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SHAPE MEMORY IN BIODEGRADABLE POLYMERIC SYSTEMS: MORPHOLOGICAL AND THERMO- MECHANICAL STUDY

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A thesis submitted to the Nanyang Technological University
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Doctor of Philosophy

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Summary

Shape-memory materials have been proposed in biomedical implantation devices due to their ability to facilitate minimally invasive surgery, particularly in cardiovascular stent interventions. Therefore, our laboratory has been developing a completely degradable bi-layer polymeric stent with self expandability, which not only plays a dual role of maintaining or increasing the lumen of a vessel without causing excessive injury as well as providing the capability to deliver one or more drugs concurrently to the target site, but will disappear completely after healing.

This thesis presents the investigations carried out to explore the shape memory / thermo-mechanical characteristics of the polymers that are used for such a polymeric stent. The main objective of this research work is to understand the mechanism responsible for the shape-memory effect in such a bi-layer polymeric system. In this work, the shape-memory characteristics of individual layers (amorphous poly (D,L-lactide-co-glycolide), P(DL)GA and semicrystalline poly (L-lactide), PLLA) were first investigated followed by the bi-layer system which consists of top layer of P(DL)GA and bottom layer of PLLA. The extent of shape memory recovery has been correlated to several factors, including the extent of strain, deformation temperatures and recovery temperatures.

Summary

These observed effects could be explained on the basis of molecular orientation and slippage effects. For amorphous P(DL)GA, the shape recovery is based on the disorientation of the oriented amorphous chains formed during programming. On the contrary, the primary mechanism of shape recovery of semicrystalline PLLA is attributed to the disorientation of the oriented amorphous chains but recovery decreases as chain orientation in the crystalline regions is increased at higher stretch ratio and deformation temperature. In addition, increased crystallinity by strain-induced crystallization is indeed unfavorable to shape recovery. In the bi-layer system, the shape recovery is still largely attributed to the disorientation of the oriented amorphous chains in both PLLA and P(DL)GA layers depending on the recovery temperature.

Finally, to better understand the experimental observations, a one-dimensional constitutive model was developed to capture the shape memory effect of amorphous polymeric system during different stages of shape memory process, i.e. the stress-strain behavior in tension, the non-isothermal and isothermal recovery behavior. The proposed model is able to capture the general profile of the polymer behavior at different stages. In addition, this model presents deeper understanding of the underlying mechanism and important parameters that govern the shape memory process. It can serve as the basis of future investigations of more complicated systems such as semicrystalline polymer and semicrystalline/amorphous polymeric multi-layer systems.

CHAPTER 1

INTRODUCTION

1.1 Background

By definition, a stent is an implantable cylindrical construction used to expand any obstructed tubular ducts in the body. Since this pioneering invention was first used in cardiology, stenting minimizes the response of acute elastic recoil and negative remodeling due to balloon angioplasty and reduces the restenosis rate down to 10 – 40% [1, 2]. However, the problems of sub acute stent occlusion and late restenosis due to intimal hyperplasia still remain. They are due to damage of artery wall during angioplasty, third body reaction and compliance mismatch between the stent and the vessel wall [2-5].

To overcome the issues mentioned above, two major breakthroughs have evolved in stent technology: *self – expanding metallic stents* incorporating shape memory property and *drug eluting stents* (DESs). Shape memory Nitinol stents are deployed with a low profile, and then are allowed to expand to their permanent shapes at the site of application without the aid of exerting additional pressure on the artery wall, thus reducing damage to artery wall and restenosis. On the other hand, DESs are polymer coated metal stents with anti-proliferative agents embedded within the polymeric matrix. Drugs such as paclitaxel, sirolimus or

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dexamethasone are used to reduce restenosis by inhibiting cell proliferation and growth of smooth-muscle cells (SMCs) [6, 7].

Even though drug eluting shape memory metallic stents further reduce the rate of in-stent restenosis, they do not represent an optimal solution. Metal stents have limited flexibility compared to the surrounding arterial walls and thus induce significant compliance mismatch. Besides, drug loading capacity is very limited since the coating can be only a few microns thick. Further, the un-biodegradable nature of the stent means that it remains in patient's body permanently and it limits patients having MRI, CT and X-ray examinations due to ferromagnetic distortions.

Furthermore, the potential release of toxic corrosion products and the permanent residence of the metallic stent may lead to long-term complications. In addition, it has been reported that the clinical need for stents is at most limited to the first 12 months following angioplasty. Therefore, biodegradable polymeric stents with the capability of self-expanding would be an ideal alternative to metal stents [3, 5, 8, 9]. Since then, a number of researchers have tried to develop biodegradable stents. The first biodegradable stent, made of woven poly (L-lactide) (PLLA) polymer strand, was developed by Duke University in the early 1980s [5].

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Another degradable stent made of PLLA was developed by Tamai *et al.* and was the first to be implanted in human body in 1999 [8]. The Igaki-Tamai stent is made of PLLA monofilament with a zigzag helical coil design and has self-expanding capability. The self-expansion can only be achieved where a heated dye in the balloon is used to trigger the expansion. Peng *et al.* [10] have also developed a self-expanding poly(caprolactone) stent using the similar concept. The stent auto expands in response to microwave or electrical heating in the balloon. However, there is concern related to these stents as heating will cause cell necrosis of the surrounding tissues.

Consequently, a completely degradable bi-layer polymeric stent with self expandability has been developed in our laboratory [11-13]. The stent can be programmed to expand at body temperature, resulting in natural deployment without need for assisting devices. Moreover, it has the potential to deliver one or more drugs concurrently to the target site.

1.2 Problem Statement of the Thesis

A novel prototype of bi-layer degradable stent made from FDA-approved polymers has been developed in our laboratory. The system consists of two layers of biodegradable polymers sandwiched together: the top layer is amorphous poly (D, L-lactide-co-glycolide) (P(DL)GA) with glass transition temperature of $\sim 40^{\circ}\text{C}$; the bottom layer is semi-crystalline poly (L-

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lactide). It utilizes the concept of shape-memory effect to deliver the stent in a minimally invasive manner. ***However, how can it be made possible to incorporate and adjust the shape memory in these biodegradable polymers such that shape-memory effect can be triggered at temperatures close to body temperature?***

To accomplish this, it is important to understand the underlying mechanism and important factors governing the shape memory effect. Most of the reported work to date has focused on shape-memory effects in physically or chemically cross-linked polymers; however, ***there is little, if any, research work conducted to investigate the shape memory mechanism in bi-layered system.***

From a practical viewpoint, it is also crucial to be able to predict the shape memory effect. Over the past decades, only a few attempts have been made in literature to develop models to quantitatively predict the shape memory effect. ***However, there is no thermo-mechanical model developed for biodegradable uncross-linked systems.***

1.3 Objectives and Scope of the Thesis

The objectives of this thesis are:

- (1) To explore the shape-memory properties of uncrosslinked polymeric systems, i.e. amorphous P(DL)GA, semicrystalline PLLA and bi-layer of P(DL)GA and PLLA;
- (2) To understand the molecular mechanism responsible for the shape memory effect in the monolayer and bi-layer polymeric systems;
- (3) To develop a model to predict the shape-memory effect of the amorphous monolayer polymeric system.

To achieve the objectives, the work of this thesis is divided into three major sections. The first section is to explore the shape-memory potential of the bi-layer polymeric system. In this bi-layer film configuration, the top layer is P(DL)GA and the bottom layer is PLLA. A preliminary study with the individual monolayer (single P(DL)GA and PLLA) was conducted to investigate the important parameters that affect the shape memory properties. The parameters studied were stretch ratio, deformation temperature and recovery temperature. Afterward, the bi-layer or the laminate system was studied.

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The second section is to understand the shape-memory mechanism in monolayer and bi-layer systems. In order to do so, molecular and morphological changes were evaluated during shape-memory programming and recovery process. Four polymer spectroscopy techniques were employed to probe the molecular orientation in various aspects: (1) optical birefringence to give orientation information averaged over the sample; (2) wide angle X-ray diffraction to provide information in the crystalline regions only and (3) Raman spectroscopy to offer molecular orientation information in both amorphous and crystalline phases. The results obtained serve as supporting and complementary information to verify the hypothesized shape-memory mechanisms.

The third section is to develop a model to correlate the experimental results with the theoretical schemes. One-dimensional constitutive models are proposed to capture the shape memory effect of the amorphous P(DL)GA during different stages of shape memory process. In addition, the proposed models are aimed to tailor and predict memory effect under isothermal and non-isothermal conditions.

1.4 Organization of the Thesis

This thesis has been divided into eight chapters. In the very first chapter, the background, the motivation that drives this research work and the scope of study has been highlighted in this chapter. In *Chapter 2* of the thesis, the background of general theory of shape memory mechanism is discussed and the various types of shape memory polymers are reviewed. In *Chapter 3*, the theory of molecular orientation is presented. A review on the theoretical explanations of orientation measurement for various techniques is also presented.

Chapter 4 outlines the methodology and materials employed to conduct all the experiments. *Chapter 5* and *6* present the two parts of the shape memory study: the former is result of the individual mono-layers that are P(DL)GA and PLLA; the latter is the result of bi-layer of P(DL)GA and PLLA. These two chapters cover the in-depth discussion of the shape memory effects under various conditions and the mechanism accompanied them.

Subsequently, *Chapter 7* presents the proposed models to predict the shape memory behavior for amorphous monolayer system under various thermo-mechanical conditions. Finally, *Chapter 8* draws a conclusion of all the works that have been done in this thesis. Recommendations for future studies are also proposed in that chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Development of Shape-memory Polymers (SMPs)

2.1.1 Introduction to shape-memory polymers

Shape-memory polymers (SMPs) are stimuli responsive materials. They have the capacity to recover a predetermined shape after subjected to significant mechanical deformation upon application of an external stimulus, which can be heat, light, pH, magnetic and electric fields etc [14-16]. In particular, polymers that undergo change in shape initiated by temperature change are called thermoresponsive shape-memory polymers, which are the main focus of this review. Generally the shape-memory effect is not linked to an intrinsic material property, meaning that polymers do not require a specific chemical composition; the effect rather results from a combination of polymer morphology and specific programming and thermo-mechanical history.

In order to exhibit shape-memory function, the polymer is needed to be ‘programmed’. During the programming process, the polymer sample is deformed and then fixed into a temporary geometry by cooling the sample as shown schematically in Figure 2.1. Upon

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heating the sample above its transition temperature (T_{trans}), it triggers the shape-memory effect, resulting in the recovery of the permanent geometry. The mechanism through which SMPs exhibit specific shape-memory functionality is related to their structural morphology, as will be discussed in the next section.

Figure 2.1 Schematic demonstration of the thermally induced shape-memory effect.

2.1.2 Molecular mechanism of the shape-memory effect

Lendlein *et al.* [14] and Gall *et al.* [17] gave an in-depth discussions of the underlying mechanism of thermally induced shape-memory effect. On the molecular level, the shape-memory polymer networks typically consist of two phases that are the reversible phase and the hard phase. The hard phases or the netpoints can either be physical or chemical in nature. Physical netpoints can be formed by polymer chains entanglements or intermolecular chain interaction of certain polymer blocks and the chemical netpoints can be in the form of covalent bonds. These covalent netpoints preserve the permanent shape of the shape-memory

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networks, while the permanent shape of the shape-memory thermoplastics is stabilized by the physical netpoints with the highest thermal transition temperature (T_{perm}).

At temperature above T_{trans} the chain segments in the reversible phase are flexible, whereas the motion of the chains is partly restricted below this thermal transition. This thermal transition can either be glass transition temperature (T_g) or melting temperature (T_m). In the case of T_g as the thermal transition, transition occurs from the rubbery state to the glassy state, limiting the flexibility of the reversible segments as the glassy modulus is at least two orders of magnitude times the rubbery modulus, the stored elastic stress is not sufficient to drive the reverse deformation in the glassy state as the load is removed.

If the thermal transition chosen for the fixation of the temporary shape is the melting temperature, strain-induced crystallization of the reversible segments occurs when the polymer is cooled below T_{trans} . In general, the crystallization obtained is incomplete; however, the crystallites formed are adequate to fix the temporary shape. Upon heating above T_{trans} , the crystallites melts and the chain segments are allowed to return to the random coil-like structures and the driving force for the recovery is provided by the entropy elasticity.

The molecular mechanism of programming the temporary and recovering the permanent geometry is demonstrated schematically in Figure 2.2 [14] for a generalized SMP network.

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The filled circles represent the fixed phases, which can be chemical or physical netpoints depending on the type of SMPs. If the rise in temperature is higher than T_{trans} , the switching segments are flexible (marked red) and the polymer can be deformed elastically. The temporary shape is fixed by cooling down below T_{trans} (marked blue). If the polymer is heated up again, the permanent shape is recovered. The SMPs can be classified into four main categories: (1) chemically cross-linked elastomers, (2) chemically cross-linked semicrystalline polymers, (3) physically cross-linked thermoplastics and (4) physically cross-linked block copolymers [18, 19]. Furthermore, the possible combinations of fixed and reversible phases present in different class of SMPs are summarized in Table 2.1.

Table 2.1 Possible combinations of fixed and reversible phases in different classes of SMPs

Category	Fixed Phase: Highest thermal transition, T_{perm}	Reversible Phase: Possible thermal transition, T_{trans}
(I) Chemically crosslinked elastomers	$T_{decomposition}$	T_g
(II) Chemically crosslinked semi-crystalline polymers	$T_{decomposition}$	T_m, T_g
(III) Physically crosslinked thermoplastics	T_m	T_g
(IV) Physically crosslinked block copolymers ^a	$T_{m,A}$	$T_{g,A}, T_{m,B}, T_{g,B}, T_{g,mix}$
	$T_{g,A}$	$T_{m,B}, T_{g,B}, T_{g,mix}$

^a Physically crosslinked block copolymers consist of a hard-segment determining block (Block A) and a switching-segment determining block (Block B).

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Figure 2.2 Schematic demonstration of the molecular mechanism of the thermally induced shape-memory effect for a polymer network with a) $T_{trans} = T_m$ and b) $T_{trans} = T_g$. [14]

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2.1.3 Chemically cross-linked SMPs

The first shape-memory polymer of commercial importance was covalently crosslinked polyethylene (PE) by means of radiation (γ -radiation, neutrons) or chemical methods. The shape memory effect of irradiated PE was first reported in 1951 and it has found broad applications as packaging films and particularly heat shrinkable products [20]. Since then, considerable work has been carried out on the synthesis of crosslinked PE and testing of their shape memory property [21-23]. Kumar *et al.* [23] have studied the effect of the radiation dose on the gel fraction of irradiated PE and recovery percentage of the stored strain. The gel content increased with the applied radiation dose (0-160 kGy). At a dose of 100 kGy, the heat shrinkage is between 94 and 100%. Furthermore, Mao *et al.* [21] have investigated the shape memory effect of slightly crosslinked PE (SXLPE) with the gel content from 5 to 20 wt%. It was reported that under certain experimental conditions the SXLPEs may exhibit good shape memory property, which is comparable to those of the commercially available shape memory PEs. However, the shape memory behavior was not very stable due to their low degree of crosslinking.

Another example of semicrystalline thermoset SMP is polycyclooctene (PCO), which undergoes cross-linking with peroxide [19, 24]. In this system, the transition temperature is T_m of PCO. Below T_m the crosslinked PCO has a three-dimensional network, which is connected by both chemical cross-links and the crystalline regions. When it is heated above

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T_m , the crystals melt and the polymer becomes amorphous with only the chemical cross-links acting as a fixed phase and the polymer can be easily deformed. Upon cooling, crystallization occurs to fix the secondary shape followed by a rapid sequence of melting, resulting to the shape recovery. It is reported that the shape memory property is dependent on degree of cross-linking and with a small amount of peroxide (2.5-5%), complete recovery is observed within 0.7s at 70°C. Besides that, other polymers such as polyvinylchlorides (PVC), polyolefins, polyamide, polytetrafluoroethylene (PTFE), polycaprolactone (PCL) and copolymers of PE and poly (vinyl acetate) (PVA) are been crosslinked and have shown shape memory properties [14].

Besides covalently crosslinked semicrystalline polymers, crosslinked thermoset epoxy has been shown to possess shape memory property [25, 26]. The crosslinked epoxy has a three-dimensional polymer network that is linked by chemical netpoints and the temperature that trigger recovery possess is glass transition temperature. Liu *et al.* examined the thermo-mechanical recovery behavior of the epoxy in three-point flexure for various pre-deformation and recovery conditions. It is observed that the relationship between the recoverable stress and strain level in SMP is governed by the stress-strain behavior at the pre-deformation temperature when the SMP is deformed above the glass transition temperature. Moreover, it is found that fast cooling raises the recoverable stress while slow heating during recovery reduces the recovery onset temperature and increase the recoverable stress. Despite the excellent shape memory property of the covalently cross-linked materials, one major

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drawback of these materials is that they cannot be reshaped or recycled once they are cross-linked.

2.1.4 Physically cross-linked (linear block copolymers) SMPs

In the early 1980s, Hayashi developed a linear segmented polyurethane (PU) thermoplastic at Mitsubishi Heavy Industries in Japan [27]. They are usually polymerized from diphenylmethane diisocyanate (MDI) and polycaprolactone diols with 1, 4- butanediol as chain extenders. The PUs are thus basically multiblock copolymers consisting of alternating sequences of soft segments with molecular weight 1000 – 10,000, and hard segments, which are built from diisocyanates and chain extenders, acting as physical crosslinks. In PUs, the physical crosslinks can be formed through polar interaction, hydrogen bonding and crystallization. The thermally induced shape memory effect is due to the formation of a phase-separated morphology, which has been described in Section 2.1.2, and the materials are categorized into two types based on the thermal transition temperature, which is either a melting temperature or a glass transition temperature.

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Linear block copolymers with $T_{trans} = T_m$

Kim and Lee et al. synthesized segmented polyurethanes with a hard segment determining block of 4,4'-diphenylmethane diisocyanate and 1,4-butanediol and polycaprolactone diols as soft segment by using pre-polymer method [28]. Effect of soft segment length ($M_n = 2,000 - 8,000$), soft segment content (50 - 90%) and maximum strain (100 – 600%) on the cyclic tensile properties and shape memory effects were studied. The transition temperature for the shape memory effect, which is the melting temperature of PCLs, can be varied in the range of 44 to 55 °C depending on the molecular weight and weight content of PCLs. Based on the result, polyurethanes that combine high molecular weight of PCL and high weight content of hard-segment determining blocks show the best shape memory property. With soft segment length below 2,000, no crystallization can be observed primarily due to poor soft segment-hard segment phase separation that leads to poor shape memory effect. In the thermomechanical cycling test, the capability of shape recovery decreases with number of cycles and it is strongly dependent on the extent of deformation: the strain recovery decreases too if the applied strain is increased, which is consistent with the results of Meng *et al* [29].

A further example of shape-memory polymers with $T_{trans} = T_m$ are linear block copolymers with a hard segment determining phase based on toluene diisocyanate (TDI) and soft segment blocks of hydroxyl-terminated *trans*-polyisoprene (HTPI) [30]. In the copolymer, a complete micro-phase separation is observed, with urethane segments organized into spherical domains acting as physical cross-links. The high degree of phase separation is

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believed due to the difference in polarity between HTTPI and TDI, which is favorable in term of shape memory effects. Results also show that the shape recovery rate depends on the soft segment content of HTTPI. With 70% soft segment content, the recovery rate is 85% compared to the mere 17% recovery rate with 30% of soft segment content. This behavior is explained with the formation of the continuous crystalline HTTPI phase when the soft segment content reaches 70%.

Furthermore, several investigations have been carried out to study the effect of mechanical and shape-memory properties through the incorporation of chain extenders such as ionic or mesogenic moieties into the hard segments of PUs system [14, 31]. The purpose of incorporating chain extenders into the hard segment is to introduce additional intermolecular interactions by possibly enhancing phase separation or increasing solubility of hard-segment blocks into the soft segment respectively. Jeong and his co-workers have synthesized a series of PUs from polycaprolactone diol ($M_n = 4,000$), MDI and 4,4'-bis-(20hydroxyethoxy)biphenyl (BEBP) or 4,4'-bis-(6-hydroxyhexoxy)biphenyl (BHBP) as mesogenic chain extenders. In this system, a higher glass transition temperature and the reduced crystallinity of the PCL soft segment phase suggests the enhanced dissolution of hard segment into the soft segment phase. As a result of that, an increase in elastic modulus and the strain fixity of 5 to 20% is observed with a strain of 100 to 300% compared to the PU system without mesogenic components [28].

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Linear block copolymers with $T_{trans} = T_g$

Polyurethane block copolymers containing a hard segment forming phase of MDI and 1,4-butanediol and a soft segment of poly (tetramethylene glycol) (PTMG) by a two-step process can be triggered by a glass transition temperature [32]. The highest thermal transition T_{perm} corresponds to the melting temperature of hard segment forming blocks and it is found to be between 200 and 240°C. The glass transition temperature of the soft segment phase with a molecular weight of 1800 increases from -15 to 1.5°C depending on the hard segment content (variation between 20 and 50 wt%). The crystallinity of the soft segment block becomes lower as the hard segment content increases. The increment in glass transition temperature and decrease in crystallinity of the soft segment are mainly due to the restrict mobility of the PTMG chains, hindering the formation of ordered crystallites.

The shape memory property is tested by thermomechanical tensile test ($\epsilon_m = 50\%$). In the test, the sample is stretched to 50% elongation at $T_g + 20^\circ\text{C}$. Subsequently, the deformed sample is quenched down to $T_g - 20^\circ\text{C}$ and is kept in this deformation for 5 minutes before the external force is released. Finally, the sample is heated up to $T_g + 20^\circ\text{C}$ to observe for any recovery. Results show that the shape fixity is more than 90% at all hard segment contents, however, the shape recovery ranges from 80 to 95% depending on the hard segment content. Surprising, no recovery is being observed when the hard segment content is less than 25 wt% or is above 50 wt%. This effect is caused by poor formation of physical crosslinks in low content of hard segment, resulting in the loss of shape memory effort. Whereas, the

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copolymer with 50 wt% of hard segment content has extensive intermolecular chain interaction among the hard segment, resulting rigid structure and low in recovery.

Another example of materials using T_g as the transition temperature are systems with poly(tetramethyl oxide)glycol (PTMO) soft-segment phase and hard-segment phase from MDI and 1,4-butanediol [33]. In this system, the transition temperature is the glass transition temperature of PTMO which can be in the range of -13 to 54°C by varying the molecular weight of the soft-segment ($M_w = 250, 650$) and the hard segment content (56 – 95 wt%). The T_g shifts to higher temperature value with increasing amount of the hard segment phase. As a result, the temperature at which the recovery is triggered rises based on the temperature series study. Furthermore, it is founded that higher hard segment content and high ratio of glassy to rubber modulus lead to higher degree of strain recovery.

2.1.5 Other thermoplastics SMPs

Polynorbornene with molecular weight of 3×10^6 g/mol is a linear, amorphous polymer showing shape memory property. It was developed by CdF Chemie and Nippon Zeon in the late 1970s [34-36]. The switching transition temperature is its glass transition temperature of 35 - 45°C and the fixed phase is based on the formation of physically crosslinked network due to the chain entanglement of the high molecular weight, linear polymer chains. Above

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the glass transition temperature, the material is in the rubbery state and softens rapidly. If the chains are being stretched quickly in this state and quenched down below the glass transition temperature, the polymer chains cannot slip off and disentanglement cannot happen. By rapid cooling, the induced elastic stress can be stored within the material. Upon heating up above T_g , the recovery of the material's original shape is observed, resulting in thermally induced shape memory effect.

There have been studies reporting that polynorbornene with high molecular weight shows strain-induced crystallization under stretching for 400% strain at 90°C and the formation of crystallites may contribute to the shape-memory effect by acting as physical netpoints in addition to entanglements [34, 36]. For this type of high molecular weight amorphous polymers to possess good shape-memory property, high precision for the programming and the recovery process is necessary; that is the time period for relaxation of the polymeric chains must be longer than the time required for deforming and cooling the polymer [14]. However, long-term storage of the polymer in temporary shape may not be easy due to the ease of relaxation of polymer. Till now, little research works have been conducted on this type of SMPs. More works can be carried out to explore the shape-memory property of the linear amorphous polymers.

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2.1.6 Polymer blends having shape-memory effect

Blending of polymers offers an attractive way to adjust the mechanical and thermal properties of the polymeric systems by varying the composition and type of polymers. Since then, numerous miscible/immiscible polymeric blends have been investigated in the past, though not with respect to shape memory behavior. Till Year 1994, Kuay [37] first studied the thermal characteristics of shape memory polymer blends for biomedical implantations. Two solution-based PUs were blended in various ratios trying to obtain a transition temperature that is nominally 37°C for biomedical applications. However, from the result these polymer blends do not deliver a reliable glass transition temperature in the temperature range of interest.

Jeong and co-workers [38] then investigated the miscibility and shape memory property of blends of poly(vinyl chloride) (PVC) and polyurethane with PCL diol as the soft segment. The results indicate that a single glass transition temperature and no endothermic melting peak of PCL are observed in all compositions, meaning that the PVC and PCL soft segment are miscible and the amorphous domain of miscible PVC/PCL segment phase acts as a reversible phase. Cyclic tensile test was carried out to test the shape memory property and it showed that PVC/PU blend by weight ratio of 8/2 reduces the hysteresis due to the presence of hard segment domain in PU. A similar study was conducted by Ajili [39] to evaluate the shape memory effect of PU/PCL blend and it was found that blend with composition 80/20

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showed good shape memory effect with recovery temperature of the melting temperature of PCL in the blend.

A patent was filed recently for blends of amorphous and semicrystalline polymers having shape memory properties [40]. In such blend system, the amorphous polymers will act as reversible phase while the crystallites in the semicrystalline polymer will act as fixed phase. The disclosure relates to the shape memory properties for blends of an amorphous polymer such as poly (vinyl acetate) (PVAc) or PMMA and semicrystalline polymer, which can be for example poly (lactic acid) or poly (vinylidene fluoride) (PVDF). In the blend systems present here, it illustrates one point that only blend with particular composition and morphology can possess good shape memory property and it requires careful control of the blending process to obtain desirable phase morphology.

2.1.7 Biodegradable SMPs

In the recent decade, SMPs are gaining great attention in area of biomedical applications especially in the minimally invasive surgery. With shape memory effect, the polymers can be implanted into the human body with a compressed shape through small incision. When the implant reaches the desired site, recovery to the application-relevant shape is triggered by the warmth of the body. After the implant remains in situ for a defined period of time to serve its

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purpose, it degrades gradually and is being absorbed. In this case, a second surgery is not required to remove the implant from the human body. When SMPs are used for biomedical applications, there are a few key points to be considered. First and foremost, the transition temperature or the recovery temperature of the SMPs should be selected near the human body temperature. And yet, the polymers should maintain the acquired mechanical strength over the lifetime of the application and degrade at a designated rate to non-toxic substances.

A number of researchers have attempted to develop biodegradable shape memory polymers. Most of the biodegradable shape memory polymers developed are based on three well-known biodegradable polymers that are poly (L-lactide) (PLLA), polyglycolide (PGA) and poly (ϵ -caprolactone) (PCL). Particularly, the choice of using PCL as switching segment is preferred due to the fact that it has a melting temperature of 60°C and it can be adjusted to the human body temperature by varying the molecular weight. For example, Lendlein [41] synthesized a AB-polymer networks made from oligo (ϵ -caprolactone) dimethacrylate as crosslinker and *n*-butyl acrylate as comonomer. The oligo (ϵ -caprolactone) dimethacrylate serves as the crystallizable switching segment. By adjusting the molecular weight of oligo (ϵ -caprolactone) dimethacrylate and weight content of *n*-butyl acrylate, the crystallinity, transition temperature and thus the shape memory property of the system can be tailored.

Furthermore, Lendlein and Langer [42] have developed a thermoplastic multi-block copolymer based on oligo(ϵ -caprolactone)diol (OCL) and oligo(*p*-dioxanone)diol (ODX).

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The switching segment is OCL while the hard segment is crystallizable ODX. The strain recovery rate studied for the system has values between 76-99%, however, the recovery stress obtainable is only between 1 and 3 MPa compared to that of shape memory alloys of 200 – 400 MPa. Soon after, Nagata *et al.* [43] synthesized photocurable biodegradable multi-block copolymers based on poly(ϵ -caprolactone) and poly(L-lactide) exhibiting shape memory effect. The transition temperature is in the range of 40 to 48°C and the strain fixity rate reduces with increasing PLLA concentration. Besides that, Ping [44] has also developed a series of biodegradable polyurethane using PCL as the switching segment. The switching temperature can be varied between 43 and 62°C and the recovery stress measured is in the range of 1 – 6 MPa. Furthermore, it is found that the recovery stress is strongly dependent on the programming condition: the recovery stress will be higher if the specimen is deformed below transition temperature.

Despite the notable shape memory properties exhibited by PCL-based SMPs, low recovery force associated with these SMPs is an issue. For that reason, there are two diverse approaches to increase the recovery force and mechanical strength for SMPs. In one approach, Min *et al.* [45] investigated the shape memory effects of polylactide-co-poly(glycolide-co-caprolactone) (PLAGC) multiblock copolymer. The copolymer show moderate shape memory properties; however, the synthesis and post treatments involved are complicated. Moreover, Wang [46] prepared a series of polyurethanes using poly(L-lactide) as soft-segment block in hope to improve the recovery force as it is known that PLLA has good mechanical strength and possesses shape memory property [46, 47]. But, the measured

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restoration force is less than 6 MPa. Furthermore, Lu *et al.* [47, 48] synthesized a series of linear segmented copolymers of PLLA and PCL with maximum recovery stress not exceeding 4 MPa. Table 2.2 gives an overview of biodegradable shape-memory polymers developed hitherto.

In an alternative approach, incorporation of particles or fibers into SMPs as the composite systems has been attempted to improve the recovery force [49, 50]. Hampikian *et al.* [51] investigated the tantalum filled SMP for the potential use as intracranial aneurysm coils. A 50% weight fraction of tantalum was added into the SMP; nevertheless the effects of the addition were small resulting in recovery stress of only 0.12 MPa. Zheng [52] has studied the shape memory effect of poly(D,L-lactide) / hydroxyapatite (HA) composites. The result showed that the composite systems have higher mechanical strength and it is also pointed out that composite ratio plays an important role in achieving memory property.

Moreover, SMP composites have been reinforced with magnetic nanoparticles (Fe_3O_4) for magnetically induced shape memory effect [53, 54]. In general, the advantage of reinforced SMPs is the increase in mechanical strength compared to the non-reinforced polymer. The disadvantages of this approach are the decrease in shape recoverability, lower drug capacity and the non-biodegradable nature of those reinforced particles. Another concern particularly related to the nanoparticles is the possible risk of triggering inflammatory as well as other adverse reactions, which has not yet been studied for the long-term effect.

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Venkatraman *et al.* [12, 13] have developed a multilayer system that exhibits partial elastic memory (PEM) for biodegradable stent application. This system consists of two layers of biodegradable polymers sandwiched together: one layer is poly (L-lactide); another layer is poly (D,L-lactide-co-glycolide) (PLGA) with glass transition temperature of 35 - 40°C. The PLLA layer is meant for the structural support while the PLGA layer is an “expandable” layer. Hence, built upon this work, this PhD work aims to study the shape memory property of this multilayer system.

Table 2.2 Biodegradable shape memory polymers

Polymer	Type of SMPs	Thermomechanical conditions	Shape memory property
Poly(ϵ -caprolactone) dimethacrylate and <i>n</i> -butyl acrylate [41]	Covalently crosslinked polymer network	$T_{trans} = 44 - 51^{\circ}C$ $\epsilon_m = 200\%$, no. of cycles = 5	$R_f = 95\%$ $R_r = 93 - 98\%$
Oligo(ϵ -caprolactone)diol and oligo(<i>p</i> -dioxanone)diol [42]	Thermoplastic multiblock copolymer	$T_{trans} = 40^{\circ}C$ $\epsilon_m = 200\%$, no. of cycles = 3	$R_f = 98 - 99.5\%$ $R_r = 77 - 99\%$ $F_{max} = 1 - 3 \text{ MPa}$
Poly(ϵ -caprolactone)diol and poly(L-lactide) [43]	Thermoplastic multiblock copolymer	$T_{trans} = 40 - 48^{\circ}C$ $\epsilon_m = 200\%$, no. of cycles = 3	$R_f = 50 - 100\%$ $R_r = 50 - 100\%$
Poly(ϵ -caprolactone)diol and 2,4-toluene diisocyanate-ethylene glycol [44]	Thermoplastic multiblock copolymer	$T_{trans} = 43 - 62^{\circ}C$ $\epsilon_m = 300\%$, no. of cycles = 1	$R_f = 94 - 100\%$ $F_{max} = 1 - 6 \text{ MPa}$
Three-arm poly(ϵ -caprolactone)triols, methylene diphenyl 4,4'-diisocyanate isocyanate and 1,6-hexanediol [55]	Thermoplastic multiblock copolymer	$T_{trans} = 45 - 47^{\circ}C$ $\epsilon_m = 100\%$, no. of cycles = 3	$R_f = 81 - 92\%$ $R_r = 91 - 99\%$
Poly(L-lactide) and poly[glycolide-co-(ϵ -caprolactone)] [45]	Thermoplastic multiblock copolymer	$T_{trans} = 40 - 49^{\circ}C$ $\epsilon_m = 200\%$, no. of cycles = 3	$R_f = 68 - 99\%$ $R_r = 88 - 99\%$
Poly(L-lactide)diols, hexamethylene diisocyanate and 1,4-butanediol [46]	Thermoplastic multiblock copolymer	$T_{trans} = 33 - 53^{\circ}C$ $\epsilon_m = 150\%$, no. of cycles = 1	$R_f = 96 - 99\%$ $R_r = 92 - 100\%$ $F_{max} = 2 - 7 \text{ MPa}$
Poly(L-lactide) and poly(ϵ -caprolactone) [47, 48]	Thermoplastic random copolymer	$T_{trans} = 42 - 62^{\circ}C$ $\epsilon_m = 100\%$, no. of cycles = 1	$R_f = 60 - 100\%$ $F_{max} = 2 - 4 \text{ MPa}$

2.2 Shape-memory Thermo-mechanical Characterization and Models

2.2.1 Thermo-mechanical characterization of SMPs

To quantify shape memory effect, it can be done by cyclic, thermo-mechanical investigations. Usually, the measurements are conducted by means of tensile tester or bending test equipped with a temperature chamber. A single cycle includes programming of the sample into temporary geometry and recovering its permanent geometry. Basically a typical test protocol is as follow:

1. First, the maximum strain ϵ_m is applied on the specimen at deformation temperature T_d .
2. Maintaining ϵ_m , the specimen is cooled down to low temperature T_L , thus fixing the temporary shape.
3. It is held at T_L for a period of time before unload the sample.
4. Under the no load condition, the specimen is heated from T_L to high temperature T_r and held at that temperature for a period of time.

The thermo-mechanical paths 1 – 4 can be repeated N times and the diagram of the three-dimensional stress-strain-temperature relationship is presented in Figure 2.3.

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Figure 2.3 Three-dimensional schematic diagram of the thermo-mechanical cycling test.

Important quantities describing the shape-memory properties of the material for a certain maximum strain are the strain recovery (R_r) and strain fixity (R_f). The strain recovery, R_r , quantifies the ability of the material to memorize its permanent geometry. On the other hand, the strain fixity, R_f , describes the ability of the material to fix the mechanical deformation which has been applied during the programming process. Both quantities are defined by the following equations respectively:

$$\text{Strain fixity: } R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\% \quad (2.1)$$

$$\text{Strain recovery: } R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \times 100\% \quad (2.2)$$

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Where: ε_u and $\varepsilon_p(N)$ represent the strain at the unload point and the residual strain after heating to T_r in the N-th cycle.

In general, the shape-memory effect is not related to a specific material property of a single group of polymer; it rather dues to combination of the polymer structure and the polymer morphology induced during programming process, thus, *understanding the programming condition-property relationship plays an important role governing the shape-memory properties*. Thereafter, considerable works on the relationship between the thermo-mechanical property and shape memory behavior has been performed using a series of Mitsubishi PU-based SMPs [27, 56-60]. The range of glass transition temperature is between 30 and 80°C. These previous studies have focused on the temperature dependence of the stress-strain response and the unconstraint strain recovery behavior.

Hu and Tobushi [27, 57, 58] have investigated the effect of different thermo-mechanical cyclic conditions, including deformation temperature T_d , deformation speed V_d , maximum strain ε_m , storage temperature T_i , fixing speed V_f , recovery temperature T_r , recovery time t_r , storage time t_s and number of cycles on the shape-memory behavior under free strain recovery response. It was found that SMPs exhibited good shape memory effects at deformation temperatures ranging from T_g to $T_g + 25^\circ\text{C}$. Furthermore, the strain recovery increases with increasing deformation speed and decreasing maximum applied strain. In practical application, SMPs may experience constraint from surrounding environment and

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will not be allowed to recover freely. As a result, Gall and Liu [17, 25] have done some works in this aspect. They studied the degree of shape recovery under various extents of constraint level.

2.2.2 Shape-memory modeling

Over the past decades, extensive researches have focused on experimental observations, physical understanding and new SMPs synthesis as mentioned in the preceding section. However, only a few attempts have been made to develop constitutive models to quantitatively predict the shape memory effect of shape-memory polymers (SMPs), which is important in the practical viewpoint. Essentially, two approaches have been used to describe the thermo-mechanical behavior of SMPs. The first approach is based on well-known standard linear viscoelastic approaches commonly used to predict the thermo-mechanical properties of polymers [61-63]. The second approach is based on the micromechanics modeling of the material during the change of state. The material is assumed to be “rubbery” at high temperature (above T_g) and “frozen” at low temperature (below T_g). During the glass transition, a fraction of the material is in glassy state while the rest of the material is in rubbery state and a rule of mixtures is applied as a micromechanical constraint [64].

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In an earlier attempt, Wayne employed a simple first-order reaction kinetics to model the recovery behavior of polyester shrink film under isothermal and non-isothermal conditions. The model was limited to amorphous polymers without strain-hardening effects and did not take into account for the recovery mechanism at the molecular level [65]. Later on, Lin *et al.* [61] derived a 4-element rheological model that described the thermo-mechanical properties of crosslinked polyurethane system. In addition, Tobushi and co-workers [62] proposed a one-dimensional constitutive model to capture the shape memory effect by modifying a standard 3-element linear viscoelastic model. The standard viscoelastic model was modified by introducing a creep strain-based friction element. The modified model consists of two springs, a dashpot and a friction element. The physical significance of the friction element is to capture the temperature dependent creep strain that remains after the unloading process. And this creep strain is irrecoverable at the low temperature but becomes recoverable at high temperature. Tobushi *et al.* [63] further improved the model by introducing the nonlinear viscous term. The nonlinear term is expressed by a power function of stress and is then added to the linear constitutive equation proposed earlier on.

Liu *et al.* [64] have used different approach, the concept of phase transitions, to develop a one-dimensional finite deformation constitutive model for shape memory thermoset by taking thermal expansion and different loading constraints into consideration. The model has been limited to small-strain deformation. In this approach, the ratio of these two phases changes as a function of temperature. By changing the ratio of these two phases, the glass

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transition during the thermo-mechanical cycle is embodied and the shape memory behavior can be captured.

Recently, Qi *et al.* [66] developed a three-dimensional finite deformation constitutive model to predict the thermo-mechanical response of amorphous SMPs in cylindrical form using the finite element code. The model employed the concept of the first order phase transition to describe the change in the deformation mechanism from entropic elasticity of the rubbery state to viscoplasticity of the glassy state as the temperature decreases. However, the predicted recovery stress deviates significantly from the experimental value.

Nguyen *et al.* [67] established a 3D finite element model for a SMP by splitting the deformation gradient into thermal and mechanical components. Compared with the experimental results by Qi *et al.* [66], the inaccuracy of the predicted recovery is still significant. The main drawback of this approach is that it is not representative of the physical processes of the glass transition and thus results in nonphysical parameters, such as the volume fractions of the glassy and rubbery phases. Nevertheless, the existing models mentioned up to now have been devoted to describe the shape memory effect of mono-SMPs, and many are limited to small strain; it has not been found in the open literature that a constitutive equation has been developed for the SMP composites, particularly the bi-laminate system.

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2.3 Summary

Shape memory polymer is a class of smart materials with the capability to recover their shape upon exposure to an external stimulus. Over the years, significant evolution has been seen and recently it has found tremendous potential in medical applications, particularly in cardiovascular intervention. For biodegradable SMPs incorporated into stent applications, the devices can be introduced into the body by minimally invasive procedures through a small incision, after which, recovering to its predetermined shape and at the same time dilating the area of arterial blockage. However, the negative aspect of the current biodegradable SMPs lie on their low recovery force.

For that reason, the challenge is to develop a biodegradable SMP system that can withstand compressive radial stresses over the lifetime of the applications, yet generate sufficient recovery stress during deployment. It can be achieved by applying composite technology and optimizing the processing – morphology relationship, having a shape-memory polymeric system that can give out adequate recovery stress with specific programming parameters. Therefore, in this thesis, the shape-memory characteristics of biodegradable bi-layer system would be investigated. Next, a model would be proposed to describe the thermo-mechanical response for the system. Lastly, the corresponding programming condition – structure – memory property relationships would be discussed to present a detailed knowledge of the molecular mechanism of the shape memory effect.

Theory on Molecular Orientation

CHAPTER 3

THEORY ON MOLECULAR ORIENTATION

3.1 Overview of Orientation Determination

As mentioned in the preceding chapter, understanding the programming-structure relationship plays an important role governing the shape-memory properties. It is essential to study how the shape memory and other physical properties are affected by the molecular orientation introduced during programming. In order to explicitly understand the properties of the material, it is necessary to know the distribution of the orientation of its structural units in either the crystalline or amorphous phase, or even in both phases. Several techniques have been employed to determine the molecular orientation of polymer.

Those techniques are optical birefringence, wide angle X-ray diffraction, nuclear magnetic resonance, infrared dichroism and Raman spectroscopy, each of which yields differing amount of information due to nature of the structural units and their different theoretical basis involved. For example, the orientation information obtained by birefringence is the average over the sample; the measurement is highly affected by the opacity of the sample. X-ray diffraction is a powerful tool that can give all molecular orientation distribution coefficients;

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however the information is limited to the crystalline regions only. On the other hand, infrared and Raman spectroscopy can provide orientation information in both amorphous and crystalline phases. The major experimental drawback in infrared measurement is the sample thickness limitation and it can only determine the second-order distribution coefficient; whereas Raman spectroscopy allows the determination of both the second and fourth-order coefficient and the sample preparation is simple. However, Raman spectroscopy is more complex in term of both fundamental theory and experimental measurement.

In the subsequent section, a theoretical introduction to the molecular orientation distribution function will be presented. Furthermore, the theoretical explanations of orientation measurement for each technique (birefringence, X-ray diffraction and Raman spectroscopy) will be presented as well.

3.2 Molecular Orientation Distribution Function

Consider a rectangular Cartesian system of coordinate axes (X, Y, Z). The molecular structural unit of a polymer with a set of coordinate axes (x, y, z) is related to the reference frame through the Euler angles (θ , ϕ , ψ) as shown in Figure 3.1. The probability of finding the orientation of a structural unit in an element $\sin\theta \, d\theta \, d\phi \, d\psi$ is described by orientation distribution function, $N(\theta, \phi, \psi)$.

Theory on Molecular Orientation

Figure 3.1 Definition of Euler angles used for specifying the orientation of the axes of a structural unit (x, y, z) with respect to the specimen axes (X, Y, Z).

The molecular orientation distribution function can be generally expressed in the following form [68-70]:

$$N(\phi, \theta, \psi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{n=-l}^l \frac{N_{lmn}}{4\pi^2} \langle P_{lmn}(\cos \theta) \rangle P_{lmn}(\cos \theta) e^{-im\psi} e^{-in\phi} \quad (3.1)$$

Where: $\langle P_{lmn}(\cos \theta) \rangle$ or $\langle P_{lmn} \rangle$ are the molecular orientation distribution coefficients of the order lmn , often called order parameters and $P_{lmn}(\cos \theta)$ are the Legendre polynomials of $\cos \theta$. The term N_{lmn} is given as [69, 70]:

$$N_{lmn}^2 = N_{l\bar{m}n}^2 = N_{lm\bar{n}}^2 = N_{l\bar{m}\bar{n}}^2 = \frac{2l+1}{2} \frac{(l+m)!(l-n)!}{(l-m)!(l+n)!} \frac{1}{[(m-n)!]^2} \quad (3.2)$$

Theory on Molecular Orientation

For the case of uniaxial symmetry, the orientation distribution function $N(\theta)$ can then be simply described as a function of the polar angle θ only in terms of spherical harmonics functions:

$$N(\theta) = \sum_{l=0}^{\infty} \left(\frac{2l+1}{2} \right) \langle P_{l00} \rangle P_{l00}(\cos\theta) \quad (3.3)$$

Where: l is even. The angular brackets used in the order parameters, $\langle P_{l00} \rangle$, indicate that the average values are taken over all orientations in the sample.

The order parameters, $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$, hereafter called P_2 and P_4 , are given further by:

$$P_2 = \langle P_{200} \rangle = \frac{1}{2} [3\langle \cos^2\theta \rangle - 1] \quad (3.4)$$

$$P_4 = \langle P_{400} \rangle = \frac{1}{8} [35\langle \cos^4\theta \rangle - 30\langle \cos^2\theta \rangle + 3]$$

(3.5)

Where: $\langle \cos^l\theta \rangle$ are determined by the following equation:

$$\langle \cos^l\theta \rangle = \frac{\int_0^\pi N(\theta) \cos^l\theta \sin\theta d\theta}{\int_0^\pi N(\theta) \sin\theta d\theta} \quad (3.6)$$

For a sample with a uniaxial orientation distribution, the order parameters, $\langle P_{l00} \rangle$, need to be determined for all the orders of l so as to obtain the molecular orientation distribution

Theory on Molecular Orientation

function $N(\theta)$ in equation 3.3. However, it is possible to predict the types of distributions from the P_2 and P_4 values. Bower *et al.* [71] and Nomura *et al.* [72] showed the graphical

representation of the state of orientation in terms of plots of P_4 against P_2 for several types of distribution function. In this graphical representation, there are four types of orientation distribution functions; (i) a monotonic decrease of the function $N(\theta)$ with increasing θ , (ii) a monotonic increase of the function $N(\theta)$ with increasing θ , (iii) the function $N(\theta)$ has at least one minimum at θ where $0^\circ < \theta < 90^\circ$, and (iv) the function $N(\theta)$ has at least one maximum at θ where $0^\circ < \theta < 90^\circ$. By obtaining the value of P_2 and P_4 , one can predict the type of orientation distribution in a system.

Very often, determination of the second order parameter, P_2 , is regarded as meaningful measures of molecular orientation distributions. For example, P_2 takes a value of -0.5 or 1 for all structural units oriented perpendicular or parallel to the stretch direction respectively; while it takes a value of zero for an isotropic system with random orientation.

Theory on Molecular Orientation

3.3 Experimental methods for determining orientation

Various techniques have been developed for characterizing the molecular orientation. The techniques used in this work are:

- 1) Optical birefringence – can give P_2 only;
- 2) X-ray diffraction – can give all order parameters;
- 3) Raman spectroscopy – can give P_2 and P_4 values.

The theory behind these three methods will be described in the following sections.

3.3.1 Birefringence

Birefringence is probably the most frequently used method to characterize the orientation. In this method, the polymer is considered to be an aggregate of polarisable structural units and it is assumed that the polarizability can be described by a component that is parallel to the z -axis of the structural unit (p_1) and a component that is perpendicular to the z -axis of the unit (p_2) as shown in Figure 3.1. It is further assumed that the electrical vector of the light is propagating along the Z axis.

Theory on Molecular Orientation

Assuming additivity of polarizability, the polarizability in the Z direction (p_{zz}) and in the X direction (p_{xx}) are given respectively by [73, 74]:

$$p_{zz} = p_1 \cos^2 \theta + p_2 \sin^2 \theta \quad (3.7)$$

$$p_{xx} = p_1 \cos^2 \psi + p_2 \sin^2 \psi \quad (3.8)$$

Eq. (3.8) can be further modified due to the relationship $\cos \psi = \cos \phi \sin \theta$ to become:

$$p_{xx} = p_2 + (p_1 - p_2) \sin^2 \theta \cos^2 \phi \quad (3.9)$$

Furthermore, the polarizability tensor is related to the refractive index tensor according to the Lorentz-Lorenz equation:

$$\frac{n_{ij}^2 - 1}{n_{ij}^2 + 2} = \frac{4\pi}{3} p_{ij} \quad (3.10)$$

The birefringence (Δn) thus depends on the refractive index and is defined as the difference between the refractive index in the Z direction and in the X direction. The birefringence and the average refractive index $\langle n \rangle$ are defined as follows:

$$\Delta n = n_{zz} - n_{xx} \quad (3.11)$$

$$\langle n \rangle = \frac{1}{2} (n_{xx} + n_{zz}) \quad (3.12)$$

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By combining Eq. (3.9), (3.10), (3.11) and (3.12) and rearranging, the following expression is obtained:

$$\Delta n = \frac{(\langle n \rangle^2 + 2)^2}{6\langle n \rangle} \frac{4\pi}{3} (p_1 - p_2) (1 - \sin^2 \theta - \cos^2 \phi \sin^2 \theta) \quad (3.13)$$

For the case of uniaxial symmetry, all angles of ϕ are probable and the average square of the cosine of ϕ is then equal to $\frac{1}{2}$. Thus, equation (3.13) becomes to:

$$\Delta n = \frac{(\langle n \rangle^2 + 2)^2}{6\langle n \rangle} \frac{4\pi}{3} (p_1 - p_2) \left(1 - \frac{3\langle \sin^2 \theta \rangle}{2}\right) \quad (3.14)$$

Following Eq. (3.14), Hermans orientation function is then defined as:

$$f^H = \frac{\Delta n}{\Delta n_{max}} = 1 - \frac{3\langle \sin^2 \theta \rangle}{2} = \frac{1}{2} [3\langle \cos^2 \theta \rangle - 1] \quad (3.15)$$

Where: the maximum or the intrinsic birefringence is given by:

$$\Delta n_{max} = \frac{(\langle n \rangle^2 + 2)^2}{6\langle n \rangle} \frac{4\pi}{3} (p_1 - p_2) \quad (3.16)$$

It should be noted that the *Hermans orientation function* is identical to the second order parameter, P_2 .

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The measured birefringence of the sample can be the result of contributions from different phases especially for the case of semicrystalline polymer. On the assumption that the crystalline (C) and amorphous (A) phases contribute to birefringence in proportion to their volume fractions, χ_c and χ_A , respectively, then the overall sample Hermans orientation function or second order parameter, f_S , is related to the crystalline, f_c and amorphous, f_A , Hermans orientation functions by the equation below [74]:

$$f_S = \chi_c f_c + \chi_A f_A \quad (3.17)$$

or

$$P_{2,S} = \chi_c P_{2,c} + \chi_A P_{2,A} \quad (3.18)$$

3.3.2 Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction is a technique that can be used to determine the orientation of both crystalline and amorphous phases, if the diffraction/scattering peaks can be properly separated. It is also only technique that can be used to measure the complete orientation distribution of the crystallographic planes. The orientation expressed by the average square of the cosine of angle θ of the crystallographic plane (hkl) can be calculated as follows [73, 75]:

Theory on Molecular Orientation

$$\langle \cos^l \theta_{hkl} \rangle = \frac{\int_0^\pi I_{hkl}(\theta) \cos^l \theta \sin \theta d\theta}{\int_0^\pi I_{hkl}(\theta) \sin \theta d\theta} \quad (3.19)$$

Where: $I_{hkl}(\theta)$ is the intensity of diffraction along the azimuthal angle θ .

For the case of uniaxially oriented poly (L-lactide), the orientation distribution coefficient of crystallites, $P_{2,c}$, can be obtained using this technique. The average cosine of the angle between the crystal c -axis and the film Z -axis, $\langle \cos^2 \theta_{c,Z} \rangle$, is related to those of the angles between the normal vector of the (110) plane and the Z -axis, $\langle \cos^2 \theta_{110,Z} \rangle$, and between the normal vector of the (200) plane and the Z -axis, $\langle \cos^2 \theta_{200,Z} \rangle$ [76], by:

$$\langle \cos^2 \theta_{c,Z} \rangle = 1 - \langle \cos^2 \theta_{110,Z} \rangle - \langle \cos^2 \theta_{200,Z} \rangle \quad (3.20)$$

Since the crystallographic c -axis is perpendicular to both the normal vectors of the (110) and (200) planes, and the α -form PLLA has a pseudo-orthorhombic conformation, Eq. (3.20) can be simplified as [69]:

$$\langle \cos^2 \theta_{c,Z} \rangle = 1 - 2\langle \cos^2 \theta_{200,Z} \rangle \quad (3.21)$$

with

$$\langle \cos^2 \theta_{200,Z} \rangle = \frac{\int_0^\pi I_{200}(\theta) \cos^2 \theta \sin \theta d\theta}{\int_0^\pi I_{200}(\theta) \sin \theta d\theta} \quad (3.22)$$

Thus, the orientation distribution coefficient of crystallites, $P_{2,c}$, can now be calculated by:

$$P_{2,c} = \frac{1}{2} [3\langle \cos^2 \theta_{c,Z} \rangle - 1] \quad (3.23)$$

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3.3.3 Raman spectroscopy

The full details of the theoretical treatment for determining the distribution of molecular orientation from polarized Raman measurement have been developed by Bower [77]. The theory will be reviewed briefly in the following section. For the Raman measurement, the scattered intensity, I_s , is given by:

$$I_s = I_0 \sum (\sum_{ij} l'_i l_j \alpha_{ij})^2$$

(3.24)

The nonindexed summation indicates that the observed intensity results from a sum over all scattering units. I_0 is a constant depending upon the incident light intensity and instrumental factors. l'_i and l_j are the direction cosine of the incident polarization vector and that of the scattered polarization vector respectively, with respect to a set of axis (X, Y, Z) of the sample. The term α_{ij} corresponds to the ij th component of the Raman tensor of the structural unit. The scattered intensity can be further expressed in the form:

$$I_s = I_0 \sum \alpha_{ij} \alpha_{pq} \quad (3.25)$$

Each component α_{ij} can be expressed as linear combination of the principal components of the Raman tensor (α_1 , α_2 and α_3) and Euler angles defining the orientation of the principal axes of the tensor with respect to the (X, Y, Z) coordinate system.

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In the case of uniaxial cylindrical symmetry with no preferred orientation about the chain axis and assuming the tensor axis coincident with the chain axis, one can write Eq. (3.25) into:

$$I_s = I_0 \sum \alpha_{ij} \alpha_{pq} = I_0 4\pi^2 N_0 \sum_l M_{l00} A_{l00}^{ijpq} \quad (3.26)$$

Where: N_0 is the number of structural units contributing to the scattered intensity and A_{l00}^{ijpq} is quadratic expression in term of principal components of the Raman tensor. The term M_{l00} is the expansion coefficient of the orientation distribution in terms of Legendre polynomials and is given by:

$$M_{l00} = \left(\frac{1}{4\pi^2} \right) \left(\frac{2l+1}{2} \right)^{1/2} \langle P_l(\cos\theta) \rangle \quad (3.27)$$

Given a specific scattering geometry, said backscattering geometry in Figure 3.2, five independent nonzero quantities $I_0 \sum \alpha_{ij} \alpha_{pq}$ can be resolved from Eq. (3.26) for uniaxially drawn sample on the assumption that the Raman tensor is cylindrical. They are [78-80]:

$$I_0 \sum \alpha_{33}^2 = b(A - 2BP_2 + 8CP_4) = I_{zz} \quad (3.28a)$$

$$I_0 \sum \alpha_{22}^2 = b(A + BP_2 + 3CP_4) = I_{yy} \quad (3.28b)$$

$$I_0 \sum \alpha_{32}^2 = b(D - EP_2 - 4CP_4) = I_{yz} \quad (3.28c)$$

$$I_0 \sum \alpha_{22} \alpha_{33} = b(F - GP_2 - 4CP_4) \quad (3.28d)$$

$$I_0 \sum \alpha_{21}^2 = b(D + 2EP_2 + CP_4) = I_{yz}(\nu = 90^\circ) \quad (3.28e)$$

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Figure 3.2 Schematic diagram of the polarized Raman back-scattering setup.

The constants A - G are given by:

$$A = \frac{8r^2 + 4r + 3}{15}$$

$$E = \frac{-2r^2 + 4r - 2}{42}$$

$$B = \frac{8r^2 - 2r - 6}{21}$$

$$F = \frac{6r^2 + 8r + 1}{15}$$

$$C = \frac{8r^2 - 16r + 8}{280}$$

$$G = \frac{12r^2 - 10r - 2}{42}$$

$$D = \frac{r^2 - 2r + 1}{15}$$

Where: $b = I_0 N_0 \alpha_3^2$ and $r = \alpha_1 / \alpha_3 = \alpha_2 / \alpha_3$. The P_2 and P_4 can, therefore, be obtained by solving the above equations (3.28a) – (3.28e).

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In these equations, there are four unknowns: b , P_2 , P_4 and r . Since the sample is thin film which is practically two-dimensional, it is extremely difficult to measure spectra of $I_0 \sum \alpha_{21}^2$ due to alignment problem and polarization scrambling by the sample. By measuring spectra $I_0 \sum \alpha_{22} \alpha_{33}$, the position of the sample needed to be adjusted in a manner that it is most affected by the birefringence effect of the sample, it may introduce errors in the measurement and thus should be avoided [79]. At this stage, there are 4 unknowns in three equations (3.28a) – (3.28c). Since the aim is to determine the order parameters, b can be eliminated by keeping the same experimental conditions and taking intensity ratios such as follows:

$$R_1 = \frac{I_{ZY}}{I_{ZZ}} = \frac{D - EP_2 - 4CP_4}{A - 2BP_2 + 8CP_4} \quad (3.29a)$$

$$R_2 = \frac{I_{ZY}}{I_{YY}} = \frac{D - EP_2 - 4CP_4}{A + BP_2 + 3CP_4} \quad (3.29b)$$

The parameter r can be directly calculated by measurement of the depolarization ratio, R_{iso} , in the isotropic sample ($P_2 = P_4 = 0$). The R_{iso} is defined as [81]:

$$R_{iso} = R_1 = R_2 = \frac{(r-1)^2}{8r^2 + 4r + 3} \quad (3.30)$$

Subsequently, P_2 and P_4 can be determined from the experimentally measured values of R_1 and R_2 .

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The order parameters, P_{l00} , mentioned above give the information about the orientation distribution of the Raman tensor (i.e. the structural unit) for the Raman band with respect to the drawn direction (i.e. Z-axis) of the specimen, rather the orientation distribution of the molecular chain with respect to Z-axis of the specimen. And very often, the principal axis of the Raman tensor is not coincident with that of the molecular chain. In order to know the orientation distribution of the molecular chain, the P_{l00} values of the Raman tensor are needed to be corrected using the angular relationship between the coordinate axes of Raman tensor and that of molecular chain.

For the case of Raman tensor with cylindrical symmetry, the order parameter of the molecular chain, $P_{l00,chain}$, is related to the order parameter of the Raman tensor by the following equation [70, 82]:

$$P_{l00,chain} = \frac{P_{l00}}{P_{l00}(\cos \Omega)} \quad (3.31)$$

Where: Ω is the tilt angle between the cylindrical symmetry axis (z-axis) of a Raman tensor for the Raman band and the molecular chain axis (c-axis), and $P_{l00}(\cos \Omega)$ are the Legendre polynomial functions.

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For the Raman band assigned to the crystalline regions only, the tilt angle can be easily determined using Eq. (3.31) by measuring the $P_{100,chain}$ for the crystalline regions, i.e. $P_{2,c}$, by WAXD. However, Raman bands are usually assigned to both the crystalline and amorphous regions and the order parameters obtain for these bands are assumed to give information about the orientation distribution contributed from both the crystalline and amorphous phases in proportion to their volume fractions. In order to obtain the order parameters for the amorphous regions from the particular band, $P_{2,a}$, the tilt angle of the Raman band assigned to both phases is first to be determined using the following equation [69]:

$$\frac{2}{3\cos^2\Omega-1}P_2 = \chi_c \left(1 - \frac{\Delta n_c}{\Delta n_a}\right) P_{2,c} + \frac{\Delta n}{\Delta n_a} \quad (3.32)$$

Where: Δn_c and Δn_a are the intrinsic birefringence for the crystalline and amorphous regions, respectively. Once the tilt angle is determined, the $P_{2,chain}$ for the Raman band assigned to both phases can then be calculated using Eq. (3.31). Subsequently, the $P_{2,a}$ value can be determined by:

$$P_{2,chain} = \chi_c P_{2,c} + \chi_A P_{2,A} \quad (3.33)$$

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3.4 Theoretical Models for Polymer Orientation

The development of molecular orientation in a polymeric material during uniaxial deformation can be described by two theoretical models: (i) so-called *affine*, and (ii) *pseudo-affine* or aggregate model. In the affine scheme, it is assumed that the polymer is in the rubbery state and the network junctions are thought to be connected by flexible chains. When the polymer is deformed by stretching, the network points move exactly as they would if they were points in a completely homogeneous medium deformed to the same macroscopic deformation. For the affine deformation mode, the Herman orientation function, f_a^H , is related to the macroscopic sample stretch ratio by the following equation [68]:

$$f_a^H = \frac{1}{5N_c} \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (3.34)$$

Where: λ is the stretch ratio $= l/l_o$ (l_o is the initial length and l is the length after drawing) and N_c is the number of chain segments between network points respectively. It is assumed that N_c is sufficiently large for the chain lengths between network points to approximate Gaussian chains. An important consequence of the affine assumption is that the model is applicable for $\lambda < \lambda_{\max} = (N_c)^{1/2}$ only, and that f_a^H depends on N_c .

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In pseudo-affine deformation scheme the polymer is assumed to behave like an aggregate of independent anisotropic units, with no extensibility in themselves. The units may or may not be embedded in a matrix. On drawing, each unit simply rotates in proportion to the macroscopic deformation of the sample [83]. The corresponding expression for the orientation function becomes [74]:

$$f^{p-a} = \frac{1}{2} \left(\frac{2\lambda^3 + 1}{\lambda^3 - 1} - \frac{3\lambda^3 \cos^{-1} \lambda^{-3/2}}{(\lambda^3 - 1)^{3/2}} \right) \quad (3.35)$$

Unlike the affine rubber scheme, pseudo-affine deformation scheme is independent of N_c and has no adjustable parameters and also has no sample- or material-dependent parameters.

CHAPTER 4

MATERIALS AND METHODS

4.1 Sample Materials

The polymers used in this project are basically aliphatic polyesters. The physical characteristics of the polymers used are listed in Table 4.1.

Table 4.1 Physical characteristics of polymers used

Properties	Polymers	
	PLLA	P(DL)GA 53/47
Glass transition temperature, T_g (°C) ^a	66	37
Melting temperature, T_m (°C) ^a	176	-
Intrinsic viscosity, IV (dl/g) ^b	8.28	0.88
Weight-average molecular weight, M_w (g/mol) ^c	1.7×10^6	8.9×10^4
Number-average molecular weight, M_n (g/mol) ^c	9×10^5	5.4×10^4
Polydispersity index, (M_w/M_n) ^c	1.9	1.6

^a Determined by modulated differential scanning calorimeter

^b Specified in certificate of analysis from manufacturer

^c Determined by size exclusion chromatography

Materials and Methods

The polymers used are homopolymer poly (L-lactide), PLLA and copolymer poly (D,L-lactide-co-glycolide), P(DL)GA 53/47, i.e. 53 mole % of D,L-lactide and 47 mole % of glycolide. Both polymers were purchased from Purac Far East, Singapore. HPLC grade dichloromethane for film preparation was purchased from Ohme Scientific, Singapore.

4.2 Sample Preparation

4.2.1 Film preparation

All film samples were prepared by the method of solution casting. Polymer solutions were formed by dissolving polymer pellets (PLLA, P(DL)GA) in dichloromethane and stirred continuously until homogenous solutions were obtained. The polymer solution was cast onto a glass plate using an automatic film applicator (Automatic Film Applicator AG2150 by BYK Gardner) that utilizes a casting knife with adjustable height and speed. For bi-layer films, the bottom layer was cast first; it hardened after solvent evaporation, another layer was then cast on top. The films were then dried in vacuum oven at 55 °C for one week to eliminate the solvent residue. Weight loss analysis by using Thermogravimetric Analysis, TGA (TA Instruments Q500) showed 0.3 ~ 1 wt% and 1 ~ 1.5 wt% residual solvent in single and double layer films respectively.

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After drying, the thickness of the solution-cast films was measured using a micrometer and the accepted thickness were found to be approximately $\sim 100 \pm 5 \mu\text{m}$ for both single and bi-layer films.

4.2.2 Preparation of oriented samples by mechanical drawing

Samples for tensile tests were cut according to ASTM D638-99 Type V. Uniaxial sample stretching was carried out on a universal Instron Testing Machine 5548. The machine was set to operate at a constant strain rate of 10 mm min^{-1} . The test gauge length was 10 mm. The machine was equipped with a temperature controlled chamber, regulating sample temperature to within $\pm 1 \text{ }^{\circ}\text{C}$. Uniaxial tensile tests were conducted at drawing temperature, $T_d = 37, 50, 65, 85$ and $120 \text{ }^{\circ}\text{C}$ at various stretch ratio, SR, depending on the type of polymers. Hence, the samples were stretched at the chosen temperature to a given stretch ratio and then immediately quenched to room temperature for subsequent measurements.

Materials and Methods

4.3 Methods

4.3.1 Shape memory measurement

Two series of shape memory measurements, i.e. (i) isothermal and (ii) isochronal recovery were undertaken. For the isothermal recovery test, the recovery was measured after immersing the drawn samples (without external constraint) in a water bath at a chosen temperature for 5 minutes. The shape memory effort was quantified by the recovery of the stretched samples and the degree of recovery R_r , was calculated from the following equation:

$$R_r(\%) = \frac{l_d - l_s}{l_d} \times 100 \quad (4.1)$$

Where: l_d is the length of the drawn sample and l_s is the length of the sample after shrinkage test.

For the isochronal measurement, it was conducted using TA Instruments Thermomechanical Analyzer, TMA (TA Instruments Q400). The heating rate of the recovery measurement was $3\text{ }^{\circ}\text{C min}^{-1}$ and the temperature of the heating process ranged from 20 to 90 $^{\circ}\text{C}$. The degree of recovery was recorded as a function of temperature.

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4.3.2 Recovery force measurement

The recovery force was measured using the Dynamic Mechanical Analysis, DMA (TA Instruments Q800). A tensile configuration was used. The stretched samples were fixed between clamps and were confined within a small environmental chamber. The experiment was conducted in non-isothermal mode, in which the force was monitored as a function of temperature.

4.3.3 Thermal characterization of samples

The thermal properties of samples were determined using TA Instruments Modulated Differential Scanning Calorimeter (MDSC 7) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen medium from $-20\text{ }^{\circ}\text{C}$ to $+200\text{ }^{\circ}\text{C}$. The glass transition temperature (T_g), the melting temperature (T_m) and the heat of fusion (ΔH_m) of the samples were measured. The perfect PLLA crystal has a melting enthalpy of 93.3 J/g [69]. Besides, the thermal property was also investigated by using Dynamic Mechanical Analysis, DMA (TA Instruments Q800). The test was carried out in tensile mode, at a heating rate of 10°C/min , an oscillation amplitude of $5.0\text{ }\mu\text{m}$ and a fixed frequency of 1 Hz . Testing was conducted over the temperature range from 20 to $100\text{ }^{\circ}\text{C}$.

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4.3.4 Molecular structure characterization

There are several experimental methods to characterize the molecular orientation in polymers:

(i) birefringence under optical polarizing microscopy, (ii) wide angle X ray diffraction, WAXD, (iii) infrared spectroscopy and (iv) Raman spectroscopy. Optical birefringence and WAXD were used to measure the average molecular orientation and the crystalline orientation distribution in the sample, respectively. Raman spectroscopy was applied to measure the molecular orientation in both amorphous and crystalline phases of the samples.

4.3.4.1 Birefringence measurement

The birefringence, Δn , was determined using polarizing microscope. For the estimation of the molecular orientation of the samples, the birefringence was measured in monochromatic light at 589nm using Leitz polarizing microscope equipped with Berek tilting compensator. Before measuring the birefringence of the sample, a darkfield was obtained first, followed by putting the samples and the compensator together under the crossed Nicols and rotating the drum until the retardation of the compensator equaled that of the specimen. By knowing the retardation and thickness of the specimen, the birefringence of the sample is obtained from retardation divided by sample thickness. Measurements were carried out at room temperature.

Materials and Methods

4.3.4.2 Wide-angle X-ray diffraction (WAXD) measurement

2D-Wide-angle X-ray diffraction measurements were employed to determine the crystalline orientation of both single PLLA and bi-layer films. Monochromatic Ni-filtered Cu K α radiation with a collimator size of 0.8mm was used. The sample-detector distance of 300mm was employed. The sample was mounted in such a manner that it is normal to the incident X-ray beam and the X-ray diffraction pattern was recorded on a flat image plate. The azimuthal intensity distribution $I(\phi)$ of (110) and (200) planes was then determined from the 2D WAXD patterns using the GADDS software to obtain intensity as a function of the azimuthal angle. The intensity profile was corrected for the background by subtracting the constant intensity level at high azimuthal angles. The orientation coefficient of crystallites was then calculated from the integrated peak intensity of (200) and (110) reflections as a function of azimuthal angle, as described in Chapter 3.

Crystallinity is obtained from equatorial scans of two-dimensional images using the peak separation method by which the amorphous halo and crystalline portion are deconvoluted. The degree of crystallinity (χ_c) was calculated as the percentage of the scattered intensity of the crystalline phase over then scattered intensity of the crystalline and amorphous phases.

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4.3.4.3 Polarized Raman spectroscopy measurement

For polarized Raman measurement, a Raman spectrometer (WITec, alpha300 S) equipped with a Olympus microscope was employed for the study. The 488 nm line of Ar-ion laser was used for excitation. In all cases, the laser beam was focused down with a 100x objective (0.95 NA) to a diameter of approximately 5 μm , generating an intensity of 20 mW at the sample. By using a 600 lines/mm holographic grating, spectral window of approximately of 2000 cm^{-1} was collected using Peltier-cooled charge-coupled device (CCD) detector 1024 x 127 pixel format. Calibration of the spectrometer was performed using silicon crystal. For sample mounting, the draw direction of the sample was aligned to the Z-axis of the laboratory coordinate system as shown in Figure 4.1.

Figure 4.1 Schematic diagram of the polarized Raman back-scattering setup. X-Y-Z are the laboratory coordinates.

Materials and Methods

Polarized Raman spectra were collected in the back-scattered geometry. A half-wave plate was used to rotate the polarization direction of the incident beam either parallel or perpendicular to the sample axis. An analyzer was set to record both parallel and perpendicularly polarized light from the scattered radiation. Spectra were obtained in three different polarization geometries: I_{ZZ} , I_{ZY} and I_{YY} . The subscripts describe the direction of laser polarization and that of scatter light polarization, respectively. In order to obtain clear Raman spectra, a total integration time of 50 s (0.5 s and 100 accumulations) was used. ScanCtrl Spectroscopy Plus software was used both for data acquisition and data evaluation.

4.35 Data analysis and statistical methods

At least three replicated measurements were performed on all tests. Data were presented in average value $\pm$ SD. Comparison between groups was done by one-way ANOVA test with post-comparison using t-test. In all statistical evaluations, $p < 0.05$ was considered as statistically significant.

Shape Memory Effect in Monolayer Systems

CHAPTER 5

THERMOMECHANICS OF SHAPE MEMORY EFFECT IN MONOLAYER POLYMERIC SYSTEMS

5.1 Introduction

In chapter 2, it is highlighted that the challenge lies with the biodegradable SMPs for stent application is the low recovery force and it can be overcome by applying composite technology and optimizing the processing condition. As a result, a multilayer biodegradable polymeric system has been developed in our laboratories. This system consists of two layers of biodegradable polymers sandwiched together: the top layer is P(DL)GA and the bottom layer is PLLA. The PLLA layer functions as structural support while the P(DL)GA layer serves as a shape memory layer.

Before exploring the shape-memory characteristics of the bi-layer system, it is important to study the shape-memory property of the individual layers, which are P(DL)GA and PLLA. In this chapter, the relationship between the thermo-mechanical conditions and shape memory behavior of the polymers (i.e. P(DL)GA and PLLA) would be studied. Next, the morphological characteristics of the polymers during programming and recovery process would be investigated in order to understand the mechanism responsible for the memory

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effect. The structural evolution in polymers during the shape memory process would be explored by means of birefringence, X-ray diffraction and Raman spectroscopy.

5.2 Shape Memory Effect in P(DL)GA

5.2.1 Thermal and dynamic mechanical properties of P(DL)GA films

Both the DSC and DMA thermograms of P(DL)GA are shown respectively in Figure 5.1. The DSC curve shows that P(DL)GA is an amorphous polymer and exhibits a glass transition temperature, which is the switching temperature (T_{trans}) for shape memory effect. The glass transition temperature is at 37°C. In the same figure, the storage modulus as a function of temperature is also presented. As far as shape recovery is concerned, the modulus drop reflects more closely the ability to recover strain as the segmental or molecular mobility increases at this temperature.

From this standpoint, the onset point for modulus drop is ascribed to the glass transition temperature, which is around 40°C. In addition, the storage modulus shows a rubbery plateau, indicating the existence of chain entanglements, which act as cross-linked points. Furthermore, the storage modulus of P(DL)GA in the glassy state ($E' = 2220$ MPa at 25°C) is

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Figure 5.1 DSC and DMA thermograms of P(DL)GA.

Figure 5.2 Effect of stretching temperature on uniaxial stress-strain behavior of P(DL)GA.

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two orders of magnitude larger than that in the rubbery state ($E' = 4$ MPa at 65°C) and in general, a large modulus ratio of the glassy state to the rubbery state is regarded as favorable to shape memory capacity.

5.2.2 Mechanical properties of P(DL)GA films

Figure 5.2 shows the tensile stress-strain behavior at 37 and 50°C . At 37°C , which is the beginning of the glass transition, P(DL)GA exhibits necking during the drawing process. This yielding behavior results in cross section contraction, whereby there is realignment of polymer chains along the stretching direction. At 80°C , the yielding disappears and the stress increases in proportion with strain till failure, showing the rubber elasticity behavior.

5.2.3 Shape memory behavior of P(DL)GA films – Strain recovery

To incorporate shape memory and recovery in a polymer, there are usually three steps: programming – fixing – recovery. A sample is deformed at deformation temperature, T_d , followed by quenching to a temperature below its transition temperature to fix the deformation. Subsequently the deformed sample is heated up to a recovery temperature, T_r , to examine the shape recovery, R_r . For the case of P(DL)GA, the shape memory effect was

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examined under two deformation temperatures that are 37°C ($T_d \sim T_g$) and 50°C ($T_d > T_g$) with two recovery temperatures, $T_r = 37$ and 50°C. It is noteworthy that the tensile stress-strain behaviors mentioned earlier actually reflect exactly the programming path. Figure 5.3 presents the result of isothermal recovery under different experimental conditions.

As illustrated in Figure 5.3, the shape recovery is higher than 90% under all the experimental conditions, indicating that P(DL)GA has good shape memory property. Furthermore, the shape memory behavior was also studied in isochronal mode via TMA, in which the recovery was monitored as a function of temperature as shown in Figure 5.4. The purpose of this isochronal experiment is to reveal the shape recovery profile and to provide information at which temperature the recovery starts occurring. As depicted in the figure, the isochronal thermal recovery curves show a sigmoidal behavior generally. For both deformation temperatures, there is slow initial recovery followed by high rate of recovery near the glass transition temperature. In all cases, complete recovery is observed. Moreover, it is worth mentioning that sample deformed at lower T_d experiences recovery at lower temperature and this behavior is also noted by Gall *et al* [25].

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Figure 5.3 Recovery as a function of stretch ratio with various deformation temperatures, T_d .

(a). $T_r = 37^\circ\text{C}$ and (b). $T_r = 50^\circ\text{C}$.

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Figure 5.4 Isochronal thermal recovery curves for P(DL)GA. Given deformation is $\lambda = 5$.

5.2.4 Shape memory behavior of P(DL)GA films – Stress recovery

To evaluate the driving force for shape recovery, data on recovery stress is presented. The recovery stress was measured as a function of temperature and the results are presented in Figure 5.5. Figure 5.5 presents the stress recovery behavior at a pre-stretch ratio of three at two deformation temperature of 37 and 50°C; other stretch ratios were studied but are not shown.

For film pre-deformed at 37°C, it can be seen that as soon as the temperature is raised above the glass transition temperature, a considerable recovery stress can be observed. It increases

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with temperature, passes through a maximum and then diminishes. As the stress recovery measurement here is isochronal, it is found that the initial increase is attributable to thermal shrinkage that leads to the observed higher stress; however, as temperature increases well beyond T_g , the increase is offset by the rapid stress relaxation, hence there is a maximum. Whereas for film pre-deformed at 50°C , the stress recovery is more gradual and the peak is broader. Similar to strain recovery, stress recovery initiates at a lower temperature in the sample that is stretched at lower temperature. Besides that, one can observe that lower deformation temperature leads to higher maximum recovery stress. However, the maximum recovery stress is relatively low. It should be noted that although the isochronal data used above are not equilibrium values, the trends are still representative of equilibrium behavior.

Figure 5.5 Recovery stress vs. temperature of recovery for P(DL)GA samples drawn to $\lambda = 3$ at $T_d = 37$ and 50°C .

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5.2.5 Structural evolution in P(DL)GA during shape memory process

Typically, SMPs consist of two phases: a thermal reversible phase and a fixed phase. For the case of P(DL)GA, the amorphous molecular chains serve as a molecular switch, while the physical crosslink acts as the fixed phase and is responsible for the permanent shape. During the programming step, deformation is applied to the sample, and generally the amorphous chains will be oriented to various extents depending on the programming conditions. Subsequent cooling down below T_g , the chain segmental motions are frozen, fixing the deformed shape and storing the internal stress generated during stretching. Upon heating up above T_g , the permanent shape is recovered, releasing the internal stress.

When the deformation temperature is at glass transition regime, i.e. 37°C, chain mobility is high enough that polymeric chains can be oriented favorably in the direction of applied force. It gives rise to chain orientation, which in turn creates a low conformational entropy state [84]. However, at higher deformation temperature, i.e. 50°C, two factors unfavorable for recovery should be taken into consideration. One is the relaxation of the oriented amorphous chain; another is the disentanglement of the physical crosslinks, resulting loss in chain orientation.

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To prove the hypothesis that greater chain orientation can be obtained at lower deformation temperature, birefringence measurement was performed on sample stretched at these two deformation temperature. The result is illustrated in Figure 5.6. It is well accepted that birefringence measurement gives an average molecular orientation in the sample and it can be seen in the figure that lower deformation temperature leads to higher value of birefringence, corresponding to a higher degree of chain orientation. In addition, almost zero birefringence is observed for all recovered samples. It is an indication that the oriented amorphous chains are returned to the coil configurations, resulting in high degree of recovery as shown in Figure 5.4 earlier on.

As for the driving force for shape recovery, it is usually associated the recovery stress with the relaxation of internal stress that is frozen in the sample after deformation. Moreover, the stored internal stress is originated from the amorphous chain orientation. Thus, the experimental results mentioned in Figure 5.5 can be explained on the basis of chain orientation. Higher maximum recovery stress is obtained with sample stretched at lower T_d because greater chain orientation can be achieved at lower T_d (not much chain relaxation), leading to the high internal stored stress.

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On the other hand, relaxation of oriented amorphous chains at high deformation temperature leads to a lower chain orientation and causes a loss in recovery stress. Thus, the mechanism of shape memory effect in P(DL)GA polymer is based on disorientation of the amorphous oriented chains formed during programming. As a result, the shape memory effect is highly affected by the degree of chain orientation.

Figure 5.6 Birefringence versus stretch ratio for P(DL)GA drawn at two deformation temperatures, T_d .

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5.3 Shape Memory Effect in PLLA

5.3.1 Mechanical properties of PLLA films

Semi-crystalline polymers are expected to behave differently under shape-memory programming and recovery. Figure 5.7 shows the tensile stress-strain curves of PLLA films obtained under various deformation temperatures. When PLLA films are subjected to deformation at 65°C (which is just below the T_g of PLLA), above a certain tensile stress opaque striations appear in plane whose normal is the direction of stretching and films exhibit yielding. In this content, yield coincides with the observation of a maximum stress in the nominal stress-strain curve. The presence of a neck indicates inhomogeneous deformation of the initially spherulitic structure; microfibrils are formed in this region, and the crystallites become highly oriented in the draw direction. After that, there is homogeneous drawing of the fibrous structure in the necked region. As the drawing temperature (T_d) rises above the glass transition temperature, PLLA first exhibits a rubbery plateau following by the onset of strain hardening. As illustrated in Figure 5.7, drawing at the higher temperature leads to higher critical strain level at which the strain hardening occurs.

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Figure 5.7 Effect of stretching temperature on uniaxial stress-strain behavior of PLLA.

5.3.2 Thermal properties of PLLA films

The DSC thermograms of undrawn and drawn PLLA films drawn at 85 and 120 °C are shown in Figure 5.8 and 5.9, respectively. For the curves, it reveals that PLLA is a semicrystalline polymer with a glass transition temperature of 66°C and a melting temperature of 176°C. In this system, the crystalline region acts as physical crosslink points to keep the original structure. On the other hand, the amorphous region serves as the switchable segments with T_g as the shape memory transition temperature. As the films are stretched, the glass transition temperature increases, suggesting that the molecular chains become more aligned along the stretch direction in the amorphous region. In addition, the

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melting peak shifts to higher temperature and crystallinity increases with deformation for both deformation temperatures. These data are quantitatively shown in Table 5.1.

There are two interesting features to be highlighted in the DSC results. The first observation is that the increase in glass transition temperature is much greater when PLLA films are stretched at 120°C than that at 85°C. Another interesting feature is that for film stretched at 85°C, there is an endothermic dip near the glass transition followed by an exothermic peak immediately above T_g (Refer to Figure 5.8). The endotherm is though is to be due to the sub- T_g physical aging of PLLA or relaxation of the oriented amorphous chains, while the exothermic transition may be associated with nucleation enhanced thermal crystallization.

In general, the temperature for cold crystallization of PLLA is around 110°C. When PLLA film is stretched, however, this crystallization peak shifts to a lower temperature, i.e. the temperature immediately above T_g , and it is attributed to the decrease in conformational entropy that gives rise to enhanced crystal nucleation, resulting from the increased orientation of polymer chains in the amorphous regions by uniaxial deformation. On the other hand, at a deformation temperature of 120°C, the rate of relaxation is much faster that any residual enthalpy of relaxation due to physical aging released during deformation, thus this transition is no longer reflected in the DSC thermogram at 120°C (Refer to Figure 5.9).

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Furthermore, the thermal characteristic of PLLA film after shape recovery at 85°C is depicted in Figure 5.10, in comparison with the undrawn and stretched films. For samples stretched at 85°C, the DSC result shows the presence of an exothermal peak immediately above T_g whereas there is a disappearance of this exothermal peak for sample after shape recovery. As mentioned in the last paragraph, the origin of the exothermal peak has been attributed to crystallization of the oriented amorphous chains during the DSC scan. The disappearance of the exotherm after shape recovery suggests that recovery process is associated with the relaxation of oriented amorphous chains that require temperature above T_g to be activated.

Table 5.1 Drawing conditions and thermal characteristics of oriented PLLA films

λ	T_d (°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g) ^a
1	undrawn	66	176	28.1
2	85	66	176	28.0
3	85	69	177	33.9
4	85	70	179	36.3
2	120	68	176	31.6
3	120	78	180	33.5
4	120	79	183	40.5

^a Endotherm of PLLA crystal.

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Figure 5.8 DSC thermograms of PLLA films stretched at 85°C.

Figure 5.9 DSC thermograms of PLLA films stretched at 120°C.

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Figure 5.10 DSC thermograms of (a) undrawn PLLA film, (b) stretched PLLA film to $\lambda = 3$ at 85°C, and (c) recovery film of (b).

5.3.3 Shape memory behavior of PLLA films – Strain recovery

Samples were recovered without constraint at 85°C for 5 minutes. The effect of stretch ratio on the degree of recovery for various deformation temperatures (i.e. $T_d = 85$ and 120°C) is demonstrated in Figure 5.11. It can be seen that the recovery decreases with both increasing stretch ratio and deformation temperatures. Furthermore, it would be worth noting that complete recovery occurs if the sample was initially drawn to $\lambda < 2$ at 85°C.

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The temperature dependence of recovery for drawn PLLA films is also presented in Figure 5.12. There are three important features of the present results. Firstly, appreciable recovery is observed in the vicinity of the glass transition temperature, but complete recovery is not achieved even at 120°C. It may be inferred that the remaining unrecoverable component is associated with the crystalline region of the polymer. Secondly, the rate of recovery is much higher for sample deformed at low T_d compared to that deformed at high T_d . Finally, deformation performed at lower T_d (i.e. 85°C) gives rise to higher degree of recovery, which is over 90% in this case.

Figure 5.11 Recovery as a function of stretch ratio with various deformation temperatures.

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Figure 5.12 Recovery as a function of temperature. Given deformation is $\lambda = 2$.

5.3.4 Shape memory behavior of PLLA films – Stress recovery

To further broaden the basis of the structure-property relationships for shape memory, data on recovery stress is presented. In the first set of measurements to be considered, the recovery stress was measured as a function of temperature and the results are presented in Figure 5.13 and Figure 5.14. It can be seen in Figure 5.13 that the general profile of the curve is similar to that of P(DL)GA; the stress increases with temperature, passes through a maximum and then diminishes. In addition, it is interesting to note that the recovery stress increases with stretch ratio and the position of the peak recovery stress shifts to higher temperature with increasing stretch ratio. It may imply that highly drawn film induces

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recovery at higher temperature during heating. Furthermore, in all cases, the samples display maximum recovery stress values much higher than those exhibited by other biodegradable shape memory polymers recently developed [42, 44].

Figure 5.14 shows the stress recovery behavior of PLLA films drawn to $\lambda = 3$ under two deformation temperatures of 85 and 120°C; other stretch ratios were studied but are not shown. It should be noted that for films stretched at lower T_d (i.e. 85°C), the stress recovery begins from a lower temperature and then rises rapidly to a peak, followed by declining gradually. Whereas for films stretched at 120°C, the stress recovery is more gradual and the peak is broader. Finally, a comparison of recovery stress and birefringence for all drawn samples is shown in Figure 5.15. It is observed that the stress optical coefficient, $C = \Delta n/\sigma$ [85], is a constant only for small values of $\lambda < 1.5$ and the complexity of the curve profile will be discussed in the section 5.3.7.

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Figure 5.13 Recovery stress vs. temperature of recovery for samples drawn to various λ at 85°C.

Figure 5.14 Recovery stress vs. temperature of recovery for samples drawn to various $\lambda = 3$.

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Upon drawing to a low stretch ratio ($\lambda = 2$) at 85°C, the WAXD pattern indicates the development of amorphous chain orientation, as evidenced by the gradual concentration of the amorphous halo in the equatorial direction. It also shows the reduction of azimuthal spread of (200) and (110) diffraction arcs in the equatorial direction, and the crystal orientation is relatively low at that point. With further stretching, the crystals continue to orient, as shown by the further reduction of azimuthal spread that represents the interchain correlation, until a pair of intense diffraction arcs for (200) and (110) planes are in the equatorial position, showing that the α crystals are highly oriented. The variation of crystalline orientation with stretch ratio can be shown more clearly by azimuthal plot as in Figure 5.17.

As illustrated in Figure 5.17, anisotropic orientation results for samples undergoing stretching, corresponding to the intensity peaks at certain azimuthal angles. The angle $\phi = 90^\circ$ refers to the equatorial axis. At first, the undrawn film shows isotropic orientation with intensity $I(\phi)$ being constant. Upon stretching to low stretch ratio, the intensity maxima appear and become azimuthally narrower with increasing stretch ratio, indicating a significant increase in the degree of molecular orientation in the crystalline region. Moreover, both (200) and (110) planes of α structure, which are parallel to the c crystallographic axis, orient along the drawing direction which is at $\phi = 90^\circ$.

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As well as the rise in orientation degree with drawing, when PLLA is stretched to $\lambda = 2$ the crystalline peaks significantly broaden and shift as shown in Figure 5.18, suggesting that there may be structure changes in the crystallites during the deformation process. At approximately the same time strain hardening starts to occur as mentioned in section 5.3.1.

At a deformation temperature of 120°C, the behavior observed differs from that observed at 85°C. Strong and spotty reflections from (200) and (110) are established at a lower stretch ratio ($\lambda = 1.5$), indicating a high level of orientation, with few changes being perceptible at higher stretch ratios.

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Figure 5.16 WAXD images for the drawn and recovered PLLA. The uniaxial drawing direction is vertical. $T_d =$ (a) 85°C and (b) 120°C .

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Figure 5.17 Azimuthal plots for the (110)/(200) reflection of the PLLA sample drawn at 85°C as a function of stretch ratio.

Figure 5.18 WAXD equatorial scans of PLLA films drawn at 85°C.

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Figure 5.16 also illustrates the WAXD images of the recovered PLLA films obtained after shape recovery. For recovered films, the films were subjected to various stretch ratios before immersing in water bath at 85°C for shape recovery. As seen in the figure, for film that were subjected to stretch ratio less than 2 at 85°C, it shows nearly complete Debye-Scherrer rings indicating that the PLLA α crystal are randomly oriented.

For those recovered films that were previously drawn to $\lambda > 2$ at 85°C, the WAXD images still show broad diffraction arcs for (200) and (110) planes in the equatorial position, suggesting that the crystals are still oriented with their c crystallographic axis parallel to the film drawing direction. Furthermore, for films that were previously deformed at 120°C to various λ , the behavior of their recovered films observed is all alike showing intense diffraction reflections from (200) and (110), representing a high level of crystal orientation still present even after recovery.

5.3.6 Structural evolution in PLLA during shape memory process

Orientation development in stretched PLLA films

As highlighted in Chapter 2, programming plays an important role controlling the shape recovery behavior. Therefore, it is essential to understand the orientation development and

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deformation mechanism of PLLA during programming. Figure 5.19 shows the measured birefringence as a function of stretch ratio. It can be seen that the higher the deformation temperature, the greater the value of birefringence. The results presented here are different from those for P(DL)GA in earlier section, where birefringence was seen to decrease with deformation temperature. The difference in trend can be attributed to differences in the morphology of the starting polymers. For P(DL)GA, the polymer is amorphous in nature, whereas the PLLA studied here is semicrystalline, with crystal acting as network points. Consequently, the polymer chains do not flow easily even at high temperature, and it results in high orientation even with high deformation temperature, consistent with the DSC results.

Figure 5.19 Birefringence versus stretch ratio for PLLA drawn at various T_d .

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The orientation development in a material can be described by using theoretical models such as *affine* and *pseudo-affine* model as described in Chapter 3. Curves of orientation function, P_2 , calculated for the affine and pseudo-affine deformation models using Eqs. (3.34) and (3.35) were superimposed with the experimental results, as shown in Figure 5.20. The calculations have been published [86]. The theoretically derived value for $\Delta n_{\max}$ is taken as 0.031 [87].

It is observed that the birefringence behavior of PLLA is close to the pseudo-affine deformation model. The small deviation may be due to the following reasons: (i) the theoretical intrinsic birefringence is determined by the summation of bond polarizability with the crystal structure and standard bond angles; however, the actual structural conformation of the polymer may vary from the theoretical models, resulting in the difference and (ii) in the pseudo-affine deformation scheme, it is assumed that the polymer behaves like an aggregate of anisotropic units and the properties of the units are those of the completely oriented polymer. Indeed, it will be shown later that the deformation process is far from pseudo-affine and homogeneous.

Since optical birefringence gives a measure of the total sample orientation, it is worthwhile to examine more closely the orientation behavior of the amorphous and crystalline phases separately in order to understand the deformation mechanism of PLLA. The crystal

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orientation ($P_{2,C}$) can be obtained from the WAXD measurements, while the amorphous orientation ($P_{2,A}$) can then be calculated according to Eq. (3.18).

Figure 5.20 Orientation function, P_2 , of PLLA as a function of stretch ratio. Theoretical predictions for affine and aggregate models are also shown.

The second order parameter of amorphous and crystalline orientation distribution function is plotted as a function of stretch ratio in Figure 5.21. The development of the orientations in the crystalline and amorphous phases in Figure 5.21 during programming can be interpreted

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as follows. The melting point of crystallites is of order of 170°C, whereas the glass transition temperature of the amorphous phase is approximately 65°C. At both drawing temperatures (85 and 120°C), the polymer behaves as a highly inhomogeneous material and the mechanical properties of the two phases will be different.

Figure 5.21 Crystalline and amorphous order parameter, $P_{2,c}$ and $P_{2,A}$ for PLLA samples as a function of stretch ratio at two deformation temperatures: 85°C and 120°C.

For drawing at 85°C and $1 < \lambda < 1.5$, it is noted that, to a first approximation, all deformation is concentrated in the amorphous regions, while the displacement of the rigid crystallites does

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not involve any significant rotation. The amorphous phase occupies 79% of the polymer volume; therefore it is the continuous phase that transmits stress to the crystallites through the interfaces. The state of stress between the crystallites is complex due to strain compatibility issues at the crystal/amorphous interfaces. This causes enhanced birefringence in the amorphous layers adjacent to the crystallites, well above that predicted by the affine model.

The stress within the amorphous regions increases with increasing draw ratio. Close to the stretch ratio of $\lambda = 1.5$, the shear stress around the crystallites is sufficient to cause the onset of significant plastic deformation, transforming the lamellar morphology into a fibrillar microstructure [88]. (It should be noted that at $T > T_g$, any observed plastic deformation is necessarily due to changes in the crystalline phase) This transformation results in a massive rearrangement of molecular orientation within the crystalline regions, giving rise to the rapid rise of the crystalline birefringence, as shown in Figure 5.22. Above $\lambda > 2$, the transformation to the fibrillar microstructure is essentially complete, and any further increase in birefringence is again confined to the amorphous regions, which already possesses a high degree of molecular orientation.

For drawing at a temperature of 120°C, the same mechanism of deformation and transformation is expected, although it starts at lower value of λ . At this higher deformation temperature, the orientation function increases more rapidly in both the crystalline and

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amorphous phases. This is expected since the yield stress of the crystalline phase decreases as a function of temperature, so the onset of lamellar to microfibrillar transformation occurs sooner. Another effect leading to an earlier onset of plasticity in the crystallites is that at higher temperature the orientation within the amorphous regions develops sooner, reaching the critical level required for yield, as seen in Figure 5.21.

Furthermore, it should be noted that the amorphous orientation function obtained at 85°C attains approximately the same degree of amorphous orientation as that at 120°C when the stretch ratio is high. This observation can be interpreted in terms of relaxation of amorphous chains and crystallization of highly oriented amorphous chains during stretching. At lower stretch ratio, the amorphous orientation is higher at 120°C; as the stretch ratio increases, the oriented amorphous chains have sufficient mobility to relax and to organize themselves into crystallites at 120°C (which is closer to the crystallization temperature), thereby reducing the overall level of amorphous orientation.

Structural basis of shape recovery and recovery stress in PLLA films

The recovery process of stretched PLLA samples can be basically described in two stages as shown in Figure 5.12. The small contraction at low temperature (below T_{trans}) could involve the recoil of oriented amorphous chains that were anchored loosely by the crystals. When

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heating to the temperature near its glass transition temperature (T_{trans}), a large-scale recovery is due to relaxation of oriented chains, corresponding to the recovery changes in second stage. The relaxation process could be associated with both the oriented amorphous and crystalline chains.

Thus, we see that the shape recovery properties of the stretched samples depend strongly on the molecular structure of the sample. In order to further delineate the molecular mechanism behind the shape recovery, the effects of the process on the crystalline and amorphous phases were examined separately. The degree of recovery, the crystallinity and the percentage difference in orientation in both crystalline (Cr) and amorphous (Am) phases (before and after recovery) are plotted against initial stretch ratio for PLLA samples, which were initially drawn to certain λ at deformation temperature T_d and subsequently recovered freely at 85°C for 5 minutes in Figure 5.22.

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Figure 5.22 Crystallinity (χ_c), degree of recovery (R_r) and percentage difference in P_2 for both phases (Cr and Am) plotted (before and after recovery) against initial stretch ratio. (a) $T_d = 85^\circ\text{C}$ and (b) $T_d = 120^\circ\text{C}$.

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There are several important features to be noted here:

1. At low initial stretch ratio ($\lambda < 2$) at 85°C, complete recovery occurs. As mentioned earlier on, at this stretch ratio, the deformation is concentrated in the amorphous regions and therefore the recovery involves mainly the relaxation of the oriented non-crystalline chains. This hypothesis can be further proved by the use of the classical rubber elasticity theory. According stress optical law, birefringence is linearly proportional to recovery stress [68].

Based on Figure 5.15, it appears that data are only well described by the stress optical law with a constant stress-optical coefficient for $\lambda < 1.5$, i.e. the first linear portion in the graph. Beyond $\lambda = 1.5$, the recovery stress ceases to rise linearly with birefringence until $\lambda = 2$. When $\lambda < 1.5$, the behavior can be modeled by a rubber-like network which is derived based on the deformation of an amorphous phase with crystallites acting as physical network points. Moreover, the validity of the model may be also due to the absence of strain-induced crystallization at such low stretch ratios.

2. As the stretch ratio increases, the extent of recovery reduces. For samples exhibiting the reduced recovery, both crystallinity and crystalline orientation is observed higher after stretching. As the deformation level is increased, strain-induced crystallization occurs from the highly oriented amorphous chains during stretching and at the same time the onset of plastic deformation occurs, transforming the lamellar morphology

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into a fibrillar microstructure preferentially oriented in the stretch direction, resulting in high crystalline orientation. These micro-fibrils then increasingly hinder long range motion and reducing shrinkage. *The low recovery in highly drawn PLLA is therefore attributed to the stabilization of the micro-fibrillar structure and the increased crystallinity* [89].

At this intermediate stretch ratios ($1.5 < \lambda < 2$), it is observed that the contribution of the crystalline phase to the recovery process is on par with that of the amorphous phase. At the intermediate ratios, therefore, the crystalline structure is affecting the recovery process, and hence the stress-optical law is no longer applicable at this region as shown in Figure 5.15 as it is derived based on deformation of an amorphous phase with physical/chemical crosslink points.

3. Samples stretched at higher deformation temperature exhibit similar but much lower values of recovery than samples stretched at lower deformation temperature. At high deformation temperature, the stress transfer between amorphous regions and crystallite is more effective due to high chain mobility, causing the crystallites to become highly plastically deformed at all stretch ratios resulting in low recovery as the crystalline orientation functions before and after recovery do not differ much (see Figure 5.22b). Therefore, the observed low recovery is primarily due to the increased crystallinity and the irrecoverable plasticity in the crystalline phase.

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Furthermore, it is interesting to infer the structural origin of recovery stress based on the current studies. As shown in Figure 5.13, the recovery stress increases with initial stretch ratio and the recovery stress at $\lambda > 3$ is substantially higher than that corresponding to $\lambda = 2$. One possible explanation lies on the amount of oriented amorphous chains or interfibrillar tie molecules present. At $\lambda = 2$, a substantial portion of the imposed stress is devoted to the transformation of the lamellar structure into fibrillar structure while there is limited amount of oriented chain molecule formation.

However, as the stretch ratio goes above $\lambda > 2$, the transformation is already quite substantial and the balance is shifted to the increased formation of tie molecules, resulting in the abrupt increase in recovery stress as $\lambda = 3$. Based on that, one can associate the amount of recovery stress with the extent of amorphous chain orientation. Another point to be highlighted is the shift of peak recovery stress to higher temperature as stretch ratio increases. This is likely associated with the better packing of the interfibrillar tie molecules with increasing stretch ratio which requires a higher temperature for the mobilization of those oriented chains [90].

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5.4 Summary

In this chapter, the shape-memory characteristics of P(DL)GA and PLLA has been explored. Though the shape-memory effects of P(DL)GA and PLLA have been studied before [47, 91], our work extends the understanding to structural changes that are occurring during deformation and recovery, which have not been studied. It is found that amorphous P(DL)GA exhibits good shape memory property with T_g as the transition temperature, having more than 90% shape recovery under all the conditions studied. Furthermore, the morphological characteristics of P(DL)GA during programming and recovery process were investigated in order to probe the mechanism responsible for the memory effect. During programming step, the amorphous chains are oriented towards the stretching direction; however, the extent of orientation depends on the programming condition. Once upon recovery, the oriented amorphous chains are able to return to the random coil configuration as indicated by the birefringence measurement. Thus, it has clearly demonstrated that the disorientation of the oriented amorphous chains is the primary mechanism responsible for the shape memory effect in P(DL)GA.

In PLLA, the amorphous chains serve as the switchable segments with T_g as the transition temperature. On the contrary, the crystalline region acts as physical crosslinks. The relationship between the programming conditions and shape memory behavior of PLLA was studied. It was found that shape recovery decreases with increasing stretch ratio and

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deformation temperature. At low stretch ratio, the shape recovery is attributed to the disorientation of the oriented amorphous chains in PLLA. At higher stretch ratio and deformation temperature, the extent of shape recovery decreases as a consequence of increased crystallinity by strain-induced crystallization and the irrecoverable plasticity in the crystalline regions due to the formation of highly oriented microfibrillar structure. Though the recovery is low, it is still associated with considerable disorientation of the amorphous chains, which represents the prominent mechanism of recovery.

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CHAPTER 6

THERMOMECHANICS OF SHAPE MEMORY EFFECT IN BI-LAYER POLYMERIC SYSTEMS

6.1 Introduction

Chapter 5 presents the shape memory characteristics of the monolayer films: P(DL)GA and PLLA. Despite the high recoverable strain level of P(DL)GA, there is significant weakness in mechanical strength and recovery stress. On the other hand, PLLA generates relatively high recovery stress; however, the level of recoverable strain attainable is low. As a result, a bi-layer biodegradable polymeric systems or composite based on P(DL)GA and PLLA films are developed in our laboratory. P(DL)GA and PLLA are chosen as the bi-layer materials for it gives the best combination in term of collapse strength and period of residence based on previous studies conducted by our group [11-13]. Thus, the top P(DL)GA layer serves as a shape memory layer while the bottom PLLA layer functions as structural support.

In this chapter, the thickness ratio of the bi-layer composite is changed and the shape-memory characteristics of the bi-layer systems under various programming conditions will be explored. Table 6.1 lists the configuration of all bi-layer films being studied for investigation of structural evolution in bi-layer system during the shape memory process, WAXD and

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polarized Raman spectroscopy is employed to examine the molecular chain behavior in crystalline and amorphous regions respectively.

Table 6.1 Configuration of bi-layer films with various thickness ratios

Abbreviation of PLLA/P(DL)GA films (thickness ratio)	PLLA	9/1	7/3	5/5	3/7	1/9	P(DL)GA
Thickness of bottom PLLA layer (μm)	100	90	70	50	30	10	0
Thickness of top P(DL)GA layer (μm)	0	10	30	50	70	90	100

6.2 Shape Memory Effect in Bi-layer System of PLLA/P(DL)GA

6.2.1 Mechanical properties of PLLA/P(DL)GA films

The stress – strain plots of PLLA/P(DL)GA films with various thickness ratios are illustrated in Figure 6.1. The neat PLLA is very brittle and it can only be drawn up to $\lambda < 3$ at 50°C. On the contrary, all bi-layer films have maximum stretch ratio up to 4 and they show typical yielding behavior and stable neck growth upon stretching, except the 1/9 samples where the content of P(DL)GA is high. During the tensile tests, no notable delamination of the layers was observed. Nevertheless, there is one interesting feature, which is strain-induced

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whitening, observed during the stretching process. This observation can be explained in term of heterogeneous deformation [92].

The deformation in this bi-layer configuration is not homogeneous when the PLLA is deformed below its own glass transition temperature and P(DL)GA is deformed above its own glass transition temperature. As a result, micro-voids may be produced and enlarged at the interface of the two components, giving rise to the whitening effect. Since the voids created are only in the range of micrometers, they do not lead to the macro-scale delamination.

Furthermore, it is interesting to find out the stress – strain behavior of bi-layer films under various deformation temperatures. Figure 6.2 shows that effect of deformation temperature on stress – strain behavior of 5/5 PLLA/P(DL)GA laminates. At deformation temperature of 50°C, the laminate behaves as a highly inhomogeneous material and the mechanical properties of the two components vary differently, in which PLLA is in the glassy state while P(DL)GA is in the rubbery state. According to this, a yield point is observed due to the glassy behavior of PLLA. As the deformation temperature rises above the glass transition temperatures of both components, the yielding disappears and it exhibits a rubbery plateau followed by the onset of strain hardening. Furthermore, the onset strain level for strain hardening occurs at higher stretch ratio when drawing at the higher temperature, which is consistent to the result of PLLA.

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Figure 6.1 Stress – strain behavior of PLLA/P(DL)GA films with various thickness ratio.

Figure 6.2 Effect of stretching temperature on stress - strain behavior of 5/5 PLLA/P(DL)GA.

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6.2.2 Thermal properties of PLLA/P(DL)GA films

Figure 6.3 shows the DSC thermograms of PLLA/P(DL)GA bi-layer films. As can be seen in the figure, the glass transition temperatures of both P(DL)GA and PLLA in the bi-layer systems remain unchanged over the whole range of thickness ratio. In order to elucidate the effect of thickness ratio on the crystallization behavior of PLLA in the bi-layer systems, the enthalpies of the PLLA melting peak are corrected with the weight fraction. And it is found that the melting enthalpy and thus the crystallization behavior of the PLLA component are not affected by incorporating a layer of P(DL)GA on top of PLLA for all thickness ratios studied. The observation is in agreement with WAXD data to be shown afterward.

According to the DSC thermograms of the bi-layer composites, these samples show three thermal transitions. In consideration of the shape memory property, the lower thermal transition, i.e. the glass transition of P(DL)GA, is taken as the shape memory transition temperature of the bi-layer systems; whereas the phase with the highest thermal transition, i.e. the crystallites in the semicrystalline PLLA, acts as the fixed phase.

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Figure 6.3 DSC thermograms of P(DL)GA/PLLA bi-layer films.

6.2.3 Shape memory behavior of PLLA/P(DL)GA films – Strain recovery

Figure 6.4 shows the shape recovery of PLLA/P(DL)GA bi-layer samples with various thickness ratios. The sample was first deformed to a certain stretch ratio at a particular deformation temperature, T_d , and was followed by the recovery process in which the stretched sample was placed in water of $T_r = 85^\circ\text{C}$. According to Figure 6.4, no statistically significant difference ($p\text{-value} > 0.05$, refer to Table 6.2) in shape recovery was observed among bi-layer samples at different thickness ratios regardless of the stretching conditions.

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Figure 6.4 Shape recoveries of bi-layer films with various thickness ratios. (a) $T_d = 50^\circ\text{C}$, (b) $T_d = 65^\circ\text{C}$ and (c) $T_d = 85^\circ\text{C}$.

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Table 6.2 Statistical analysis test result (ANOVA’s p-value) on shape recovery of bi-layer samples with various thickness ratios subjected to $T_r = 85^{\circ}\text{C}$

Stretch ratio, λ	$T_d = 50^{\circ}\text{C}$	$T_d = 65^{\circ}\text{C}$	$T_d = 85^{\circ}\text{C}$
2	0.469	0.125	0.947
3	0.665	0.436	0.092
4	0.983	0.001	0.197
5	-	0.392	0.706

Theoretically, PLLA has the shape-memory capability; however, its intrinsic brittleness limits its shape-memory property for wide application especially for deformation temperature below its glass transition. Nevertheless, the finding is surprising and encouraging as shown in Figure 6.4, by which it illustrates that laminating PLLA with P(DL)GA can exhibit shape-memory ability upon high deformation and these bi-layer films regardless of the thickness ratios can yield the same degree of recovery when subjected to the same programming condition. The degrees of recovery of all samples are over 90% when they were deformed at 50°C .

Though the thickness ratio of these bi-layer samples has little effect on the shape recovery, it is important to further evaluate the effects of temperatures (either T_d or T_r) and degree of deformation on the shape recovery. Three deformation temperatures, T_d of 50°C , 65°C and 85°C were chosen for the study as it is interesting to explore how the shape recovery would be varied when P(DL)GA is in rubbery state while PLLA is under different states

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respectively, i.e. glass state ($T_d = 50^\circ\text{C}$), glass transition state ($T_d = 65^\circ\text{C}$) and rubbery state ($T_d = 85^\circ\text{C}$). Results, as shown in Figure 6.5, illustrate two interesting features: shape recovery drops with increasing deformation temperature and stretch ratio. This trend is in accordance with that of PLLA.

Figure 6.5 Shape recovery of 5/5 PLLA/P(DL)GA samples as a function of deformation temperature, T_d .

On the other hand, the relationship between the shape recovery and recovery temperature (T_r) is shown in Figure 6.6. The bi-layer composites were first stretched to $\lambda = 3$ at deformation

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temperature, T_d , and then were quickly cooled to room temperature. Subsequently, the shape memory tests were carried out in hot water of various recovery temperatures, T_r .

Figure 6.6 Shape recovery of 5/5 PLLA/P(DL)GA samples as a function of recovery temperature, T_r for samples subjected to $\lambda = 3$ at different deformation temperatures.

From Figure 6.6, it is clear that the shape recovery increases with rising recovery temperature and lower deformation temperature gives relatively higher degree of recovery irrespective of the recovery temperature. When the recovery temperature is at 37°C , which is well below the glass transition temperature of PLLA, the recoveries of all samples are low. However, as the recovery temperature increases to 65°C , which is above and in the regime of glass transition

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of P(DL)GA and PLLA, respectively, samples that are deformed at lower T_d yield a much higher recovery compared to samples deformed above the glass transition of both P(DL)GA and PLLA ($T_d = 65$ and 85°C). The results illustrated here are interesting and it should be related to the morphologies and phase structures of both components at various thermo-mechanical conditions, which will be discussed in detail later. In summary, both low deformation temperature and stretch ratio give high shape recovery for bi-layer samples.

6.2.4 Shape memory behavior of PLLA/P(DL)GA films – Stress recovery

In this section, the stress recovery results for the PLLA/P(DL)GA bi-layer films are presented and compared with the monolayer samples. In the stress recovery test, the pre-deformed samples were held constraint during the recovery and the recovery stress was monitored as a function of temperature. Figure 6.7 presents the stress recovery behavior at a pre-stretch ratio of three at deformation temperature of 50°C ; other stretch ratios and deformation temperatures were studied but not shown. In Figure 6.7, the general profile of the curve is similar to that of single P(DL)GA and PLLA films; the stress increases with temperature, passes through a maximum and then diminishes. It is worth noted that the overall stress generated by the bi-layer sample is much greater than that generated by single P(DL)GA films.

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Figure 6.1 demonstrates that the PLLA/P(DL)GA bi-layer films have higher modulus than the single P(DL)GA film. The increase in stiffness is due to incorporating higher elastic modulus of PLLA into P(DL)GA. Initially, when the both samples (single P(DL)GA film and bi-layer PLLA/P(DL)GA film) were pre-deformed at 50°C, a higher drawing force was required to deform the bi-layer composite due to the higher stiffness of the bi-layer system and the stored internal energy was higher. Nevertheless, when the samples are heated under full strain constraint, release of stored internal energy and recovery of a state of higher entropy occurs. Since bi-layer sample has higher stored internal energy, therefore it results in higher recovery stress generated during the stress recovery test.

Figure 6.7 Stress recovery of single P(DL)GA film and PLLA/P(DL)GA composite under strain constraint.

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Thus, increased stiffness in the bi-layer composites is critical for the enhanced recoverable stress during recovery and particularly this high recovery force could be used to overcome obstacles such as expanding obstructed arteries in stent application.

6.2.5 WAXD of PLLA/P(DL)GA films

The shape recovery properties of PLLA/P(DL)GA bi-layer films have been demonstrated in *Section 6.2.3*, now we should extend the understanding to structural changes in both PLLA and P(DL)GA, especially in the amorphous phase, that are occurring during deformation and recovery. Firstly, characterization of the structural changes in the PLLA crystalline phase would be carried out using WAXD. Secondly, the characterization of the structural evolution in the amorphous phases in the PLLA/P(DL)GA bi-layer films would be conducted by polarized Raman spectroscopy.

Figure 6.8 shows the WAXD 2θ plot for PLLA/P(DL)GA films with various thickness ratios. As mentioned in *Section 5.3.5*, PLLA exhibits two strong diffraction peaks at $2\theta = 16.5^\circ$ (5.25 Å) and $2\theta = 18.9^\circ$ (4.62 Å), corresponding to the (110)/(200) and (203) planes characteristic of α crystal structure. Whereas for P(DL)GA, it exhibits only an amorphous halo. Upon addition of P(DL)GA, all the peak intensities are lowered, however, the peak positions still remain unchanged. In addition, the crystalline lamellae size does not vary with

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sample thickness ratio based on the peak width at half height measurement. The results indicates that the crystal structures of PLLA crystals present in the bi-layer films remains intact despite the addition of P(DL)GA, which is consistent with the DSC results.

Figure 6.8 WAXD 2θ plot for various PLLA/P(DL)GA bi-layer samples.

In order to elucidate the effect of the thickness ratios and the stretching conditions on the crystal orientation of PLLA crystals in the bi-layer composites, 2D WAXD images of PLLA/P(DL)GA bi-layer films are presented both in Figure 6.9 and 6.10. As shown in Figure 6.9, both single PLLA and bi-layer films show highly oriented patterns of only PLLA α -form

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crystal upon drawing, indicating by the presence of strong diffraction arcs of (200) and (110) in the equatorial direction and the presence of four weak arcs of (203) reflection of PLLA crystal as well. Moreover, the depression in the intensity of diffraction arcs with thickness ratio is due to the decrease of the crystal concentration per unit volume within the bi-layer films.

Figure 6.9 WAXD images of (a) single PLLA, (b) 9/1 PLLA/P(DL)GA sample, (c) 5/5 sample and (d) 1/9 sample. The stretching condition for (a) – (d) samples is: $T_d = 85^\circ\text{C}$ and $\lambda = 4$.

As can be observed in Figure 6.10, upon drawing at 50 and 65°C, the WAXD patterns show general reduction of azimuthal spread of (200) and (110) diffraction arcs in the equatorial direction with increasing stretch ratio, indicating that PLLA crystals are oriented to a considerable extent in bi-layer films. This is an astonishing observation as neat PLLA is impossible to be stretched to high extent below its glass transition temperature. Furthermore, the degree of PLLA crystal orientation ($P_{2,c}$) of bi-layer films was calculated and presented quantitatively in Figure 6.11. Figure 6.11 reveals that there is no significant difference in term of crystalline orientation across all PLLA/P(DL)GA bi-layer films, suggesting sample

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thickness ratio has little effect on PLLA crystalline orientation. In addition, above $\lambda > 2$, samples show a high degree of crystal orientation (above 0.9) with negligible changes in $P_{2,c}$ value with further stretching. It is due to the complete transformation of the lamellar morphology to the fibrillar microstructure.

Figure 6.10 2D WAXDS images of stretched 5/5 PLLA/P(DL)GA films under various stretching conditions.

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Figure 6.11 Plot of crystalline orientation (P_{2c}) as a function of thickness ratio for PLLA/P(DL)GA bi-layer films, which were drawn at $T_d = 85^\circ\text{C}$.

To investigate how the crystal orientation of PLLA within the bi-layer system is influenced by the stretching condition, plot of P_{2c} under various stretching conditions is presented in Figure 6.12. Upon drawing to a low stretch ratio ($\lambda = 2$) at 50°C (below the T_g of PLLA), the PLLA crystal orientation is relatively low at that point. With further stretching, the crystal orientation rises abruptly to higher value, as shown by the further reduction of azimuthal spread in the equatorial position in Figure 6.10, indicating that the α crystals are oriented progressively. At deformation temperature above glass transition temperature of PLLA, a high level of crystal orientation has been observed even at low stretch ratio ($\lambda = 2$), and it has leveled off at higher stretch ratios.

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Figure 6.12 Plot of crystalline orientation ($P_{2,c}$) as a function of stretch ratio for 5/5 PLLA/P(DL)GA bi-layer films, which were drawn at various T_d .

6.2.6 Polarized Raman studies of amorphous orientation in PLLA/P(DL)GA films

Characterization of the structural changes in the PLLA crystalline phase has been done using WAXD in *Section 6.2.5*. Moreover both WAXD and shape recovery studies show that sample thickness ratio has trivial impact; therefore, the characterization of the structural evolution in the amorphous phases in the PLLA/P(DL)GA bi-layer films would be conducted by polarized Raman spectroscopy, focusing on 5/5 PLLA/P(DL)GA bi-layer films only.

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6.2.6.1 Structure characterization of semicrystalline PLLA bottom layer by Raman

Prior to the study of molecular orientation for the crystalline and amorphous regions of the PLLA bottom layer in the bi-layer system, it is first necessary to assign the Raman bands of PLLA to their respective crystalline and amorphous regions and to determine the tilts angles for the Raman bands. Hence, single PLLA films were first employed for the band assignment and tilt angle determination, before studying the molecular orientation in bi-layer film with aid of the obtained information.

Assignment of Raman bands of PLLA

Figure 6.13 depicts the Raman spectra of the isotropic crystalline PLLA at various temperatures. As it can be seen, the peaks at 520, 708 and 919 cm^{-1} disappear over the melting temperature (T_m) of PLLA. This can be an indication that these peaks are assigned only to the crystalline regions of PLLA and it is agreed well with the result of the previous studies [69]. On the other hand, other peaks are present below and above T_m , suggesting that these peaks are associated with both crystalline and amorphous phases to various extents. Furthermore, the information about different phases contribute to the peak intensity can be qualitatively obtained by comparing the full width at half maximum (FWHM) of each band, which is normalized to the FWHM of each band at 25°C [93]. The bands assignments are summarized in Table 6.3 and are agreed well with the results by other workers [69, 94, 95].

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Figure 6.13 Raman spectra of an isotropic crystalline PLLA film at various temperatures.

Determination of tilt angle (Ω) for the Raman band assigned to both the crystalline and amorphous regions

Figure 6.14 presents the polarized Raman spectra of oriented PLLA in different polarization geometries. Of particular interest for this study, the bands at 873, 1042, 1092 and 1765 cm^{-1} were used for the study of the molecular orientation in the amorphous regions of the PLLA film. In Figure 6.15, the P_2 values for those Raman bands assigned to both the crystalline and amorphous phases of PLLA are calculated as described in Chapter 3 and correlated with sample stretch ratio.

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Table 6.3 Raman band assignments and assignment of the Raman bands to the crystalline and amorphous regions of PLLA^a

Raman band (cm ⁻¹)	Assignment of bands for various phases of PLLA			Band assignment
	Current study	Tanaka <i>et al.</i> [69]	Kister <i>et al.</i> [96]	
1765M – 1774M	Cr / Am	Cr / Am	Cr / Am	$\nu\text{C=O}$
1751M	Am >> Cr	Am > Cr	Cr / Am	$\nu\text{C=O}$
1454S	/	Cr / Am	Cr / Am	$\delta_{\text{as}}\text{CH}_3$
1388M	Cr > Am	/	/	$\delta_{\text{s}}\text{CH}_3$
1297M	Cr / Am	Cr >> Am	Cr / Am	δCH
1181M	Cr / Am	Cr / Am	Cr / Am	$\nu_{\text{as}}\text{COC} + r_{\text{as}}\text{CH}_3$
1128S	Cr / Am	Cr / Am	Cr / Am	$r_{\text{as}}\text{CH}_3$
1092S	Cr / Am	Cr >> Am	Cr / Am	$\nu_{\text{s}}\text{COC}$
1042S	Am > Cr	Cr / Am	Cr / Am	$\nu\text{C-CH}_3$
919M	Cr	Cr	Cr	$r\text{CH}_3 + \nu\text{CC}$
873VS	Cr / Am	Cr / Am	Cr / Am	$\nu\text{C-COO}$
736M	Cr / Am	Cr >> Am	Cr / Am	$\delta\text{C=O}$
708M	Cr >> Am	Cr >> Am	Cr	$\gamma\text{C=O}$
520w	Cr	Cr	Cr	$\delta\text{C-CH}_3 + \delta\text{CCO}$
398M – 411M	Cr / Am	Cr / Am	Cr / Am	δCCO

^a Abbreviations: VS = very strong; S = strong; M = medium; w = weak; s = symmetric; as = asymmetric; Cr: crystalline phase; Am = amorphous phase; Cr / Am = mixed contribution from both phases; Cr > Am = more attribution to Cr rather than Am; Cr >> Am = even more attribution to Cr rather than Am; / = not determined.

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Figure 6.14 Polarized Raman spectra of oriented PLLA with stretch ratio of 2.

As it can be seen, P_2 values obtained from Raman bands at 873 and 1042cm^{-1} increase positively as the stretch ratio becomes higher, it means that the z-axes of the Raman tensors for these Raman bands have a tendency to align towards the drawing direction. In contrast, Raman bands at 1092 and 1764cm^{-1} show a monotonic decrease in P_2 values, suggesting that the z-axes of these Raman tensors become oriented away from the uniaxial drawn direction. The difference in P_2 values from one Raman band to another is due to their difference in tilt angle (Ω). As mentioned in Chapter 3, the P_2 values obtained for the Raman band, in fact, represent the orientation distribution of the principal axis of the Raman tensor with respect to the drawn direction (i.e. Z-axis) of the sample.

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Figure 6.15 Plot of P_2 values of Raman bands as a function of stretch ratio. Error bars are superimposed for 873cm^{-1} .

Figure 6.16 Plot of the right-hand term in Eq. 3.32 against P_2 values for the Raman bands assigned to both the crystalline and amorphous regions of drawn PLLA.

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In order to obtain the order parameter of the molecular chain ($P_{2, chain}$) with respect to the Z-axis of the sample, the obtained P_2 values needs to be corrected for the tilt angle according to Equation 3.32. Referring to Equation 3.32 (refer to page 49), four parameters (i.e. χ_c , Δn , Δn_c and Δn_a) are needed to be known before tilt angle can be calculated. The birefringence (Δn) and the degree of crystallinity (χ_c) of the stretched PLLA sample were determined and presented previously in Section 5.3.6 and 5.3.7 respectively. As for the intrinsic birefringence, the Δn_c and Δn_a values for PLLA are reported as 0.0207 and 0.0587, respectively [69]. For each Raman band assigned to both the crystalline and amorphous regions of PLLA, the right-hand side term of Equation 3.32 is plotted against the P_2 value as shown in Figure 6.16. The plot shows linear correlation between the two parameters that goes through the origin for each Raman band. The tilt angle for each Raman band can then be calculated from the slope of the plot, and they are given in Table 6.4, which are consistent with a previous study [69].

Table 6.4 Tilt angles of the Raman bands that are assigned to both the crystalline and amorphous regions of PLLA

Raman band (cm ⁻¹)	Tilt angle, Ω (°)
873	49.6
1042	44.4
1092	60.1
1764	69.8

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Orientation measurement of PLLA bottom layer in bi-layer film

Once the tilt angles for the Raman bands assigned to both the crystalline and amorphous regions of PLLA are known, then $P_{2,\text{chain}}$ values can be determined by using Equation 3.31. Subsequently, the second order of the molecular orientation distribution function for the amorphous regions only ($P_{2,\text{am}}$) can be calculated using Equation 3.33 based on the known values of $P_{2,\text{c}}$ and $P_{2,\text{chain}}$. Table 6.5 presents the averaged $P_{2,\text{c}}$ and $P_{2,\text{am}}$ values of PLLA in stretched PLLA/P(DL)GA bi-layer films. The $P_{2,\text{c}}$ values were obtained from WAXD measurement. The $P_{2,\text{am}}$ values, on the other hand, were calculated from averaging the values for the Raman bands at 873, 1042, 1092 and 1764 cm^{-1} . It is important to realize that the assumption of axially symmetrical Raman tensor with certain degree of tilt angles is still valid and not affected by drawing.

Table 6.5 Order parameters, $P_{2,\text{c}}$ and $P_{2,\text{am}}$ of PLLA in uniaxially stretched PLLA/P(DL)GA bi-layer film under various deformation temperatures

λ	$T_d = 50^\circ\text{C}$		$T_d = 65^\circ\text{C}$		$T_d = 85^\circ\text{C}$	
	$P_{2,\text{c}}$	$P_{2,\text{am}}$	$P_{2,\text{c}}$	$P_{2,\text{am}}$	$P_{2,\text{c}}$	$P_{2,\text{am}}$
2	0.26 ± 0.02	0.38 ± 0.02	0.69 ± 0.02	0.16 ± 0.02	0.83 ± 0.02	0.02 ± 0.05
3	0.55 ± 0.01	0.47 ± 0.01	0.80 ± 0.01	0.15 ± 0.05	0.91 ± 0.02	0.11 ± 0.05
4	0.77 ± 0.01	0.55 ± 0.03	0.87 ± 0.00	0.39 ± 0.05	0.92 ± 0.02	0.26 ± 0.06

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As noted in Table 6.5, the evolution of the molecular orientation in both crystalline and amorphous phases of PLLA depends on the deformation temperature. For samples drawn at 85°C, the result of bi-layer film is similar to the result obtained on single PLLA film discussed above. At $T_d = 85^\circ\text{C}$, the transformation from the lamellar to the fibrillar morphology has been essentially completed above $\lambda > 2$ and hence $P_{2,c}$ almost levels off. At this point, sharp diffraction arcs in the equatorial direction are observed by WAXD, indicating high level of crystalline orientation. Nevertheless, the development of molecular orientation in the PLLA amorphous regions still continues even after the development of crystallite orientation has been almost ceased at $\lambda > 2$.

However, drawing at lower temperature whereby the neat PLLA would simply break up upon stretching beyond $\lambda = 2$, both crystalline and amorphous orientation of PLLA in bi-layer film increase with stretch ratio. At drawing temperature of 65°C which is approximately the glass transition temperature of PLLA, the molecular chains in the amorphous region, which is less rigid, would first experience stretching. Between stretch ratio of 2 and 3, the amorphous orientation remains constant with stretch ratio. The explanation for this is that PLLA has undergone the transformation from lamellar to fibrillar structure during this stage. In addition, it is supported by the general concentration of diffraction arcs in the equatorial direction in the WAXD measurement. After that, a further rise in molecular orientation is observed in the amorphous phase due in part to the stretching of intercrystalline strands or tie molecules in the direction of drawing.

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For stretching bi-layer film at 50°C (below the glass transition temperature of PLLA), cool drawing of PLLA in bi-layer film occurs whereby both crystalline and amorphous phases are largely immobilized. Though both phases are in rigid state, local segmental motions can still occur. The results in Table 6.5 illustrate, in the first place, that most of the deformation is concentrated in the amorphous regions, while the rigid crystallites do not show any significant rotation. Subsequently, increase of both $P_{2,c}$ and $P_{2,am}$ values can be seen, although the rate of increase is different. Once the built-up shear stress in the crystallites exceeds the critical resolved shear stress level, massive rearrangement of molecular chains in the crystalline regions occurs, giving rise to an increase in crystalline orientation. The onset of plastic deformation starts at a higher stretch ratio due to the restricted mobility at that deformation temperature. Therefore, amorphous orientation is comparable to that of crystalline orientation except at high stretch ratio.

6.2.6.2 Structure characterization of amorphous P(DL)GA top layer by Raman

Similar to the study of molecular orientation of the PLLA bottom layer in the bi-layer system, it is first necessary to assign the Raman bands of amorphous P(DL)GA and to then determine the tilts angles for the Raman bands. Hence, single P(DL)GA films were first employed for the band assignment and tilt angle determination, before studying the molecular orientation of P(DL)GA in bi-layer film with aid of the obtained information.

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Raman band assignment and tilt angle (Ω) determination

Polarized Raman spectra of P(DL)GA with different polarization geometries are shown in Figure 6.17. The peaks between $2800 - 3150 \text{ cm}^{-1}$ were employed to analyze the molecular orientation behavior of amorphous P(DL)GA layer. The strong peak at 2949 cm^{-1} is assigned to the symmetric CH_3 stretching [97, 98]. In order to obtain quantitative information regarding the order parameter and tilt angle, a commercial software package Peak Fit was employed to de-convolute the peaks mixed with multiple components. A typical fitting is shown in Figure 6.18. Through numerical fitting with a number of Mixed Gaussian and Lorentzian line shapes of different widths and peak heights, the peak height of the intensity at 2949 cm^{-1} was used for the P_2 determination.

As given in Table 6.6, the P_2 values were calculated according to Equation 3.29. The P_2 value obtained from Raman band at 2949 cm^{-1} rises negatively as the stretch ratio increases. Knowing that the limiting values of P_2 are 1 and -0.5 for perfect orientation at 0° and 90° from the drawn direction, respectively, the obtained P_2 values indicate that the CH_3 group is highly oriented perpendicular to the drawn direction with stretching.

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Figure 6.17 Polarized Raman spectra of single P(DL)GA film for different polarization combinations. (a) Raman shifts: 750 – 1900 cm^{-1} and (b) 2800 – 3150 cm^{-1} .

Figure 6.18 Deconvolution of the band over the range from 2800 to 3150 cm^{-1} .

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Table 6.6 Order parameter P_2 of single P(DL)GA films specimens stretched at 50°C

λ	P_2	$P_{2,chain}$
2	-0.0315	0.067
3	-0.0453	0.096
4	-0.1649	0.350

In order to obtain the order parameter of the molecular chain ($P_{2, chain}$) with respect to the Z-axis of the sample, an angular correction is required to obtain the $P_{2, chain}$ according to Equation 3.32. As mentioned above, four parameters (i.e. χ_c , Δn , Δn_c and Δn_a) are required for the tilt angle calculation. Being the fact that P(DL)GA is an amorphous polymer, two parameters, χ_c and Δn_c , can be omitted and thus the P_2 value can be simply corrected by correlating it with the birefringence (Δn) of the sample. A reference value of 0.065 is taken for the intrinsic birefringence (Δn_a) of P(DL)GA [99]. In that case, a tilt angle of 82.1° is obtained based on calculation. After knowing the tilt angle, the P_2 values for the molecular chains ($P_{2, chain}$) were then calculated from those for the P_2 values from 2949 cm⁻¹ Raman band. The results are also shown in Table 6.6, demonstrating high degree of chain orientation at high stretch ratio.

Orientation measurement of P(DL)GA top layer in bi-layer film

Once the tilt angle for the Raman band at 2949 cm⁻¹ is known, then $P_{2,chain}$ values or rather values for the case of amorphous P(DL)GA can be determined. The calculated $P_{2,am}$ values

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for P(DL)GA are listed in Table 6.7. The P(DL)GA in bi-layer film shows the same orientation trend as pure P(DL)GA does: stretch ratio increases the amorphous chain orientation and lower deformation temperature gives higher degree of molecular orientation in all stretch ratios.

Table 6.7 Order parameters, $P_{2,am}$ of P(DL)GA in uniaxially stretched PLLA/P(DL)GA bi-layer film under various deformation temperatures

λ	$T_d = 50^{\circ}\text{C}$ $P_{2,am}$	$T_d = 65^{\circ}\text{C}$ $P_{2,am}$	$T_d = 85^{\circ}\text{C}$ $P_{2,am}$
2	0.18 ± 0.04	0.10 ± 0.04	0.06 ± 0.03
3	0.27 ± 0.02	0.22 ± 0.04	0.19 ± 0.03
4	0.35 ± 0.02	0.26 ± 0.00	0.20 ± 0.04

For samples drawn above glass transition temperature of P(DL)GA (50°C and 65°C), the $P_{2,am}$ value of P(DL)GA gradually increases with stretch ratio, which indicates that the molecular chain segments orient steadily towards the draw direction from the onset of deformation. In addition, the attained orientation of P(DL)GA in bi-layer film is higher compared to that in the pure P(DL)GA film. However, drawing at 85°C shows that the $P_{2,am}$ value was found to be close to zero at low stretch ratio ($\lambda = 2$), indicating a negligible chain orientation. This low $P_{2,am}$ value has to be ascribed mostly to the relaxation of the chains in the amorphous regions for the relaxation occurs rapidly at this temperature.

Shape Memory Effect in Bi-layer Systems

6.3 Mechanism of Shape Memory Properties of PLLA/P(DL)GA Bi-layer Film

In the preceding Chapter 5, it demonstrates that both single layers (amorphous P(DL)GA and semicrystalline PLLA) exhibit diverse shape memory behaviors. For single P(DL)GA film, it exhibits good shape memory property with complete shape recovery. On the contrary, single PLLA film shows incomplete shape recovery. The loss in recovery is ascribed to formation of highly oriented micro-fibrillar structure and the increased crystallinity. Moreover, it is found that recovery is associated with disorientation of the amorphous chains, which represents the primary mechanism of recovery, and oriented crystallites do not “recover”.

According to the investigation performed in this chapter, the shape-memory effect of PLLA/P(DL)GA bi-layer films is remarkably different from the individual single components and the traditional shape-memory polymers such as polyurethane. In the following section, a shape-memory mechanism of the semicrystalline/amorphous polymeric laminates would be proposed for the PLLA/P(DL)GA bi-layer system based on the phase morphologies of the materials.

Shape Memory Effect in Bi-layer Systems

In the system, crystalline regions in the PLLA act as physical crosslinks to keep the original structure. In contrast, amorphous regions in both P(DL)GA and PLLA serve as a reversible phase, which undergo deformation involving molecular orientation during stretching/programming. When the sample is brought to temperature below T_{trans} and the load is removed, the temporary shape is kept and the internal energy is stored in the system (both in PLLA and P(DL)GA to various degrees). Subsequently, when the temperature increases, the sample recovers to its original shape with the stress releasing instantaneously.

Furthermore, based on the current observation, it should be pointed out that shape recovery response of the bi-layer system is strongly influenced by the deformation temperature (T_d) and the recovery temperature (T_r). The shape memory mechanism under various conditions is illustrated in Figure 6.19. When deformation is performed below the glass transition temperature of PLLA (50°C), the degree of shape recovery is high with over 90%.

This phenomenon can be explained as follows: P(DL)GA is in rubbery state at this deformation temperature, amorphous orientation increases with stretching; moreover, as it is laminated with PLLA, P(DL)GA also acts as stress concentrators upon being subjected to stretching. It helps the amorphous PLLA chains orient better because of the locally increased stress levels induced by P(DL)GA, particularly at the interfacial areas.

Shape Memory Effect in Bi-layer Systems

Nonetheless, the crystalline orientation is suppressed at this low temperature despite the better orientation in the amorphous regions of PLLA at this temperature. It is because the crystallites, constituting about 20% of the material, are surrounded by the amorphous chains and connected to the bulk via certain tie molecules. At this deformation temperature that is below T_g of PLLA, the surrounding amorphous chains exhibit a solid-like behavior and inhibit crystallite rotation. Thus, most of the orientation is concentrated in the amorphous regions of P(DL)GA and PLLA in the stretched sample. When the sample is heated to a recovery temperature of 85°C (above T_g of both P(DL)GA and PLLA), almost complete shape recovery is obtained as illustrated in Figure 6.4a. This happens because of the disorientation of the oriented non-crystalline chains in both materials.

But if the deformation temperature is at the T_g of PLLA (i.e. 65°C), the molecular chains in the amorphous regions of PLLA start to have adequate capability to move, so amorphous orientation increases with stretch ratio. In addition, the crystallite orientation is highly promoted. It is due to the efficient transfer of stress from the surrounding amorphous chains to the crystallites at such a temperature, promoting the crystal orientation. However, amorphous orientation in both P(DL)GA and PLLA is lower compared to that at T_d of 50°C. This is expected since the rate of relaxation increases with increasing deformation temperature. As a result, the degree of shape recovery decreases. The loss in recovery is attributed to the plastic crystallite deformation of PLLA and the reduced amorphous orientation that accounts for recovery.

Shape Memory Effect in Bi-layer Systems

Samples stretched at higher deformation temperature (above the T_g of PLLA) exhibit similar but much lower values of recovery than samples stretched at lower deformation temperature. At high deformation temperature (85°C), the stress transfer between amorphous regions and crystallite is more effective due to high chain mobility, causing the crystallites to become highly plastically deformed at all stretch ratios along with the new crystal formation due to strain-induced crystallinity as evidenced from the X-ray crystallinity measurement.

At the same time, the amorphous chains experience greater relaxation and result in lower orientation levels. Therefore, the highly oriented crystallites and the increased crystallinity hinder the disorientation of oriented amorphous chains during the recovery process, leading to lower recovery at high deformation temperature. This indicates that increase in amorphous orientation and diminution of crystal transformation induced at low deformation temperature help to enhance shape recovery.

Besides deformation temperature, recovery temperature also plays a critical role to the shape recovery as demonstrated in Figure 6.6. When the recovery temperature is at the glass transition of P(DL)GA, but is well below the T_g of PLLA, only oriented amorphous chains in P(DL)GA have sufficient chain mobility to recoil and recover to its original conformation at this temperature. Furthermore, the recovery process would be slight hindered by the rigid molecular chains of PLLA, resulting in low shape recovery.

Shape Memory Effect in Bi-layer Systems

(a)

(b)

(c)

Shape Memory Effect in Bi-layer Systems

Figure 6.19 Schematic diagrams of shape memory mechanism of amorphous P(DL)GA / semicrystalline PLLA bi-layer system under various conditions: (a) T_d below T_g of PLLA (50°C), (b) T_d at T_g of PLLA (65°C) and (c) T_d above T_g of PLLA (85°C).

However, if the recovery temperature is at the T_g of PLLA (which is above T_g of P(DL)GA), oriented amorphous chains in both P(DL)GA and PLLA have the chain mobility to recoil to their respective original conformations. Therefore, samples that are deformed at $T_d = 50^\circ\text{C}$ gives much higher recovery since orientation is concentrated in the amorphous regions of PLLA and P(DL)GA. Whereas, samples that are deformed at higher T_d suffer from lower recovery for the attained crystal transformation is not reversible at this temperature. When the recovery temperature is above the glass transition temperatures of both materials; the degree of recovery increases as there is certain extent of crystallite orientation being recoverable at this high temperature due to greater chain mobility to regain the Gaussian conformation. Thus, through careful selection of bi-layer composition and proper programming conditions, a bi-layer system with good performances can be achieved.

Modeling of Shape Memory Behavior

CHAPTER 7

MODELING OF SHAPE MEMORY BEHAVIOR IN BIOMEDICAL POLYMERIC SYSTEMS

7.1 Introduction

For biomedical devices using the concept of thermally induced shape-memory effect, the shape memory polymer will typically undergo a thermomechanical loading-unloading cycle illustrated in Figure 2.3. The polymer is first isothermally programmed or deformed from its initial shape to a temporary shape by applying a mechanical force at temperature T_d . Subsequently, the temporary shape of the material can be maintained by lowering the temperature to T_L and removing the external load. The polymer can largely maintain this shape as long as the temperature remains unchanged. The shape recovery or device deployment is activated by raising the temperature to T_r where the desired initial shape is recovered. Generally, T_d and T_r are above the glass transition temperature T_g , while T_L is below the glass transition temperature.

In practical viewpoint, it is highly desirable that the thermomechanical behavior of polymer (the deformation and recovery behavior) can be predicted. In chapter 5, it is demonstrated that various factors such as deformation temperature, deformation extent and recovery temperature affect the recovery property. In an attempt to capture these effects on the

Modeling of Shape Memory Behavior

thermomechanical behavior of polymer, a one-dimensional thermomechanical constitutive model was developed for amorphous polymer and it serves as the foundations for the development of model for semi-crystalline and bi-layer polymeric system.

7.2 Description of Constitutive Model

This work was based on the behavior of amorphous P(DL)GA polymer which regains its initial shape upon heating illustrated in chapter 5. The proposed model combined a ‘Kelvin’ unit (a network spring and a viscous dashpot in parallel) and a Hookean spring in series. The model and the steps in deformation and recovery are shown in Figure 7.1 (a) – (d). At temperature above the glass transition temperature ($T_d \geq T_g$), the model is stretched to a certain stretch ratio, λ . During the stretching, macromolecular chains undergo large conformational changes and orient towards the drawn direction, leading to the reduction in the configurational entropy of the molecular chains. Subsequently, it is quenched to temperature below T_g followed by the removal of the external load. Before the model coming to a complete frozen state (shape memory), slight strain reduction occurs due to complete contraction of the elastic spring element. However, the shape recovery is largely interrupted at this temperature due to significant reduction in the mobility of macromolecular chains, which is represented by the dashpot having high viscosity at that stage. The shape recovery process is invoked as the temperature rises above T_g , where the viscosity of the dashpot reduces and the deformed ‘Kelvin’ unit recovers to its original state.

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Figure 7.1 Proposed mechanical model for shape memory process.

The proposed model developed is meant for *uniaxial tension* only and it consists of three basic elements, which will be discussed in relations, where appropriate, to the possible molecular mechanisms involved.

The elastic element

The series elastic element is used to represent the initial transient response before the onset of recoverable plastic deformation. In this region, the deformation is assumed to approximately follow Hooke's law. Therefore, a Hookean spring is used with the following equation:

$$\sigma = E \varepsilon_s = E \ln \lambda_s \quad (7.1)$$

Where: E is the elastic modulus and it is assumed to be time-independent.

Modeling of Shape Memory Behavior

The viscous element

The viscous element can be modeled by many equations such as Newtonian, Arrhenius, Argon and Eyring or even WLF equation [21, 61, 100, 101]. In the generalized form,

$$\dot{\epsilon}_G = \frac{d\epsilon_G}{dt} = \frac{\sigma_V}{\eta} \quad (7.2)$$

Where: η is the apparent viscosity. In this model, the Eyring process is used to represent the dashpot. Applying Eyring theory, one can correlate strain rate to the true stress σ_v by [102]:

$$\dot{\epsilon}_G = \frac{\sigma_V}{\eta} = A \sinh \left(\frac{\sigma_V V}{kT} \right) \quad (7.3)$$

Where: A is a constant, V the activation volume; k the Boltzmann constant and T the temperature in Kelvin. The activation volume represents the volume of polymer segment required to move as a whole in order for plastic deformation to take place. By substituting

$\dot{\epsilon}_G = \frac{\dot{\lambda}_G}{\lambda_G}$ and rearranging, equation (7.3) becomes

$$\sigma_V = \frac{kT}{V} \ln \left(\frac{\dot{\lambda}_G}{A\lambda_G} + \sqrt{\left(\frac{\dot{\lambda}_G}{A\lambda_G} \right)^2 + 1} \right) \quad (7.4)$$

It should be pointed out that the viscous element is in parallel with the network element. This means that the model will return to its original form whenever the viscosity is reduced and this corresponds well with the recovery behavior of the polymer whereby the apparently permanent plastic deformation is recovered on heating up above T_g . However, negligible

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amount of deformation is recovered at room temperature as the viscosity is high at that temperature.

The network element

The reversibility of the large deformation leads to the concept of rubber elasticity. As demonstrated in chapter 5, the material response at temperature above T_g shows rubber-like hyperelastic behavior. Several models, such as Mooney-Rivlin model, Wang and Guth three chain model and Ball *et al.* model, can be used to capture this behavior [103, 104]. In this model, Arruda-Boyce eight-chain model [103] is used here to represent the network element.

The eight-chain equation is given as:

$$\sigma_G = \frac{G}{3} \sqrt{N} L^{-1} \left[\frac{\lambda_{chain}}{\sqrt{N}} \right] \frac{(\lambda_G^2 - \lambda_G^{-1})}{\lambda_{chain}} \quad (7.5)$$

$$\text{and } \lambda_{chain} = \frac{(\lambda^2 + \frac{2}{\lambda})}{\sqrt{3}}$$

Where: G is the rubbery shear modulus; N is the number of statistical links between the two crosslinks. In amorphous thermoplastics, which do not have a cross-linked structure, the value of N is related to the number of chain segments between points of physical entanglement in the polymer chain. λ_{chain} is the chain stretch and L is the Langevin function defined as

$$L(\beta) = \coth \beta - \frac{1}{\beta} \quad (7.6)$$

Modeling of Shape Memory Behavior

There are several models [102, 104, 105] which have a general arrangement of elements similar to the proposed model; however, they differ in the specific term of the viscous and network elements. Our model is specified on grounds of simplicity and yet it gives an adequate representation of the uniaxial deformation and recovery behavior studied here.

Construction of constitutive equation

Stress-strain behavior

The applied total stress, σ , is the sum of stresses σ_V and σ_G and is itself equal to the stress in the elastic spring element. Thus,

$$\sigma = \sigma_V + \sigma_G$$

(7.7)

In addition, the total stretch ratio, λ , is determined from the multiplicative decomposition of the elastic spring extension, λ_s , and dashpot extension, λ_G [102, 105]. Therefore, it takes the form:

$$\lambda = \lambda_s \lambda_G \tag{7.8}$$

Substituting equations (7.1), (7.4), (7.5) and (7.8) into equation (7.7), it becomes:

$$E \ln \left(\frac{\lambda}{\lambda_G} \right) = \frac{kT}{v} \ln \left(\frac{\lambda_G}{A \lambda_G} + \sqrt{\left(\frac{\lambda_G}{A \lambda_G} \right)^2 + 1} \right) + \frac{G}{3} \sqrt{N} L^{-1} \left[\frac{\lambda_{chain}}{\sqrt{N}} \right] \frac{(\lambda_G^2 - \lambda_G^{-1})}{\lambda_{chain}} \tag{7.9}$$

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Assuming that the model is stretched with a constant crosshead speed of α mm/s, then the relation between stretch ratio and time can be expressed as follow:

$$\lambda = 1 + \left(\frac{\alpha}{l_0}\right)t \quad (7.10)$$

Where: l_0 is initial length of the sample and t is the time.

Equation (7.9) is solved numerically using *Mathematica* to obtain λ_G as a function of time, t . By knowing λ and λ_G at each time increment, true stress can be calculated using equation (7.1). Furthermore, the results are presented in terms of nominal stress, σ_{nom} , which is simply taken as σ/λ assuming incompressibility of the material.

Non-isothermal recovery

The shape recovery process is a temperature and time dependent phenomenon. It can occur either under the influence of constant heating rate on the temperature dependent recovery (non-isothermal recovery) or as a time dependent recovery under constant temperature condition (isothermal recovery). In this section, the nonisothermal recovery behavior would be investigated. As illustrated in Figure 7.1, when the sample is quenched to temperature below T_g by removing the specimen out of the temperature chamber, strain reduction due to the complete contraction of the elastic spring element occurs before reaching a complete frozen state. In other words, the subsequent recovery of the stretched samples can be explained by the recovery of the ‘Kelvin’ unit. The constitutive equation for prediction of nonisothermal recovery is derived as below.

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When the sample is in complete frozen state, the stress (σ) is equal to zero, thus equation (7.7) becomes:

$$0 = \sigma_V + \sigma_G \quad (7.11a)$$

By substituting equations (7.2) and (7.5), equation (7.11a) can be expressed respectively as:

$$0 = \eta \frac{d\epsilon_G}{dt} + \frac{G}{3} \sqrt{N} L^{-1} \left[\frac{\lambda_{chain}}{\sqrt{N}} \right] \frac{(\lambda_G^2 - \lambda_G^{-1})}{\lambda_{chain}} \quad (7.11b)$$

And

$$0 = \frac{\eta}{\lambda_G} \frac{d\lambda_G}{dt} + \frac{G}{3} \sqrt{N} L^{-1} \left[\frac{\lambda_{chain}}{\sqrt{N}} \right] \frac{(\lambda_G^2 - \lambda_G^{-1})}{\lambda_{chain}} \quad (7.11c)$$

In the frozen state, the viscosity (η) is very large for the dashpot element. Hence, there is no recovery at this stage. During the recovery process whereby the sample is heated up above T_g , the viscosity of the dashpot starts to reduce, leading to the spring back of the ‘Kelvin’ unit to its original state as shown in Figure 7.1(d). According to the Eyring theory, the temperature dependence of viscosity can be expressed as [106]:

$$\eta = B e^{\frac{E_p}{RT}} \quad (7.12)$$

Where: B is a constant, E_p is the activation energy, and R is the gas constant. B and E_p are used as tuning parameters for the viscosity-temperature dependency.

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Equation (7.12) resembles the Arrhenius-type behavior. Alternatively, we may use the WLF temperature dependence [101]:

$$\eta = \eta_{T_g} \exp \left(\frac{-C_1(T-T_g)}{C_2+(T-T_g)} \right) \quad (7.13)$$

Where: η_{T_g} is the viscosity at the glass transition temperature, $C_1 = 40.16$ and $C_2 = 51.6$ are universal constants [61].

As the non-isothermal recovery process is conducted under a constant heating rate (β in K/s), the relationship between time and temperature can be expressed as:

$$\frac{dT}{dt} = \beta \rightarrow \frac{1}{dt} = \frac{\beta}{dT} \quad (7.14)$$

Combining equations (7.12) and (7.14) into (7.11c), the equation is solved numerically to obtain the correlation of ε_G on temperature.

Isothermal recovery

In isothermal recovery, it is a time dependent recovery under constant temperature condition. As illustrated in Figure 7.1(c), when the model is in complete frozen state (shape memory), the strain is being stored in the ‘Kelvin’ unit while the elastic spring element is completely contracted. Subsequently, during the recovery process, the sample is subjected to a constant temperature that is above T_g , the recovery of the stretched sample is due to the contraction of the ‘Kelvin’ unit with respect to time.

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In other words, it resembles to the creep recovery process. Then the following equation can be simply used to represent the isothermal recovery [101]:

$$\varepsilon_G(t) = \varepsilon_{G,max} \left(e^{-\frac{t}{\tau}} \right) \quad (7.15)$$

Where: ε_G is the strain at time t , $\varepsilon_{G,max}$ is the maximum strain of the model at the moment of load release, i.e., after the complete retraction of the elastic element, and τ is the time constant and is a fitting parameter.

7.3 Identification of material parameters

In order to successfully implement the constitutive model, the material parameters must be appropriately identified. In the model developed in this work, there are 8 material parameters, among which 5 are fitting parameters. The necessary experiments are described herein, and the materials parameters for P(DL)GA are then determined from such experiments.

1. Young's modulus, E

The value of Young's modulus E can be obtained as a best fit to the slope of the first part of the stress-strain curve. Alternatively, the initial Young's modulus can be described by the following expression [66]:

$$E(T) = \frac{E_r}{1 + \exp\left[-\frac{T-T_r}{W}\right]} + (E_g) \left[1 - \frac{1}{1 + \exp\left[-\frac{T-T_r}{W}\right]} \right] \quad (7.16)$$

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Where: E_r is the rubbery extensional modulus and E_g is the elastic modulus in the glassy state respectively. Among these parameters, T_r and W are the fitting parameters in which W characterizes the width of the transition region and T_r is a reference temperature that is close to T_g . By curve fitting, it is found that W gives a value of 4.23 and $T_r = 39.6^\circ\text{C}$. Figure 7.2 shows the plot of modulus as a function of temperature. A value of 1491MPa is taken as elastic modulus at 37°C .

Figure 7.2 Dependence of apparent/effective modulus on temperature.

2. Eyring activation volume, V

The material parameters which model the viscous dashpot consist of activation volume, V , and a constant, A . These two parameters can be determined by conducting isothermal uniaxial tensile test at various levels of strain rate as shown in Figure 7.3. In order to

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determine the constants from the tests at various strain rates, equation (7.3) is first rearranged to be the equation of a line by assuming high value of σ :

$$\ln \dot{\epsilon} = \ln A + \frac{\sigma V}{kT} \quad (7.17)$$

The values at peak yield for σ and strain rate ($\dot{\epsilon}$) are used to plot the curve of $\ln \dot{\epsilon}$ vs. peak stress as shown in Figure 7.4. The values of V can be then extracted from the slope of the resulting curve.

Figure 7.3 True tensile stress versus stretch ratio curves for P(DL)GA at 37°C.

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One can see that the experimental data lies on a straight line and it gives support the use of Eyring viscous dashpot in the model. Values of $1870 \text{ \AA}^3$ is obtained for activation volumes at 37°C . It is to be noted that there is no peak in stress at yield when the tensile tests were low strain rates or when the deformation is conducted at 50°C ; therefore the yield points were identified as the point whereby there is a change on slope. The stress at that point was taken as the yield stress.

Figure 7.4 Rate dependence of yield stress of P(DL)GA at 37°C .

3. Rubber modulus, G

The material parameters required to capture the strain hardening behavior are the rubbery modulus, G , and the number of rigid links between entanglements, N . An approximate value for the rubber modulus, G can be determined by fitting the isothermal uniaxial tensile stress-

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strain curve at temperature above T_g and the test was conducted at a moderately rapid rate to minimize entanglement drift. In this work, $G = 0.98$ MPa were obtained.

7.4 Results

In this section, the results from model's predication are compared with the experimental results and the interpretation of the modeling results with the experimental results is elaborated. The material parameters in the model are listed in Table 7.1.

Table 7.1 Material parameters used in the simulation

Material parameters	$T_d = 37^{\circ}\text{C}$	$T_d = 50^{\circ}\text{C}$
E (MPa)	1491	170
V ($\text{\AA}^3$)	1870	1660
A (s^{-1})	2.98×10^{-4}	9×10^{-4}
G (MPa)	0.89	0.89
N	13	40
B (Pa.s^{-1})	8×10^{-4}	1×10^{-3}
E_p (kJ.mol^{-1})	73.7	76.4
τ (s)	17.1	-

Figure 7.5 shows the comparison of the results from the numerical simulations and experiments of isothermal uniaxial tensile curves at difference temperature. At temperature at the start of glass transition of P(DL)GA, i.e. 37°C , the stress-strain curve obtained by simulation shows a pronounce yield peak followed by drop in stress, and then significant strain hardening. One discrepancy between the experimental and simulation curves lies at the high stretch ratio where the theoretical curve rises more steeply than the experimental curve.

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The difference can be interpreted by the assumption that there is break down of some physical entanglements at high stretch ratio. Thus N does not remain constant but increases slightly [107]. As the temperature increase, the height of yield peak drops rapidly, reflecting the marked temperature sensitivity of the viscous elements. A higher value of N was used at high deformation temperature, implying that there is longer chain or more number of chain segments between physical entanglement points. It is worth noting that the experimental result is obtained based on the thin films subjected to uniaxial tension, which develops a state of plain stress, that is stresses perpendicular to the plane of the film relaxed to zero. The ideal sample for uniaxial testing, is of course, a fibre. Therefore, the measurements on film and application of uniaxial model are not exactly compatible. But still, generally speaking, it can be seen that the proposed model is able to capture the general profile of the stress-strain behavior of the material reasonably at different programming conditions.

Figure 7.5 Uniaxial tensile stress-strain curve of P(DL)GA at a constant strain rate of $1.67 \times 10^{-2} \text{ s}^{-1}$ at various deformation temperatures.

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Figure 7.6 shows the comparison of the temperature dependence recovery of specimen measured by TMA and that from numerical simulations. It can be clearly seen that the proposed model describes the behavior reasonably well. To avoid repetition, the model parameters for sample deformed at 50°C followed by recovery are presented in Table 7.1. When the deformed model is at low temperature, the viscosity of the dashpot in the ‘Kelvin’ unit is high enough to resist the recoverable elastic entropic force of the network element. Therefore, the recovery is small at temperatures below the T_g of the stretched sample. During the recovery process where the sample is being heated up, the viscosity, η , which obeys the Eyring’s equation, is reduced; the sample is quickly recovered on the glass transition regime.

Figure 7.6 Comparison of non-isothermal recovery for experimental and simulated results. The P(DL)GA sample was stretched to $\lambda = 3$ at 37°C before subjected to recovery test.

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Furthermore, the numerical simulation of the isothermal recovery experiment was also conducted to characterize the recovery behavior at a constant temperature. Figure 7.7 shows the comparison between the simulation and the experimental results. Upon immersing the sample at a temperature above its glass transition temperature, the ‘Kelvin’ unit started to shrink to its original state due to the release of the entropic restoring force of the network spring. Generally, the model predicts the decrease of strain with time. However, single relaxation mechanism is used in the model instead of multiple relaxations, which are usually involved in the real experiment.

Figure 7.7 Stretch ratio response in the isothermal recovery process. The P(DL)GA sample was stretched to $\lambda = 4$ at 37°C before subjected to the isothermal recovery test at 37°C.

Conclusions and Recommendations

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

8.1.1 Shape memory of biodegradable polymeric systems

(a) Monolayer polymeric system - Amorphous P(DL)GA

A systematic study of the shape memory effect in amorphous P(DL)GA has been presented. Amorphous P(DL)GA consists of two phases: the thermal reversible “phase” consists of the amorphous molecular chains; the fixed “phase” consists of the physical entanglements, which is responsible for the permanent shape. The effects of deformation temperature ($T_d = 37$ and 50°C), stretch ratio ($\lambda = 1.5 - 5$) and recovery temperature ($T_r = 37$ and 50°C) on shape recovery were evaluated. The shape recovery was higher than 90% under all the experimental conditions studied, indicating that P(DL)GA exhibited good shape memory property.

The shape memory behavior is related to the morphological changes during the programming and recovery process probed by birefringence measurement. During programming, the amorphous chains are forced to orient towards the stretching direction, however, the extent of orientation depends on the programming condition. High stretch ratio and low deformation

Conclusions and Recommendations

temperature give higher chain orientation of P(DL)GA. Lower chain orientation obtained at high deformation temperature is due to relaxation of the amorphous chains. Furthermore, near zero birefringence was observed for P(DL)GA after recovery process. It was meant that the oriented amorphous chains are able to return to the random coil configuration after recovery, irrespective of the details of the molecular orientation.

Moreover, the recovery stress generated during the constrained recovery process increases with increasing stretch ratio and with reducing deformation temperature. It is related to the amount of stored internal energy, which originates from the amorphous chain orientation. Higher recovery stress is obtained with P(DL)GA deformed at lower temperature, because higher chain orientation can be achieved and then stored, leading to release of high recovery stress upon the recovery. However, the overall recovery stress is relatively low. Thus, the mechanism of shape memory effect in amorphous P(DL)GA polymer is based on disorientation of the oriented amorphous chains formed during programming.

(b) Monolayer polymeric system – Semicrystalline PLLA

In PLLA, the crystalline region acts as physical crosslinks to maintain the original shape. On the other hand, the amorphous region serves as the switchable segments with T_g as the shape memory transition temperature. During programming ($T_g < T_d < T_m$), the deformation mechanism of semicrystalline PLLA was found to be more complex even though the overall molecular orientation (from birefringence) seemed to follow closely the pseudo-affine deformation model.

Conclusions and Recommendations

In general, higher orientation is obtained at higher deformation temperatures for semicrystalline PLLA due to the development of a highly oriented microfibrillar structure and increased crystallinity in the amorphous regions. At a low stretch ratio and moderate deformation temperature, molecular orientation is concentrated in the amorphous regions and molecular orientation in the crystalline regions is found to progress less rapidly than in the amorphous regions. At a high draw ratio, the crystals slip and shear along certain crystallographic planes, attaining high crystalline orientation, whereas the amorphous chains undergo processes of molecular orientation and relaxation concurrently, depending on the extent of deformation and deformation temperature.

During recovery, it was found that the degree of recovery was affected by the programming condition. The degree of shape recovery decreases with increasing stretch ratio and deformation temperature. At low stretch ratio, the shape recovery is attributed to the disorientation of the oriented amorphous chains in PLLA. At higher stretch ratio and deformation temperature, the extent of shape recovery decreases as a consequence of increased crystallinity by strain-induced crystallization and the irrecoverable plasticity in the crystalline regions due to the formation of highly oriented microfibrillar structure. Though the recovery is low, it is still associated with considerable disorientation of the amorphous chains, which represents the primary mechanism of recovery.

Conclusions and Recommendations

(c) Multilayer polymeric system – Semicrystalline PLLA /amorphous P(DL)GA bi-layer

In this bi-layer system, crystalline regions in the semicrystalline PLLA act as physical crosslinks to keep the original structure. On the other hand, amorphous regions in both P(DL)GA and PLLA serve as a reversible phase, which undergo deformation involving molecular orientation during programming. The orientation behavior of PLLA/P(DL)GA bi-layer exhibited diverse orientation behaviors under different programming conditions. At deformation temperature below the glass transition temperature of PLLA, deformation is concentrated in both the amorphous P(DL)GA and the amorphous regions of PLLA. However, the crystalline orientation of the rigid PLLA crystallites is suppressed at this low temperature.

At deformation temperature near the glass transition of PLLA, the molecular chains in the amorphous regions of PLLA has adequate mobility, thus, the molecular chains in the amorphous regions of PLLA and P(DL)GA experience chain orientation during stretching. In addition, the PLLA crystallites undergo fibrillar transformation and the crystal orientation is highly promoted. At even higher deformation temperature that is above glass transition of PLLA, there is high degree of PLLA crystal orientation and new crystal formation due to strain-induced crystallization during stretching. However, the attained chain orientation in the amorphous regions is lower compared to that at lower drawing temperature and it is due to the relaxation experienced by the amorphous chains. Furthermore, the orientation of the PLLA amorphous phase is always higher than that of the P(DL)GA amorphous phase.

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As for the recovery process, it was found that shape recovery decreases with both increasing deformation temperature and stretch ratio. Nonetheless, recovery increases with increasing recovery temperature. Furthermore, the thickness ratio of the bi-layer sample did not affect the extent of shape recovery regardless of the programming condition. The shape recovery is largely attributed to the disorientation of the oriented amorphous chains in both PLLA and P(DL)GA layers depending on the recovery temperature.

When the recovery temperature is at the glass transition of P(DL)GA, but is well below the T_g of PLLA, only oriented amorphous chains in P(DL)GA can recover to its original random coil conformation. Furthermore, the recovery process would be slightly hindered by the rigid molecular chains of PLLA, resulting in low shape recovery. When the recovery temperature is above the glass transition temperatures of both materials, oriented amorphous chains in both P(DL)GA and PLLA have the chain mobility to recoil to their respective original conformations. Furthermore, the recovery stress generated is greater as compared to that generated by P(DL)GA.

8.1.2 Modeling of shape memory behavior

A one-dimensional thermo-mechanical model was developed for P(DL)GA to describe qualitatively and quantitatively the shape memory behavior, i.e. the stress-strain behavior in tension, the non-isothermal and isothermal recovery behavior. The model consists of three

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elements: a 'Kelvin' unit (a network spring and a viscous dashpot in parallel) and a Hookean spring in series. This model is most suitable for amorphous polymer, which exhibits complete shape recovery. The important model parameters were determined.

Numerical simulations of the uniaxial tensile experiments under various isothermal conditions agreed with the experimentally obtained stress-strain behavior. For the case with recovery process, the model captured the shape recovery behavior reasonably well. However, the model did not fully capture the isothermal recovery behavior, implying the existence of a more complicated relaxation behavior that was not captured by the single relaxation mode proposed in the current model. This model serves as the foundation and enables the investigations of the more complicated systems such as semicrystalline polymer and semicrystalline/amorphous polymeric bi-layer system.

8.1.3 Summary

In the first part of the project, the shape-memory potential of the single-layer polymeric systems (PLLA and P(DL)GA) was explored under various programming and recovery conditions. It was demonstrated that P(DL)GA showed good recovery property but with low recovery stress. On the other hand, PLLA generated relatively high recovery stress; however, the level of recoverable strain attainable was low. As a result, in the second part of the project, a bi-layer biodegradable polymeric composite based on P(DL)GA and PLLA were studied for the shape-memory property and the mechanism behind it. It was clearly shown

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that moderate stretching at low deformation temperature leads to high shape recovery. So, through proper programming conditions, a bi-layer system with good recovery performance and adequate recovery stress can be achieved. In the last part of the work, a one-dimensional constitutive model was developed to capture the shape memory effect of amorphous polymeric system during different stages of shape memory process. In general, the model is found to correlate well to the experimental results. In conclusion, it can be said that the results and conclusions have clearly addressed the objectives outlined in chapter one.

8.2 Recommendations

Here are some recommendations for the future work that can be conducted.

(1) Shape recovery test in bending mode and in stent form

Stents are typically cylindrical in shape and the stresses that induced into the stent materials can be in the form of tension, compression, bending or even a combination of both. Therefore, it is important to investigate the shape memory characteristics in bending mode that fundamentally influences the recovery stress or the radial strength. The bending recoverability can be examined in term of bending angle and the sequence of the bi-layer components. Furthermore, although the recovery measurements have been conducted in a

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sink condition at 37°C to mimic the physiological conditions, an expansion (or recovery) study of stent made of respective components is required to verify the results.

(2) The effect of drug on shape-memory property

The results reported in this work are based on the shape-memory effects in pure biodegradable polymers. However, in stent application, drugs will be embedded into the polymeric matrix. Therefore, it is important to find out the effect of drug (drug type, drug concentration, drug size) on the shape-memory property of the polymeric films.

(3) Bi-layer polymeric system made of alternative components for stent application

In this work, it was found that increased crystallinity hinders the shape recovery to certain extent and the amorphous chains play a crucial role in shape recovery. Therefore, it will be of great interest to investigate the shape memory characteristics of a bi-layer system made of different components with lower crystallinity, various molecular weights (length of amorphous chain varies) or even lower glass transition temperature.

(4) Extension of the proposed thermo-mechanical model

The model developed in this thesis caters to the thermo-mechanical behavior of amorphous polymer. It could be further refined and modified to extend the study from at least three aspects: (i) Incorporation of a parameter governing the slipperiness of entanglements into the

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network element. The idea driven it is that the number of physical crosslinks or entanglements might decrease as a polymer is deformed to large strain level in the programming step [104]. (ii) In the isothermal recovery, it will be beneficial to improve and refine the model by introducing multiple relaxation time constants as usually more than one of the relaxation modes is operative during the recovery process. (iii) It will be interesting to extend the applicability of the model to semicrystalline polymer by incorporating more elements to represent the crystalline phase [108]. (iv) Furthermore, it would be of great interest that improving the model such that it can be used to predict the shape-memory of bi-layer system. The co-existence of the semicrystalline and amorphous components and their contribution to the recovery response can be treated following composite model. Nevertheless, extension of the thermo-mechanical model is a complex problem that involve other material or model parameters. It will be advantageous to obtain the model parameters by fitting to the experimental data using a genetic algorithm method. The relaxation spectrum may be easier to deal with by considering the possible molecular segmental motions in terms of Rouse theory. For the bi-layer structure, some material parameters such as Young's modulus can be predicted using the classical lamination theory [109, 110].

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List of Publications

LIST OF PUBLICATIONS

International Journal Papers

1. Wong, Y.S. and S.S. Venkatraman, *Recovery as a measure of oriented crystalline in poly(L-lactide) used as shape memory polymer*. Acta Materialia, 2010. **58**(1); p.49 – 58.
2. Wong, Y.S., Z.H. Stachurski, and S.S. Venkatraman, *Orientation and structure development in poly(lactide) under uniaxial deformation*. Acta Materialia, 2008. **56**: p. 5083-5090.
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