APPLICATIONS OF POLYBENZOXAZINES FOR IMPROVEMENT IN PROCESSABILITY AND PROPERTY

by

LIN JIN

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Thesis Advisor: Dr. Hatsuo Ishida

Department of Macromolecular Science and Engineering

CASE WESTERN RESERVE UNIVERSITY

May, 2010
CASE WESTERN RESERVE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis/dissertation of

__________________________
Lin Jin

candidate for the _______Ph.D.______ degree *

(signed)_________ Hatsuo Ishida____________________
(chair of the committee)

_________Joao Maia___________________________
_________Lei Zhu_____________________________
_________Syed Qutubuddin_____________________

(date) 1/21/10__________

*We also certify that written approval has been obtained for any
Proprietary material contained therein.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE OF CONTENTS</td>
<td>i</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
<tr>
<td><strong>CHAPTER 1: Introduction</strong></td>
<td></td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>References</td>
<td>7</td>
</tr>
<tr>
<td><strong>CHAPTER 2: Development of Thermo-oxidatively Stable Coating System in the 450 - 800°C Range Based on Polybenzoxazine Resins, POSS and Glass Microbeads</strong></td>
<td>10</td>
</tr>
<tr>
<td>Introduction</td>
<td>11</td>
</tr>
<tr>
<td>Experimental</td>
<td>14</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>18</td>
</tr>
<tr>
<td>Conclusions</td>
<td>30</td>
</tr>
<tr>
<td>References</td>
<td>31</td>
</tr>
<tr>
<td>Tables</td>
<td>33</td>
</tr>
<tr>
<td>Schemes</td>
<td>34</td>
</tr>
<tr>
<td>Figures</td>
<td>36</td>
</tr>
</tbody>
</table>
### CHAPTER 3: Bis(benzoxazine-maleimide)s as a Novel Class of High Performance Resin: Synthesis and Properties

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>46</td>
</tr>
<tr>
<td>Experimental</td>
<td>47</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>50</td>
</tr>
<tr>
<td>Conclusions</td>
<td>56</td>
</tr>
<tr>
<td>References</td>
<td>65</td>
</tr>
<tr>
<td>Tables</td>
<td>66</td>
</tr>
<tr>
<td>Schemes</td>
<td>68</td>
</tr>
<tr>
<td>Figures</td>
<td>69</td>
</tr>
</tbody>
</table>

### CHAPTER 4: Using Allyl Benzoxazine Monomers as Replacement for Styrene in Vinyl Ester Resin

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>86</td>
</tr>
<tr>
<td>Experimental</td>
<td>87</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>89</td>
</tr>
<tr>
<td>Conclusions</td>
<td>92</td>
</tr>
<tr>
<td>References</td>
<td>101</td>
</tr>
<tr>
<td>Tables</td>
<td>102</td>
</tr>
<tr>
<td>Schemes</td>
<td>103</td>
</tr>
<tr>
<td>Figures</td>
<td>105</td>
</tr>
</tbody>
</table>

BIBLIOGRAPHY 118
LIST OF TABLES

CHAPTER 2
Table 2.1 Summary of TGA results of main-chain benzoxazine, OctaSilane POSS and glass sphere systems with varying polymer and OctaSilane POSS contents 33

CHAPTER 3
Table 3.1 Thermal Properties of Bis(benzoxazine-maleimide) monomers 68
Table 3.2 Thermal Properties of Poly[ Bis(benzoxazine-maleimide)] thermosets 69

CHAPTER 4
Table 4.1 Viscosities of VE Resin Prepolymer blends with St/ pC-ala/BF-ala 103
Table 4.2 Thermal properties of Copolymers 104
LIST OF SCHEMES

CHAPTER 2

Scheme 2.1 Preparation of oligomeric benzoxazine (BZ-atdms) 34
Scheme 2.2 Demonstration of coating preparation 35

CHAPTER 3

Scheme 3.1 Preparation of Bis(benzoxazine-maleimide) monomers 70
Scheme 3.2 Structure of benzoxazine and bismaleimide counterpart monomers 71

CHAPTER 4

Scheme 4.1 Preparation VE Resin Prepolymer and VE Resin Copolymers 105
LIST OF FIGURES

CHAPTER 2

Figure 2.1 ¹H NMR spectrum of oligomeric benzoxazine BZ-atdms 36

Figure 2.2 TGA thermograms under oxidative environment for the mixture of OctaSilane POSS and 11 µm sodalime glass beads with oligomeric benzoxazine(a), BA-a(b), epoxy(c) and polystyrene(d) as matrices. 37

Figure 2.3 TGA thermograms under oxidative environment for the mixture of the oligomeric benzoxazine and 11 µm sodalime glass beads with Octasilane POSS(a), aluminum oxide(b), or titanium dioxide(c) 38

Figure 2.4 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine with the oxazine ring in the main chain with 11 µm sodalime glass microbeads and OctaSilane POSS with BZ:POSS 2.5:4.5(a), 3:4(b), 3.5:3.5(c) and 4:3(d) 39

Figure 2.5 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine, OctaSilane POSS and 4 µm treated E-glass sphere with BZ:POSS 2.5:4.5(a), 3:4(b), 3.5:3.5(c) and 4:3(d) 40

Figure 2.6 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine, OctaSilane POSS and 11 µm treated sodalime glass sphere with BZ:POSS 2.5:4.5(a), 2:5(b), 3:4(c), 3.5:3.5(d) and 4:3(e) 41

Figure 2.7 Raman Spectra for Octasilane POSS and oligomeric benzoxazine (BZ-atdms) 42
Figure 2.8 Optical Image of oligomeric benzoxazine, OctaSilane POSS and glass sphere (11 µm) (4:3:3) blends (top middle); Raman Image for peak at 2150 cm⁻¹ (left bottom); Raman Image for peak at 1600 cm⁻¹ (right bottom)

Figure 2.9 Optical Micrographs of Uncoated Carbon/Carbon Composite Surface (top middle), Coated before curing Carbon/Carbon Composite Surface (left bottom), Coated, cured and baked Carbon/Carbon Composite Surface (right bottom)

Figure 2.10 Isothermal Weight Loss Measurements for Coated and Uncoated Carbon/Carbon Composite at 700°C in air

CHAPTER 3

Figure 3.1 ¹H NMR spectra of Bis(benzoxazine-Maleimide)s

Figure 3.2 ¹³C NMR spectra of Bis(benzoxazine-Maleimide)s

Figure 3.3 FTIR spectra of Bis(benzoxazine-maleimide)s

Figure 3.4 DSC curve of Bis(benzoxazine-maleimide)s

Figure 3.5 DSC curve of benzoxazine and bismaleimide counterpart monomers

Figure 3.6 DSC curve of Bis(MI-npda) monomer with the monomer containing PTS, styrene and AIBN

Figure 3.7 DSC curve of Bis(MI-npda) after each cure stage

Figure 3.8 DSC and TGA curves of themosets polymerized at 250°C of Bis(MI-npda)

Figure 3.9 Isothermal TGA curves of themosets from Bis(MI-npda)

Figure 3.10 FTIR spectra of Bis(MI-npda) after each heating stage

Figure 3.11 FTIR spectra of Bis(MI-npda) after post curing
Figure 3.12 Temperature dependence of storage moduli of Poly[Bis(benzoxazine-maleimide)] thermosets

Figure 3.13 Temperature dependence of loss moduli of Poly[Bis(benzoxazine-maleimide)] thermosets

Figure 3.14 TGA of Poly[Bis(benzoxazine-maleimide)] thermosets

CHAPTER 4

Figure 4.1 $^1$H NMR spectra of VE Resin Prepolymer, benzoxazine monomer pC-ala and BF-ala

Figure 4.2 DSC curves of VE Resin Prepolymer and pC-ala blends

Figure 4.3 Viscosities of VE Resin Prepolymer blends with St, pC-ala and BF-ala at shear rate 100/s

Figure 4.4 Time dependence of viscosities at 120°C with shear rate of 100/s for VE Resin Prepolymer blends with St, pC-ala and BF-ala

Figure 4.5 Storage Modulus for VE Resin Copolymers with St and pC-ala

Figure 4.6 Tan δ for VE Resin Copolymers with St and pC-ala

Figure 4.7 FTIR of VER Resin Copolymer with pC-ala(deuterated) after each heating stage

Figure 4.8 pC-ala Content vs Time with isothermal treatment at 80°C and 150°C

Figure 4.9 Storage Modulus for VE Resin Copolymers with St, pC-ala and BF-ala

Figure 4.10 Tan δ for VE Resin Copolymers with St, pC-ala and BF-ala

Figure 4.11 TGA for VE Resin Copolymers with St, pC-ala and BF-ala in N$_2$

Figure 4.12 TGA for VE Resin Copolymers with St, pC-ala and BF-ala in air
ACKNOWLEDGMENTS

First, I would like to thank my research advisor, Prof. Hatsuo Ishida for his guidance, criticism, encouragement and philosophies these years. I truly appreciate his care about the students’ growth in research and life. I would like to thank Dr. Tarek Agag for all the fruitful discussions about the research and the teaching of the knowledge for the labs.

I also want to extend my gratitude to Barb for her assistance and kindness and all the past and present group members: Yuki, Lookwah, Pedro, Andrey, Carlos, Jia and Mohamed for their help and friendship. Besides, I would like to thank all the friends I have met in Cleveland, and Linxia and Mingming for their support.

Last, I would like to thank my family for their patience and support during all these years.
Applications of Polybenzoxazines for Improvement in Processability and Property

Abstract

by

LIN JIN

Polybenzoxazines obtained from the polymerization of benzoxazine monomers or oligomers has been used for various applications: to simplify the technology adopted for protection, to improve the processability of high performance material and to replace the environmental hazards in resins.

Novel siloxane-containing benzoxazine oligomers with benzoxazine rings in the main chain have been synthesized and mixed with octasilane polyhedral silsesquioxane (OctaSilane POSS) and glass sphere to form a thermo-oxidatively stable coating on a carbon/carbon composite after polymerization and baking. The coating method is very simple and inexpensive compared with the conventional approaches, such as chemical vapor deposition. The effectiveness of the coating has also been demonstrated.

A new class of benzoxazine-containing monomers, namely bis(benzoxazine-maleimide)s have been synthesized to improve the poor processability of bismaleimides. A new approach of using high boiling point nonpolar solvent has been developed to prepare the monomer, which is difficult to synthesize using the traditional method of
synthesizing benzoxazines. In the meantime, by the combination of two types of polymers: benzoxazine and bismaleimides, high thermally stable thermosets with high $T_g$ have been obtained.

Benzoxazine monomers have also been introduced into vinyl ester resins to replace styrene for environmental concern. With the incorporation of allyl-containing benzoxazines, the dynamic mechanical property and the thermal stability of the resins have been improved, while the processibility of the resin is maintained.
CHAPTER 1

Introduction
Phenolic resins have been in use commercially as a thermosetting resin since the early twentieth century. The resin has many desirable properties such as good electrical properties and mechanical strength, dimensional stability, chemical and heat resistance, flame retardance and low smoke generation. Therefore, they have been widely used in construction, appliance industries and high technology applications in electronics and aerospace industry. However, they have several serious shortcomings which are connected with the fundamental polymerization mechanism. The usage of strong acid or base as catalysts brings in the corrosion of processing equipment, and the release of volatiles during polymerization causes the internal micro voids as structural defects [1,2]. Thus, it has been a challenge to develop a novel class of materials which can overcome the drawbacks of traditional phenolic resins while maintaining their physical and mechanical properties.

Among the numerous attempts to develop alternative resins for traditional phenolic resins to overcome its associated drawbacks, polybenzoxazines have been created as a novel class of phenolic resin, showing great commercial potential because they have mechanical and physical properties comparable or even superior to conventional phenolic, epoxy, bismaleimide and polyimide resins.

Benzoxazine monomers are heterocyclic compounds that were first synthesized by Holly and Cope through Mannich condensations of phenols with formaldehyde and amines [3]. Subsequently, Burke et al. improved the procedure for preparing benzoxazine monomers by a number of variations [4,5]. Later, the opening of benzoxazine rings by a
phenol group to form dimeric structures was observed [6], but it was not until Schreiber that the potential of benzoxazines for the preparation of phenolic materials with improved properties was first introduced [7,8]. Reiss et al. further demonstrated the use of monocyclic benzoxazines as precursors to oligomeric species with thermally initiated and phenol catalyzed systems [9].

The mechanism for the formation of the benzoxazine ring structure has been proposed. The evidence suggests that amine reacts with formaldehyde and forms aminomethylol group as intermediate immediately after mixing, then it further reacts to form 1,3,5-triaza-like structure. With time, it reacts with phenol and formaldehyde to form the oxazine ring [10]. At elevated temperature, benzoxazine monomer with or without initiator/catalyst undergoes cationic ring opening polymerization and forms the polymer consisting of phenolic groups that are linked by Mannich base as repeating units [5].

This family of phenolic resins produces no condensation byproducts and almost no shrinkage during the polymerization and requires no harsh catalysts for the synthesis or polymerization. Unlike traditional phenolic resins, the benzoxazine resin provides great molecular design flexibility by using a derivative of phenol, a primary amine and formaldehyde. The other attractive characteristics of benzoxazine resin include rapid development of properties as a function of conversion, low melt viscosity, good mechanical properties, excellent electrical properties and ease of processing [11-16].

Due to its fascinating advantages, tremendous work has been done in benzoxazine chemistry, basically in two categories. First is to understand the fundamental relationship
between its structure and its appealing properties [10,17-20]; second is to further improve the property for specific applications as high performance materials by either introducing new functional groups by blending or as part of the monomer structure [21-45]. This has also been achieved by extending benzoazine structure from monofunctional monomers to difunctional monomers and even main-chain oligomers [11,46-50].

This thesis focuses on utilizing both monomeric and oligomeric benzoazine chemistry to improve their properties for specific functions, including simplifying the technology adopted for thermo-oxidative protection of carbon/carbon composites, improving the processability of high performance bismaleimides without sacrificing thermal and mechanical properties and replacing the environmental hazards in vinyl ester resins.

In the first part, the main-chain benzoazine oligomers containing siloxane repeating units have been synthesized. This benzoazine exhibits high thermo-oxidative stability. The benzoazine has been used as a matrix for the fillers: octasilane polyhedral silsesquioxane (OctaSilane POSS) and glass sphere with high char yield. Then the mixture is applied to carbon/carbon composites, which suffer from thermo-oxidative degradation at temperature as low as 500 °C and the reduction of mechanical properties, as a thermo-oxidative protective coating in the mid temperature range of 450-800 °C. The synergism of thermo-oxidative stability of the mixture has been observed, which can be partially attributed to the retention of filler degradation and homogeneous distribution of the filler particles by the matrix. A convenient and inexpensive method has been
adopted to coat the carbon/carbon composites and the effectiveness of the coating has been demonstrated by thermo-oxidative degradation test for protected composites.

In the second part, a series of bis(benzoxazine-maleimide)s has been synthesized and characterized as a novel class of high performance resin. The study was motivated by the outstanding performance of resin from monofunctional benzoxazine functionalized with maleimide groups and the demands to improve the processability of bismaleimides with high glass transition temperature. Instead of using traditional methods of synthesizing benzoxazine: either solvent or solventless processes, the synthesis of these bis(benzoxazine-maleimide)s have been achieved by adopting a new approach: using non-polar high boiling point solvents and increasing temperatures. Due to the non-polar nature of the solvents, the oxazine ring formation process for difficult structure is accelerated without much side reactions going on even at high temperature. The new class of the resin exhibits high thermal stability, good dynamic mechanical property along with excellent processability.

In the third part, allyl containing benzoxazine monomers are used to replace styrene in vinyl ester resins. Styrene is used as a reactive diluent in vinyl ester resin for good processability; however, it causes health and environmental risks due to its volatile nature. To avoid the potential danger, benzoxazine monomers with allyl functionalities are introduced to vinyl ester resin. At elevated temperature, the new vinyl ester prepolymer blends show comparable viscosity with the styrene containing blend, indicating its good processability. Improved dynamic mechanical property and thermal stability is also obtained by using the benzoxazines as reactive diluents because of its
superior properties. Considering environmental safety and human health, besides the technological interest, it is urgent and important to develop this new resin without styrene.

All the work aims to improve the processability, properties or safety for the materials by incorporating benzoxazines.
References


42. Su YC, Chen WC, Ou KL, Chang FC. *Polymer* 46, 3758, 2005.


CHAPTER 2

Development of Thermo-oxidatively Stable Coating System in the 450 - 800°C Range Based on Polybenzoxazine Resins, POSS and Glass Microbeads
2.1 Introduction

Carbon/carbon composites are attractive materials because of their many unique properties, including good electrical conductivity, fire retardant characteristics, and resistance to erosion. Carbon/carbon composites offer exceptional thermal stability, provided that the surface is properly protected from thermo-oxidative degradation; therefore, they are promising in a wide range of applications, such as rocket nozzles, supersonic aircraft brakes, thermal insulation in inert furnaces, and anodes for lithium-ion battery systems [1-4].

However, unprotected carbon/carbon composites suffer from thermo-oxidative degradation at temperature as low as 500°C, which results in the reduction of mechanical properties [5-7]. The brittleness of the carbon matrix also leads to matrix cracking due to the weight loss during pyrolysis and subsequent thermal shrinkage upon cooling [8]. The cracks penetrate deep into the core of the material, leading to accelerated thermo-oxidative decomposition beyond the surface degradation. For these reasons, the usage of carbon/carbon composites at increased temperature in oxidizing atmosphere requires effective oxidation-protective layered coatings.

To achieve oxidative protection at high temperatures, various methods have been developed. Williams et al. used silicon carbide with an over-coating of glass [9]. Titanium carbide and boron nitride were applied by chemical vapor deposition to composites by Naslain. et al. [10]. Ehrburger et al. [11] and McKee et al. [12-14] introduced glassy or liquid films of boron oxide or borates as the coating systems. Singh et al. [15] and Soraru et al. [16] employed silicon oxycarbide, which is stable up to
temperatures above 1000°C, through decomposition of hydrocarbon substituted silicates or through sol-gel processing. The thermo-oxidative stability of carbon/carbon composites in the mid-temperature range of 450-800°C has received little attention, due in part to the historical interest of carbon/carbon composite to be in the very high temperature regime where there almost no materials that can compete with its thermal and mechanical properties. On the other hand, there are many materials that can compete with carbon/carbon composites for performance in the mid-temperature range, in particular mechanical strength. While the thermal stability of carbon/carbon composite in inert atmosphere in the mid-temperature range remains a strong attraction, mechanical strength retention during service must be much better than in the high temperature regime to justify the use; however, carbon does degrade noticeably above 500°C [17], thus thermo-oxidative protected carbon/carbon composite is desirable for the use in the mid-temperature range.

Polybenzoxazines, a class of ring-opening phenolic resins has been developed in the past 15 years. A Mannich condensation of a phenolic derivative, formaldehyde, and a primary amine affords a ring compound that polymerizes through cationic polymerization. Upon polymerization, a polymer with a phenolic hydroxyl group and a tertiary amine bridge as a repeating unit is produced. This class of polymers exhibit many attractive properties, including low melt viscosity, high thermal stability, good mechanical properties, and rich molecular design flexibility [18-22]. Of particular interest in the current project is the high char yield of polybenzoxazines. Polybenzoxazines usually exhibit char yield in the range from 35% to 75% when heated under nitrogen to 800°C.
Traditionally, polybenzoxazines are derived from benzoxazine monomers, of either monofunctional, difunctional or higher functionality. However, the film formability of these benzoxazine resins is poor. Recently, a new extension in polybenzoxazine research has been reported. Unlike monomeric precursors for polybenzoxazines reported in the past, the new material is based on linear polymers containing benzoxazine moieties as repeating units in the main chain [23-24]. These polymers can be processed into self-supporting, flexible films, and the benzoxazine ring-containing resin can be further polymerized to form crosslinking networks. Such a polymer is ideally suited for applications, such as coating, where film formation is needed.

In this study, a new, high-char yield benzoxazine resin was synthesized as a matrix for fillers that provides high char yield under air. A coating system for carbon/carbon composite that is stable under thermo-oxidative conditions in the temperature range between 450 and 800°C has been developed using convenient and inexpensive technology.
2.2 Experimental

2.2.1 Materials

Aminopropyl-terminated poly(dimethylsiloxane) (M<sub>w</sub>=700-1000 g/mol) was purchased from Gelest Inc. 4,4-Dihydroxy benzophenone was kindly supplied from Kennedy&Klim Inc. Solid E-glass spheres with an average diameter of 4 μm and the softening temperature of 843°C, sodalime glass microbeads with an average diameter of 11 μm and the softening temperature of 730°C were kindly supplied from Potters Industries Inc. Octasilane polyhedral oligomeric silsesquioxane (OctaSilane POSS) was purchased from Hybrid Plastic Company. Vinyl trimethoxysilane was purchased from United Chemical Technologies Inc. Aluminum oxide (3 μm APS Powder. S.A. 80-120 m<sup>2</sup>/g) was obtained from Alfa AESAR A Johnson Matthey Company. Titanium dioxide was provided by JT BakerChemical Co. Triethylamine (99%), formaldehyde solution (37%w/w), 1,4-dioxane (99.9%), toluene(99.9%), methanol and tetrahydrofurane (THF) were obtained from Fisher Scientific Company. All chemicals were used as received.

2.2.2 Preparation of oligomeric benzoxazine (BZ-atpdms)

In a 100ml round bottom flask, a mixture of 4,4-dihydroxy benzophenone (5.1 mmol, 1.1 g), formaldehyde aqueous solution (37Wt.%， 20 mmol, 1.6 g), and aminopropyl-terminated poly(dimethylsiloxane) (4.9 mmol, 4.2 g) in 14 ml 1,4-dioxane was stirred at 100°C for 50 h with one drop of triethylamine which was added to the mixture as a reaction catalyst. The product was purified by washing with cold methanol.
$^1$H NMR spectra (Acetone, ppm, δ, 600 MHz): 0.1 (s, Si-CH$_3$), 0.6 (s, Si-CH$_2$), 1.6 (s, Si-CH$_2$-CH$_2$), 2.7 (s, Si-CH$_2$-CH$_2$-CH$_2$-N), 4.1 (s, C-CH$_2$-N), 5.0 (s, N-CH$_2$-O), 6.5-7.8 (m, Ar).

2.2.3 Preparation of blends

Benzoxazine resin was dissolved in THF using a magnetic stirrer. Then, OctaSilane POSS was added followed by the addition of glass sphere with certain ratios as listed in Table 2.1. The overall solid content with THF is about 30%. The mixture was stirred as much as possible until the viscosity increased to the extent that the glass beads did not segregate any more. In order to compare the effectiveness of the new benzoxazine, it was replaced with polystyrene, epoxy and bisphenol-A/aniline type monomeric benzoxazine (6,6’-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine); hereinafter abbreviated as BA-a). The epoxy resin used was of an electronic grade cresol-novolak type (Epon 164). For epoxy and BA-a substitution, melt mixing instead of solution mixing was used. The effectiveness of OctaSilane POSS is investigated by replacing the weight percentage of OctaSilane POSS with the same weight of titanium dioxide and aluminum oxide. E-glass microbeads with 4µm diameter were intended to replace 11µm sodalime glass sphere to achieve better mixing. The E-glass microbeads were treated with 0.1% vinyl trimethoxy silane in reflux toluene for 6 hrs to minimize aggregation. The glass was centrifuged and dried in vacuum oven overnight at 100°C after treatment. 11µm sodalime glass spheres received the same treatment to be used as a comparison with untreated systems. The organic matrix/OctaSilane POSS/glass beads blends were heated in a convection oven with different temperature profiles. The temperature profiles used were: 160°C(1 hr), 190°C(1 hr),
210°C(2 hrs), 250°C(0.5 hr) for the blend with oligomeric benzoxazine; 140°C(0.5 hr), 160°C(0.5 hr), 170°C(0.75 hr), 180°C(0.75 hr), 190°C(1.25 hrs), 200°C(1.25 hrs) for the blend with BA-a; 200°C(2 hrs) for the blend with epoxy. Since a commercial form of polystyrene was used, the components were just mixed without any heat treatment.

2.2.4 Preparation of coatings on Carbon/Carbon Composites

Carbon/carbon composites were treated with 0.2% vinyl trimethoxy silane in toluene under reflux for 2 hrs to increase their affinity to coating suspension. The treated carbon/carbon composites were dip-coated twice in benzoxazine solution/OctaSilane POSS/glass beads mixture in THF, then they were dried in a saturated THF environment in order to obtain uniform-thickness coating. After drying, the coating was polymerized and the composite was baked in a convection oven by the following temperature profiles: 160°C(1 hr), 190°C(1 hr), 210°C(2 hrs), 250°C(0.5 hr), 300°C(10 min), 400°C(10 min), 500°C(10 min), 600°C(10 min), 700°C(5 min), 800°C(5 min), 900°C(5 min). Coating, curing and baking were each carried out 2 times.

2.2.5 Measurements

$^1$H NMR spectra were acquired in deuterated acetone on a Varian Oxford AS600 at a proton frequency of 600 MHz. The average number of transients for $^1$H NMR is 64. A relaxation time of 10s was used for the integrated intensity determination of $^1$H NMR spectra. Size exclusion chromatography (SEC) was carried out using three µStyragegel™ columns, pore sizes of 10$^5$, 10$^3$ and 50nm respectively, and with THF as an elutent.
dual detection system was used consisting of refractive index detector (Waters model 410) and UV absorption detector (Waters model 440) at a fixed UV frequency of 252 nm. Thermogravimetric analyses (TGA) were performed on High Res TGA 2950 (TA Instruments) with a heating rate of 10°C/min under air purge with a flow rate of 90ml/min. The experiments started from ambient temperature to 900°C and all the experiments were repeated twice. Micro Raman scattering studies were performed at room temperature with a Horiba Jobin Yvon LabRam HR800 spectrometer equipped with a charge coupled detector and two grating systems (600 and 1800 lines/mm). A HeNe laser (λ = 632.8 nm) was focused on the sample with an Olympus microscope at an optical power of 17 mW and a spot size of 1 μm². Raman shifts were calibrated with a silicon wafer using the 520 cm⁻¹ peak. Coated carbon/carbon composite specimens were placed on glass slides, digital micrographs were taken by an Olympus BH-2 optical microscope (OM). Coated specimens were kept in a convection oven at 700°C up to 1300 hrs to investigate their thermo-oxidative stabilities. The residual weight was measured by a chemical balance at specified time intervals.
2.3 Results and Discussion

2.3.1 Preparation of oligomeric benzoxazine (BZ-atpdms)

To develop a new coating for carbon/carbon composites, it is required to have high thermo-oxidative stability. While many benzoxazine resins offer high char yield with carbonaceous residues, they do not survive under air. Thus, the new benzoxazine resin needs to yield coating that is thermo-oxidatively stable at least above 800°C. For this purpose, oligomeric benzoxazine (Poly(BZ-atdms)) containing siloxane repeating units has been developed. This oligomeric benzoxazine is of main-chain type where oxazine rings are in the main chain of a linear polymer. These oxazine groups can then be used to crosslink the linear oligomer. The reaction pathway is shown in Scheme 2.1. The structure is confirmed by $^1$H NMR and also characterized by SEC. Figure 2.1, the $^1$H NMR spectrum of Poly(BZ-atdms), shows the resonance of the methyl group next to silicon at 0.1 ppm, the methylene group next to silicon at 0.6 ppm, and the two consecutive methylene groups at 1.6 and 2.7 ppm, respectively. The characteristic benzoxazine resonances appear at 4.1 and 5.0 ppm, and the polymeric aromatic structure shows resonances in the range 6.5-7.8 ppm. SEC was used to characterize molecular weight of Poly(BZ-atdms). The as-synthesized product has a number average molecular weight of 836, a weight average molecular weight of 6387 and PDI of 7.64. The broadness of molecular distribution is due to the existence of small molecules from starting materials and remaining solvents, shown as a multiple peaks among and after main peak. These impurities can be successfully removed by washing the crude reaction products with cold methanol, as indicated by the disappearance of the massive peaks in
GPC spectrum. The purified product has a number average molecular weight of 8640, a weight average molecular weight of 15225 and PDI of 1.76. The degree of polymerization is between 8 and 15. No further purification has been attempted due to the application demands to simplify the procedure. The purity of washed material is sufficient and the impurities remaining in the material are expected to be effectively incorporated into network structure upon polymerization without sacrificing properties.

2.3.2 Blends Formula

Fillers are also added to increase the thermo-oxidatively stable char yield. There are several requirements for a filler to effectively meet the purpose. The filler particles must be distributed evenly in the matrix so as to protect the composite surface evenly. Upon char formation, the film must be air tight to act as an oxidation barrier. The crack formation needs to be minimized upon film formation and cooling, if necessary. In addition, the coating procedure should be simple, not requiring costly instrumentation and able to be performed under ambient conditions. Furthermore, addition of the filler(s) should not lead to significant difficulty in processing or coating. In order to satisfy these requirements, we have developed a three-phase system comprised of a benzoxazine resin, POSS and glass microbeads.

A high char yield benzoxazine resin is used as a short-term support until the fillers form an even film. Both the benzoxazine resin and the POSS of choice dissolve in a common solvent so that they are molecularly mixed. The POSS molecule chosen (OctaSilane POSS) has only a few organic groups so as to produce high concentration of silica, a thermo-oxidatively stable material. As POSS is sometimes called molecular silica, these silica nanoparticles will distribute evenly throughout the char produced by
the polybenzoxazine. However, both polybenzoxazine and POSS char will lead to powdery residues. Thus, the thermo-oxidatively stable coating will be mechanically weak and can be easily scraped off the surface of carbon/carbon composite. Also, these particles will not form an airtight film. In order to produce an airtight film, we added the third component, glass microbeads. The concept and procedure is demonstrated in Scheme 2.2.

2.3.3 Justification of the Blend Formula

2.3.3.1 Matrix

Thermo-oxidative stabilities of four different types of polymers have been compared for the most suitable candidate for a matrix: polystyrene, an example of an ordinary polymer with no char yield under air; epoxy, an effective film former; Bisphenol-A/aniline type monomeric benzoxazine (hereinafter abbreviated as BA-a), a standard of traditional benzoxazine resin; and our newly synthesized oligomeric benzoxazine. For forty percent by weight of four matrix materials were mixed with 30 wt% of OctaSilane POSS and 30 wt% of glass sphere (11µm). The concentration of OctaSilane POSS and glass beads were kept constant. TGA results are shown in Figure 2.2. The mixture with polystyrene as the matrix material starts to degrade at around 100°C and shows a sharp drop of residual weight in the 270-380°C region. The drop corresponds to the degradation of polystyrene by about 40% of total weight, which is consistent with the amount of this material added. There is another minute degradation process up-to 500°C. The char yield for modified PS film is 40%, much less than the expected value of around 53% (30% contribution from glass sphere and 23% contribution from OctaSilane POSS as its inorganic content). Therefore, it is hypothesized that the
presence of PS interferes with OctaSilane POSS’s ability to form thermo-oxidatively stable char due to degradation process of molecularly distributed PS component.

For the mixture with epoxy matrix, the degradation starts at around 200°C. A gradual loss in residual weight is observed till 550°C and the char yield is 53%, which is the expected value considering no contribution from the matrix as a char at high temperature. It is interesting to compare the result of the epoxy matrix with that of BA-a. Both epoxy and BA-a have zero char yield under thermo-oxidative environment; therefore, at first thought, it might be reasonable to expect the same char yield from both blends. In fact, the mixture with BA-a matrix shows a similar trend as epoxy matrix but the overall curve has an upward shift for the degradation processes with a slower rate, eventually achieving 58% char yield.

For the mixture with oligomeric benzoxazine, the degradation starts at relatively high temperature of 270°C. The degradation is relatively mild with two-stage weight loss process in the region of 300-550°C and 700-800°C. It reaches a maximum rate of weight loss at 440°C and 750°C respectively for the two stages. The char yield is 74%, which is higher than calculated value using the additivity rule of approximately 65% total char, in which 30% contribution from glass sphere, 23% contribution of OctaSilane POSS and 12% contribution of polymer are expected. The extra 9% can be assumed as the synergism caused by the char formation of polybenzoxazine.

The observation of a 13% reduction of char yield in the case of polystyrene matrix, matches with the expected char yield for the epoxy matrix, and the 5% and 9% addition to the expected value for BA-a benzoxazine and oligomeric benzoxazine, respectively, clearly indicate the significance of the matrix char formation process at lower
temperatures onto the overall char yield. Since these three matrices do not leave any residues at 800°C under air, no contribution in the char yield by themselves was anticipated.

The carbon matrix is gradually decomposed in air as the temperature increases. During this decomposition process, the degradation kinetics of OctaSilane POSS molecules can be influenced. Since a POSS molecule is relatively small, it can evaporate at a high temperature either by itself, or co-evaporate with the decomposed fragments of the matrix molecules. The longer the time of OctaSilane POSS is in the matrix, the greater the formation of non-evaporating silica nano-particles, resulting in higher char yield. Therefore, it appears that the decomposition process of OctaSilane POSS is strongly influenced by the matrix structure. No effect is expected on the char formation process of glass beads, though the morphology of the glass film formation is predicted to be significantly influenced. But it is possible that, due to the phase change of glass sphere at high temperature, the degradation of some carbonized char can be reduced or even suppressed by mixing with glass film, making it a synergism.

Overall, polystyrene type film is not promising as it has no char yield under air, despite the fact that it can form equally good film at room temperature as other matrices studied. Rather, it interferes with the formation of thermo-oxidatively stable char. Epoxy shows no synergism, while BA-a reveals synergism with lower thermo-oxidative stability than the main-chain type, oligomeric benzoxazine. It is obvious that Poly(BZ-atdms) is the best, as it was designed to leave thermo-oxidatively stable residue which then helps OctaSilane POSS to further enhance the char formation.

2.3.3.2 Filler
In order to evaluate the effect of fillers on the char formation, the same amount of OctaSilane POSS was replaced with either titanium dioxide or aluminum oxide. Titanium dioxide and aluminum oxide modified mixtures show similar trends in TGA results, as shown in Figure 2.3. The difference is that aluminum oxide modified mixture degrades earlier than the titanium oxide mixture but ends up with higher char yield of 66%, while the yield of the titanium dioxide modified mixture is about 64%. Both char yields are approximately 10% lower than that of oligomeric benzoazine mixture with OctaSilane POSS. Basically, both titanium dioxide and aluminum oxide are stable under all the experimental conditions used. Thus, the extra loss can be explained by an adverse catalytic effect on the benzoxazine char formation. Both aluminum oxide and titanium dioxide are hydrophilic with hydroxyl groups on the surface. We have observed that the surface hydroxyl groups can harm the char formation of benzoxazine resins. To further verify this, degradation products need to be analyzed further in detail. It is worth mentioning that both of these fillers cannot dissolve in THF while OctaSilane POSS dissolves completely, and the POSS used is less hydrophilic as it has no silanol groups in the molecule. Therefore, the OctaSilane POSS modified system shows better homogeneity and thermo-oxidative stability.

2.3.4 Optimization of Blends Formula

TGA results for blends of oligomeric benzoazine, OctaSilane POSS, and soldalime glass sphere (11µm) with different benzoazine-POSS ratios are shown in Figure 2.4. Glass sphere content is kept constant as 30%. The ratio between benzoazine and OctaSilane POSS was varied to evaluate any synergistic effect between them and also to optimize the thermo-oxidative stability on the new blends. In the meantime, more
OctaSilane POSS is added to the blend to examine the limitation of POSS content without any adverse effect in processibility. The extreme ratio that can be achieved is 2.5:4.5 (Poly(BZ-atdms): OctaSilane POSS). Above this ratio, the heterogeneity occurs by precipitation of glass sphere as oligomeric benzoxazine is not sufficient to form the film with well-dispersed additives. All of these four systems show two major degradation processes in the ranges of 300 - 550°C and 700 - 800°C. As expected, higher the amount of OctaSilane POSS in the system, higher the char yield and better thermo-oxidative stability. The char yield results are summarized in Table 2.1. From the calculation, adding 5% more of OctaSilane POSS component can help to obtain 2% more in char yield. The calculated value assumes no synergism and totals only the sum of contributions of all three components as those components were thermo-oxidatively degraded separately. In fact, the blend with benzoxazine-POSS ratio of 3.5:3.5 has 6% increase in char yield compared with that of 4:3, which is beyond the expectation by simple addition. However, by adding more OctaSilane POSS beyond 3.5:3.5, it shows increase of around 2% as the calculated results. As a whole, the blend with benzoxazine:OctaSilane POSS:glass sphere ratio at 4:3:3 has 74% char yield, having 9% increment beyond the char yield calculated by the additivity rule, while the blends with ratios ranging from 3.5:3.5:3 to 2.5:4.5:3 show around 12% increase over the calculated value. Therefore, it is believed that more synergistic effects are expected for the systems with ratios between 3.5:3.5 and 2.5:4.5 than that for the 4:3 blend.

The first glass used was sodalime beads with 11 µm in average diameter. Upon demonstration of the feasibility, we also tested E-glass microbeads of 4 µm, which are ideal for the temperature range of interest: 450-800°C, as E-glass liquefies at 843°C in
comparison to the sodalime softening temperature of 730 °C. Thus, it forms a glassy film within the temperature range of interest: 450-800°C, below the softening temperature of the glass, and helps to form the film to hold the powdery residues of polybenzoxazine and POSS during baking on carbon/carbon composites. However, E-glass beads of 4 μm do not mix easily with benzoxazine oligomer and OctaSilane POSS due to the hydrogen bonding interaction via the surface hydroxyl groups and adsorbed water molecules. This leads to aggregate formation of glassbeads in a hydrophobic environment of the matrix resin. 0.1% Vinyltrimethoxy silane is used to treat the surface of glass sphere to make it less hydrophilic and lower the possibility of aggregation. Also, the sodalime and E-glass microbeads are not available in the same diameter, which makes it difficult to distinguish the effect of the chemical component from the effect of the particle size effect. Figure 2.5 is the TGA results for the blends of oligomeric benzoxazine, OctaSilane POSS and treated E-glass microbeads with different benzoxazine-POSS ratios. The results are also summarized in Table 2.1. The ratio of benzoxazine and OctaSilane POSS is varied between 4:3 and 2.5:4.5, and the four blends show similar trends of decomposition during heating process. Two major degradation processes are in the temperature ranges 300-640°C and 640-700°C. The second drop of weight is much sharper than the first one. From 700°C to 900°C, the char is stable without decomposition. Comparing the E-glass microbeads systems with sodalime microbeads systems, it is believed that glass sphere with smaller size helps to retard decomposition of polybenzoxazine-POSS matrix up-to 640°C. But the degradation process of E-glass mixture is more intensive in a narrow temperature range of about 50°C above 640°C. After 700°C, E-glass sphere blends are
stable while sodalime glass sphere mixtures still decompose till 800°C. Overall, the char yield is comparable, despite minor difference.

As previously assumed, surface treatment of glass spheres with silane helps to improve dispersion uniformity by reducing the interactions between glass particles. It is of interest to observe the influence of surface treatment on sodalime glass sphere blends. Instead of 2.5:4.5 (benzoxazine:OctaSilane POSS) as the extreme ratio achieved, 2:5 blend is homogeneously made. Figure 2.6 shows the TGA results for 5 different ratio systems. Char yield data are also summarized in Table 2.1. For the 2:5 system, the thermo-oxidative degradation curve is situated between the curves of 2.5:4.5 and 3:4. Adding more OctaSilane POSS beyond the 2.5:4.5 ratio does not further increase thermo-oxidative stability, because the polybenzoxazine content is not sufficient as a matrix to suspend the filler upon heating. Compared with untreated sodalime glass sphere systems, treated systems show similar thermo-oxidative stability under all examined temperature with the same degradation trends. It can be concluded that using 2:5:3 or 2.5:4.5:3 blends with any type of glass spheres achieve the best thermo-oxidative stability. No significant change in thermo-oxidative stability has been observed after the surface treatment.

2.3.5 Dispersion Investigation by Raman Spectroscopy

Raman spectroscopy was used to evaluate the homogeneity of three components’ blends. Glass sphere shows negligible intensity in Raman spectrum. The spectra of octasilane POSS and oligomeric benzoxazine are shown in Figure 2.7. The characteristic peak at 1600 cm\(^{-1}\) from the benzoxazine spectrum and peak at 2150 cm\(^{-1}\) from the OctaSilane POSS spectrum are used as the representative of two components for taking Raman image. A blend with ratio 4:3:3 of benzoxazine: OctaSilane POSS:glass sphere
(11µm) was used as an example for demonstrating the effectiveness of mixing. Raman images and optical image are shown in Figure 2.8. In the Raman images, the spherical object corresponds to the glass spheres, which did not show the sign of aggregation in the optical image. Both images of 1600 and 2150 cm⁻¹ scattering show consistent trends, indicating the efficient blending of benzoxazine and OctaSilane POSS on approximately 0.7 µm scale at least, limited by the spatial resolution of image.

2.3.6 Coating on Carbon/Carbon Composite

Oligomeric benzoxazine:OctaSilane POSS:glass sphere (11µm untreated) with ratio of 4:3:3 was used as a coating on carbon/carbon composites to demonstrate the effectiveness of the current coating for thermo-oxidative protection of carbon/carbon composites. The specimen was coated, cured and baked to form a glassy film on surface of the composites two times. Optical micrographs of these three stages are shown in Figure 2.9. In the middle of the top row is the uncoated carbon/carbon composite surface. Carbon fibers embedded in carbon matrix are observed. The one on the left side at bottom row is the 1st time coated surface before oxazine polymerization and baking. It is shown that glass sphere is dispersed in the benzoxazine and OctaSilane POSS matrix. The boundaries of glass sphere can be clearly identified, and the dimensions of the glass sphere are consistent with its average size of 11µm. The coated specimen was further cured and baked twice, and its micrograph is shown on the right side. It can be seen that the glass spheres are no longer in the shape of solid particles and turn into a film with a gloss, having benzoxazine and POSS chars dispersing in it. The surface is wrinkled, not smooth, this is partially due to the shrinkage of the coating material upon cooling from the treatment. After the first treatment and cooled to room temperature, microcracks form
on the surface, while after the second treatment, the microcracks have been covered with uneven thickness compared with the covered portion before the second treatment. No uncoated area is exposed, implying the complete coverage of the composite surface. The coating thickness is about 100-200μm for the surfaces in all directions.

2.3.7 Isothermal Weight Loss Measurements for Carbon/Carbon Composites

To test the protection efficiency, an isothermal weight loss analysis was carried out at 700°C in air for both coated (PBz:POSS:11μm untreated glass spheres = 4:3:3) and uncoated carbon/carbon composites. The results are shown in Figure 2.10. A dramatic difference of about 40% in the residual weight for the coated composite is observed for all the time up-to 1300 hrs. For the uncoated composite, a substantial weight loss of 12% is observed after about 10 hrs, and the degradation was gradually changed into steady state with a constant rate of 0.05%/hr. The initial increase for the coated composite in residual weight is related to the oxidation of surface coating material, which was not fully oxidized during the baking procedure due to the short time period process. The coated composite show negligible decomposition for up to 400 hrs and then changed to an almost constant degradation rate of about 0.03%/hr up to 1300hrs. This degradation is partially due to the formation of microcracks on the surface from the severe environment. Only 11μm untreated glass spheres were used as the coating component for this test, as the variation of particle size and the surface treatment does not significantly affect their thermo-oxidative stability. Though these results are the preliminary proof of concept, the situation can be improved if a better and more careful coating technology is applied based on the current materials. All together, the remarkable improvement in thermo-oxidative stability of carbon/carbon composite has been achieved, making the use of the blends as
an oxidative-protective coating material in the mid-temperature range of 450-800°C a promising endeavor without the use of expensive instrumentation or processing conditions.
2.4 Conclusions

We have synthesized a novel, main-chain type, oligomeric benzoxazine (BZ-atpdms) as a highly thermo-oxidative stable matrix material. It has been incorporated with octasilane POSS and glass spheres to form an effective oxidative-protective coating for carbon/carbon composites. The composition has been optimized by varying the benzoxazine and OctaSilane POSS ratio. The effectiveness of the coating has been demonstrated.
References

Table 2.1 Summary of TGA results of main-chain benzoxazine, OctaSilane POSS and glass sphere systems with varying polymer and OctaSilane POSS contents

<table>
<thead>
<tr>
<th>SYSTEM*</th>
<th>Calculated Value**</th>
<th>Char Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>11 µm untreated</td>
</tr>
<tr>
<td>4:3:3</td>
<td>65%</td>
<td>74%</td>
</tr>
<tr>
<td>3.5:3.5:3</td>
<td>67%</td>
<td>80%</td>
</tr>
<tr>
<td>3:4:3</td>
<td>69%</td>
<td>82%</td>
</tr>
<tr>
<td>2.5:4.5:3</td>
<td>71%</td>
<td>83%</td>
</tr>
<tr>
<td>2:5:3</td>
<td>73%</td>
<td>85%</td>
</tr>
</tbody>
</table>

*: System A:B:C= Weight ratio of main-chain benzoxazine:OctaSilane POSS:glass sphere

**: Based on the simple addition of the char yield of each component considering the concentration of the each component.
Scheme 2.1 Preparation of oligomeric benzoxazine (BZ-atdms)
Scheme 2.2 Demonstration of coating preparation
Figure 2.1 $^1$H NMR spectrum of oligomeric benzoxazine BZ-atdms
**Figure 2.2** TGA thermograms under oxidative environment for the mixture of OctaSilane POSS and 11 µm sodalime glass beads with oligomeric benzoxazine(a), BA-a(b), epoxy(c) and polystyrene(d) as matrices.
Figure 2.3 TGA thermograms under oxidative environment for the mixture of the oligomeric benzoxazine and 11 µm sodalime glass beads with Octasilane POSS(a), aluminum oxide(b), or titanium dioxide(c)
Figure 2.4 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine with the oxazine ring in the main chain with 11 µm sodalime glass microbeads and OctaSilane POSS with BZ:POSS 2.5:4.5(a), 3:4(b), 3.5:3.5(c) and 4:3(d)
Figure 2.5 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine, OctaSilane POSS and 4 µm treated E-glass sphere with BZ:POSS 2.5:4.5(a), 3:4(b), 3.5:3.5(c) and 4:3(d)
Figure 2.6 TGA thermograms under oxidative environment for the mixture of oligomeric benzoxazine, OctaSilane POSS and 11 µm treated sodalime glass sphere with BZ:POSS 2.5:4.5(a), 2:5(b), 3:4(c), 3.5:3.5(d) and 4:3(e)
Figure 2.7 Raman Spectra for Octasilane POSS and oligomeric benzoxazine (BZ-atdms)
Figure 2.8 Optical Image of oligomeric benzoxazine, OctaSilane POSS and glass sphere (11 µm) (4:3:3) blends (top middle); Raman Image for peak at 2150 cm$^{-1}$ (left bottom); Raman Image for peak at 1600 cm$^{-1}$ (right bottom)
Figure 2.9 Optical Micrographs of Uncoated Carbon/Carbon Composite Surface (top middle), Coated before curing Carbon/Carbon Composite Surface (left bottom), Coated, cured and baked Carbon/Carbon Composite Surface (right bottom)
Figure 2.10 Isothermal Weight Loss Measurements for Coated and Uncoated Carbon/Carbon Composite at 700°C in air
CHAPTER 3

Bis(benzoxazine-maleimide)s as a Novel Class of High Performance Resin: Synthesis and Properties
3.1 Introduction

High performance materials have been developed in the last several decades to meet the requirement for advanced technology development. Generally with excellent performance, the materials have the processing difficulty. Thus, it is very important to develop material with good processability and high performance for industrial application. Holly and Cope discovered the chemistry to form monomeric aromatic oxazines in 1944 using a phenolic derivative, formaldehyde, and a primary amine via Mannich reaction [1]. Only recently has there been a detailed study in the polymerization of benzoxazine monomers and the properties of the resultant polymers [2]. The monomers polymerize through cationic ring opening polymerization either with thermally activated polymerization without an added initiator or with an initiator. Upon polymerization, a polymer with a phenolic hydroxyl group and a tertiary amine bridge as a repeating unit is produced. Benzoxazine monomers exhibit many attractive properties, including low melt viscosity, no release of volatiles during polymerization and no need for harsh catalysts. In addition, the polymer is characterized by low volumetric shrinkage on curing; low moisture absorption; superb properties in chemical resistance, flame retardance, electrical properties, thermal stability and mechanical properties; and very rich molecular design flexibility [2-6]. These fascinating characteristics make benzoxazine a promising candidate as matrix for high-performance composites. Thus, it has excellent application opportunities in many other fields, such as the electronics and aerospace industries.

Bismaleimide (BMI) is another class of high performance thermosetting resins due to their excellent thermomechanical properties compared with typical phenolic and
epoxy resins as well as most high-performance polymers. Thus, the maleimide structure has been introduced into many polymeric systems aiming at improving thermal-stability with high $T_g$ [7-9]. However, it is well known that the unmodified BMI resins have some shortcomings, such as brittleness because of their high crosslinking density after polymerization and poor processability, poor solubility in ordinary solvents and high melting and polymerization temperature [10,11].

It is expected that combining benzoxazine and maleimide chemistry will generate the new material having the best attributes of them. The incorporation of the maleimide functionality into the monofunctional benzoxazine resulted in an increased char yield and glass-transition temperature without increasing the viscosity of the monomer significantly [12,13]. Recently, monofunctional benzoxazines with maleimide containing various additional crosslinking sites were synthesized to develop low-viscosity benzoxazine monomers, with high glass-transition temperature above 200°C. Chaisuwan and Ishida studied maleimide and nitrile-functionalized benzoxazine as a high performance material with good processability for advanced composite applications [14]. Agag and Takeichi investigated maleimidobenzoxazine monomers with allyl and propargyl functionality for excellent thermo mechanical performance [15].

Motivated by the good performance of monofunctional benzoxazine containing maleimide, we have developed a new class of bifunctional benzoxazine containing maleimide, namely bis(benzoxazine-maleimide)s. It has been very difficult to synthesize these monomers using the standard methods known in the literature to prepare benzoxazine. In order to synthesize these monomers, a new method, developed in our laboratory [16] using a nonpolar high boiling point solvent has been used. This facile
method yielded benzoxazines with high purity prior to purification procedure. The optimum processing conditions of the monomers and the properties of the polymers derived therefrom have been investigated.
3.2 Experimental

3.2.1 Materials

4,4’-Oxydianiline (ODA) 97%, 4,4’-diamo diphenyl methane (DDM) 98%, maleic anhydride 99%, phosphorus pentoxide 98% and styrene 99% were purchased from Aldrich Chemical Company. 4,4’-(p-Biphenylenedioxy) dianiline (BPDA) was obtained from Wako Pure Chemical Industries Ltd. 1,4-Bis-(4-aminophenoxy) benzene (DPDA) was supplied by Ken Seika Co. p-Toluensulfonic acid (PTS) 99% was provided by Fluka. 2,2’-Azobisisobutyronitrile was purchased from Polysciences Inc. Sulfuric acid, N,N’-dimethylformamide (DMF), xylenes (o-, m-, p-isomers), hexanes (a mixture of isomers), tetrahydrofuran, methanol and ethanol were obtained from Fisher Scientific Company. Styrene was washed with sodium hydroxide solution and dried to remove the inhibitors and kept in refrigerator. All the other chemicals were used as received. 1-(4-Hydroxy-phenyl) pyrrole-2,5-dione (HPMI) was synthesized according to the reported method [17]. 2,7-Bis(4-aminophenoxy)naphthalene (NPDA) was prepared according to the reported method [18].

3.2.2 Preparation of Bis(benzoxazine-maleimide)s

3.2.2.1 Preparation of 1,1’-(3,3’-(4,4’-oxybis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3-diyi))bis(1H-pyrrole-2,5-dione) [Bis(MI-oda)]

A mixture of ODA (2 g, 10 mmol), HPMI (3.78 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a mole ratio of 1:2:4 was added into a 100 ml flask. Xylenes (30 ml) was added into the flask and the mixture was stirred at 130°C for 5h. The solution was cooled to room temperature and then poured into hexanes to obtain
yellow powder. The powder was redissolved in tetrahydrofuran and reprecipitated in methanol to yield a pale yellow powder (Yield: 60%) with a melting point of 116-118°C. 

$^1$H NMR spectra (DMSO, ppm, δ): 4.64 (s, C-CH$_2$-N-), 5.44 (s, N-CH$_2$-O-), 6.82-7.13(m, Ar) 7.15 (s, -CH=CH-).

$^{13}$C NMR spectra (DMSO, ppm, δ): 49.34(C-CH$_2$-N-), 79.24(N-CH$_2$-O-), 134.52 (-CH=CH-), 170.10 (C=O).

IR spectra (KBr, cm$^{-1}$): 1773, 1714 (imide I), 1147 (imide III), 935 (out-of-plane C-H), 691 (imide IV)

Elem. Anal. (C$_{36}$H$_{26}$N$_4$O$_7$) Calcd: C, 69.00%; H, 4.18%; N, 8.94%. Found: C, 68.97%; H 4.53%; N 9.36%.

### 3.2.2.2 Preparation of 1,1’-(3,3’-(4,4’-methylenebis(4-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3-diyl))bis(1H-pyrrole-2,5-dione) [Bis(MI-ddm)]

Bis(MI-ddm) was synthesized from DDM (1.98 g, 10 mmol), HPMI (3.78 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) in a manner similar to bis(MI-oda) with a melting point of 110-112°C.

$^1$H NMR spectra (DMSO, ppm, δ): 3.71 (s, Ar-CH$_2$-Ar), 4.62 (s, C-CH$_2$-N-), 5.43 (s, N-CH$_2$-O-), 6.78-7.04(m, Ar) 7.15 (s, -CH=CH-).

$^{13}$C NMR spectra (DMSO, ppm, δ): 48.93(C-CH$_2$-N-), 79.00(N-CH$_2$-O-), 134.50(-CH=CH-), 170.10(C=O).

IR spectra (KBr, cm$^{-1}$): 1774, 1712 (imide I), 1149(imide III), 934(out-of-plane C-H), 691(imide IV)
3.2.2.3 Preparation of 1,1'-(3,3'-(4,4'-(1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3-diyl))bis(1H-pyrrole-2,5-dione) [Bis(MI-dpda)]

Bis(MI-dpda) was similarly synthesized from DPDA (2.92 g, 10 mmol), HPMI (3.78 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a melting point of 108-110°C.

$^1$H NMR spectra (DMSO, ppm, δ): 4.66 (s, C-CH2-N-), 5.45 (s, N-CH2-O-), 6.82-7.14 (m, Ar) 7.15 (s, -CH=CH-).

$^{13}$C NMR spectra (DMSO, ppm, δ): 49.31 (C-CH2-N-), 79.21 (N-CH2-O-), 134.52 (-CH=CH-), 170.10 (C=O).

IR spectra (KBr, cm$^{-1}$): 1772, 1713 (imide I), 1149 (imide III), 936 (out-of-plane C-H), 692 (imide IV)

Elem. Anal. (C$_{42}$H$_{30}$N$_4$O$_8$) Calcd: C, 70.19%; H, 4.21%; N, 7.80%. Found: C, 69.90%; H 4.37%; N 7.85%.

3.2.2.4 Preparation of 1,1'-(3,3'-(4,4'-(biphenyl-4,4'-diylbis(oxy)))bis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3-diyl))bis(1H-pyrrole-2,5-dione) [Bis(MI-bpda)]
Bis(MI-bpda) was similarly synthesized from BPDA (3.68 g, 10 mmol), HPMI (3.78 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a melting point of 114-116°C.

\(^1\)H NMR spectra (DMSO, ppm, \(\delta\)) \(\text{ppm, } \delta\): 4.68 (s, C-CH\(_2\)-N-), 5.48 (s, N-CH\(_2\)-O-), 6.82-7.57 (m, Ar) 7.15 (s, -CH=CH-).

\(^1\)C NMR spectra (DMSO, ppm, \(\delta\)) \(\text{ppm, } \delta\): 49.25 (C-CH\(_2\)-N-), 79.14 (N-CH\(_2\)-O-), 134.54 (-CH=CH-), 170.11 (C=O).

IR spectra (KBr, cm\(^{-1}\)) \(\text{ppm, } \delta\): 1773, 1715 (imide I), 1150 (imide III), 937 (out-of-plane C-H), 692 (imide IV).

Elem. Anal. (C\(_{48}\)H\(_{34}\)N\(_4\)O\(_8\)) Calcd: C, 72.54%; H, 4.31%; N, 7.05%. Found: C, 72.61%; H 4.75%; N 7.31%.

3.2.2.5 Preparation of 1,1'-(3,3'-(4,4'-(naphthalene-2,7-diylbis(oxy))bis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6,3-diyl))bis(1H-pyrrole-2,5-dione) [Bis(MI-npda)]

Bis(MI-npda) was similarly synthesized from NPDA (3.42 g, 10 mmol), HPMI (3.78 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a melting point of 123-124°C.

\(^1\)H NMR spectra (DMSO, ppm, \(\delta\)) \(\text{ppm, } \delta\): 4.68 (s, C-CH\(_2\)-N-), 5.47 (s, N-CH\(_2\)-O-), 6.84-7.87 (m, Ar) 7.16 (s, -CH=CH-).

\(^1\)C NMR spectra (DMSO, ppm, \(\delta\)) \(\text{ppm, } \delta\): 49.20(C-CH\(_2\)-N-), 79.09(N-CH\(_2\)-O-), 134.52(-CH=CH-), 170.09 (C=O).
IR spectra (KBr, cm\(^{-1}\)): 1775, 1713(imide I), 1144(imide III), 937(out-of-plane C-H), 691(imide IV)

Elem. Anal. (C\(_{46}H_{32}N_4O_8\)) Calcd: C, 71.87%; H, 4.20%; N, 7.29%. Found: C, 73.09%; H 5.06%; N 7.41%

3.2.2.6 Preparation of bis(4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenyl)methane (P-ddm)

A mixture of DDM (1.98 g, 10 mmol), phenol (1.88 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a mole ratio of 1:2:4 was added into a 100 ml flask. Xylenes (20 ml) was added into the flask and the mixture was stirred at 130\(^\circ\)C for 2h. The solution was precipitated into hexanes and redissolved in chloroform and washed three times with 1N sodium hydroxide solution and water. The solution was dried over anhydrous sodium sulfate and the chloroform was evaporated afterward. The target compound was further purified by column chromatography with hexanes/ethyl acetate (6:4) to afford white powder.

\(^1\)H NMR spectra (CDCl\(_3\), ppm, \(\delta\)): 3.78 (s, Ar-CH\(_2\)-Ar), 4.57 (s, C-CH\(_2\)-N-), 5.31 (s, N-CH\(_2\)-O-), 6.77-7.10 (m, Ar)

3.2.3 Polymerization of Bis(benzoxazine-maleimide)s

Solutions of 30% solid content of the monomers in DMF were prepared. Then, the solutions were cast over dichlorodimethylsilane-pretreated glass plates. The films were dried in an air circulating oven at 100\(^\circ\)C for 24hr to remove the solvent. The films as fixed on glass plates were polymerized stepwise at 120, 140, 160, 200, 250\(^\circ\)C for 1hr
each, and then slowly cooled to room temperature. The films have brown color with thickness ranging from 0.1 to 0.8 mm.

### 3.2.4 Measurements

$^1$H and $^{13}$C NMR spectra were acquired in deuterated dimethyl-sulfoxide on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency. The average number of transients for $^1$H and $^{13}$C is 64 and 1024, respectively. A relaxation time of 10s was used for the integrated intensity determination of $^1$H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddtion of 32 scans was recorded at a resolution of 4 cm$^{-1}$. Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples. Elemental analysis was performed by MHW Labs.

TA Instruments DSC model 2920 was used with a heating rate of 10°C/min and a nitrogen flow rate of 60mL/min for all tests of differential scanning calorimetric (DSC) study. All samples were crimped in hermetic aluminum pans with lids. Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with an amplitude of 10 μm and a ramp rate of 3°C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10°C/min in a nitrogen atmosphere at a flow rate of 40mL/min.
3.3 Results and Discussion

3.3.1 Preparation of Bis(benzoxazine-maleimide) Monomers

The novel monomers, comprising of both benzoxazine and bismaleimide moieties, were prepared by the reaction of HPMI and paraformaldehyde with different diamines, as shown in Scheme 3.1. The conventional methods, using a solventless method [19] or solvent method [2] with chloroform or dioxane for synthesizing benzoxazine, were inappropriate for bis(benzoxazine-maleimide) monomers. There are two main reasons for this: first, the starting phenol, HPMI, has poor solubility in common organic solvent used as the ordinary benzoxazine synthesis; and second, the reaction of diamines with formaldehyde afforded a stable triaza gel structure, which was difficult to be broken by phenols. All these retard the desired monomer formation. To overcome this difficulty, a new method was developed in our laboratory by using high boiling point nonpolar solvents such as xylenes or dichlorbenzene at higher reaction temperature (130°C). These solvents increased the solubility of HPMI and accelerated the breakage of triaza gel by HPMI. As a consequence, monomer formation proceeded smoothly without generating significant side reaction as the solvents are nonpolar. The monomers of various diamine have been prepared because of historical difficulty in preparing these monomers. All the monomers were easily soluble in common polar and nonpolar solvents, such as dimethylsulfoxide, dimethylformamide, dioxane, ethyl acetate, chloroform and tetrahydrofuran.

The chemical structures of the monomers were confirmed by $^1$H, $^{13}$C NMR, FT-IR and elemental analysis. Figure 3.1 shows the $^1$H NMR spectra of all the bis(benzoxazine-maleimide) monomers. The characteristic proton resonances of the
oxazine ring appear as two singlets at 4.62-4.68 and 5.42-5.48 ppm which are assigned to 
–CH\textsuperscript{*2}-N- and –O-CH\textsuperscript{*2}-N-, respectively. The singlet at 7.15-7.16 ppm is assigned to the protons of –CH\textsuperscript{=}CH*- in the maleimide structure. The multiplet at 6.78-7.88 ppm is assigned to the protons of the aromatic ring.

Figure 3.2 shows the \textsuperscript{13}C NMR spectra for all the monomers. The characteristic carbon resonances of the oxazine ring show at 49.36-50.01 ppm for C-C\textsuperscript{*}H\textsubscript{2}-N- and at 78.52-79.84 ppm for N-C\textsuperscript{*}H\textsubscript{2}-O- respectively. The peak at 134.52-135.24 ppm is attributed to the double bond carbon in the maleimide structure and the one at 170.11-170.81 ppm is due to the carbon from the carbonyl group.

The IR spectra of all the novel monomers shown in Figure 3.3 exhibit the typical antisymmetric and symmetric stretching modes of the carbonyl in the cyclic maleimide ring at about 1773 and 1716 cm\textsuperscript{-1}, respectively. The band at 1144 cm\textsuperscript{-1} due to the C-N-C bending mode of the maleimide ring and the band at 828 cm\textsuperscript{-1}, which is assigned to the imide CH wagging of the vinylene group, are clearly observed. Also a characteristic absorption for the maleimide structure is seen at 694 cm\textsuperscript{-1} for the =C-H out-of-plane bending mode. [13,14] For the benzoxazine structure, the bands at 1234 cm\textsuperscript{-1} due to the -C-O-C- antisymmetric stretching of the oxazine group and the band at 938 cm\textsuperscript{-1} due to the out-of-plane C-H vibration of the benzene ring to which an oxazine ring is attached are observed.

DSC thermograms of all the bis(benzoxazine-maleimide)s monomers are shown in Figure 3.4. DSC result is extremely sensitive to the small amount of impurities in sample, thus the results we obtained are based on the samples with the highest purity we achieved. The results are summarized in Table 3.1. Both bis(MI-ddm) and bis(MI-oda)
show two exotherms, and the 1st exotherms are broad and the onset of the peaks are around 160°C. The exothermic maxima are observed at 211°C and 311°C for bis(MI-ddm), 218°C and 314°C for bis(MI-oda), respectively. The onset of the 1st exothermic peaks is at least 30°C lower than those from the monomers containing naphthalene and biphenyl structures. This is because methylene or oxy linkage allows the molecule to rotate easily and increases the flexibility. For bis(MI-dpda) and bis(MI-bpda), the DSC thermograms are very similar to each other. The 1st exotherm has the onset at around 190°C and reaches the maximum at 214 and 221°C, respectively. The 2nd exotherm reaches the maximum at 306 and 314°C, respectively. For bis(MI-npda), two separate exotherms are observed with maxima at 232°C and 311°C. Because of the rigidity from naphthalene structure, the exothermic transitions happened at relatively higher temperature compared with the other monomers.

For all the monomers, the first exotherm is more pronounced than the second one which appears at higher temperature above 300°C. This behavior is different from the benzoxazine monomers with maleimide functionality we have previously synthesized [14, 15].

To better understand the significance of the exotherms, we compared with the benzoxazine monomer based on phenol and DDM (P-ddm) and bismaleimide (DDM-BMI) counterparts. The structures are shown in Scheme 3.2 whereas the DSC thermograms are shown in Figure 3.5. P-ddm and DDM-BMI have the maximum exotherm at 237 and 207°C, respectively, which are both in the range of the 1st exotherm of bis(benzoxazine-maleimide)s monomers. Thus, it is assumed that the 1st exotherm of
bis(benzoxazine-maleimide)s monomers is the combination of ring-opening polymerization of benzoxazine and addition-polymerization of bismaleimide.

To further prove this hypothesis, one monomer, bis(MI-npda), is chosen to mix with two different types of catalysts for maleimide and benzoxazine polymerization respectively. DSC results of this experiment are shown in Figure 3.6. $p$-Toluenesulfonic acid (PTS) is known to be an effective catalyst for benzoxazine polymerization [20]. Five wt% PTS is added into the monomer and dissolved in acetone, and a film was casted on a glass plate till dried. The DSC thermogram shows a significant shift of the onset and maximum of the 1st exotherm to the lower temperature range, 138 and 191°C, respectively. The lowering of the exotherm is expected due to the catalytic effect of PTS on cationic ring-opening polymerization of benzoxazine. In addition, copolymerization between maleimide in bis(MI-npda) and styrene at 2:1 ratio and 1wt% AIBN is investigated. AIBN can be used as a free radical initiator for this polymerization. An exotherm maximized at 98°C is observed from the free radical copolymerization in the DSC thermogram and a significant decrease of the evolved heat for the peak at 232°C is shown. These results indicate the maleimide polymerization is part of the 1st exotherm. The 2nd exotherm above 300°C could be mainly attributed to degradation, as we can observe about 2-4% weight loss at around 350°C for the crosslinked polymer from the TGA thermogram. In addition, the reaction of hydroxyl group from polybenzoxazine and double bond of bismaleimide might contribute to the 2nd exotherm as well [23]. The phenomenon will be discussed in details in the polymerization behavior section.

3.3.2 Polymerization Behavior of the Bis(benzoxazine-maleimide)s
The polymerization behavior of bis(benzoxazine-maleimide)s was studied by DSC by stepwise heating at 120°C, 140°C, 160°C, 200°C, 250°C for 1hr each. The final polymerization temperature was restricted to 250°C in order to prevent observable degradation. The polymerization behavior shows the same trend for all the monomers, and, thus, the result of bis(MI-npda) as an example is shown in Figure 3.7. The DSC traces of bis(MI-npda) monomer have two exotherms: the first exotherm has the onset at 200°C with a maximum at 232°C, followed by the second one with the maximum at 311°C. The total exothermic heat generated is 254J/g. From the DSC thermograms of the monomer after each heating stage, it can be seen that the first exothermic peaks gradually decreases after each heating cycle and disappeares by the end of the polymerization at 250°C, while the second exotherm does not show much change and a peak still remains with significant intensity even after the polymerization at 250°C. The residual exothermic heat observed is 38J/g. It is well known to us that traditional bismaleimide resin requires severe conditions to achieve complete polymerization, such as 10hr at 280°C [21] Also thermal and thermooxidative degradation is observed during the polymerization of bismaleimides [22]. Thus, it is assumed that the residual exotherm after the heating cycles adopted in this study is attributed to the polymerization and degradation. To confirm this, we compared the TGA result with the DSC thermogram for the polymerized sample in Figure 3.8. The onset of degradation observed as residual weight and derivative weight from TGA matches the onset of the 2nd exotherm, suggesting that it is the degradation process. To further understand it, the degradation was studied by the isothermal TGA in air shown in Figure 3.9. The sample, polymerized stepwise in air at 120, 140, 160, 200, was heated to 250°C and kept for 1hr and then heated to 300°C for
another hour. The initial 0.1% weight loss during the process of heating to 250°C is believed to come from the water absorption during the sample transfer. It is followed by two degradation processes, and the 2\textsuperscript{nd} weight loss is more rapid than the 1\textsuperscript{st} one, which is reasonable as the higher temperature leads to the higher rate of degradation. Overall, 4% weight loss degradation is observed after 300°C treatment.

The polymerization behavior is also monitored by FTIR for bis(MI-npda) after each heating stage, as shown in Figure 3.10. IR spectra indicate that the characteristic peaks due to the benzoxazine structure at 1033 and 938 cm\(^{-1}\) disappear by the 250°C heating cycle, suggesting that the ring opening reaction of the benzoxazine has completed by the end of the 250°C treatment. At the same time, the characteristic absorption of the maleimide at 694 cm\(^{-1}\) is gradually consumed by its homopolymerization and nearly disappears by the 250°C treatment. In addition, the intensity of the absorption at 828 cm\(^{-1}\) due to the imide CH wagging of the vinylene group decreases upon the polymerization, and it does not completely disappear after polymerization at 250°C as it is associated with absorption from the other =CH group of aromatic rings. Furthermore, the band at 1144 cm\(^{-1}\) gradually decreases with the appearance of a new band at 1186 cm\(^{-1}\) which is due to the C-N-C bending mode of the succinimide, indicating that maleimide has been converted into succinimide. The IR results show the disappearance of maleimide and benzoxazine structure by the 250°C, indicating that the complete polymerization is achieved.

The degradation study was further performed by FTIR, as shown in Figure 3.11. The sample was heated to 300°C for 1hr and the spectrum was taken after that to compare with those of lower temperature polymerization. The dramatic decrease of intensity of
peak at around 1715 cm\(^{-1}\) shows the degradation of maleimide components in the thermoset. Maleimide is rather difficult to achieve complete homopolymerization, so in the thermoset, also due to the rigidity of the network structure, some part might form short chain oligomers as reacting with several double bonds instead of forming the long chain molecules. They have relatively poor resistance to thermal degradation as they are not well anchored in the network. When undergone harsh heat treatments, the maleimide components suffer from the evaporation of these short chain oligomers. This situation is similar to the evaporation of amine during benzoazine thermal degradation process [24,25].

### 3.3.3 Dynamic Mechanical Analysis (DMA) of Crosslinked Poly[bis(benzoxazine-maleimide)]s

The viscoelastic properties for the crosslinked poly[bis(benzoxazine-maleimide)] are studied by DMA. Figures 3.12 and 3.13 show the temperature dependence of the storage moduli and loss moduli for the polybenzoazine films polymerized at 250\(^\circ\)C. The thermal properties are summarized in Table 3.2. The storage modulus is maintained at approximately the same value for a wide temperature range up to 300\(^\circ\)C. The glass transition temperature (\(T_g\)) determined as the peak temperature of the \(\alpha\)-transition of the loss modulus ranges from 289 to 307\(^\circ\)C for the crosslinked polybenzoazines studied. On the other hand, the benzoazine (P-ddm) without maleimide group has \(T_g\) of 212\(^\circ\)C. Introduction of maleimide group lead to a significant increase in \(T_g\) by about 80\(^\circ\)C because maleimide group brings about a higher crosslink density and increased rigidity. The increase in \(T_g\) is also seen in copolymers of benzoazines with bismaleimide (DDM-
BMI) [23]. While the polybenoxazines derived from phenol and aniline (P-a) and bisphenol-A and aniline (BA-a) have \( T_g \) at 146 and 154°C, respectively, the copolymers of these benzoazines with DDM-BMI show corresponding increased \( T_g \) to 240 and 268°C, respectively. This is compared with the \( T_g \) of DDM-BMI at 222°C. The increase in \( T_g \) for the copolymers compared with the homopolymers derived from both benzoxazine and bismaleimide implies that extra crosslink sites are formed during the polymerization, such as the reaction of the hydroxyl group from polybenzoxazine with the double bond of bismaleimide [23]. The higher \( T_g \) of crosslinked poly[bis(benzoxazine-maleimide)] may be explained by the molecularly dispersed bismaleimide and benzoxazine.

3.3.4 Thermal Stability of Crosslinked Poly[bis (benzoxazine-maleimide)]s

The thermal stability of the novel crosslinked poly[bis(benzoxazine-maleimide)] is determined by thermogravimetric analysis (TGA). Figure 3.14 shows the TGA thermograms of polymer films under \( \text{N}_2 \) atmosphere. The poly[bis(benzoxazine-maleimide)] films were thermally treated at 250°C for 1h in air. The results are summarized in Table 3.2. For all the polymers studied, the 5% weight loss temperatures, \( T_d5 \), varies from 374°C to 383°C. This is an improvement from polybenzoxazines (P-ddm) based on DDM with phenol which has \( T_d5 \) of 364°C. DDM based bismaleimide has \( T_d5 \) of 477°C, and its’ alloys with P-a and BA-a has \( T_d5 \) of 344 to 425°C and 310 to 428°C, respectively [23]. Overall, bismaleimide containing polybenzoxazines shows an increase in \( T_d5 \) compared with neat polybenzoxazines, indicating the improved thermal stability of the material. This is because the rotation of the imide is hindered as the imide group has a
planar five-membered ring structure, and it forms the partial conjugation with the benzene ring [12]. The evaporation of amine happens at 200-300°C and could not be avoided with benzoxazine as our previous research has shown. The thermal degradation of polybenzoxazines has three main stages: evaporation of the amine followed by the simultaneous breakage of the phenolic linkage and degradation of the Mannich base [24,25]. On the other hand, bismaleimide polymer does not have the weak point from amine, and it shows high T₆₅.

The char yield at 800°C in N₂ varies from 55% to 62% for the crosslinked poly[bis(benzoxazine-maleimide)]s, which is much higher than that of polybenzoxazines based on P-ddm at 46%. DDM based bismaleimide has char yield of 51%, while the alloys has about 45% to 53% [23]. Therefore, the crosslinked poly[bis(benzoxazine-maleimide)]s have higher char yields than bismaleimide with its alloys, as the degradation of bismaleimide at higher temperature around 500°C is more intensive compared with benzoxazine counterpart.
3.4 Conclusions

We have synthesized a novel class of bis(benzoxazine-maleimide) monomers as high performance thermosets from hydroxyphenylmaleimide, para-formaldehyde and different types of aromatic diamines, including 4,4’-oxydianiline, 4,4’-diamino diphenyl methane, 1,4-bis-(4-aminophenoxy) benzene, 4,4’-(p-biphenylenedioxy) dianiline, 4,4’-(9H-fluorene-9,9-diyl)dianiline, 4,4’-(naphthalene-2,7-diylbis(oxy))dianiline. The thermally activated polymerization behavior of the monomers undergoes ring-opening polymerization from benzoxazine and addition polymerization from maleimide. The crosslinked polymers under current study shows excellent thermal stability and high $T_g$ with easy processibility, indicating synergestic effect of benzoxazine and maleimide resin.
References


Table 3.1 Thermal Properties of Bis(benzoxazine-maleimide) monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>1st exotherm</th>
<th>2nd exotherm</th>
<th>Total exotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset(°C)</td>
<td>Max(°C)</td>
<td>Max(°C)</td>
</tr>
<tr>
<td>Bis(MI-oda)</td>
<td>164</td>
<td>218</td>
<td>314</td>
</tr>
<tr>
<td>Bis(MI-ddm)</td>
<td>158</td>
<td>211</td>
<td>311</td>
</tr>
<tr>
<td>Bis(MI-dpda)</td>
<td>191</td>
<td>214</td>
<td>306</td>
</tr>
<tr>
<td>Bis(MI-bpda)</td>
<td>194</td>
<td>221</td>
<td>314</td>
</tr>
<tr>
<td>Bis(MI-npda)</td>
<td>200</td>
<td>232</td>
<td>311</td>
</tr>
<tr>
<td>P-ddm</td>
<td>229</td>
<td>237</td>
<td>-----</td>
</tr>
<tr>
<td>DDM-BMI</td>
<td>181</td>
<td>207</td>
<td>-----</td>
</tr>
<tr>
<td>Type</td>
<td>$T_g$ (°C)</td>
<td>Weight-Loss Temperature (°C)</td>
<td>Char yield at 800°C (%)</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon''_{\text{max}}$</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>Bis(MI-oda)</td>
<td>301</td>
<td>383</td>
<td>410</td>
</tr>
<tr>
<td>Bis(MI-ddm)</td>
<td>300</td>
<td>379</td>
<td>407</td>
</tr>
<tr>
<td>Bis(MI-dpda)</td>
<td>303</td>
<td>376</td>
<td>401</td>
</tr>
<tr>
<td>Bis(MI-bpda)</td>
<td>289</td>
<td>374</td>
<td>407</td>
</tr>
<tr>
<td>Bis(MI-npda)</td>
<td>307</td>
<td>379</td>
<td>407</td>
</tr>
<tr>
<td>P-ddm</td>
<td>212</td>
<td>364</td>
<td>390</td>
</tr>
<tr>
<td>DDM-BMI$^a$</td>
<td>222</td>
<td>477</td>
<td>482</td>
</tr>
</tbody>
</table>

$^a$ Data were obtained from ref [23]
Scheme 3.1 Preparation of Bis(benzoxazine-maleimide) monomers
Scheme 3.2 Structure of benzoxazine and bismaleimide counterpart monomers
**Figure 3.1** $^1$H NMR spectra of Bis(benzoxazine-Maleimide)s
Figure 3.2 $^{13}$C NMR spectra of Bis(benzoxazine-Maleimide)s
Figure 3.3 FTIR spectra of Bis(benzoxazine-maleimide)s
Figure 3.4 DSC curve of Bis(benzoxazine-maleimide)s
Figure 3.5 DSC curve of benzoxazine and bismaleimide counterpart monomers
Figure 3.6 DSC curve of Bis(MI-npda) monomer with the monomer containing PTS, styrene and AIBN.
Figure 3.7 DSC curve of Bis(MI-npda) after each cure stage
Figure 3.8 DSC and TGA curves of thermosets polymerized at 250°C of Bis(MI-npda)
Figure 3.9 Isothermal TGA curves of themosets from Bis(MI-npda)
Figure 3.10 FTIR spectra of Bis(MI-npda) after each heating stage
Figure 3.11 FTIR spectra of Bis(MI-npda) after post curing
Figure 3.12 Temperature dependence of storage moduli of Poly[Bis(benzoxazine-maleimide)] thermosets
Figure 3.13 Temperature dependence of loss moduli of Poly[Bis(benzoxazine-maleimide)] thermosets
Figure 3.14 TGA of Poly[Bis(benzoxazine-maleimide)] thermosets
CHAPTER 4

Using Allyl Benzoxazine Monomers as Replacement for Styrene in Vinyl Ester Resin
4.1 Introduction

The most common commercial vinyl ester resins are epoxy-based thermosetting resins which are polymerized by the free-radical mechanism. Generally, the resin is blended with styrene so as to lower the viscosity of the resultant resin solution, making it easily handled in the reinforced plastic processes and incorporating styrene molecules as part of the crosslinked structure. Compared to epoxies, the vinyl esters are less expensive and easy to work with. At the same time, they have been designed to retain most of the desirable properties of epoxy. Vinyl ester resins offer excellent mechanical (tensile strength, toughness, elongation and fatigue resistance) and adhesive properties (better wetting, the compatibility with and bond strength to glass, graphite fibers and to high-strength organic fibers such as polyamide), low viscosity which is suitable for vacuum assisted resin transfer molding (VARTM), and good thermal stability. The chemical resistance of vinyl ester resin is the intermediate of epoxy and polyester resins. The alkali resistance of the epoxy is due to relatively few ester linkages and the hindrance afforded by the methyl group of the methacrylic acid. The acid and oxidizing chemical resistance of the polyester comes from the steric hindrance protection by the copolymerized styrene. Based on its many advantages, vinyl ester resin is a prime candidate as a matrix in large composite structures for transportation, infrastructure and marine applications [1-6].

However in many commercial applications, where liquid molding techniques are desired from processibility point of view, using styrene as a low viscosity reactive diluent causes health and environmental risks due to the volatile nature of the dilutent. Therefore,
it is urgent and important to replace styrene in vinyl ester resin without sacrificing its excellent processability and performance.

Polybenzoxazine is a promising class of thermosets as an alternative to epoxies, phenolic resins, bismaleimides, cyanate esters, and polyimides. Benzoxazine can be synthesized from a phenolic derivative, formaldehyde, and a primary amine via Mannich reaction. Benzoxazine monomers polymerize through cationic ring opening polymerization. Upon polymerization, a polymer with a phenolic hydroxyl group and a tertiary amine bridge as a repeating unit is produced. Benzoxazine monomers exhibit many attractive properties, including low melt viscosity, no release of volatiles during polymerization and no need for harsh catalysts. In addition, the polymer is characterized by low volumetric shrinkage upon polymerization; low moisture absorption; superb chemical resistance, flame retardance, electrical properties, thermal stability and mechanical properties; and very rich molecular design flexibility [7-11].

Utilizing the advantages of benzoxazine, it is proposed that benzoxazine monomers containing allyl group as reactive diluents are used to replace styrene in vinyl ester resin. Allyl benzoxazine monomers have less environmental concerns than styrene. It is expected that allyl group can copolymerize with vinyl ester resin via the free radical mechanism and benzoxazine can polymerize cationically during post-curing of the resin to form a more thermostable network.
4.2 Experimental

4.2.1 Materials

P-Cresol (98%), allyl amine (98%), styrene reagent plus (St) (99%), benzoyl peroxide (BPO), dicumyl peroxide (Di-Cup) (98%) and hydroquinone (99+%) were purchased from Aldrich Chemical Company. Paraformaldehyde (96%) and methacrylic acid stabilized (99.5%) were obtained from Acros. D.E.R. 331 epoxy resin was provided by the Dow Chemical Company. Imidazol was supplied by Shikoku Chemicals Corp. Toluene-4-sulfonic acid monohydrate (PTS) (99%) was purchased from Fluka. Bisphenol F isomers were kindly supplied by Solvay. Benzoyl peroxide was recrystallized in 1:1 chloroform:ethanol. Styrene was filtered through a basic alumina column. All the other chemicals were used as received.

4.2.2 Preparation of 3-allyl-6-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (pC-ala)

A mixture of p-Cresol (1mol, 108.1g), allylamine (1mol, 57.1g) and paraformaldehyde (2mol, 60g) in 350 ml toluene was heated to reflux for 15 hours. The solvent was removed by a rotavapor and vacuum oven overnight at 50°C. No further purification was done. Light yellowish transparent viscous liquid was obtained and the yield was 90%. The analytical data for the monomer is also available in ref 12 [12].

4.2.3 Preparation of bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methane (BF-ala)

A mixture of bisphenol F isomers (1 mol, 200g) and allyl amine (2mol, 114.2g) in 1800ml toluene were kept at 50°C until dissolved. Then paraformaldehyde (4mol, 120g) was added drop wise and the mixture was heated to reflux overnight. After the reaction,
the solvent was removed by a rotavapor and vacuum oven overnight at 50°C. Light yellow solid was obtained. (Yield: 80 %)

4.2.4 Synthesis of VE Resin Prepolymer

VE resin prepolymer was synthesized from the reaction of epoxy resin, diglycidyl ether of bisphenol A (DGEBA, D.E.R. 331 with equivalent weight 186-190g/eq) with methacrylic acid, using imidazol as a catalyst and hydroquinone as an inhibitor. 140g diglycidyl ether of bisphenol A, 64g methacrylic acid, 0.21g hydroquinone and 0.64g imidazol were mixed together using mechanical stirrer. The reaction was carried out under nitrogen at 70°C for 30min and 5 hours at 100°C until reaction completed, which was confirmed by $^1$H NMR. The product was stored in a refrigerator.

4.2.5 Preparation of VE Resin Copolymers with Styrene (St)/3-allyl-6-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (pC-ala)/ bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methane (BF-ala)

VE resin prepolymers with same mole concentration of St, pC-ala and BF-ala and their combinations were mixed respectively using 1-2% BPO and/or Di-Cup initiators in chloroform and cast on glass treated with dichlorodimethyl silane. The film was heated to 50°C for 2hours, 80°C for 1.5hours, 150°C for 1.5hours and 180°C for 30min. Kapton film was used to cover the film to exclude air after removing most solvent at 50°C treatment.

4.2.6 Measurements

$^1$H NMR spectra were acquired in deuterated chloroform on a Varian Oxford AS600 at a proton frequency of 600 MHz. The average number of transients for $^1$H NMR was 64. A relaxation time of 10s was used for the integrated intensity determination of $^1$H
NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddition of 32 scans was recorded at a resolution of 4 cm\(^{-1}\). Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples.

A differential scanning calorimeter (DSC), TA Instruments DSC model 2920, was used with heating rate of 10\(^{\circ}\)C/min and a nitrogen flow rate of 60mL/min for all tests. All samples were crimped in hermetic aluminum pans with lids. Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with amplitude of 10 \(\mu\)m and a ramp rate of 3\(^{\circ}\)C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10\(^{\circ}\)C/min in a nitrogen atmosphere at a flow rate of 40mL/min. The mixtures without initiator and solvent were mixed at 40\(^{\circ}\)C homogeneously using stirrer to measure viscosity. Viscosity was measured using Anton Paar MCR501 with constant shear rate at 100 s\(^{-1}\) at different elevated temperatures. The samples used for viscosity measurements were prepared by melt mixing at 40\(^{\circ}\)C without solvent or initiators.
4.3 Results and Discussion

4.3.1 Preparation of VE Resin Prepolymer

The pathway of VE resin prepolymer synthesis is described in Scheme 4.1. The formation was followed by $^1$H NMR as shown in Figure 4.1. The peaks at 7.13 and 6.81 ppm correspond to the aromatic hydrogens. The vinyl hydrogens (CH$_2$*=C-C=O) are represented by peaks at 6.14 and 5.60 ppm, and the multiple peaks in the range of 3.85-4.40 ppm are attributed to the reacted epoxy hydrogens (O-CH$_2$*-CH*-CH$_2$*-O). The methyl hydrogens of methacrylic acid is observed at 1.95 ppm, and the peak at 1.63 ppm is originated from the methyl hydrogens from bisphenol A.

4.3.2 Polymerization and Processing Behavior of VE Resin Prepolymer and St/pC-ala blends

The DSC thermograms of pC-ala monomer and its blend with VE Resin prepolymer are shown in Figure 4.2. A broad exotherm with onset at about 180°C and maximum at 230°C is observed for the pC-ala monomer. It is expected that the exotherm is the combination of allyl polymerization with benzoxazine ring-opening polymerization. On the other hand, VE resin prepolymer with 2% BPO as catalyst shows a sharp exothermic peak centered at 115°C, which is in agreement with the easy curing procedure of vinyl ester resin. Copolymerization of vinyl with allyl has been investigated thoroughly by others [13], providing the reactivity ratio of the components, showing that allyl tends to copolymerize with a vinyl compound. A mixture with the ratio of 10:4 of VE resin prepolymer with pC-ala is used as the example blend for comparison with
traditional vinyl ester resin. Two free radical initiators with different initiating temperatures were used to compare the polymerization behavior. The blend with 2% BPO shows two separate exotherms with maxima at 100 and 208°C, and the blend with 2% Di-Cup shows two overlapped peaks in the range of 115 to 200°C. It is expected that BPO can initiate vinyl polymerization at lower temperature, but with the limited reactivity of allyl functionality at lower temperature, it is not sufficient to polymerize allyl groups effectively, which leads to the contribution to exotherm at higher temperature. Di-Cup is known to initiate polymerization above 100°C and is efficiently used for ally polymerization [14]. By using Di-Cup, vinyl polymerization is suspended to higher temperature too, making polymerization of vinyl and allyl to take place simultaneously, or at least successively, which makes it possible to achieve a valid copolymerization of two components for the resin. The properties of mixture with different catalysts are also discussed in the following section.

The other major concern for replacing styrene in vinyl ester resin is processability. With low viscosity of styrene, vinyl ester resin can be processed using liquid molding technology, such as vacuum assisted resin transfer molding. Apparently, pC-ala is more viscous at room temperature, but it reduces its viscosity rapidly at higher temperature. A comparison of viscosity for two blends with the same molar concentration of styrene to VE Resin prepolymer and pC-ala to VE Resin prepolymer (10 g VE Resin prepolymer : 21.6 mmol pC-ala and 10 g VE Resin prepolymer : 21.6 mmol St) is made at different elevated temperatures, as shown in Figure 4.3. VE Resin prepolymer was prepared and stored in a refrigerator for a certain time, which is expected to increase the viscosity in comparison to fresh synthesized batch due to shelf life of the prepolymer; however, the
comparison was made using exactly the same resin at the same time. The results are summarized in Table 4.1. Viscosities were obtained at shear rate of 100 s$^{-1}$. It is clearly observed that, at lower temperature, the blend with pC-ala shows higher viscosity and the difference between the blends decreases with increased temperature. Especially at the processing temperature of about 100$^\circ$C, the blend with pC-ala is comparable with the blend with St. The other interesting observation is at 120$^\circ$C, VE-St blend starts to polymerize even without an initiator within 10 minutes. This leads to the large standard deviation of viscosity data at 120$^\circ$C and is shown in Figure 4.4 for time dependence of viscosity at 120$^\circ$C. The dramatic increase of viscosity for the VE-St blend in Figure 4.4 corresponds to the gelation observed after the viscosity measurement, while VE-pC-ala blend was still liquid. At 120$^\circ$C, VE-pC-ala shows longer shelf-life than VE-St mixture. This is partially due to the reactivity difference of vinyl group from St and allyl group from pC-ala, as the former one has a higher reactivity and can react at milder conditions. The data for the blend with BF-ala will be discussed in Section 4.3.4.

4.3.3 Dynamic Mechanical Properties of VE Resin Copolymers (St or pC-ala)

Figures 4.5 and 4.6 show the normalized storage moduli and tan $\delta$ versus temperature obtained from VE resin copolymers with St and pC-ala with different experimental compositions or conditions. The copolymers have the same feed mole concentration for St and pC-ala. For VE-pC-ala copolymers, Four samples were made with different initiators. BPO and DiCup are used as free radical initiator with different initiating temperatures and PTS is used for catalyzing benzoxazine polymerization. The other VE-pC-ala copolymer was compression molded instead of using oven for polymerization. In Figure 4.5, the glassy storage moduli for all the copolymers are in the
range of 1.50 – 3.00 GPa. After the glass transition, the rubbery modulus for VE-St copolymer is 3 to 4 times higher than that of VE-pC-ala copolymers. This indicates that the crosslinking density of VE-St copolymer is higher. Glass transition temperatures are usually determined at the peak position from $E''$; however, due to the crosslink nature of the material, no $E''$ peak is observed. Thus, the glass transition temperatures for copolymers are determined by the peak position of $\tan \delta$ in Figure 4.6 as in the literature [4]. The results are also summarized in Table 4.2. VE-St copolymer shows a $T_g$ at 179°C. The closest counterpart from VE-pC-ala copolymer is the resin with 2% DiCup, showing a $T_g$ at 174°C. Increasing the amount of DiCup to 2.5% has little influence on $T_g$, displaying $T_g$ at 171°C. By applying compression-molding technology, the resin does not show increased $T_g$ as expected from higher polymerization efficiency due to the processing method. Using other initiator besides DiCup lower the $T_g$ significantly. $T_g$ is 147°C for resin with 1%BPO and 142°C for copolymer with 1%BPO and 1%PTS. This shows that BPO does not initiate allyl polymerization effectively. By catalyzing cationic ring-opening polymerization of benzoaine using PTS, the formation of the phenolic structure, which is a free radical inhibitor, hinders the free radical polymerization of allyl group to vinyl network. The less effective polymerization reduces the crosslink density and thus increases the molecular chain mobility. Therefore, the $T_g$ is lower. Moreover, the intensity of the $\tan \delta$ peak is related to the amount of the material undergoing the transition. For all the VE-pC-ala copolymers, the intensities of $\tan \delta$ are higher than that of VE-St, showing more potion of material undergoing the transition. This is consistent with lower crosslink density observed from storage moduli.
The reduction of crosslink density and chain rigidity is unexpected considering the copolymerization efficiency of the vinyl and allyl functionalities in the blends. It is suspected that part of pC-ala evaporates during the polymerization procedure both by compression molding and heating in the oven. This is confirmed by monitoring polymerization of copolymers using deuterated pC-ala in the blend for FTIR study to avoid overlapping of the band positions in the CH stretching region. The results are shown in Figure 4.7. Deuterated paraformaldehyde was used to synthesize pC-ala and the synthesized benzoxazine was mixed with VE prepolymer. The characteristic peak of C-D stretch at 2142 cm\(^{-1}\) from deuterated portion of benzoxazine is observed for the blend, and it gradually decreases till it almost disappears by heat treatment, implying its significant evaporation. To further understand the evaporation of pC-ala, the blend was heated isothermally at 80°C and 150°C, respectively, for prolonged time. The intensity of the band at 2142 cm\(^{-1}\) is used to calculate pC-ala content by comparison with the original spectrum at room temperature, and time dependence of the content for both conditions is shown in Figure 4.8. It can be seen that after 1.5hrs at 80°C, part of the copolymerization condition for blends, about 50% benzoxazine monomer remains while after 1.5hrs at 150°C, only less than 5% monomer can be observed. This is in consistence with the disappearance of peak at 2142 cm\(^{-1}\) after polymerization treatment. Overall, it can be concluded that both St and pC-ala tend to evaporate by elevated temperature, but it is easier to polymerize St at lower temperature before its evaporation. In order to successfully replace styrene without sacrificing the property of the resin, another difunctional benzoxazine monomer (BF-ala) is used.

4.3.4 VE Resin Copolymer with BF-ala
BF-ala is synthesized from allyl amine, formaldehyde and bisphenol F isomers. Allyl amine has high reactivity towards formaldehyde and the formation of benzoxazine tends to have oligomeric molecules as the side product. Due to the presence of isomeric structure from phenol, the resultant benzoxazine monomer mixture has relatively low viscosity at temperatures above room temperature, implying the potential good processability. The viscosity of the blend by melt mixing without initiator was measured and also shown in Figures 4.3 and 4.4. It can be seen that at temperature up to 100°C, VE prepolymer with BF-ala show about 10 times higher viscosity of prepolymer with pC-ala. This is understandable as the result of using higher viscosity component. Nevertheless, viscosity of prepolymer with BF-ala at 100°C is about 0.4 Pa.s. This is within the processable window for commercial processing technology such as resin transfer molding, as typical guideline for such technique is about 0.6 Pa.s or less. At 120°C, the blend with BF-ala starts to polymerize, showing the same trend as that with St. This gelation process is believed to be related to the catalytic effect of impurities in BF-ala isomers. As a whole, replacing styrene by BF-ala will not create any further difficulty for processing procedure. On the other hand, it still requires higher temperature for the processing, which will consume more energy for the production.

Dynamic mechanical analyses have been done for the copolymer with BF-ala and comparison with copolymer of pC-ala and St has been made in Figures 4.9 and 4.10. Five copolymers with the same mole ratio of double bond functionality from St, pC-ala, BF-ala, St/pC-ala(1:1) and St/BF-ala(2:1) to VE prepolymer were used to demonstrate the difference. In Figure 4.9, storage moduli of copolymers at glassy state are in the same range, while the rubbery plateau moduli can be divided into three regimes. Even by
adding small amount of St with pC-ala as co-diluents for the copolymer, the evaporation of pC-ala portion is still significant, evidenced by the low rubbery storage moduli observed, indicating lower crosslink density. On the other hand, with BF-ala, it even shows higher storage moduli in rubbery region than that with St, implying improved chain rigidity due to higher crosslink density. The improvement is also observed with mixture of BF-ala and St, and this could potentially broaden the application window by lowering the viscosity of the blend, so the technology with more severe requirements for materials can be used. The copolymer with BF-ala shows a higher T\text{g} at 182°C, consistent with observation of higher crosslink density from storage moduli. The T\text{g} for copolymer with BF-ala/St is 172°C, comparable to those with pC-ala (and St). Moreover, the copolymers containing BF-ala show smaller intensities for tan δ peaks, indicating less portion of material are undergoing the transition. All the results imply an effective copolymerization of BF-ala with vinyl has been achieved and improved dynamic mechanical property of the copolymers obtained.

**4.3.5 Thermal and Thermo-oxidative Stability of VE Resin Copolymers**

In Figure 4.11, thermal stability of VE-St, VE-pC-ala and VE-BF-ala copolymers was evaluated in N\textsubscript{2} with TGA. The 5% weight decomposition temperature: T\text{d}5; 10% weight decomposition temperature: T\text{d}10; and char yield are also summarized in Table 4.2. By replacing St with pC-ala, it is shown that the stability of copolymer is higher up to 320°C, and T\text{d}5 reveals at least 30°C improvement. Polybenzoxazine based on monomer pC-ala has T\text{d}5 at 337°C [12], while polystyrene tends to degrade at lower temperature. For example, typically PS loses about 10% of its molecular weight even when it is fabricated [15]. Thus, it is logical to observe the improved thermal stability by switching
to a more stable component, even though pC-ala tends to evaporate during copolymerization. On the other hand, \( T_{d,10} \) of copolymer with St is about 15°C higher than that with pC-ala. For copolymer with BF-ala, it shows a comparable degradation trend as copolymer with St up to 305°C with a slight upwards feature, and the degradation between 200 and 305°C is attributed to the amine part as the weak portion in benzoxazine structure in the network [16, 17]. A dramatic decrease in weight loss profile from TGA analyses is seen in 300-450°C for all the copolymers. Copolymer with St and pC-ala show the same trend while the copolymer with BF-ala end up with 10% improvement in char yield due to the contribution of thermal stability from benzoxazine. pC-ala is a monofunctional monomer, and under experimental processing conditions, benzoxazine cannot polymerize completely. A significant portion will evaporate and not be anchored into network, leading to easy degradation with high temperatures. The copolymer with St has pendant benzene ring in every repeating unit as the side chain for polymer, easily decomposed at high temperature as they are not fixed in the network. On the other hand, an improved char yield is observed by incorporating more immobilized molecule difunctional benzoxazine BF-ala, as expected. For the application of vinyl ester, generally it is not above 200°C. Therefore, the incorporation of benzoxazine into vinyl ester with improved thermal stability up to at least 305°C is appropriate for the resin.

VE-pC-ala and VE-BF-ala copolymers show comparable thermo-oxidative stability up to 300°C, which is slightly better than VE-St copolymer, in consistence with the results in \( N_2 \). In all, benzoxazine modified VE resin show better stability in 400-600°C region, indicating benzoxazine components tend to carbonize at higher temperature than St. It is expected that no char yield difference is observed for TGA
analyses in air, as no stable element is present in copolymers to survive in thermo-
oxidative environment. Overall, copolymer with BF-ala show improved thermal and
thermo-oxidative stability at temperature higher than 450°C, and both copolymers
containing benzoxazine diluents show slight improvements compared with copolymer
containing St at lower than 300°C, even considering the evaporation of pC-ala along with
polymerization.
4.4 Conclusion

We have developed vinyl ester resins using 3-allyl-6-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (pC-ala) and bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methane (BF-ala) to replace a traditionally used vinyl ester resin that is diluted by styrene (St). By investigation of viscosity for the blends, it demonstrated that the new vinyl ester resin has similar processability at elevated temperature as the traditional resin. Improved dynamic mechanical property is achieved for the VE-BF-ala copolymers. New resins also have comparable or better thermal and thermo-oxidative stability compared with VE-St resin. Overall, it is promising to replace environmental hazard: styrene, by bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methane (BF-ala) without sacrificing much of processability and with improved properties.
References


Table 4.1 Viscosities of VE Resin Prepolymer blends with St/ pC-ala/BF-ala

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Viscosities (Pa s)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VE-St</td>
</tr>
<tr>
<td>25</td>
<td>2.262 ± 0.145</td>
</tr>
<tr>
<td>40</td>
<td>0.612 ± 0.043</td>
</tr>
<tr>
<td>60</td>
<td>0.162 ± 0.007</td>
</tr>
<tr>
<td>80</td>
<td>0.067 ± 0.003</td>
</tr>
<tr>
<td>100</td>
<td>0.036 ± 0.001</td>
</tr>
<tr>
<td>120</td>
<td>0.057 ± 0.046</td>
</tr>
</tbody>
</table>

<sup>a</sup> Viscosities were obtained at shear rate of 100/s
Table 4.2 Thermal properties of Copolymers

<table>
<thead>
<tr>
<th>Feeding Composition&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C, tanδ)</th>
<th>T&lt;sub&gt;d5&lt;/sub&gt; (°C, N₂)</th>
<th>T&lt;sub&gt;d10&lt;/sub&gt; (°C, N₂)</th>
<th>Char yield (%, N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18%St+2%BPO</td>
<td>179</td>
<td>271</td>
<td>351</td>
<td>9.7</td>
</tr>
<tr>
<td>29%pC-ala+2%DiCup</td>
<td>174</td>
<td>306</td>
<td>335</td>
<td>9.4</td>
</tr>
<tr>
<td>28%BF-ala+2%DiCup</td>
<td>182</td>
<td>285</td>
<td>326</td>
<td>21.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> VE prepolymer content = 100% - monomer content
Scheme 4.1 Preparation VE Resin Prepolymer and VE Resin Copolymers
Figure 4.1 $^1$H NMR spectra of VE Resin Prepolymer, benzoxazine monomer pC-ala and BF-ala
Figure 4.2 DSC curves of VE Resin Prepolymer and pC-ala blends
Figure 4.3 Viscosities of VE Resin Prepolymer blends with St, pC-ala and BF-ala at shear rate 100/s
Figure 4.4 Time dependence of viscosities at 120°C with shear rate of 100/s for VE Resin Prepolymer blends with St, pC-ala and BF-ala
Figure 4.5 Normalized Storage Modulus for VE Resin Copolymers with St and pC-ala
Figure 4.6 Tan δ for VE Resin Copolymers with St and pC-ala
Figure 4.7 FTIR of VER Resin Copolymer with pC-ala(deuterated) after each heating stage.
Figure 4.8 pC-ala Content vs Time with isothermal treatment at 80°C and 150°C
Figure 4.9 Storage Modulus for VE Resin Copolymers with St, pC-ala and BF-ala
Figure 4.10 Tan δ for VE Resin Copolymers with St, pC-ala and BF-ala
Figure 4.11 TGA for VE Resin Copolymers with St, pC-ala and BF-ala in N₂
Figure 4.12 TGA for VE Resin Copolymers with St, pC-ala and BisF-ala in air
BIBLIOGRAPHY


Han JC, He XD, Du SY. *Carbon* 33, 473, 1995.


Ishida H, Ohba S. *Polymer* 46, 5588, 2005.


Low HY, Ishida H. *Polymer* 40, 4365, 1999.

McKee DW. *Carbon* 24, 737, 1986.


Soraru GD, Andrea GD, Campostrini R, Babonneau F. *J. Am. Ceram. Soc.* 78, 379,
1995.