Micro-mechanics of interfacial debonding: demolding of hot-embossed polymeric microfluidic substrate

Jeffry William Tani

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**MICRO-MECHANICS OF INTERFACIAL
DEBONDING: DEMOLDING OF HOT-EMBOSSSED
POLYMERIC MICROFLUIDIC SUBSTRATE**

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(B. Eng. (Hons), Nanyang Technological University)

**A THESIS SUBMITTED
FOR THE DEGREE OF DOCTOR OF
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IN MANUFACTURING SYSTEMS AND
TECHNOLOGY (MST)**

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2014

DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in this thesis.

This thesis has also not been submitted for any degree in any university previously.

Jeffry William Tani

24 August 2014

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by

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Abstract

Hot-embossing is one well-known micro-molding technique to fabricate the highly potential polymeric microfluidic devices. During the process, demolding which involves separation of polymer substrate from the mold is one crucial factor in determining the success of replication, because demolding defects are extremely prone to occur.

This thesis aims to develop an in depth understanding in the demolding mechanics of the hot-embossed polymeric substrate based on analytical, experimental and numerical studies in order to facilitate successful and efficient mass production of the microfluidic devices. An understanding of the previously unknown main demolding-failure mechanism is also established.

In addition, the influence of eight essential parameters on the demolding process and demolding failure has also been systematically studied. With the developed understanding of each parameter, it has been demonstrated that optimal processing conditions to achieve successful and efficient replications can be eventually accomplished. Moreover, the findings can also be readily utilized to provide optimal processing and design guidance for industrial application of polymer micro-molding as well as other novel replication processes.

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2. Prof Lallit Anand, SMA Fellow, MIT

Summary

Polymer-based microfluidic technology has shown great promise and potential for life science and many other applications with its advantages such as the use of tiny amount of sample, cost-reduction, and access to simple medical diagnostic tests that formerly require expensive and extensive lab work. Hot-embossing is one well-known micro-molding technique to fabricate the polymeric microfluidic devices. In the micro-replication process, demolding which involves separation of polymer substrate from the mold is one crucial factor in determining the success of replication. This is because demolding defects are extremely prone to occur, particularly during demolding of high aspect ratio micro-channels.

This thesis aims to develop an in depth understanding in the demolding mechanics of the hot-embossed polymeric substrate based on analytical, experimental and numerical studies in order to facilitate successful and efficient mass production of microfluidic devices. Initial analytical study has revealed the three main factors that correlate to demolding mechanics. They are the adhesion and friction at the contacting interfaces, thermal residual stress formed due to differential cooling, and mechanical properties of the polymer substrate. Demolding has also been characterized experimentally through the use of a metric named demolding energy. Then, a new numerical model that incorporates a robust constitutive material model and an experimentally characterized interfacial model with a uniquely different set of boundary conditions was developed. Its robust predictive capability has been experimentally validated both quantitatively and qualitatively. And, an

understanding of the previously unknown main demolding-failure mechanism has been established.

The influence of eight essential parameters on the demolding process and demolding failure have been systematically studied, namely, channel geometry, polymer substrate thickness, demolding temperature, demolding rate, demolding method, embossing temperature, channel design (shape of the channel cross-section), and adhesion of polymer substrate to the mold. With the developed understanding of each parameter, it has been demonstrated that optimal processing conditions to achieve successful and efficient replications, even at a high aspect ratio of two, can be established. Most importantly, the findings obtained in this thesis can be applicable and readily utilized to provide optimal processing and design guidance for industrial application of polymer micro-molding as well as other novel replication processes.

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Chapter 1 Introduction

In this chapter, the importance and significance of the present work will be outlined. This will be done by considering the status of microfluidics technology and the identification of some of the major research gaps. The motivation of the present work will also be outlined.

1.1 Microfluidic devices

Microfluidics is the science and technology of systems that process or manipulate small amounts of fluids, typically 10^{-9} to 10^{-18} litres, by using channels with dimensions of tens to hundreds of micrometers. It has emerged as a distinct new field and has the potential to influence subject areas from chemical synthesis and biological analysis to optics and information technology [1]. The first applications of microfluidic technologies have been in analysis, for which they offer a number of useful capabilities such as the ability to use very small amounts of samples and reagents, ability to carry out separations and detections with high resolution and sensitivity, low cost, short times for analysis, and small footprints for the analytical devices [2]. Besides its small size, it also has laminar flow characteristics of fluid in the micro-channels which is different from the flow characteristics in macro-channels. Thus, fluids do not mix convectively when two fluid-streams come together in a micro-channel. The mixing occurs based on the result of diffusion of molecules across the interface between the fluids. This characteristic is indeed

advantageous in many circumstances. It is also capable of controlling concentrations of molecules in space and time.

According to Whitesides, the field of microfluidics has four parents which are molecular analysis, bio-defence, molecular biology, and microelectronics. The first field is in micro-analytical methods such as gas-phase chromatography (GPC), high pressure liquid chromatography (HPLC) and capillary electrophoresis (CE) which revolutionized chemical analysis with capillary format. The combination of those methods with the power of laser in optical detection made it possible to achieve high sensitivity and high resolution only by using very small amounts of sample. The second reason for the development of microfluidic systems is the realization that chemical and biological weapons pose major military and terrorist threats. Therefore, it is possible to develop field-deployable microfluidic systems which can detect and sense chemical as well as biological threats. From the molecular biology point of view, microanalysis in molecular biology is getting more popular especially with the explosion of genomics. One of the examples is the DNA sequencing which requires higher throughput, sensitivity, and resolution that can be offered by microfluidics. The fourth contribution is from microelectronics. Microfluidics was initially hoped to be applicable to photolithography and associated technologies which had been successful in silicon microelectronics and micro-electromechanical systems (MEMS). In fact, some of the earliest works in microfluidics were made with silicon and glass. However, they have largely been displaced by plastics with time due to their advantages.

Some of the applications of microfluidic devices are lab-on-a-chip, drug screening devices, screening devices for protein crystallization, flow-focusing devices, separations coupled to mass spectroscopy, bio-analyses, polymerase chain reaction (PCR), cell counting and sorting, electrophoretic separations, nucleic acid extraction, DNA sequencing, cell culture studies, single cell manipulation, and immunoassays. Microfluidic devices can also be used as micro-channels for cooling microelectronic circuits, grayscale photo-masks consisting of channels filled with different dye concentrations, pressurized elastomeric chambers acting as tunable lenses, a tunable microfluidic dye laser, and fluidic circuits for implementing DNA computing. Besides the mentioned possible applications, there are many more areas in which the beneficial microfluidics technology may be applicable. Therefore, it is a very promising field to explore.

1.1.1 Polymeric microfluidic devices

Microfluidic devices can be fabricated with different materials such as silicon, glass or polymer. Silicon is no longer used frequently because it is costly. Furthermore, it is opaque to visible and UV light in that it cannot be used with conventional optical methods of detection. Silicon is also more rigid and brittle such that it is more difficult to fabricate. On the other hand, glass is expensive when compared to polymer. In addition to the consideration of materials cost, many more steps are required during fabrication of microfluidic devices with silicon or glass, such as cleaning, resist coating, photolithography, development, and etching. Hazardous wet chemicals such as HF are usually involved. The higher number of processing steps involved adds to the final

cost. Furthermore, neither silicon nor glass has all the properties, especially permeability to gases, required for work with living mammalian cells [1].

Limitation on the geometrical design with silicon or glass is also one of the crucial considerations due to the isotropic etching process, particularly by the wet etching method. Another issue can arise due to the surface chemistry of silicon such as in a continuous flow system in which the biomolecules (oligonucleotides, DNA or proteins) tend to bond with the silicon surface groups, and thus stick to the silicon surfaces [3].

Figure 1.1 Pictures of polymeric microfluidic devices (Reference: www.asme.org)

On the other hand, polymers have been gaining increasing attention in recent years as the more potential materials for microfluidic devices (see Figure 1.1), mainly because of the much cheaper cost and easier mass-replication processes such as by injection-molding or hot-embossing. The popularity has also been supported by the availability of the many different kinds of polymers nowadays. The different kinds of polymers can correspond to different mechanical properties, optical characteristics, temperature stability, resistance

against chemicals such as organic solutions, alkalines or acids, and even biodegradability for some types of polymers [3]. Some of the other beneficial properties which may be required for specific applications are high rigidity, high transparency, low birefringence, excellent water vapour barrier, low water absorption, good blood compatibility, excellent biocompatibility, and good melt processability/flowability. Therefore, it has become much more straightforward and practical to select suitable polymeric materials which can be optimally used for the different kinds of applications. In addition to that, the growing interest of single-use disposable microfluidic devices has further enhanced and supported the use of polymeric materials.

1.2 Research motivation

During the micro-fabrication process of microfluidic devices by replication technique, there are two basic steps required which are molding (filling of the polymer into the mold cavities) and demolding (separation of the replicated polymer from the mold). The two most well-known replication techniques are injection-molding and hot-embossing. Despite the well-developed injection-molding technology, hot-embossing has become more popular because it has a simpler set-up and can replicate delicate micro-features with higher aspect ratio as well as lower inner stress [4].

Extensive research has been carried out both experimentally and numerically on filling of the mold by the polymer melt during the molding process with the aim of optimizing the replicated pattern accuracy as well as improving process yield through efficient and fast filling [5-10]. Complete filling can be achieved

by applying sufficient molding temperature, load, and time. However, apart from problems encountered in the replication process, the quality of the molded or embossed part is also dependent on the demolding process.

The replicated features may be severely deformed, or even fractured during demolding. Such problems are more prone to arise during replication of high aspect ratio micro-features or micro-channels [11-13]. And, most importantly, the high aspect ratio micro-channels can provide more advantages during applications due to their larger surface area, such as higher packing densities and higher throughput in flow systems, increased sensitivities and improved detection limits in sensor technology, increased reaction rates for application as micro-reactors, and further miniaturization of the devices [3, 14]. The demand for high aspect ratio micro-channels have also been increasing in the field of micro-lenses [15], tissue engineering [16], liquid crystal displays, and microfluidics [17]. Demolding failure in the replicated polymer has also been known to occur when the polymer sticks to the mold which can eventually render the mold unusable [14].

In spite of the importance in demolding, there has not been any rigorous systematic study on this topic, particularly on demolding mechanics. The existing experimental studies of demolding have only consisted of qualitative evaluations of the effect of mold materials [18-19], mold coating [5, 20], demolding temperature [21], and the layout of features on the mold [22]. The few existing quantitative research on demolding has so far been limited to finite element simulation of the demolding process without consideration in the preceding molding process [5, 11, 22-24]. There were also simplifications

in the models in terms of the overall channel geometry as well as boundary conditions. In addition, there is still no widely accepted interfacial model that can represent the bonding between the mold and replicated substrate. And, the implemented material models were only limited to simple linearly elastic material properties. In short, there has been no known numerical model that can simulate as well as predict the real micro-replication process both quantitatively and qualitatively.

A few research groups have tried to measure the required demolding force based on studies of the influence of demolding temperature [11, 25] and combined influence of demolding temperature and channel geometry [23]. However, these studies were still limited to rather low aspect ratio micro-channels which were far below 0.5. Furthermore, brittle silicon molds which are not suitable for mass-replications due to their very short life-span were commonly used. Dirckx et al. have used aluminum instead of silicon molds, but the aluminum molds had rough surface finishing due to the micro-machining process. The rough surface finishing may have an effect on demolding and the performance of the microfluidic devices.

Apart from the demolding temperature and channel geometry, it is believed that there are still a lot of important parameters that affect demolding mechanics that have not been identified yet. Moreover, it is also extremely crucial to develop an in-depth understanding in the still unknown demolding-failure mechanism through quantitative and qualitative studies on demolding. As the demolding mechanics is heavily dependent on the interfacial properties that involve both adhesion and friction, the level of thermal stress developed during differential thermal contraction prior to demolding has to be taken into

consideration. These are the focus of the current work. Through an understanding of these issues, the optimal conditions for successful demolding can be readily established.

1.3 Research objectives

The main objectives of the work in this thesis are:

- Development of an in-depth understanding in the replication processes, particularly the demolding mechanics, based on the analytical, experimental, and numerical analyses.
- Development of numerical model that can simulate and predict experiments both quantitatively and qualitatively with the use of constitutive model of the amorphous thermoplastic material. Systematic studies on the interfacial model, the modeling of the whole replication processes including molding and demolding, and the non-simplified model including its unique boundary conditions will be performed.
- Development of an in-depth understanding in the main demolding-failure mechanism.
- Systematic studies on the influence of the crucial parameters that can affect the replication processes via hot-embossing through a combination of numerical studies and experimental verification. The parameters include channel geometry, polymer substrate thickness, demolding temperature, demolding rate, demolding method, embossing temperature, channel design (shape of the channel cross-section), and adhesion between the mold and the polymer substrate.

-
- Prediction and determination of the final optimal processing guidelines to achieve successful and efficient replications.
 - A secondary aim is the development of a robust experimental technique and data analysis method using cheap durable aluminum molds for mass-replications of microfluidic devices. The aluminum molds have optical surface finishing and high aspect ratio micro-features of up to 2.

1.4 Organization of the thesis

This chapter (Chapter 1) has introduced the topic of microfluidics technology that includes its abundant benefits for different kinds of applications as well as the challenges in fabrication of the microfluidic devices which are caused by the demolding process. The existing research gaps, research motivation, and objectives of this thesis work have been outlined.

Chapter 2 presents a brief review on the existing replication techniques that includes the issues encountered and the parameters involved in the replication processes. The fracture mechanics theory will be correlated and applied to the demolding process. And, the constitutive theory in the large strain thermo-mechanical behavior of amorphous polymers in a temperature range spanning their glass transition temperature which will be eventually used as the material model is also presented.

Chapter 3 presents the different demolding experimental techniques and experimental set-ups used in this thesis work. The reliability of the chosen experimental technique as well as the developed experimental set-ups, and the implemented data analysis method are evaluated.

Chapter 4 initially reviews the existing numerical research work by others, and identifies the relevant research gaps. Then, the development of the implemented model in this thesis work is elaborated in detail, including the advantages of the new model. Finally, the new numerical model is also experimentally validated.

Chapter 5 presents the experimental characterization of the interfacial properties between the mold and polymer substrate, and the tensile properties of the polymer substrate. The testing apparatuses and specimens for both characterization tests will be discussed in detail.

Chapter 6 presents the development of the main demolding-failure mechanism, and the detailed discussions on the effect of the parameters on the fabrication of hot-embossed polymer substrates. Correlations between the studied parameters and the demolding-failure mechanism will also be explored and presented.

Chapter 7 presents the findings on the influence of the parameters on both thermal cooling and the demolding processes based on both experimental and numerical results.

Chapter 8 presents an approach in predicting and determining the optimal processing conditions to achieve successful and efficient replications, which is followed by experimental verification.

Chapter 9 summarizes this thesis with final conclusions. In addition, several possible future works are proposed.

Chapter 2 Literature Review

There are many different techniques to fabricate micro-channels for microfluidic applications. This chapter will elaborate in detail on some of these techniques, and the issues encountered during the replication of the micro-channels. Particular focus will be given to the demolding step and the different parameters that affect demolding. This is because demolding has a significant influence on the quality of the molded microfluidic part. Consideration of the fracture mechanics during demolding will be explored in order to build a better understanding in the mechanics of demolding. Lastly, the application of the thermo-mechanically-coupled constitutive theory of amorphous polymer as a material model in numerical simulation will be discussed.

2.1 Fabrication of micro-channels

In the fabrication of micro-channels for microfluidic applications, there are two important aspects to be considered. Firstly, the appropriate micro-fabrication technique has to be selected from the various techniques that are available nowadays. This is important because each technique has its own advantages and disadvantages. The second crucial aspect is the importance of having a proper understanding of the challenges and limitations of each fabrication process.

2.1.1 Micro-fabrication techniques

There are two general techniques to fabricate microfluidic devices, namely: the direct technique and the replication technique. The basic difference is on the use of master mold in the replication technique.

2.1.1.1 Direct techniques

In the direct technique, the micro-device or channel is fabricated without the use of any mold. In other words, each micro-channel is made directly through the appropriate removal of material from a basic block. This technique allows rapid fabrication of a single device because there is no need to fabricate master mold. On the other hand, the overall fabrication throughput will be very limited by the fabrication time of each individual device when aiming at mass-production.

Nowadays, there are several available direct techniques such as laser based technologies (laser photo-ablation), optical lithography in deep resists (X-ray lithography, UV LIGA), stereo-lithography, and layering techniques [3]. Nevertheless, due to the inherent disadvantage of low fabrication throughput, direct techniques are not utilized for fabricating large quantities of microfluidic devices. Some of the direct techniques are only used to fabricate the master mold which will then be used for further repetitive productions with the replication techniques.

2.1.1.2 Replication techniques

In the replication technique, a master mold (mold tool) is used as the negative (inverse) structure of the desired replicated structure. Such replication techniques, which are also known as molding, are widely used commercially for mass production because of the low average cost coupled with the high throughput of the manufacturing process. The only costly fabrication step is the fabrication of master mold. However, the master mold can generally be used to replicate structures for many cycles, which still makes the technique very favorable from the cost perspective. In addition, molding also offers flexibility in design in that the master mold can be fabricated with various kinds of fabrication technologies which allow different types of geometries. The master mold can generally be fabricated by lithography, deep reactive ion etching (DRIE), micro-machining or electroplating methods [3].

There are many micro-replication techniques available nowadays such as nano-imprint lithography (NIL), hot embossing lithography (HEL), mold assisted lithography (MAL), step and flash lithography (SFIL), UV casting, soft lithography, injection molding, reaction injection molding, thermoforming, hot embossing, and injection compression molding [3-4, 26-27].

A. Nano-Imprint Lithography (NIL)

Nano-imprint lithography (NIL) is a replication technique (see Figure 2.1) that involves two main process sequences which are pattern lift off and oxygen plasma reactive ion etching in order to remove the residual layers [28]. Sub micron features of up to 10 nm have been achieved and non-flat surfaces have

also been successfully patterned. However, loss of aspect ratios has been recorded especially due to the lift off method (35% of master mold), and high aspect ratios have not been demonstrated yet [29]. Other problems faced by this technique include the filling of molds for high aspect ratio structures which can only be remedied by the application of higher temperature ($T_g + 90^\circ\text{C}$).

Figure 2.1 Nano-imprint lithography process sequences for direct lift off (left) and oxygen plasma reactive ion etching (right) [28, 30]

B. Hot Embossing Lithography (HEL)

Hot embossing lithography (HEL) is a development from NIL in which there are two different methods for pattern transfer (direct lift off or RIE). In direct RIE method, the residual PMMA resist acts as a form of mask for a subsequent round of etching by CHF_3 RIE [29]. Deeper channels have also been achieved by using a multi layer technology with the expense of having additional processing steps. Both NIL and HEL utilize thermal cured thermoplastic polymers. The additional step in HEL is the coating of

additional silane by deposition (see Figure 2.2) through the gas phase or immersion in a solution [31]. Then, the remaining resist layer is removed by acetone. One limitation experienced by both the NIL and HEL processes is the flow behavior of the polymer during the imprinting process which is highly dependent on the kind of patterning mold used [32].

Figure 2.2 Hot embossing lithography (HEL) processes with deposition of silane layer [31]

C. Mold Assisted Lithography (MAL)

Replication technique via mold assisted lithography (MAL) uses molding of a monomer via a vacuum contact printer with UV curing [33]. One promising advantage of this technique is the direct compatibility with the current Si technology. However, the drawback of this technique is the additional process step of dry etching to remove the residual polymer layer which prolongs the cycle time. Furthermore, it is also difficult to achieve high aspect ratio structures without any aid of multilayer technology.

D. Step and Flash Lithography (SFIL)

Step and flash lithography (SFIL) is a technique that uses photo-curable thermoset polymers (see Figure 2.3). It has been used in conjunction with layer technology to enable the creation of high aspect ratio structures or channels. Some of the advantages are the less demanding process conditions (room temperature and low pressure), and the ability to pattern non-flat structures [34-35]. Nevertheless, the method requires good adhesion of the etch barrier to the transfer (base) layer. Furthermore, the transfer layer should be un-reactive to the etch barrier solution. Another drawback of this technique is the additional step to etch the transfer layer down by using halogen breakthrough RIE followed by oxygen RIE [36].

Figure 2.3 Step and flash lithography (SFIL) processes [36]

E. UV Casting

UV casting is usually used to replicate commercial 3D polymeric micro-channels in large areas under cost effective conditions with its simple process requirements. A liquid resin is initially poured on the mold insert. Subsequently, a substrate backing is attached to the liquid resin. Then, it is UV irradiated to initiate photo-polymerization until it has the desired properties before it is demolded or ejected. The advantage of UV casting technique (see Figure 2.4) is mainly attributed to its non-stringent requirements for temperature and pressure. In addition, the process can also be carried out in non-clean room conditions.

Figure 2.4 UV casting processes [12]

However, the materials used for UV casting usually consist of a mixture of polymeric acrylate oligomers, cross-linker multifunctional acrylate, and photo-initiator [12]. This mixture is imperative so that the final polymer has the

important characteristics such as high curing rate, good mechanical strength, and high dimensional stability.

F. Soft Lithography

Soft lithography is a replication technique with significant advancement in microfluidic systems development by using elastomeric polymers [3]. This technique also uses positive relief master mold which may be fabricated in silicon. Then, an elastomeric polymer is cast onto the silicon stamp and allowed to cure at room temperature or at a slightly elevated temperature to speed up the curing process. After curing, the elastomeric polymer will be separated from the stamp. The advantage of this technique is that the mold is not exposed to excessive pressure as well as heat. Therefore, fabrication of a metal electroform is not necessary. Moreover, the mold can even be made from softer materials such as photoresists. Most importantly, it has been reported that three dimensional microfluidic devices has been successfully fabricated by performing this technique [3]. However, the vast majority of work done by this technique has been with the use of PDMS as the material which will further restrict the choices of polymers used.

G. Injection Molding

Injection molding (see Figure 2.5) has been adapted as one of the widespread standard processes to fabricate polymer parts. Injection molding processes start with the raw polymer material which is generally used in granular form.

These granules are then fed into the cylinder through the heated screw where they subsequently become molten. The molten polymer is then injected forward into the mold cavity under high pressure. The entire mold is then cooled whereupon the polymer substrate is ejected.

Figure 2.5 Schematic diagram of an injection molding machine [3]

It is important to note that there is an additional consideration when injection molding is performed at the micron level [3]. At macro level, the cavity can be held at a temperature below the solidification temperature of the polymer. This will allow rapid fabrication, and thus minimize the cycle time. However, for structures at the micron level, the cavity has to be heated up to a temperature closer to the melting point of the polymer material in order to ensure complete flow into the mold cavity. This is essential because the surface to volume ratio increases significantly at the micron level.

The advantage of injection molding is that this technique has been well established in the macroscopic production of polymer parts over many decades. Thus, there exists vast know-how and machine technology that can be made

use of for micro-injection molding. Most importantly, the required cycle time for production in this technique is extremely short.

H. Reaction Injection Molding

Reaction injection molding is quite similar to injection molding. The difference is on the raw material used in that instead of using one type of polymeric material, two components are injected into the closed molding tool. This technique allows fabrication of parts from polymers that are not thermoplastic such as thermosetting material and elastomer. However, fabrication of micro parts by reaction injection molding turns out to be difficult because good mixing of the material components has to be achieved at micro scale, and the ensuing chemical reaction required to form the micro structures of the molding tool requires a comparatively long time [4]. Hence, cycle time will be longer. Nevertheless, with the possibility of UV-curing instead of thermal initiation of the polymerization, reaction injection molding has become one of the preferable choices.

I. Thermoforming

Micro-thermoforming is used to form thin thermoplastic films. The polymer film is inserted into a molding tool. Then, the film is clamped and heated up prior to pressing into the mold insert by gas. After pressing, it will be cooled down and demolded (see Figure 2.6).

Figure 2.6 Thermoforming processes [4]

The problem encountered in micro-thermoforming is that the film may not fill the micro structures completely. On the other hand, the film cannot be heated until it is too hot and soft because the permeability of polymers for gases increases with temperature. Nevertheless, with the flexibility of the thin films, successful demolding is easy to achieve. One crucial drawback is the inappropriateness for replicating high aspect ratio structures as the thin film cannot be stressed too much [4].

J. Hot Embossing

Nowadays, hot embossing is one of the most widely used replication technique to fabricate channel structures for microfluidic applications. This is because

the processes required for this technique are extremely straightforward and simple (see Figure 2.7). This technique usually involves heating of the mold and polymer substrate to temperature above the glass transition temperature (T_g) of the thermoplastic polymer, so that the polymer softens. After heating, pressure is applied and held for some time to replicate/stamp out the features of the mold. The time when pressure is maintained onto the mold and polymer substrate is usually known as holding time. Then, cooling of the mold and polymer substrate is performed by lowering down the temperature of the platens of the hot embossing machine which are in contact with both the mold and polymer substrate. When the desired temperature which is also known as demolding temperature has been reached, the polymer substrate is further separated or demolded from the embossing mold. Hence, the demolded substrate will now contain the features of the mold.

Figure 2.7 The hot embossing processes: heating, molding/embossing, cooling, and demolding [13]

Besides the simplicity of its processes, hot embossing has evolved into a popular fabrication technique because it is suitable for producing delicate micro-channels with high aspect ratios on thin layers and with low inner stress [4]. Moreover, the inner stresses developed during forming are very low due to the short flow path of polymer into the mold cavity. This is in contrast to injection molding. In addition, the hot embossing process is also very flexible because different mold inserts and various substrates can be used. Furthermore, it allows large scale production of devices up to 200 mm in diameter. It can also be combined with automated handling systems which will further reduce the cycle time.

K. Injection Compression Molding

Injection compression molding is a combination of injection molding and hot embossing to overcome the problem of heating the polymer by the tool in the latter replication technique [4]. The molten polymer is injected from a screw into the semi-closed molding tool before it is pressed into the mold cavity by closing the tool. With this technique, the problem of longer flow into mold cavity in injection molding can be avoided. In other words, this technique inherits both benefits of injection molding and hot embossing. However, this technique may not be preferable to hot embossing because of its higher initial set-up cost.

From the above consideration of the different replication techniques, it can be seen that hot embossing appears to be one of the most promising techniques for fabricating microfluidic devices. Some advantages of hot embossing include the simplicity and cheaper cost in set-up, suitability in replicating micro-channels on thermoplastic polymers with high aspect ratio and low inner stress, and possibility in large scale production with automated systems. Therefore, it is believed that hot embossing is a suitable technique to produce high quality micro-channels for microfluidic applications at low cost.

2.1.2 Issues encountered in micro-replication process

In micro-replication process, there are generally two basic steps that determine the success of the replication. The first step is to replicate the mold patterns known as molding, while the second step is to remove the replicated substrate from the mold known as demolding. In most cases, the first step is not as hard to accomplish. In addition, studies of the hot-embossing process that focuses on pattern formation have been quite extensively reported [5-9]. Conversely, issues and challenges often arise during demolding to the extent that significant deformation experienced during demolding may cause the replicated substrate to be damaged. Polymer fracture and breakage of the replicated part can also occur. Unfortunately, there are few studies on demolding available in the literature. Thus, it is obvious that demolding should be further understood and studied in order to achieve successful replication.

2.1.2.1 Demolding related defects

Several types of defects can be formed during demolding. These include part warping or breakage (see Figure 2.8 and 2.10), and plastic deformation/distortion on the replicated channels or features (see Figure 2.8 and 2.9). Such demolding related defects including broken or distorted features have been observed in hot embossing [20-22, 37-40], injection molding of micro-features [41-42], thermal nano-imprint lithography (NIL) [11], and PDMS casting [43]. When there is good adhesion between the substrate and mold, cohesive failure of the substrate material can occur during demolding. This substrate residue can cause contamination to the mold and may render the mold unusable. Another costly defect is when a broken mold feature becomes stuck on the replicated substrate after demolding (see Figure 2.11). In this case, the mold has to be replaced.

Figure 2.8 SEM micrographs showing defects on PMMA due to demolding from Si mold (polymer breakage & deformation at top and bottom of channels) [11]

Figure 2.9 SEM micrograph showing the distorted T-shape pattern (PMMA) after demolding from nickel mold [22]

The bulge defect as shown in Figure 2.12 is also a commonly observed defect. It generally occurs on one side of a feature and it is widely attributed to the thermal stress associated with the differential thermal contraction between the mold and polymer substrate during cooling to a lower temperature [21-22, 38-39]. It can be correlated to demolding at the demolding temperature. Demolding is generally performed at lower temperature in order to ensure that the polymer substrate has adequate strength to overcome the demolding stress without any deformation. Nevertheless, lower demolding temperature may create higher thermal stress such that the bulge defect is more prone to occur. This type of defect can be problematic because it can inhibit the replicated channels from being properly sealed with a cover plate.

Figure 2.10 SEM micrograph of broken PMMA that was embedded on a bulk metallic glass mold [37]

Figure 2.11 SEM micrograph of COC molding by hot-embossing showing the broken silicon mold embedded on the replicated COC substrate [20]

The potential challenges in the formation of defects faced during demolding become more significant when higher aspect ratio micro-channels are replicated. Higher aspect ratio micro-channels are in high demand, and they have essential as well as potential applications in the field of microlenses, tissue engineering, liquid crystal displays, and microfluidics. This is due to the

benefits of higher aspect ratio micro-channels during their applications such as increased sensitivity and improved detection limit due to the enhanced surface and cross sectional area in sensor technology, further miniaturization, higher packing density and throughput in continuous flow systems, and enhanced reaction rate due to the larger cross sectional area in micro-reactors whereby catalyst or reactant is grafted onto the surface of channels [14, 43]. This further shows the importance of tackling the challenges that are prone to arise in demolding in order to successfully fabricate the microfluidic devices.

Figure 2.12 SEM micrograph showing bulge defects on PMMA that was hot-embossed on nickel mold due to high thermal stress generated during thermal cooling [22]

2.1.2.2 Main factors that affect success in demolding

In the micro-fabrication of polymeric micro-channels by hot-embossing, the main factors that contribute to the success of demolding process can be grouped into three aspects. They are adhesion, friction, and material properties. Adhesion always plays a role at any interfaces that are in contact, while

friction is mainly involved at the sidewall interfaces of mold and polymer substrate. A defect or failure can only occur during demolding when the stress experienced by both mold and polymer substrate has reached their respective yield or fracture strength.

A. Adhesion

Adhesion is always involved in any contact between two interfaces, which are the mold and polymer substrate in this replication process. If the interfacial adhesion property between mold and polymer substrate is too strong, there may be potential high stress experienced by the polymer during the interfacial separation process or demolding. This may further lead to plastic deformation or even severe breakage. One feasible solution to reduce the interfacial adhesion is by tailoring and changing the surface properties of the mold materials with the use of self-assembled monolayer (SAM) method [44]. The modified surface can be flexibly altered to hydrophilic or hydrophobic according to the SAM properties in order to match with the relevant applications either as adhesion promoters or anti-sticking layers.

In the case of replication via hot-embossing, the interface of mold is preferable to be hydrophobic so that the adhesion strength between mold and polymer substrate can be minimized, which further eases demolding. Therefore, it is very important to understand and evaluate the effect of SAMs on the adhesion properties of materials when using them as adhesion promoters or anti-sticking layers. Several tests have been generally used to evaluate the adhesion

properties of materials such as atomic force microscopy (AFM) [45-46], pull-off test [47], double cantilever beam test [48], and four-point bending test [44].

In addition, a research group has reported a work on variable temperature chemical force microscopy with the use of scanning probe microscopy (SPM) tip with different SAMs to model the hot-embossing mold-polymer interaction over a temperature range spanning the glass transition of the polymer [49]. They evaluated the most suitable SAM on silicon mold through further evaluation on the measured water drop contact angle and adhesion force. Other research groups have also reported on the use of different coating materials on silicon mold through sputtering and dipping processes [37, 50]. With the coatings, they have successfully lowered the surface energy, friction as well as the wear of the coated silicon mold.

Besides the above mentioned methods, mold release agent in the form of spray is also ubiquitous. And, the steps required in applying the mold release agent are much more straightforward. However, most importantly, those methods may not be applicable in major applications of microfluidic devices, especially for chemical or biological purposes [3]. This is to prevent any unwanted chemical reaction from occurring due to the coating residue that may still stick on the demolded polymer substrate. The potential sample contamination is further dependent on the atomic compositions of the altered surface. Hence, the best scenario is still to successfully demold the replicated substrates without any surface treatment on the mold. Lastly, it is important to note that adhesion is temperature-dependent in that demolding temperature may be one of the crucial parameters in determining the success of demolding.

B. Friction

Unlike adhesion, friction is only involved during sliding of two interfaces. In the case of fabrication of micro-channels through replication, friction is mainly involved at the vertical sidewall interfaces of the micro-channels. This happens due to the differential thermal contraction behavior between the mold and polymer substrate. Thus, the polymer substrate is constrained from thermally contracting by the mold due to its much lower coefficient of thermal contraction. With the constraint, normal force on the vertical sidewall interfaces increases during cooling from embossing to demolding temperature, and it is indeed the normal force that corresponds to how significant the frictional force will be. The frictional force may eventually generate high stress on polymer substrate during demolding that may lead to demolding defect or even failure in most cases. Apart from the contribution of differential thermal shrinkage, the mold surface finishing as well as its adhesion properties also play an important role in determining how severe the frictional force during demolding will be.

As mentioned above in adhesion section, coatings on mold have been found to improve demolding by lowering both the surface energy and frictional property [50]. It has also been reported that channels with draft angle such as silicon mold produced by KOH etching can be demolded more easily [51-52]. This occurs due to the weaker mechanical asperity interaction that directly correlates to friction. Nevertheless, with the draft angle, there is limitation in the overall shape of the micro-channels, and the limitation is restricted in some specific applications such as microlense fabrication in which accuracy is highly important [18]. Moreover, it may not be a simple task to fabricate mold

that has channels with draft angle, and at the same time, is made of materials other than silicon that are suitable for repetitive mass-production.

C. Material properties

Besides adhesion and frictional properties between the mold and polymer substrate, the material properties of polymer substrate is also an extremely important key factor. Demolding defects or failures can only occur when the stress generated in the polymer substrate during demolding has reached its yield or fracture strength. Moreover, mechanical properties of polymeric materials are highly dependent on both temperature and rate. This dependency further signifies the importance of processing parameters that are related to temperature and rate in order to achieve successful demolding. Conversely, the mold is generally made of materials with much higher mechanical strength than the polymer, so that repetitive replications can be achieved simply with a single mold. Therefore, mold failure is relatively rare, except in silicon mold which is brittle and not suitable for repetitive replications.

2.2 Hot-embossing

As elaborated in Section 2.1.1.2, hot-embossing is chosen and used as the replication technique in the author's research work to fabricate polymeric microfluidic devices. This section further discusses the methodology and the different parameters that may affect demolding of hot-embossed polymer substrate.

2.2.1 Methodology

The procedure in performing hot-embossing is extremely simple and straightforward. Initially, a polymer substrate material is placed into contact with a patterned mold. Then, both of these are heated to an embossing temperature that is generally above the glass transition temperature of the polymer substrate so that it softens. When the equilibrium temperature has been reached, the polymer substrate is pressed on the patterned mold under a certain amount of pressure known as the embossing pressure. The embossing pressure will be held for a specified duration which is also known as holding time in order to allow the softened polymer to flow into the mold cavity. Finally, the mold and the embossed part are cooled down to the demolding temperature, and then the polymer substrate which now has the exact patterns as in mold is removed or demolded from the mold. The trajectories of temperature and embossing pressure over time in hot-embossing are illustrated in Figure 2.13.

Figure 2.13 Schematic process profile of hot-embossing with a relation between embossing temperature (T_E), glass transition temperature (T_g), demolding temperature (T_D), room temperature (T_R), and embossing pressure (P_E) with time (t_1 to t_5)

2.2.2 Parameters that affect demolding

In order to develop a deeper understanding in demolding, critical parameters that affect demolding should be further considered and studied. All of the critical parameters indeed contribute to and affect the three main factors mentioned in Section 2.1.2.2 which are adhesion, friction, and material properties. Having defined the three main factors that contribute to the success of demolding process, the next step is to further evaluate how the processing and mold parameters affect these factors and influence the demolding behaviour. The processing parameters can be grouped into hot-embossing parameters (embossing temperature, embossing load, and holding time), and demolding parameters (demolding temperature, and demolding rate), whereas mold parameters include channel geometry and mold surface finishing.

2.2.2.1 Hot-embossing parameters

A. Embossing temperature

Embossing temperature is one crucial parameter in hot-embossing process that affects the flowability of the polymeric materials into the mold cavities. Generally, the polymer is embossed at a temperature above its glass transition temperature (T_g) so that it gets softened. The flow of the polymer is further eased with the application of an embossing load for a period of time in order to replicate the mold patterns. Considering a fixed set of embossing load and holding time, it can be intuitively predicted that there exists a minimum embossing temperature which results in complete filling of polymer into the mold cavities.

The amount of thermal shrinkage is defined from the difference between embossing and demolding temperatures. As there is usually huge difference in thermal contraction behaviour between mold and polymer substrate, the polymer will be constrained from contracting especially by the mold features during thermal cooling process. This further creates thermal stress that leads to difficulty in demolding. With higher thermal stresses, higher frictional forces are experienced during demolding. Therefore, with all other parameters being constant, the minimum embossing temperature which generates complete filling may most probably be an optimum temperature that results in the easiest demolding. Moreover, a lower embossing temperature means a shorter processing cycle time.

Nevertheless, there has not been any in-depth study on the effect of embossing temperature on demolding behaviour. Worgull et al. has only observed that static coefficient of friction increased significantly with higher embossing temperature due to the better filling of PMMA onto the micro-roughness of the brass and copper molds [53]. Hence, the hypothesis mentioned above is still merely based on intuition and knowledge about the differential thermal shrinkage. Nevertheless, it is apparent that the embossing temperature may affect both adhesion and friction.

B. Embossing load

Similar to embossing temperature, embossing load also plays an important role in accomplishing complete filling of polymer into the mold cavities. Assuming that embossing load is adequate to achieve complete filling, the

specified embossing load or pressure that is maintained for a period of time is known as holding pressure which has been found to affect demolding [54]. In this work, the embossing pressure was maintained not only at the embossing temperature, but also during cooling to the demolding temperature.

The thermal shrinkage was reported to be less severe due to higher constraint provided by the higher holding pressure. The ejection force was found to be lower during demolding of the tubular injection molded polycarbonate that had been molded under higher holding pressure. Friction tests by another research group also revealed that the static coefficient of friction decreased significantly with higher holding pressure when a hot-embossed PMMA was separated from a flat brass mold [53]. They also reported that there was a reduction in shrinkage of polymer during cooling to demolding temperature. Thus, the embossing load and holding pressure may affect both adhesion and friction in the demolding process.

C. Holding time

As illustrated in Figure 2.13, holding time is the period of time when embossing pressure is maintained at the embossing temperature. Holding time may also affect the final profile of the replicated micro-channels. If there is inadequate time, the mold features may not be fully imprinted into the polymer substrate. In this way, holding time can affect both adhesion and friction factor with correlation to the quality of polymer filling. Figure 2.14 shows the comparison in replication quality of PMMA substrates at two

different holding times. It has been observed that too short holding time may result in bad replication fidelity [55].

Figure 2.14 SEM micrographs of replicated channel on PMMA showing bad replication due to inadequate holding time (left) and complete replication with longer holding time [55]

2.2.2.2 Demolding parameters

A. Demolding temperature

Unlike hot-embossing parameters that mainly affect the quality of polymer filling into mold cavities, demolding parameters mainly contribute to the final replication fidelity through the demolding process. Demolding temperature is one of the most important parameters to control in tackling potential demolding challenges. This is because demolding temperature has an impact on all the three main factors that affect success in demolding. Adhesion and friction are known to be temperature dependent. Moreover, the polymeric material properties are extremely dependent on temperature as well.

In practice, it has been reported that there exists an optimum demolding temperature at which the demolding force is a minimum [11, 25, 37]. Park et al. and Trabadelo et al. have studied how temperature influenced the demolding behaviour by investigating silicon wafer nanoimprinting of PMMA

using a commercial imprinting machine [11, 25]. Dirckx et al. have obtained results that exhibited a similar trend by performing demolding tests on hot-embossed PMMA and PC [37]. They further grouped demolding at varying temperatures into two regions which were adhesion-dominated and friction-dominated. Adhesion-dominated behavior occurred at higher temperatures, while friction-dominated behavior was found at lower temperature. The easiest demolding was found to be at the temperature range in between those two regions.

High demolding temperature may lead to strong adhesion, while low demolding temperature may enhance the frictional effect due to the more severe thermal shrinkage. Combined with the temperature-dependent material properties, demolding at low temperature may lead to breakage due to brittleness of the materials. On the other hand, demolding performed at high temperature may lead to loss in replication fidelity such as stretching, shearing, or wrinkling in the replicated features as a result of the low mechanical strength of the material.

B. Demolding rate

In terms of the manufacturing point of view, demolding rate affects the production throughput. Nevertheless, the most essential goal is to achieve successful fabrication without demolding defects. Demolding rate may be crucial because the mechanical strength of polymers is also highly dependent on strain rate. In this way, it may be possible to find an optimum condition for

successful demolding, while maximizing production throughput at the same time.

It may also be useful to investigate the effect of demolding rate on the adhesion and friction properties between the mold and substrate material. It has been reported that it is possible to perform kinetically controlled, adhesiveless transfer printing using microstructured stamps [56]. They utilized a PDMS stamp to perform inking and printing onto a glass substrate at high and low peel rates, respectively, without the use of any adhesives. This was achieved by accounting for the viscoelastic nature of the elastomer stamp and controlling adhesion through the peeling rate. Their results suggested that demolding rate may affect the outcome of demolding.

2.2.2.3 Thermal shrinkage

Thermal shrinkage occurs during cooling from the embossing temperature to the demolding temperature. In other words, the extent of thermal shrinkage is determined from the difference between embossing and demolding temperatures. The difference in the thermal contraction behavior between mold and polymer substrate materials causes thermal stresses to be generated during cooling. The polymer which has a higher coefficient of thermal contraction is constrained from contracting fully during cooling. A schematic diagram that shows the generated thermal stress is illustrated in Figure 2.15. Such thermal stresses can also cause the bulge defect as shown in Figure 2.12.

Figure 2.15 Schematic diagram showing the thermal compressive stress built up during thermal cooling with an assumed shrinkage center

It has been found through numerical simulation [13, 22, 57] that the generated thermal stress in a substrate was higher at locations further away from shrinkage center. Therefore, demolding failure was more prone to occur at micro-channels located furthest away from the shrinkage center where high stresses existed. One way to reduce the stress at the micro-channels located further away from the centerline was to build an auxiliary microstructure that served as a stress barrier at the edge of the mold [22]. However, it may not be easy to do this in practice since the orientation of microstructures and the stress barriers have to be kept coincident to the shrinkage center. It has also been reported that another feasible way to minimize the effect of thermal shrinkage is by increasing the holding pressure during cooling process [54].

Another obvious method to minimize the effect of thermal shrinkage is by performing demolding at higher temperature. However, the adhesion and frictional properties, as well as the mechanical strength of the polymer substrate are also temperature-dependent. Thus, it is reasonable to predict that there is an optimum demolding temperature which corresponds to the

combination of the most effective value of thermal shrinkage, and the adhesion, frictional and material properties.

2.2.2.4 Channel geometry

High aspect ratio micro-channels are known to be beneficial for applications of microfluidic devices. However, the limitation to achieve higher aspect ratio micro-channels is the challenge to demold successfully with no demolding defect. This issue has been reported by a number of researchers in qualitative terms, but there has been no attempt to correlate these with any systematic quantitative study [11-13].

Furthermore, there may be changes in adhesion and friction at the interfaces for the different channel geometry. This is because the extent of thermal stress is also dependent on the overall and relative geometry of mold and polymer substrate. Thus, it is essential to conduct a systematic study to quantify the stresses during demolding because developing such an understanding can enable successful demolding of high aspect ratio micro-channels during hot-embossing. This will also enable the processing conditions to be optimized to achieve successful demolding.

2.2.2.5 Mold surface finishing

It is commonly known that the quality of surface finishing can affect both adhesion and friction properties of the interface. Surface roughness affects the total area of contact between two interfaces that further influences the total

energy needed to overcome adhesion between the surfaces. In addition, mechanical adhesion in terms of mechanical interlocking between asperities can also alter adhesion at the interface. Therefore, mold surface finishing can influence the outcome of demolding.

Sasaki et al. have investigated the effect of mold surface roughness on demolding force of injection molded polymer substrates [58]. Their results indicated that there existed an optimum surface roughness in which the least demolding force was required for all the different types of polymers that they tested. For higher surface roughness, scratch marks were observed on the demolded substrates. The observations matched with the larger demolding force required to overcome the higher friction experienced with high surface roughness. Conversely, as surface roughness became very low, the demolding force increased again. They suggested that such a phenomenon occurred because the meniscus force or van der Waals force of attraction in the smooth surfaces was larger than the scratching force.

2.3 Demolding mechanics

The negative consequence of replication technique by hot-embossing is the formation of bonded interfaces between the mold and polymer substrate. In fact, demolding is the step to separate the replicated polymer substrate from the embossing mold. Therefore, demolding involves fracture of the bonded interfaces. Fracture mechanics is a study about fracture-related failure of either homogeneous or inhomogeneous body, which has been studied extensively. This section explores the relevance of fracture mechanics to debonding of

interfaces in order to build a better understanding in the mechanics of demolding.

2.3.1 Contributors of demolding force

It has been discussed in Section 2.1.2 that demolding is an extremely challenging step that determines the success of the micro-replication process. In order to understand the demolding mechanics, the basic knowledge about what contributes to demolding force should first be clearly determined. One basic contributor that makes the polymer substrate adhere to the mold is adhesion. Adhesion can arise based on different interactions such as chemical and molecular interactions. Adhesion due to chemical interaction includes covalent bonding, acid-base interaction, and inter-diffusion, while adhesion due to molecular interaction includes van der Waals force, and hydrogen bonding. In addition, adhesion can also be contributed by mechanical interaction such as the interlocking of surface roughness or asperities [59]. Wu has further grouped adhesion into three basic categories which are thermodynamic adhesion, chemical adhesion, and mechanical adhesion [60]. While chemical and mechanical adhesion refer to adhesion involving chemical bonding and mechanical interlocking, respectively, thermodynamic adhesion refers to equilibrium interfacial forces or energies associated with reversible processes such as work of adhesion, and heat of wetting.

Figure 2.16 Schematic diagram of forces that contribute to the demolding force with an assumed shrinkage center

The various contributors to demolding force are shown schematically in Figure 2.16. Adhesion due to intermolecular force as well as mechanical interlocking of surface roughness exists in all of the interfaces including horizontal and vertical interfaces. For the vertical interfaces which are the channel sidewalls, frictional force arises upon demolding. As demolding is generally performed at a temperature below the embossing temperature, there will be thermal stress generated on the channel sidewalls due to the different thermal contraction behavior between the mold and polymer substrate. Thus, the higher the thermal stress is, the more significant the frictional force will be, which causes demolding to be more difficult.

2.3.2 Fracture mechanics

Fracture mechanics can be applied to the demolding phenomenon because demolding represents the task to create fracture on the interfaces between the

mold and polymer substrate. Although demolding involves fracture of interfaces between two dissimilar materials, the fundamentals of fracture mechanics which only involves a homogeneous body will still be discussed as the approach remains useful for the development of interfacial fracture mechanics that deals with two inhomogeneous bodies [61]. As fracture mechanics has been studied thoroughly and extensively these days, it will not be elaborated in great detail.

2.3.2.1 Strain energy approach

Fracture mechanics was initially developed by Griffith. In many cases, fracture phenomena can generally be described by using the energy balance approach developed by him [62-63]. Griffith's work was on brittle fracture in a linear elastic material. Consider the situation shown in Figure 2.17 which shows a preexisting crack in an elastic body that is subjected to an external load (P) along the vertical x -direction. Based on the theory of the conservation of energy, the total amount of work done by the applied load should be equal to the sum of total change in the internal energy of the body, the kinetic energy of the body, and energy consumed by propagating the crack or increasing the crack area [64]. However, for the quasi static case in which kinetic energy may be considered to be negligible, and for ideal brittle fracture in which plastic deformation does not occur, a final relationship can be expressed in terms of changes in crack area as:

$$\frac{\partial U}{\partial A} + \frac{\partial \Gamma}{\partial A} = \frac{\partial W}{\partial A} \quad 2-1$$

where:

U Elastic strain energy

Γ Energy consumed to create new surface area

W External work

A Crack area

Figure 2.17 An elastic body with an initial crack (a) that is subjected to external load (P) along the x-direction

During a typical situation in which the body subjected to external load is stationary while the crack propagates (fixed-grip situation), the external work can be neglected [64]. This can happen in a fracture test that operates under displacement control. In this case, the energy consumed in propagating the crack indeed comes from the strain energy that is previously stored and then released from the body. Hence, the term $\frac{\partial U}{\partial A}$ is widely known as strain energy release rate which acts as a parameter for determining the occurrence of crack propagation. If the stored energy exceeds the critical strain energy release rate, the crack will propagate. Therefore, according to Griffith's theory, the strain

energy release rate is the energy spent on the newly created surface area in the body which is equal to 2γ (two crack surfaces) [62-63].

Irwin further extended Griffith's work to ductile materials that considers plastic deformation. In other words, he partitioned the critical strain energy release rate to cover both surface energy and energy spent on dissipative mechanism [65]. The expressions for both of their works so that crack can propagate are eventually expressed as:

$$-\frac{\partial U}{\partial A} \geq G_c = 2\gamma \quad (\text{Griffith}) \quad \text{or} \quad 2\gamma + \frac{\partial U^p}{\partial A} \quad (\text{Irwin}) \quad 2-2$$

where:

- G_c Critical strain energy release rate
- γ Surface energy
- U^p Dissipative energy

The fracture criteria concepts stated above can also be described graphically in Figure 2.18 and 2.19. The strain energy release rate of equation 2-2 is basically the slope of the curve $U(a, x_0)$ under the fixed-grip condition. Stable crack length (initially a_0) corresponds to the minimum energy of the system. When the system changes in such a way that there is another extra displacement (Δx) which is enough to reach the fracture resistance of the system, the energy curve shifts, and the crack propagates to a new stable length ($a_0 + \Delta a$). This corresponds to the new minimum energy condition of the system. As illustrated in Figure 2.19, the energy consumed in creating the

new surface area by crack propagation is supplied by the previously stored energy in the system (shaded area ΔU) [66].

Figure 2.18 Schematic representation of strain energy fracture criterion. A stable crack length corresponds to the minimum energy of the system [37]

Figure 2.19 Schematic representation of load and displacement curve for strain energy fracture criterion. The additional displacement (Δx) causes the crack to propagate by consuming some of the energy stored in the system (ΔU)

2.3.2.2 Stress intensity approach

Another alternative approach other than the strain energy approach is the stress intensity approach which predicts the stress field in the vicinity of the crack caused by any remote load or stress. The detailed derivations have already been well-described in fracture mechanics literatures, so they will not be repeated here. In this approach, the stress field component can be expressed in the form of equation 2-3, with f as a function of the angular coordinate measured from the plane of crack (see Figure 2.17) [67]. The stress intensity factor (K) is defined by equation 2-4 [64].

$$\sigma_{ij}(r, \theta) = \frac{K}{\sqrt{2\pi r}} f(\theta) \tag{2-3}$$

$$K = Y\sigma\sqrt{\pi a} \tag{2-4}$$

where:

- σ_{ij} Stress component
- K Stress intensity factor
- r Radial coordinate measured from crack tip
- θ Angular coordinate measured from plane of crack
- $f(\theta)$ Function of angle θ
- Y Dimensionless parameter (dependent on both specimen and crack geometry)
- σ Far-field tensile stress due to applied load
- a Crack length

As illustrated in equation 2-3, stress goes to infinity at the crack tip ($r = 0$) which is commonly known as stress singularity. Therefore, the fracture criteria

cannot be directly determined based on the maximum stress experienced at the crack tip. The crucial idea about this approach is the similitude of the crack tip stress field. It means that two systems having the same stress intensity factor will have identical stress field at the vicinity of crack in spite of differences in the far-field loading. Fracture takes place when the applied stress increases in such a way that the stress field at the crack tip reaches the critical value. The fracture criteria can be determined based on the critical stress intensity factor (K_c), above which an existing crack will propagate.

Figure 2.20 Three different types of basic loading mode

There are generally three modes to describe different crack surface displacement (see Figure 2.20). Mode I is opening or tensile mode where the crack surfaces move directly apart. Mode II is sliding or in-plane shear mode where the crack surfaces slide over in parallel direction with respect to the crack extension. Mode III is tearing or anti-plane shear mode where the crack surfaces move in perpendicular direction relative to the crack extension. Through substitution of the stress field solution into the strain energy

equations, correlation between strain energy release rate and stress intensity factor can be defined (equation 2-5 and 2-6) which further shows their equivalence [64-65].

For single-mode loading:

$$\begin{aligned}
 G_I &= \frac{\kappa+1}{8\mu} K_I^2 \\
 G_{II} &= \frac{\kappa+1}{8\mu} K_{II}^2 \\
 G_{III} &= \frac{K_{III}^2}{2\mu}
 \end{aligned}
 \tag{2-5}$$

For plane problems with mixed-mode loading:

$$G = \frac{K_I^2}{E'} + \frac{K_{II}^2}{E'} + \frac{\beta(1+\nu)K_{III}^2}{E'}
 \tag{2-6}$$

where:

- G Strain energy release rate
- K Stress intensity factor
- κ Bulk modulus
- μ Shear modulus
- E' Effective modulus (E for plane stress and $E/(1-\nu^2)$ for plane strain)
- β Constant (0 for plane stress and 1 for plane strain)

2.3.3 Interfacial fracture mechanics

The previous Section 2.3.2 makes an assumption of fracture in elastic homogeneous body. Nevertheless, demolding involves interfacial fracture in

two different bodies that has a certain bonding property formed during the initial replication process. Due to the two different bodies (materials), there is discontinuity in material properties which further causes discontinuity in stress state. This can result in shear load at the interface although the far-field load is purely tensile [68]. For example, the discontinuity leads to mixed-mode loading even though tensile loading (mode I) is applied on a system with flat interface.

2.3.3.1 Interfacial adhesion

The key characteristic in separating interfaces of two inhomogeneous bodies is the work that has to be done in order to overcome the adhesion. The work of adhesion (W_A) is defined as the decrease in Gibbs free energy per unit area when an interface is formed from two individual surfaces [60]. Hence, the work of adhesion can also be considered as the reversible work per unit area required to separate the two adhered surfaces. By applying the Dupré relation, the work of adhesion can be expressed in terms of the surface energy of both materials and the interfacial energy between the two materials (equation 2-7) [69].

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad 2-7$$

where:

W_A Work of adhesion

γ_i Surface energy of material i

γ_{ij} Interfacial surface energy between material i and j

However, for low energy systems such as interfaces between metallic molds and polymer substrates, the work of adhesion can be approximated based on the polar (dipole-dipole, induced-dipole, etc) and dispersive (non-polar) components of surface energy as expressed in equation 2-8 below [60]. Nevertheless, the work of adhesion mentioned in equation 2-8 only includes thermodynamic adhesion from intermolecular attractions, while the mechanical adhesion which is based on mechanical interlocking due to asperities is not considered yet. For a low energy system involving a metallic mold and a polymer substrate, it can be expected that mechanical adhesion plays a more significant role than thermodynamic adhesion.

$$W_A = 4 \left[\frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} + \frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} \right] \quad 2-8$$

where:

W_A Work of adhesion

γ_i^p Polar component of surface energy of material i

γ_i^d Dispersive component of surface energy of material i

2.3.3.2 Stress intensity factor

It has been mentioned above that mixed-mode loading tends to happen during fracture even though the whole system is only exposed to single-mode loading. The Dundurs parameters (α and β) are generally used to characterize the elastic mismatch and how great the contribution of a particular mode of loading to the overall mixed-mode loading [61]. The parameter α is related to the tensile mismatch, while β is related to the coupling of tension and shear at

the interface. For a homogeneous material, a far-field tensile stress will not create any shear stress on the interface which is also represented by $\beta = 0$. On the other hand, a larger value of β implies more significant shear stress at the interface (mode II) despite the application of only pure tensile loading on the system (mode I).

$$\alpha = \frac{\mu_2(\kappa_1 + 1) - \mu_1(\kappa_2 + 1)}{\mu_2(\kappa_1 + 1) + \mu_1(\kappa_2 + 1)}$$

$$\beta = \frac{\mu_2(\kappa_1 - 1) - \mu_1(\kappa_2 - 1)}{\mu_2(\kappa_1 + 1) + \mu_1(\kappa_2 + 1)}$$

2-9

where:

α, β Dundurs parameters

μ_i Shear modulus of material i

κ_i Bulk modulus of material i

The stress field at the vicinity of an interfacial crack is a complex function that involves complex stress intensity factor [68, 70]. The complex stress intensity factors (K_I and K_{II}) reduce to conventional stress intensity factors (K_I and K_{II}) for a crack in a homogeneous body. Generally, the determination of the complex stress intensity factor is quite complicated, and they are commonly found through numerical means. The strain energy release rate for a crack in a bimaterial interface can also be correlated to the complex stress intensity factor as shown in equation 2-12 with the assumption of no tearing (mode-III loading) [71]. In addition, the phase angle (Ψ) defines the relative contribution of shear to tensile loading (equation 2-13) [61].

In reports by other researchers, interfacial toughness has been found to increase due to the bigger contribution of shear stress in mixed-mode loading (higher phase angle) [72-73]. Most importantly, the increase in interfacial toughness caused by the increasing phase angle has been found to be attributed to the frictional interaction of asperities [74], and shielding of crack tip by asperities [72]. The findings are crucial as demolding of replicated polymer substrate involves fracture of interfaces with features which may resemble the asperities. Moreover, features are generally much bigger than asperities, and this may lead to more significant increase in interfacial toughness.

$$\sigma_{22} + i\sigma_{12} = \frac{K_1 + iK_2}{\sqrt{2\pi r}} r'^{\varepsilon} \quad 2-10$$

$$\varepsilon = \frac{1}{2\pi} \ln\left(\frac{1-\beta}{1+\beta}\right) \quad 2-11$$

$$G = \frac{1-\beta}{2} \left(\frac{1}{E_1} + \frac{1}{E_2}\right) (K_1^2 + K_2^2) \quad 2-12$$

$$\psi = \tan^{-1}\left(\frac{K_2}{K_1}\right) \quad 2-13$$

where:

- i Square root of (-1)
- σ_{ij} Stress component
- K_i Components of the complex stress intensity factor
- r Radial coordinate measured from crack tip
- ε Bimaterial constant
- β Dundurs parameter

G	Strain energy release rate
E'	Effective modulus (E for plane stress and $E/(1-\nu^2)$ for plane strain)
Ψ	Phase angle

2.3.4 Application of the interfacial fracture mechanics on demolding

This section further explores the application of fracture mechanics to demolding. This is achieved by considering the analogy of interfacial fracture to demolding of replicated polymer substrate from embossing mold.

2.3.4.1 Several different approaches

There have been a lot of different analytical interfacial fracture mechanics models developed by researchers with different assumptions and approaches [66, 75-80]. The different models will not be repeated and elaborated in detail in this section. However, one common feature in all these models is that they were based on a consideration of flat interfaces in between two bonded materials. Therefore, when correlating demolding of replicated polymeric micro-channels to the developed models, the features or channels are assumed to be very small when compared to the overall size of the system such that they do not cause any effect on the macroscopic demolding behavior.

Figure 2.21 Schematic diagram of a demolding process with initial crack of a , vertical displacement of δ , and demolding load of P

To apply the strain energy approach on demolding by considering the Griffith fracture criterion, the strain energy release rate can be expressed in four different LEFM methods based on the obtained demolding load-displacement data [66]. The four different methods are area method (see Figure 2.19), compliance method (equation 2-14), load method (equation 2-15), and displacement method (equation 2-16). The energy method is based on the elastic energy stored in the polymer substrate due to the elastic deformation or bending of the polymer by neglecting the contribution of shear stress for simplicity. As shown in Figure 2.21, the model has an initial crack length (a) at the edge of the polymer substrate, and the polymer is subjected to load P with vertical deflection of δ .

The polymer substrate can be modeled as a cantilever beam in that the value of the compliance can be obtained from the simple beam theory ($C = \frac{\delta}{P} = \frac{a^3}{3EI}$).

Hence, the load and displacement methods can be further derived and expressed from equation 2-14 into equation 2-15 and 2-16, respectively. With the assumption of negligible shear stress on the interface, the final strain energy release rate equations are based on pure tensile mode (Mode I).

$$G_{IC} = \frac{P^2}{2b} \frac{dC}{da} \quad 2-14$$

$$G_{IC} = \frac{6P^2 a^2}{Eb^2 t^3} \quad 2-15$$

$$G_{IC} = \frac{3\delta^2 Et^3}{8a^4} \quad 2-16$$

where:

- G_{IC} Strain energy release rate (Mode-I)
- P Applied load (demolding load)
- δ Displacement at the loading point
- C Beam compliance
- a Crack length
- b Polymer substrate width
- t Polymer substrate thickness
- E Flexural modulus

A lot of the analytical models are still based on linear elastic fracture mechanics which does not take any dissipative mechanism into consideration [66, 75-79]. The work of Irwin has assumed that there exists a tiny plastic zone at the crack tip which further contributes to the overall fracture energy [75]. Nevertheless, plastic dissipation on the body of polymer substrate which is not close to crack tip may also be prone to occur during the peel test (demolding), especially when the adhesion between mold and polymer substrate is extremely strong. With the occurrence of plastic deformation, the determination of correlation between total fracture energy and true intrinsic

fracture energy becomes much more complicated. The total fracture energy includes both true intrinsic fracture energy and the plastic work done.

Georgiou et al. have developed an analytical model that considers the complex bending and unbending processes that happen during peeling with a crucial parameter known as the root rotation angle [80]. They eventually developed an equation that correlates the total fracture energy and true intrinsic fracture energy (equation 2-17). The essential step in their model is the determination of the characteristic length of deformation (Δ). They have reported two different approaches (the linear-elastic stiffness and the critical, limiting maximum stress approach) in order to determine the parameter. However, the required steps further shows the complexity involved in applying the elastic-plastic peel test analytical model. Furthermore, the model is only mainly used to determine the correlation between total fracture energy and true intrinsic fracture energy in a system especially for the evaluation of adhesive applications.

$$G_c = \left(\frac{\Delta}{h}\right) \frac{2G^2}{\sigma_y h} + \frac{\sigma_y^2 h}{2E} \tag{2-17}$$

where:

- G_c True intrinsic fracture energy (critical strain energy release rate)
- G Total fracture energy
- Δ Characteristic length of deformation
- σ_y Yield strength
- E Elastic modulus
- h Substrate thickness

2.3.4.2 Effect of mold features on the interfacial fracture

Previous sections of fracture mechanics have focused on models with the assumption of negligible features at the interface. The features are assumed to be so tiny when compared to the system that they do not affect the overall interfacial fracture process. Nevertheless, features or channels in the application of microfluidic devices are generally big enough to cause significant changes or effects on the interfacial fracture (demolding) process. This issue has been frequently related to the occurrence of plastic deformation or even breakage of the micro-features during demolding.

Evans et al. has studied on the hypothesis of crack tip shielding by asperities [72, 74, 81]. They have proposed that in a brittle interface with sharp crack tip, there will be region near the tip where the separation on the fractured interfaces is of the order of the roughness amplitude of the surfaces as shown in Figure 2.22. This concept has also been used to correlate to demolding of replicated polymeric substrate with features [37].

Figure 2.22 Schematic diagram showing the asperity interaction in the vicinity of crack tip as proposed by Evans et al. [37, 72, 74]

The study by Evans et al. shows that the shear loading which arises due to mixed-mode loading may cause the asperities to come into contact laterally. This contact further creates shielding effect to the crack tip that leads to increase in the overall fracture toughness. Moreover, friction between the asperities enhances the overall toughness through possible plastic dissipation. They have proposed a dimensionless parameter (χ) that is related to the increase in fracture toughness due to the crack tip shielding [72, 81].

$$\chi = \frac{Eh^2}{\Lambda\Gamma_o} \quad 2-18$$

where:

- χ Dimensionless parameter related to crack tip shielding
- E Elastic modulus
- h Height of roughness
- Λ Spacing of roughness
- Γ_o Intrinsic fracture toughness of the interface (work of adhesion)

In their work, they have concluded that no shielding is evident for lower values of the dimensionless parameter ($\chi \leq 10^{-4}$) until the phase angle is close to $\pi/2$ (tendency to mode-II loading). On the other hand, above the value of 1 ($\chi > 1$), it is found that the shielding effect saturates and there is no increase in toughness even with roughness features that are taller in height. A research group in MIT has tried to correlate the dimensionless parameter to demolding of amorphous thermoplastic material [37]. They defined the parameters in equation 2-18 according to material properties and geometries of a typical microfluidic device ($E \approx 3$ GPa, $h \approx 10$ -200 μm , $\Lambda \approx 0.5$ -5 mm, $\Gamma_o \approx 0.05$ -50

J/m²). With the defined range of parameters, they found that the dimensionless parameter lay between 1.2 and 2.4×10^7 . The results eventually imply that demolding of replicated polymeric micro-channels from embossing mold lies on an extreme regime based on the work of Evans et al. This means that the mechanical interaction of the features may enhance the fracture toughness significantly. In other words, the feature is one extremely crucial factor in causing difficulty in demolding.

2.3.4.3 Effect of thermal cooling after hot-embossing

In hot-embossing, the polymer substrate which is going to replicate the patterns in embossing mold has to be heated to elevated temperature (above T_g) so that it softens and flows into the mold cavities with the application of embossing load. Thus, the consequence is the possible development of thermal stress during thermal cooling as demolding is generally executed at temperature below T_g of the relevant polymer substrate. The key factor that causes thermal stress is the difference in thermal contraction behavior between mold and polymer substrate. As mold is generally made of metals for excellent durability and moderate cost, its coefficient of thermal expansion can be one to three orders lower than that of polymers.

In microfluidic applications, there are both horizontal and vertical interfaces that form the micro-channels (see Figure 2.16). As temperature cools down after hot-embossing, both the mold and polymer substrate are going to thermally contract towards their own respective shrinkage centers. In this way,

there may be different interactions in terms of thermal stress in the two different interfaces.

Cannon et al. have studied cracks at the edge of residually stressed thin films and developed an expression for the strain energy release rate as well as crack extension criterion for cracks that are long compared to the film thickness (equation 2-19) [82]. In addition, Dirckx et al. have further utilized the work of Cannon et al. by assuming that mold is rigid and only considering the thermal contraction of polymer substrate in order to describe the generated thermal stress. During the thermal contraction of the polymer substrate, it is assumed that the polymer substrate is completely constrained from contracting for simplicity. Thus, thermal stress will build up based on equation 2-20.

On the other hand, Wu has further considered the contribution of thermal contraction behavior of mold to the overall thermal residual stress (equation 2-21) [60]. By correlating both equations (equation 2-19 and 2-21), it is feasible to develop an expression for strain energy release rate and fracture criterion merely for the horizontal interfaces (equation 2-22). From equation 2-22, it can be concluded that as demolding temperature decreases (higher ΔT), the thermal stress will increase accordingly and eventually reach a state in which the strain energy release rate is equal to the intrinsic interfacial toughness that is mainly contributed by mechanical and thermodynamic adhesion. At that particular state, the horizontal interfaces between the mold and polymer substrate will separate. For cases in which the thermal stress is not large enough to cause interfacial fracture on the horizontal interfaces, demolding may become easier due to the induced thermal residual stress.

$$G = \frac{\sigma^2(1-\nu)t}{E} \geq G_c \quad 2-19$$

$$\sigma = E\varepsilon = E\alpha\Delta T \quad 2-20$$

$$\sigma = E\varepsilon = E\Delta\alpha\Delta T \quad 2-21$$

$$G = E(1-\nu)(\Delta\alpha\Delta T)^2 t \geq G_c \quad 2-22$$

where:

- G Strain energy release rate
- G_c Intrinsic interfacial toughness
- σ Residual stress (thermal stress)
- ν Poisson's ratio
- t Film (polymer substrate) thickness
- E Elastic modulus
- α Linear coefficient of thermal expansion
- $\Delta\alpha$ Difference in the coefficient of thermal expansion between mold and polymer substrate
- ΔT Change in temperature

On the other hand, thermal cooling may cause detrimental effect on the vertical interfaces during demolding. Unlike the horizontal interfaces in that fracture or separation can possibly occur due to the generated thermal stress, the vertical interfaces of the mold act as barriers that constrain the polymer substrate from thermal contraction. Typically, the thermal stress increases with further decrease in demolding temperature (higher ΔT). The thermal stress enhances the compressive force acting on the vertical interfaces that leads to

further increase in frictional force during demolding. With the defined thermal stress as expressed in equation 2-21, the compressive force acting on the vertical interface can be estimated (equation 2-23).

$$F = \sigma.A = E\Delta\alpha\Delta TA \quad 2-23$$

where:

- F Compressive force on the vertical interface (sidewall)
- σ Residual stress (thermal stress)
- E Elastic modulus
- α Linear coefficient of thermal expansion
- ΔT Change in temperature
- A Cross-sectional area of the polymer substrate

Hence, it can be seen that there is a difference in contribution of thermal cooling to demolding of horizontal and vertical interfaces which acts in opposite ways. Lower demolding temperature may lead to fracture on horizontal interfaces, while at the same time, it increases the compressive force on the vertical interfaces. Furthermore, the material properties of polymer substrate are also drastically affected by temperature. Therefore, with the combined effect of thermal cooling on both horizontal and vertical interfaces, and the temperature-dependent material properties, an optimum temperature that leads to easiest and successful demolding could possibly exist. This further shows the important influence of temperature on demolding.

2.3.4.4 Determination of demolding energy

As demolding is the process of separating the embossed polymer substrate from the mold through the process of interfacial fracture, demolding energy that represents fracture energy is one essential parameter in the study of demolding mechanics. The parameter “demolding energy” acts as a measure of strength of the bond between the mold and polymer substrate. It includes the effects of both adhesion and friction, and energy dissipation due to the possible plastic deformation. In addition, demolding energy can be easily measured in a demolding experiment which is similar to an interfacial fracture test. Demolding energy per unit area (demolding energy normalized by area) is also a useful parameter for comparing demolding of molds with different channel geometry (see Section 3.4.3).

Several of the different approaches mentioned in Section 2.3.4.1 have been applied to determine the demolding energy per unit area in one of the demolding experiments. Both compliance and load methods are based on Mode-I fracture with the assumption of negligible effect of features to macroscopic demolding behavior. In the particular demolding experiment with micro-machined mold having feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart, the interfacial crack was found to propagate regularly with each crack extension length of 4.6 mm which is the sum of channel width and spacing. Through the plot of demolding load-displacement curve (see Figure 3.19) and thorough observation during the experiment, it was observed that the crack propagates once the load has dropped to the lowest point right after reaching peak load during demolding of each individual channel (see detail in Section 3.4.1). On the other hand, the area

method is purely based on the calculation of the obtained demolding load-displacement data.

The parameters needed in both the compliance and load methods are obtained from the demolding load-displacement curve. Figure 2.23 shows the similarity in the calculated results based on the three different methods. However, the area method was found to be more applicable than the other methods. Assessment based on area method is efficient and robust because unlike the compliance and load methods, it involves the whole data of the demolding load-displacement curve. This means that it will take into account any phenomenon that may happen during the demolding event such as the mixed-mode interfacial fracture between two inhomogeneous materials (mold and polymer substrate), and the possible plastic dissipation mechanism. The area method simply considers the area under the demolding load-displacement curve in the assessment.

Figure 2.23 Plot of demolding energy per unit area versus crack length determined by several different fracture mechanics methods on mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (demolding at RT with rate of 1.5 mm/min)

On the other hand, the compliance and load methods only consider and utilize several points of the whole demolding load-displacement data. Another drawback is that it may be difficult to define the exact crack extension length that propagates during demolding, as several channels may possibly be demolded at one time. Moreover, the number of channels that is demolded at a time may not be constant which is further dependent on the set of channel geometry used. This can be further seen on the characteristics of experimental data described in Section 3.4.1 based on the different sets of channel geometry. Therefore, the area method is considered as the most suitable method for analyzing the demolding experimental results.

2.4 Large-strain thermo-mechanical behaviour of amorphous polymers in a temperature range which spans their glass transition

In order to achieve a rigorous numerical study, constitutive models of the materials used during the replication process should be implemented, particularly for the polymer substrate. This is because the embossing mold generally has much more superior material properties compared to the polymer substrate. Therefore, in many cases, it is adequate to simply apply the linear elastic model for the embossing mold. Over the past 30 years, a huge amount of effort has been devoted to the development of constitutive models to represent the large-deformation elastic viscoplastic behavior of amorphous thermoplastic materials [83-88].

Nevertheless, hot-embossing requires heating of the polymer substrate to above its glass transition temperature. Thus, a constitutive model developed by Srivastava et al. is used in this work. This constitutive model describes the thermo-mechanically-coupled large-deformation isotropic elastic-viscoplastic behavior of amorphous polymers in a temperature range which spans their glass transition temperature and in a wide range of strain rates [89]. The constitutive model will not be elaborated in detail in this report, but the main features of the model will be summarized. The crucial kinematic ingredient of the elastic-viscoplastic constitutive theory is the micro-mechanism decomposition of the deformation gradient into elastic and plastic parts (equation 2-24).

$$F_{ij} = F_{ik}^{e(\alpha)} F_{kj}^{p(\alpha)} \quad 2-24$$

The variable α denotes the local micro-mechanism of deformation, and there are three micro-mechanisms incorporated in the constitutive model ($\alpha = 1, 2, 3$) as shown in Figure 2.24. The role of each micro-mechanism is as follow:

- The first micro-mechanism ($\alpha = 1$)
 - The non-linear spring represents an “elastic” resistance to intermolecular (and perhaps intra-molecular) energetic bond stretching.
 - The dashpot represents thermally activated plastic flow due to “inelastic mechanisms” such as chain segment rotation and relative slippage of the polymer chains between neighboring mechanical cross-links.

-
- The non-linear spring in parallel with the dashpot represents an “energy storage” mechanism due to the local inelastic incompatibilities caused by viscoplastic flow mechanisms. Such a defect energy is introduced only for the first micro-mechanism, even the role of this defect energy decreases as molecular mobility increases when the temperature approaches and exceeds T_g .
 - The second and third micro-mechanisms ($\alpha = 2,3$)
 - The non-linear springs represent resistances due to changes in the free energy upon stretching the molecular chains between mechanical cross-links.
 - The dashpots represent thermally activated plastic flow due to slippage of the mechanical cross-links, which are relatively strong below T_g , but are progressively destroyed at temperature above T_g . The fact that two such mechanisms are employed is necessitated by the experimentally observed increased complexity of the response of amorphous polymers as the temperature transitions across the glass transition. Any defect energy is neglected in the second and third micro-mechanisms.

Figure 2.24 Schematic spring-dashpot representation of the constitutive model as developed in Srivastava et al. [89]

In the constitutive model, there are quite a number of material parameters that require calibration by fitting the experimental stress-strain data of the relevant amorphous thermoplastic materials. Large strain compression experiments in a temperature range from room temperature to approximately 40°C above the glass transition temperature, and in strain rate ranging from 10^{-3} to 10^{-1} s^{-1} with true strain exceeding 100% were performed for the calibration purpose. The material parameters for cyclic olefin copolymer (Topas 8007) which is the amorphous polymer used throughout this work, have been calibrated based on the constitutive model and compression experiments by Jena et al. [90]

By implementing the constitutive model into a user material subroutine with a three-dimensional single element finite element simulation and the calibrated material parameters, comparison between experimental and numerical true stress-true strain curves based on compression test is as shown in Figure 2.25.

The results further show the reliability of the constitutive model to reasonably and accurately reproduce the true stress-true strain curves of the large strain compression tests at different temperature and strain rate which also involve both loading and unloading. In addition, the constitutive model is also capable of capturing the “elastic recovery” upon unloading. More importantly, the constitutive model has also been successfully implemented to predict different types of experiments such as plane-strain forging, blow-forming, hot-embossing, and thermal bonding [89-90].

Figure 2.25 Fitting of the constitutive model to experimental true stress - true strain curves (Topas 8007 with $T_g = 78^\circ\text{C}$) at temperatures ranging from 22 to 120°C at three different strain rates: (a) 0.001 s^{-1} , (b) 0.01 s^{-1} , and (c) 0.1 s^{-1} . The experimental data is plotted as solid lines, while the model fit is plotted as dashed lines [90]

Chapter 3 Experimental

This chapter will elaborate on the experimental techniques and equipment used to characterize the demolding of hot-embossed polymer substrate by measuring the demolding energy. The commonly used techniques for investigating interfacial fracture are discussed and further compared to the demolding situation in hot-embossing applications. In addition, the experimental set-up, experimental procedures and parameters, as well as the implemented data analysis method will also be elaborated in detail. Then, the reliability of the overall experiments is eventually evaluated and justified.

3.1 Demolding – Experimental techniques

After each hot-embossing process, the replicated polymer substrate needs to be separated from the embossing mold. Thus, a proper and reliable experimental technique is crucially required for the demolding process without damaging the replicated part. Some common experimental techniques used in studying interfacial fracture are the pull test, four-point bending test, wedge test, double cantilever beam (DCB) test, and peel test. The characteristics of each test will be examined so that the most appropriate testing technique for evaluating the demolding process can be selected.

3.1.1 Pull test

The pull test is a straightforward and simple test which only involves normal tensile load F (see Figure 3.1). Generally, the tensile stress at which the bonding fails is considered as the strength of the adhesive joint or interface. As the substrates are pulled apart during the test, stress will be generated on the interfaces between the two bonded substrates. Failure will only occur at a certain level of force which is also known as the maximum force. For all its simplicity, the pull test has one distinct disadvantage in that the progress in failure is rapid and uncontrolled. Hence, it is not feasible to attempt to control the location and progress of interfacial failure during the test. Therefore, this testing method may not be suitable for demolding study of replicated polymer from patterned mold. Furthermore, the polymer substrate may need to be bonded or fixed on one of the platens to enable the load to be applied. More importantly, the pull test is known to produce huge scatter in the resulting data [91-92].

Figure 3.1 Schematic diagram of a pull test

3.1.2 Four-point bending test

The four-point bending test is a fracture test which is based on bending to introduce fracture on the interface of two bonded substrate materials as shown in Figure 3.2 below. As can be observed from the schematic diagram, a notch or pre-crack is initially introduced prior to the bending test in order to create a proper and controlled crack growth. Due to the bending involved during the test, this technique may not be appropriate for evaluating the interface when one of the substrates is rigid as in the case of hot embossing which utilizes a rigid embossing mold. Moreover, the channels or patterns in the mold can hinder initiation and propagation of the interfacial crack. Thus, the four-point bending test is not a suitable choice for demolding study.

Figure 3.2 Schematic diagram of a four-point bending test

3.1.3 Wedge test

The wedge test involves the introduction of a sharp wedge in between the interface of two bonded substrates in order to create interfacial fracture (see Figure 3.3). Wedge test is straightforward in process, and it is a constant displacement test in such a way that crack growth is stable. In addition, it is a test for conducting mode I fracture. In order to study different modes of

fracture, an asymmetrical wedge should be used instead. One drawback in the wedge test is that it is generally used for delaminating two similar adherends. Hence, it will not be applicable for demolding of rigid mold from a much more flexible replicated substrate material. Moreover, there can be a lot of difficulty involved when a wedge is introduced on the bonded interfaces with patterns.

Figure 3.3 Schematic diagram of a wedge test

Another drawback of the wedge test is that huge variations in testing results are commonly observed due to variations in the insertion angle of the wedge. In addition, this test is also known to be sensitive to the other experimental parameters such as the blade insertion distance and insertion speed which further makes this testing method difficult to implement in practice [93].

3.1.4 Double cantilever beam (DCB) test

DCB test requires simple set-up and there exists very well-known bending mechanics such that analysis of the results of this method is quite straightforward. DCB test is executed by pulling the two bonded adherends apart from each other as illustrated in Figure 3.4. The increasing applied load will result in enhanced deflection of both materials where the crack will

propagate once the critical strain energy release rate or critical stress intensity factor has been reached. With this testing method, either constant load or constant displacement based fracture test can be conducted. Nevertheless, similar to the wedge test, the DCB test is generally used to test two similar or identical adherends in terms of their stiffness. Therefore, this method will not be a suitable technique for studying the demolding of a more flexible replicated substrate from a rigid mold. Furthermore, the peeling angle is not changeable (always 90°) in that the interfacial fracture can only involve mode I fracture.

Figure 3.4 Schematic diagram of a double cantilever beam (DCB) test

3.1.5 Peel test

The peel test is almost similar to the DCB test. The only difference is that in the peel test, one material is generally much more flexible than the other material (see Figure 3.5). Therefore, loading is only applied on the flexible material, while the more rigid material remains stationary. With such testing conditions, it is an ideal technique to perform demolding in hot-embossing applications. Most importantly, the mold patterns will not be an issue that can

inhibit the propagation of the interfacial crack during demolding in this testing method.

Figure 3.5 Schematic diagram of a peel test

During the application of load on the more flexible material, localized stress will build up on the peel front until the crack propagates when failure criteria has been reached. The geometry of the test makes it possible to control the location and progress of failure. The peeling rate can also be controlled which permits the study of rate-dependent and time-dependent phenomena such as the visco-elasticity of polymeric materials. Another essential advantage of the peel test is that the peel angle can be altered accordingly so that different modes of fracture can be investigated. The different modes of fracture performed with different peel angles are illustrated in Figure 3.6. Eventually, with all the suitable characteristics of peel test, it is chosen as the most appropriate testing technique for the study of demolding mechanics.

Figure 3.6 Schematic diagrams showing the different modes of fracture with three possible different peel angles (90° , 135° , and 180°)

3.2 Experimental set-up

The two basic steps required in the experiments are hot-embossing of polymer substrate on to the mold, followed by demolding of the replicated polymer substrate from the mold. Thus, a hot-embossing machine will be required. In addition, a specialized demolding apparatus should also be developed in order to perform the demolding experiment. It is also crucial for the demolding set-up to mimic the typical demolding in practice so that the obtained experimental results are relevant and applicable to the real hot-embossing applications, especially during the fabrication of microfluidic devices. Most importantly, the demolding set-up should be able to measure and obtain accurate results. Apart from the hot-embossing and demolding apparatus, embossing mold and polymer substrate are required as the testing specimens. This section will further describe in detail the experimental set-up and specimens used in the study of demolding during hot-embossing.

3.2.1 Hot-embossing apparatus

The two essential features in the hot-embossing machine in order to obtain consistent experimental results are the capability in controlling the applied embossing load as well as the temperature of the specimens. The embossing load should also be evenly distributed throughout the whole heating platens, while the system should be able to maintain the desired temperature at all time. The hot-embossing apparatus used in the experiments is the automatic hot-press machine (Instron) as shown in Figure 3.7. It also has the capability to control the embossing rate as well as maintain the embossing load for a specified amount of time.

Each of the two heating platens is equipped with three cartridge heaters (Hasco type Z110-8x50/160) and located inside an oven chamber. Then, the whole assembly is mounted in an Instron electromechanical load frame. The bottom heating platen is fixed to the frame base, whereas the upper heating platen is connected to a load-cell with an extension rod. The cartridge heaters are further controlled by a temperature control system. In addition, the oven chamber is also built with its own heating capability which has thermocouple installed in it to measure the ambient temperature inside the oven. To obtain a more accurate temperature measurement, two thermocouples are also installed in each heating platen.

Figure 3.7 Photos and schematic diagrams of the hot-embossing apparatus (Instron): (a) Experiment on micro-machined mold, and (b) Experiment on diamond-ruled mold

As illustrated in Figure 3.7, there are two different hot-embossing set-ups (heating platens) for performing hot-embossing on the two types of different molds. Due to the limitation in the overall size of micro-machined mold, demolding was performed using a different machine. After each hot-embossing process of the micro-machined mold, the specimens were cooled down to room temperature and further transferred to another Instron machine equipped with demolding fixture (see Section 3.2.2). It is noted that only demolding at room temperature was performed for experiments on micro-machined mold.

Unlike experiments on the micro-machined mold, the experiments on the diamond-ruled mold also involved demolding at elevated temperature. Therefore, the heating platens underwent some minor amendments due to the combined hot-embossing and demolding processes on the same apparatus (see Figure 3.7b). The bottom heating platen has two mounting-holes for fixing the

mold during the whole process, while the top heating platen has the demolding fixture. The mechanical drawing of the heating platens can be found in Appendix B.2.

3.2.2 Demolding apparatus

In order to obtain reliable and consistent demolding experimental results, there are two important demolding apparatus which are the demolding machine and demolding fixture. The demolding machine should have a motion control system so that consistent testing rate can be achieved in each experiment. Furthermore, the applied load should be captured accurately by the load-cell of the demolding machine. Hence, proper selection of load-cell with suitable load capacity is extremely essential. A load-cell with too huge load-capacity is not capable of measuring small loads. Apart from the demolding machine, a demolding fixture is also needed to transfer the load from the demolding machine to the embossed polymer substrate for demolding purpose.

The Instron machine (frame model 5569) equipped with demolding fixture used during demolding experiments on micro-machined mold is as shown in Figure 3.8a. As demonstrated in the schematic diagram in Figure 3.8b, demolding was performed by utilizing the rod-based demolding fixture. Demolding load was applied to the projecting end of the embossed polymer substrate via a steel bar (rod) located at the front edge of the mold which has initially been fixed to the base of the machine.

During the upward movement of the demolding fixture at a specified rate, the bar started to lift the projecting end of the polymer substrate once they were in

contact. While lifting, a crack between the embossed polymer substrate and mold was initiated, and it further propagated as the demolding fixture continued to move upwards. At the same time, all of the applied demolding load and displacement data were measured and captured into the system. Demolding was only considered to be successfully completed under two possible scenarios. The first scenario was when the embossed polymer substrate has been successfully separated from the mold. And, the second scenario was when the polymer substrate has undergone severe plastic deformation or even cohesive failure like breakage in such a way that it slipped through the demolding bar while experiencing severe bending.

Figure 3.8 (a) Photo of the demolding machine (Instron frame model 5569) with the rod-based demolding fixture used during experiments on micro-machined mold, and (b) Schematic diagram of the rod-based demolding fixture

Similar to the experiments on the micro-machined mold, demolding experiments on the diamond-ruled mold also utilizes a demolding bar (see Figure 3.9). As some of the experiments involved demolding at elevated temperature, demolding was performed inside an oven chamber with heating platens to maintain a consistent temperature at both specimens. Therefore, demolding was performed by using the same hot-press machine which was initially used for hot-embossing purpose (see Section 3.2.1). The top heating platen has mounting holes on both left and right sides so that demolding can be performed by using either one or both sides with the assembly of two through-holes steel plates and steel bars. This specially-designed demolding fixture was also meant for further study of two different demolding approaches, namely one-sided (see Figure 3.9a) and two-sided demolding (see Figure 3.9b).

On the other hand, the bottom heating platen has two mounting holes to fix the mold during the entire hot-embossing and demolding processes. After the polymer substrate has been hot-embossed onto the mold, temperature was then set to the required demolding temperature in both the heating platens and oven chamber. Demolding was eventually performed once the specimens have reached equilibrium demolding temperature based on the temperature readings on both heating platens and oven chamber. As before, the demolding load and displacement data were measured and recorded into the system during demolding.

(a)

(b)

Figure 3.9 Photos and schematic diagrams of the demolding fixture used during experiments on diamond-ruled molds: (a) One-sided demolding, and (b) Two-sided demolding

It should be noted that the load-cell was carefully chosen based on the comparison in the measured demolding load and the quoted accuracy of the load cell. Therefore, the performance of the chosen load-cell to accurately capture all of the loadings measured during the demolding experiments has also been justified. In all of the demolding experiments involving both micro-machined and diamond-ruled molds, a load-cell with loading capacity of 500 N was used. Based on the information obtained from Instron, the quoted accuracy of the load-cell is found to be equal to or better than 0.025% of the load-cell rated output (0.125 N for the 500 N load-cell), or 0.25% of the indicated load, whichever is greater.

3.2.3 Molds

To produce a robust and reliable mold especially for repetitive replications, mold material should be properly selected. The list of possible mold materials used to fabricate microfluidic devices via hot-embossing is as follows:

- Silicon (unsuitable for repetitive replications, especially without coating due to its brittleness [20])
- Steel (excellent wear properties with poor machinability)
- Nickel (challenges in fabrication of micro-sized channels with electroplating technique [94])
- Bulk metallic glass / BMG (excellent wearability and surface finishing, but with high cost)
- Brass (good wearability and machinability with low cost)
- Aluminum alloy (good wearability and machinability, low cost, feasibility in fabrication by hot-embossing with the use of silicon as master mold [95], and fabrication by diamond-ruling method that can produce optical surface finishing)

In microfluidic applications, surface finishing of the mold is one extremely crucial consideration. Most of the microfluidic devices can only function properly with excellent or optical surface finishing. Apart from the surface finishing, fabrication of the micro-devices by replication techniques requires the mold to be robust enough to survive the huge amount of repetitive replications. In addition, low cost is definitely beneficial for industrial applications of polymer micro-molding. Therefore, aluminum alloy (6061-T6)

is eventually chosen as the mold material due to the advantages that it can provide when compared to the other remaining materials.

In this thesis work, two different types of aluminum molds based on different fabrication technique will be used. The first is the micro-machined mold made by the conventional CNC machining tool, while the second is the diamond-ruled mold made by a special diamond tool. In both types of molds fabricated by different tools, patterned and flat molds will be fabricated. Patterned mold will be used for replication of micro-channels into polymer, while flat mold will be used for interfacial model analysis (see Section 4.2.2) and characterization of interfacial property (see Section 5.1).

3.2.3.1 Micro-machined molds

This type of molds was machined by computer numerical controlled (CNC) machining tool from a sheet of aluminium alloy 6061-T6 with overall dimensions of 100 mm by 53 mm and 8 mm thick. There are two different micro-machined molds used in this thesis work which are patterned and flat molds. The features or channels of the patterned mold (see Figure 3.10a) are located in the middle region, while the flat mold (see Figure 3.10b) does not have any channel at all. There are two mounting holes at both sides of each mold so that it can be mounted on the base of demolding machine during demolding.

After machining the patterned mold, all of the top surfaces of mold features were lightly and manually polished with very fine grain-sized silicon carbide paper (FEPA P4000) in order to remove the minor burrs formed during the

micro-machining process. Unlike patterned mold, polishing was not performed on the flat mold. Then, each of the two molds was eventually cleaned with soap to remove the grease applied during machining, followed by rinsing with acetone and DI water.

Figure 3.10 Photos and schematic diagrams of micro-machined molds: (a) Patterned mold with feature dimensions of $360\text{ }\mu\text{m}$ high, $800\text{ }\mu\text{m}$ wide, and 3.8 mm spaced apart, and (b) Flat (featureless) mold

Inspection of the mold feature dimensions as well as surface roughness of both molds was performed with Form TalySurf profilometer and white light confocal microscope, respectively. The final surface finishing of the patterned mold is as illustrated in Figure 3.11. It can be clearly seen that the feature is free of burr. However, there is inevitable cutting mark on the surface of mold due to the contact with cutting tool during milling process. The surface roughness (R_a) of both patterned and flat molds was found to be approximately 300 nm (see Figure 3.12). It should be noted that the channel geometry of the patterned mold was made larger than the conventional dimensions of microfluidic devices due to the limitation in the available machining capability. Nevertheless, they will serve the same purpose in demolding study.

Figure 3.11 Images of micro-machined mold showing the surface finishing quality taken by: (a) Scanning electron microscopy (SEM), and (b) Optical microscope

Figure 3.12 White light confocal microscopy micrograph of a micro-machined mold showing the surface roughness profile ($R_a \approx 300$ nm)

3.2.3.2 Diamond-machined molds

As mentioned above, there is limitation in the surface finishing and channel geometry of micro-machined mold due to the constraint in the available machining facility. However, it is commonly known that better surface finishing and smaller channel geometry are generally required for better performance of microfluidic devices. Those two issues can be eventually tackled by fabricating the embossing molds with the use of high technological precision machining technique by using diamond tools. Therefore, this thesis work will also include and mainly focus on the demolding study of diamond-machined molds.

The machining techniques used to fabricate the patterned and flat molds are known as diamond-ruling and diamond-turning, respectively. Both methods were performed with the use of special diamond tools. The advantage of the diamond-ruling method is that it can fabricate aluminum mold with optical surface finishing, and extremely tight tolerance of $2\text{ }\mu\text{m}$ in the channel

geometry. Similar to diamond-ruling method, diamond-turning method also produces flat aluminum mold with optical surface finishing.

The overall dimensions of both the diamond-ruled (patterned) and diamond-turned (flat) molds were 20 mm wide by 50 mm long and 10 mm thick. Similar to the micro-machined patterned mold, the diamond-ruled molds have features or channels in the middle region and two mounting holes on both sides of each mold (see Figure 3.13a). In the fabrication of the patterned molds, mold features were initially fabricated with the use of diamond tools. Then, the overall sizes of the mold and mounting holes were obtained by further conventional machining process with CNC machining tools.

Figure 3.13 Photos and schematic diagrams of diamond-machined molds: (a) Diamond-ruled patterned mold with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart, and (b) Diamond-turned flat (featureless) mold

On the other hand, there was no feature in the diamond-turned mold (see Figure 3.13b). A cylindrical piece of aluminum alloy was initially diamond-turned in order to obtain optical surface finishing. Then, the final geometry was eventually achieved by using wire-cutting method, and the mounting holes were drilled with conventional CNC machining tool. Before all of the molds were used in experiments, they were all cleaned with acetone and DI water. Due to the optical surface finishing quality ($R_a \approx 40 \text{ nm}$) obtained from the fabrication techniques (see Figure 3.14), additional polishing step was not performed at any of the diamond-machined molds.

Figure 3.14 White light confocal microscopy micrograph of a diamond-machined mold showing the surface roughness profile with optical surface finishing quality ($R_a \approx 40 \text{ nm}$)

Inspection on the channel geometry of the diamond-ruled molds was also performed by using white light confocal microscope (see Figure 3.15). The figures further show that the micro-channels have been successfully fabricated with excellent quality by the diamond tool. In addition, observation by SEM has also demonstrated the good quality of the fabricated micro-channels (see Figure 3.16).

(a)

Figure 3.15 White light confocal microscopy micrograph of a diamond-ruled mold with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart showing: (a) Excellent quality of the fabricated micro-channels, and (b) Measurement of the channel geometry

Figure 3.16 Scanning electron microscopy (SEM) micrographs showing all of the six diamond-ruled molds

As focus of the thesis work is on micro-channels with excellent surface finishing, there are seven molds with different sets of channel geometry that

cover a wide range of channel dimensions (see Table 3.1). In addition, a wide range of aspect ratio from 0.05 to 2 is also included in which aspect ratio of 2 is already considered quite high for microfluidic applications with amorphous thermoplastic polymer as the base material. It should be noted that there are only six diamond-ruled molds used in the experiments (mold 1, 2, 3, 5, 6, and 7), while mold 4 only exists in the numerical simulation. The model of mold 4 is purposely built so that the effect of channel spacing on the thermal cooling process can be numerically studied (see Section 7.1.2).

Table 3.1 List of the seven diamond-ruled molds with their respective channel geometry (Note: mold 4 is only used in the numerical simulation)

Mold	Width (μm)	Spacing (μm)	Depth (μm)	AR (feature)	AR (channel)
1	100	1000	50	0.05	0.5
2	100	500	100	0.2	1
3	100	500	200	0.4	2
4	100	100	50	0.5	0.5
5	100	100	100	1	1
6	100	100	150	1.5	1.5
7	100	100	200	2	2

3.2.4 Polymer substrates

The specimens used to replicate the micro-channels from the patterned mold are made of amorphous thermoplastic material known as cyclic olefin copolymer (COC). It is also known as Topas. There are several Topas grades available in the market such as 8007, 5013, 6013, 6015, and 6017. The

different grades primarily differ with one another in the heat deflection temperature. Further information about the different grades of Topas can be found in the Topas datasheet of the manufacturer. Topas is chosen as the substrate material because it has a lot of advantages such as low density, high transparency, low birefringence, extremely low water absorption, excellent water vapor barrier properties, high rigidity, strength and hardness, very good blood compatibility, excellent biocompatibility, very good resistance to acids and alkalis, very good electrical insulating properties, and very good melt processability/flowability.

In this thesis work, Topas 8007 will be used throughout the whole experiments. Topas 8007 has the lowest glass transition temperature (T_g) out of all the available grades which is about 78°C . The substrate material made of Topas 8007 can be prepared with two different techniques such as injection or compression molding. Injection-molded substrate is much easier and more efficient to produce because the process only needs a very short cycle time. However, there may be issues in the injection-molded substrate in that the produced substrate tends to contain residual stress and some degree of polymer chain orientation. This can happen during the injection molding process because the polymer-melt flows to fill the mold cavity through a tiny gate. It has also been reported that the polymer chain orientation of a substrate material could affect the replication accuracy during hot-embossing [6].

Unlike the injection-molded substrate, the compression-molded substrate does not experience any of those issues. This is simply because of the different processes involved during the molding of polymer substrate. In compression-molded substrate, polymer granules were initially placed inside a metal (steel)

mold cavity with the desired dimensions. Then, they were heated up to the melting temperature of the polymeric material so that the polymer granules could easily fill the mold cavity while pressing load was applied. Thus, there was no long or complicated flow of the polymer-melt while filling the mold cavity. Nevertheless, one drawback of the compression molding process is the requirement of a much longer cycle time.

Figure 3.17 Photos of: (a) Injection-molded polymer substrate, and (b) Compression-molded polymer substrate before cutting

Figure 3.17 shows the polymer substrates prepared by the two different techniques. The injection-molded polymer substrate (see Figure 3.17a) was 36 mm wide by 60 mm long, and its thickness was varied from 1, 1.5 to 2 mm. On the other hand, the compression-molded polymer substrate was initially larger before it was cut into the same sizes as the injection-molded substrate by a plastic cutter (see Figure 3.17b). Polymer substrate with the mentioned sizes was used for the experiments on micro-machined mold. However, it was further cut into smaller pieces using a plastic cutter so that it can fit the smaller-sized diamond-ruled molds (see Figure 3.18). The overall dimensions of the polymer substrate used on the diamond-ruled molds were 10 mm wide by 35 or 50 mm long, and the thickness was varied from 1, 1.5 to 2 mm. The shorter polymer substrate (35 mm long) was used for one-sided demolding, while the longer substrate was used for two-sided demolding. The length was varied so that there was enough front projecting portion of substrate material to reach the demolding bars for demolding purpose. Section 3.5.2 will further explore the effect of the differently prepared polymer substrates to the obtained experimental results.

Figure 3.18 Photo of a smaller injection-molded polymer substrate which was cut and used for experiments on diamond-ruled molds

3.3 Experimental details

The sections below will describe the processes involved in conducting experiments that includes the relevant detailed procedures as well as the experimental parameters.

3.3.1 Experimental procedure

One whole complete test involves several steps that include heating, hot-pressing, thermal cooling, and demolding. Prior to each experiment, the mold was cleaned with acetone and subsequently rinsed with DI water. The embossing mold was initially placed on top of the bottom heating platen, and the polymer substrate was subsequently placed on top of the mold. Both of them were eventually put in contact in between the two heating platens equipped with cartridge heaters inside an oven chamber by moving the top platen downward. Then, the whole assembly was heated to the embossing temperature. Once the temperature readings from the heating platens and oven chamber had reached the embossing temperature, a delay of three minutes was purposely allowed prior to the application of load so that the specimens could achieve equilibrium temperature. During the heating process, contact was achieved and maintained by applying contact load-threshold of 10 N.

Then, the motion control system was switched to displacement-control with a specified ramp rate. At this moment, the polymer substrate was progressively pressed with the previously set embossing load. The load was further constantly held for a short period of time known as holding time. The hot-pressing step was followed with cooling to demolding temperature. For

experiments on micro-machined molds, demolding was only performed at room temperature with the use of different demolding machine due to the larger size of the mold. Therefore, after cooling to room temperature, the specimens were transferred to another Instron machine equipped with demolding fixture, and the mold was mounted at both sides from the through-holes to the base of the demolding machine (see Section 3.2.2).

Conversely, for experiments on diamond-machined molds, demolding was performed at various temperatures with the same machine used during hot-embossing (see Section 3.2.2). Thus, the specimens remained inside the same machine during cooling to demolding temperature. During demolding, the demolding bar which was already assembled on the top heating platen would lift the front projecting portion of the polymer substrate.

3.3.2 Experimental parameters

The relevant parameters used for all of the experiments are described below (see Table 3.2 and 3.3). Some of the parameters were varied over a certain range so that the effect of the parameters could be studied. The other remaining experimental parameters were held constant to isolate the effect of the more important parameters which were the focus of this thesis work. On the other hand, some of the embossing parameters such as embossing temperature, embossing load, and holding time were chosen based on prior experience which resulted in complete filling of the mold cavities.

For the experiments on micro-machined molds, the embossing temperature and demolding rate were set as 100°C and 1.5 mm/min, except during study of

the effect of embossing temperature and demolding rate, respectively. Similarly, the default embossing temperature was also set as 100°C during experiments on diamond-machined molds, except during the experimental study of the effect of embossing temperature. In addition, the default demolding rate tested on diamond-machined molds was 50 mm/min, unless stated otherwise.

Table 3.2 List of the experimental parameters and the values (micro-machined molds)

Parameter	Value
Embossing temperature	100 – 112 °C
Embossing load	1200 N
Embossing load ramp rate	0.5 mm/min
Holding time	30 s
Demolding temperature	25°C (room temperature)
Demolding rate	0.1 – 70 mm/min
Demolding method	One-sided

Table 3.3 List of the experimental parameters and the values (diamond-machined molds)

Parameter	Value
Embossing temperature	100 – 110 °C
Embossing load	300 N
Embossing load ramp rate	0.5 mm/min
Holding time	30 s
Demolding temperature	25 - 70°C
Demolding rate	1 & 50 mm/min
Demolding method	One-sided or Two-sided

3.4 Data analysis method

All of the relevant metrics of demolding will be calculated based on the demolding load-displacement data obtained from each demolding experiment. Therefore, in-depth understanding in the characteristic of experimental data as well as reliable data analysis method should be developed.

3.4.1 Characteristic of experimental data

Based on all of the results, there are two general types of demolding experimental data in terms of the shape of the demolding load-displacement curve. The first type has a unique demolding characteristic in that only a single individual channel will be demolded at a time (see Figure 3.19). This happens continuously until all of the channels have been demolded. It can be observed from the figure that the demolding load-displacement curve has a certain number of peaks and troughs. At the beginning of demolding process, demolding load increases up to a peak until interfacial fracture from the first channel is about to propagate to the next following channel. Then, the demolding load drops to a certain level which corresponds to the end of demolding of that particular channel.

In other words, each peak and trough corresponds to demolding of an individual channel. Eventually, demolding load reduces to zero which corresponds to the end of demolding process. There are eight sets of peak and trough in the demolding load-displacement curve. However, there are nine channels replicated on the polymer substrate, which means that it is lack of a set of peak and trough. This happens because during demolding of the eighth

channel, the strain energy stored in the deflected polymer substrate is adequate to create interfacial fracture up to the last channel. This can also be noticed by observing the tiny increase in load and displacement during demolding of the eighth channel prior to sudden drop to zero.

Figure 3.19 Plot of demolding load-displacement curve (left) and the corresponding schematic diagram of demolding with demolding load P and vertical displacement x (right) tested on micro-machined mold with feature dimensions of $360\text{ }\mu\text{m}$ high, $800\text{ }\mu\text{m}$ wide, and 3.8 mm spaced apart (total of 9 replicated channels)

Unlike the first type of demolding load-displacement curve, the second type is different in such a way that more than a single channel can be demolded at once. Therefore, there is no predictable number of peaks and troughs during demolding when compared to the total number of replicated channels. As illustrated in Figure 3.20, there are only two sets of peak and trough despite the replication of fifty micro-channels. This phenomenon is mainly dependent on the channel geometry and the polymer substrate thickness. If the channel spacing is too narrow such that each channel is very close to the neighboring channels, it may not be feasible to demold a single channel at a time. In addition, the polymer substrate thickness also plays a role because its flexural

rigidity changes with different thickness. This will further affect the deflection of polymer substrate upon demolding as well as the ability to store initial strain energy before releasing some to create new interfacial fracture.

Despite the different characteristics in demolding load-displacement curves, there is no difference in approach for determining the demolding difficulty in terms of demolding energy. The only difference is that with a known set of peaks and troughs, additional information such as the demolding energy for individual channels can be calculated. Nevertheless, the most essential result which is the total demolding energy required to separate the polymer substrate from embossing mold can always be determined.

Figure 3.20 Plot of demolding load-displacement curves tested on diamond-ruled mold with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart (total of 50 replicated channels)

3.4.2 Peel test assessment method

Separation of the hot-embossed polymer substrate from mold is performed by peeling method from the front projecting portion of the polymer substrate with

the use of demolding bar. The important parameters in characterizing the demolding event will be obtained from the measured demolding load-displacement data during the demolding experiment. Hence, it is extremely crucial to have a reliable assessment method in order to draw a valid and reliable conclusion.

From the obtained demolding load-displacement curve, further assessment was performed by applying one of the fracture mechanics methods known as area method. As mentioned in Section 2.3.4.4, assessment based on the area method is efficient and robust because it involves the whole data of the demolding load-displacement curve. This means that it will take into account any phenomenon that may happen during the demolding event such as the mixed-mode interfacial fracture between two inhomogeneous materials (mold and polymer substrate), and any possible plastic dissipation mechanism. In the area method, the area under the demolding load-displacement curve is used for assessment. Referring to Figure 3.19 and 3.20, the total energy spent during the whole complete demolding process can be calculated as the total area under the whole demolding load-displacement curve. This total energy is also considered as total demolding energy.

On the other hand, the energy required to demold each individual channel can also be calculated based on the obtained demolding load-displacement curve (see Figure 2.19). However, it should be noted that this only applies to a demolding event with visible and defined peaks and troughs that correspond to demolding of a single channel. In Figure 3.19, the highlighted area is the energy required to demold a single channel. It shows two different highlighted areas that correspond to demolding energy of the first and second channels.

Similarly, determination of demolding energy for following channels follows the same method in that the point in the demolding load-displacement curve is always located at the trough where each successive channel is demolded. During the determination of demolding energy per channel, it should be noted that the initial increase in demolding load for subsequent channels after the first channel is assumed to be linearly elastic. On the whole, demolding can be eventually characterized and quantified in terms of the demolding load-displacement curve, total demolding energy, and possibly demolding energy per channel for further in-depth analysis, especially under varying both processing and mold parameters.

3.4.3 Demolding energy per unit area

Demolding energy per unit area (J/m^2) is the amount of demolding energy spent (Joule) per unit area of crack growth (m^2). It is an important metric in demolding study especially when demolding results from molds with different channel geometry are compared. In other words, the demolding energy is normalized by the amount of surface area that is created from the interfacial fracture or separation of polymer substrate off from mold. The newly created surface area upon demolding includes both top and bottom horizontal surfaces, as well as the vertical sidewall surfaces. Hence, with demolding energy per unit area, valid comparison in experimental results can be obtained, particularly when the number of channels replicated from each of the different molds varies from one another.

3.5 Reliability of experiments

After detailed elaborations on the experimental technique, experimental set-up, experimental procedures and parameters, and the data analysis method, the reliability of the whole system has to be considered and evaluated. To accomplish reliable conclusions out of the experimental work, the obtained demolding experimental results under each of the varying parameters should be consistent. Furthermore, study on the effect of utilizing injection and compression-molded polymer substrate to the obtained demolding experiment results is also performed.

3.5.1 Repeatability of demolding experimental results

Before a good interpretation of demolding experimental results can be achieved, repeatability of the obtained results should be first assessed. This is to further ensure the level of reliability of the experiments and thus, the withdrawn conclusions. Figure 3.21 shows the plots of calculated total demolding energy and demolding energy per channel which are based on average of three experiments with micro-machined mold. The standard deviation of all experiments on micro-machined mold is found to be less than 10%.

Figure 3.21 Plot of: (a) Total demolding energy, and (b) Demolding energy per channel tested on micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (demolding at RT with rate of 1.5 mm/min and 2 mm thick substrate)

There is also identical observation in the repeatability of the demolding experimental results on diamond-ruled molds. Standard deviation always falls below 10% in all of the experiments performed under different sets of parameters. The small degree of deviations in the plots (see Figure 3.21 and 3.22) has successfully demonstrated the consistency of the obtained results. In conclusion, the implemented experimental technique and data analysis method have proven to give reliable and consistent experimental results. Hence,

reasonable interpretation as well as solid conclusion can eventually be accomplished.

Figure 3.22 Plot of total demolding energy tested on diamond-ruled mold with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart (demolding rate of 50 mm/min and 2 mm thick substrate) at (a) 25, 40, and 50°C, and (b) 60°C

3.5.2 Comparison between injection and compression-molded polymer substrates

Study on the various parameters that affect demolding will involve a lot of experiments. Therefore, a huge number of polymer substrates will be required. It has been commonly known that injection molding requires much shorter cycle time to produce polymer substrates when compared to compression molding. Thus, it may be much more efficient and easier to produce injection-molded polymer substrate rather than compression-molded polymer substrate. As mentioned in Section 3.2.4, there may be issues regarding to injection-molded polymer substrate such as the residual stress and polymer chain orientation which is determined by the flow of polymer melt from the injection gate into the mold cavity. Conversely, compression molding technique can prevent such issues from happening. With the consideration in the benefits of each polymer substrate preparation techniques, further evaluation to study on the influence of the differently prepared polymer substrates to demolding experimental results is performed.

Experiments on a micro-machined mold with identical experimental parameters were performed by using the two different polymer substrates. As demonstrated in Figure 3.23, it is found that both tests give relatively similar results. Moreover, there is also comparable trend and value in terms of the demolding energy per channel for both of the experiments with injection-molded and compression-molded polymer substrates. The obtained results eventually suggest that the effect of residual stress and polymer chain orientation in the injection-molded polymer substrate may have been relieved during the heating step of the hot-embossing process. Hence, it can be

concluded that injection-molded polymer substrate can be used to perform all of the experiments in this thesis work.

Figure 3.23 Plot of: (a) Total demolding energy, and (b) Demolding energy per channel tested on micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (demolding at RT with rate of 1.5 mm/min and 2 mm thick substrate), showing the influence of the differently prepared polymer substrates (injection-molded versus compression-molded)

Chapter 4 Numerical analysis and development of model

In this chapter, the numerical model used to study the fabrication process of hot-embossed polymeric device will be outlined. The drawback of work reported by others is initially discussed. Then, our implemented numerical model and its advantages are further elaborated. Numerical simulation was performed by using ABAQUS/Standard, and for simplicity, all of the numerical model used are restricted to two-dimensions with plane-strain idealization. The performance of the implemented numerical model is eventually justified with experimental validation.

4.1 Current research work by others

In spite of its importance, there has not been any rigorous or extensive numerical study of the micro-replication of polymeric micro-channels, particularly the demolding process. Several researchers have developed simplified two dimensional numerical models with only a single or double channeled polymer adhered to an embossing mold, and simulated the demolding process by only incorporating the thermal residual stress that corresponds to thermal cooling [5, 11, 22-24]. The interfacial model used was mainly a frictional model that was assumed to have no temperature dependency. In addition, simple linearly elastic material properties were used in the material model. There have also been reports of demolding studies that utilized the cohesive zone model (CZM) as the interfacial model that

implemented a specific traction-separation behavior on the interfaces [12, 14]. The cohesive zone model is not straightforward to implement because the different fracture modes at the interfaces must first be characterized. In both of the reported works by Chan Park and Yeo, they made an assumption of identical fracture properties between mode I and II. Apart from this, there was also a simplification in their model which only considered a few channels.

Figure 4.1 Illustration of a simplified model with its boundary conditions during thermal cooling and demolding

The general simplification of the numerical model with the imposed boundary conditions is as illustrated in Figure 4.1. The crucial drawback of the simplified model is the difficulty in imposing proper sets of boundary conditions such that the model can behave in a way that truly reflects the real processes. In other words, no work which considers the full geometry of polymer substrate with the complete number of channels has been made to date. This can be extremely essential because both mold and polymer substrate cannot thermally contract towards their own real shrinkage center as a result of

the simplification. Hence, thermal stress due to cooling cannot be accurately obtained. For example, as shown in Figure 4.1, both the mold and polymer substrate will thermally contract towards AC which is not the real shrinkage center of both specimens.

Secondly, there may be a certain bending behaviour of the polymer substrate during demolding, especially by the generally known peeling method. Therefore, it is also not feasible to impose a set of boundary conditions such that the simplified model is not over-constrained during demolding. For example, during demolding of the simplified model, the polymer substrate tends to slide upwards at AC and it is not allowed to tilt when a demolding load is applied at node D. As a result of the two factors, the final demolding outcome will be affected.

In addition to the simplification of the model, no work on the whole micro-replication process which involves hot-pressing, thermal cooling, and demolding combined in a single model has been reported. Such comprehensive analysis of the entire micro-replication process is essential as this will permit assessment of the effect of the hot-pressing step to both the cooling and demolding results, because residual stresses may be generated in the polymer substrate during the hot-pressing. Most importantly, none of the previously reported models has been validated experimentally. They were only used for trend studies in the influence of certain parameters to demolding.

Therefore, in short, there has been no known numerical model that can reasonably and accurately simulate as well as predict the real micro-replication process both quantitatively and qualitatively. The quantitative results include

considerations based on the measured demolding load-displacement curve, and the calculated demolding energy. On the other hand, the qualitative results refer to the capability of the model in predicting demolding outcome of the polymer substrate in terms of its replication fidelity.

4.2 Material and interfacial model

In the numerical simulation of the replication processes, there are two important models which are the material and interfacial models. The material model is required to characterize the properties of both the mold and polymer substrate under different conditions, while the interfacial model is used to determine the properties at the interfaces between the mold and polymer substrate that are formed during replication.

4.2.1 Material model

The polymer substrate (Cyclic olefin copolymer – Topas 8007) is modelled with the constitutive theory that represents the large deformation, thermo-mechanically coupled, elastic-viscoplastic behaviour of amorphous thermoplastic material spanning the glass transition temperature (see Section 2.4) developed by Srivastava et al [89]. The material parameters for Topas 8007 were obtained from calibration based on large strain compression experiments which were done and extracted from the work of Jena et al [90].

As the constitutive model of the polymeric material was calibrated based on compression tests, it cannot predict any fracture or polymer breakage that may

happen due to tensile stresses during demolding. It should be recognized that for demolding at lower temperatures, brittle failure which is preceded by the crazing phenomenon in the polymeric material (see Section 5.2) can occur. Therefore, the temperature-dependent and rate-dependent tensile properties of COC – Topas 8007 have also been characterized based on tensile tests. The possible onset of crazing as a precursor to fracture can be predicted through an analysis on the maximum principal stress experienced by the polymer substrate during demolding, and by comparing this to the fracture strength of the polymer.

On the other hand, the aluminum mold is simply modelled as an isotropic linear elastic solid with the properties of aluminum alloy (AA6061-T6). The simple material model for the mold can be justified based on the superior properties of aluminum alloy when compared to Topas 8007. This further means that the mold is unlikely to plastically deform during the micro-replication process. The material properties of the aluminum mold used in the simulation is tabulated in Appendix A.2.

4.2.2 Interfacial model

Apart from implementing the constitutive model for the polymeric material, it is also imperative to develop an appropriate interfacial model before the micro-replication process can be simulated. A unique interfacial model has to be developed for modelling the displacements and stresses at the interfaces between the mold and polymer substrate because there is some bonding between these two materials which have very different properties. An

analytical analysis will be developed, and it will be further verified experimentally so as to confirm the applicability of the final interfacial model that is to be implemented.

4.2.2.1 Analytical analysis

As mentioned in Section 2.3.4.3, the consequence of the thermal cooling process after hot-embossing is the development of thermal stress on the polymer substrate. The key factor that causes thermal stress is the significant difference in thermal contraction behavior between the mold and polymer substrate. Microfluidic devices generally consist of micro-channels that have both horizontal and vertical interfaces. Nevertheless, the effect of thermal stress on these two kinds of interfaces is totally different.

Based on equation 2-22, the strain energy release rate on the horizontal interfaces at different demolding temperature can be calculated and plotted (see Figure 4.2a). When the strain energy release rate is equal to the intrinsic interfacial toughness of the interface, the adhesion between the mold and polymer substrate will break. The intrinsic interfacial toughness is mainly contributed by the mechanical and thermodynamic adhesion in the case of the aluminum mold and Topas 8007 substrate. In this study, the intrinsic value was not calibrated. However, it can be easily concluded that when demolding temperature decreases, the adhesion becomes weaker. Moreover, it is also possible for the temperature effect to destroy all the adhesion on the horizontal interfaces prior to demolding.

Figure 4.2 Plot of (a) Strain energy release rate on horizontal interfaces, and (b) Compressive force on vertical interfaces, at different demolding temperature with embossing temperature of 100°C

On the other hand, based on equation 2-23, the compressive force acting on the vertical interfaces shows the converse effect. As illustrated in Figure 4.2b, the compressive force increases with lower demolding temperature. This further creates more difficulty in demolding because higher frictional force will be encountered. Hence, the analytical results have shown that thermal stress indeed helps in demolding of horizontal interfaces, but worsens in the demolding of vertical interfaces.

It should be noted that demolding is generally performed at a temperature lower than the embossing temperature. This is to ensure that the polymer substrate has adequate strength in order to withstand the high stress experienced during demolding without experiencing any defects. Therefore, based on the analytical results, it can be deduced that the thermal stress on the vertical interfaces is the only factor which contributes significantly to the difficulty in demolding, while adhesion contribution on horizontal interfaces is minor or even negligible at demolding temperature. Thus, it may be reasonable to only consider frictional factor on the vertical interfaces in the interfacial model which will also incorporate thermal stress contribution.

4.2.2.2 Experimental analysis

The experimental analysis is used to validate and support the findings from the analytical analysis. There are two different types of aluminum mold used in the experimental work which are the micro-machined and diamond-machined molds. Hence, in the experimental analysis, both types of molds will be used and analyzed. Demolding at only room temperature was performed on the micro-machined molds, while demolding at varying temperature was conducted on the diamond-machined molds.

A. Micro-machined molds

In order to validate the hypothesis obtained from the analytical analysis, studies on demolding of hot-embossed polymer substrate from both flat and patterned molds was carried out. As illustrated in Figure 4.3a with the

assumed shrinkage center, debonding in the flat mold only involves interfacial fracture on horizontal interface. On the other hand, it can be seen from Figure 4.3b that demolding from a patterned mold involves interfacial fracture on both the horizontal and vertical interfaces. In both experiments on flat and patterned molds, the polymer substrate covered an identical projected area of contact (40 mm x 36 mm). Nevertheless, it should be noted that the actual total area of contact or adhesion between mold and substrate is higher on patterned mold due to the additional vertical surfaces. In addition, identical hot-embossing and demolding conditions were used in both experiments (see Table 3.2).

Figure 4.3 Schematic diagram of demolding on: (a) Flat mold, and (b) Patterned mold, corresponding to interfacial fracture on only horizontal interface, and both horizontal and vertical interfaces, respectively

The demolding energies for the flat and patterned molds were found to be extremely different (see Figure 4.4b). Total demolding energy per unit area instead of only total demolding energy is calculated and utilized due to the different actual total area of contact between the two. Unlike the patterned mold, the demolding load tested on the flat mold does not involve any peak and trough (see Figure 4.4a). This happens due to the absence of the vertical interfaces or mold features. The percentage of total demolding energy per unit area spent on flat mold is found to be only 0.96% of the energy per unit area spent on patterned mold. Thus, based on the obtained results, it can be concluded that the contribution of adhesion between mold and polymer substrate from the horizontal interfaces to demolding at room temperature is almost negligible. On the other hand, the thermal stress generated during cooling process combined with the frictional property on the vertical interfaces are found to have a significant influence on the demolding energy.

Figure 4.4 Plot of: (a) Demolding load-displacement curve, and (b) Total demolding energy per unit area, obtained from experiments on flat and patterned micro-machined molds

B. Diamond-machined molds

Similarly, demolding of polymer substrate from both flat and patterned molds fabricated by diamond tools is also compared. It should be noted that the demolding study on diamond-machined molds is performed at varying temperature in order to consider the effect of temperature on demolding. This is mainly because of the temperature-dependent adhesion property on the horizontal bonded interfaces. It has already been commonly known that adhesion becomes stronger at higher temperature. Therefore, it may be feasible that the frictional interfacial model which mainly focuses on the vertical interfaces may not be robust enough to accurately simulate demolding at elevated temperature.

In all of these experiments, the polymer substrate covered an identical area of 20 mm x 10 mm on the molds. It is also noted that identical hot-embossing and demolding conditions were used in both types of experiments (see Table 3.3). Figure 4.5 shows the calculated total demolding energy tested on both

flat and several of the patterned molds at different demolding temperatures. It can be observed that the total demolding energy spent on the flat mold is relatively much lower than the total demolding energy spent on the patterned molds. Almost no energy is required to demold the hot-embossed polymer substrate from the flat mold at room temperature. On the other hand, as expected from the temperature-dependent adhesion property, the obtained total demolding energy tested on the flat mold increases with increase in demolding temperature.

Figure 4.5 Plot of the total demolding energy calculated from experiments on flat and patterned molds at varying demolding temperatures (the two plots are made in different scale for clear observation)

The relative percentage of the total demolding energy spent on flat mold with respect to all of the used patterned molds is as shown in Table 4.1. It should be noted that no demolding energy (0 mJ) is required during demolding on flat mold at room temperature. Therefore, there is negligible contribution of adhesion on the horizontal interfaces to demolding at room temperature. There is no data for demolding at 70°C for mold 3, 5, 6, and 7 because the polymer substrate has already experienced severe plastic deformation during demolding at 60°C. Thus, no additional demolding experiments at 70°C were carried out.

It can be deduced from Table 4.1 that, for low demolding temperatures of between 25 to 50°C, the adhesion of the horizontal bonded interfaces contribute very little to the overall total demolding energy of the patterned molds. As expected, the adhesion factor becomes more prominent when demolding is performed at higher temperatures. Quite high percentage values are observed during demolding from mold 1 and 2 at 60°C when compared to the other patterned molds at the same demolding temperature. The high values arise because of the relatively low aspect ratio micro-channels of the two molds. As a result, they are more similar to flat mold in terms of the overall demolding difficulty, and thus the percentage values become higher.

Table 4.1 List of the percentage of demolding energy spent on flat mold divided by demolding energy spent on patterned molds at varying demolding temperatures (experiments)

Demolding Temperature	Mold					
	1	2	3	5	6	7
25	0%	0%	0%	0%	0%	0%
40	5.31%	1.63%	0.80%	1.18%	0.36%	0.12%
50	13.51%	5.10%	2.45%	2.96%	0.36%	0.20%
60	42.61%	21.73%	0.23%	0.24%	0.14%	0.04%
70	1.95%	1.20%	-	-	-	-

On the other hand, it can also be seen from Table 4.1 that the calculated percentage values are quite small for the demolding of mold 1 and 2 at 70°C, and mold 3, 5, 6, and 7 at 60°C. This is due to the plastic deformation experienced by the polymer substrate during demolding on the patterned molds. At higher temperature, the polymer substrate becomes more prone to plastic deformation due to the increase in both adhesion and frictional properties, as well as the decrease in mechanical strength of the polymeric material. The occurrence of such plastic deformation causes higher demolding energy to be spent. Unlike the patterned molds, no plastic deformation is observed during demolding of flat mold even at 60 and 70°C which corresponds to much lower demolding energy. Hence, the calculated percentage values are relatively much smaller.

Figure 4.6 Pictures showing the interfacial bonding on both horizontal and vertical interfaces based on the three different regions (leftmost, center, and rightmost): (a) Before thermal cooling, and (b) After thermal cooling to 60°C (numerical simulation)

Nevertheless, the calculated percentage values in Table 4.1 may have been overestimated because some of the bonded horizontal interfaces on the patterned molds may have separated during the thermal cooling process. This phenomenon can be observed through additional analysis based on the numerical simulation (see Figure 4.6). Such separation can happen due to the interaction of polymer substrate with the mold features during thermal contraction. As the mold features are constraining the polymer substrate from thermally contracting, both ends of the polymer substrate may tend to move upwards through sliding on the vertical interfaces. As illustrated in Figure 4.6b, only some of the initial bonded interfaces may still remain bonded, especially in the middle region of the replicated micro-channels. In contrast, during thermal cooling on the flat mold, all of horizontal interfaces between the mold and polymer substrate still remain in contact. And, this makes the consideration in the bonded area of horizontal interface based on the flat mold over-estimated when compared to the patterned molds.

On the whole, the generally low percentage values of less than about 5% in the relative demolding energy spent on flat mold with respect to patterned molds clearly show that it is reasonable to neglect the contribution of adhesion on the horizontal interfaces of the micro-channels in the numerical model. Moreover, the elaborated experimental analyses on both micro-machined (see Section 4.2.2.2 A) and diamond-machined molds (see Section 4.2.2.2 B) have also revealed the agreement to the initial finding based on the analytical analysis (see Section 4.2.2.1).

4.2.2.3 Final implemented interfacial model

Based on the obtained results from both analytical and experimental analyses, a summary of conclusions can be drawn on the implemented interfacial model. Firstly, the frictional interfacial model can be implemented in the numerical model to yield reliable results. It has several benefits when compared to the other fracture mechanics model such as the surface-based cohesive model. Some of the benefits are the simplicity during implementation in numerical model, the much shorter computational time, and the much easier characterization and calibration of the interfacial friction property between mold and polymer substrate.

There are several steps involved during the replication process of microfluidic devices, and the steps involve change in temperature. Therefore, the implemented frictional interfacial model will be temperature-dependent. In addition, it has also been mentioned that microfluidic devices generally consist of micro-channels which have both horizontal and vertical interfaces. In the numerical model, frictional model will be implemented on all of the contacting interfaces including both horizontal and vertical interfaces.

With only frictional property implemented as the interfacial model, Coulomb friction interaction will be used to represent the interfacial property between the mold and polymer substrate. The implemented Coulomb friction interaction on ABAQUS/Standard uses penalty friction formulation and hard contact pressure-overclosure [96]. The temperature-dependent interfacial friction property between aluminum mold and Topas 8007 substrate will be further elaborated and characterized in Section 5.1. Justification on the final

implemented interfacial model will also be performed through experimental validations (see Section 4.5).

4.3 The effect of hot-pressing step in the numerical studies

During replication by hot-embossing, the thermoplastic polymer substrate is initially hot-pressed against a mold at above the glass transition temperature of the polymeric material. In the hot-pressing step, the softened polymer is in contact with the mold as it flows into and fills the mold cavities. This may induce internal stresses in the polymer substrate prior to the thermal cooling process. The residual stresses that are induced due to the application of embossing load may affect the level of thermal stresses generated within the polymer substrate after thermally cooled to the demolding temperature, and therefore affect the degree of difficulty in demolding. As mentioned above, such a study has not been reported yet.

One of the main considerations in incorporating the hot-pressing step in numerical simulation is the requirement of a much longer computational time. A huge number of elements should also be used in the model so that severe distortion of the elements during the hot-pressing step can be prevented. As a result, the computational time is increased quite substantially. Therefore, the investigation on the influence of the hot-pressing step on the generated stress in the polymer substrate as well as the final demolding process was performed on a simple single-channeled model.

The numerical model was created based on the micro-machined mold used in the experiments. However, the channel depth was reduced from 360 μm to

100 μm in this study, because there was difficulty in the convergence of the numerical result when the channel was 360 μm deep during the hot-pressing step. The difficulty arose because there was extremely severe distortion on the elements when the polymer substrate was hot-pressed into the deeper mold cavities. Despite this simplification and modification, the model can still serve to verify the influence of the hot-pressing step on the generated thermal stress after thermal cooling, and eventually on the demolding outcome.

4.3.1 Single-channeled model

In this study, two identical models with only a single channel (100 μm deep, 800 μm wide, and spaced at 3.8 mm) were used. The first model begins with a piece of polymer substrate that is located on top of the mold prior to the hot-pressing step (see Figure 4.7). On the other hand, the second model begins after the polymer substrate has been hot-pressed and there is already complete filling of polymer substrate into the mold cavities (see Figure 4.8). It should be noted that the mesh was made much denser and finer on the region near the mold feature. This is to ensure that severe distortion of elements can be accommodated, and accurate quantitative results can be achieved. The model was meshed with quadrilateral, linear order plane strain elements (ABAQUS/Standard element type CPE4HT). Then, the interfacial friction property was applied based on the characterization and calibration of the interfacial property on the micro-machined mold (see Section 5.1).

The first model incorporates all of the three steps involved during replication via hot-embossing which are hot-pressing, thermal cooling, and demolding.

The numerical simulation started with an even temperature distribution in both the mold and polymer substrate at the embossing temperature, because they were initially heated in between two heating-platens inside an oven chamber during experiments. Then, an evenly distributed load (pressure) was applied on the top surface of polymer substrate (AC) through an analytical rigid surface (shown as a line in Figure 4.7) that represents the top heating platen. The embossing load was gradually increased in a period of 470 seconds and held for another 30 seconds. During the hot-pressing step, both the leftmost and rightmost sides of the polymer substrate (AB and CD) as well as the mold (EF and GH) have displacement boundary condition of $u_1 = 0$, and were constrained against in-plane rotation. The bottom horizontal surface of mold (FH) was also fixed with boundary condition of $u_2 = 0$.

Then, cooling from embossing to demolding temperature (room temperature) based on isothermal condition was simulated with displacement boundary condition of $u_1 = 0$ on the leftmost sides of both polymer substrate (AB) and mold (EF), and $u_2 = 0$ on the bottom horizontal surface of mold (FH). At the same time, the embossing load applied through the analytical rigid surface was gradually released to zero in 300 seconds, while the total duration required for the thermal cooling process was set at 1200 seconds. The displacement boundary condition of $u_1 = 0$ applied on both AB and EF basically assumes that both the mold and polymer substrate are thermally contracting towards the left. After cooling to room temperature, demolding was further performed by applying a prescribed velocity on the bottom right corner node of the polymer substrate (node D), while maintaining the previous boundary conditions applied during the thermal cooling process. The prescribed velocity boundary

condition represents the demolding rate used in experiments. During demolding, the analytical rigid surface also moved upward so that it would not constrain the movement of polymer substrate. Eventually, the demolding load and displacement was obtained from node D.

Figure 4.7 Numerical model that includes all of the three steps involved in replication process (hot-pressing, thermal cooling, and demolding)

Conversely, there are only two steps involved in the second model which are thermal cooling and demolding. In terms of the application of boundary conditions in the model, they were all identical to the boundary conditions applied in the first model that incorporated the hot-pressing step. The boundary conditions applied during cooling were $u_1 = 0$ at AB and BE, and $u_2 = 0$ at EF, while during demolding, a prescribed velocity was applied at node D. In addition, both models have relatively similar number of elements for valid comparison.

Figure 4.8 Numerical model that only includes two processing steps (thermal cooling, and demolding)

4.3.2 Result

The results obtained from both numerical models are further compared in order to investigate if hot-pressing step had a significant influence on the data. After the hot-pressing step, it is found that there is a maximum residual stress (Von Mises) of 4.932 MPa on the two inner corner edges of the polymeric channel (see Figure 4.9). The highest residual stress arises at those regions because of contact with the corner edge of the mold feature where stress concentration is located. Based on the results obtained from the model, it can be seen that there is indeed an initial residual stress generated on the polymer substrate due to the applied embossing load.

Figure 4.9 Contour plot of residual stress (Von Mises) on polymer substrate after the hot-pressing step

During the following thermal cooling step, thermal stress gradually increases on both polymer substrate and mold because there is mismatch in thermal contraction behaviour between the two. Figure 4.10 shows the contour plot of thermal stress after cooling from embossing to demolding temperature which is room temperature. Both models show the relatively similar thermal stress distribution on the polymer substrate. Nevertheless, the maximum thermal stress of the model with hot-pressing step (44.55 MPa) is slightly higher than that of the model without the hot-pressing step (41.93 MPa). The observed result further demonstrates the small influence of the initial residual stress generated on the polymer substrate during the application of embossing load on the final overall thermal stress in the polymer substrate after cooling to the demolding temperature.

In addition, it has been found that the difference in the maximum thermal stress calculated from both models (2.62 MPa) is less than the maximum

initial residual stress formed during the application of embossing load (4.932 MPa). There are two reasons that cause this difference. Firstly, during thermal cooling to room temperature, the embossing load gradually decreases to zero because it is no longer constantly held. As the load decreases, there will be elastic recovery on the polymer substrate that may relieve some of the initial residual stress. Secondly, the region with the maximum thermal stress is not located at the same region (elements) where the initial residual stress is highest after the hot-pressing step.

Figure 4.10 Contour plot of thermal stress (Von Mises) on polymer substrate after thermally cooled to room temperature: (a) Model with hot-pressing step, and (b) Model without hot-pressing step

Before conclusion on the effect of hot-pressing step on the overall result can be drawn, final comparison in demolding outcome should be made. Figure 4.11 shows the comparison in the obtained demolding load-displacement curves from both models. Demolding load obtained from the model with hot-pressing step is found to be slightly higher than the model without hot-

pressing step. The result follows the obtained trend in thermal stress, as the difficulty in demolding is directly related to the amount of thermal stress generated on the polymer substrate. Nevertheless, there is only a small difference of 6.28% in the calculated demolding energy. Therefore, it can be concluded that it is reasonable to neglect the hot-pressing step in the numerical model. By doing so, quite a significant amount of computational time can be saved. Moreover, severe distortion of elements due to the hot-pressing step can be prevented as well.

Figure 4.11 Plot of demolding load-displacement curves obtained from models with and without hot-pressing step, showing the relatively similar results

4.4 Implementation of new model

With consideration of the drawbacks and limitations of the previous research by others, both the material and interfacial model have been developed. Furthermore, as the hot-pressing step has been proven to cause minor influence to thermal stress and the overall demolding result, it is reasonably valid to skip the hot-pressing step in numerical model without the need to

compromise on the obtained results. This section will further elaborate in detail about the final implementation as well as the advantages of the new model.

4.4.1 Final numerical model

The final numerical model used in this thesis work considers the full geometry of both mold and polymer substrate with the real dimensions as used in experiments (see Section 3.2.3 and 3.2.4). Figure 4.12a and Figure 4.12b show the full geometry model of tests on micro-machined and diamond-ruled molds, respectively. By neglecting the hot-pressing step, the polymer substrate is assumed to have completely filled the mold cavities. The model is built under plane strain idealization in that the width of both specimens is only incorporated during the calculation of demolding load.

Similar to the previous single-channeled model, the mesh was made much finer in the regions near the mold features. In addition, two different types of elements were used in the model. Polymer substrate with regions near the mold features was meshed with full-integration, quadrilateral, linear order plane strain elements (element type CPE4HT). On the other hand, the remaining regions of polymer substrate as well as all the regions of the mold were meshed with reduced-integration element (element type CPE4RHT). The reduced-integration element only has one integration point, while the full-integration element has four integration points. The full-integration elements were only used in important regions that are susceptible to high stress, so that accurate results can be obtained. Conversely, the remaining regions were

meshed with reduced-integration elements in order to minimize the total computational time. The interfacial friction property was applied on all of the contacting interfaces based on the calibrated values with the respective molds.

Figure 4.12 Final numerical model with full geometry: (a) Micro-machined mold, and (b) Diamond-ruled mold

To prevent rigid body motion during the thermal cooling process, displacement boundary condition of $u_1 = 0$ was applied on a single node in the middle of the mold (node C), and $u_2 = 0$ was applied on all of the nodes at the bottom surface of mold (AB). On the other hand, the polymer substrate has no set boundary condition at all during the cooling process. This is to accommodate for simulation of the real thermal contraction that happens on the polymer substrate without providing any unreal constraints. Nevertheless, it should be highlighted that the imposed boundary condition on polymer

substrate is highly dependent on the actual experimental set-up. For example, during rare cases in which the polymer substrate is anchored to the substrate holder, or there is very high frictional contact between polymer substrate and its holder, the currently imposed boundary condition (no set boundary condition) on polymer substrate may not be a good approximation. In addition, temperature was set on both mold and polymer substrate to cool down from embossing to demolding temperature based on isothermal condition.

While performing demolding, node C and the bottom surface of the mold (AB) were still fixed at $u_1 = 0$, and $u_2 = 0$, respectively. This set of boundary conditions corresponds to the mold that was mounted during demolding experiments. In addition to the mentioned boundary conditions, prescribed velocity boundary condition was applied on node D that was located at the front projecting portion of polymer substrate. In the models of both the micro-machined and diamond-ruled molds, node D was located at 5 mm in front of the mold where the demolding bar was in contact with the polymer substrate during demolding experiments. The applied prescribed velocity boundary condition varied with the value of demolding rate. It should be noted that there was no other boundary condition applied on the polymer substrate, except the temperature and prescribed velocity boundary conditions. Finally, the important demolding load-displacement data were obtained from node D.

4.4.2 Advantages of the new model

There are several crucial advantages of the new model used in this thesis work. One of the factors that will make the model robust is the use of the constitutive

theory of the amorphous thermoplastic material (COC – Topas 8007) which can model the large deformation, thermo-mechanically coupled elastic-viscoplastic behavior in a temperature range spanning the glass transition temperature. The tensile properties of Topas 8007 have also been characterized and calibrated so that premature fracture or breakage on the polymer substrate during demolding can be predicted.

Apart from the material model, a temperature-dependent and rate-dependent interfacial friction model is also applied on all of the bonded interfaces. This interfacial model can capture both temperature-dependent and rate-dependent effects that correspond to demolding temperature and demolding rate in experiments, respectively. Most importantly, the applied interfacial model only requires simple characterization and calibration. In addition, the amount of computational time is also minimized. Lastly, the frictional property at different testing temperatures and testing rates have also been characterized and calibrated based on the two different types of molds which are the micro-machined and diamond-machined molds.

It has been shown above that the hot-pressing step only has a small effect on the overall results. This demonstrates that the hot-pressing step can be skipped without having to significantly compromise on the obtained results. The last essential advantage of the new implemented model is the consideration in the full geometry of both the mold and polymer substrate. A full geometry model will require much more elements in numerical simulation, and thus prolong the required computational time. Nevertheless, it can simulate all of the real experimental phenomena which cannot be accurately performed by a simplified model with no consideration of the full geometry. The beneficial

performance of the new model will be elaborated in detail from the perspectives of both the thermal cooling and demolding processes.

A. Thermal cooling

There are two factors which can render the simplified model to be incapable of reflecting a real experiment. The first factor is the incorrect modelling of thermal contraction during thermal cooling such that both the mold and polymer substrate are not thermally contracting towards their own real shrinkage centers. The shrinkage center of both the mold and polymer substrate has already been predetermined through the assumption on the imposed boundary conditions in a simplified model (see Figure 4.1). Moreover, it is also not an easy task to determine the shrinkage center of the polymer substrate because it is generally thin with irregular arrangement of channels. In addition to that, the channels may have a comparable dimension in terms of order of magnitude when compared to the polymer substrate thickness. Unlike the simplified model generally used by others, there is no boundary condition set on the polymer substrate in the new model used in this thesis work. In this way, the polymer substrate can thermally contract in a free manner without any unreal or artificial constraint.

Figure 4.13 Contour plot of: (a) Thermal stress (Von Mises), and (b) Equivalent plastic strain, on the polymer substrate that was replicated on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart after thermally cooled to room temperature

Based on the obtained results from the model, it can be observed that only one side of the channels on the polymer substrate has higher thermal stress as well as plastic strain (see Figure 4.13). The exact side of the channels with the high thermal stress and plastic strain further depends on the relative location of the channel with respect to the thermal shrinkage center of the polymer substrate. As illustrated in fig. 13, the highest thermal stress and plastic strain experienced on the leftmost and rightmost channels are located in opposite directions.

To have a better illustration, the plot of maximum localized thermal stress on each channel tested on the micro-machined mold (see Figure 4.14a) shows that the polymer substrate tends to thermally contract towards channel five which experiences the lowest thermal stress. Similarly, Figure 4.15a shows that the shrinkage center of the polymer substrate tested on the diamond-ruled mold is located in between channel twenty and thirty. In other words, there exists a unique trend in the obtained thermal stress which is further dependent on the relative location of the particular channel to the shrinkage center. It should be

noted that the further the channel is located away from the shrinkage center, the higher the thermal stress will be.

Figure 4.14 Plot of: (a). Max. localized thermal stress (Von Mises), and (b) Max. localized equivalent plastic strain, in each channel of polymer substrate that was replicated on a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart after thermally cooled to room temperature (channel 1 is the channel closest to the applied demolding load)

An identical trend is also observed in the amount of plastic strain experienced on each channel (after thermal cooling) during testing on both the micro-machined and diamond-ruled molds (see Figure 4.14b and Figure 4.15b). Therefore, the observed results have further demonstrated the capability of the

model to simulate the thermal cooling process without the need to pre-determine an assumed shrinkage center. Furthermore, most importantly, the model can also capture the correct thermal stress and plastic strain generated on the polymer substrate in which a simplified model fails to deliver. This is because the extent of both generated thermal stress and plastic strain is extremely dependent on the relative location between the particular channel and the respective shrinkage center.

Figure 4.15 Plot of: (a). Max. localized thermal stress (Von Mises), and (b) Max. localized equivalent plastic strain, in each channel of polymer substrate that was replicated on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart after thermally cooled to room temperature (channel 1 is the channel closest to the applied demolding load)

B. Demolding

The second factor is the issue of over-constrain on the polymer substrate experienced in the simplified model during demolding. This issue can happen due to the applied boundary conditions. As illustrated in Figure 4.1 that shows the general simplified model, the polymer substrate is generally fixed with zero horizontal displacement on one vertical side (AC) during demolding. As a result, this will further constrain the polymer substrate from bending during demolding by peeling method. Furthermore, the polymer substrate tends to slide upwards based on the vertical line (AC). The mentioned issues is illustrated in Figure 4.16 in which a simplified model was purposely created, so that its overall performance can be observed based on the deformed shape of the polymer substrate during demolding and after demolding.

Figure 4.16 Plot of deformed shape of polymer substrate that was simulated on a simplified model with a single mold feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (numerical simulation): (a) During demolding, and (b) After demolding

To have a better visualization on the performance of the implemented new model, both Figure 4.17 and Figure 4.18 show the deformed shape of polymer substrate during demolding as well as its final shape after demolding. It can be observed from Figure 4.17a and Figure 4.18a that the polymer substrate was subjected to bending during demolding. It is mainly this bending phenomenon that causes the simplified model to give inaccurate results. The polymer substrate bends during demolding because there is interlocking interaction between the features of the mold and polymer substrate. And, this bending may influence the maximum stress that is experienced in the polymer substrate. Furthermore, it can be seen that the polymer substrate tilts when demolding reaches completion (see Figure 4.17b and Figure 4.18b). This is identical to the experimental observation because one side of the polymer substrate still hangs on the demolding bar, while the other side sits on the mold.

Figure 4.17 Plot of deformed shape of polymer substrate that was replicated on a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (numerical simulation): (a) During demolding, and (b) After demolding

Figure 4.18 Plot of deformed shape of polymer substrate that was replicated on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart (numerical simulation): (a) During demolding, and (b) After demolding

With the comparison in the deformed shape of polymer substrate during demolding and after demolding between the new model and the simplified model, it can be clearly seen that the simplified model has over-constrained

the polymer substrate. Hence, the advantages of the new implemented model have been successfully demonstrated in terms of both the thermal cooling and demolding processes.

4.5 Experimental validation of new numerical model

The last step required to prove the performance of the new numerical model is by validating the numerical results with experiments. The experimental validation of the new numerical model used in this thesis work will be conducted both quantitatively and qualitatively. The quantitative results include the measured demolding load-displacement curve, and the calculated demolding energy. On the other hand, the qualitative results refer to the capability of the model in predicting the replication fidelity of the demolded polymer substrate.

4.5.1 Demolding load-displacement curve and demolding energy

A. Micro-machined mold

Figure 4.19 shows the plots of three different quantitative comparisons between experimental and numerical results. It can be observed that there was close agreement in the shape and magnitude of the demolding load-displacement plot obtained from numerical simulation with that of the experimental curve (see Figure 4.19a). Moreover, the numerical model can also reasonably and accurately capture all of the peaks and troughs that

correspond to demolding of individual channels. However, the first peak of the experimental demolding load is smaller than that of the simulated demolding load. This happens due to the rounded channel profile on one side of the first channel which is in contact with the front edge of the mold. During the hot-embossing process, there was nothing to constrain the polymer from flowing on the front edge of mold which further created the inevitable rounded channel profile. Unlike that which was encountered experimentally, the replicated polymer substrate is assumed to have complete perpendicular channel profile in the numerical model.

Comparable total demolding energy was also observed in both the experimental and numerical simulation results (see Figure 4.19b). It should be noted that the experimental results were averaged from three tests. Another interesting finding is that the numerical model can be used to determine the demolding energy required for demolding the individual channels with a unique trend that was similar to that determined experimentally as shown in Figure 4.19c. As expected due to the rounded channel profile on one side of the first channel, the experimental demolding energy for the first channel is much lower when compared to the numerical result.

Figure 4.19 Plot of: (a) Demolding load-displacement curve, (b) Total demolding energy, and (c) Demolding energy per channel, tested on a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (2 mm thick substrate and demolding at 25°C), showing the comparison between experimental and numerical simulation results

B. Diamond-ruled molds

Generally, there are three possible scenarios on the outcome of the demolded polymer substrate. Firstly, successful demolding with no defect is the most desired scenario and the main aim of demolding. However, demolding defects can also arise. The other two remaining scenarios are the two common demolding defects which are polymer brittle failure (breakage) and severe plastic deformation (distortion).

Some of the experimental and numerical results based on the measured demolding load-displacement data and calculated total demolding energy from tests on diamond-ruled molds are plotted in Figure 4.20, Figure 4.21 and Figure 4.22. All the three different scenarios are observed and highlighted in the plots. As illustrated through the comparison in experimental and numerical results, it can be concluded that the model can successfully predict and reproduce the experimental results which involve different set of parameters as well as different demolding outcomes. The different set of parameters include mold geometry, demolding temperature, polymer substrate thickness, demolding method, and demolding rate (see Section 6.2). It should be noted that the polymer breakage in numerical simulation is determined based on analysis in the maximum principal stress generated on the polymer substrate relative to the respective tensile strength.

Figure 4.20 Plot of: (a) Demolding load-displacement curve, and (b) Total demolding energy, tested on a diamond-ruled mold (mold 1) with feature dimensions of 50 μm high, 100 μm wide, and 1 mm spaced apart, showing the comparison between experimental [E] and numerical simulation [S] results

It can also be observed from the plots that during demolding at high temperature (typically 60 or 70°C), the numerical model may not result in a complete demolding load-displacement curve (see Figure 4.20a, Figure 4.21a, and Figure 4.22a). This happens because of convergence issues in the model due to the occurrence of severe plastic deformation on the polymer substrate. Hence, it was not possible to continue running the simulation. In such cases, the experimental total demolding energy is only calculated based on the same final displacement where the numerical simulation has stopped in order to

have fair comparison in the plots. In spite of the convergence issue, there were ample results which show that distortion of polymer substrate had occurred, and thus a firm conclusion can be drawn.

Figure 4.21 Plot of: (a) Demolding load-displacement curve, and (b) Total demolding energy, tested on a diamond-ruled mold (mold 3) with feature dimensions of 200 μm high, 100 μm wide, and 500 μm spaced apart, showing the comparison between experimental [E] and numerical simulation [S] results

Another important finding based on the demolding load-displacement curve and calculated total demolding energy is that the values obtained from the model during demolding at high temperature (typically 60 or 70°C) were found to be lower than the experimental results. This can be attributed to the fact that the implemented interfacial model may have underestimated the adhesion between the mold and polymer substrate on the horizontal interfaces which still remain in contact after the thermal cooling process. This can happen because adhesion becomes more prominent at higher temperature. However, most importantly, the model can still predict the unsuccessful demolding with plastic deformation that may occur when demolding is performed at high temperature. On the other hand, the model works very well during demolding at lower temperatures that also involve both successful demolding and unsuccessful demolding (broken polymer). The remaining experimental and numerical results can be found at Appendix C.

(a)

Figure 4.22 Plot of: (a) Demolding load-displacement curve, and (b) Total demolding energy, tested on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart, showing the comparison between experimental [E] and numerical simulation [S] results

4.5.2 Replication fidelity

A. Micro-machined mold

The capability of numerical model in predicting experimental results quantitatively has been demonstrated. The next validation step is to investigate if the model can predict the final replication quality at the end of the micro-replication process which is demolding. Figure 4.23 shows the contour plot of equivalent plastic strain on polymer substrate after cooling and demolding. After thermally cooled from embossing to demolding temperature, it was

found that more prominent plastic strain only exists at the corner edges of channels (see Figure 4.23a). The plastic strain arises due to the constraint provided by the mold features during the mismatched thermal contraction between the mold and polymer substrate.

Figure 4.23 Contour plot of equivalent plastic strain on a 2 mm thick substrate after: (a) Cooling to room temperature, and (b) Demolding, that was replicated on a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart

Post cooling, there is a maximum localized equivalent plastic strain of about 0.24 on the outermost channel. Nevertheless, the higher value of plastic strain only appears in several tiny elements which are located at the corner edges of the channels. Those regions are tiny enough such that they do not affect the overall shape of the replicated channels. A profile plot of an outermost (leftmost) channel as illustrated in Figure 4.25 demonstrates the still well-maintained overall shape and dimensions of the replicated channel after the thermal cooling process. On the other hand, there is a slight increase in the

maximum localized equivalent plastic strain of about 1.4% after the polymer substrate has been demolded (see Figure 4.23b). Despite the slight increase in plastic strain, no significant defect is observed on the demolded polymer.

As mentioned in Section 4.2.1, demolding failure such as fracture can only be determined by comparing the maximum principal stress generated on the polymer substrate during demolding with its tensile (fracture) strength. Based on the analysis of stress-evolution in Figure 4.24, it can be seen that the localized maximum principal stress in the polymer substrate did not exceed the tensile strength of Topas 8007. This indicates that no polymer breakage or fracture will occur during demolding. The peaks and valleys in the plot correspond to the evolution of demolding stress during demolding from one channel to another. The excellent agreement of the plot of channel profiles during post-cooling and post-demolding further demonstrated the good replication fidelity of the demolded polymer substrate (see Figure 4.25).

Figure 4.24 Plot of the evolution of localized maximum principal stress on a 2 mm thick substrate during demolding from a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart at 25°C

Figure 4.25 Plot of channel profile (channel 9 – channel furthest away from the demolding load) obtained from numerical simulation with replication on a micro-machined mold with feature dimensions of 360 μm high, 800 μm wide, and 3.8 mm spaced apart (demolding at 25°C with 2 mm thick substrate)

From the above, it can be seen that the numerical simulation result correlates well with the experimental data. The polymer substrate was successfully demolded without any visible defect in the experiment. Additional inspection on the demolded polymer substrate was performed with both the white-light confocal microscope and the scanning electron microscope (SEM) (see Figure 4.26). Due to the limitation in the lens used in the white-light confocal microscope, only half of the channel can be captured (see Figure 4.26a), while the SEM image in Figure 4.26b shows the complete and well-replicated channel. It can be seen from Figure 4.27 that the profiles of the replicated channel after demolding obtained both experimentally and from numerical simulation showed excellent agreement with the channel profile in the mold, thus demonstrating good replication fidelity. The channel profile data of both the mold and replicated polymer were obtained using the white-light confocal microscope.

Figure 4.26 Images showing the replicated channel quality of a 2 mm thick polymer substrate that was demolded from a micro-machined mold at 25°C based on: (a) White-light confocal microscope, and (b) SEM

Figure 4.27 Plot of channel profiles comparing the mold and replicated 2 mm thick polymer substrate that was demolded from a micro-machined mold at 25°C (experiment and numerical simulation results)

B. Diamond-ruled molds

Comparison of the experimental and numerical results for tests using the diamond-ruled molds under the different set of studied parameters has also revealed the good predictive capability of the model. It was found that there is a bulge defect on the outermost channel of the replicated polymer based on observation under the SEM (see Figure 4.29a). This defect arises due to the high thermal stress generated during the thermal cooling process. As it can be seen through the numerical simulation result shown in Figure 4.28a (Left) and Figure 4.29a, the new model has successfully predicted the bulge defect.

Figure 4.28 Plot of: (a) Maximum localized equivalent plastic strain, and (b) Evolution of localized maximum principal stress and Von Mises stress during demolding, on polymer substrates that were replicated on a diamond-ruled mold (mold 1) with feature dimensions of 50 μm high, 100 μm wide, and 1 mm spaced apart (numerical simulation)

Channel profile (experiment)

(c)

Image (simulation)

Figure 4.29 Images showing replication on a diamond-ruled mold (mold 1) with feature dimensions of 50 μm high, 100 μm wide, and 1 mm spaced apart based on both experimental and numerical results: (a) Bulge defect on outermost channel due to thermal cooling process to 25°C (2 mm thick substrate), (b) Successful demolding (one-sided demolding at 25°C with 1.5 mm thick substrate), and (c) Unsuccessful demolding with plastically deformed substrate (one-sided demolding at 70°C with 2 mm thick substrate)

In addition, the model can also be used to predict successful demolding as well as failed demolding. Successful demolding which is predicted based on the final generated plastic strain and analysis in the maximum principal stress on the polymer substrate from numerical model (see Figure 4.28 (Left) and Figure 4.30 (Left)) correlates well with the experimental inspections on the demolded polymer substrates under white-light confocal microscope and SEM (see Figure 4.29b and Figure 4.31a).

Figure 4.30 Plot of: (a) Maximum localized equivalent plastic strain, and (b) Evolution of localized maximum principal stress and Von Mises stress during demolding, on polymer substrates that were replicated on a diamond-ruled mold (mold 3) with feature dimensions of 200 μm high, 100 μm wide, and 500 μm spaced apart (numerical simulation)

As mentioned earlier, two common demolding defects exist, namely, severely deformed polymer and broken polymer. Demolded polymers with severe plastic deformation such as distorted channels or overall part warping have been observed based on our numerical studies. As illustrated in Figure 4.29c, Figure 4.31c and Figure 4.33b, the obtained numerical results show good agreement with the experiments. The relevant numerical analyses in both plastic strain and maximum principal stress generated on the plastically deformed polymer substrate are as shown in Figure 4.28 (Right), Figure 4.30 (Right), and Figure 4.32 (Right).

(a)

White-light confocal microscope image (experiment)

SEM image (experiment)

Channel profile (experiment)

(b)

Image (simulation)

Images (experiment)

(c)

Image (simulation)

Figure 4.31 Images showing replication on a diamond-ruled mold (mold 3) with feature dimensions of 200 μm high, 100 μm wide, and 500 μm spaced apart based on both experimental and numerical results: (a) Successful demolding (one-sided demolding at 25°C with 2 mm thick substrate), (b) Unsuccessful demolding with polymer breakage (one-sided demolding at 25°C with 1 mm thick substrate), and (c) Unsuccessful demolding with plastically deformed substrate (one-sided demolding at 60°C with 1 mm thick substrate)

In some of the experiments, the polymer substrates also broke before demolding can be finished (see Figure 4.31b and Figure 4.33a). The polymer breakage can occur when the stress experienced on the polymer substrate during demolding has reached its tensile strength. Detailed numerical analyses on the generated maximum principal stress on the polymer substrate during demolding have also revealed that the maximum stress has exceeded its tensile strength (see Figure 4.30b (Left) and Figure 4.32b (Top)).

(b)

Figure 4.32 Plot of: (a) Maximum localized equivalent plastic strain, and (b) Evolution of localized maximum principal stress and Von Mises stress during demolding, on polymer substrates that were replicated on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart

Images (simulation): demolding rate of 1 mm/min (top) and 50 mm/min (bottom)

Figure 4.33 Images showing replication on a diamond-ruled mold (mold 5) with feature dimensions of 100 μm high, 100 μm wide, and 100 μm spaced apart based on both experimental and numerical results: (a) Unsuccessful demolding with polymer breakage (two-sided demolding at 25°C with 1 mm thick substrate), and (b) Unsuccessful demolding with plastically deformed substrate (one-sided demolding at 60°C with 2 mm thick substrate, and demolding rate of 1 and 50 mm/min)

Therefore, it is apparent from the above results that the new model can successfully be used to predict the outcome of thermal cooling process as well as both successful and failed demolding, even under different sets of parameters. The implemented model can thus be used with confidence to further study the effect of the different parameters, and to eventually determine the optimal parameters for both the fabrication and demolding processes. As a result, efficient and successful replications can be accomplished.

Chapter 5 Characterization of interfacial and material (polymer substrate) properties for model

This chapter discusses the interfacial and material characterization of the mold-substrate system. The characterization of the interface between the mold and hot-embossed polymer substrate involves calibration and determination of the frictional properties for the numerical simulation studies. In addition, characterization in tensile properties of the polymer substrate is elaborated in detail, particularly for the prediction of failure or breakage during demolding.

5.1 Interfacial friction properties (calibration test)

The friction test was conducted to obtain the friction characteristics on the interface between the mold and hot-embossed polymer substrate for the numerical studies. The importance and significance of the frictional property on those interfaces has been described and justified in Section 4.2.2 both analytically and experimentally. The implementation of the frictional model to demolding even at elevated temperature is one of the essential contributions of the work in this thesis.

5.1.1 Testing set-up

The testing set-up involved in the friction calibration test includes flat molds, polymer substrates, a temperature control system, and the sliding-test platform.

5.1.1.1 Molds and polymer substrate

There are two categories of experiments in this thesis work which utilize either the micro-machined molds or the diamond-ruled molds. Hence, these two different type of molds were used in the friction calibration test. Both molds were purposely made flat with no feature for calibration purposes.

The micro-machined mold was fabricated using the method described in Section 3.2.3.1, and it has overall dimensions of 100 mm by 53 mm and 8 mm thick (see Figure 3.10b). On the other hand, the flat diamond-ruled mold used was fabricated with a diamond tool (see Figure 5.1) by diamond-turning method that can produce identical optical surface finishing when compared to diamond-ruling method (see Figure 5.2).

Figure 5.1 Photo of a flat (featureless) diamond-turned mold

Initially, a thick cylindrical piece of aluminum (AA6061-T6) was diamond-turned, and subsequently cut into the desired dimensions by wire-cutting

method. Then, two through-holes and mounting holes were drilled by CNC-machining method for accommodating the cartridge heaters. The diamond-turned mold was made much thicker so that it can accommodate the cartridge heaters in the middle of the mold to facilitate testing at elevated temperatures. The overall dimension of the mold was 60 mm by 60 mm and was 20 mm thick. The polymer substrate used in all of the calibration tests has dimensions of 36 mm by 30 mm and was 2 mm thick.

Figure 5.2 White light confocal microscopy micrograph of a flat diamond-turned mold showing the optical surface finishing ($R_a \approx 40$ nm)

5.1.1.2 Temperature control system

To conduct friction calibration tests at elevated temperatures, a temperature control system (Hasco type Z126/1/2/16) installed with two cartridge heaters (Hasco type Z110-8x50/160) was used. In addition, four thermocouples were used and installed on the mold in order to obtain accurate and reliable temperature readings. Two thermocouples were located on the left and right side of mold, while the other two were placed on the top surface of mold with

optical surface finishing. The temperature control system has a user-friendly interface in which temperature can be easily set through the front panel by simply tuning the number.

5.1.1.3 Sliding-test apparatus

The sliding-test apparatus consists of a flat plane in which the flat mold is mounted, a metal sled (made of aluminum), nylon filament that connects the load cell to the specimen-covered sled through its eye screw, a low-friction pulley, and supporting base that can be connected to the base of Instron machine (frame model 5569). The apparatus is based on ASTM D1894 and is as shown in Figure 5.3. The polymer substrate is not visible in the figure because it is located in between the flat mold and sled.

Figure 5.3 Photos of: (a) Complete sliding-test apparatus, and (b) Detailed sliding-test configuration, for testing at room temperature

For the sliding test performed at elevated temperatures, the testing configuration with both cartridge heaters and thermocouples is as shown in Figure 5.4. The load-cell for the sliding-test has a load capacity of 10 N with quoted accuracy to be equal to or better than 0.025% of the rated output (0.0025 N), or 0.25% of the indicated load, whichever is greater. Nevertheless, during the sliding-test at the highest temperature tested (70°C), a load-cell with a load capacity of 50 N was used because the measured load exceeded 10 N. Thus, proper selection of the load-cell has further ensured the accuracy and reliability of the measured load.

Figure 5.4 (a) Photo of a sliding-test configuration for testing at elevated temperatures, and (b) Schematic diagram of the testing configuration with red points where thermocouples are located

5.1.2 Sliding-test procedure and parameters

Prior to each test, the mold was cleaned with acetone and further rinsed with DI water. Then, the polymer substrate was hot-embossed onto the flat mold with the embossing parameters as described in Section 3.3.2 by using the hot-embossing apparatus. After hot-embossing and cooling to the corresponding sliding-test temperature, the specimens were transferred to the sliding-test apparatus on a different Instron machine. When the sliding-test was performed at room temperature, the specimens were only transferred after cooling to

room temperature. On the other hand, sliding-tests at elevated temperatures were performed by carefully transferring the specimens when they had reached the desired sliding-test temperature (the temperature in the first set-up was typically about ten degrees higher to accommodate for the drop in temperature after transfer to the second machine). The mold was mounted on the plane and the temperature of the specimens was maintained by inserting two cartridge heaters through the two-through holes in the mold.

The sled was eventually attached on the polymer by using double-sided tape with adequate bond strength. As the sled was initially at room temperature, an adequate amount of time was further allowed for both the specimens and sled to reach equilibrium temperature prior to the final sliding test. Eventually, the sled was pulled by the nylon filament that was connected to the load-cell through the low-friction pulley which created sliding between polymer and mold. At the same time, the sliding load and displacement were measured and recorded. Table 5.1 lists the sliding-test parameters which are identical to the demolding parameters used during experiments.

Table 5.1 List of sliding-test parameters and the values

Parameter	Value
Testing temperature	25°C (micro-machined mold)
	25 – 70°C (diamond-turned mold)
Testing (sliding) rate	0.1 – 60 mm/min (micro-machined mold)
	1 & 50 mm/min (diamond-turned mold)

5.1.3 Determination of coefficient of friction

The final coefficient of friction is calculated and obtained from the measured sliding load-displacement curve. Based on the Coulumb friction law, coefficient of friction in the relevant sliding-test can be calculated from the sliding load divided by the normal load (equation 5-1). In this case, the normal load is the total weight of both sled and eye screw, because they are the ones exerting a vertically downward force on the polymer substrate. During the sliding-test, there are two states which are static and dynamic. Static friction is the friction between two objects that are not moving relative to each other, while dynamic friction is the friction when two objects that are moving relative to and rubbing against each together. In other words, the sliding-load should be as large as the static frictional load in order to begin the interfacial sliding between the polymer and mold. On the other hand, while the polymer is sliding on the mold, the required sliding-load decreases to the dynamic frictional load.

$$F_S = \mu.F_N \tag{5-1}$$

where:

- F_S Sliding (frictional) load
- μ Static (or dynamic) coefficient of friction
- F_N Normal load

As shown in Figure 5.5, the highest sliding load is the load required to begin the interfacial sliding (static), while the subsequent lower sliding load is the load required to constantly slide the polymer relative to the mold (dynamic).

In the sliding-test with the micro-machined mold, there appears to be regular fluctuation in the sliding load as displacement increases (see Figure 5.5a). This is due to the surface roughness formed during the micro-machining process which prohibits the polymer to slide smoothly on the mold. Moreover, the polymer has also replicated the exact surface roughness of the mold which further inhibits smooth sliding.

On the other hand, during the dynamic friction state with the diamond-turned mold, the measured sliding load is constant (see Figure 5.5b). This occurs due to the smooth optical surface finish of the mold such that the sliding phenomenon is steady and constant. With both data of static and dynamic friction, the static and dynamic coefficients of friction can be eventually determined. However, for simplicity, most studies only consider and focuses on the static coefficient of friction. In addition, it has also been shown through experimental validation (see Section 4.5) that the implementation of only static friction can provide reasonably good results in numerical simulation.

Figure 5.5 Plots of sliding load-displacement curve performed on: (a) Micro-machined mold (25°C and 50 mm/min), and (b) Diamond-turned mold (55°C and 50 mm/min)

5.1.4 Influence of temperature, sliding rate, and surface finishing of mold on friction

As mentioned in Table 5.1, friction calibration tests with micro-machined mold only involve testing at room temperature, but with varying sliding rates. The plot of static coefficient of friction with different sliding rates in Figure 5.6 is based on the averaged results that are obtained from three experiments in each sliding rate. By implementing the analysis of variance method (ANOVA) with two significance levels, it can be finally concluded that there is negligible change in the friction with different sliding rate (see Table 5.2). Hence, the static coefficient of friction can be generalized to be equal to 0.4. The relevant details and equations regarding ANOVA are available in the textbook by Montgomery [97].

Figure 5.6 Plot of static coefficient of friction under varying sliding rates (mm/min) tested on a flat micro-machined mold at 25°C

Table 5.2 ANOVA result with single factor experiment (sliding rate) on a micro-machined mold

Sliding rate (mm/min)	ANOVA ($\alpha = 1\% \text{ \& } 5\%$)	Effect
0.1 to 60 mm/min	Fo (1.03) < F _{0.01,9,20} (3.46)	No
	Fo (1.03) < F _{0.05,9,20} (2.39)	No

On the other hand, the frictional property between the polymer substrate and the diamond-turned mold was evaluated at elevated temperatures under two different sliding rates. Similarly, analysis based on the ANOVA method was performed in order to analyze the obtained results. However, ANOVA method based on two-factor factorial experiment was applied because there were two factors involved in the tests. The ANOVA result shows that only temperature affects the resulted static coefficient of friction, while the sliding rate and interaction between testing temperature and sliding rate do not give any significant impact (see Table 5.3). It can be observed from the plot in Figure 5.7 that the static coefficient of friction gradually decreases from room

temperature to 50°C, and then increases quite significantly up to 70°C which is just about 8°C below the polymer’s T_g. In addition, it can also be observed that the obtained static coefficient of friction remains relatively similar in each testing temperature at the two different sliding rates. This independency to the performed range of sliding rate also agrees with the results obtained from tests on a micro-machined mold. Nevertheless, as expected based on the difference in the surface finishing between micro-machined and diamond-turned mold, the static coefficient of friction on a micro-machined mold tested at room temperature ($\mu_s = 0.4$) is much higher than that on a diamond-turned mold ($\mu_s = 0.26$).

Figure 5.7 Plot of static coefficient of friction under varying testing temperatures (°C) and two different sliding rates (mm/min) tested on a flat diamond-turned mold

Table 5.3 ANOVA result with two-factor factorial experiment (testing temperature and sliding rate) on a diamond-turned mold

Factor	ANOVA ($\alpha = 1\% \text{ \& } 5\%$)	Effect
Testing temperature (25 – 70°C)	Fo (276.21) > F _{0.01,9,40} (2.89)	Yes
	Fo (276.21) > F _{0.05,9,40} (2.12)	Yes
Sliding rate (1 & 50 mm/min)	Fo (0.0059) < F _{0.01,1,40} (7.31)	No
	Fo (0.0059) < F _{0.05,1,40} (4.09)	No
Interaction between testing temperature and sliding rate	Fo (0.004) < F _{0.01,9,40} (2.89)	No
	Fo (0.004) < F _{0.05,9,40} (2.12)	No

As the polymer substrate is hot-embossed on the mold, the polymer replicates the exact surface finishing of mold, and it fills completely into the nano-roughness or asperities of the mold. The particular trend observed in the friction test results at varying temperatures may be further correlated to two dominant components such as the adhesion component and deformation component. During friction test which involves sliding, there will be collision between the tiny asperities of polymer and mold. With increase in temperature, the strength of the polymeric material decreases, while adhesion increases at the same time. At the initial increase in temperature from room temperature, the effect of increase in adhesion may be suppressed by the decrease in the strength of the polymeric asperities. This may further lower the friction coefficient. Nevertheless, with further increase in temperature, adhesion may eventually become more dominant and thus the friction coefficient increases. A similar trend has also been observed by Saha in his work on determining the dynamic coefficient of friction of PMMA ball against FDTS coated silicon sample under varying temperatures with ball-on-disc micro-tribometer [50].

5.2 Tensile properties of cyclic-olefin copolymer (Topas 8007)

Characterization in tensile properties of the polymeric material used for the replication process is obtained by performing tensile testing until fracture. The tensile properties are extremely essential, particularly for predicting the possible fracture or breakage in polymer substrate during demolding. As the constitutive theory for the amorphous polymer (COC – Topas 8007) is developed and calibrated based on compression tests (see Section 2.4), it is not feasible to predict failure in terms of fracture in the numerical simulation. Thus, the tensile properties serve as an additional means for failure prediction.

5.2.1 Specimens

Tensile test specimens with dog-bone shape based on ASTM D638 were initially produced by utilizing the rectangular pieces of injection-molded polymer substrate. The rectangular pieces of polymer substrate were machined into dog-bone shape with the CNC tool. Then, the side edges were carefully polished in order to remove any tiny irregularities formed during the micro-machining process. The tensile test specimen has an overall length and width of 60 and 15 mm, respectively, and a gauge length of 20 mm with 2 mm thickness.

5.2.2 Testing procedure and parameters

The tensile tests were performed by using the universal tensile testing Instron machine (frame model 5566) equipped with 1k N load-cell. A non-contact

video extensometer system was used to capture the extension in the specimens for accurate result. As the tensile test involves testing at elevated temperature, all of the tensile tests were executed inside an environmental temperature chamber. An addition, a thermocouple was installed such that it was in contact with a side of tensile specimen that was clamped by the tensile-test jig, in order to accurately capture the temperature reading on the specimen.

Tensile test specimen was initially fixed into the tensile-test jig prior to heating. During heating, the specimen and testing fixture were thermally expanding which further created compressive stress on the specimen. Hence, the load frame was constantly and accordingly adjusted so that no pre-stress was experienced by the specimen. Then, the tensile test was eventually performed after the specimen had reached equilibrium temperature. Tensile test parameters are chosen based on the relevant demolding parameters (see Table 5.4). The obtained results in the following section are based on three tests for each set of tensile test parameters.

Table 5.4 List of tensile test parameters and the values

Parameter	Value
Testing temperature	25 – 70°C
Testing (displacement) rate	1 & 50 mm/min

5.2.3 Influence of temperature and strain rate on mechanical properties of COC – Topas 8007

The tensile test results performed at varying temperatures and two testing rates are as shown in Figure 5.8. It was found that the polymeric material (COC – Topas 8007) crazes at lower testing temperature ranging from 25 to 50°C. The crazing phenomenon results in brittle failure without any significant plastic deformation. Nevertheless, the polymer starts to experience significant plastic deformation when tested at 60 and 70°C. This phenomenon is also known as cold-drawing [98].

As it can be seen from the true stress-true strain curves, there is an initial elastic response followed by a yield peak. At the yield peak, a neck forms in the specimen and the load drops dramatically. This is further followed by the cold-drawing process in which the tensile load remains relatively constant while displacement continues to increase. During this stage of deformation, the neck propagates along the gauge section of the specimen as the polymer chains are re-aligned in the tensile direction. When the neck has travelled the full gauge length of the specimen, the polymer chains become fully aligned in the tensile direction. Subsequently, they start to stretch. The stretching eventually causes slight increase in the load prior to failure.

Figure 5.8 Plot of tensile true stress – true strain curves (Topas 8007) at temperatures ranging from 25 to 70°C performed at two different testing rates: (a) 1 mm/min, and (b) 50 mm/min

Based on the results shown in Figure 5.9, the elastic modulus of the polymer is found to decrease with increase in temperature. The drop in elastic modulus is much more significant at 60 and 70°C when compared to tests at lower temperature. Furthermore, the rate-dependency of the elastic modulus can also

be observed when comparing results with testing rates of 1 and 50 mm/min. A similar trend is observed in the comparison of yield and tensile strength in terms of both temperature and testing rate. Tensile strength is only for specimens with brittle failure, while yield strength is for specimens that experience severe plastic deformation.

Figure 5.9 Plot of elastic modulus and yield (or tensile) strength of Topas 8007 at temperatures ranging from 25 to 70°C performed at two different testing rates: (a) 1 mm/min, and (b) 50 mm/min

In the cases with severe plastic deformation, the tested specimens also have final fracture strength at large strain that is much higher than the yield strength. Based on both comparisons in elastic modulus and strength, it can be concluded that the transition between brittle and ductile failure lies in the temperature ranging in between 50 and 60°C in both the different testing rates.

Evaluation on the fracture strength based on the different sets of tensile test parameters is further plotted in Figure 5.10. It was found that the rate-dependency in fracture strength becomes more significant at higher temperature.

Figure 5.10 Plot of fracture strength of Topas 8007 at temperatures ranging from 25 to 70°C performed at two different testing rates (1 and 50 mm/min)

Chapter 6 Analysis of demolding process I – Demolding-failure mechanism & Parameters that affect the fabrication of hot-embossed polymer substrate

Different types of demolding failure have been observed both experimentally and in numerical simulations. However, the exact causes for the different types of failure are not known. An in-depth understanding of the demolding process, particularly the optimal conditions to achieve successful demolding without any failure or defects can only be developed through proper analysis of the main factors that lead to demolding failures. Knowledge of the main factors that can hinder demolding or cause demolding failure will make it possible to understand how each parameter can affect the fabrication process of a hot-embossed polymer substrate. Through this, the key parameters that can have the most significant impact on the demolding outcome can be identified. This chapter will scrutinize and determine the main factors which increase the demolding difficulty, followed by detailed elaborations on the essential parameters that can affect the replication process.

6.1 Analysis of demolding-failure mechanism

Until now, there has not been any thorough study on the main mechanisms that cause demolding failure of a hot-embossed polymer substrate. It has been generally known and accepted that the adhesion and friction cause increased bonding on contact between the mold and polymer substrate during hot-

embossing, leading to a higher demolding force. However, the main mechanism that can lead to demolding failure in the polymer substrate remains unclear. It is crucial to develop a deeper understanding in the demolding process so that approaches to avoid demolding failure can be established.

Fu et al. has reported a demolding failure criteria based on the shear stress generated on the feature sidewall between the mold and stainless steel substrate in micro-metal injection molding [57]. Interlocking features were strengthened by the thermally induced stress after the specimens have cooled down to the demolding temperature. Based on their analysis, it was suggested that the shear-mechanism on the contacting feature sidewalls was the main mechanism that caused the demolding failure. However, no experimental and numerical simulation work was conducted to further support their analytical conclusion.

In addition to the above factor, from the study in this thesis, the existence of high demolding stress has also been found in both the replicated features and base layer of polymer substrate. The base layer is the bulk polymer substrate beneath the replicated features. High demolding stresses can indeed arise due to the bending experienced by both the features and base layer of the polymer substrate (see Figure 6.1a). Based on the analysis in the maximum principal stress on the polymer substrate (see Figure 6.1b), it has been revealed that bending of the substrate causes high stress to be located on the corner edges of channel which are the transition region between the features and base layer. On the other hand, the maximum principal stress due to shear-mechanism on the contacting sidewalls was found to be much less significant. Therefore, it is

the high stress induced due to bending that can eventually influence the demolding failures such as polymer breakage or distorted channel.

Figure 6.1 (a) Plot showing the bending experienced by both features and base layer of polymer substrate during demolding, and (b) Contour plot of maximum principal stress showing the location of high stress on polymer substrate during demolding

In other words, bending is found to be the main mechanism that causes demolding failure. Two kinds of demolding failure based on the bending-mechanism have been observed experimentally (see Figure 4.29c, Figure 4.31c, and Figure 4.33a). As illustrated in Figure 4.33a, it can be seen that the

high stress generated on the corner edge of channel has reached the polymeric tensile strength, and thus a crack starts to initiate in that particular location and propagates through the base layer. Similarly, as shown in Figure 4.31c, the bending of the polymeric feature during demolding at high temperature (60°C) caused the stress at the corner edge of the channel to surpass the yield strength of the polymer, which led to distortion of the channel. Thus, the finding obtained in this thesis work differs from that obtained by Fu et al., and it has also proven that bending plays a much more important role in influencing demolding failures rather than the shearing on contacting interfaces.

Considering that the feature dimensions for microfluidic applications are in the micron-scale, the second moment of area of the embossed polymer substrate tends to be small because of the smaller dimensions, which inadvertently make the substrate more prone to bending stress. On the whole, it can be seen that bending should be minimized in order to maximize the chances of accomplishing successful demolding in hot embossing.

6.2 Parameters that affect the fabrication of hot-embossed polymer substrate

There are a number of different parameters that can affect the fabrication process of hot-embossed polymer substrate, particularly the demolding outcome. The list of parameters that will be studied in this thesis work is as follows:

- Channel geometry
- Polymer substrate thickness

-
- Demolding temperature
 - Demolding rate
 - Embossing temperature
 - Channel design (shape of the channel cross-section)
 - Adhesion of the polymer substrate to mold
 - Demolding method

It has been shown that demolding failure is mainly caused by bending experienced by the polymer substrate during demolding. Based on theoretical considerations, bending can be correlated to the flexural rigidity (EI). Flexural rigidity is defined as the force couple required to bend a rigid structure to a unit curvature. In the context of demolding, it can be considered as a measure of how easy bending can occur in the polymer substrate when a demolding load is applied. Since bending should be minimized to avoid the high stress that may lead to demolding failure, a high enough flexural rigidity is preferable. In considering how the parameters can influence the demolding difficulty in the following section, the effect of some of these parameters on the flexural rigidity will be examined. This will enable an in-depth understanding to be developed so that knowledge of how the parameters contribute to demolding difficulty may be utilized to prevent the demolding failure from happening.

A. Channel geometry

As mentioned above, bending of the replicated features in the polymer substrate during demolding can generate high stress which can lead to failure. The dimensions of the replicated features and the flexural rigidity of the polymer substrate depend on the fabricated channel geometry. As a result, channel geometry can affect the demolding difficulty.

Figure 6.2 shows the schematic diagrams of demolding on two molds with different channel geometry and aspect ratio using the peeling method. The protruded feature of the polymer substrate experiences bending. With higher aspect ratio of micro-channels or micro-features, the flexural rigidity (in terms of second moment of area) and moment arm tend to decrease and increase, respectively. Based on the simple bending theory (see Equation 6-1), stress due to bending increases with lower flexural rigidity or longer moment arm. Therefore, the proneness to demolding defects may be significantly enhanced. This is consistent with the reported studies based on numerical simulation [99] which showed a significant increase in stress generated on polymer substrate during demolding when the aspect ratio of the micro-channel increased.

In addition to the geometry-dependent bending properties of the replicated features, the extent of thermal stress is also further dependent on the overall channel geometry. Higher thermal stress may lead to enhanced demolding difficulty, and thus facilitate the more severe bending experienced by the polymer substrate.

$$\sigma = \frac{My}{I} \tag{6-1}$$

where:

- σ Stress due to bending
- M Moment about the neutral axis
- y Perpendicular distance to the neutral axis
- I Second moment of area

Figure 6.2 Schematic diagrams showing the deflection or bending of a replicated (protruded) feature on polymer substrate during demolding with: (a) Higher, and (b) Lower aspect ratio

B. Polymer substrate thickness

The simple bending theory also clearly suggests that the thickness of polymer substrate plays an important role in determining the severity of bending experienced by the polymer substrate. There has been no attempt to study the

influence of polymer substrate thickness to demolding yet. The polymer substrate thickness may create a significant impact on the demolding outcome because the thickness can easily alter the value of the second moment of area based on the correlation in equation 6-2. The fact that the thickness is multiplied by three times makes it more impactful and crucial. As illustrated in Figure 6.3, it can be observed that there is a significant increase in the flexural rigidity of the polymer substrate when the substrate is progressively thickened by 0.5 mm. In addition, based on the different perspective, polymer substrate thickness also affects the overall size of the microfluidic device as well as the amount of raw material used during fabrication.

$$I = \frac{bt^3}{12} \quad 6-2$$

where:

- I Second moment of area
- b Width of polymer substrate
- t Polymer substrate thickness

Figure 6.3 Plot showing the correlation of polymer substrate thickness (width of 10 mm) to the resulting second moment of area, and the percentage of increase in flexural rigidity (EI)

C. Demolding temperature

The flexural rigidity of polymer substrate is dependent on two factors which are Young's modulus (E) and second moment of area (I). It has been shown that the second moment of area is geometry-dependent. On the other hand, Young's modulus is known to be temperature-dependent. The temperature-dependence of the Young's modulus of the Topas 8007 in the present work has already been determined (see Figure 5.10). The modulus decreases with increase in temperature, which further means that the polymer substrate will be more susceptible to bending during demolding. Furthermore, it should be noted that there is reduction in both yield and tensile strength at higher temperature as well.

Demolding temperature also affects other factors such as the adhesion and friction. Both adhesion (see Figure 4.5) and frictional (see Figure 5.8)

properties tend to be larger at higher demolding temperature. At the same time, thermal stress will be less significant due to smaller thermal contraction. In other words, the combined interaction of several factors (adhesion, friction, thermal stress, and material properties) will eventually determine the demolding outcome. In addition, from the manufacturing point of view, demolding temperature can also affect the cycle time and energy efficiency of the processes. Therefore, demolding temperature is an extremely crucial parameter, but its effect may not be straightforward.

D. Demolding rate

The demolding rate is important because Young's modulus is also known to be rate-dependent. The rate-dependency of Young's modulus was found to be quite significant, particularly at higher temperature (see Figure 5.10). It was also observed that both the yield and tensile strength varied with testing rate. Based on the characterization of interfacial properties between the mold and polymer substrate in this thesis work, it is found that friction does not change at the two tested sliding rates (see Section 5.1). Therefore, the influence of demolding rate is only affected through its effect on the material properties. Based on this, a faster demolding rate which will enhance the flexural rigidity of the polymer substrate may be preferable. Moreover, optimal production throughput can be accomplished at the same time.

E. Embossing temperature

For a fixed demolding temperature, embossing temperature is a crucial parameter that will further determine the magnitude of thermal stress generated on the polymer substrate prior to demolding. Thus, an embossing temperature that is too high may not be preferable because the interfacial bonding developed between the mold and polymer substrate has to be minimized. Consequently, an optimal embossing temperature is one at which complete filling can be achieved, and at the same time, ease of demolding is possible. The above serves to underline the importance of this parameter.

F. Channel design (shape of the channel cross-section)

The most common and conventional shape of the channel cross-section used in microfluidic devices is rectangular or square-shaped channel which is as illustrated in Figure 6.4a. A lot of challenges arise during demolding of this type of channel design, particularly the high aspect-ratio micro-channels. Therefore, an attempt to fabricate tapered micro-channels has been reported [100]. The reason for the development of tapered micro-channel is mainly to ease the demolding process. Nevertheless, there may be limitations in the applications of tapered micro-channels such as in micro-lense application in which high accuracy is required [22].

suitability for use as compressive, deformation-based valves where the cross-sectional areas of micro-channels can be maximized without compromising the ability to completely collapse the channel structure and stop the fluid flow.

It is noted that even though the results of the easier demolding have been demonstrated through experiments on mold with tapered channels, the formation of thermal stress during cooling process and the evolution of stress during demolding on such channel have never been analyzed yet. Therefore, these three different channel designs will be studied through numerical simulation. Figure 6.4a demonstrates the model with conventional rectangular-shaped channels, while Figure 6.4b shows the model with tapered-channels that have a tapered angle of about 5.7° . In addition, the model with semi-circular or bell-shaped channels is as illustrated in Figure 6.4c. The different channel design may provide different interfacial mechanical interlocking between the mold features and the replicated polymeric features.

G. Adhesion of the polymer substrate to mold

There are two different adhesions during the replication process of polymer substrate on aluminum mold via hot-embossing (see Section 2.3.1). They are the thermodynamic and mechanical adhesion. Thermodynamic adhesion is correlated to the surface energy of the mold, while mechanical adhesion is dependent on the mechanical interlocking developed in between surface roughness or asperities at the substrate-mold interface. The presence of the two types of adhesion means that there may also be two possible ways to mitigate demolding difficulty.

The first feasible way to ease demolding through thermodynamic adhesion is by altering the surface energy of the mold. One of the simplest and easiest methods is through the application of mold release agent on the mold surfaces. The mold release agent is commonly available in the form of spray, and thus straightforward to apply. Silicon molds have also been successfully coated with different types of coating materials by performing sputtering and dipping processes [50]. The different practices serve an identical purpose which is to reduce the surface energy of the mold, so that the adhesion and friction between the mold and polymer substrate can be minimized. However, there can be limitation in the use of coated-molds because the coating materials may stick on the demolded polymer substrate as residues. As a result, sample contamination can potentially occur. The consideration in this issue is extremely crucial in major applications of microfluidic devices, particularly for chemical or biological purposes. Therefore, it is generally more preferable to use an uncoated mold for replication purposes.

Another feasible way to mitigate the demolding difficulty is by suppressing the effect of mechanical adhesion based on the control in the mold surface finishing. Rougher mold surface finishing will provide stronger mechanical interlocking on the contacting interfaces when compared to the smoother mold surface finishing. Besides the stronger mechanical interlocking, rougher mold surface finishing will involve larger contacting area due to the irregularities of the interfaces. And, the larger contacting area will eventually lead to higher influence of thermodynamic adhesion. In the current work, the effect of mold surface finishing has been demonstrated through characterization in the interfacial friction property on both micro-machined and diamond-machined

molds, in which the value is found to be much larger on the rougher micro-machined mold (see Section 5.1.4).

The influence of interfacial adhesion between the mold and substrate on demolding will be studied through both numerical simulation and experiment. Experiments on molds with different surface finishing quality by utilizing micro-machined and diamond-ruled molds will be performed. In addition, numerical models with different interfacial friction property which can represent both different scenarios of coated molds and molds with different surface finishing quality will also be built and examined.

H. Demolding method

Demolding method is defined as the way to apply the demolding load on the replicated polymer substrate for removal purpose. In this thesis work, two different demolding methods will be examined which are one-sided demolding (see Figure 6.5a) and two-sided demolding (see Figure 6.5b). As mentioned in the experimental chapter, the polymer substrate used for demolding by two-sided method has a longer length. This is to accommodate for the application of additional demolding load on the other projecting side of the polymer substrate.

Figure 6.5 Plot of the two different demolding methods: (a) One-sided demolding, and (b) Two-sided demolding

These two different demolding methods were studied because they are the two most possible and ubiquitous ways of performing demolding in the current manufacturing set-up. As illustrated in Figure 6.5, demolding can be performed from either one side or both sides of the projecting portion of the polymer substrate. Both methods can be performed with different kinds of demolding fixtures such as demolding strip, demolding stop, ejector pin (see Figure 6.6), or demolding bar which is used in this thesis work (see Figure 3.8 and Figure 3.9). The numerical models for these two demolding methods can reflect the use of the above mentioned demolding fixtures.

Figure 6.6 Schematic diagrams showing the different operation of demolding fixtures that are commonly observed as the current manufacturing practices [37]: (a) Use of demolding strips (μ FAC project), (b) Use of demolding stops to clamp the replicated substrate (μ FAC II project), and (c) Use of ejector pins, for demolding purposes

It can be intuitively predicted that the bending behavior of the polymer substrate in the two demolding methods would be different. This will have an impact on the stresses in the polymer substrate, and on the possible demolding-failure mechanism. Furthermore, the difference in demolding technique is also another parameter that has not been studied and reported by any research group yet. Hence, determination of the most effective demolding method may be beneficial, especially with the aim of achieving successful demolding.

Based on the detailed elaborations of the possible effect of the eight different parameters outlined above, it can be seen that not every parameter can be correlated to the flexural rigidity of the polymer substrate. However, it is obvious that each parameter can play an important role in determining the final demolding outcome. All the parameters can be classified into two categories so that a clear overview on the main contribution of each parameter to the demolding-failure mechanism can be developed. The two major categories are:

1. Bending properties of the polymer substrate :

a. Flexural rigidity (EI)

Channel geometry, polymer substrate thickness, demolding temperature, and demolding rate

b. Bending behavior due to the application of demolding load

Demolding method

2. Interfacial bonding (adhesion) properties between the mold and polymer substrate:

Embossing temperature, channel design (shape of the channel cross-section), and adhesion property of the mold

It will be shown that the optimal processing conditions can be determined both experimentally and by using numerical simulations through a deeper understanding in the influence of the above two categories of parameters on demolding. It should be noted that the channel geometry may not be a flexible parameter that can always be adjusted for achieving optimal process. This is because channel geometry is dependent on the specific requirements of the desired applications of the microfluidic devices, such as the need of high aspect ratio micro-channels for much better performance in certain applications. Nevertheless, this emphasizes the importance of optimizing by adjusting the other parameters. Thorough studies on the effect of all the eight parameters on both thermal cooling and demolding process will be discussed in the next following chapter.

Chapter 7 Analysis of demolding process II – Influence of thermal cooling & Effect of the different parameters on demolding

In this chapter, the influence of all of the eight different parameters on the two main processes involved during hot-embossing which are the thermal cooling and demolding processes will be thoroughly examined. Systematic studies will be performed on these two processes based on both experiments and numerical simulation. Then, with the knowledge on the influence of each parameter on both thermal cooling and demolding outcome, the optimal conditions for the fabrication of microfluidic devices by hot-embossing can be predicted and determined.

7.1 Influence of thermal cooling based on the different parameters

In hot-embossing, thermal cooling always happens before demolding is performed. As a result of thermal cooling combined with the mismatch in thermal contraction behavior between the mold and polymer substrate, thermal stresses arise. One consequence of the generated thermal stress is the possible occurrence of plastic deformation on the replicated polymer substrate. Apart from that, it also increases the demolding difficulty. The influence of each of the different parameters on the thermal cooling process will be further examined.

7.1.1 Differential thermal shrinkage

It has been found from the numerically simulated results that the thermal stress generated on the polymer substrate after thermal cooling process varies from one channel to another. An identical trend was also observed in the plastic strain that developed in the polymer substrate because of the generated thermal stress (see Figure 4.14 and Figure 4.15). The results indicate that highest thermal stress and plastic strain are experienced on the two outermost channels. Both values start to decrease as one move inwards towards the inner channels, and the minimum values are found to be located at the vicinity of the thermal shrinkage center.

This observed trend can be correlated to the relative distance between the thermal shrinkage center and the referred channel. The two outermost channels experience the highest thermal stress and plastic strain because their locations are the furthest away from the shrinkage center. As the distance of the channel position to the shrinkage centre decreases, the smaller the thermal stress and the plastic strain in the channel will be. This occurred because the longer relative distance of the outermost channels to the shrinkage center corresponds to higher thermal contraction when compared to the other inner channels.

For this reason, the bulge defect is more prone to occur in the outermost channel of polymer substrate (see Figure 4.29a). Therefore, if no bulge defect is detected in the outermost channels after the thermal cooling process, good replication fidelity of the remaining channels could be assured. This affords us an efficient method to perform inspection tasks to ensure good replication in a

manufacturing environment such that substrates which have defects due to the thermal cooling process, typically bulge defect, can be readily identified and rejected.

7.1.2 Channel geometry

The effect of both channel spacing and depth to the thermal cooling process in terms of the generated thermal stress and plastic strain on the polymer substrate will now be considered. Referring to Table 3.1, both the channel spacing and the depth of the diamond-ruled molds were varied, while the channel width was kept constant. The plots in Figure 7.1 reveal that higher thermal stress (see Figure 7.1a) and plastic strain (see Figure 7.1b) are generated on the polymer substrates which have wider channel spacing. This occurred because thermal contraction in the polymer substrates with wider channel spacing was constrained by fewer channels when compared to those with narrower channel spacing. In addition, the availability of a higher number of channels in sharing the load developed from the thermal contraction also leads to lower thermal stress and plastic strain.

It can also be observed from Figure 7.1 that, for a given channel spacing, the polymer substrates with shallower channel experienced higher thermal stress and plastic strain. The higher values arise because of the influence of the base polymer layer where the replicated features are standing on. Under the same polymer substrate thickness, a shallower channel corresponds to thicker base layer. As a result, there will be more substrate material above the replicated

features which could provide more constraint during the thermal cooling process, and hence, higher stress is generated.

Figure 7.1 Plot of: (a) Maximum thermal stress (Von Mises stress), and (b) Maximum localized equivalent plastic strain, on 2 mm thick substrates that were replicated on the different diamond-ruled molds and thermally cooled to 25°C (numerical simulation)

An undesirable outcome of the effect of thermal stress is plastic deformation that can commonly exist as the bulge defect. As illustrated in Figure 7.2a (numerical simulation) and Figure 4.29a (experiment), a bulge defect was

formed on the outermost channel of the polymer substrate replicated on mold 1. On the other hand, no bulge defect was detected when the channel spacing is reduced from 1 mm (mold 1) to 100 μm (mold 4). Thus, it can be seen that wider channel spacing can enhance the proneness to bulge defect. Hence, channel spacing should be minimized.

The simulation results in Figure 7.2b demonstrated that more significant plastic strain was formed on the mold with wider channel spacing (mold 2) than in the mold with narrower channel spacing (mold 5). However, the bulge defect did not form in both of these cases. The same trend applies to molds with different channel depth as it can be seen from the comparison in contour plot of equivalent plastic strain between mold 4 and 5. The obtained results further suggest that polymer substrate with more packed channels or narrower channel spacing is preferable based on consideration of the fabrication process. It is apparent that both channel spacing and channel depth should be properly considered and designed so that unwanted bulge defects can be prevented from occurring.

Figure 7.2 Contour plot of equivalent plastic strain on the outermost channel of a 2 mm thick substrate showing the comparison in diamond-ruled molds with: (a) Channel spacing of 100 μm and 1 mm, and (b) Channel spacing of 100 and 500 μm , after thermally cooled to 25°C

7.1.3 Polymer substrate thickness

The influence of the polymer substrate thickness to thermal cooling process can be directly correlated to the thickness of base layer. For a fixed channel geometry, variation in the polymer substrate thickness will only alter the thickness of base layer. As mentioned above in Section 7.1.2, the base layer can have a detrimental impact on the replicated features of polymer substrate when it is cooled down to lower temperature. This is mainly due the constraint developed by the excess material on the base layer. As expected, both thermal stress (see Figure 7.3a) and plastic strain (see Figure 7.3b) formed on the polymer substrate increase with the use of thicker substrate. This trend applies to all of the molds. It should be noted that the values of thermal stress and plastic strain during testing on mold 1 are much higher because of the relatively much wider channel spacing (1 mm) and shallower channel (50 μm) when compared to the other molds.

Figure 7.3 Plot of: (a) Maximum thermal stress (Von Mises stress), and (b) Maximum localized equivalent plastic strain, on the 1, 1.5, and 2 mm thick substrates that were replicated on the different diamond-ruled molds and thermally cooled to 25°C (numerical simulation)

The above results indicate that the detrimental effects of thermal cooling can be minimized by utilizing a thinner substrate. When a 2 mm thick substrate replicated on mold 1 was cooled down to room temperature, the bulge defect (see Figure 7.4a) was formed. However, when a thinner polymer substrate of 1

mm was used, the bulge defect was much less severe (see Figure 7.4b). Thus, using a thinner polymer substrate will always be more advantageous.

Figure 7.4 Contour plot of equivalent plastic strain on the outermost channel of a: (a) 2 mm thick substrate, and (b) 1 mm thick substrate, showing the comparison in the formed bulge defect after thermally cooled to 25°C on diamond-ruled mold (mold 1)

7.1.4 Demolding temperature

In this study, the embossing temperature was fixed at 100°C as complete replication was possible at this temperature. It will be demonstrated that demolding temperature significantly influences the thermal stress and resultant plastic strain in the replicated polymer substrate. It can be seen from Figure 7.5a that thermal stress increases with lower demolding temperature. However, the results show that there is a slight drop in the maximum thermal stress at

50°C. This happens because during the thermal cooling transition phase from 60 to 50°C, the polymer substrate slides slightly upwards with relative to the mold. The slight upward movement on the contacting features between the mold and polymer substrate permits some thermal stress-relief.

In line with expectations, the plastic strain increases when the polymer substrate is cooled to lower temperatures (see Figure 7.5b). Similar to thermal stress, the highest plastic strain is observed when demolding is performed at the lowest temperature (25°C). It should be noted that both the thermal stress and plastic strain are relatively much higher during testing on mold 1 when compared to the other molds. This happens because the channels in mold 1 have the widest channel spacing (see Section 7.1.2).

Figure 7.5 Plot of: (a) Maximum thermal stress (Von Mises stress), and (b) Maximum localized equivalent plastic strain, on a 2 mm thick substrate that was replicated on the different diamond-ruled molds and thermally cooled to demolding temperature ranging from 25 to 70°C (numerical simulation)

From the above results, it is apparent that demolding temperature is an extremely crucial parameter because it determines the magnitude of generated thermal stress which has a significant effect on demolding difficulty. Appropriate choice of the demolding temperature is also a useful means to mitigate the bulge defect. Figure 7.6 demonstrates the comparison in the bulge defect formed on the outermost channel of replicated polymer substrate at the varying demolding temperature. It can be observed that the severity of the bulge defect is affected by the chosen demolding temperature. It is apparent that a demolding temperature of 70°C can significantly reduce the formation of bulge defect when compared to the lower demolding temperatures. Hence, it can be concluded that thermal cooling to a higher demolding temperature is a better approach to minimize thermal stress and possible plastic deformation.

Figure 7.6 Contour plot of equivalent plastic strain showing the comparison in the bulge defect formed on the outermost channel of a 2 mm thick substrate that was replicated on a diamond-ruled mold (mold 1) and thermally cooled to: (a) 25°C, (b) 40°C, (c) 60°C, and (d) 70°C

Furthermore, the above results also demonstrate that, control of both the polymer substrate thickness and demolding temperature can be an efficient approach in tackling the bulge defect issues, rather than resorting to build an auxiliary structure to protect the outermost channels from the formation of intolerable bulge defect [22]. The efficacy of adopting such an approach has been successfully demonstrated (see Figure 7.7) through the use of a thin polymer substrate (1 mm) and high demolding temperature (70°C).

Figure 7.7 Contour plot of equivalent plastic strain showing the minor bulge defect formed on the outermost channel of a 1 mm thick substrate that was replicated on a diamond-ruled mold (mold 1) and thermally cooled to 70°C

7.1.5 Embossing temperature

The embossing temperature (prior to demolding) also has an effect on the magnitude of generated thermal stress and plastic strain in the polymer substrate after cooling. As illustrated in Figure 7.8a, the polymer substrate experiences higher thermal stress when it is hot-embossed at a higher temperature. An identical trend is also observed for the generated plastic strain in the polymer substrate (see Figure 7.8b). The finding is in line with expectations because the use of a higher embossing temperature, under a fixed

demolding temperature, will lead to greater thermal contraction. Therefore, the embossing temperature can affect the demolding difficulty through its influence on the generated thermal stress. Consequently, it is always better to perform hot-embossing at the lowest possible temperature, whilst ensuring complete replication of the polymer substrate into the mold cavity is achieved.

Figure 7.8 Plot of: (a) Maximum thermal stress (Von Mises), and (b) Maximum localized equivalent plastic strain, on a 2 mm thick polymer substrate that was replicated on a diamond-ruled mold (mold 2) at varying embossing temperature and thermally cooled to 25°C, showing the influence of embossing temperature

7.1.6 Channel design (shape of the channel cross-section)

The effect of the shape of the channel cross-section will now be studied. Two numerical models that include tapered and bell-shaped channels were built and their effect on the thermal cooling process was investigated. To ensure fair comparison, the channel geometry of both models were modeled based on the channel depth and average width as in the diamond-ruled mold (mold 3) that has a conventional rectangular-shaped channel. The obtained results as shown in Figure 7.9 have revealed that the three different shapes of channel cross-section have their own influence to the outcome of thermal cooling process.

Figure 7.9 Plot of: (a) Maximum thermal stress (Von Mises), and (b) Maximum localized equivalent plastic strain, on a 2 mm thick polymer substrate that was replicated on a diamond-ruled mold (mold 3) and thermally cooled to 25°C, showing the influence of the three different channel design (shape of channel cross-section)

The conventional rectangular-shaped channel has the highest thermal stress, while the bell-shaped channel created the smallest thermal stress (see Figure 7.9a). The magnitude of the plastic strain generated also follows the same trend (see Figure 7.9b). It was apparent that the molds with sharper corners had higher thermal stress and plastic strain. This is because the mold acts as a constraint to shrinkage of the polymer substrate during thermal contraction, and the sharp corners will act as points of the stress concentration. The rectangular-shaped channel has the worst stress concentration because it has a channel with the sharpest edge (see Figure 7.10a). The stress concentration can be reduced by having a slight tapered angle on the mold (see Figure 7.10b), while a rounded-corner profile eliminates any stress concentration. Hence, the bell-shaped channel can result in the best outcome (see Figure 7.10c).

Figure 7.10 Plot showing the deformed shape of the two outermost replicated channels on a 2 mm thick polymer substrate after thermally cooled to 25°C: (a) Conventional rectangular-shaped channel, (b) Tapered channel, and (c) Bell-shaped channel

7.1.7 Adhesion of the polymer substrate to the mold

Two types of adhesion are encountered in the replication of a polymer by hot-embossing using an aluminum mold. They are thermodynamic and mechanical adhesion. Generally, the first can be altered by using coated molds, while the latter is affected by the quality of surface finish of the molds. The main objective of altering both thermodynamic and mechanical adhesion is to lower the adhesion of the replicated polymer to the mold to facilitate ease of demolding. A lower adhesion also translates into lower interfacial friction between the mold and polymer substrate. To study the effect of adhesion to the mold on demolding, two different interfacial models were used. In the first model, the interfacial friction between the mold and polymer substrate that was determined experimentally was used in the analysis, while the second model assumes that the interfacial friction was halved.

Figure 7.11 Plot of: (a) Maximum thermal stress (Von Mises), and (b) Maximum localized equivalent plastic strain, on the polymer substrates that were replicated on diamond-ruled molds (mold 1 – 1 mm, mold 2 – 1 mm, mold 3 – 1.5 mm, and mold 7 – 2 mm thick substrate) and thermally cooled to 25°C, showing the influence of reduced adhesion property which can correspond to coated mold or smoother surface finishing of mold

It can be observed from Figure 7.11 that both thermal stress (see Figure 7.11a) and plastic strain (see Figure 7.11b) obtained using the original molds which have higher adhesion are much higher than those from molds with lower friction (lower adhesion). Thus, the adhesion of the replicated polymer

substrate to the mold has also shown a significant effect on the ease of demolding based on the generated thermal stress.

7.1.8 Demolding method

There are two types of demolding method, namely: one-sided demolding and two-sided demolding. A detailed analysis of these two demolding methods will be investigated in a later section. One key difference between these demolding methods is the length of the polymer substrate. This is because in the two-sided method, polymer substrate has to be longer to enable the demolding load to be applied on both side of the polymer substrate. The influence of the length of the polymer substrate will now be examined. It can be seen from Figure 7.12 that both generated thermal stress (see Figure 7.12a) and plastic strain (see Figure 7.12b) in the slightly different polymer substrates are relatively similar. Thus, it can be concluded that the slightly longer polymer substrate used with the two-sided method does not lead to any significant difference in the outcome of thermal cooling process.

Figure 7.12 Plot of: (a) Maximum thermal stress (Von Mises), and (b) Maximum localized equivalent plastic strain, in each channel of a 2 mm thick polymer substrate that was replicated on a diamond-ruled mold (mold 3) and thermally cooled to 25°C, showing the comparison in the two slightly different substrates for one-sided and two-sided demolding purposes

7.2 Effect of the different parameters on demolding

The influence of different parameters on the thermal cooling process was considered in detail in the previous section. In this section, the effect of each parameter on demolding will now be evaluated.

7.2.1 Channel geometry

As the variations in channel geometry involve channel depth and spacing, the effect of channel geometry on demolding is further divided into three different groups which are aspect ratio of replicated polymeric features, channel depth, and channel spacing. The aspect ratio of replicated polymeric features can correspond to change in both of the channel depth and channel spacing at the same time. Therefore, the influence of channel depth and channel spacing will also be individually investigated.

7.2.1.1 Aspect ratio of replicated features

As tabulated in Table 3.1, there are two different aspect ratios. The first is the aspect ratio of channel which is defined as the ratio of channel depth divided by channel width, while the second is the aspect ratio of replicated feature which is defined as the ratio of channel depth divided by channel spacing. Aspect ratio of the micro-channel is a general term which is commonly used by researchers. It should be noted that despite the different definitions, both aspect ratios share a similarity in that a higher aspect ratio of the micro-channels generally corresponds to a higher aspect ratio of the replicated features.

In the present work, the aspect ratio of replicated feature will be the main focus. The importance of the replicated features in the polymer substrate on the demolding outcome has been described in Section 6.2. This is mainly influenced by the bending phenomenon experienced by the replicated features which can cause demolding failure. It has also been mentioned that the aspect ratio of the replicated features will influence the magnitude of stress experienced under bending during demolding based on the simple bending theory.

Figure 7.13 shows the experimentally and numerically calculated demolding energy per unit area during demolding of the replicated polymer substrate from diamond-ruled molds which involve a wide range of aspect ratios, substrate thicknesses, and demolding temperatures. The plots reveal that aspect ratio of the replicated features has a significant influence on the demolding difficulty. It can be observed that the demolding energy per unit

area generally increases when polymer substrates with higher aspect ratio features are demolded. This trend applies to all of the three demolding energy per unit area plots that demonstrate different scenarios of both successful demolding (see Figure 7.13a (Left)) as well as failed demolding in terms of polymer breakage (see Figure 7.13b (Left)) and deformed substrate (see Figure 7.13c (Left)). It can also be observed that there is an increase in plastic strain in the demolded polymer substrates with higher aspect ratio (see Figure 7.13 (Right)). Therefore, it is apparent that demolding can cause failure in features with high aspect ratio.

Figure 7.13 Plot of demolding energy per unit area calculated from both experiments (E) and numerical simulations (S), and maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrates after thermal cooling and demolding processes (numerical simulation), showing the influence of aspect ratio of the replicated features: (a) Successful demolding, (b) Polymer breakage, and (c) Deformed substrate

Next, correlation of the influence of aspect ratio to the influence of channel depth will be considered. This can be seen from Figure 7.13a where it is apparent that the demolding energy per unit area at aspect ratio of 0.5 is relatively lower than that at smaller aspect ratios of 0.2 and 0.4. This can happen because of a much shallower channel ($50\text{ }\mu\text{m}$) for the mold with aspect ratio of 0.5, when compared to the other two (100 and $200\text{ }\mu\text{m}$), which causes the demolding of polymer substrate with an aspect ratio of 0.5 easier. Furthermore, it is also found that polymer substrate with a feature aspect ratio of 0.4 broke during demolding, while no breakage occurred during demolding for a polymer substrate with a higher feature aspect ratio of 1 (see Figure 7.13b). This was similarly due to the much deeper channel (200 and $100\text{ }\mu\text{m}$, respectively). The separated effect of channel depth will be examined in the following Section 7.2.1.2.

The observed demolding difficulty at higher aspect ratio can be correlated to the bending phenomenon experienced by the polymer substrate during demolding. Figure 7.14 illustrates how aspect ratio affects the bending phenomenon in the polymer substrate during demolding. The two models show the deformed shape of polymer substrate just prior to the end of demolding based on the consideration of the lowest and highest aspect ratio of features used in this work. It can be seen that there is much more severe bending in the polymer substrate that has replicated features with an aspect ratio of 2 (see Figure 7.14b) when compared to that with aspect ratio of 0.05 (see Figure 7.14a).

Figure 7.14 Plot of deformed shape of polymer substrate during demolding from diamond-ruled mold with feature aspect ratio of: (a) 0.05, and (b) 2, showing the comparison in the bending behavior

Furthermore, it is also possible to quantitatively correlate the bending phenomenon to demolding difficulty by considering the stress-evolution on the polymer substrate during demolding (see Figure 7.15). The magnitude of the stress generated in the polymer substrate during demolding was found to increase drastically with increase in aspect ratio of replicated features. This finding is much more obvious from the stress-evolution during demolding of polymer substrate with aspect ratio of 1.5 and 2.

Figure 7.15 Plot of evolution of localized maximum principal stress on the polymer substrate during demolding from diamond-ruled molds, showing the influence of aspect ratio of the replicated features

In conclusion, both the quantitative and qualitative results obtained from experiments and numerical simulations indicated the increasing demolding difficulty during replication of polymer substrate with higher aspect ratio micro-features. The above findings demonstrated good agreement to reports based on qualitative analyses by other researchers claiming that demolding failures frequently occurred in high aspect ratio micro-channels. Most

importantly, the present studies have also successfully unveiled the main mechanism that contributes to the drastic increase in demolding difficulty. With the analysis afforded by our model and the known demolding-failure mechanism, it is possible to evaluate the influence of the other parameters so that successful fabrication of microfluidic devices with high aspect ratio micro-channels can be accomplished.

7.2.1.2 Channel depth and channel spacing

Since the aspect ratio of replicated feature can involve a change in both channel depth and spacing at once, the individual effect of channel depth and spacing will be further examined in this section. It can be seen from Figure 7.16a that an increasing trend in demolding energy per unit area is obtained with increasing channel depth. Identical trend is also observed when a substrate with more densely packed channels that corresponds to narrower channel spacing is demolded (see Figure 7.16b). Although the plots in Figure 7.16 only demonstrate the increasing demolding difficulty based on successful demolding scenarios, it should be noted that polymer breakage or deformed substrate is not uncommon during tests on molds with either deep or narrowly spaced channels at the different set of parameters that are not shown here.

In considering the thermal cooling and demolding processes, it is interesting to note that the demolding energy per unit area has a trend which is converse to the trend for the generated thermal stress after thermal cooling. For a fixed polymer substrate thickness, thermal stress is found to increase with either shallower channel or wider channel spacing (see Figure 7.1a). Furthermore,

thermal stress has a direct effect on the demolding difficulty since it increases the friction forces for sliding at the vertical interfaces between the mold and polymer substrate.

Figure 7.16 Plot of demolding energy per unit area calculated from both experiments (E) and numerical simulations (S) during demolding of 2 mm thick substrate from diamond-ruled molds after thermally cooled to 25°C, showing the individual effect of (a) Channel depth, and (b) Channel spacing

The contrast in the obtained trends can be further correlated and supported by the tendency of polymer substrate with deeper or more narrowly spaced channels to experience more severe bending during demolding. Considering a fixed channel spacing, deeper channel indeed corresponds to higher aspect ratio of the feature. Similarly, a narrower channel spacing under a fixed channel depth also means higher aspect ratio of the feature. In other words, consideration in the magnitude of the generated thermal stress prior to demolding only cannot fully predict the final demolding difficulty. It is the bending phenomenon that will eventually determine how difficult the demolding process will be.

7.2.2 Polymer substrate thickness

The influence of polymer substrate thickness will now be considered. Unique demolding energy trends were observed for the three different polymer substrate thicknesses used to replicate the channels of diamond-ruled molds (see Figure 7.17). Figure 7.17a indicates a decrease in demolding energy when thinner polymer substrate is used, while conversely, Figure 7.17c indicates an increasing trend in demolding energy with the use of thinner polymer substrate. It is noted that the demolding energy obtained for a 1 mm thick substrate from diamond-ruled mold (mold 7) is lower than that for the 1.5 mm thick substrate. The obtained smaller demolding energy is due to early breakage in the polymer substrate after demolding of just six out of the fifty replicated channels. Also, it is quite arduous to demold the 1.5 mm thick substrate as it can be observed from the increase in plastic strain of about 15% in spite of the

absence in polymer breakage (see Figure 7.18c). Nevertheless, based on the increasing severity in the demolding outcome from 1.5 mm to 1 mm thick substrate, the term “increasing trend in demolding energy” can still be reasonably used.

Besides the two trends observed in Figure 7.17a and Figure 7.17c, a V-shaped trend in demolding energy was observed in Figure 7.17b. All three different trends share a common feature in that there existed a minimum demolding energy which corresponds to the easiest demolding. Easiest demolding is always an optimal aim so that efficient and successful demolding can be achieved, while minimizing the chances of demolding defects from arising. Successful demolding can also be numerically represented by the plastic strain on the demolded polymer substrate that remains constant after the thermal cooling process (see Figure 7.18a, Figure 7.18b, and Figure 7.18c).

Figure 7.17 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of replicated polymer substrates from diamond-ruled molds after thermally cooled to 25°C, showing the effect of polymer substrate thickness: (a) Decreasing trend, (b) Slight V-shaped trend, and (c) Increasing trend, of demolding energy with the use of thinner substrates

The conditions under which the demolding process ends up with extremely high demolding energy and defects have also been identified. This is demonstrated through the relatively high demolding energy spent in demolding the 1 mm thick substrate from the diamond-ruled molds (mold 3, 6, and 7) which resulted in polymer breakage (see Figure 7.18c). The polymer breakage was evident from both experimental observation (see Figure 7.21a)

and numerical simulation which is based on an analysis of the evolution of demolding stress in the polymer substrate (see Figure 7.20).

Lastly, there is also a scenario in which the polymer substrate survives possible demolding defects despite the relatively high demolding energy. This scenario can be seen from the demolding results of 2 mm thick substrate from diamond-ruled mold 1 & 2 (see Figure 7.17a), and 1 mm thick substrate from diamond-ruled mold 5 (see Figure 7.17b). As illustrated in Figure 7.18a, there is no increase in plastic strain after demolding from mold 2 at all three different thicknesses. It is also noted that although there is a slight increase of 4% in plastic strain during demolding from diamond-ruled mold 5 (see Figure 7.18b), the overall replication fidelity of the demolded 1 mm thick substrate was still well-maintained. Nevertheless, such scenarios may not be considered as an optimal demolding condition because lower demolding energy can still be achieved with other substrate thicknesses (see Figure 7.17a and Figure 7.17b).

Figure 7.18 Plot of maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the influence of polymer substrate thickness

The obtained quantitative and qualitative results have revealed the crucial role that the polymer substrate thickness plays in accomplishing both efficient and successful demolding. Its role is indeed mainly dependent on its bending stiffness (flexural rigidity). Thicker polymer substrates have higher bending stiffness so that extreme bending can be prevented. This can be observed through a comparison of the deformed shape of polymer substrate during demolding. As illustrated in Figure 7.19, the bending experienced by the polymer substrate during demolding becomes more severe in thinner polymer substrates. It can be seen that the thinnest polymer substrate (1 mm) did not possess adequate bending stiffness and was severely bent during demolding from the diamond-ruled mold 6 (see Figure 7.19c), and eventually broke prior to the end of demolding. The difference in influence of the polymer substrate thickness to demolding outcome in terms of the demolding stress is summarized in Figure 7.20.

The important influence of bending stiffness of the substrate can also be observed for demolding at elevated temperature (60°C). In spite of the unsuccessful demolding in all the three different substrate thicknesses, the benefit of higher flexural rigidity in the 2 mm thick substrate in minimizing plastic deformation during demolding (see Figure 7.18d) is still apparent. An identical trend in plastic deformation was also obtained experimentally (see Figure 7.21b).

Figure 7.19 Plot of deformed shape of polymer substrate during demolding from diamond-ruled mold (mold 6) with substrate thickness of: (a) 2 mm, (b) 1.5 mm, and (c) 1 mm, showing the comparison in the bending behavior

Finally, based on the set of processing parameters considered, it can be concluded from Figure 7.17 that the most efficient and successful demolding can be achieved with 1 mm, 1.5 mm, and 2 mm thick substrates during demolding from diamond-ruled mold 1 & 2, 3 & 5, and 6 & 7, respectively. In other words, there exists an optimal polymer substrate thickness. Interestingly, there is a correlation between the optimal substrate thickness and the aspect ratio of replicated features. It is noted that the aspect ratio of the replicated features increases from mold 1 to mold 7, which further means that thicker substrate is required for efficient and successful replication on mold with higher aspect ratio micro-features. This can be attributed to the combined effect of the individual parameters on the bending phenomenon in the substrate. It has been previously concluded that bending is more prone to

occur during demolding of mold with high aspect ratio micro-features. Therefore, thicker substrate is required to compensate and minimize the bending experienced on the polymer substrate during demolding.

Figure 7.20 Plot of evolution of localized maximum principal stress on the polymer substrate during demolding from diamond-ruled mold (mold 6), showing the influence of polymer substrate thickness

In spite of the preference for a thinner substrate (which leads to lower thermal stress) based on thermal cooling considerations, it has been found from the above work that the selection of an optimal polymer substrate thickness should mainly be based on a consideration of the demolding process. Generally, it can be concluded that molds with higher aspect ratio micro-channels tend to be more sensitive to the selection of an appropriate substrate thickness to ensure that the bending stiffness is adequate to prevent severe bending. On the other hand, there is much more flexibility in the selection of substrate thickness on molds with lower aspect ratio micro-channels. Nevertheless, an optimal polymer substrate thickness exists whereby, not only is the overall size of the

microfluidic devices and the amount of raw material used can be minimized, but most importantly, efficient and successful fabrication of the devices can also be accomplished.

Figure 7.21 Photos showing: (a) Polymer breakage during demolding of a 1 mm thick substrate from diamond-ruled mold (mold 6) at 25°C, and (b) Deformed substrates comparing the deformation of 2 mm and 1 mm thick substrates during demolding from diamond-ruled mold (mold 5) at 60°C

7.2.3 Demolding temperature

The influence of demolding temperature involves the combined interaction of several factors which include adhesion, friction, thermal stress, and material properties. The experimental and simulation results on the effect of demolding temperature on demolding energy are shown in Figure 7.22a. The respective Figure 7.22b, Figure 7.22c, and Figure 7.22d are plotted with two molds each

for clearer presentation. It can be seen that there exists a minimum demolding energy which represents the optimal demolding temperature. The demolding energy is higher at both ends of the demolding temperature range.

At the higher temperature end, which is close to the glass transition temperature of the polymeric material (78°C), severe plastic deformation always arises with all molds. Despite the relatively low thermal stress, defects can easily form due to high friction and adhesion, and the much weaker material properties in terms of strength and flexural rigidity. As expected from the proneness of bending phenomenon in mold with higher aspect ratio micro-features, polymer substrates replicated on such molds tend to plastically deform at lower demolding temperature of 60°C instead of 70°C (see Figure 7.22a, Figure 7.23a, and Figure 7.23b). One such example can be experimentally (see Figure 7.25a) and numerically (see Figure 7.24 and Figure 7.25b) observed in the 2 mm thick substrate demolded from diamond-ruled mold 7 at 60°C in which the channels were severely distorted.

Figure 7.22 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of 2 mm thick substrates from diamond-ruled molds, showing the effect of demolding temperature: (a) All diamond-ruled molds, (b) Mold 1 & 2, (c) Mold 3 & 5, and (d) Mold 6 & 7

At the low temperature end (25°C), the demolding energy was high for all the six diamond-ruled molds. The high demolding energy is mainly contributed by the high friction and thermal stress, because adhesion between the mold and substrate is very low at 25°C. Nevertheless, because of the superior material properties of the polymer at 25°C, the substrate is less prone to the development of any demolding defect. This observation is evident from the high number of successful demolding cases in spite of the several unsuccessful demolding cases involving polymer breakage during demolding of thin substrate (1 mm) from molds with high aspect ratio micro-features for demolding temperature of 25°C (see Figure 7.26c).

Figure 7.23 Plot of maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrates after thermal cooling and demolding processes (numerical simulation), showing the influence of demolding temperature

Because of the higher demolding difficulty at either lower or higher temperature, there exists an optimal demolding temperature that is located in between the two extreme temperatures. The beneficial effect of the optimal demolding temperature can be demonstrated more clearly through testing on molds with high aspect ratio micro-features. As illustrated in Figure 7.22d, the optimal demolding temperature for demolding of a 2 mm thick substrate from diamond-ruled mold 7 was found to be at 40°C at which the plastic strain formed from demolding (see Figure 7.23c) is minimum. Another example is the demolding of a 1.5 mm thick substrate from diamond-ruled mold 6 in which the optimum demolding temperature was also found to be at 40°C (see Figure 7.23d).

Figure 7.24 Plot of evolution of localized maximum principal stress and Von Mises stress on the polymer substrate during demolding from diamond-ruled mold 7 at elevated temperature (60°C) that resulted in plastic deformation (distorted channel)

Lastly, it is important to note that there exists a correlation between the optimal demolding temperature and the feature aspect ratio. Based on the plots in Figure 7.22a with 2 mm thick substrates, the optimal demolding

temperature during demolding from diamond-ruled mold 1, 2, 3, and 5 is 50°C, while the optimal demolding temperature during demolding from diamond-ruled mold 6 and 7 is 40°C. This indicates that the optimal demolding temperature tends to become lower for replication on molds with higher aspect ratio micro-features. The shift in the optimal demolding temperature is mainly caused by the need to have higher strength and flexural rigidity so that the polymer substrate can withstand the more severe bending phenomenon. On the other hand, the higher optimal demolding temperature during demolding from molds with lower aspect ratio micro-features can already provide adequate strength and flexural rigidity to endure the less severe bending.

Figure 7.25 Images showing the unsuccessful demolding (distorted channel) of a 2 mm thick substrate from diamond-ruled mold 7 at 60°C based on: (a) Experiment, and (b) Numerical simulation. It is noted that the simulation cannot finish due to convergence difficulty as a result of the severe channel distortion on the polymer substrate.

7.2.3.1 Combined influence of demolding temperature and polymer substrate thickness on the optimal demolding temperature

The influence of mold channel geometry, particularly its feature aspect ratio to the optimal demolding temperature has been investigated and discussed above. As polymer substrate thickness also significantly affects the flexural rigidity property, it can be intuitively predicted that there may be a possible shift in the optimal demolding temperature when combined with the influence of mold channel geometry. Three different scenarios have been observed both experimentally and numerically. Firstly, there is no change in the optimal demolding temperature (50°C) with variation in polymer substrate thickness for demolding from a mold with relatively low aspect ratio micro-features (see Figure 7.26a). This can happen because the demolding process only involves minor bending phenomenon, despite the use of a thin polymer substrate.

The second scenario is as illustrated in Figure 7.26b. When thinner polymer substrates (1 and 1.5 mm) are used to replicate the mold with relatively high aspect ratio micro-features ($AR = 1$) instead of the 2 mm thick substrate, the optimal demolding temperature shifts from 50°C to a lower temperature of 40°C. The thinner polymer substrates have a much lower second moment of area so that there is a need for the demolding temperature to compensate for the decrease in the flexural rigidity. This is eventually achieved from the enhanced Young's modulus through the application of a lower demolding temperature. In addition to the increase in Young's modulus, the enhanced

strength of the polymer substrate also helps to withstand the bending stress experienced during demolding.

Figure 7.26 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of replicated polymer substrates from diamond-ruled molds, showing the combined effect of demolding temperature and polymer substrate thickness: (a) Mold 2, (b) Mold 5, and (c) Mold 6

Lastly, there is also a scenario in which there is no existence of optimal demolding temperature. In this case, successful demolding cannot be simply achieved with any change in demolding temperature. As shown in Figure 7.26c, the optimal demolding temperature during demolding of 1.5 and 2 mm thick substrates from diamond-ruled mold 6 is at 40°C. However, all of the demolding tests at 25, 40 and 50°C performed on a 1 mm thick polymer substrate ended up with polymer breakage. The main reasons that cause this unsuccessful demolding are the extremely low flexural rigidity of a thin substrate and the relatively high feature aspect ratio of diamond-ruled mold 6 (AR = 1.5). In this scenario, the increase in both strength and flexural rigidity of polymer substrate through application of a lower demolding temperature is still insufficient to withstand the severe bending encountered during demolding. This demonstrates that successful demolding may not be

accomplished through proper selection of demolding temperature alone. In other words, it is very important to consider the combined effect of both demolding temperature and polymer substrate thickness so that successful demolding can be achieved.

Besides having the best chance of success, demolding performed at the optimal demolding temperature will also influence the time and energy efficiency of the whole replication processes. This is because mass replication via hot-embossing involves many repetitive temperature cycles. Therefore, if demolding can be successfully performed at a higher temperature, the temperature difference between embossing and demolding temperature can be narrowed and at the same time, the overall cycle time can also be minimized.

7.2.4 Demolding rate

A study on the influence of demolding rate on both micro-machined and diamond-ruled molds was carried out. The total demolding energy required to separate the replicated polymer from both types of molds shows a general trend in that it increases with faster demolding rate (see Figure 7.27a and Figure 7.28 (Left)). During replications on the micro-machined mold, the demolding rate has a noticeable effect on the demolding energy, but no change in the generated plastic strain on the demolded polymer substrate was observed (see Figure 7.27b). Similarly, during replications on the diamond-ruled molds with relatively lower aspect ratio micro-features, there is no distinctive influence of demolding rate on the generated plastic strain, except for the increasing demolding energy (see Figure 7.28a).

Figure 7.27 Plot of: (a) Total demolding energy calculated from both experiments (E) and numerical simulations (S), and (b) Maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the effect of demolding rate during demolding of a 2 mm thick substrate from micro-machined mold at 25°C

Although the optimum demolding condition is associated with the condition at which the demolding energy is minimum, it may not be the best scenario for selecting the optimal demolding rate. This was observed based on a demolding study on the effect of demolding rate using molds with higher aspect ratio micro-features that can cause significant demolding difficulty. Figure 7.28b

shows that a slower demolding rate can result in smaller demolding energy, but unfortunately, it can also induce much more plastic strain on the demolded polymer substrate.

Another scenario that reflects the observed phenomenon is illustrated during demolding of a 2 mm thick substrate from diamond-ruled mold 5 at 60°C (see Figure 7.28c). Even though both of the tested demolding rates end up with severe plastic deformation, the obtained results can still demonstrate the distinct opposite trend of demolding energy and generated plastic strain. In this case, in spite of the lower demolding energy during demolding at 1 mm/min, the generated plastic strain is much higher than that at 50 mm/min. This trend is also evident based on the comparison in the stress-evolution on the polymer substrate during demolding with the corresponding yield strength at the two different demolding rates (see Figure 4.32b). Moreover, the two differently deformed substrates after demolding can also be easily distinguished in experiments (see Figure 4.33b).

Figure 7.28 Plots of total demolding energy calculated from both experiments (E) and numerical simulations (S), and the maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation) that show the effect of demolding rate during replication on diamond-ruled molds

The observed phenomenon happens because with the faster demolding rate, both of the strength and flexural rigidity of the polymer substrate increase. Furthermore, it has already been proven that there is no significant change in the interfacial friction property at the tested range of demolding rate on both micro-machined and diamond-ruled molds. Thus, it is clear that demolding rate only affects the material properties of the polymer. As a result, based on the consideration in the tested range of demolding rate in this work, it can be concluded that a faster demolding rate can always perform better despite the

requirement of higher demolding energy when compared to the slower demolding rate. In addition, a faster demolding rate not only suppresses the formation of defect better than the slower demolding rate, but it can also accommodate for the maximum production throughput.

7.2.5 Embossing temperature

Three different embossing temperatures with a fixed demolding temperature of 25°C were used to investigate on its effect to demolding of replicated polymer substrates from micro-machined and diamond-ruled molds. It should be noted that complete filling of polymer into the mold cavities is always achieved at all of the tested embossing temperatures. Based on the experimental and numerically simulated results, it is found that demolding becomes harder to perform when the polymer substrate is hot-embossed at a higher temperature (see Figure 7.29a and Figure 7.30a). This is indeed attributed to the more severe thermal stress that is generated due to the higher thermal contraction at higher embossing temperature.

(a)

(b)

Figure 7.29 Plot of: (a) Total demolding energy calculated from both experiments (E) and numerical simulations (S), and (b) Maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the effect of embossing temperature during demolding of a 2 mm thick substrate from micro-machined mold at 25°C

In spite of the increasing demolding energy with the application of higher embossing temperature, there is a scenario in which there is no increase in the generated plastic strain on the demolded polymer substrate at all of the three different embossing temperatures (see Figure 7.30b). This can happen because of the much easier demolding from the diamond-ruled mold 2 that has a low feature aspect ratio. Conversely, as a result of the enhanced thermal stress at higher embossing temperature, there is also a scenario in which more additional plastic strain arises during demolding of polymer substrate that is hot-embossed at a higher temperature (see Figure 7.29b). For the case of molds with relatively higher feature aspect ratio, embossing temperature is expected to significantly affect the generated plastic strain during demolding.

In other words, demolding energy always increases with the application of higher embossing temperature, while the formation of plastic strain due to demolding is dependent on how difficult the demolding process is. Considering a fixed demolding temperature, it should be recognized that thermal stress is always more severe when the polymer substrate is hot-embossed at a higher temperature. Therefore, higher plastic strain will also be formed during the thermal cooling process. Moreover, at the same time, there will be higher chance of developing bulge defect, and it may eventually deem the replicated polymer substrate unusable. Based on the mentioned arguments, it is always optimal to perform the hot-embossing process at the lowest possible temperature as long as complete filling is accomplished.

(a)

Figure 7.30 Plot of: (a) Total demolding energy calculated from both experiments (E) and numerical simulations (S), and (b) Maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the effect of embossing temperature during demolding of a 2 mm thick substrate from diamond-ruled mold 2 at 25°C

7.2.6 Channel design (shape of the channel cross-section)

The influence of channel design (shape of the channel cross-section) on demolding was only studied numerically due to the unavailability of molds with tapered and bell-shaped channels. It should be noted that the mold with rectangular-shaped channels is based on diamond-ruled mold 3. Similarly, both molds with tapered and bell-shaped channels also follow the overall channel geometry of the diamond-ruled mold 3, except their own respective distinct differences such as tapered angle and rounded-corner channel profile.

Figure 7.31 Plot of: (a) Total demolding energy calculated from numerical simulations, and (b) Maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the effect of channel design during demolding of a 2 mm thick substrate at 25°C

As illustrated in Figure 7.31a, the calculated total demolding energy demonstrates that it is the most difficult to demold the replicated polymer substrate from mold with the conventional rectangular-shaped channels, followed by molds with bell-shaped and tapered channels, respectively. This is in line with the finding that the highest thermal stress was formed during replication on the mold with rectangular-shaped channels (see Figure 7.9a). In

addition, the sharp corners and vertical channel sidewalls also contribute to the demolding difficulty. The numerical simulations indicate that no additional plastic strain arises during demolding (see Figure 7.31b) in all the three molds.

Figure 7.32 Plot of evolution of localized maximum principal stress on the polymer substrate during demolding of a 2 mm thick substrate from the different kinds of molds, showing the influence of channel design

An interesting finding based on the comparison in demolding energy between molds with tapered and bell-shaped channels is observed. Higher thermal stress is initially experienced in the polymer substrate replicated on mold with tapered channels. However, despite the higher thermal stress, demolding from the mold with tapered channels is found to be easier than that with bell-shaped channels. The much easier demolding is influenced by the slanted channel sidewalls of the tapered channels that eventually lead to much weaker mechanical interlocking between the mold features and replicated polymeric features. Furthermore, the lower stress and shorter demolding displacement when compared to the other two molds (see Figure 7.32) have also

demonstrated the same agreement. On the whole, although tapered and bell-shaped channels can provide easier demolding when compared to the conventional rectangular-shaped channels, the suitability and functionality of each channel design to a certain application should be first considered so that maximum performance can be achieved.

7.2.7 Adhesion of the polymer substrate to the mold

7.2.7.1 Numerical study on the effect of both thermodynamic and mechanical adhesion

As shown in Figure 7.33a, the lower adhesion to the mold which can correspond to either reduced thermodynamic adhesion through application of coating layer on mold or reduced mechanical adhesion through smoother surface finishing quality of mold leads to easier demolding. It should be noted that the lower adhesion property was implemented numerically by applying half of the temperature-dependent interfacial friction values that were initially characterized on the diamond-ruled molds (shown as higher adhesion in the plots).

The beneficial effect of the lower adhesion property becomes more obvious during demolding of replicated polymer from mold with higher aspect ratio micro-features such as the diamond-ruled mold 7. This can be observed in Figure 7.33b which is based on the comparison in plastic strain developed on the polymer substrate after thermal cooling and the demolding processes. Besides its significant reduction in the demolding energy, there is also no additional increase in plastic strain after demolding, which is in contrast to the

increased plastic strain during demolding from the same mold that has higher adhesion property. Hence, it is apparent that lower adhesion of the polymer substrate to the mold may also prevent unwanted demolding failures from happening.

Figure 7.33 Plot of: (a) Total demolding energy calculated from numerical simulations, and (b) Maximum localized equivalent plastic strain comparing the plastic strain generated on the polymer substrate after thermal cooling and demolding processes (numerical simulation), showing the effect of adhesion property on demolding from diamond-ruled molds (mold 1 – 1 mm, mold 2 – 1 mm, mold 3 – 1.5 mm, and mold 7 – 2 mm thick substrate)

7.2.7.2 Experimental study on the effect of mechanical adhesion

The effect of thermodynamic adhesion was only studied through numerical simulation because the experimental work does not involve any mold coating. It should be noted that two different methods were used to fabricate the molds, and both methods result in quite distinctive surface finishing in terms of the surface roughness. The different surface roughness led to quite different experimental values of the interfacial friction. Thus, the influence of mechanical adhesion due to the different surface roughness could be experimentally investigated.

Due to the limitation in the micro-machining method, the channel geometry of the micro-machined mold is relatively much larger than the channel geometry of the diamond-ruled molds. As a result, the two types of molds will only be compared based on their respective feature aspect ratio. In addition, only two diamond-ruled molds (mold 2 and 3) are used for comparison with the micro-machined mold because they generate a relatively similar maximum thermal stress on the polymer substrates after thermally cooled to room temperature. In this way, it was possible to suppress their differences other than due to friction that arises from the different surface roughness. The demolding energy was normalized to the total area of the replicated polymer substrate so that reasonable comparison can be made to provide useful insights.

Figure 7.34 Plot of demolding energy per unit area calculated from experiments, showing the effect of adhesion property of mold based on its different surface finishing by the two different mold fabrication methods (micro-machining and diamond-ruling)

In spite of the lower feature aspect ratio, the demolding energy per unit area for demolding from the micro-machined mold was found to be higher than the demolding energy per unit area for the diamond-ruled molds (see Figure 7.34). The observed finding is attributed to the much higher interfacial friction in the micro-machined mold. Therefore, the results confirmed the detrimental influence of the rougher surface finishing on demolding difficulty.

Both of the numerically simulated and experimental results have indicated that optimal demolding can be better achieved with the use of molds that have lower adhesion property such as coated mold or mold with smooth surface finishing. Nevertheless, despite the advantages of coated molds, it should be noted that the use of coated molds may not be a suitable and optimal solution, particularly in chemical or biological applications due to the potential sample contaminations. Conversely, the use of molds with smooth surface finishing quality is always preferable to minimize demolding difficulty.

7.2.8 Demolding method

7.2.8.1 Comparison study in the performance of one-sided and two-sided demolding

The difference in one-sided and two-sided demolding will next be considered. Based on intuition, two-sided demolding is expected to provide easier demolding when compared to one-sided demolding. This is because the application of load on both sides of the polymer substrate in two-sided demolding may lead to less bending in the polymer substrate. However, this perception was not found to be valid in all situations.

The performance of one-sided and two-sided demolding will only be studied in terms of polymer substrate thickness and demolding temperature on all the diamond-ruled molds with varying channel geometry. The other parameters such as the demolding rate and embossing temperature are fixed in this comparison study. In addition, only uncoated mold with conventional rectangular-shaped channels is considered.

7.2.8.1.1 Influence of polymer substrate thickness with a fixed demolding temperature of 25°C

During demolding of the replicated polymer substrate from the diamond-ruled mold 1, both demolding methods can accomplish a successful demolding. At all three substrate thicknesses, the two-sided demolding was found to utilize higher demolding energy when compared to the one-sided demolding (see Figure 7.35). The higher demolding energy is attributed to the two demolding

loads applied on both sides of the polymer substrate, instead of only one demolding load applied during one-sided demolding. This trend only applies to diamond-ruled mold 1 due to the lowest tested feature aspect ratio that corresponds to much easier demolding. In this particular case, the two-sided demolding does not contribute to prevent bending because there is no severe bending in the polymer substrate even in one-sided demolding. Therefore, in terms of demolding energy, one-sided demolding can perform better.

Figure 7.35 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of replicated polymer substrate from diamond-ruled mold 1 at 25°C, showing the effect of demolding method

The remaining molds that have higher feature aspect ratio do not show identical demolding behavior. Based on tests on 1 mm thick substrates, one-sided demolding was found to be better for all of the tested molds (see Figure 7.36a). During demolding of molds with higher aspect ratio micro-features such as mold 3 and mold 7, successful demolding cannot be achieved by both demolding methods. Although there was polymer breakage in both cases, one-

sided demolding was still found to perform better. It can be observed based on the consideration in the stress-evolution on polymer substrate during demolding. As illustrated in Figure 7.37a, polymer breakage occurs earlier during the two-sided demolding for mold 3. As the polymer experiences more severe bending during the two-sided demolding, the polymer fractured during demolding of the third channel, while it only happened on the eighth channel via one-sided demolding.

Figure 7.36 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of replicated polymer substrate from diamond-ruled molds at 25°C with substrate thickness of: (a) 1 mm, (b) 1.5 mm, and (c) 2 mm, showing the effect of demolding method

A clear difference in performance of the two demolding methods is evident during demolding from diamond-ruled mold 5 in which successful demolding can only be achieved by the one-sided demolding that involves less severe bending. The difference in bending experienced on the polymer substrate during demolding by the two demolding methods is as shown in Figure 7.38. Lastly, demolding with no defect was achieved during demolding of diamond-ruled mold 2 that has relatively lower feature aspect ratio. Similarly, the higher demolding energy spent via two-sided demolding was caused by the higher level of bending when compared to one-sided demolding. Nevertheless, in this case, the polymer substrate can still survive the demolding stress.

Figure 7.37 Plot of evolution of localized maximum principal stress on the polymer substrate during demolding of: (a) 1 mm thick substrate from diamond-ruled mold 3, (b) 1.5 mm thick substrate from diamond-ruled mold 5, and (c) 2 mm thick substrate from diamond-ruled mold 7, showing the two opposite influence of two-sided demolding method in the three cases when compared to one-sided demolding method

With an increase of 0.5 mm in the polymer substrate thickness, the flexural rigidity will increase, and this is expected to mitigate the high level of bending experienced on the 1 mm thick substrate. As expected from the enhanced flexural rigidity, two-sided demolding results in lower demolding energy during demolding of diamond-ruled mold 2 and 3 (see Figure 7.36b (Left)). However, the two-sided demolding still causes severe bending on the polymer substrate to arise during demolding of molds with higher aspect ratio micro-features (diamond-ruled mold 5 and 7) as shown in Figure 7.36b (Right). This is in contrast to the one-sided demolding which finishes with successful demolding on these two molds. Comparison in the stress-evolution on the polymer substrate during demolding from diamond-ruled mold 5 by the two methods as shown in Figure 7.37b has further indicated the detrimental influence of the two-sided demolding method. In other words, based on tests with 1.5 mm thick substrates, two-sided demolding can only perform better at molds with lower aspect ratio micro-features, while one-sided demolding perform better for molds with higher aspect ratio micro-features.

Figure 7.38 Plot of deformed shape of polymer substrate during demolding of the ninth channel on a 1 mm thick substrate from diamond-ruled mold 5 by: (a) One-sided demolding, and (b) Two-sided demolding, showing the comparison in the bending behavior

On the other hand, when a thicker polymer substrate of 2 mm was used for replications, two-sided demolding becomes the best method to minimize demolding energy for all the molds. Figure 7.36c shows the lower trend in demolding energy spent with the two-sided demolding in all cases. In addition, Figure 7.39 also demonstrates the benefit of two-sided demolding that contributes to less severe bending on the polymer substrate during demolding. The same agreement can also be observed in the much lower stress-evolution on the polymer substrate that is demolded by two-sided method (see Figure 7.37c).

Figure 7.39 Plot of deformed shape of a 2 mm thick polymer substrate just prior to being fully-demolded from diamond-ruled mold 7 by: (a) One-sided demolding, and (b) Two-sided demolding, showing the comparison in the bending behavior

Based on the above results, it can be concluded that two-sided demolding can only perform better than one-sided demolding when there is adequate flexural rigidity in the polymer substrate. When the flexural rigidity was low, two-sided demolding will cause more severe bending on the polymer substrate rather than the one-sided demolding. It should also be recognized that higher flexural rigidity is required during demolding of molds with higher aspect ratio micro-features due to the much higher demolding difficulty. As a result, successful and optimal demolding can only be achieved by two-sided

demolding with the use of 2 mm thick substrate during demolding of diamond-ruled mold 5, 6, and 7 that have higher range of feature aspect ratio. On the other hand, 1.5 mm thick substrate can already provide adequate flexural rigidity for two-sided demolding method to accomplish successful and optimal demolding of the lower feature aspect ratio diamond-ruled mold 2 and 3.

7.2.8.1.2 Influence of demolding temperature with a fixed polymer substrate thickness of 2 mm

During demolding of the 2 mm thick substrates at lower temperature range between 25 to 50°C, it was found that two-sided demolding always suppressed the bending phenomenon at all molds such that all the respective demolding energies are also lower (see Figure 7.40a). This can happen because the flexural rigidity of the polymer substrate was adequately high. It should be noted that the flexural rigidity decreases with increase in temperature based on the reduced Young's Modulus.

However, at higher temperature that corresponds to reduced flexural rigidity, complication in determining whether two-sided demolding can perform better than one-sided demolding arises. In spite of the reduced flexural rigidity when demolding is performed at higher temperature, two-sided demolding can still mitigate the unwanted defect during demolding of molds with lower feature aspect ratio due to the relatively lower demolding difficulty. As shown in Figure 7.40b with high demolding temperature that is just 8°C below the T_g of the polymer, two-sided demolding can indeed help to prevent severe deformation that occurs during demolding by the one-sided method on

diamond-ruled mold 1 and 2. Similarly, Figure 7.40c (Left) also demonstrates that demolding of the replicated polymer from diamond-ruled mold 3 at 60°C, which cannot be achieved by the one-sided method, was successfully performed by the two-sided method. This finding can be correlated to Figure 7.41a which shows the significantly reduced demolding stress experienced on the polymer substrate during demolding from mold 3 at 60°C by the two-sided method due to the non-occurrence of severe bending on the polymer substrate.

Figure 7.40 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of 2 mm thick substrates from diamond-ruled molds at: (a) 50°C, (b) 70°C, and (c) 60°C, showing the effect of demolding method

On the other hand, the less superior performance of the two-sided demolding can be observed during demolding of molds with higher feature aspect ratio that is carried out at high temperature of 60° (see Figure 7.40c (Right)). In such cases, the two-sided demolding appears to worsen the demolding outcome. Despite the failed demolding by one-sided method on diamond-ruled mold 5, 6, and 7, the polymer substrate demolded by the two-sided method was found to be more severely deformed. This finding can be observed based on both the experimental and numerical results. During the experiment by two-sided demolding, the extremely severe bending causes the polymer substrate to slip away from the demolding bar such that it cannot be separated from the mold (see Figure 7.42b). On the other hand, even though the polymer substrate was also plastically deformed during demolding by one-sided method as shown in Figure 7.42a, it was still successfully separated from the mold. Such inferior performance of the two-sided demolding can also be numerically observed through the higher demolding stress experienced on the

polymer substrate that was demolded by the two-sided method (see Figure 7.41b).

Figure 7.41 Plot of evolution of localized maximum principal stress and Von Mises stress on the polymer substrate during demolding of 2 mm thick substrates at 60°C from: (a) Diamond-ruled mold 3, and (b) Diamond-ruled mold 6, showing the two opposite influence of two-sided demolding method in the two cases when compared to one-sided demolding method

Hence, the same conclusion is obtained as in the previous section whereby two-sided demolding can only perform better when there is adequate flexural rigidity. In the case with varying demolding temperatures and fixed substrate thickness of 2 mm, two-sided demolding remains as the optimal demolding method when demolding is performed at lower temperature range of 25 to 50°C. At higher demolding temperature above 60°C, two-sided demolding is only found to be easier and more beneficial during demolding of lower feature aspect ratio. Conversely, it worsens when performed at molds with higher feature aspect ratio because the flexural rigidity is no longer adequately strong. In other words, there is a unique difference in bending behavior created on the polymer substrate when two demolding loads are applied on both sides of the polymer substrate, and this bending behavior is extremely dependent on its flexural rigidity.

Figure 7.42 Images taken from experiments during demolding of 2 mm thick substrate from diamond-ruled mold 6 at 60°C by: (a) One-sided method, and (b) Two-sided method, showing the worse influence of two-sided demolding method to the demolding outcome

7.2.8.2 Findings of the study in demolding method

7.2.8.2.1 Four different possible scenarios based on the two demolding methods

Based on all the results obtained from tests with different sets of parameters by the two demolding methods, it can be deduced that there are four possible scenarios in the final demolding outcome. The first two scenarios correspond to the situation where there is adequately strong flexural rigidity in the

polymer substrate, while the last two scenarios correspond to weaker or inadequate flexural rigidity. Two plots of demolding tests on two different molds at different demolding temperature as illustrated in Figure 7.43 will further help to indicate the four scenarios clearly. The four different scenarios are as follows:

1. Success with both one-sided and two-sided demolding methods

In this scenario, two-sided demolding is preferable because it requires lower demolding energy when compared to one-sided demolding. This is mainly attributed to the less significant bending experienced on the polymer substrate during demolding by the two-sided method. Such an example is evident from Figure 7.43b during demolding of a 2 mm thick substrate from diamond-ruled mold 5 at 40°C.

2. One-sided demolding fails, but two-sided demolding succeeds

It can be clearly concluded that two-sided demolding performs better than one-sided demolding. This situation is demonstrated in Figure 7.43a during demolding of a 2 mm thick substrate from diamond-ruled mold 3 at 60°C in which the two-sided demolding successfully prevents deformation from occurring. Successful demolding can be achieved because of the less severe bending phenomenon.

3. One-sided demolding succeeds, but two-sided demolding fails

In this case, one-sided demolding is the optimal demolding method. Examples of such situation are observed during demolding of 1 and 1.5 mm thick substrates from diamond-ruled mold 5 at 40°C (see Figure 7.43b). This can happen because there is different bending behavior on the

polymer substrate during demolding by the two-sided method such that more significant bending can arise when there is inadequate flexural rigidity.

4. Both one-sided and two-sided demolding methods fail

In terms of the final demolding outcome that only considers the usability of the demolded polymer substrate, it may not be feasible to select a better demolding method between the two. Nevertheless, based on consideration in the level of plastic deformation, one-sided demolding can perform better than the two-sided demolding because the polymer substrate is always more severely deformed when demolded by the two-sided method in such scenario. As mentioned in the third scenario, this is mainly due to the different bending behavior on the polymer substrate that arises during demolding by the two-sided method. In addition, when premature polymer breakage occurs during demolding, two-sided demolding is found to fracture earlier than the one-sided method. This scenario is demonstrated in Figure 7.43a during demolding of 1 and 1.5 mm thick substrates from diamond-ruled mold 3 at 60°C. Higher demolding energy is also spent during demolding by the two-sided method.

Figure 7.43 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of replicated polymer substrates from: (a) Diamond-ruled mold 3 at 60°C, and (b) Diamond-ruled mold 5 at 40°C, showing the four possible scenarios in the demolding outcome based on the two demolding methods

If only successful demolding outcome is considered based on the four possible scenarios, it can be deduced that the two-sided demolding has a higher chance to outperform one-sided demolding. This can be seen from the first two scenarios in which two-sided demolding can perform better than the one-sided demolding. On the other hand, there is only one successful demolding scenario left (third scenario) which can only be better executed by the one-sided

demolding. Hence, the finding of this study has revealed the advantages of two-sided demolding to the final demolding outcome by the capability to suppress the bending phenomenon which further eases the demolding process.

Unfortunately, the beneficial performance does not apply to every demolding case. Two-sided demolding can help to ease demolding and prevent demolding defect from arising when there is adequate flexural rigidity. However, at the same time, it can also worsen the demolding process when the flexural rigidity of the polymer substrate is too weak. Moreover, it should also be noted that demolding of molds with higher aspect ratio micro-features generally involves more severe bending phenomenon, and thus stronger flexural rigidity is required in order to achieve successful demolding. As a result, special consideration in the flexural rigidity property should be made.

The flexural rigidity property can be influenced by demolding temperature and demolding rate based on the Young's modulus, and polymer substrate thickness based on the second moment of area. As it has been shown that faster demolding rate can always perform better, the flexural rigidity property eventually depends on the contribution of both demolding temperature and polymer substrate thickness. In other words, polymer substrate thickness and demolding temperature should be properly considered and selected in order to ensure that two-sided demolding method can help to result in optimal demolding outcome.

7.2.8.2.2 Influence of two-sided demolding on the optimal demolding temperature

It has been previously found that there exists an optimal demolding temperature which corresponds to the lowest demolding energy during demolding by one-sided method (see Section 7.2.3). Similarly, there is also an optimal demolding temperature when demolding is performed by the two-sided method. Nevertheless, the two-sided method may contribute to the change in the optimal demolding temperature, particularly due to the different bending behavior experienced on the demolded polymer substrate. As illustrated in Figure 7.44, the optimal demolding temperature during demolding of diamond-ruled mold 6 and 7 by one-sided method is initially found to be at 40°C. When demolding is executed by two-sided method, the optimal demolding temperature shifts to a higher temperature of 50°C.

(a)

Figure 7.44 Plot of total demolding energy calculated from both experiments (E) and numerical simulations (S) during demolding of 2 mm thick substrates from: (a) Diamond-ruled mold 6, and (b) Diamond-ruled mold 7, showing the influence of demolding method to the optimal demolding temperature

During demolding of the two molds that have quite high feature aspect ratio by the one-sided method, the polymer substrates were exposed to significant bending. In contrast to one-sided method, the two-sided method provides a much easier demolding with no severe bending phenomenon. As a result of the suppressed bending, the polymer substrate no longer requires such a strong flexural rigidity, and thus the optimal demolding temperature shifts to a higher value.

Chapter 8 Prediction of final optimal conditions for hot-embossing

Two processes involved during replication of polymer substrates that includes both thermal cooling and demolding have been thoroughly studied. As there are eight different parameters that can affect the replication process, the influence of each parameter to the thermal cooling and demolding processes will be further summarized in this section. Based on the outcome of thermal cooling process, no severe critical defect that causes intolerable change in the overall channel fidelity is observed during tests at all molds under the different sets of parameters, except diamond-ruled mold 1 in which severe bulge defect is prone to arise. Bulge defect is the only critical issue faced during the thermal cooling process that can deem the replicated polymer substrate unusable due to the incapability of sealing the demolded polymer with a cap layer.

On the other hand, based on the obtained results from all the performed tests, higher chance in the development of defects is found to arise during the demolding process rather than the thermal cooling process. Hence, besides the thermal cooling process, demolding process should also be scrutinized as the demolding outcome will eventually determine the usability of the replicated substrate through consideration in its final replication fidelity. The sequence of the eight studied parameters as elaborated below is purposely arranged from the most to the least important based on the consideration in the final

demolding outcome. The summarized influence of the parameters to both processes is as follow:

- Channel geometry

Thermal stress and plastic strain due to thermal contraction is found to be higher when channel spacing is wider or channel depth is shallower, which further means that channel geometry should be properly designed. This issue becomes more critical as bulge defect may develop due to the high thermal stress. This type of defect has been observed during replication on diamond-ruled mold 1 which has the widest channel spacing and shallowest channel depth from all the tested molds.

In terms of demolding process, the obtained results have demonstrated that channel geometry corresponding to higher feature aspect ratio generally generates higher demolding difficulty. Higher demolding stresses as well as demolding failures have been commonly observed during replications on molds with such a high feature aspect ratio, typically above 1. However, the channel geometry may not be flexibly controlled because it also depends on the requirements of certain applications. Moreover, despite the higher demolding difficulty, channel geometry that corresponds to higher feature aspect ratio has been reported to provide more advantages during applications as microfluidic devices when compared to the lower feature aspect ratio. Therefore, it may be more preferable and optimal to prevent such bulge defect as well as demolding failures from arising through control in the other remaining parameters.

- Polymer substrate thickness

During thermal cooling process, thicker polymer substrate contributes to higher thermal stress and plastic strain when compared to a thinner substrate. Therefore, one feasible way to prevent the formation of bulge defect on the polymer substrate can be achieved by utilizing thinner polymer substrate.

In spite of the preference in thinner substrate based on the lower thermal stress after the thermal cooling process, the final selection of optimal polymer substrate thickness is found to be primarily dependent on the demolding process. This dependency arises because thinner polymer substrate is more prone to result in demolding failures, particularly during demolding of molds with higher feature aspect ratio.

In short, molds with higher feature aspect ratio tend to be more sensitive towards the selection of substrate thickness in order to ensure that there is adequately strong flexural rigidity in the polymer substrate. Conversely, with less severe bending involved during demolding of molds with lower feature aspect ratio, there is more flexibility in the selection of substrate thickness such that thinner substrate can also accomplish successful demolding. Lastly, it can be firmly concluded that an optimal polymer substrate thickness always exists whereby not only the overall size of the microfluidic devices and the amount of raw material used can be minimized, but most importantly, efficient and successful fabrication of the devices can also be accomplished.

- Demolding temperature

Based on a fixed embossing temperature, lower demolding temperature will correspond to more significant thermal contraction, and thus the thermal stress and plastic strain will be higher as well. Similar to the polymer substrate thickness, demolding temperature can also act as an aid to help preventing bulge defect by performing demolding at a higher temperature.

However, at the same time, it is found that demolding performed at too high temperature which is close to the T_g of the polymer experiences a very high proneness to demolding defects in the form of deformed substrate or distorted channels, and thus make demolding at too high temperature not applicable. On the other hand, when demolding is performed at the lower range temperature, there is possibility in experiencing polymer breakage, especially during demolding of molds with high feature aspect ratio. In the case when the polymer does not fracture, the demolding process generally spends higher energy at lower demolding temperature.

Hence, the best scenario is to perform the demolding at the optimal demolding temperature where the minimum demolding energy exists. This optimal demolding temperature is located in between the high range temperature close to the T_g of polymer and the low range temperature of 25°C. The minimum demolding energy can also be correlated to the lowest chance of developing demolding defects. Based on the obtained experimental and numerical results, the optimal demolding temperature during demolding of molds with higher feature aspect ratio is found to be

lower than that with lower feature aspect ratio. The decrease in the optimal demolding temperature is mainly attributed to the need of higher strength and flexural rigidity in the polymer substrate that is gained from the increase in Young's modulus, in order to withstand the more severe bending phenomenon. In conclusion, besides having the highest chance of achieving successful demolding at the optimal demolding temperature, it can also determine the time and energy efficiency of the whole replication processes that involve a lot of repetitive temperature cycles.

- Demolding rate

It should be noted that demolding rate does not give any influence to the thermal cooling process. In terms of demolding process within the tested range of demolding rate, faster demolding rate is found to always perform better than slower demolding rate. This is because demolding rate contributes to the flexural rigidity property through the Young's modulus. With faster demolding rate, Young's modulus will be enhanced, and thus the flexural rigidity becomes stronger. Besides that, the strength of the polymer is increased as well.

Even though higher demolding energy is required with faster demolding rate, the benefit of the enhanced strength and flexural rigidity becomes readily visible during difficult demolding situation by minimizing the formation of plastic deformation better than the slower demolding rate. During the opposite case in which no deformation arises, faster demolding

rate can also outperform slower demolding rate because it is capable of maximizing the production throughput.

- Demolding method

Identical to demolding rate, there is also no impact on the thermal cooling process by this parameter because it is only performed during demolding. Based on comparison in the three different successful demolding scenarios performed by the two tested demolding methods, there is higher chance of the two-sided demolding method to outperform the one-sided demolding method. The two-sided demolding can help to minimize the required demolding energy, and most importantly, it can also help to prevent deformation that arises when performed by the one-sided method. This is achieved by the change in the bending behavior on the polymer substrate in such a way that bending phenomenon is suppressed.

Although two-sided demolding can help to ease demolding, it can also worsen demolding when the flexural rigidity of the polymer substrate becomes inadequate. In this situation, the bending behavior on the polymer substrate becomes different and severe. This scenario becomes more prone to occur during demolding of molds with higher feature aspect ratio. In such cases, one-sided demolding method may succeed and become more preferable. Therefore, if two-sided demolding is to be implemented, special consideration in the flexural rigidity of the polymer substrate as well as the mold feature aspect ratio should be first made. This is to eventually ensure that the benefits of the implemented two-sided demolding can be gained.

- Embossing temperature

Considering a fixed demolding temperature, higher embossing temperature creates larger temperature difference. As a result, higher thermal stress and plastic strain will be developed during the thermal contraction. Similarly, demolding is also found to be more difficult to perform when the polymer substrate is hot-embossed at higher temperature, which is mainly caused by the higher thermal stress. Therefore, lowest embossing temperature that can still achieve complete filling of the polymer substrate into the mold cavities during the hot-pressing step is always an optimal processing condition. Furthermore, the optimal embossing temperature can be predicted through the hot-embossing simulation that is based on the robust implemented interfacial and material models in this thesis work. In this way, the optimal embossing temperature can be efficiently determined without the need to perform trial and error experiments.

- Channel design (shape of the channel cross-section)

Based on identical channel geometry, a bell-shaped channel is found to generate the smallest thermal stress and plastic strain after thermally cooled to demolding temperature, followed by the tapered-channel and rectangular-shaped channel, respectively. The smallest thermal stress and plastic strain is attributed to the rounded corner of a bell-shaped channel such that there is no stress concentration. However, the easiest demolding process is observed during demolding of mold with the tapered-channel, followed by the bell-shaped channel and rectangular-shaped channel, respectively. In spite of the higher thermal stress developed on the tapered-

channel when compared to bell-shaped channel, the slanted channel sidewalls of the tapered-channel provide a much weaker mechanical interlocking between the mold features and replicated polymeric features which eventually results in easier demolding.

On the other hand, both thermal cooling and demolding processes experienced on the rectangular-shaped channel are found to be the worst, particularly due to the sharp corners of the channel and the vertical channel sidewalls. In conclusion, despite the differences in the thermal cooling and demolding outcomes, the suitability and functionality of each channel design to a certain application should be first considered so that maximum performance can be achieved. Nevertheless, it should be noted that all of the obtained knowledge in both thermal cooling and demolding processes based on the different parameters which are only studied on the conventional rectangular-shaped channel can still be applicable to the remaining two channel designs.

- Adhesion of the polymer substrate to the mold

Adhesion of the polymer substrate to the mold is grouped into two which are thermodynamic and mechanical adhesion. The two types of adhesion share a similarity in that weaker thermodynamic and mechanical adhesions correspond to lower interfacial friction property. Hence, both thermal cooling and demolding processes result in better outcomes with weaker adhesion. Nevertheless, it should be noted that weaker thermodynamic adhesion is generally achieved by additional application of coating layer on

the mold, which further deem this method not suitable for every application, especially in chemical or biological applications. The suitability in the use of coated molds is extremely dependent on the potential sample contaminations that should be prevented. In contrast to the use of coated mold based on the weaker thermodynamic adhesion, the use of mold with smoother surface finishing quality that corresponds to weaker mechanical adhesion is always preferable to minimize the development of thermal stress as well as demolding difficulty.

As the eight different parameters are summarized and elaborated above, there are two different characteristics which are fixed parameters and variable parameters. A fixed parameter is one in which the effect can be predicted and established even at the initial stage without the need for any further investigation in order to accomplish the best demolding outcome. Such parameters include demolding rate, embossing temperature, channel design, and adhesion of the polymer substrate to the mold. On the other hand, a variable parameter refers to those in which its effect is also dependent on other factors (remaining variable parameters and channel geometry) such that an optimal condition exists to achieve the best and most efficient demolding outcome. Unlike fixed parameters, further investigation is required so that the optimal conditions of the variable parameters can be predicted and customized. Variable parameters include polymer substrate thickness, demolding temperature, and demolding method.

Channel geometry is not included in these two characteristics even though high feature aspect ratio has been found to enhance the demolding difficulty which has to be avoided. Nevertheless, it has been mentioned above that the channel geometry heavily depends on the requirements in the applications of microfluidic devices. As high feature aspect ratio that also corresponds to high aspect ratio micro-channel has been known to beneficially generate better performance, it may not be reasonably practical to neglect and avoid such channel geometry. Therefore, this high demolding difficulty should be successfully suppressed by simply focusing and adjusting the variable parameters.

Table 8.1 Optimal processing conditions during replications on each of the diamond-ruled mold with the highlighted minimum values of respective demolding energy. It should be noted that the two fixed parameters of demolding rate and embossing temperature are set as 50 mm/min and 100°C with rectangular-shaped channel design and adhesion of polymer substrate to mold as illustrated in Figure 5.7

Mold	Demolding method	Substrate thickness	Demolding temperature	Demolding energy (mJ)	
				Experiment	Simulation
1	1	1	50	0.0572	0.0550
	2	1	50	0.1102	0.1043
2	1	1	50	0.1100	0.1017
	2	1	50	0.1192	0.1099
3	1	1.5	50	0.4151	0.3822
	2	1.5	50	0.2549	0.2351
5	1	2	50	0.5145	0.4699
	2	2	50	0.3729	0.3354
6	1	2	40	1.8208	1.6665
	2	2	50	0.5854	0.5166
7	1	2	40	5.6060	5.1604
	2	2	50	0.7140	0.6225

In addition, a robust demolding-failure mechanism which is based on bending phenomenon experienced on the polymer substrate has been discovered. As the bending phenomenon is heavily correlated to the flexural rigidity property

of the polymer substrate, it can be firmly concluded that the polymer substrate thickness, demolding temperature, and demolding rate plays an important role in determining the success of demolding process. The influence of demolding method to the final demolding outcome which is based on the unique change in bending behavior of the polymer substrate has also been identified. Lastly, an in depth understanding in the interfacial bonding (adhesion) between the mold and polymer substrate which are influenced by embossing temperature, channel design, and adhesion of polymer substrate to mold has also been developed. This means that final optimal processing conditions that lead to successful as well as efficient outcomes can be eventually predicted and determined.

Finally, based on all the experimental and numerical tests on all molds with the possible combinations of the different parameters (see Appendix C.1), the most optimal processing conditions for the replication processes of each diamond-ruled mold are obtained and tabulated in Table 8.1. An optimal processing condition for the micro-machined mold cannot be predicted because only two parameters (demolding rate and embossing temperature) were studied. Besides the two parameters, it also only helps to investigate the influence of mechanical adhesion based on the different surface finishing quality between the micro-machined and diamond-ruled molds.

Figure 8.1 SEM micrographs showing the good replication fidelity of the replicated channels on the demolded polymer substrates from: (a) Diamond-ruled mold 1, (b) Diamond-ruled mold 2, (c) Diamond-ruled mold 3, (d) Diamond-ruled mold 5, (e) Diamond-ruled mold 6, and (f) Diamond-ruled mold 7, which were hot-embossed and demolded with the optimal processing conditions

Based on the consideration in minimum required demolding energy, the optimal processing condition during demolding of each mold is further highlighted in Table 8.1. It should be noted that both one-sided and two-sided demolding methods can succeed, but there is difference in the spent demolding energy. Two-sided demolding is found to outperform one-sided demolding during demolding of diamond-ruled mold 3, 5, 6, and 7 that have higher range of feature aspect ratio, particularly due to the capability in suppressing the bending phenomenon.

On the other hand, one-sided demolding spends lower demolding energy during demolding of diamond-ruled mold 1 and 2. As it has been discussed in Section 7.2.8.1.1, the lower demolding energy by the one-sided method can arise due to the quite easy demolding on diamond-ruled mold 1 that has the lowest feature aspect ratio. In the case of demolding from diamond-ruled mold 2, the thin substrate causes the change in bending behavior during the two-sided demolding in such a way that it bends slightly more than during demolding by the one-sided method. Nevertheless, the bending is still not severe and there is still adequate mechanical strength to withstand the demolding stress. Thus, the use of 1 mm thick substrate in this demolding case can still result in lower demolding energy when compared to thicker substrate of 1.5 mm.

Figure 8.2 Plots of channel profile comparing the molds and replicated polymer substrates obtained from white-light confocal microscope that show the good replication fidelity of the replicated channels on the demolded polymer substrates from: (a) Diamond-ruled mold 1, (b) Diamond-ruled mold 2, (c) Diamond-ruled mold 3, (d) Diamond-ruled mold 5, (e) Diamond-ruled mold 6, and (f) Diamond-ruled mold 7, which were hot-embossed and demolded with the optimal processing conditions

There is also a unique increasing trend in the optimal polymer substrate thickness used on the diamond-ruled molds with increasing feature aspect ratio. As expected, this can happen because higher flexural rigidity is required during demolding of molds with high feature aspect ratio that involve more severe bending phenomenon. Similarly, the optimal demolding temperature during demolding of diamond-ruled mold 6 and 7 by the one-sided method shifts to lower temperature of 40°C in order to accommodate the significant bending experienced on the polymer substrate during demolding.

Besides the minimum demolding energy obtained from the optimal processing conditions, the excellent replication fidelity of the micro-channels on the demolded polymer substrates has also been verified through observation under SEM as shown in Figure 8.1. Furthermore, same agreement is observed through the plotted channel profile that compares the initial channels on the mold with the replicated channels (see Figure 8.2). Lastly, in real-life manufacturing process, as both demolding methods can achieve successful demolding, the selection of optimal demolding method may not be only dependent on the minimum required demolding energy. The optimal demolding method may instead be selected based on the available manufacturing set-up such as the arrangement of ejector-pins or demolding bars.

Chapter 9 Conclusions and Future Work

In this chapter, the conclusions and main contributions of this thesis will be summarized. In addition, some recommendations for future work will also be proposed.

9.1 Conclusions

The critical importance of an interfacial study on demolding mechanics has been identified based on the known challenges encountered in fabricating and demolding of microfluidic devices. This is an area that has not been studied in detail. Therefore, the main objective of this thesis work is to develop an in depth understanding of the replication processes via hot-embossing, particularly the demolding mechanics. This was done based on analytical, experimental, and numerical studies.

Initial studies using the analytical model based on the interfacial fracture mechanics revealed that the mismatched thermal cooling in the mold and polymer substrate during replication created thermal stress on the vertical channel sidewalls between the mold and polymer substrate. Such thermal stresses had a significant effect on demolding difficulty.

A new numerical model that incorporates both a robust material and an interfacial model have also been developed. A constitutive model of the mechanical properties of the COC Topas 8007 polymeric material has been implemented in the model. Furthermore, analytical analysis based on the strain

energy release rate on horizontal interfaces, and compressive force on vertical interfaces under varying demolding temperature which was then further supported by experimental analysis on flat and patterned molds has revealed that it is reasonable to neglect the contribution of adhesion on the horizontal interfaces of the micro-channels in the model even during demolding at elevated temperature. Therefore, the implemented interfacial model only utilizes the experimentally characterized temperature-dependent interfacial friction between the mold and polymer substrate.

The model has also considered all the steps involved in hot-embossing that includes hot-pressing, cooling, and demolding. However, the hot-pressing step was found to have a minor influence on the thermal cooling and demolding outcomes, and can thus be neglected. In addition, a non-simplified model that incorporates the complete geometry of both the mold and polymer substrate with a uniquely different set of boundary conditions has been shown to be capable of reflecting the real replication processes that include both thermal cooling and demolding. The above could not be achieved in the existing simplified models that have been reported by other research groups. Finally, the predictive capability of our new model has been experimentally validated through comparisons of both quantitative and qualitative results.

However, there is one minor limitation in the performance of the new model that is based on the implemented interfacial friction behaviour. The numerical model tends to underestimate the quantitative experimental results during demolding at high temperature close to the T_g of the polymer (between 60 to 70 °C). It has been shown that this can be attributed to underestimation of the adhesion between the bonded horizontal interfaces between the mold and

polymer substrate after thermal contraction. Despite this, the numerical model can still successfully predict the demolding defects at high temperature in terms of substrate deformation or distortion, and provide an indication whether the demolding process is likely to be successful. Premature fracture in the polymer substrate could also be successfully predicted by comparing the stress states during demolding with the temperature and rate-dependent tensile properties of the polymer which was characterized experimentally.

It has also been established that the bending experienced by the polymer substrate during demolding is the major cause of demolding-failure. It was shown both through simulation and experimental studies that the tendency for such failure can be analyzed through the concept of flexural rigidity of the polymer substrate, such that in cases where the bending phenomenon can be suppressed, demolding failure can be prevented. The demolding mechanics model revealed that the three main factors are (i) the adhesion and friction at the interfaces between the mold and polymer substrate, (ii) the magnitude of residual stress formed due to differential cooling prior to demolding, and (iii) the mechanical properties of the polymer substrate, mainly its strength to withstand the demolding stress.

The effect of eight essential parameters on the demolding process and demolding failure was scrutinized, namely, channel geometry, polymer substrate thickness, demolding temperature, demolding rate, demolding method, embossing temperature, channel design (shape of the channel cross-section), and adhesion of polymer substrate to the mold. The channel geometry, polymer substrate thickness, demolding temperature, and demolding rate influence the flexural rigidity of the polymer substrate, while

the demolding method affects the bending behaviour of the polymer substrate during demolding. On the other hand, the remaining three parameters influence the interfacial bonding between the mold and polymer substrate which directly affect the demolding difficulty.

The influence of these eight parameters on both thermal cooling and demolding outcome was also carried out. The experimental and numerical results indicated that the parameters can be classified into two groups, namely, fixed parameters and variable parameters. A fixed parameter is one in which the effect can be predicted and established even at the initial stage without the need for any further investigation in order to achieve the best demolding outcome. Such parameters include demolding rate, embossing temperature, channel design, and adhesion of polymer substrate to the mold. On the other hand, a variable parameter refers to those in which its effect is also dependent on other factors (remaining variable parameters and channel geometry) such that an optimal condition exists to achieve the best and most efficient demolding outcome. Variable parameters include polymer substrate thickness, demolding temperature, and demolding method. The optimal conditions of variable parameters have to be generally customized based on the specific channel geometry. It should be noted that selection in channel geometry may not be flexible because it is highly dependent on the requirements of its applications. A channel with beneficial high feature aspect ratio is more prone to demolding failure. Despite the much higher demolding difficulty of features with high aspect ratio, this study has demonstrated that successful demolding can still be efficiently achieved if the three variable parameters are considered and optimized. Finally, the optimal processing conditions during replications

on each of the diamond-ruled molds have also been determined, and it has been further proven that the established optimal processing conditions can help to accomplish successful and efficient replications.

As this thesis work has only considered aluminum mold and Topas 8007 polymer substrate, the recommended procedures for others to follow in order to successfully and efficiently produce microfluidic devices through replication techniques, especially when dealing with different polymer substrate/mold pairs have also been determined. The summary of the recommended procedures is as follow:

1. Channel geometry should be initially designed and decided according to application requirements of the microfluidic devices. In this step, polymer substrate material may have also been chosen due to its required properties.
2. Characterize and calibrate constitutive parameters for the thermo-mechanical response of the chosen amorphous polymeric material (Anand et al. theory [87]) based on large-strain compression experiments. Constitutive parameters for some of the widely used polymers are already available such as PMMA, PC, Zeonex-690R [89], and cyclic olefin copolymer – TOPAS [90].
3. Characterize the temperature and rate-dependent tensile properties of the chosen polymer which are useful for prediction of premature fracture during demolding.
4. Characterize the interfacial friction properties for the chosen mold and polymer substrate as a function of temperature and sliding rate.

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5. Based on the remaining seven different essential parameters (excluding the already finalized channel geometry), fixed parameters (demolding rate, embossing temperature, channel design, and adhesion of polymer substrate to the mold) can be first considered as their effects have been clearly identified, and they are relatively easy to control. The calibrated constitutive model by Anand et al. can be utilized to simulate and predict the lowest embossing temperature that can achieve complete replications, whereas faster demolding rate can be decided based on the capability of available set-up. Lastly, channel design and adhesion of polymer substrate to mold are dependent on application requirements as well as chosen mold material, respectively.
 6. Then, the remaining variable parameters (polymer substrate thickness, demolding temperature, and demolding method) should be focused and optimized. Generally, these variable parameters will be highly dependent on the chosen channel geometry.
 7. The most effective way to achieve an optimal set of variable parameters is by numerical simulation. The numerical simulation will include the constitutive material model and the calibrated interfacial model. In addition, it also involves complete geometry of both mold and polymer substrate with properly defined boundary conditions.
 8. Following the obtained optimal processing conditions through numerical simulations, perform the real replication process to validate the successful and efficient replications.

In summary, the main contributions of this thesis work are:

- Development of an in-depth understanding in the replication processes, particularly the demolding mechanics, based on the analytical, experimental, and numerical studies.
- Study of the replication processes with the use of molds that are made of aluminum alloy (AA6061-T6) which are cheap in cost and durable for repetitive replications. Most importantly, the molds have optical surface finishing and high feature aspect ratio of up to two, so that the aimed benefits during applications of microfluidic devices can be achieved. Such study with the combined beneficial characteristics of extremely smooth surface finishing quality and high feature aspect ratio have not been reported previously.
- Development of new numerical model that has been experimentally validated, which can successfully predict both successful and unsuccessful demolding both quantitatively and qualitatively. The quantitative results include considerations based on the demolding load-displacement curve, and the demolding energy, while the qualitative results refer to the capability of the model in predicting the final replication fidelity of the demolded substrate.
- Systematic study of the influence of the eight crucial parameters that can affect the replication processes via hot-embossing which involve thermal cooling and demolding. The parameters include channel geometry, polymer substrate thickness, demolding temperature, demolding rate, demolding method, embossing temperature, channel design (shape of the channel cross-section), and adhesion of polymer substrate to the mold. The obtained

knowledge on the influences of the different parameters may also be applicable to other kind of replication techniques.

- Development of an in-depth understanding of the main demolding-failure mechanism and demolding mechanics that are used to determine how the eight crucial parameters contribute to demolding failure, and how the demolding failure can be prevented.
- Prediction and determination of the final optimal processing conditions to accomplish successful and efficient replications. For example, the efficient and successful demolding of replicated polymer substrate from mold with the highest feature aspect ratio of two has been demonstrated through the use of its optimal processing conditions.
- Development of recommended procedures for other mold/polymer substrate pairs to accomplish both successful and efficient replications.

9.2 Future work

9.2.1 Exploration on different mold and polymer substrate materials

Mold can be made of various types of materials, and each material has its own properties. In fact, different mold's material properties may contribute differently to demolding phenomenon. Several most common materials used as mold are aluminum, silicon, and nickel. There are several factors that may affect demolding based on the choice of mold materials. They are the thermodynamic adhesion formed due to molecular interaction, mechanical adhesion due to interlocking in between asperities, and the thermal contraction

behavior of the mold material. Thermodynamic adhesion can be calculated based on equation 2-8 with the polar and dispersive components of surface energy of the relevant materials (see Appendix A.1). The calculated work of adhesion for the three different materials when paired with COC is as shown in Table 9.1. It is found that aluminum has the lowest thermodynamic adhesion when compared to silicon and nickel. Nevertheless, it can be generally expected that the thermodynamic adhesion is weak enough such that the mechanical adhesion due to surface roughness interlocking becomes more dominant.

Table 9.1 Calculated work of adhesion (mJ/m^2) and thermal contraction mismatch of different mold materials when paired with COC

Mold material	W_A (paired with COC) (mJ/m^2)	Thermal contraction mismatch ($\Delta\alpha$)
Aluminum	17.57	46
Silicon	44.71	67.5
Nickel	76.55	57

Thermal cooling is a definite step that is required in replication by hot-embossing prior to demolding. As it has been mentioned in Section 2.3.4.3, thermal cooling gives different effects to horizontal and vertical interfaces of the micro-channels. Thus, the thermal contraction mismatch which can be approximated by the difference in the coefficient of linear thermal expansion between the mold and polymer substrate ($\Delta\alpha$) plays a very important role in determining the level of difficulty in demolding. The mismatched thermal contraction between the three different mold materials and polymer substrate (COC) has also been illustrated in Table 9.1.

For simplicity in comparison of the three different mold materials, it is assumed that all three mold materials have identical surface roughness. Therefore, it can be further assumed that mechanical adhesion due to interlocking in between asperities is identical among all molds. As a result, the factors left to consider are only the thermodynamic adhesion and the mismatched thermal contraction behavior.

Prediction on how the different mold materials may affect the demolding process can be further grouped into two aspects which are the horizontal and vertical interfaces. Based on equation 2-23 that describes the compressive force on the vertical interfaces, it can be concluded that compressive force increases with higher value of mismatched thermal contraction, which eventually causes more difficulty in demolding. However, prediction on horizontal interfaces may not be straightforward. Interfacial fracture on the horizontal interfaces can only occur when the strain energy release rate has reached the critical value which is contributed by the combination of both mechanical and thermodynamic adhesion (equation 2-22). Therefore, the overall insight on the effect of mold materials can be further grouped into two possible scenarios:

1. Interfacial fracture on the horizontal interfaces has not happened yet ($G < G_c$)

As thermal contraction mismatch becomes higher, thermal residual stress on the horizontal interfaces increases during thermal cooling. This may indeed help to ease demolding. Nevertheless, the thermodynamic adhesion may also need to be considered. For example, nickel has higher thermal contraction mismatch than aluminum, but at the same time, the work of

adhesion between nickel and COC is also higher when compared to aluminum and COC. The larger work of adhesion means that higher thermal stress may be needed to break the relevant bond/adhesion. Thus, the two factors should be considered and relatively compared in order to draw a reasonable conclusion regarding to the effect of different mold materials to demolding difficulty.

2. Interfacial fracture on the horizontal interfaces has happened ($G \geq G_c$)

If the thermal stress induced during the thermal cooling process is sufficient to create interfacial fracture, there may be no longer any bonding left on the horizontal interfaces between the mold and polymer substrate. In such situation, higher thermal contraction mismatch may give a direct impact on the demolding difficulty, such that the compressive force on the vertical interfaces will increase. Therefore, enhanced demolding difficulty can be readily expected. As a result, it can be eventually predicted that molds with the order of decreasing demolding difficulty are silicon, nickel, and aluminum, respectively.

It should be noted that the discussion on the effect of different mold materials is not meant to draw a solid conclusion, but rather to provide a possible general overview of the effect. In real-life applications, surface roughness of the mold is entirely dependent on the mold fabrication process. Hence, the assumption of having identical surface roughness may not be valid, because mechanical adhesion may differ from each mold material. On the other hand, different polymer substrate material will also correspond to different work of

adhesion and value of mismatched thermal contraction between the mold and polymer substrate. In addition, significant influences can also be contributed by the different material properties and T_g of the chosen polymeric material. On the whole, with the developed numerical model and demolding-failure mechanism, as well as the already understood demolding mechanics and influences of the different crucial parameters, it thus becomes feasible to efficiently predict and determine the optimal processing conditions for replications using different mold and polymer substrate materials.

9.2.2 Application of the developed numerical model in other replication processes

Predictive capability of the developed new numerical model has been demonstrated. It is thus feasible to apply the developed model in other novel replication processes so that in depth understanding in those replication processes can be further developed. Moreover, it is also possible to efficiently predict and determine the optimal processing conditions for those different replication processes.

9.2.3 Application of surface-based cohesive behavior to model the adhesion on the horizontal interfaces

It has been mentioned that there is minor limitation in the current implemented interfacial friction model such that the numerical results have quantitatively underestimated the experimental results during demolding at high temperature

that is close to T_g of the polymer. This is attributed to the underestimation of the adhesion on some of the still bonded horizontal interfaces between the mold and polymer substrate after the differential thermal contraction. Surface-based cohesive behavior that is based on characterized different fracture modes can be possibly applied only on the horizontal interfaces in order to consider the adhesion properties. In this way, more accurate quantitative results during demolding at high temperature can be numerically obtained.

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Appendices

A. Material Properties

A.1 Representative properties of selected materials

Material	CTE ($\mu\text{m/m}^\circ\text{C}$) at 25 $^\circ\text{C}$	Surface energy (mJ/m^2) at 25 $^\circ\text{C}$		References
		Polar	Dispersive	
COC	70	0.35	33.55	[105]
Aluminum	24	44	4.6	[37, 106]
Silicon	2.5	19	16	[107-108]
Nickel	13	0.28	43.72	[109-110]

COC = Cyclic-Olefin Copolymer

A.2 Material properties of aluminium alloy (AA6061-T6) mold used in finite element simulation

Material	Elastic Modulus (GPa)	Poisson's Ratio	Linear CTE ($\mu\text{m/m}^\circ\text{C}$)	Density (kg/m^3)	Thermal Conductivity (W/m K)	Specific Heat (J/kg K)
Aluminum	70	0.33	24	2700	167	896

B. Mechanical drawing

B.1 Diamond-machined mold

Diamond-turned flat mold

Diamond-ruled mold 1

Diamond-ruled mold 2

Diamond-ruled mold 3

Diamond-ruled mold 5

Diamond-ruled mold 6

Diamond-ruled mold 7

B.2 Experimental set-up for diamond-ruled molds

Bottom heating platen

Top heating platen

Fixture to support demolding bar

Demolding bar

C. Experimental and numerical simulation results of tests on diamond-ruled molds

C.1 Demolding energy

Mold 1

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	0.2139	0.2280	0.0144	6.33%	-	-
40				0.1189	0.1225	0.0068	5.58%	-	-
50				0.1095	0.1126	0.0050	4.47%	-	-
60				0.1792	0.2053	0.0079	3.87%	-	-
70				3.6355	4.4898	0.4068	9.06%	Yes	-
25	1.5	1	50	0.1798	0.1860	0.0135	7.28%	-	-
40				0.0795	0.0805	0.0035	4.37%	-	-
50				0.0659	0.0674	0.0048	7.06%	-	-
60				0.1468	0.1676	0.0096	5.71%	-	-
70				2.4099	3.0363	0.2092	6.89%	Yes	-
25	1	1	50	0.1776	0.1724	0.0082	4.77%	-	-
40				0.0789	0.0808	0.0041	5.06%	-	-
50				0.0550	0.0572	0.0035	6.11%	-	-
60				0.1110	0.1292	0.0094	7.31%	-	-
70				1.5989	2.0217	0.1655	8.19%	Yes	-
25	2	2	50	0.5220	0.5369	0.0303	5.64%	-	-
40				0.2173	0.2293	0.0107	4.66%	-	-
50				0.1463	0.1518	0.0078	5.15%	-	-
60				0.2366	0.2755	0.0186	6.77%	-	-
70				0.5721	0.7280	0.0415	5.70%	-	-
25	1.5	2	50	0.4669	0.4905	0.0274	5.58%	-	-
40				0.1974	0.2056	0.0095	4.60%	-	-
50				0.1190	0.1235	0.0049	3.99%	-	-
60				0.2070	0.2339	0.0157	6.71%	-	-
70				0.5157	0.6486	0.0468	7.22%	-	-
25	1	2	50	0.3766	0.4062	0.0247	6.08%	-	-
40				0.1660	0.1742	0.0096	5.52%	-	-
50				0.1043	0.1102	0.0059	5.36%	-	-
60				0.1710	0.2003	0.0178	8.90%	-	-
70				0.4120	0.5114	0.0378	7.39%	-	-

Mold 2

Mold 2

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	0.7281	0.7968	0.0459	5.77%	-	-
40				0.3732	0.3998	0.0202	5.06%	-	-
50				0.2804	0.2979	0.0182	6.11%	-	-
60				0.3482	0.4026	0.0274	6.81%	-	-
70				4.4396	6.0717	0.5577	9.19%	Yes	-
25	1.5	1	50	0.5448	0.5923	0.0375	6.33%	-	-
40				0.2779	0.3029	0.0169	5.58%	-	-
50				0.1982	0.2112	0.0094	4.47%	-	-
60				0.2423	0.2735	0.0215	7.87%	-	-
70				3.4357	4.5250	0.4099	9.06%	Yes	-
25	1	1	50	0.3654	0.3882	0.0236	6.08%	-	-
40				0.1754	0.1869	0.0103	5.52%	-	-
50				0.1017	0.1100	0.0070	6.36%	-	-
60				0.1454	0.1661	0.0098	5.90%	-	-
70				2.8987	3.8659	0.3245	8.39%	Yes	-
25	2	2	50	0.6723	0.7169	0.0429	5.99%	-	-
40				0.3368	0.3560	0.0176	4.94%	-	-
50				0.2509	0.2664	0.0172	6.46%	-	-
60				0.3092	0.3513	0.0274	7.80%	-	-
70				0.7019	0.9187	0.0762	8.30%	-	-
25	1.5	2	50	0.5424	0.5788	0.0214	3.70%	-	-
40				0.2465	0.2614	0.0152	5.82%	-	-
50				0.1682	0.1755	0.0080	4.57%	-	-
60				0.2284	0.2560	0.0133	5.20%	-	-
70				0.5638	0.7290	0.0515	7.06%	-	-
25	1	2	50	0.4223	0.4633	0.0264	5.70%	-	-
40				0.1832	0.1945	0.0150	7.70%	-	-
50				0.1099	0.1192	0.0075	6.32%	-	-
60				0.1787	0.2057	0.0147	7.17%	-	-
70				0.4378	0.5841	0.0496	8.49%	-	-
25	2	1	1	0.7190	0.7492	0.0331	4.41%	-	-
			50	0.7281	0.7968	0.0459	5.77%	-	-
Embossing temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
100	2	1	50	0.7281	0.7968	0.0459	5.77%	-	-
105				0.7888	0.9061	0.0561	6.19%	-	-
110				0.8693	1.0562	0.0737	6.98%	-	-

Mold 3

Mold 3

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	1.2988	1.3745	0.0823	5.99%	-	-
40				0.7529	0.8138	0.0402	4.94%	-	-
50				0.5646	0.6196	0.0400	6.46%	-	-
60					12.2192	15.3560	1.5043	9.80%	Yes
25	1.5	1	50	0.8503	0.9202	0.0524	5.70%	-	-
40				0.4803	0.5137	0.0395	7.70%	-	-
50				0.3822	0.4151	0.0262	6.32%	-	-
60				8.3163	10.5199	1.1039	10.49%	Yes	-
25	1	1	50	14.3945	16.6776	1.1690	7.01%	Yes	Yes
40				4.7848	5.6738	0.5056	8.91%	Yes	Yes
50				3.9624	4.8781	0.4859	9.96%	Yes	Yes
60				6.7781	8.6549	0.9568	11.05%	Yes	-
25	2	2	50	0.9533	1.0340	0.0655	6.33%	-	-
40				0.5545	0.5984	0.0334	5.58%	-	-
50				0.3918	0.4239	0.0334	7.87%	-	-
60				0.4813	0.5544	0.0447	8.06%	-	-
25	1.5	2	50	0.5592	0.5985	0.0357	5.96%	-	-
40				0.3350	0.3679	0.0236	6.41%	-	-
50				0.2351	0.2549	0.0183	7.19%	-	-
60				17.5489	21.7377	1.8203	8.37%	Yes	-
25	1	2	50	22.3386	27.1811	2.5670	9.44%	Yes	Yes
40				10.3473	12.3975	1.1045	8.91%	Yes	Yes
50				12.6055	15.3030	1.4952	9.77%	Yes	Yes
60				13.4844	17.3087	1.7957	10.37%	Yes	-
25	2	1	1	1.2908	1.3285	0.0581	4.37%	-	-
50			1.2988	1.3745	0.0823	5.99%	-	-

Mold 5

Mold 5

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	0.9136	1.0002	0.0570	5.70%	-	-
40				0.5065	0.5498	0.0423	7.70%	-	-
50				0.4699	0.5145	0.0325	6.32%	-	-
60				9.1009	10.6567	1.0116	9.49%	Yes	-
25	1.5	1	50	0.8404	0.9246	0.0646	6.99%	-	-
40				0.6128	0.6686	0.0464	6.94%	-	-
50				0.6953	0.8022	0.0599	7.46%	-	-
60				9.0118	10.9224	1.1792	10.80%	Yes	-
25	1	1	50	7.6303	8.5313	0.7204	8.44%	-	-
40				5.2974	5.9594	0.5309	8.91%	-	-
50				7.1195	8.0665	0.7881	9.77%	-	-
60				7.6001	9.2828	1.0559	11.37%	Yes	-
25	2	2	50	1.0550	1.1507	0.0801	6.96%	-	-
40				0.5347	0.5841	0.0375	6.41%	-	-
50				0.3354	0.3729	0.0268	7.19%	-	-
60				37.6255	47.7891	4.2407	8.87%	Yes	-
25	1.5	2	50	26.5551	32.9005	2.4119	7.33%	Yes	Yes
40				24.3924	29.0701	2.2038	7.58%	Yes	Yes
50				21.8057	26.7418	2.2376	8.37%	Yes	Yes
25	1	2	50	20.5744	25.8943	2.3641	9.13%	Yes	Yes
40				18.8348	23.5201	2.2955	9.76%	Yes	Yes
60	2	1	1	3.8217	4.8241	0.4226	8.76%	Yes	-
			50	7.2243	8.6002	0.8164	9.49%	Yes	-

Mold 6

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	2.7901	2.9924	0.2194	7.33%	-	-
40				1.6665	1.8208	0.1380	7.58%	-	-
50				3.7259	4.2450	0.3552	8.37%	-	-
60				18.4285	22.6351	2.4615	10.87%	Yes	-
25	1.5	1	50	12.6278	13.8612	1.0129	7.31%	-	-
40				8.4356	9.3295	0.5985	6.41%	-	-
50				9.7487	11.1202	0.8548	7.69%	-	-
60				15.2711	19.3730	2.1511	11.10%	Yes	-
25	1	1	50	17.2348	19.8888	1.7422	8.76%	Yes	Yes
40				11.3839	13.0155	1.2356	9.49%	Yes	Yes
50				10.3215	11.9519	1.1864	9.93%	Yes	Yes
25	2	2	50	2.0725	2.2648	0.1799	7.94%	-	-
40				0.8410	0.9189	0.0773	8.41%	-	-
50				0.5166	0.5854	0.0455	7.77%	-	-
60				39.7572	51.5676	5.3499	10.37%	Yes	-

Mold 7

Mold 7

Demolding temperature (°C)	Thickness (mm)	Demolding method	Demolding rate (mm/min)	Simulation	Experimental			Condition	
				Demolding energy (mJ)	Average energy (mJ)	S.D.	% S.D.	Deformation	Fracture
25	2	1	50	8.9181	9.8950	0.7939	8.02%	-	-
40				5.1604	5.6060	0.4177	7.45%	-	-
50				6.6299	7.4967	0.6200	8.27%	-	-
60				24.5852	31.2217	3.2715	10.48%	Yes	-
25	1.5	1	50	22.7585	25.3460	2.1403	8.44%	-	-
40				13.6082	15.0085	1.3371	8.91%	-	-
50				14.5638	16.7668	1.6382	9.77%	-	-
60				14.8246	18.9961	2.1607	11.37%	Yes	-
25	1	1	50	11.5292	13.6166	1.3165	9.67%	Yes	Yes
25				2.6717	2.9329	0.2290	7.81%	-	-
40				1.0299	1.1276	0.0915	8.11%	-	-
50				0.6225	0.7140	0.0585	8.19%	-	-
60	1.5	2	50	42.8390	56.3106	6.2526	11.10%	Yes	-
25				36.7334	46.8760	4.5215	9.65%	Yes	Yes
25				14.6909	19.0520	1.9832	10.41%	Yes	Yes
25				8.7619	9.4880	0.7510	7.92%	-	-
25	2	1	1	8.9181	9.8950	0.7939	8.02%	-	-
25			50	8.9181	9.8950	0.7939	8.02%	-	-
25	1.5	1	1	22.5555	23.7227	2.0946	8.83%	-	-
25			50	22.7585	25.3460	2.1403	8.44%	-	-

C.2 Demolding load-displacement curves

Mold 1

Mold 2

Mold 3

Mold 5

Mold 6

Mold 7