SYNTHESIS AND CHARACTERIZATION OF HIGH TEMPERATURE
RESISTANT BISMALEIMIDE BASED RESINS
AND THEIR COMPOSITES

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SYNTHESIS AND CHARACTERIZATION OF HIGH TEMPERATURE RESISTANT BISMALEIMIDE BASED RESINS AND THEIR COMPOSITES

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF HIGH TEMPERATURE RESISTANT BISMALEIMIDE BASED RESINS AND THEIR COMPOSITES

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Bismaleimide resins are important in aerospace applications as matrix component of composite materials due to their high thermal and mechanical properties. 4,4'-bismaleimidodiphenylmethane (BMI) which is the most widely used bismaleimide, was synthesized starting from maleic anhydride and 4,4'-diaminodiphenylmethane (MDA). N,N'-diallylaminodiphenyl methane (ADM), N,N'-diallylaminodiphenyl sulfone (ADS) and N,N'-diallyl p-phenyl diamine (PDA) were synthesized by allylating primary aromatic diamines. Nine different prepolymers with 1:1, 1.5:1 and 2:1 molar ratios of BMI/diallyl compound were prepared and cured. The effect of increase in BMI ratio on thermal properties of the resin systems were investigated via Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analyzer (TGA).

DSC results showed that the curing temperature of the resins increased due to the increase in BMI ratio in the resins. Thermal gravimetric analysis showed that incorporation of BMI monomer improved the thermal stability of the resins.

BMI/ADM resin system showed better thermal stability compared to BMI/ADS and BMI/PDA resins. Processing characteristics of resins having 1:1 and 1.5:1 mole ratio of BMI/ADM were investigated by viscosity measurements and these resins were found to be suitable for composite production with Resin Transfer Molding (RTM). Composites were manufactured by RTM technique using two different mole ratios of BMI/ADM resins as matrix component. The effect of different matrix composition on thermal and mechanical properties of the composites were investigated.

The concept of this thesis work was arised from the requirements of some projects carried out in Tübitak-SAGE.

Keywords: Bismaleimide resins, composite, thermal properties, resin transfer molding.

ÖZ

YÜKSEK SICAKLIK DAYANIMLI BİSMALEİMİD ESASLI REÇİNELERİN VE KOMPOZİTLERİNİN SENTEZ VE KARAKTERİZASYONU

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Isıl ve mekanik özelliklerinden dolayı bismaleimid reçineleri, kompozit malzemelerin matris elemanları olarak havacılık uygulamalarında önemlilerdir. En çok kullanılan bismaleimid olan 4,4'-bismaleimidodifenilmetan (BMI), maleik anhidrit ve 4,4'-diaminodifenilmetandan başlayarak sentezlenmiştir. N,N'-diallilaminodifenil metan (ADM), N,N'-diallilaminodifenil sülfon (ADS) ve N,N'-diallil p-fenil diamin (PDA), birincil aromatik aminlerin allillenmesi ile sentezlenmiştir. BMI/diallil bileşikleriyle 1:1, 1.5:1 ve 2:1 mol oranlarına sahip 9 farklı prepolimer hazırlanmış ve kür edilmiştir. BMI oranındaki artışın reçinelerin ısıl özelliklerine olan etkisi Diferansiyel Taramalı Kalorimetre (DSC) ve Isıl Gravimetrik Analiz Cihazı (TGA) ile incelenmiştir.

DSC sonuçları, reçinelerdeki BMI oran artışına bağlı olarak kür sıcaklığının arttığını göstermiştir. Isıl gravimetrik analiz, eklenen BMI monomerinin, reçinelerin ısıl dayanıklılığını arttırdığını ortaya çıkarmıştır. BMI/ADS ve BMI/PDA reçinelerine kıyasla, BMI/ADM reçine sistemi, daha iyi ısıl dayanıklılık göstermiştir.

1:1 ve 1.5:1 BMI/ADM mol oranına sahip reçinelerin proses edilme özellikleri viskozite ölçümleri ile incelenmiştir ve bu reçinelerin Reçine Transfer Kalıplama (RTM) ile kompozit malzeme üretimine uygun olduğu tespit edilmiştir. İki farklı BMI oranıyla hazırlanan BMI/ADM reçineleri matris eleman olarak kullanılarak, RTM tekniği ile kompozit malzeme üretimi gerçekleştirilmiştir. Farklı matris kompozisyonun, kompozitlerin ısıl ve mekanik özelliklerine etkisi incelenmiştir.

Bu tez çalışmasının kapsamı, Tübitak-SAGE'de yürütülmekte olan bazı projelerin ihtiyaçlarından ortaya çıkmıştır.

Anahtar kelimeler: Bismaleimid reçineleri, kompozitler, ısıl özellikler, reçine transfer kalıplama

To My Family

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LIST OF ABBREVIATIONS

BMI   4,4'-bismaleimidodiphenylmethane

ADM   N,N'-diallylaminodiphenyl methane

ADS   N,N'-diallylaminodiphenyl sulfone

PDA   N,N'-diallyl p-phenyl diamine

RTM   Resin Transfer Molding

NMR   Nuclear Magnetic Resonance

FTIR   Fourier Transform Infrared Spectroscopy

ATR   Attenuated Total Reflactance

DSC   Differential Scanning Calorimetry

TGA   Thermal Gravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 Polyimides

Polyimides are one of the most stable and environmentally resistant thermoset polymer systems. They are attractive in high temperature applications as matrix resins of composite materials for aerospace applications since they possess outstanding properties such as thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties and superior chemical resistance [1,2]. Polyimides which are derived from polymerizable monomers, contain imide functionality in their backbone (Figure 1.1).

$$R' \overset{\displaystyle \overset{O}{\|}}{-C} - N - \overset{\displaystyle \overset{O}{\|}}{C} - R''$$
$$|$$
$$R$$
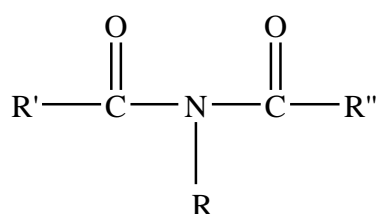
Figure 1.1 Imide functional group

Most of the developments in modern polyimide chemistry can be traced to pioneering work at DuPont in the 1950s and 1960s [3,4]. These efforts included the modification of nylon chemistry to produce polyimides in a two-step process. Kapton [TM] polyimide was formed by the condensation of an aromatic diamine, and dianhydride in the first step, to form polyamic acid followed by

cyclodehydration reaction in the second step. The reaction route for the synthesis of Kapton ^{TM} polyimide is shown in Figure 1.2.
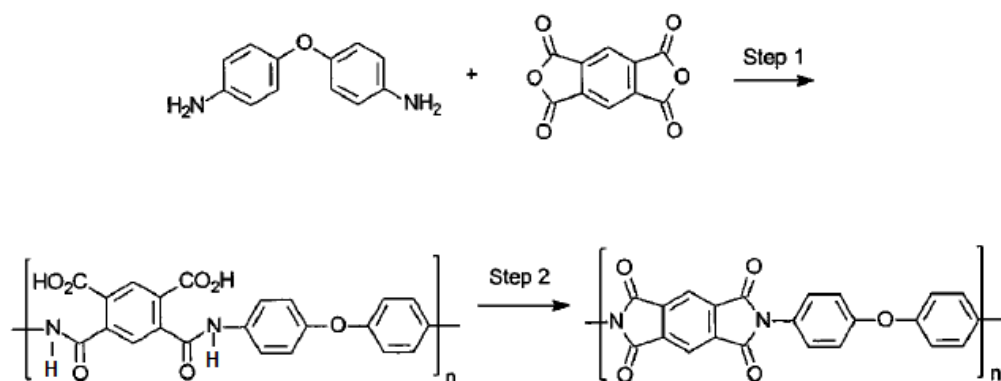
Figure 1.2 Reaction route for the synthesis Kapton ^{TM} polyimide [5].

A way of classification of polyimides can be done on the basis of the final curing reaction. There are two types of polyimides: condensation and addition polyimides [6].

1.1.1 Condensation Polyimides

Condensation polyimides are formed in a two step condensation polymerization process. In the first step, an aromatic dianhydride is reacted with an aromatic diamine to form a polyamic acid precursor. The second step involves the cyclization step by condensing out of a solvent molecule [7]. Due to their excellent thermal and oxidative stability, they can be used as matrix resins at high temperatures up to 350°C. A major limitation of condensation polyimides is the difficulty in processing the resin due to the evolution of volatile byproducts. Long cure cycles to prevent void formation, high pressures needed to minimize the effects of volatile content and long processing times are other limitations of condensation polyimides [6].

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1.1.2 Addition Polyimides

Addition polyimides are formed by the addition polymerization of low molecular weight polyimide resins. There are no volatile byproducts during the curing reaction so that problems occurred due to void formation are eliminated. Acetylene terminated polyimides, PMR polyimides and bismaleimides are the three important class of addition polyimides [8,9].

1.1.2.1 Acetylene-Terminated Oligomers

A class of thermosetting polyimides that possess good thermal and mechanical properties are systems terminated with acetylene endcaps. One acetylene terminated system that has received considerable attention is Thermid 600. It was developed at the Hughes Aircraft Company under US Air Force funding in the 1970's [10-12].

These polyimides are quite attractive for high temperature application because of their high T_g's (about 370 °C), good thermo-oxidative stability, resistance to humidity at elevated temperature and good dielectric properties. However, a major drawback of acetylene terminated oligomers is their narrow processing window. In general, these systems exhibit high melting point (195-200°C) and very short time of flow in the molten state (100-180 s) [10]. This makes them difficult to process, especially in the fabrication of large and complex structures.

1.1.2.2 PMR Polyimides

PMR polyimides, developed in the mid-1970's at the NASA Lewis Research Center are produced by dissolving an aromatic diamine, a dialkyl ester of tetraxarboxylic acid and a monofunctional nadic ester endcapping agent in a solvent, such as alcohol [13]. PMR stands for Polymeric Monomer Reactants

and -15 stands for a molecular weight of 15,000. It is widely regarded as one of the leading high-temperature matrix resins for polymer-matrix-composite for aircraft engine components.

The polymerization of PMR-15 consists of two steps. First, short chains of imide oligomers with norbornene endcaps are formed when 5-norborbornene-2,3-dicarboxylic acid monomethyl ester (NE), dimethyl ester of 3,3', 4,4'-benzophenone-tetracarboxylic acid (BTDE), and 4,4'-methylene dianiline (MDA) are combined in a low boiling alcohol, such as methanol. In the second step, crosslinked network structure due to the reaction of norbornene endcaps is formed [8]. Synthetic route for PMR-15 is shown in Figure 1.3.
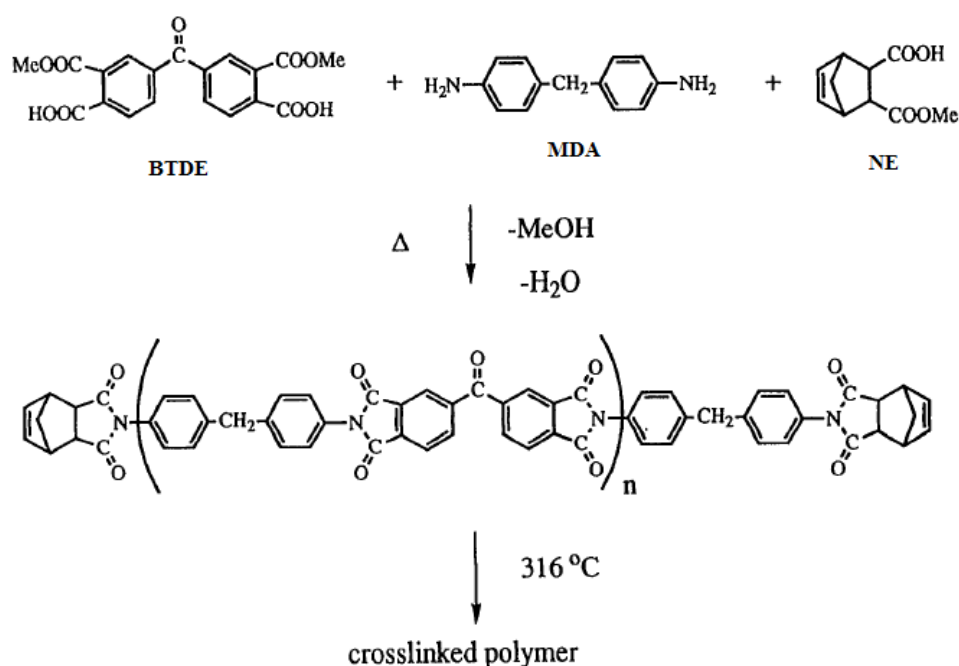
Figure 1.3 Reaction scheme of PMR-15

The attractive features of PMR-15, such as low raw material cost, use of a low boiling solvent which is easily removed during processing, good thermo-oxidative stability at elevated temperatures and excellent mechanical property

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retention for long-term use (1,000-10,000 h) at elevated temperatures (288-316°C) [14] make PMR-15 a leading candidate for a variety of aerospace applications [15,16].

However, one of the monomers of PMR-15, methylene dianiline (MDA) is a suspected mutagen, carcinogen and a liver toxin. The Occupational Safety and Health Administration (OSHA) imposes strict regulations on the handling of MDA during the fabrication of PMR-15 composites [17]. There have been several non-MDA polyimides formulated and sold; however, their elevated temperature performance is not good as the original formulation. The other disadvantages of PMR-15 are inadequate resin flow for fabricating complex structures, mismatch between fiber and resin in composite applications and the tendency towards microcraking of its composites [14].

1.2 Bismaleimides

Bismaleimides have become a leading class of thermosetting polyimides. They can be processed at relatively low temperatures (<175 ºC) by a variety of manufacturing techniques such as autoclave curing, filament winding and resin transfer molding and then cured at high temperatures to yield highly crosslinked networks with high glass temperatures (200-400ºC). They exhibit a balance of thermal and mechanical properties which make them popular for use in advanced composites, structural adhesives and electronic applications. They are the most important resins currently used in the aerospace industry due to their high performance-to-cost ratio and good processibility [18].

1.3 Synthesis of Bismaleimides

Bismaleimide (BMI) monomers are synthesized from maleic anhydride and a diamino compound. The synthesis route is shown in Figure 1.4. For temperature-resistant resins, aromatic diamines (2) are reacted with maleic anhydride (1) in

an inert organic solvent at room temperature, forming the corresponding bismaleamic acid (3) as an intermediate. Then, the cyclodehydration of the intermediate in the presence of acetic anhydride and fused sodium acetate as a catalyst forms the bismaleimide (4).
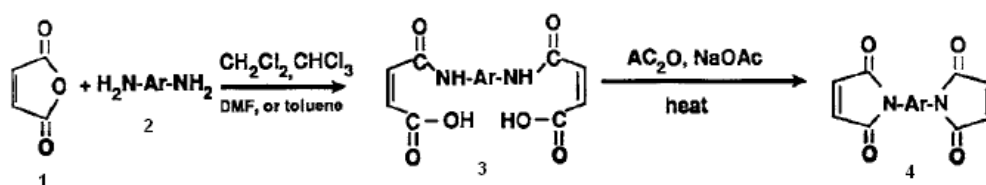
Figure 1.4 The general synthesis route of bismaleimide

A wide variety of bismaleimides is synthesized starting from different diamines to improve or modify the processing characteristics of the resin formulations. However, 4,4'-bismaleimidodiphenylmethane is the most widely used BMI in commercial resin formulations prepared from 4,4'-diaminodiphenylmethane and maleic anhydride. Due to its rigid ring, regular backbone structure and network forming ability, 4,4'-bismaleimidodiphenylmethane has excellent thermal stability. In addition, due to the methyl linkage between aromatic groups, it possesses the highest crosslink density among all bismaleimides so T_g of cured resins can reach 450 ℃ [18]. The chemical structure of 4,4'-bismaleimidodiphenylmethane is shown in Figure 1.5.
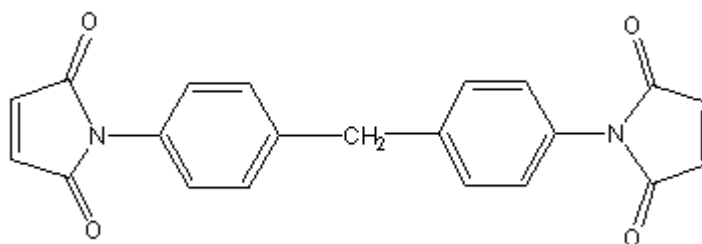
Figure 1.5 Chemical structure of 4,4'-bismaleimidodiphenylmethane

1.4 Structure-Property Relationship of Bismaleimides

The maleimide double bonds of BMI can undergo addition polymerization reactions. The reactivity of the maleimide double bond is a result of the electron-withdrawing nature of carbonyl functional groups, which create an electron deficiency. Therefore, bismaleimides can easily undergo homopolymerization and copolymerization reactions. As a consequence of the aromatic nature and highly crosslinking density of the cured structure, homopolymerization of BMIs gives a highly crosslinked brittle products.

Bismaleimide resins have attracted great attention in advanced composites manufacturing since they process in a way similar to epoxies. They can be processed at low temperatures, without evolution of by products. The imide functional groups reveal high polymer backbone stiffness and the network structures of bismaleimide resins result in materials with enhanced thermal and mechanical resistance.

However, unmodified bismaleimides suffer from hard, brittle structures forming due to their high crosslinking densities after curing, high temperatures needed for curing, poor solubility in ordinary solvents and narrow processing windows [19-21]. Considering the mechanical properties, they are high-modulus, low-strength materials with very low elongation at break [22]. Therefore, improving processibility and fracture toughness while retaining thermal stability is the important factor for the advancement of bismaleimide resins in composite applications. Bismaleimides are modified with a variety of compounds such as diamines, epoxy resins and olefinic materials in order to increase the molecular weight between chains. Increasing the molecular weight between chains helps to reduce the brittleness, improve processibility and toughness of bismaleimides.

1.5 Types of BMI Resins

1.5.1 BMI/Diamine Resins

One of the most common approaches for toughening of BMIs is the reaction of a BMI with a nucleophile, such as an aromatic diamino compound. In a system containing a bismaleimide monomer and a diamine, polymerization proceeds via addition reactions between the amine groups and the maleimide double bonds and also homopolymerization reactions between the maleimide double bonds [24-27].

Since the double bond of the maleimide is very reactive, it can undergo a chain extension reaction with primary and secondary amino compounds via the nucleophilic attack of the amine group on the maleimide double bond. This reaction is known as Michael addition reaction which is shown in Figure 1.6. Finally, crosslinking and further chain extension occur as a consequence of the homopolymerization reactions (Figure 1.7) particularly at higher temperatures. The maleimide double bonds of the BMI readily react in the molten state by free radical polymerization [8,28].
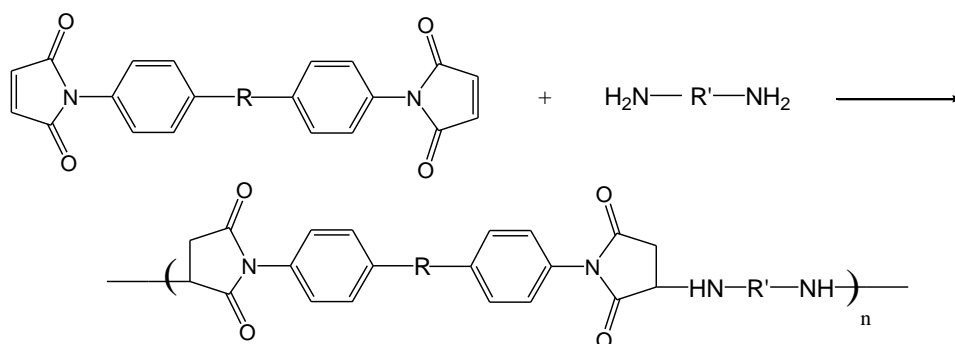
Figure 1.6 Chain extension due to Michael addition reaction
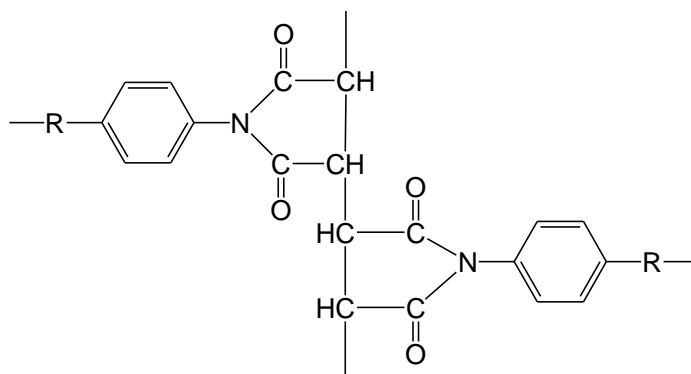
Figure 1.7 Crosslinking due to homopolymerization

Chain extension via primary amine addition reaction proceeds at relatively low temperatures without the elimination of volatiles while higher temperatures are required for homopolymerization of the bismaleimide. Tungare et al. [29] reported that amine addition occurs at 125 °C while crosslinking reaction competes with the chain extension reaction above 150°C.

Modification by diamines to reduce the brittleness of bismaleimide was first studied in 1973 by Crivello [30]. The formation of a linear high molecular weight polymer called polyaspartimide was reported when an exact 1:1 molar ratio of bismaleimide and diamine were employed in solution.

Different reactant ratios of the monomers yield resins with different thermal and mechanical properties. Considering the resin composition on T_g, Leung and colleagues [31] reported that increasing the concentration of BMI from 1:1 to a 2:1 mole ratio results increase in T_g. Donnellan and Roylance [26,32] investigated the effects of changing the compositions of BMI and MDA on resin properties. It was reported that curing at a lower temperature or increasing the diamine ratio favors the chain extension mechanism so crosslinking density decreases.

On the other hand, increasing the amount of BMI in the composition, yield stress and modulus increase while fracture toughness [32,33] decreases.

The reaction product of 4,4'-bismaleimidodiphenylmethane and 4,4'-diaminodiphenylmethane, the trade name known as Kerimid 601 [34] was prepolymerized in melt or in solution to such an extent that the resulting prepolymer is soluble in aprotic solvents such as dimethylformamide, N-methylpyrrolidone and the like.

1.5.2 BMI/Epoxy Resins

Modification of bismaleimides by epoxy compounds is a well-developed technique used to improve their processibility and toughness. Epoxy resins exhibit many desirable properties such as excellent chemical and solvent resistance, good thermal and electrical properties, good adhesion to various substrates, and easy processibility [35-41].

Bismaleimide-epoxy blends of optimum composition may yield resins with excellent thermal and mechanical properties. Such blends have been reported in the literature. EA 9655 and EA 9102 which are bismaleimide-modified epoxy resins were formulated by the Hysol division of Dexter Corporation. Resins with good heat resistance were produced by modification of epoxies with bismaleimide-anhydride copolymer Kerimid 601 was blended with 1,2-polybutadiene epoxide in the presence of an organic epoxide to prepare electric insulators with good heat resistance, adhesion and dimensional stability [42].

BMI modified epoxy and siliconized epoxy intercrosslinked network having varied concentrations of bismaleimide were developed by Kumar et al. [43,44]. According to their results, the mechanical and thermal properties were increased with an increasing percentage of BMI content whereas the values of the strain

fracture toughness were decreased with increasing BMI content. The T_g of such systems revealed values in the range 160-190°C due to the varying concentration of BMI.

The modification of BMI with epoxy-like compounds helps to improve the processibility and toughness of BMI; however, one disadvantage associated with addition of epoxy resin is that it reduces the thermal stability of bismaleimides.

1.5.3 BMI/Allyl Compounds

Allyl-compound-modified BMI resins are one of the most successful BMI resins. The prepolymers show good processability and the cured BMI resins possess high thermal stability, high glass transition temperature, and good toughness [45]. O,O'-diallylbisphenol A (DABA) is the most common allyl type modifier for BMI systems.

A two-component bismaleimide system (Matrimid 5292 A and B^{TM}), composed of 4,4'-bismaleimidediphenyl methane and o,o'-diallyl bisphenol A (DABA), was developed by the Ciba Geigy Corporation to improve mechanical properties and processability of BMI [46]. It is one of the leading matrix resins for fiber reinforced composite for advanced aerospace application. The components of Matrimid 5292 are given in Figure 1.8.
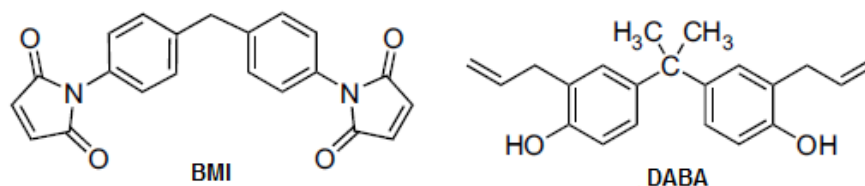
Figure 1.8 The components of Matrimid 5292 (Component A: 4,4'-bismaleimidodiphenyl methane, BMI and component B: o,o'-diallyl bisphenol A, DABA)

During the curing process of such resins, allyl compound copolymerizes with BMI via an ene type linear chain-extension reaction followed by the Diels-Alder reaction. The brittleness of the cured resin is improved, compared with the conventional bismaleimide resins [47]. The curing reactions of such BMI resins are shown in Figure 1.9.
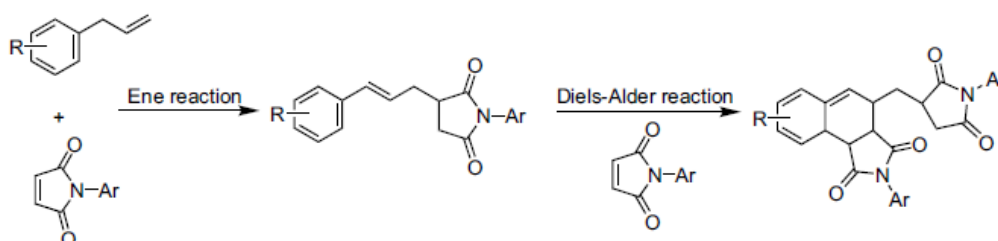
Figure 1.9 Curing reactions of BMI-allyl type compounds

It was reported that allyl groups reacted with maleimide groups at around 130°C via the Ene reaction to yield an intermediate, and subsequently reacted with maleimide groups at around 200°C via the Diels-Alder reaction to form crosslinking networks [45,48,49]. Homopolymerization of maleimide groups were also existed during the curing process (Figure 1.10).
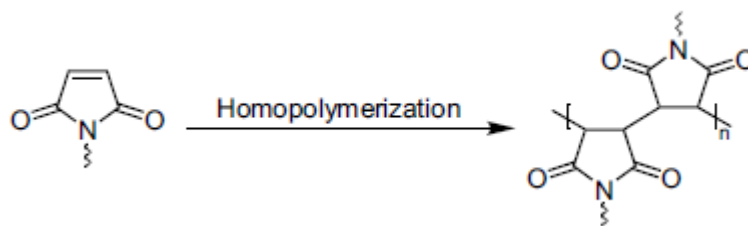
Figure 1.10 Homopolymerization of BMI

Allyl compounds are one of the most successful modifiers for BMI, however, these systems need to be cured and post-cured at high temperatures such as 220-250°C [50]. Then, the main target of researchers have become to reduce the cure and post-cure temperature of the bismaleimide resins and improve the toughness of the resin systems with no reduction in thermal stability. In order to merge the advantages of BMI/diamine resins (low cure temperature) and BMI/allyl type resins (high thermal stability, low process temperature), allyl amine compounds were synthesized and the modified BMI systems were formulated.

Liang and Gu [50] achieved allylation of 4,4'-diaminodiphenylmethane (MDA) and prepolymers in various mole ratios of BMI and the allyl amine compound were prepared . It was reported that, the cured prepolymer system which had the 100:40 weight ratio of BMI:diallyl amine compound revealed the best thermal and mechanical properties (%38 char yield at 800°C, 86.4 MPa tensile strength, 11.8 MPa impact strength) among the others.

In another study, Aijuan Gu [51], prepared N-allyl diaminodiphenyl ether (Figure 1.11) by allylization of diaminodiphenylether and it was copolymerized with BMI to prepare a resin sytem suitable for resin transfer molding (RTM) process.

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The characteristics of the resin system showed that the resin could meet the requirements of (RTM) , and the neat resin system displayed high mechanical properties (85.3 MPa tensile strength (25°C), 12.5 MPa impact strength) after cured and post-cured at 200°C.
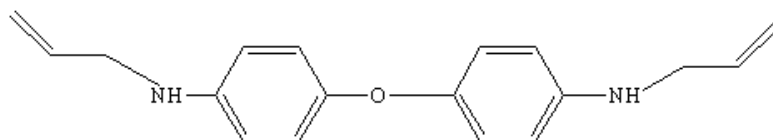
Figure 1.11 Structure of N-allyl diaminodiphenyl ether

1.6 Composites

A composite material is defined as a combination of two or more components, usually a selected filler or reinforcing agent and a compatible matrix binder. The components and the interface between them can usually be physically identified, and the properties of the interface generally control the properties of a composite. The composite property is noticeably different from the properties of each of the constituents. [52,53]. Different reinforcement and matrix systems can be used to obtain a broad spectrum of composite materials having specific characteristics.

Today, composites are highly preferred materials mainly used in high technology industries. The reasons that composite materials are favored over conventional materials are their higher specific strength, higher specific stiffness, higher corrosion and impact resistance, improved fatigue life. Today, composite materials are widely used in industries such as automobile, electronics, aircraft components, space vehicles and sporting goods. (Figure 1.12)

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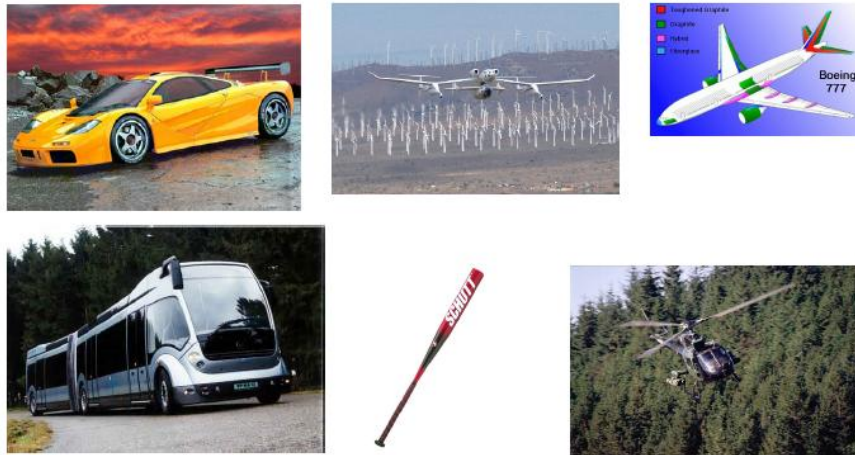
Figure 1.12   Use of composites in different industries

A way of classification of the composites can be done on the basis of the reinforcement employed such as fibrous, laminar and particulate. Another way of classification based on type of the matrix material can be polymeric, ceramic, metallic and intermetallic matrix composites [52,54].

Polymer matrix composites are now an important class of engineering materials. In addition, mostly fiber reinforced ones are preferred for high technology applications due to their lower weight and superior mechanical properties.

The demands of the aerospace community which aims to produce high performance materials have lead to the development of fiber reinforced composites. For many years, aluminum and steel which provide high strength and high stiffness were the main material of the aerospace components. However, corrosion and fatigue problems of metals used in structural parts and also demand for the lightweight materials supported the development of fiber reinforced composites. Today, it seems that fiber reinforced composites have successfully replaced aluminum and steel in many engineering applications.

The main components of fiber reinforced polymer matrix composites are the fiber which provides strength and stiffness to the composite and the matrix which provides the rigidity and the shape to the structure.

1.7 The Components of Composites

1.7.1 Fiber

The main functions of the fiber reinforcement in a composite material are:
- To carry the load. In a 70 to 90% of the load in a strucrural composite is carried by fibers,
- To provide high strength, stiffness and other mechanical properties in the composites,
- To provide electrical conductivity or insulation, depending on the fiber used [53].

Mostly used types of fibers for composite manufacturing are carbon, glass, aramid or boron fibers. The fibers are sold and used in many different forms and architectures. The discussion of the reinforcement forms is a discussion on how fibers can be joined together. The type and the arrangement of the fiber directly affects properties of the composite and process design.

The most common commercial form of fibers is woven fabric which is described as a planar material made by interlacing yarns (a twisted bundle of continous filaments, often used for weaving) and tows (an untwisted bundle of continous filaments, usually with specific count) in various specific patterns [55]. The most common types of fabric weaves are illustrated in Figure 1.13.
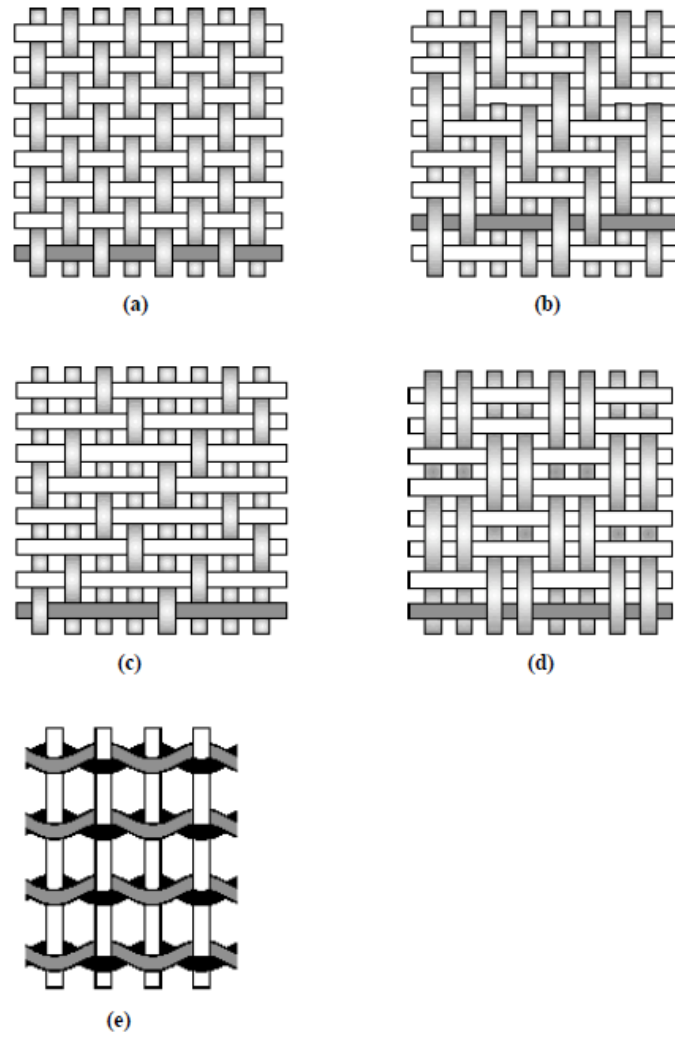
Figure 1.13 Fabric weave styles a) plain, b) twill, c) satin, d) basket, e) leno

The plain weave is the simplest form which is formed by interlacing yarns in an alternating over-and-under pattern. The maximum fabric stability and firmness with minumun yarn slippage results from this weave. This weave is the most resistant to in-plane shear and considered to be a stiff weave [55]. Plain weave carbon fabric was used as the reinforcement of the composite manufactured in this study.

1.7.1.1 Carbon Fiber Reinforcement

The demand for reinforcement fibers with strength and modulus higher than those of glass fibers has led to the development of carbon or graphite fibers. Since the mechanical properties of carbon fibers have gradually increased through improvements in starting materials and production methods, carbon fibers are today predominant as the high-strength and high-modulus reinforcing agents used in the fabrication of resin matrix composites [55].

The carbon and graphite fibers are produced using PAN-based or pitch-based precursors. The general flow diagram of carbon fiber manufacturing from PAN and pitch is shown in Figure 1.14. The precursor undergoes a series of operations. In the first step, the precursors are oxidized by exposing them extremely high temperatures. Later, they go carbonization and graphitization processes. During these processes, precursors go through chemical changes that yield high stiffness-to-weight and strength-to-weight properties. The successive surface treatment and sizing process improve its resin compatibility and handleability [53].

```
                    Two Types of Precursors
                            |
    Textile  ◄──────────────┴──────────────►  Pitch
  Polyacrylonitrile                          (Isotropic)
     (PAN)                                        |
       |                                        Heat
       |                                      Treatment
       |                                       at 350°C
       |                                          |
  Wet spinning                               Mesophase
  and stretching                               Pitch
  followed by                               (Anisotropic)
  stabilization at
  220°C in air                              Melt spinning
       |                                    and drawing
       |                                    followed by
       |                                    heat stabilization
       ▼                                        ▼
  PAN Filament                              Pitch Filament
       |_____|
                            |
                            | Heating and stretching
         Carbonization      | at 1000°C in an inert
                            | atmosphere
                            ▼
              Relatively low modulus, high strength
                        Carbon fibers
                            |
         Graphitization     | Heating to 2000°C
                            | with or without stretching
                            ▼
                  Carbon/Graphite Fibers
        (without stretching. relatively high modulus, low strength
              with stretching improved strength)
```

Figure 1.14 Flow diagram in carbon fiber manufacturing [56]

PAN refers to polyacrylonitrile, a polymer fiber of textile origin. Pitch-fiber is obtained by spinning purified petroleum or coal tar pitch and lower cost precursor than PAN [53]. PAN-based fibers are most widely used for the fabrication of carbon fibers. Pitch carbon fibers have very high modulus values, but their tensile strength and strain to failure are lower than those of PAN carbon fibers [56].

1.7.2 Matrix

The important functions of a matrix material in a composite system include the following [53]:

- The matrix material binds the fibers together and transfers load to the fibers. It provides rigidity and shape to the structure.

- It isolates the fibers so that individual fibers can act separately. This stops or slows the propagation of a crack.

- The matrix provides a good surface finish quality and aids in the production net-shape or near-net-shape parts.

- The matrix provides protection to reinforcing fibers against chemical attack and mechanical damage.

- Depending on the matrix material selected, performance characteristics such as ductility, impact strength, etc. are also influenced. A ductile matrix will increase the toughness of the structure.

- The failure mode is strongly affected by the type of matrix material used in the composite as well as its compatibility with the fiber.

The matrix materials are generally polymers, ceramics or metals. The polymer matrices, also called resins, are the most common and they are usually divided into two general classifications: thermosets and thermoplastics.

Thermosets have historically been the principal matrix material for composites. Epoxies, phenolics, polyesters, cyanate esters and polyimides can be classified as important thermoset polymers while thermoplastic resins include polymers such as polyamides, polypropylene, polyphenylene sulfide.

1.8 Composite Manufacturing Techniques

Polymer matrix composite manufacturing techniques can be classified as short (discontinuous) fiber composite manufacturing, and continuous composite manufacturing techniques. Continous composite manufacturing techniques can be classified into two: thermoset and thermoplastic composite manufacturing.

In advanced *thermoplastic* composite manufacturing, the initial raw material is in solid state and needs to be melted to obtain the final product. Heat and pressure are applied to have the highly viscous resin system and the fibers move together. In these processes, resin and fibers deform together and take the shape of the final part. The advantage of processing thermoplastic composites is that the process cycle time is very short since no chemical reaction occurs during processing, as a result they can be used for high-volume production methods. Thermoplastic tape winding, thermoplastic pultrusion, autoclave processing, diaphragm forming, compression molding are common processing techniques for advanced thermoplastic composites.

Advanced *thermoset* composite manufacturing processes involve the impregnation of a preform fabric with thermoset resin. The resin systems are cured at elevated temperatures or sometimes at room temperature to obtain the final shape. The processes that fall into this class are prepreg lay-up , wet lay-up, filament winding, pultrusion, roll wrapping and all liquid composite molding (LCM) processes such as resin transfer molding (RTM) or vacuum assisted RTM (VARTM).

1.9 Resin Transfer Molding (RTM) Process

Resin transfer molding (RTM), also known as liquid transfer molding process, is one of the most popular manufacturing processes for producing polymer matrix fiber reinforced composite materials.

The main steps of a typical RTM process are summarized below:

1) *Preparing the preform:* Fabric layers are cut in desired dimensions and placed in the mold cavity. The dimensions should match the size of the mold cavity.

2) *Closing the mold:* Upper mold is clamped to the other one by compacting the the fabric preform between two mold parts. The mold is heated to a specified temperature.

3) *Resin injection and cure:* The thermosetting resin is injected into the mold cavity through inlet port at selected tempearature and pressure. Sometimes a vacuum is created inside the mold to assist in resin flow as well as to remove air bubbles. After resin fills the entire mold cavity, the vacuum is turned off and the pressure inside the mold is increased to ensure that the remaining porosity is collapsed. (Figure 1.15)

4) *Final processing and demolding:* The part solidifies after curing for a certain time depending on the chemistry of the resin system. The upper mold is opened and the composite part is removed from the mold.
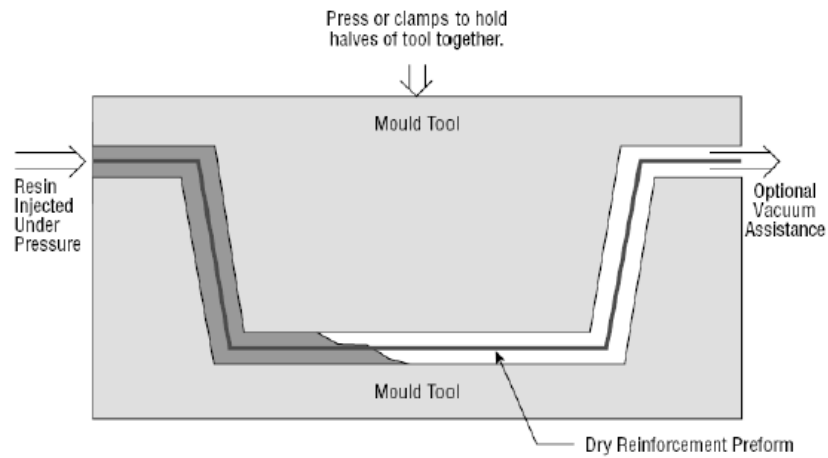
Figure 1.15 Schematic view of Resin Transfer (RTM) Molding Process [57]

1.9.1 Applications of RTM Process

The RTM process is suitable for making small-to large sized structures in small-to medium volume quantities. Some industry applications of RTM process include:

- Automative industry (automative panels, sport car bodies)
- Aerospace and military (wing and engine part, aircraft structures)
- Sporting goods (bicycle frames, hockey sticks)
- Consumer products (chairs, swim pool panels, solar collectors)
- Corrosion resistance applications (chemical storage tanks, tubes..)

1.9.2 Advantages of RTM Process

RTM provides opportunities to use continuous fibers for the manufacture of structural components in low-to-medium volume environments. Some of its major advantages over other composites manufacturing techniques include [53]:

1) Initial investment cost is low because of reduced tooling costs and operating expenses.
2) Moldings can be manufactured close to dimensional tolerances.
3) RTM processing can make complex parts at intermediate volume rates.
4) RTM provides for the manufacture of parts that have a good surface finish on both sides.
5) Higher fiber volume fractions can be achieved.
6) A wide variety of reinforcement materials can be used.
7) RTM offers low volatile emission during processing because of the closed molding process.
8) RTM offers production of near-net-shape parts, hence low material wastage and reduced machining cost.
9) The process can be automated, resulting in higher production rates with less scrap.

1.9.3 Limitations of RTM Process

Although RTM has many advantages compared to other fabrication processes, it also has the following limitations [53].

1) The manufacture of complex parts require good amount of trial-and-error experimentation or flow simulation modelling to make sure the porosity and dry fiber- free parts are manufactured.

2) The tooling design is complex.

3) The resin system should have low viscosity sufficient pot-life at injection temperature.

4) Good adhesion between the resin matrix and the reinforcement should be provided.

5) No volatile material should be released upon curing.

1.10 Aim of This Study

Bismaleimides are one of the most important components of matrix resins of composite materials for aerospace industry where lightweight structures with considerable strength are needed. However, unmodified bismaleimides suffer from brittleness due to their high crosslinking densities after curing. The aims of this study are:

1) To synthesize 4,4'-bismaleimidodiphenylmethane (BMI), which is the most widely used bismaleimide in commercial resin formulations,

2) To synthesize three different diallylamino compound by allylization of diamine precursors,

3) To accomplish the modification of BMI with diallylamino compounds in order to improve processibility and toughness of BMI,

4) To manufacture composite systems which have good thermal and mechanical properties with RTM process.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

The chemicals for the synthesis of BMI which are maleic anhydride, sodium acetate, acetic anhydride, and N,N-dimethylformamide (DMF) were obtained from Merck and 4,4'-diaminodiphenyl methane (MDA) was obtained from Fluka. For the synthesis of diallylamino compounds, primary aromatic diamines which are 4,4'-diaminodiphenyl methane (MDA) (Fluka), 4,4'-diaminodiphenyl sulfone (Fluka) and p-phenylenediamine (Merck) were used as received. The solvent, N,N-dimethylformamide (DMF) (Merck) and the allylating agent, allyl chloride (Aldrich) were used without further purification.

3K plain weaving carbon fiber fabric was obtained from DOST Kimya for composite production. The properties of the fabric is given in Table 2.1.

Table 2.1 Properties of carbon fiber fabric

Property	HS (High strength)
Filament diameter, μm	5,5-8,0
Density, g/cm^3	1,75-1,80
Tensile strength, MPa	3105-4555
Tensile modulus, GPa	228-262
Elongation at break, %	1,3-1,8
Thermal conductivity, W/mK	8,1-9,3

2.2. Instrumentation

2.2.1 Nuclear Magnetic Resonance (NMR)

^{1}H-NMR and ^{13}C-NMR spectrum of the samples were recorded on a Bruker Ultrashield Superconducting 400 MHz Spectrometer using $CDCl_3$ and d-DMSO as the solvents.

2.2.2 Fourier Transform Infrared Spectrometer (FTIR)

FTIR analysis were carried out on a Perkin Elmer Spectrum One Spectrometer. The FTIR spectrums of materials were obtained by ATR (Attenuated Total Reflactance) accesory with 4000-650 cm^{-1} scan range, and 4 resolution.

2.2.3 Differential Scanning Calorimetry (DSC)

Thermal properties of materials were investigated with Perkin Elmer Diamand DSC under N_2 atmosphere at a heating rate of 10°C/min.

2.2.4 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis of samples were performed using Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer. TGA curves were obtained at a heating rate of 10˚C/min under N_2 atmosphere.

2.2.5 Viscosity Measurements

The viscosity data of the resins were obtained isothermally using shear for liquid holder of Metravib +450 model Dynamic Mechanical Analyzer under 5 Hz freqency and 0.0001 mm displacement.

2.2.6. X-ray Analysis

The non-destructive testing were performed using Vidisco Fox-Rayzor X-Ray Instrument to investigate the interior structural details of composites. X-ray data of materials were collected at 270 Kv, 24 pulse and 70 cm distance.

2.2.7. Tensile Tests

Instron Tensile Testing Machine TM1102 was used to obtain the tensile properties of the composite specimens. The drawing rate was 2 mm/min and tests were done at room temperature. The test were performed in compliance with ASTM D638 (Standard Test Method for Tensile Properties of Plastics). Five samples were used for each resin tranfer molded composites. The shape and dimensions of the specimens are exhibited in Figure 2.1 and Table 2.2.
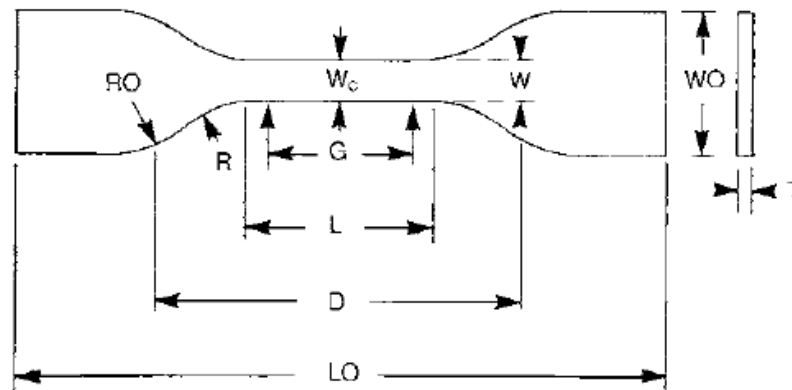

Figure 2.1 Representation of tensile test specimen

Table 2.2 Dimensions of tensile test specimen

Symbol	Dimensions, mm
W, Width of narrow section	6
L, Length of narrow section	33
WO, Width overall	19
LO, Length overall,	115
G, Gage length	25
D, Distance between grips	65
R, Radius of fillet	14
RO, Outer radius	25

Tensile strength at break (MPa), Young's modulus (GPa) and percent elongation (%) at break values were derived from the stress-strain curve of composites.

Tensile strength is defined as the load recorded in breaking the test specimen divided by the original cross-sectional area of the test piece. Young's modulus shows the stiffness of the material and is calculated from the slope of the stress-strain curve in the elastic deformation region. Percent elongation at break is the change in gage length at the point of specimen rupture relative to the original specimen gage length and expressed as a percent.

2.2.8 Izod Impact Tests

Impact testing measures the energy absorbed by a specimen prior to fracture and provides information about the resistance of a material to fracture or break (toughness). Composite specimens having dimensions of 55 mm x 10 mm x 3.5 mm were used in unnotched izod impact tests. Tests were performed by using a impact tester of Inston Dynatup 9250 HV according to ASTM D256 at room temperature.

2.3 Procedure

2.3.1 Synthesis of BMI

Synthetic route of 4,4'-bismaleimidodiphenyl methane (BMI) is a two-step process. The first step involves the formation of amic acid intermediate and in the second step bismaleimide is synthesized as a result of the cyclization of amic acid intermediate.

BMI was synthesized according to the procedure reported by Varma et al.[58]. 4,4'-diaminodiphenylmethane (MDA) (0.5 mol, 99.14 g) was dissolved in DMF (800 ml) in a four-necked 2-liter reactor fitted with a mechanical stirrer, 50 ml/min flow rate of nitrogen inlet, reflux condensor and a thermometer. Maleic anhydride (1.1 mol, 107.91 g) was dissolved in DMF (200 ml) and added dropwise at room temperature over 30 min. The temperature was increased to 50°C gradually and stirred at 50°C for 2 hours. During this period, amic acid intermediate formation occured and the color of the solution turned colorless to yellow.

First, fused sodium acetate (0.55 mol, 45.12 g) and then acetic anhydride (250 ml, 270.50 g) were added dropwise to the solution in order to achieve the cyclodehydration of the amic acid. The temperature of the reaction mixture was maintained for one hour at 50°C. At the end of the reaction period, color of the solution turned from yellow to brown. The solution was then poured into cold water. The precipitate was collected by vacuum filtration, repeatedly washed with water and dried at 60°C in a vacuum oven. The light brown bismaleimide powder was purified by recrystallization from 50/50 v/v chloroform-ethanol solution.

The product was obtained with a good yield (90-95%). The schematic representation of synthesis of BMI is given in Figure 2.2.
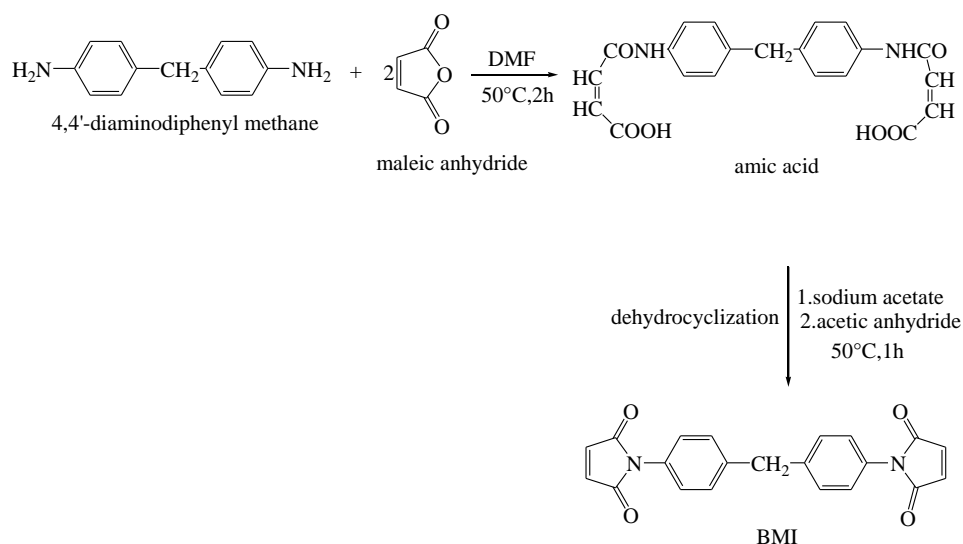

Figure 2.2 Synthetic route of BMI

2.3.2 Synthesis of Diallylamino Compounds

Three different diallyl compounds were synthesized by allylating 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone and p-phenylenediamine using the procedure reported in literature [59]. The corresponding diamine (0,5 mol) was dissolved in dimethyl sulfoxide (DMSO) (300 ml) and was charged into a one-liter three-necked flask equipped with a reflux condenser, a thermometer and a dropping funnel. Aqueous 48% sodium hydroxide solution (1.15 mol, 95.8 g) was added to the solution at room temperature, and then allyl chloride (1.15 mol, 88.0 g) was added dropwise over 2 hours at 40°C. After completion of the dropping, the solution was stirred at 50°C for 4 hours and then stirred overnight at room temperature. Toluene (300 ml) and distilled water (500 ml) were added to the solution successsively, organic layer was seperated and washed two times with aqueous 15% sodium chloride solution (500 g) and two

31

times with distilled water (500 ml). The solvent was evaporated and the product was dried at vacuum. The products were obtained 70-75% yield. The general synthetic route and the structure of synthesized diallylamino compounds which are N,N'-diallylaminodiphenyl methane (ADM), N,N'-diallylaminodiphenyl sulfone (ADS) and N,N'-diallyl p-phenyl diamine (PDA) are given in Figure 2.3 and Figure 2.4.
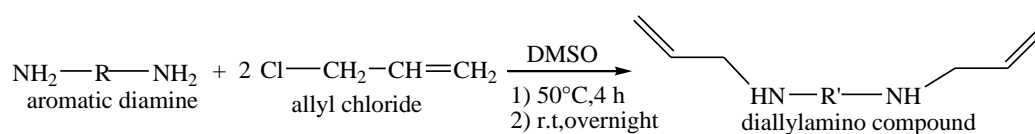
$$NH_2-R-NH_2 \;+\; 2\; Cl-CH_2-CH{=}CH_2 \quad \xrightarrow[\substack{1)\;50°C,4\;h \\ 2)\;r.t,overnight}]{DMSO} \quad HN-R'-NH$$

aromatic diamine   allyl chloride   diallylamino compound

Figure 2.3 General synthetic route of diallylamino compounds

R : —[phenyl]—CH$_2$—[phenyl]—

↓

HN—[phenyl]—CH$_2$—[phenyl]—NH
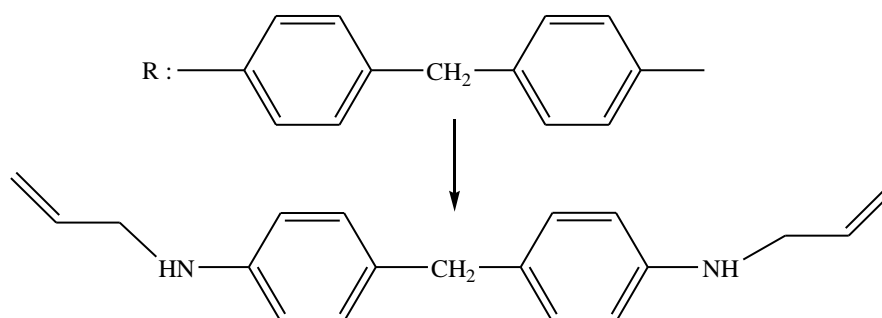
Figure 2.4.a Structure of N,N'-diallylaminodiphenyl methane (ADM)
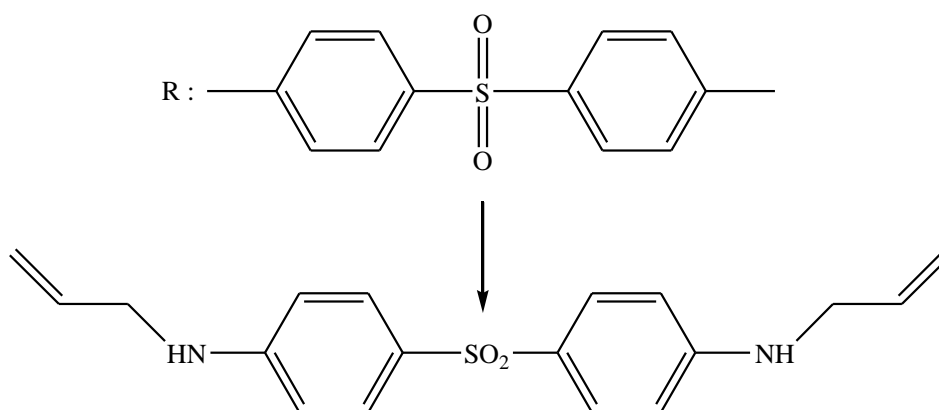
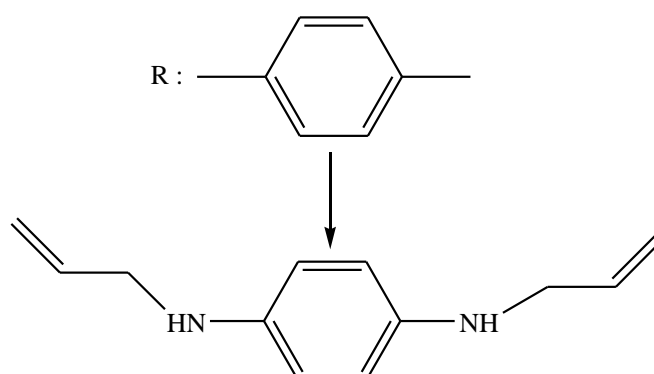**Figure 2.4.b** Structure of N,N'-diallylaminodiphenyl sulfone (ADS)

Figure 2.4.c Structure of N,N'-diallyl p-phenyl diamine (PDA)

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The physical properties of ADM, ADS and PDA are summarized in Table 2.3.

Table 2.3 Physical properties of diallylamino compounds

	ADM	ADS	PDA
Appearance at 25°C	Red-brown liquid	Pale yellow pasty liquid	Dark-brown liquid
Viscosity at 25°C (Pa.s)	0.44	2.04	0.06
Solubility	Soluble in acetone, ethanol, DMF	Soluble in ethanol, DMF	Soluble in ethanol, DMF

2.3.3 Preparation of Neat Resins

For each system, 3 different molar ratios of BMI to allyl compound (1:1,1.5:1 and 2:1) were heated with stirring in a flat-bottom flask with a magnetic stirrer and temperature was maintained at 120°C, until a clear homogeneous melt was obtained. The melt solution was maintained at 120°C for additional 10 min and the resultant product was defined as prepolymer. The compositions of 9 prepolymers are presented in Table 2.4 as molar ratios and corresponding weight of each component.

Table 2.4 Compositions of prepolymers

Prepolymer System	BMI:diallyl (mole ratio)	Weight, g (BMI:diallyl)
BMI/ADM	1:1	10.00 : 7.77
BMI/ADM	1.5:1	10.00 : 5.18
BMI/ADM	2:1	10.00 : 3.88
BMI/ADS	1:1	10.00 : 9.17
BMI/ADS	1.5:1	10.00 : 6.11
BMI/ADS	2:1	10.00 : 4.58
BMI/PDA	1:1	10.00 : 5.25
BMI/PDA	1.5:1	10.00 : 3.50
BMI/PDA	2:1	10.00: 2.63

The prepolymers were degassed while hot at 120°C and cured with the following cure cycles in air circulating oven.

BMI/ADM sytem : 150°C/1h+180°C/2h+200°C/6h

BMI/ADS sytem: 180°C/2h+200°C/4h+250°C/6h

BMI/PDA system: 150°C/1h+180°C/2h+200°C/3h

2.3.3.1 Possible Polymerization Reactions

The reaction mechanism of BMI with allyl group compounds is very complicated. Polymerization reactions begins upon the mixing of components at 120°C and polymer formation continues during the curing step. In this study, BMI can react with both amine and allyl groups according to different reaction routes as well as crosslinking reaction takes place due to the reaction between maleimide groups of BMI. Mainly three types of reactions taking place between BMI and allyl type compounds were reported [45,48,49].

These reactions are i) 'Ene' reaction ii) Michael amine addition reaction and iii) Homopolymerization of BMI. In general, the double bonds of the maleimide ring in BMI, and the allyl groups react via the ene-type linear chain extension reaction between 100-200°C. The reaction process is roughly outlined in Figure 2.5.
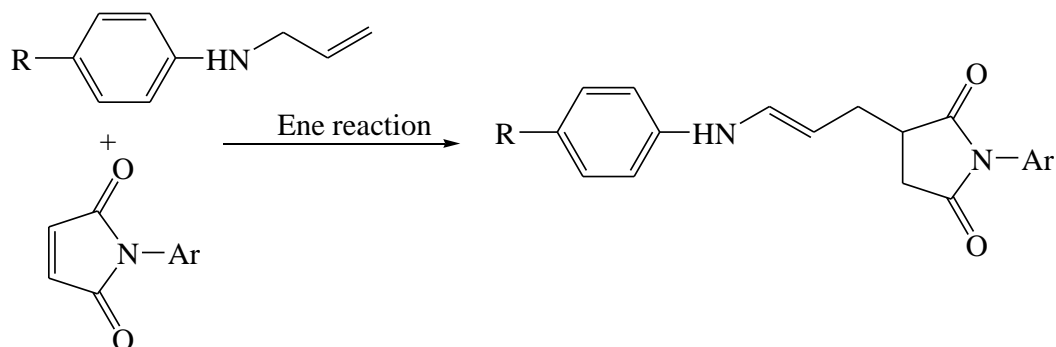

Figure 2.5 Chain extension with 'Ene' reaction

Moreover, Michael amine addition reaction can occur between the amine group and maleimide double bond of BMI. Figure 2.6 illustrates the chain extension reaction between BMI and a secondary amine group. Homopolymerization of BMI (Figure 2.7) during curing gives a highly crosslinked network structure.
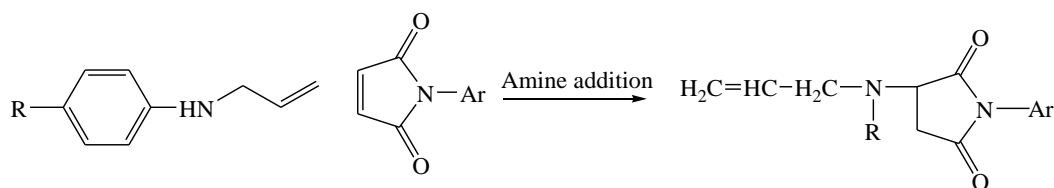
Figure 2.6 Amine addition reaction between BMI and secondary amine group
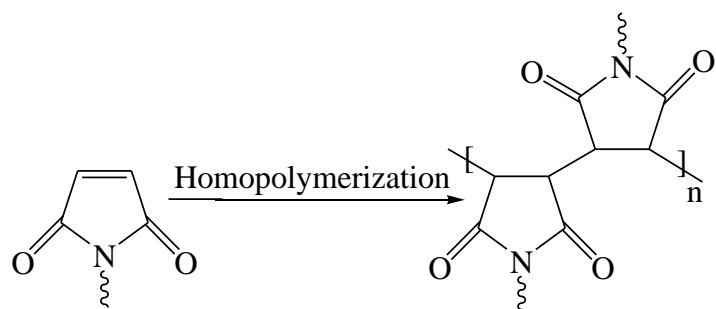
Figure 2.7 Crosslinking due to homopolymerization of BMI

2.3.4 Production of Composites by RTM Process

The main steps followed in the production of composites by RTM technique are given as a flowchart in Figure 2.8.
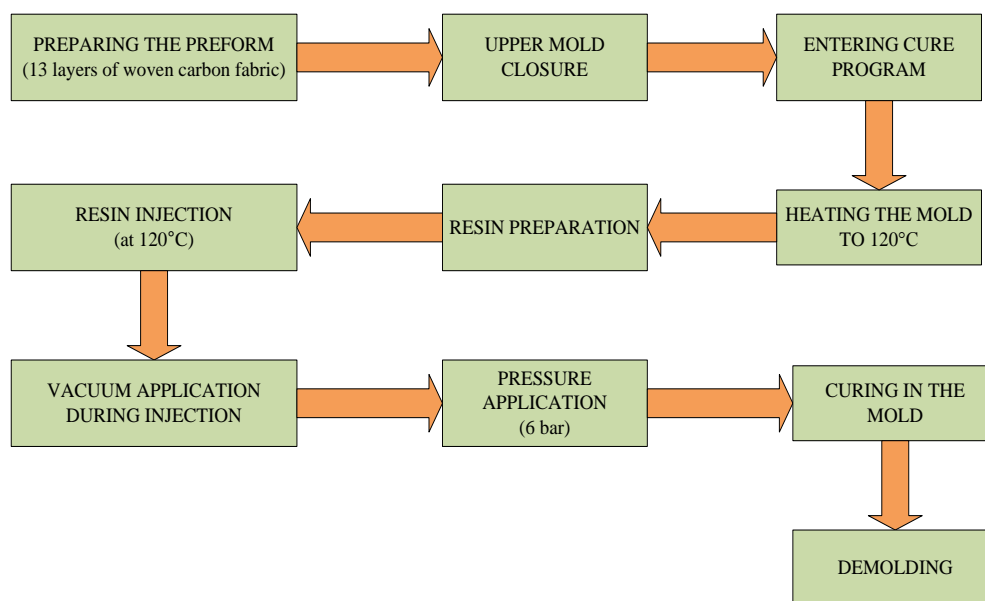

Figure 2.8 Main steps followed in RTM process

First, the mold surface was cleaned and a release agent was sprayed onto the mold surface for easy removal of the part. 13 layers of carbon fabric were cut in 19x12.5 cm dimensions and were placed in the mold cavity all in the same orientation (warp ↑, weft →) as shown in Figure 2.9.
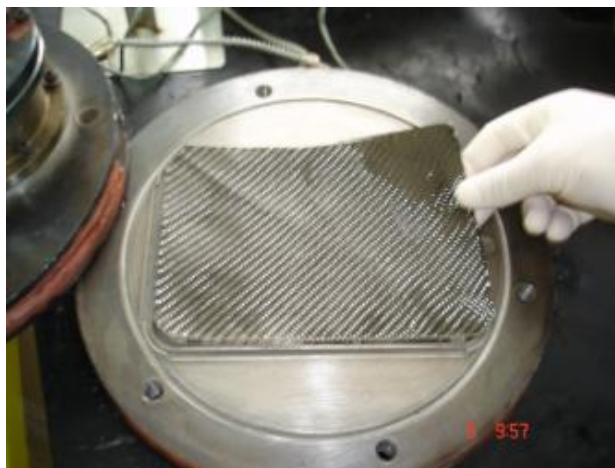
Figure 2.9 Placing carbon fabric layers in the lower mold cavity

The upper mold was closed and clamped. The mold was heated to the injection temperature (120°C) of the resin and the curing program was entered to the temperature board as 150°C/1h+180°C/2h+200°C/6h. The resin was prepared by mixing desired quantities of BMI and ADM in evaporator embedded in silicon oil bath. The components were stirred at 120°C until a clear homogeneous solution was formed. The solution was maintained at 120°C for additional 10 min, and vacuumed for a minute. Prepared resin was immediately injected through inlet ports into the mold which was heated to 120°C before. The outlet resin port was connected to vacuum pump and 0.5 bar vacuum was created inside the mold to assist in resin flow as well as to remove air bubbles. After the mold was completely filled with resin, the vacuum was turned off and the outlet port was closed. Then, 6 bar positive pressure was applied into the mold to ensure that the remaining porosity was prevented. Resin injection port as well as vacuum and pressure ports are shown in Figure 2.10.
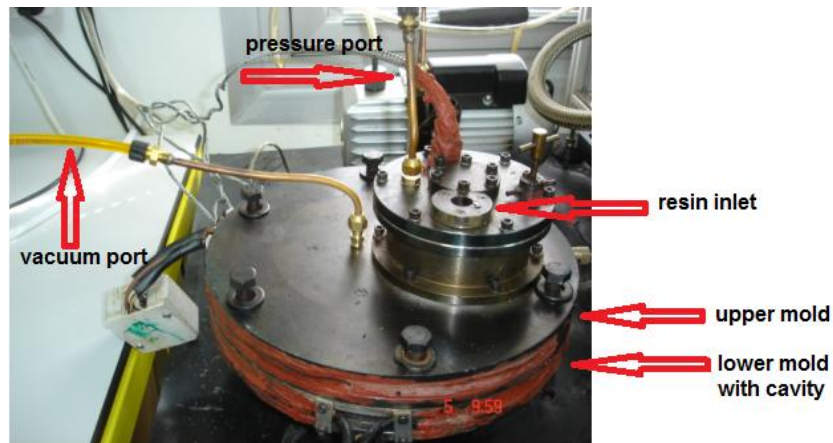
Figure 2.10 General view of RTM

After curing program was completed, the mold was left to cool to room temperature and the composite plate was removed from the mold. In the study, 2 composites which differ in matrix resin compositions were produced with RTM process. The components of the composites and weight compositions of matrix resins are given in Table 2.5.

Table 2.5 Components and compositions of the composites

	Matrix Resin Composition	Reinforcement	Weight of composite, g	Resin/fabric weight, g
Composite 1	BMI/ADM 1:1 mole ratio 60.00 g BMI/46.61 g ADM	13 layers of carbon fabric	112. 53	53.01/59.52
Composite 2	BMI/ADM 1.5:1 mole ratio 60.00 g BMI/31.07 g ADM	13 layers of carbon fabric	113. 78	53.54/60.24

CHAPTER 3

RESULTS & DISCUSSION

3.1. Characterization of BMI

4,4'-bismaleimidodiphenyl methane (BMI) synthesized in this study was a pale brown powder at room temperature with a molecular weight of 358.36 g/mol and a density of 1.35 g/cm^3. The solubility of the monomer was tested with different solvents and it was found that it is highly soluble in solvents like dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide etc. and partly soluble in acetone, dichloroethane.

3.1.1. Characterization by NMR Spectroscopy

The ^{1}H- NMR and ^{13}C-NMR spectra of BMI were obtained in CDCl$_3$. According to ^{1}H- NMR spectra (Figure 3.1), the signals appeared at 7.3 ppm are due to the protons of aromatic groups. The olefinic protons of maleimido group are observed at 6.8 ppm and the signal at 4 ppm indicates the presence of CH$_2$ protons. ^{13}C-NMR spectrum of BMI is shown in Figure 3.2. The signal at 169 ppm is due to carbonyl groups. The carbons of aromatic groups give signals at 126, 129 and 140 ppm, olefinic carbons are at 134 ppm and the CH$_2$ carbon is at 41 ppm. The signals observed at 77 ppm are due to CDCl$_3$.
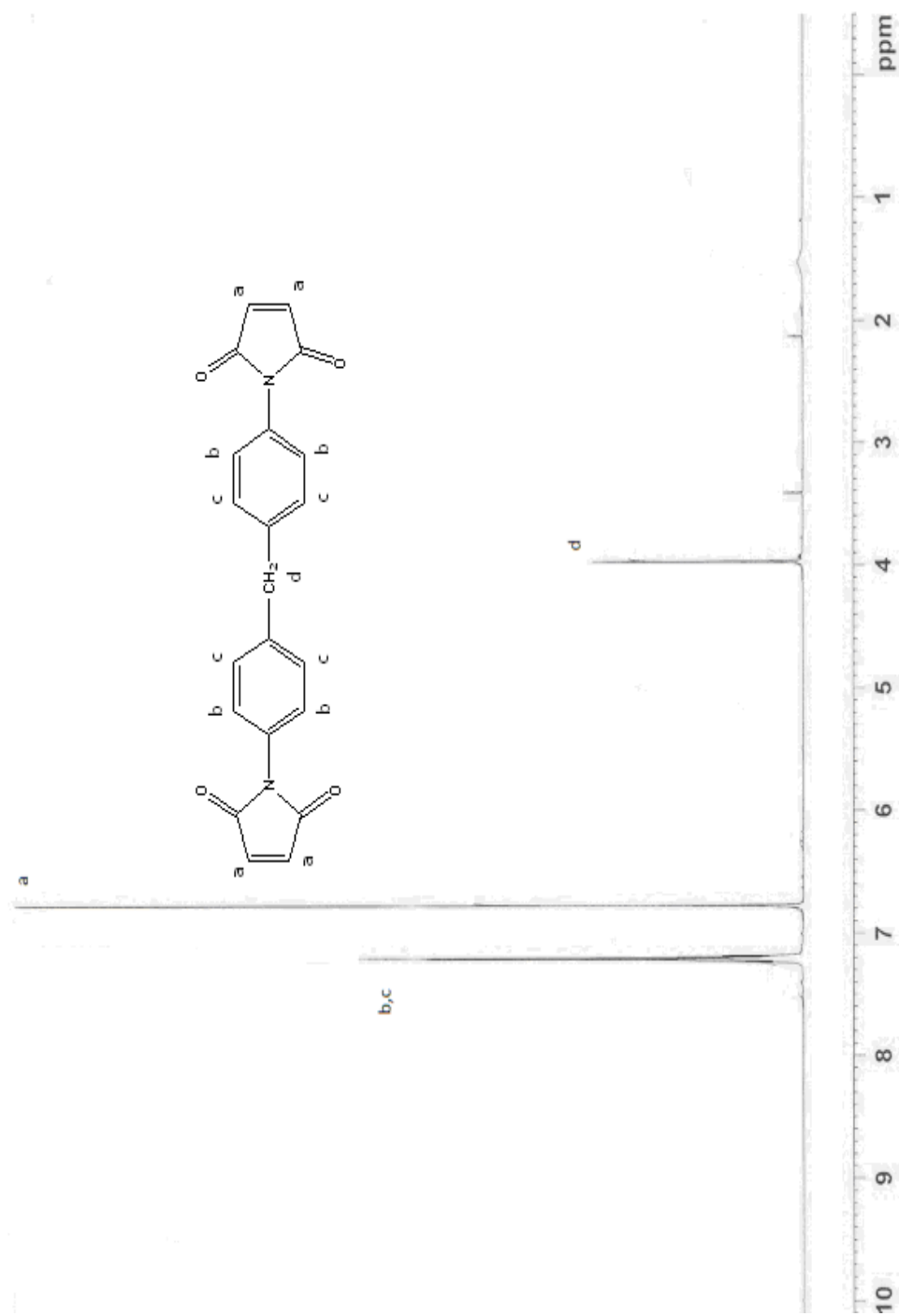
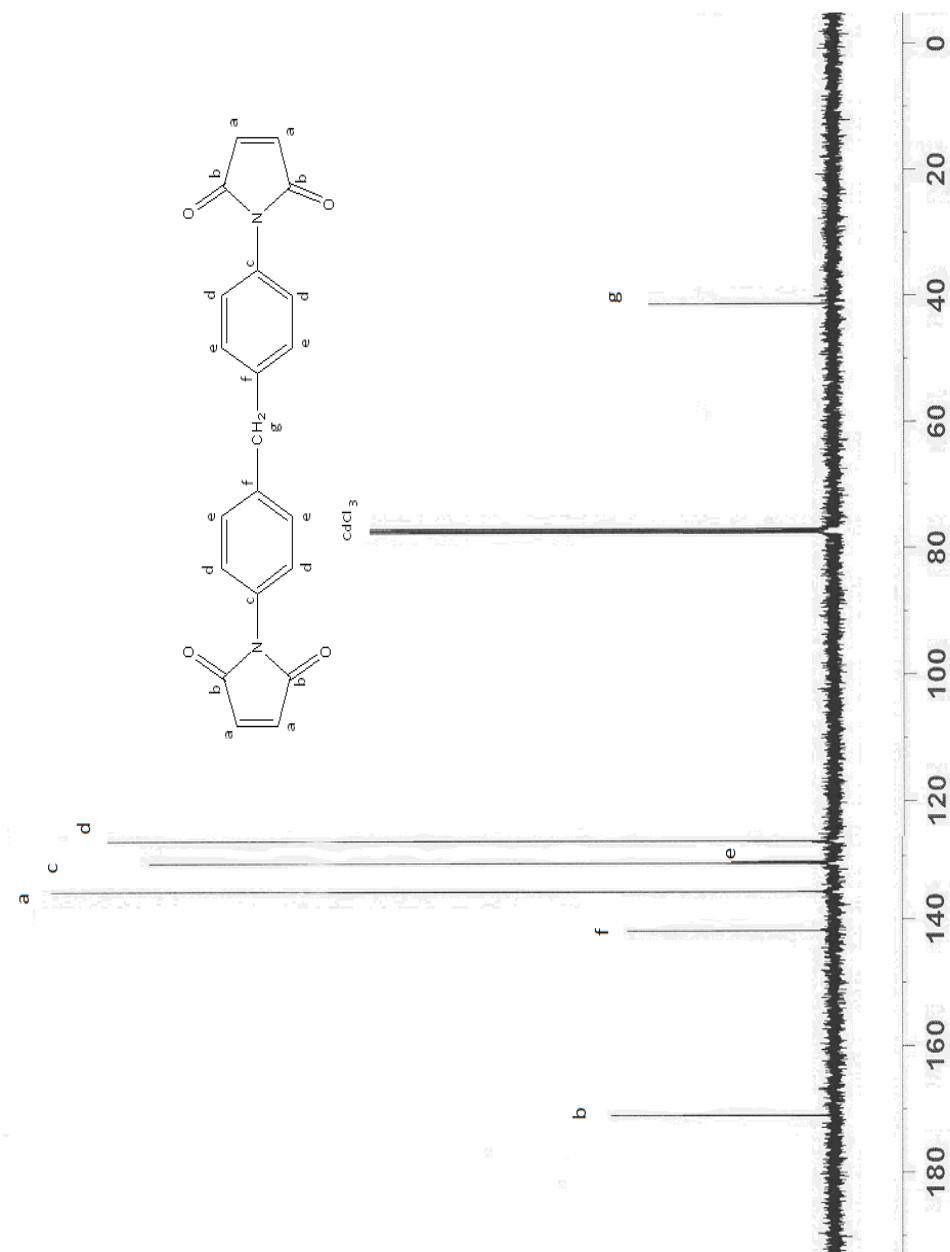**Figure 3.1** ^{1}H-NMR Spectrum of BMI

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Figure 3.2 ^{13}C-NMR Spectrum of BMI

42

3.1.2. FTIR Analysis

FTIR spectrum of BMI demostrating the characteristic bands is given in Figure 3.3. The strong imide C=O band appears at 1702 cm^{-1} while the aromatic ring absorption appears at 1510 cm^{-1}. The strong bands at 1392 and 1147 cm^{-1} are due to the C−N−C stretching. =C−H vibration of the maleimide group is observed at 3106 cm^{-1}. Other identified bands of the maleimide ring are at 829 and 686 cm^{-1} [58,60].

The obtained spectrum of BMI was searched within the library of the instrument and a perfect match with pure BMI with a 99% probability was obtained according to the library search.
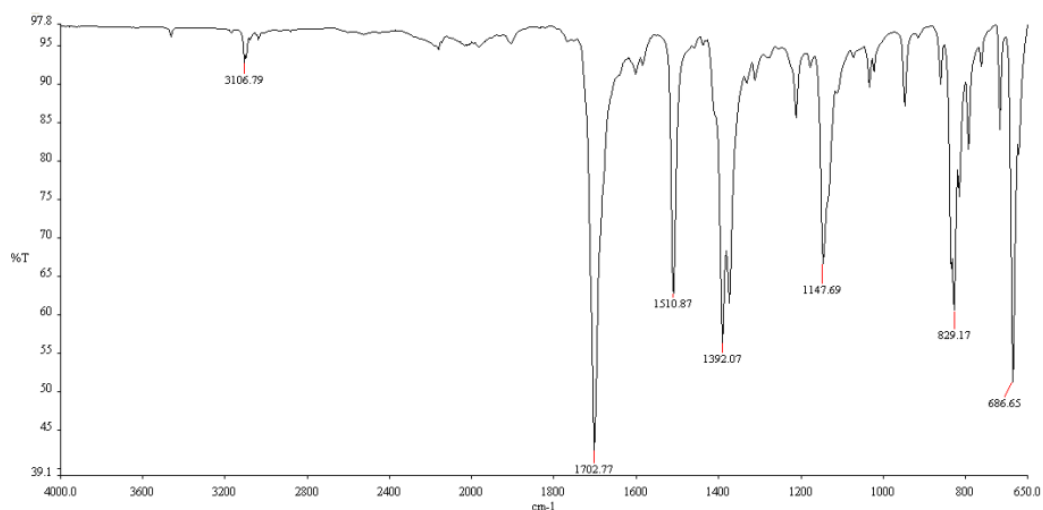
Figure 3.3 FTIR Spectrum of BMI

3.1.3. Thermal Analysis

Thermal analysis of BMI monomer was performed using differential scanning calorimetry (DSC) under nitrogen. DSC (Figure 3.4) shows a sharp endothermic peak at 155.75 ℃ which is the melting point of the BMI powder [61] and a broad exotherm associated with the curing reaction of BMI. This curing reaction involves the homopolymerization of BMI by bond formation between maleimide double bonds [58]. A highly crosslinked network structure is obtained as a result of homopolymerization reaction.

According to the spectrum, onset temperature of the exotherm (T_1) , maximum peak temperature of the exotherm (T_{exo}), and end temperature of the exotherm (T_2), were found as 193.29 ℃, 230.68 ℃ , 268.29 ℃, respectively. T_1 and T_2 were calculated automatically by the software by extrapolating the front side and back side of the exothermic peak to the baseline.
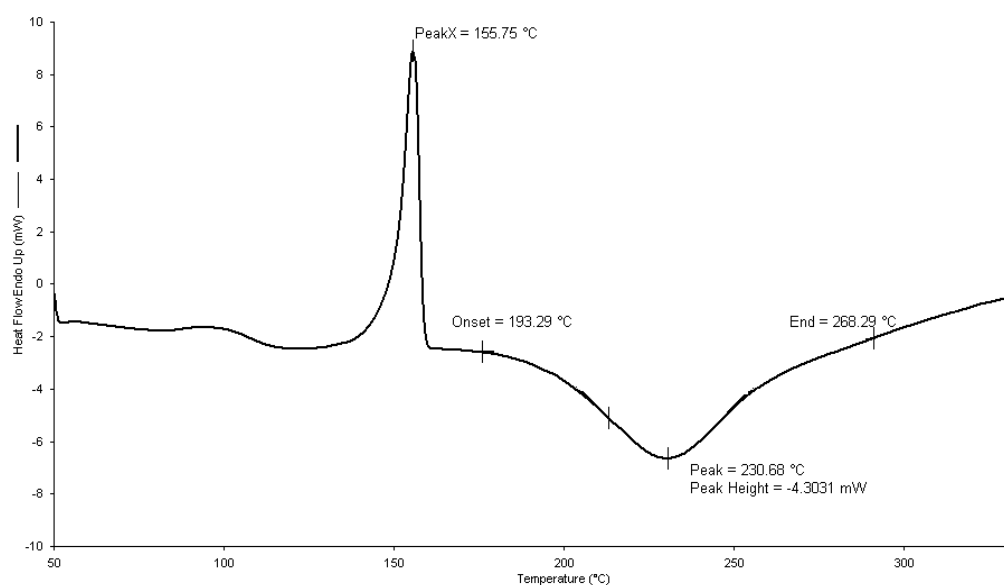

Figure 3.4 DSC Scan of BMI

3.2 Characterization of Diallylamino Compounds

3.2.1 Characterization by ^{1}H-NMR Spectroscopy

1H-NMR spectra of diallylamino compounds were obtained by using d-DMSO as the solvent. NMR results of N,N'-diallylamino diphenyl methane (ADM), N,N'-diallylamino diphenyl sulfone (ADS) and N,N'-diallyl p-phenyl diamine (PDA) are given in Figure 3.5, Figure 3.6 and Figure 3.7, respectively.

In NMR spectra of ADM (Figure 3.5), the peaks between 6-7 ppm are attributed to the aromatic protons. The peaks at 5.1 and 5.8 ppm are assigned to the allyl protons, and the peak at 3.7 ppm is arised from the secondary amine proton. The methylene groups are observed at 3.5 and 3.6 ppm [59].

In NMR spectra of ADS (Figure 3.6), aromatic protons give signals between 6.5-7.5 ppm. Allylic protons are observed at 5.1 and 5.8 ppm. The secondary amine proton and methylene protons give signals at 3.9 and 3.6 ppm, respectively.

Similar to the previous spectra, aromatic protons are observed at 6.7 ppm, and the peaks due to the allyl group are observed between 5 and 6 ppm in NMR spectra of PDA (Figure 3.7). The peaks at 3.9 and 3.4 ppm are observed due to the amine proton and methylene protons, respectively.

The peak observed at 2.5 ppm in all spectra arises from the solvent (d-DMSO).
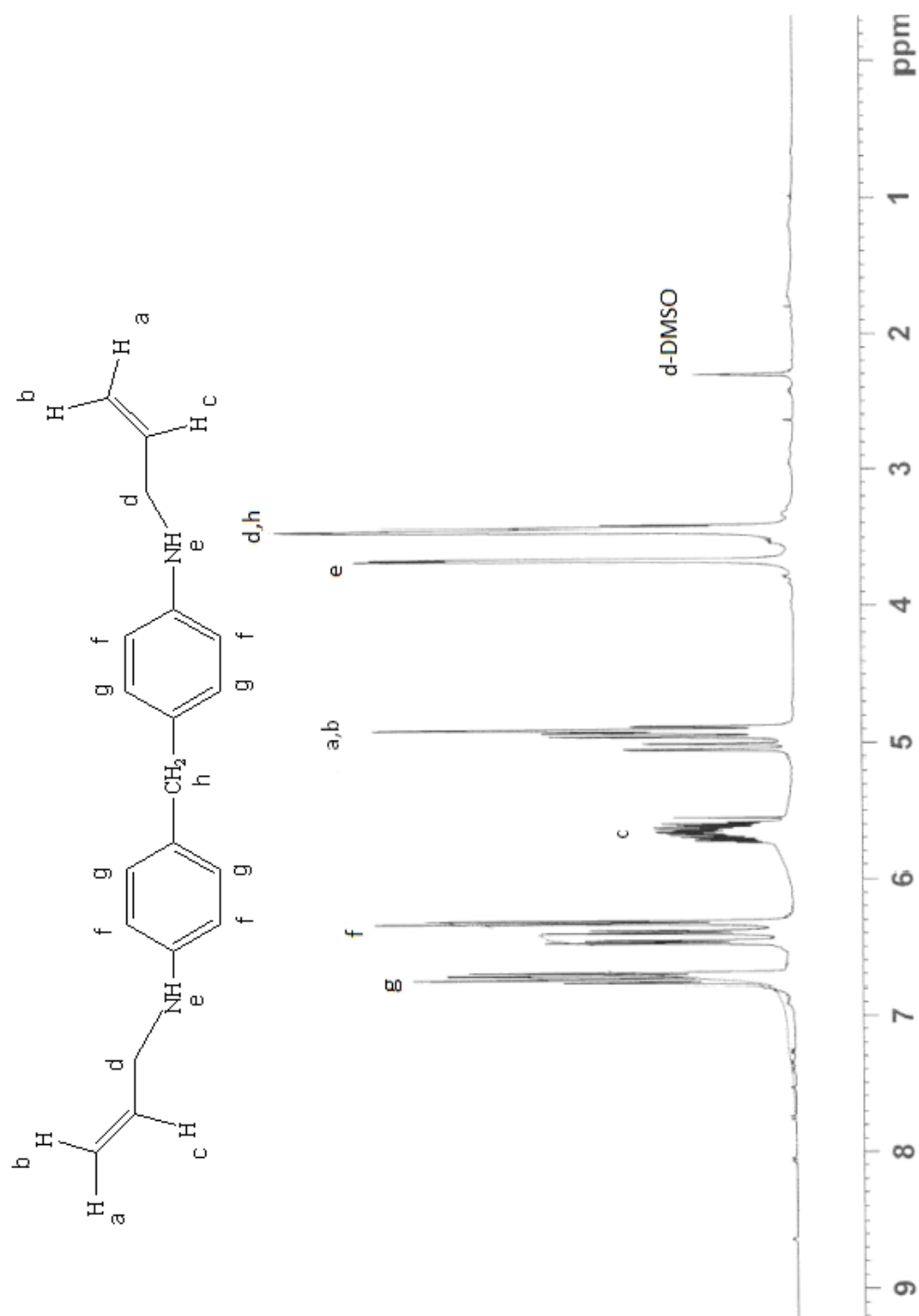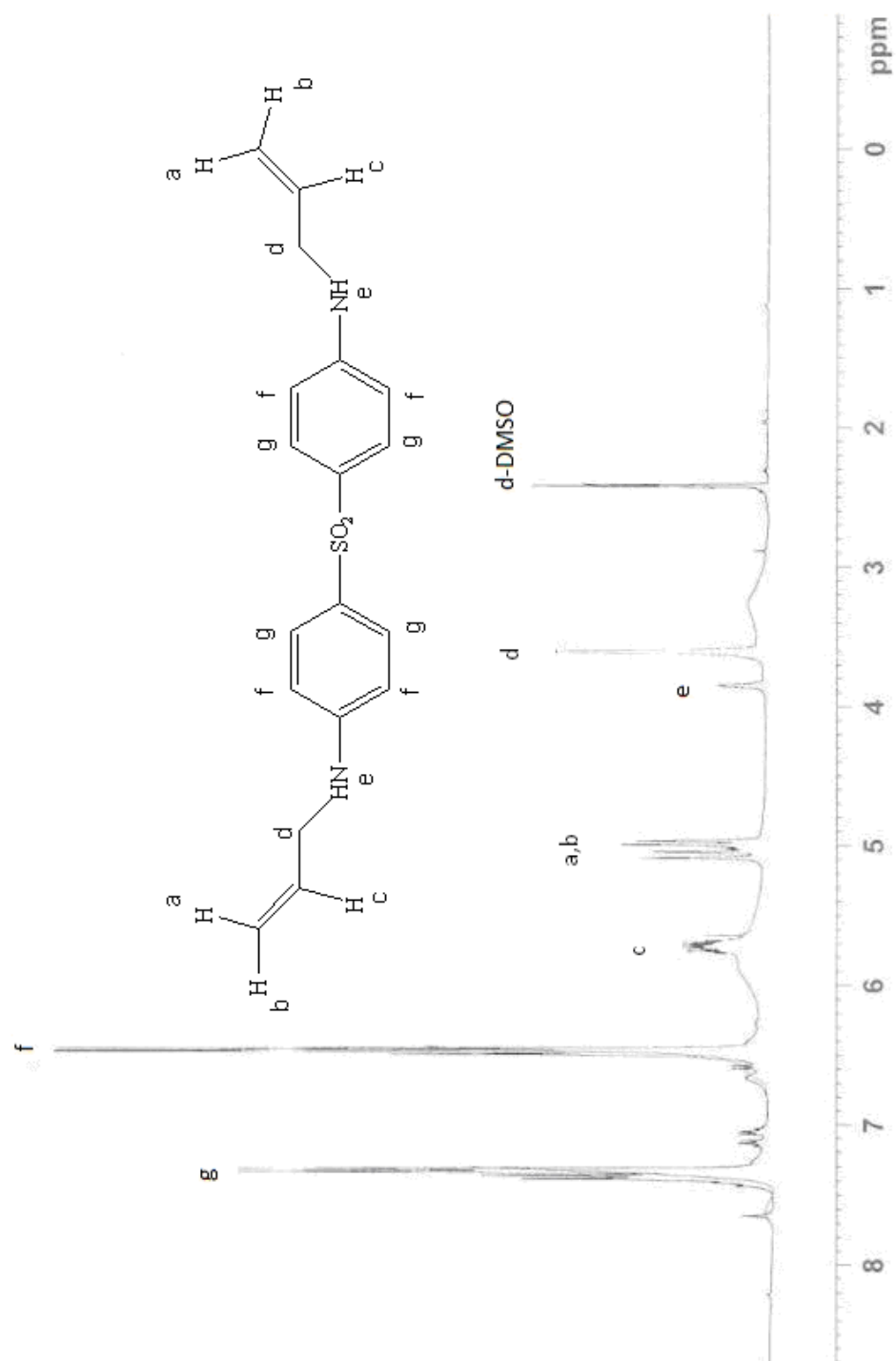
Figure 3.5 ^{1}H-NMR spectum of ADM

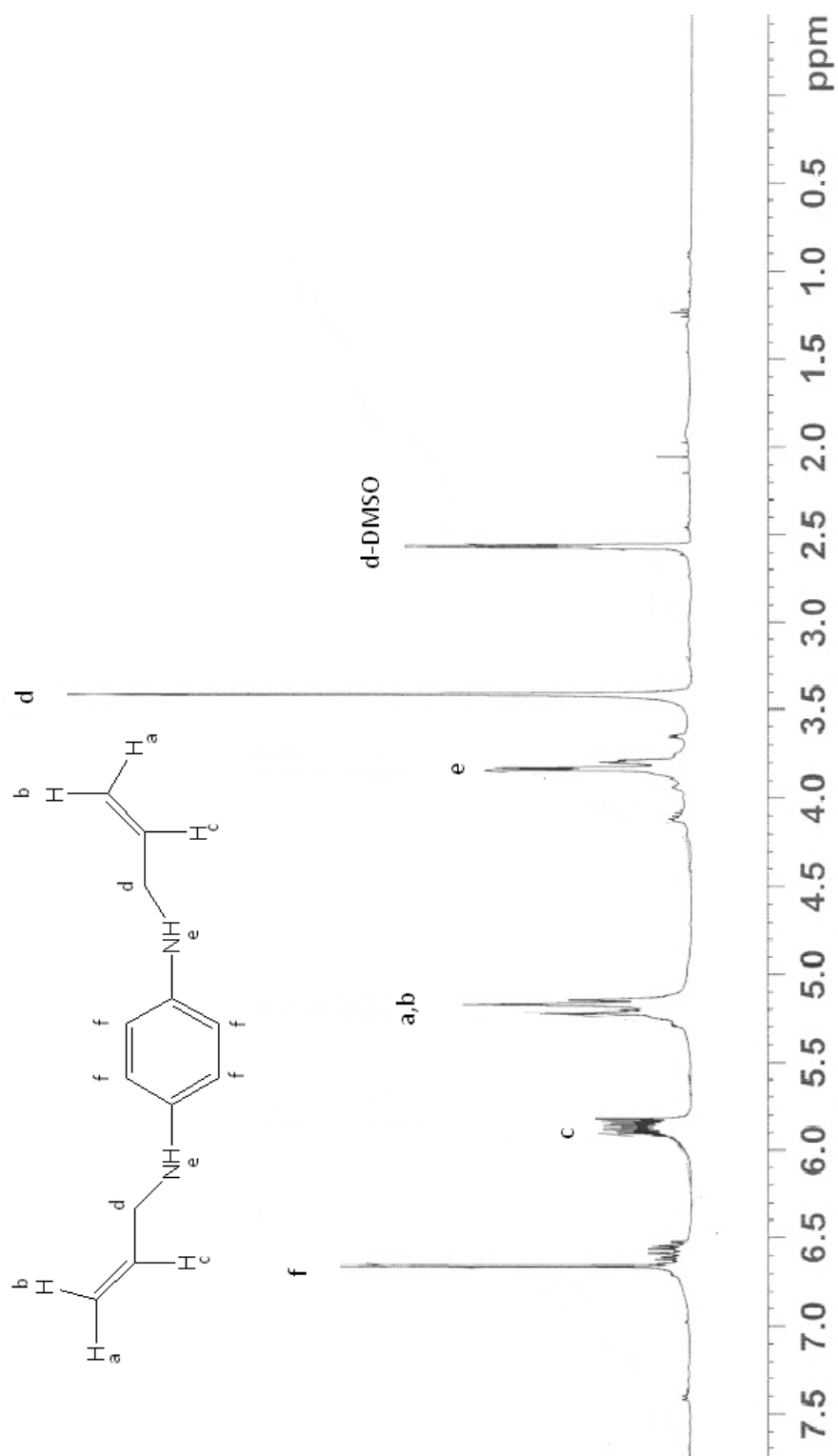**Figure 3.6** ¹H-NMR spectum of ADS

47

Figure 3.7 ¹H-NMR spectum of PDA

48

3.2.2 FTIR Analysis

The formation of diallylamino compounds can be successfully investigated by comparing the FTIR spectra of diallylamino compounds with the FTIR spectra of diamines that are the primary amines used as precursors. The FTIR spectra of three diamines which are 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl sulfone and p-phenylenediamine are given in Figure 3.8, Figure 3.10 and Figure 3.12, respectively. The spectra of all diamines exhibit characteristic peaks between 3200-3500 cm^{-1} for aromatic primary amine groups resulting from the symmetric and asymmetric N−H vibration. Other common peaks observed at ~1500 cm^{-1}, ~1620 cm^{-1} and between 900-675 cm^{-1} are assigned to aromatic groups of primary amines [62].

The FTIR spectra of diallylamino compounds which are ADM, ADS and PDA are shown in Figure 3.9, Figure 3.11 and Figure 3.13, respectively. The characteristic bands due to primary amine groups between 3300-3500 cm^{-1} disappear in the spectra of diallyl compounds. In contrast to the strong primary amine peaks, a weak single peak at ~3300 cm^{-1} appears due to the secondary amine groups [62]. In addition, C−H stretching and C−H bending vibrations due to the allyl groups are confirmed by the peaks at ~3010 and ~915 cm^{-1}, respectively [60,63]. The signals observed at ~2900 cm^{-1} result from the asymmetric stretch of CH_2 groups [62]. Other common peaks at ~1500 cm^{-1}, ~1600 cm^{-1} and between 900-675 cm^{-1} due to aromatic groups that exist in spectra of primary amines are also observed in spectra of diallylamino compounds.
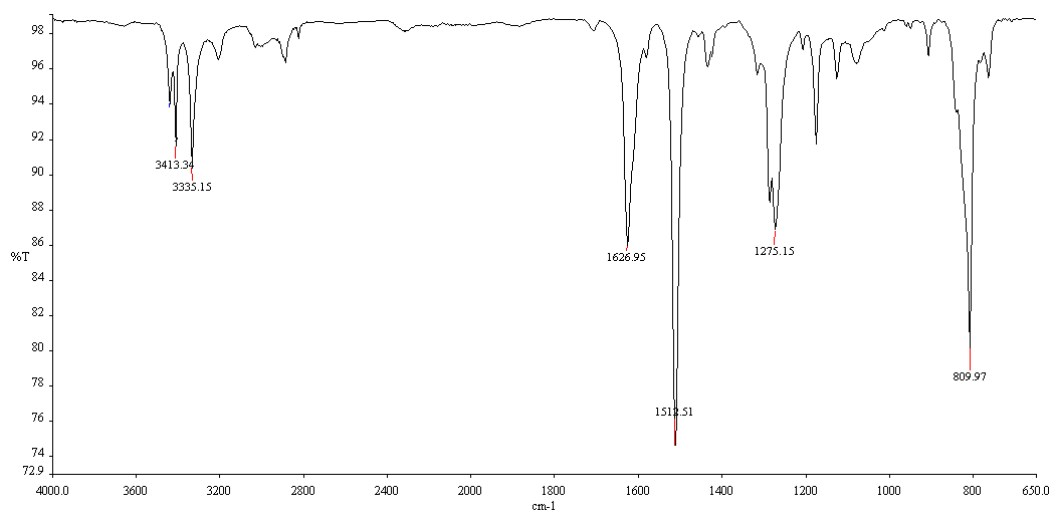
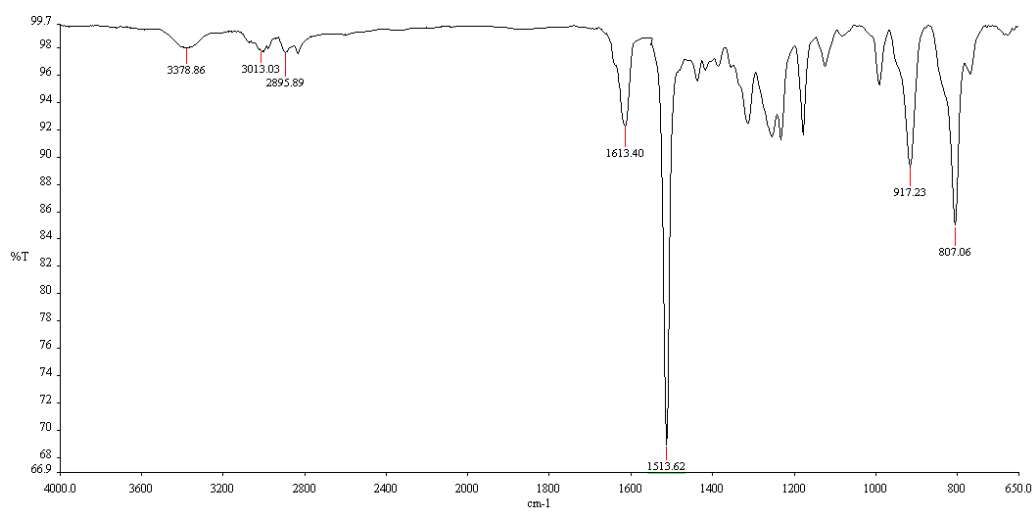**Figure 3.8** FTIR spectrum of 4,4'-diaminodiphenyl methane

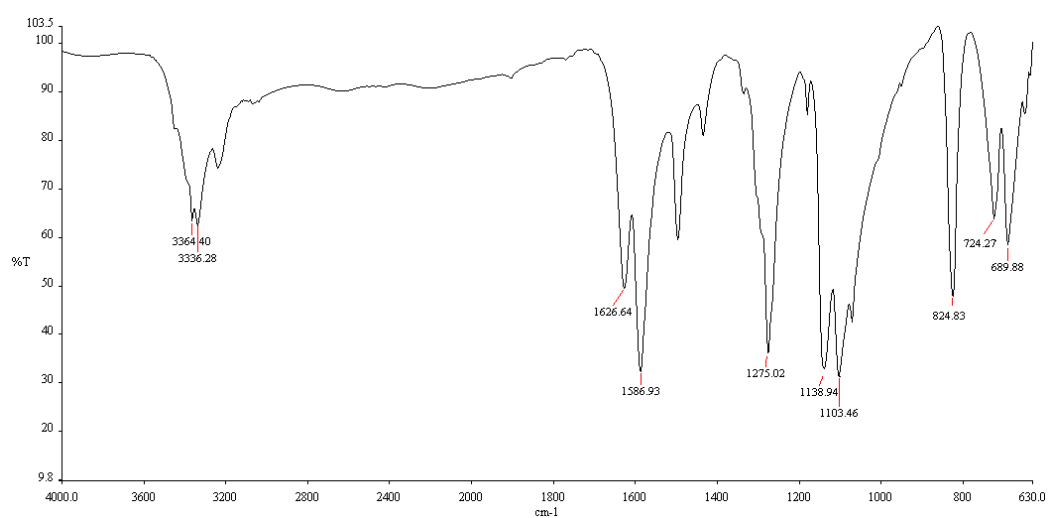**Figure 3.9** FTIR spectrum of N,N'-diallylamino diphenyl methane (ADM)

50

Figure 3.10 FTIR spectrum of 4,4'-diaminodiphenyl sulfone
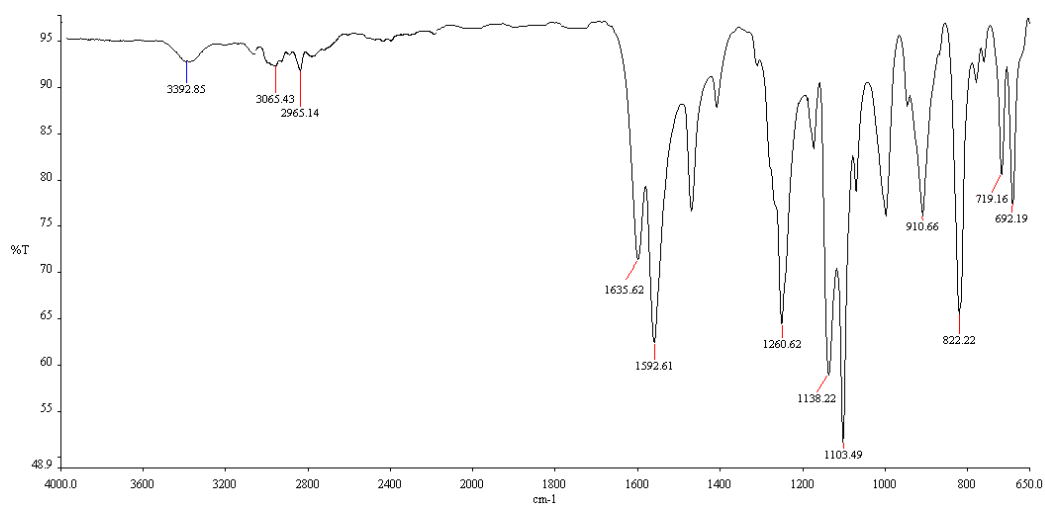

Figure 3.11 FTIR spectrum of N,N'-diallylamino diphenyl sulfone (ADS)
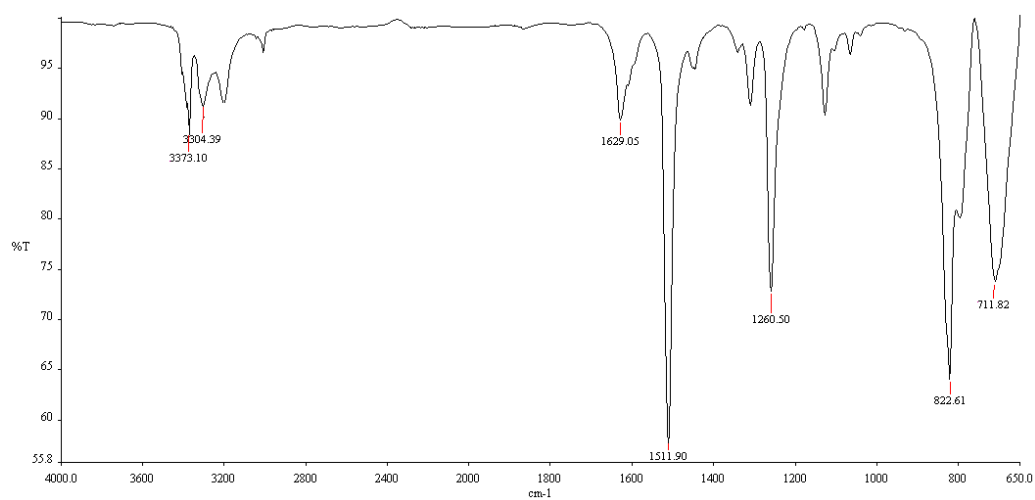
51

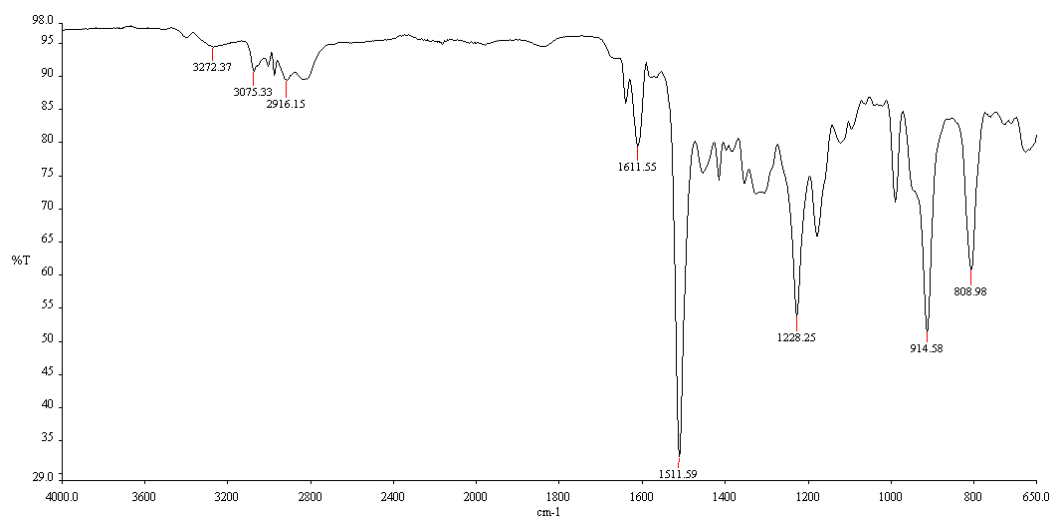**Figure 3.12** FTIR spectrum of p-phenylenediamine

Figure 3.13 FTIR spectrum of N,N'-diallyl p-phenyl diamine (PDA)

3.3 Characterization of BMI/Diallylamino Prepolymers

3.3.1 FTIR Analysis

FTIR spectra of prepolymers in three different mole ratios of BMI to diallyl compounds (1:1, 1.5:1 and 2:1) were investigated.

FTIR spectra for the mixture of BMI and ADM of varying mole ratios are presented in Figure 3.14.a. The characeric peaks due to the BMI content of the resin can be observed at 1702 cm^1 (imide carbonyl), and 1510 cm^{-1} (aromatic group) in all spectra. As the concentration of BMI increases, it is clearly observed that the intensity of peaks increases. The peak at 917 cm^{-1} indicating the allyl groups does not appear in the spectrum since the allyl groups were consumed in the reaction with maleimide double bonds of BMI.

Another important signal to investigate the reaction of BMI with ADM is the existence of $=C-H$ vibration of bismaleimide at 3105 cm^{-1}. This peak is widely accepted as a reference to follow the conversion of BMI double bonds [35]. 4000-2000 cm^{-1} IR region of Figure 3.14.a was magnified and given in Figure 3.14.b. The small peak at 3105 cm^{-1} due to the excess BMI can be observed in the spectrum of 2:1 mole ratio of BMI/MDA, however there is a reduction in the intensity of the peak as the BMI concentration decreases and it is poorly resolved in the spectrum of 1:1 mole ratio of BMI/MDA. This confirms the reaction of BMI maleimide bonds with allyl groups in equivalent mole ratio (1:1).

FTIR spectra BMI/PDA and BMI/ADS resins are presented in Figure 3.15.a and Figure 3.16.a, respectively. The peaks due to bismaleimide at 1702 and 1510 cm^{-1} becomes more intense as going from spectrum 1:1 mole ratio through 2:1 mole ratio of BMI/MDA. $=C-H$ vibration of bismaleimide for BMI/PDA is

observed at 3107 cm^{-1} and for BMI/ADS at 3105 cm^{-1} . These peaks almost disappear in both figures for spectra of 1:1 mole ratio but the intensity of the peak increases as the BMI content increases due to unreacted maleimide functional groups.
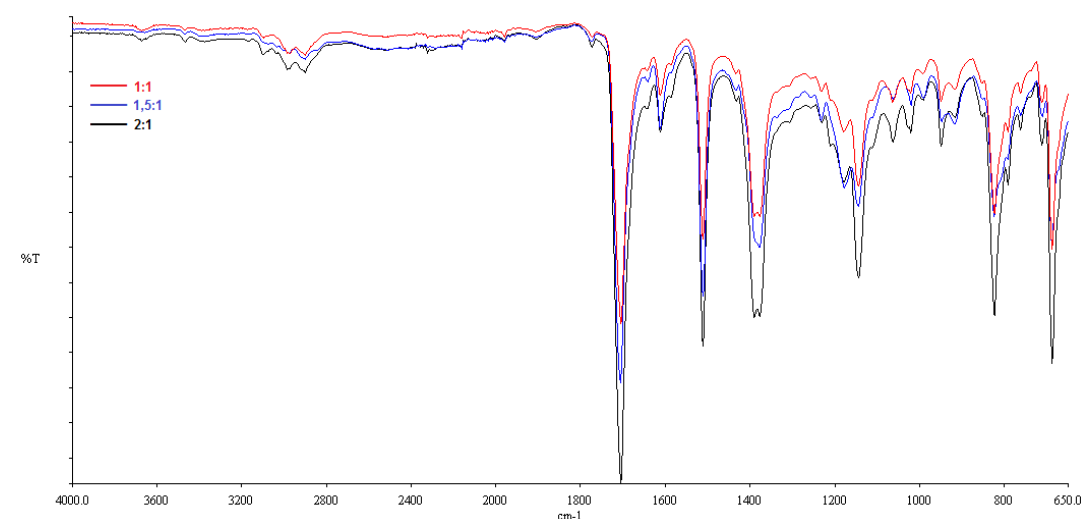

Figure 3.14.a FTIR spectra of BMI/ADM resins (BMI/ ADM 1:1 mole ratio; BMI/ ADM 1.5:1 mole ratio; BMI/ ADM 2:1 mole ratio)
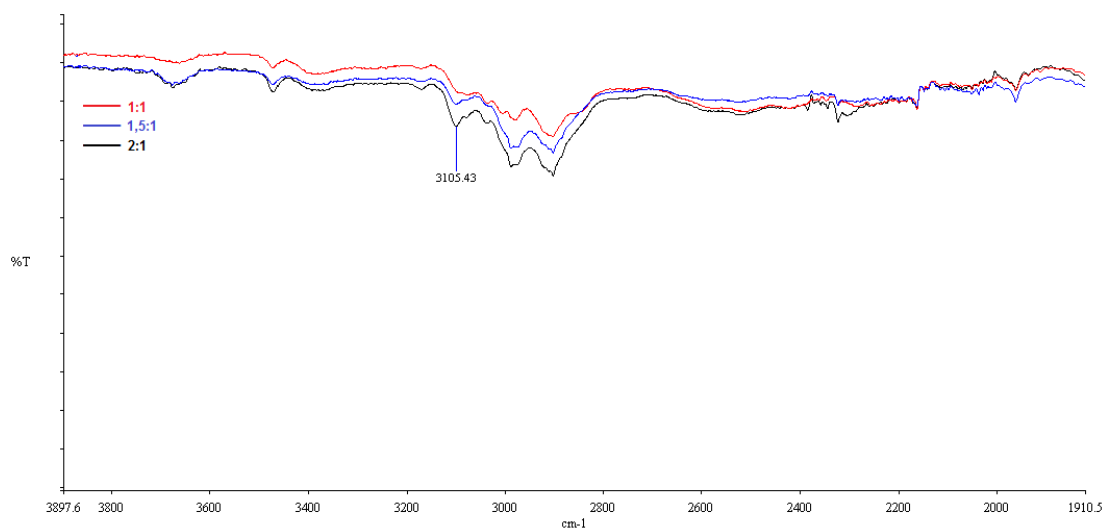

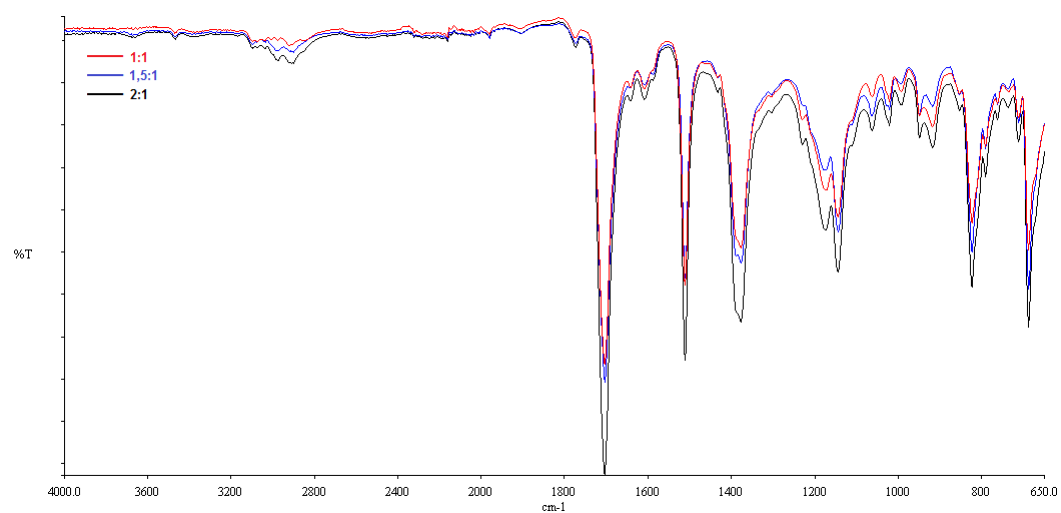**Figure 3.14.b** Magnified FTIR spectra of BMI/ADM resins

Figure 3.15.a FTIR spectra of BMI/PDA resins (BMI/PDA 1:1 mole ratio;
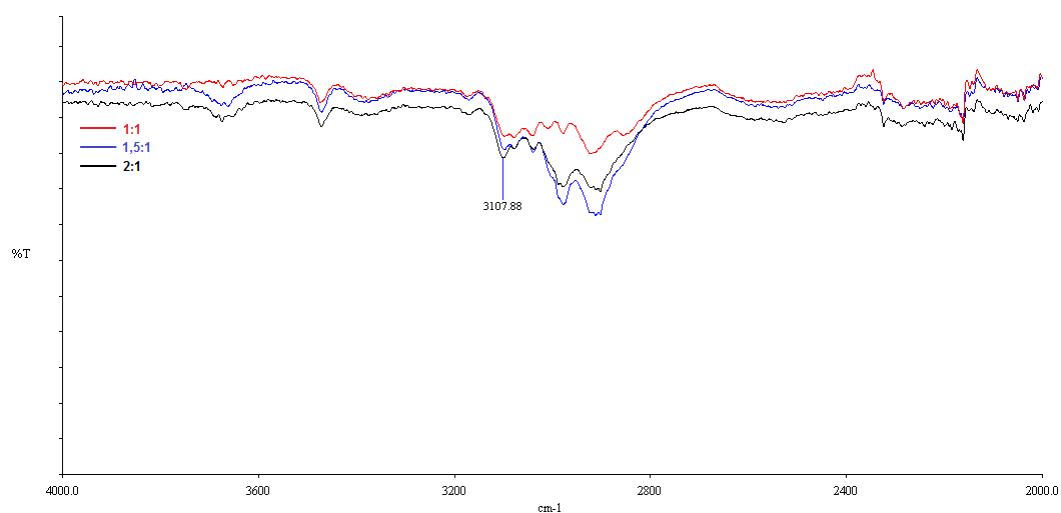BMI/PDA 1.5:1 mole ratio; BMI/PDA 2:1 mole ratio)

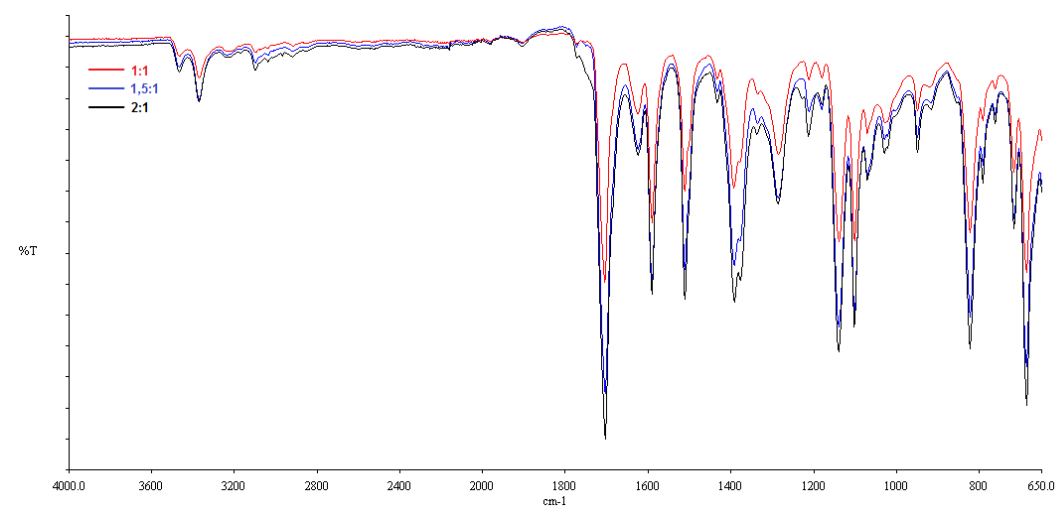
Figure 3.15.b Magnified FTIR spectra of BMI/PDA resins

Figure 3.16.a FTIR spectra of BMI/ADS resins (BMI/ADS 1:1 mole ratio; BMI/ADS 1.5:1 mole ratio; BMI/ADS 2:1 mole ratio)
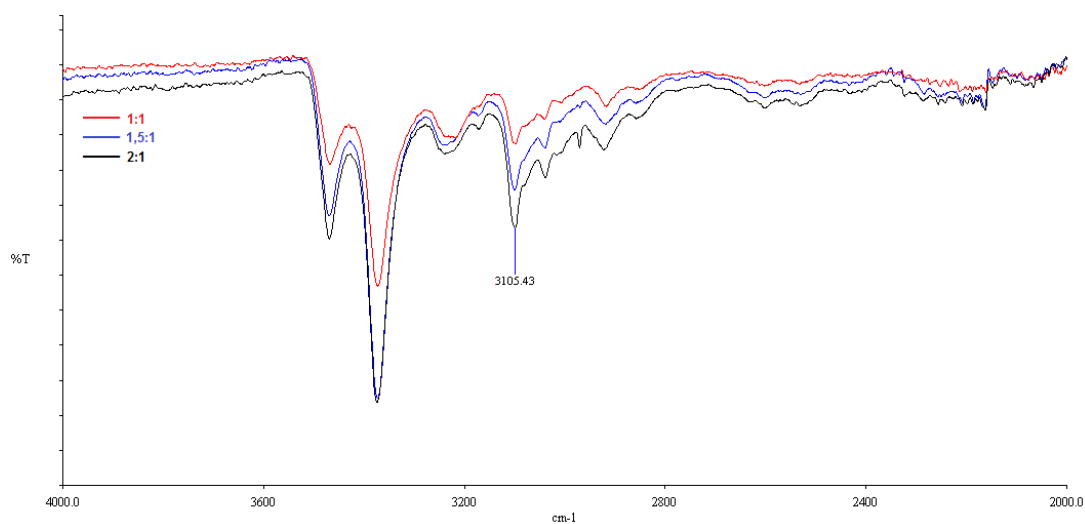

Figure 3.16.b Magnified FTIR spectra of BMI/ADS resins

3.3.2 Thermal Analysis

Thermal analysis of prepolymers were performed using differential scanning calorimetry in nitrogen atmosphere. DSC thermograms of the BMI modified diallylamino compounds containing 1, 1.5 and 2 mole ratio of BMI/ADM, BMI/PDA and BMI/ADS prepolymers are given in Figure 3.17, Figure 3.18 and Figure 3.19, respectively.

 It is observed that all thermograms show a wide exotherm resulting from the curing reaction of the resins. Mainly, three types of reactions occur in curing process: i) 'ene' reaction (addition reaction between maleimide double bonds and allyl groups), ii) Diels-Alder reaction, iii) BMI homopolymerization (reaction between maleimide double bonds of BMI) [45,48,49].

To compare the curing behavior of prepolymers, several thermal characteristics were determined from their DSC traces. The onset temperature (T_1), the exothermic peak temperature (T_{exo}), and the temperature for completion of the reaction (T_2) were determined. The T_1 and T_2 were obtained by extrapolating the front side or back side of the exothermic peak to the baseline and the results are listed in Table 3.1.

Similar behaviours were observed in all thermograms. The higher BMI ratio in the prepolymers results in higher curing temperature so T_{exo} shifts to higher temperatures when the concentration of BMI increases. In addition, the intensities of the peaks increases due to the heat evolved by the homopolymerization of excess BMI. The relative reactivity of prepolymers may be judged on the basis of T_{exo} values. The exothermic peak temperature of BMI/ADS resins are much more higher than BMI/ADM and BMI/PDA resins so the reactivitiy of BMI towards ADS is not high as the reactivity of BMI

towards ADM and PDA, accordingly, high temperatures are needed to cure BMI/ADS resin, completely.

Table 3.1 DSC data of prepolymers

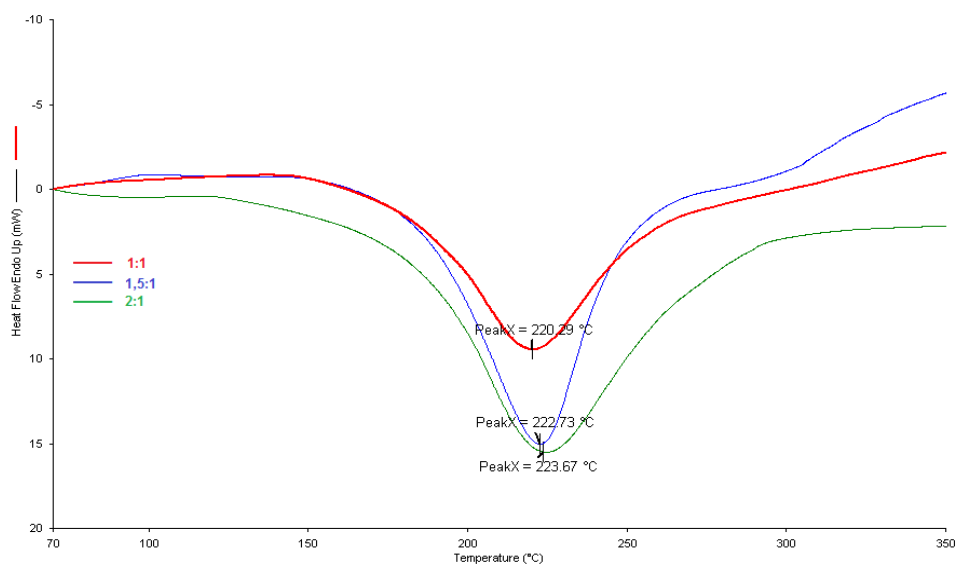| Prepolymer-mole ratio	$T_1(°C)$	$T_{exo}(°C)$	$T_2(°C)$
BMI/ADM-1:1	182.60	220.29	250.39
BMI/ADM-1.5:1	183.59	222.73	260.33
BMI/ADM-2:1	185.73	223.67	276.92
BMI /PDA-1:1	139.80	194.40	237.50
BMI /PDA-1.5:1	141.30	201.51	241.57
BMI /PDA-2:1	146.65	215.17	246.55
BMI/ADS-1:1	209.83	281.00	334.05
BMI/ADS-1.5:1	210.71	284.39	338.59
BMI/ADS-2:1	225.21	287.18	338.62

Figure 3.17 DSC thermograms of BMI/ADM prepolymers (BMI/ADM 1:1 mole ratio; BMI/ADM 1.5:1 mole ratio; BMI/ADM 2:1 mole ratio)
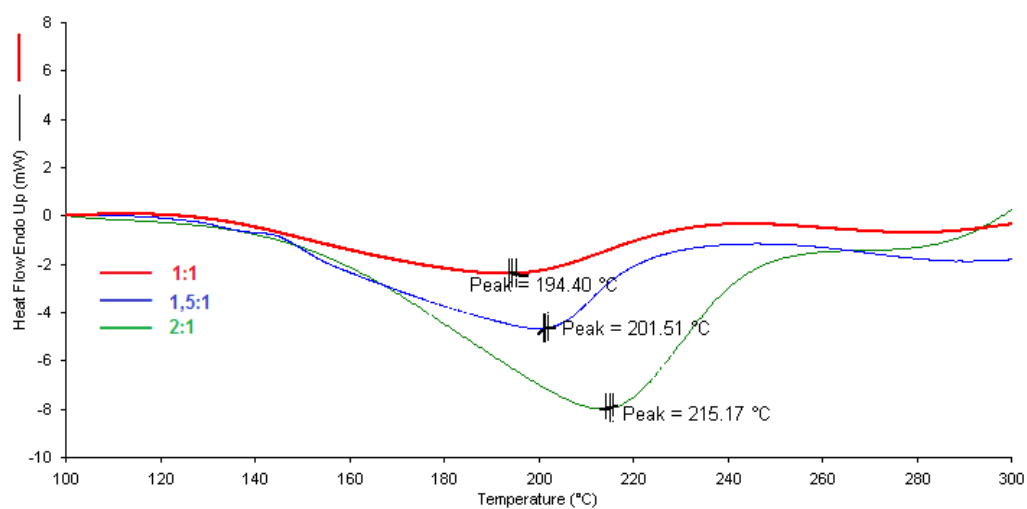
58

Figure 3.18 DSC thermograms of BMI/PDA prepolymers (BMI/PDA 1:1 mole ratio; BMI/PDA 1.5:1 mole ratio; BMI/PDA 2:1 mole ratio)
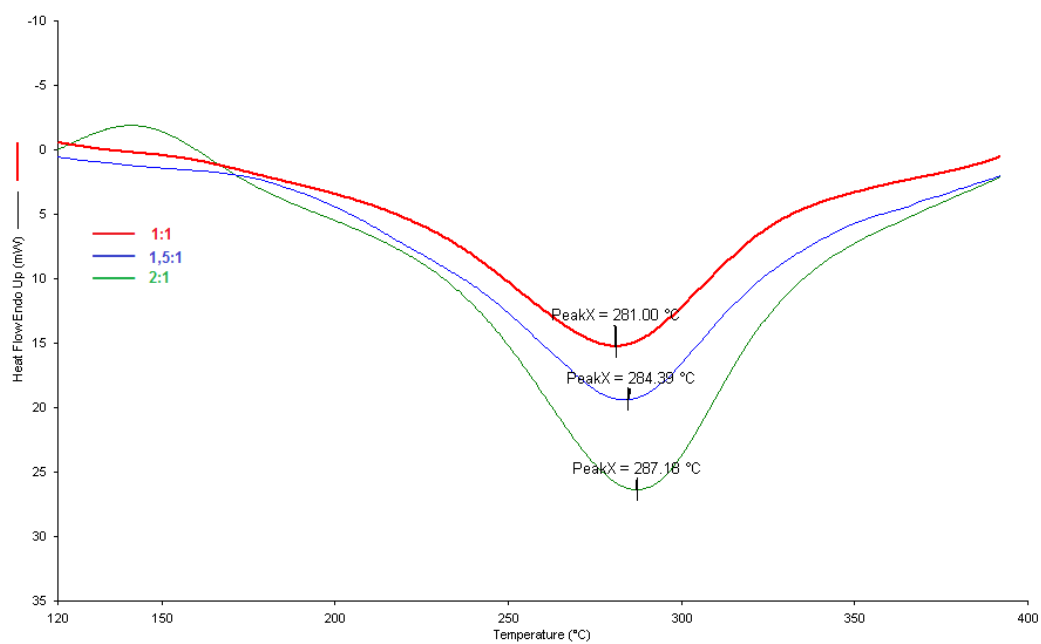

Figure 3.19 DSC thermograms of BMI/ADS prepolymers (BMI/ADS 1:1 mole ratio; BMI/ADS 1.5:1 mole ratio; BMI/ADS 2:1 mole ratio)

3.4 Characterization of Cured Resins

3.4.1 Thermal Gravimetric Analysis (TGA)

Prepolymers were completely cured and the investigation of thermal stabilities of samples were followed in TGA under nitrogen with a scan range 50-850°C, heating rate of 10°C/min. Figure 3.20 , Figure 3.21 and Figure 3.22 show the primary TGA curves of cured systems BMI/ADM, BMI/PDA and BMI/ADS, respectively.
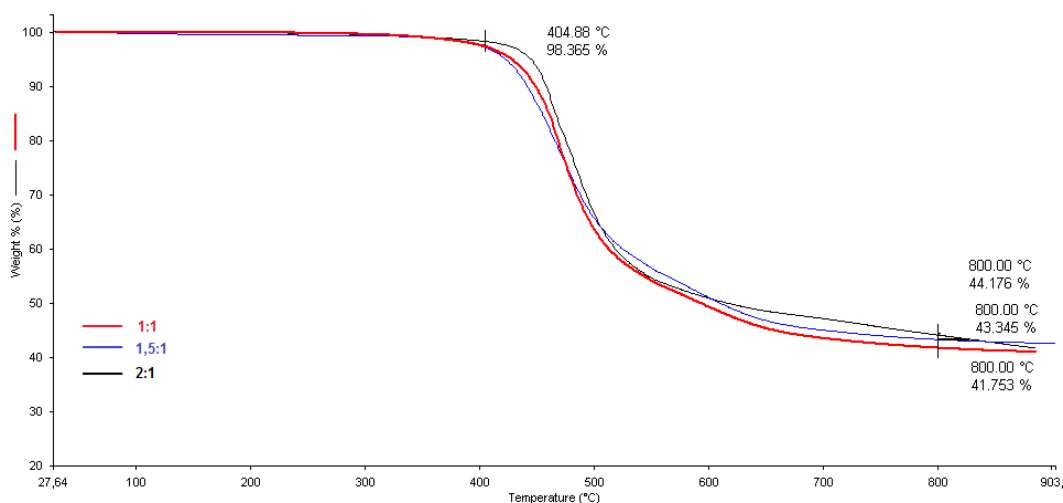

Figure 3.20 TGA curves of BMI/MDA resins (BMI/ ADM 1:1 mole ratio; BMI/ ADM 1.5:1 mole ratio; BMI/ ADM 2:1 mole ratio)
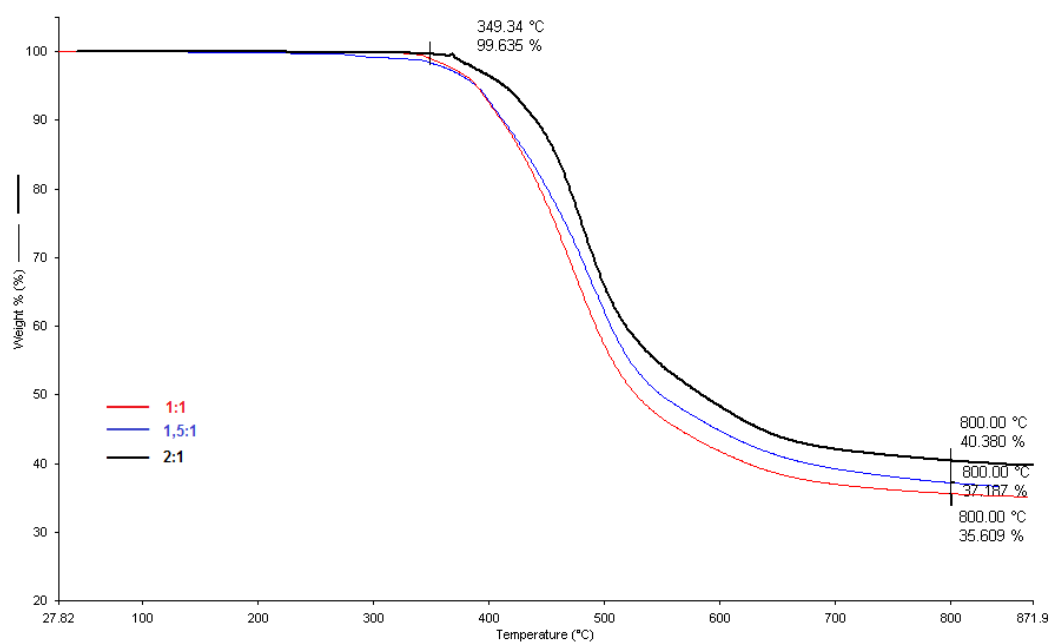
Figure 3.21 TGA curves of BMI/PDA resins (BMI/PDA 1:1 mole ratio;
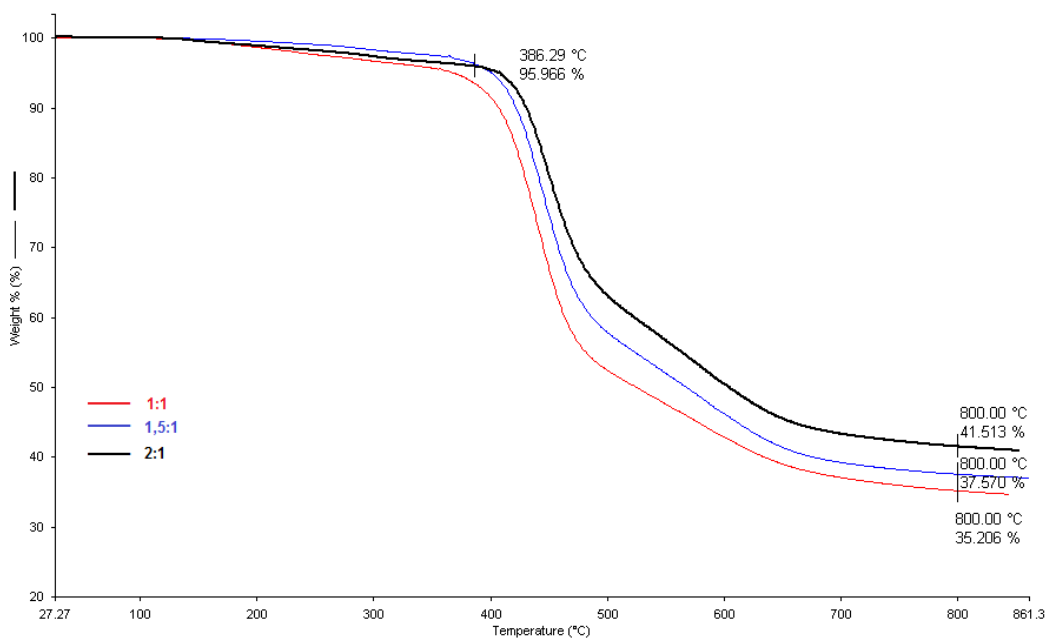BMI/PDA 1.5:1 mole ratio; BMI/PDA 2:1 mole ratio)

Figure 3.22 TGA curves of BMI/ADS resins (BMI/ADS 1:1 mole ratio;
BMI/ADS 1.5:1 mole ratio; BMI/ADS 2:1 mole ratio)

The temperature of initial decomposition (Td_i), the maximum polymer decomposition temperature (Td_{max}) and char yield at 800°C (Y_c) were determined from the TGA traces and are listed in Table 3.2. Td_{max} results were calculated as the peak temperature of first derivative of % weight vs temperature curves and are given in Figure 3.23, 3.24 and 3.25 for cured resin systems. The results are summarized in Table 3.2. There is an increasing trend in Td_i, Td_{max} and Y_c values as the concentration of BMI increases in the resin content. The delay in decomposition by the incorporation of BMI is mainly due to the thermally stable aromatic-heterocyclic structure of BMI and the formation of intercrosslinking network. BMI/ADM system shows the highest values of Td_i, Td_{max} and Y_c. Therefore, the thermal stability of systems increase in the order BMI/ADM> BMI/ADS> BMI /PDA. Td_i, Td_{max} and Y_c values reach 404.88, 490.52 and %44.18 respectively for BMI/ADM system having BMI/ADM mole ratio of 2:1 which can be considered to be a resin system with a good thermal stability.

Since BMI/MDA system shows the best reactivity towards BMI and excellent thermal properties of all the resin systems, it is decided as the matrix component of the composite sytem.

Table 3.2 TGA data of cured resins

Cured resin systems	Td_i (°C)	Td_{max} (°C)	Y_c at 800°C(%)
BMI/ADM-1:1	369.27	473.25	41.75
BMI/ADM-1.5:1	372.39	481.45	43.35
BMI/ADM-2:1	404.88	490.52	44.18
BMI /PDA-1:1	332.07	440.01	35.61
BMI /PDA-1.5:1	335.78	443.83	37.19
BMI /PDA-2:1	349.34	450.11	40.38
BMI/ADS-1:1	348.96	465.45	35.21
BMI/ADS-1.5:1	361.80	467.41	37.57
BMI/ADS-2:1	386.29	469.61	41.51
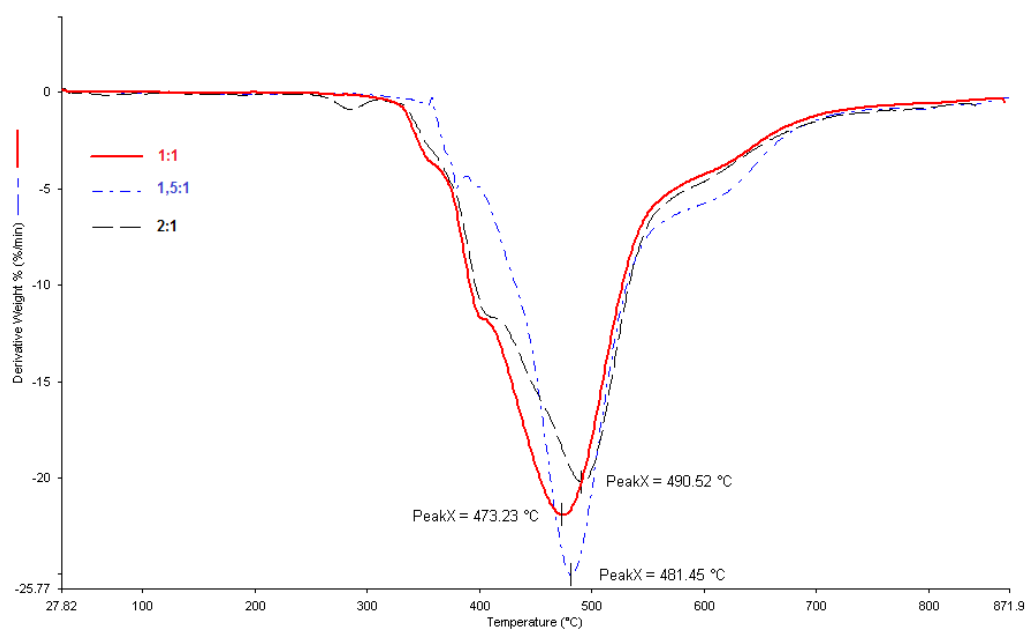
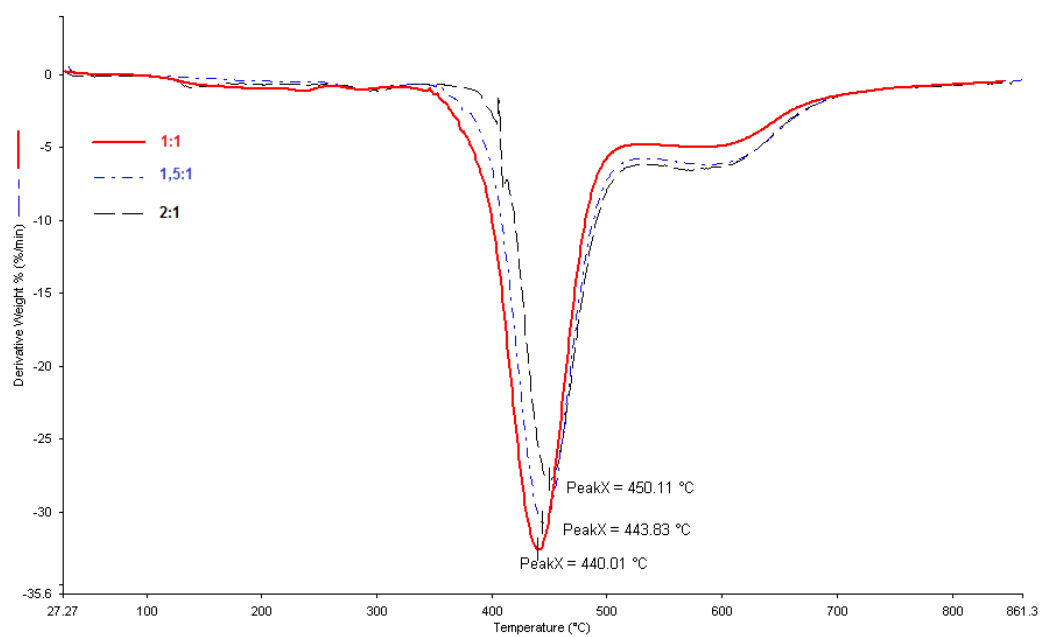**Figure 3.23** Td_{max} results of BMI/ADM resins

63

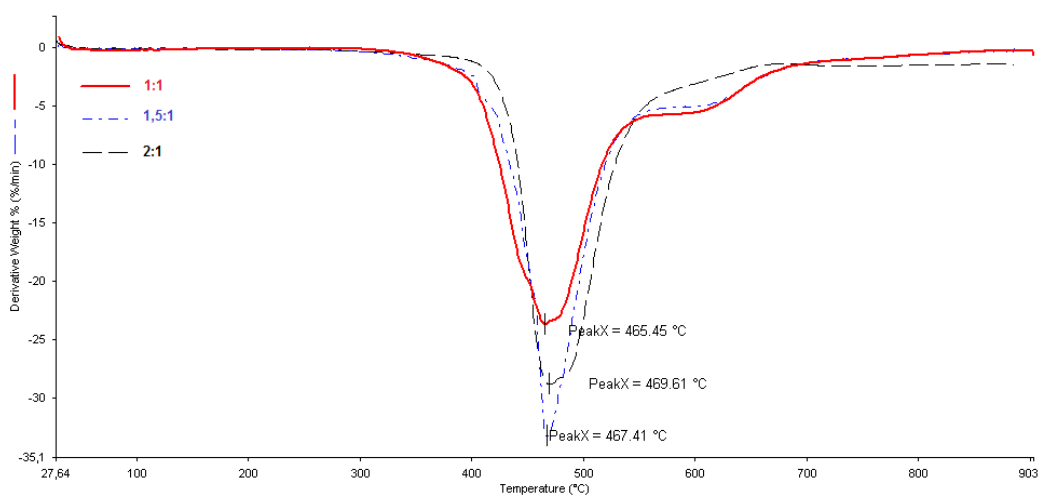**Figure 3.24** Td_{max} results BMI/PDA resins

Figure 3.25 Td_{max} results of BMI/ADS resins

3.5 Processing Characteristics of BMI/ADM Resins

The first important key factor in the processing properties of a matrix is whether the resin is suitable for RTM technique or not. The matrix which is intended to be used in RTM technique must have a low viscosity at the injection temperature and the pot life should be sufficient in order to tranfer the resin. The pot life reflects the length of time in which the resin injection is possible and it can be obtained from the viscosity-time plot at the injection temperature.

The viscosity-time correlations of 1:1 and 1.5:1 compositions of BMI/ADM resins at 120°C are given in Figure 3.26 and Figure 3.27, respectively. As seen from the curves, the stochiometry of the components have a great effect on the viscosity of the resins. At the beginning, the viscosities of both resins begin with 2.5 Pa.s at 120°C. After being maintained for 50 min (3000 s), the viscosity of BMI/ADM mole ratio of 1:1 is stil 2.5 Pa.s while the the viscosity of BMI/ADM mole ratio of 1.5:1 reaches 7 Pa.s. BMI/ADM mole ratio of 1:1 retains its viscosity value of 2.5 Pa.s for approximately 3500 s, indicating a pot life of about 60 min. The viscosity of BMI/ADM mole ratio of 1.5:1 stays constant for about 2000 s, indicating a pot life time of about 35 min. It is seen that the pot life of both resins are long enough for RTM process.
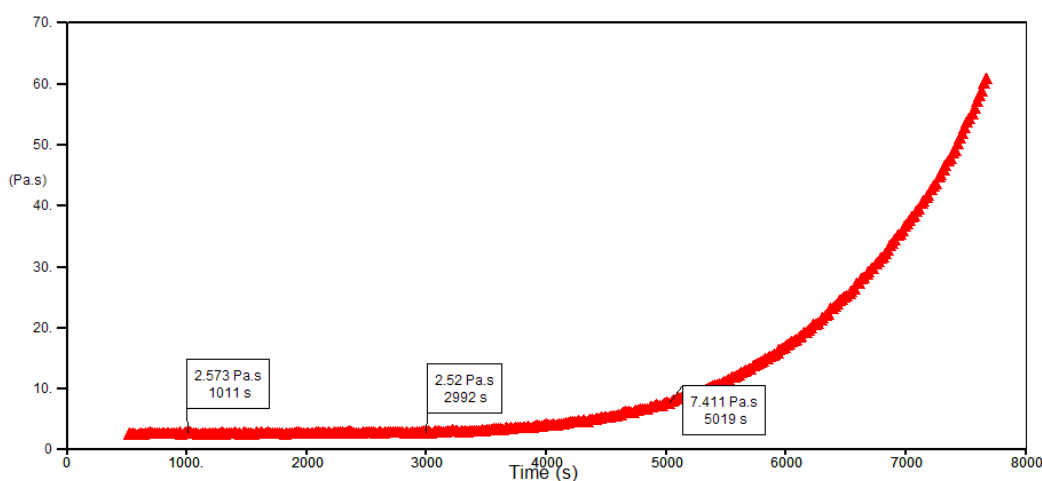

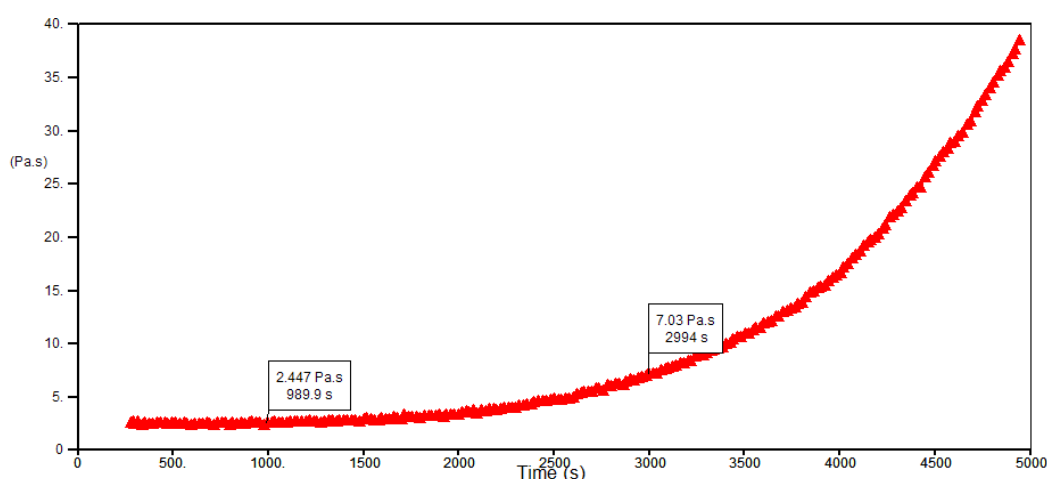**Figure 3.26** Viscosity-time plot at 120°C for BMI/ADM mole ratio of 1:1

Figure 3.27 Viscosity-time plot at 120°C for BMI/ADM mole ratio of 1.5:1

The same plot is obtained for BMI/ADM mole ratio of 2:1 in order to see the effect of increasing BMI concentration on viscosity. As seen from Figure 3.28, the viscosity is 3.4 Pa.s at the very beginning of the measurement and it increases immediately and sharply afterwards. It reaches 9.2 Pa.s after 3000 s while the viscosities of BMI/ADM mole ratio of 1:1 and 1.5:1 are 2.5 and 7.0 Pa.s, respectively at that time. It is observed that even small increases in concentration of BMI lead high viscosity values of the resins. The plot for BMI/ADM mole ratio of 2:1 resin system shows that although this resin system exhibits good thermal properties, it is not possible to process it with RTM technique because of high viscosity at injection temperature and time shortage for injecting it to the mold.
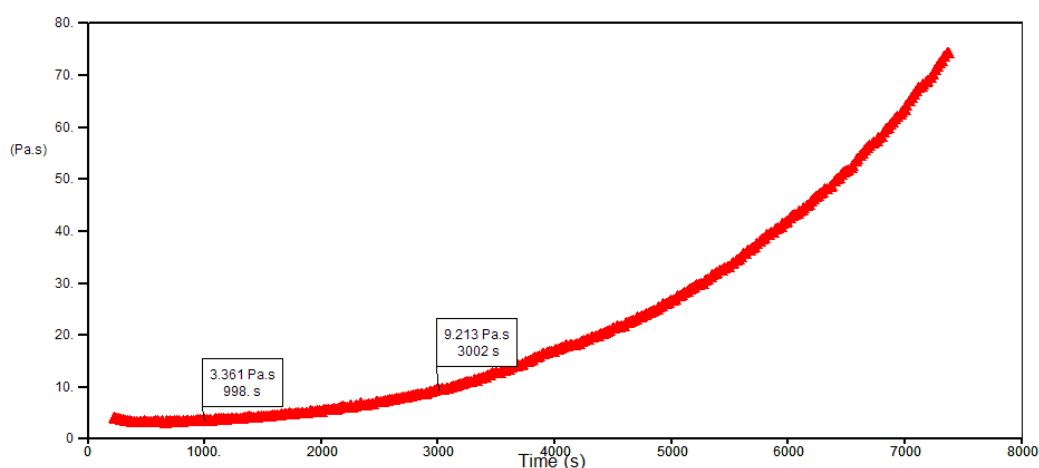
66

Figure 3.28 Viscosity-time plot at 120°C for BMI/ADM mole ratio of 2:1

3.6 Characterization of Composites

Two different composites (composite 1 and composite 2) were manufactured by using BMI/ADM mole ratio of 1:1 and 1,5:1 as the matrix resins while all other parameters were held the same. The effect of different matrix systems on thermal and mechanical properties of the composites were investigated.

3.6.1. X-Ray Analysis

Non-destructive testing of composites were performed and the composite structures were monitored by X-ray tomography. Both of the composite materials exhibited similar X-ray photographs. Figure 3.29 shows the general X-ray tomograph of composite 1 of which   and the magnified views of two sections are given in Figure 3.30.a and Figure 3.30.b. Structural defects such as delamination, fiber pullout, fiber fracture or matrix cracking were not observed within the material. No voids or local porosity except a few microholes of 0.2 mm diameter were detected which means that solvent evaporation during curing process was successfully prevented. The material seems homogenous within the

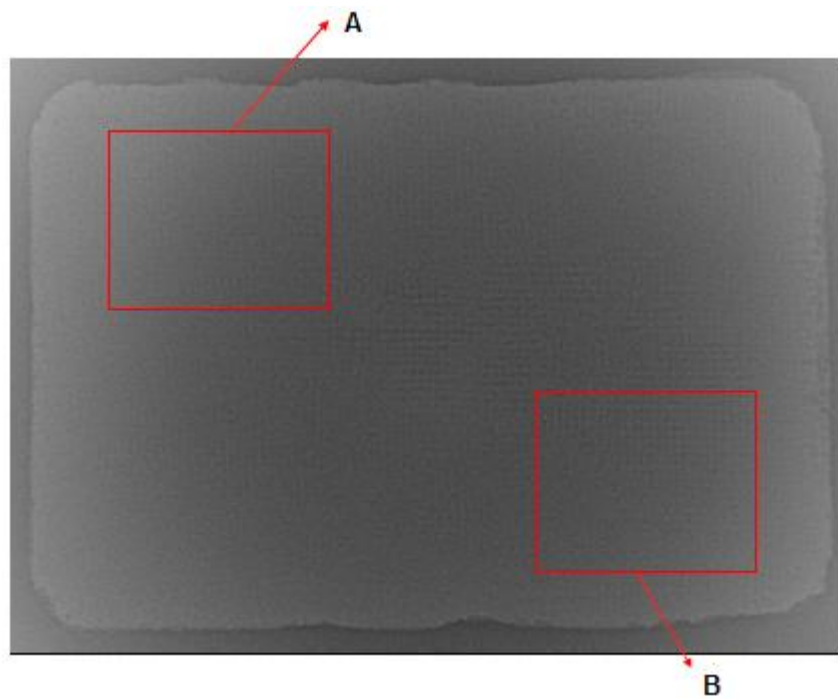structure, therefore the prepared resin and the carbon fabric were well-matched for this composite system.

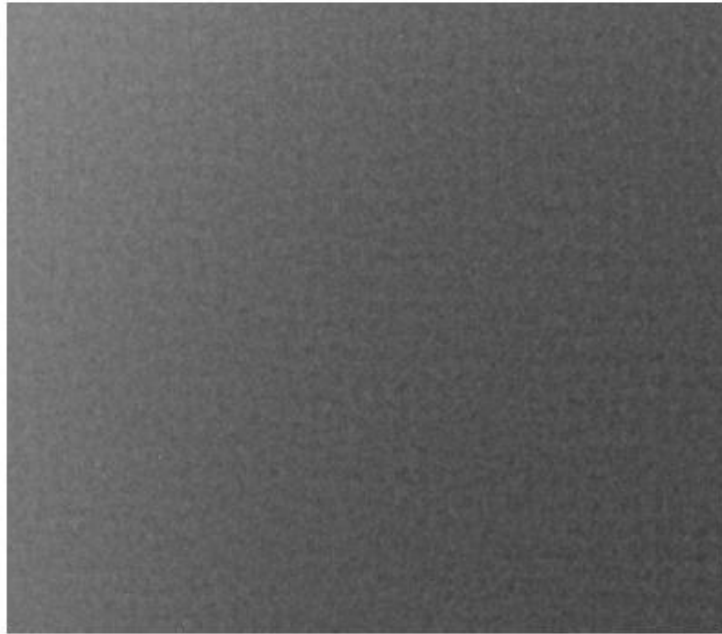

Figure 3.29 X-Ray photograph of Composite 1

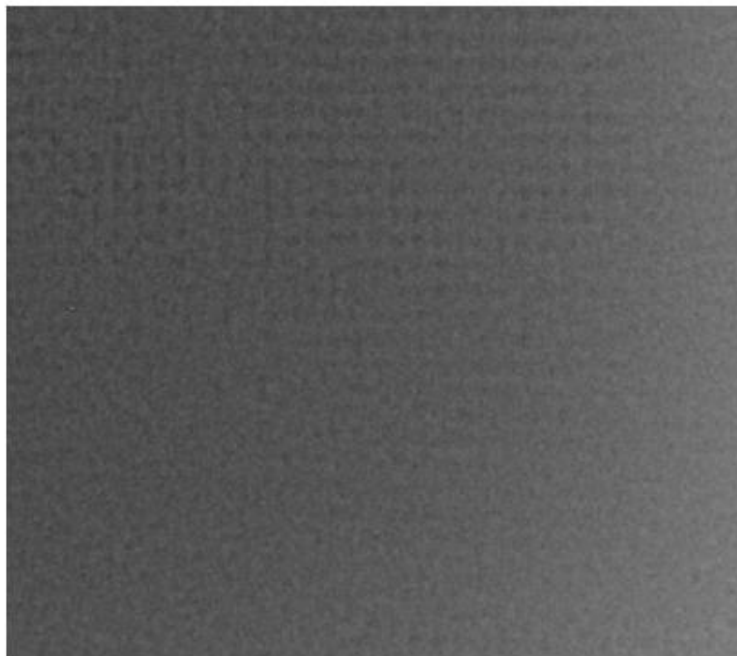**Figure 3.30.a** Magnified X-Ray view of section A

Figure 3.30.b Magnified X-Ray view of section B

3.6.2 Glass Transition Temperature (T_g)

The glass transition temperature of composite 1 and composite 2 were determined by DSC at a heating rate of 10°C/min and are presented in Figure 3.31 and 3.32. The single T_g value obtained for both systems confirm the presence of intercrosslinked network structure. T_g was obtained as 242°C for composite 1 and 257°C for composite 2. By the incorporation of BMI into the system, T_g increaes with increasing BMI concentration. The increase in T_g value may be due to the homopolymerization reaction of BMI rather than 'ene' reaction. BMI homopolymerization leads to the thermally stable C−C linkage and enhances crosslinking density resulting an increase in T_g, whereas 'ene' reaction makes chain extension effect and reduces the crosslinking density [64].
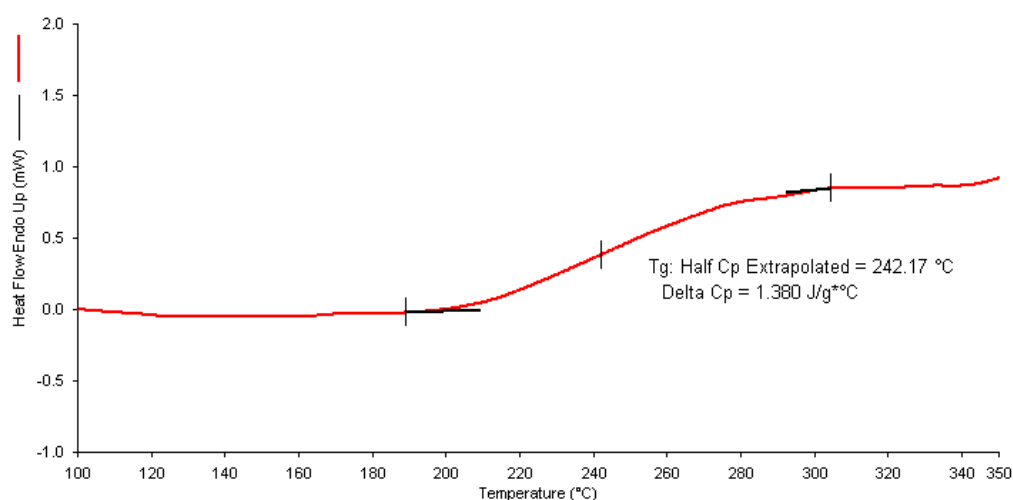

Figure 3.31 Glass transition temperature of composite 1
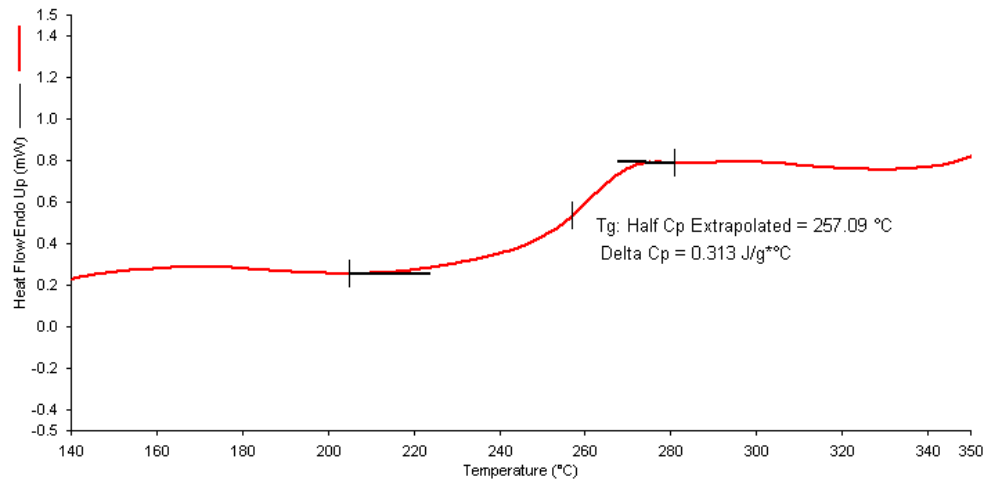
Figure 3.32 Glass transition temperature of composite 2

3.6.3 Tensile Tests

Tensile testing was applied to 5 specimens of composite 1 and composite 2 and the mechanical characteristics of materials were evaluated in terms of tensile strength, percent elongation at break and Young's modulus.

The difference in mechanical properties of composites which have different mole ratios of BMI can be examined from stress-percent elongation curves of composite 1 and composite 2 illustrated in Figure 3.33. The arithmetic mean values of tensile strength and Young's modulus belonging to composite 1 were calculated and found as 556 MPa, 31.8 GPa, respectively. The results of composite 2 are 587 MPa, for tensile strength and 32.6 GPa for Young's modulus.
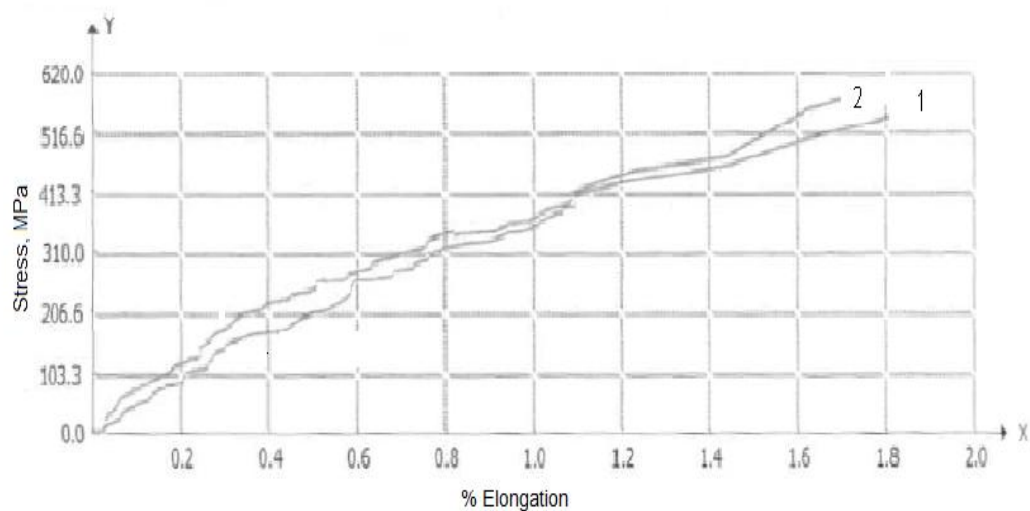
Figure 3.33 Stress-% Elongation curve for composite 1 and 2

It is observed that composite 2 exhibits slightly higher tensile strength and Young's modulus. This small difference in results is the result of higher BMI content in the matrix resin of composite 2. The effect is due to the rigidity imparted by BMI due to the formation of intercrosslinked network.

The values of % elongation at break were found as 1.80 % and 1.75 % for composite 1 and composite 2, respectively. Low elongation values indicate that the materials are very brittle and the difference between two results is very small. Therefore, increase in BMI concentration makes a slight difference between % elongation values. The difference may be attributed to the aromatic, rigid structure of BMI which decreases the elastic properties of the composite.

3.6.4 Izod Impact Tests

The resistance to impact loading of composite 1 and 2 were measured by izod impact testing. The impact test curves of composite 1 and composite 2 are given in Figure 3.34 and 3.35, respectively as load versus displacement curve. The area under the curves represent the energy absorbed by the material before the fracture and gives information about the toughness of the material. The energy values for composite 1 and composite 2 were calculated as 0.624 and 0.730 Joule. Impact strength of materials were obtained dividing the energy by the cross-sectional area of the specimen and calculated as 19.2 and 22.5 kJ/m^2.
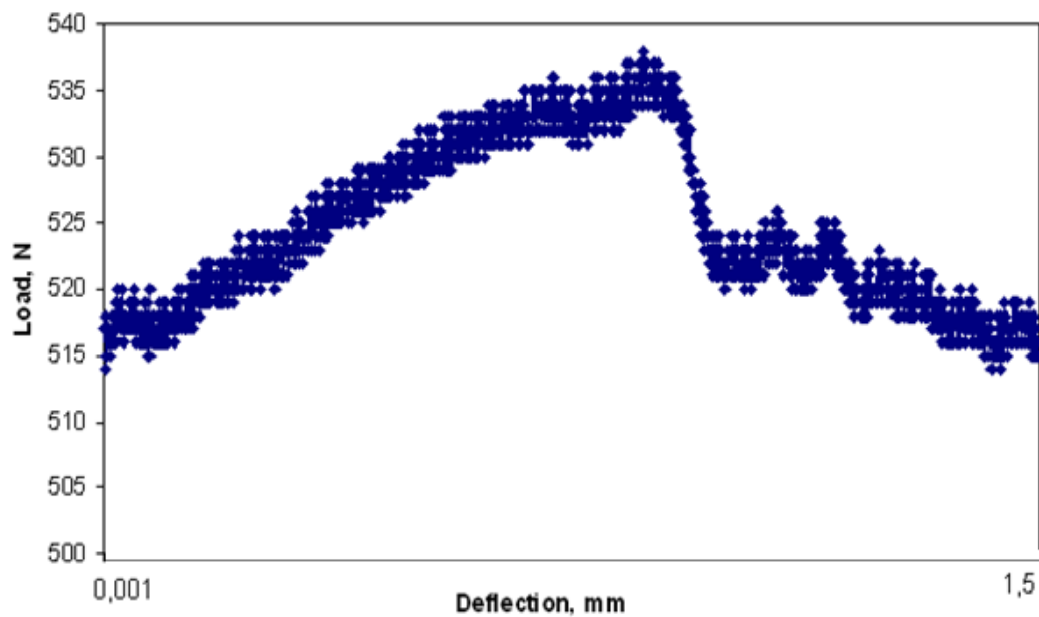

Figure 3.34 Impact test curve for composite 1
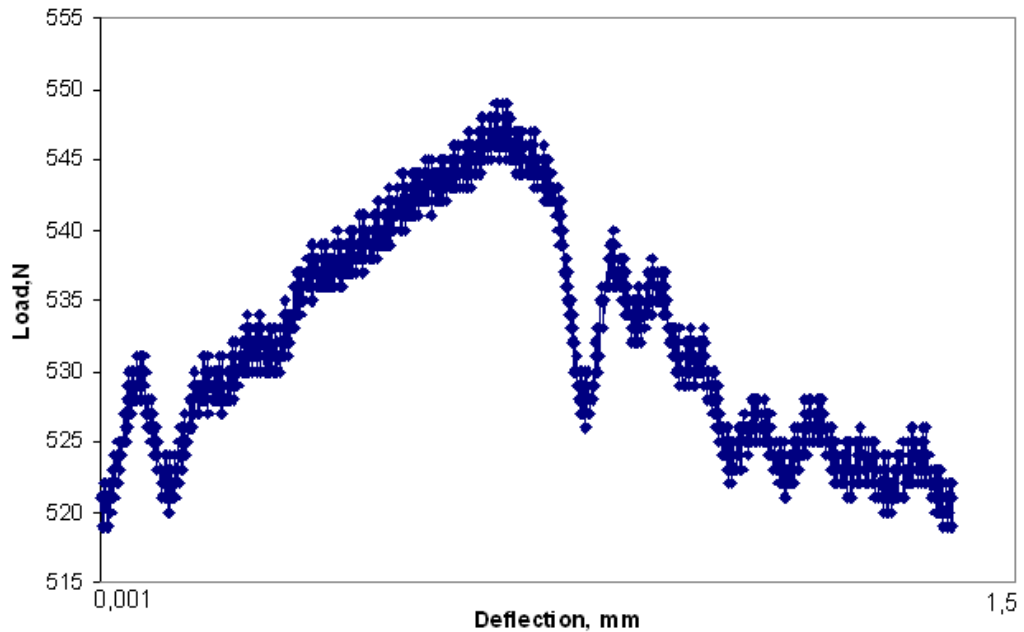
Figure 3.35 Impact test curve for composite 2

According to the results, it is observed that increase in the BMI content in the matrix resin has an increasing effect on impact strength value. Also in literature [50,51], impact strength of cured resins are reported to increase by the incorporation of BMI to the system. However, there is an optimum ratio of BMI which gives the maximum value of impact strength and after that point, further increase in BMI ratio results decraese in toughness. The reason is that energy absorption of the material becomes harder because of the rigidity imparted by BMI and high crosslink density.

The effect of further increase in BMI content on the mechanical properties of composite systems could not be observed in this study since high viscosity of BMI/ADM resin having mole ratio of 2:1 were not suitable for composite manufacturing with RTM process.

CHAPTER 4

CONCLUSION

4,4'-bismaleimido diphenylmethane (BMI) was successfully synthesized starting from 4,4'-diaminodiphenylmethane (MDA) and maleic anhydride. Three different diallyl compounds (ADM, ADS and APD) were synthesized by allylating primary aromatic diamines. BMI was modified with diallyl compounds and 9 prepolymers with 1:1, 1.5:1 and 2:1 molar ratios of BMI/allyl compound were prepared and cured. The effect of increase in BMI ratio on resin properties were investigated in terms of FTIR, DSC and TGA results.

DSC thermograms of all prepolymers showed a wide exotherm resulting from the curing reaction of the resins. The higher BMI ratio in the prepolymers resulted in higher curing temperature and increase in the intensities of the peaks due to the heat evolved by the homopolymerization of excess BMI.

According to TGA results, the thermal stability of resin systems increased in the order BMI/ADM> BMI/ADS> BMI/PDA. Td_i, Td_{max} and Y_c values reached 404.88°C, 490.52°C and %44.18, respectively for BMI/ADM system having BMI/ADM mole ratio of 2:1 which can be considered to be a resin system with a good thermal stability.

According to viscosity-time correlations of BMI/ADM, it was observed that BMI/ADM molar ratio of 1:1 and BMI/ADM molar ratio of 1.5:1 resin systems

are suitable for RTM system considering the viscosities at injection temperature and pot life.

Two different composites were manufactured by RTM processing which the matrix was BMI/ADM molar ratio of 1:1 and 1.5:1, the reinforcement was carbon fabric. Composites were characterized in terms of thermal and mechanical properties. Finally, BMI/ADM resin sytem seems to be a good candidate for matrix component of high performance composite systems.

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