การเพิ่มสมบัติของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารโมโนแอนไฮไดรด์และไดแอนไฮไดรด์

นางสาววารีรัตน์ ปู่นุช

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PROPERTY ENHANCEMENT OF POLYBENZOXAZINE MODIFIED WITH MONOANHYDRIDES AND DIANHYDRIDES

Miss Wareerat Punuch

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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Thesis Title	PROPERTY ENHANCEMENT OF POLYBENZOXAZINE MODIFIED WITH MONOANHYDRIDES AND DIANHYDRIDES
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วารีรัตน์ ปู่นุช : การเพิ่มสมบัติของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารโมโนแอนไฮไดรด์และไดแอนไฮไดรด์. (PROPERTY ENHANCEMENT OF POLYBENZOXAZINE MODIFIED WITH MONOANHYDRIDES AND DIANHYDRIDES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศราวุธ ริมดุสิต, หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาสมบัติทางกลและทางความร้อนของพอลิเบนซอกซาซีน (PBA-a) เพื่อให้มีสมบัติทางกลและทางความร้อนที่ดี คือ มีอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วและอุณหภูมิการสลายตัวทางความร้อนที่สูง รวมไปถึงแสดงสมบัติยืดหยุ่นที่ดี โดยนำพอลิเบนซอกซาซีนมาดัดแปรด้วยสารแอนไฮไดรด์สองประเภท คือโมโนแอนไฮไดรด์ (มีแอนไฮไดรด์ 1 หมู่) ได้แก่ พาทาลิก แอนไฮไดรด์ (PA) และ แนพทาลิก แอนไฮไดรด์ (NA) และ ไดแอนไฮไดรด์ (มีแอนไฮไดรด์ 2 หมู่) ได้แก่ ไพโรเมลลิทิก ไดแอนไฮไดรด์ (PMDA) และ แนพทาลีน เทรทาคารบอกซิลิก ไดแอนไฮไดรด์ (NTDA) จากผลการทดลองพบว่า การเติมสารแอนไฮไดร์ทั้งสองประเภทสามารถพัฒนาสมบัติทางกลและทางความร้อนของพอลิเบนซอกซาซีนได้ แต่ให้สมบัติเด่นที่แตกต่างกัน ค่าอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารไดแอนไฮไดรด์มีค่าสูงกว่าพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารโมโนแอนไฮไดรด์ คือ PBA-a:NTDA (304 องศาเซลเซียส) > PBA-a:PMDA (296 องศาเซลเซียส) >> PBA-a:NA (247 องศาเซลเซียส) > PBA-a:PA (223 องศาเซลเซียส) และยังมีค่าสูงกว่าพอลิเบนซอกซาซาซีน ทั้งนี้เนื่องจากความหนาแน่นของการเชื่อมขวางของปฏิกิริยาเอสเทอริฟิเคชั่นระหว่างหมู่ฟีนอลิกไฮดรอกซิลของพอลิเบนซอกซาซีนและหมู่แอนไฮไดรด์ของสารแอนไฮไดรด์ นอกจากนี้อุณหภูมิการสลายตัวทางความร้อนที่สิบเปอร์เซ็นต์โดยน้ำหนักที่หายไป ภายใต้แก๊สไนโตรเจนมีค่าสูงถึง 430 องศาเซลเซียส และปริมาณเถ้าที่เหลือ ณ อุณหภูมิ 800 องศาเซลเซียสของพอลิเมอร์อัลลอยนี้ยังมีค่าสูงถึง 63 เปอร์เซ็นต์ และพบอีกว่าค่า LOI ที่คำนวณได้ของทุกอัตราส่วนของพอลิเมอร์ผสมมีค่ามากกว่า 26 จึงจัดอยู่ในสารประเภทดับไฟได้เอง ยิ่งไปกว่านั้นยังพบว่า ค่าความแข็งแรงภายใต้แรงดึง ค่าระยะยืด ณ จุดขาด ของพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารโมโนแอนไฮไดรด์ยังให้ค่าดังกล่าวที่สูงกว่าพอลิเบนซอกซาซีนที่ดัดแปรด้วยสารไดแอนไฮไดรด์ และจากผลดังกล่าวแสดงให้เห็นว่าพอลิเบนซอกซีนที่ดัดแปรด้วยสารไดแอนไฮไดรด์ให้สมบัติทางความร้อนที่ดีในขณะที่พอลิเบนซอกซีนที่ดัดแปรด้วยสารโมโนแอนไฮไดรด์ให้สมบัติทางกลที่ดี

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก	....
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KEYWORDS: POLYBENZOXAZINE / ANHYDRIDE / CROSS-LINKING / THERMAL PROPERTIES / MECHANICAL PROPERTIES

WAREERAT PUNUCH: PROPERTY ENHANCEMENT OF POLYBENZOXAZINE MODIFIED WITH MONOANHYDRIDES AND DIANHYDRIDES. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., pp.

Recent development of polybenzoxazine (PBA-a) focuses primarily on broadening their thermal and mechanical properties such as their glass transition temperature (T_g), degradation temperature (T_d) as well as their flexibility and toughness. In this research, It is revealed that the incorporation of mono and dianhydrides can improve both properties of PBA-a but different manner. PBA-a property enhancement by monoanhydrides (i.e. phthalic anhydride, PA and napthalic anhydride, NA) and dianhydrides (i.e. pyromellitic dianhydride, PMDA and naphthalene tetracarboxyllic dianhydride, NTDA) are systematically investigated and compared. The Tg of the alloys was found to be in order of PBA-a:NTDA (304 $^{\circ}$C) > PBA-a:PMDA (296 $^{\circ}$C) >> PBA-a:NA (247 $^{\circ}$C) > PBA-a:PA (223 $^{\circ}$C). Furthermore, The Tg of the alloys was observed to be significantly higher than that of the neat PBA-a owing to the enhanced crosslink density by the anhydride addition. This greater crosslink density results from additional ester linkage formation which is a covalent interaction between phenolic hydroxyl groups of PBA-a and anhydride groups in anhydride as confirmed by Fourier transform infrared spectroscopic technique. From thermogravimetric studies, the alloys display relatively high Td reported at 10% weight loss up to 430 $^{\circ}$C under nitrogen atmosphere and substantial enhancement in char yield at 800 $^{\circ}$C with a value of up to 63% by weight. On the other hand, it was found that tensile strength and elongation at break of monoanhydrides modified PBA-a are significantly greater than that those of dianhydrides modified system comparing at the same mole fraction of modifiers. The above results suggest effective methods to improve thermal properties of the PBA-a with an incorporation of the dianhydrides while better mechanical properties require monoanhydrides as a PBA-a modifiers.

Department: Chemical Engineering
Student's Signature ....
Field of Study: Chemical Engineering
Advisor's Signature ....
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CHAPTER I

INTRODUCTION

1.1 Overview

Recently, there has been an increasing high temperature requirement from the aerospace industry and other industrial applications such as composite matrices, protecting coatings, and microelectronic materials using a thermosetting polymer.

Polybenzoxazines are a newly developed addition polymerized phenolic systems, having a wide range of interesting properties and potential to overcome several shortcomings of conventional novolac and resole type phenolic resin. For example, hexamethylenetetramine (hexamine) is required as curing agent in the curing process of novolac-hexamine. Volatiles such as water or ammonia compounds, etc. must be eliminated [1]. Benzoxazine resin can be easily synthesized from bisphenol-A, formaldehyde and amine by employing solution or solventless methods [2]. The polymerization of benzoxazine resin proceeds via ring opening of oxazine rings by thermal cure. In addition, they do not require catalysts for polymerization or provide a self-polymerizable cross-link system [3-7], do not produce by-product upon curing and there is no corrosion of processing equipment. At present, there are many companies in the world which have been produced benzoxazine for trading including multiplicity requirements of individual applications i.e. Huntsman Company, Henkel Corporation and Shikoku Chemicals Corporation.

There are two main methods to develop the performance of polybenzoxazine. First method is the modification of the structure of benzoxazine monomers. However, disadvantages of the molecular modification to obtain high performance polymer include difficulty of the resin preparation, the purification process, and the high cost of raw materials used. The other is the blends or composites with other high-temperature polymers like epoxy resin [8-11], polyimide [12, 13], dianhydrides [14-16]. Takeichi et al. [13] investigated the thermal property of the polymer alloys between bisphenol-A-aniline type (BA-a) resin and polyimide based on bisphenol A di(phthalic anhydride) ether (BPADA) and oxydianiline (ODA). The authors reported that the glass transition temperatures (T_gs) and thermal stabilities in both systems of PBA-a:polyamic acid (PAA) and PBA-a:polyimide (PI) increased as the imide component increased. At the same ratio, T_gs of PBA-a:PAA alloys were slightly higher that than of PBA-a:PI alloys due to the formation of aromatic ester group (AR-COOR) in the PBA:PAA alloys. Furthermore, carboxylic acid in the backbone of PAA was proved to be a quite effective catalyst for the ring-opening polymerization of benzoxazine and would polymerize at lower temperature probably. Furthermore, they reported that the chemical bonding could be expected in the systems of polybenzoxazine modified with dianhydride.

Recently, a novel PBA-a modified with dianhydrides was successfully prepared by reacting bisphenol-A-aniline-based benzoxazine resin (BA-a) with 3,3’,4,4’ bizophenonetetracarboxylic dianhydride (BTDA) [14, 16]. The copolymers showed significant enhancement in their mechanical and thermal properties. It is worthy to note that the synergism of T_g was observed in the PBA-a modified with BTDA, i.e. the T_g value of PBA-a:BTDA copolymer at the weight ratio of 60/40 (mole fraction of BTDA = 0.4) was reported to be 255 °C which was significantly higher than that of unmodified PBA-a, i.e. 173 °C. Furthermore, FTIR spectra reveals ester linkage formation between hydroxyl group of PBA-a and anhydride group of dianhydride, thus flexible PBA-a was obtained by the utilize of ester linkage.

In the recent time, there was an investigation on the effects of aromatic tetra carboxylic dianhydrides on thermomechanical properties of PBA-a modified with dianhydrides [15], i.e. pyromellitic dianhydride (PMDA), 3,3’,4,4’ bipheneyl tetra carboxylic dianhydride (s-BPDA), and 3,3’,4,4’ bizophenonetetracarboxylic dianhydride (BTDA). The authors suggested that properties of PBA-a were improved by addition dianhydride. The copolymer films exhibited excellent toughness, excellent thermal stability, and good mechanical properties. T_g value of the neat PBA-a was substantially enhanced by blending with the aromatic carboxylic dianhydrides. The effect of types of dianhydrides on T_g was found to be as follows: PBA-a:PMDA>PBA-a:s-BPDA>PBA-a:BTDA. Furthermore, degradation temperature (T_d) and char yield at 800 °C of the copolymer films were also improved with an incorporation of the aromatic carboxylic dianhydrides.

The high performance of PBA-a modified with dianhydrides have been developed for more broad applications, i.e., thermal insulation materials, protecting coatings, high-temperature adhesives, tape-automated bonding (TAB), chip-on-film, and packaging application.

In this work, we demonstrate an ability of benzoxazine resin to react with mono and dianhydries i.e. phthalic anhydride (PA), 1,8-napthalic anhydride (NA), 1,4,5,8-naphthalenetetracarboxylic dianhydrides (NTDA) and pyromellitic dianhydrides (PMDA) to yield novel high performance thermosetting copolymers. The modification is very simple and highly practical for industrial use. mechanical, thermal and thermomechanical properties of the copolymer were systematically investigated.

1.2 Objectives

1. To study the suitable mole ratio of polymeric systems between benzoxazine resin (BA-a) modified with mono and dianhydrides i.e. phthalic anhydride (PA), 1,8-napthalic anhydride (NA), 1,4,5,8-naphthalenetetracarboxylic dianhydrides (NTDA) and pyromellitic dianhydrides (PMDA) on its curing and processing conditions.
2. To evaluate mechanical and thermal properties of polybenzoxazine modified with the mono and dianhydrides and compare the effects of types of anhydrides on the benzoxazine resin.

1.3 Scopes of Research

1. Synthesis of benzoxazine resin by solventless synthesis technology.

2. Preparation of polymeric systems between the benzoxazine modified with monoanhydrides and dianhydrides i.e. phthalic anhydride (PA), 1,8-napthalic anhydride (NA), pyromellitic dianhydrides (PMDA) and 1,4,5,8-naphthalene tetra carboxylic dianhydride (NTDA) at various molar percentage of anhydride from 0 to 67 using N,N-dimethylformamide (DMF) as a solvent.

3. Examination of physical, chemical, thermal and mechanical properties of the polybenzoxazine modified with monoanhydrides and dianhydrides alloy films using

- Fourier Transform Infrared Spectroscope (FTIR)
- Dynamic Mechanical Analyzer (DMA)
- Thermogravimetric analyzer (TGA)
- Universal Testing Machine (Tensile test)
- Solvent Extraction

CHAPTER II

THEORY

2.1 Chemical Reaction of Polymerization

Polymerization, in polymer chemistry, is the process of reacting monomer molecules together in a chemical reaction to form three-dimension networks or polymer chains. There are many forms of polymerization and different systems exit to categorize them. In the case of a thermosetting polymer, Prime [1] stated that “the chemistry of the polymerization begins to branch and then to cross-link” The proposed chemical reaction of polymerization is presented in Figure 2.1

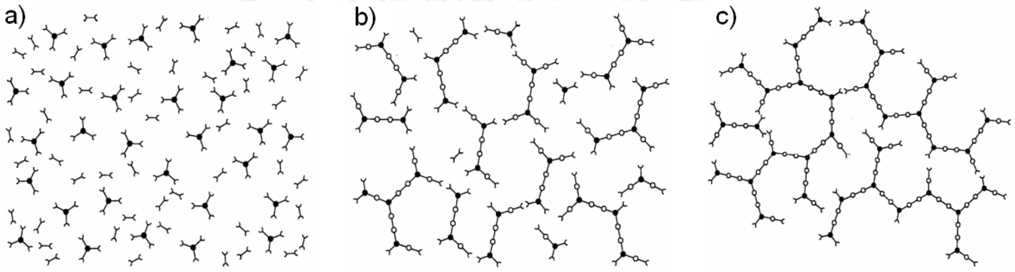

Figure 2.1 Schematic, two-dimensional representation thermoset cure. cure starts with A-stage or uncured monomers and oligomers (a), continues with formation of a gelled but incompletely cross-linked network (b), and ends with the fully cured, C-stage thermoset (c).

The mechanism of polymerization process typically involves several steps that can give rise to complex kinetics. The polymerization reaction is accompanied by dramatic physical change in the reaction medium. At the early stages, cure begins by the growth and branching of chains. As the reaction progresses in B-stage, the molecular weight, the viscosity and the glass transition temperature (T_g) of the medium of the forming polymer increases. The molecular mobility, in turn, decreases. The most dramatic decrease in the mobility is associated with the crosslinking of polymer chains. Eventually several chains become linked together into a network of infinite molecular weight. The abrupt and irreversible transformation from a viscous liquid to an elastic gel or rubber is called the gel point. The gel point of a chemically cross-linking system can be defined as the instant at which the weight average molecular weight diverges to infinity.

2.2 Polymer Alloy

Polymeric material, exhibiting macroscopically uniform physical properties throughout its whole volume that comprises a compatible polymer blend, a miscible polymer blend.

2.2.1 Compatible Polymer Blend

Immiscible polymer blend that exhibits macroscopically uniform physical properties. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the component polymers.

2.2.2 Miscible Polymer Blend

Polymer blend that is a single-phase structure. Miscibility is sometimes assigned erroneously on the basis that a blend exhibits a single T_g or is optically clear. The miscible system can be thermodynamically stable or metastable. For components of chain structures that would be expected to be miscible, miscibility may not occur if molecular architecture is changed, e.g., by crosslinking.

2.3 Benzoxazine Resin

Benzoxazine resin is a story class of phenolic resin which was developed to defeat almost all shortcomings of the phenolic resins and are expected to replace conventional phenolic, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in numerous respects and they demonstrate several remarkable properties that have not been regularly observed by other well-known polymers, as follow excellent process ability owing to low melt viscosity [1], solvent-less method for benzoxazine resin preparation [10], near-zero shrinkage upon polymerization [11], 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 $^{\circ}$C and 220 $^{\circ}$C [12] and gelation takes place in a matter of minutes to tens of minutes at these temperatures if no initiators are employed [13].

Additionally, the ring opening mechanism occurs by breaking of a C-O bond of the oxazine ring as shown in Fig. 2.2 and benzoxazine cure without the support of strong acid catalysis, do not release by-products during the polymerization. The curing behavior of the as-synthesized benzoxazine precursor studied is autocatalytic. The fantastic molecular design flexibility of the polybenzoxazines allows the properties of cured materials to be tailored for the particular requirements of personality applications.

Furthermore, good mechanical properties, such as Tensile Strength = 64 MPa, Tensile Modulus = 5.2 GPa, elongation at break (%) =1.3 [17], high thermal stability (T_d = 334°C; 5%wt loss) 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 [4, 18], much higher than cure temperature, the glass transition temperature (T_g) exhibit in the range 160-340 $^{\circ}$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 an desirability applicant as non-flammable materials for the transportation industry.

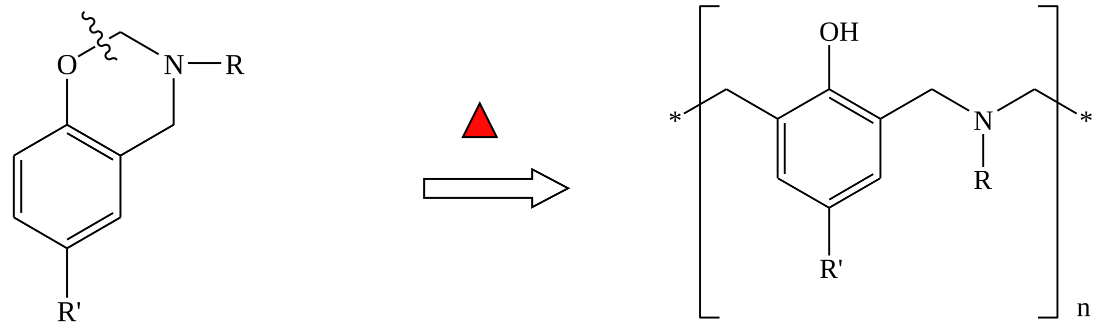

Figure 2.2 Ring opening mechanism of benzoxazine monomers

Finally, low dielectric constants (ε = 3.6 or lower), long-term immersion studies indicate that these materials have a low rate of water absorption and low water absorption [1, 11, 17, 19] that bisphenol-A and aniline based polybenzoxazine saturated at 1.9% by weight [19], 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 [20]. Table 2.1 compares the properties of polybenzoxazine with those of the state- of-the-art matrices [1].

2.4 Raw Materials for Benzoxazine Resin

2.4.1 Synthesis of Bifunctional Benzoxazine Monomer using Bisphenol A

2.4.1.1 Bisphenol A

Bisphenol A is produced by reacting phenol with acetone in the presence of an acid catalyst (Figure 2.3). Common catalysts are aqueous acids or acid clays. Promoters such as thioglycolic acid and resorcinol are also used.

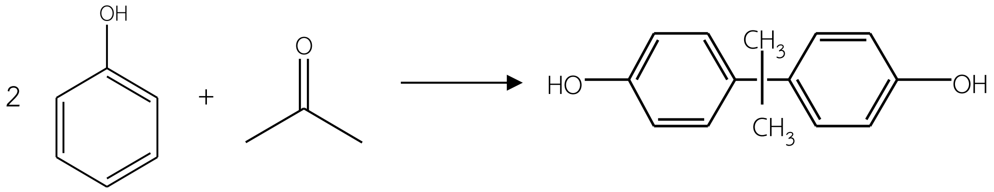

Figure 2.3 Synthesis of bisphenol A.

2.4.1.2 Formaldehyde

Formaldehyde is an unstable colorless gas, which is commercially supplied in 37% aqueous solution, as a solid cyclic trimer (trioxan), and as a solid polymer (paraformaldehyde) which used in this work. Almost all formaldehyde produced is derived from methanol either by oxidative dehydrogenation using silver or copper catalyst (Equation 2.1) or by oxidation in the presence of Fe_2O_3 and MoO_3 (Equation 2.2)

$$CH_3OH \xrightarrow{\text{Cat}} HCHO + H_2 \qquad (2.1)$$

In the oxidative dehydrogenation, the generated hydrogen is oxidized to water upon addition of air.

$$CH_3OH + 0.5O_2 \longrightarrow HCHO + H_2O \qquad (2.2)$$

2.4.1.3 Aniline

The classical method of synthesis of aniline is the reduction of nitrobenzene with hydrogen in the vapor phase using a copper/silica catalyst (Figure 2.4). Nitrobenzene is produced in the nitration of benzene using a mixture of nitric acid and sulfuric acid.

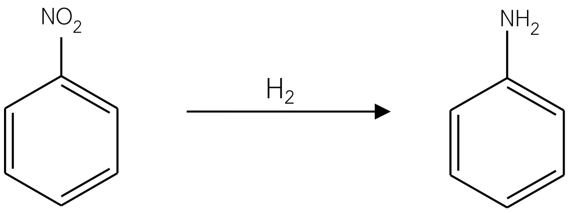

Figure 2.4 Synthesis of aniline by nitrobenzene.

Recently Aristech Chemical completed a 90,000-ton aniline plant using plant using phenol as the feedstock. This technology was developed by Halcon, and it is also used by Mitsui Toatsu in Japan. The animation of phenol is conducted in the vapor phase using an alumina catalyst, and yields are very high.

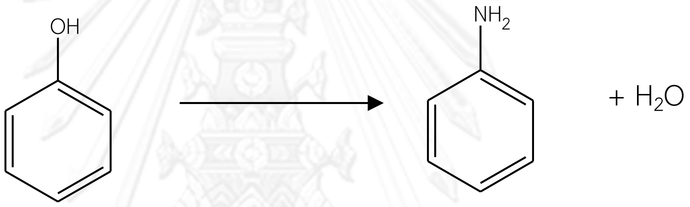

Figure 2.5 Synthesis of aniline by phenol.

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

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

The benzoxazine resins 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 Figure 2.6 and Figure 2.7 an example of the monomer synthesis is Benzoxazine monomer.

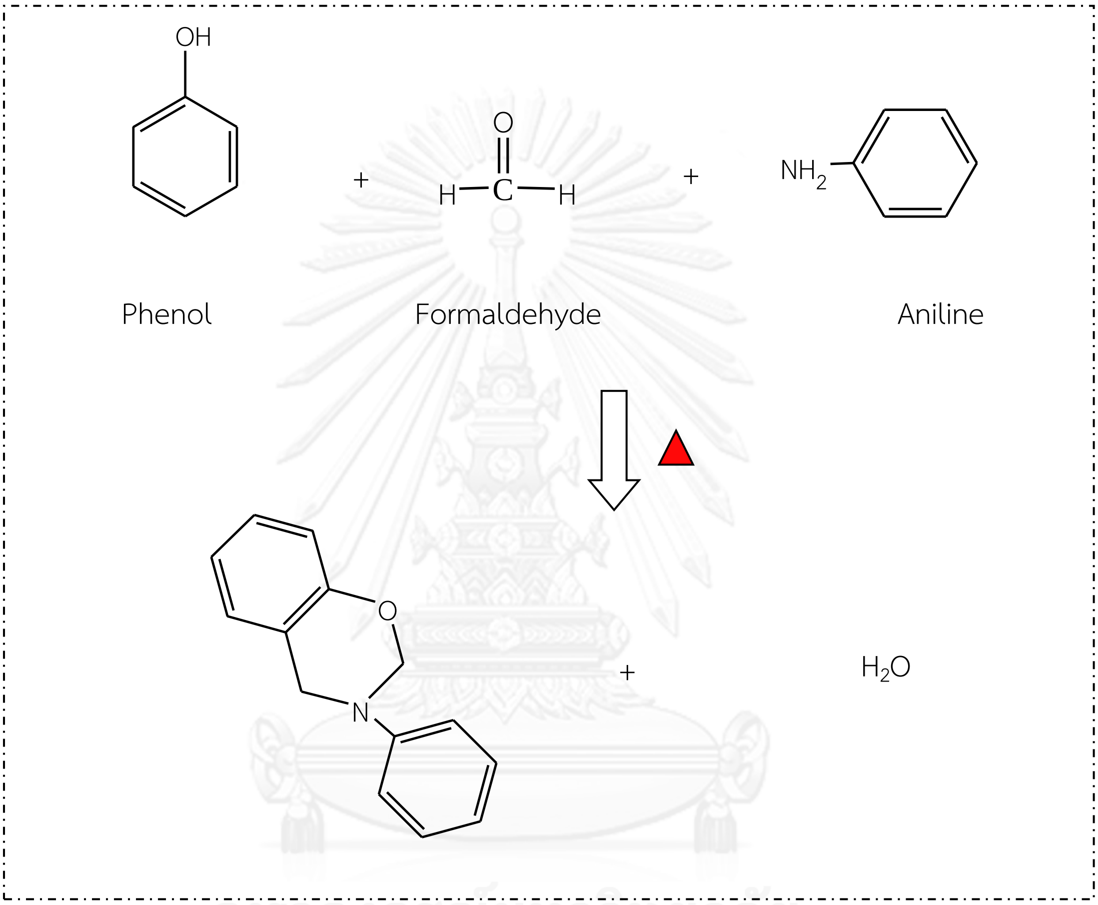

Figure 2.6 Schematic synthesis of monofunctional benzoxazine monomer.

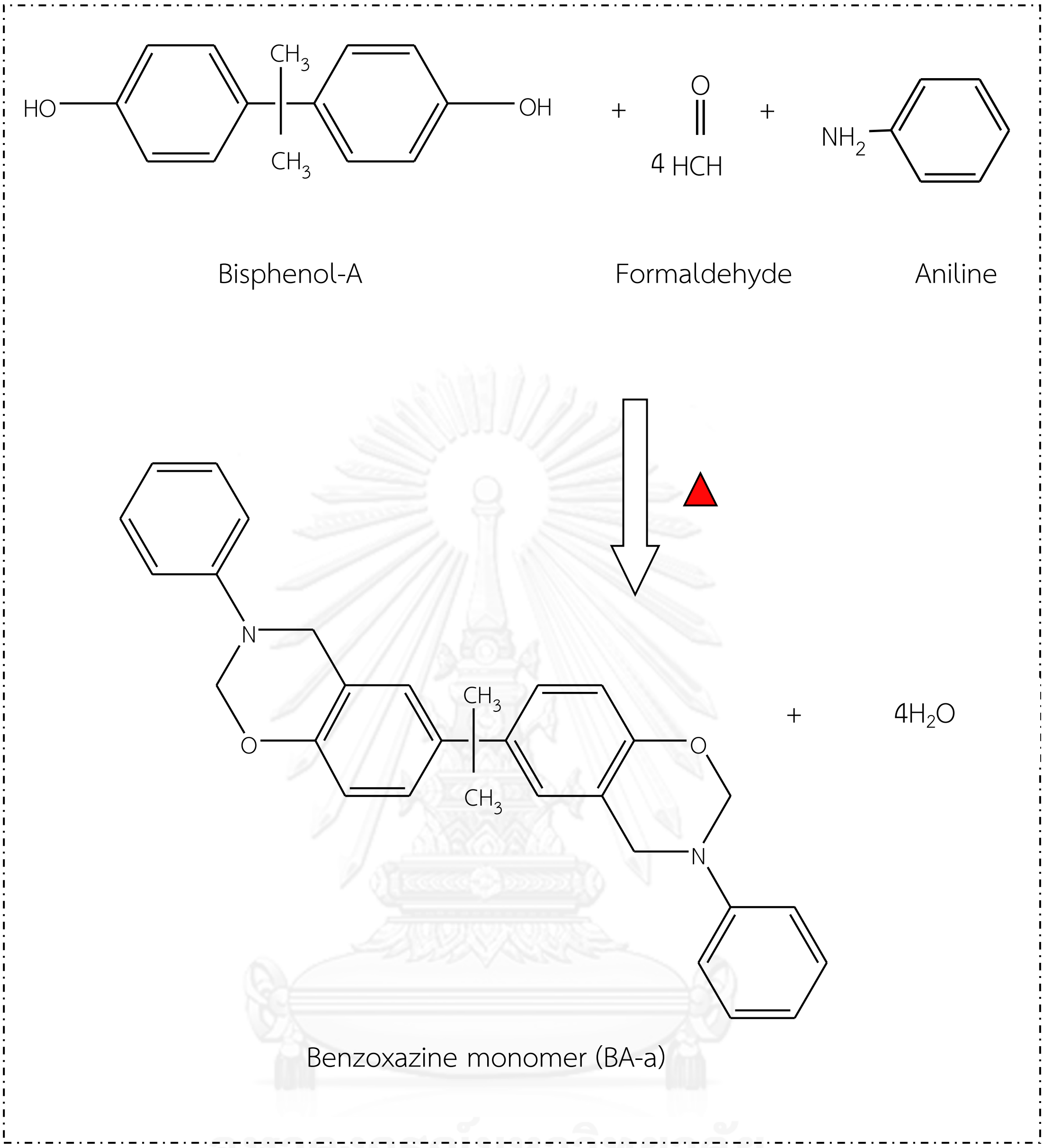

Figure 2.7 Schematic synthesis of bifunctional benzoxazine monomer [21].

In this work, we synthesized bifunctional benzoxazine monomer in our laboratory. Raw materials are bisphenol-A, formaldehyde, aniline as seen Figure 2.7 For the reason that bisphenol-A is low cost and plentiful.

2.5 Anhydride

Anhydride has been used to substance in produce polymers such as polyimides. They have various types of anhydride. For example,

2.5.1 Phthalic anhydride (PA)

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_2O_5 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.

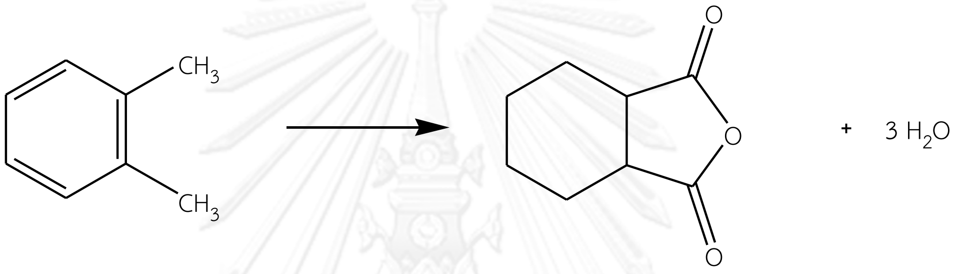

Figure 2.8 The production of phthalic anhydride is produced by oxidizing o-xylene.

Secondly, the air oxidation of naphthalene derived from petrochemical sources or coal is still being used to produce phthalic anhydride. The processes and catalysts were similar [22].

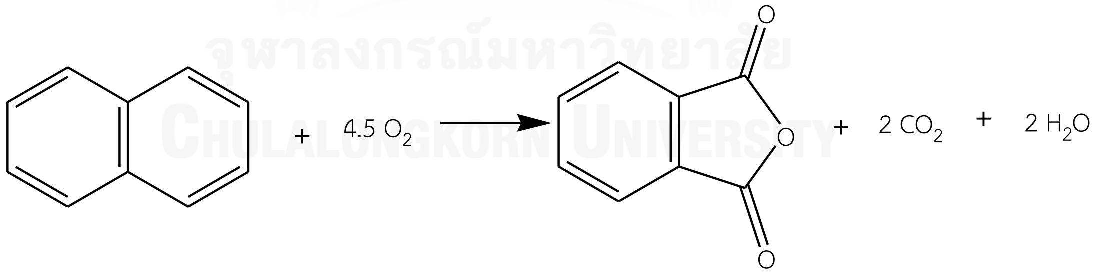

Figure 2.9 The production of phthalic anhydride is produced by air oxidizing of naphthalene.

Table 2.2 Physical and chemical properties of phthalic anhydride (PA).

Physical State	Thin flakes.
Color	White
Vapor Pressure	< 0.01 mmHg @ 20 °C
Boiling Point	284-295 °C @ 760 mmHg
Freezing / Melting Point	132 °C
Flash Point	152 °C (306 °F)
Solubility in water	0.62 g/100 g water @ 20 °C
Solubility in other solvents	Soluble in acetone.
Molecular Formula	$C_8H_4O_3$
Molecular Weight	148.12
Chemical Stability	Stable under conditions of use and storage. Heat will contribute to instability.

2.5.2 1,8-Napthalic anhydride (NA)

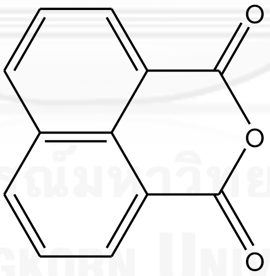

Figure 2.10 Structure of 1,8-Napthalic anhydride (NA).

Table 2.3 Physical and chemical properties of 1,8-napthalic anhydride (NA) [23].

Physical State	Powder
Color	Beige
Boiling Point	407.5 °C
Freezing / Melting Point	267 - 269 °C
Flash Point	272 °C
Solubility in water	decomposes
Molecular Formula	$C_{12}H_6O_3$
Molecular Weight	198.17

2.5.3 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA)

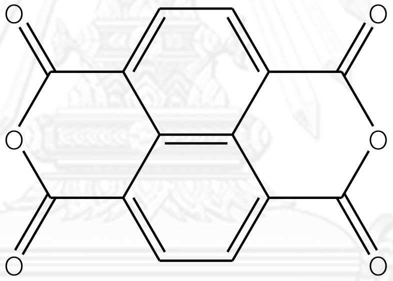

Figure 2.11 Structure of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA)

Table 2.4 Physical and chemical properties of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) [24].

Physical State	Powder
Color	Light brown
Boiling Point	607 °C
Freezing / Melting Point	>300 °C
Sensitive	Moisture sensitive
Molecular Formula	$C_{14}H_4O_6$
Molecular Weight	268.18

2.5.4 Pyromellitic dianhydride (PMDA)

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.

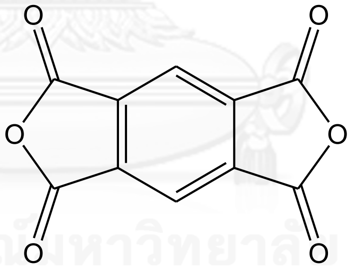

Figure 2.12 Structure of pyromellitic dianhydride (PMDA)

Table 2.5 Physical and chemical properties of pyromellitic dianhydride (PMDA) [25].

Physical State	Powder
Color	white to light beige
Vapor Pressure	< 0.01 hPa @ 20 °C
Boiling Point	397 - 400 °C @ 760 mmHg
Freezing / Melting Point	283 - 287 °C
Flash Point	380 °C (716.00 °F)
Solubility in water	Decomposes
Solubility in other solvents	Soluble in acetone.
Molecular Formula	$C_{10}H_2O_6$
Molecular Weight	218.12
Chemical Stability	Stable under normal temperatures and pressures. Moisture sensitive.

2.6 Solvent

Dimethylformamide is an organic compound. Commonly abbreviated as DMF, this colorless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded samples often have a fishy smell due to impurity of dimethyl amine. Its name is derived from the fact that it is a derivative of form amide, the amide of formic acid.

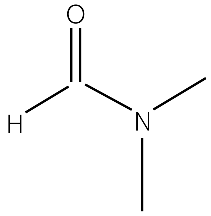

Figure 2.13 Structure of dimethylformamide (DMF)

Table 2.6 Physical and chemical properties of dimethylformamide (DMF) [26].

Physical State	Liquid
Color	Colorless
Vapor Pressure	516 Pa
Boiling Point	152 - 154 °C
Freezing / Melting Point	- 60 °C
Flash Point	380 °C (716.00 °F)
Solubility in water	Miscible
Molecular Formula	$(CH_3)_2NC(O)H$
Molecular Weight	73.09

CHAPTER III

LITERATURE REVIEWS

Ardhyananta et al. [27] reported the improvement of thermal stability, mechanical property, flame resistance, and flexibility of bisphenol-A-aniline based polybenzoxazine by alloying with polydimethylsiloxane (PDMS) since PDMS is one of the most important silicones that have inorganic main chain, showing both high flexibility (Figure 3.1) and many intriguing properties, e.g. good oxidative stability, low surface energy, high hydrophobicity, high gas permeability, and good biocompatibility [28]. The alloys at 7wt% and 13wt% of PDMS revealed higher thermal stability, i.e. the degradation temperatures at 10 % weight loss are 352 °C and 368 °C, respectively. These values are greater than that of pure polybenzoxazine (326 °C). It was reported that the glass transition temperature determined from E” peak of DMA results presented two values. The higher T_g was in the range of 176-185 °C, while the lower T_g was in the range of 63-72 °C. These T_g values correspond to those of polybenzoxazine and PDMS components, respectively. This behavior revealed the phase separation of the alloy in micro-scale. In addition, the char yield at 850 °C of the alloys increased with increasing PDMS content. The values of residual weight were in the range of 40 to 46%, presenting the enhancement of the flame retardancy. In addition, they reported that the obtained alloy film render higher tensile strength and elongation at break than neat polybenzoxazine due to the toughening effect of PDMS. In recent times, the effect of pendant groups of polysiloxane, e.g. PDMS, PMPS, and PDPS on thermal properties have been reported by Ardhyanant et al. [28]. The phenyl group of polysiloxanes as PMPS and PDPS improved their compatibility with polybenzoxazine. The alloying could enhance the glass transition temperature because of high crosslink density by plasticizing effect of polysiloxanes. Moreover, polybenzoxazine/PDMS alloy exhibited the optimum improvement of degradation temperature, while polybenzoxazine/PDPS presented the most effectiveness of flame retardancy. That means the thermal properties of the polybenzoxazine/polyimide-siloxane alloys depends on the types of polysiloxanes.

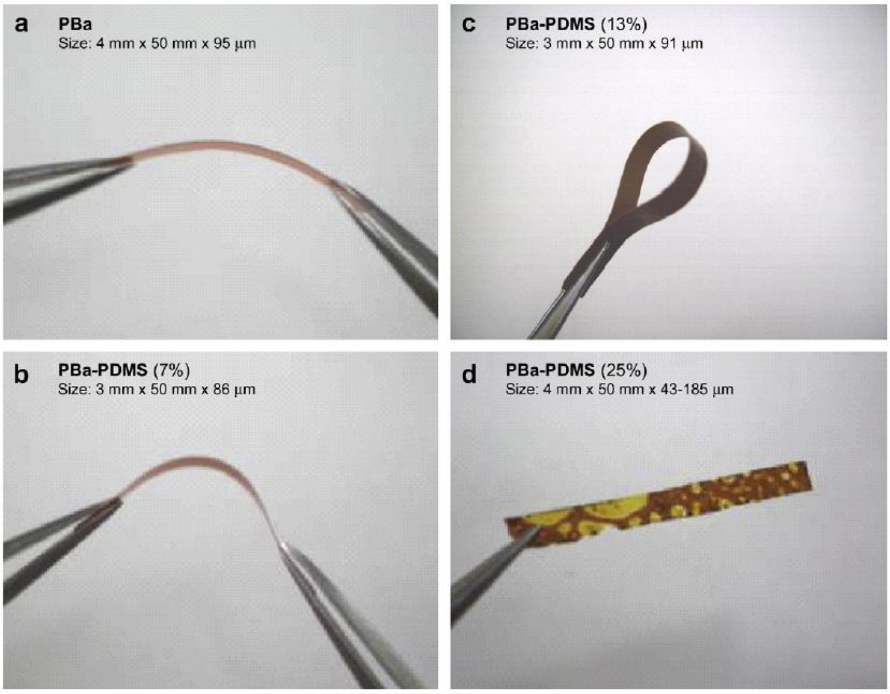

Figure 3.1 Photographs of pristine PBa (a) and PBa–PDMS hybrids prepared by sol–gel method at 7 (b), 13 (c) and 25 wt% (d) PDMS contents.

In order to enhance the miscibility of the alloy between polybenzoxazine and polysiloxanes, the polybenzoxazine alloying with PDMS-containing polyimide as polyimide-siloxane with hydroxyl functional group (PI-Si) was developed by Takeichi et al.[11]. The researcher reported that only one glass transition temperature was observed at 300 °C because crosslinked polymer networks were formed. It is worthy to note that in case of polybenzoxazine alloyed with polyimide-siloxane without hydroxyl functional group (PISi), the synergy of char yield was reported at certain content of PISi as presented in Figure 3.2 [29]. The phenomenon could be due to a large amount of aromatic ring in the blends with some chemical interaction between polybenzoxazine and PISi.

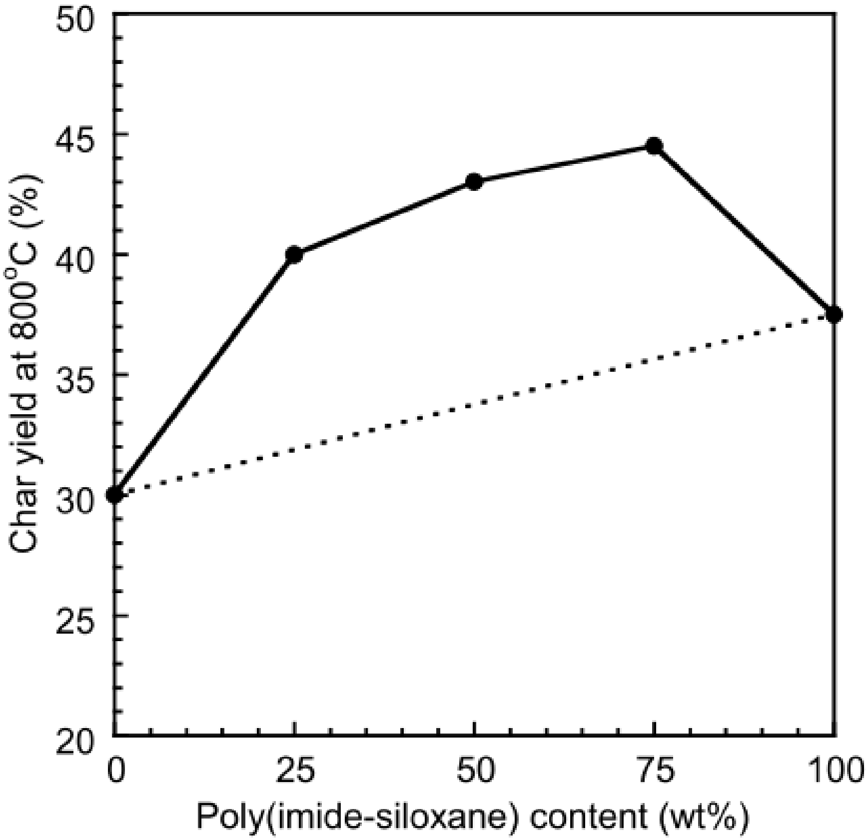

Figure 3.2 Char yield of polybenzoxazine/polyimide-siloxane alloys.

Takeichi et al. [13] prepared the polymeric blends using a bifunctional benzoxazine resin, 6,6'-(1-methylethylidene)bis(3,4-dihydro-3-2H-1,3-benzoxazine) and a polyamic acid (PAA, intermediate compound to synthesize polyimide) or soluble polyimide (PI) derived from bisphenol A di(phthalic anhydride) ether (BPADA) and oxydianiline (ODA). The results of loss modulus (E") and loss tangent (tan δ) exhibited only one glass transition temperature (T_g) in both systems of PBZ/PAA and PBZ/PI. That means these blending systems were miscible. The T_g s was shifted to higher temperature when increasing the content of imide. In comparison at the same ratio, the T_gs of PBZ/PAA alloys were slightly higher than that of PBZ/PI alloys. For example at 30 wt% of PBZ, the T_g of PBZ/PI alloys are 205 °C, while that of PBZ/PAA is higher than 215 °C. That indicates the formation of cross-linked structure in the alloys of PBZ/PAA. In aspect of thermal stability of PBZ/PI alloys and PBZ/PAA alloys, the value of degradation temperature increased with the increase of imide content.

In addition, the synergism of char yield was observed as shown in Figure 3.3. It was presented that an interpenetrating polymer network (IPN) structure occurred in the systems. The PAA was imidized in situ with the polymerization of benzoxazine. This leads to the formation of aromatic ester group (AR-COOR). The proposed reaction between PAA and benzoxazine is presented in Figure 3.4. The researchers explained that the combination of PBZ and PAA contains IPN structure, while that of PBZ and PI is supposed to be pure semi-IPN structures.

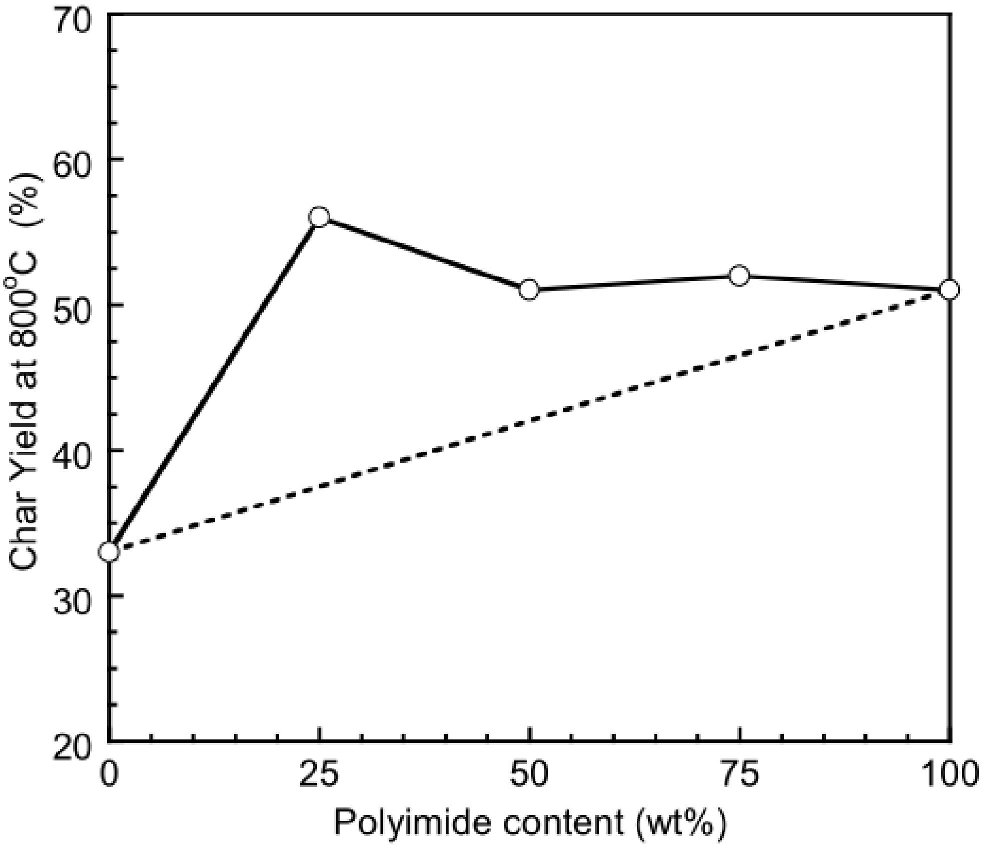

Figure 3.3 Char yield of polybenzoxazine/polyimide blends.

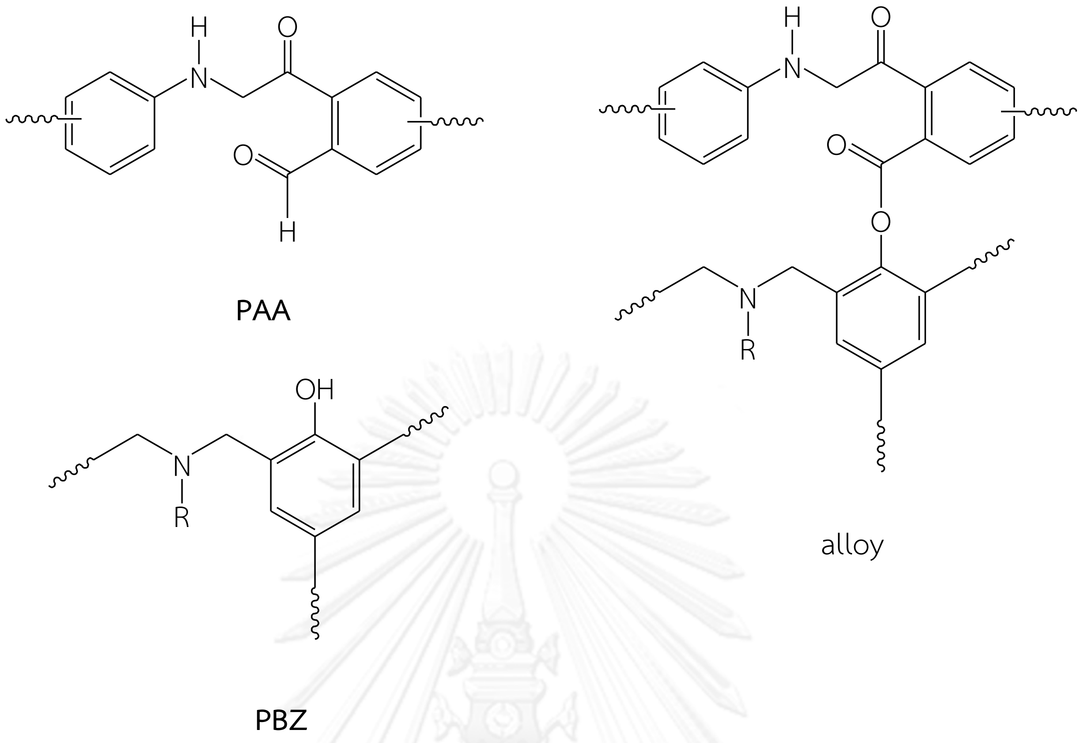

Figure 3.4 Proposed reactions between PAA and PBZ.

As previously mentioned in the section of the PBA-a:PAA alloys, Takeichi et al. [13] reported that the chemical bonding between carboxylic acid of PAA to generated aromatic ester group (AR-COOR). Thus, the chemical bonding could be expected in the systems of polybenzoxazine modified with dianhydride. Recently, a novel PBA-a modified with dianhydrides was successfully prepared by reacting bisphenol-A-aniline-based bifunctional benzoxazine resin (BA-a) with 3,3’,4,4’ bizophenonetetracarboxylic dianhydride (BTDA) were studies by C. Jubsilp, T. Takeichi, S. Rimdusit, (2011) [30] and S. Rimdusit, B. Ramsiri, C. Jubsilp, I. Dueramae, (2012) [14]. From their works, the result from FTIR spectra in Figure 3.3(c). Showed that the chemical interactions between hydroxyl group of PBA-a and anhydride group of BTDA occur to generated ester linkages at spectrum of 1730 cm^{-1}. When PBA-a was modified with dianhydride, the ester linkage was formed. That is able to make the rigid PBA-a flexible. Furthermore, The PBA-a:BTDA copolymer at the weight ratio of 60/40 was reported to be 255 °C. This value is significantly higher than that of unmodified PBA-a, i.e. 173 °C as presented in Figure 3.5. The T_g improvement of PBA-a is attributed to the increase in crosslink density of the copolymers determined by dynamic mechanical analysis (DMA). In addition, the resulting PBA-a:BTDA copolymer displays relatively high thermal stability with T_d up to 364 $^{\circ}$C and considerable enhancement in char yield of up to 61% vs. that of 38% of the PBA-a as exhibited in Figure 3.6.

In the recent time, there was an investigation on the effects of aromatic tetracarboxylic dianhydrides on the thermomechanical properties of PBA-a:dianhydride alloys [15]. Three different tetracarboxylic dianhydrides were determined, i.e. pyromellitic dianhydride (PMDA), 3,3’,4,4’ biphenyltetracarboxylic dianhydride (s-BPDA), or 3,3’,4,4’ benzophenonetetracarboxylic dianhydride (BTDA). The authors discussed that the rendered copolymer of PBA-a and three types of dianhydride could be potential candidates for high performance materials with excellent mechanical integrity for high temperature applications.

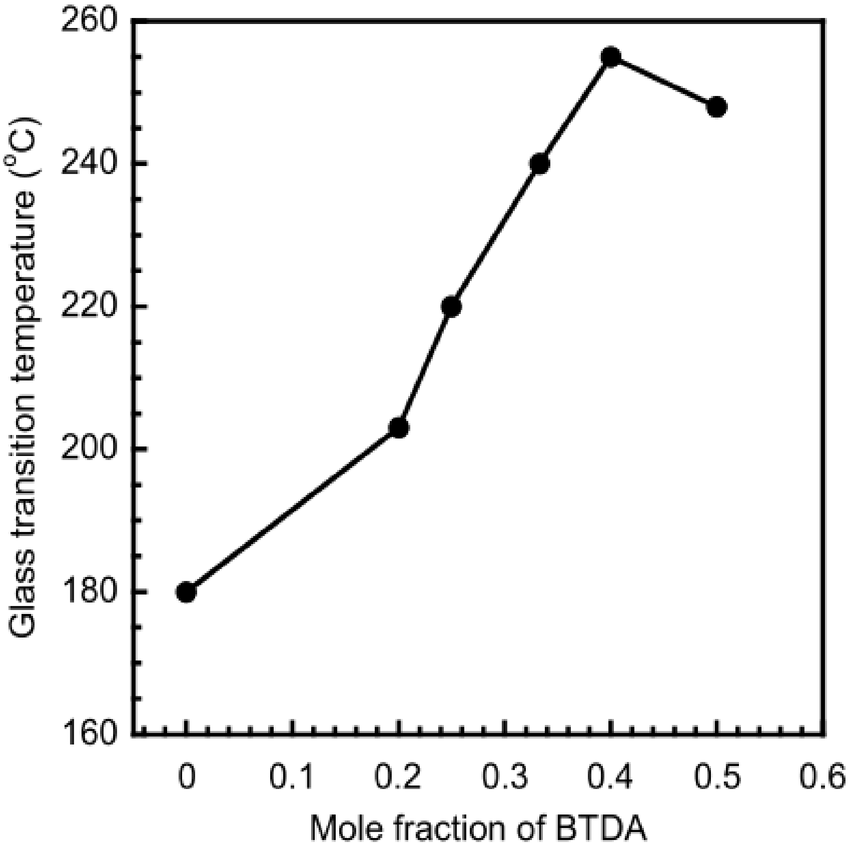

Figure 3.5 Glass transition temperature of polybenzoxazine/dianhydride alloy at various BTDA mole fractions.

The glass transition temperatures (T_g) of the copolymers were reported to be in the order of PBA-a:PMDA > PBA-a:s-BPDA > PBA-a:BTDA. The difference of the glass transition is relevant to the rigidity of dianhydride components. All types of dianhydride render significantly higher T_g than that of neat PBA-a due to the improved crosslink density. Moreover, the decomposition temperature at 10 % weight loss of neat PBA-a was 361 ^{o}C, while those of the copolymers increased in the order of PBA-a:PMDA (426 ^{o}C) > PBA-a:s-BPDA (422 ^{o}C) > PBA-a:BTDA (410 ^{o}C). This thermal stability could be related to the aromatic skeleton of the dianhydride component, i.e. phenylene unit > biphenyl unit > benzophenone unit [36]. Moreover, the properties of polybenzoxazine modified with dianhydrides are shown in table 3.1.

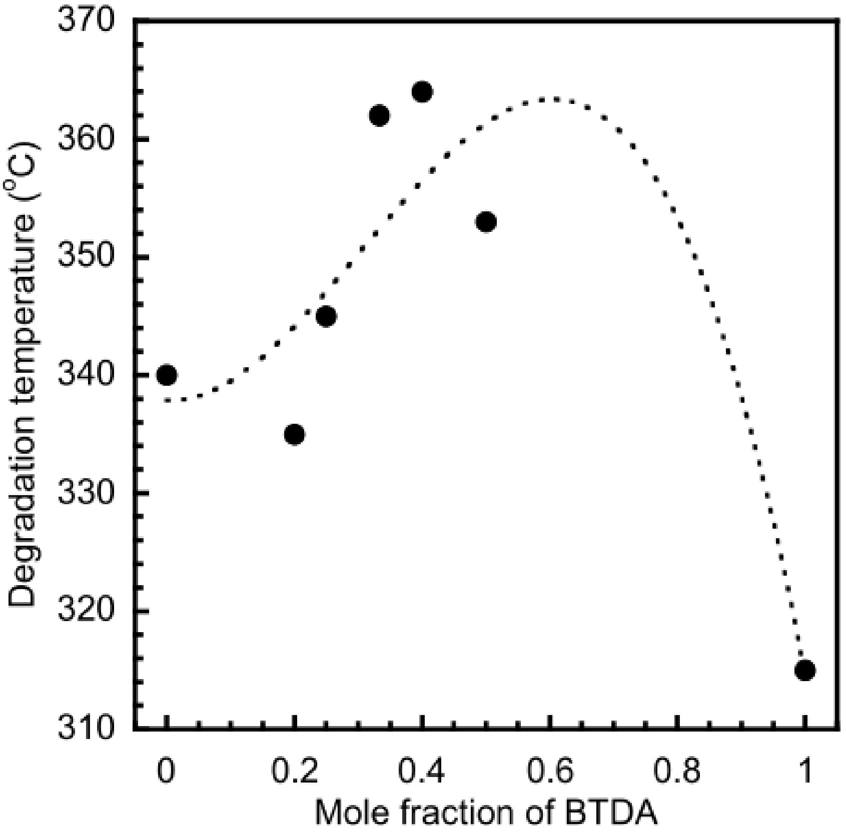

Figure 3.6 Degradation transition temperature of polybenzoxazine/dianhydride alloy at various BTDA mole fractions.

Table 3.1 Properties of polybenzoxazine modified with dianhydrides.

Composition (molar ratio)	T_g ($^\circ$C)		E' at rubbery plateau (MPa)	Crosslink density (mol/m^3)	T_d ($^\circ$C) at 10% weight loss	Char yield at 800 $^\circ$C (%)
	from DSC	from E''				
BA-a/BTDA						
100/0	165	166	45	4014	361	32.9
75/25	206	224	212	6311	396	58.8
60/40	239	263	302	7630	410	61.7
50/50	236	249	270	6670	420	61.5
BA-a/PMDA						
75/25	229	210	294	6796	375	57.0
60/40	306	296	554	8656	426	60.2
50/50	263	290	613	7885	418	55.7
BA-a/s-BPDA						
75/25	219	191	184	6101	389	55.8
60/40	257	270	325	7664	422	62.3
50/50	242	243	242	6507	439	59.2

CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

Materials used in this research are benzoxazine resin, anhydrides, Dimethylformamide (DMF; AR grade) as solvent. 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. Anhydrides have four types i.e. Phthalic anhydride (PA; 99%), 1,8-Napthalic anhydride (NA; 97%) Pyromellitic dianhydride (PMDA; 99%) and 1,4,5,8-Napthalene tetra carboxylic dianhydride (NTDA; 98%) were supplied from Acros organics, and Finally, Dimethylformamide (DMF) solvent purchased from Fisher Scientific.

4.2 Synthesis of Benzoxazine Monomer

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 [1]. 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.

4.3 Preparation of Benzoxazine-Anhydride Alloying Films

The benzoxazine monomer (BA-a) was blended with various mole percentage of anhydride from 0 to 67 mol%. The mixture were dissolved in Dimethylformamide (DMF) 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 to partially remove the DMF solvent, followed by thermal curing at 120, 150, 170 °C for 1 h each and 190, 210 °C 230 °C for 2 h each. Finally all film samples will be fully cured at 240 °C for 1 h to guarantee complete curing of the mixtures.

4.4 Sample Characterizations

4.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure and network formation behavior of sample was studied by a Fourier transform infrared spectroscopy (FTIR). 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 128 scans at a resolution of 4 cm^{-1} and a spectral range of 4000-650 cm^{-1}. For Dianhydrides before synthesis, a small amount of a powder sample was casted as thin film on a potassium bromide (KBr) window.

4.4.2 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 7x10x0.1 mm^3 (WxLxT). 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 δ) were then obtained. The glass transition temperature (T_g) was taken as the as the maximum point on the loss modulus curve in the DMA thermograms.

4.4.5 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 850 °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/anhydride polymeric alloys were reported at their 10% weight loss and char yields of the above specimens were also reported at 800 °C.

4.4.6 Universal Testing Machine (Tension Mode)

The tensile strength and tensile modulus of the BA-a/anhydride polymeric alloys were determined using a universal testing machine (model 5567) from Insron 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 using five specimens per test condition.

4.4.7 Solvent Extraction

The polymer alloy films after curing at 240 °C for 10 h were immersed in 10 ml of chloroform to determine the nature of crosslinking network formation. The mass of the residual solid was weighed after 30 day immersion.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Preparation of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

PBA-a:anhydride alloying films were produced by blending benzoxazine monomer with monoanhydrides or dianhydrides at desirable mole ratios in dimethylformamide solvent (DMF) using 3 g of solid monomer mixture in 3 ml of DMF. During the solution mixing, it could be observed that PA and PMDA tended to be readily dissolved in BA-a/DMF solution whereas solutions of BA-a:NA and BA-a:NTDA were more difficult to obtain. In the latter case, NA or NTDA will be dissolved in hot DMF (80 °C). The NA or NTDA homogenous solution was obtained by magnetic stirring for about 10 min. The resulting solution was then poured into molten benzoxazine resin (80 °C). The brown and transparent solutions of BA-a/NA as well as BA-a/NTDA solutions were obtained after 10 min using magnetic stirring. The mixtures of BA-a:PA and BA-a:PMDA are light yellow and light red-brown in color. While, the mixtures of BA-a:NA and BA-a:NTDA were dark red-brown in color as seen in Figure 5.1. Thereafter, all the solution was cast and vacuum dried at 80 °C for 24 hr to partially remove the DMF solvent, followed by thermal curing at 120, 150, 170 °C for 1 hr each and 190, 210 °C 230 °C for 2 hrs each. Finally all film samples will be fully cured at 240 °C for 1 hr.

After curing at temperature up to 240 °C, the visual appearance of PBA-a:PA and PBA-a:PMDA were found to be transparent red brown in color and PBA-a:NA and PBA-a:NTDA films were transparent dark brown in color, respectively as illustrated in Figure 5.2. The thickness of the obtained films is about 100 μm.

5.2 Fourier Transform Infrared Spectroscopy (FT-IR) Study of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

FTIR spectra of benzoxazine resin (BA-a) and polybenzoxazine (PBA-a) are showed in Figure 5.3a and Figure 5.3b, respectively. Characteristic absorption bands of the BA-a resin were found at 1232 cm^{-1} assigned to C-O-C stretching mode of oxazine ring whereas the band around 1497 cm^{-1} and 936 cm^{-1} were attributed to the tri-substituted benzene ring. Following the curing phenomenon, an infinite three dimensional network was formed from benzoxazine ring opening by the breakage of C-O bond and after that the benzoxazine monomers will be transformed from a ring structure to a network polymer structure. During this process, the backbone of benzoxazine ring, the tri-substituted benzene ring around 1497 cm^{-1}, became tetra-substituted benzene ring centered at 1488 cm^{-1} and 878 cm^{-1} which led to the formation of a phenolic hydroxyl group-based polybenzoxazine (PBA-a) structure. The presence of a phenolic hydroxyl group is also confirmed by the appearance of a new absorption peak at about 3300 cm^{-1}. The spectroscopic result evidently suggested that the benzoxazine monomers (BA-a) were thermally polymerized through a ring opening reaction to form a corresponding polybenzoxazine (PBA-a) which rendered phenolic hydroxyl groups. This newly formed hydroxyl group was expected to react with anhydride modifiers in the following alloying step.

The chemical transformation of PBA-a, monoanhydrides i.e., phthalic anhydride (PA), or napthalic anhydride (NA), and dianhydrides i.e., pyromellitic dianhydride (PMDA) or naphthalene tetra carboxylic dianhydride (NTDA) as well as their network formation reactions between the PBA-a and both groups of anhydride modifiers upon thermal curing were systematically investigated and the resulting spectra are illustrated in Figures 5.4-5.7. The spectra of the monoanhydrides and dianhydrides provided characteristic absorption peaks in the range of 1790-1763 cm^{-1} due to symmetric stretching and 1858-1831 cm^{-1} due to asymmetric stretching of carbonyl groups as seen in Figures 5.4b-5.7b.

After a fully cured stage, the IR spectra of PBA-a:PA, PBA-a:NA, PBA-a:PMDA and PBA-a:NTDA alloys revealed the disappearance of the absorption peak at about 936 cm^{-1} and the reduction of the 1497 cm^{-1} bands of the oxazine ring. Meanwhile, the new band at about 1486-1491 cm^{-1}, which was ascribed to tetra-substituted benzene ring, was clearly observed. The chemical interaction between phenolic hydroxyl groups of PBA-a and carbonyl groups of anhydride occurred to generate ester linkage as confirmed by the appearance of the band at about 1730-1712 cm^{-1} due to C=O stretching band of the ester linkage. In general, IR spectra for esters exhibit an intense band in the range 1750-1705 cm^{-1} [31]. This peak varies slightly depending on the different structure and the nature of the anhydrides used. The PBA-a:anhydride copolymer spectra are showed in Figures 5.4a-5.7a. We can see that the carbonyl stretching bands from the anhydride moieties at 1858-1831 cm^{-1} and 1790-1763 cm^{-1} completely disappeared. Furthermore, the free carboxylic acid vibration band occurred after thermal curing of the PBA-a:anhydride mixtures can also be seen as a band at 1669-1651 cm^{-1} due to C=O stretching band [32]. The proposed reaction models of those monoanhydrides and dianhydrides modified PBA-a alloys are shown in Scheme 1 and Scheme 2 which was proposed in our previous works [14-16]. The reaction was also similar to the ester formation between a diglycidyl ether of bisphenol A based epoxide resin (DGEBA) and dodecyl succinic anhydride (DDSA) as reported by Ghaemy and Riahy [33].

5.3 Dynamic Mechanical Properties of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

Recently, dynamic mechanical analysis (DMA) at a selected fixed frequency over a range of temperature has widely used as useful analytical techniques for the characterization 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.

The storage modulus that provides the materials stiffness of the alloy films at glassy state region reflecting their molecular rigidity of the PBA-a:PA and PBA-a:PMDA alloying films was depicted in Figure 5.8, while those of PBA-a:NA and PBA-a:NTDA were shown in Figure 5.9. All alloys were fully cured to yield highly cross-linked structures. The storage modulus of solid polymer alloys at glassy state was higher than that of the neat PBA-a and values increases when the anhydride fraction in the alloys increases. The storage modulus at room temperature (35 °C) of the PBA-a:anhydride alloying films at various anhydride contents exhibited the values in the range of 2.6-3.4 GPa, which are higher than that of the neat PBA-a of 2.57 GPa as shown in Table 5.1. In addition, The storage modulus at room temperature (35 °C) of PBA-a:anhydride alloy films exhibited a maximum value at 60 mol% for PBA-a:mono-anhydride and 40 mol% for PBA-a:di-anhydride, values of 2.9 GPa for PBA-a:PA, 3.0 GPa for PBA-a:PMDA, 3.2 GPa for PBA-a:NA, and 3.4 GPa for PBA-a:NTDA.This is due to higher crosslink density and greater aromatic content of the anhydride. We can see that the storage modulus of PBA-a:anhydride alloy films is approximately the same as that of typical polyimide films with reported value in the range of 2.2-3.5 GPa [13, 30].

The glass transition temperature (T_g) value determined from the maximum point of loss modulus curve, of the PBA-a:PA and PBA-a:PMDA alloying films was depicted in Figure 5.10, while those of PBA-a:NA and PBA-a:NTDA were shown in Figure 5.11. The transparent cured anhydride modified PBA-a alloy films suggested the good compatibility between anhydride and BA-a components. The appearance of a single T_g in viscoelastic measurements indicated that no phase separation in the cured alloy films. From the figures, The T_g value of the neat PBA-a was determining to be about 178 °C and those of PBA-a:anhydride alloying films were determine to be in the range of 183-304 °C. In addition, the ultimate T_g values of the alloys were reported to be in the order of PBA-a:NTDA (304 °C) > PBA-a:PMDA (296 °C) >PBA-a:NA (247 °C) > PBA-a:PA (223 °C). It is attributed to the fact that di-anhydride (NTDA and PMDA) possess greater amount of reactive functional group to form the network than mono-anhydride (PA and NA). That means the crosslink densities of the alloys with di-anhydride is higher than those of the alloys with mono-anhydride. In addition, NTDA and NA possess more amounts of aromatic rings than PMDA and PA, respectively. Therefore, the crosslink densities of the alloys with NTDA and NA are higher than those of the alloys with PMDA and PA. The increase of crosslink density could hinder the molecular mobility and lead to the increase of the glass transition temperatures.

From our result, it is found that T_g values of anhydride modified PBA-a were increased according to the decrease of structure flexibility and number of reactive functional on the anhydrides. All types of anhydrides provide significantly higher T_g than that of the neat PBA-a due to the improved crosslink density from the additional ester linkage formation between phenolic hydroxyl group of PBA-a and anhydride group of anhydride as depicted in FTIR spectra results in further T_g improvement of the alloys [14-16]. In a tight network structure, in which rubbery plateau modulus is greater than 10^7 Pa such as in our case, the non-Gaussian character of the polymer network become more and more pronounced and equation from theory of rubbery elasticity is no longer applicable. The approximate relation expressed in the equation below proposed by Nielsen [34, 35] is thus preferred and is reported to better describe the elastic properties of dense network. As consequence, a crosslink density of these alloy networks, ρ_x, can be estimated from a value of the equilibrium storage shear modulus in rubbery region (G_e’) which equals to $E_e^{'}/3$ as followed:

$$\log \frac{E_e^{'}}{3} = 7.0 + 293\,(\rho_x) \qquad (5.1)$$

Where $E_e^{'}$ (dyne/cm^2) is an equilibrium tensile storage modulus on rubbery plateau, ρ_x (mol/cm^3) is crosslink density which is the mole number of network chain per unit volume of the polymers.

From the same table, it was obviously that the modulus in rubbery plateau of PBA-a:anhydride alloy films also increased with the content of the four anhydrides with the ultimate values observed again at 60 mol% for PBA-a:mono-anhydride and 40 mol% for PBA-a:di-anhydride. Crosslink density values of the PBA-a and its alloys, i.e., PBA-a:PA, PBA-a:PMDA, PBA-a:NA, and PBA-a:NTDA, calculated from Equation (5.1) are 3,980 mol/cm^3, 6,816 mol/cm^3, 8,655 mol/cm^3, 7,417 mol/cm^3, and 8,751 mol/cm^3, respectively. It is evident that the crosslink density of the neat PBA-a was greatly enhanced by an addition of anhydride, corresponding to an enhancement in their T_g values discussed previously. An effect of crosslink density which is one key parameter on T_g of anhydride modified PBA-a network.

Loss tangent (tan δ) of the PBA-a and their alloys of various anhydride types is illustrated in Figure 5.12 and Figure 5.13. A peak height of tan δ of the alloys were reported to be in the order of PBA-a:PA > PBA-a:NA > PBA-a:PMDA > PBA-a:NTDA, while the peak position of their alloys clearly shifted to higher temperature. The result suggested that an increase in crosslink density cause a restriction of the chain's segmental mobility in aromatic carboxylic anhydride modified PBA-a alloys thus a more elastic nature of the alloy films compared to the neat PBA-a. In addition, the width-at-half-height of tan δ curves was broader in their PBA-a alloys, which suggested a more heterogeneous network in the resulting polymer alloys possibly due to a hybrid polymer network formation. Furthermore, the obtained transparent alloy films and single tan δ peak observed in each alloy suggested no macroscopic phase separation in their PBA-a alloy films.

5.4 Thermal Stability of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

In general, the thermal stability of the materials can be determined by measuring the thermally induced weight loss of the materials as a function of the applied temperature. That could be represented in terms of the thermal degradation temperatures (T_d) and char yields, investigated by thermo gravimetric analysis.

The degradation temperature reported at 10% weight loss (T_d) under nitrogen atmosphere of the PBA-a:PA and PBA-a:PMDA alloying films was depicted in Figure 5.14, while those of PBA-a:NA and PBA-a:NTDA were shown in Figure 5.15. The T_d

values are also summarized in Table 5.2. In this study, the molar percentages of anhydride were varied from 0 to 67%. From the results, the T_d of PBA-a was reported to be 347 °C. The T_d values were systematically increased with the increasing of anhydride content (all types of anhydride). This could be attributed to the formation of poly (aromatic ester) in the alloys, i.e. the T_d value of polyester was reported to be 355-440 °C [36]. The obviously increasing of T_d was corresponded to the FTIR spectra as previously reported. The formation of additional crosslinking site via ester linkage (between the carbonyl groups in the aromatic carboxylic anhydride and phenolic hydroxyl groups of the neat PBA-a) was found to effectively enhance the T_d of resulting BA-a: anhydride alloys. Moreover, the increase of crosslink density and the presence of an aromatic structure of aromatic carboxylic anhydride in PBA-a could suppress segmental decomposition via gaseous fragments thus providing an observed enhancement in T_d of the samples. However, it could be observed that all four types of anhydride are able to enhance the T_d of PBA-a with different degree of T_d improvement, i.e. at 20 mol% of anhydrides, the alloys with PA and NA (mono-anhydrides) provided the T_d increase for 8 °C and 16 °C, respectively; while, the T_d values of the alloys with PMDA and NTDA (di-anhydrides) could increase the values for 26 °C and 31 °C, respectively. When increasing the molar content of anhydride as much as 40 mol%, the alloys with PA and NA (mono-anhydrides) provided the increase of T_d for 20 °C and 28 °C, respectively; while, the T_d values of the alloys could be increased for 79 °C and 83 °C with the addition of PMDA and NTDA (di-anhydrides), respectively. That is because di-anhydride could form the denser network structure than the mono-anhydride modified alloys. In comparison between two types of mono-anhydride, it could be observed that, the T_d of PBA-a:NA (at 60 mol%) alloys (390 °C) is much higher than that of PBA-a: PA (375 °C). The degree of T_d improvement is different because of the difference in the amount of aromatic rings in anhydride structures. The anhydride structures with greater aromatic rings led to greater crosslink density and higher thermal stability of the alloys. From the table, the T_d values of four pure anhydrides are decreased as follows: NTDA (360 °C) >

PMDA (290 ^{o}C) >> NA (258 ^{o}C) > PA (200 ^{o}C). Therefore, the alloys of anhydrides with higher crosslink density possibly tended to provided higher T_d.

Moreover, interesting feature in the TGA thermograms was the amount of carbonized residue or char yield at 800 ^{o}C of all samples which was tested under nitrogen atmosphere for PBA-a:PA and PBA-a:PMDA alloying films was depicted in Figure 5.16, while those of PBA-a:NA and PBA-a:NTDA were shown in Figure 5.17. The char yield values are also summarized in Table 5.2. The ultimate char yield values of the neat PBA-a was determined to be approximately 25%. The char yield values of the alloys, i.e. PBA-a: mono-anhydride and PBA-a: di-anhydride were increased with the content of anhydride (0 to 40 mol%). However, it could be observed that all four types of anhydride are able to enhance the char yield of PBA-a with different degree of char yield improvement. The char yield values of PBA-a alloyed with di-anhydride are higher than those of the PBA-a alloys with mono-anhydride. At 20 mol% of anhydrides, the alloys with PA and NA (mono-anhydrides) provided the increase of char yield for 15% and 16%, respectively; while, the char yield values of the alloys could be increased for 26% and 31% with the addition of PMDA and NTDA (di-anhydrides) respectively. It could be because more functional groups (for chemical reaction) of di-anhydride could lead to greater crosslink density. As a consequence, greater functionality of anhydride is the key factor to improve the thermal stability of the PBA-a. Additionally, in comparison between two types of di-anhydride (PBA-a:PMDA and PBA-a:NTDA), the alloys with NTDA provided high char yield as compared to the alloys with PMDA. This could be explained by compact network structure presented in naphthalene based PBA-a [37]. And the alloys with NTDA (greater aromatic content unit in the molecular structure) could have greater crosslink density leading to higher char yield [38]. From calculation, the crosslink density of PBA-a:NTDA (8,751 mol/m^3) > PBA-a:PMDA (8,655 mol/m^3).

Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resins in accordance to Van Krevelen and Hoftyzer equation [39].

$$LOI = 17.5+ 0.4\ CR \qquad (5.2)$$

Where CR = char yield of the sample.

All samples had LOI values, calculated based on their char yield, to be in the range of 33.3 to 42.6. These LOI values were significantly higher than that of the neat PBA-a (i.e. 27.5). Furthermore, the LOI value also exhibited a maximum value at 60 mol% of PBA-a:monoanhydride and 40 mol% of PBA-a:dianhydride. As a result, On the basis of LOI values, such materials can be classified as self-extinguishing polymers which require LOI value to be at least 26.

5.5 Tensile Behaviors of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

Mechanical properties of materials are of great importance in engineering applications. 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). The effects of the aromatic carboxylic anhydride on flexural properties of their PBA-a alloys at various molar percentages of anhydride from 0 to 67% were investigated by a universal testing machine. The tensile modulus, tensile strength, and elongation at break as a function of molar percentages of anhydride of both systems have no linear relationship with the compositions of alloys. However, synergistic behaviors were found with the maximum value at 60 mol% for PBA-a: mono-anhydride and 40 mol% for PBA-a:dianhydride.

The tensile modulus values as a function of molar percentages of anhydride of the PBA-a:PA and PBA-a:PMDA alloying films were illustrated in Figure 5.18, while those of PBA-a:NA and PBA-a:NTDA were shown in Figure 5.19. Tensile modulus at room temperature of these alloys were slightly higher than that of the neat PBA-a. The values are revealed in a range of 2.2-2.6 GPa at all of the tested compositions whereas that of the neat PBA-a was determined to be 2.1 GPa. It is possible to be ascribed to greater crosslink density (calculated from DMA as formerly mentioned) and increasing aromatic in structure of anhydrides. The tendency is in good agreement with the results from DMA mentioned above.

Figures 5.20 and 5.21 exhibit the plot of the tensile strength as a function of molar percentages of anhydride.The tensile strength of these alloys were observed to be significantly greater than that of the neat PBA-a (i.e. 62.1 MPa). Tensile strengths of PBA-a:PA, PBA-a:NA, PBA-a:PMDA, and PBA-a:NTDA alloying films were ranging from 94.1 to 137.9 MPa, 114.1 to 202.0 MPa, 75.8 to108.5 MPa, and 84.0 to 161.6 MPa, respectively. This behavior was attributed to an enhancement in crosslink network density from additional esterification reaction between the phenolic hydroxyl groups of PBA-a and the carbonyl group of anhydride.

In comparison on the maximum strength values of all alloys, it could be found that NA (202.0MPa) > NTDA (161.6MPa) > PA (137.9MPa) > PMDA (108.5MPa). This could be because the structures of NA and NTDA possesses greater amount of aromatic ring than those of PA and PMDA. However, it could be noticed that the alloys with mono-anhydride have higher tensile strength than those with di-anhydride.

Strain hardening behavior in elongation, i.e. the rapid increment of the elongation, is highly needed for different polymer processing methods such as film processing. Most polymers without long chain branching show any strain hardening behavior in the elongation. It has been observed that incorporation of small amount of crosslinked polymer in a linear polymer remarkably enhances the strain hardening behavior in elongation. This happens when the linear polymer and precursor of crosslinked polymer are compatible. In general, strain hardening is resulted from molecular orientation, which increases the modulus and tensile strength.

The area under the curve refers to the energy absorption capability of the materials. Figures 5.22 and 5.23 show elongation at break as a function of molar percentages of anhydride. From the results, it is clearly revealed a remarkable improvement in elongation at break as a result of alloying the PBA-a modified with any types of four investigated anhydrides. Elongation at break of PBA-a:PA, PBA-a:NA, PBA-a:PMDA, and PBA-a:NTDA alloying films were ranging from 9.3 to 14.8 %, 6.1 to 9.3%, 4.6 to 7.1 %, and 3.6 to 5.7 %, respectively. In other words, elongations at break of the alloys with the mono-anhydrides and di-anhydrides were approximately seven times and a three times of the neat polybenzoxazine (i.e. 2.3%), respectively.

In comparison on the maximum elongation values of all alloys, it could be found that PA > NA > PMDA > NTDA.This could be attributed to the fact that mono-anhydrides have lower amount of chemical functional group, which leads to lower crosslink density than di-anhydrides. That means the alloys with mono-anhydride are more flexible than those with di-anhydride. Moreover, lower amounts of aromatic rings of PA and PMDA could lead to more flexible than the alloys with NA and NTDA [36].

5.6 Solvent Extraction of Monoanhydride and Dianhydride Modified PBA-a Alloy Films

Solvent extraction of polymer alloy films from PBA-a: mono-anhydride and PBA-a: di-anhydride after thermal cure at 80-240°C for 10 h was quantitatively studied by immersing a given weight of sample in chloroform as solvent. The percentages of extraction were calculated from the weight before and after 30 days of chloroform immersion, and were summarized in Table 5.3. The data from the experiment exhibit the ability of network formation of the PBA-a: anhydride at different anhydride types and molar percentage of anhydride.

The specimens at 66.7 mol% of PA and NA and 50 mol% of PMDA and NTDA were found to change from their original state. The color of the chloroform was changed from colorless to light yellow after immersing for 30 days whereas the solvent of the other molar percentage of anhydride remained colorless throughout the whole calculation period. As a result, the samples at 66.7 mol% of mono-anhydride and 50 mol% of di-anhydride tended to exhibit the weakest network. The phenomenon was also reported by Rimdusit et al. [47]; therefore, percent extraction in the solvent extraction was rather high, i.e. 3.9-6.6%. The percent of solvent extraction of other specimens were determined to be 0.6-0.9%. It is attributed that the excess amount of added anhydride could lead to the defect in the network such as dangling ends because it could not completely form the network with PBA-a. The possible network defects in thermoset might be terminal chain end, chain entanglement, and loop [40, 41]. The formation and network defect could lower crosslink density of the network which led to lower T_g of the alloys. Furthermore, the excess anhydride (not reacted with PBA-a) could dissolve in the chloroform. Additionally, this is likely due to an ability of the benzoxazine monomer to react among themselves (self-polymerizability) besides their ability to react with the anhydride [14].

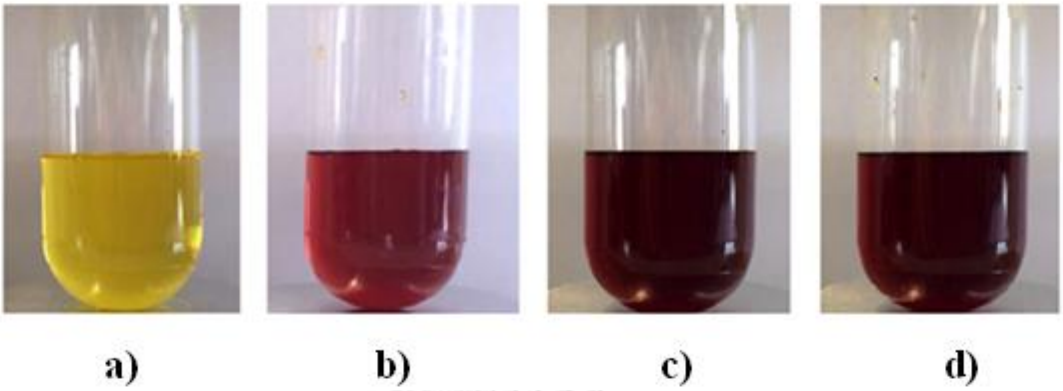

Figure 5.1 Photographs of homogenous solutions (3 g of solid monomers in 3 ml of DMF) of BA-a:PA (a), BA-a:NA (b), BA-a:PMDA (c), BA-a:NTDA (d).

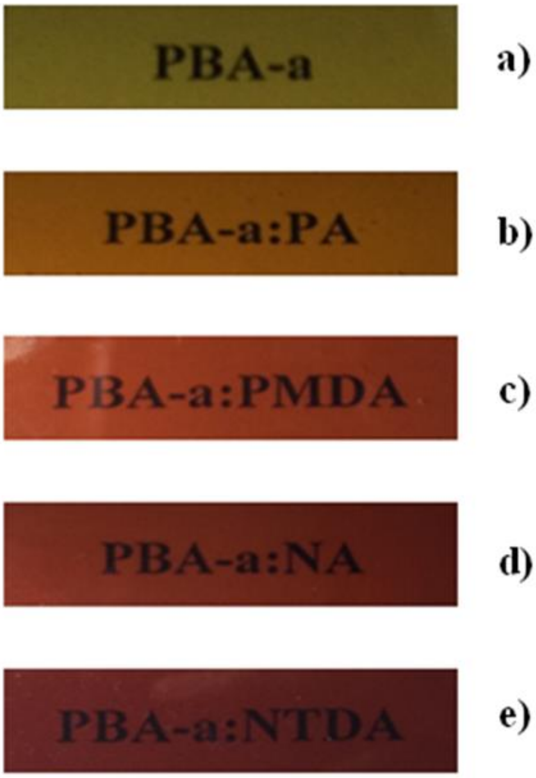

Figure 5.2 Photographs of neat PBA-a (a), PBA-a:PA (b), BA-a:PMDA (c), BA-a:NA (d), BA-a:NTDA (e) revealing homogenous and transparent polymer films.

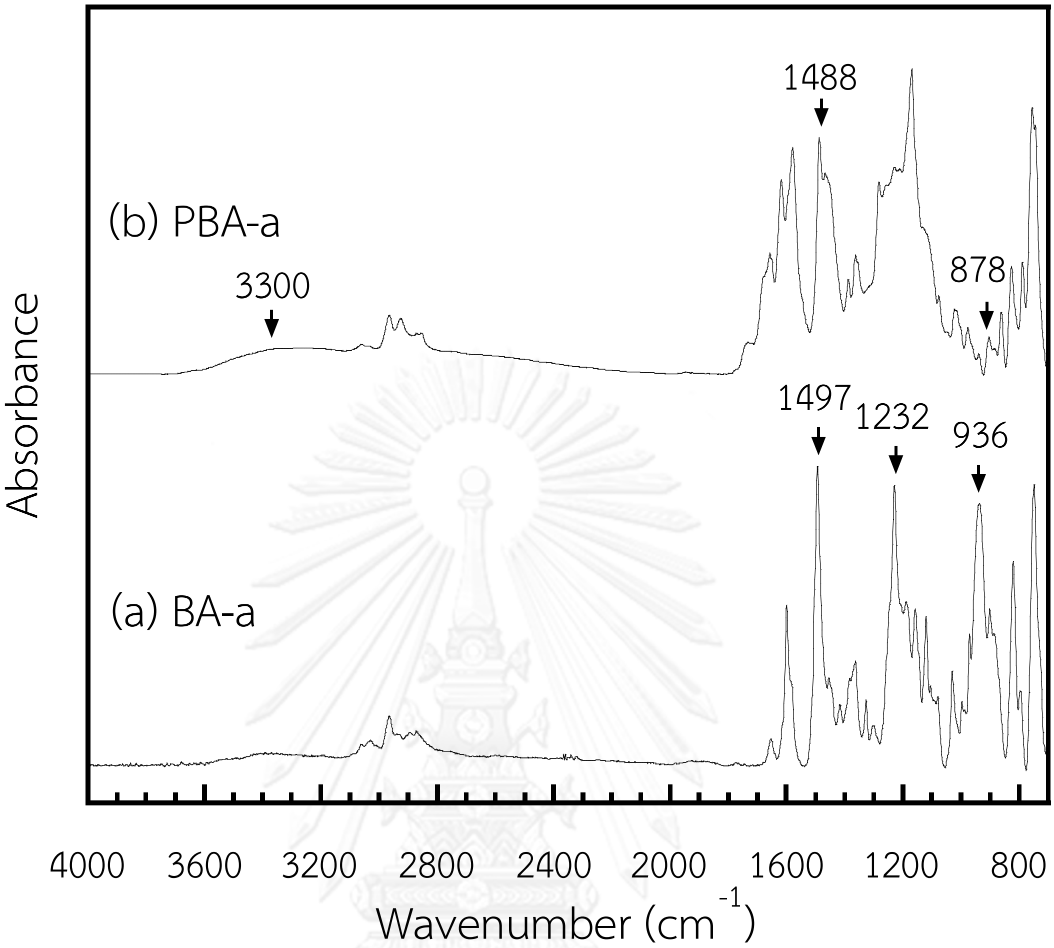

Figure 5.3 FTIR spectra of a) BA-a monomer and b) PBA-a after fully cured.

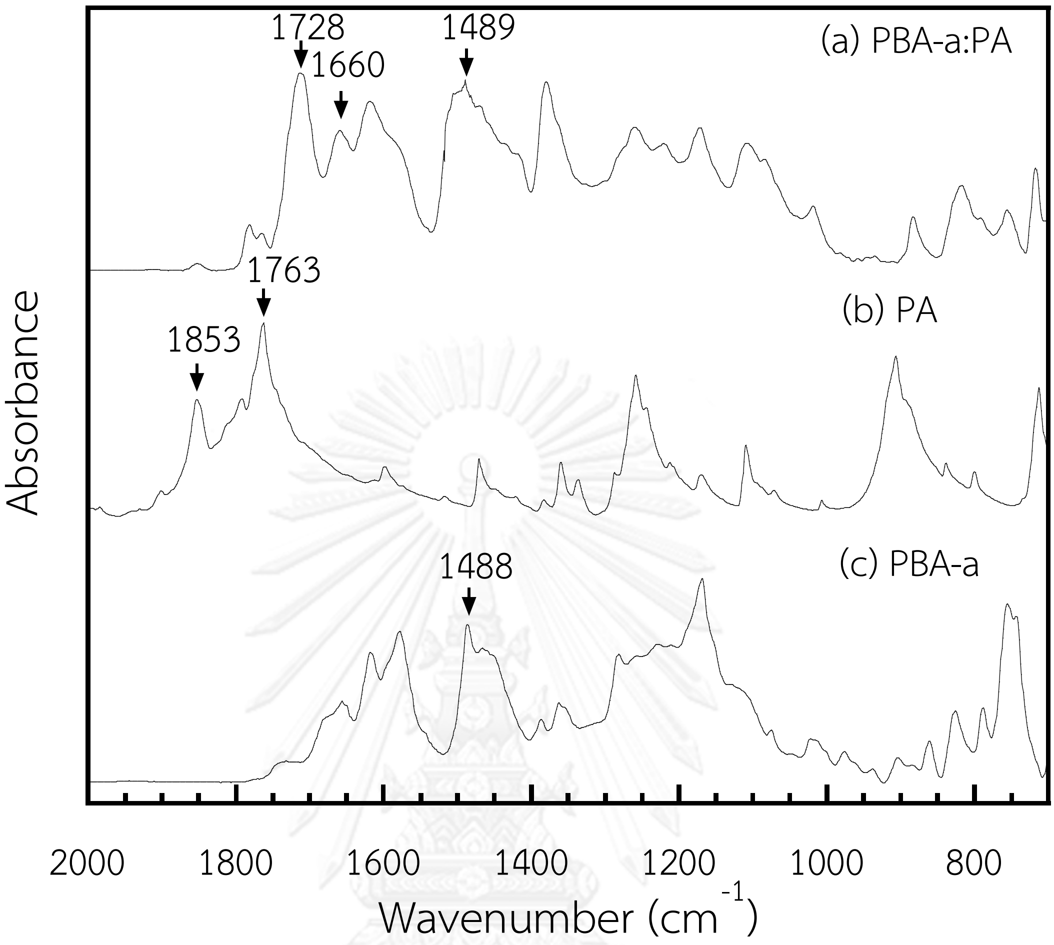

Figure 5.4 FTIR spectra of a) PBA-a:PA after fully cured., b) PA and c) PBA-a

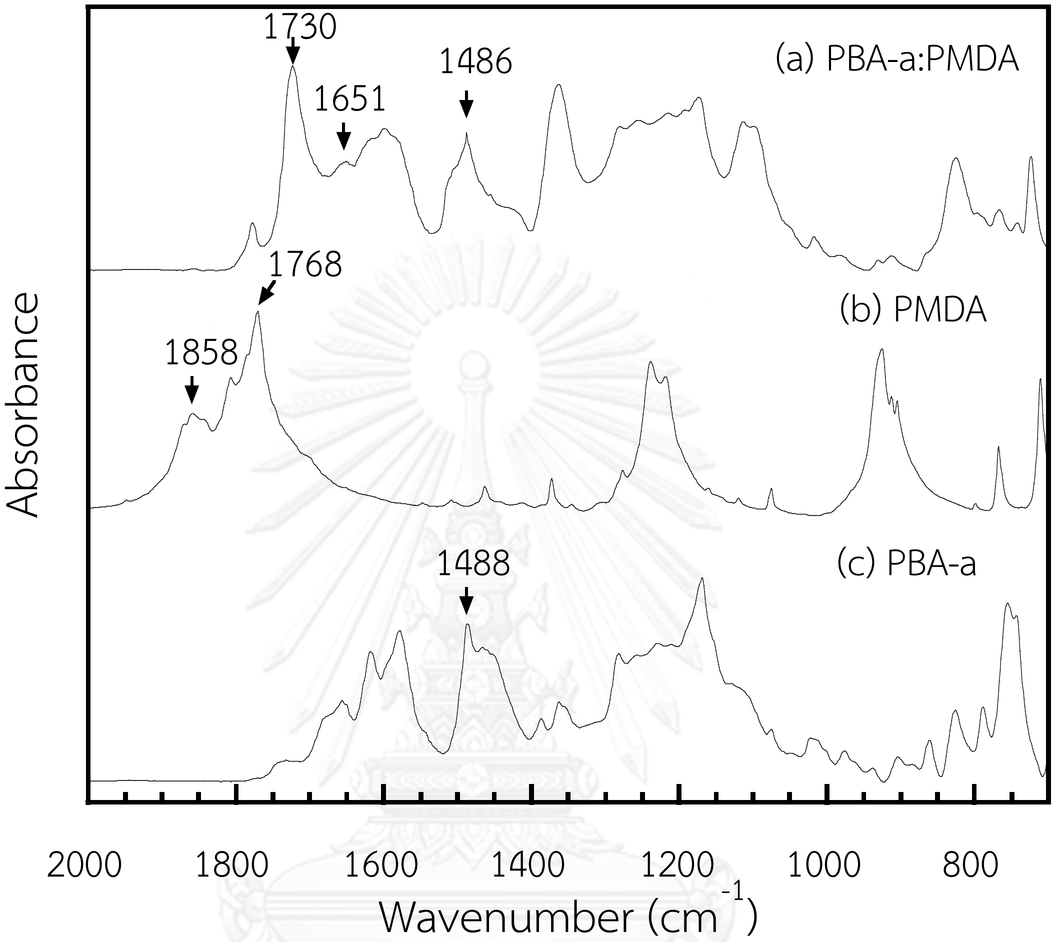

Figure 5.5 FTIR spectra of a) PBA-a:PMDA after fully cured., b) PMDA and c) PBA-a

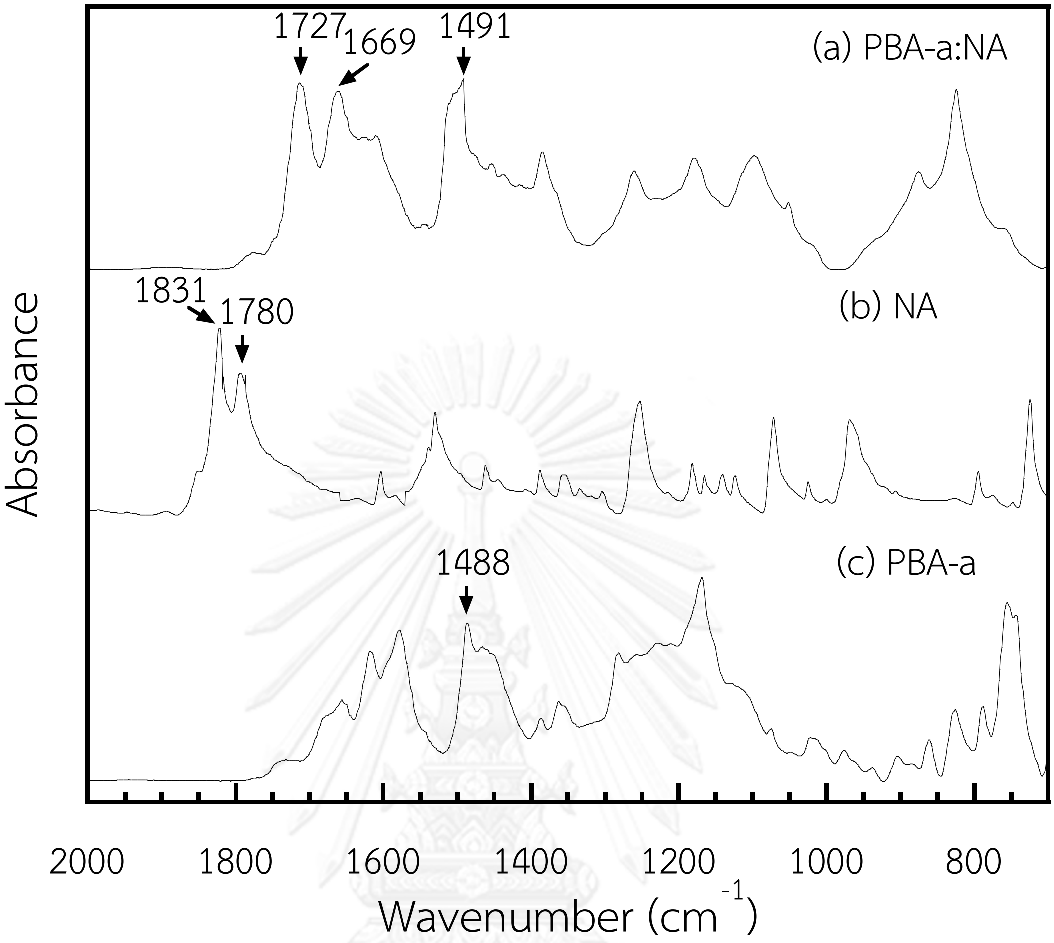

Figure 5.6 FTIR spectra of a) PBA-a:NA after fully cured., b) NA and c) PBA-a

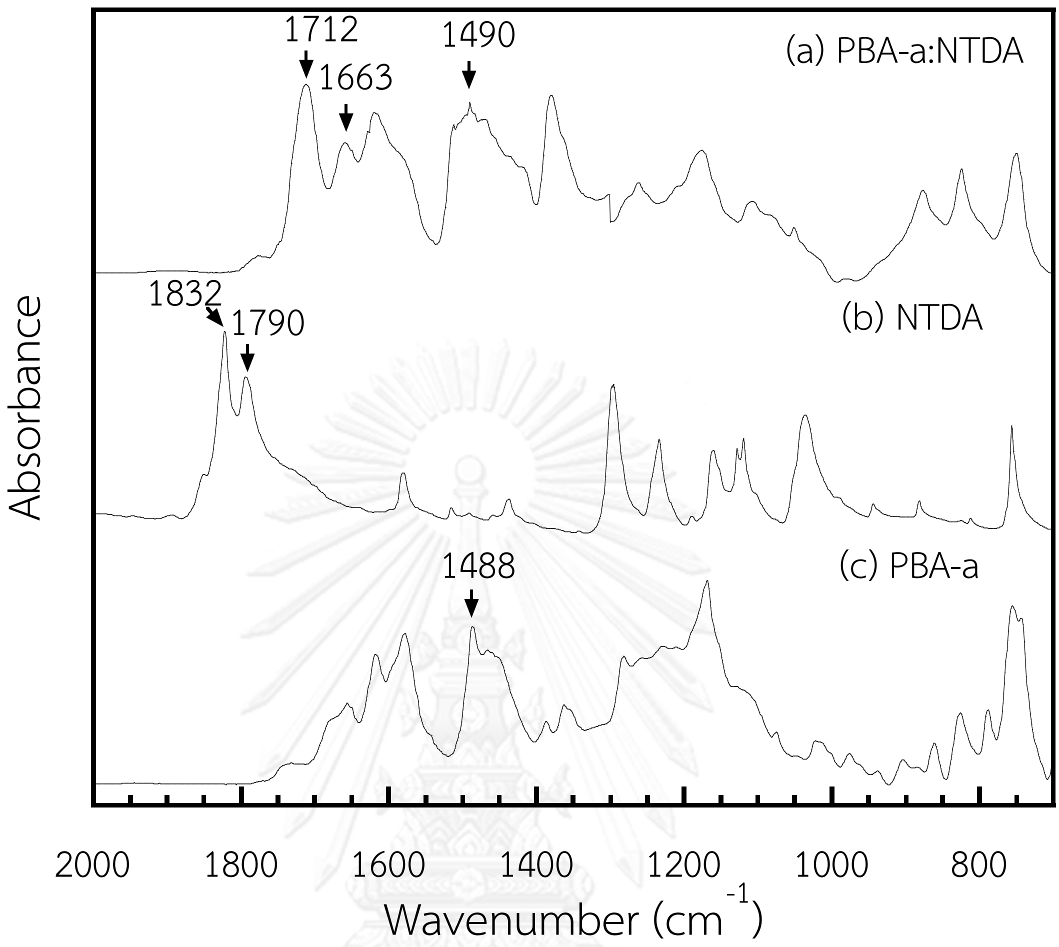

Figure 5.7 FTIR spectra of a) PBA-a:NTDA after fully cured., b) NTDA and c) PBA-a

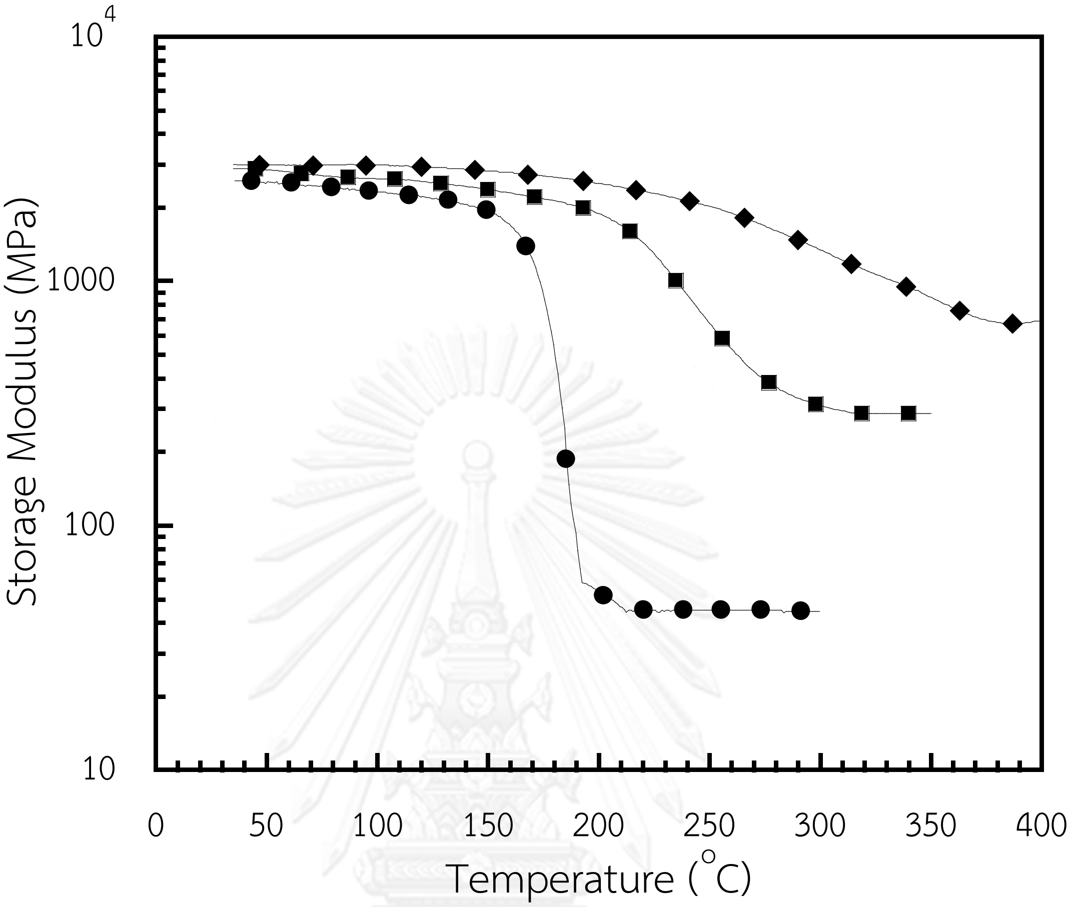

Figure 5.8 Storage modulus of PBA-a: anhydride alloying films: (◆) 40 mol% of PMDA, (■) 60 mol% of PA, and (●) PBA-a.

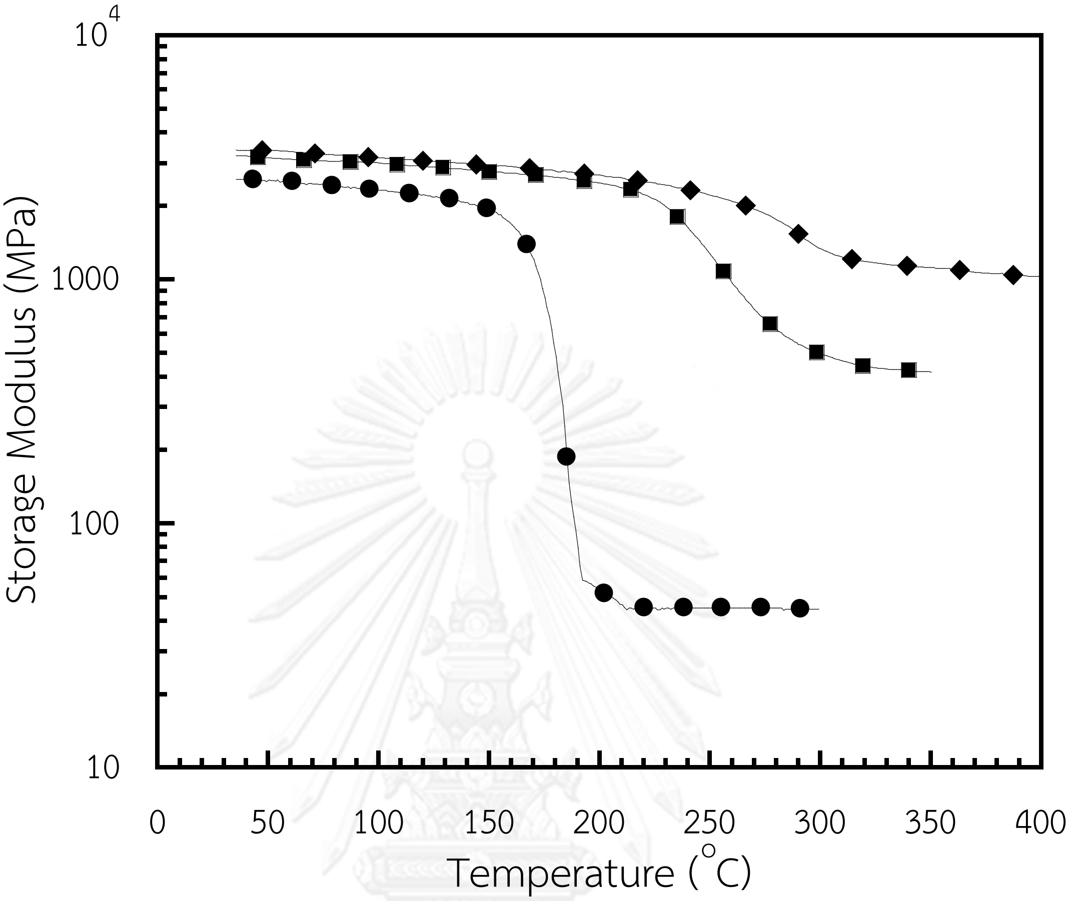

Figure 5.9 Storage modulus of PBA-a: anhydride alloying films: (◆) 40 mol% of NTDA, (■) 60 mol% of NA, and (●) PBA-a.

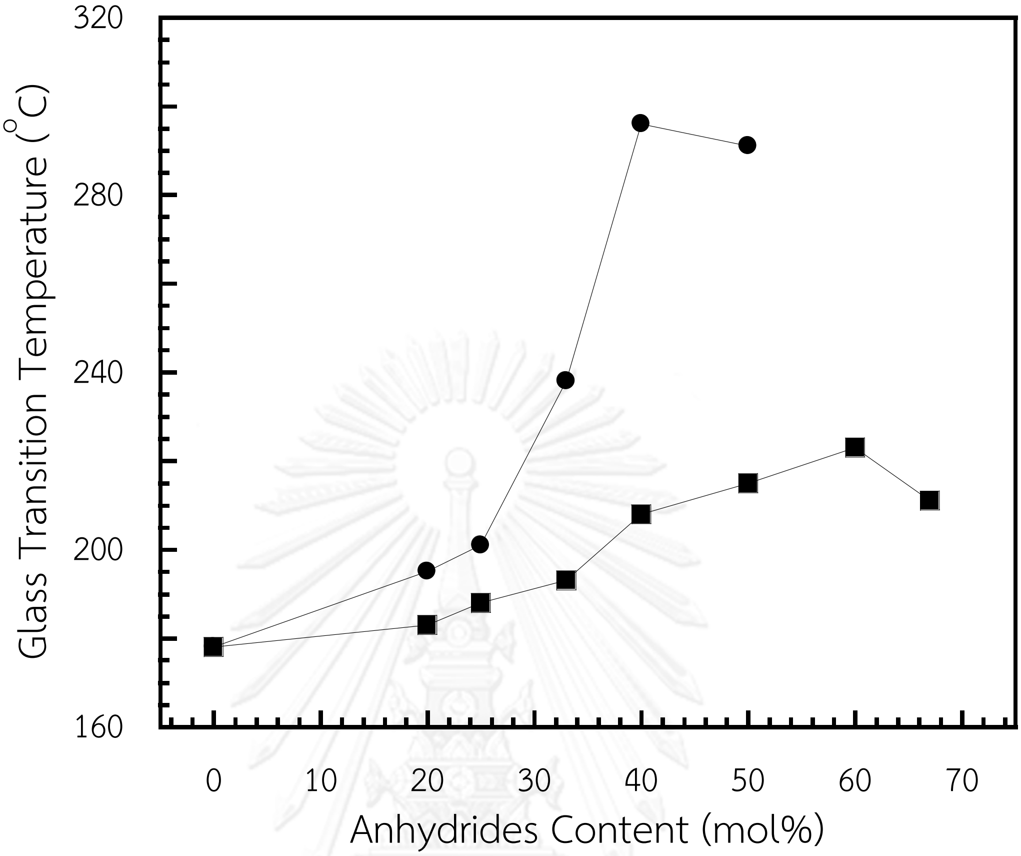

Figure 5.10 Glass transition of PBA-a: anhydride alloying films: (●) PBA-a:PMDA and (■) PBA-a:PA.

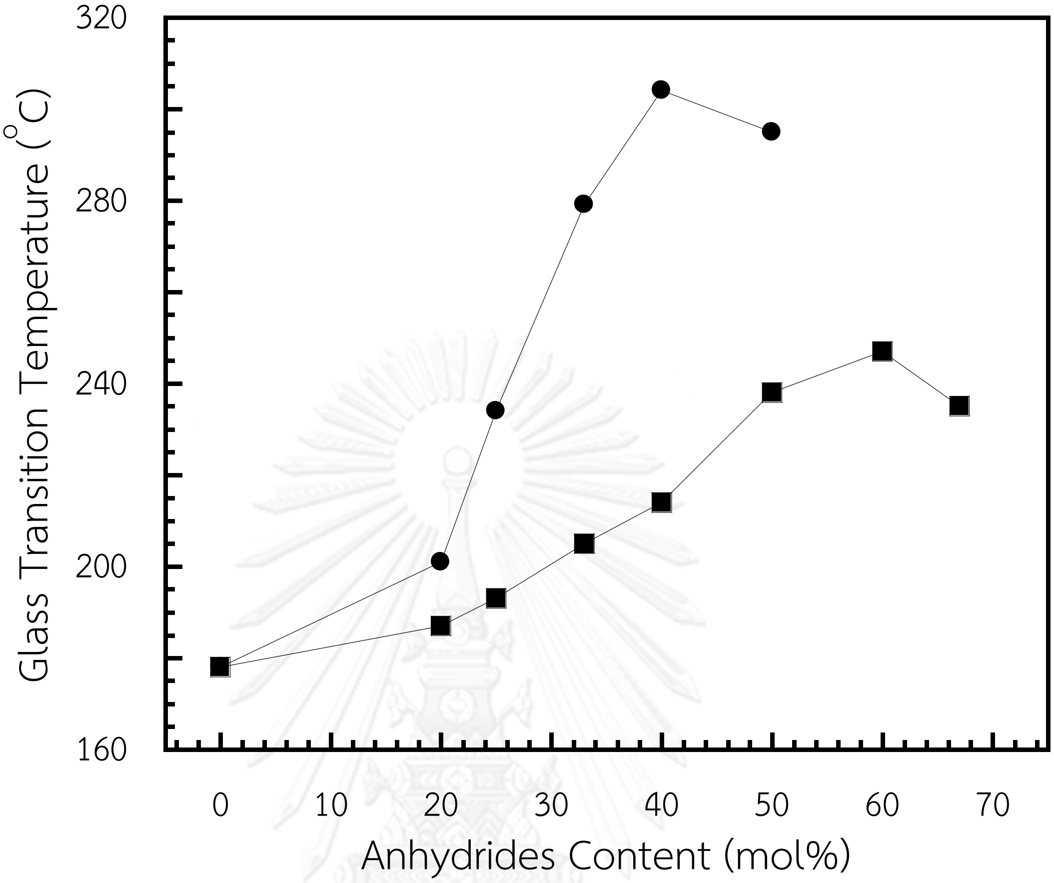

Figure 5.11 Glass transition of PBA-a: anhydride alloying films: (●) PBA-a:NTDA and (■) PBA-a:NA.

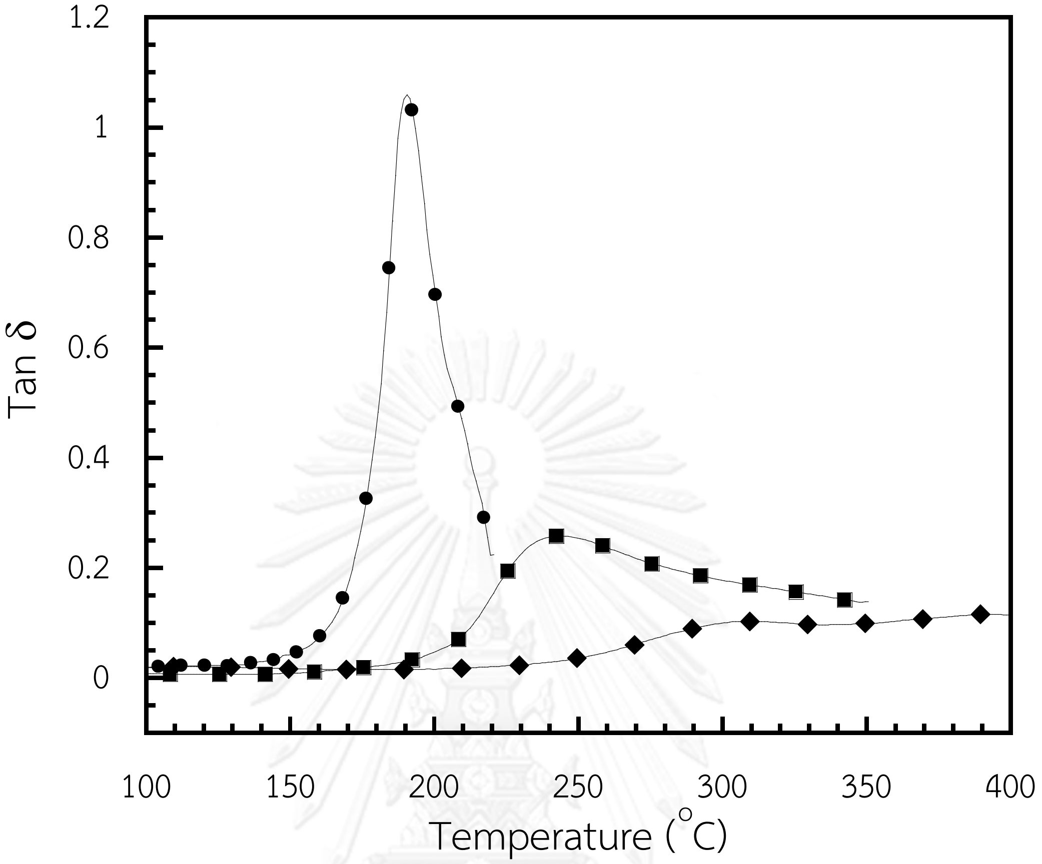

Figure 5.12 Loss tangent of PBA-a: anhydride alloying films: (◆) 40 mol% of PMDA, (■) 60 mol% of PA, and (●) PBA-a.

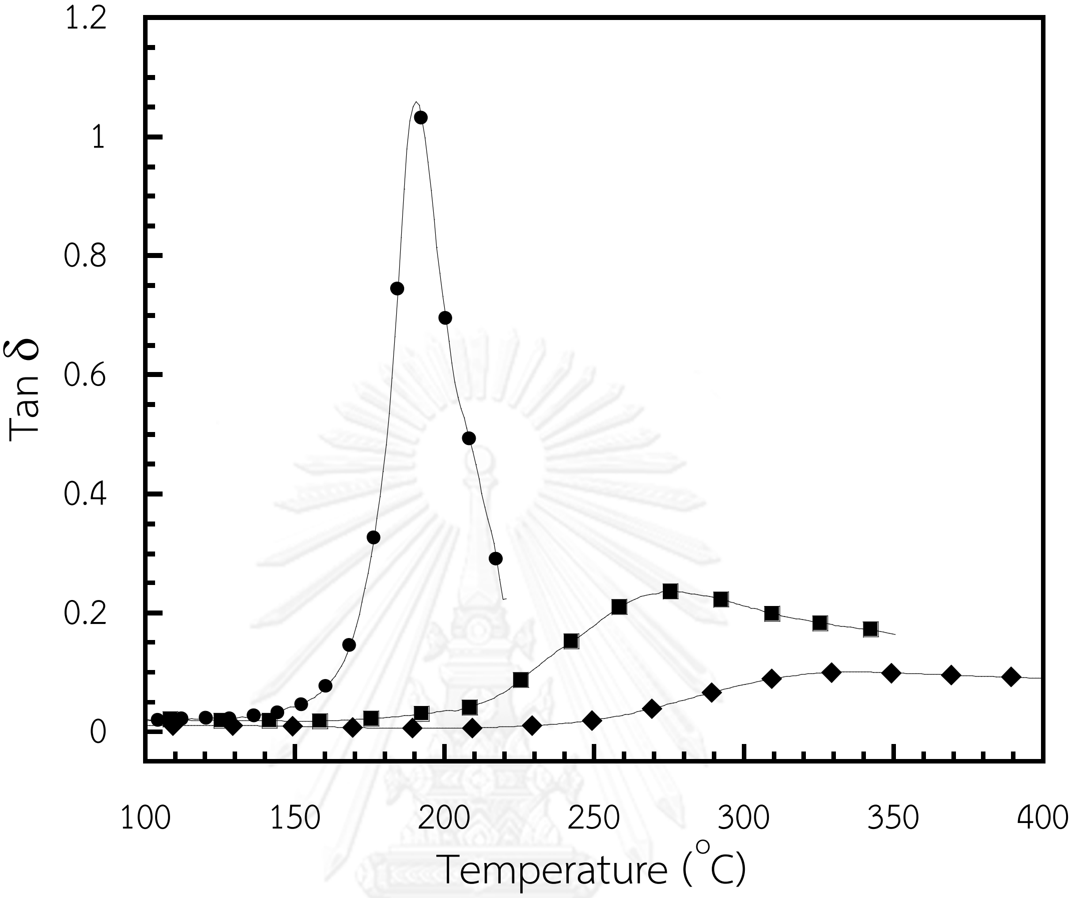

Figure 5.13 Loss tangent of PBA-a: anhydride alloying films: (◆) 40 mol% of NTDA, (■) 60 mol% of NA, and, (●) PBA-a.

Table 5.1 Glass transition temperature, storage modulus (E’) at 35 °C, rubbery plateau (E’), and crosslink density at various molar percentage of anhydride modified PBA-a alloy films.

Molar percentage of anhydride (%)	PBA-a:PA				PBA-a:PMDA				PBA-a:NA				PBA-a:NTDA			
	Tg (°C)	Storage modulus (E’) at 35 (°C)	E’ rubbery plateau (MPa)	Crosslink density (mol/m^3)	Tg (°C)	Storage modulus (E’) at 35 (°C)	E’ rubbery plateau (MPa)	Crosslink density (mol/m^3)	Tg (°C)	Storage modulus (E’) at 35 (°C)	E’ rubbery plateau (MPa)	Crosslink density (mol/m^3)	Tg (°C)	Storage modulus (E’) at 35 (°C)	E’ rubbery plateau (MPa)	Crosslink density (mol/m^3)
0	178	2.57	44	3,980	178	2.57	44	3,980	178	2.57	44	3,980	178	2.57	44	3,980
20	183	2.63	145	5,748	195	2.72	272	6,133	187	2.70	215	6,332	201	2.87	290	6,776
25	188	2.69	150	6,133	201	2.84	292	6,172	193	2.76	275	6,697	234	2.95	426	7,346
33.3	193	2.74	253	6,172	238	2.86	442	6,283	205	2.80	280	6,724	279	3.20	780	8,242
40	208	2.78	256	6,283	296	2.99	1,031	8,655	214	2.93	307	6,860	304	3.35	1,110	8,765
50	215	2.91	260	6,613	291	2.84	922	8,490	238	3.20	369	7,133	295	3.44	938	8,516
60	223	2.98	337	6,998	-	-	-	-	247	3.27	417	7,417	-	-	-	-
66.7	211	2.88	301	6,831	-	-	-	-	235	3.10	374	7,153	-	-	-	-

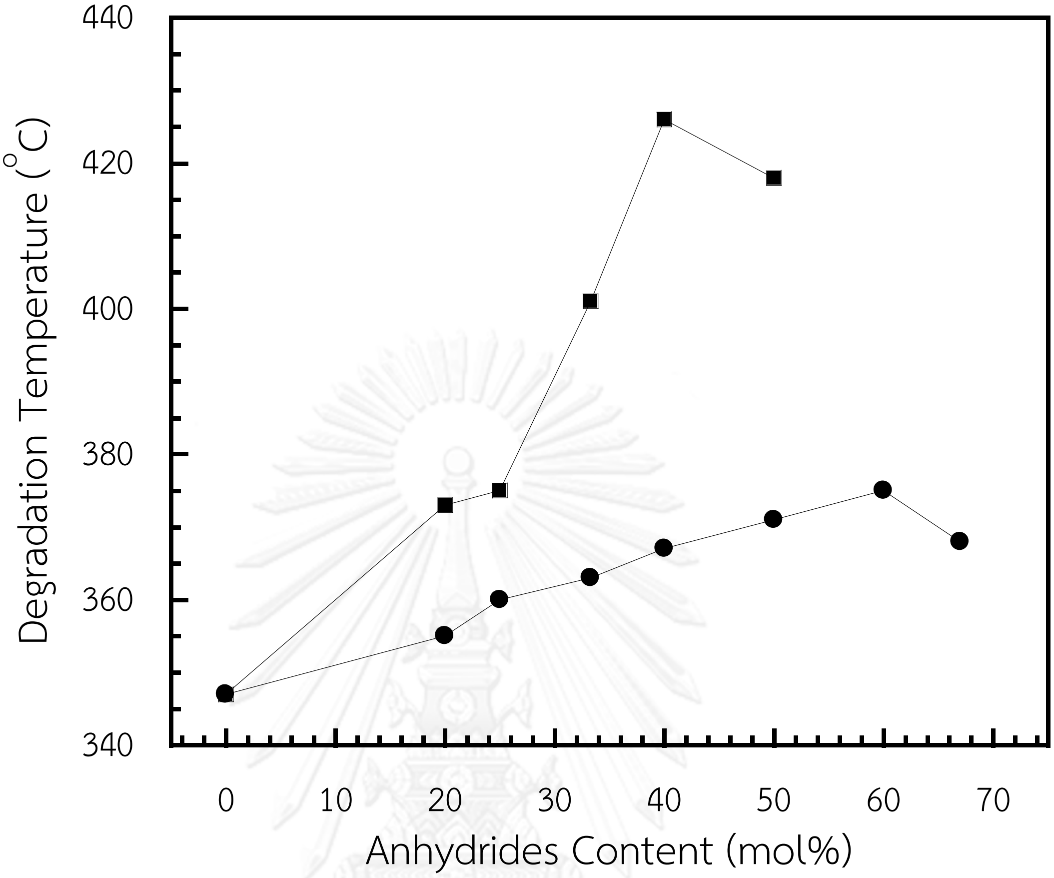

Figure 5.14 Degradation temperature of anhydride modified PBA-a alloy films: (●) PBA-a:PA and (■) PBA-a:PMDA.

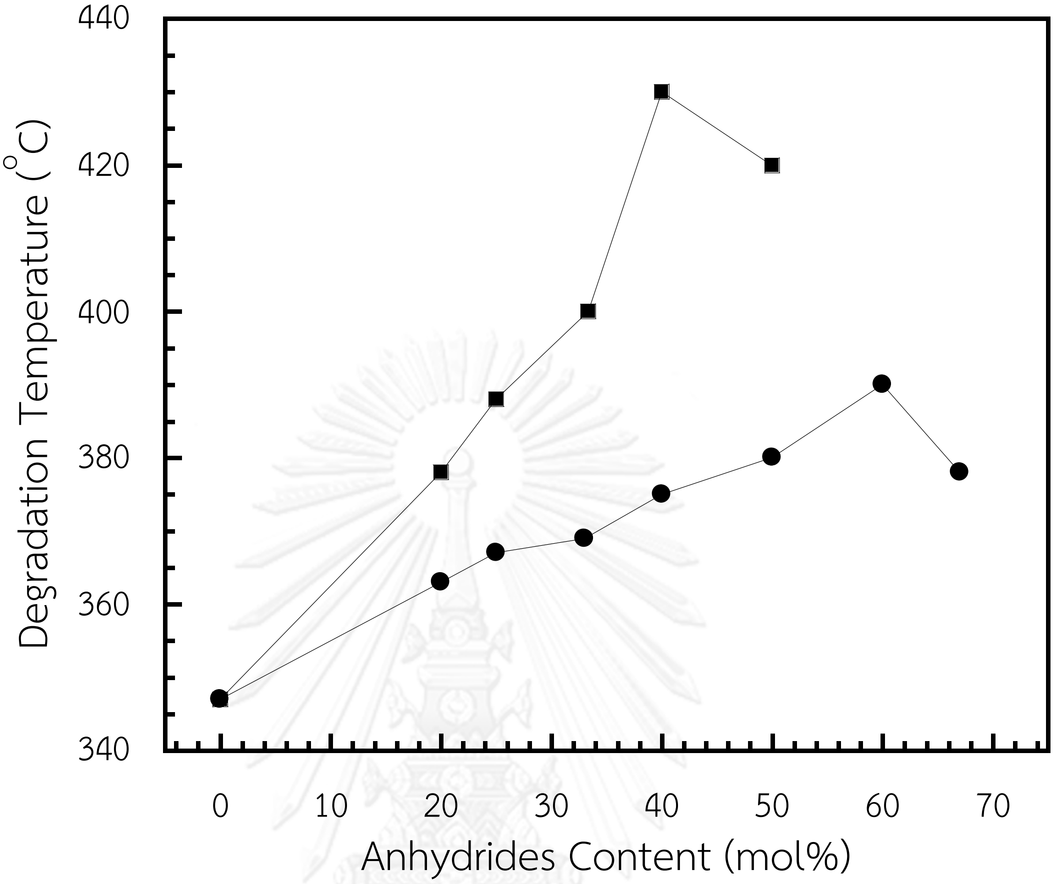

Figure 5.15 Degradation temperature of anhydride modified PBA-a alloy films: (●) PBA-a:NA and (■) PBA-a:NTDA.

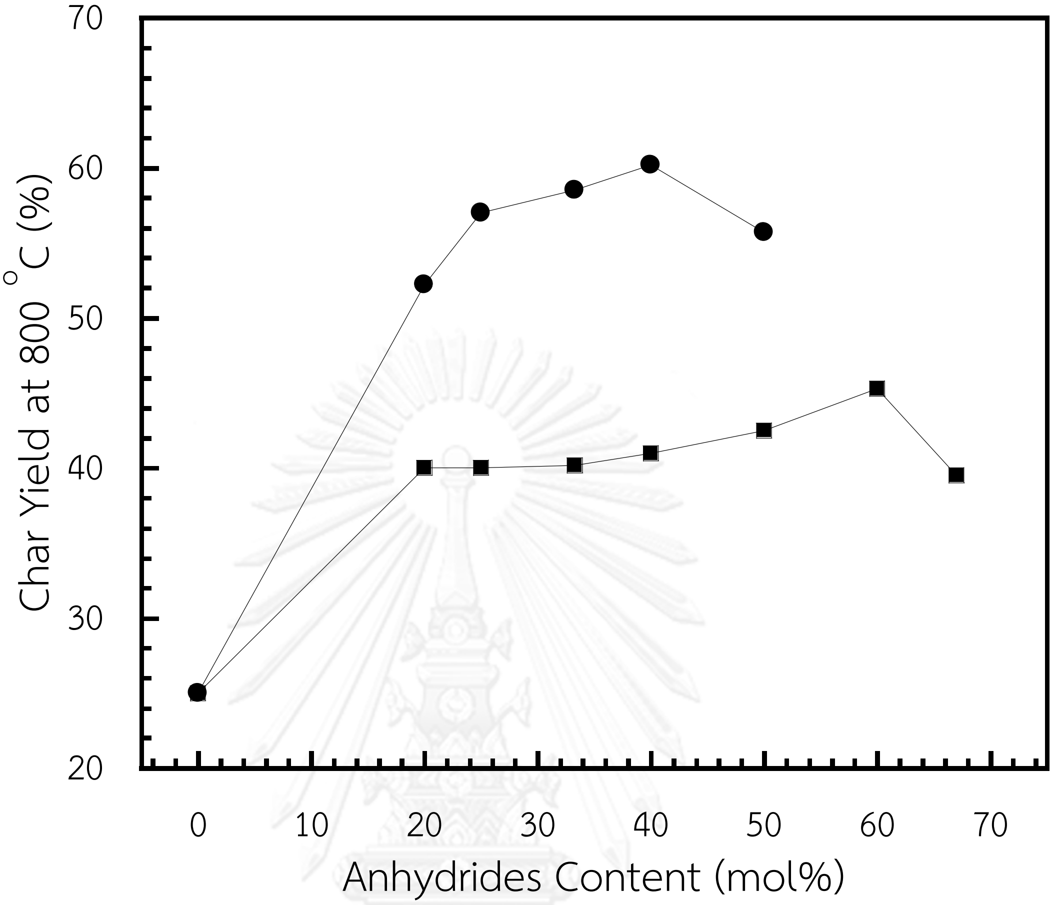

Figure 5.16 Char yield of anhydride modified PBA-a alloy films: (●) PBA-a:PA and (■) PBA-a:PMDA.

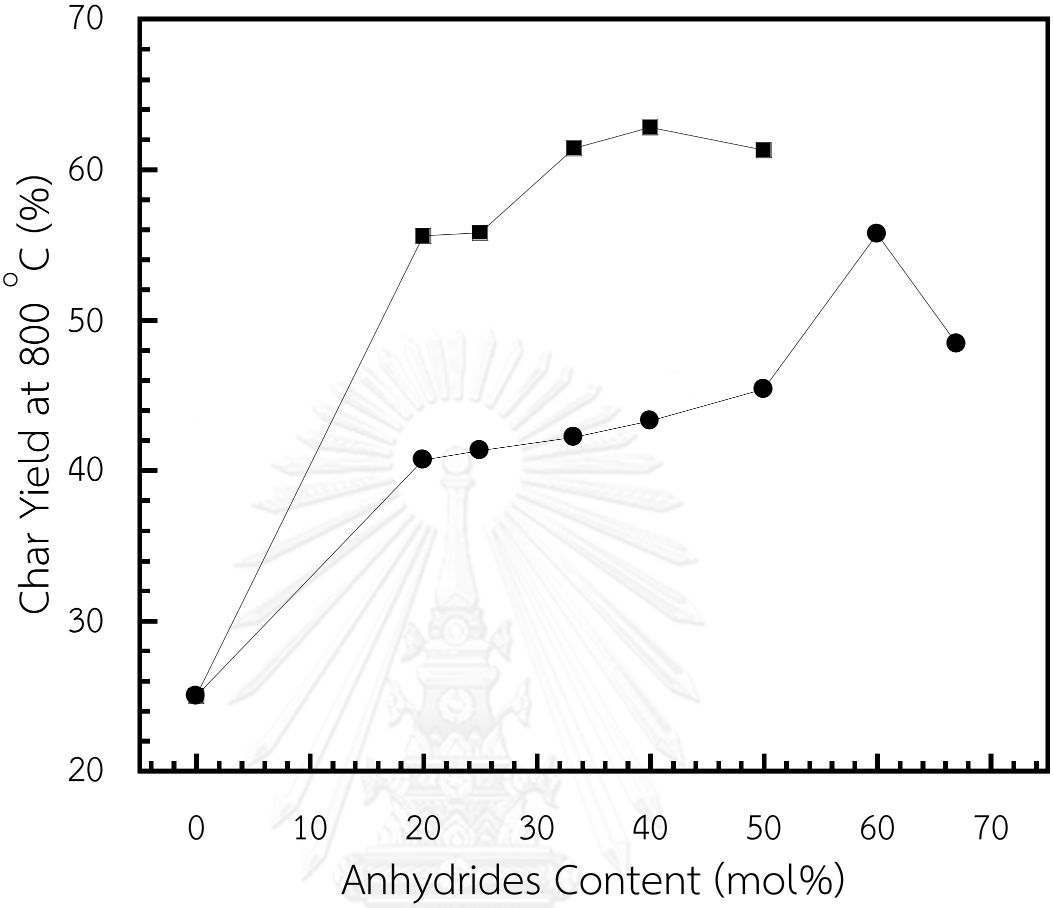

Figure 5.17 Char yield of anhydride modified PBA-a alloy films: (●) PBA-a:NA and (■) PBA-a:NTDA.

Table 5.2 Degradation temperatures (T_d) at 10% weight loss and residual weights (char yield) at 800 °C of polybenzoxazine and anhydride alloying films which were determined from TGA.

Molar percentage of anhydride (%)	PA		PMDA		NA		NTDA	
	T_d (°C)	Char yield (%)	T_d (°C)	Char yield (%)	T_d (°C)	Char yield (%)	T_d (°C)	Char yield (%)
0	347	25.0	347	25.0	347	25.0	347	25.0
20	355	40.0	373	52.2	363	40.7	378	55.6
25	360	40.0	375	57.0	367	41.3	388	55.8
33.3	363	40.2	401	58.5	369	42.2	400	61.4
40	367	41.0	426	60.2	375	43.3	430	62.8
50	371	42.5	418	55.7	380	45.4	420	61.3
60	375	45.3	-	-	390	55.7	-	-
66.7	368	39.5	-	-	378	46.4	-	-
100	200	0	290	0	258	0	360	0

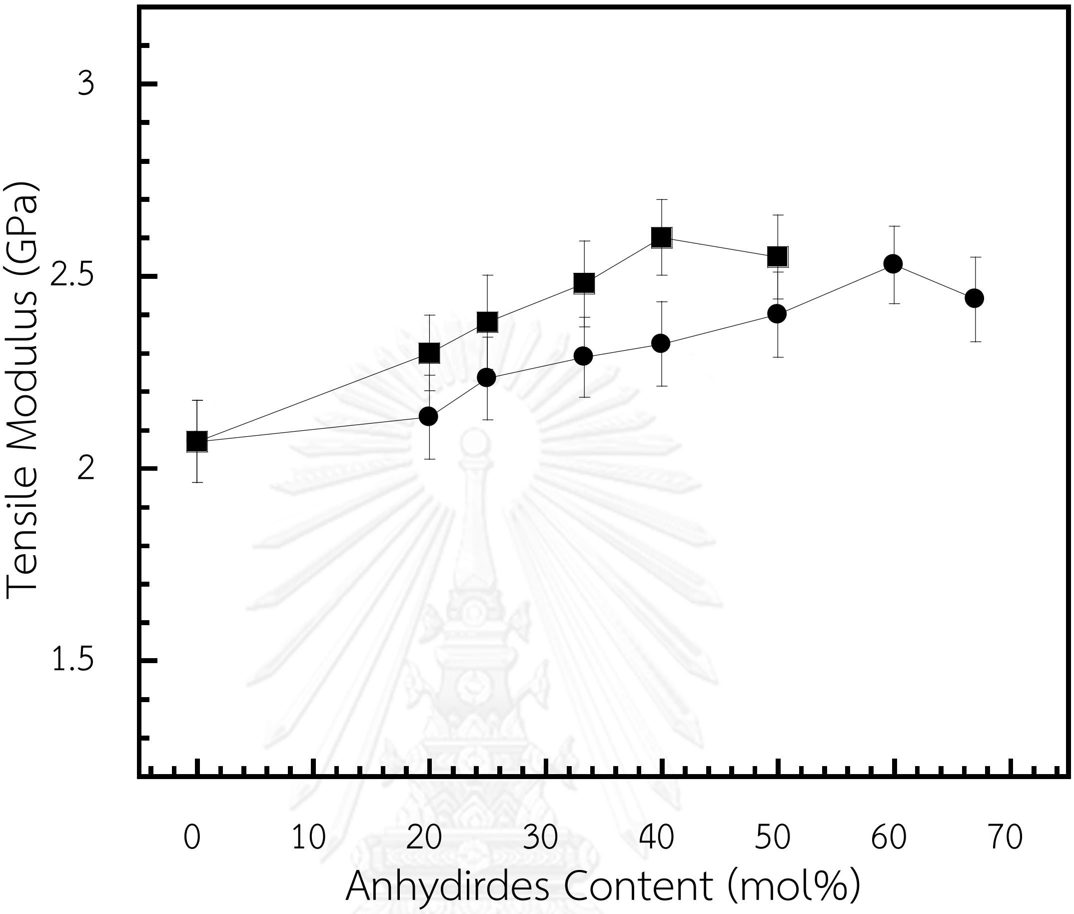

Figure 5.18 Tensile modulus of anhydride modified PBA-a alloy films: (●) PBA-a:PA, and (■) PBA-a:PMDA.

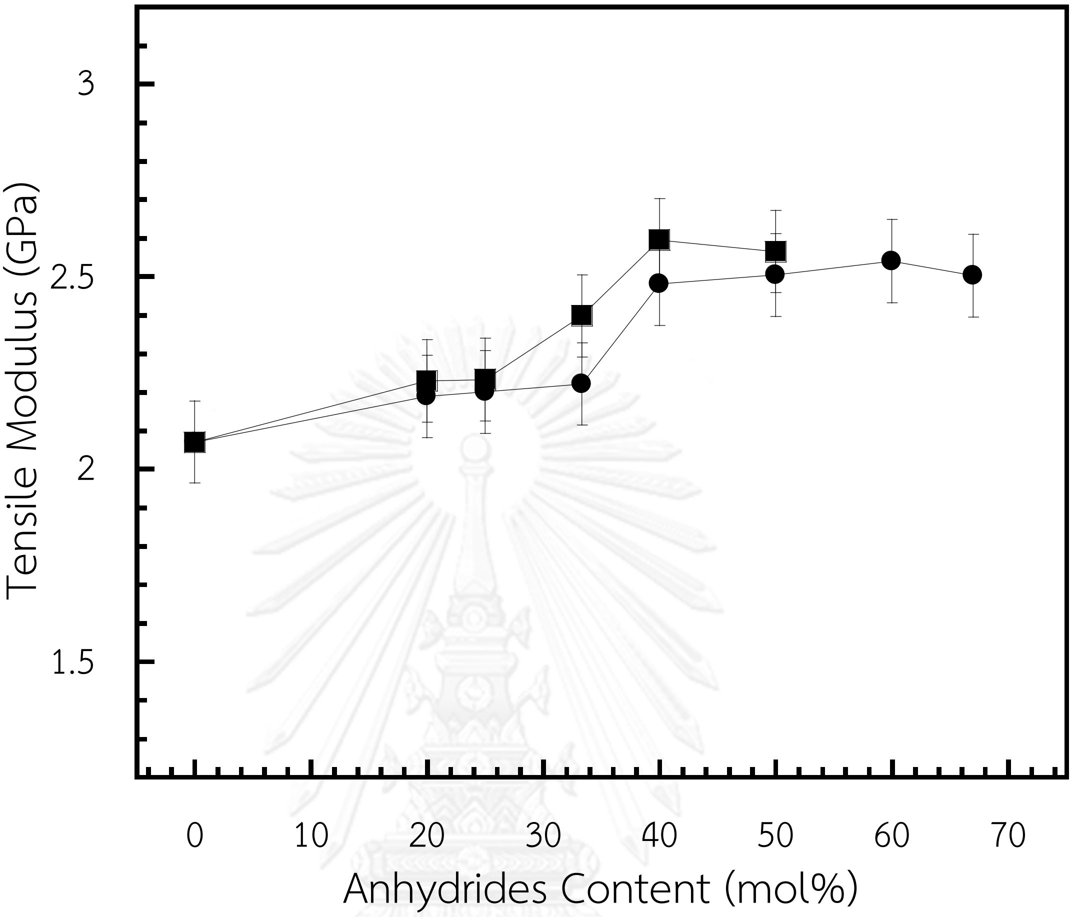

Figure 5.19 Tensile modulus of anhydride modified PBA-a alloy films: (●) PBA-a:NA, and (■) PBA-a:NTDA.

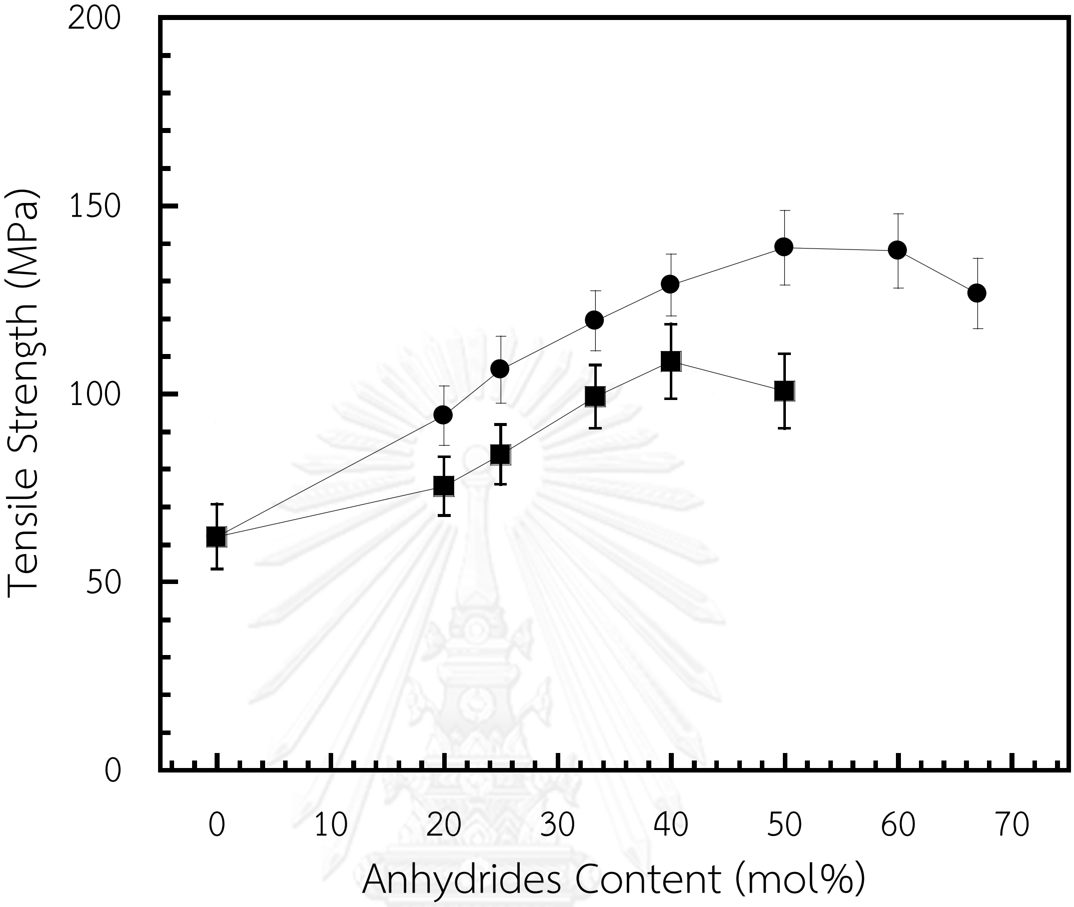

Figure 5.20 Tensile strength of anhydride modified PBA-a alloy films: (●) PBA-a:PA, and (■) PBA-a:PMDA.

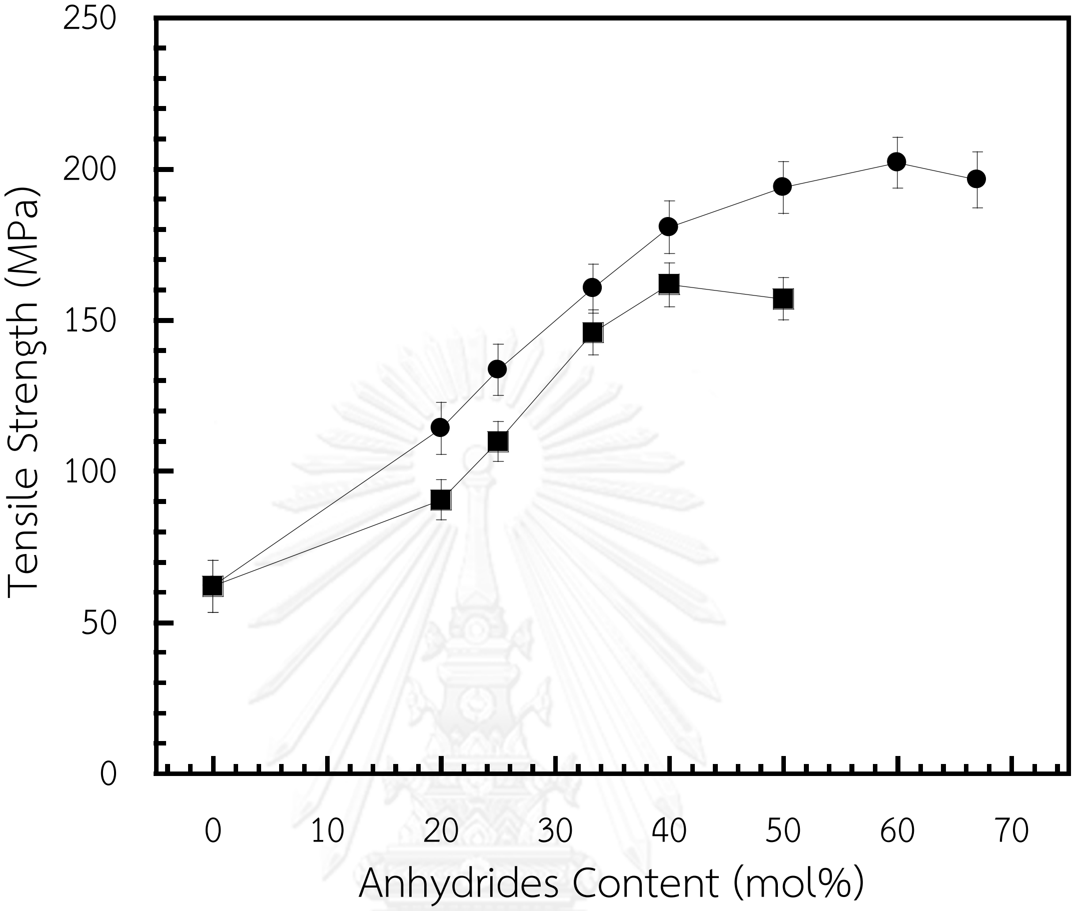

Figure 5.21 Tensile strength of anhydride modified PBA-a alloy films: (●) PBA-a:NA, and (■) PBA-a:NTDA.

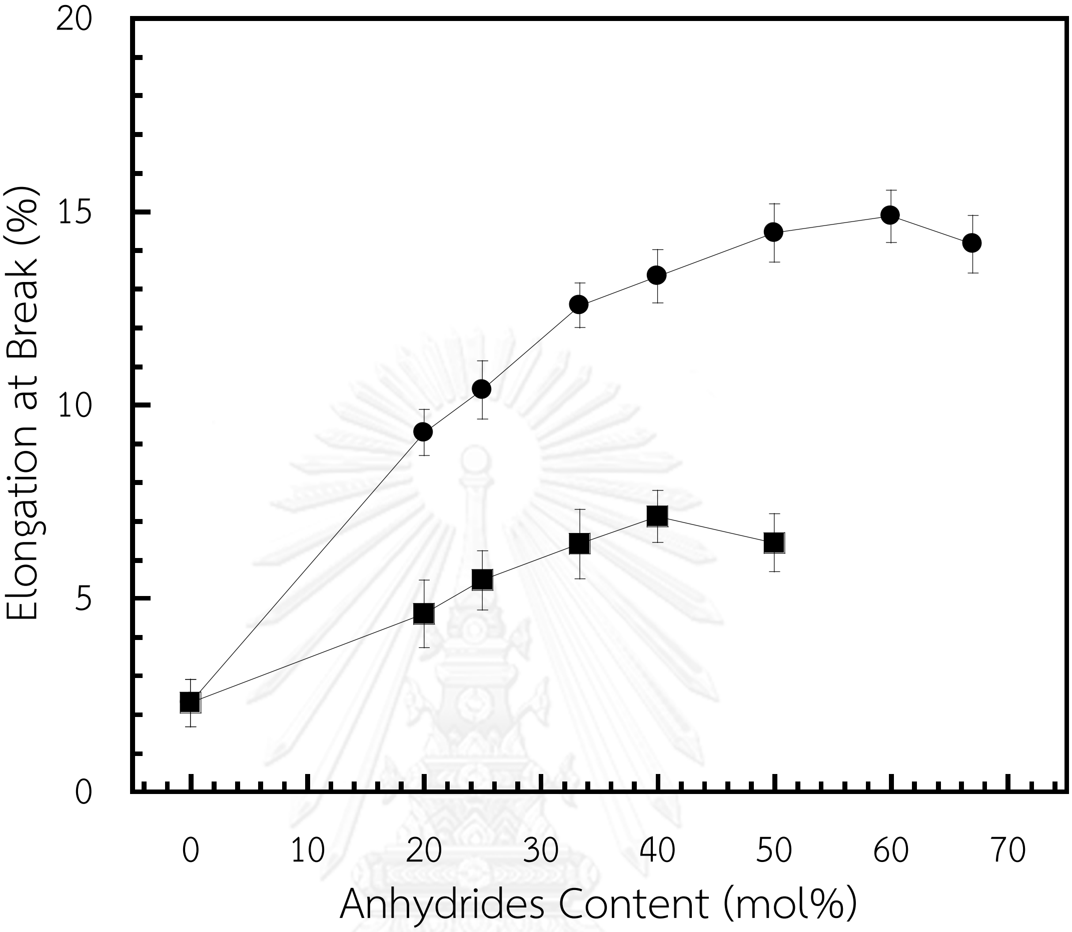

Figure 5.22 Elongation at break of anhydride modified PBA-a alloy films: (●) PBA-a:PA, and (■) PBA-a:PMDA.

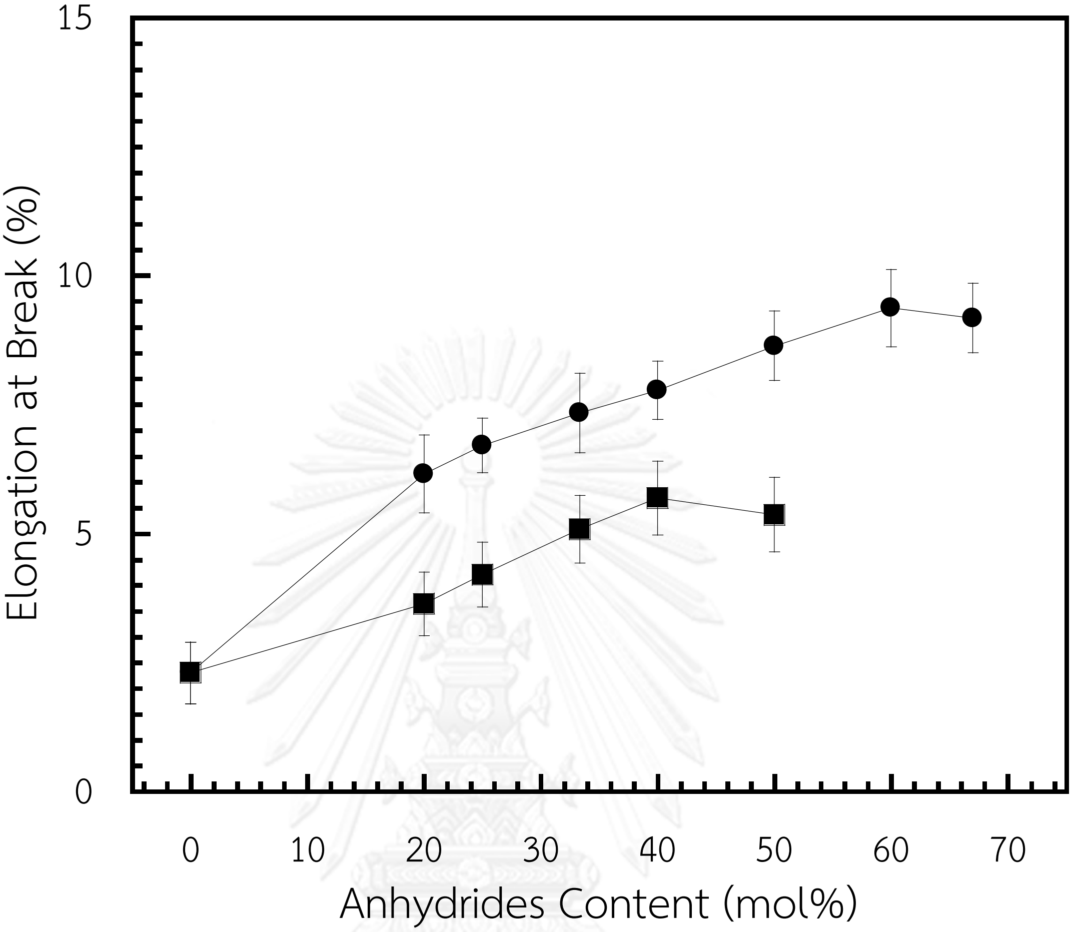

Figure 5.23 Elongation at break of anhydride modified PBA-a alloy films: (●) PBA-a:NA, and (■) PBA-a:NTDA.

Table 5.3 Solvent extraction data at various mass fractions of anhydride modified PBA-a alloy films.

Molar percentage of anhydride (%)	PBA-a:PA			PBA-a:PMDA			PBA-a:NA			PBA-a:NTDA		
	Mass of specimen (mg)		Percent extraction (%)	Mass of specimen (mg)		Percent extraction (%)	Mass of specimen (mg)		Percent extraction (%)	Mass of specimen (mg)		Percent extraction (%)
	Initial	After immersion for 30 days		Initial	After immersion for 30 days		Initial	After immersion for 30 days		Initial	After immersion for 30 days	
0	115.2	114.5	0.61	115.2	114.5	0.61	115.2	114.5	0.61	115.2	114.5	0.61
20	130.1	128.9	0.92	142.5	141.3	0.84	134.1	133.0	0.82	145.6	144.4	0.82
25	133.6	132.5	0.82	143.5	142.1	0.98	135.5	134.3	0.89	146.4	145.1	0.89
33.3	134.9	133.7	0.89	144.3	143.0	0.90	136.2	135.0	0.88	147.4	146.1	0.88
40	136.2	135.1	0.81	144.5	143.3	0.83	135.6	134.5	0.81	149.4	148.2	0.80
50	136.8	135.6	0.88	146.7	140.9	3.95	135.9	134.8	0.81	150.8	145.2	3.71
60	138.1	137.0	0.80	-	-	-	136.6	135.6	0.73	-	-	-
66.7	138.8	131.6	5.19	-	-	-	137.2	128.1	6.63	-	-	-

CHAPTER VI

CONCLUSIONS

Enhancement on thermal and mechanical properties of the alloys of bisphenol A aniline based polybenzoxazine (PBA-a) modified with mono and dianhydrides were observed and compared. Both mono and di-anhydrides can be alloyed with benzoxazine monomer to form a uniform and transparent specimen without sign of phase separation.

FT-IR spectra confirmed the formation of ester linkage between phenolic hydroxyl groups of PBA-a and anhydride groups of anhydride.

The thermal properties of the alloy films were investigated by the DMA and TGA. The T_g, T_d and weight residue were found to be more effectively enhanced by di-anhydride than mono-anhydrides. Moreover, the anhydride with greater amount of aromatic rings could provide greater values of T_g, T_d and weight residue. Therefore, the values are arranged in order as follows: NTDA > PMDA >> NA > PA.

Whereas mechanical properties of the alloy films such as tensile strength and elongation at break were more greatly improved by monoanhydride than the dianhydride.

Finally, The optimum content of monoanhydride (NA and PA) and dianhydride (NTDA and PMDA) in polybenzoxazine-anhydride alloy films were investigated to be 60 mol% and 40 mol%, respectively.

It is highly possible that the combination of the two types of anhydrides with benzoxazine resin might provide a benzoxazine copolymer with optimal properties in both thermal and mechanical characteristics and will be reported in our future work.

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