NANYANG
TECHNOLOGICAL
UNIVERSITY

**FABRICATION, CHARACTERIZATION AND APPLICATIONS
OF CYCLOSILOXANE BASED HYBRID RESIN
AND NANOCOMPOSITES THEREOF**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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AND NANOCOMPOSITES THEREOF**

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

The development of high-performance polymers/composites/nanocomposites has been one of main concerns nowadays, especially considering the consumption of finite resources. Silicones, which can be made from sand, have been widely used as high-performance polymers since their initial use in World War II. In order to push the limit of silicones, cyclosiloxane polymer was developed to improve the thermal stability. However, the limited data on cyclosiloxane polymer has provided little insight into structure-properties relationship.

This thesis aims to study the structure-properties relationship of cyclosiloxane polymer, reinforce cyclosiloxane polymer by additives and nanofillers, and explore applications of cyclosiloxane polymer/composites/nanocomposites.

Through a review of the literature, the limitations in current knowledge about cyclosiloxane polymer were identified. The kinetics study was performed to better understand and control the curing process of hydrosilylation reaction between cyclosiloxanes. To better understand the structure-properties relationship, the structure of cyclosiloxane was firstly identified. It was found that cyclosiloxane polymer is a layered structure in nano-size but isotropic in bulk.

After identifying the structure, possible reinforcement methods were proposed. By adding vinyl terminated polydimethylsiloxane (PDMS), which can be covalently bonded to the layered structure, a simultaneously improved toughness, and stiffness was observed. It is proposed that PDMS exists as two phases in cyclosiloxane polymer. The homogeneously dispersed PDMS chains anchor different layered structures together, forming a 3D connected network, contributing to both toughness and stiffness while the phase separated PDMS particles only contribute to toughness, while reducing other mechanical properties.

Graphene oxide (GO) was basally modified and used to toughen the cyclosiloxane polymer matrix. A 153 increase in toughness with only 0.8 wt% graphene loading was observed. ‘Double side tape’ toughening mechanism is proposed to explain the toughening behavior and formation of micro-cracks. The increase of thermal conductivity when allylamine modified GO (GO-AA) was added into cyclosiloxane polymer is also explained by ‘double side tape’ effect of GO-AA nanosheets, which act as a staircase for phonon transfer and contribute to thermal conductivity.

Based on Thermal interface materials (TIMs) considerations, cyclosiloxane polymer was used as matrix and multi-walled carbon nanotubes (MWCNTs) were used as thermally conductive fillers. MWCNTs were modified by silica coating and/or siloxanes with double bonds before incorporating into cyclosiloxane polymer. The resulting increase in thermal conductivity was explained by alleviating modulus mismatch by silica coating, covalent bonds between the matrix and MWCNTs fillers, as well as dispersion. The insulate behavior of MWCNT-cyclosiloxane polymer nanocomposites except raw MWCNTs indicated possible candidates for TIMs.

In summary, cyclosiloxane polymer was studied from structure to properties, as well as the relationship between them. Based on the layered structure, possible reinforcement methods were carried out, and the corresponding mechanisms are proposed. Finally, MWCNTs-cyclosiloxane polymer nanocomposites were fabricated toward TIMs.

Acknowledgements

I would like to express my appreciation and thanks for help and suggestions given by my supervisor, Professor Hu Xiao of School of Materials Science and Engineering (MSE), Nanyang Technological University (NTU). He has given me much support on my Ph.D. research work, especially my research freedom and flexibility. I would like to express my thanks to Dr. Liu Ming, who is a principle investigator in Temasek Laboratories@NTU. She is co-PI of my project and has given me much advice during my Ph.D. study, in both research and life.

I would like to thank Temasek Laboratories@NTU who has provided financial support and research lab for my Ph.D. research.

I would like to express my special thanks to Dr. Zhang Liying, Dr. Tang Xiuzhi, Dr. Liang Yen Nan, Dr. Chen Xuelong, Dr. Tay Sock Peng, Dr. He Xuehan, Dr. Cai Yufeng, Dr. Cheah Jun Wei Jason, Dr. Mu Chenzhong, Ms Zhang Fan and Ms Chen Ye for their help and suggestions on my Ph.D research. I would also like to thank my colleagues, group members and friends during my Ph.D. study. You have given me much support during my Ph.D. study.

Sincere thanks to MSE and NTU, who have provided me lots of opportunities to study with and collaborate with world-class researchers. I have gained a lot in NTU, and I know this experience will be my precious treasure in my future life.

Lastly, I want to thank my family. Special thanks to my parents, my wife and my daughter-Song Jingyi Annie. I want to express my thanks to my wife. She has given me much support on my Ph.D. study and given birth to our baby as well as taking care of her. Thanks to all my family members.

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Abbreviations

AFM	Atomic Force Microscopy
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
GO-AA	Allylamine Modified Graphene Oxide
HPPs	High Performance Polymers
HRR	Heat Release Rate
MWCNTs	Multi-Walled Carbon Nanotubes
PCFC	Pyrolysis-Combustion Flow Calorimetry
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TIMs	Thermal Interface Materials
TMA	Thermomechanical Analysis
XPS	X-ray photoelectron spectroscopy

Chapter 1

Introduction

This chapter provides a framework for this thesis by presenting a brief background of the challenges of present high-performance polymers and introduces cyclosiloxane polymer as a candidate. The hypothesis that cyclosiloxane polymer is a layered structure is put forward in this chapter, followed by objectives of this thesis based on this hypothesis. The objectives consist of curing kinetics study, basic characterizations, toughening of cyclosiloxane polymer, and functionalization of cyclosiloxane polymer. A dissertation overview is listed in this chapter, followed by the key findings and outcomes corresponding to the objectives.

1.1 Hypothesis/Problem Statement

High-Performance Polymers (HPPs) which are also called thermally stable or heat-resistant polymers can provide long-term services at elevated temperatures and have resistance to chemical reagents, radiation, and oxidative degradation¹. Many scientists and engineers have been making efforts to develop new high performance polymers to meet the requirements of operation in harsh environments such as high temperature, high pressure, and oxidizing and corroding atmospheres.² One representative high-performance polymer is polyimide which has been most widely used in various fields due to its excellent mechanical properties, electrical properties and resistance to extreme environments conditions.³ Various types of research from molecular design to nanocomposite fabrication have been done to qualify the present high-performance polymers to fit the stringent requirements^{1,3,4} but the final polymers or nanocomposites still suffer from limited improvements, sacrifice of other properties and high processing costs. The commonly used or researched high-performance polymeric materials are composed primarily of carbon backbones which originate from limited resources such as coal, petroleum oil, and natural gas. Besides being produced from non-renewable resources, the release of toxic substances generated during production process lead to contamination of our environment, which has been a growing issue which needs to be solved urgently.

Being aware of the issues listed and discussed above, governments have put much effort on seeking sustainable resources to meet the needs of the public. In this case, there is a great need for the investigation of alternative polymer materials from renewable resources.

Silicon-containing polymers or organosilicon polymers (normally called silicones) which can be prepared from sand are one of the possible high-performance polymers. They are being categorized as organic-inorganic hybrid materials since they possess advantages of the inorganic backbones and the organic side groups.⁵ The word ‘Silicone’ was first coined by Frederick S. Kipping⁶ (1863-1949, University College, Nottingham, England)

after several years of research on organosilicon compounds. Though the molecule synthesized by Kipping was actually a cyclic trimer, the misleading name ‘Silicone’ has persisted till today. Nowadays the word ‘Silicone’ refers to polymers that are based on siloxane backbones (-Si-O-) with substitution of other organic groups, and these polymers are also called siloxane polymers or polysiloxanes.^{7,8}

Figure 1.1 General molecular structure of silicones or polysiloxane.

R₁ and R₂ are organic groups attached to Si atoms.

Since first being commercialized by Dow Corning Corporation in the 1940s, a variety of silicones emerged both in academics and industries, especially after their excellent performances were recognized by the military during World War II. Of all these silicones, polydimethylsiloxane (PDMS, Figure 1.2) has been investigated and applied the most. The linear polysiloxanes have found applications in personal and house care, textiles and coatings, as well as engineering materials⁹.

Figure 1.2 Molecular structure of polydimethylsiloxane. R = CH₃, OH, Vinyl, etc..

Despite the outstanding performance at elevated temperatures compared to other organic counterparts, PDMS still suffers from decomposition which leads to failure of

performance above 200 °C¹⁰. In this case, modifications of PDMS have been done to improve its properties but have produced only limited improvements.^{7,11,12}

Silicone resin, which contains less organic parts, can be used at temperatures above 1000 °C. However, the processing is complicated, and the small molecular species generated during processing may cause defects in the final products. In addition, the operating temperature normally depends on the final sintering temperature, at which the final materials is rather an ‘inorganic ceramic’ than a silicone resin. It is a great challenge to get a defect-free silicone resin and the complicated curing procedure further hindered its applications.

Based on the discussions above, a new silicone based high-performance polymer which can (1) operate at high temperatures higher than the operating temperature of PDMS and (2) can be produced in an easier way than silicone resins is highly desired. Strategies on reinforcement and functionalization of this new polymer are also needed to better utilize this material and composite thereof.

In a typical PDMS decomposition process, the long chain bites back, generating cyclic siloxanes (cyclosiloxanes) which evaporate quickly.^{13,14} If cyclic siloxanes are directly used as monomers to synthesize an organic-inorganic hybrid polymer network, the decomposition process can be suppressed. In this research, cyclosiloxanes which contain four Si atoms (these kinds of monomers are categorized as D₄) have been chosen as monomers since they are the dominant decomposition products and are much more economical to make of use than other decomposition products such as D₅.

Highly crosslinked polymer network usually leads to brittleness in materials.¹⁵ The cyclosiloxane based hybrid is a highly crosslinked polymer network, so it is intrinsically brittle in nature. The inter defects (weak interaction between structures) and intra defects (dangling bonds) makes the cyclosiloxane polymer more brittle. The dangling bonds inside cyclosiloxane polymers act as structural defects which may deteriorate the mechanical properties. Effective toughening can be resulted by first understanding and

bridging the defects. Thermal conductivity enhancement via simultaneous enhancement in toughness can be achieved by modified nano-fillers.

1.2 Objectives

This research project aims to better understand the relationship between cyclosiloxane based polymer network structure and properties, and exploring toughening mechanism and possible functional properties of the modified polymer network or nanocomposites.

In order to develop cyclosiloxane based high performance polymers or its nanocomposites, specific objectives are listed as below:

1. To study the curing kinetics of the cyclosiloxane polymer to better understand and control the hydrosilylation reaction between cyclosiloxanes, as well as basic characterizations of it to identify the structure, based on which reinforcement strategies are put forward.
2. To study the reinforcement and toughening mechanisms of covalently bonded additives to better understand how they contribute to the reinforcement of toughening of cyclosiloxane polymer.
3. To study the reinforcement mechanism and possible functionalization of nanofillers such as CNTs and Graphene to better understand the structure-property relationship of nanocomposites.

1.3 Dissertation Overview

The thesis addresses the issue of developing green high-performance polymers through suppressing the decomposition process and sealing the dangling bonds inside the polymer networks to improve mechanical properties and render possible functionalization.

Chapter 1 provides an introduction to my research, a brief and rational research background which presents the current challenges, the research objectives, and dissertation overview.

Chapter 2 presents a comprehensive review of published literature and summarizes the current state of research into cyclosiloxane polymers. This chapter concludes a summary of past research on it, knowledge gaps which have not been covered by past research and potential areas for further studies and novel research.

Chapter 3 presents the methodology adopted to study cyclosiloxane based polymer and its nanocomposites. The experimental processes, instruments, methods for data analysis and some particular methods used are detailed in this chapter.

Chapter 4 presents the results and discussions of the findings from kinetics study and basic property study of this cyclosiloxane based polymer network. The experimental conditions are explored and possible applications of neat cyclosiloxane hybrid polymer are suggested in this chapter.

Chapter 5 presents the results and discussions of the findings of PDMS modified cyclosiloxane polymer. The roles of PDMS at different loadings are discussed and possible toughening mechanism was proposed.

Chapter 6 presents the results and discussions of the findings of cyclosiloxane/Graphene nanocomposites. The influence of covalent bonds on mechanical properties and thermal conductivity is discussed. A possible toughening mechanism was proposed to explain the toughening effect of Graphene.

Chapter 7 presents the results and discussions of the findings of Multi-Walled Carbon Nanotubes (MWCNTs) nanocomposites. The roles of covalent bonds and silica coating in enhancing thermal conductivity are discussed.

Chapter 8 summarizes the overall findings of this thesis and highlighted the significant achievements of this work. Recommendations for future work are presented.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. The identification of the structure of cyclosiloxane hybrid polymer, which acts as a mainline connecting problems and solutions together. The cyclosiloxane polymer is a layered structure at nano scale but isotropic at the macro scale. The following reinforcement/toughening strategies are suggested based on its unique structure.
2. Assessing the mechanical properties of vinyl terminated PDMS reinforced cyclosiloxane hybrid materials and proposing mechanism to explain it. A simultaneous improvement in toughness and stiffness were observed. More than 200% improvement in toughness was observed with PDMS loading from 0.04 wt% to 0.08 wt%. It is proposed that the vinyl PDMS exist as two phases in cyclosiloxane polymer. The homogeneously dispersed PDMS chains contribute to both stiffness and toughness, while the separated PDMS particles are responsible for toughening effect and decrease in other mechanical properties.
3. Assessing the mechanical properties of modified graphene oxide reinforced cyclosiloxane hybrid materials and a proposing mechanism to explain it. Graphene Oxide was basally functionalized by allylamine and incorporated into cyclosiloxane polymer via solventless in-situ polymerization. The cyclosiloxane/graphene nanocomposite showed 153% improvement in toughness with 0.8 wt% loading of modified graphene oxide. It is proposed that the 'double side tape' graphene can bind layered structures together to toughen the cyclosiloxane polymer. The 'double side tape' graphene acts as a staircase for phonon transfer which contributes to the thermal conductivity of cyclosiloxane/graphene nanocomposites.
4. Assessing the thermal conductivity of nanocomposites and proposing a mechanism to explain the improvements. The influence of silica coating and surface modification by siloxanes with double bonds is discussed. The insulating behavior of MWCNTs-cyclosiloxane polymer nanocomposites except for the one with raw MWCNTs indicated their being possible candidates for thermal interface

materials.

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Chapter 2

Literature Review

This chapter presents a review of available literature, which contains all the research and related research that has been done during the past decades. This review of literature covers three parts regarding respectively cyclosiloxane polymers, toughening agents, and thermally conductive fillers. Excellent properties and applications of cyclosiloxane polymer are summarized, but it is pointed out that the reinforcement of cyclosiloxane polymer is still a problem. By reviewing rubber phases and nano-fillers as toughening agents, toughening strategies are put forward according to the structure of cyclosiloxane polymer. The review of thermally conductive fillers reveals that graphene and multi-walled carbon nanotubes (MWCNTs) show prospects for improving the thermal conductivity of the cyclosiloxane polymer matrix, and the challenge of dispersion is highlighted here. This review highlights the need for further study of cyclosiloxane polymer and composites thereof to improve their performance. The limited information on the cyclosiloxane hybrid polymer materials indicates opportunities and potential for research: to better understand the structure - property relationships, to create knowledge and to bring light on this material and the potential for transfer from laboratory to industry.

2.1 Introduction

This chapter presents a review of published literature in related fields, which comprise of high-performance polymers and cyclosiloxane hybrid polymers. The study of cyclosiloxane hybrid polymers including basic properties and demonstrated applications is reviewed as well as the history of cyclosiloxane hybrid polymers, followed by a discussion which identifies key points from the review of the literature. The gaps are highlighted to address the inspiration and importance of this thesis.

Work in which cyclosiloxane parts were used as part of a polymer or the core of some dendrimers is not summarized here since it is not highly related to this thesis topic.

2.2 High-Performance Polymers, Organic-inorganic Hybrid Materials and Cyclosiloxane Polymer Hybrid

2.2.1 Definition and Types of High-Performance Polymers

Generally, materials which can be used at high temperature are called high-temperature materials (HTMs), in which the term ‘high temperature’ depends on the application or service environment. HTMs have various applications and are widely used in aerospace, high-temperature processing or heat treatment equipment, energy conversion processes, high-temperature devices and so on.^{1,2} However, thermal stability is not the only criteria for HTMs because the application conditions are always coupled with other requirements such as anti-oxidation, chemical resistance, mechanical properties, thermal conduction and even high-temperature electric conductivity.

Apart from metals, alloys, and ceramics, polymers are also good candidates for high-temperature applications due to their light weight, easy processing and low cost. High-performance polymers (HPPs) which are also called thermally stable or heat-resistant polymers are a set of polymers which can perform long-term service at elevated temperatures and have resistance to chemical reagents, radiation, and oxidative

degradation³. It is arbitrary to classify HPPs into different types since there are many ways of classifying them according to different standards. However, when it comes to normally used HPPs, some types of HPPs should be noted. Polyimide (PI), polysulfone (PSU), polyetherimide (PEI), poly(phenylene sulfide) (PPS), polyetheretherketone (PEEK) and polyetherketone (PEK) are the most commonly used ones⁴. Besides the types listed above, researcher also introduce fluorine atoms or phenol groups into polymers to synthesize fluoropolymers or aromatic polymers which are categorized as HPPs since polymers with fluorine and phenol groups incorporated are thermally stable, chemical resistant, etc.⁵

2.2.2 The Art of Organic-Inorganic Hybrid Materials

Though a lot of research has been done on the high performance polymers mentioned in 2.2.1, they are all pure organic compounds (carbon based) which generally arise from finite resources such as petroleum, coal, and natural gases. The inevitable running out of these resources pushes the investigation of alternative polymer materials. In this case, silicon based materials are considered as good candidates since silicon is 60 times more abundant in the earth's crust than carbon and, in principle, they can be synthesized from sand and carbon dioxide, which suggests that they are sustainable. Siloxane polymers, which are normally called silicones or polysiloxanes, are a type of materials composed of -Si-O- backbones with monovalent organic radicals attached to each silicon atom⁶ and these polymers are one of the most important silicon-containing polymers. Polysiloxanes are categorized as organic-inorganic hybrid materials since this material is inorganic in backbone and organic in the side groups⁷. The properties of organic-inorganic hybrid materials benefit from both the organic parts, which provide elasticity, flexibility and toughness, and the inorganic parts, which provide high-temperature resistance, anti-oxidation, high strength, and hardness. (Figure 2.1)

Figure 2.1 Combination benefits of organic-inorganic hybrid materials.

2.2.3 From Linear Polysiloxane to Cyclosiloxane Polymers

Due to the combination of benefits from both inorganic –Si-O- backbones and organic side groups, polysiloxanes usually have high chain flexibility, low glass transition temperatures, good cold and heat stability including anti-oxidation, excellent dielectric properties, good weathering properties, and biocompatibility^{6,8}. They have found applications in molding, automotive industry, aviation, aerospace, electronics industry, and medical devices^{8,9}. The most widely used polysiloxane is polydimethylsiloxane (PDMS) which is representative of the polysiloxane family, and has found many applications in the fields mentioned above. As mentioned in Chapter 1, in order to push the thermal limit to a higher value, cyclosiloxane monomers are considered to suppress the decomposition process, contributing to thermal stability.

2.3 Cyclosiloxane Polymers

2.3.1 Various Cyclosiloxane Polymers

Generally in this thesis, polymers synthesized from cyclosiloxanes are called cyclosiloxane polymers. Cyclosiloxanes are normally called D_n , where n is the number of siloxane units in the cyclosiloxane molecule (Figure 2.2). D_3 , D_4 and D_5 are the most commonly used cyclosiloxanes¹⁰. However, in order to form a cyclosiloxane polymer hybrid, functional groups which can provide connections or bridges between cyclic

components should be introduced onto cyclosiloxanes. In general, Si-H, Si-C=C and Si-OH groups are most commonly used. In this thesis, the cyclosiloxane polymer will be polymers synthesized from D₄ cyclosiloxanes and the term cyclosiloxane polymer stand for D₄ cyclosiloxane polymer, unless otherwise stated.

Figure 2.2 Different types of cyclosiloxanes.

2.3.2 Discovery of Cyclosiloxane Polymers

In 1993, DuPont Corporation crosslinked cyclosiloxane with functional groups via hydrosilylation method and categorized the product as high-temperature polymers.¹¹ In this report, the thermal stability and the decomposition method was investigated. It was pointed out that this cyclosiloxane polymer hybrid was thermally stable up to 400 °C with only 2-4 wt% loss being observed. The weight loss below 525 °C was mainly due to cleavage of organic groups, while above 525 °C decomposition of cyclosiloxane polymer hybrid network occurred followed by complex reformation of the network, giving a high char yield (84%) at 950 °C in nitrogen. Similar thermal stability was observed with 82% char yield at 950 °C in air expect for a slight increase (0.4%) above 200 °C due to oxidation. In conclusion, this kind of organic-inorganic cyclosiloxane polymer hybrid

showed very good thermal stability at elevated temperatures and is a possible candidate high-performance polymer.

Figure 2.3 Organic-inorganic polymer hybrid synthesized from cyclosiloxanes¹¹.

2.3.3 Applied as Preceramic Polymers

Through a controlled heat treatment, polymers which can be converted into ceramic are called preceramic polymers.¹² The ceramic derived from preceramic polymers after heat treatment is called polymer derived ceramic^{13,14} and has found applications in many areas such as aerospace. There are various types of preceramic polymers, and Si-containing polymers have been researched most because of high ceramic yields after heat treatment¹⁵. Due to excellent high thermal stability (stable up to 1200 °C in air) of silicone oxycarbide (SiCO), which can only be produced from pyrolysis of polysiloxanes¹⁴, polysiloxane preceramic polymers has drawn much attention during the past decades¹⁶.

Figure 2.4 Types of preceramic organosilicon polymers¹⁴.

Due to high char yield of cyclosiloxane polymers, they have been explored as preceramic polymers to produce SiCO ceramic. Nyczyk et al.¹⁷ studied the curing process of several preceramic polymers and revealed that cyclosiloxane polymers showed the best thermal stability and were good candidates to produce SiCO ceramic protective coatings.

Schiavon et al.¹⁸ performed decomposition kinetics study in which both thermal stability and activation energy for the degradation process were determined for a series of preceramic polymers. The relationships between properties and polymer network structure were discussed. It was also pointed out that high crosslinking density in the preceramic polymers contributes to the increase of ceramic yields, which is a desirable feature of preceramic polymers.

Sousa et al.¹⁹ investigated two preceramic polymers - one was a linear polysiloxane crosslinked with cyclosiloxane and the other one was a cyclosiloxane polymer. The mineralization process was studied and the temperature for reorganization reactions of

siloxane sites was about 600 °C. The redistribution of Si sites was present till 800 °C. At 1000 °C the resulting SiCO ceramic was a mixture of random distributed SiO_4 , SiO_3C , SiC_2O_2 and SiC_4 . Further study by XRD (Figure 2.5) showed that the SiCO produced by pyrolysis at 1000 °C is an amorphous material, while from 1200 °C the presence of β -SiC indicates beginning of the crystallization process.

Figure 2.5 XRD pattern of cyclosiloxane polymer generated by pyrolysis for 2 h at various temperatures¹⁹.

2.3.4 Applied as Pure Polymer

Redondo et al.²⁰ investigated the gas permeability of this cyclosiloxane polymers and it was found that cyclosiloxane polymer membrane showed lower gas permeability (O_2 , N_2 , CO_2 , CH_4 and H_2) but higher selectivity coefficients (O_2/N_2 and CO_2/CH_4) than PDMS membrane, which resulted from a decrease in the free volume. This indicated possible application in gas separation processes.

Inspired by the report from DuPont Corporation¹¹, Zheng and McCarthy²¹ performed a further study on this unique cyclosiloxane polymer (Figure 2.6). They found that, apart from good thermal stability, this cyclosiloxane polymer showed hard material behaviour but elasticity during nanoindentation test with a few hundred of nanometres indentation. It was found that this material showed more than 90% transmittance in visual light range while reduced transmittance in UV range due to the presence of platinum catalyst. AFM results showed that the surface roughness is around 0.1 nm, indicating very smooth surface which might be used as a mold to replicate very small features. After optical, mechanical and surface tests, they reported that cyclosiloxane is ‘an unusual material that has multiple uses’ which is still being explored.

Figure 2.6 Synthesis and structure of cyclosiloxane polymer²¹.

Because of high transparency, thermal stability, high modulus, low surface roughness (<0.1 nm), low surface energy and low viscosity precursors, the cyclosiloxane polymer hybrid can be used as replica material.²² In order to demonstrate the replica properties, Zheng an. McCarthy²² used cyclosiloxane polymer as a mold material for nanoimprinting lithography and capillary force lithography. Cyclosiloxane polymer hybrid could replicate sub-10 nm features of anodized aluminum master and transmit these features to an epoxy granddaughter (nanoimprinting lithography) and a PMMA granddaughter (capillary force lithography), demonstrating that a cyclosiloxane polymer hybrid could be a candidate replica material.

Figure 2.7 AFM height images and section analysis data

- (a) Anodized Al foil master,
- (b) cyclosiloxane polymer daughter,
- (c) epoxy granddaughter (nanoimprinting lithography),
- (d) PMMA granddaughter (capillary force lithography)²².

Apart from hydrosilylation method to cyclosiloxane polymer, Yoo²³ et al. reported an initiated chemical vapor deposition (iCVD) method to prepare a cyclosiloxane polymer

coating. In this report the authors deposited two separated polymer layers- cyclosiloxane polymer (p(V4D4)) and poly(1H,1H,2H2H-perfluorodecylacralate) (p(PFDA)) on hydrophilic textured fabrics via a solventless iCVD method. The coating of cyclosiloxane polymer and p(PFDA) significantly changed from hydrophilic surface to superhydrophobic surface, enhanced water repellency, increased the durability against mechanical and chemical stresses, and resistance to UV and ultrasonic.

Figure 2.8 A schematic structure of cyclosiloxane coated fabric²³.

2.3.5 Other Cyclosiloxane Polymers

As mentioned in 2.3.1, other than D₄ cyclosiloxane polymer, there are also other cyclosiloxane polymers or polymers incorporating cyclosiloxane. In order to better understanding the advantage and disadvantages of pure D₄ cyclosiloxane polymer, other types of polymer involving cyclosiloxane should be reviewed for comparisons.

To the best of my knowledge, there has been limited work on other pure cyclosiloxane polymers, probably due to complicated way to fabricate them and low synthesis yields, resulting in very high prices.

Kurian et al.²⁴ synthesized D₅ cyclosiloxane polymer via a hydrolysis-polycondensation method. D₅ cyclosiloxane polymer showed the lowest glass transition temperature (-151 °C) till now and it was thermally stable up to at least 700 °C, which might be due to the reduction in organic parts compared to D₄ cyclosiloxane polymer. However, this D₅ cyclosiloxane polymer was a powder-like brittle solid and could not be shaped.

Figure 2.9 Synthesis of D₅ cyclosiloxane polymer²⁴.

There are also many other reports incorporating cyclosiloxanes into polymer networks²⁵⁻³² hydrosilylation, condensation or other ways, the main idea of introducing cyclosiloxane was to increase the thermal stability of the polymer or fabricating new kinds of preceramic polymers and high-temperature adhesives^{27,30,31}. Other studies involving cyclosiloxane also showed promising applications in other fields such as optical and encapsulation of light emitting diodes (LED).^{33,34}

2.4 Gap in Cyclosiloxane Polymers and Solutions

2.4.1 Gap

Thus cyclosiloxanes have proved that they are a good candidates as monomers for high-performance polymers since it has many advantages such as high-temperature stability, low surface energy, elasticity, transparency, low surface roughness, etc²¹. The application in preceramic polymer to produce SiCO ceramics has been well studied¹⁹, but the cyclosiloxane polymer was researched as an intermedia material toward to final application materials such as ceramic parts or coatings. Limited application has been researched except replica material²². Although Zheng and McCarthy²¹ have proved that the mechanical properties of cyclosiloxane polymer is good since it is elastic and has a high modulus, the literature published to date has failed to mention the brittleness which results from high crosslink density and which remains a challenge if cyclosiloxane is to be applied directly as a polymer. To the best of my knowledge, there has been no report on the reinforcement of cyclosiloxane polymers including toughening.

Reinforcement of cyclosiloxane polymer especially toughening can enable it to meet higher application requirements and possible functionalization of it will make it qualified for new applications such as thermally conductive resin for electronic device encapsulation.

2.4.2 Possible Solutions – From Structure To Property

Reinforcement of polymers can be achieved by modifying structure and add particles/fillers to tune the mechanical properties. Since cyclosiloxane is brittle in nature, the main issue that needs solving is toughening.

Traditional ways to toughen polymers is adding rubber phase into them, effective but large quantity needed.³⁵ Recently, the development of nanotechnology has provided more opportunities for toughening brittle polymers. The nanosized fillers, such as graphene and carbon nanotubes have broadened the ways to reinforce polymers as well as providing the polymer nanocomposite with multi-functionalities, such as electrical conductivity and thermal conductivity.

In the following part (2.5), the toughening of brittle polymer matrix as will be reviewed.

2.5 Toughening of Polymer Thermoset

2.5.1 Rubber Phase

Blending of polymer thermosets with rubber phase is routinely employed to improve the toughness of a matrix. The toughening mechanism of rubber phase is shown in Figure 2.10 regardless of whether the rubber phase is produced via phase separation³⁶⁻⁴⁰ or added as rubber particles⁴¹.

Figure 2.10 A schematic representation of the different toughening mechanisms from rubber phase toughened polymers.⁴²

Of all possible rubber phases, PDMS is one of the most widely used materials to toughen polymer thermosets. Usually, PDMS separates from epoxy phase and forms rubber particles that contribute to the increase of toughness, but a large amount is needed (15-20 wt%) to achieve the desired toughness. This excessive amount of PDMS would deteriorate other mechanical properties⁴³.

In the most researched epoxy thermosets, pure PDMS was rarely used as toughening agent because of poor compatibility between siloxane segments and epoxy segments⁴⁴. In order to overcome this problem, the interaction between PDMS and epoxy was created by introduction of bridges between them or directly incorporating siloxane chain into epoxy chains^{45,46}. The nature of cyclosiloxane polymers is same as PDMS. However, this still cannot guarantee compatibility between them. Zhu et al.⁴⁷ studied the influence of homogeneously dispersed PDMS via coupling reaction on toughening brittle silicone resin, which also has the same nature as PDMS. It was found that the enhanced inelastic deformation was the main reason why fracture toughness increased. In this paper, it was also found that the compatibility of the PDMS depended on the chain length of the PDMS, which means longer chains are less compatible with silicone resin and the separated domains did not toughen silicone resin. Zhou et al.⁴⁸ studied the toughening effect of long chain and short chain PDMS and they found that a proper combination of long chain and short chain PDMS could effectively toughen silicone resin and the effectiveness depended on the particle size. Submicron sized particles are more effective than particles larger than a few tens of micros and the deformation of grains induced by long chain PDMS was responsible for the increased fracture toughness. (Figure 2.11)

Figure 2.11 Schematic illustration of long chain PDMS formed particles (b) is the same as (a) except for the grains which are omitted.⁴⁸

2.5.2 Graphene/Graphene Oxide/Modified Graphene Oxide

Graphene, since its discovery by Geim, Novoselov et al.⁴⁹, has drawn much attention due to its two dimensional structure (2D)⁵⁰. The high theoretical surface-to-mass ratio of $\sim 2600 \text{ m}^2/\text{g}$ ⁵¹, high strengths, and high elastic moduli⁵² has made it an ideal material for various applications. The electrically conductive and thermally conductive nature⁵³⁻⁵⁷ has widened its application fields out of strong scientific and technological interest. Graphene can be prepared by mechanical exfoliation, epitaxial growth, chemical vapor deposition and the reduction of graphene oxide^{58,59} (GO). The first three methods give graphene with relatively perfect structure. However, GO can be prepared by oxidizing inexpensive graphite with high yield and the highly hydrophilic nature of GO, which results from oxygen-containing groups, makes it form stable aqueous colloids⁵³ which is critical for large-scale use and easy processing. Defect-free graphene which has perfect structure is brittle while oxygen-containing groups on GO can help to dissipate strain energy and hinder crack propagation.⁵² In particular, GO offers a tremendous opportunity via chemical functionalities of epoxide and hydroxyl groups on its basal plane and carboxyl groups on the edge⁶⁰.

Particularly in polymer composites, chemically modified graphene has provided new insight to composite research. The modification of GO, as mentioned above, has been a promising way to fabricate polymer composite since it can provide modified GO in mass production⁶⁰.

In polymer composites, GO was either simply blended into a polymer matrix⁶¹⁻⁶⁴ or chemically modified to get a better dispersion (by both covalent and non-covalent bonding to polymer matrix)⁶⁵⁻⁶⁷. When it comes to mechanical properties, chemically modified GO is favourable because of the good interaction between the modified GO and polymer matrix, the dispersion of the modified GO sheets, and the homogeneity of the polymer composite.⁶⁶ Processing of graphene-polymer composites can be summarized into three methods⁶⁶: (a) melt intercalation in which melt blending and mechanical mixing are used to disperse graphene nanosheets into polymer matrix. The absence of organic solvents and easy processing make it economically attractive and scalable method for industries; (b) solution dispersion in which the blending of polymer/monomer

and graphene nanosheets is conducted in solvents. Sonication is often used in this method to get better dispersion. This method is the widely used for fabrication of elastomer/graphene composites⁶⁸⁻⁷⁰; and (c) in situ polymerization in which the graphene nanosheets was mixed with monomers with or without solvent, followed by in situ polymerization. As polymerization goes on, the space between graphene layers increases and finally a polymer composite with exfoliated graphene nanosheets is obtained. All the three methods mentioned above have been used according to different requirements and polymer/monomers conditions.

Figure 2.12 A schematic representation for solution dispersion to fabricate TPU/graphene composite.⁷¹

Due to the high surface area and outstanding mechanical properties from unique structure, graphene has been used to reinforce polymer matrix at lower loadings, compared to other carbon filler such as carbon nanotubes.^{53,59,72} Rafiee et al.⁷³ first studied the toughening effect of graphene in composites in 2010 and found that with only 0.125 wt% loading of

modified graphene, the toughness was increased by 65%, showing a better result than for carbon nanotubes composite (11% increase in toughness at 2.5 wt% loading). Meanwhile, the Young's modulus of 0.125 wt% loading of modified graphene composite increased by 50%. It was found that crack deflection appeared to play a significant role in toughening. Following this work, researcher studied the toughening effect of graphene in various matrixes, from polymer^{43,74} to ceramic⁷⁵. In summary, toughening mechanisms of graphene can be categorized into following types: crack deflection^{73,75-83}, crack bridging^{75,76,79,81,82,84}, sheet wrapping⁷⁵, pull-out^{75,76,79,82}, micro-cracks^{43,85,86}, void⁴³, layer breakage⁴³, crack pinning,^{54,74,81,87} plastic zone deformation^{77,81}, crack branching⁷⁹, crack necking⁷⁹, bi-furcation^{54,83,87}, and so on.

Figure 2.13 Percentage of enhancement in fracture toughness in epoxy upon addition of graphene nano-filler observed in literature.⁸³

A summary of graphene loadings in epoxy versus toughness is shown in Figure 2.13. As can be observed from the plot, the toughening effect can give more than 30% increase with a low graphene loading. However, the number of stacked layers, the

functionalization degree, the size of graphene sheets and the dispersion is critical for the scattering of data collected.⁸³

To push the limit to lower graphene loadings for toughening effect, Park, et al.⁸⁶ studied epoxy toughening with low graphene loading, and they found that with only 0.04 wt% functionalized graphene loading, the epoxy composite showed 50% improvement in fracture toughness. The formation of micro-cracks at low graphene loading was responsible for the increase of toughness.

2.6 Thermally Conductive Polymer and Composite thereof

2.6.1 Significance Thermally Conductive Polymer and Composites

Thermal dissipation is critical to the performance, lifetime, and reliability of electronic devices⁸⁸ and thermal management in new applications such as light emitting diodes still remains a challenge.

The thermal conductivity of polymers can be calculated from the Debye equation:

$$\lambda = \frac{C_p v l}{3} \quad (2.1)$$

where C_p is the specific heat capacity per unit volume; v is the average phonon velocity; and l is the phonon mean free path. Typically in amorphous polymers, l is extremely small due to phonon scattering, leading to a very low thermal conductivity of polymers.⁸⁹

To meet the requirement of new applications, the development of polymer-based composite with enhanced thermal conductivity is in great need.

2.6.2 Graphene-Based Thermally Conductive Composites

Traditionally, heat conductive fillers, such as aluminum oxide, boron nitride, metal particles, diamond, carbon nanotubes (CNTs) and graphene are introduced into polymers to enhance thermal conductivity. CNTs and graphene stand among fillers with highest

thermal conductivity, 1000-4000 W/mK and 2000-6000 W/mK, respectively⁸⁸. The light weight compared with metal and ceramic fillers is another advantage of CNTs and graphene.

2.6.3 Carbon Nanotubes (CNTs) Based Thermally Conductive Composites

CNTs has been successfully incorporated into various polymer matrixes such as silicone^{90,91}, polystyrene⁹², epoxy⁹³⁻⁹⁷, polyurethane⁹⁸, and so on. It was reported that the structure, defects, size, purification and functionalization of CNTs have an influence on thermal conductivity of CNTs and thus influence thermal conductivity of CNTs/polymer composites.^{89,99} For the CNTs/polymer composites, the interfacial resistance plays a critical role in thermal conductivity of the composites since the interfacial barrier caused scattering of phonons which leads to decrease in thermal conductivity⁹⁹. The strong interfacial phonon causes a large difference between experimental data and theoretical data⁹⁴. In order to minimize the difference, functional groups which could provide a strong interaction between polymer and CNTs were introduced to get better dispersion and reduce the interfacial resistance^{97,100,101}, contributing to higher thermal conductivity at same CNTs loadings. Another way to enhance the phonon transportation between the polymer matrix and CNTs is to introduce an intermediate which alleviates the modulus mismatch between polymer and CNTs and improves the interaction between them⁹⁴. Typically, silica was coated onto CNTs to perform alleviation effect and lots of research has proved the feasibility^{91,102,103}. It was proved that the thickness of silica coating^{103,104} and the functionalization of silica coating¹⁰⁵ have an effect on composite thermal conductivity. Another art of CNTs coated with silica is that the insulate silica shell can make CNTs nonconductive, which is critical for electronic packaging⁹⁴. Cui et al.⁹⁴ studied the influence of silica coating of CNTs on thermal conductivity, and found that silica coating could help to alleviate the modulus mismatch and thus contributed to thermal conductivity(67% improvement at 1 wt%). Silica coated CNTs have been studied in various matrices and thermal conductivity enhancement was observed in all of them^{91,102-105}.

Figure 2.14 A schematic illustrating the fabrication of silica coated CNTs.⁹⁴

2.7 Evaluation of Literature Review

This review of literature has covered three parts regarding cyclosiloxane polymers, toughening agent, and thermally conductive fillers. This review has highlighted the need for further study of cyclosiloxane polymer and composites thereof in order to better understand structure – property relationship. This review focuses on toughening of a polymer matrix and of thermally conductive polymer/composites.

The issue of brittleness has long been the problem of highly crosslinked polymer thermosets. Though various toughening agents have been used and many toughening mechanisms have been put forward, a lack of knowledge on toughening silicone resins, of which cyclosiloxane polymer is one, still remains a problem because silicone resins are organic-inorganic hybrid materials, in which case it is difficult to assess the toughness in normal way. In this case, only a few papers have been published on toughening of silicone resins, especially the resins whose structures are clearly known. The traceable publications were based on commercial silicone resins whose formula tends to be kept

secret and contribute little to structure–property relationship knowledge and toughening mechanism development.

Having brought the challenge of toughening to bright, it is very important to find a proper toughening way and create an understanding of toughening mechanisms in cyclosiloxane polymers. To the best of my knowledge, toughening of cyclosiloxane polymer remains unknown since there is no publication on this yet. Though published papers have described the properties of cyclosiloxane polymers, their structure has not been identified. In order to better understand the structure – property relationship and develop a series of reinforcement/toughening mechanisms, identification of the structure is critical.

With the capability of identifying structure of cyclosiloxane polymer, the reinforcement/toughening strategies can be employed. The strategies should be designed according to the structure of cyclosiloxane polymers to make it better candidate for high performance polymer.

Considering low viscosity of monomers, the cyclosiloxane polymer/composite should be possible candidate for thermal interface materials. The easy processing makes it suitable for direct coating and infusing into the gap between thermal management parts. The key part here is how to improve the thermal conductivity of cyclosiloxane polymer. Due to hydrophilic nature of GO and oxidized CNTs, they are hard to be dispersed in hydrophobic cyclosiloxane monomers. Chemical modification of these fillers is to be conducted and the thermal conductivity of resulting composites is assessed.

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Chapter 3

Experimental Methodology

This chapter presents the principles behind the research experiments carried out. Non-isothermal differential scanning calorimetry (DSC) was chosen to study the curing kinetics. Rheological testing and fourier transform infrared spectroscopy (FTIR) were used to further characterize the curing behaviors. Morphological tests, such as atomic-force microscopy (AFM), scanning electron microscope (SEM) and transmission electron microscopy (TEM) were selected to study the structure of the cyclosiloxane polymer. Mechanical tests such as the three-point bending test, nanoindentation and compression were used to study how the rubber phase or nano-fillers influence the mechanical properties of cyclosiloxane polymer composites. The discussion of the experimental approach and justifications of how the selected approaches were appropriate to fulfill the objectives of this thesis are given here.

3.1 Introduction

From previous literature review of cyclosiloxane polymer, it was shown that the reinforcement/toughening of this hybrid polymer remains as an issue of concern for high performance applications. Limited literature and the lack of understanding of cyclosiloxane polymer further challenge the task of reinforcement.

The aim of this thesis is to develop cyclosiloxane based high-performance polymers or composites, and the specific objectives are listed as below:

1. To study the curing kinetics of the cyclosiloxane polymer to better understand and control the hydrosilylation reaction between cyclosiloxanes, as well as basic characterizations of it to identify the structure, based on which reinforcement strategies are put forward.
2. To study the reinforcement and toughening mechanisms of covalently bonded additives to better understand how they contribute to the reinforcement of toughness of cyclosiloxane polymer.
3. To study the reinforcement mechanism and possible functionalization of nanofillers such as CNTs and Graphene to better understand the structure-property relationship of nanocomposites.

In order to fulfill the specific objectives, the thesis will be divided into four parts: Kinetics Study, PDMS Toughened Cyclosiloxane Polymer, Graphene/Cyclosiloxane Polymer Nanocomposites and CNTs/Cyclosiloxane Polymer Nanocomposites. The experimental methodology will be given according to each chapter respectively.

3.2 The Chemistry behind Materials Fabrication

In general, there are three methods to synthesize silicon-containing polymers: polycondensation, sol-gel process and hydrosilylation.^{1,2} However, polycondensation and sol-gel process are less preferred due to the use of solvent, the evolution of small molecule during fabrication process, the high processing temperature and long processing

time are also making the processes less popular, especially for large scale production. Hydrosilylation, or catalytic hydrosilylation, involves reactions in which Si-H bonds are added onto unsaturated multiple bonds³, in particular carbon-carbon and carbon-heteroatom bonds. As illustrated by Figure 3.1, compared to polycondensation and sol-gel process, hydrosilylation does not generate any byproduct and the reaction can be conducted at a lower temperature in the presence of Karstedt's catalyst - a platinum based catalyst.

Figure 3.1 Methods for synthesis of silicon containing polymers.

3.3 Sample Preparation

3.3.1 Chemical list

The chemicals used in this thesis are listed in Appendix Table A.1 for reference.

3.3.2 General Fabrication Method for Cyclosiloxane Polymer and Composite

Cyclosiloxane Polymer: Equal amount (weight ratio was 1:1) of 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^V) were mixed together by a magnetic stirrer, followed by addition of 0.1 wt% platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst). The mixture was subject to magnetic stirring till proper viscosity

was obtained before being poured into molds and cured at room temperature for 24 h followed by 150 °C for 24 h. A molecular structure of the cyclosiloxane polymer is given in Figure 3.2.

Cyclosiloxane PDMS composites: A certain amount of PDMS was dissolved in D_4^H and D_4^V (Mass ratio of D_4^H : D_4^V was 1:1 and the content of vinyl terminated PDMS used here was 0.2 wt%, 0.4 wt%, 0.6 wt%, and 0.8 wt%, respectively.) by sonication for 5 mins. The subsequent steps were the same as in the cyclosiloxane polymer preparation procedure described in the previous session. The samples were partially cured before being cut into required dimensions and subjected to further curing.

Cyclosiloxane graphene or CNTs nanocomposites: Certain amount of graphene or CNTs was dissolved in D_4^H and D_4^V (Mass ratio of D_4^H : D_4^V was 1:1 and the content of GO or GO-AA used here was 0.02 wt%, 0.04 wt%, 0.06 wt%, 0.08 wt%, and 0.10 wt%, and the content of MWCNTs used was 0.5 wt%.) by sonication for 4 h. The subsequent steps were the same as in the cyclosiloxane polymer preparation procedure described in the previous session. The samples were partially cured before being cut into required dimensions and subjected to further curing.

Figure 3.2 Fabrication of cyclosiloxane hybrid polymer.

3.3.3 Modification of GO

GO was prepared according to a modified Hummer's method⁴ and dried in vacuum oven overnight before being modified by allylamine. Dried GO (100 mg) was suspended in Dimethylformamide (DMF, 100 ml), and the mixture was probe sonicated for 20 minutes to form a stable suspension. Allylamine (10 ml) was added into GO suspension and the obtained mixture was heated up to 50 °C for 48 h under continuous stirring. The solid product was separated by vacuum filtration and washed with sufficient amounts of ethanol and DI water to remove DMF and residual allylamine. After dehydration by freeze drying, the fluffy GO-AA was stored in a desiccator for further use. A schematic illustration of the allylamine treated GO is given in Figure 3.3.

Figure 3.3 Modification of GO by allylamine (Red: top basal; Blue: bottom basal).

3.3.4 Modification of Multi-Walled Carbon Nanotubes (MWCNT)

Acid-treated MWCNTs (1 g) were ultrasonically dispersed into a fixed-volume mixture of ethanol (250 mL), DI water (50 mL) and NH_4OH (8 mL, 25.0-28.0 wt%) for 30 min, followed by vigorous mechanical agitation for another 15 min to obtain a stable and homogeneous suspension. Immediately afterward, 10 mL of tetraethoxysilane (TEOS) was quickly added to the above solution and kept at room temperature for 12 h under stirring. After the reaction, the mixture was centrifuged at a moderate speed (4000 rpm). In order to fully remove free silica particles, the resultant sediment was ultrasonically re-dispersed in water for 15 min, and centrifuged. The same procedure was repeated at least four cycles. Finally, a darkish product was obtained by vacuum dried at 50 °C for 24 h, yielding silica-coated MWCNTs(CNT-2).

The acid treated CNTs or silica coated MWCNTs (CNT-2) (0.5g) was ultrasonically dispersed into a mixture solution of ethanol (250 mL), DI water (50 mL) and ammonium (8 mL, 25.0-28.0 wt%) for 30 min, followed by vigorous mechanical agitation for another 15 min to obtain a stable and homogeneous suspension. KBM-1003 or KBM-1403 (10 mL) was introduced successively to the flask and the whole system reacted at 30 °C for 24 h. When the reaction was completed, the products were separated from the mixture by centrifugation (7,500 rpm) in ethanol. The silane modified CNTs or silane modified silica coated MWCNTs were obtained by dried in a vacuum oven at 50 °C for 24 h. Schematic

illustrations of the two CNTs treatment methods are given in Figure 3.4.

Figure 3.4 Modifications of MWCNTs.

3.4 Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) Used For Kinetics Study

3.4.1 Principle of DSC

DSC is a thermal analysis technique that qualitatively and quantitatively measures the temperatures and heat flow associated with transition in samples as a function of time and temperature. A DSC measuring cell usually contains two parts: a furnace and sensors for both sample and reference pans. The principle behind DSC is that when the sample undergoes a physical transformation such as phase transitions, or chemical change such as reaction or decomposition, there will be more or less heat flowing to the sample compared with reference to main the temperatures of both same. Any physical or chemical change in sample side will lead to a peak, whether it is endothermic or exothermic. The generated peak or peaks is correlated with the heat content of the

transition. Analyzing the peaks gives us information about physical transformation or chemical reaction.

Figure 3.5 A schematic graph of heat-flux DSC.

3.4.2 Isothermal versus Non-isothermal DSC Test

DSC has been widely used for curing kinetics study. In kinetics study, isothermal⁵⁻⁸ and non-isothermal^{9,10} are most commonly used. In a non-isothermal DSC experiment, temperature and conversion contributions are not separated, and this will lead to ambiguous kinetic triplets, especially in model-fitting methods¹⁰. Isothermal DSC experiments can better provide information about kinetics models, but still non-isothermal DSC experiment was chosen to study cyclosiloxane polymer curing kinetics for the following reasons:

- a. Isothermal DSC experiment has limited temperature range. Low temperature leads to difficulty in complete cure while high temperature leads to significant cur before it reaches the set temperature.
- b. Non-zero conversion cannot be avoided in isothermal experiments.¹¹ The heating up period to set temperature cannot be taken into account while the samples have already been partially cured.
- c. Strictly isothermal DSC experiments are impossible.¹¹ Especially for cyclosiloxane polymer cure process, the heat generated during curing will lead to a change in sample temperature.

A detailed discussion is shown in Section 4.2.

3.4.3 Theory of Curing Kinetics - DSC

Kinetics deals with parameterization of process. For cure process, the reaction rate can be expressed by following equation:

$$d\alpha/dt = k(T)f(\alpha)h(P) \quad (3.1)$$

where α is the extent of conversion, t is the time, $k(T)$ is the rate constant, which depends on temperature, $f(\alpha)$ is the reaction model which depends on extent of conversion, and $h(P)$ is pressure dependence. Usually $h(P)$ is ignored in most of the thermal analysis. For our system, there are no gases reactants or products, so there is little dependence on pressure during the curing process. In this case, the reaction rate can be simplified as follows:

$$d\alpha/dt = k(T)f(\alpha) \quad (3.2)$$

$k(T)$ is usually assumed to follow the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3.3)$$

where A is the pre-exponential factor or Arrhenius frequency factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature of the sample. In the DSC test, the data can be correlated with fractional conversion and reaction rate. They are assumed to follow the following equation:

$$\alpha = \frac{\int_0^t (\frac{dH}{dt}) dt}{\Delta H_0} \quad (3.4)$$

where H is heat flow, t is the reaction time, ΔH_0 is the total reaction exothermic heat, and α is the reaction conversion. Based on eq. 3.4, the reaction rate can be described as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} = k(T)f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3.5)$$

For this kinetics study, n -th order kinetics (model kinetics) and isoconversional method (model free kinetics) are employed here.

The Borchardt and Daniels method¹² is most widely used in n-th order kinetics analysis. For this method the following equation stands:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \quad (3.6)$$

Taking the logarithm of eq. (11) yields eq. (12):

$$\ln k(T) = \ln \frac{d\alpha/dt}{(1-\alpha)^n} = \ln A - \frac{E_a}{RT} \quad (3.7)$$

By dividing curve into 20 segments (Figure 3.5) which is evenly spaced by temperature, a plot of $\ln k(T)$ versus $1/T$ should be a straight line. The activation energy (E_a) and pre-exponential factor (A) can be obtained from the slope and intercept of this plot respectively.

Figure 3.6 Illustration of analysis of DSC curve by Borchardt and Daniels method.

However, the Borchardt and Daniels method is based on an assumption that E_a is independent of α . This method is strictly applicable only for simple or elementary reactions. In most cases, this assumption is not valid because the overall process usually contains several reactions which involve multiple steps of both chemical and physical process. Activation energy varies with overall α , in which case E_a should be better expressed as $E_a(\alpha)$ ^{13,14}. Thus, the Borchardt and Daniels method can only be applied to a single linear peak. Furthermore, the unknown reactions model and false mechanistic assumptions may invalidate the Borchardt and Daniels method, so a model free kinetics method is preferable.

Another widely used n -th order kinetics model is the Kissinger method¹⁵. Because of its easy use, the Kissinger method has also been used for determining activation energies. In this method, the following equation stands:

$$\ln \frac{\beta}{T_p^2} = \ln \left(-\frac{AR}{E_a} f'(\alpha) \right) - \frac{E_a}{RT_p} \quad (3.8)$$

where $f'(\alpha) = df(\alpha)/d\alpha$. In the Kissinger method, a plot of $\ln \frac{\beta}{T_p^2}$ versus $1/T_p$ should be straight line the slope of which yields the activation energy. In Kissinger method, it is assumed that $f'(\alpha)$ is constant and independent of α . But for most reactions, a variation of α_p with heating rate β will result in systematic error in calculating kinetics parameters.

All the model free kinetics methods are based on the isoconversional principle which assumes that the reaction rate at constant extent of conversion is only a function of temperature¹¹. Taking logarithm of eq. (10) leads to the following equation:

$$\ln \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E_a(\alpha)}{RT} \quad (3.9)$$

Based on the assumption, when α is constant, $f(\alpha)$ is also constant. Thus differentiating with respect to T^{-1} yields:

$$\frac{d \ln \frac{d\alpha}{dt}}{dT^{-1}} = -\frac{E_a(\alpha)}{R} \quad (3.10)$$

Isoconversional methods fall into two categories: differential and integral. The most common differential isoconversional method is the Friedman method¹⁶. In this method, the following equation stands:

$$\ln \beta \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E_a(\alpha)}{RT_\alpha} \quad (3.11)$$

where β stands for heating rate (dT/dt). Because Friedman method does not make use of any approximations, it is more accurate than integral method such as Ozawa method, which will be introduced later in integral methods.

Among all the integral methods, the Ozawa¹⁷ and/or Flynn and Wall¹⁸ equation is the most widely known:

$$\ln \beta = \text{const} - 1.052 \left(\frac{E_a(\alpha)}{RT_\alpha} \right) \quad (3.12)$$

But the crude temperature integral approximation leads to inaccurate values of E_a . Based on the Ozawa isoconversional method, ASTM E698 provides a better evaluation method of thermal analysis. The method assumes that the extent of the reaction at the exothermal peak is constant and independent of heating rate. The ASTM E698 method can be expressed as the following equation:

$$\beta \frac{d\alpha}{dt} = A e^{-\frac{E_a}{RT_p}} (1 - \alpha_p) \quad (3.13)$$

where T_p and α_p are peak temperature and the conversion extent at it, respectively. Plotting of logarithm of heating rates versus peak temperatures can provide the information to calculate kinetics parameters. However, there are also some limitations of ASTM E698. First it is not applicable to reactions that are partially inhibited. Second it cannot work with reactions that include simultaneous or consecutive reaction steps. Third it cannot be applied to materials that undergo phase transitions if the reaction rate is significant at the transition temperature.

In this thesis, the Borchardt and Daniels method, the Kissinger method, the ASTM E698 method and the Friedman method are used and assessed.

3.4.5 FTIR principle

FTIR is a technique which can give infrared spectrum of absorption or transmission of a solid, liquid or gas. The principle of FTIR lies in the absorption of specific wavelengths of light by groups or molecules. In other words, every group has its own absorption at certain wavelengths/wave numbers, corresponding to vibrational movement of dipoles. Usually, for FTIR, the mid-infrared ($4000 - 400 \text{ cm}^{-1}$) is mostly used. In this range, the characteristic absorption peaks corresponding to different groups are usually sharp and sensitive. In this case, FTIR can be used to perform qualitative detection to determine functional groups or do structure analysis. For specific samples, the area of certain peak is related to the concentration of absorption bond, so FTIR can be used to do quantitative determination.

In this thesis, FTIR was used to monitor reaction process and verify the modification of modification of nano-fillers. It is a useful and reliable tool to study the chemical structure of samples.

For liquid samples, KBr pallets are used. In a typical FTIR test for liquid sample, the background was firstly scanned with loading of pure KBr pallet. After background collection, a small amount of liquid sample was dropped on the surface of KBr pallet, and the KBr pallet underwent FTIR test. The collected spectrum was baseline-corrected before further analysis. In curing study, another KBr pallet was used to cover the liquid sample, forming a sandwich structure (Figure 3.7), in case of any monomer evaporation, which results in inaccuracy of the collected spectrum.

Figure 3.7 A sandwich-structured sample for FTIR curing monitoring.

For solid samples, the background collection is the sample with liquid sample. The solid sample is ground into powder by mortar and then mixed with KBr. The well-ground mixture is pressed into a pallet and undergoes FTIR analysis. The collected spectrum is baseline-corrected before further analysis.

3.4.6 FTIR analysis

This part is related to the analysis of FTIR monitored curing process.

Since Si-CH₃ group does not change during hydrosilylation reaction, it was chosen as internal standard. The area of Si-H stretching ($A(\text{Si-H})$ centered at ca. 2160cm^{-1} , from 2100cm^{-1} to 2200cm^{-1}) and the area of Si-CH₃ bending ($A(\text{Si-CH}_3)$ centered at ca. 1260cm^{-1} , from 1220cm^{-1} to 1300cm^{-1}) were calculated and $A(\text{Si-H})/A(\text{Si-CH}_3)$ was used to monitor the reaction.

The conversion by FTIR can be calculated from the following equation:

$$\alpha = 1 - \frac{[V]_t}{[V]_0} \quad (3.14)$$

where α stands for conversion, $[V]$ stands for Si-vinyl groups concentration. The subscripts 0 and t stand for reaction time. Because the molar ratio of $D_4^H:D_4^{Vi}$ was 1.43:1 (mass ratio was 1:1), so the zero reaction time Si-H concentration can be expressed as following:

$$[H]_0 = 1.43 [V]_0 \quad (3.15)$$

Because Si-H and Si-vinyl were equally consumed, the following equation is obtained:

$$[H]_0 - [H]_t = [V]_0 - [V]_t \quad (3.16)$$

Based on the equations above, the conversion can be expressed as follows:

$$\alpha = 1.43 \left(1 - \frac{[H]_t}{[H]_0} \right) \quad (3.17)$$

In FTIR study eq. (3.17) can be expressed as follows:

$$\alpha = 1.43 \left(1 - \frac{A(Si-H)_t/A(Si-CH_3)}{A(Si-H)_0/A(Si-CH_3)} \right) \quad (3.18)$$

3.4.7 Sample Preparation and Test Method for DSC and FTIR

A mixture of D_4^H , D_4^V and Karstedt's catalyst was prepared before isothermal DSC test (TA instruments, Q10, USA) and stored in fridge to prohibit reaction before test. In order to minimize sample size effect, 4-5 mg sample was used. Hermetic aluminum pans were used for DSC tests. A series of non-isothermal curing were conducted from 0 °C to 300 °C with different heating rates of 1, 5, 10, 15 °C/min. All the DSC measurements were carried out in high-purity nitrogen (protection gas flow: 60 mL/min and purge gas flow: 40 mL/min).

FTIR analysis was conducted in a FTIR spectrometer (Perkin-Elmer Frontier, MA, USA). KBr pellets were used to support sample solution and FTIR spectrum was recorded at specific cure time. The sample was cured at room temperature (25 °C) and kept in dry box in case of side reaction between Si-H and moisture.

3.5 Rheometer

Rheology is the study of the deformation and flow of matter. Shear stress, shear rate and viscosity are usually determined from a rheology test. Besides normally studied rheology

test regarding to viscosity of liquid or soft matter, it can be used to monitor the crosslinking reaction of thermosets. Gel point is a point where material change from liquid to solid which is caused by the growth of structure during thermoset curing¹⁹. In a typical thermoset curing process, storage modulus (G') describes solid like behaviour while loss modulus (G'') describes liquid like behaviour. If $G' > G''$, the material behaves like solid; if $G' < G''$, the material behave like liquid; when $G' = G''$, where the cross section of storage modulus and loss modulus occurs, it is defined as gel point²⁰.

In this thesis, the rheology study was performed to obtain the gel point of cyclosiloxane polymer at different temperatures. The rheology test was performed on a Discovery Hybrid Rheometer-3 (TA Instruments, USA) with an environmental test chamber. Rheometer was firstly calibrated and zero gapped before test. Parallel aluminium plates with a diameter of 25 mm were used for curing process rheology test. The uncured samples were loaded at loading gap and then the top plated was lowered down to trim gap to remove excessive samples before go to test gap. 500 μm gap was adopted in this thesis. Oscillation mode with a frequency of 1 Hz and shear strain of 0.03% was employed. The samples were kept at different temperatures until the storage modulus does not change. The time when gel points appeared was plotted against temperature at which samples were cured. This diagram acts as a guide for the process of cyclosiloxane polymer formation.

3.6 Mechanical Tests

3.6.1 Tensile Test

Tensile test is one of the normally used methods to evaluate how the mechanical properties change in samples. When fillers or additives are added into a polymer matrix, the structure change will lead to increase or decrease in Young's modulus.

Tensile test was performed according to ASTM D638 and V type samples were prepared with a thickness of ~ 1 mm. An Instron 5567 (USA) with load cell of 500 N was used to

test samples at a constant cross-head of 1 mm/min at room temperature. A preload was applied to eliminate the impulsive force on specimens and improve the consistency of the measurements. The Young's modulus was calculated from the slope of stress-strain curve within elastic range.

Figure 3.8 A picture of the sample for tensile test.
Inset is a schematic graph of ASTM D638V sample.

3.6.2 3-point Bending test

According to previous publications^{21,22}, there is no standard like ASTM D790 to quantify the toughness of silicone resin. Unlike normally organic polymer/composite like epoxy which can be easily notched in a well-developed way, the cyclosiloxane is hard to notch, in which case ASTM D790 is not suitable. In this thesis, the toughness was characterized via 3-point bending test of rectangular samples without notch. During 3-point bending test, the top of the samples undergoes compression while the bottom undergoes tension where the initial crack begins followed by fast crack propagation, leading to catastrophic failure of the sample. Analysis of fracture surfaces allowing identifying and putting forward toughening mechanisms.

3-point bending test was carried out using Tensile Tester Instron 5567 (Instron, USA)

with a 500 N load cell. The sample thickness was about 1 mm and the width was about 10 mm. All the samples were carefully polished before bending tests at a sample span of 16 mm with a 2 mm/min crosshead speed. 4-6 samples were tested for each system. Relative toughness was calculated by the following equation:

$$T = \frac{\int_0^{\epsilon_f} \sigma \, d\epsilon}{\int_0^{\epsilon_{fn}} \sigma_n \, d\epsilon} \quad (3.19)$$

Where T is relative toughness, σ is flexural stress (MPa), ϵ is flexural strain and ϵ_f is final flexural strain (σ_n and ϵ_{fn} stand for flexural stress and final flexural strain of neat cyclosiloxane polymer).

Figure 3.9 (A) A picture of 3-point bending test and (B) a schematic graph of samples under load.

One thing should be noted here is the sample thickness. In polymer materials, critical thickness is defined as an absolute thickness dimension below which a macroscopically brittle polymer no longer exhibits brittle fracture and instead deforms in a ductile fashion.^{23,24} In order to minimize the effect of thickness and eliminate deceptive results which might lead us to wrong analysis, all samples tested were more than 0.5 mm which is much larger than reported critical thickness (less than 5 micrometers) of similar silicone resins^{25,26} and thickness of samples were similar for each test.

3.6.3 Compression Test

Compression test is used to establish the compressive force of a material and the recovery after compression. Compression is used to determine the material behavior under a load. Compression test was employed in this thesis to study the compression properties such as compression strength. The compression sample dimension is 25.4 mm*25.4 mm*12.7mm. Compression test was performed by using Tensile Tester Instron 8801 (Instron, USA) with a crosshead speed of 1 mm/min. The tests were conducted till complete failure of the samples.

3.6.4 Nanoindentation

Nanoindentation is a non-destructive hardness test technique which provides mechanical properties such as hardness, modulus and creep behaviour of materials. Compared with traditional hardness test such as macro or microindentation, less sample is used, even coating with a few micron meters can also be tested. In a typical nanoindentation test, a nano-sized tip, for example Berkovich tip, indents on the surface of material with a constant rate of increase load or depth, and then unloads at the same constant. Creep behaviours can be studied by holding at fixed load.

During materials tests, micro-indenter was also employed to study the hardness of materials. However, compared with microindentation, nanoindentation is preferred due the following reasons:

- a. Cyclosiloxane polymer is transparent, so it is hard to control the tips during test and the indentation trace is not clear via microscope.
- b. The cyclosiloxane tended to break during tip indentation.
- c. Part of the deformation bounced back, which lead to inaccuracy of hardness test.

The nanoindentation data was analyzed by the following method:

- a. The hardness was calculated by the following equation:

$$H = \frac{P_{max}}{A_r} \quad (3.20)$$

where H is hardness, P_{max} is maximum load, and A_r is residual indentation area. A_r is a function of height of contact (h_c):

$$A_r = f(h_c) \quad (3.21)$$

height of contact can be calculated from the following equation:

$$h_c = h - h_s \quad (3.22)$$

where h is the maximum height of indentation. For h_s , the following equation stands:

$$h_s = \varepsilon \frac{P_{max}}{S} \quad (3.23)$$

where S is stiffness and ε is a constant (ε is 0.75 for Berkovitch tip). S can be expressed by the following equation:

$$S = \frac{dP}{dh} \quad (3.24)$$

Reduced modulus is given by:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{A_r}} S \quad (3.25)$$

Figure 3.10 A schematic graph of nanoindentation

Nanoindentation was performed on a nano-indenter (Micro Materials Ltd., Wrexham, United Kingdom) with a Berkovitch-type diamond tip. The tip indented with a rate of 1 mN/s to 5 mN and was held at 5 mN for 5 seconds before unloading with a rate of 1 mN/s. The temperature was held at 22-23 °C during the test. For each sample, 5 points were indented to guarantee the reliability of the data.

3.7 Morphology test

3.7.1 Atomic Force Microscopy (AFM)

AFM images were taken by AFM Cypher S (Asylum Research, OXFORD instrument, USA) in air condition. The AFM imaging was conducted in tapping mode, in which a mechanically oscillated cantilever with is driven at a fixed frequency is moved along the sample surface. In other words, AFM images are taken by measuring the force between a cantilever probe and the sample surface. AFM can give height, amplitude and phase information about the samples by presenting different colors. It is a useful tool to study cyclosiloxane structure. Besides topography information, AFM can also give accurate structure details such as height, distance and surface roughness. In addition, AFM can build 3D image for better presentation.

In this thesis, AFM was used for characterization of surface properties as well as the structure of cyclosiloxane polymer. For bulk samples, the samples were bound onto a magnetic disk by double-side tape before test. For cyclosiloxane polymer structure study, the cyclosiloxane polymer was firstly ground into powder, and the powder was sonicated for 1 day. The solution was dropped onto a heated silicon wafer before AFM test.

3.7.2 Scanning Electron Microscope (SEM)

SEM was employed to study the fracture surface of samples. In SEM, electron beam is produced at the top of the column. After accelerating, the electron beam passes through a combination of lenses and apertures to focus and hit on the surface of the sample. When the electron beam hit the sample surface, secondary electrons, backscattered electrons, characteristic X-rays, continuum X-rays, and secondary fluorescence X-rays are generated. Detection of different signals gives different information about sample surface. Secondary electrons escape easily from the surface and are used to image the topography of samples. Backscattered electrons have intensity proportional to average atomic number and thus are used for imaging different regions. Characteristic X-ray gives the elemental information about the sample and can be used for elemental analysis.

SEM provides morphologies of sample surface and, theoretically, can give morphology pictures with high roughness which AFM fails to obtain (Usually for AFM, the sample surface roughness should be less than 2 μm). SEM is very useful especially when morphology of fracture surfaces is needed.

Figure 3.11 A schematic graph of SEM and electron beam interaction.

SEI images were taken by FE-SEM 7600F (JEOL, Japan) and the samples were bind onto sample holder by conductive carbon tape. The samples were coated with platinum before test.

3.7.3 Transmission Electron Microscopy (TEM)

TEM was employed to study the morphology of GO, GO-AA, modified CNTs and cyclosiloxane polymer/nanocomposites. In TEM chamber, a high energy beam of electrons is shone from an electron gun through a combination of condenser lens which restrict electron beam under vacuum. After hitting on the very thin sample, part of the beam is transmitted through the sample. The transmitted beam is then focused by objective lens into an image and hit on phosphor screen, allowing the user to see the image. The contrast in the image represents how much electrons transmit through the sample which depends on the thickness and composition of the sample.

When the electrons in TEM pass through the sample, by adjusting the magnetic lenses, they are scattered by the electrostatic potential which is determined by the elements of the sample. The diffracted electrons undergo Bragg Scattering, generating diffraction patterns. Diffraction patterns provide information about space group symmetries in crystals and the crystal's orientation to the beam path.

TEM images were taken by JEM-2010 (JEOL, Japan). For GO and GO-AA samples, GO or GO-AA was firstly dispersed in ethanol by ultrasonication and the suspension was dropped onto copper grid before test. For cyclosiloxane polymer and composites thereof, the cyclosiloxane polymer or composite was firstly grind into powder by mortar. The powder was dispersed in ethanol and sonicated for ~ 1 week to exfoliate the structure. The suspension was dropped onto copper grip before test.

3.8 Thermal Related Test

3.8.1 Thermalgravimetric Analysis (TGA)

To evaluate thermal stability, TGA was performed by using a TA 2950 (TA instruments, USA). TGA is a technique showing physical or chemical changes of materials which are measured as a function of weight and temperature/time. TGA can provide information about physical or chemical phenomena including dehydration, decomposition, oxidation, and so on. TGA is very useful in determining the thermal stability of tested samples and analyzing thermal decomposition mechanisms in inert or oxidative atmosphere. In a typical TGA test, T_{d5} (temperature at which 5 wt% loss occurs) and weight retention are used to evaluate the thermal stability of samples. TGA test in air can provide information about anti-oxidation property of samples.

In order to eliminate the size effect, the sample weight was kept around 20 mg. TGA test was run with a heating rate of 10 °C/min from room temperature to 900 °C in both air and nitrogen with a flow rate of 60 mL/min. The test was performed under nitrogen protection with a flow rate of 40 mL/min.

3.8.2 Dynamic Mechanical Analysis (DMA)

DMA test was performed on DMA Q800 (TA instruments, USA) in air. Single cantilever sample clamp was employed to test the storage modulus. The sample is rectangular with a thickness of ~ 1 mm and a width of ~ 12.5 mm. In this thesis DMA was employed to evaluate the mechanical property of samples under a fixed frequency (1 Hz) at room temperature.

Figure 3.12 A sample clamped in DMA chamber.

3.8.3 Thermomechanical Analysis (TMA)

When subjected to temperature change, material tends to change in shape or dimensions. TMA is a technique which is used to measure a change of a dimension of the sample as a function of temperature.

In this thesis, TMA was used to test homogeneity of cyclosiloxane polymer. If cyclosiloxane polymer is isotropic, it will show the same coefficient of thermal expansion in all directions. To test the thermal expansion behavior, TMA test was run on TMA 2940 (TA Instruments, USA). A preload of 0.01 N was applied to the sample. A rectangular sample was used in TMA test with a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$ from room temperature to $200\text{ }^{\circ}\text{C}$ under the protection of nitrogen with a flow rate of $50\text{ mL}/\text{min}$.

3.8.4 Pyrolysis-Combustion Flow Calorimetry (PCFC)

PCFC measures the heat release rate (HRR) from combustion of the fuel gases generated from a solid sample during controlled pyrolysis in an inert atmosphere.²⁷ The fuel gases is brought to another chamber by inert gas flow and mixed with excessive oxygen. The heat generated from combustion of the flowing gas stream is measured by oxygen consumption calorimetry. The heat release rate depends on gas fuel released from sample decomposition. In this case the heat release rate is proportional to the mass generation rate of gas fuel. PCFC usually present in a plot of HRR as a function of temperature. The heat release capacity (HRC) is defined as the peak of heat release rate divided by heating rate. If the heating rate is 1 K/s, the values are the same for HRC and HRR. Total heat released can be calculated from integration of the HRR curve over the complete time of the test.

In this thesis, PCBC was employed to test the flammability of cyclosiloxane polymers. PCFC test was performed by FTT micro calorimeter (Fire Testing Technology, UK). Samples were tested from room temperature to 900 °C with a heating rate of 1 °C/s. The sample weight was kept around 10 mg to minimize the size effect.

3.8.5 Pycnometer, Heat Capacity and Thermal Conductivity

Gas pycnometer Ultrapyc 1200e (QuantachromeCorp Instrument, USA) was used to measure the true density of samples in Helium atmosphere. Three specimen were tested for each sample.

Modulated Differential Scanning Calorimeter (MDSC, TA instruments, USA) was used to get the heat capacity of cyclosiloxane and composite thereof by TA 2920 (TA Instruments, USA) with a heating rate of 3 °C/min in nitrogen. In MDSC, the sample is given a non-linear heating or cooling rate to separate the kinetic from the thermodynamic data. This is usually done by applying a series of heating or cooling micro-steps and thus allows users to get Cp curve. In this case, MDSC removes kinetic noises from transitions

and give more accurate data.

XFA 500 Xenon Flash Apparatus (LINSEIS, USA) was used to determine the thermal diffusivity. This equipment used a laser flash method (Figure 3.13) to test thermal diffusivity. The flash lamp gives a laser flash on the sample from one side and heats the sample. The IR detector on the other side of the sample detects the time-dependent temperature rise. In a typical thermal diffusivity test, a round samples with a diameter of 12.5 mm and thickness of 2-3 mm was used. Before test, the samples were firstly coated with gold and graphite to ensure accurate results.

Figure 3.13 A schematic graph of laser flash method for thermal conductivity test.

Thermal conductivity was calculated by the following equation:

$$K = \alpha \rho C_p \quad (3.26)$$

where K is thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$), α is thermal diffusivity (mm^2s^{-1}), ρ is density of the samples (g cm^{-3}) and C_p is specific heat capacity ($\text{Jg}^{-1}\text{K}^{-1}$).

3.9 Other Tests

3.9.1 Raman Spectroscopy

Raman Spectroscopy is a technique which is used to detect vibrational, rotational, and other low-frequency modes in materials. Raman spectroscopy is collected by detecting the change in the polarizability of molecule due to light interaction. When a light beam hits a molecule, photons are absorbed and scattered by it. The molecule which absorbs

photons is excited by photons to a virtual energy state for a short period of time before an inelastic scattering which results in scattering of a photon of either lower energy (Stokes Raman Scattering) or higher energy (Anti-Stokes Raman scattering) than the incoming light. Raman shift is recorded in wavenumbers. The Raman shift can be expressed by the following equation:

$$\Delta\omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) \quad (3.27)$$

where $\Delta\omega$ is the Raman shift, λ_0 is the excitation wavelength, and λ_1 is the scattered Raman light wavelength. $\Delta\omega$ is only related to material composition and the intensity is proportional to the concentration of materials. The plot of Raman shift versus intensity is the Raman spectrum.

Raman Spectrum was recorded using a Witec alpha300 SR Confocal Raman Spectrometer (WITec, Germany) with 488 nm wavelength laser and 50 scans were recorded for each sample to ensure the accuracy. For powder samples, the powder was firstly suspended in ethanol and the suspension was sonicated to get a better dispersion. The suspension was dropped on a silicon wafer which was cleaned by ultra-sonication to form a uniform layer.

3.9.2 X-ray photoelectron spectroscopy (XPS)

XPS is a surface analysis technique that measures the elemental composition of materials. In XPS, an X-ray beam hit the surface of sample and photoelectrons are emitted. The emitted photoelectrons are collected and analyzed. In a typical XPS spectrum, intensity which is presented in the form of number of photoelectrons detected versus binding energy of the electrons detected. For each element, the characteristic peaks have specific binding energy values which can be used to determine each element.

XPS is widely used in characterizing carbon materials such as graphene and CNTs. In this thesis, XPS was employed to characterize GO and GO-AA graphene nanosheets to further prove the structures of GO and GO-AA. XPS was carried out on a VG ESCALAB 220I-XL system (Thermo VG Scientific Ltd. UK). The energy calibration was made

against the N1s peak and C1s peak during analysis. Peak deconvolution was applied by OriginPro 8.5.0 SR1 to separate peaks for different bonds.

3.9.3 UV-Vis Spectrum

In a typical UV-Vis test, a beam of light with changing wavelength goes through the samples, and the detector collect how much light can go through the sample. By plotting the transmittance as a function of wavelength, a UV-Vis spectrum is presented.

In this thesis, UV-Vis was employed to test the optical transparency of cyclosiloxane polymers and composites thereof. A UV-2501 PC (Shimadzu, Japan) was used to test UV-Vis spectrum. The equipment was firstly baselined correct in air before testing samples. The self-standing bulk samples with a thickness of 4 mm were fixed on sample holder by double side tape. The wavelength is from 900 nm to 200 nm with a medium scanning speed.

3.9.4 Optical Microscope

Optical microscope is a common method to visually observe materials. Optical images were taken in transmission mode using Olympus BX 53 fluorescence microscope (Olympus, Japan).

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Chapter 4

Fundamental Study of Cyclosiloxane Polymer Including Kinetics Study and Basic Characterizations

This chapter presents and discusses the curing kinetics and basic characterizations of cyclosiloxane polymer. In a curing kinetics study, the curing process is evaluated by model-fitting and model-free methods. The E_a dependency on conversion is explained by structure growth. Fourier transform infrared spectroscopy (FTIR) and rheological testing further explain the curing behaviors. Morphological characterizations reveal that the cyclosiloxane polymer has a layered structure but thermomechanical analysis (TMA) results shows that it is isotropic in bulk. The hypothesis that cyclosiloxane is a layered structure is confirmed, but only at the micro-scale. This lays the foundation for reinforcement strategies.

4.1 Introduction

This chapter presents the fundamental studies of cyclosiloxane polymer including, curing kinetics study by DSC, and curing monitoring study by FTIR and Rheometer and basic characterizations of cyclosiloxane polymer. In the DSC kinetics study, the Borchardt and Daniels, the Kissinger, ASTM E698 and the Friedman methods are used and assessed. Subsequently, FTIR was employed to monitor the curing reaction data and was correlated to the rheological behavior of the curing system. All the curing studies revealed details about the hydrosilylation reaction. The results and experimental methods can act as guides for processing and further study of similar polymer thermosets. The hypothesis that cyclosiloxane polymer is a layered structure was verified by morphology imaging. Further characterization shows that cyclosiloxane polymer is a layered structure at the nano scale but is isotropic in the bulk. The identified structures laid the fundamentals for the work in the rest of this thesis.

Due to the limited literature available on cyclosiloxane polymer, as mentioned in Chapter 3, there is a lack of information concerning both kinetics studies and structure characterization. Curing kinetics and modeling of hydrosilylation in silicones have been studied by DSC¹⁻³, but all the materials used in the literature are commercially available silicones containing various additives. The additive influenced the kinetics parameters and thus led to deviation in kinetics calculation. Some reported the hydrosilylation reaction monitored by FTIR, but they all focused on hydrosilylation of bifunctional monomers or linear bifunctional polydimethylsiloxanes⁴⁻⁶ and hydrosilylation of mono-functional reactants⁷. For cyclosiloxane polymer, both of the monomers are tetra-functional and, to the best of my knowledge, there is no publication concerning the kinetics of similar curing processes. Besides, the published literature only demonstrated the properties⁸ and potential applications⁹ of cyclosiloxane polymer, the structure of it was still unknown at the start of this work.

The study presented in this chapter fills this gap in the study of this polymer. The observations and data presented in this chapter are discussed to better understand the

chemistry and physics behind the reaction and the structure of resulting cyclosiloxane polymer hybrids.

4.2 Kinetics Study - DSC

According to Eq. 3.2, $k(T)$ is constant during an isothermal experiment. The shape of the kinetic curve is determined by the reaction model, which can be easily identified from the conversion-time profile obtained by an isothermal DSC measurement. According to Figure 4.1 which shows the characteristic α vs. time for accelerating, decelerating and autocatalytic reactions, accelerating and autocatalytic profiles demonstrate a plateau before conversion starts to increase while a decelerating profile demonstrates a quick increase in conversion and conversion approaches 1 with a plateau. The isothermal (90 °C) curing process profile of cyclosiloxane polymer. The isothermal DSC curve at 90 °C showed a decelerating reaction profile. It is unfavorable in isothermal DSC measurement because significant cure before the sample reaches set temperature leads to loss of information. Based on the discussion above, non-isothermal measurement was adopted to study the curing kinetics of cyclosiloxane polymer.

Figure 4.1 Characteristic conversion vs. time profile for different types of reaction, and conversion vs. time curve of cyclosiloxane polymer from isothermal DSC measurement at 90 °C (Dash line).

Figure 4.2 shows DSC curves with different heating rates from 0 °C to 300 °C and the DSC curves show shoulders following the main curing peak. There are two possible factors contributing to the shoulders after hydrosilylation exothermal peaks; (1) solidification makes diffusion harder during cure process, and (2) increase in steric hindrance which derived from hydrosilylation of the third and fourth Si-vinyl groups. As the heating rate increased, the appearance of the shoulder became less significant because of overlapped fast cure process.

Table 4.1 shows the summarized results of DSC curves. The onset temperature and peak temperature increased with heating rate, which is normal in thermoset curing¹⁰. Previous research showed that for different heating rate, either the total heat enthalpy did not change much^{3,11} or even there was a decrease at the highest heating rate, no explanation was given¹². However, for the cyclosiloxane being studied in this thesis, the lowest reaction rate and the highest reaction rate showed lower total heat enthalpy than the others. This phenomenon is probably due to the tetra-functional monomers which react and grow like a dendrimer. At low heating rate (1 °C/min), there was enough time for structure growth, the reaction turned from chemical control to diffusion control when the macromolecules formed were too large to diffuse quickly. The reaction resulted in lots of unreacted dangling bonds being buried inside the cyclosiloxane polymers due to steric hindrance, leading to relatively lower total heat enthalpy. At high heating rate (20 °C/min), there was relatively less time for macromolecule diffusion and the sample quickly turned from liquid to gel, which also limited the diffusion. The high steric hindrance of dangling bonds resulted in more unreacted dangling bonds, thus leading to lower total heat enthalpy.

Figure 4.2 Heat flow curves versus temperature obtained at different heating rates.

Table 4.1 Summary of DSC results with different heating rates.

Heating rate (°C/min)	T_{onset}^* (°C)	T_p^{**} (°C)	ΔH_0^{***} (J/g)
1	40.02	67.99	540.7
5	56.41	91.33	663.5
10	63.85	96.91	635.6
15	76.45	105.35	646.6
20	79.30	114.00	417.1

* T_{onset} is the onset temperature of DSC curve.

** T_p is the peak temperature of DSC curve.

*** ΔH_0 is the total curing enthalpy.

Figure 4.3 shows plots of the conversion and reaction rate of curing process versus temperature with different heating rates. The highest reaction rates (da/dt) shifted to higher temperature with increasing heating rates, which is common in DSC since a higher heating rate leads to delay in peak temperature. However interestingly, the conversion for 10 °C/min, 15 °C/min and 20 °C/min showed higher values than that for 5 °C/min in a certain range (>120 °C for 10 °C/min and 15 °C/min; >150 °C for 20 °C/min).

This is probably because the cure process shifted from chemical control to diffusion control. For curves with a heating rate of 5 °C/min, 10 °C/min and 15 °C/min, at same temperature, higher heating rates might lead to smaller macromolecules due to higher curing speed. The smaller molecules are easier to diffuse inside sample, leading to higher reaction rate at a higher heating rate in diffusion control process. For sample with heating rate of 20 °C/min, the heating rate was too fast, leading to delay in the shift from chemical control to diffusion control.

Figure 4.3 (A) Conversion versus temperature and (B) reaction rate versus temperature.

The Borchardt and Daniels method was firstly used to calculate the activation energy from a single temperature ramp DSC curve (10°C/min), which is shown in Figure 4.4. In Borchardt and Daniels method, the following equation stands:

$$\ln K(T) = \ln \frac{da/dt}{(1-\alpha)^n} = \ln A - \frac{E_a}{RT} \quad (4.1)$$

By dividing the curve into 20 evenly spaced segments (Figure 3.5) by temperature, a plot of $\ln K(T)$ versus $1/T$ obtained should be a straight line. Tentative reaction orders from 1 to 3 were examined. By analyzing via OriginPro 8.5.1, tentative reaction order $n = 1.18, 1.19, 1.20, 1.21, 1.22$ and 1.23 showed the best fitting ($R = 0.9978$). In other words, when $n = 1.18, 1.19, 1.20, 1.21, 1.22$ and 1.23 , straight line fitting curves were obtained from the experimental data. In this case, middle value $n = 1.20$ was selected to calculate the parameters, an activation energy (E_a) of 79.90 ± 0.50 KJ/mol was obtained from the

slope and the Y-intercept was determined to be 23.33 ± 0.19 . $k(T)$ can be expressed by the following equation:

$$k(T) = 23.33 \exp\left(-\frac{9610.30}{T}\right) \quad (4.2)$$

Figure 4.4 Borchardt and Daniels method: (A) tentative reaction orders and (B) fitting curve of selected reaction order.

The Kissinger and ASTM E698 methods were also employed to calculate the activation energy, which are shown in Figure 4.5. The activation energies obtained from the Kissinger and ASTM E698 methods are 68.23 ± 5.50 KJ/mol and 74.26 ± 5.46 KJ/mol, respectively. The E_a values calculated are close to that from the Borchardt and Daniels method. But all the three methods discussed above have a common limitation, they can only be used in linear single peak kinetics analysis. However, multiple cure peaks and/or shoulders due to shift from chemical to diffusion control^{13,14} are more commonly observed and a more appropriate method is needed. For cyclosiloxane polymer cure process, the above three methods can only be used to analyze the significant exothermal peak which account for almost 80% of the reaction while they cannot be used to analyze the shoulders arise from diffusion control and high steric hindrance due to the unique tetra-functional cyclosiloxane structures. In order to fully understand the kinetics behind the cure process, model free kinetics analysis was used to interpret E_a vs. α dependency.

Figure 4.5 (A) Kissinger plot and (B) ASTM E698 plot.

Figure 4.6 shows Friedman plots at different conversions from 5% to 95%, calculated activation energies at different conversions, and a schematic graph of structure growth. The activation energies calculated from the Friedman method were much higher than those calculated using the Borchardt and Daniels, the Kissinger and ASTM E698 methods. This is because the Borchardt and Daniels, the Kissinger and ASTM E698 methods only used peak temperature, which means that it is only applicable to a single peak while the Friedman method considered the entire reaction including the shoulders. From Figure 4.6 it can be concluded that the activation energy was almost the same during the initial curing period (from 5% to 40% conversion). From 40% conversion, the activation energy started to decrease and reached its lowest point at 80% conversion, followed by an increase till the end of reaction. There are various explanations for the E_a dependency on different conversions, such as autocatalytic reaction mechanism, shift from chemical control to diffusion control, polymer chains mobility, viscosity change, phase transition, systematic errors, experimental errors and side reactions^{12,15-28}. However, most of these kinetics studies were done on epoxy systems. Considering tetra-functional structures of cyclosiloxane monomers, as well as the cyclosiloxane polymer molecule structures, possible explanations are suggested as follows:

1. Similar E_a value from 5% to 40% conversion (Region 1, Figure 4.6B) indicates that curing reaction during this conversion is a single reaction. Ideally, in Region 1, the

- molecular growth is chain-like, which is accomplished by reaction of para groups from the tetra-functional monomers (Region 1, Figure 4.6C).
2. From 40% conversion onwards (Region 2, Figure 4.6B), E_a started to decrease till 80 % conversion. As for the decrease in E_a , viscosity change, autocatalytic reaction, or shift from chemical control to diffusion control²⁸⁻³¹ were believed to be the main causes in other systems such as curing of epoxy. However, in this unique tetra-tetra functional hydrosilylation reaction, this cannot be explained by one single reason. In Region 2, the reaction shifted from chemical control to diffusion control and increasing crosslinking lead to higher viscosity, which made the diffusion harder. These two causes will lead to an increase of E_a . Contrary to that, E_a decreased with conversion in Region 2. In this isoconversional method, higher conversion corresponded to a higher temperature, so the viscosity was lower at a higher temperature. It allowed easier diffusion of intermediate macromolecules, leading to decreased E_a . From molecule level, it is probably due to the clicking of chain-like structures. (Region 2, Figure 4.6C) In this case, Region 2 could be divided into two parts: mild decrease in E_a (40-70% conversion) and dramatic decrease in E_a (70-80% conversion). The mild decrease in E_a with the conversion from 40% to 70% was due to easier diffusion at higher temperature, as discussed earlier. Once the chain-like molecules reacted with each other, much lower diffusion energy was needed since the structure can well fit in each other once the molecule moved to the right position, causing dramatic decrease in E_a (70-80% conversion). Based on the discussion above, the decreased E_a was a consequence of the shift from chemical control to diffusion control, viscosity change, and clicking of chain-like structures.
 3. After 80% conversion, E_a started to increase. It corresponds to the shoulders in the non-isothermal DSC measurement. One possible reason is the solidification of samples impeded diffusion process from occurring. In this case, the dendrimer-like intermedia molecules (Region 3, Figure 4.6C) formed by clicking of chain-like molecules could not diffuse easily, and high steric hindrance from the structure made it harder to react further, thus leading to the increase of E_a . From molecular structure of dendrimer-like intermedia, another possible reason is that solidification of samples made rearrangement of molecular structure harder, and the unreacted dangling bonds,

such as Si-H and Si-vinyl (Black arrows, Region 3, Figure 4.6C), were embedded in the intermedia structure, and it cost more energy to rearrange structure for hydrosilylation reaction.

Figure 4.6 (A) Friedman plot, (B) E_a vs. conversion dependency, and (C) schematic graph of structure growth.

4.3 FTIR monitored reaction

Figure 4.7 shows the FTIR monitored conversion versus time. During the first two hours at room temperature, conversion increased dramatically and then slowed down. The

conversion at which it slowed down is about 40%, corresponding to the conversion where the reaction shifted from chemical control to diffusion control in the former non-isothermal DSC kinetics analysis. When further cured at 150 °C, conversion quickly went up in the first 5 minutes, which is due to high diffusion speed at high temperature. Following at about 80% conversion reaction started to slow down due to solidification of increasing steric hindrance. The 80% conversion corresponds to non-isothermal DSC kinetics analysis where the E_a started to go up and solidification occurred. After 4 h the 93% conversion did not change and stayed same even cured for 24 h at 150°C. Though curing at 150 °C for 4 h allows a full cure of cyclosiloxane polymer, the bulk samples were still cured for 24 h to guarantee the samples were fully cured in case of any size effect.

Figure 4.7 Curing process monitored by FTIR (A) conversion versus time at room temperature and (B) further cured at 150°C after cured at room temperature for 24 h.

Figure 4.8 shows the FTIR spectrum of uncured cyclosiloxane polymer and fully cured cyclosiloxane polymer which was further cured at 150 °C for 24 h. The remaining peaks at 1598 cm⁻¹ and 3054 cm⁻¹ are attributed to Si-vinyl groups, indicating that this curing process is not 100% completed. These unreacted vinyl groups were a consequence of increasing steric hindrance during curing process and they are embedded in the cyclosiloxane polymer network. The dangling bonds are possible weak points where the mechanical properties are not as good as highly crosslinked parts. Sealing dangling bonds might be possible ways to reinforce cyclosiloxane polymer.

Figure 4.8 FTIR spectrum of the uncured sample and fully cured sample.

4.4 Rheology

To accurately evaluate the relationship between structures and viscoelastic behavior, experiments need to be done within a region where the viscoelastic properties are independent of strain. In this case, an oscillation strain sweep was conducted to determine the linear viscoelastic region. Oscillation strain sweep of cyclosiloxane monomers mixture without any curing is shown in Figure 4.9. The region within which storage modulus does not change is the linear viscoelastic region. As can be seen from the curve, linear viscoelastic region is from $10^{-3}\%$ to more than $10^{-1}\%$. In this case, 0.03% oscillation strain was chosen as fixed parameter for all the remaining rheology curing tests.

Figure 4.9 Oscillation strain sweep of cyclosiloxane monomers mixture.

A plot of temperature versus gelation time at that temperature is shown in Figure 4.10 and the accurate data is shown in Table 4.2. Gelation time is defined as the time when gel point³² occurred at that temperature. The plot of temperature versus gelation time gives us a guide of processing time at different temperatures. As we can see, with increasing curing temperature, the gelation time was reduced. The area below the line is liquid area while the area above the line is the solid area. The points on the line indicate where the cyclosiloxane mixture changes from liquid to solid.

Figure 4.10 A plot of temperature versus gelation time at different temperatures.

Table 4.2 Gelation time of cyclosiloxane polymer at different temperatures.

Temperature (°C)	Time (h)
30	0.025
50	0.083
60	0.433
70	1.400
80	4.280
90	12.300

Figure 4.11 shows the oscillation rheology test result (the mixture was cured for 10 h before loading onto Rheometer for test) of curing process of cyclosiloxane polymer at room temperature. The gel point appeared at 12.3 h. Combined with FTIR results shown in Figure 4.7 (A), the conversion of 12.3 h (738 min) is about 45%, which verifies the explanation of isoconversional DSC kinetics study that at about 40% conversion the reaction shifted from chemical control to diffusion control. The slight difference is probably due to different test conditions because the rheology test was conducted under constant strain and air flow while DSC and FTIR experiments were conducted in static state.

Figure 4.11 Oscillation rheology result of cyclosiloxane mixture cured for 10 h.

4.5 Characterizations of Cyclosiloxane Polymer

4.5.1 DSC

A DSC curve of cyclosiloxane polymer is shown in Figure 4.12. The cyclosiloxane polymer was firstly cooled down to $-90\text{ }^{\circ}\text{C}$. The sample was then heated up to $200\text{ }^{\circ}\text{C}$ (first heating curve), cooled down to $-90\text{ }^{\circ}\text{C}$ (cooling curve), and then heated to $150\text{ }^{\circ}\text{C}$ (second heating curve) with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. There was no obvious peak or plateau change within this range except some small peaks at terminal temperature arising from isothermal of sample. This indicates that cyclosiloxane polymer is stable within this temperature range because there was no detectable physical or chemical change occurring.

Figure 4.12 A DSC curve of cyclosiloxane polymer.

4.5.2 TGA

TGA curves of cyclosiloxane polymer up to $900\text{ }^{\circ}\text{C}$, both in nitrogen and air, are shown in Figure 4.13 and Table 4.3 summarizes the results of them. Cyclosiloxane showed good thermal stability up to $400\text{ }^{\circ}\text{C}$ without any noticeable weight change in nitrogen, the

weight loss above 400 °C was due to cleavage of the organic side groups from Si³³. The weight loss from 500 °C to 900 °C was due to degradation of the siloxane ring network and rearrangement of the network from polymer to ceramic³⁴. TGA curve in air showed the same trend except for a weight gain at 200 – 300 °C mainly due to oxidation of cyclosiloxane polymer. Cyclosiloxane polymer showed the similar behavior in TGA with earlier decomposition temperature but similar weight retention at 900 °C. The high stability of cyclosiloxane polymer and high weight retention at 900 °C indicated that it is a good candidate to be a high-performance polymer.

Figure 4.13 TGA curves of cyclosiloxane polymer in nitrogen and air.

Table 4.3 TGA results of cyclosiloxane polymer.

Atmosphere	T _{d5} * (°C)	Weight retention at 900 °C (%)
Nitrogen	604	86.65
Air	497	86.15

* Td5: Temperature at which 5 wt% loss occurs

4.5.3 SEM

SEM was used to characterize the structure of cyclosiloxane polymer. Cyclosiloxane polymer was ground into powder by a mortar and pasted onto a conductive carbon tape and coated by platinum before SEM imaging. Figure 4.14 shows the morphology of powder sample. It can be clearly seen that cyclosiloxane showed a layered structure with a smooth surface. Forming of this structure was mainly a result of crosslinking of 2D like monomers. The monomers are not strictly 2D since the organic bonds are out of the plane, hence cyclosiloxane polymer is not pure 2D polymer³⁵. The delamination of the layered structure should be due to weak connections between layers. When subject to grinding, the layers tend to slide away or peel off, leaving a smooth, layered structure.

Figure 4.14 SEI image of cyclosiloxane polymer powder sample.

4.5.4 TEM

In order to further characterize the layered structure, the ground cyclosiloxane polymer powder was suspended in ethanol and subjected to sonication for ~ 1 week to exfoliate the layered structure. The suspension was dropped onto a copper grid for TEM imaging. Figure 4.15 shows the TEM image of cyclosiloxane polymer. TEM image further confirms the layered structure with a few tens of layers stacking together. A few trials were made to find a single layered structure but failed. This is mainly because

connections between layers are not fully weak but range from weak to relatively stronger. This can be explained by the structure growth mechanism. At the beginning of structure growth (curing process), the layered structures stack together with covalent bonds between layers. Less defects and dangling bonds contribute to the connections between layers. In this case, the small layered structures are hard to delaminate. When the structure grows bigger, the steric hindrance increases and more dangling bonds are left after cure, leading to less covalent bonds (weaker connection) between stacked layered structures. Sonication of cyclosiloxane polymers destroyed these weak connections but not the strong connections. This is why a single layer is hard to be obtained. The missing of a diffraction pattern indicates the amorphous nature of the cyclosiloxane polymer

Figure 4.15 TEM image of cyclosiloxane polymer. Inset is diffraction pattern image of it.

4.5.5 AFM

AFM was used to characterize the surface of cyclosiloxane polymer for the first time. Figure 4.16 shows the AFM height image of cyclosiloxane polymer surface. The AFM image showed a smooth surface with only 0.46 nm surface roughness.

Figure 4.16 AFM height image of cyclosiloxane polymer surface.

AFM image of a powder sample of cyclosiloxane polymer after being cleaned by sonication is shown in Figure 4.17. A stacked layered structure was clearly seen from the height image of one piece of micro-sized polymer debris. The section analysis showed that the thickness of each layer was around a few tens of nanometers, which indicated that each layer did not consist of single sheet.

The AFM image also shows that in this piece of cyclosiloxane polymer debris, the directions of the layered structure were not the same. Layered structures in areas A, B and C had different stacking directions and area D with no clear layered structure might be a transition area connecting areas with different layered structure stacking directions.

Figure 4.17 (Top) AFM image of grinded powder of cyclosiloxane polymer and (bottom) section analysis of it.

Figure 4.18 shows AFM image of one thin piece of cyclosiloxane polymer. The thickness was about 30 nm, but the fluctuation from section analysis proved that this thin piece was still a stack of cyclosiloxane polymer layers with a thickness of around 1-5 nm.

Figure 4.18 AFM image of a thin piece of cyclosiloxane polymer.

4.5.6 TMA

In 4.5.5, SEM, TEM and AFM images have proved that cyclosiloxane polymer is naturally a layered structure, and AFM has shown that the layered structures have different directions. Though the nano-sized layered structure has been proved by previous morphology characterizations, the bulk structure remains unclear. If cyclosiloxane polymer is a pure layered structure or has oriented structure, the properties in different directions should be different. In this case, TMA was used to evaluate thermal expansion properties at different directions. One flat piece of cyclosiloxane polymer was used to test coefficients of thermal expansion (CTE) by TMA, both in plane and out of plane directions. The thermal expansion curves are shown in Figure 4.19. CTE obtained from the slope of thermal expansion curves were 124.1 ppm/°C and 124.3 ppm/°C for in plane and out of plane, respectively. This indicates that cyclosiloxane polymer is isotropic in the bulk. So the cyclosiloxane polymer is a layered structure at the nano scale but isotropic in the bulk.

Figure 4.19 Thermal expansion curves of a flat piece of cyclosiloxane polymer.

4.6 Conclusion

In this chapter, non-isothermal DSC was used to do hydrosilylation kinetics of cyclosiloxane polymer. The curing kinetics of this tetra-functional cyclosiloxanes was evaluated by model fitting and model free isoconversional methods for the first time. The solventless curing process showed a decelerating reaction process, and E_a dependency on conversion was attributed to a combined influence of shift from chemical control to diffusion control, increasing steric hindrance from tetra-functional structure, dendrimer-like intermedia, phase transition and inevitable errors. The E_a dependency was also analyzed from view of structure growth. Curing process monitored by FTIR and Rheometer verified the assumptions/explanations from DSC kinetics.

The cyclosiloxane polymer was characterized by TGA/DSC, the high thermal stability and high ceramic yield indicated that it is a good candidate for high performance polymer. The micro structure was characterized by SEM, TEM and AFM. The morphology images proved the hypothesis that cyclosiloxane has a layered structure in nano-size. The similar CTE from TMA test indicated that cyclosiloxane polymer is isotropic in bulk. (Figure 4.19)

This chapter corresponds to objective 1 stated in 1.2.

Figure 4.19 A schematic drawing of cyclosiloxane polymer structure.

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Chapter 5

PDMS Reinforced Cyclosiloxane Polymers

This chapter presents cyclosiloxane polymers reinforced by vinyl terminated polydimethylsiloxane (PDMS) which can react with the dangling Si-H bonds. Mechanical properties such as hardness, modulus and toughness are assessed. Simultaneous improvements in stiffness and toughness are observed at low loading (<0.1 wt%) of PDMS. It is proposed here that the PDMS exists as two phases: homogeneously dispersed PDMS single chains, which are responsible for simultaneous improvements in toughness and stiffness, and phase separated PDMS particles, which contribute to toughness but lead to deterioration of other mechanical properties. The simultaneous improvement of stiffness and toughness is a combined effect of the two phases.

5.1 Introduction

This chapter presents cyclosiloxane polymers reinforced with vinyl terminated PDMS, corresponding to objective 2 stated in 1.2. The mechanical properties were evaluated by tensile test, compression test, nanoindentation test, DMA and 3-point bending test. Reinforcements in all mechanical tests are observed and the reinforcement mechanisms are proposed.

Reinforcement of polymer materials can be achieved by various methods, of which, adding stiff fillers such as Carbon Nanotubes (CNTs)¹⁻³, Graphene or modified Graphene nanosheets⁴⁻⁷ and ceramics⁸ has been proven to be an effective method which also offers the possibility of rendering functionalities such as electrical conductivity and thermal conductivity^{2,8-14}. However, despite the high strength or stiffness/hardness achieved by adding such stiff fillers, the reinforcement was usually achieved by sacrificing other mechanical properties such as toughness. The compromise is highly unfavorable for real applications, especially for materials subject to various or continuous loads. Efforts have been made to fabricate stiff yet tough materials through nanocomposites route¹⁵⁻¹⁷ or mimicking natural structures.¹⁶ However, the high cost involved due to large quantity of nano-fillers and complicated processing method limited possible applications. Apart from stiff nano-fillers, polydimethylsiloxane (PDMS) has been widely used to toughen thermosets¹⁸⁻²³ by simply physical blending or through creating chemical covalent bonds. However, to the best of my knowledge, PDMS usually does not improve other mechanical properties such as modulus or hardness, since it is softer than the matrix materials. the large quantity of PDMS added in order to achieve the satisfying toughening effect usually cause deterioration other mechanical properties such as strength or stiffness²². From toughening mechanism point of view, some authors suggested that the presence of these PDMS particles which dissipate energy by yielding around them are the main reason of PDMS toughening effect^{21,23-25}. This mechanism sounds reasonable; however, it offers little insight into the structure-property relationship and no guidance for the design of new resin materials. Based on this, an engagement of high cross-link density domains toughening mechanism was proposed²². The residual Si-OH groups after

synthesis were purposely designed to crosslink prepolymer molecules to form grains which had higher cross-link density. The rubber phase particles helped the grains deform and absorbed more energy, contributing to higher toughness of silicone resins. However, this mechanism is complicated yet not clearly understood since they incorporated two kinds of PDMS with different chain length and the structure of silicone resin was unknown. A simple and clear model is needed to better understand the toughening mechanism of PDMS.

During our screening of materials for reinforcement, it was found that cyclosiloxane polymer is a layered structure at nano scale but isotropic in bulk due to different orientations of nano-sized layers (Chapter 3). The problem and disadvantage of this materials lie in the intrinsic brittleness, which results from the weak connections between the layers. Besides, steric hindrance and excessive Si-H bonds caused the presence of dangling bonds which act as defects as well as possible crosslinking sites. Considering the nature of cyclosiloxane polymer and PDMS are both polysiloxane, it makes it ideal matrix to study how PDMS works inside the matrix, both in toughening and reinforcement of other mechanical properties.

To better understand the reinforcement mechanism of PDMS, PDMS reinforced cyclosiloxane polymers are researched in this chapter. The PDMS here used is vinyl terminated (Figure 5.1). The vinyl groups can react with the Si-H groups, sealing the dangling bonds and anchoring layered structures to each other. It is commonly accepted that that if you add a soft segment into hard parts, the overall mechanical properties such as hardness or modulus will decrease with increasing soft segment loading. Contrary to that, an increase in hardness, modulus and toughness were observed with certain PDMS loadings. A reinforcement mechanism for the simultaneously improved stiffness/hardness and toughness is proposed in this chapter which may guide new materials design.

Figure 5.1 Structure of vinyl terminated PDMS.

5.2 Tensile Test

Figure 5.2 shows the Young's modulus of PDMS reinforced cyclosiloxane polymers obtained from the tensile test. A significant increase of 11.4% in Young's modulus was observed at 0.2 wt% loading of PDMS. The extent of increase declined upon further increasing the PDMS content, merely 0.6% enhancement was observed when the PDMS content was increased to 0.8 wt%. This phenomenon is contrary to previously published results that only a continuous decrease in mechanical properties with increasing PDMS content was observed due to the formation of soft PDMS microparticles caused by phase separation²³. The strains at break are not applicable here because the failure of samples occurred at clamp area instead of the middle part of the samples (inset picture of Figure 5.2).

Figure 5.2 Young's modulus of PDMS reinforced cyclosiloxane polymers.

Inset is a picture of samples after tensile test.

5.3 Compression Test

Figure 5.3 shows the compression curves and compression strength of PDMS reinforced cyclosiloxane polymers. Compression strength represents the capacity of a material to resist compression and indicates the strength limit when material is under compression stress. The compression strength showed a similar trend with Young's modulus. A 44.5%

increase in compression strength was observed with only 0.2 wt% PDMS. Further increase of PDMS content lead to a decrease in compression strength, increases of 11.6% and 17.6% were observed for 0.4 wt% and 0.6 wt% loading of PDMS, respectively, while a 2.2 % decrease in compression strength was observed at 0.8 wt% loading of PDMS. The compressive modulus can be calculated from the slope of the compression curve. However, for this compression, the compressive modulus is not accurate because of fluctuations in the curves which resulted from cracks during compression. By comparing the compression curves, it is obvious that all the samples reinforced by PDMS had a higher compressive modulus than cyclosiloxane polymer. 0.2 wt% PDMS reinforced cyclosiloxane showed the highest compressive modulus.

Figure 5.3 (A) Compression curves and (B) compression strength of PDMS reinforced cyclosiloxane polymers.

5.4 Nanoindentation

Nanoindentation curves and hardness of PDMS reinforced cyclosiloxane polymers at various loadings are shown in Figure 5.4, and Table 5.1 summarizes the results of nanoindentation. The hardness showed an upward peak like a trend with increasing PDMS content and reach its highest value at 0.4 wt% loading with 12.7% improvement, which is similar to trend of Young's modulus and compression strength. For all samples except 0.8 wt% PDMS loading in cyclosiloxane polymer, the 5 nanoindentation curves overlapped with each other perfectly, which, to some extent, indicated the homogeneity

of the samples. Indentation depth around 1400 nm was obtained when the force was held at 5 mN for 5 s for pure cyclosiloxane to its nanocomposite containing up to 0.6 wt% of PDMS indicates that cyclosiloxane polymers and its composites were hard, while after unloading the displacement almost return to its original value with some remaining displacement resulting from holding, indicating elasticity. The reduced modulus did not show any trend but fluctuated with PDMS content.

At 0.8 wt% of PDMS loading, a large error bar was observed. The abnormality was attributed to the presence of a soft segment, which is probably the PDMS phase. The distinct hardness determined at different spot within the same specimen proved the existence of PDMS phase due to phase separation.

After nanoindentation, SEM and AFM were used to find the nanoindentation traces. However, the traces could not be observed though a few trials were made. This is consistent with Zheng's observation²⁶. So the deformation during nanoindentation was elastic deformation in which case it could regain its original dimensions after the force was unloaded. Holding at maximum load did not lead to permanent deformation, and the indentation depth recover with time, which is defined as creep recovery. It can be concluded that holding at maximum depth did not lead to failure of the structure because creep recovery occurred after force was released.

Figure 5.4 Nanoindentation curves of cyclosiloxane polymer reinforced by (A) 0%, (B) 0.2 wt%, (C) 0.4wt%, (D) 0.6 wt%, (E) 0.8 wt% PDMS, and (F) hardness versus PDMS content. .

Table 5.1 Hardness and reduced modulus of cyclosiloxane polymers reinforced by PDMS.

PDMS content (wt%)	Hardness (GPa)	Reduced modulus (GPa)
0	0.229 ± 0.003	1.466 ± 0.015
0.2	0.221 ± 0.002	1.276 ± 0.002
0.4	0.258 ± 0.005	1.303 ± 0.007

0.6	0.232 ± 0.002	1.288 ± 0.009
0.8	0.220 ± 0.092	1.358 ± 0.123

5.5 DMA

DMA was used to test the storage modulus of PDMS reinforced cyclosiloxane polymer. The storage moduli for cyclosiloxane polymers with 0 wt%, 0.2 wt%, 0.4 wt%, and 0.8 wt% PDMS loadings were 676 MPa, 765 MPa (13.2% ↑), 753 MPa (11.4% ↑) and 716 MPa (5.9 % ↑), respectively. According to ISO 6721-1, the storage modulus represents the stiffness and is proportional to the energy stored under load. When PDMS was added into cyclosiloxane polymer, the increase in storage modulus represented the stiffening effect of cyclosiloxane polymer. Similarly, the increase showed an upward peak, reaching its highest value at 0.2 wt% PDMS loading.

5.6 Three-point bending and toughness

Figure 5.5 (A) shows the representative curves of PDMS reinforced cyclosiloxane polymers. Figure 5.5 (B) shows the flexural modulus and flexural strength and Figure 5.5 (C) shows the calculated relative toughness from the area under the stress-strain curves. The toughness of neat cyclosiloxane polymer without any PDMS was normalized to 1 to intuitively present the data.

The flexural modulus and flexural strength showed the similar trend as previously discussed mechanical properties. At 0.2 wt% loading of PDMS, the flexural modulus and flexural strength showed the highest values with 22.6% and 94.5% improvement, respectively. The improvement of 0.4 wt%, 0.6 wt% and 0.8 wt% PDMS loading cyclosiloxane polymers in flexural modulus is 5.8%, 8.2% and 7.0%, respectively, while improvement in flexural strength is 57.4%, 86.5% and 38.7%, respectively. The improvement observed in tensile modulus, compression strength, hardness, flexural modulus and flexural strength indicated that certain loadings of PDMS made cyclosiloxane polymer harder or stiffer.

The low flexural strain of neat cyclosiloxane polymer indicated that this material is brittle. Here the area under the stress-strain curve was calculated and normalized as toughness of PDMS reinforced cyclosiloxane polymers. From the representative curves (Figure 5.5 (A)) and mechanical properties (Figure 5.5 (B)) of cyclosiloxane polymers, it can be concluded that PDMS contributes to both flexural modulus and flexural strain. Though the modulus of cyclosiloxane polymer with more than 0.2 wt% loading of PDMS decreased with increasing PDMS, the modulus was still more than that of neat cyclosiloxane polymer. Meanwhile, the dramatic increase in flexural strain ($\sim 70\%$ and $\sim 140\%$ improvement for 0.4 wt% and 0.8 wt% loading of PDMS, respectively) contributed to the toughness. The toughness improvement for 0.2 wt%, 0.4 wt%, 0.6 wt% and 0.8 wt% PDMS loadings is 207.0%, 210.4%, 208.7% and 73.7%, respectively.

Figure 5.5 (A) Representative 3-point bending curves against flexural strain, (B) flexural modulus, flexural strength and (C) toughness of PDMS reinforced cyclosiloxane polymers versus PDMS contents.

5.7 SEM

Figure 5.6 shows selected SEI images of fracture surfaces from three-point bending tests aimed to investigate the reinforcement mechanism of PDMS. Neat cyclosiloxane polymer gave a smooth fracture surface and straight cracks, typically observed from intrinsically brittle materials and cyclosiloxane polymer with 0.2 wt% loading PDMS showed similar smooth fracture surface as neat resin (Figure A.1). When 0.4 wt% PDMS was added into cyclosiloxane polymer, the PDMS phase started to separate from the cyclosiloxane polymer matrix, forming PDMS particles with diameters of approximately 50-70 nm. The amount of PDMS particles increased with loading content while the size remained unchanged. The presence of nano-size particles induced a micro-size tail, or also known as crack-pinning (red circles, Figure 5.6 (D) and (F)). This micro-sized ‘crack-pinning’ should be one of the main reasons why the toughness increased at such loadings.

Figure 5.6 SEI images of fracture surfaces after 3-point bending test

(A) and (B): Neat cyclosiloxane polymer;

(C) and (D) 0.4 wt% PDMS; (E) and (F) 0.8 wt% PDMS

The white arrows indicate the crack direction.

5.8 Proposed Reinforcing Mechanisms for Simultaneously Improved Hardness/Stiffness and Toughness

Simultaneous improvement in all the mechanical properties, including Young's modulus, compression strength, compressive modulus, hardness, storage modulus, flexural modulus, flexural strength, and toughness were obtained through adding PDMS, but within certain loading (0.2 wt% - 0.6 wt%). Obviously, the liquid PDMS rubber phase is soft than the solid cyclosiloxane polymer matrix, and there is an unassured question how PDMS works inside cyclosiloxane polymer to achieve simultaneous improvement in toughness and other mechanical properties in such a low loading (< 1 wt%). The underlying mechanisms accounted for the observations arise from the phenomena are:

- a. The improvements in mechanical properties except toughness observed when soft PDMS was added into hard cyclosiloxane polymer matrix.
- b. The improvements obtained through the addition of a tiny amount of PDMS ($< 1\%$) compared to the usual amount (15 wt% - 20 wt%²⁷) used to toughen brittle thermosets.

When it comes to the reinforcement mechanisms of PDMS in cyclosiloxane polymer, the polymer structures and in what phases PDMS exists should be taken into consideration. According to the cyclosiloxane polymer network analyzed in the previous chapter, the structure is built up of layers with a few tens of nanometer in thickness and the connections between layers are weak since the layered structure could be separated by grinding and sonication in ethanol. However, during structure growth, due to the steric hindrance and the excessive Si-H bonds, there were lots of dangling Si-H bonds inside the cyclosiloxane polymer. The weak connections between the layered structures and dangling bonds are intrinsic defects which may lead to poor mechanical properties such as brittleness. A possible way to achieve reinforcement is through bridging the flake-like structures by sealing the dangling bonds. In this case, the vinyl terminated PDMS was employed to seal the dangling Si-H bonds and bridge the layered structures. When then PDMS content exceeded a critical amount, PDMS separated from cyclosiloxane polymer matrix and formed rubber phase particles which further toughened the matrix.

Based on the results and discussions above, a reinforcing mechanism for covalently bonded PDMS was proposed. The PDMS was proposed to exist as two phases in the cyclosiloxane polymer: (1) homogeneously dispersed PDMS existed as single chain,

which can bridge the layers, and (2) PDMS particles with a diameter of 50-70 nm, which can insert between layers and dissipate energy. A schematic graph of structure of PDMS toughened cyclosiloxane polymer is shown in Figure A.2

When cyclosiloxane polymer was subject to a force, no matter tension, compression or a combination of both, the force can be divided into two forces: one is parallel to the layer and the other one is vertical to the layer. (Figure 5.7) Base on this, the reinforcing mechanisms is proposed in the following sections.

Figure 5.7 Illustration of cyclosiloxane polymer subject to force.

5.8.1 Homogeneously Dispersed PDMS

Because cyclosiloxane polymer with 0.2 wt% loading of PDMS showed a smooth fracture surface (Figure A.1) without observation of any PDMS particles. In this case, PDMS is homogeneously dispersed in cyclosiloxane matrix. The homogeneously dispersed PDMS exist as single chain, and the terminal vinyl groups can react with dangling Si-H bonds in layered structures, bridging layered structures. For homogeneously dispersed PDMS, the simplest type is PDMS chains which directly bridge two layered structures together. Here in this section, the simplest model is adopted to illustrate how homogeneously dispersed PDMS works in cyclosiloxane polymer

(Figure 5.8). However it should be noted that the actual situation is much more complicated because the PDMS chain can go through one or more layered structures. PDMS chains can seal dangling bonds, reducing defects and bridging layered structures. When a force is applied to the sample, PDMS chains will be stretched and anchored one layer of the structure to another (Figure 5.8). Going through layered structures enables one PDMS chain to anchor three or more of them, even though those between PDMS ends are non-covalently bonded. To some extent, stretching of PDMS chain from coil state contributes to larger strain under force, toughening cyclosiloxane polymer matrix. So the reinforcement of mechanical properties should be attributed to the homogeneously dispersed PDMS chains while it is also responsible for the toughening effect at 0.2 wt% loading.

Figure 5.8 A schematic graph of cyclosiloxane polymer with homogeneously dispersed PDMS under force.

5.8.2 Separated PDMS particles

The PDMS phase also exists in particle form, which is inserted between two layered structures. Figure 5.9 gives a schematic illustration of the toughening mechanism of PDMS particles. At loading of PDMS is 0.4 wt% or more, PDMS tends to separate and

form PDMS particles with a diameter of 50 – 70 nm. The presence of phase separated PDMS rubber particles dissipated the stress and contributed to strain increase when the sample was subjected to force and achieved toughening effect of the cyclosiloxane polymer matrix. Thus, for samples with 0.4 wt% or more loading of PDMS, the toughening effect comes from both homogenously dispersed PDMS and separated PDMS particles.

However, when the loading of PDMS is 0.8 wt%, more soft PDMS particles increase the distance of layered structures, leading to a lower crosslinking density and weak connections between layered structures. As a consequence, the mechanical properties decreased²⁸.

Figure 5.9 A schematic graph of cyclosiloxane polymer with phase separated PDMS particles under force.

5.8.3 Summary of Proposed Reinforcement Mechanisms

In the PDMS reinforced cyclosiloxane polymers, the reinforcement depends on which phase is dominant. When the loading content of PDMS is 0.2 wt%, homogeneously dispersed PDMS is dominant and the polymer is reinforced in both stiffness and toughness. When the loading of PDMS is equal to or more than 0.4 wt%, the dominant phase is separated PDMS particles and stiffness starts to decrease but the toughness is

still maintained at a high value. If the loading of PDMS is 0.8 wt%, too many PDMS particles leads to increase of distance between layered structures and lead to reduced mechanical properties. The coalescence of micro-sized cracks is another reason why toughness drops.

To sum up, cyclosiloxane polymer was strengthened, stiffened and toughened by soft covalently bonded PDMS in a certain loading range. The mechanism of reinforcement was proposed to explain the phenomena. Defects can be decreased by homogeneously dispersed PDMS phase, in which case stiffness and toughness are improved simultaneously. Separated PDMS phases can dissipate stress and contributes to toughness while deteriorating other mechanical properties. The reinforcement depends on which PDMS phase was dominant. However, when PDMS content is 0.8 wt%, the toughness dropped because the PDMS particles can expand the distance between layers, leading to a smaller failure strain (Figure 5.5A), and thus lead to decreased toughness at 0.8 wt% loading.

Though satisfying reinforcement in toughening and other mechanical properties were achieved, UV-Vis and thermal stability of PDMS reinforced cyclosiloxane polymers were evaluated to explore possible optical or high-temperature applications.

5.9 UV-Vis

Figure 5.10 shows a depictive picture of PDMS reinforced cyclosiloxane polymers and the UV-vis results from them. The UV-vis results show that the samples turned from transparent to translucent with increasing PDMS content. Neat cyclosiloxane showed ~80% transmittance from 400 nm to 800 nm. Samples with 0.4 wt% PDMS loading showed a reduced transmittance but still as high as 70%. If PDMS loading was further increased, the transmittance decreased dramatically. The decrease in transmittance is due to phase separation of PDMS^{29,30} which is usually immiscible with most of the polymers. The absorption below 400 nm is due to Pt derived from the catalyst²⁶. It should be noted that

when the PDMS content is low enough (≤ 0.4 wt%) the change in transmittance is not significant (the sample thickness is 4 mm).

Figure 5.10 A depictive picture of PDMS reinforced cyclosiloxane polymers. Inset picture is UV-Vis results of the samples. The sample thickness is around 4 mm.

5.10 TGA

Figure 5.11 shows the TGA curves of PDMS reinforced cyclosiloxane polymers in nitrogen and Table 5.2 summarizes the results of them. T_{d5} (temperature at which 5 wt% loss appears) and weight retention at 800 °C of PDMS reinforced cyclosiloxane polymers showed the same trend that with increasing PDMS loading content both T_{d5} and weight retention at 800 °C decreased. This is mainly due to lower thermal stability of PDMS than that of cyclosiloxane polymer. The cyclosiloxane polymer starts to decompose at 375 °C, at which stage the main weight loss is due to cleavage of organic side groups from Si atoms³¹, followed by mineralization process at higher temperatures³² while PDMS chain tends to bite back to form volatile cyclic siloxanes at around 400 °C, leading to a sharp decrease in weight till almost 0% retention at 600 °C^{33,34}.

Figure 5.11 TGA curves of PDMS reinforced cyclosiloxane polymers in nitrogen.

Table 5.2 T_{d5} and Weight retention at 800 °C of PDMS reinforced cyclosiloxane polymers.

PDMS content/%	$T_{d5}/^{\circ}\text{C}$	weight retention at 800°C/%
0	602	87.56
0.2	592	86.58
0.4	584	86.02
0.6	581	85.96
0.8	578	85.61

5.11 Conclusion

In this chapter, vinyl terminated PDMS was successfully incorporated into cyclosiloxane polymer via hydrosilylation at very low loadings (< 1 wt%). The PDMS reinforced cyclosiloxane polymers were characterized by tensile test, compression, DMA, nanoindentation and 3-point bending test. Simultaneous improvement in stiffness/hardness and toughness were observed. SEI images of fracture surface of PDMS reinforced cyclosiloxane polymers showed that PDMS separated and formed particles with diameter of 50 – 70 nm.

Based on the layered structure of cyclosiloxane polymer, reinforcing mechanisms are proposed in this chapter. PDMS exists in two phases in cyclosiloxane polymer, one is homogeneously dispersed and the other one is phase separated. Homogeneously dispersed PDMS is responsible for

reinforcement in all mechanical properties including toughness. Phase separated PDMS particles are responsible for toughness at high loadings (≥ 0.4 wt%), but deteriorate other mechanical properties. The mechanical properties of PDMS reinforced cyclosiloxane is an outcome of combination of homogenously dispersed PDMS and separated PDMS particles.

This chapter corresponds to objective 2 stated in 1.2.

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Chapter 6

Toughening Effects of Basally Functionalized Graphene Nanocomposites on Cyclosiloxane Polymer and Thermal Conductivity of Nanocomposites Thereof

This chapter presents the cyclosiloxane polymer based graphene nanocomposite. The mechanical properties evaluated by a 3-point bending test are shown and a 153% improvement in toughness with only 0.08 wt% of basally functionalized graphene oxide (GO-AA) is observed. Following the mechanical properties, the thermal conductivity of graphene-cyclosiloxane polymer nanocomposites is presented and the corresponding ‘double side tape’ mechanism of GO-AA is proposed to explain the toughening mechanism and reinforcing effect in thermal conductivity. GO-AA acts as double side tape in the cyclosiloxane polymer matrix to bind layered structures together, contributing to toughening of the matrix. It also acts as a staircase for phonon transfer and reduces phonon scattering when the phonon transfer is between layers.

6.1 Introduction

In this chapter, modification of graphene oxide (GO) by allylamine is presented and the nanocomposites made from graphene and cyclosiloxane are assessed by 3-point bending test and thermal conductivity test. This chapter corresponds to objective 3 stated in 1.2. An increase in toughness and thermal conductivity with low loading of basally functionalized graphene oxide (GO-AA) is presented and the corresponding reinforcing mechanisms are proposed.

Traditionally, rubber and thermoplastic toughening agents are used for improving toughness, but the large amount used (15-20 wt%)¹ causes degradation of other mechanical properties and thermal stability, which can be proved by research presented in Chapter 5. Comparing with traditional counterparts, nanofillers such as carbon fiber, carbon nanofiber, carbon nanotubes, or nano-size metallic oxide and graphene attract a lot of attention since they were proven to improve toughness and stiffness simultaneously, contributed by the large surface area and specific chemical modification towards better interfacial interaction between polymer matrix and nanofillers, without loss in thermal stability.²⁻⁴

Graphene, among all these nanofillers, has emerged as an superior choice in terms of its high specific area, maximizing extended two-dimensional geometry, and the wrinkled surface which is critical for interfacial interaction between the fillers and matrix.⁵ Various studies have been done on the toughening mechanism of graphene inside ceramics⁶⁻⁹ and polymers^{1,5,10-16}. Several toughening mechanisms were proposed, which can be summarized as graphene pull-out, crack bridging, crack pinning, crack deflection, and microcracks.

Graphene-based nanocomposites have drawn much attention due to excellent mechanical property enhancement and possible multi-functionalization of polymer matrix. By introducing graphene into polymer matrix, a remarkable improvement in mechanical properties of polymer matrix can be achieved and this has qualified it for harsher

environmental conditions, widening its fields of application. As discussed previously, graphene was used to toughen brittle thermoset polymers and various toughening mechanisms have been proposed to explain the toughening effects of graphene nanosheets.¹²⁻¹⁴ However, due to its high cost, a low loading of graphene inside nanocomposites (within 0.5 wt%) is desired for industrial applications.^{5,15,16} Furthermore, most of the studies related were based on epoxy systems, and very few papers talked about toughening of silicone resins. To the best of my knowledge, no report has been published on toughening of this cyclosiloxane based polymer with the incorporation of a low loading of graphene nanosheets.

The layered structures of cyclosiloxane polymer make the well-established toughening methods ineffective. The solventless process also makes it challenging to disperse the nanofiller in the matrix. In this case, graphene is suitable for toughening cyclosiloxane polymer because graphene is a two-dimensional material and it can bind layers together once graphene is modified by groups which can react with cyclosiloxane polymer.

Motivated by the discussion above, it was decided to investigate the toughening effects of graphene nanosheets in cyclosiloxane hybrid matrix. The content of graphene in nanocomposites was kept within 0.1 wt%. Graphene oxide (GO) was chemically functionalized via a facile method and both of unfunctionalized and functionalized GO were incorporated into cyclosiloxane hybrid matrix via solventless process. The enhanced mechanical properties were observed and possible toughening mechanisms are proposed. The thermal conductivity of graphene-cyclosiloxane polymer nanocomposites was studied as one of possible functionalities and the mechanism of enhancing thermal conductivity was discussed. This work paves the way to the practical applications of cyclosiloxane polymer hybrids.

6.2 Characterizations of Basally Functionalized Graphene Oxide (GO-AA)

Chemicals containing amine groups are believed to be potential reducing agents for GO.¹⁷ And in theory, both carboxyl groups and epoxide groups on GO nanosheets are likely to

react with amine groups. Figure 6.1 shows modification of GO by allylamine and characterizations of GO as well as GO-AA by FTIR, TGA and TEM.

FTIR spectroscopy was utilized to verify the chemical linkages between GO and allylamine. As shown in Figure 6.1 (B), the peaks corresponding to oxygen-containing groups in GO-AA were much reduced when compared to those in GO, indicating obvious reduction has occurred. Although C=O stretching vibration peak (1732 cm^{-1}) in GO-AA disappeared due to the reduction, no obvious peaks corresponding to amide groups can be observed. The peak at 1058 cm^{-1} corresponding to stretching vibration of epoxide groups disappeared accompanied by the emergence of three new peaks located at 1573 cm^{-1} (N-H), 1431 cm^{-1} (C-N), and 1214 cm^{-1} (C-O), which were consistent with the typical ring-opening reaction between -NH_2 and -C-O-C- .¹⁸⁻²⁰ Additionally, the new peak at 932 cm^{-1} observed in GO-AA ascribed to -C=C- further confirmed the successful grafting of allylamine.²¹ According to the widely accepted Lerf-Klinowski model²², carboxyl groups are believed to be distributed at the edge of GO nanosheets while the epoxide groups are basally decorated. Based on the discussion above, it is believed that the GO-AA was basally functionalized by allylamine molecules. Thus, the subsequent in-situ polymerization of cyclosiloxanes will selectively occur on the basal plane, which promotes the expansion and exfoliation of GO-AA nanosheets in the toughened/high performance polymer composites.

The results of thermogravimetric Analysis (TGA) of GO and GO-AA are shown in Figure 6.1 (C). The poor thermal stability of GO with a low onset thermal degradation around $150\text{ }^{\circ}\text{C}$ and 32 wt% weight loss between 150 to $350\text{ }^{\circ}\text{C}$ were due to the cleavage of labile oxygen-containing groups on GO.²² In contrast, the removal of most of the oxygen-containing groups from GO-AA improved the thermally stability with only 15 wt% weight loss between 150 to $350\text{ }^{\circ}\text{C}$, and the final residual of GO-AA at $800\text{ }^{\circ}\text{C}$ was determined as 51 wt%.

Figure 6.1 (E) and (F) show the TEM images and the respective selected-area electron diffraction (SAED) of GO and GO-AA. Rougher surface of GO-AA was resulted due to

the introduction of allylamine and the SAED patterns with only one set of points are expected from single graphene sheet.

Figure 6.1 (A) Schematic graph of modifying GO by allylamine, (Red: Top surface Blue: Bottom surface). (B) FTIR spectra of GO and GO-AA, and (C) TGA curves of GO and GO-AA in nitrogen. TEM images of GO (E) and GO-AA (F), Inset pictures are SAED patterns (Scale bar 500 nm).

Figure 6.2 (A) shows the Raman spectra which revealed the structural changes of GO upon surface modification. The Raman spectrum of GO demonstrates two main peaks at 1354 cm^{-1} and 1581 cm^{-1} , corresponding to D band and G band, respectively. The drastic intensity increase of D and G band in GAC and GAT indicated that the formation of more sp^3 and sp^2 carbon structures. The D band represents the defects of graphene, while the G band is due to the first order scattering of the E_{2g} phonon of the sp^2 carbon atoms of graphene.²³ The G band of GO-AA shifted to 1573 cm^{-1} suggested that GO was successfully reduced by allylamine. The I_D/I_G increased from 0.92 for GO to 1.03 for GO-AA, indicating the removal of oxygen functional groups and the conversion of sp^3 carbon of GO to sp^2 carbon in the reduced GO. Another difference which should be noticed is 2D bands of GO and GO-AA. 2D bands located at 2718 cm^{-1} are sensitive to layers of graphene.^{24,25} The missing 2D peak in GO-AA indicates the existence of single layered graphene and the success in the exfoliation of the graphene nanosheets.

Figure 6.2 (B) shows the N1s XPS spectrum of GO and GO-AA while Figure 6.2 (C) and (D) show the C1s XPS spectrum of GO and GO-AA, respectively. C1s XPS peak locations and relative area are shown in Table 1. Compared with N1s XPS spectra of GO, a peak at 399.50 eV which corresponds to C-N bonds indicates successful grafting of allylamine onto graphene nanosheets.²⁶ To further understand the bonding chemistry of allylamine, C1s XPS peaks were deconvoluted into separate peaks. No peak for C(O)-N (287.43 eV) and C(O)-O (289.42)²⁷ can be deconvoluted from the XPS spectra of GO-AA while C-N peak (286.48 eV) suggests the covalent reaction of epoxide groups and amine groups. As discussed above, carboxyl groups are believed to be distributed on the edge of graphene while epoxide groups are basally decorated. The absence of C=O and C(O)-N signals proved that GO-AA was basally functionalized by allylamine. Variance in percentage of C=O between spectra of GO and GO-AA reveals changes in the proportions of oxygen-containing functional groups. The deconvoluted C1s spectrum of GO shows strong C-O signal (286.52 eV) while the one of GO-AA showed decreased intensity. Taking all the points above into consideration, the XPS spectra of GO and GO-AA further proved that modification of graphene nanosheets by allylamine and reduction of GO occurred simultaneously and the GO-AA is basally functionalized.

Figure 6.2 (A) Raman spectra of GO and GO-AA, (B) N1s XPS spectra of GO and GO-AA, C1s XPS spectra of (C) GO and (D) GO-AA.

6.3 Stability of Graphene Suspensions and Dispersion of Graphene Nanosheets

The suspension stability of GO in D_4^V played a crucial role in determining the GO final dispersion state in the nanocomposite obtained via the solventless in-situ polymerization process. This directly correlates with mechanical, electrical, thermal, and other functional properties.²⁸ Figure 6.3 shows the digital images of GO and GO-AA suspensions in D_4^V and the final nanocomposites. GO started to aggregate at 5 min and precipitated at 10 min after sonication, while the GO-AA suspension remained stable at 30 min after sonication. Distinct dispersion state of GO and GO-AA in the D_4^V matrix was clearly visible from the digital images in Figure 6.3 (B). Observation of 0.04 wt% nanocomposites by microscope (Inset images of Figure 6.3 (B). Large images are available in Figure A.3) further proven the improved dispersion of GO-AA in nanocomposite since aggregation of GO can be easily observed while GO-AA were distributed evenly in nanocomposites. The improved

dispersion of GO-AA inside D_4^V was mainly contributed by the decrease in hydrophilicity after modification by allylamine, resulting in improved compatibility of graphene nanosheets with the hydrophobic D_4^V monomer, an great advantage for the solventless process.

Figure 6.3 (A) Visual pictures of GO and GO-AA suspensions in D_4^V after sonication; (B) Visual picture of final GO and GO-AA nanocomposites; Inset pictures are microscope graphs of 0.04 wt% GO nanocomposite and 0.04 wt% GO-AA nanocomposite.

6.4 3-Point bending Tests and Toughness

The toughening effects of GO-AA were demonstrated by the flexural modulus, flexural strength, and relative toughness through 3-point bending tests. Representative curves are shown in Figure 6.4 (A). The relative toughness was calculated according to equation 3.19 and is shown in Figure 6.4 (B). Figure 6.4 (C) and (D) compare the flexural modulus and flexural strength of GO and GO-AA nanocomposites. Figure 6.4 (C) shows that the flexural modulus of GO nanocomposites fluctuates as a function of graphene content while the flexural strength decreases with increasing graphene content. Compared with GO nanocomposites, the flexural modulus of GO-AA nanocomposites increased with

graphene content, maximized at 0.04 wt% before decrease at higher loading. The flexural strength increases with graphene content, but less significant when graphene loading is lower than 0.04 wt%. The insignificant effect of GO on modulus is due to the weak graphene-matrix interfacial interaction resulting from their incompatibility. Together with aggregation of GO nanosheets, these two reasons caused the decrease of flexural strength.¹⁶ For GO-AA nanocomposites, better dispersion and covalent bonds between graphene nanosheets and the cyclosiloxane hybrid matrix are the two main contributing factors for the increase of flexural modulus before it peaks at 0.04 wt% graphene loading, as well as for the increase of flexural strength with graphene loading from 0.02 wt% to 0.1 wt%. The subsequent decrease of flexural modulus might be due to poor dispersion above weight fraction of 0.04% which reduces the effective area for interaction.¹⁰ Apart from the two main reasons mentioned above, the wrinkled surfaces of graphene nanosheets also played an important role in enhancing the mechanical properties of nanocomposites. The wrinkled surfaces of graphene nanosheets, together with covalent bonds between graphene nanosheets and matrix, provide better interfacial interactions. In this case, the graphene nanosheets acted as interlocks and load transfers in the matrix, improving the mechanical properties (The wrinkled surfaces of graphene nanosheets can be observed in SEI image of graphene traces from fracture surface (Figure A.4 and A.5)).⁵

Figure 6.4 (B) shows the roughness calculated from the area under the stress-strain curve. It can be seen that the toughness of GO-AA nanocomposite increased with GO-AA loading while that of GO nanocomposites decrease with GO loading. The toughness results shows that the toughness of GO-AA nanocomposites was increased by 34.9%, 86.6%, 117.4%, 153.5% and 136.4% for 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8wt% and 1.0 wt% loading of GO-AA, respectively. To the best of my knowledge, the best toughening effect with low loading graphene is 50% increase with 0.04 wt% loading of graphene, followed by a decrease in toughness¹⁶. Our result showed that at 0.04 wt% loading of GO-AA, 86.6% increase in toughness was observed and the toughness continued to increase till 153.5% improvement with 0.08 wt% of GO-AA.

Figure 6.4 (A) Representative curves of nanocomposites; (B) Toughness of GO and GO-AA nanocomposites; Flexural modulus and flexural strength of (C) GO nanocomposites and (D) GO-AA nanocomposites.

As can be seen from SEI images from fracture surfaces after 3-point bending test, cyclosiloxane polymer matrix without graphene displayed a very smooth crack surface (Figure 6.5, (A)), and occasionally a small number of straight cracks can be observed. The smooth surfaces and straight crack indicated the intrinsic brittle nature of cyclosiloxane polymer matrix. The fracture surface of 0.04 wt% GO nanocomposite (Figure A.6) was chosen for discussion here, as the representative of all the GO nanocomposites prepared. Smooth fracture surface was observed except some aggregation of GO (Red arrows). The hydrophilicity of GO and hydrophobicity of cyclosiloxane polymer matrix lead to poor dispersion of GO in D_4^V monomer and subsequent aggregation during the curing process, which caused defects in the hybrid matrix.

Figure 6.5 (C)-(F) show typical fracture surfaces of GO-AA nanocomposites demonstrating better dispersion without aggregation. Interestingly, different toughening

mechanisms were observed at various GO-AA loadings. 0.02 wt% GO-AA nanocomposite showed a smooth fracture surface (Figure 6.5 (B)), and only few sites of crack pinning (red arrow, Figure 6 (B)) was observed in which case the crack front was stopped by graphene nanosheet, forming a graphene-tail morphology. Crack-pinning can be observed in all GO-AA nanocomposites, but it should be pointed out that crack pinning itself is insufficient to achieve a satisfactory toughening effect of the hybrid matrix at low graphene loadings (Figure 6.4 (B)). When GO-AA loading was increased to 0.04%, straight cracks with sub-cracks or microcracks can be observed (Figure 6.5 (C)). The number of cracks and microcracks grew with GO-AA loading (Figure 6.5 (D)-(H)). When the GO-AA loading is 0.08 wt%, the cracks were bamboo-like with many microcracks. The formation of bamboo-like microcracks absorbed the fracture energy, leading to increased toughness. However, when GO-AA loading is 0.10 wt%, the coalescence of microcracks (Red arrow, Figure 6.5 (F)) resulted in the formation of rougher surfaces, facilitated major crack propagation and reduced the toughness (Figure 6.4 (B)).

Though graphene pulling-out can be detected by SEM in GO-AA nanocomposites (Figure A.7), it is still quite a challenge to study the graphene nanosheets dispersion by SEM at such low loading of graphene⁵. Cyclosiloxane polymer tended to coat on graphene nanosheets. The strong connections between graphene and cyclosiloxane polymer matrix forced the crack to propagate within cyclosiloxane polymer matrix instead of along graphene nanosheets surfaces, thus leaving a wrinkled graphene trace with small flat surfaces (Figure A.5).

Figure 6.5 Fracture surfaces of cyclosiloxane polymer with (A) 0, (B) 0.02 wt GO-AA, (C) 0.04 wt% GO-AA, (D) 0.06 wt% GO-AA, (E) 0.08 wt% GO-AA and (F) 0.1 wt% GO-AA. The white arrows indicate crack propagation directions.

6.5 Proposed Toughening Mechanism

Various toughening mechanisms have been proposed to explain graphene toughening effect in polymer matrix^{5,7,10,14-16,29}. Crack pinning and microcracks are responsible for

the toughening effect. However, an insight into the structure should be taken into consideration to explain the toughening effect. Cyclosiloxane polymer is layered structure at nano-size but isotropic in bulk and this has been proved in chapter 4. Considering this, a double sided tape mechanism is proposed here to explain the toughening effect of GO-AA nanosheets and the forming of microcracks. The GO-AA nanosheets are covalently bonded to layered structures at nano-size and act as interlocks and load transfer which contributes to mechanical properties. This effect resembles a double-sided tape which bonds two parts together, forming a 'sandwich' structure. When no filler is added, the interaction between layered structures is weak. Though covalent bonds exist between them, due to steric hindrance, they are much less than that inside layered structures, leading to weak boundary between layered structures. The crack tends to propagate along the weak boundary, resulting in brittleness. GO tends to aggregate during the polymerization process, and aggregations act as weak points which facilitate the crack propagation, leading to decrease in toughness. During the in-situ polymerization process with the presence of GO-AA, the layered structures formed on the basal surfaces of GO-AA, starting with double bonds which provided reactive sites. The size of GO and GO-AA used in this paper is approximately 10 μm while the size of a single layer of cyclosiloxane is 1 – 2 μm . This allows one single 'double side tape' GO-AA to anchor many layered structures on it (Figure 6.6), forming a 3D connected network at such low loadings, which pure cyclosiloxane polymer and GO nanocomposites failed to form.

Figure 6.6 In-situ polymerization of cyclosiloxane hybrid polymer on surface of GO-AA. TEM sample was prepared by exfoliating layered structure with GO-AA via sonicating GO-AA nanocomposite in ethanol for ~1 week.

As discussed above, when a crack is initiated, it tends to propagate between layered structures along the weak boundaries. However, if the crack meets a GO-AA nanosheet, the crack will be deflected or tilted along the surface directions of GO-AA (Red arrows, Figure 6.7). If the crack is stopped by GO-AA, crack pinning morphology (Figure 6.7A) will be observed. Crack pinning was observed in all GO-AA containing cyclosiloxane nanocomposites, but it cannot be the main mechanism responsible for 153% improvement at only 0.8 wt% loading of GO-AA. In most cases, the deflected or tilted crack continues to propagate along GO-AA surface, leaving graphene trace (Figure 6.7B). When the deflected or tilted crack along GO-AA surface meets weak boundaries existing between layered structures anchored to surface of 'double side tape' GO-AA, part of the crack will propagate along weak boundaries (orange arrows, Figure 6.7), forming microcracks (black arrows, Figure 6.7C) with directions deviated from GO-AA surface. Formation of microcracks allows absorbing more energy during cracking, toughening cyclosiloxane hybrid polymer. There are cases when parts of cracks are pinned, deflected or tilted while the rest continues to propagate, forming a bifurcation morphology (Figure 6.7D). Bifurcation allows the crack to change height during propagation³⁰ and absorb more energy, contributing to toughness of cyclosiloxane hybrid polymer.

Figure 6.7 Crack propagation behaviors in GO-AA nanocomposites and formation of (A) crack pinning, (B) graphene trace, (C) graphene trace with microcracks and (D) crack bifurcation. (The white arrows indicate the crack directions)

6.6 TEM

A TEM image of cyclosiloxane polymer nanocomposite with GO-AA nanosheets is shown in Figure 6.8. The wrinkled morphology (red arrows) was from wrinkled graphene

surfaces, and the inset SAED pattern indicated the presence of graphene sheet. Based on the in-situ polymerization process, the presence of only one set of diffraction pattern indicated that GO-AA was well dispersed in cylcosilxoane polymer. The TEM image proved that GO-AA inserted into layered structures and acted as ‘double sided tape’ which bound layered structures together. More TEM images are presented in Figure A.8.

Figure 6.8 A TEM image of cyclosiloxane polymer nanocomposite with GO-AA nanosheets. Inset is SAED pattern of it.

6.7 Thermal conductivity

Figure 6.9 shows the thermal conductivity of GO and GO-AA nanocomposites. The thermal conductivity of GO and GO-AA nanocomposites showed same trend with increasing graphene loadings. The thermal conductivity first slightly decreased and then increased with graphene loading, but GO-AA nanocomposites have higher thermal conductivity than that of GO nanocomposites with same graphene loadings. The thermal conductivity of GO-AA nanocomposite reached its highest value with only 0.10 wt%

graphene loading, increased by 24.7 % compared to hybrid matrix while for GO nanocomposite with the same graphene loading the thermal conductivity was increased only 15.3 %.

Figure 6.9 Thermal conductivity of GO and GO-AA nanocomposites.

Based on the research done over the last decades, the thermal conductivity of composites was proved to be dependent on interfacial resistance, distribution, dispersion and alignment of fillers.³¹ Normally, interfacial thermal resistance was thought to be the main cause for the scattering of phonons, which is the primary mechanism of heat conduction in most polymer composites.³² Taking the layered structures of cyclosiloxane polymer into consideration, the ‘double side tape’ GO-AA nanosheets being inserted between layers acted as staircase (Figure 6.10) and it can provide a intermedia flat for phonon transfer, in which case, less phonons are scattered during transfer from one layer to another. The covalent bonds between graphene nanosheets and cyclosiloxane polymer matrix in GO-AA nanocomposites effectively reduce the interfacial thermal resistance, and enhance phonon transmission on interfaces, leading to higher thermal conductivity than that of GO nanocomposite of same graphene loadings. Besides covalent bonds, wettability can also influence interfacial thermal resistance. Good wettability of GO-AA (Figure 6.3 (A) and Figure A.5) provided better physical contact between graphene and cyclosiloxane polymer matrix, but the poor wettability of GO (Figure A.6) leads to bad

physical contact, aggregations, and voids, which are not in favorable for thermal conductivity in the nanocomposites.

Figure 6.10 A proposed enhancing mechanism of GO-AA in thermal conductivity.

Dispersion of nanofillers is another critical issue with regard to thermal conductivity of nanocomposites. It was reported that better dispersion contributes to higher thermal conductivity,³²⁻³⁵ and it is true when thermal conductivity network for phonon propagation in composites is formed. Contrary to expectations, the thermal conductivity of both nanocomposites is less than that of pure hybrid matrix when the graphene loading is very low (0.02 wt% and 0.04 wt% GO-AA & 0.02 wt%, 0.04 wt% and 0.06 wt% GO). At such low loading of graphene, the phonon can only be transmitted inside the cyclosiloxane based hybrid, through interfaces between matrix and along graphene nanosheets. In this case, insufficient graphene nanosheets act as defects inside the nanocomposites, and the phonon scattering at interfaces is the main cause for decreased thermal conductivity at such low graphene loadings.

6.8 Thermal Stability

Figure 6.11 shows TGA curves of GO and GO-AA nanocomposites and Table 6.1 summarizes the TGA results. All the samples tested showed better thermal stability than cyclosiloxane polymer matrix. T_{d5} (the temperature where 5% weight loss) and weight retention at 800 °C firstly increased and then decreased with graphene content. The phenomenon can be explained by transfer of phonons, which is necessary for heat conduction in polymers. For low graphene loading, the filler-polymer coupling and filler-filler interfacial coupling are too weak and hinder the transfer of phonons, thus causing increased thermal resistance. However, when graphene loading is higher, the filler-filler interfacial coupling is enhanced since the distance between fillers are smaller, resulting in decrease of the thermal stability^{36,37}. The relatively poorer thermal stability of GO-AA nanocomposites at higher graphene loadings (>0.04 wt%) is due to better dispersion of GO-AA, in which case the filler-filler interfaces coupling is stronger since there is less aggregation of GO-AA.

Figure 6.11 TGA curves of GO and GO-AA nanocomposites.

Table 6.1 Results of TGA.

Sample Name	$T_{d5}/^{\circ}\text{C}$	Weigh Retention at 800°C/%
Cyclosiloxane polymer	602	86.08
0.02 wt% GO	615	87.47
0.04 wt% GO	613	87.88
0.08 wt% GO	612	87.46

0.02 wt% GO-AA	616	87.74
0.04 wt% GO-AA	610	87.41
0.08 wt% GO-AA	608	87.03

6.9 Conclusion

In this chapter, modification of graphene oxide (GO) by allylamine to introduce vinyl groups onto the surface of graphene nanosheet via a facile method is presented. Cyclosiloxane polymer nanocomposites containing GO and GO-AA were fabricated and the mechanical properties were evaluated by 3-point bending. A 155% increase in toughness with 0.08 wt% loading was observed. Taking the layered structure of cyclosiloxane polymer into consideration, a ‘double sided tape’ toughening mechanism is proposed in this chapter to explain the toughening effect of GO-AA.

Thermal properties were evaluated by thermal conductivity and thermal stability. A 24.7% increase in thermal conductivity with 0.1 wt% loading of GO-AA. A staircase enhancing mechanism in thermal conductivity is proposed based on the layered structure of cyclosiloxane polymer. TGA showed that with graphene nanosheets the thermal stability of cyclosiloxane polymer nanocomposite was improved.

The toughened cyclosiloxane polymer nanocomposites with enhanced thermal conductivity are proved to be good candidates for high-performance polymers. This chapter corresponds to objective 3 stated in 1.2.

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Chapter 7

MWCNTs–Cyclosiloxane Polymer Nanocomposite toward Thermal Interface Materials

This chapter presents modifications of multi-walled carbon nanotubes (MWCNTs) by silica coating and/or siloxanes with double bonds. The thermal conductivity of the fabricated MWCNTs – cyclosiloxane polymer nanocomposites are presented and discussed. Coating MWCNTs with silica alleviates the modulus mismatch and enhancing the phonon transfer. Covalent bonds between MWCNTs and the cyclosiloxane polymer matrix reduce phonon scattering at interfaces, contributing to thermal conductivity. The results show that MWCNTs-cyclosiloxane polymer nanocomposites are possible candidates for thermal interface materials.

7.1 Introduction

In this chapter, modification of MWCNTs by silica coatings and/or siloxanes with double bond to fabricate non-covalently bonded or covalently bonded MWCNTs – cyclosiloxane polymer nanocomposites. The assessment of thermal conductivity is presented and the corresponding enhancing mechanism is discussed. This chapter corresponds to objective 3 stated in 1.2.

Thermal interface materials (TIMs) are essential for efficient thermal management in electronic packaging, energy storage media, organic solar cells, heat-sink materials, and so on.^{1,2} Excellent thermal conductive and electrical insulating properties are desired for TIMs but lower percolation of electrical conductivity makes it one of the main bottlenecks in electronic packaging.³ Possible methods have been explored to overcome this problem, such as adopting non-conductive fillers^{4,5} or coating conductive fillers with non-conductive materials to enhance phonon transmittance between filler-polymer interfaces⁶. However, large amount of non-conductive filler content (30-60 vol%)^{7,8} is needed to get satisfactory thermal conductivity and the resulting high viscosity makes it difficult to process during application procedure which also lies in the non-conductive material coated fillers, especially when the polymer matrix is high viscous epoxy resin, on which research has been carried out for decades⁹⁻¹¹. Thus, new polymer matrix and fillers are in great need to develop new TIMs which has excellent thermal conductivity, good electrical insulating properties and easy processibility.

Low viscous TIMs can be achieved by using matrix or monomers which have low viscosity and using high efficient thermally conductive fillers in case of any high viscosity resulting from high filler volume. Cyclosiloxane polymer¹² whose monomers are liquid with low viscosity has been proved to be possible candidate for TIMs in chapter 6.

Among all the fillers, carbon based fillers are the most promising¹³. As stated in Session 2.6, CNTs has a thermal conductivity of 1000-4000 W/mK, ranking the second to

graphene among all the thermally conductive fillers. However, compared to graphene, CNTs can be easily coated by silica to make CNTs insulating³ which is desired for TIMs. In this case, MWCNTs were coated with silica and/or modified by siloxanes with double bonds to be used as thermally conductive fillers.

Based on the discussion above, MWCNTs – cyclosiloxane polymer nanocomposites were explored as candidates for TIMs.

7.2 Characterizations of Modified MWCNTs

Modifications of MWCNTs are provided in Figure 3.4, chapter 3. The names and corresponding marks are shown in Table 7.1.

Table 7.1 Names and corresponding marks of MWCNTs.

Names of MWCNTs	Mark
Raw MWCNTs	CNT-1
MWCNTs@silica	CNT-2
MWCNTs-KBM 1003	CNT-3
MWCNTs@silica-KBM 1003	CNT-4
MWCNTs-KBM 1403	CNT-5
MWCNTs@silica-KBM 1403	CNT-6

FTIR results are shown in Figure 7.1. The appearance of peaks from 1041–1130 cm^{-1} indicated Si-O-Si bonds in the samples¹⁴, implying successful silica coating in CNT-2, CNT-4 and CNT-6. The peaks appeared at 2851 cm^{-1} and 2922 cm^{-1} in CNT-2 were attributed to Si-CH₃ in silica coating. Peaks located at 3062 cm^{-1} and 3025 cm^{-1} in CNT-3 and CNT-4 indicated the presence of double bonds from KBM-1003, while peaks located at 3087 cm^{-1} and 3068 cm^{-1} in CNT-5 and CNT-6 indicated the presence of double bonds from KBM-1403.

Figure 7.1 FTIR of raw MWCNTs and modified MWCNTs.

TGA curves of MWCNTs and modified MWCNTs in air are shown in Figure 7.2, and the final char yield at 900 °C are summarized in Table 7.2. From the TGA curves, it can be clearly seen that for CNT-3, CNT-4, CNT-5 and CNT-6, there is an increase in weight from 120 °C due to oxidation of siloxanes graft onto surfaces of MWCNTs, while for raw MWCNTs (CNT-1) and silica coated MWCNTs (CNT-2), there is no obvious oxidation weight gain. From the char yield at 900 °C, the coating fractions (weight percentage) can be roughly calculated. However, the oxidation process is not a purely burning off of MWCNTs; it is a process with complicated reactions occurring at the same time. The fractions of coatings are not accurate. So in this thesis, same weight percentage were used to compared different MWCNTs fillers.

Figure 7.2 TGA curves of raw MWCNTs and modified MWCNTs in air.

Table 7.2 Char yield of raw MWCNTs and modified MWCNTs at 900 °C.

Name of MWCNTs	Char yield at 900 °C/%
CNT-1	10.32
CNT-2	70.79
CNT-3	69.85
CNT-4	41.05
CNT-5	39.61
CNT-6	43.90

Figure 7.3 shows TEM images of raw MWCNTs (CNT-1) and silica coated MWCNTs (CNT-2). As can be seen from Figure 7.3 (B), the MWCNTs were successfully coated by silica with a thickness of 20-30nm. More TEM of silica coated MWCNTs are available in Figure A.9.

Figure 7.3 TEM images of (A) raw MWCNTs and (B) silica coated MWCNTs.

7.3 MWCNTs-Cyclosiloxanes Mixture and Nanocomposites Thereof

Figure 7.4 shows the visual pictures of MWCNTs-cyclosiloxanes mixture after sonication with a loading percentage of 0.5 wt%. It can be clearly seen that for raw MWCNTs (CNT-1) and silica coated MWCNTs (CNT-2), the dispersion was not good since aggregation of MWCNTs can be easily seen by unaided eyes. The tilted bottles of mixtures showed an intuitional presentation of viscosity. The mixture from raw MWCNTs was already a viscous paste which could not flow freely after being tilted while the others showed a much lower viscosity, indicating an easy process.

The high viscosity of raw MWCNT-cyclosiloxane mixture did not only lead to difficult in processing such as being transferred from bottles to mold, it also made the degas process difficult, in which case, a bubble free sample was hard to fabricate. While for all the other MWCNTs-cyclosiloxane mixtures, the lowered viscosity made the process procedure much easier.

Figure 7.4 Visual pictures of MWCNTs-cyclosiloxane mixture.

Figure A.10 shows the visual picture of MECNTs-cyclosiloxane polymer nanocomposites with 0.5 wt% loading of MWCNTs. As can be seen from the picture, the pure cyclosiloxane polymer was transparent while when MWCNTs was added in the samples became opaque.

7.4 Thermal Conductivity

Figure 7.5 shows the thermal conductivity of MWCNTs-cyclosiloxane polymer nanocomposites with MWCNTs loading of 0.5 wt%. Table 7.2 summarizes the results of thermal conductivity. With 0.5 wt% loading of raw MWCNTs (CNT-1), the thermal conductivity was increased by only 8.9%, while 0.5 wt% of silica coated MWCNTs (CNT-2), the thermal conductivity was increased by 30.9%, more than three times of raw MWCNTs achieved. When it comes to the number of MWCNTs, silica coated MWCNTs

was much less than raw MWCNTs due to the silica coating. The dramatic increase is due to the presence of silica coating, whose modulus (30-70 GPa) is between MWCNTs (270-950 GPa) and cyclosiloxane polymer matrix (~1.5 GPa), decreasing the modulus mismatch³, thus contributing to the thermal conductivity of the nanocomposites. Comparing raw MWCNTs (CNT-1), MWCNTs-KBM 1003 (CNT-3) and MWCNTs-KBM 1403 (CNT-5), it can be concluded that, covalent bond did have an influence on thermal conductivity because of enhanced thermal interfaces¹³. Compared with MWCNTs-KBM 1003 and MWCNTs-KBM 1403, KBM 1403 showed a much higher thermal conductivity with an improvement of 63.0%. It seemed that the presence of phenyl groups could provide anchored structures which can significantly improve interfacial interactions, contributing to the thermal conductivity. Another factor is dispersion, which will be further discussed in 7.6. The same effect was observed by comparing CNT-2, CNT-4 and CNT-5, all of which are silica coated MWCNTs.

Figure 7.5 Thermal conductivity of MWCNTs-cyclosiloxane polymer nanocomposites with 0.5 wt% MWCNTs loading.

Table 7.3 Thermal conductivity results of MWCNTs-cyclosiloxane polymer nanocomposites with 0.5 wt% MWCNTs loading.

Sample	Thermal conductivity/W/mK	Improvement
Cyclosiloxane polymer matrix	0.338	N/A

CNT-1	0.368	8.9%
CNT-2	0.440	30.2%
CNT-3	0.351	3.8%
CNT-4	0.461	36.4%
CNT-5	0.551	63.0%
CNT-6	0.464	37.3%

7.5 Electrical Conductivity

Electrical conductivity of MWCNTs-cyclosiloxane polymer nanocomposites was tested. However, only sample with 0.5 wt% loading of raw MWCNTs gave an electrical conductivity of 9.3×10^{-3} S/m (The V-I curve is shown in Figure A.11). Other samples showed same insulating behaviour as cyclosiloxane polymer, and could not be detected by equipment. By comparing raw MWCNTs (CNT-1) and silica coated MWCNTs (CNT-2), it can be concluded that the electrically insulating silica coating changed the electrical behaviour of raw MWCNTs, from conductive to non-conductive. As to CNT-3 and CNT-5, the non-conductive behaviour was probably due to the damaged structure of carbon nanotubes, leading to a dramatic decrease in electrical conductivity. Based on the discussion above, the MWCNTs-cyclosiloxane polymer nanocomposites are possible candidates for TIMs.

7.6 SEM

Figure 7.6 shows the SEI images of fracture surface of MWCNTs-cyclosiloxane polymer nanocomposites. As can be seen from SEI images, raw MWCNTs (CNT-1) aggregated and the MWCNTs entangled with each other, which are not preferable for thermal conductivity but might form an electrically conductive path. Though coated with silica, CNT-2 also aggregated and formed MWCNT clusters. It is interesting that CNT-3 (MWCNTs-KBM 1003) also showed aggregation of MWCNTs, and this might be the cause of low thermal conductivity of this nanocomposite. For CNT-4 (MWCNTs@silica-KBM 1003), CNT-5 (MWCNTs-1403) and CNT-6 (MWCNTs@silica-1403), the samples showed that MWCNTs were well dispersed. However, for CNT-4, CNT-5, and

CNT-6, the MWCNTs could hardly been seen. This is because the strong interaction between MWCNTs and cyclosiloxane polymer matrix made it hard to be pulled out.

Figure 7.6 Fracture surfaces of cyclosiloxane polymer nanocomposites with 0.5 wt% loading of (A) CNT-1, (B) CNT-2, (C) CNT-3, (D) CNT-4, (E) CNT-5 and (F) CNT-6.

7.7 Conclusion

In this chapter, MWCNTs were modified by silica coating/and or siloxanes with double bonds, and incorporated into cyclosiloxane polymer to fabricate nanocomposite toward

TIMs. Silica coating alleviated the modulus mismatch between MWCNTs and cyclosiloxane polymer matrix, contributing to the thermal conductivity. Covalent bond between MWCNTs and polymer matrix enhanced the interfacial interactions and increase the thermal conductivity of nanocomposite. SEI images showed that samples with better dispersion showed a higher thermal conductivity, indicating the dispersion is also a very important factor. Electrical conductivity test showed that all sample except raw MWCNTs was insulate, indicating possible candidates for TIMs.

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Chapter 8

Conclusions and Future Work

This chapter concludes the thesis by reviewing the objectives set out in chapter 1 and summarizing the results and achievements corresponding to each objective. The identification of structure shows that cyclosiloxane is a layered structure and the following reinforcement in mechanical properties and thermal properties is based on this. The reinforcing mechanisms which are put forward on the basis of layered structure are emphasized and this provided an insight into structure-properties relationship. Future work such as high-performance polymers/composites/nanocomposites and CMCs is suggested beyond the scope of this thesis

8.1 Conclusions

The review of published literature showed a limited knowledge of cyclosiloxane polymer, which can be used as candidate for high performance polymers. Due to limited literature on cyclosoiloxane polymer, there is lack of knowledge in structure and properties relationship. This thesis described the work carried out with the objective to study the structure, structure-properties relationship, possible reinforcing method and possible applications as TIMs.

In summary, the work presented in this thesis is based on the mainline – cyclosiloxane polymer. From structure study of cyclosiloxane polymer to possible reinforcing methods, and finally to possible applications, this thesis gives a knowledge of cyclosiloxane polymer and composites/nanocomposites thereof as well as guidance for materials design.

Through a review of the literature (chapter 2), the limitations in current knowledge about cyclosiloxane polymer were identified. The kinetics study was performed to better understand and control the curing process of hydrosilylation reaction between cyclosiloxanes. To better understand the structure-properties relationship, the structure of cyclosiloxane was firstly identified. It was found that cyclosiloxane polymer is a layered structure at the nano-size but isotropic in bulk. Chapter 4 discusses kinetics study and basic characterizations of cyclosoiloxane polymer. Kinetics study was performed to better understand the curing process of hydrosilylation of cyclosiloxanes. The curing kinetics was studied by model fitting method and non-model fitting method, confirmed and further studied with FTIR and rheology test. Through this part, besides curing mechanism, a processing guide was given. The following characterizations showed that cyclosiloxane polymer has layered structure in nano-size while is isotropic in bulk. This chapter corresponds to objective 1 stated in 1.2.

After identifying the structure, possible reinforcement methods were proposed. By adding vinyl terminated polydimethylsiloxane (PDMS), which can be covalently

bonded to the layered structure, a simultaneously improved toughness, and stiffness was observed. (Chapter 5) It is proposed that PDMS exists as two phases in cyclosiloxane polymer. The homogeneously dispersed PDMS chains anchor different layered structures together, forming a 3D connected network, contributing to both toughness and stiffness while the phase separated PDMS particles only contribute to toughness, while reducing other mechanical properties.

Graphene oxide (GO) was basally modified and used to toughen the cyclosiloxane polymer matrix. (Chapter 6) A 153 increase in toughness with only 0.8 wt% graphene loading was observed. ‘Double side tape’ toughening mechanism is proposed to explain the toughening behavior and formation of micro-cracks. The increase of thermal conductivity when allylamine modified GO (GO-AA) was added into cyclosiloxane polymer is also explained by ‘double side tape’ effect of GO-AA nanosheets, which act as a staircase for phonon transfer and contribute to thermal conductivity.

Based on Thermal interface materials (TIMs) considerations, cyclosiloxane polymer was used as matrix and multi-walled carbon nanotubes (MWCNTs) were used as thermally conductive fillers. (Chapter 7) MWCNTs were modified by silica coating and/or siloxanes with double bonds before incorporating into cyclosiloxane polymer. The resulting increase in thermal conductivity was explained by alleviating modulus mismatch by silica coating, covalent bonds between the matrix and MWCNTs fillers, as well as dispersion. The insulate behavior of MWCNT-cyclosiloxane polymer nanocomposites except raw MWCNTs indicated possible candidates for TIMs.

In summary, cyclosiloxane polymer was studied from structure to properties, as well as the relationship between them. Based on the layered structure, possible reinforcement methods were carried out, and the corresponding mechanisms are proposed. Finally, MWCNTs-cyclosiloxane polymer nanocomposites were fabricated toward TIMs.

8.2 Future Work

Though a series work has been done on cyclosiloxane polymer, there is still a lot of research need carrying out on this material, both academically and industrially.

8.2.1 High-Performance Polymers/Composites/Nanocomposites

8.2.1.1 Cyclosiloxane Polymers Modified by PDMS or Other Additives

Though PDMS has been proved that it can simultaneously improve toughness and stiffness of cyclosiloxane polymer, the influence of PDMS chain length and combination of PDMS with different lengths is yet unknown. Chances are there that higher toughness can be achieved without significant loss in thermal conductivity and/or transparency. These materials can be used as flame retardant coatings where transparency is important.

Other additives which can increase the refractive index are also in great need, especially for applications such as optical lens or LED adhesive. Increase of refractive index can be achieved by incorporation of phenyl groups or sulfur. This can be done from monomer modification or copolymerization with other phenyl- or sulfur-containing cyclosiloxane monomers. However, the incorporation of phenyl group or sulfur will lead to other problems such as smelly odor or brittleness. A balance of properties should be investigated.

8.2.1.2 Cyclosiloxane Polymer Composites/Nanocomposites

Electrically conductive polymer composites based on cyclosiloxane polymer should be investigated for sensors and electromagnetic shielding applications. Electrically conductive fillers such as metal particles, carbon fibers, carbon nanotubes, graphene and so on should be incorporated into cyclosiloxane polymer to make it electrically conductive. The key points of developing such composites/nanocomposites are dispersion of the fillers and forming of conductive paths. In this case, the modification of fillers is critical. Mixture of fillers with different compositions, sizes

and morphologies should be investigated. Usually a combination of different fillers results in better performance in electrical conductivity.

8.2.2 Ceramic Matrix Composites (CMCs)

Cyclosiloxane polymer has been researched as preceramic polymers and the resulting SiCO ceramic is a highly thermally stable material. By incorporating ceramic fillers, the resulting cyclosiloxane polymer composite can be turned into composites which are composed of SiCO and ceramic fillers. By combining SiCO ceramic and high performance fillers, such as SiC, BN, and Si_3N_4 , composites which can perform service on server conditions can be fabricated. This kind of materials has promising applications in space technology, turbine , burner components, and so on.

APPENDIX

Table A.1 Key chemicals used in this thesis.

Name	Company and country
1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, 99%	Alfa Aesar, USA
2,4,6,8- tetramethylcyclotetrasiloxane, 97%	Alfa Aesar, USA
platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex	Alfa Aesar, USA
Poly(dimethylsiloxane), vinyl terminated	Sigma-Aldrich, USA
average Mw ~25,000	
Allylamine, 98%	Alfa Aesar, USA
Sulfuric acid (A. R. 95-98%)	Sigma-Aldrich, USA
Nitric acid (A. R. 67%)	Sigma-Aldrich, USA
Potassium permanganate	Alfa Aesar, USA
Hydrogen Peroxide, 30%	VWR, USA
N,N-dimethylformamide	Sigma-Aldrich, USA
Tetraethyl orthosilicate, 99.999%	Sigma-Aldrich, USA
Multi-walled carbon nanotubes	Nanocyl, Belgium
Vinyltrimethoxysilane (KBM-1003)	Shin Etsu Silicone, Japan
p-Styryltrimethoxysilane (KBM-1403)	Shin Etsu Silicone, Japan
Ammonium hydroxide solution purum, ~28% NH₃ in H₂O (T)	Sigma-Aldrich, USA
Ethanol, 94%-96%	Alfa Aesar, USA

Figure A.1 Fracture surface of cyclosiloxane with 0.2 wt% loading of PDMS.

Figure A.2 A schematic graph of structure of PDMS reinforced cyclosiloxane polymer.

Figure A.3 Microscope images of (A) 0.04 wt% GO and (B) 0.04 wt% GO-AA cyclosiloxane polymer nanocomposites.

Figure A.4 An SEI image of graphene trace from GO-AA-cyclosiloxane polymer nanocomposite.

Figure A.5 An SEI image of graphene trace from GO-AA-cyclosiloxane polymer nanocomposite.

Figure A.6 Fracture surface of cyclosiloxane polymer nanocomposite with 0.04 wt% GO.

Figure A.7 Crack pinning and pulling-out of graphene.

Figure A.8 TEM images of cyclosiloxane polymer nanocomposites with GO-AA nanosheets.

Figure A.9 TEM images of silica coated MWCNTs.

Figure A.10 A visual picture of MWCNTs-cyclosiloxane polymer nanocomposites with 0.5 wt% MWCNTs loading.

Figure A.11 V-I curve of MWCNTs-cyclosiloxane polymer composites with 0.5 wt% raw MWCNTs. (dimensions of sample: $1.27 \times 1.27 \times 3.788 \text{ mm}^3$, the V-I curve was tested on side faces)