

สมบัติทางกลเชิงความร้อนของพอลิเบนซอกลูซีนที่ดัดแปรด้วยสารไดแอนไฮไดรด์



นางสาวบุณชฎริกา รามศิริ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

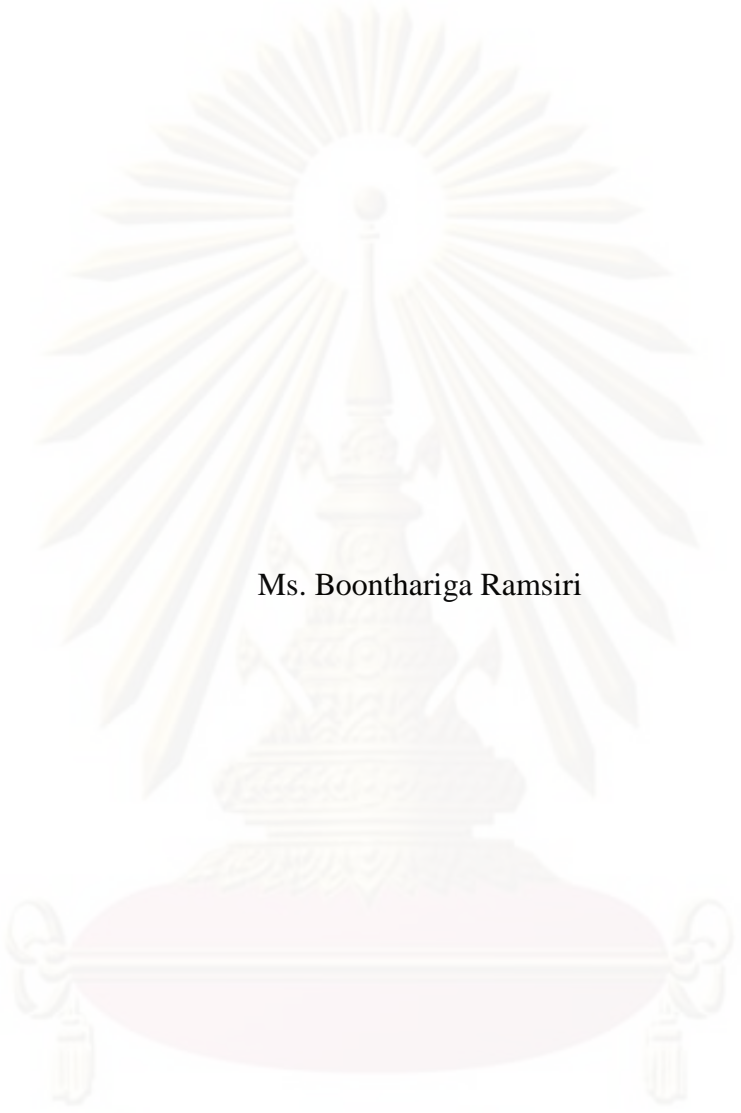
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2552

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

THERMOMECHANICAL PROPERTIES OF POLYBENZOXAZINE  
MODIFIED WITH DIANHYDRIDES



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A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2009

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บุษกริภา รามศิริ : สมบัติทางกลเชิงความร้อนของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารไดแอนไฮไดรด์. (Thermomechanical Properties of Polybenzoxazine Modified with Dianhydrides) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศราวุธ ริมคุสิต, อ. ที่ปรึกษาร่วม: ดร. จันจิรา จัปศิริป์, 99 หน้า.

ในงานวิจัยนี้ศึกษาพอลิเมอร์ผสมระหว่าง เบนซอกซาซีนเรซิน (BA-a)กับไดแอนไฮไดรด์ ซึ่งในงานวิจัยนี้ศึกษาไดแอนไฮไดรด์ 3 ชนิดคือ BTDA PMDA และ s-BPDA ที่อัตราส่วนโดยโมลของ เบนซอกซาซีนเรซินกับไดแอนไฮไดรด์ต่างๆ คอสมบัติทางกล และทางความร้อน ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว และค่าสตอเรจมอดุลัสของแผ่นฟิล์มของ BA-a:BTDA BA-a:PMDA และBA-a:s-BPDA มีค่าสูงอย่างมากกว่า พอลิเบนซอกซาซีน (PBA-a) เนื่องจากความหนาแน่นในการเชื่อมขวางของ ปฏิกิริยาเอสเทอร์ฟิเคชันระหว่าง หมู่ไฮดรอกซิลของ พอลิเบนซอกซาซีนกับ หมู่คาร์บอกซิลิกของ ไดแอนไฮไดรด์ที่ ผ่านกระบวนการบ่มด้วยความร้อน และค่าสูงสุดของอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของ BA-a:PMDA > BA-a:s-BPDA > BA-a:BTDA ที่ 1.5:1 โดยโมล นอกจากนี้อุณหภูมิการสลายตัวด้วยความร้อนที่ สิบเปอร์เซ็นต์โดยน้ำหนักที่หายไป ภายใต้ก๊าซไนโตรเจน และปริมาณของแก๊สที่เหลือ ณ อุณหภูมิ 800 องศาเซลเซียสของ พอลิเมอร์อัลลอยนี้มีค่าสูงกว่า พอลิเบนซอกซาซีน และพบอีกว่าค่า LOI ที่คำนวณจากสูตรของทุกอัตราส่วนโดยโมลของ BA-a:BTDA BA-a:PMDA และ BA-a:s-BPDA นี้ มีค่าเกินขอบเขตที่วัสดุสามารถติดไฟเองได้ ซึ่งค่านี้ต้องมากกว่า 26 จึงจัดอยู่ในสารประเภทดับไฟได้เอง มากไปกว่านั้น ความแข็งแรงภายใต้แรงดึงยึด ความยืดสูงสุด ณ จุดขาด มอดุลัสภายใต้แรงดึง และความเหนียวของ พอลิเบนซอกซาซีนมีค่าเพิ่มขึ้น โดยการอัลลอยกับ BTDA PMDA หรือ s-BPDA เช่นกัน จากผลดังกล่าวแสดงว่าสามารถขึ้นฟิล์มที่ยืดหยุ่น และแข็งแรง อีกทั้งสมบัติทางกล และทางความร้อนที่เหมาะสมที่สุดที่อัตราส่วนเท่ากับ 1.5:1 โดยโมล จากคุณสมบัติดังกล่าวส่งผลให้ได้พอลิเมอร์อัลลอยที่เหมาะสมสำหรับการใช้งานเป็นฟิล์มที่ทนความร้อนสูง เช่น การบรรจุหีบห่อทางอิเล็กทรอนิกส์ สารเคลือบที่ทนความร้อน และเมทริกซ์สำหรับวัสดุเชิงประกอบ เป็นต้น

ภาควิชา..... วิศวกรรมเคมี.....  
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# 5170584121: MAJOR CHEMICAL ENGINEERING

KEYWORDS: DIANHYDRIDES / POLYBENZOXAZINE / POLYMER  
ALLOYS / THERMOMECHANICAL PROPERTIES

BOONTHARIGA RAMSIRI: THERMOMECHANICAL PROPERTIES  
OF POLYBENZOXAZINE MODIFIED WITH DIANHYDRIDES.

THESIS ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D.,

THESIS CO-ADVISOR: CHANCHIRA JUBSILP, D.Eng., 99 pp.

In this research, we have been studied mixture between benzoxazine resin (BA-a) and dianhydrides, i.e. 3, 3', 4, 4' benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA) or 3, 3', 4, 4' biphenyltetracarboxylic dianhydride (s-BPDA) at various mole ratios of BA-a: dianhydrides on thermal and mechanical characteristics. The glass transition temperature ( $T_g$ ) and the storage modulus ( $E'$ ) values of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA films were observed to be significantly higher than that of the neat polybenzoxazine (PBA-a) owing to the enhanced crosslink density. This greater crosslink density resulted from esterification reaction between the hydroxyl group of polybenzoxazine and the carboxylic group of dianhydride, which formed by thermal curing. The maximum  $T_g$  values of BA-a: PMDA > BA-a: s-BPDA > BA-a: BTDA were observed at an alloy composition of 1.5: 1 mole ratio. Moreover, the degradation temperature ( $T_d$ ) reported at 10 percent weight loss under nitrogen atmosphere and char yield at 800 °C of the polymer alloys were found to be much greater than those of the neat polybenzoxazine (PBA-a) while the calculated LOI of all BA-a: dianhydride alloys were above the self-extinguishable limit i.e. > 26. In addition, tensile strength, tensile elongation at break, tensile modulus, and toughness of PBA-a increased by alloying with BTDA or PMDA or s-BPDA. These results suggested the alloys to be casted to yield tougher and stronger films. The ultimate mechanical and thermal properties for BA-a: dianhydrides were also obtained at 1.5:1 mole ratio. The obtained alloy sample is appropriate for an application as polymeric film for high temperature resistance material such as electronic packaging, thermal resistance coating and matrix for composite materials.

Department : Chemical Engineering

Field of Study : Chemical Engineering

Academic Year : 2009

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Advisor's Signature Sarawut Rimdusit

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## ACKNOWLEDGEMENTS

I am sincerely grateful to my advisor, Assoc. Prof. Dr. Sarawut Rimdusit and Dr. Chanchira Jubsilp, for their invaluable guidance and value suggestions including constant encourage throughout this study. Furthermore, I deeply appreciate all the things. I have learnt from them and for the opportunity to work in their group. I really enjoyed our meetings and pleasure with my thesis. I am also grateful to Assoc. Prof. Dr. Muenduen Phisalaphong, as the chairman, Assoc. Prof. Dr. Siriporn Damrongsakkul and Dr. Pratana Kewsuwan, who have been members of my thesis committee for the kind advices and good comments.

This work is supported by the research grant for TRF Research Scholar (S. Rimdusit) and by the 2009 Overseas Research Grants of The Asahi Glass Foundation. Additional fund is also provided by the research allowance from university income, SWU, Government budget 2009 (C. Jubsilp).

The authors would like to thank Mektec International Corporation (MIC), Chulalongkorn University for the assistance on thermogravimetric analysis (TGA) and Bisphenol A is kindly supported by Thai Polycarbonate Co., Ltd.

Additionally, I would like to extend my grateful thanks to all members of Polymer Engineering Laboratory of the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, for their assistance, discussion, and friendly encouragement in solving problems. Finally, my deepest regard to my family and parents, who have always been the source of my unconditional love, understanding, and generous encouragement during my studies. Also, every person who deserves thanks for encouragement and support that cannot be listed.

จุฬาลงกรณ์มหาวิทยาลัย

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# CHAPTER I

## INTRODUCTION

### 1.1 Overview

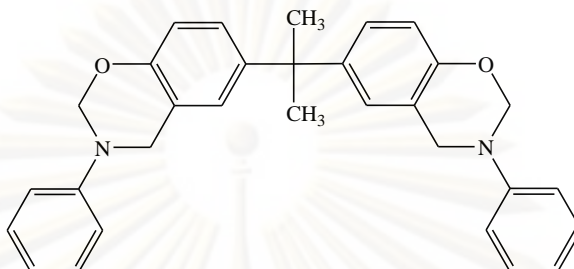
Polybenzoxazine (PBA-a) is a newly developed addition polymerized phenolic systems, which are formed from phenol and formaldehyde in the presence of amines. It has a wide range of interesting properties and potentials to overcome several shortcomings of conventional novolac and resole type phenolic resin, while retaining their benefits like near zero shrinkage upon curing, the glass transition temperature ( $T_g$ ) much higher than cure temperature, fast mechanical property build-up as a function of degree of polymerization, high char-yield, low CTE, low viscosity, low moisture absorption and excellent electrical properties [1]. The alternative for phenol and amine permits design flexibility and polymer property tailoring [1]. Polybenzoxazines have excellent thermal and non-flammable properties. Furthermore, benzoxazines are able to polymerize simply through heating without strong acids catalyst, and with producing harmful by-products during the cure process.

Moreover, there are many ways to develop the performance of polybenzoxazine into two methods. Firstly, the modification of the structure of benzoxazine monomers [2-6] and the other is the blends or composites with other high-temperature polymers like polyimide [7], inorganic fillers such as clay[8-9] and metal oxide [10], and high-temperature stable material i.e. multi-walled carbon-nanotube [11], titania [12], and silsesquioxane [13].

At present, there are many companies in the world which has been produced benzoxazine for trading including multiplicity requirements of individual applications i.e. Huntsman Company and Henkel Corporation.

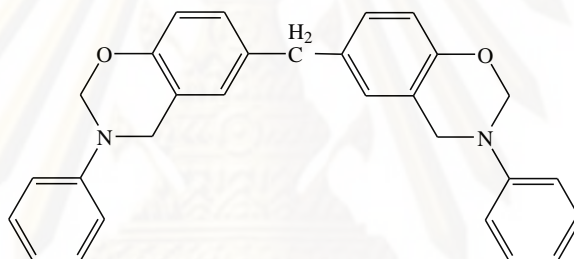
1. **Huntsman** [14] has sale volume in PCB/Electronic Industry (1000T/year). In addition, Huntsman still develops many types of benzoxazine as following.

- Bisphenol A Benzoxazine (N-Phenyl Bisphenol A Benzoxazine)



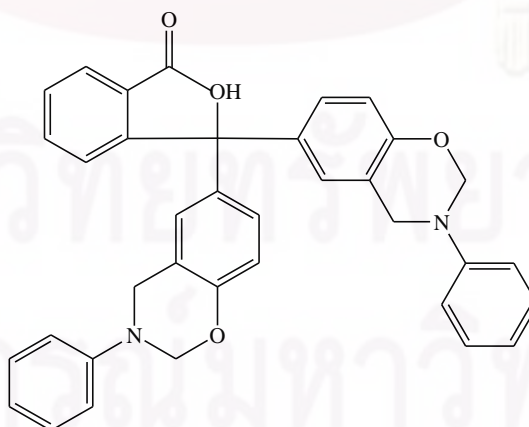
**Figure 1.1:** Bisphenol A Benzoxazine [14].

- Bisphenol F Benzoxazine (N-Phenyl Bisphenol F Benzoxazine)



**Figure 1.2:** Bisphenol F Benzoxazine [14].

- Phenolphthalein Benzoxazine (N-Phenyl Phenolphthaleine Benzoxazine)

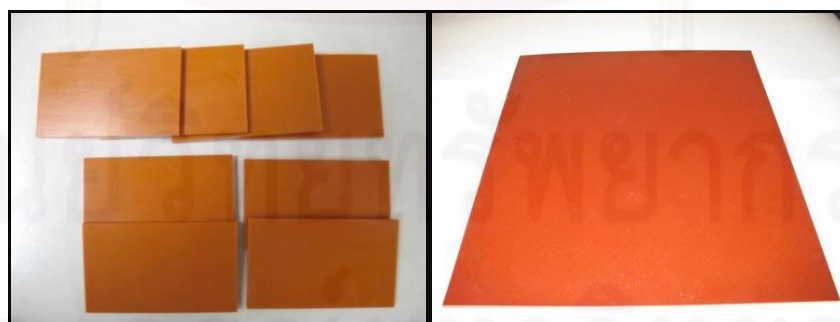


**Figure 1.3:** Phenolphthalein Benzoxazine [14].

And polymer blend by using benzoxazine blend with many chemical materials such as

- Epoxy resins
- Cyanate Esters
- Maleimides / Bismaleimides
- Isocyanates
- Polyamides
- Phosphazenes
- Thermoplastics (PPO)
- Acrylates / Vinylmonomers
- Triazine compounds
- Anhydrides

2. **Henkel Corporation** [15] Epsilon 99100 benzoxazine RTM/VART resin system from Henkel Corp. (Bay Point, CA) is designed for composite structure in aerospace applications. The resin is stable at ambient temperatures for over a year as a one-part resin. The system features a broad processing window for large parts and intricate shapes, viscosity stability, low heat release during cure, low cure shrinkage for improved translation of strength in the final part, fire retardancy for aircraft fuselage and interior applications, high hot/wet property retention, improved UV-resistance, and thermal resistance. The 180°C cure resin is also resistant to solvents, has high compressive strength and modulus, and has hot/wet glass transition temperature of 165°C as shown in Figure 1.4.



**Figure 1.4:** benzoxazine RTM/VARTM resin system [16].



Polymer alloys from polybenzoxazine and polyimide yielded deep wine and transparent films. The tensile properties of the polyimide-polybenzoxazine alloy films show that the bisphenol-A based on polybenzoxazine (BA-a) enhanced the modulus of polyimide, while polyimide improved the toughness of PBA-a. The thermal stabilities of PBA-a was improved significantly by alloying with polyimide. The alloying with polyimide is an excellent method to modify the properties of PBA-a, which should be effective for the microelectronic applications [7].

Therefore, polybenzoxazines were improved by addition dianhydride like pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), and which were selected for using high performance material like polyimides including eliminate disadvantages of polybenzoxazine such as the brittle property and expectation in enhancement of both the thermal and the mechanical properties of polybenzoxazines as a high performance polymer.

Moreover, the high performance of polybenzoxazine-dianhydride alloys produce to suitable for more broad applications, i.e., in thermal insulation materials, protecting coating, high-temperature adhesives, tape-automated bonding (TAB), chip-on-film, and packaging application.

In this study, we prepared the high performance polymer alloys of polybenzoxazine and dianhydride, studying the effect of mole ratios and types of the dianhydrides in polybenzoxazine on thermal and mechanical characteristics.

## 1.2 Objectives

1. To study the suitable mole ratio of polymeric alloys between benzoxazine resin and dianhydrides, such as BTDA, PMDA, and s-BPDA on curing and processing conditions.

2. To evaluate mechanical and thermal properties of polybenzoxazine modified with dianhydrides and compare the effect of types of dianhydride in benzoxazine resin on thermal and mechanical properties.

### 1.3 Scopes of the Study

1. Synthesis of benzoxazine resin by solvent-less synthesis technology.
2. Preparation of polymeric alloys between the benzoxazine resin and dianhydrides, such as BTDA, PMDA, or s-BPDA at various mole ratio of the benzoxazine resin and dianhydride i.e. 4:1, 3:1, 2:1, 1.5:1, 1:1, 1:0 in N-methyl-2-pyrrolidinone (NMP) as solvent.
3. Evaluation of the curing condition or crosslinking process of the polymeric alloys.
  - ❖ Determining functional groups by Fourier Transform Infrared Spectroscopy (FTIR).
  - ❖ Finding curing condition by Differential Scanning Calorimeter (DSC).
4. Examination of thermal and mechanical properties of the polymeric alloys.
  - ❖ Dynamic mechanical analysis (DMA).
  - ❖ Differential scanning calorimetry (DSC).
  - ❖ Thermogravimetric analysis (TGA).
  - ❖ Tensile testing.
5. Finding densities of benzoxazine-dianhydride alloying films by Densitometer.

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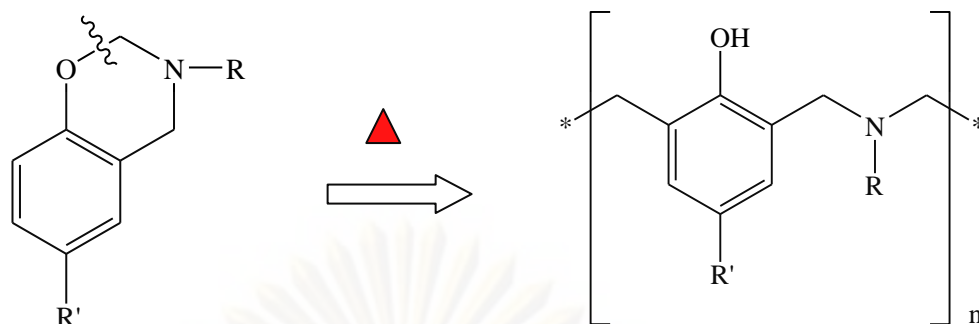
## CHAPTER II

### THEORY

#### 2.1 Benzoxazine resin

Benzoxazine resin is a story class of phenolic resin which was developed to defeat almost all shortcomings of the phenolic resins and was expected to replace conventional phenolic, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in numerous respects. They demonstrate several remarkable properties that have not been regularly observed by other well-known polymers, as follow excellent processability owing to low melt viscosity [1], solvent-less method for benzoxazine resin preparation [17], near-zero shrinkage upon polymerization [18], fast mechanical property build-up as a function of degree of polymerization [1] and benzoxazine resins can be synthesized from low-cost raw materials. The ring opening polymerization is readily achieved by basically heating the purified monomer typically at temperatures in the range between 160°C and 220°C [19] and gelation takes place in a metter of minutes to tens of minutes at these temperatures if no initiators are employed [20].

Additionally, the ring opening mechanism occurs by breaking of a C-O bond of the oxazine ring as shown in Figure 2.1 [21] and benzoxazines cure without the support of strong acid catalysis, do not release by-products during the polymerization [22]. The curing behavior of the as-synthesized benzoxazine precursor studied is autocatalytic [23]. The fantastic molecular design flexibility of the polybenzoxazines allow the properties of cured materials to be tailord for the particular requirements of personality applications.



**Figure 2.1:** Ring opening mechanism of benzoxazine monomers [21].

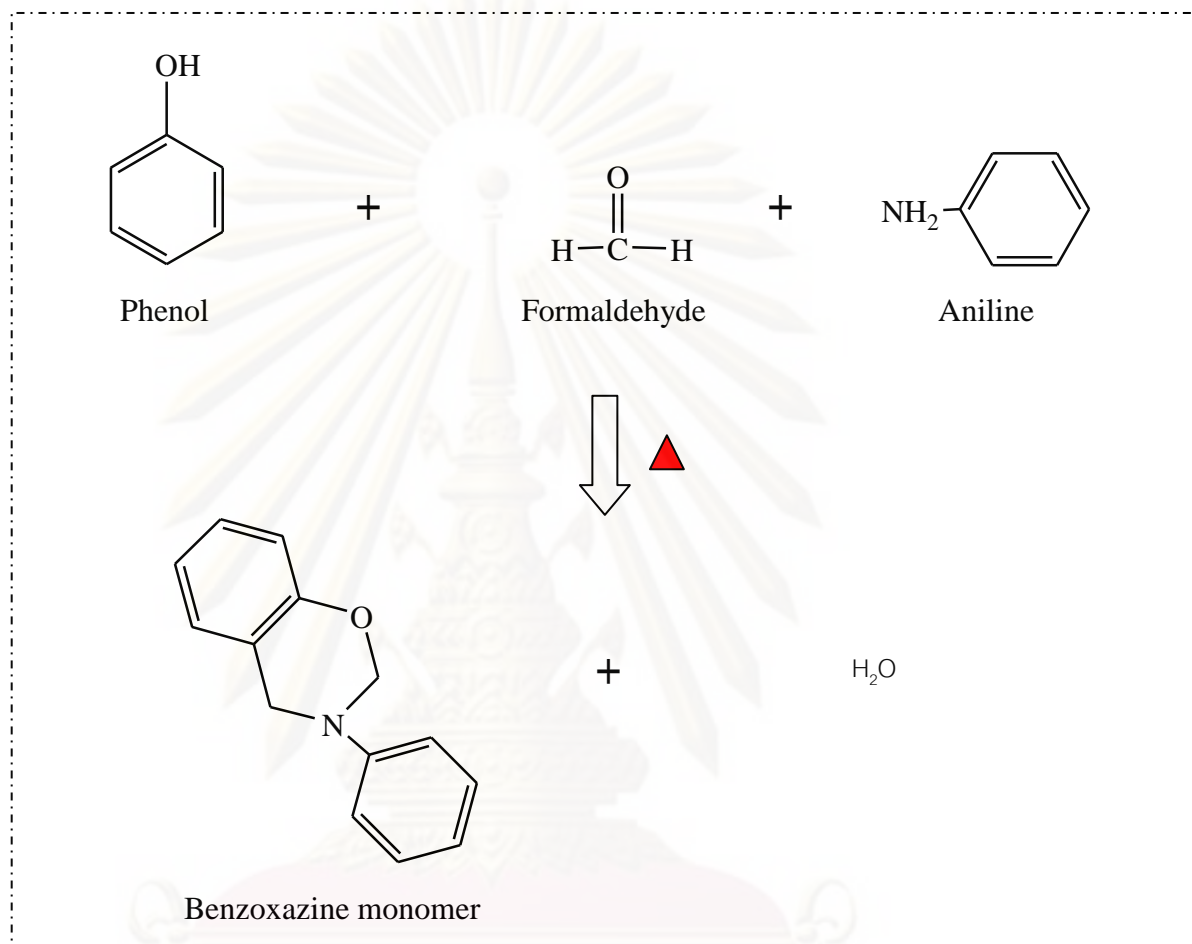
Furthermore, good mechanical properties, such as Tensile Strength = 64 MPa, Tensile Modulus = 5.2 GPa, elongation at break (%) = 1.3 [24], high thermal stability ( $T_d = 334^\circ\text{C}$ ; 5 % wt loss[24]) which is possibly owing to the stabilization of the Mannich bridges by the very strong intramolecular hydrogen bonding between the phenolic OH groups and the nitrogen atom of Mannich bridge [25,26], much higher than cure temperature, the glass transition temperature ( $T_g$ ) exhibit in the range  $160$ - $340^\circ\text{C}$  depending on the structure, high char-yield due to char formation usually increases with increased content of benzene content and char yield, no dark smoke, self extinguishing, low heat release rate, and low total heat release make them a desirability applicant as non-flammable materials for the transportation industry.

Finally, low dielectric constants ( $\epsilon = 3.6$  or lower), long-term immersion studies indicate that these materials have a low rate of water absorption and low water absorption [1, 18, 24, 27] that bisphenol-A and aniline based polybenzoxazine saturated at 1.9% by weight [27], and low coefficient of thermal expansion (CTE), propose an abnormal combination for electronic packaging materials. Their composites are comparable to polyimides and other high performance polymer, but are easily processable [28]. Table 2.1 compares the properties of polybenzoxazine with those of the state-of-the-art matrices [1].

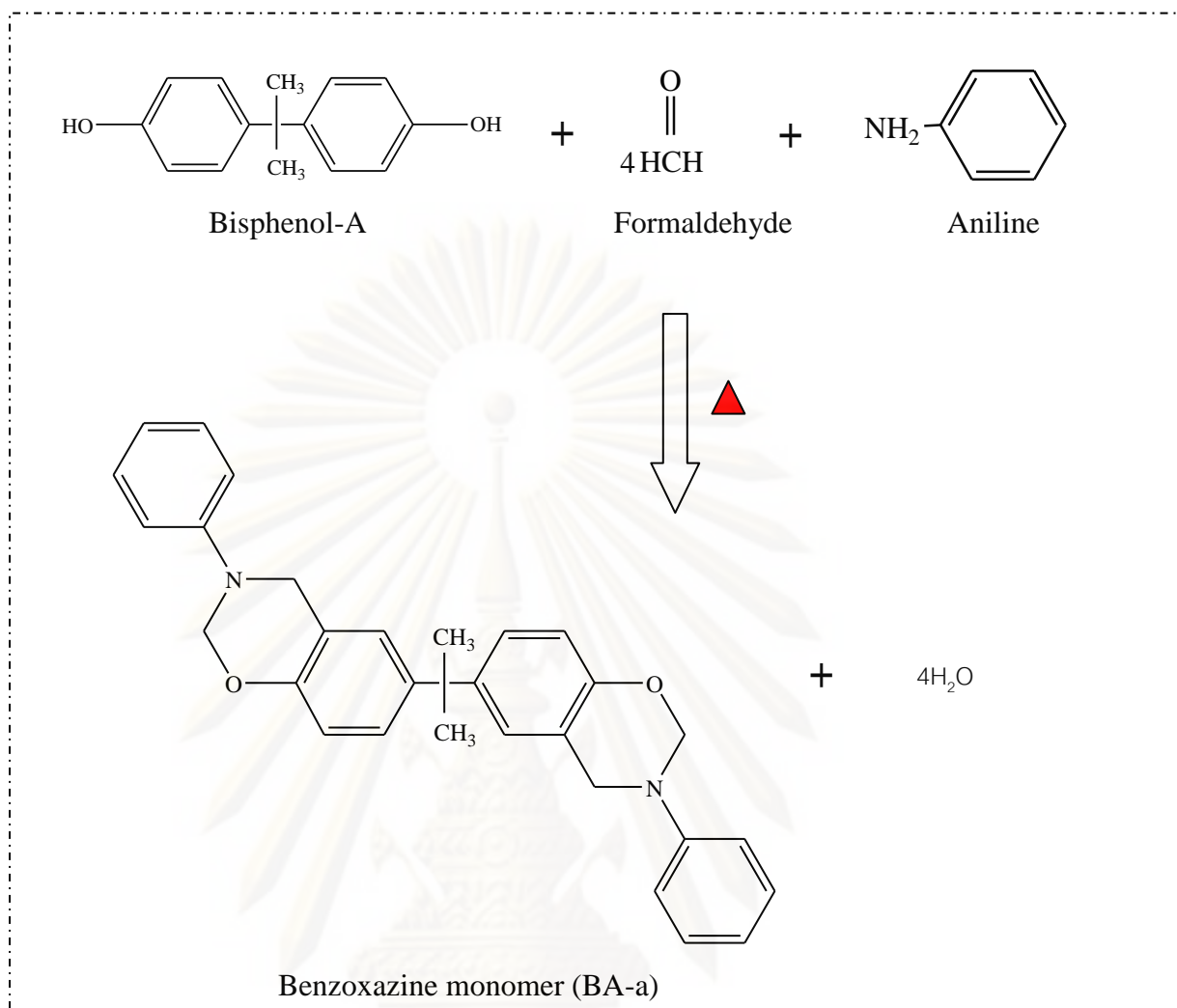
**Table 2.1:** Comparative properties of various high performance polymers [1].

<b>Property</b>	<b>Epoxy</b>	<b>Phenolics</b>	<b>Toughened BMI</b>	<b>Polybenzoxazine</b>
<b>Density (g/cc)</b>	1.2 - 1.25	1.21 - 1.32	1.2 - 1.3	1.19
<b>Max use temperature (°C)</b>	180	200	~ 200	130 - 280
<b>Tensile strength (MPa)</b>	90 - 120	24 – 45	50 - 90	100 - 125
<b>Tensile modulus (GPa)</b>	3.1 - 3.8	-	3.5 - 4.5	3.8 - 4.5
<b>Elongation (%)</b>	3 - 4.3	0.3	3	2.3 - 2.9
<b>Dielectric constant (1 MHz)</b>	3.8 – 4.5	04/10	3.4 - 3.7	3 - 3.5
<b>Cure temperature (°C)</b>	RT – 180	150 – 190	220 - 300	160 - 220
<b>Cure shrinkage (%)</b>	> 3	0.002	0.007	~ 0
<b>TGA onset (°C)</b>	260 - 340	300 – 360	360 - 400	380 – 400
<b>Tg (°C)</b>	150 - 220	170	230 - 380	170 - 340

The benzoxazine resin can be synthesized from phenol, formaldehyde and amines [1] that can be classified into a monofunctional and a bifunctional type depending on a type of phenol used as shown in Figures 2.2 and 2.3. An example of the monomer synthesis is



**Figure 2.2:** Schematic synthesis of monofunctional benzoxazine monomer.



**Figure 2.3:** Schematic synthesis of bifunctional benzoxazine monomer.

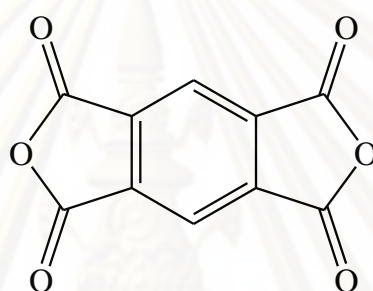
In this work, we synthesized bifunctional benzoxazine monomer in our laboratory. Raw materials are bisphenol-A, formaldehyde, aniline as seen Figure 2.1.2 For the reason that bisphenol-A is low cost and plentiful.

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## 2.2 Dianhydrides

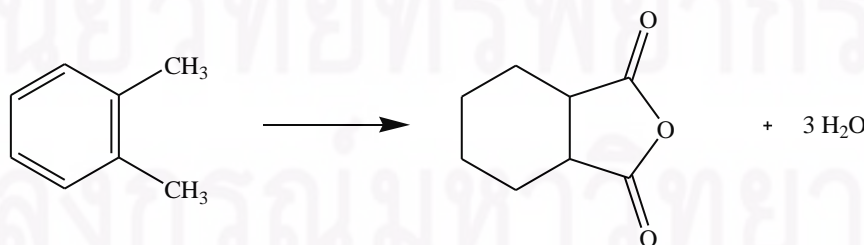
Dianhydride have been used to substance in produce polymers such as polyimides [7]. They have vaious types of dianhydride. For example,

➤ **Pyromellitic dianhydride (PMDA)** is prepared by the vapor phase oxidation of durene, which is 1, 2, 4, 5 tetramethylbenzene, using a supported vanadium oxide catalyst. The synthesis is completely analogous to the synthesis of phthalic anhydride [31, 32].



**Figure 2.4:** Pyromellitic dianhydride (PMDA).

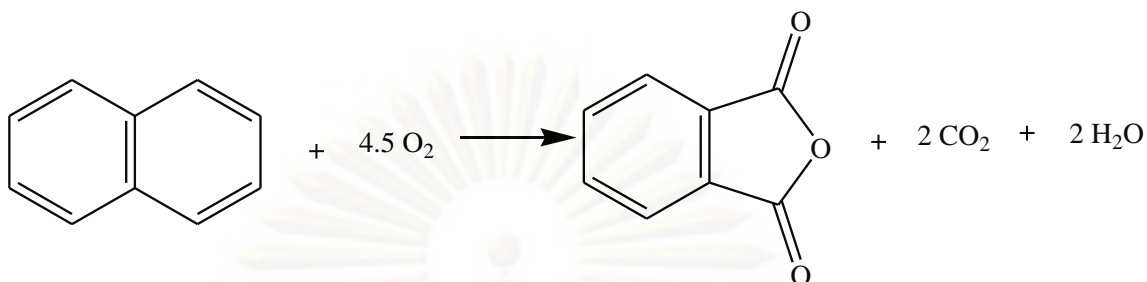
➤ There are two methods of productive phthalic anhydride in industry system. Firstly; about 71% of phthalic anhydride is produced by oxidizing o-xylene. This reaction either conducted in the vapor phase using a fixed or fluidized bed catalyst base on V<sub>2</sub>O<sub>5</sub> or a liquid-phase oxidation. The liquid-phase oxidation is conducted 150°C using soluble acetates or naphthenates of cobalt, manganese, or molybdenum in combination with bromine as a promoter [33].



**Figure 2.5:** The production of phthalic anhydride.



Secondly, the air oxidation of naphthalene derived from petrochemical sources or coal is still being used to produce phthalic anhydride. The processes and catalysts are similar [25].

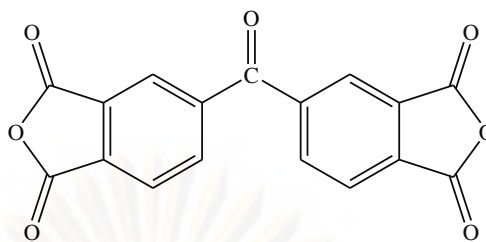


**Figure 2.6:** The production of phthalic anhydride.

**Table 2.2:** PHYSICAL AND CHEMICAL PROPERTIES OF PMDA [34].

<b>Physical State</b>	Powder
<b>Color</b>	white to light beige
<b>Vapor Pressure</b>	< 0.01hPa @ 20 °C
<b>Boiling Point</b>	397 - 400 °C @ 760mmHg
<b>Freezing / Melting Point</b>	283 - 287 deg C
<b>Flash Point</b>	380 deg C (716.00 deg F)
<b>Solubility in water</b>	Decomposes.
<b>Solubility in other solvents</b>	Soluble in acetone.
<b>Molecular Formula</b>	C <sub>10</sub> H <sub>2</sub> O <sub>6</sub>
<b>Molecular Weight</b>	218.12
<b>Chemical Stability</b>	Stable under normal temperatures and pressures. Moisture sensitive

➤ 3,3',4,4' –benzophenonetetracarboxylic dianhydride (BTDA)

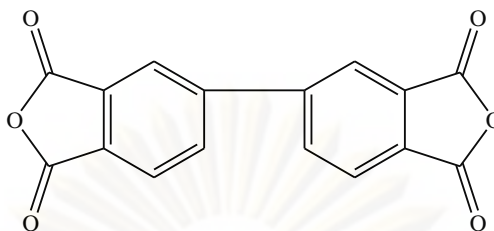


**Figure 2.7:** 3, 3', 4,4' –benzophenonetetracarboxylic dianhydride (BTDA).

**Table 2.3:** PHYSICAL AND CHEMICAL PROPERTIES OF BTDA [35]

<b>Synonyms</b>	4,4'-Carbonyldiphthalic anhydride
<b>Empirical Formula (Hill Notation)</b>	$C_{17}H_6O_7$
<b>Appearance</b>	White or light yellow powder
<b>Molecular Weight</b>	322.23
<b>Vapor density</b>	1.4 (vs. air)
<b>Density</b>	$1.57 \text{ g/cm}^3$
<b>Vapor pressure</b>	$<0.1 \text{ mmHg (0 } ^\circ\text{C)}$
<b>Auto ignition temp.</b>	$975 \text{ } ^\circ\text{F}$
<b>Melting Point</b>	$218\text{-}222 \text{ } ^\circ\text{C}$
<b>Chemical Stability</b>	Sensitive to humidity
<b>Assay</b>	96 %

➤ **3,3',4,4' –biphenyltetracarboxylic dianhydride (s-BPDA)**



**Figure 2.8:** 3, 3', 4, 4' –biphenyltetracarboxylic dianhydride (s-BPDA).

**Table 2.4:** PHYSICAL AND CHEMICAL PROPERTIES OF s-BPDA [36].

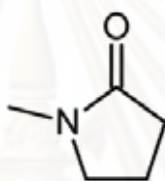
IUPAC Name	5-(1,3-dioxo-2-benzofuran-5-yl)-2-benzofuran-1,3-dione
Nomenclature	3,3',4,4'-Biphenyl tetracarboxylic dianhydride (s-BPDA)
Synonyms	4,4'-Biphthalic anhydride, 4,4'-Biphthalic dianhydride
Physical State	Light grey, odorless powder
Molecular Formula	C <sub>16</sub> H <sub>6</sub> O <sub>6</sub>
Molecular Weight	294.215240 [g/mol]
H-Bond Donor	0
H-Bond Acceptor	6
Purity	99.5% min
Sp. Gr.	1.56
Melting Point	300

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### 2.3 Solvent

**N-methyl-2-pyrrolidinone (NMP)** [36] is a chemical composite with 5-membered lactam structure. It is a clear to faintly yellow liquid miscible with water and solvents like ethyl acetate, chloroform, benzene and lower alcohols or ketones. It also belongs to the group of dipolar aprotic solvents which includes also dimethylformamide, dimethylacetamide and dimethyl sulfoxide. Other names for this compound are: 1-methyl-2-pyrrolidone, N-methyl-2-pyrrolidinone, and m-pyrrole, and pharماسolve.



**Figure 2.9:** N-methyl-2-pyrrolidinone (NMP).

N-Methylpyrrolidone is used to recover pure hydrocarbons while processing petrochemicals and in the desulfurization of gases. Owing to its good solvency properties N-methyl-2-pyrrolidone is used to dissolve an ample range of chemicals, particularly in the polymers field. It too used as a solvent used for surface treatment of textiles, resins and metal coated plastics or as a paint stripper [38]. In the pharmaceutical industry, N-methyl-2-pyrrolidone is used in the formulation for drugs by both oral and transdermal delivery routes.

N-Methyl-2-pyrrolidone and its derivatives are used as intermediates for the synthesis of agrochemicals, pharmaceuticals, textile auxiliaries, plasticizers, stabilizers and specialty inks. It is also employed as a nylon precursor. The rubber industry uses it for SBR latex production and the electronics industry for printed circuit board manufacturing [39]. NMP is also used in lithium cell creation.

World fabrication capacity for NMP was 226 million lb in 2006. NMP has attractive properties such as low volatility, low flammability, and relatively low toxicity. Nevertheless, it has been identified as a reproductive toxicant, first by California in 2001 and then by the European Commission in 2003. In the face of

growing regulation, some manufacturers are considering option solvents for some applications, especially where worker exposure is hard to control, such as in paint stripping and cultivation [40].

**Table 2.5:** properties of N-methyl-2-pyrrolidinone (NMP).

<b>Molecular formula</b>	C <sub>5</sub> H <sub>9</sub> NO
<b>Molar mass</b>	99.13 g/mol
<b>Density</b>	1.028 g/cm <sup>3</sup>
<b>Melting point</b>	-24 °C
<b>Boiling point</b>	202-204°C






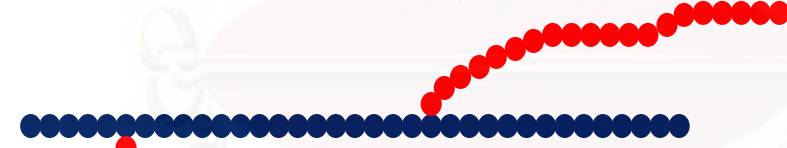

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## 2.4 Copolymers

A further type of polymer structure arises when two or more kinds of mer are mixed in a single polymer chain. For example, ethylene and propylene may be copolymerized to give a copolymer, which have properties somewhat different from the parent homopolymer polyethylene and polypropylene. To be able to describe the copolymer chain structure fully it is necessary to know how the two types of mer are arranged within the chain. Three possible distinct copolymer classes can be envisaged at once, and all three types are found among engineering polymer materials: the alternating copolymer, the random copolymer and the block copolymer [41].

The structures of these basic copolymer classes are shown schematically in table 2.7, together with the graft copolymer and the terpolymer [42].

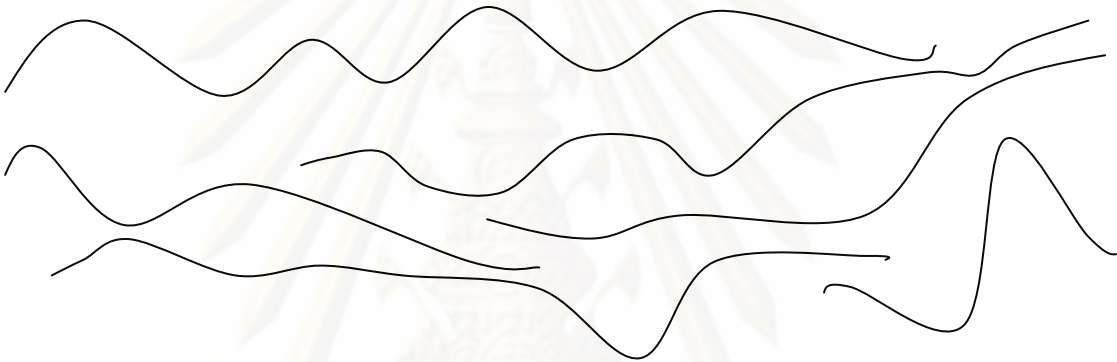
**Table 2.6:** Classification of copolymers [40].

	<b>Alternating</b>
	<b>Random</b>
	<b>Block</b>
	<b>Graft</b>
	<b>Random terpolymer</b>

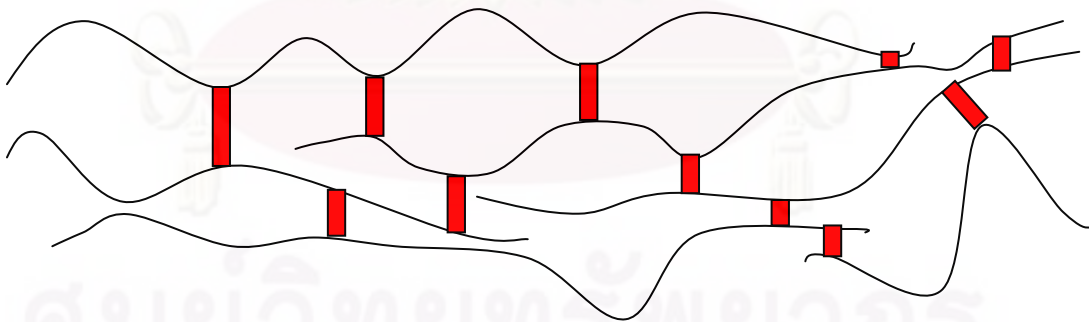
## 2.5 Thermosets [41]

Thermosets before hardening, like thermoplastics, are independent macromolecules. But in their final state, after hardening, they have a three-dimensional structure obtained by chemical crosslinking produced after (spray-up molding or filament winding) or during the processing (compression or injection molding, for example).

Figures 2.10 and 2.11 schematize the molecular arrangements of these polymers.



**Figure 2.10:** Thermoset before crosslinking or thermoplastic.



**Figure 2.11:** Thermoset after crosslinking.

Some polymers are used industrially in their two forms, thermoplastic and thermosets, for example, the polyethylene or VAE.

Thermoset consumption is roughly 15-20% of the total plastic consumption. The links created between the chains of the thermosets limit their mobility and possibilities of relative displacement and bring certain advantages and disadvantages.

## Advantages

- Infusibility: thermosets are degraded by heat without passing through the liquid state. This improves some aspects of fire behavior: except for particular cases, they do not drip during a fire and a certain residual physical cohesion involves a barrier effect.
- When the temperature increases the modulus retention is better, due to the three-dimensional structure.
- Better general creep behavior, the links between the chains restricting the relative displacements of the macromolecules, one against the other.
- Simplicity of the tools and processing for some materials worked or processed manually in the liquid state.

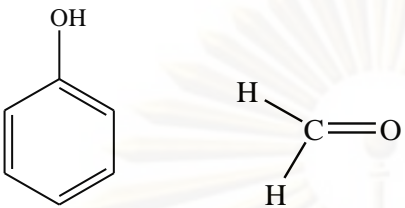
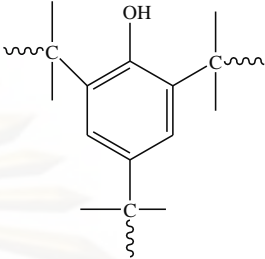
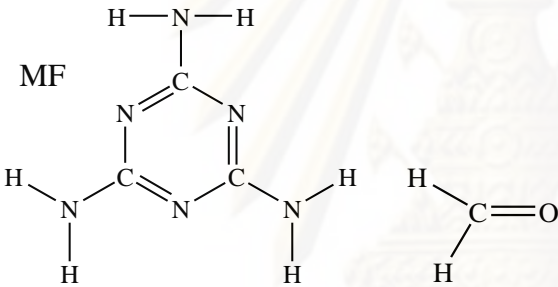
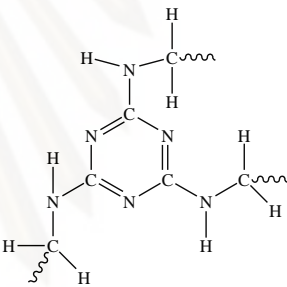
## Disadvantages

- The chemical reaction of crosslinking takes a considerable time that lengthens the production cycles and, often, requires heating, that is, an additional expenditure.
- The processing is often more difficult to monitor, because it is necessary to take care to obtain a precise balance between the advances of the crosslinking reaction and the shaping.
- Certain polymers release gases, in particular water vapor, during hardening.
- The wastes are not reusable as virgin matter because of the irreversibility of the hardening reaction. At best, they can be used like fillers after grinding.
- The infusibility prevents assembly by welding.

In a similar way, unsaturated polyesters UP can be crosslinked by molecules such as styrene to produce network polymers. The second types are represented by important thermosets such as PF, MF and EP (Table 2.8) [41].

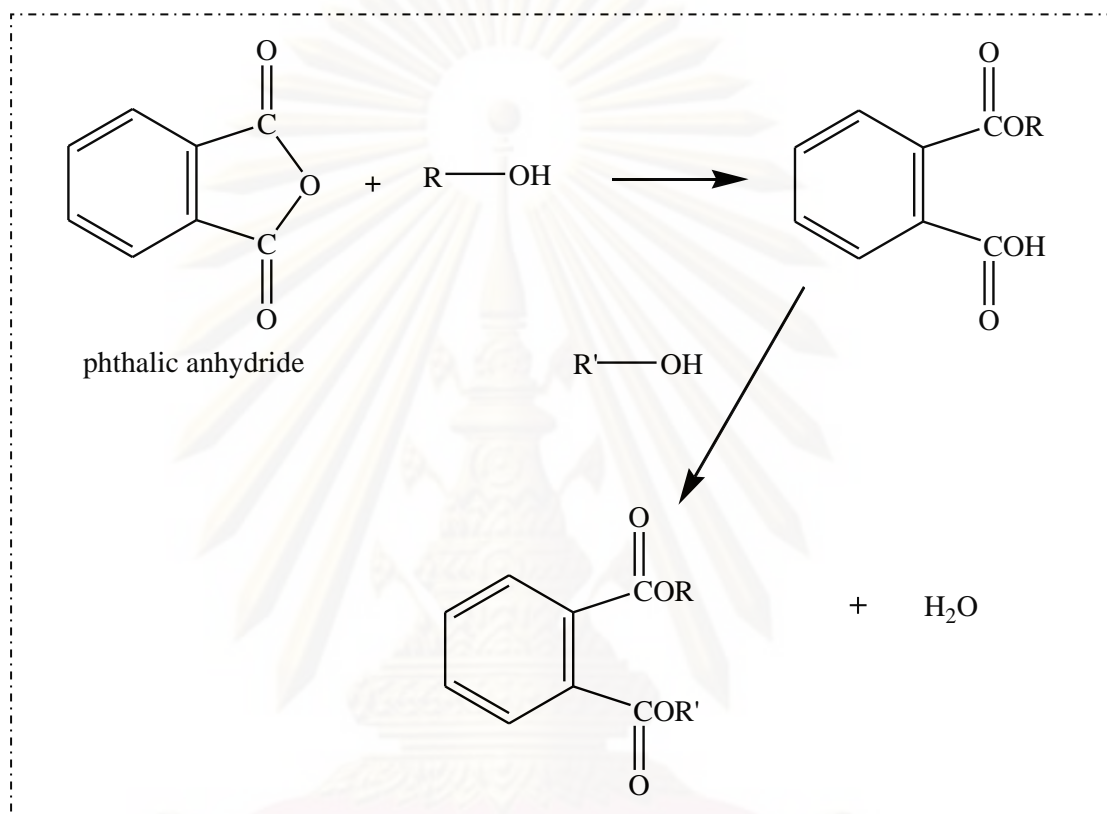


**Table 2.7:** Synthetic network polymers thermosets [41].

Type	Starting materials	Network polymer
PF	 <p>Phenol</p> <p>formaldehyde</p>	 <p>and similar units randomly connected by a variety of links</p>
MF	 <p>Melamine</p> <p>formaldehyde</p>	 <p>and similar units randomly connected by a variety of links</p>

## 2.6 Reaction

Esterification proceeds of phthalic anhydride have two steps as shown in Figure 2.12 [43].

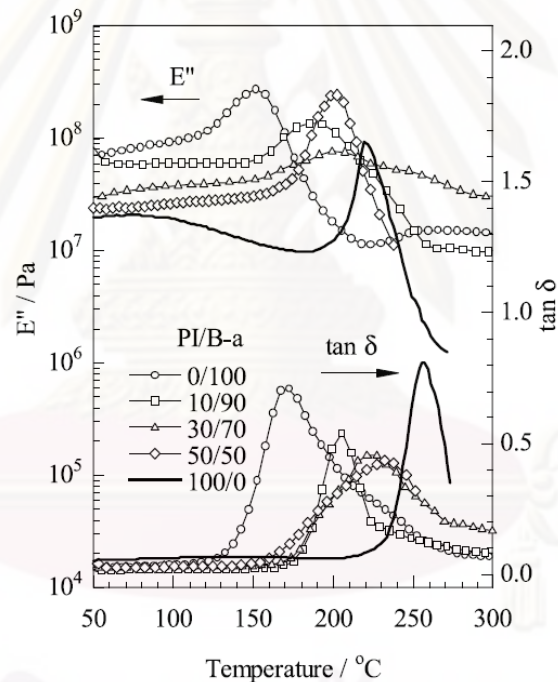


**Figure 2.12:** Esterification of phthalic anhydride [43].

## CHAPTER III

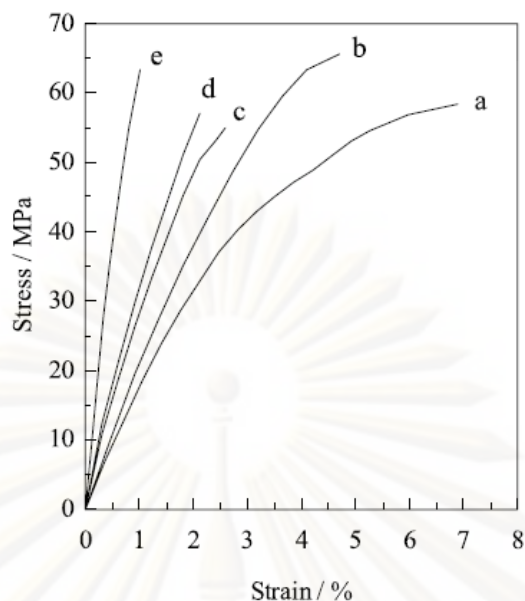
### LITERATURE REVIEWS

Takeichi, Y. Guo, S. Rimdusit, 2005 [7] The cast films polyimide (PI)/Benzoxazine (BA-a) were yellow and transparent, similar with that of the blend solution, and became deep wine-color and transparent after the cure at 240 °C. From Figure 3.1, it is clear that all the samples of polymer alloys from PI/BA-a have only one glass transition temperature ( $T_g$ ) from both loss modulus ( $E''$ ) and  $\tan\delta$  maxima. The  $T_g$  shifted to higher temperature as PI content increased.



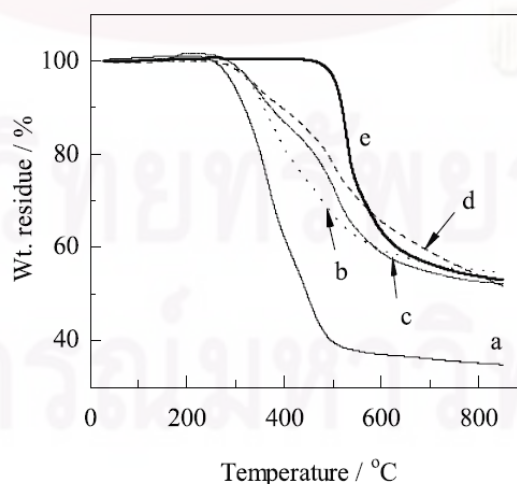
**Figure 3.1:** Loss modulus ( $E''$ ) and  $\tan \delta$  of PI/B-a films with various ratios.

The stress-strain curves for PI/BA-a films are shown in Figure 3.2. The tensile properties of the PI/BA-a films confirmed that the polyBA-a enhanced the modulus of PI, while PI improved the toughness of polyBA-a.



**Figure 3.2:** Tensile properties of PI/BA-a films after cured at 240 °C/2 h with PI/BA-a ratio of 100/0 (a), 50/50 (b), 30/70 (c), 10/90 (d), and 0/100 (e).

The thermal stabilities of polymer alloy films from PI/BA-a were investigated by thermogravimetric analysis (TGA), and shown in Figure 3.3. The initial decomposition temperatures (defined at 5 and 10% weight loss) of the polymer alloys from PI/BA-a increased obviously with the increase of PI content due to higher thermal stability of PI than that of polyB-a. They also notice that char yield increased by the addition of only small amount of PI. These polymers have good thermal stability.

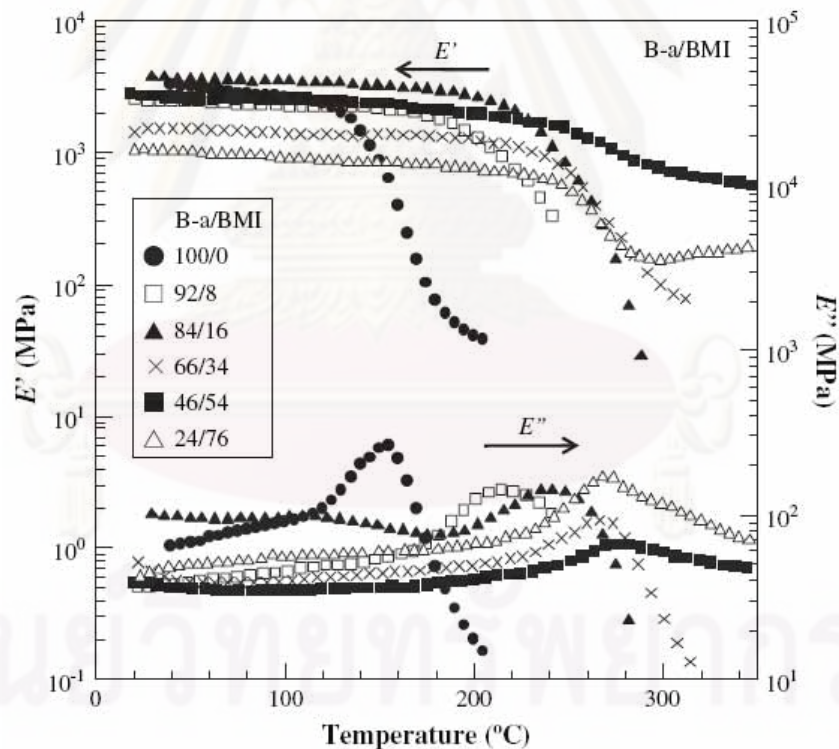


**Figure 3.3:** TGA of PI/BA-a films with PI/BA-a ratio of 0/100 (a), 10/90 (b), 30/70 (c), 50/50 (d), and 100/0 (e).

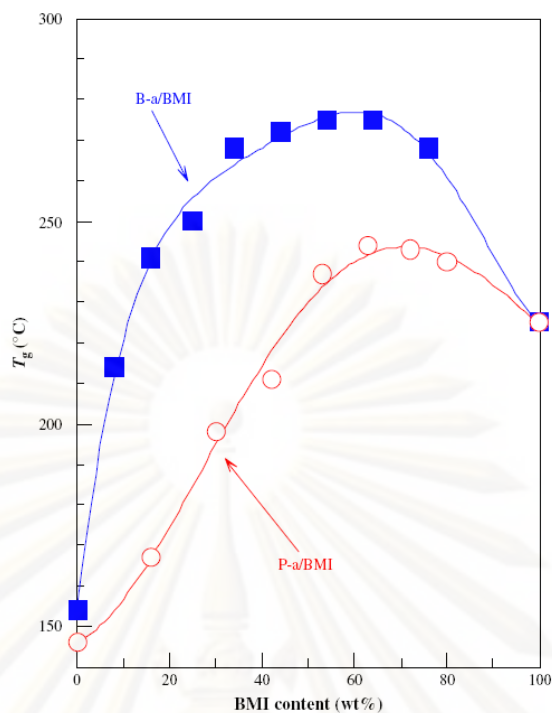
**T. Takeichi, Y. Saito, T. Agag, H. Muto, and T. Kawauchi, 2008 [44]**

Polymer alloys were prepared by blending bismaleimide (BMI) and benzoxazine followed by heat treatment. The obtained alloy films had improved toughness than the neat benzoxazine films and the toughness of alloy films increased with the increase of BMI content.

The viscoelastic properties of benzoxazine/BMI alloys were studied using dynamic mechanical analysis (DMA). The temperature dependence of the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of neat polybenzoxazines and the polymer alloys are shown in Figure 3.4. The  $T_g$  estimated from the maximum of  $E''$  is summarized in Table 3.1 and the shift of glass transition temperature ( $T_g$ ) against BMI content is plotted in Figure 3.5.



**Figure 3.4:** Viscoelastic analysis of B-a/BMI polymer.

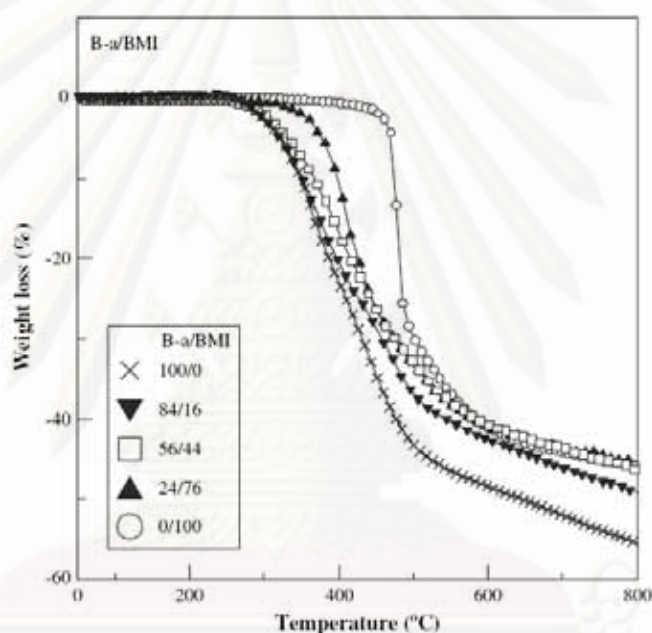


**Figure 3.5:** Influence of BMI content on Tg (from E'') alloys at various ratios.

**Table 3.1:** Thermal properties of benzoxazine/BMI polymer alloy.

Benzoxazine	BMI Content (wt%)	Softening Temperature (°C)	DMA Tg from E'' (°C)	TGA T <sub>5</sub> (°C)	TGA T <sub>10</sub> (°C)	TGA Char yield at 800 (°C) %
<b>BA-a</b>	0	172	154	310	338	45
	8	213	214	315	342	47
	16	231	241	321	351	50
	25	248	250	327	360	51
	34	262	268	332	366	52
	44	254	272	333	367	53
	54	-	275	338	366	57
	64	-	275	351	379	57
	76	-	268	380	399	55
	87	-	-	428	435	53
-	100	222	222	477	482	51

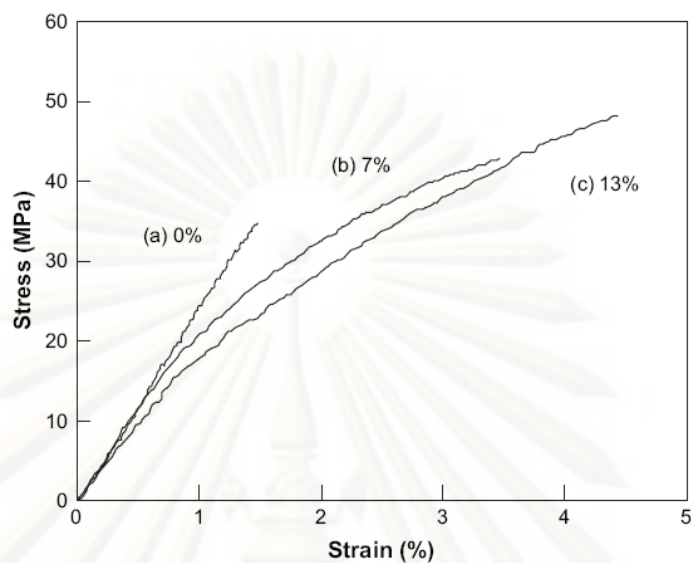
The thermal stability of the polymer alloys were investigated by thermogravimetric analysis (TGA). The TGA profiles of alloys blended at various ratios are shown in Figure 3.6. The values of 5 and 10% weight loss temperatures ( $T_5$  and  $T_{10}$ ) and the char yield at 800 °C are shown in Table 3.1. The  $T_5$  and  $T_{10}$  gradually shifted to higher temperature with the increase of BMI content, indicating that the addition of BMI was effective for the improvement of the thermal stability of polybenzoxazine. Furthermore, the char yield of the polymer alloys increased when compared to the homopolymers, showing that the flame retardancy is also improved by alloying.



**Figure 3.6:** TGA curves of BA-a/BMI polymer alloys at various ratios.

**H. Ardhyananta, M. H. Wahid, M. Sasaki, T. Kawauchi, H. Ismail, and T. Takeichi, 2008** [45] The tensile properties of the hybrid films were examined. The Figure 3.7 shows stress–strain curves of various PBA-a–PDMS hybrid films and the results are summarized in Table 3.2. Pristine polybenzoxazine (PBA-a) possesses high modulus, but low elongation at break, corresponding to the brittleness of the film. As the content of polydimethylsiloxane (PDMS) increases, tensile modulus slightly decreases but tensile strength and elongation at break increase, clearly showing that the in situ formed PDMS acts as a toughener. Moreover, homogeneous hybrid films were obtained up to 13 wt% PDMS content and the flexibility increased with the

increase of PDMS content (Figure 3.8). However, at ca. 25 wt% PDMS content, macroscopic phase separation occurred and the film became brittle.



**Figure 3.7:** Stress–strain curves of pristine PBA, and PBA–PDMS hybrids at 7 (b) and 13 wt%.



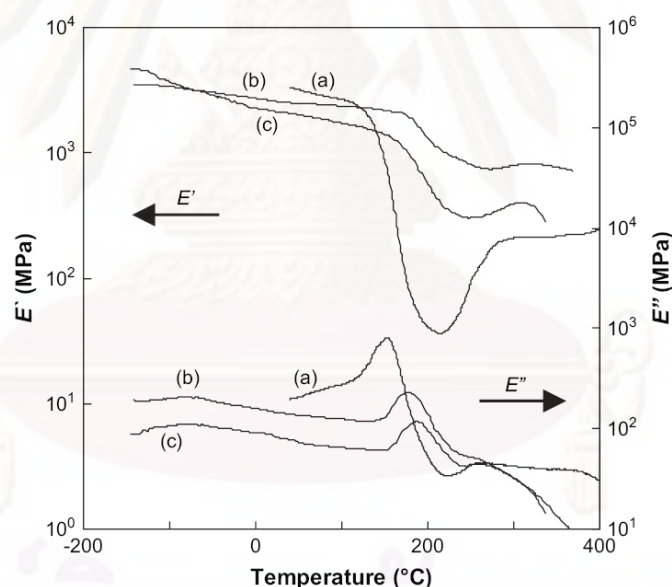
**Figure 3.8:** Photographs of pristine PBA-a (a) and PBA-a–PDMS hybrids prepared by sol–gel method at 7 (b), 13 (c) and 25 wt% (d) PDMS contents.



**Table 3.2:** Tensile properties of PBA-a and PBA-a–PDMS hybrids.

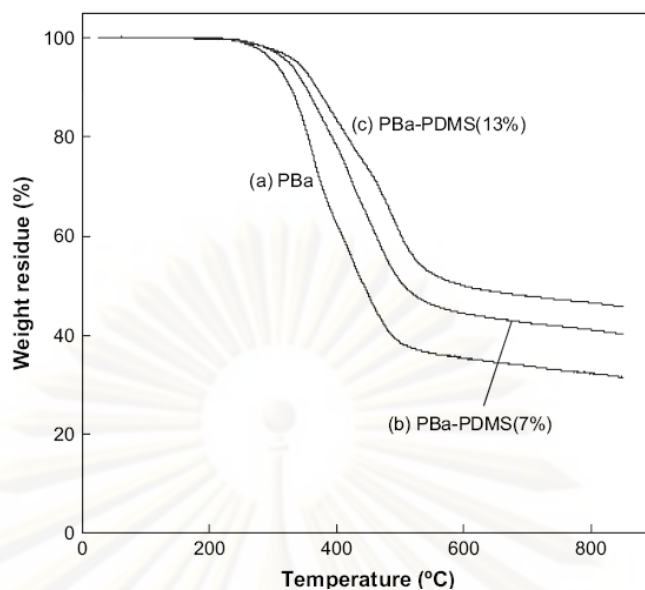
Code	PMDS Content (wt%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
<b>PBA-a</b>	0	$3.3 \pm 0.16$	$35 \pm 2.12$	$1.5 \pm 0.33$
<b>PBA-a-PDMS(7%)</b>	7	$2.6 \pm 0.15$	$42 \pm 1.58$	$3.5 \pm 0.23$
<b>PBA-a-PDMS(14%)</b>	13	$2.2 \pm 0.13$	$48 \pm 1.62$	$4.4 \pm 0.17$

Viscoelastic properties of PBA-a–PDMS hybrids were investigated by DMA. The storage modulus ( $E'$ ) and loss modulus ( $E''$ ) are plotted in Figure 3.9 and the results are summarized in Table 3.2. Tg of benzoxazine resin (Ba) component shifts to higher temperature with the increase of PDMS content. These results suggest that crosslink density of PBa increased by the addition of PDMS.



**Figure 3.9:** DMA of pristine PBA, and PBA–PDMS hybrids at 7 (b) and 13 wt% of PDMS.

Thermogravimetric analysis (TGA) of the hybrids was examined (Figure 3.10). The 5 and 10% weight loss temperatures increased with increasing PDMS content. Moreover, the weight residue at 850 °C of hybrids increased with the increase of the PDMS content, indicating that the flame retardancy is also improved.



**Figure 3.10:** TGA curves of pristine PBa (a), PBa–PDMS hybrids with 7 (b) and 13 wt% (c) of PDMS content under argon atmosphere at a heating rate 5 °C/min.

**T. Grubb, V. Ulery, T. Smith, G. Tullos, H. Yagci, L. Mathias, M. Langsam, 1999** [46] Polyimide has been synthesized from various aromatic tetracarboxylic dianhydrides and sterically hindered diamines in 1-methyl-2-pyrrolidinone (NMP). The thermal properties of polyimide were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods, are listed in Table 3.3. The glass transition temperature ( $T_g$ ) of the polyimides decreased with decreasing rigidity of the dianhydride in the order pyromellitic dianhydride (PMDA) > 3,3',4,4'–biphenyltetracarboxylic dianhydride (S-BPDA) > 3,3',4,4'–benzophenonetetracarboxylic dianhydride (BTDA), the values of 5 and 10% weight loss temperatures ( $T_5$  and  $T_{10}$ ) and the char yield at 800 °C as Table 3.3.

**Table 3.3:** Thermal properties of polyimides synthesized.

Dianhydride	$T_g$ (°C)	TGA 5% wt loss (°C)		Char yield at 1000 °C (%)
		Air	N <sub>2</sub>	
PMDA	373	422	504	58
S-BPDA	345	450	505	60
BTDA	300	415	503	53

**X. Zhao, Y. F. Li, S. J. Zhang, Y. shao, X. L. Wang, 2007** [47] studied polyimides that were prepared by polycondensation of 2-amino-5-[4-(40-aminophenoxy)phenyl]-thiazole (APPT) with various aromatic dianhydride, such as pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). It was observed from an Instron 1122. Tensile Apparatus with 100×5 mm specimens at drawing rate of 100 mm/min that polyimide based on APPT-BTDA had tensile strength of 105.4 MPa, elongations at breakage of 6%, and tensile modulus of 2.19 GPa as shown in Table 3.4, which indicated strong and tough materials but polyimide based on APPT-PMDA were brittle film because of rigidity structure of the polymer chains.

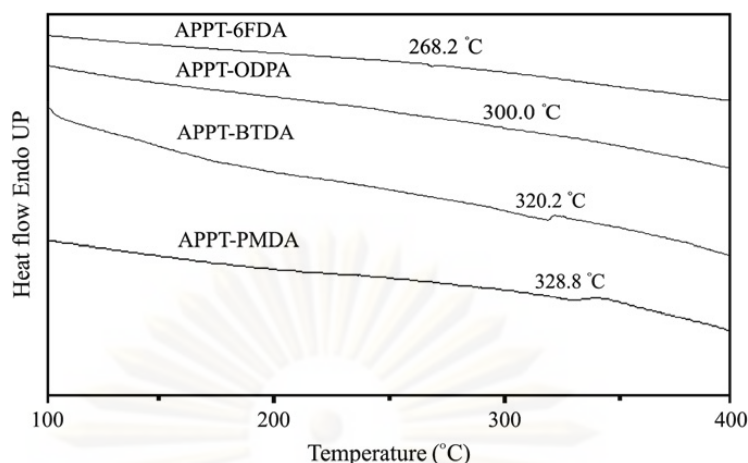
**Table 3.4:** Mechanical properties of the polyimides.

Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
APPT-BTDA	105.4	2.19	6

The thermal properties of the polyimides, which were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods, are listed in Table 3.5. DSC curves of the polyimides are shown in Figure 3.11. The experimental results indicate that APPT-PMDA have higher glass transition temperature than APPT-BTDA by dint of the structure of the dianhydride component.

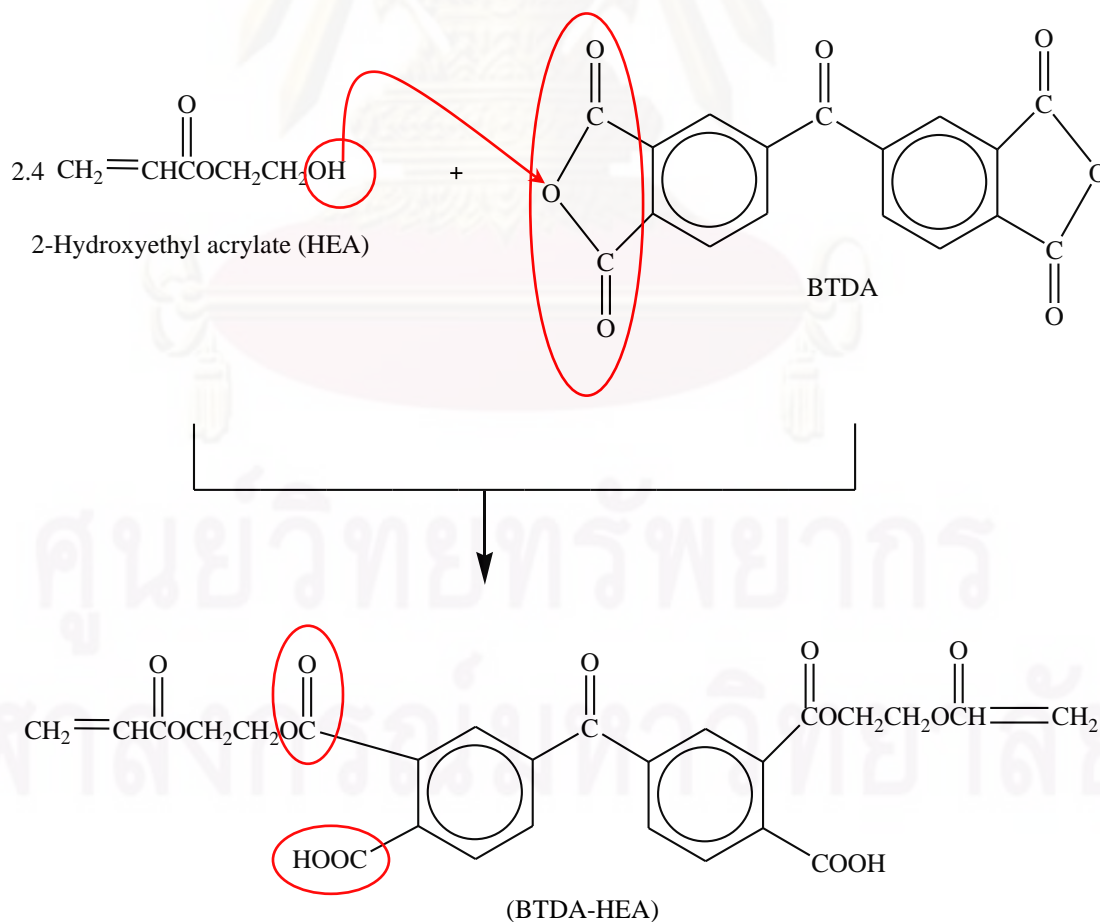
**Table 3.5:** Data of thermal analysis of the polyimides.

Polymer		T <sub>g</sub> <sup>a</sup> (°C)		In N <sub>2</sub> <sup>b</sup> (°C)		In air <sup>b</sup> (°C)	Char yield <sup>c</sup> (%)
T <sub>5</sub>	T <sub>10</sub>	T <sub>5</sub>	T <sub>10</sub>	T <sub>5</sub>	T <sub>10</sub>		
APPT-BTDA		320.2	489	523	439	482	59.31
APPT-PMDA		328.8	507	548	458	499	63.33



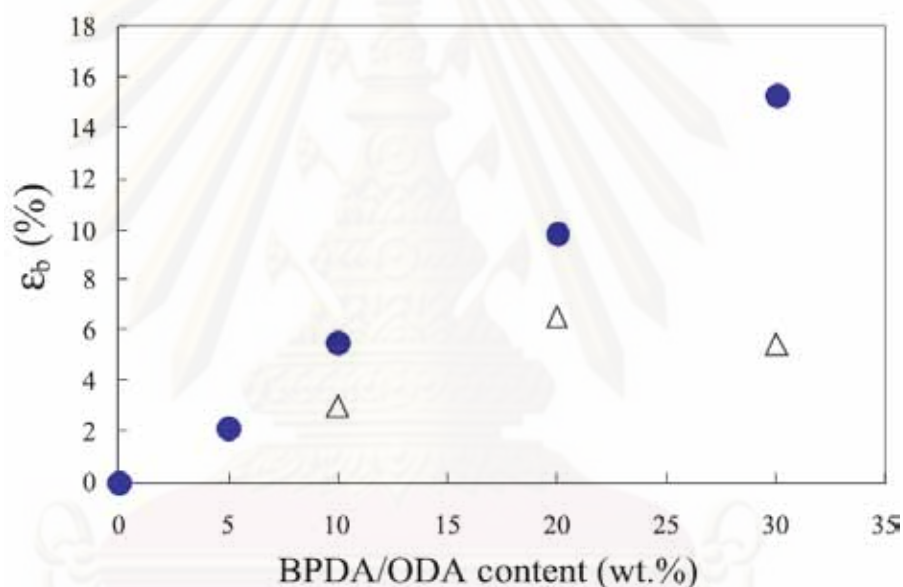
**Figure 3.11:** DSC thermograms of PIs at heating rate of 20 °C/min in nitrogen.

**W.Chiang and S.Chan, 1991** [48] Figure 3.12 summarizes the synthesis reaction of hydroxyethyl acrylate (HEA) and benzo- phenone tetracarboxylic dianhydride (BTDA). The half ester intermediate (BTDA-HEA) with pendant acid group was the addition reaction product of benzo- phenone tetracarboxylic dianhydride ( BTDA) and hydroxyethyl acrylate (HEA) with the molar ratio of 1 : 2 : 4.



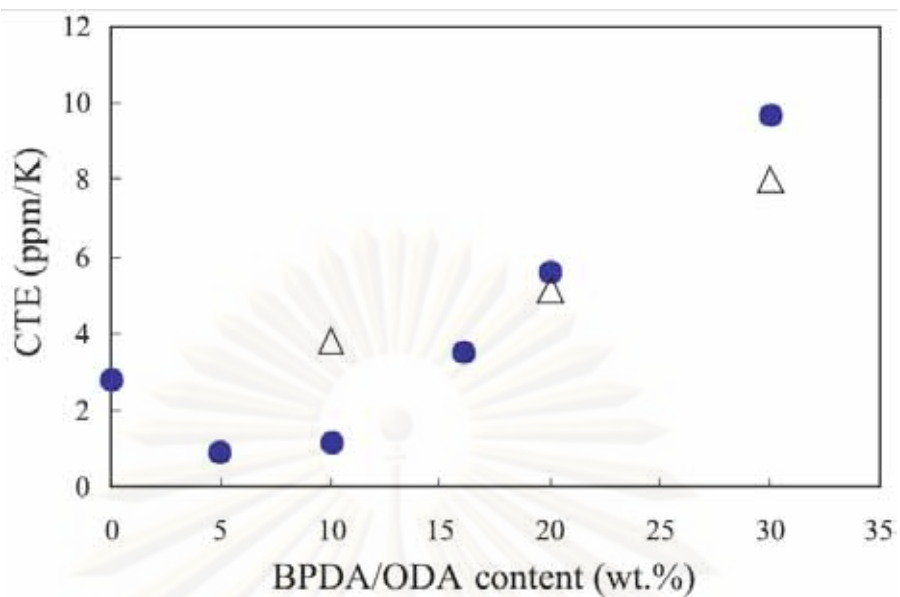
**Figure 3.12:** Syntheses of HEA and BTDA.

N. Sensui, J. Ishii, A. Takata, Y. Oami, and M.Hasegawa, 2008 [49]. This is revealed that the pyromellitic dianhydride(PMDA)-p-phenylenediamine(PDA)/2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA)-4,4'-oxydianiline (ODA) blend system was miscible over the whole blend compositions, whereas the PMDA-PDA/3,3',4,4' -biphenyltetracarboxylic dianhydride(s-BPDA)-ODA blend system was essentially immiscible. a-BPDA-ODA as a flexible component was much more effective than s-BPDA/ODA in reducing the crystallinity of PMDA/PDA. Consequently, it was also much more effective to significantly improve the film toughness of originally very brittle PMDA/PDA as shown in Figure 3.13.



**Figure 3.13:** Influences of blending of a-BPDA (●) or s-BPDA (△) into PMDA-PDA on the elongation break ( $\epsilon_b$ ).

Blending of only small amounts of a-BPDA/ODA (5–10 wt.%) into PMDA/PDA caused an unexpected further decrease in an originally ultra-low coefficient of thermal expansion (CTE,  $2.8 \text{ ppm K}^{-1}$ ) of homo PMDA/PDA film as seen Figure 3.14. PMDA-PDA90/a-BPDA-ODA10 blend system achieved an ultra-low CTE of  $0.9 \text{ ppm K}^{-1}$  in addition to sufficient film flexibility.



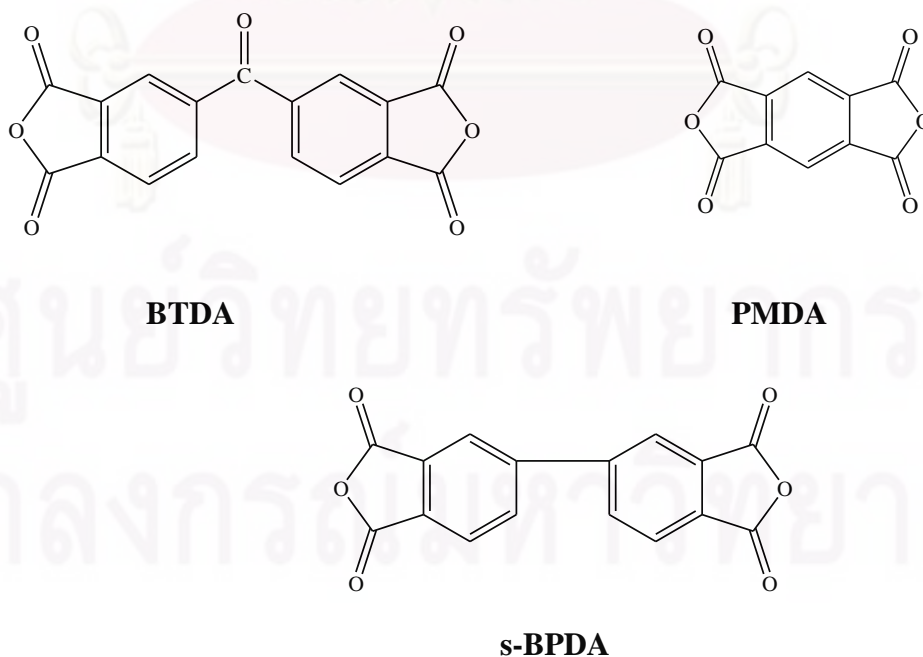
**Figure 3.14:** Influences of blending of a-BPDA (●) or s-BPDA (△) into PMDA-PDA on low coefficient of thermal expansion (CTE).

## CHAPTER IV

### EXPERIMENTAL

#### 4.1. Raw Materials

Materials used in this research are benzoxazine resin, dianhydrides, 1-Methyl-2-Pyrrolidone (NMP) as solvent, and releasing agent. Benzoxazine resin is based on bisphenol-A, aniline and formaldehyde. The bisphenol-A (polycarbonate grade) was supported by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Panreac Quimica S.A. Company. Dianhydrides have three types i.e. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA; 96%) was supplied by Aldrich, 1,2,4,5-Benzenetetracarboxylic anhydride (PMDA ; 99%) purchased from Acros organics, and 3,3',4,4' -biphenyltetracarboxylic dianhydride (s-BPDA) was obtained from JAXA, Japan (Prof. R. Yokota). Finally, 1-Methyl-2-Pyrrolidone (NMP) solvent purchased from Fluka Chemical Co, and releasing agent was used as-received from Huntsman.



**Figure 4.1:** Chemical structures of dianhydrides.

## 4.2 Resin Preparation

### 4.2.1 Benzoxazine Resin Preparation

Benzoxazine resin (BA-a) was synthesized from bisphenol-A, paraformaldehyde, and aniline at mole ratios of 1:4:2. The mixture was heated to 110°C in an aluminum pan and was mixed until a homogeneous mixture was obtained for 30 min to yield a light yellow solid monomer product, according to the patented solventless method [17]. The resulting benzoxazine monomer is solid at room temperature with transparent yellow color. The as-synthesized monomer was ground into fine powder and taken for material characterization.

### 4.2.2 Preparation of Benzoxazine-Dianhydride Alloying Films

The benzoxazine monomer (BA-a) was blended with various mole ratios of Dianhydride (DA), i.e., BA-a/DA (1:0), BA-a/DA (4:1), BA-a/DA (3:1), BA-a/DA (2:1), BA-a/DA (1.5:1), and BA-a/DA (1:1). The mixture were dissolved in N-methyl-2-pyrrolidinone (NMP) and stirred at 80°C until the clear homogeneous mixture was obtained. The solution was cast onto teflon sheet and dried at room temperature for 24 h. Additional drying was carried out at 80 °C for 24 h. followed by thermal curing at 120 °C to 240 °C for 10 h to guarantee complete curing of the mixtures.

## 4.3 Characterization Methods

### 4.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectra of all samples under various curing conditions were acquired by using a Spectrum GX FT-IR spectrometer from Perkin Elmer with an ATR accessory at room temperature. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm<sup>-1</sup> and a spectral range of 4000-650 cm<sup>-1</sup>. For Dianhydrides before synthesis, a small amount of a powder sample was casted as thin film on a potassium bromide (KBr) window.



### 4.3.2 Differential Scanning Calorimetry (DSC)

The curing behavior and glass transition temperature of benzoxazine resin alloyed with dianhydrides at various mole ratios were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. All samples were put in aluminum pans with lids. The thermogram was obtained using a heating rate of 10°C/min from 30°C to 350°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min. The sample with a mass in a range of 8-10 mg was sealed in an aluminum pan with lid. The glass transition temperature was obtained from the temperature at half extrapolated tangents of the step transition midpoint.

### 4.3.3 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the dynamic mechanical properties. The dimension of specimens was  $6.8 \times 10 \times 0.1 \text{ mm}^3$  (W×L×T). The test was performed in a tension mode. In a temperature sweep experiment, a frequency of 1 Hz and a strain value of 0.1% were applied. The temperature was scanned from 30 °C to the temperature beyond the glass transition temperatures ( $T_g$ ) of each specimen with a heating rate of 2°C /min under nitrogen atmosphere. The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent or damping curve ( $\tan \delta$ ) were then obtained. The glass transition temperature ( $T_g$ ) was taken as the maximum point on the loss modulus curve in the DMA thermograms.

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#### 4.3.4 Thermogravimetric Analysis (TGA)

The degradation temperature ( $T_d$ ) and char yield of the benzoxazine-dianhydride alloys at various mole fractions of Dianhydrides were studied using a Diamond TG/DTA from Perkin Elmer Instrument Technology. The testing temperature program was ramped at a heating rate of 20°C/min from room temperature to 1000°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min. The sample mass used was measured to be approximately 8-15 mg. Weight loss of the samples was measured as a function of temperature. The degradation temperatures ( $T_d$ ) of BA-a/dianhydride polymeric alloys were reported at their 5% weight loss and char yields of the above specimens were also reported at 800°C.

#### 4.3.5 Universal Testing Machine (Tension Mode)

The tensile strength and tensile modulus of the BA-a/Dianhydride polymeric alloys were determined using a universal testing machine (model 5567) from Instron Co., Ltd. The test method was a tension mode and tested at a crosshead speed of 2 mm/min. The specimen gauge length was 2.0 cm. The dimension of the specimens is 5 cm in length, 1 cm in width, and about 100 microns in thickness. The tensile properties were determined based on ASTM D882 and according to the [7] using five specimens per test condition.

#### 4.3.6 Density Measurement

The densities of benzoxazine resin alloyed with Dianhydride were determined by water displacement method according to the ASTM D 792-00 (Method A). The dimension of specimens was in rectangular shape 20×20×0.1 mm<sup>3</sup> (L×W×T). All measurements were performed at room temperature. The density is calculated by a following equation:

$$\rho = \left( \frac{A}{A - B} \right) \times \rho_o \quad (4.1)$$

Where

$\rho$  = Density of a specimen, g/cm<sup>3</sup>

A = Weight of a specimen in air, g

B = Weight of a specimen in the auxiliary liquid, g

$\rho_0$  = Density of water at a given temperature, g/cm<sup>3</sup>

The average value from at least three specimens was calculated.



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## CHAPTER V

### RESULTS AND DISCUSSION

#### 5.1 Preparation of Polybenzoxazine-Dianhydride Alloying Films

Benzoxazine-dianhydride alloying films were produced by blending benzoxazine monomer with dianhydride in n-methyl-2-pyrrolidinone (NMP) at a given mole ratios. The solubility of BA-a: BTDA and BA-a: PMDA in NMP is greater than BA-a: s-BPDA because BA-a: BTDA and BA-a: PMDA were observed to require shorter dissolving time than BA-a: s-BPDA at same temperature. The cast films of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA resin mixtures were transparent light orange, transparent dark orange and transparent yellow in color, respectively. Thereafter, this cast films were air dried at 60°C and vacuum dried at 80°C to partially remove NMP, followed by gradual thermal cure at 120 – 240 °C for 10 hr.

After curing at elevated temperature up to 240°C, the color of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA films became transparent red brown, transparent dark brown, and transparent light brown, respectively, as shown in Figure 5.1. The obtained thickness of the films was about 100 µm. It was well known that polybenzoxazine (PBA-a) film was very brittle and could hardly be bent as shown in Figure 5.2a. Interestingly, all compositions of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films exhibited greatly improved flexibility compared to the neat PBA-a as can be seen in Figures 5.2-5.4.

#### 5.2 Fourier Transform Infrared Spectroscopy Investigation

FT-IR spectra of benzoxazine resin (BA-a) and polybenzoxazine (PBA-a) are shown in Figure 5.5a and Figure 5.5b, respectively. Characteristic absorption bands of the BA-a resin were found at 936 and 1228 cm<sup>-1</sup> both assigned to C-O-C stretching mode of oxazine ring (Figure 5.5a). As the curing phenomenon proceeded, an infinite

three dimensional network was formed from benzoxazine ring opening by the breakage of C-O bond and then the benzoxazine molecule transformed from a ring structure to a network structure. During this process, the tri-substituted benzene ring ( $1492\text{ cm}^{-1}$ ), backbone of benzoxazine ring became tetra-substituted benzene ring ( $1488\text{ cm}^{-1}$ ) which led to the formation of a phenolic hydroxyl group-based polybenzoxazine (PBA-a) structure as shown in Figure 5.5b. In addition, an indication of ring opening reaction of BA-a upon thermal treatment could also be observed from the appearance of a broad peak about  $3300\text{ cm}^{-1}$  which was assigned to the phenolic hydroxyl groups formation. The result evidently suggested that benzoxazine monomers (BA-a) thermally polymerized through a ring opening reaction to form the corresponding polybenzoxazine (PBA-a) and which rendered phenolic hydroxyl groups to be reacted with dianhydrides [43].

The chemical structures of benzoxazine resin, the dianhydride modifier and their network formation reactions were studied by FT-IR spectroscopic technique. The chemical transformation of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA at 1.5:1 mole ratio upon thermal curing were investigated by FT-IR and the resulting spectra are shown in Figures 5.6, 5.7, and 5.8, respectively. The important characteristic infrared absorptions of BA-a monomer structures were clearly observed again at  $936$  and  $1492\text{ cm}^{-1}$  due to the tri-substituted benzene ring and  $1228\text{ cm}^{-1}$  from the asymmetric stretching of C-O-C group [7, 12, 23, 45, 50, 53] as illustrated in Figures 5.6a, 5.7a, and 5.8a, respectively. On the other hand, BTDA [7], PMDA [52], and s-BPDA dianhydrides provided the strong carbonyl characteristic absorption peaks in the range of  $1770$ - $1784$  and  $1854$ - $1859\text{ cm}^{-1}$  as seen in Figures 5.6b, 5.7b, and 5.8b.

After fully cured stage, the BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA polymer alloys, at 1.5:1 mole ratios revealed the disappearance of the absorption peaks at  $936\text{ cm}^{-1}$  and the reduction of the  $1492\text{ cm}^{-1}$  bands, as shown in Figures 5.6c, 5.7c, 5.8c. Meanwhile, the new band at  $1488\text{ cm}^{-1}$ , which was ascribed to tetra-substituted benzene ring, was observed. These spectra indicated that the Mannich bridge linkage and phenolic hydroxyl groups were produced by the ring-opening polymerization of BA-a [7, 53-54]. According to the polymerization mechanism proposed by Dunkers and Ishida, this ring-opening polymerization of benzoxazine

(BA-a) was formed by the breaking a C-O bond of the oxazine ring and then the benzoxazine molecule transformed from a ring structure to a three dimensional network structure [55-56].

For dianhydrides, the carbonyl stretching bands of anhydride in the range of 1770-1784 and 1854-1859  $\text{cm}^{-1}$  were found to shift to 1775-1779 and 1714-1723  $\text{cm}^{-1}$  upon thermal cure with the above benzoxazine monomers. The phenomenon was ascribed to the appearance of carbonyl stretching bands of aromatic ester [57]. The obtained FT-IR spectra suggested that the esterification reaction between the phenolic hydroxyl group of polybenzoxazine and the carboxylic carbonyl group of dianhydride could take place during the thermal curing. The proposed reaction model of these resin mixtures were shown in Figure 5.9-5.11 which were similar to the esterification of di-(2-ethylhexyl)phthalate and hydroxyl group of allyl alcohol [43] as well as reaction between BTDA dianhydride and hydroxyl group of 2-hydroxyethyl acrylate (HEA) [48].

For BTDA, the carbonyl between the two phenyl rings in BTDA did not participate in the network formation of hydrogen bonding due to no significant frequency shifts in the benzophenone carbonyl band was observed [58].

Moreover, this three dimensional network structure of ring-opening reaction of polybenzoxazine as well as the esterification reaction between benzoxazine and dianhydrides brought about an increase in crosslink density of the resulting alloys as well as improvement on thermal performance of the resulting films. These observations were discussed in the following sections.

### **5.3 Differential Scanning Calorimetry (DSC)**

The curing reaction of BA-a: BTDA at 1.5:1 mole ratio by differential scanning calorimetry using a heating rate of 10  $^{\circ}\text{C}/\text{min}$  under nitrogen flow at a temperature range of 30-350  $^{\circ}\text{C}$  is shown in Figure 5.12. From the DSC thermograms, after vacuum drying at 80 $^{\circ}\text{C}$ , the BA-a: BTDA alloying film showed endothermic peak at 200 $^{\circ}\text{C}$  which corresponded to boiling point of NMP solvent (Bp. = 202 $^{\circ}\text{C}$ ). This endothermic peak decreased with the increase of heat treatment temperature, and

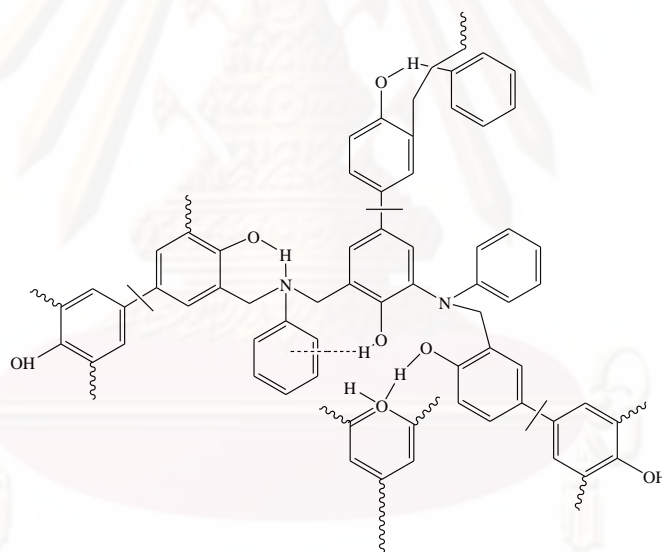
completely disappeared after 150°C heat treatment. This implied that the NMP was completely removed from the BA-a: BTDA alloying film at this heat treatment stage.

Furthermore, the BA-a: BTDA alloying films possessed an exothermic peak at 242°C, and the area under the exothermic peak was observed to decrease as the cure temperature increased, and completely disappeared after the cure temperature at 240°C. This suggested that the fully cured stage was achieved at up to 240°C heat treatment.

Other thermal properties of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films were also evaluated from differential scanning calorimetry (DSC) using a heating rate of 10°C/min at a temperature range of 30-350 °C. The results from DSC experiments on BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films at various mole ratios (i.e., 1:1, 1.5:1, 2:1, 3:1, 4:1, and 1:0) are shown in Figure 5.13-5.15, respectively and the numerical results are also summarized in Table 5.1.

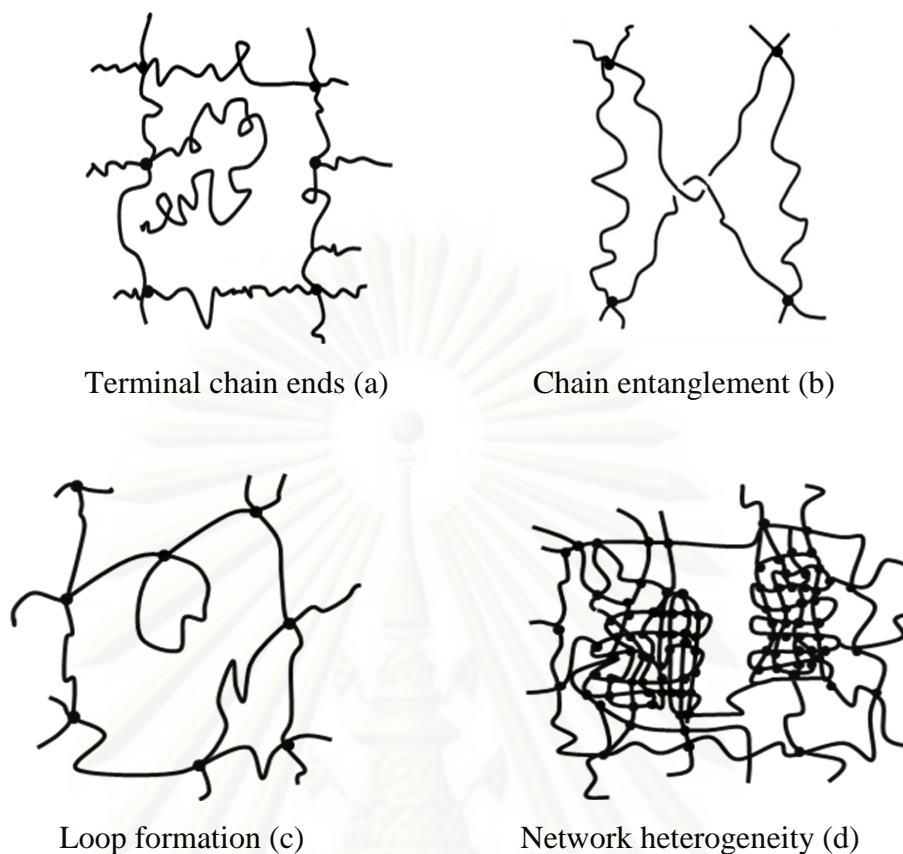
Figures 5.13-5.15 provided the glass transition temperatures ( $T_g$ ) of the neat polybenzoxazine (PBA-a) and the cured BA-a: dianhydride alloys at various mole ratios. From the thermograms, the glass transition temperature of the neat PBA-a was determined to be 163 °C and those of the cured BA-a: BTDA alloys, BA-a: PMDA alloys and BA-a: s-BPDA alloys were in the range of 191- 239°C (Figure 5.13), 178-306°C (Figure 5.14), and 170–257°C (Figure 5.15), respectively. The glass transition temperature ( $T_g$ ) values of benzoxazine alloying with BTDA, PMDA or s-BPDA dianhydrides were found to be much higher than the neat PBA-a and were found to increase with the amount of the dianhydride modifiers up to about 1.5:1 mole ratio. The obtained high  $T_g$  value of BA-a: dianhydride alloys might attribute to the improved crosslink structure and their high aromatic content from the presence of dianhydrides in the polymer network [59]. The crosslink structure resulted from esterification reaction between polybenzoxazine and dianhydrides was observed by FT-IR. Furthermore, BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films consistently showed a maximum  $T_g$  at the composition of 1.5:1 mole ratio. In addition, the  $T_g$  values of the cured BA-a: dianhydride alloying films at up to 1:1

mole ratio were found to be lower than at 1.5:1 mole ratio. This was possibly due to an excess of the dianhydrides in the polymer alloys thus causing the network defects such as dangling ends, in the cured BA-a:dianhydride. The possible network defects in thermosets might be terminal chain ends (a), chain entanglement (b), loop formation (c), and network heterogeneity (d) as shown in Figure 5.32 [60-61]. The formation and network defects such as dangling or terminal chain ends above could lower crosslink density of the network which led to lower T<sub>g</sub> of the sample. The chloroform extraction of all alloy samples up to 1:1 mole ratio revealed no weight change in those materials. This suggested no free dianhydride was presented in these alloys up to 1:1 mole ratio, however, it was expected that greater amount of the anhydride i.e. more than 1:1 mole ratio, might cause the mass loss from the above solvent extraction due to free anhydride presented in the specimen.



**Figure 5.32:** Hydrogen-bonded network structure for polybenzoxazine (PBA-a) [62].





**Figure 5.33:** Possible network defects in thermosetting polymers [60-61].

Moreover, the ultimate Tg values of BA-a: PMDA (i.e. 306 °C) > BA-a: s-BPDA (i.e. 257 °C) > BA-a: BTDA (i.e. 239 °C) were observed at 1.5:1 mole ratio as depicted in Figure 5.16. These Tg values showed a similar trend as that found in polyimides derived from i.e. PMDA > s-BPDA > BTDA [63-68]. This observation implied that the Tg values were also dependent on the structure of the dianhydride components used. The stiffness/bulkiness of these dianhydride moieties were as follows: PMDA > s-BPDA > BTDA [69]. Thus the stiffer the dianhydride, the larger the Tg of the alloy obtained. At 1.5:1 mole ratio, the BA-a: PMDA had the highest Tg due to the most rigid polymer chains of this dianhydride compared with the other two.

#### 5.4 Dynamic Mechanical Properties (DMA)

Dynamic mechanical analysis (DMA) is useful to investigate thermomechanical properties of polymeric materials, especially the transitions and relaxations of the materials. Knowledge of the transitions and relaxations of the materials will lead to an understanding of how materials behave at different

temperature and to an identification of a suitable service temperature. The change in molecular mobility of the specimen when temperature changed was conveniently investigated by dynamic mechanical analysis.

In this section, dynamic mechanic properties of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films at various mole ratios (i.e., 1:1, 1.5:1, 2:1, 3:1, 4:1, and 1:0) were evaluated and the thermograms are shown in Figure 5.17-5.23 as well as Table 5.2.

Generally, the storage modulus of the materials demonstrated the deformation resistances of material when external force were applied sinusoidally. The storage moduli at room temperature (35°C) of the BA-a: dianhydride alloying systems at various anhydride contents exhibited the values in the range of 2.63-3.4 GPa were higher than that of the neat PBA-a of 2.57 GPa as shown in Table 5.2. This might be due to higher crosslink density and greater aromatic content of the polymer alloys with a greater amount of the dianhydride. In addition, the storage modulus of the BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films showed a maximum value at an alloy composition of 1.5:1 mole ratio. The anhydride content greater than this ratio would result in the formation of network defects such as dangling chains ends as discussed previously thus lower the modulus of the polymer alloys. However, a type of dianhydride was found to show no significant effect on the modulus values of the alloys.

The effects of polybenzoxazine-dianhydride contents on the rubbery plateau modulus of their polymer alloys are shown in Table 5.2. The storage modulus in the rubbery plateau region tended to increase with the content of the three dianhydrides (BTDA, PMDA, and s-BPDA) with the ultimate values observed again at 1.5:1 mole ratio.

According to crosslink density of polymer network, the value can be estimated by equation (1) derived from the statistical theory of rubber elasticity by Nielson [59].

$$\log\left(\frac{E'}{3}\right) = 7.0 + 293(\rho_x) \quad (1)$$

Where  $E'$  is a storage modulus in a rubbery plateau region.

$\rho_x$  is crosslink density of the specimen.

The crosslink density of PBA-a and its polymer alloys calculated from equation (1) are shown in Figure 5.20-5.22 and Table 5.2. We can see clearly that the crosslink density of the neat PBA-a was enhanced by an addition of BTDA or PMDA or s-BPDA dianhydrides, which was in the same trend as an enhancement in their  $T_g$  values by an addition of all three dianhydrides.

Figure 5.17-5.19 displays the plot of loss modulus as a function of temperature of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films, respectively at various mole ratios. The glass transition temperature or  $T_g$  of each specimen was taken at the maximum point on the loss modulus curves. From Figures 5.17-5.19, and Table 5.2, polybenzoxazine and its alloys showed only single glass transition temperature. The glass transition temperature ( $T_g$ ) value of the neat PBA-a was determined to be about 178°C and those of dianhydride-polybenzoxazine alloying films were found to be in the range of 184-296 °C. This result suggested all compositions of BA-a: dianhydride alloying films was homogeneous and no phase separation occurred in these polymer alloys. The glass transition temperature ( $T_g$ ) value of the neat PBA-a was clearly enhanced by alloying with the BTDA or PMDA or s-BPDA dianhydrides. This can be owing to enhanced crosslink density partly via esterification reaction between phenolic hydroxyl groups of polybenzoxazine and dianhydrides as depicted in FT-IR spectra [59] as well as a greater amount of aromatic content from the dianhydride addition. The BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films showed a maximum behavior in  $T_g$  at a composition of 1.5:1 mole ratio. This was probably due to an ability of the benzoxazine monomers to react with each other besides their ability to react with carboxylic groups of the dianhydrides via esterification reaction. Therefore, benzoxazine monomers were expectedly consumed more than dianhydrides. In addition, the ultimate  $T_g$  values of BA-a: PMDA (i.e. 296°C) > BA-a: s-BPDA (i.e. 266 °C) > BA-a: BTDA (i.e. 263 °C)

were observed as shown in Figure 5.23. The Tg values tended to depend on the structure of the dianhydride components used as we can see that the BA-a: PMDA had the highest Tg due to the presence of most rigid phenyl unit compared with the other two [64-66].

Moreover, we could see that a higher crosslink density of the obtained alloys provided a greater storage modulus and glass transition temperature (Tg) of the alloy specimens.

The effect of a crosslinked density on Tg of polymer network can be accounted for using the Fox-Loshaek equation (2) [70].

$$Tg = Tg(\infty) - \frac{k}{M_n} + k_x \rho_x \quad (2)$$

Where  $Tg(\infty)$  is the glass transition temperature of infinite molecular weight linear polymer.

$k$  and  $k_x$  are the numerical constants.

$M_n$  is the number averaged molecular weight which equals infinity in the cross-linked system, therefore, this term can be neglected.

$\rho_x$  is the crosslinked density.

According to the Fox-Loshaek equation, the cross-linked density is one key parameter affecting Tg of the polymer networks. Figures 5.20-5.22 illustrate Tg and cross-linked density of BA-a: Dianhydride alloys at various mole ratios. As seen from this figure, the Tg of the polymer network increased when its cross-linked density increased, which was in excellent agreement with our DMA results.

Moreover, it can be noticed that the glass transition temperatures observed from DMA thermograms exhibited an optimum value at the alloy composition of 1.5:1 as those obtained by DSC experiment of Figure 5.16.

### 5.5 Thermogravimetric Analysis (TGA)

Thermogravimetry (TG) is a branch of thermal analysis which examines the mass change of a sample as a function of temperature. Thermal degradation of BA-a: dianhydride alloying films at various mole ratios, i.e., 1:1, 1.5:1, 2:1, 3:1, 4:1, and 1:0 was investigated by thermogravimetric analysis (TGA). The degradation temperature (Td) is one of the key parameters used to determine thermal stability of polymers.

The degradation temperature (Td) reported at 10 percent weight loss under nitrogen atmosphere of the BA-a: PMDA, BA-a: s-BPDA, and BA-a: BTDA alloying films was depicted in Figure 5.24-5.26, respectively and also summarized in Table 5.3. The Td of the neat polybenzoxazine (PBA-a) was determined to be 361°C. The Td of all ratios of BA-a: dianhydride alloying films were in the range of 373 to 426 °C. The Td values of all ratios of BA-a: dianhydrides were higher than that of the neat polybenzoxazine films (about 12 - 65°C). The Td value of neat polybenzoxazine films was observed to systematically increase with increasing dianhydrides contents. This is possibly due to the formation of poly (aromatic ester) which had higher thermal stability than the neat polybenzoxazine (i.e. reported Td ~ 320-400 °C [71-72]) and the enhanced crosslink density of the PBA-a with an addition of the dianhydrides via esterification reaction between the hydroxyl group of the polybenzoxazine and the carbonyl group of the dianhydrides as mentioned previously [73-74].

Moreover, interesting feature in the TGA thermograms was the amount of carbonized residue (char yield) at 800°C of the BA-a: PMDA, BA-a: s-BPDA, and BA-a: BTDA alloying films which was tested under nitrogen atmosphere as showed in Figure 5.24-5.26 and Table 5.3. The char yields of BA-a: PMDA, BA-a: s-BPDA, and BA-a: BTDA alloying films provided the values as high as 60 % at 800°C which was much greater than that of the neat PBA-a (i.e. 32.9 percent at 800°C). Furthermore, the maximum char yields of BA-a: PMDA, BA-a: s-BPDA, and BA-a: BTDA alloying films were also attained at 1.5:1 mole ratio of BA-a and the dianhydrides. The high char yield value of these dianhydride-modified polybenzoxazine can also be attributed to their greater aromatic content in the molecular structure and enhanced crosslinked density of the resulting polymer alloys.

In principle, the greater the char yield, the higher the flame retardancy of the polymer. Therefore, these polymer alloys tended to provide a sample with potentially substantial improvement in its flame retardancy which was highly useful in some applications.

In the report of Hongshen Li et al. [75], polyimide derived from 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene exhibited a char yield of 48.8 % at 800 °C under nitrogen atmosphere by comparison with other polyimides, which was attributed to the presence of high fluorine content in the polymer backbone. In our research, the high char yields of BA-a: PMDA, BA-a: s-BPDA, and BA-a: BTDA alloying films at 1.5:1 mole ratios did not require any presence of fluorine moieties in these alloys. It is expected that the flame retardancy of BA-a: dianhydride alloying films is at least as high as that of polyimide derived from similar dianhydrides [64-66, 75-76].

Char yield of the material can be applied as a decisive factor for estimating its limiting oxygen index (LOI) using Van Krevelen and Hoftyzer equation (3) [77-80].

$$\text{LOI} = 17.5 + 0.4 \text{ CR} \quad (3)$$

Where CR = char yield of the sample.

The dianhydride-polybenzoxazine alloying films provided theoretical LOI values, derived from their char yield, to be in the range of 38.3 to 42.4. These LOI values were significantly higher than that of the neat polybenzoxazine (i.e. 30.7). Furthermore, the LOI value also exhibited a maximum value at an alloy composition of 1.5:1 mole ratio of BA-a: dianhydride. As a result, these polymer alloys can be classified as self-extinguishing polymers which require LOI value to be at least 26.

### 5.1.6 Tensile Properties

Mechanical properties of materials are of great importance in engineering application. When a mechanical force is applied to a specimen, the deformation of the specimen is described in terms of its stress-strain behavior. The stress-strain behavior quantifies the stress (mechanical load) required to achieve a certain amount of strain (deformation). Tensile properties of polybenzoxazine-dianhydride alloying film at various mole ratios, i.e., 1:1, 1.5:1, 2:1, 3:1, 4:1, and 1:0 were investigated by a universal testing machine.

Figure 5.27 and Table 5.4 show tensile modulus as a function of dianhydride content. Tensile modulus at room temperature of the PBA-a: dianhydride alloying films exhibited the values in a range of 2.33-2.68 GPa at all of the tested compositions whereas that of the neat PBA-a was determined to be 2.09 GPa. Tensile modulus of the BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films were slightly higher than that of the neat PBA-a. In addition, the tensile modulus of the BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films showed a maximum value at an alloy composition of 1.5:1 mole ratio. It may possible be attributed to greater crosslink density which was calculated from DMA as mentioned formerly and increasing aromatic in structure of dianhydrides. The difference in the storage modulus ( $E'$ ) of the BA-a: s-BPDA, BA-a: PMDA, and BA-a: BTDA are not significant and the tendency is in good agreement with the results from DMA mentioned above.

Figure 5.28 and Table 5.4 exhibit tensile strength of the BA-a: dianhydride polymer alloys as a function of dianhydride contents. Tensile strengths of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA (4:1 to 1:1 mole ratios) alloying films were ranging from 70.1 MPa to 88.4 MPa, 70.8 MPa to 82.2 MPa, 62.4 MPa to 95.7 MPa, respectively. Tensile strength of PBA-a (i.e. 25 MPa) was found to greatly increase by alloying with BTDA or PMDA or s-BPDA dianhydrides. In addition, tensile strength of BA-a: dianhydride alloying films were observed to be about three times greater than that of the neat polybenzoxazine. This behavior was attributed to an enhancement in crosslink network density from additional esterification reaction between the phenolic hydroxyl group of polybenzoxazine and the carboxylic carbonyl

group of dianhydride and from a greater amount of rigid aromatic rings from an incorporation of the dianhydride in those alloys. Last but not least, the difference in the tensile strength of the three types of polymer alloys, i.e. BA-a: s-BPDA, BA-a: PMDA, and BA-a: BTDA, were insignificant.

Figure 5.29 and Table 5.4 showed elongation at break as a function of dianhydride mole ratio. Elongation at break of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films varied from 4.65% to 6.06%, 4.43% to 5.41%, and 4.16% to 5.35%, at the mole ratio of 4:1 to 1:1, respectively. Elongation at break of PBA-a (i.e. 1.97 percent) substantially increased by alloying with those dianhydrides and BA-a: dianhydrides alloying films was approximately two and a half time of the neat polybenzoxazine. The reason for this behavior would be explained by the formation of an ester group in the resulting network structure of the alloy which was confirmed by FT-IR. The ester group in our polymer alloy structure help improve flexibility of the obtained polymer alloys. The resulting poly (benzoxazine ester) also clearly rendered a hybrid network with higher elongation at break. However, an effect of types of dianhydride on the elongation at break of the polymer alloys was not significant.

The toughness of a specimen refers to the total amount of energy required to cause failure, that is, the total area under the stress-strain curve. The toughness of -a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films at 1.5:1 mole ratios depicted in Figure 5.30. Their toughness is much higher than that of the neat polybenzoxazine owing to the polymer alloys had a more flexible ester group in their structures. These films exhibited improvement on their thermal and mechanical integrity as well as higher flexibility which were highly unique characteristics for high performance applications. Finally, in significant difference was observed on the effect of different type of dianhydride on the alloy's toughness.



### 5.1.7 Density Measurement

In this study, the density measurement was determined based on water displacement principle (ASTM D792) for all specimens. The density of polybenzoxazine, BTDA, PMDA, s-BPDA are 1.19 g:cm<sup>3</sup> [1, 27], 1.57 [34], 1.68 [33], 1.625 [35], respectively.

$$\rho = \left( \frac{A}{A - B} \right) \times \rho_o \quad (3)$$

Where

$\rho$  = Density of a specimen, g/cm<sup>3</sup>

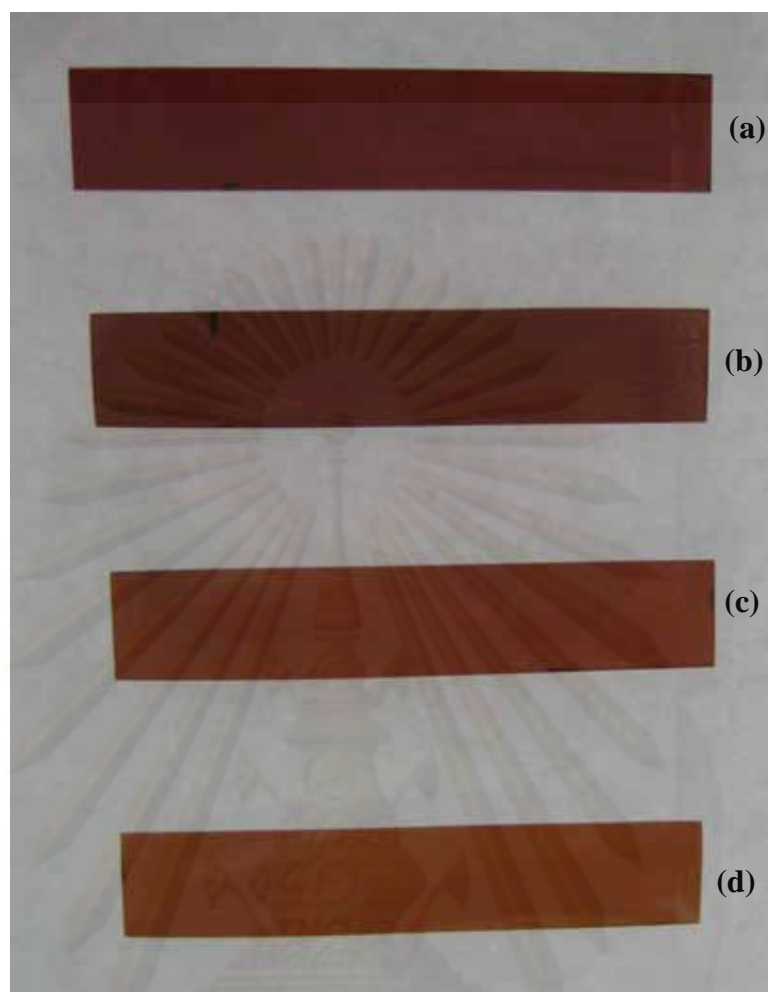
A = Weight of a specimen in air, g

B = Weight of a specimen in water, g

$\rho_o$  = Density of water at a given temperature, g/cm<sup>3</sup>

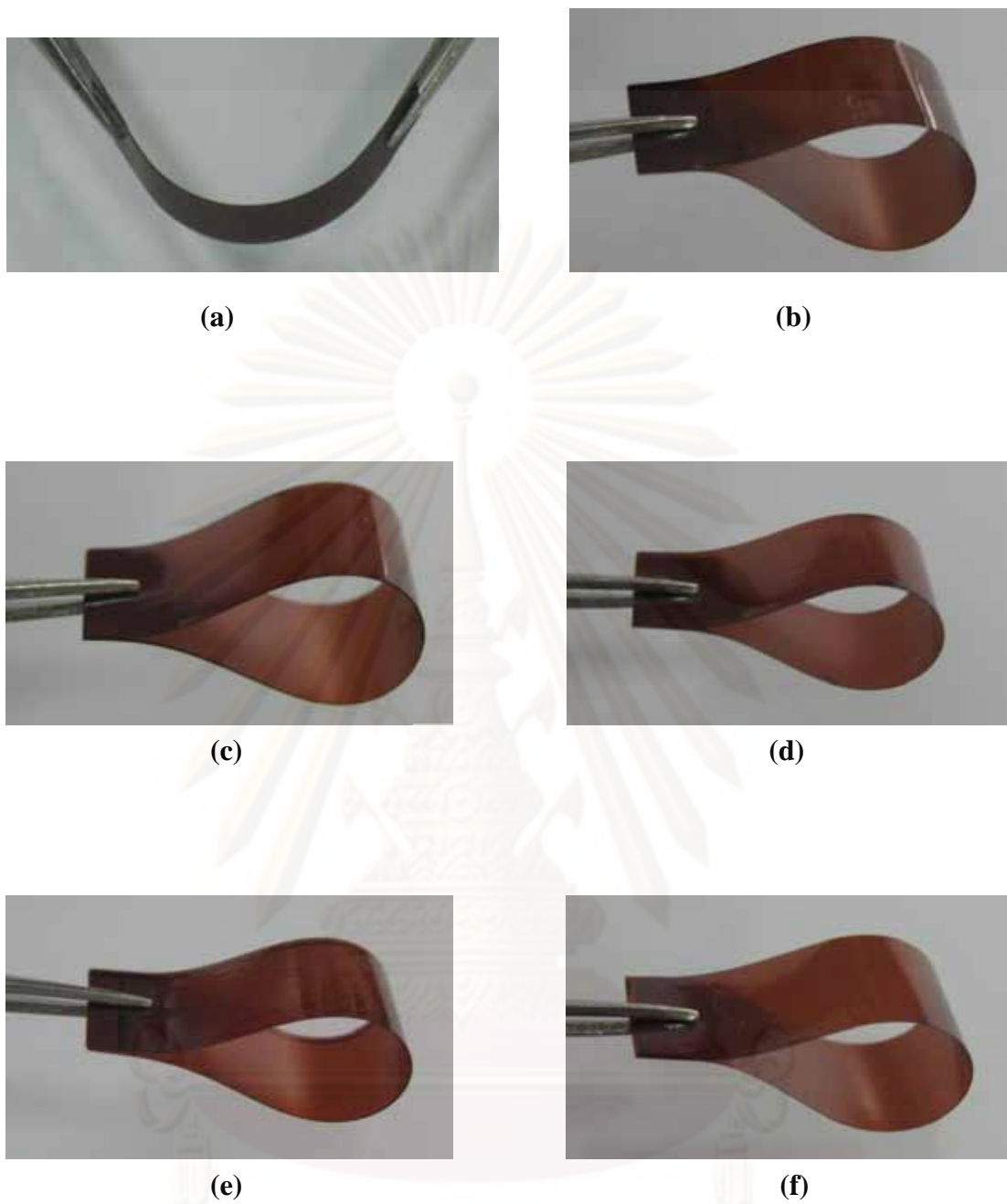
The averaged value from at least three specimens was calculated.

Figure 5.31 exhibits the density of all three types of polybenzoxazine-dianhydride alloying films at various mole ratios. From the obtained result, the density of all composition of BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA were ranging from 1.22 to 1.26 g/cm<sup>3</sup>, 1.23 to 1.28 g/cm<sup>3</sup>, 1.23 to 1.27 g/cm<sup>3</sup>, respectively. The densities of the polybenzoxazine-dianhydrides alloying films were observed to increase with increasing dianhydride content and they were between the neat polybenzoxazine and the pure dianhydrides.



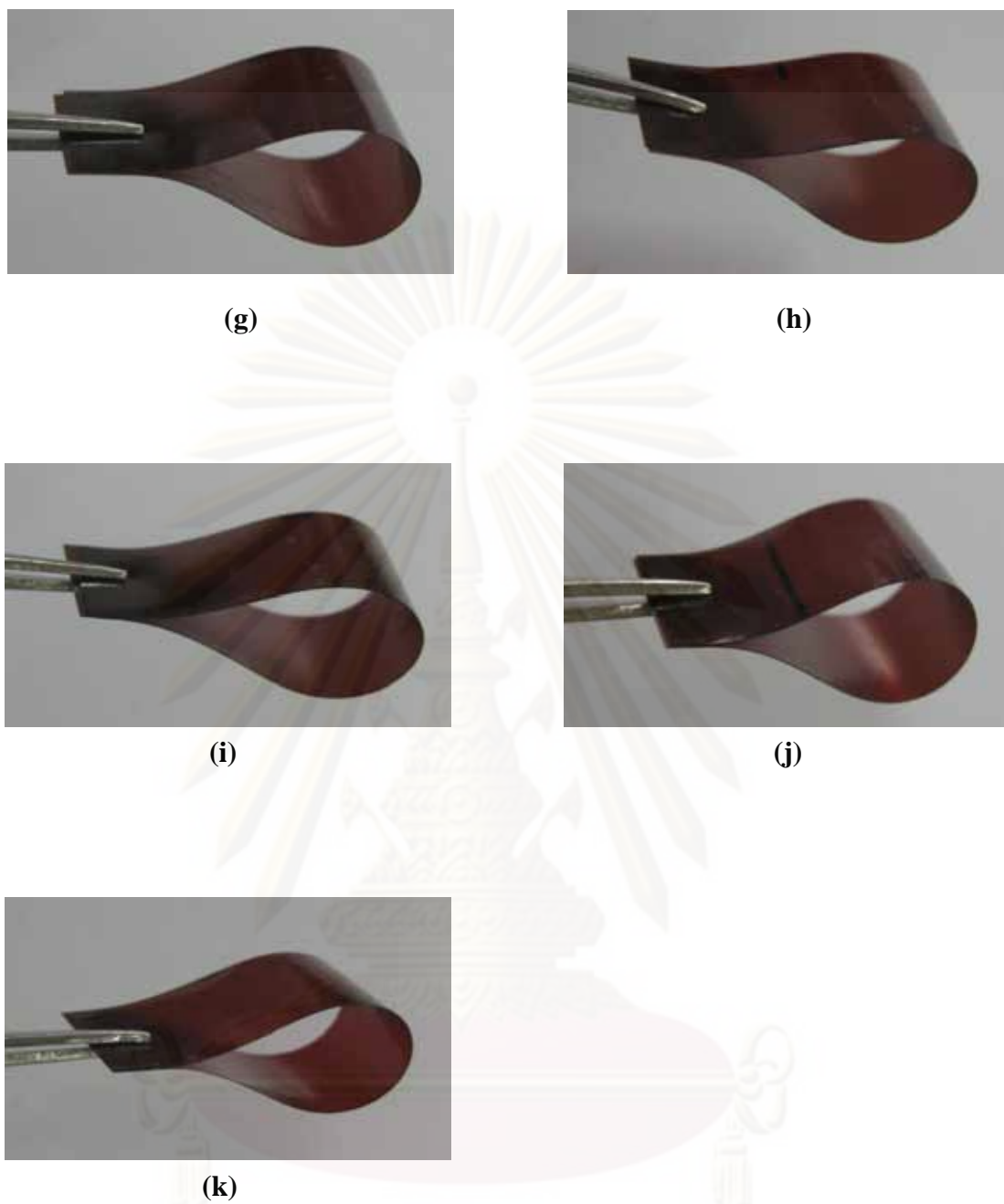
**Figure 5.1:** Photographs of neat PBA-a (a), BA-a/PMDA 1.5/1 mole ratio (b), BA-a/BTDA 1.5/1 mole ratio (C), BA-a/s-BPDA 1.5/1 mole ratio (d)  
; size ~ 0.1mm thick.

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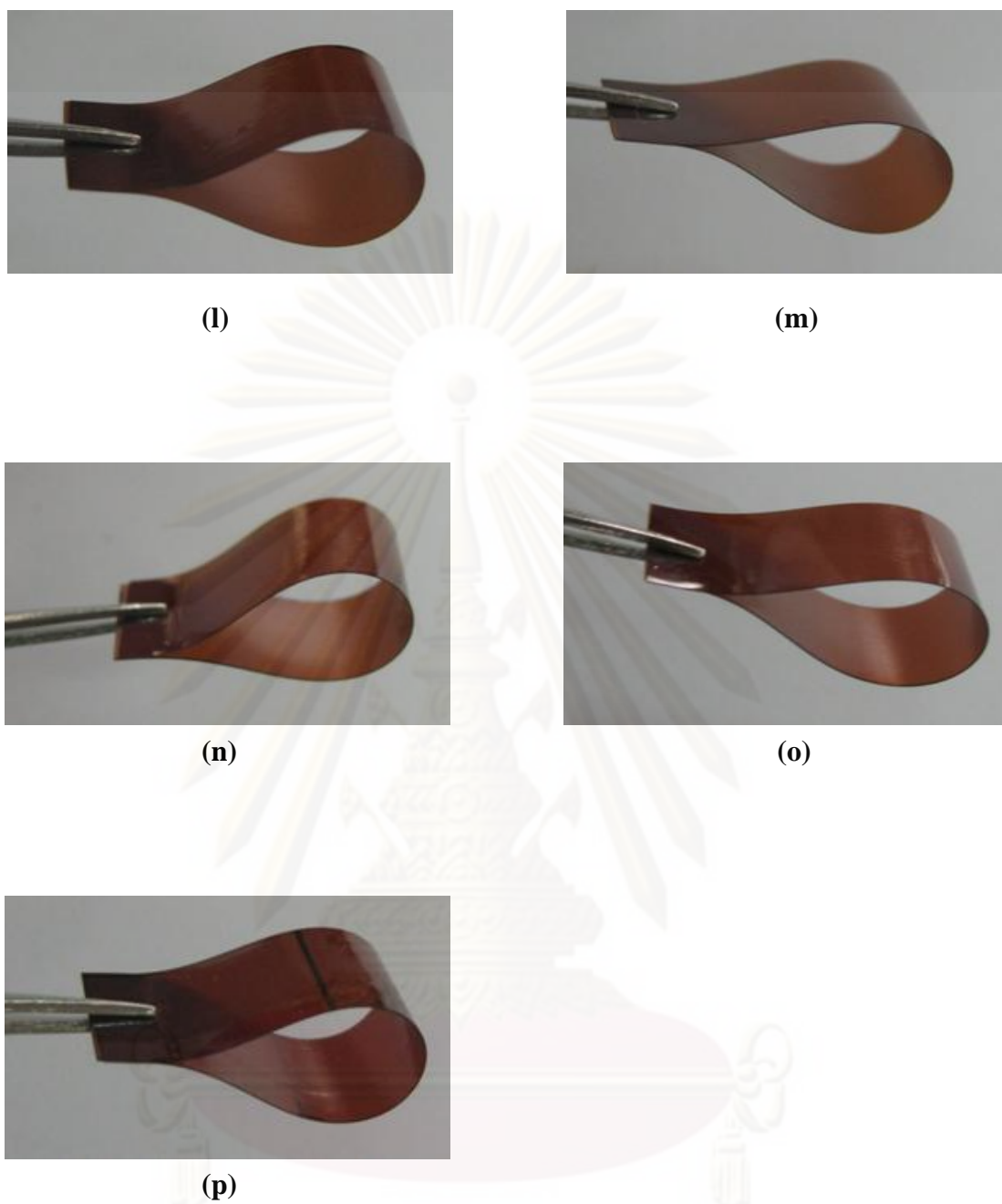


**Figure 5.2:** Photographs of Benzoxazine/BTDA alloying films at various mole ratios: PBA-a (a) BA-a/BTDA 1/1 (b), BA-a/BTDA 1.5/1 (c), BA-a/BTDA 2/1 (d), BA-a/BTDA 3/1 (e), BA-a/BTDA 4/1 (f); size ~ 0.1mm thick.

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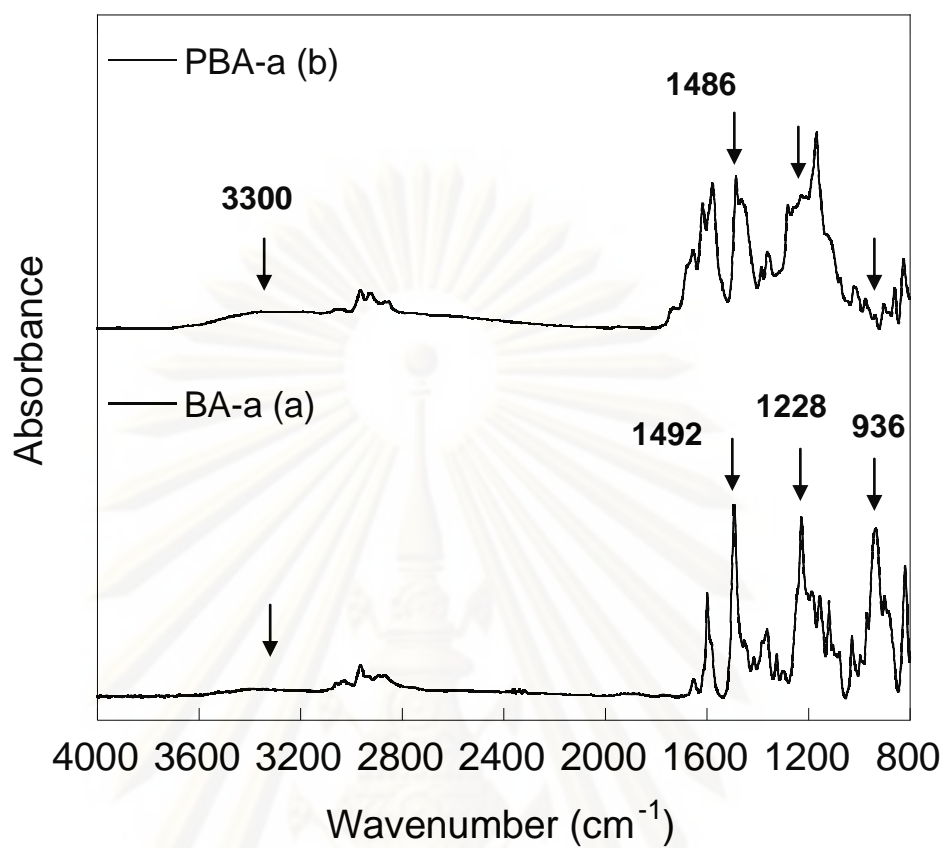


**Figure 5.3:** Photographs of Benzoxazine/PMDA alloying films at various mole ratios: BA-a/PMDA 1/1 (g), BA-a/PMDA 1.5/1 (h), BA-a/PMDA 2/1(i), BA-a/PMDA 3/1 (j), BA-a/PMDA 4/1 (k); size ~ 0.1mm thick.

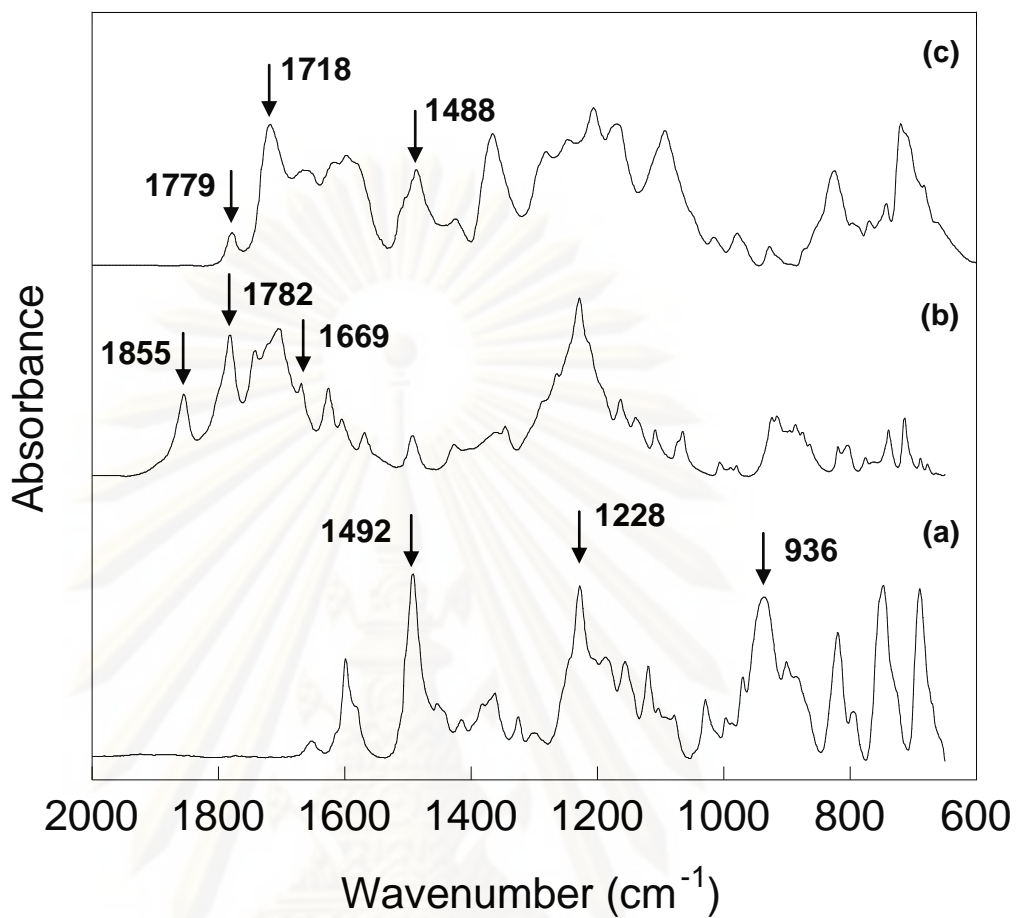


**Figure 5.4:** Photographs of Benzoxazine/s-BPDA alloying films at various mole ratios: BA-a/s-BPDA 1/1 (l), BA-a/s-BPDA 1.5/1 (m), BA-a/s-BPDA 2/1(n), BA-a/s-BPDA 3/1 (o), BA-a/s-BPDA 4/1 (p); size ~ 0.1mm thick.

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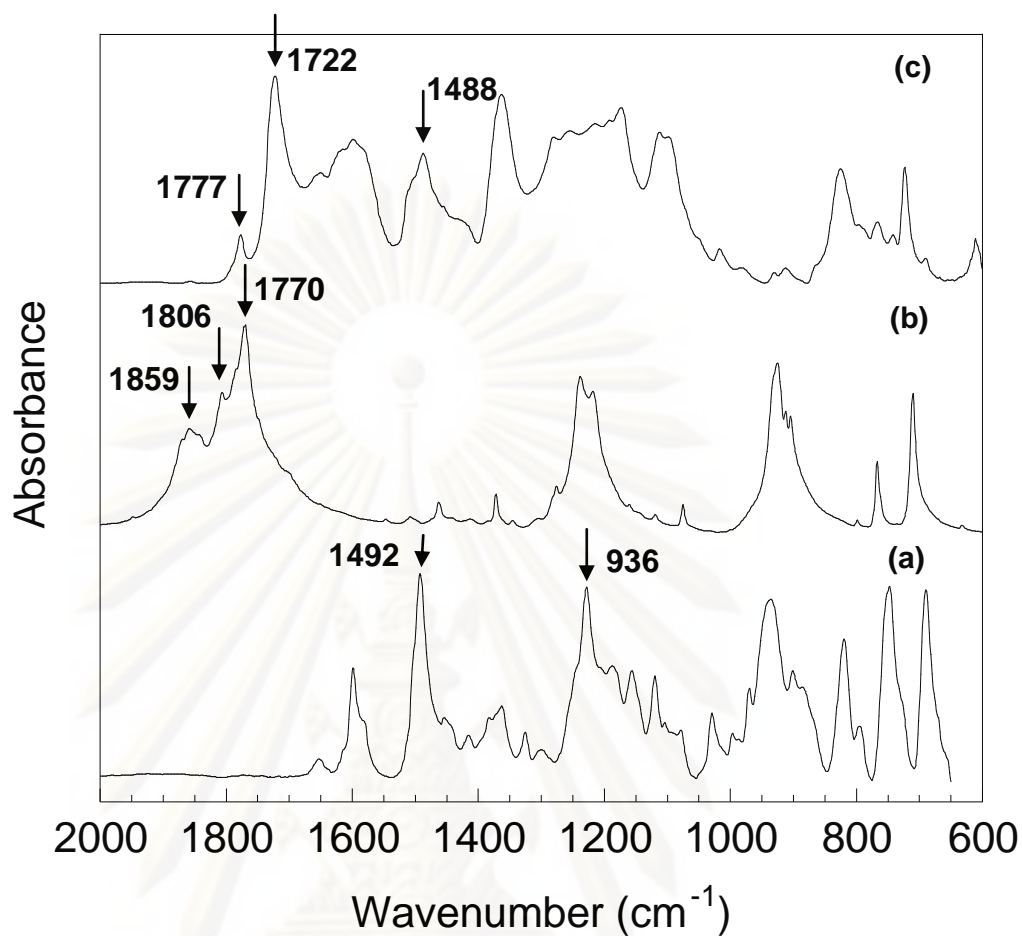
**Figure 5.5:** FTIR spectra of a) BA-a monomer b) PBA-a after fully cured.



**Figure 5.6:** FTIR spectra of a) BA-a monomer b) BTDA  
c) BA-a/BTDA 1.5/1 mole ratio after fully cured.

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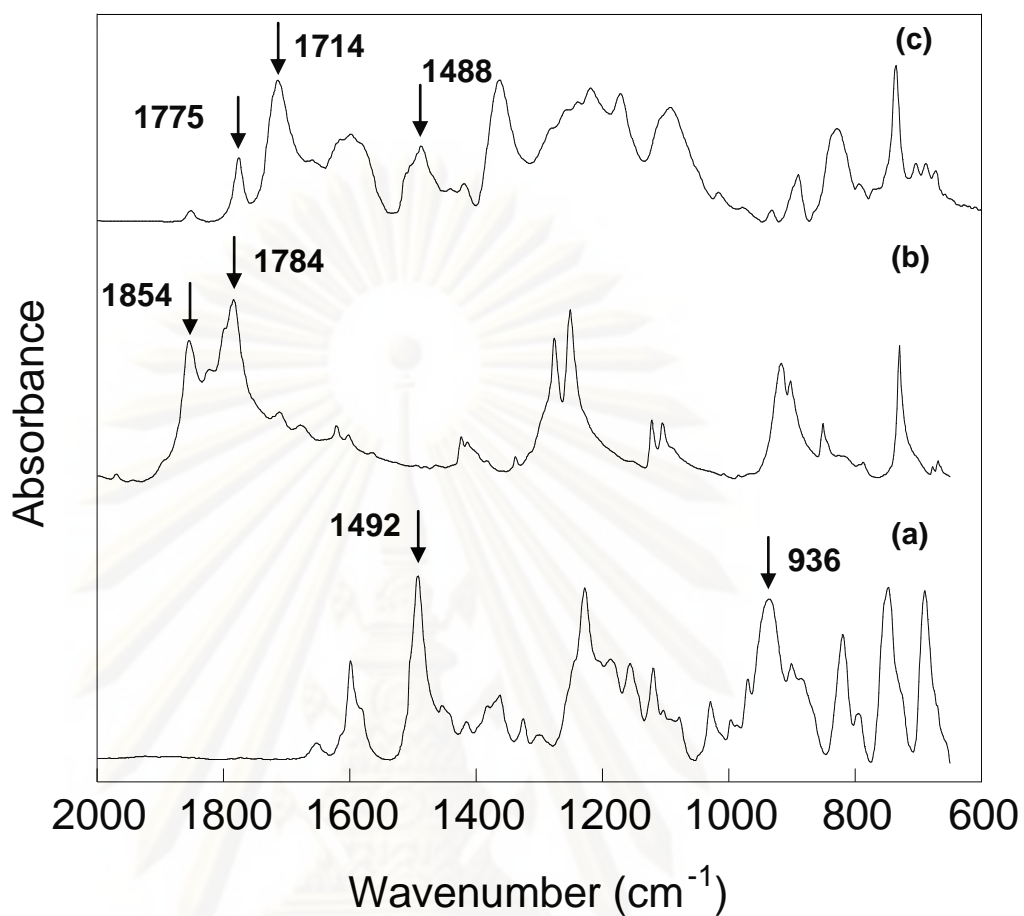


**Figure 5.7:** FTIR spectra of a) BA-a monomer b) PMDA  
c) BA-a/PMDA 1.5/1 mole ratio after fully cured.

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**Figure 5.8:** FTIR spectra of a) BA-a monomer b) s-BPDA  
c) BA-a/s-BPDA 1.5/1 mole ratio after fully cured.

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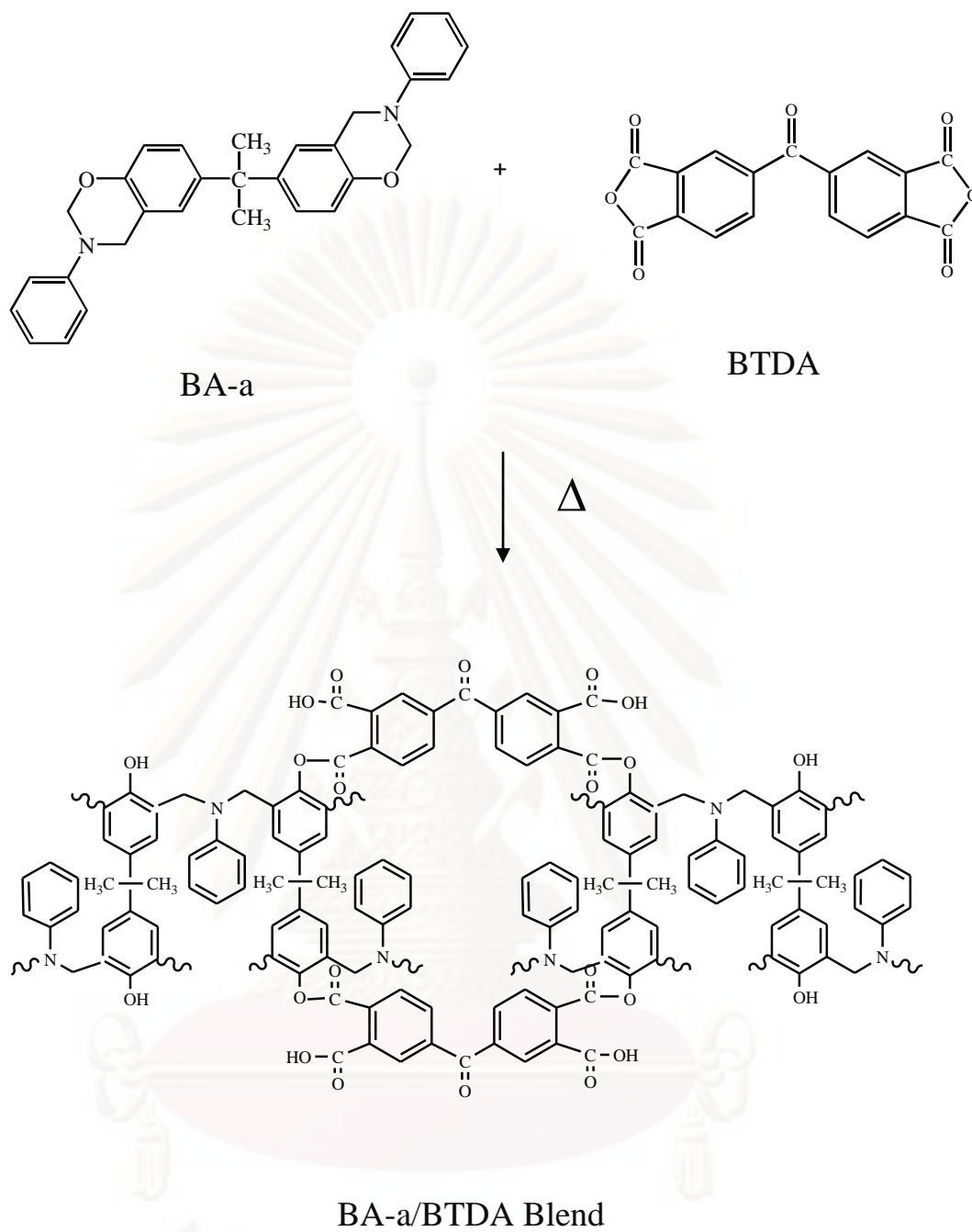
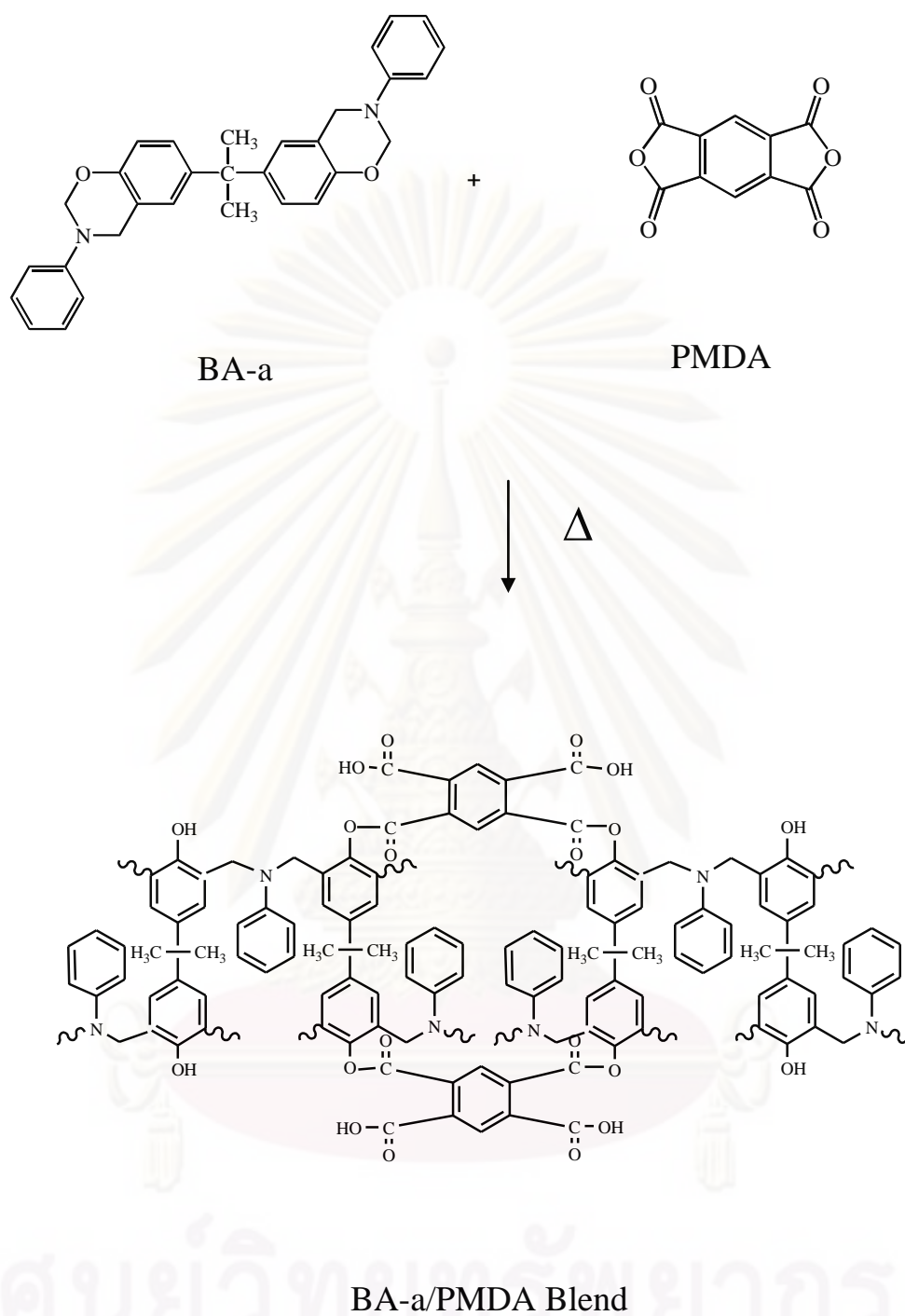
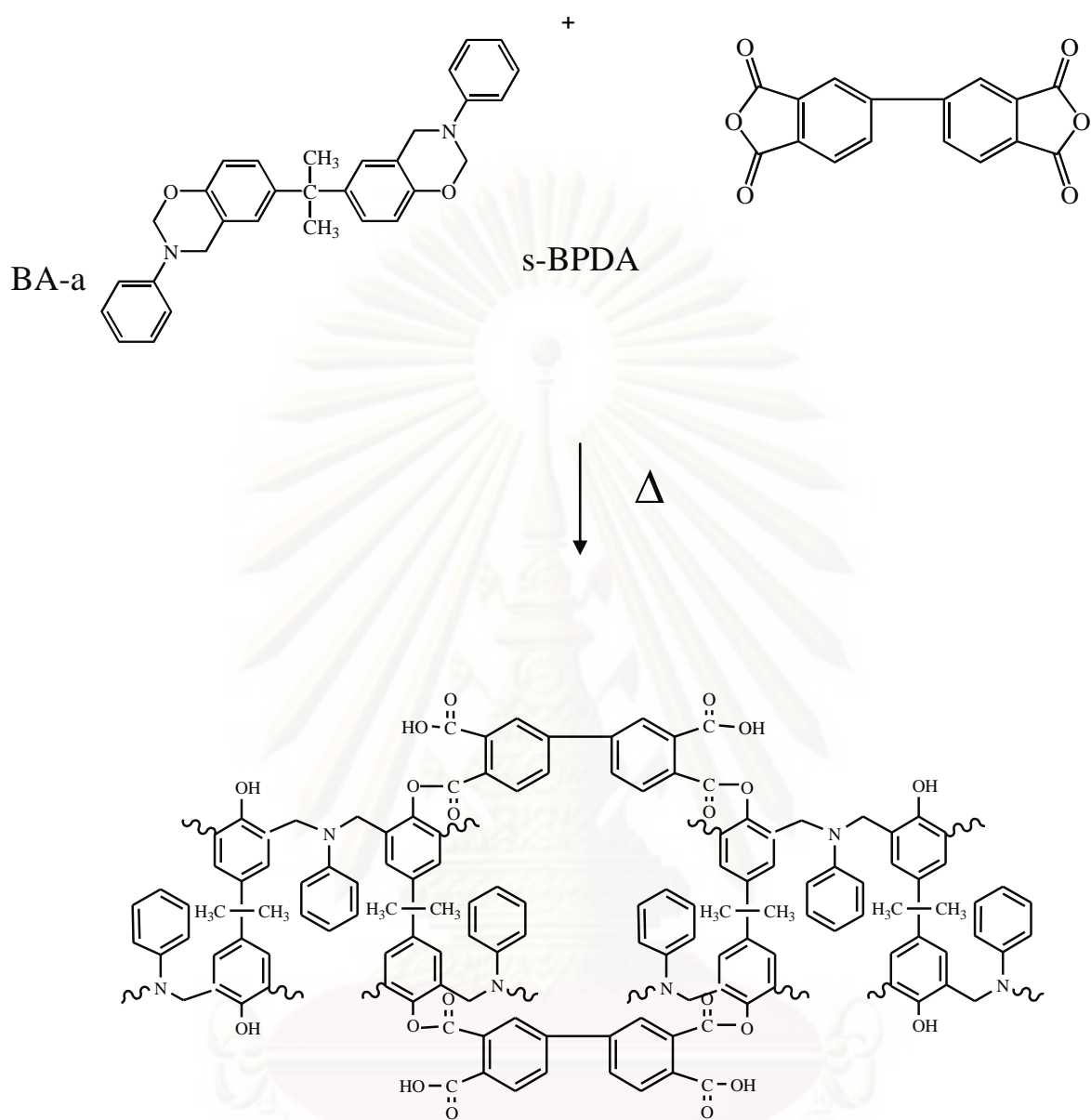


Figure 5.9: Model compound of BA-a/BTDA Blend.

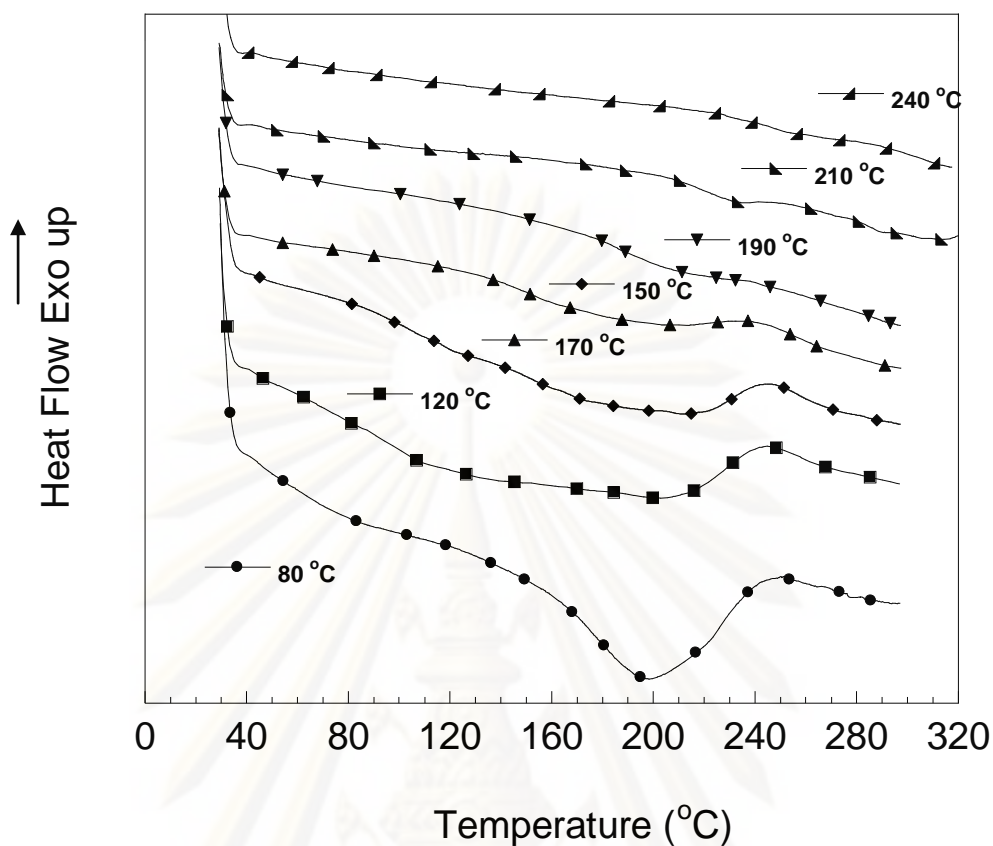


**Figure 5.10:** Model compound of BA-a/PMDA Blend.

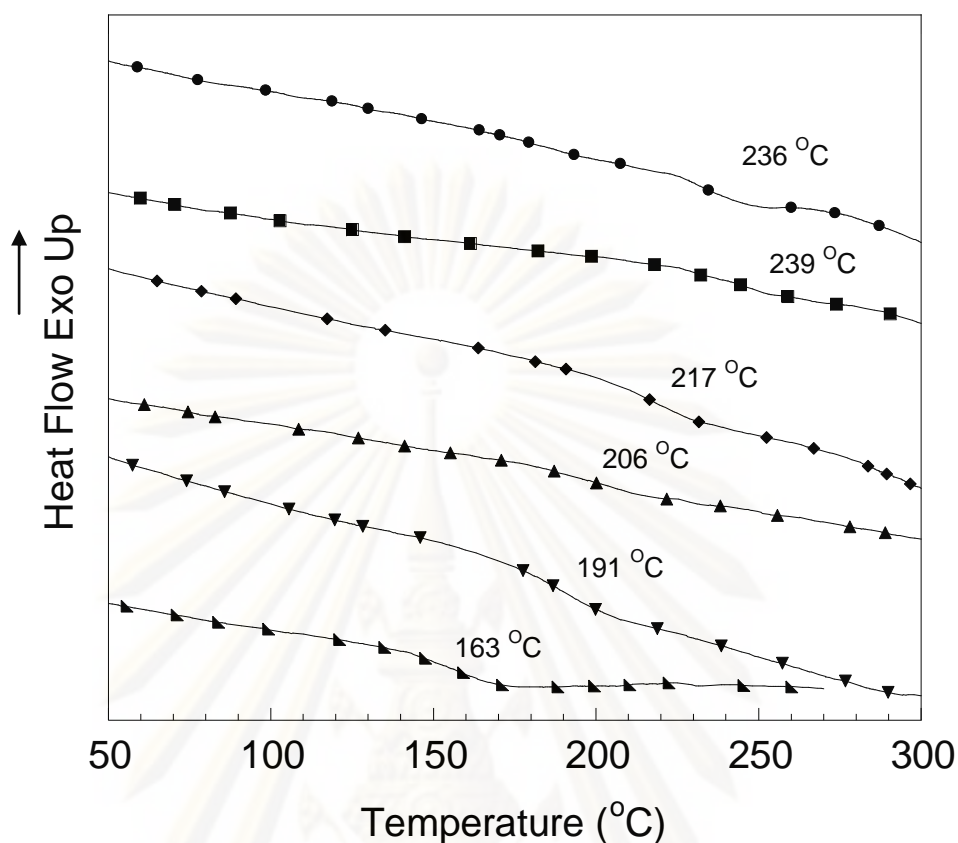


BA-a/s-BPDA Blend

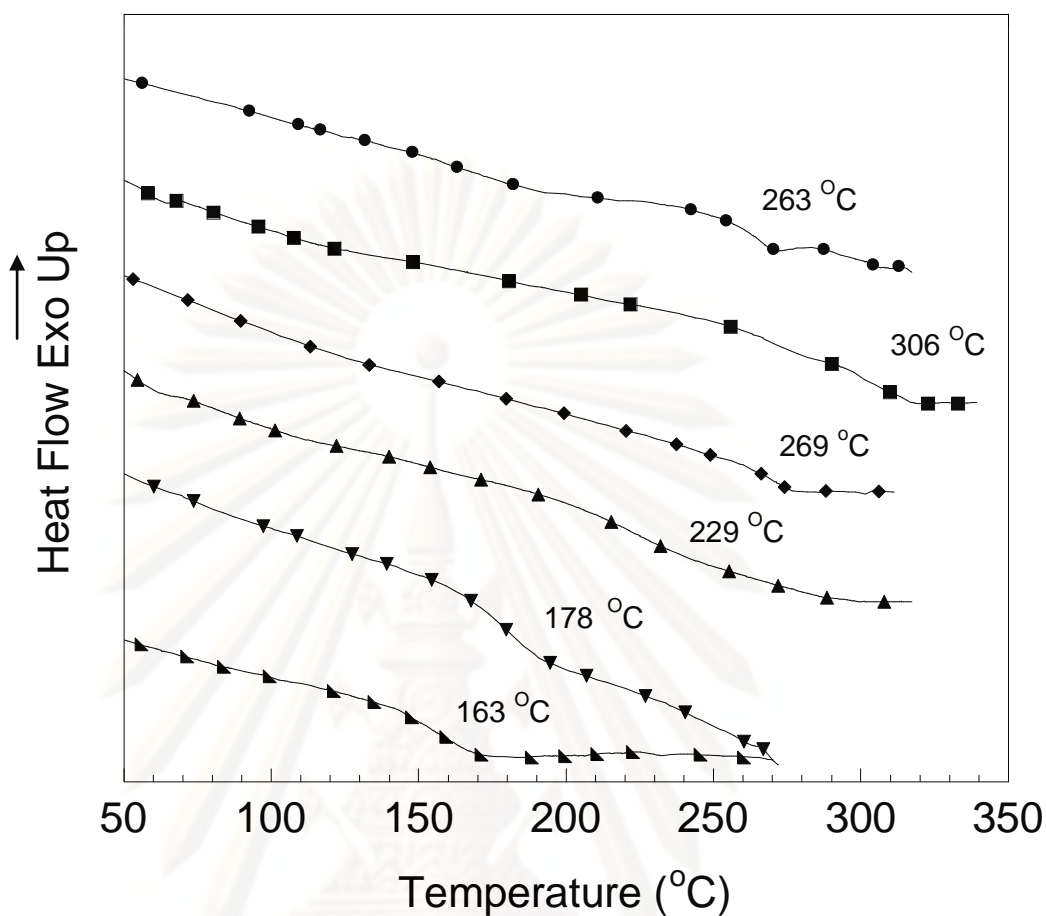
**Figure 5.11:** Model compound of BA-a/s-BPDA Blend.



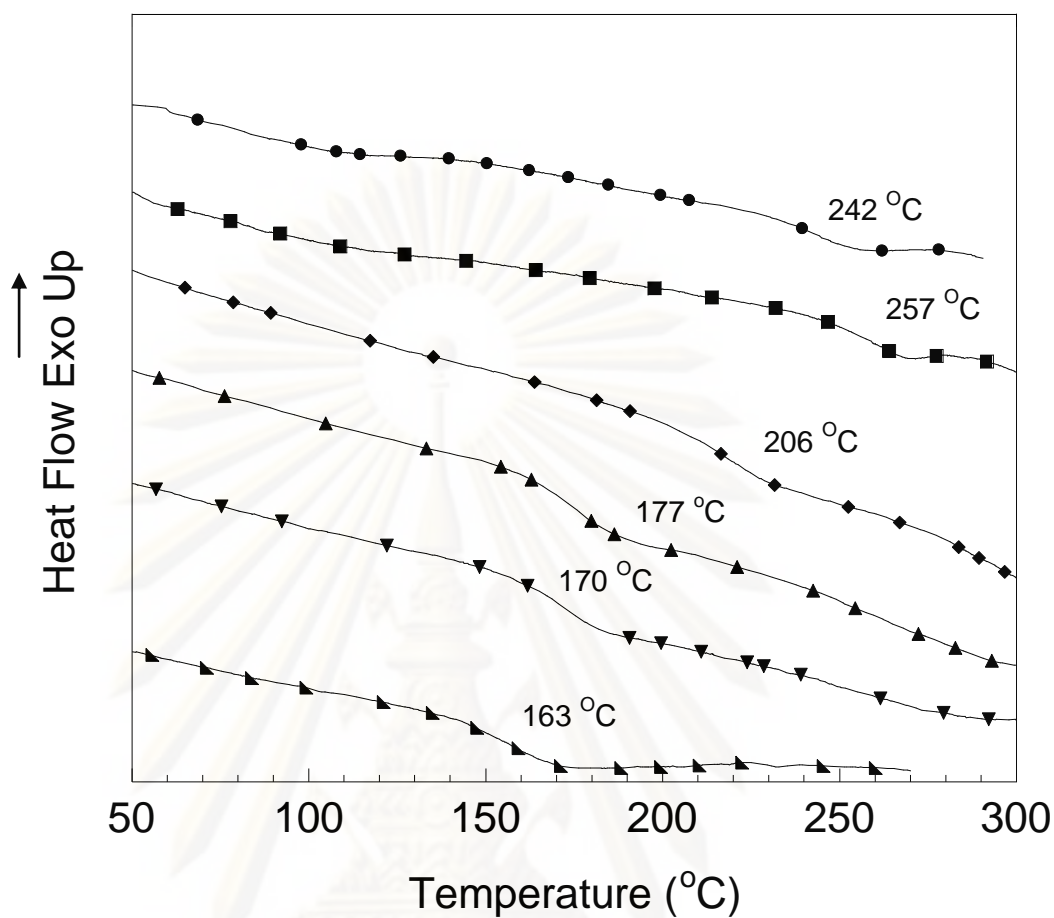
**Figure 5.12:** DSC thermograms of the benzoxazine alloying with BTDA at 1.5/1 mole ratio at various curing conditions: (●) 60 °C/24hr + vacuum 80 °C/24hr, (■) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr (◆) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr + 150°C/1hr, (▲) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr + 150°C/1hr + 170 °C/1hr(▼) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr + 150°C/1hr + 170 °C/1hr + 190°C/2hr, (▴) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr + 150°C/1hr + 170°C/1hr + 190°C/2hr +210°C/2hr , (◀) 60 °C/24hr + vacuum 80 °C/24hr + 120 °C/1hr + 150°C/1hr + 170°C/1hr + 190°C/2hr +230°C/2hr+240°C/1hr.



**Figure 5.13:** DSC thermograms of Benzoxazine/BTDA alloying films at various mole ratios: (●) BA-a/BTDA 1/1, (■) BA-a/BTDA 1.5/1, (◆) BA-a/BTDA 2/1, (▲) BA-a/BTDA 3/1, (▼) BA-a/BTDA 4/1 and (▴) Polybenzoxazine.



**Figure 5.14:** DSC thermograms of Benzoxazine/PMDA alloying films at various mole ratios: (●) BA-a/PMDA 1/1, (■) BA-a/PMDA 1.5/1, (◆) BA-a/PMDA 2/1, (▲) BA-a/PMDA 3/1, (▼) BA-a/PMDA 4/1 and (▴) Polybenzoxazine.



**Figure 5.15:** DSC thermograms of Benzoxazine/s-BPDA alloying films at various mole ratios: (●) BA-a/s-BPDA 1/1, (■) BA-a/s-BPDA 1.5/1, (◆) BA-a/s-BPDA 2/1, (▲) BA-a/s-BPDA 3/1, (▼) BA-a/s-BPDA 4/1 and (▴) Polybenzoxazine.

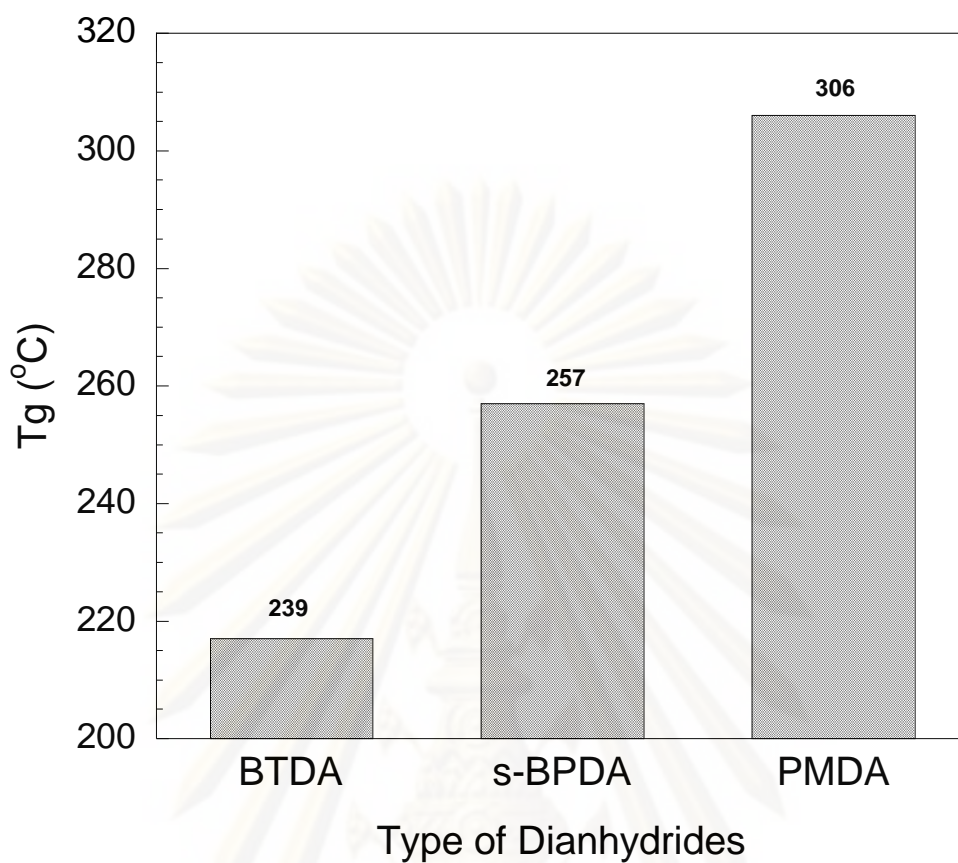


**Table 5.1:** Glass transition temperature (T<sub>g</sub>) of Polybenzoxazine and Dianhydride alloying films from DSC.

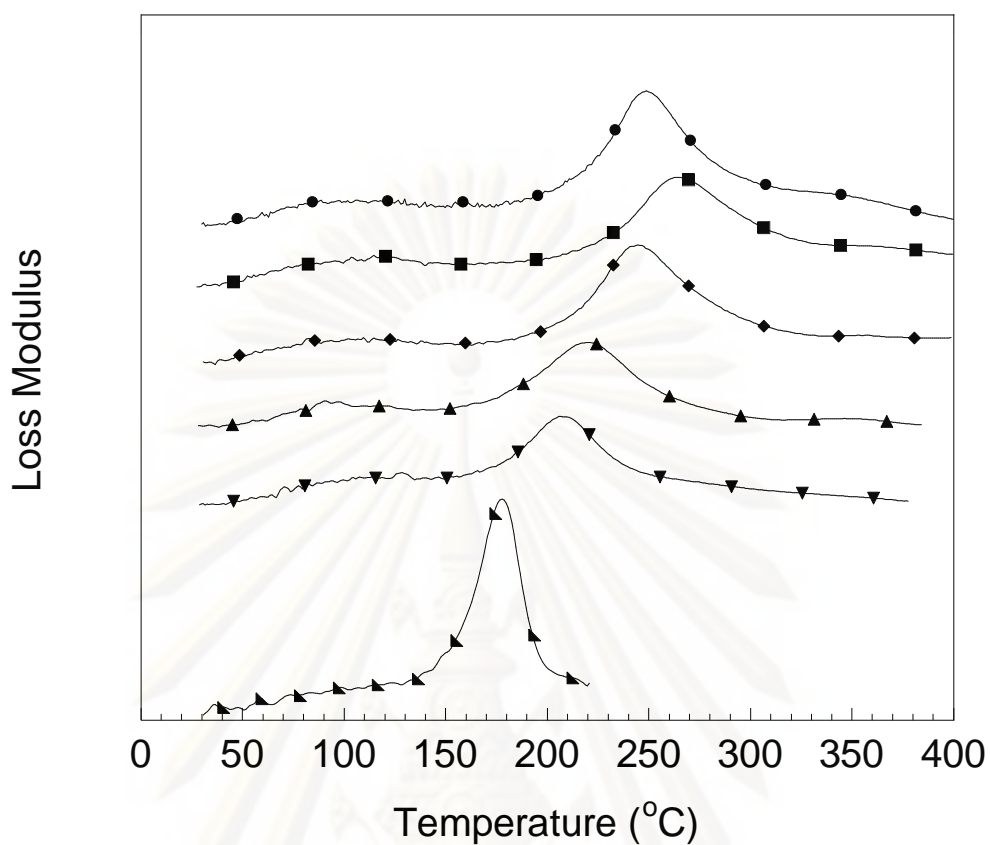
Benzoxazine :Dianhydrides	T <sub>g</sub> (°C)		
	BTDA	PMDA	s-BPDA
1:0	163	163	163
4:1	191	178	170
3:1	206	229	177
2:1	217	269	206
1.5:1	239	306	257
1:1	236	263	242



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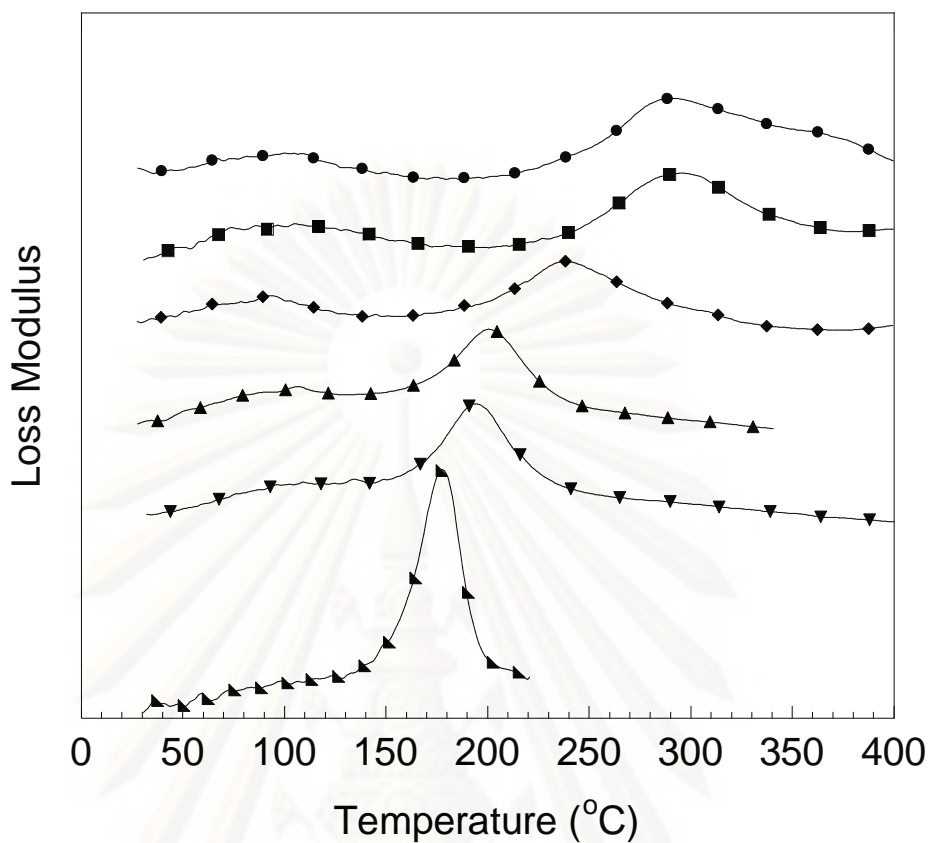
**Figure 5.16:** Glass transition temperature (DSC) of Benzoxazine/Dianhydrides alloying films at 1.5/1 mole ratio.



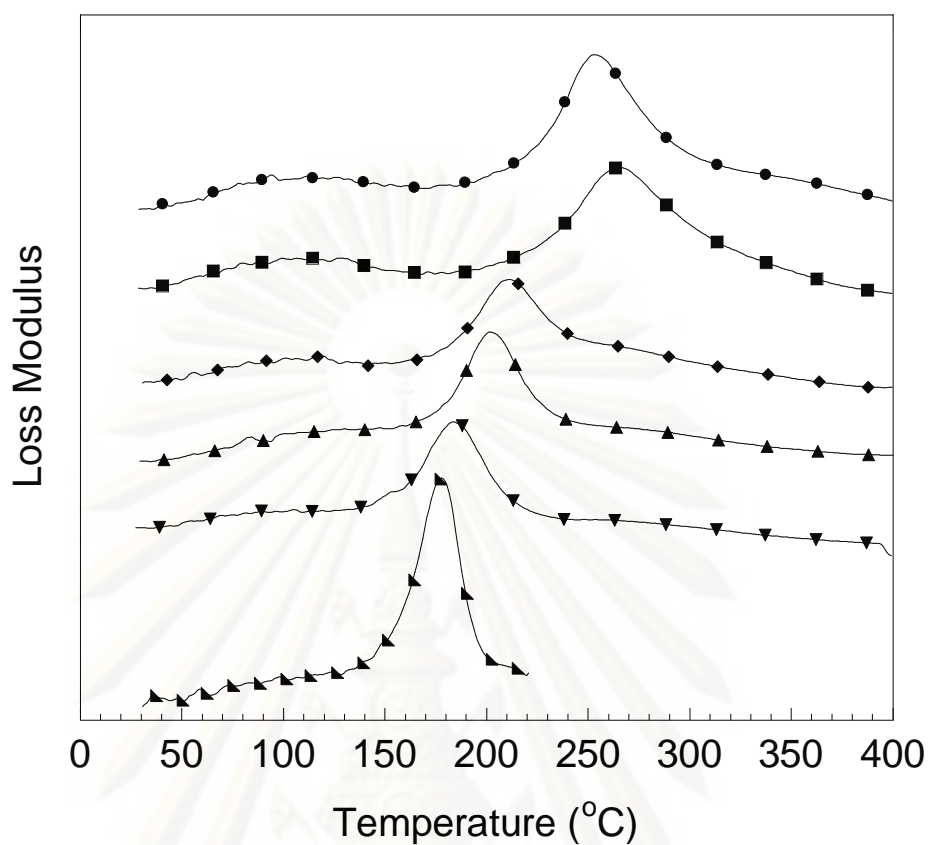
**Figure 5.17:** Loss modulus (DMA) of Benzoxazine/BTDA alloying films at various mole ratios: (●) BA-a/BTDA 1/1, (■) BA-a/BTDA 1.5/1, (◆) BA-a/BTDA 2/1, (▲) BA-a/BTDA 3/1, (▼) BA-a/BTDA 4/1 and (▴) Polybenzoxazine.

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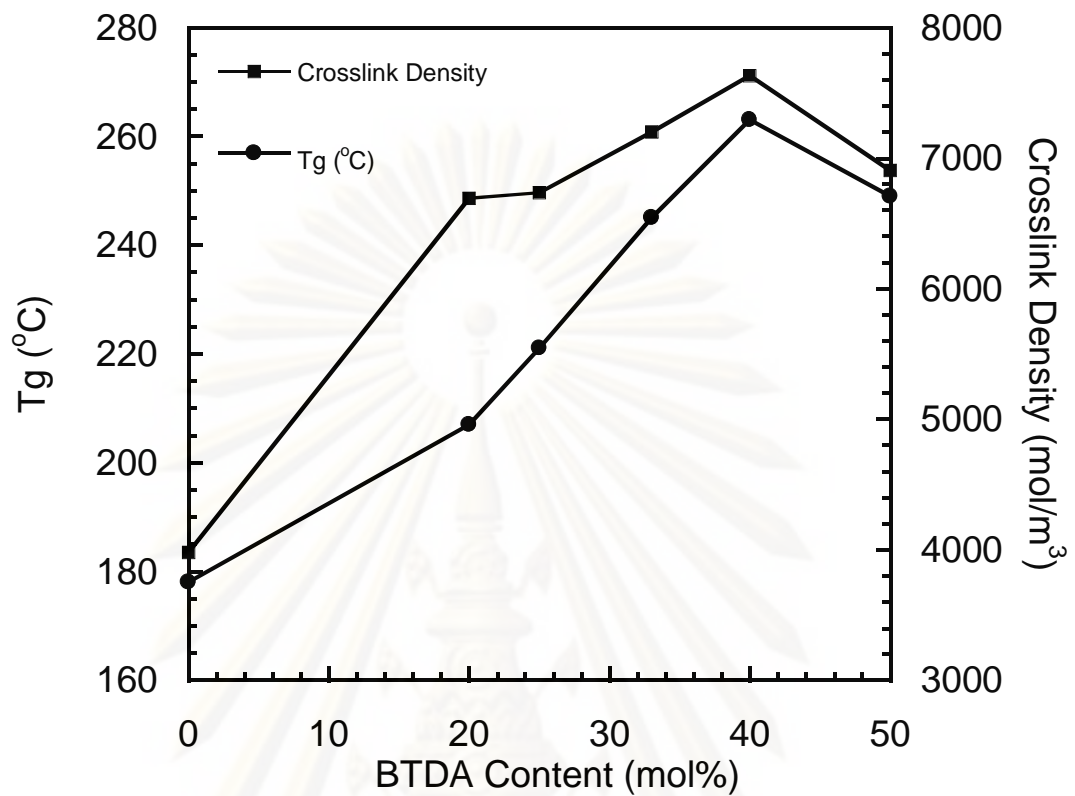
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**Figure 5.18:** Loss modulus (DMA) of Benzoxazine/PMDA alloying films at various mole ratios: (●) BA-a/PMDA 1/1, (■) BA-a/PMDA 1.5/1, (◆) BA-a/PMDA 2/1, (▲) BA-a/PMDA 3/1, (▼) BA-a/PMDA 4/1 and (▲) Polybenzoxazine.



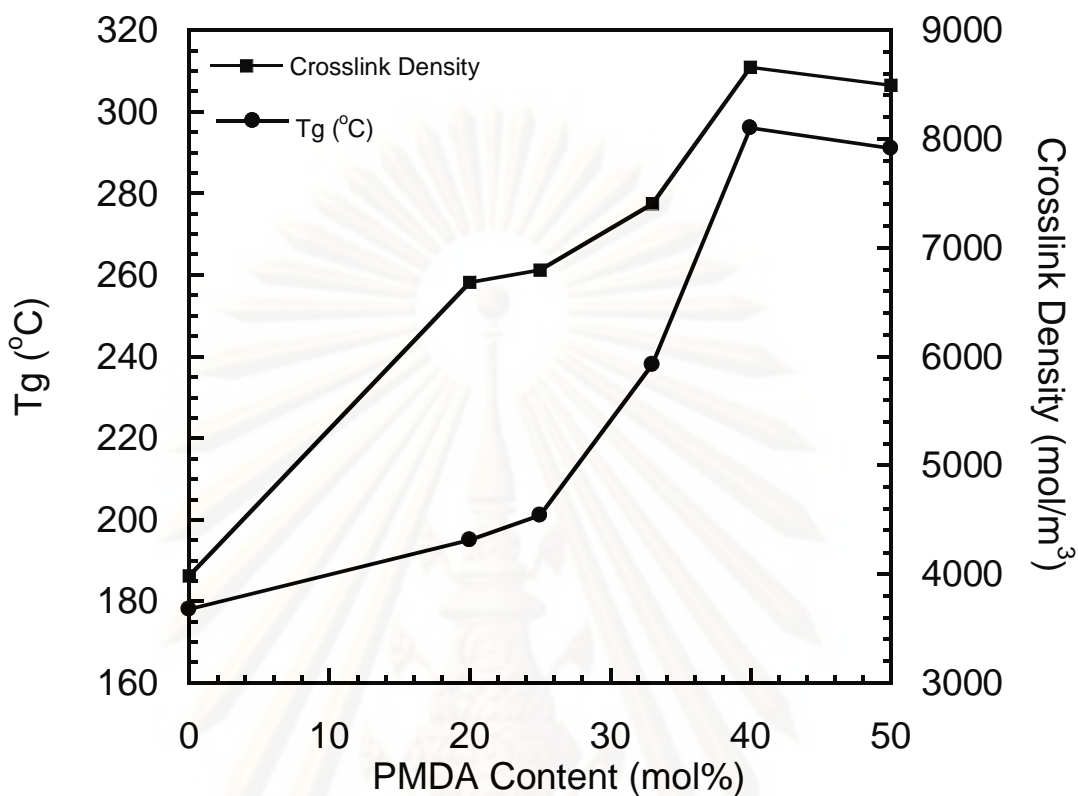
**Figure 5.19:** Loss modulus (DMA) of Benzoxazine/s-BPDA alloying films at various mole ratios: (●) BA-a/s-BPDA 1/1, (■) BA-a/s-BPDA 1.5/1, (◆) BA-a/s-BPDA 2/1, (▲) BA-a/s-BPDA 3/1, (▼) BA-a/s-BPDA 4/1 and (▲) Polybenzoxazine.



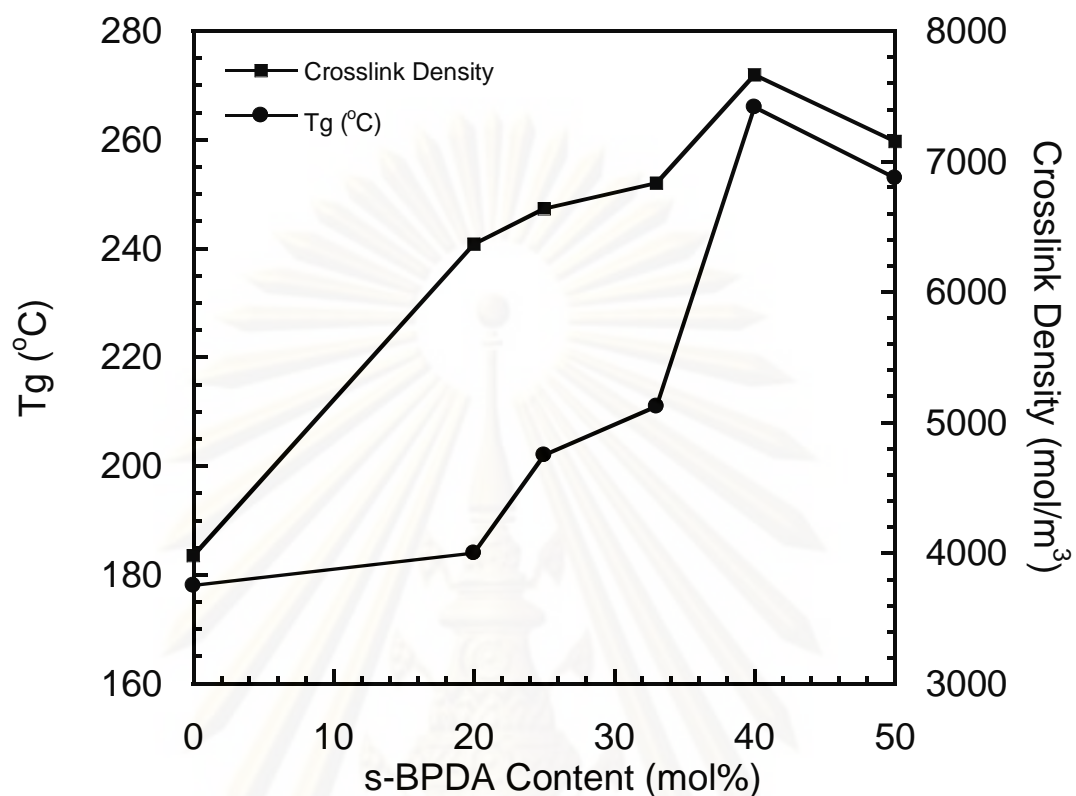
**Figure 5.20:** Glass transition temperature (Tg) and crosslink density of Benzoxazine/BTDA alloying films at various BTDA content (mol%).

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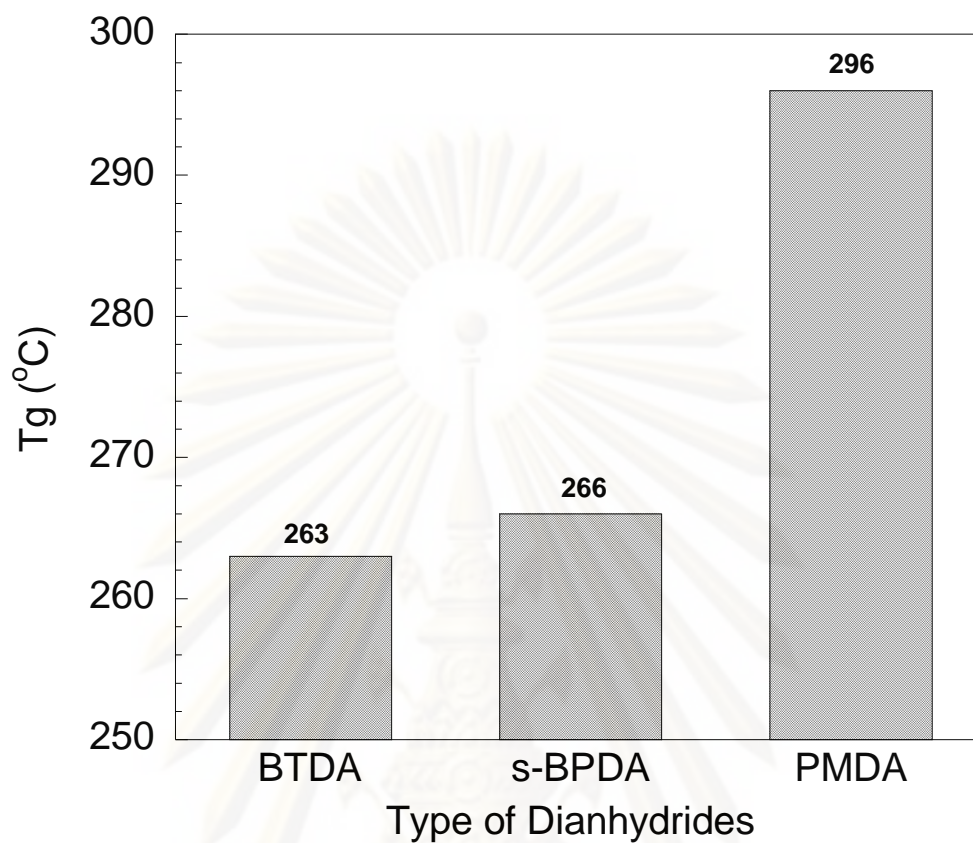


**Figure 5.21:** Glass transition temperature (Tg) and crosslink density of Benzoxazine/PMDA alloying films at various PMDA content (mol%).



**Figure 5.22:** Glass transition temperature (Tg) and crosslink density of Benzoxazine/s-BPDA alloying films at various s-BPDA content (mol%).

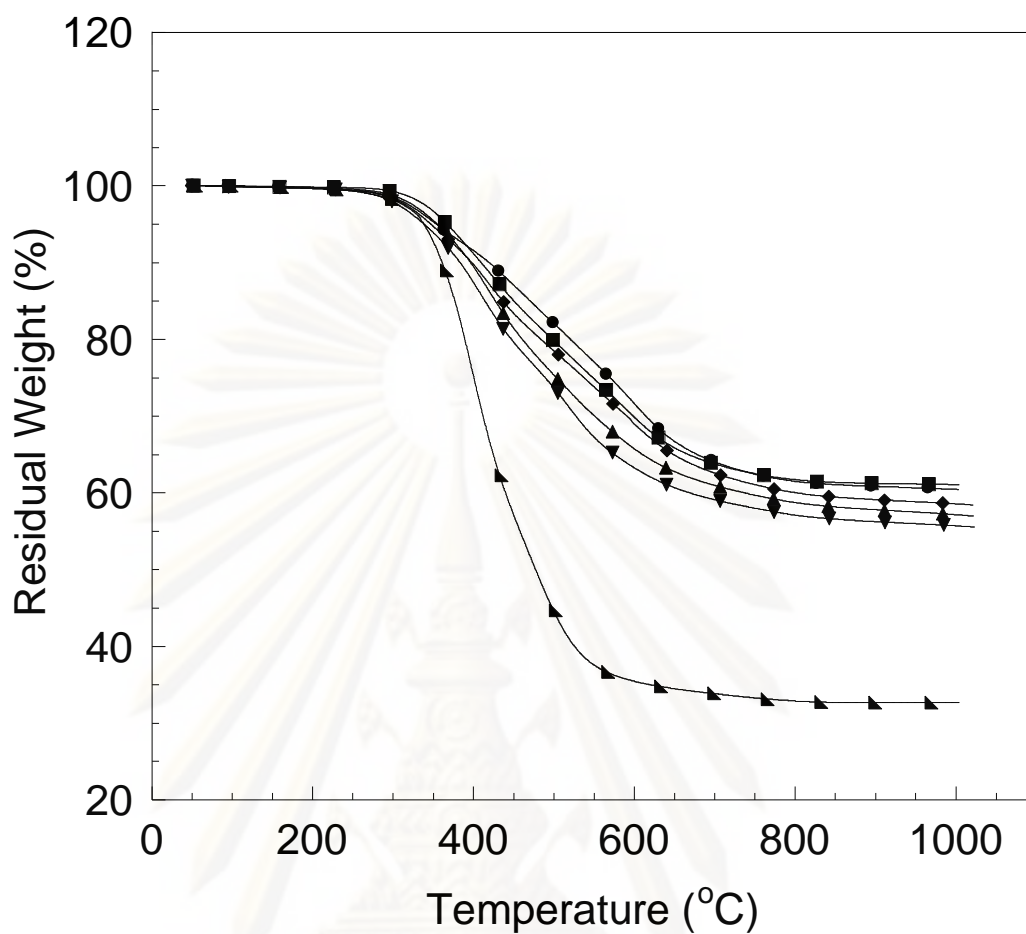




**Figure 5.23:** Glass transition temperature (loss Modulus, DMA) of Benzoxazine/Dianhydrides alloying films at 1.5/1 mole ratio.

**Table 5.2:** Glass transition temperature (T<sub>g</sub>, Loss modulus), Storage modulus (E') at 35°C, Rubbery plateau (E'), and Crosslink density of Polybenzoxazine and Dianhydride alloying films which were determined from DMA.

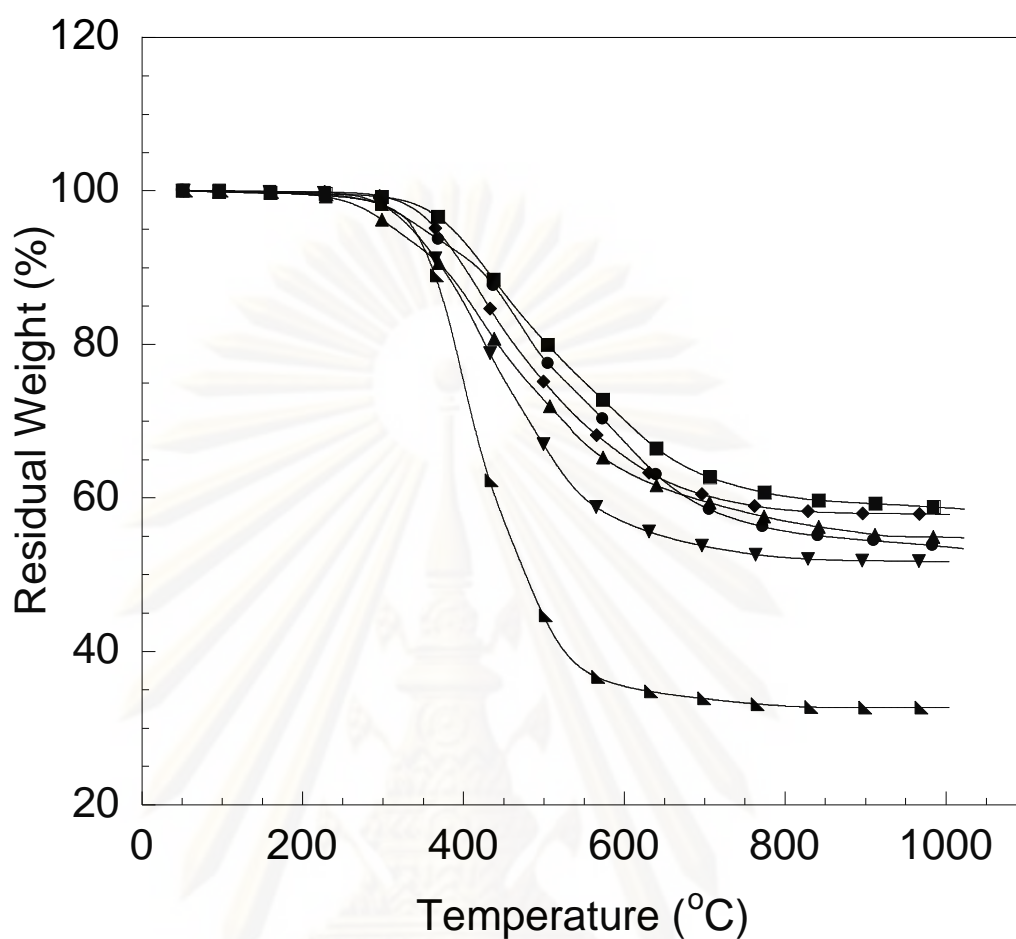
BA-a:DA	BTDA				PMDA				s-BPDA			
	T <sub>g</sub> (°C) DMA	Storage modulus (E') at 35°C (MPa)	E' rubbery plateau (MPa)	Crosslink Density (mol/m <sup>3</sup> )	T <sub>g</sub> (°C) DMA	Storage modulus (E') at 35°C (MPa)	E' rubbery plateau (MPa)	Crosslink Density (mol/m <sup>3</sup> )	T <sub>g</sub> (°C) DMA	Storage modulus (E') at 35°C (MPa)	E' rubbery plateau (MPa)	Crosslink Density (mol/m <sup>3</sup> )
1:0	178	2.57	44	3981	178	2.57	44	3981	178	2.57	44	3981
4:1	207	2.63	274	6691	195	2.72	272	6681	184	2.89	220	6366
3:1	221	2.8	282	6734	201	2.84	292	6791	202	2.91	264	6636
2:1	245	2.88	386	7200	238	2.86	442	7400	211	2.96	301	6831
1.5:1	263	2.94	516	7630	296	2.99	1031	8656	266	3.41	528	7664
1:1	249	2.89	316	6903	291	2.84	922	8490	253	3.3	374	7153



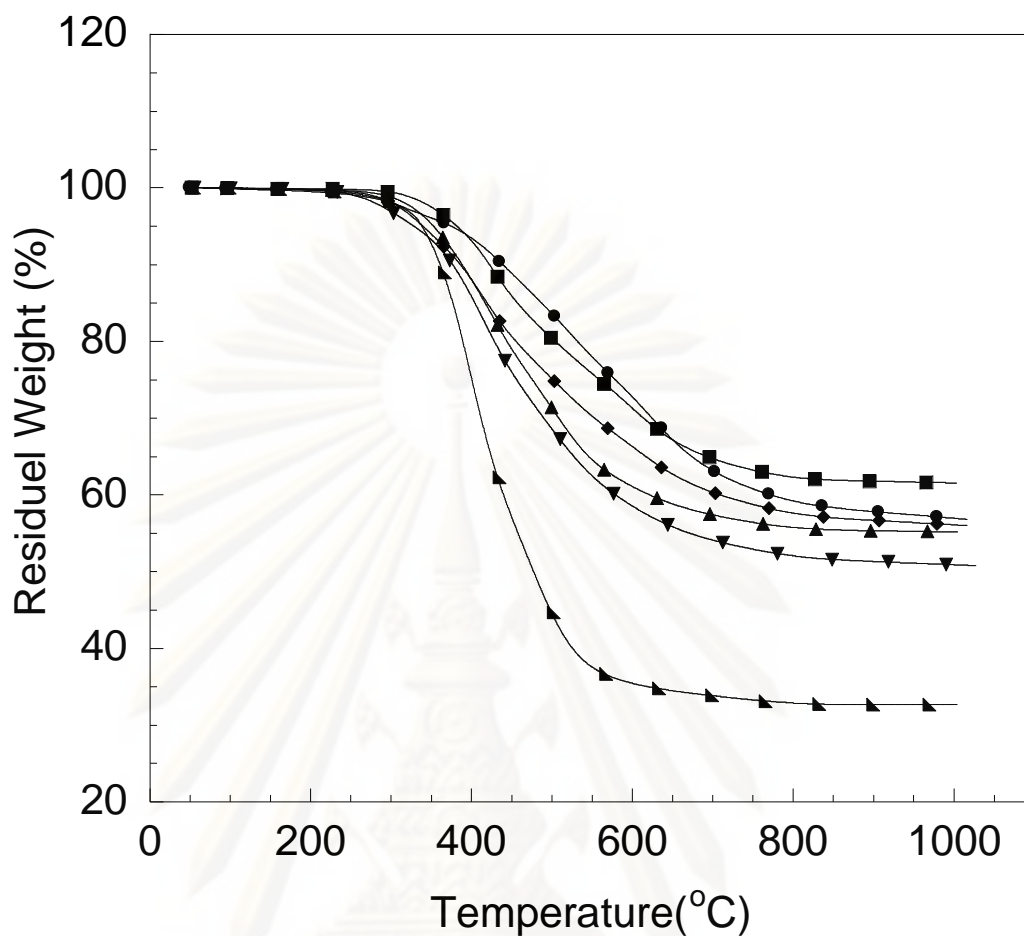
**Figure 5.24:** Thermal degradation of Benzoxazine/BTDA alloying films at various mole ratios: (●) BA-a/BTDA 1/1, (■) BA-a/BTDA 1.5/1, (◆) BA-a/BTDA 2/1, (▲) BA-a/BTDA 3/1, (▼) BA-a/BTDA 4/1 and (▴) Polybenzoxazine.

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**Figure 5.25:** Thermal degradation of Benzoxazine/PMDA alloying films at various mole ratios: (●) BA-a/PMDA 1/1, (■) BA-a/PMDA 1.5/1, (◆) BA-a/PMDA 2/1, (▲) BA-a/PMDA 3/1, (▼) BA-a/PMDA 4/1 and (♣) Polybenzoxazine.



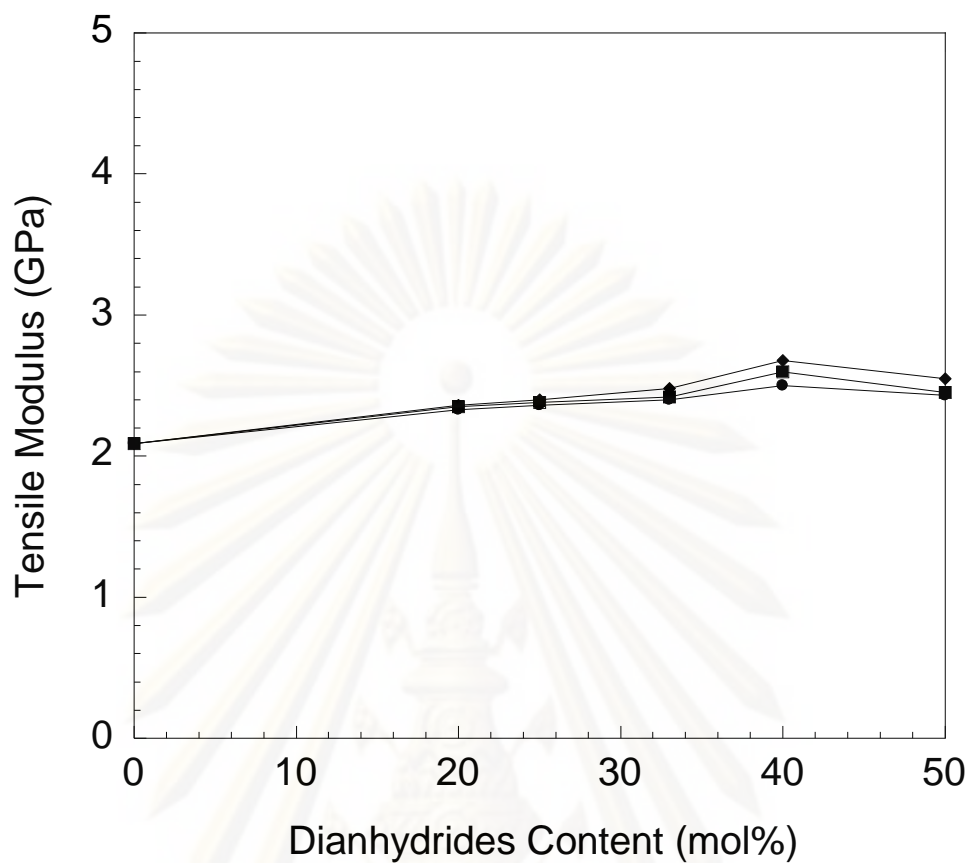
**Figure 5.26:** Thermal degradation of Benzoxazine/s-BPDA alloying films at various mole ratios: (●) BA-a/s-BPDA 1/1, (■) BA-a/s-BPDA 1.5/1, (◆) BA-a/s-BPDA 2/1, (▲) BA-a/s-BPDA 3/1, (▼) BA-a/s-BPDA 4/1 and (♣) Polybenzoxazine.

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**Table 5.3:** Degradation temperatures ( $T_d$ ) at 10% weight loss, residue weights (char yield) at 800°C, and LOI of Polybenzoxazine and Dianhydride alloying films which were determined from TGA.

Benzoxazine:Dianhydride	BTDA			PMDA			s-BPDA		
	$T_d$ (°C)	Char yield (%)	LOI	$T_d$ (°C)	Char yield (%)	LOI	$T_d$ (°C)	Char yield (%)	LOI
1 : 0	361	32.9	30.7	361	32.9	30.7	361	32.9	30.7
4 : 1	384	57.1	40.3	373	52.2	38.4	377	52.1	38.3
3 : 1	396	58.8	41.0	375	57.0	40.3	389	55.8	39.8
2 : 1	398	60.0	41.5	401	58.5	40.9	386	57.6	40.6
1.5 : 1	410	61.7	42.2	426	60.2	41.6	422	62.3	42.4
1 : 1	420	61.5	42.1	418	55.7	39.8	439	59.2	41.2



**Figure 5.27:** Tensile modulus of Benzoxazine/Dianhydride alloying films at various compositions: BA-a/BTDA(●), BA-a/PMDA (■), BA-a/s-BPDA (◆).

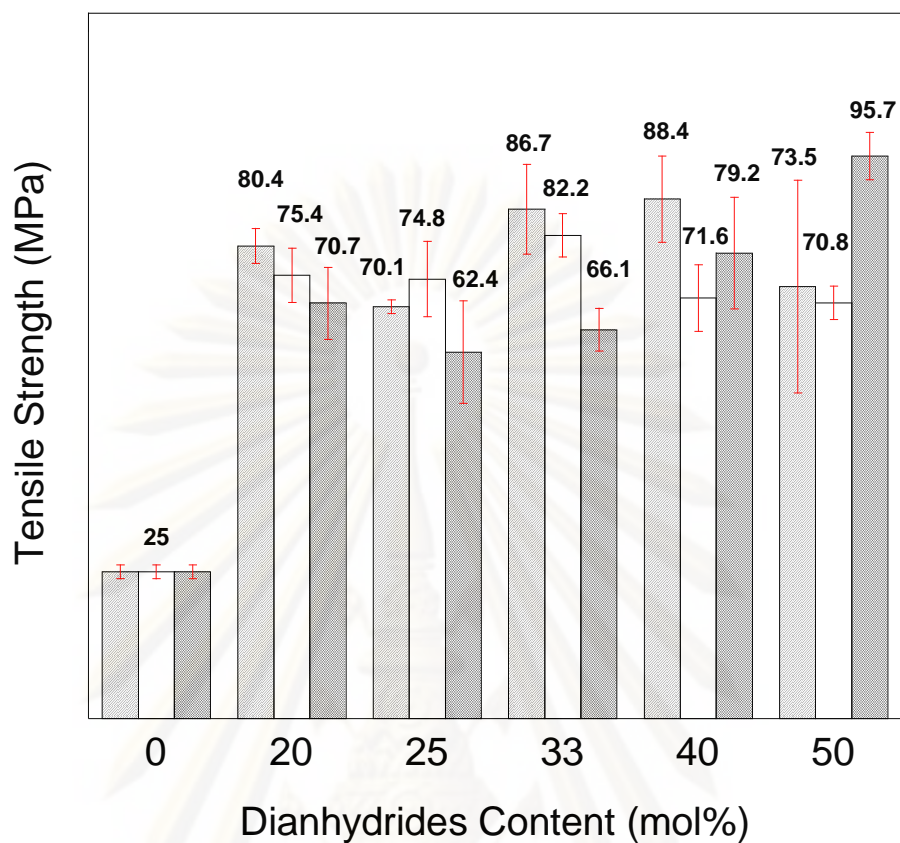
**Table 5.4:** Mechanical properties of Polybenzoxazine and Dianhydride alloying films.

<b>BA-a:BTDA</b>	<b>Tensile Strength (MPa)</b>	<b>Tensile modulus (GPa)</b>	<b>Tensile elongation at break (%)</b>
1:0	25.00	2.09	1.97
4:1	70.70	2.33	4.21
3:1	62.37	2.36	4.16
2:1	66.14	2.40	4.75
1.5:1	79.20	2.50	5.35
1:1	95.74	2.43	5.35

<b>BA-a/PMDA</b>	<b>Tensile Strength (MPa)</b>	<b>Tensile modulus (GPa)</b>	<b>Tensile elongation at break (%)</b>
1:0	25.00	2.09	1.97
4:1	75.42	2.35	4.60
3:1	74.79	2.38	4.47
2:1	82.22	2.42	5.41
1.5:1	71.56	2.60	5.22
1:1	70.77	2.45	4.43

<b>BA-a/s-BPDA</b>	<b>Tensile Strength (MPa)</b>	<b>Tensile modulus (GPa)</b>	<b>Tensile elongation at break (%)</b>
1:0	25.00	2.09	1.97
4:1	80.41	2.36	4.85
3:1	70.06	2.40	4.98
2:1	86.66	2.48	5.55
1.5:1	88.40	2.68	6.06
1:1	73.51	2.55	4.65

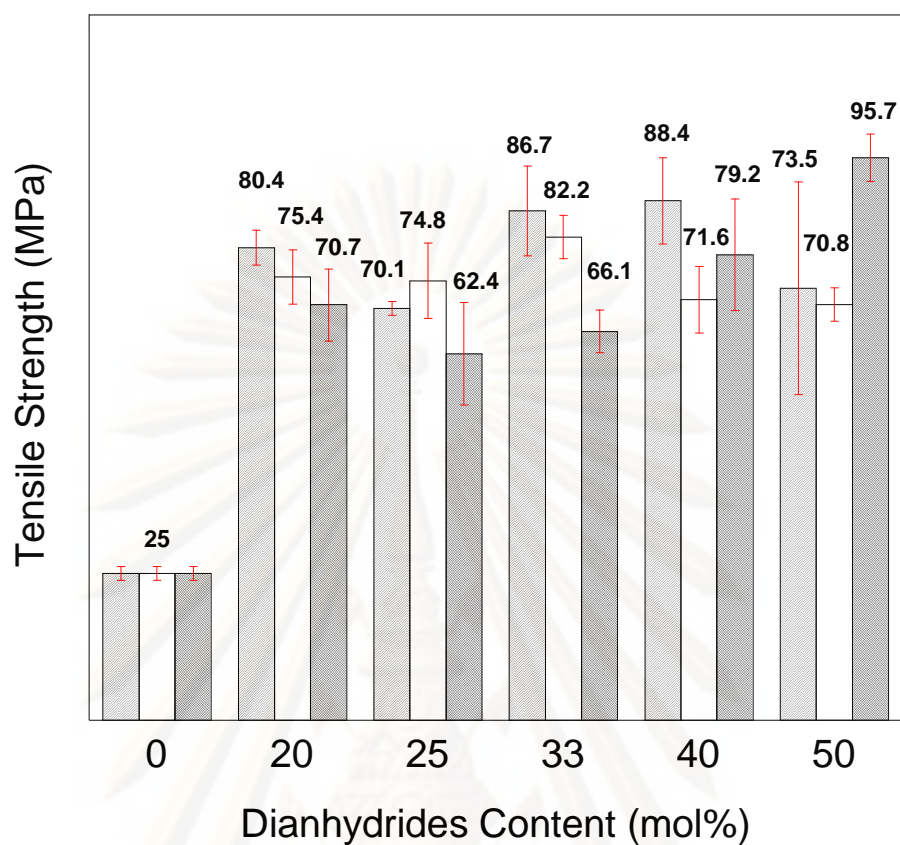




**Figure 5.28:** Tensile strength of Benzoxazine/Dianhydride alloying films at various mol% of dianhydrides: BA-a/BTDA (▨), BA-a/PMDA (□), BA-a/s-BPDA (▩).

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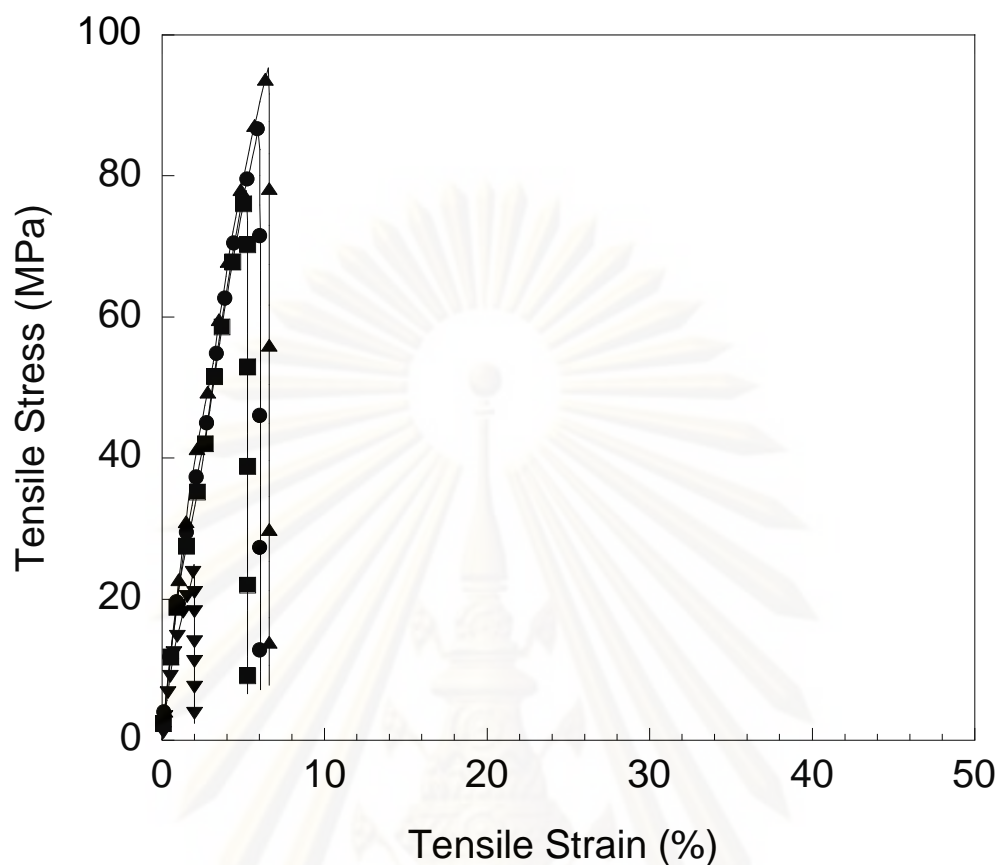
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**Figure 5.29:** Elongation at break of Benzoxazine/Dianhydride alloying films at various mol% of dianhydrides: BA-a/BTDA (▨), BA-a/PMDA (□), BA-a/s-BPDA (▩).

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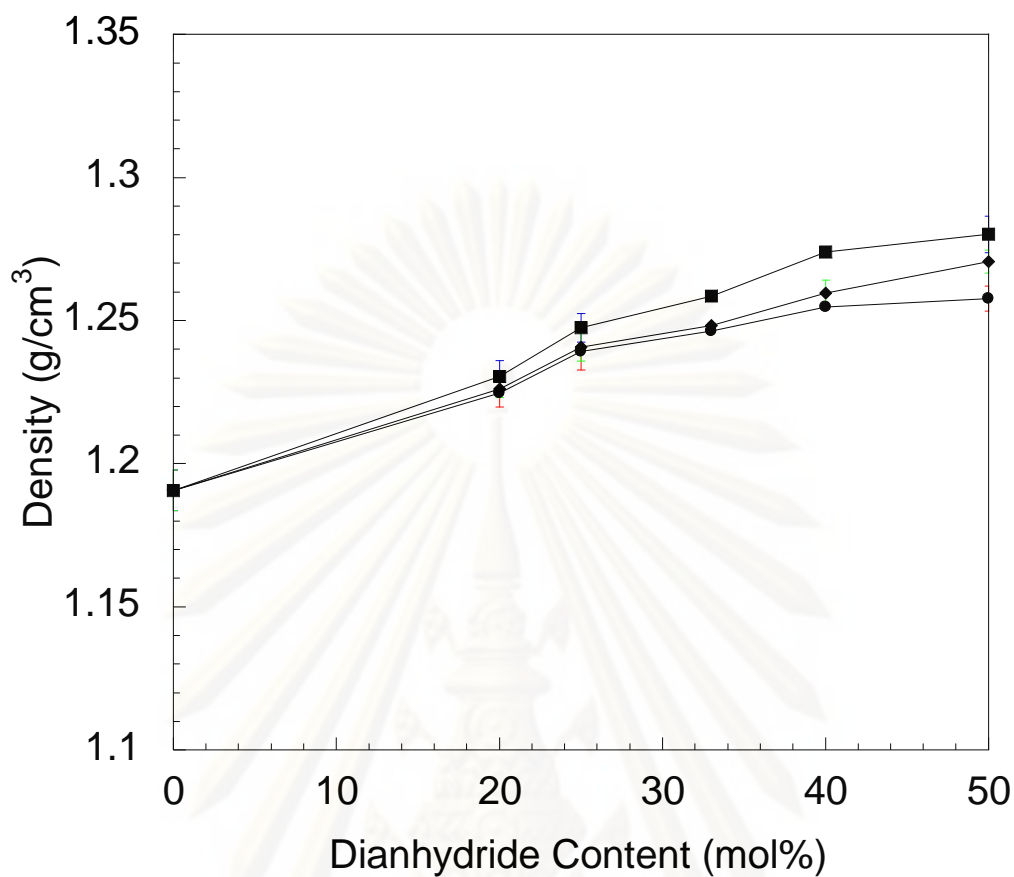
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**Figure 5.30:** Stress-strain curve of Benzoxazine/Dianhydride alloying films at various type of dianhydrides: BA-a/BTDA 1.5/1 mole ratio (●), BA-a/PMDA 1.5/1 mole ratio (■), BA-a/s-BPDA 1.5/1 mole ratio (▲), and polybenzoxazine (▼).

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**Figure 5.31:** Density of Benzoxazine/Dianhydride alloying films at various mol% of dianhydrides: BA-a/BTDA (●), BA-a/PMDA (■), BA-a/s-BPDA (◆).

## CHAPTER VI

### CONCLUSIONS

Polymeric alloying films were prepared from benzoxazine resin (BA-a) and BTDA, PMDA, or s-BPDA dianhydrides followed by thermal curing. It is clear that the NMP was completely removed from the BA-a: BTDA alloying film at 150°C heat treatment and the fully cured stage was achieved at up to 240°C heat treatment.

From FI-IR spectroscopy, the obtained network structures were due to reaction between the hydroxyl group of polybenzoxazine and the carboxylic group of dianhydrides. The T<sub>g</sub> value and crosslink density of the neat PBA-a were substantially enhanced by alloying with the BTDA, PMDA, or s-BPDA. The BA-a: BTDA, BA-a: PMDA, and BA-a: s-BPDA alloying films at a 1.5:1 mole ratio exhibited maximum in the T<sub>g</sub> values. Moreover, the effect of types of dianhydrides on T<sub>g</sub> values was found to be as follows: BA-a: PMDA > BA-a: s-BPDA > BA-a: BTDA. The storage modulus in a glassy state of the BA-a: dianhydride alloying films was slightly higher than that the neat PBA-a. Whereas type of the dianhydride showed negligible effect on the mechanical properties of the resulting alloys.

Furthermore, the T<sub>d</sub> value and the weight residue at 800 °C of the alloying films were found to be enhanced with the amount of those dianhydrides. Therefore, the introduction of dianhydrides into PBA-a improved the thermal stability of the resulting polymeric alloying films. In principle, the greater the char yield, the higher the flame retardancy of the polymer. The LOI of dianhydride-polybenzoxazine alloying films was much higher than the neat polybenzoxazine (i.e. 30.7) and the LOI of the entire BA-a: dianhydride alloys were above the self-extinguishable limiting i.e. > 26.

Last but not least, tensile strength, tensile elongation at break, tensile modulus, and toughness of PBA-a increased by alloying with BTDA or PMDA or s-BPDA. These films could be casted into flexible and strong films. The difference in tensile strength, tensile elongation at break, tensile modulus, and toughness of the

three types of dianhydrides were not significant. The optimum mechanical and thermal properties of BA: dianhydrides were obtained at 1.5:1 mole ratio.



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## **APPENDIX**

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## APPENDIX

### Characterization of Polybenzoxazine and Dianhydride Alloying Films

**Appendix A-1** The density of polybenzoxazine and dianhydride alloys.

Benzoxazine:Dianhydrides	Density (g/cm <sup>3</sup> )		
	BTDA	PMDA	s-BPDA
1:0	1.19	1.19	1.19
4:1	1.2247	1.2304	1.2261
3:1	1.2392	1.2475	1.2408
2:1	1.2464	1.2586	1.2482
1.5:1	1.2548	1.2740	1.2597
1:1	1.2577	1.2801	1.2706
0:1	1.57	1.68	1.625

## VITAE

Ms. Boonthariga Ramsiri was born in Bangkok, Thailand on July 10, 1986. She graduated at high school level at Bodindecha (Sing Singhaseni) 2 School, Thailand in 2004. In 2008, she received Bachelor's Degree in Chemical Engineering from the Department of Chemical Technology, Faculty of Science, Chulalongkorn University Bangkok, Thailand. After graduation, she continues her studies on a Master's Degree of Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University Bangkok, Thailand.



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