

A STUDY OF POLYURETHANE-MODIFIED EPOXY
AND ITS NANOSILICA FILLED COMPOSITES

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UNIVERSITI SAINS MALAYSIA
2009

**A STUDY OF POLYURETHANE-MODIFIED EPOXY
AND ITS NANOSILICA FILLED COMPOSITES**

by

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**Thesis submitted in fulfillment of the
requirements for the Degree
of Doctor of Philosophy**

November 2009

ACKNOWLEDGEMENTS

First and foremost, I would like to express my appreciation and utmost gratitude to my project supervisors, Prof. Jamil Ismail, Assoc. Prof. Mohamad Abu Bakar and Prof. Ismail Abd. Rahman. Their relentless guidance, advice, encouragement and support have been vital to the completion of my candidature.

I would also like to thank the School of Chemical Sciences and its staffs especially En. Burhanudin, En. Ali, En. Sobri, En. Fahmi, Mr. Aw Yeong and Puan Ami for their guidance on instrument handling. My thanks also go out to Cik Jamilah, Mr. Muthu and En. Johari from the Electron Microscope Unit of the School of Biological Sciences as well as Cik Ella from Intel Technology Sdn. Bhd. who dedicated extra effort and time in helping me complete my analyses.

I would like to acknowledge Intel Technology Sdn. Bhd. for the Student Fellowship awarded to me and the research grant awarded to this project. I also appreciate the mentoring from Dr. Chee Choong Kooi and the help from Dr. Chong Kim Foong for arrangement of laboratory usage at Intel Technology Sdn. Bhd.

And most importantly, I would like to thank my parents for their unconditional love, understanding, encouragement and support. Last but not least, a special thanks to my friends for their warmth and kindness which makes my pursuit of the postgraduate degree an enjoyable one.

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LIST OF SYMBOLS

δ	Solubility parameter <u>OR</u> Phase shift <u>OR</u> Chemical shift
ρ	Density
α	Coefficient of linear thermal expansion <u>OR</u> Fractional conversion
γ	Gruneisen constant
Δ	Time delay
ΔH	Enthalpy of reaction

LIST OF ABBREVIATIONS

ACA	Anisotropic conductive adhesives
B	Bulk modulus
CED	Cohesive energy density
CTE	Coefficient of thermal expansion
C_v	Specific heat
DER331	Bisphenol epoxy resin
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DOE	Design of experiment
DSC	Differential scanning calorimetry
DTG	Derivative of thermogravimetry analysis
E'	Storage modulus
E''	Loss modulus
E_a	Apparent activation energy
EDX	Energy dispersive x-ray analysis
EEW	Epoxy equivalent weight
EG	Ethylene glycol
f	Frequency
F	Force response
FTIR	Fourier transform infra-red
g	Geometry factor
G	Molar lattice energy
^1H	Proton
HDI	1, 6 - hexamethylene diisocyanate
ICN	Intercrosslink network
IPN	Interpenetrating polymer network
IR	Infra-red
KBr	Kalium bromide
L	Amplitude
M	Formula weight
M'	Storage modulus
M''	Loss modulus
$ M^* $	Complex modulus
MDA	4, 4'- diamino diphenyl methane

MDI	4, 4' - methylene diphenyl diisocyanate
MW	Molecular weight
n	Degree of polymerization
NMR	Nuclear magnetic resonance
p	Extent of reaction
PCB	Printed circuit board
PDMS	Polydimethylsiloxane
PEEK	Poly(ether ether ketone)
PEG 400	Poly(ethylene glycol) 400
phr	Parts per hundred of rubber
PMMA	Poly(methyl methacrylate)
PPG 1000	Poly(propylene glycol)
ppm	Part per million
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PU	Polyurethane
r	Molar ratio
rpm	Rotation per minute
SEM	Scanning electron microscopy
Tan δ	Loss tangent
TDI	Toluene diisocyanate
T _{0.5}	Degradation temperature (50 % degradation)
T _e	Degradation end temperature
T _{end}	Cure end temperature
TEM	Transmission electron microscopy
TEOS	Tetraethoxy silane
T _i	Degradation onset temperature (2 nd degradation step)
T _g	Glass transition temperature
TGA	Thermogravimetry analysis
TIM	Thermal interface material
TMA	Thermomechanical analysis
TMS	Tetramethylsilane
T _o	Degradation onset temperature (at 5 % degradation)
T _{o(tan)}	Degradation onset temperature (at tangent)
T _{onset}	Cure onset temperature
T _p	Degradation peak temperature
T _{peak}	Cure peak temperature
UF	Underfill
v/v	By volume
Vol %	Percent volume
w/w	By weight
wt %	Percent weight
wt loss	Weight loss
ZnSe	Zinc selenide

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SUATU KAJIAN EPOKSI TERUBAHSUAI-POLIURETANA DAN KOMPOSITNYA BERSAMA PENGISI SILIKA NANO

ABSTRAK

Kajian ini adalah mengenai pengubahsuaian kimia ke atas resin epoksi menggunakan prabahan-poliuretana (prabahan-PU) yang beraneka panjang rantai dan kearomatikan. Prabahan-PU dengan nisbah diol-diisosianat 1:3 adalah optima untuk penambahan secara kimia ke dalam epoksi. Kajian ini berbeza daripada kajian lain yang sedia ada dari segi penambahan kimia PU serta penggunaan PU yang berberat molekul, dan darjah pempolimeran rendah. Faktor-faktor pembezaan tersebut telah menyumbang kepada keelakan masalah-masalah pemisahan fasa, pengurangan suhu peralihan kaca (T_g) dan kestabilan terma yang lazim berlaku. Namun, penggunaan kaedah kemasukan secara kimia telah menghadkan kuantiti PU yang boleh ditambah kepada kurang daripada 6 phr.

Pengubahsuaian dengan PU mengubah sifat epoksi sebelum dan selepas matang. Perubahan tersebut lazimnya bergantung kepada struktur PU. Dalam epoksi yang belum matang, pengubahsuaian dengan PU meningkatkan kestabilan terma dan keupayaan sistem untuk membasahi permukaan. Secara bandingannya, epoksi dengan prabahan aromatik adalah lebih stabil secara terma daripada epoksi dengan prabahan alifatik. Akan tetapi, tren yang bertentangan diperhatikan dari segi keupayaan membasahi permukaan. Kelikatan meningkat dengan pengubahsuaian PU di mana prabahan aromatik mengakibatkan peningkatan yang paling ketara.

Didapati bahawa prabahan-PU memangkinkan tindakbalas epoksi-amina, tanpa dipengaruhi oleh struktur PU. Ketumpatan sambung-silang meningkat dalam

termoset yang diubahsuai dengan prabahan alifatik tetapi berkurang dengan prabahan aromatik. Kesan-kesan ini ditunjukkan melalui pencirian modulus simpanan (E') dan kelenturan termoset. Kuasa pelekatan meningkat dengan pengubahsuaian PU alifatik tetapi berkurang dengan PU aromatik. Penambahan prabahan-PEG400-HDI, secara khasnya, memplastik termoset. Kesan ini ditunjukkan dalam pencirian T_g , E' dan koefisien pengembangan terma (CTE). Prabahan aromatik pula meningkatkan kerapuhan termoset, ditunjukkan oleh kelenturan dan morfologi permukaan retak. Pengubahsuaian PU tidak mempengaruhi kestabilan terma termoset. Ciri ini adalah berlainan daripada yang ditunjukkan oleh epoksi belum matang.

Kajian ini juga merangkumi penentuan kaedah optima untuk taburan 9 % berat silika nano dalam epoksi tanpa pelarut. Didapati bahawa selain daripada kadar dan tempoh masa campuran yang optima, penggunaan media bebola dan haba dapat memecahkan gumpalan silika dengan berkesan. Kehadiran 9 % berat silika nano memangkinkan tindakbalas epoksi-amina, tetapi ia merupakan halangan fizikal kepada tindakbalas lengkap pematangannya, sepertimana ditunjukkan oleh keputusan analisis DSC. Taburan silika nano yang berkesan menghasilkan komposit satu fasa.

Penambahan PU kepada epoksi terisi silika nano menunjukkan potensi untuk memecahkan gumpalan silika dengan lebih lanjut disebabkan peningkatan dalam interaksi antara silika dan matrik; ini mencadangkan terdapatnya potensi untuk menyesuaikan silika nano kepada epoksi. Akan tetapi, turutan penambahan PU ini telah mengakibatkan masalah pembentukan fasa kedua dalam komposit. Kehadiran fasa kedua telah mengakibatkan pemisahan fasa dalam matriks, kemerosotan kestabilan terma dan CTE yang tidak tetap. Dalam komposit terubahsuai-PU yang berisi silika nano, interaksi antara silika nano dan matrik, pembentukan gel mikro bertentangan dengan pengurangan ketumpatan sambung-silang adalah kesan-kesan bertentangan yang secara keseluruhannya mempengaruhi T_g , E' and sifat kelenturan.

A STUDY OF POLYURETHANE-MODIFIED EPOXY AND ITS NANOSILICA FILLED COMPOSITES

ABSTRACT

This study describes the chemical modification of epoxy resin with polyurethane-precursors (PU-precursors) of varying chain length and aromaticity. PU-precursors with diol-diisocyanate ratio of 1:3 are optimum for a chemical incorporation into epoxy. Differentiating the present study from other available PU-epoxy systems are the chemically incorporated PU, as well as the use of PU with low molecular weight (MW) and low degree of polymerization (n). These differentiating factors have been attributed to the successful aversion of phase separation, reduced glass transition temperature (T_g) and thermal stability, that has otherwise been common in PU-incorporated epoxy systems. Nevertheless, confining to chemical incorporation has limited the incorporated PU quantity to less than 6 phr.

Modification with PU changes the properties of the un-cured and cured epoxies and the changes are generally dependent on PU structures. In the un-cured epoxies, PU modification generally enhances thermal stability and wetting capability. Comparatively, epoxies with aromatic precursors are thermally more stable than the epoxies with aliphatic precursors. However, a reverse trend prevails for the wetting capability. Viscosity is increased with PU modification where the aromatic precursors result in the most significant increase.

PU-precursors are found to catalyze the epoxy-amine curing reaction but no particular trend can be ascribed to the PU structures. Thermosets modified with aliphatic PU experienced increased crosslink density but those modified with aromatic

PU experience reduction. This is evident from the storage modulus (E') and flexural properties of the thermosets. Modification with aliphatic PU increases adhesion strength but aromatic PU reduces it. In particular, the incorporation of PEG400-HDI-precursor plasticizes the thermoset, as shown by its T_g , E' and coefficient of thermal expansion (CTE) properties. Meanwhile, aromatic PU increases brittleness of thermoset, exhibited by its flexural properties and fracture surface morphology. PU modification does not affect thermal stability of the resultant thermosets which differs from its effects on the un-cured epoxy.

This study also includes evaluations for optimum dispersion of 9 weight % (wt %) nanosilica in solventless epoxy. It has been found that apart from optimum mixing rate and duration, the use of ball media and heat significantly breaks down the nanosilica clusters. The presence of 9 wt % nanosilica has been shown to catalyze the epoxy-amine reaction but is a physical hindrance to completion of cure reactions, evidenced by DSC results. Effective nanosilica dispersion has nevertheless resulted in single phased composite.

PU incorporation into the nanosilica filled epoxy has shown potential of further cluster dispersion due to increased silica-matrix interaction, suggesting a potential for compatibilizing nanosilica to epoxy. Nevertheless, this sequence of PU incorporation has resulted in the formation of a second PU-silica phase. Its presence has been attributed to the occurrence of phase separation, reduced thermal stability and increased CTE fluctuation over temperature cycle. In the filled PU-modified composites, the adverse effects of nanosilica-matrix interaction, microgel formation versus lowered crosslink density collectively affects its T_g , E' and flexural properties.

CHAPTER 1

INTRODUCTION

1.1 Overview

Epoxy resin is an important thermosetting polymer material due to its varied uses. Modification of epoxy further extends its applications which encompass some novel materials. The common modification routes include physical blending, interpenetrating polymer network (IPN) and intercrosslink network (ICN) formations and filler incorporation. Reports have shown that these modifications result in improved physical, mechanical and thermal properties but at the same time posed further challenges with undesirable traits that need to be overcome. These continue to motivate research on epoxy as versatile core material of thermoset systems for decades to come.

1.2 Literature review

1.2.1 Epoxy

Epoxy has been widely and variedly used, due to its many positive attributes. The types of epoxies are differentiated by their structures and chemical compositions. Of these, the most commonly used is the diglycidyl ether of bisphenol A¹⁻³ due to its good wetting, adhesion⁴, electrical insulating and mechanical capabilities⁵, high chemical and thermal resistance⁶, high strength to weight ratio and low shrinkage during cure⁷. Its primary applications include coating, adhesives, industrial tooling and structures^{6,8} and electronics packaging. Stringent application requirements related to performance, processing and exposure to extreme conditions continue to increase demand for improved materials. Modification of epoxy was a means to cope with such demands. Listed subsequently are some notable examples of modification. Epoxy

underfill (UF) is incorporated with silica fillers to reduce its coefficient of thermal expansion (CTE) ⁹. In another example, epoxy is filled with silver and conductive metal particles for respective applications as thermal interface material (TIM) ¹⁰ and anisotropic conductive adhesives (ACA) ^{11 - 13}. Electronic packaging molding compound ¹⁴ and antifouling coating material ¹⁵ is toughened by physically or chemically incorporating polyurethane (PU) or polydimethylsiloxane (PDMS).

Modifications have yielded property enhancements for epoxy. Yet, inherent issues still exist and these motivate continuous studies and improvements. For one, CTE mismatch still exist between substrate and UF ¹⁶ with UF having higher CTE. Unfortunately, CTE reduction of UF with microsilica filler has reached its threshold loading. As a result, UF-substrate delamination remains an inherent issue. Although nanosilica incorporation is a promising development ^{17, 18} its tendency to agglomerate remains a challenge before it can be fully benefited. While continuous researches on nanocomposites are being carried out, a viable alternative to mitigate UF-substrate delamination is adhesion enhancement ^{19, 20}.

Another example is in the coating and construction materials where the filled epoxies still endure stress induced by cure shrinkage ²¹ and thermal cycling ^{22, 23} that leads to epoxy-substrate delamination. Since both effects are inherent ²⁴, strong bonding of epoxy to its substrate is again a viable alternative to offset them.

The above examples point to the importance of good adhesion between epoxy and substrate and the need to improve this aspect. This has generally been acknowledged and a survey has shown that steps were taken to improve adhesion. Ultraviolet/ozone treatment on soldermask has been used to enhance surface polarity and improve UF adhesion to soldermasks (substrate). Sham et al. ²⁵ reported adhesion improvement with this method, but Luo and Wong ^{26, 27} have argued that the improvement was not significant. Chemical etching, flame treatment, primer

application and abrasion of the substrate surface²⁸ are all methods that have been used to improve adhesion of the coating and construction materials. Though yielding results, these methods incur additional cost and time while etchants used are environment hazards. This leaves the adhesion enhancement through modification of epoxy. Nevertheless, research in this area has been scarce. Fan et al.¹⁹ had attempted the introduction of additives (coupling agents, primers and hetero-ring active chemicals) with no positive outcome, opening this area for further exploration. At this point, it must be noted that modification of epoxy rather than utilizing new material is preferred to avoid any drastic change to process parameters.

To attempt epoxy modification, the additives used by Fan et al. will not be used to avoid similar failure. Nevertheless, to provide good adhesion, the modifier of choice must be able to interact with both epoxy and substrate as suggested by Esfandeh et al.²⁹. PU seems a suitable choice. It has been shown to form blends, IPN and ICN with epoxy. Once assimilated with epoxy, its carbonyl and –NH groups can interact with substrate surface and is expected to enhance adhesion. In fact, Al-Zharani et al.³⁰ found PU-based material to be better adhesive than epoxy-based material in their study of waterproofing coating. Another positive attribute of PU is its versatility.

1.2.2 Polyurethane

Versatility of PU arises from the interplay of its hard and soft segments. The former composed of derivatives of aromatic diisocyanate (eg. toluene diisocyanate, TDI and methylene diisocyanate, MDI) and low molecular weight (MW) dihydroxyl (diol) monomers that can cluster into ordered hard domains³¹. The latter is derived from aliphatic diisocyanates (eg. hexamethylene diisocyanate, HDI) and high MW dihydroxyl (diol) monomers that form soft domains³². The ultimate property of PU depends on the composition, length and ratio of the hard and soft segments. A

majority of hard segments in the PU would result in rigid behavior while a majority of soft segments will bring to elastomeric properties.

1.2.3 Polyurethane-modified epoxy

PU modification of epoxy has been investigated but the focus has largely been on mitigating epoxy brittleness. Adhesion capability of PU-modified epoxy remains un-explored. Regardless of the study objective, existing works demonstrated that PU can be assimilated through chemical incorporation or physical blending. Chemical incorporation utilizes the reaction between isocyanate group of PU and pendant hydroxyl group of epoxy^{1, 15, 33}. Preparation of blends, on the other hand, involves physical mixing of PU and epoxy^{34, 35}.

The resultant epoxy system of chemically incorporated PU are characterized by improved toughness but compromised glass transition temperature (T_g), thermal stability and homogeneity^{1, 15, 33}. The observed characteristics are the effect of PU soft segments. PU formation from toluene diisocyanate (TDI) and poly(propylene glycol) 1000 (PPG1000) in these works resulted in high MW, soft and flexible structures that provide the resilient characteristics to toughen the epoxy system; but plasticize the resultant system causing lower T_g and promote phase separation. The PU phase with thermally weak urethane linkage becomes prominent as a result of the phase separation causing the overall system to appear thermally less stable.

As for the physically blended PU and epoxy, heterogenous microstructure is reported³⁵. It is inevitable as PU and epoxy are immiscible. Although not reported, thermal stability of the blends is expected to be lower. It is because the blend will be characterized by distinct degradations of PU and epoxy where the temperature associated with the former is lower.

The key learning from the literature review is to avoid phase separation by evading epoxy and PU blends as well as high MW, soft structures. Nevertheless, the threshold of diol MW that induces phase separation is not known.

From the same review of PU-modified epoxy systems, it can be observed that there is a lack of systematic studies on the effect of PU structures on system properties. Versatility of PU could have been used to support the diversity required of epoxy. The need for diversity is illustrated by the storage and elastic moduli requirements of epoxy where UF requires low moduli³⁶ to accommodate thin, large dies but coating material requires high value¹⁵. Another example is the glass transition, where structural application needs high T_g but microelectronics packaging requires low T_g for reliability^{37,38}.

1.2.4 Nanosilica dispersion

Microsized fillers have been traditionally used to reinforce epoxy. But filler sizes have since been reduced to nanoscale. The progression to nanofillers is encouraged by the unique features of resultant nanocomposites that is not displayed by its micro-counterparts^{39,40}. In the case where discrete dispersion of nanofillers can be achieved, nanocomposites possess improved thermal, mechanical^{41,42} and barrier properties⁴³. Meanwhile, the nano-progression in electronics packaging materials is necessitated by technology that sees a move towards smaller bump pitch^{36,44}.

Nanocomposite technology nevertheless faces a major challenge where its fillers have a tendency to aggregate and agglomerate. This tendency increases with decreasing filler size^{45,46}. Heterogeneity, rigidity and low impact strength will happen⁴⁶⁻⁴⁸ if excessive aggregation occurs. Aggregates are also crack initiation sites upon impact^{46,48,49}. Various techniques have been deployed to reduce agglomeration. The technique used depends on the physical state of the matrix. High dispersive forces are

usually employed for nanofiller dispersion in liquid matrix ⁵⁰ while surface modification of nanofillers is carried out if viscous matrix is involved. The latter is achieved through the use of surfactants ^{51 - 53}, coupling agents ^{54, 55} and chemical modification of nanofiller surface ^{56, 57}.

For nanosilica in particular, its dispersion in polymer matrix is commonly improved through chemical modification of silica surface. Lai et al. ⁵⁸ demonstrated improved nanosilica dispersion in poly (ether ether ketone) (PEEK) by stearic acid modification of the silica surface. The improved dispersion was accompanied by enhanced Young's and storage moduli and increased thermal stability of the resultant nanocomposite. Sun et al. ⁵⁹ reported that poly(vinyl chloride) (PVC) was significantly reinforced and toughened by nanosilica treated with γ -methylacryloxypropyl trimethyl silane and dimethyl dichlorosilane. Simultaneous improvement in nanosilica dispersion was also observed. Kang et al. ⁶⁰ reported reduced CTE and improved T_g in nanosilica-epoxy composites when nanosilica is modified with aminopropyl-methyldiethoxysilane. It can be inferred from the above review that nanosilica dispersion can be improved by compatibilizing the silica to matrix and reducing interaction between particles. Instead of modifying nanosilica, modifying the epoxy matrix by increasing its polarity could achieve the same outcome. It means that PU-modified epoxies have the potential of improving nanosilica dispersion. This hypothesis is supported by the work from Lee et al. ⁶¹ that shows that nanosilica with enhanced hydrophilicity interacts better with PU matrix which resulted in better dispersion.

1.2.5 Nanosilica-filled PU-modified epoxy

Studies on nanosilica-filled PU-modified epoxy systems have not been reported, prompting the speculation that the present study on this system is novel. A closely related systems of montmorillonite-filled PU-epoxy IPN evaluated by Jia et al.^{62 - 64} are, nevertheless, encouraging. They have shown that the montmorillonite fillers interact well with the epoxy and PU through the silanol groups on filler surface and reduce phase separation of the IPN as a result.

1.3 Problem statements

The discussion in Section 1.2 reveals critical areas that should be dealt with as far as epoxy is concerned :

- Increasing demands for better mechanical, adhesion properties and reduced CTE in advanced applications calls for more versatile material. Epoxy needs to be improved upon while there has been no suitable substitute for epoxy.
- Reduction of CTE with maximum allowable silica fillers in epoxy has reached its limit while resin-substrate delamination remains an inherent issue. Improvement of adhesion by chemical modification of epoxy seems viable but has not been explored.
- Mitigating epoxy resin brittleness with incorporation of PU is often accompanied by the negative effects of reduced T_g , thermal stability and matrix heterogeneity. Chemically incorporated PU of low MW could be a viable choice, but this remains relatively un-explored.
- Systematic studies of the effect of PU structure on the properties of the resultant PU-modified epoxy systems are scarce, although PU(s) are versatile through the variation of its hard and soft segments.

- Nanocomposites are better than the conventional microcomposites in thermal, mechanical and barrier properties, provided the nanofillers are well dispersed. Due to the tendency for nanofillers to agglomerate, effective implementation of nanocomposite has been limited. Attempts to improve dispersion, by nanofiller surface modification and optimizing dispersion metrology have yielded results but these processes means additional time and cost.
- Nanosilica-filled PU-modified epoxy has not been explored.

1.4 Research objectives

This research project aims to explore the modification of epoxy-amine system with PU, centering on the effect of PU modification and the resultant structural change on the processability and properties of the modified systems. It includes the study on effect of chemically incorporated PU that is added in stoichiometric proportion. It also involves characterization of the effects of PU structures on thermoset properties.

Also of interest is the dispersibility of nanosilica in solventless epoxy. The aim of the present study is also to understand the effect of PU modification on nanosilica dispersion and properties of the resultant composites using the parameters that produce optimum dispersion.

The above aims are achieved through fulfilling the objectives as follows :

- To synthesize, characterize and test the properties of PU-precursors.
- To prepare and characterize properties of PU-modified epoxies.
- To evaluate the cure characteristics and properties of PU-modified thermosets.
- To determine optimum conditions of nanosilica dispersion in epoxy and PU-modified epoxies respectively.
- To evaluate the effect of PU modification on properties of nanosilica-epoxy composites.

1.5 Choice of materials

As noted earlier, epoxy resins are generally classified into two main categories, namely the glycidyl and non-glycidyl epoxies, differentiated by their structures. For uses in coatings, adhesives, electrical and electronic packaging and structural applications, the glycidyl epoxies are the common choice. It has been observed that the diglycidyl ether of bisphenol-A (DGEBA)^{3, 5, 65 - 68} with epoxy equivalent weights (EEW) of 180 – 190 g/eq is favoured. Based on the above reasons, the choice of epoxy for this project is DER331. Its properties are listed in Appendix A. With pendent hydroxyl group, DER331 enables chemical reaction with isocyanate-terminated PU.

As for the material for epoxy curing, commonly used hardeners are amines, anhydrides, polyamides, phenols, isocyanates and polymercaptans⁶⁹. The choice and stoichiometry of hardeners are application specific as it affects the properties of the cured thermosets. Amines are used for coating materials, amides for structural applications⁷⁰ and printed circuit board (PCB), phenolic-formaldehyde for interior of food cans and anhydride⁷¹ for UF material of the electronic packaging. Specifically, anhydride was the choice for microelectronic packaging materials because its resultant thermosets have the highest heat distortion values and the best aging stability. However, it has been subsequently phased out due to its tendency to absorb moisture⁷² and outgas³⁷, both of which compromise curing, thermomechanical and adhesion properties as well as reliability. Anhydrides have also been phased out due to its sensitizing nature⁷³ that poses health hazard. Among the hardeners, aromatic amines are the favored choice to replace anhydride^{66, 68, 74, 75}. Its preference is attributed to the higher T_g and rigidity⁷⁶ as well as thermal and chemical resistance in the resultant thermoset. Methylene dianiline (MDA) has been commonly used for microelectronics packaging, coating and structural applications⁷⁶ and will hence be used in the present study.

For the PU-precursors, variation of long and short chain as well as aliphatic and aromatic structures is desired to enable study on PU versatility. Taking into consideration the key learning from Section 1.2.3, MW of PU(s) will be kept low. For these reasons, combinations of poly(ethylene glycol) (PEG400) and ethylene glycol (EG) to hexamethylene diisocyanate (HDI) and methylene diphenyl diisocyanate (MDI) will be used.

1.6 Thesis layout

This thesis consists of nine chapters. The first chapter is an overview, which covers the literature survey on the progress and inherent issues which leads to the problem statements, research objectives and the scope of this work. Chapter 2 gives the basic principles and theory involved in this study while Chapter 3 describes the materials used as well as the detail experimental procedures and techniques. Chapter 4 presents the synthesis, characterization and properties of the PU-precursors. Chapter 5 discusses the preparation, characterization and properties study of the PU-modified epoxies. Chapter 6 elaborates on the isothermal cure and properties of the resultant thermosets. Subsequently Chapter 7 moves the discussion to fundamental metrology of nanosilica dispersion in solventless epoxy and the effect of PU incorporation on the nanosilica dispersion. Chapter 8 discusses the effect of PU modification on nanosilica-epoxy composites. Finally, Chapter 9 provides a conclusion and suggestions for further investigation.

CHAPTER 2

BASIC PRINCIPLES AND THEORY

2.1 Stepwise addition reaction

Bifunctional monomers such as diisocyanate and diol undergo stepwise polymerization by addition reaction producing molecules as linear chains. The basic quantities used to describe the change are degree of polymerization, n , associated with molecular chain; molar ratio, r , associated with functional groups; and extent of reaction, p , associated with the reaction between functional groups. A general equation that relates these quantities is given by Eq. (2.1) ⁷⁷.

$$n = (1+r) / [(2r(1-p)+1-r)] \quad (2.1)$$

where $r = N_{\text{hydroxy}} / N_{\text{diiso}}$, the ratio of total number of hydroxyl group, N_{hydroxy} and total number of isocyanate group, N_{diiso} .

For a complete reaction, $p=1$ and Eq. (2.1) reduces to Eq. (2.2).

$$n = (1+r) / (1-r) \quad (2.2)$$

Eq. (2.2) predicts the value of n while the ratio r predicts the linear chain structure related to the functional groups at the terminal or chain end. Based on the equation, n can be controlled by varying the ratio r . It is also related to molecular weight (MW) according to Eq. (2.3).

$$\text{MW} = n \times (\text{formula weight of the repeating unit}) \quad (2.3)$$

2.2 Structure-property relationship

2.2.1 Chemical composition

Uniqueness of a polymer is characterized by the relationship between its properties and chemical composition and structure of molecular chain. Variation in chemical structure gives rise to polymers that range from rubber to thermoplastics. The wide range of properties is a result of interactions between the repeat units or segments that constitute the molecular chains. While most polymers are amorphous, those with chemical structures that provides stereo regularity of the chain produces semicrystalline polymers. All the above features influence polymer bulk properties such as viscoelastic and thermomechanical properties, strength, toughness, modulus and melt viscosity. Interaction in a particular polymer changes if transformation from homopolymer to copolymer with a second polymer type occurs. The bulk properties changes henceforth.

2.2.2 Molecular structure and molecular weight

Polymers with high molecular weight (MW) are likely to have chains that entangle, which will be reflected in the bulk properties. Transforming the linear chains to branched and networked structures via grafting and crosslinking processes respectively will impose further modification to the bulk properties. The property change will reflect the general increase in segmental and chain mobility restrictions.

2.2.3 Modulus

Modulus is a measure of polymer resistance to deformation by external force in the elastic region at constant temperature. It is the force required to incur a unit of reversible or elastic deformation. Elastic deformation is a reversible extension of the chain conformation in response to applied stress. In the bulk state, elastic deformation

characterizes the synchronized motion of the chains. The resistance to deformation is a result of cohesion within the bulk polymer and is associated with the chemical structure and molecular weight of the polymer. In fact, modulus measurement is one of the most widely used techniques to characterize the structure-property relationship of polymers. The technique involves stress-strain measurement where modulus is determined from the slope of the stress versus strain curve.

Alternatively, bulk modulus of a polymer, B , can be related to its cohesive energy density, CED. The latter represents the energy required to move a detached segment into vapor phase according to Eq. (2.4)⁷⁸.

$$B = 8.04 (\text{CED}) = 8.04\delta \quad (2.4)$$

where δ is the solubility parameter of polymer.

Eq. (2.4) is based on the Lennard-Jones potential, which is the interaction energy between a pair of isolated molecules. When extended to interaction in a polymer system, it gives rise to molar lattice energy, G , between the repeat units or segments. The relationship between G and δ is given by Eq. (2.5)⁷⁸.

$$\delta = \rho \Sigma G / M \quad (2.5)$$

where ρ and M are the density and the formula weight of the repeat unit of a polymer respectively.

In summary modulus is influenced by the chemical composition of a polymer.

2.2.4 Viscoelasticity

Response of a polymer to external force is governed by its elastic and viscous components. Elasticity arises from elastic and reversible deformation or Hookian behavior while viscous behavior is due to relative motions of molecular chains passing each other or chain slippage. During deformation, a part of the force is stored elastically and reversibly and the remainder is converted to frictional heat or work to drive chain slippage. Both properties are defined as the storage and loss moduli respectively. Relative contribution of each component determines the overall viscoelastic properties of the polymer. The ratio of loss modulus to storage modulus is the damping ($\tan \delta$) and is a measure of how well the material can disperse energy. These properties are dependent of the polymer microstructures. They can be measured, for example, by subjecting the polymer to sinusoidal mechanical deformation at fixed frequency and amplitude while the response to the sinusoidal force is recorded. The technique that uses this principle is the dynamic mechanical analysis (DMA).

2.2.5 Thermal expansion

Polymer responds to the change in temperature with a volume change. Based on a crystal lattice model, Gruneisen⁷⁹ suggested a formula relating coefficient of linear thermal expansion, α , to bulk modulus, B, and specific heat, C_v , of a substance as shown in Eq. (2.6).

$$\alpha = C_v \gamma / 3B \quad (2.6)$$

where γ is the Gruneisen constant.

Eq. (2.6) shows that increasing bulk modulus will reduce thermal expansion. Table 2.1 compares some experimental values of linear thermal expansion coefficient for polymers and inorganic materials. The general trend is that $\alpha_{\text{polymers}} > (\alpha_{\text{metals}} \approx \alpha_{\text{ionic}}) > \alpha_{\text{covalent}}$. Some examples of the effect of fillers on thermal expansion coefficient of polymer are given in Table 2.2. Hence, incorporation of inorganic fillers generally reduces coefficient of linear thermal expansion.

Table 2.1 : Linear expansion coefficients at T=298 K ⁷⁹.

Materials	α (10^{-6} K^{-1})
Si	4.68
SiN ₄	2.7
PMMA	70
PS	70
PP	68
Polyisoprene rubber	223

Table 2.2 : Linear expansion coefficient of filled polymer systems at 293 K ⁸⁰.

Polymers	α (10^{-6} K^{-1})
Polyketone	111
Polyketone (54 %wt crystallinity)	102
Polyketone (30 %wt CaCO ₃)	87
Polyketone (30 %wt long glass fibres)	33

An analogue to the concept of B in Eq. (2.6) is the free volume within the polymer. Conceptually, free volume is inversely proportional to B. Hence, structural changes that reduce free volume will reduce CTE. This includes increasing MW and crosslink density within the polymer ⁸¹.

2.2.6 Adhesion

Adhesion characterizes the interaction between two surfaces. The adhesion strength is the force needed to overcome the interaction in order to separate the surfaces. The interaction may involve strong chemical bonding, ionic and polar

attraction, hydrogen bonding or Van der Waals interactions depending on the chemical structures of the surfaces. Adhesion between the polymer-substrate or polymer-filler systems is generally the interest in polymer systems.

Failure of adhered polymer-substrate assembly may be adhesive or cohesive in nature. The former is due to interfacial interaction while the latter is related to CED of the polymer matrix. Cohesive failure implies at good adhesive strength as the applied external force causes break within the polymer matrix instead of the polymer-substrate interface.

2.3 Dynamic Mechanical Analysis (DMA)

Typical sinusoidal deformation at frequency f , amplitude L and force response F of a polymer is illustrated in Figure 2.1⁸². There is a characteristic time delay, Δ , which is due to inherent viscoelastic nature of the polymer causing out-of-phase situation between deformation and force response. The out-of-phase situation is also termed as phase shift, δ . For a perfect elastic material the deformation and force responses are in phase. Using these raw data, the elastic and viscous components as well as other desired properties of the polymer are calculated :

- The phase shift, $\delta = 2\pi f\Delta$.
- Complex modulus, $|M^*| = (F/L)g$, where g is the geometry factor.
- Storage modulus, $M' = |M^*| \cos \delta$.
- Loss modulus, $M'' = |M^*| \sin \delta$.
- $\tan \delta = M''/M'$

The quantities M' , M'' , and $\tan \delta$ are temperature dependent.

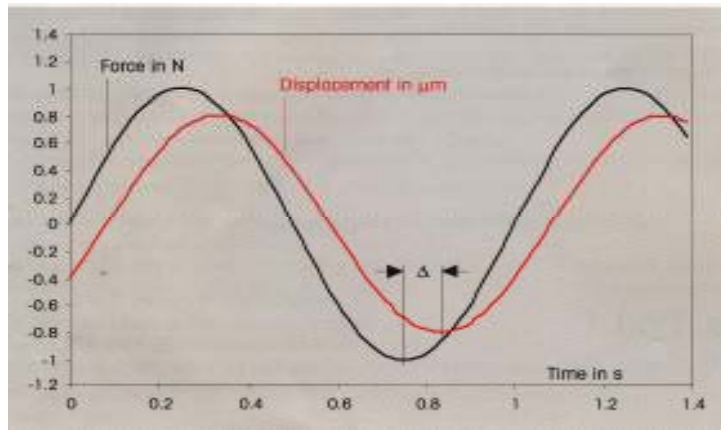


Figure 2.1 : Force and displacement at a frequency (f) of 1 Hz ⁸².

Under non-isothermal measurement, the profile of each quantity as a function of temperature exhibits two distinct regions of practically constant value. These regions correspond to the glassy and rubbery states, separated by a stepwise break which is the relaxation process or glass transition. Typical output of a non-isothermal measurement is given in Figure 2.2 ⁸². Measurement of deformation in either bending, tension or compression mode, the quantities obtained are called Young's storage, E' and loss moduli, E'' respectively.

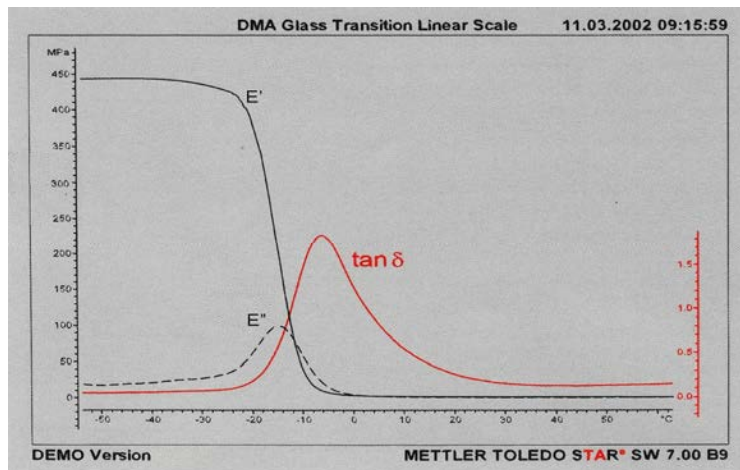


Figure 2.2 : The storage, loss moduli and $\tan \delta$ versus temperature curves ⁸².

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Design of experiment

Figure 3.1 outlines the design of experiments (DOE) that will be carried out in subsequent chapters. Systems to be evaluated can be categorized into un-filled and filled. Under each category, both the PU-modified and non-modified systems will be prepared and studied.

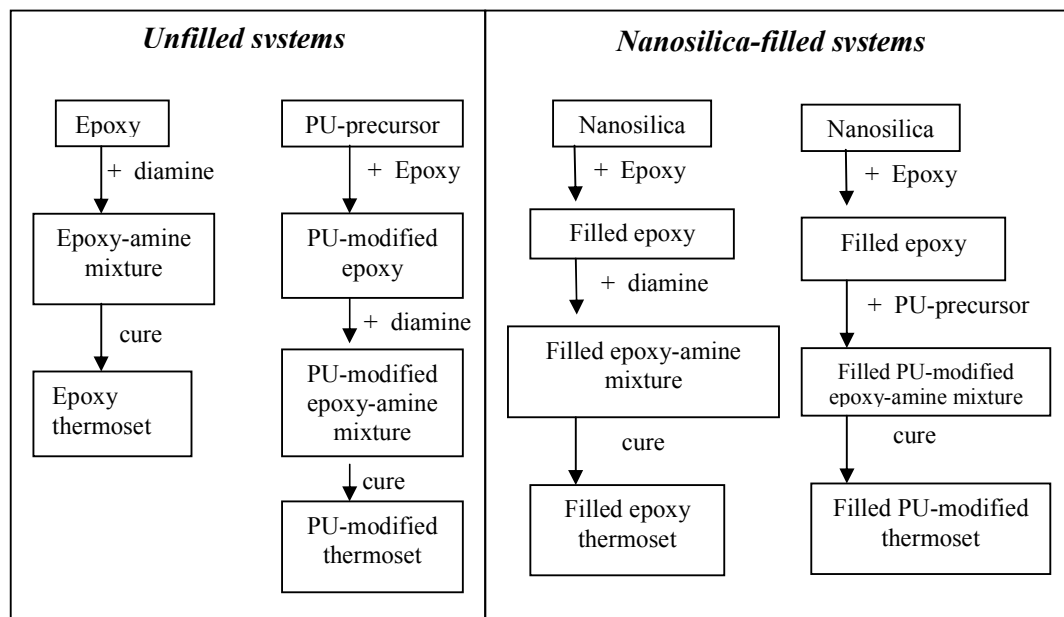


Figure 3.1: Design of experiment (DOE).

3.2 Materials and work station

The materials used in this project are listed in Table 3.1. Diols and diisocyanates were for polyurethane-precursor (PU-precursor) synthesis while epoxy and diamine were the base material for the matrix. Materials needed for nanosilica synthesis were also listed in the same table. All reagents were purchased and used without further purification except for the diols which were treated to remove traces of water. Treatment was carried out by passing the diols through numerous silica gel columns until the silica gel remain blue. Here, the silica gel acted as a drying agent as well as moisture indicator.

The work station for all PU-precursor synthesis was an environment-controlled glove box measuring 60 x 90 x 120 cm. It is set to 45 % relative humidity and 30 °C by suction with a 1 horse-power pump for 30 minutes. The glove box also acted as a safety measure that prevents direct contact with toxic diisocyanates.

3.3 Synthesis

3.3.1 PU-precursors

Two types of PU-precursors based on HDI and MDI were prepared. A typical HDI-based precursor with diol-diisocyanate mole ratio of 1:3 was prepared as follows : 1.00 g of PEG400 and 1.26 g of HDI were homogenized in a sealed glass vial using a magnetic stirrer. It was conducted at ambient temperature (30 °C) for 24 hours. The rest of the HDI-based precursors were prepared in similar manner.

As for the MDI-based precursors, a typical preparation for precursor with diol-diisocyanate mole ratio of 1:3 was as follows : 1.00 g of PEG400 and 1.88 g of MDI were homogenized in a 90 °C silicon oil bath for 15 minutes. Preparation of EG-MDI-

precursor was conducted in a similar manner. 90 °C was used as it allows the MDI to melt and subsequently react with the diol. Temperatures above 80 °C⁸³ are commonly used for MDI-based reactions.

Quantities of diol and diisocyanate for the preparation of the rest of PU-precursors are listed in Table 3.2. Reaction completion was tracked using the Fourier Transform Infra-red (FTIR) technique based on the disappearance of characteristic –OH band at ~ 3450 cm⁻¹.

Table 3.2: Preparation of PU-precursors.

Reactants		Diol-diisocyanate mole ratio	PU-precursors	Diol (g)	Diisocyanate (g)
HDI	PEG400	1 : 1	PEG400-HDI (r = 1)	1.00	0.42
		1 : 2	PEG400-HDI (r = 0.5)	1.00	0.84
		1 : 3	PEG400-HDI (r = 0.33)	1.00	1.26
		1 : 5	PEG400-HDI (r = 0.2)	1.00	2.10
		1 : 10	PEG400-HDI (r = 0.1)	1.00	4.20
	1 : 100	PEG400-HDI (r = 0.01)	0.20	8.40	
	EG	1 : 3	EG-HDI	1.00	8.13
MDI	PEG400	1 : 3	PEG400-MDI	1.00	1.88
	EG	1 : 3	EG-MDI	0.20	2.42

Table 3.1 : Materials used

Materials	Structure	Descriptions			Source
		Weight	T _m (°C)	Purity (%)	
Diols					
Poly(ethylene glycol) (PEG400)	$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$	MW = 380 - 420	4 - 8	100	Merck
Ethylene glycol (EG)	$\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$	MW = 62.07	-13	99.5	Merck
Diisocyanates					
1, 6 - hexamethylene diisocyanate (HDI)	$\text{OCN}-(\text{CH}_2)_6-\text{NCO}$	MW = 168.19	-55	98	Sigma Aldrich
4, 4' - methylene diphenyl diisocyanate (MDI)	$\text{OCN}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NCO}$	MW = 250.25	70	98	TCI Japan
Epoxy					
Diglycidyl ether of bisphenol-A based epoxy DER331		EEW = 182 - 192 % epoxide = 22.4 - 23.6	> 25	100	Dow Plastics
Diamine					
4, 4' - diamino diphenyl methane (MDA)	$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2$	MW = 198.27	88	> 97	Fluka
Materials for nanosilica synthesis					
Tetraethoxysilane (TEOS)	$(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}$	MW = 208.33	- 82	> 98	Fluka
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	MW = 46.07	- 114	99.5	System
Ammonium hydroxide	NH_4OH	MW = 35.05	- 72	25	Merck

Note : T_m = Melting temperature
 MW = Molecular weight (g/mol)
 EEW = Epoxy equivalent weight (g/eq)

3.3.2 PU-modified epoxies

This project focuses on PU-modified epoxies with chemically incorporated PU-precursors. Hence, stoichiometric quantity of PU-precursor was first determined. For PEG400-HDI-precursor it was determined by stage-wise addition of epoxy to 1.25 g of precursor, prepared in Section 3.3.1. The mixture was monitored with FTIR technique. At each stage, the need to add epoxy was determined by the following criteria : When only the –NCO band ($\sim 2270 \text{ cm}^{-1}$) was detected, epoxy was added. When both the –OH and –NCO bands were detected, the mixture was left to react. Stoichiometric quantity was reached when both the –OH and –NCO bands were just depleted. Stoichiometric quantities for the rest of the PU-precursors were determined in the same way.

Upon determination of the stoichiometric quantity, subsequent preparation of PU-modified epoxies involved homogenizing desired quantities of PU-precursors with epoxy in a 90 °C silicon oil bath. The duration needed for complete reaction of PU-precursor and epoxy was tracked with FTIR technique until both –NCO and –OH bands were depleted. In all, the PU-modified epoxies prepared for the present study are listed in Table 3.3.

Table 3.3: PU-modified epoxies prepared.

PU-modified epoxies	% wt of PU-precursor in epoxy		
	Partial stoichiometric quantity	Stoichiometric quantity	In excess of stoichiometric quantity
PEG400-HDI-modified epoxy	2.77	4.87	10, 20
EG-HDI-modified epoxy	0.30	0.67	-
PEG400-MDI-modified epoxy	2.93	5.85	-
EG-MDI-modified epoxy	2.05	3.83	-

3.3.3 Nanosilica

Nanosilica was synthesized based on the modified Stober method by Vejayakumaran et al.⁸⁴. Mixture of 6.0 ml TEOS, 0.7 ml distilled water and 30.0 ml ethanol were first sonicated for 2 hours. Then, 6.0 ml ammonium hydroxide (25 %) was added drop-wise, over a period of 3 hours. The mixture was next sonicated for an hour and silica nanoparticles were harvested by centrifugation. Repeated ethanol agitation and centrifugation were then carried out on the nanosilica to eliminate impurities. Finally, the nanosilica was dried at 80 °C for 24 hours and calcined at 500 °C for another 24 hours to remove water and other volatile impurities.

3.3.4 Filled epoxies

A 250 ml round bottom flask was set up in a heating mantle. 87.00 g of epoxy (approximately 75 ml), 8.60 g of nanosilica (prepared in Section 2.3.3) and 45.0 ml of zirconia (Zr) media were added alternately in small quantities to the round bottom flask. The composite was then mixed. Optimized mixing condition will be evaluated in Chapter 7. The resultant system is epoxy filled with 9 wt % of nanosilica.

Filled PU-modified epoxy was prepared as follows : 1.25 g of PEG400-HDI-precursor prepared in Section 3.3.1 was added into 26.83 g of filled epoxy prepared above and homogenized in a 90 °C silicon oil bath for 20 minutes. The filled EG-MDI-modified epoxy was prepared in the same manner where 1.25 g of EG-MDI-precursor and 34.49 g of filled epoxy were used.

3.3.5 Epoxy-amine mixtures

10.00 g of epoxy was added with 2.65 g of diamine (MDA) and stirred for 2 - 3 min in 90 °C silicone oil bath to just melt the solid MDA and homogenize the mixture. While still in liquid, the mixture was promptly transferred into PP vials and stored in a – 20 °C freezer. The quantity of epoxy and diamine used allows 1 epoxy equivalent weight (EEW) of epoxy to react with 0.25 mole of diamine. PU-modified epoxy and amine mixtures, both filled and un-filled, were prepared in the similar manner. Reactant quantities are listed in Table 3.4. Fresh samples were prepared weekly.

Table 3.4: Preparation of epoxy-amine mixtures.

Epoxy-amine mixtures		PU-modified epoxy (g) used	Diamine (g) needed
Mixtures	% wt PU-precursor		
PEG400-HDI-modified epoxy-amine	2.77	10.00	2.58
	4.87	10.00	2.52
	10	10.00	2.39
	20	10.00	2.12
EG-HDI-modified epoxy-amine	0.30	10.00	2.64
	0.67	10.00	2.63
PEG400-MDI-modified epoxy-amine	2.93	10.00	2.57
	5.85	10.00	2.50
EG-MDI-modified epoxy-amine	2.05	10.00	2.60
	3.83	10.00	2.55
Filled PEG400-HDI-modified epoxy-amine	4.87	10.00	2.29
Filled EG-MDI-modified epoxy-amine	3.83	10.00	2.32