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NAFTOKSAZİN GRUPLARI İÇEREN POLİMERLERİN SENTEZLENMESİ VE POLİMERLERİN ISISAL KÜRLEŞME ÖZELLİKLERİNİN KARAKTERİZASYONU

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LIST of ABBREVIATIONS

BMI	: bismaleimide
BPA	: bisphenol A
BZ	: benzoxazine
CNE	: o-cresol novolac epox
CTE	:coefficient of thermal expansion
DGEBA	: diglycidyl ether of bisphenol A {2,20-bis (4-glycidyloxy phenyl) propane}
DMA	: dynamic mechanical analysis
DMF	: dimethyl formamide
DMSO	: dimethyl sulfoxide
DSC	: differential thermal analysis
EPAN	: ethynyl phenyl azo novolac
EPN	: novolac epoxy resin
FTIR	: fourier transform infra red
FTMS	: fourier transform mechanical spectroscopy technique
GC/MS	: gas chromatography-mass spectrum
MMT	: montmorillonite clay
OMMT	: organically modified montmorillonite clay
PBZ	: poly(benzoxazine)
PC	: polycarbonate
PCL	: poly(1 -caprolactone)
PU	: polyurethane
PVP	: poly(N-vinyl-2-pyrrolidone)
RT	: room temperature
RTM	: resin transfer molding
TEM	: transmission electron microscopy
Tg	: glass transition temperature
TGA	: thermo gravimetric analysis
VBP	: vinyl phenol–butyl acrylate copolymer
VP	: poly(p-vinyl phenol)
VRTM	: vacuum resin transfer molding
XRD	: X-Ray Diffraction

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LIST of SYMBOLS

Dk	: Dielectric constant
f	: Functionality
M	: Monomer
k	: Rate constant
μm	: Micrometer
Δ	: Heat
B-a	: Bisphenol A-based benzoxazine {bis(4-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane}
Va	: benzoxazine from poly(p-vinyl phenol)
Vba	: benzoxazine from vinyl phenol–butyl acrylate copolymer
Terp-Bz	: terpene diphenol-based benzoxazine

SYNTHESIS AND CHARACTERIZATION OF NAPHTHOXAZINE-FUNCTIONALIZED POLY(PROPYLENE OXIDE) AMINES AND THEIR THERMAL CURING PROPERTIES

SUMMARY

Recently, high performance polymeric materials have received considerable studies for their wide application in electronics, biomaterials, and other industrials. Among the developed materials, polybenzoxazines possess outstanding properties of small shrinkage in curing, low water absorption, good thermal stability, and high glass transition temperatures. These advantages of naphthoxazines receive considerable increase on the studies of naphthoxazines and their corresponding polymers.

In this study, naphtoxazine-functionalized polymers were prepared by the reaction of linear (Diamines) and branched (Triamines) reactive elastomer Jeffamine series having various molecular weights, with *p*-formaldehyde, and 2-naphthol [1,2]. The structures of the resulting polymers were characterized by FTIR and ^{1}H-NMR. In addition, cure behavior of polymers were studied using DSC which indicated a single exothermic curing peak between 230-251 ^{o}C based on benzoxazine functionality. Hydrophilicity of polymers with B-a and effect of naphtoxazine functionality on hydrophilicity of these trunk polymers were investigated by water contact angle measurements. Also, Surface topography of polymers were represented by AFM images.

NAFTOKSAZİN GRUPLARI İÇEREN POLİMERLERİN SENTEZLENMESİ VE POLİMERLERİN ISISAL KÜRLEŞME ÖZELLİKLERİNİN KARAKTERİZASYONU

ÖZET

Sentetik polimerler bilimsel, endüstriyel ve bilinen ev ürünlerindeki kullanımları nedeniyle modern hayatta önemli rol oynar. Fenolik reçineler plastic uygulamalarda oldukça sık kullanılır.

Son zamanlarda yüsek performanslı polimerik malzemeler; elektronik, biyomalzeme ve diğer endüstriyel alanlarındaki geniş kullanım yelpazeleri sebebiyle önemli çalışmalara konu olmuştur. Naftoksazin yapılı polimerler; reçineleşme sırasındaki ufak hacim değişiklikleri (büzüşme), düşük miktada su absorplamaları, ısısal dayanımları ve yüksek camsı geçiş sıcaklıkları gibi göze çarpan özelliklere sahiptirler. Bu özellikler naftoksazin ve naftoksazin polimerleri hakkında yapılan çalışmaların önemli bir şekilde artmasına sebep olmuştur.

Bu çalışmada, iki ve üç uçlu serilerinden oluşan farklı molekül ağırlığına sahip Jeffamin, p-formaldehit ve 2-naftol kullanılarak 1,4-diokzan varlığında naftoksazin yapılı polimerler elde edildi. Sonuçta oluşan polimerler FTIR ve ^{1}H-NMR ile karakterize edildi. Bununla beraber, polimerlerin kürleşme özellikleri DSC de oluşan ekzotermik pikleri (230-251 ^{o}C) ile kanıtlandı. Suyun kontakt açıları kullanılarak, polimerlerin (B-a monomeri ile) hidrofil özelliği ile naftoksazin fonksiyonlarının polimerler üzerindeki etkileri araştırıldı. Ayrıca polimerlerin yüzey topografileri AFM görüntüleri ile açıklandı.

1. INTRODUCTION

Synthetic polymers played an important role in modern life because of their scientific, industrial, and household applications. Phenolic resins are widely used in plastic industry in numerous applications. Naphthoxazine is type of phenolic resin materials possessing heterolytic structures consisting of naphthlene and oxazine rings combined with an oxygen atom and a nitrogen atom. Polynaphthoxazine is synthesized by ring opening polymerization of the oxazine rings at high temperature without any catalyst and formation of byproduct [3]. Polynaphthoxazines are widely used in biomaterials, electronics, and other industrials because of their high performance; small shrinkage in curing, low water absorption, good thermal stability, and high glass transition temperatures. Moreover, naphthoxazine group can also be incorporated to various polymeric structures which ultimately leads to the improved properties of the trunk polymer.

Poly(propyleneoxide) amines (PPOA), also called as Jeffamines, are used as epoxy curing agents and lead tough, clear, impact-resistant coatings (for decoupage and furniture, reinforced composites, electrical encapsulation, and lamination), castings, and adhesives. They are light in color, low in viscosity and completely miscible with a wide variety of solvents. In addition, the utility of PPOA with Mw up to 2500 as intermediates in preparation of acrylates that are used as ultraviolet light-curible buffer coatings and top coatings for optical fibers [4]. In addition, surface moisture absorption ability and, therefore, surface electrical resistivity [5] can easily be adjusted by the segmental length of the Jeffamines. Jeffamines can be in the form of monoamine, diamines, and triamines which are available in variety of molecular weights. Therefore, telechelic poly(propyleneoxide) amines can be used as cross-linkers, chain extenders, and precusors for block and graft copolymers. Recently, naphthoxsazine-based telechelic macromonomers have been synthesized [6].

The hydrophilicity of polymers is an important parameter which can change the area of their applications. Naphthoxazine functionality could affect the hydrophilicity of

the resulting polymers. Hydrophilicity of the polymers can be measured by water contact angle on the surface of the polymer films.

In this study, Jeffamines with various diamine series, namely, D-230, D-400, D-2000 and triamine series, namely, T-403, T-5000 are functionalized with naphthoxazine units in order to extend the properties of these polymers.

2. THEORETICAL PART

2.1 High Performance Polymers

High performance plastics are replacing traditional materials in hostile environments. They possess characteristics such as exceptional strength, lightweight, temperature resistance (usually in excess of 160 °C), chemical resistance and dimensional stability. In addition, plastics are relatively easy to process and can be coloured (or transparent) and moulded to create innovative and attractive structures.

However, it is not only the excellent temperature capabilities of these polymers and compounds that have caused their high growth. In many applications, their chemical, wear resistance, and other properties are more important. Despite their high average price in comparison to other engineering plastics, demand for these polymers has been growing dramatically in performance applications, including electrical, automotive, and industrial uses. In the automotive market, demands for improved fuel efficiency, lower emissions, and longer maintenance cycles are also favoring more consumption of high-temperature plastics.

2.1.1 Some Examples for High Temperature & High Performance Materials

2.1.1.1 PBI (PolyBenzImidazole)

PBI offers excellent dimensional stability and strength at the highest sustained temperatures of any plastics up to 750°F, with excursions possible up to 1000°F [7].

2.1.1.2 Polyimide

Polyimide material provides a unique combination of strength, toughness, wear resistance, chemical stability at temperatures up to 550°F. It can be used for insulators, spacers, and other electrical components that must stand up to extreme temperatures [8].

2.1.1.3 Polyimide Film

Polyimide film is a high performance polymer which combines excellent physical, electrical, and mechanical properties at temperatures as low as 269°C and as high as 400°C. It is typically orange and transparent in appearance. Polyimide offers excellent dimensional stability combined with excellent chemical resistance there are no known solvents. It is typically used for wire and cable tapes, formed coil insulation, flexible printed circuit board substrates, and magnet wire, transformer and capacitor insulation.

2.1.1.4 Polyamide

Polyamide offers dimensional stability, chemical resistance, and retains its strength at temperatures of up to 550°F. Polyamide is a slightly lower cost replacement for polyimide.

2.1.1.5 PolyAmide-Imide

PolyAmide-Imide has high dielectric properties and low thermal expansion, and is much less expensive than some advanced polymers. It is also available in glass and carbon-filled versions to enhance its already excellent characteristics. Because of its wide temperature range and dimensional stability, polyAmide-Imide is ideal for connector bodies, insulators, spacers and other high-temperature electrical parts.

2.1.1.6 PolyEtherImide

PolyEtherImide has good dielectric properties and low thermal expansion, and is considerably less expensive than some other polymers. Its 30% glass-filled version, PEI 2300, has a excellent dimensional stability and a wide operating temperature range. PEI 2300 is an excellent choice for for insulators, spacers, connectors, and structural parts [9].

2.1.1.7 PEEK (PolyEtherEtherKetone)

PEEK offers exceptional chemical resistance combined with heat resistance to 480°F. It does not degrade with exposure to water or steam, and is flame and radiation-resistant. Glass and carbon-fiber reinforced grades are also available for improved dimensional stability, stiffness, compressive strength, and heat dissipation.

Because of these properties, PEEK can withstand the chemical and mechanical stresses present during downhole operations. Connector bodies, insulators and spacers may be manufactured from PEEK.

2.1.1.8 PPS (PolyPhenylene Sulfide)

Bearing grade PPS offers exceptional chemical resistance combined with heat resistance to 425°F. It does not degrade with exposure to water or steam, nor to hydrocarbon or other organic compounds. Many different bearing grades of PPS are available which are filled with solid lubricants for lower friction and higher wear resistance. Glass and carbon-fiber reinforced grades are also available for improved dimensional stability, stiffness, compressive strength, and heat dissipation. PPS materials are suitable for bearing, thrust, and wear surfaces and structural components.

2.1.1.9 Glass-Epoxy Industrial Laminates

Glass-epoxy laminate are specified for their extremely high strength and high dimensional stability over temperature. These materials they are frequently used for insulators, spacers and structural parts which must stand vibration, shock, and high temperatures.

2.2 Phenolic Resins

2.2.1 Phenolic Resin Chemistry

Despite the emergence of several new classes of thermosets, high performance polymers and several other new generation materials that are superior in some respects, phenolic resins retain industrial and commercial interest, a century after its introduction [10].

Phenolic resins are a large family of polymers and oligomers, composed of a wide variety of structures are prepared by the reaction of phenol or substituted phenol with an aldehyde, especially formaldehyde, in the presence of an acidic or basic catalyst [11].

Their thermosetting character and the exotherm associated with the reaction presented technical barriers to commercialization. In 1900, the first U.S. patent was granted for a phenolic resin, using the resin in cast form as a substitute for hard

rubber [12]. Polymeric phenolic compounds have a wide range of applications, including fields such as aerospace, construction, and electronics [13]. This recognition emerges from the fact that these resins have several desirable characteristics, such as superior mechanical strength, heat resistance and dimensional stability, as well as, high resistance against various solvents, acids and water. They are inherently flame resistant, and evolve low smoke upon incineration [13,14].

There are three core reasons for the broad application range of these materials. One, the synthesis of phenolic prepolymers by electrophilic aromatic substitution is relatively simple and inexpensive. Two, methods for their conversion into thermoset networks are well established. Three, these networks are highly aromatic and thus, they are resistant to thermal oxidation.

2.2.2 Monomers

2.2.2.1 Phenol

This is the monomer or raw material used in the largest quantity to make phenolic resins. As a solid having a low melting point, phenol, C_6H_5OH, is usually stored, handled in liquid form at 50–60°C, and stored under nitrogen blanket to prevent the formation of pink quinones. Iron contamination results in a black color. The most widely used process for the production of phenol is the cumene process. Benzene is alkylated with propylene to produce cumene (isopropylbenzene), which is oxidized by air over a catalyst to produce cumene hydroperoxide (CHP). With acid catalysis, CHP undergoes controlled decomposition to produce phenol and acetone; α-methylstyrene and acetophenone are the by-products [15]. Other commercial processes for making phenol include the Raschig process, using chlorobenzene as the starting material, and the toluene process, via a benzoic acid intermediate.

Table 2.1: Substituted Phenols Used for Phenolic Resins.

Substituted Phenol	Resin Application
Cserol (*o*-, *m*-, *p*-)	Coatings, epoxy hardeners
p-t-Butylphenol	Coatings,
p-Octyphenol	Carbonless paper, coatings
p-Nanophenol	Carbonless paper, coatings
p-Phenylphenol	Carbonless paper
Bisphenol A	Low color molding compounds, coatings
Ressolcinol	Adhesives
Cashew nutshell liquid	Friction particles

2.2.2.2 Substituted Phenols

Phenol itself is used in the largest volume, but substituted phenols are used for specialty resins (Table 2). Substituted phenols are typically alkylated phenols made from phenol and a corresponding α-olefin with acid catalysts [16]. Acidic catalysis is frequently in the form of an ionexchange resin (IER) and the reaction proceeds preferentially in the para position. For example, in the production of *t*-butylphenol using isobutylene, the product is >95% para-substituted. The incorporation of alkyl phenols such as cresol into the resin reduces reactivity, hardness, cross-link density, and color formation, but increases solubility in nonpolar solvents, flexibility, and compatibility with natural oils.

2.2.2.3 Formaldehyde

In one form or another, formaldehyde is used almost exclusively in the production of phenolic resins, regardless of the type of phenol. It is frequently produced near the site of the resin plant by either of two common processes using methanol (qv) as the raw material. In the silver catalyst process, the reaction takes place at 600–650 °C and produces water and hydrogen as by-products. The more common metal oxide process operates at 300–400 °C. The gaseous formaldehyde is absorbed in water, and the final product is a formalin solution containing 36–50% formaldehyde. Of the various chemical forms of formaldehyde, the aqueous form is preferred for making phenolic resins, even though at least half of this form is water. The water serves to moderate the reaction and is readily removed in processing equipment [17].

2.2.2.4 Aqueous Formaldehyde

Water solutions of formaldehyde consist mainly of telomers of methylene glycol having <100 ppm of the formaldehyde as CH_2O [18].

Alcohols form hemiformals with aqueous formaldehyde according to the 2.1. where $n = 1, 2, 3$, etc.

$$\begin{aligned} ROH + HOCH_2OH &\rightleftharpoons ROCH_2OH + H_2O \\ RO(CH_2O)_nH + HOCH_2OH &\rightleftharpoons RO(CH_2O)_{n+1}H + H_2O \end{aligned} \tag{2.1}$$

However, a second mole of alcohol or hemiformal does not add at the ordinary pH of such solutions. The equilibrium constant for hemiformal formation dependson the nature of the R group of the alcohol. Using NMR spectroscopy, a group of alcohols including phenol has been examined in solution with formaldehyde [19,20]. The spectra indicated the degree of hemiformal formation in the order of methanol > benzyl alcohol > phenol.

Hemiformal formation provides the mechanism of stabilization; methanol is much more effective than phenol in this regard. The large value for the hemiformal formation constant of methanol and its low molecular weight explains the high efficiency of methanol in stabilizing formalin solutions. Phenol, on the other hand, is inefficient, and phenol hemiformals are only formed by careful removal of water [21].

2.2.2.5 Other Aldehydes

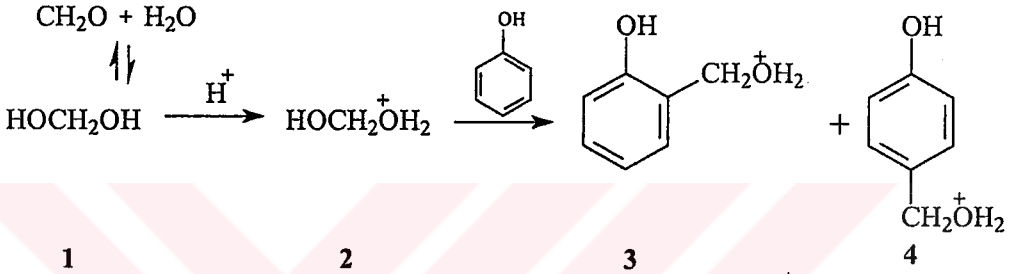
The higher aldehydes react with phenol in much the same manner as formaldehyde, although at much lower rates. Examples include acetaldehyde, CH_3CHO; paraldehyde, $(CH_3CHO)_3$; glyoxal, OCH CHO; and furfural. The reaction is usually kept on the acid side to minimize aldol formation. Furfural resins, however, are prepared with alkaline catalysts because furfural self-condenses under acid conditions to form a gel.

2.2.3 Polymerization

Phenolic resins are prepared with strong acid or alkaline catalysts. Occasionally, weak or Lewis acids, such as zinc acetate, are used for specialty resins.

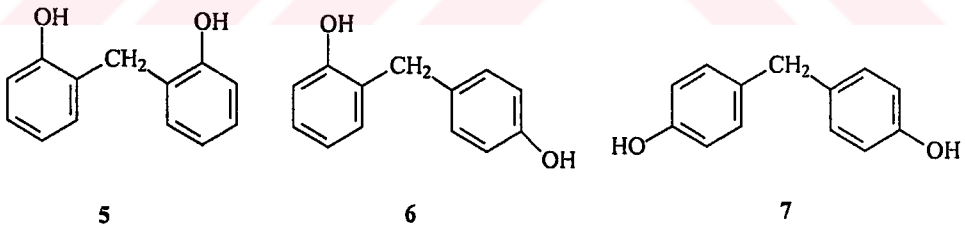
2.2.3.1 Strong-Acid Catalysts, Novolak Resins

Phenolic novolaks are thermoplastic resins having a molecular weight of 500–5000 and a glass-transition temperature *T*g of 45–70°C. The phenol–formaldehyde reactions are carried to their energetic completion, allowing isolation of the resin; formaldehyde–phenol molar ratios are between 0.5:1 and 0.8:1. Methylene glycol **1** is converted to the corresponding hydrated carbonium ion **2**, which adds to the *ortho-* and *para-* positions of phenol with the elimination of water to form the corresponding *ortho-* **3** and *para-* **4** benzylic ions. The benzylic carbonium ions are in equilibrium with the corresponding benzylic alcohols, observed by NMR as transient species in the formation of novolak resins [22].



(2.2)

In the next step the hydrated benzylic carbonium ions **3** and **4** react with free *ortho-* and *para-* positions on phenols to form methylene-linked bisphenols, 2,2_ **5**, 2,4_ **6**, and 4,4_ **7** (2.3).



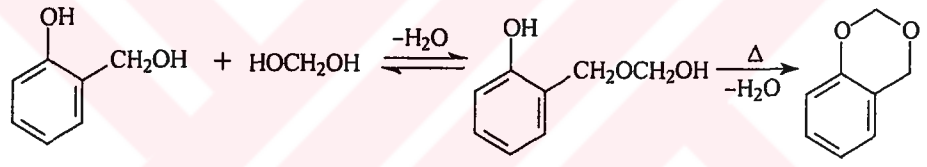
(2.3)

Continued reaction leads to the formation of novolak polymers having a molecular weight of up to 5000. Acid-catalyzed resins contain 50–75% 2,4-linkages **6**. The reaction rate is proportional to catalyst, formaldehyde, and phenol concentrations, and inversely proportional to the concentration of water. The rate of formation of the benzyl alcohol intermediate is 5–10 times lower than the rate to form the methylene-linked bisphenol **3**.

At typical molecular weights of 500–1000, novolak molecules are essentially linear because of the much lower reactivity of doubly-reacted phenolic units. In higher

molecular weight polymers, the low concentration of end groups and unreacted phenol causes branching. In the curing process, end groups are more reactive than the backbone groups.

Thus a branched resinhaving a higher content of end groups than a corresponding linear equivalent may gel sooner and cure faster because of the higher resin functionality. The typical acid catalysts used for novolak resins are sulfuric acid, sulfonic acid, oxalic acid, or occasionally phosphoric acid. Hydrochloric acid, although once widely used, has been abandoned because of the possible formation of toxic chloromethyl ether by-products. The type of acid catalyst used and reaction conditions affect resin structure and properties. For example, oxalic acid, used for resins chosen for electrical applications, decomposes into volatile by-products at elevated processing temperatures. Oxalic acid catalyzed novolaks contain small amounts (1–2% of the original formaldehyde) of benzodioxanes formed by the cyclization and dehydration of the benzyl alcohol hemiformal intermediates (2.4).

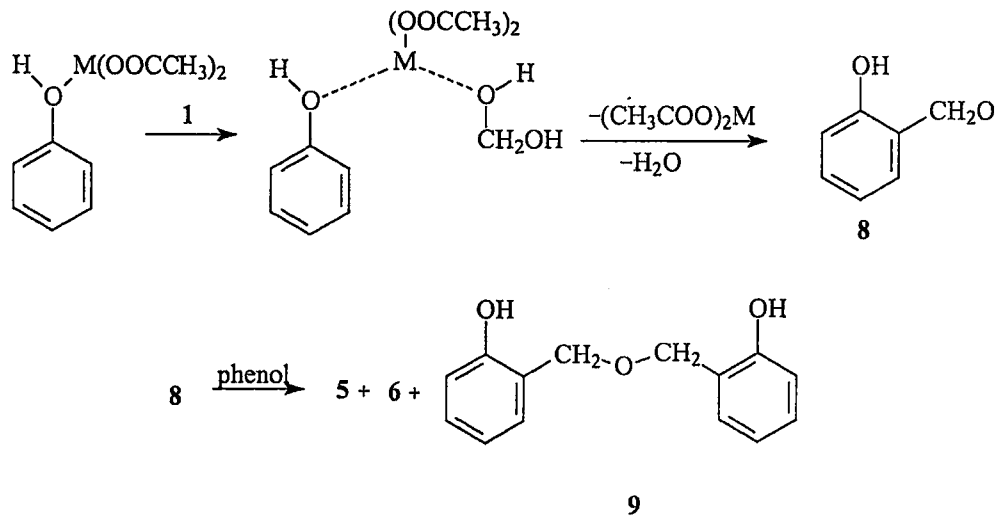


(2.4)

Benzodioxane is reasonably stable at neutral pH, but may decompose when the resin is cured, serving as a source of labile formaldehyde. Benzodioxanes are not found in sulfuric or sulfonic acid catalyzed resins, since the stronger acid readily catalyzes the second step in the reaction sequence.

2.2.3.2 Neutral Catalysts, High Ortho Novolaks

In the range of pH 4–7, formaldehyde substitution of the phenolic ring is possible, using divalent metal catalysts containing Zn, Mg, Mn, Cd, Co, Pb, Cu, and Ni; certain aluminum salts are also effective. Organic carboxylates are required as anions in order to obtain suf.cient solubility of the catalyst in the reaction medium, as well as to provide a weak base. Acetates are most convenient and economical. Although lead acetate is highly effective because of its excellent solubility properties, it has been largely eliminated because of lead toxicity. Zinc and calcium salts are probably the most widely used catalysts [23]. Novolaks produced from these catalysts exhibit a high content of 2,2- methylene units. The mechanism proposed for the ortho-directing effect involves chelation of the phenolic unit with the metal ion. (2.5)



(2.5)

Zinc acetate catalyst produces essentially 100% *o*-methylol phenol **8** in the first step. The second step gives an approximately equal quantity of 2,2'-5,45% and 2,4%-diphenylmethylene (6,45 %) bridges, indicating little chelate-directing influence. In addition, a small quantity (10%) of methylene ether units **9** (dibenzyl ether) is observed at moderate reaction temperature. High ortho novolaks have faster cure rates with hexa. The gel time with hexa is one-third of that with a strong acid catalyzed novolak.

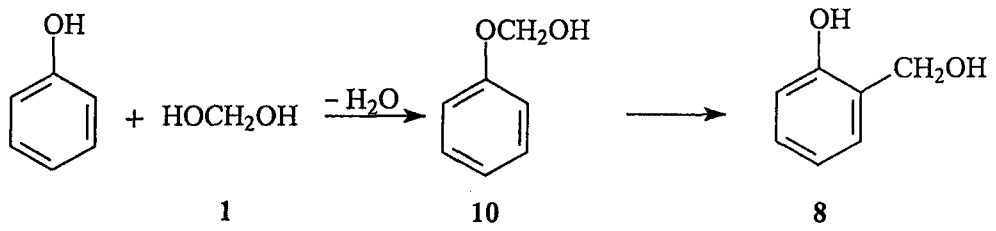
2.2.3.3 Alkaline Catalysts, Resols

Resole-type phenolic resins are produced with a molar ratio of formaldehyde to phenol of 1.2:1 to 3.0:1. For substituted phenols, the ratio is usually 1.2:1 to 1.8:1. Common alkaline catalysts are NaOH, $Ca(OH)_2$, and $Ba(OH)_2$. While novolak resins and strong acid catalysis result in a limited number of structures and properties, resoles cover a much wider spectrum.

Resols may be solids or liquids, water-soluble or -insoluble, alkaline or neutral, slowly curing or highly reactive. In the first step, the phenolate anion is formed by delocalization of the negative charge to the ortho and para positions. Alkaline catalysts are also effective in the polymerization–depolymerization of methylene glycol. The mechanism of the formaldehyde addition to the phenolate is still not completely understood. The most likely mechanism involves the contribution of phenol hemiformals **10**.

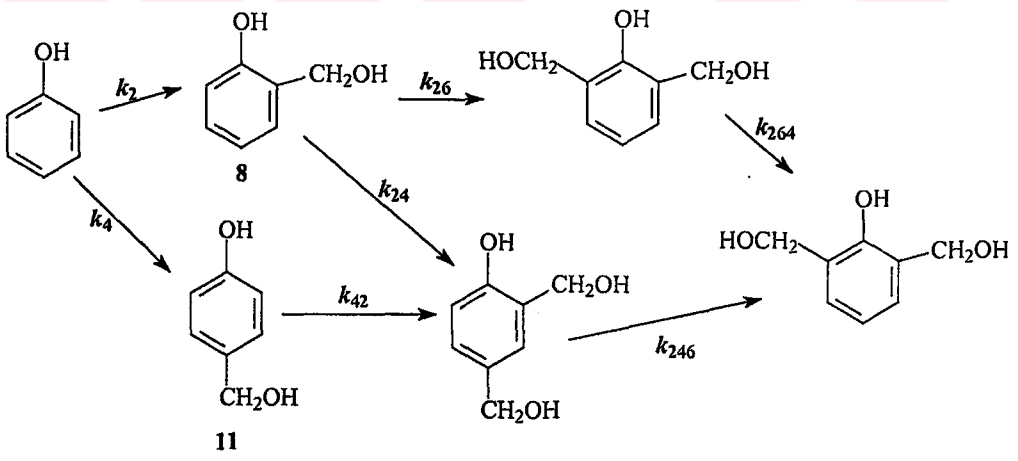
Rate studies show that base-catalyzed reactions are second order and depend on the phenolate and methylene glycol concentrations. The most likely path involves a

nucleophilic displacement by the phenoxide on **1**, with the hydroxyl as the leaving group. In alkaline media, the methylolated quinone intermediate is readily converted to the phenoxide by hydrogen-ion abstraction [24].



(2.6)

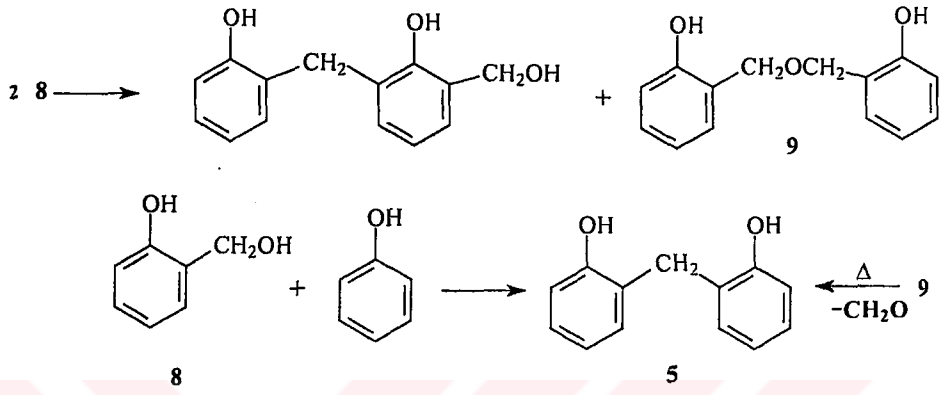
The ratio of ortho-to-para substitution depends on the nature of the cation and the pH. Para-substitution is favored by K^+ and Na^+ ions and higher pH, whereas ortho substitution is favored at lower pH and by divalent cations, such as Ba^{2+}, Ca^{2+}, and Mg^{2+}. For the reaction scheme shown in (2.7), seven different rate constants must be determined. Despite different solution concentration, temperatures, and methods of analysis, comparing reaction rates [27-29] from each study using an NaOH catalyst gave fairly close agreement that rate constants increase with methylol substitution. In fact, dimethylol-substituted phenols react with formaldehyde two to four times faster than phenol. As a result, unreacted phenol remains high in resole resins (5–15%) even though the formaldehyde/phenol ratio is as high as 3:1 (2.7).



(2.7)

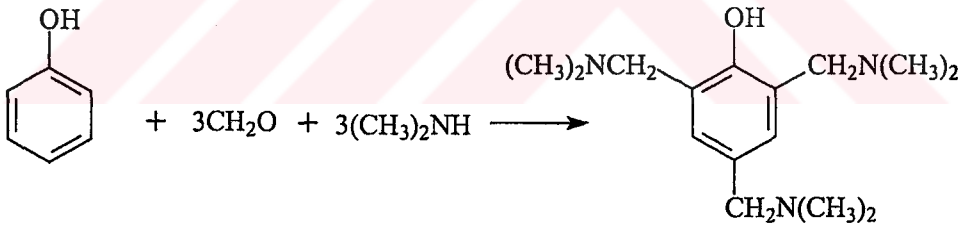
The rate studies show that *k*264 is by far the fastest reaction (by a factor of 4–6) than *k*2 or *k*4, with *k*24 the second fastest (by a factor of 2–4) [23-25]. Although monomeric methylolated phenols are used in certain applications, such as in fiber bonding, higher molecular weight resins are usually desirable.

Molecular weight is increased by further condensation of the methylol groups, sometimes after the initial pH has been reduced. Dibenzyl ether **9** and diphenylmethylene formation are shown in the following. The formation of diphenylmethylene bridges is favored above 150°C and under strongly alkaline conditions; dibenzyl ether formation is favored at lower temperatures and near neutral pH (2.8).



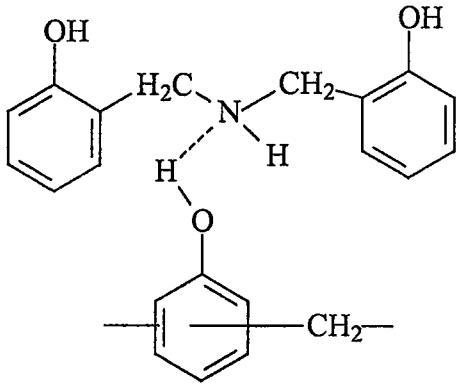
(2.8)

Special resoles are obtained with amine catalysts, which affect chemical and physical properties because amine is incorporated into the resin. For example, the reaction of phenol, formaldehyde, and dimethylamine is essentially quantitative (2.9) [30].



(2.9)

In practice, ammonia is most frequently used. With hexa, the initial reaction steps differ, but the final resole resins are identical, provided they contain the same number of nitrogen and CH_2 groups. Most nitrogen from ammonia or hexa is incorporated as dibenzylamine with primary, tertiary, and cyclic amine structures as minor products (2.10).



(2.10)

Compared to the resin catalyzed with NaOH, this resin has higher molecular weight, less free phenol, lower water solubility, and a higher *T*g. This increase in *T*g is higher than that expected if only phenol and formaldehyde were used, and is a result of the hydrogen-bonding interaction between the backbone amine units and the phenolic hydroxyls (2.10). Taking advantage of this effect, hexa and ammonia have been frequently used to produce solid, grindable, and water-insoluble resoles for molding compounds.

2.2.3 Manufacture

2.2.3.1 Materials of Construction

Compatibility of the materials of construction and the process chemicals is extremely important. The reactors are usually made of stainless steel alloys. Copper is avoided because of the possible presenceof amines. Glass-lined reactors are occasionally used for nonalkaline resins. Because the use of HCl has been largely discontinued, material requirements are less stringent. The reactor contains a bottom discharge, which for solid heat-reactive resins must be large. Solid resole resins are discharged for rapid cooling in order to quench the thermosetting reactions. Resin coolers are made up of vertical plates with internally circulating water. The product can also be discharged to a large cooled surface. Discharges to belt and drum flakers are highly automated; however they can only be used for less-reactive resins.

Novolak resins can be stored molten in heated holding tanks under nitrogen. Because novolaks are used mainly in pulverized form with hexa and additives, a process that includes belt flaking and feeding directly into the blending and pulverizing system is preferred. Liquid and solution resole resins are cooled in the reactor by using jacket cooling and vacuum refluxing. Discharged products are filtered and pumped to

refrigerated intermediate holding areas or packaged for shipping. The stability of liquid resole products varies greatly from product to product and depends on the storage temperature. The viscosity of a liquid resole resin increases but the water miscibility decreases as time and temperature increase. Generally, resoles, both liquids and solids, must be refrigerated.

2.2.3.2 Novolak Resins

In a conventional novolak process, molten phenol is placed into the reactor, followed by a precise amount of acid catalyst. The formaldehyde solution is added at a temperature near 90°C and a formaldehyde-to-phenol molar ratio of 0.75:1 to 0.85:1. For safety reasons, slow continuous or stepwise addition of formaldehyde is preferred over adding the entire charge at once. Reaction enthalpy has been reported to be above 80 kJ/mol (19 kcal/mol) [31,32]. The heat of reaction is removed by refluxing the water combined with the formaldehyde or by using a small amount of a volatile solvent such as toluene. Toluene and xylene are used for azeotropic distillation. Following decantation, the toluene or xylene is returned to the reactor.

The reaction is completed after 6–8 h at 95 °C; volatiles, water, and some free phenol are removed by vacuum stripping up to 140–170°C. For resins requiring phenol in only trace amounts, such as epoxy hardeners, steam distillation or steam stripping may be used. Both water and free phenol affect the cure and final resin properties, which are monitored in routine quality control testing by gas chromatography (GC). Oxalic acid (1–2 parts per 100 parts phenol) does not require neutralization because it decomposes to CO, CO_2, and water; furthermore, it produces milder reactions and low color. Sulfuric and sulfonic acids are strong catalysts and require neutralization with lime; 0.1 parts of sulfuric acid per 100 parts of phenol are used.

2.2.3.3 High Ortho Novolaks

The process for high ortho novolaks is similar to the one used for those catalyzed by strong acid. Zinc acetate is used at concentrations higher than the acids, typically 2% or more. The formaldehyde/phenol ratio is similar (0.75–0.85) but yields are 5–10% lower than those produced with strong acids, and reaction times are longer. Problems with gel particles and bulk gelation occur more frequently because small amounts of reactive dibenzyl ether groups are present. Overall, the process is more expensive because of higher raw material costs, lower yields, and longer cycle times. Another

process employs a pH maintained at 4–7 and a catalyst that combines a divalent metal cation and an acid. Water is removed continuously by azeotropic distillation and xylene is recycled. The low water content increases the reaction rate. The dibenzyl ether groups are decomposed by the acid; the yield of 2,2_-methylene ca be as high as 97% [33].

2.2.3.4 Resoles

Like the novolak processes, a typical resole process consists of reaction, dehydration, and finishing. Phenol and formaldehyde solution are added all at once to the reactor at a molar ratio of formaldehyde to phenol of 1.2–3.0:1. Catalyst is added and the pH is checked and adjusted if necessary. The catalyst concentration can range from 1 to 5% for NaOH, 3 to 6% for $Ba(OH)_2$, and 6 to 12% for hexa. A reaction temperature of 80–95°C is used with vacuum-reflux control. The high concentration of water and lower enthalpy compared to novolaks allows better exotherm control. In the reaction phase, the temperature is held at 80– 90°C and vacuum-refluxing lasts from 1 to 3 h as determined in the development phase. Solid resins and certain liquid resins are dehydrated as quickly as possible to prevent overreacting or gelation. The endpoint is found by monitoring the gel time, which decreases as the reaction progresses. Automation includes on-line viscosity measurement, GC, and gel-permeation chromatography (GPC).

2.2.3.5 Phenolic Dispersion

These systems are predominantly resin-in-water systems in which the resin exists as discrete particles. Particle size ranges from 0.1 to 2 μm for stable dispersions and up to 100 μm for dispersions requiring constant agitation. Some of the earliest nonaqueous dispersions were developed for coatings applications. These systems consist of an oil-modified phenolic resin complexed with a metal oxide and a weak solvent. In the postdispersion process, the solid phenolic resin is added to a mixture of water, cosolvent, and dispersant at high shear mixing, possibly with heating. The cosolvent, frequently an alcohol or glycol ether, and heat soften the resin and permit small particles to form. On cooling, the resin particles, stabilized by dispersant and perhaps thickener, harden and resist settling and agglomeration. Both resole and novolak resins have been made by this process [27]. The *in situ* process is simpler because it requires less material handling [34]; however, this process has been used

only for resole resins. The principal application for this type of product is believed to be wood binding, especially for waferboard applications.

2.2.3.5 Cyanate Ester Resins

Cyanate ester resins, sometimes called triazines or cyanurates after the cured structure that they produce, are derived from phenols and phenolic resins. Specifically the starting phenols are reacted with cyanogen chloride, ClCN, and base to give the resins. In the cure step the cyanate groups trimerize to form triazine rings when heated in the range 180–250°C. Performance is generally intermediate between aromatic amine cured epoxides and toughened bismaleimides. Glass transition temperature *T*g is about 250°C and the heat distortion temperature is about 250°C dry and 175°C wet. Electrical propertiesare excellent due to very low residual chlorine content. Principal applications are printed wiring boards and structural composites [35].

2.2.3.6 Benzoxazine Resins

Benzoxazine resins are prepared by the reaction of phenol, formaldehyde, and an amine. In one particular example a benzoxazine is prepared from bisphenol A, formaldehyde, and aniline to give 2,2_-bis(3-phenyl-4- dihydro-1,3,2-benzoxazine) propane. When heated to about 200∘C the methylene bond to oxygen breaks and reforms onto the available ortho positions of adjacent moieties to give dibenzylamine structures. Resin formulations have been developed and formulated, in some cases with epoxy and phenolic resins to give ternary systems with *T*g as high as 170°C [35-38].

2.2.4 Applications

2.2.4.1 Coatings

For coatings applications, phenolic resins are grouped into four classes, depending on heat reactivity and the type of phenol. Substituted phenols are more compatible with oil and hydrocarbons, whereas heat-reactive resins require polar solvents. Depending on its nature, the resin can be used alone or as a modifying resin that acts as an adhesion promoter, a chemical cross-linker, or a hardening agent. In these cases the primary resin may be an alkyd, polyester, or epoxy. nonpolar hydrocarbon solvent. The resin exists as droplets that have particle sizes of 1–20 μm and are dispersed in

the continuous phase. Aqueous dispersions are prepared either *in situ* during the preparation of the resin itself or by high shear mixing. Aqueous dispersions are alternatives to solutions of liquid and solid resins. They are usually offered in 50% solids and may contain thickeners and cosolvents as stabilizers and to promote coalescence. Both heat-reactive (resole) and nonheatreactive (novolak) systems exist that contain unsubstituted or substituted phenols or mixtures. A related technology produces large, stable particles that can be isolated as discrete particles [39]. In aqueous dispersion, the resin structure is designed to produce a hydrophobic polymer, which is stabilized in water by an interfacial agent. Aqueous dispersions are used in fiber bonding, paper coating, friction and abrasive applications, and laminates and wood bonding. Phenolic dispersions improve the strength of latex-contact adhesive applications. Epoxy-modified phenolic dispersions are prepared by dispersion of the phenolic epoxy resin. The systems are used for baked primer applications and bonding requirements. Minimum baking conditions are 20 min at 150°C [37].

2.2.4.2 Adhesives

Contact adhesives are blends of rubber, phenolic resin, and additives supplied in solvent or aqueous dispersion form; they are typically applied to both surfaces to be joined [40]. Evaporation of the solvent leaves an adhesive film that forms a strong, peel-resistant bond. Contact adhesives are used widely in the furniture and construction industries and also in the automotive and footwear industries. The phenolic resins promote adhesion and act as tackifiers, usually at a concentration of 20–40%. In solvent-based contact adhesives, neoprene is preferred, whereas nitrile is used in specialty applications. The type and grade of phenolic resin selected control tack time, bond strength, and durability. Phenolic resins substantially increase open time and peel strength of the formulation [40]. For example, higher methylol and methylene ether contents of the resin improves peel strength and elevated temperature resistance. Adhesive properties are also influenced by the molecular weight distribution of the phenolic; low molecular weight reduces adhesion [41].

2.2.4.3 Carbonless Copy Paper

In carbonless copy paper, also referred to as pressure-sensitive record sheet, an acid-sensitive dye precursor, such as crystal violet lactone or *N*-benzoylleucomethylene blue, is microencapsulated with a high boiling solvent or oil within a cross-linked

gelatin [42,43] or in synthetic mononuclear microcapsules. Microcapsules that have a starch binder are coated onto the back of the top sheet. This is referred to as a coated-back (CB) sheet. The sheet intended to receive the image is treated on the front (coated-front (CF)) with an acid. When the top sheet is mechanically impacted, the dye capsules rupture and the dye solution is transferred to the receiving sheet where the acid developer activates the dye.

2.2.4.4 Molding Compounds

Molding compounds were among the earliest applications for solid phenolic resins. Molding neat phenolic resin was almost impossible and the strength, especially on impact, was poor without reinforcement. Combining the resin, usually a novolak, with hexa, wood-flour, or asbestos reinforcement, as well as pigments and additives, gave a moldable thermoset. The molded articles exhibit high temperature, flame, and chemical resistance, retention of modulus at elevated temperature, and hardness. Systems that have good electrical properties can be formulated at low cost. Resins can be compounded with a choice of fillers for a variety of applications.

2.2.4.5 Abrasives

Abrasive materials are either bonded or coated. Bonded phenolic abrasives have superior strength and shock resistance compared to sintered ceramic compositions. The higher stability permits higher rotational speeds for resin-binder wheels; however, temperatures are lower than with ceramic wheels. Coated abrasives, such as sheets, disks, and drums, are used for polishing and finishing. Here, too, the abrasives, such as aluminum oxide and silicon carbide, have replaced the flint and garnet of common sandpaper. These industrial coated abrasives are manufactured from cloth or tough paper base. First, a coat of medium viscosity liquid resole resin is laid down on a continuous web of the backing. The web passes wet-side-down over a pan of grit, which adheres to it electrostatically and remains embedded in the resin layer. Altering the strength of the applied electrostatic field and the speed of the web can control the amount of grit deposited, which varies from an open to a closed dense mass of abrasive. The uncured coated sheet is partially dried in a low temperature oven at 60 °C, and a second, thinner coating of lower viscosity liquid resole resin is applied as a top to anchor the grit thoroughly. The coated web is taken off in rolls to be cured at 107–120 °C for 3–4 h.

2.2.4.6 Friction Materials

Phenolic friction materials are made from molding compounds developed to meet the extraordinary demands required by frictio elements in the transportation industries. Friction materials are used for brake linings, clutch facings, and transmission bands. A moderately high coefficient friction, which is temperature-independent, is needed. In addition, the materia must be high in strength, low in wear and abrasion, and resistant to moisture an hydraulic fluids.

2.2.4.7 Foundry Resins

In the foundry industry, phenolic resins are used as th binder for sand in the manufacture of shell molds and cores. The two mating halves are joined by clamps or a bonding agent to form a shell mold into which the molten metal is poured for castings. The shell is formed by depositing a resin–sand mix on a hot metal pattern plate. After a certain period the pattern is inverted and the excess resin–sand is removed. The sand particles are bonded by an oven cure, and the shell is ejected from the pattern plate.

2.2.4.8 Laminates

Laminate manufacture involves the impregnation of a web with a liquid phenolic resin in a dip-coating operation. Solvent type, resin concentration, and viscosity determine the degree of fiber penetration. The treated web is dried in an oven and the resin cures, sometimes to the B-stage (semicured). Final resin content is between 30 and 70%. The dry sheet is cut and stacked, ready for lamination. In the curing step, multilayers of laminate are stacked or laid up in a press and cured at 150–175°C for several hours. The resins are generally low molecular weight resoles, which have been neutralized with the salt removed. Common carrier solvents for the varnish include acetone, alcohol, and toluene. Alkylated phenols such as cresols improve flexibility and moisture resistance in the fused products.

2.2.4.9 Air and Oil Filters

Liquid resole resins are used to coat and penetrate the cellulose fibers of filters and separators in order to increase strength and stiffness and protect against attack by the environment. The type of phenolic to be used depends on both the final property requirements and the papermaking process. The resins used in air and oil filters are

moderate-to-low molecular weight, catalyzed by caustic in one step; 10–20% alcohol is added; solids content is in the range of 50–60%. These resins are designed to penetrate the sheet thoroughly, yet not to affect the porosity of the paper. In the B-stage, the resin must have sufficient flexibility to permit pleating; the C-stage should have stiffness and resistance to hot oil.

2.2.4.10 Wood Bonding

This application requires large volumes of phenolic resins (5–25% by weight) for plywood, particle board, waferboard, and fiberboard. Initially, phenolic resins were used mainly for exterior applications, whereas UF was used for interiors. However, the concern over formaldehyde emission has caused the replacement of UF by phenol–formaldehyde adhesives. Different phenolic resins are used for different types of wood; for example, plywood adhesives contain alkaline-catalyzed liquid resole resins. Extension with a filler reduces cost, minimizes absorption, and increases bond strength. These resins have an alkaline content of 5–7% and are low in free phenol and formaldehyde.

Because many resins have a highwater content and limited storage stability, they are frequently made at or near the mill producing the plywood product. The plywood veneers are dried, coated with resin, stacked for pressing, and cured at 140–150 °C.

2.2.4.11 Fiber Bonding

In fiber bonding, the resin is used as a binder in such products as thermal insulation batting, acoustic padding, and cushioning materials. All these materials consist of long fibers (glass or mineral fiber, cotton, polyester) laid down in a randomly oriented, loosely packed array to form a mat. They are bonded with resin to preserve the special insulating or cushioning quality of the mat.

2.2.4.12 Composites

There has been substantial progress in improving the processability of phenolics in composite materials [44-46] to the point where a varietyof materials are available for pultrusion, filament winding, and resin-transfer molding. More complicated composite systems are based on aramid and graphite fibers.

Epoxy resins are usually superior to phenolics because of better adhesion, lower shrinkage on curing, and a much lower volatile content. Nevertheless, there are many

specific applications for phenolic resins, including formable laminates and sheet-molding compounds having low flammability and smoke generation. These systems are suitable for aircraft interiors. Another area is in binders for carbon–carbon composites for applications such as in ablative coatings of reentry vehicle and aircraft brakes. The high char yield and the strength and porosity of the char are important in these applications. Finally, phenolic novolaks are effective curing agents for epoxies, and epoxidized novolaks are being used in applications requiring high functionality and high crosslink density.

2.2.4.13 Nanocomposites

Work conducted at Toyota in nylon-6 nanocomposites has generated several commercial products and stimulated substantial interest in a variety of polymer/nanoclay systems. The melt intercalation and curing behavior of phenolic resin were investigated using layered silicates such as montmorillonite and alkyl ammonium modified layered silicates. It was found by X-ray diffraction that the uncured phenolic was effectively intercalated. Depending on the surface treatment, the resulting interaction between organic modifier and phenolic resin played an important role in determining the stable nauostructure and the final morphology of the layered silicate composite [47,48].

2.2.4.14 Liquid-Injection Molding

In LIM, monomers and oligomers are injected into a mold cavity where a rapid polymerization takes place to produce a thermoset article. Advantages of these processes are low cost, low pressure requirement, and flexibility in mold configuration. Conventional systems, such as isocyanate with polyol, release little or no volatiles. The generation of substantial volatiles in the mold is obviously undesirable and has represented a significant obstacle to the development of a phenolic-based LIM system. A phenolic LIM system based on an anhydrous high ortho liquid resole has been reported [49,50]. Formaldehyde ispresent in the form of both methylol and phenolic hemiformals. A formaldehyde/ phenol ratio of ≈1.5–1.0 is used at a pH of 4–7. Divalent salts catalyze the reaction at 80–90°C for 5–8 h and the water is removed by an azeotropic solvent. Uncatalyzed resoles have excellent storage stability.

2.2.4.15 Foam

Phenolic resin foam is a cured system composed of open and close cells with an overall density of 0.16–0.80 g/cm3. Principal applications are in the areas of insulation and sponge-like floral foam. The resins are aqueous resoles catalyzed by NaOH at a formaldehyde/phenol ratio of ≈2:1. Free phenol and formaldehyde content should be low, although urea may be used as a formaldehyde scavenger.

2.2.4.16 Honeycombs

Honeycomb structures usually involve resin-treated papers and fiberglass, sometimes with a core filler and surface skins bonded to the honeycomb. Uses can be in aircraft interior panels as well as more demanding parts. Phenolic resin-impregnated aramid paper honeycomb cores have been developed for fighter aircraft applications. These new honeycom structures provide greater structural strength than other honecomb products currently available. One particular part application is the inlet cowl, which incorporates a complex structure, core machining, and core forming [51].

2.2.4.17 Spheres

Hollow spherical fillers have become extremely useful for the plastics industry and others. A wide range of hollow spherical fillers are currently available, including inorganic hollow spheres made from glass, carbon, fly ash, alumina, and zirconia; and organic hollow spheres made from epoxy, polystyrene, UF, and phenol–formaldehyde. Although phenol–formaldehyde hollow spheres are not the largest volume product, they serve in some important applications and show potential for future use.

2.2.4.18 Fibers

The principal type of phenolic fiber is the novoloid fiber [52]. The term novoloid designates a content of at least 85 wt% of a cross-linked novolak. Novoloid fibers are sold under the Trademark Kynol, and Nippon Kynol and American Kynol are exclusive licensees. Novoloid fibers are made by acid-catalyzed crosslinking of melt-spun novolak resin to form a fully cross-linked amorphous network. The fibers are infusible and insoluble, and possess physical and chemica properties that distinguish them from other fibers. Applications include a variety of flame- and chemical-

resistant textiles and papers as well as composites, gaskets, and friction materials. In addition, they are precursors for carbon fibers.

The fibers are prepared from a high molecular weight novolak resin. Uncured fibers are prepared by melt-spinning the novolak. These fibers are then immersed in aqueous formaldehyde solution containing an acidic catalyst. As heat is applied curing commences and the novolak resin is transformed into a cross-linked network through the formation of methylene and dibenzyl ether linkages. The final cross-linked structure is free of molecular orientation, and the density of cross-linking is low. The fiber contains ≈5 wt% unreacted methylol groups, which can be utilized in the formation of novoloid-fiber composites, or be reduced by heating the cured fiber to 180 °C.

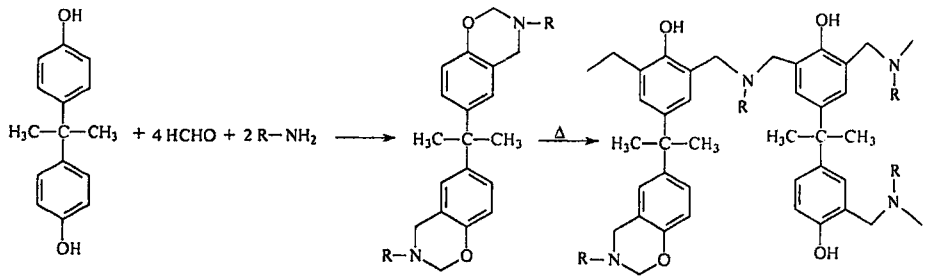
Applications for novoloid fibers include a variety of flame-resistant protective clothing, safety accessories, and flame barriers for upholstered furniture. As an asbestos replacement, novoloid fibers have been used in gasketing, packings, brake linings, and clutch facings. In electrical applications, novoloid fibers and papers can be used as flameproof coatings and as wrapping tapes in wire and cable applications.

2.3 Benzoxazines

Benzoxazines is interesting addition-cure phenolic system based on oxazine-modified phenolic resin that undergoes a ring-opening polymerization to give polybenzoxazine, which is effectively a poly(aminophenol). The precursors are formed from phenol and formaldehyde in the presence of amines. The choice for phenol and amine permits design flexibility and polymer property tailoring. The as-synthesized mixture consists of monomer, and oligomers that contain phenolic groups. For practical applications, the mixture is good enough, but for controlled structure and properties, the monomer is freed of the oligomers. The ring-opening polymerization can be catalyzed by acidic catalysts that permits a wide cure temperature. In the presence of acidic catalysts (e.g. phenols), the cure temperature window can be reduced from 160–220 °C to about 130–170 °C (i.e. a decrease of 30–50 °C). The synthesis and polymerization of BZ are depicted in (2.11).

2.3.1 Features of polybenzoxazines

These new materials, belonging to the addition cure phenolics family were developed to combine the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of advanced epoxy systems [53].



(2.11)

The polybenzoxazines overcome several shortcomings of conventional novolac and resole-type phenolic resins, while retaining their benefits. PBZ resins are expected to replace traditional phenolics, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in many respects. The molecular structure of PBZ offers super design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements. The physical and mechanical properties of these new polybenzoxazines are shown to compare very favorably with those of conventional phenolic and epoxy resins. The resin permits development of new applications by utilizing some of their unique features such as [54,55]:

- Near zero volumetric change upon polymerization
- Low water absorption
- Tg much higher than cure temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low CTE
- Low viscosity
- Excellent electrical properties

The high TGA decomposition onset temperature (for dihydroxy benzophenone–aniline system, it is ,400 °C) is attributed to the very strong intramolecular H-bonding between phenolic OH and the Mannich bridge. Char-yield as high as 82% has been

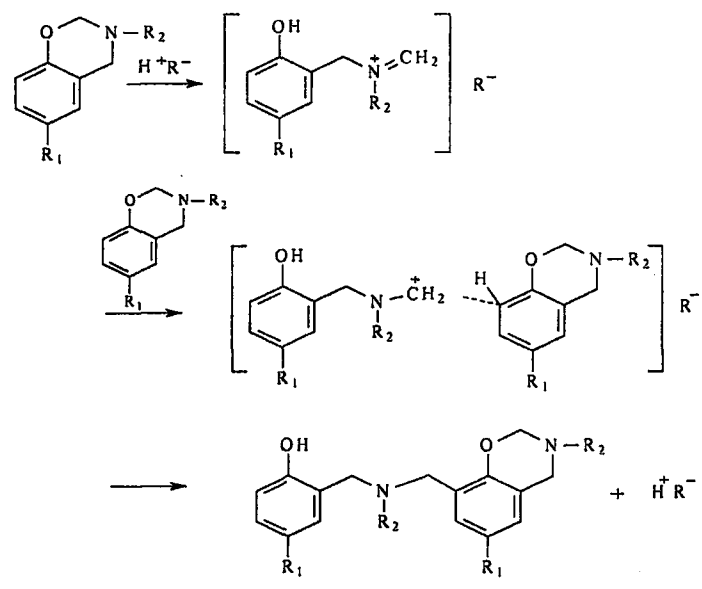
claimed. Their composites are comparable to polyimides and other high performance polymers, but are easily processable [56].

The ring-opening polymerization of these new materials occurs with either near-zero shrinkage or even with a slight expansion upon cure. It is proposed that the volumetric expansion of the BZ resin is mostly due to the consequence of molecular packing influenced by inter and intramolecular hydrogen bonding. The role of hydrogen bonding on the volumetric expansion has been studied by systematically changing the primary amine used in the BZ monomer synthesis.

In comparison to the other known expanding monomers and spiro ortho compounds, this resin has been shown to have a high potential for structural/engineering applications [57]. Polybenzoxazines have the lowest heat release during combustion and is therefore, more flame resistant, surpassing that of phenolics and polyetherimides, the current aerospace matrices of choice.

2.3.2 Cure mechanism and cure kinetics

Polymerization of BZ with a free ortho position can occur through a ring-opening reaction. No volatile by-products are evolved and no strong catalyst is required for the reaction [58]. The reaction site of the ring-opening polymerization in monofunctional aromatic amine-based BZ has been investigated through a systematic manipulation of the monomer chemistry [59]. The ionic ring openning reaction of polybenzoxazine is shown in 2.12.



(2.12)

Thus, selective protection or activation of sites on the arylamine ring towards electrophilic aromatic substitution has allowed a series of materials to be developed, which contain varying amounts of phenolic Mannich base bridges, arylamine Mannich base bridges, and methylene bridges. Electron-donating alkyl substituent groups at one or both the meta positions on the arylamine ring facilitate ring-opening/ degradation at lower temperatures. This opening of rings in a step other than the polymerization reaction greatly increases the numbers of methylene linkages.

The reaction was carried out at 140 °C for 5h. N,N-Bis (2-hydroxy-3,5-dimethylbenzyl) phenylamine and N-(2-hydroxy-3,5-dimethylbenzyl) phenylamine were isolated as the main products at an early stage. This result indicates that this compound produces several inter- and intramolecular rearrangement products. Based on these data, some possible reaction pathways were proposed. In the presence of p-toluene sulfonic acid monohydrate, 3,30[4,40-methylenediphenyl] bis(3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine) was isolated as one of the intermediates. The polymerization generally manifests autocatalysis. The ring-opening polymerization of BZ was monitored by rheological analysis utilizing both conventional isochronic and a new multi frequency approach that can observe the critical gel [60].

The activation energies were calculated for the process. The methylamine-based Bz has higher activation energy for the gelation process than the aniline-based one. The cure kinetics of BZ precursor has been analyzed by torsional braid analysis [61], and gelation and glass transition during curing were studied. Two specific glass transitions were obtained at the curing temperature of 220 °C. The time–temperature-transformation spectra were also generated. BZ is also cationically polymerizable [62]. Electrochemical polymerization of PBZ in acetonitrile/alkaline aqueous solution has also been reported [63].

2.3.3 Structure–property relations

The physical, mechanical and thermal properties of polybenzoxazines are primarily decided by the nature of the diphenol and the amine. The system derived from 4,40-dihydroxy benzophenone and aniline provides a combination of high thermal stability (5% weight loss at 400 °C) and high Tg (340 °C). Table 1 typically illustrates the structure–property relation for three different BZs [75]. It is seen that the thermal capability for dihydroxy benzophenone-based system is achieved at the

cost of mechanical performance. The impact property is good for PBZ derived from aliphatic amine.

Similar to BZs, naphthoxazines were obtained from hydroxy naphthalene with aniline and formaldehyde [68]. The polynaphthoxazine also showed a Tg higher than the cure temperature. Thermal properties in terms of the weight loss after isothermal ageing in static air, the decomposition temperature from thermogravimetric analysis, and the change of dynamic storage moduli at high temperatures also confirmed their superior thermal characteristics. Thus, the thermal and mechanical properties of polybenzoxazine thermoset networks containing varying amounts of phenolic Mannich bridges, arylamine Mannich bridges, and methylene bridges were investigated [66].

Table 2.2: Structure-property relation for polybenzoxazine [Bis benzoxazine formed from:1,2 and 3]. [59]

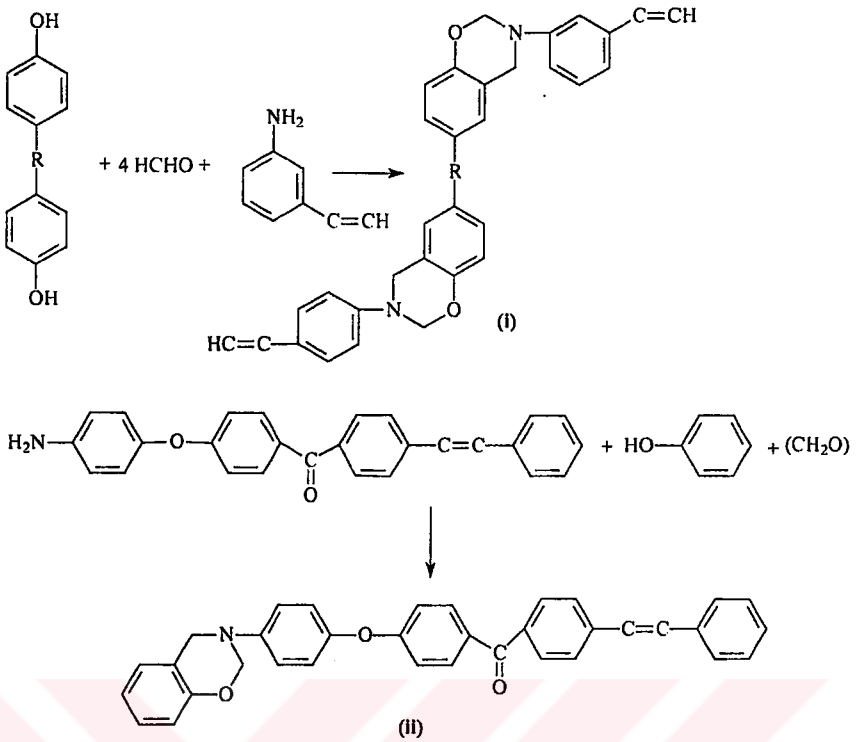
Properties	1. BPA+methyl amine	2. BPA + aniline	3. Dihydroxy benzophenone + aniline
Tensile Strength(MPa)	103	126	6.2
Tensile Modulus(GPa)	3.8	4.5	>6
Strain at break (%)	2.6	2.9	2.3
Impact strength(J/m)	31	18	-
Polymer Density	1.122	1.195	1.250
T_g (°C)	180	170	340

In materials based on, m-toluidine and 3,5-xylidine, the onset of thermal degradation is delayed until around 350 °C with no significant effect on the final char-yield. Materials with additional amounts of arylamine Mannich bridges and methylene bridges show improved mechanical properties, including higher crosslink densities and rubbery plateau moduli. Regulation of the viscosity of a difunctional BZ resin is achieved by addition of a monofunctional BZ monomer or a difunctional epoxy monomer as reactive diluents to further improve processibility [66].

The glassy state properties, such as stiffness at room temperature, are unaffected by the incorporation of the monofunctional BZs. The thermal stability of the monofunctional modified polybenzoxazine is not significantly affected below 200

°C. Properties sensitive to network structure, however, are affected. The incorporation of the monofunctional BZ reduces crosslink density and produces a looser network structure, while the difunctional epoxy increases crosslink density and leads to a more connected network structure. The relatively low crosslink density of BZ has been overcome by synthesizing pendant BZ functional vinyl polymer by reacting poly(4-vinylphenol) (VP) with formalin and aniline [67]. The pendant phenol polymer was obtained by homopolymerization of vinyl phenol (VP) or its copolymerization with butyl acrylate (VBP). The corresponding BZs (Va and VBa, respectively) were reacted with bisphenol A epoxy (DGEBA) and o-cresol novolac epoxy (CNE). The curing reaction proceeded rapidly at higher temperatures without a curing accelerator. The reaction induction time or cure time of the molten mixture from VP-based BZ and epoxy resin was found to decrease, in comparison to those of conventional BPA-based BZ and epoxy resin. The cured resins from VP-based BZ and epoxy resin showed higher Tg; mechanical properties, electrical insulation, and water resistance compared to the one from VP and epoxy resin (phenol–epoxy reaction) using imidazole as the catalyst. In the case of CNE, the net gain in Tg was not substantial. The improvement in flexural properties was also marginal. The electrical requirements of new printed wire boards are beyond the capabilities of epoxies.

The dielectric constant *D*k (3–3.5) and dissipation factor (0.006–0.012) of selected and structurally modified PBZ systems are inferior only to cyanate esters and they find application in printed wire boards [67]. Whereas selection of suitable precursors can lead to high char-yielding PBZ, this can also be achieved by the incorporation of additional curing sites such as acetylene on the BZ backbone.

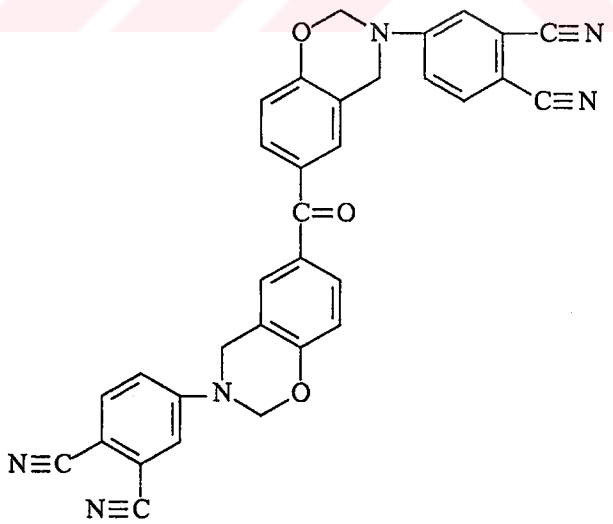


(2.13)

The synthesis is achieved using amino phenyl acetylene in place of amine. They are polymerized in the range 190–200 °C. DMA analyses showed a Tg of the order of 329–368 8C, much higher than those of the nonacetylene BZs [63]. The high thermal stability of this class of polybenzoxazines is a combined result of the independent polymerization of both the terminal acetylene groups and the BZ rings. The thermal capability is a combined effect of the acetylene and BZ as these properties are dependant also on the backbone structure. Mechanistic investigations revealed that the acetylene group polymerizes to form short chains of polyenes, almost simultaneously with the ring-opening polymerization of BZ [69].

In fact the thermal stability depends on the atmosphere of curing. Thus, polymerization in air conferred better thermal stability and char-yield than the polymerization done in an inert atmosphere. Both the ring-opening polymerization and the acetylene polyene formation are faster in air. The syntheses of two typical acetylene-containing polymers (i) with terminal acetylene and (ii) with phenyl acetylene groups are shown in (2.13) [70]. The phenyl ethynyl benzoxazine (structure ii) required very high cure temperature (i.e. 350 °C) for cure completion, typical of phenyl ethynyl group polymerization.

Another strategy to improve Tg and thermal stability is by fluorination of BZ. Thus, a fluorinated polybenzoxazine was synthesized by the ring-opening polymerization of hexafluoroisopropylidene-containing BZ monomer. Substantial development of Tg occurred at low degrees of conversion. The thermal stability also improved upon fluorination [71]. Fluorinated PBZ with fluorine groups on the amine (viz. 3,4-dihydro-3-pentafluorophenyl-2H-1,3-benzoxazine) was obtained in high yield from pentafluoroanilin [72]. This monomer, synthesized by a non-conventional route is a potential precursor for a polybenzoxazine in electronic applications in view of its low *D*k, low flammability, low refractive index, low coefficient of friction and high glass transition temperature. PBZ with phthalonitrile groups manifested good thermal characteristics [73]. The phthalonitrile-functional polybenzoxazines (Pth-PBZ, structure in (2.14) showed good char retention up to 80% at 800 °C. In air, the char-yield is up to 70% at 600 °C with T5 in the range 380–420 °C. Tg is in the range 275–300 °C. Unlike conventional phthalonitrile polymers, these systems require a relatively lower cure temperature, of the order of 250 °C. The unreacted nitrile groups react further during degradation accounting for the high char residue. The polymers are classified as flame resistant. The superior thermal stability is evident from the comparative thermal properties of different phthalonitrile-based polymer substantial.

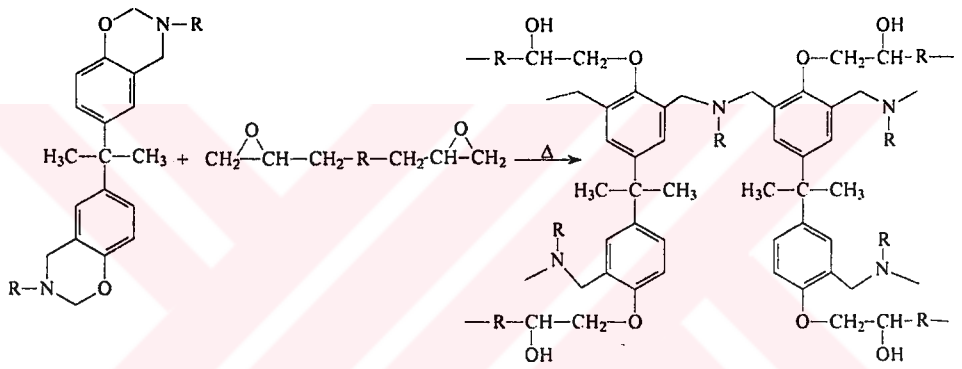


(2.14)

2.3.4 Reactive blending of polybenzoxazines

Despite high modulus and Tg; polybenzoxazines have surprisingly low crosslink density in comparison to other thermosets. Hydrogen-bonding is adequate to induce rigidity and constrain the mobility in the glassy state. The reactive blending with

epoxy resins allows the network to achieve higher crosslinking. The co-reaction proceeds via the ring-opening polymerization of BZ followed, by reaction of the generated phenol with the epoxy, probably catalyzed by the amine group. The proposed reaction sequences can be found in (2.15). Epoxy ring-opening by the generated amine is totally not ruled out. Copolymerization leads to a significant increase in the glass transition temperature [73]. Reaction of DGEBA with BPA-based benzoxazine (B-a) increased the Tg of the latter from about 143 to about 153 °C for an epoxy-content of 35%. Further increase in epoxy decreases Tg to below that of pure PBZ. The copolymer exhibits strain at breakage that is up to twice the strain for pure BZ and a flexural strength significantly improved with minimal sacrifice in modulus.



(2.15)

The flexural strength increased from 125 to 170 MPa on enhancing the epoxy-content to 50%. Interestingly, the increase is almost linear to the epoxy-content as shown in Fig.1. The modulus decreased from 4.4 to 3.4 GPa, translating to an increase in strain at break from 3 to 6.3%. A corresponding decrease occurred in the storage modulus determined by DMA. By understanding the structural changes induced by variations of epoxy-content and their effect on material properties, network can be tailored to specific performance requirements. Thermally stable systems resulted on using BPA based BZ as a hardener of the epoxy resin[74]. The curing reaction proceeded without any accelerator. The molding compound showed good thermal stability under 150 °C, which corresponded to the injection molding temperature. Above 150 °C, the curing reaction proceeded rapidly. The cured epoxy resin showed good heat resistance, water resistance, electrical insulation, and mechanical properties compared with the epoxy resin cured by the bisphenol-A type novolac. PBZ–EPOXY system has been projected as a high performance matrix for several applications [75]. These systems are processable by traditional techniques

such as prepreg, RTM and VRTM etc. for composite fabrication. The system, not requiring any refrigeration, is stable at ambient conditions indefinitely. Suitably formulated, their Tg can be boosted to ,200 °C, and they possess excellent mechanical properties and low moisture absorption.

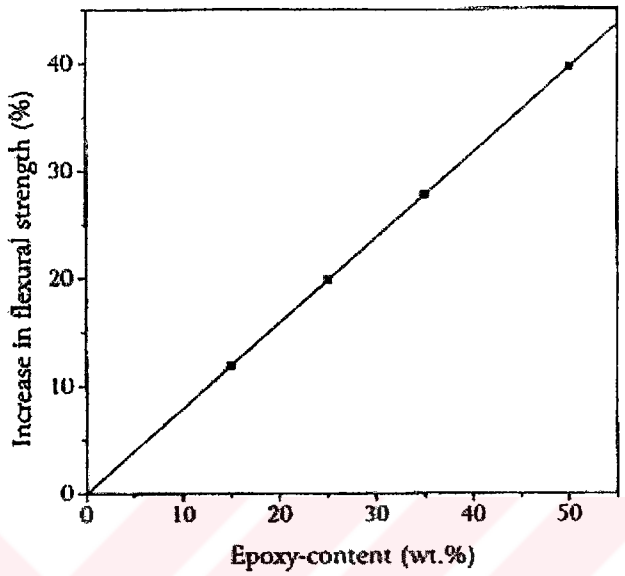
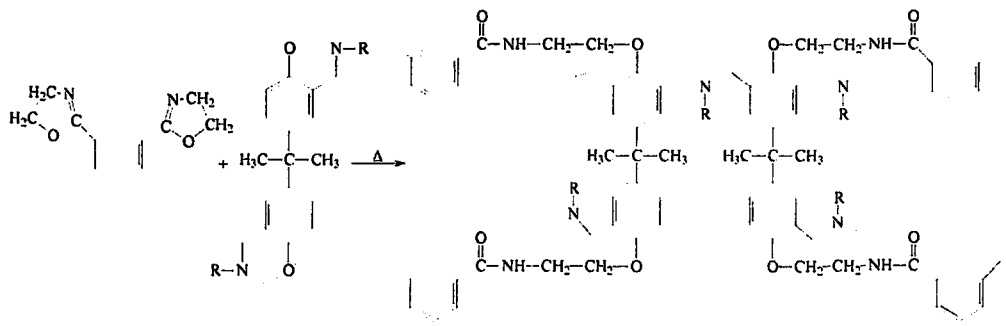


Figure 2.1: Relative increase in fluxtural strenth with epoxy-content for polybenzoxazineepoxy blend.

BZ can be used for functionalization of the polymeric systems as a means of cross linking. Thus, polysiloxanes are fictionalized with these groups and their adhesion properties in glass fiber-reinforced composites are improved [76]. BPA-based BZ can be cured by bisoxazoline in the presence of triphenylphosphine as a catalyst at 170 °C [77]. The blend is processable by melt impregnation, RTM etc. The phenolic hydroxyl groups generated by the ring opening reaction of the BZ ring react with the oxazoline ring at 200 °C as shown in (2.16) completed in less than 30 min at this temperature as evident from DMA. The system flows easily at 100–140 °C, and has good thermal stability. The melt viscosity of the molding compound is around 0.1–1.0 Pa s at 140 °C, even after 1.5 h, but increases rapidly at 180 °C.



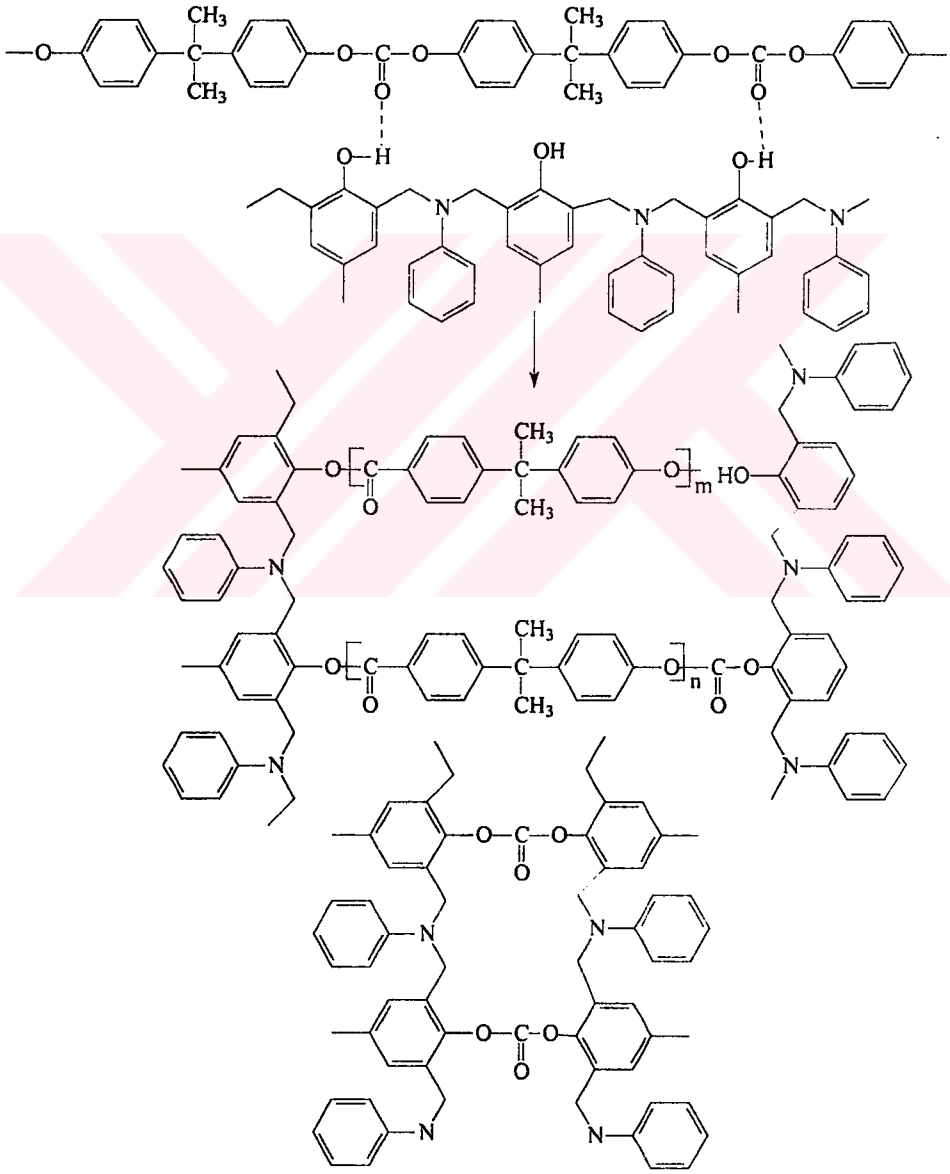
(2.16)

The cured resin showed good heat resistance (Tg ,195 °C), water resistance (0.28% absorption), electrical insulation (volume resistivity of 3.5 £ 1016 ohm cm), and mechanical properties (KIC ,0.93 MPa m1/2), that are only marginally superior to cured resin from BPA-type novolac and bisoxazoline. On the other hand, when BPA-based benzoxazine (B-a) containing oligomers (oligo-B-a) was cured with bisoxazoline, the cure time and temperature could be lowered, compared with those from pure B-a and bisoxazoline [75]. Above 160 °C, the curing reaction of oligo-B-a with bisoxazoline (1,3-PBOX) proceeded more rapidly than that of B-a with bisoxazoline. The cured resin from oligo-B-a and bisoxazoline showed better heat resistance (Tg -232 °C) and water resistance (0.23 absorption), than the cured resin from B-a and bisoxazoline. However, the fracture toughness showed a reverse trend (KIC-0.75 against 0.93 MPa m1/2 for the latter). In another study, two poly functional BZ monomers, viz. 8,80-bis (3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) and 6,60-bis(2,3-dihydro-3-phenyl-4H-1, 3-benzoxazinyl) etone, were co-cured in an autoclave [79]. These two polybenzoxazines showed mechanical and thermal properties similar to or beter than BMIs and some polyimides. They also showed very high char-yield after carbonization in a nitrogen atmosphere. Thermally stable blends result when phenyl nitrile functional BZs are blended with nitrile systems and cured [80]. Ortho-, meta-, and paraphenylnitrile-functional BZs were polymerized at different compositions with phthalonitrile-functional monomers, providing copolybenzoxazines of high thermal stability and easy processibility. The copolymer char-yield increased from 59 to 77 wt% and Tg from 180 to 294 8C with only 30 mol% of phthalonitrile-functional monomer.

2.3.5 Non-reactive blends and composites of benzoxazine

PBZ is amenable for matrix modification by fillers, reinforcements and polymer blends. The thermal properties of physical blends containing BZ monomer and polycarbonate (PC) were studied by non-isothermal DSC, TGA and FTIR [81]. The ring-opening reaction and subsequent polymerization reaction of the BZ were inhibited significantly by the presence of polycarbonate. The glass-transition temperature of the resulting blends decreased as the concentration of polycarbonate increased and deviated markedly from the Fox equation. An earlier degradation event appeared in the blend with 11 and 33 wt% of PC. Intermolecular hydrogen bonding between PC and cured polybenzoxazine appeared after 1h of isothermal curing at

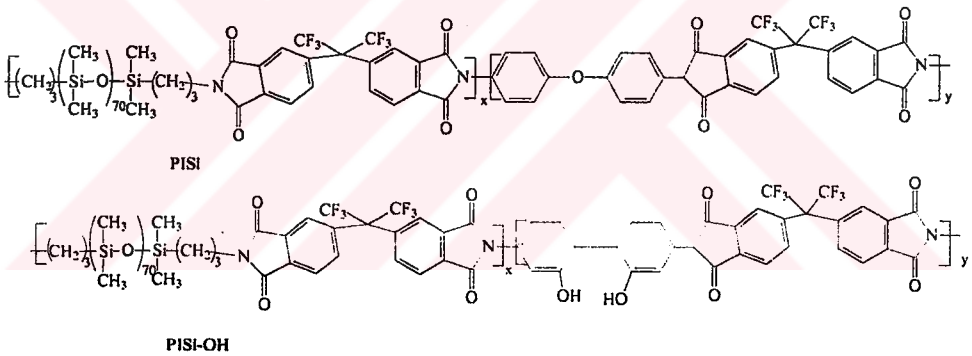
180 °C, and continued throughout the entire curing process. Subsequent studies confirmed a possible cross-reaction between PC and the ringopene BZ that led to PC-grafted and PC-cross linked PBZ [82]. The chain fragmentation in PC and polybenzoxazine blend upon thermal polymerization was investigated by size exclusion chromatography. Molecular weight reduction of PC via trans esterification between the hydroxyl groups of ring-opened BZ and the carbonate groups from PC was observed. In addition, excess heat of reaction compared to the expected value was detected from DSC and was assigned to the exotherm associated with the exchange reaction.



(2.17)

The proposed PBZ-PC interaction leading to grafts and crosslinks is shown in (2.17). Improved systems are reported to result due to synergism on melt blending BZ resins with poly(1-caprolactone) (PCL) [83]. The PCL-content was varied in the range 0–

15 wt%. The Tgs of the BZ blends were found to be slightly lower than that of neat polybenzoxazine resin. The blends showed improved mechanical properties, including higher crosslink densities, rubbery plateau moduli, and flexural strengths compared to pure polybenzoxazine. Unlike the previous case of PC-modification, the thermal stability at the mid-temperature range was enhanced, evident from the delayed onset of decomposition temperature and the disappearance of the first degradation event. However, at higher PCL loading, only one Tg resulted, and the Tg value of the resulting blend appeared to be higher in the blend with a greater amount of PCL [81]. Phase separatio occurred when a BZ monomer (B-a) was blended with soluble poly(imide–siloxane)s [84]. The soluble poly(imide–siloxane)s with and without pendent phenolic groups (structures PISi–OH and PISi, respectively, in (2.18) were prepared from the reaction of 2,20-bis(3,4-dicarboxylphenyl) hexafluoropropane dianhydride with a,v-bis(aminopropyl) dimethylsiloxane oligomer (PDMS; molecular weight ¼ 5000) and 3,30-dihydroxybenzidine or 4,40-diaminodiphenyl ether.



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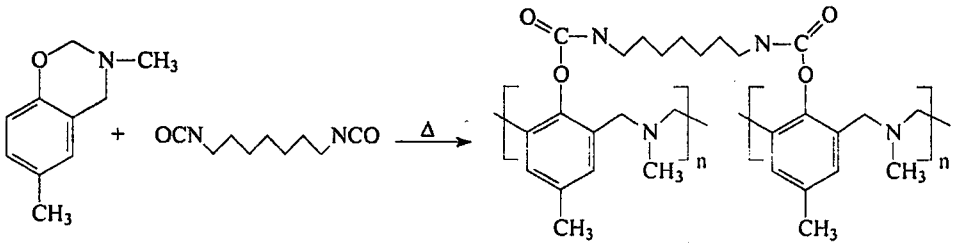


(2.19)

In the presence of poly(imide–siloxane)s, the cure onset shifted from 200–240 to 130–140 °C. Viscoelastic measurements of the cured blends containing poly(imide–siloxane) with OH functionality (i.e. PISi–OH) showed two glass-transition temperatures, one at 255 °C and another at around 250–300 °C, indicating phase separation between PDMS and the combined phase consisting of polyimide and

polybenzoxazine components, due to the formation of AB crosslinked polymer. For the blends containing PISi, however, in addition to the Tg due to PDMS, two Tgs were observed in high-temperature ranges, 230–260 and 300–350 °C, indicating further phase separation between the polyimide and PBa components due to the formation of semi-interpenetrating networks. In both cases, Tg increased with increasing poly(imide–siloxane)-content. Thus, the Tg of PBa increased from 160 to about 300 °C on enhancing the polyimide siloxane-content to 20% in the case of PiSi–OH. For PISi, the Tg increase was to about 225 °C.

As the siloxane-content increased, tensile strength and modulus decreased implying an improved toughness caused by the addition of poly(imide–siloxane). The thermal stability of PBa also was enhanced by the addition of poly(imide –siloxane) [85].

Urethane–benzoxazine copolymer films were prepared by blending a monofunctional BZ monomer, viz.3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa), and polyurethane (PU) prepolymer that was synthesized from 2,4-tolylene diisocyanate and polyethylene adipate polyol (Mw , 1000) in 2:1 molar ratio, followed by casting as films and thermal curing at 190 °C [86]. Their synthesis is depicted in (2.19). The poly(urethane–benzoxazine) films exhibited only one glass transition temperature, indicating good miscibility between PU and polybenzoxazine (Pba) due to the in-situ copolymerization of B-a and PU prepolymers. The Tg of the polyurethane was enhanced with increased Pba-content. Films containing less than 50% of Pa had the characteristics of an elastomer, with an elongation at break of more than 200%. These elastic films exhibited good resilience with excellent reinstating behavior. Films containing more than 60% of Pa had the characteristics of a plastic. Up to 15% Pba, the films were elastomeric with tensile strength of the order of 2–6 MPa. The value shot up to the range 280 MPa when the Pa-content exceeded 15%. The variations in tensile strength and elongation for different copolymers illustrating their evolution from elastomer to plastic nature, are shown in Fig.2. Poly(urethane–benzoxazine) films showed excellent resistance to solvents such as THF, DMF, NMP and DMSO [87].

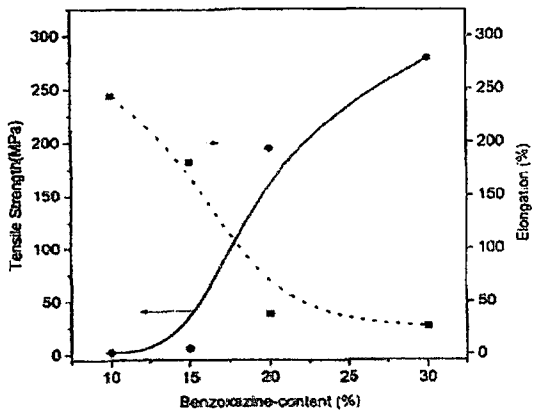
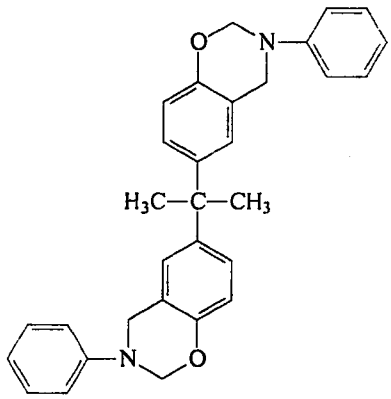


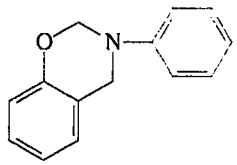
Figure 2.2: Variation of mechanical properties with polybenzoxazine-content for benzoxazine-modified PU film.

Amine-terminated butadiene–acrylonitrile copolymer (ATBN) and CTBN were introduced to polybenzoxazine by modification of the monomer prior to curing. On a comparative scale, ATBN is more effective than CTBN in improving the fracture toughness of PBZ [88]. This was attributed to the better distribution of rubber particles in an ATBNmodified matrix than for the CTBN-modified one. DMA confirmed the existence of two networks in the ATBN-modified matrix [89]. The BZ resin permits compounding with a variety of additives, including nanoparticles such as montmorillonite, to make nanocomposites [90,91]. Thus, polybenzoxazine–clay hybrid composites were prepared from a BZ precursor based on BPA and aniline or bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane, (B-a, structure in (2.11)) and surface treated montmorillonite. The dispersity of organically modified montmorillonite (OMMT) at the molecular level in the polybenzoxazine matrix was confirmed by XRD. The Tg of the hybrid material was enhanced vis-a`-vis the base polymer. The reinforcement effect of OMMT was reflected in the enhanced high temperature storage modulus of the composite. The additive also delayed the thermal decomposition of the matrix in the high temperature regime. The isothermal degradation studies indicated good thermal stabilization. This was attributed to the formation of OMMT nano-barriers minimizing the permeability of volatile degradation products in the material. Several types of polybenzoxazine/clay hybrid nanocomposites have been prepared from OMMT and mono- or bifunctional benzoxazine{3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa) or bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (B-a), respectively} [92]. OMMT was prepared by a cation exchange of MMT with ammonium salts of amines such as tyramine, phenylethylamine, aminolauric acid, and dodecyl amine, with the

structures given in (2.20). Strong hydrogen-bonding existed between PBZ and poly(N-vinyl-2-pyrrolidone) (PVP) on blending the two polymers, via interaction between OH group of phenol and the carbonyl groups of PVP. This caused a positive deviation in the Tg-versus composition curve for the two systems. A Tg maximum was observed at around 50/50 composition of the two components as seen in Fig.3.

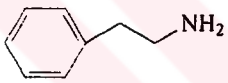


Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane. (B-a)

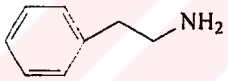


3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa)

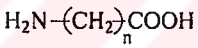
(2.20)



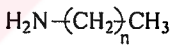
Phenyl ethylamine



Tyramine



Aminolauric acid



Dodecylamine

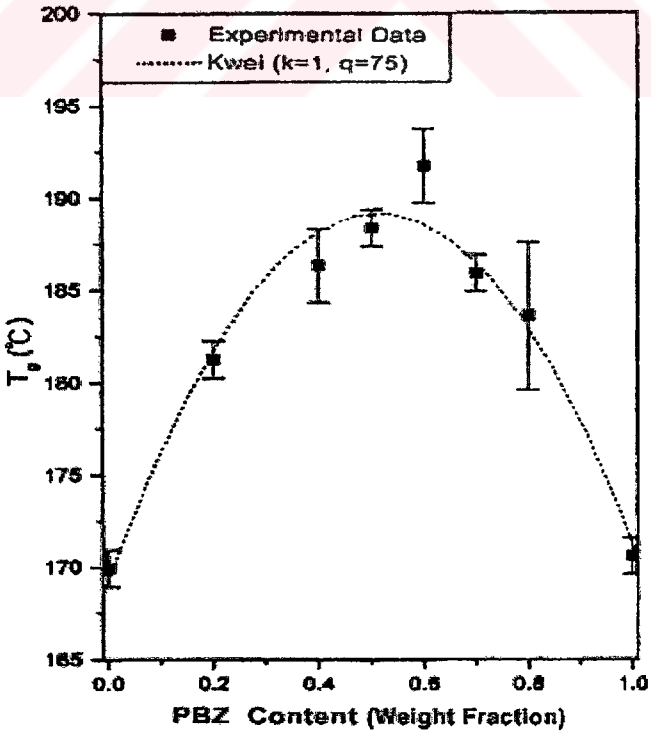


Figure 2.3: Dependence of *T*g on blend composition for polybenzpxazine/poly(*N*-vinyl-2-pyrrolidone) system.

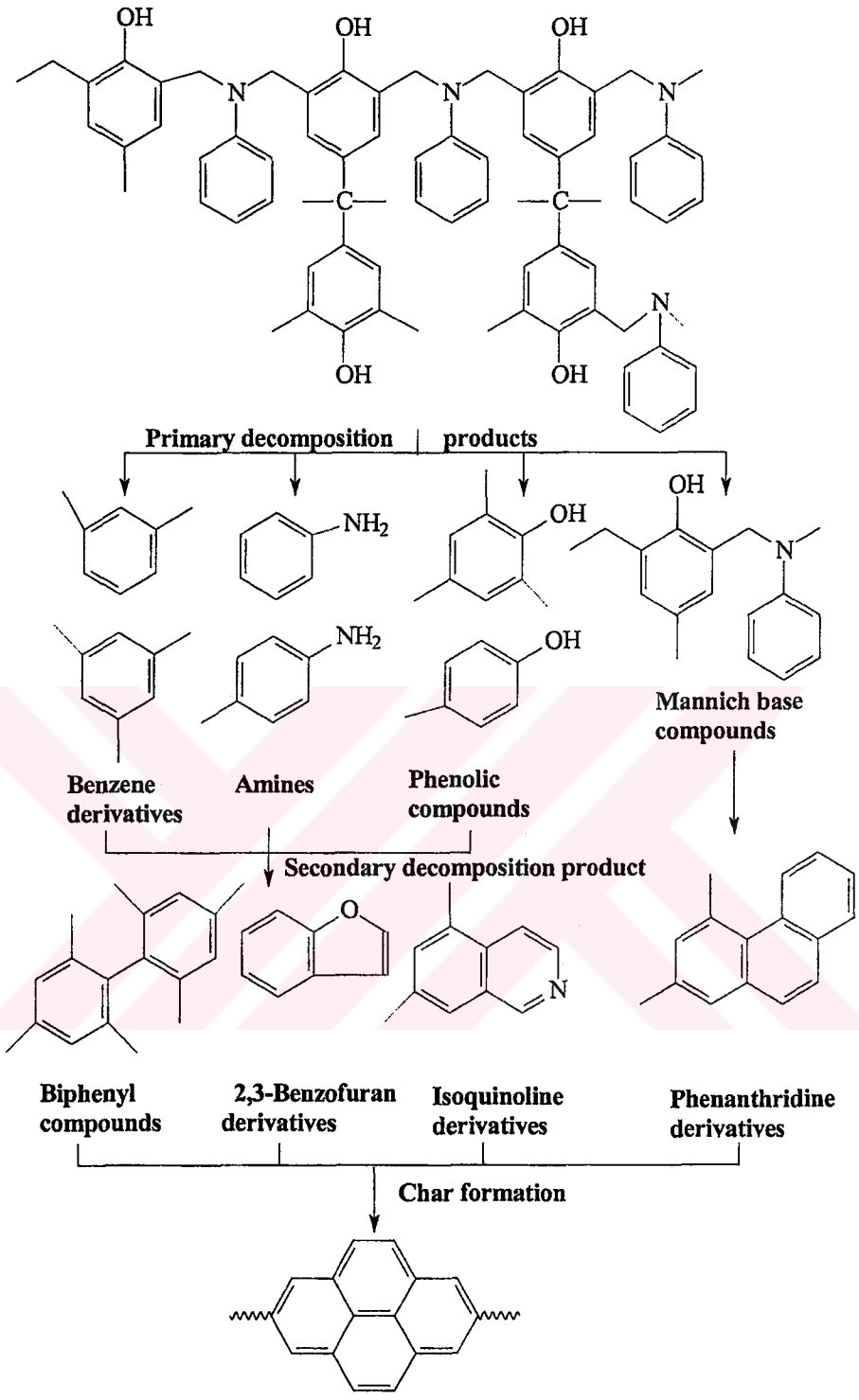
The Tg-composition curve conformed to the Kiwi equation, accounting for specific polymer–polymer interaction. These interactions were corroborated by FTIR investigations [93]. Polybenzoxazine/clay nanocomposites were prepared by both melt method and solvent methods.

XRD measurements of the nano composites showed that the blending method and the kind of solvent play crucial roles in the dispersion of OMMT in the polybenzoxazine matrix. The inclusion of any type of OMMT significantly lowered the curing exotherm of BZs. The hybrid nanocomposites exhibited higher Tg; higher modulus and enhanced thermal stability. The effect of clay was more significant at around 2–5 wt % loading. The blending also reduced the exothermicity of curing significantly. An immiscible polymer–clay nanocomposite has been synthesized, consisting of dispersed layers of OMMT in a polybenzoxazine matrix, as shown by thermogravimetry, wide-angle X-ray diffraction (WAXD), and TEM [94]. Protonated amines showed high ion-exchangeability. The spacing of the silicate layers was strongly dependent on the size or molecular weight of the amine derivative and the solvent type. Binary solvents (5% methanol in toluene) exhibited superior ability to swell OMMT. WAXD results revealed that the silicate layer expansion of all polybenzoxazine-OMMT nanocomposites prepared from either melt or solution methods were similar, with about a 48 A increment. This was correlated with TEM results that showed the aggregation of silicate layers, indicating that all prepared OMMT are immiscible with the polymer matrix. The compatibility between amine modifying agents and BZ dictated the characteristics of the nanocomposites. The curing reaction in the synthesis of polybenzoxazine–montmorillonite (MMT) nanocomposites shows autocatalytic characteristics for fairly good conversion range [95]. Inclusion of boron nitride, on the other hand, results in highly conducting polybenzoxazine composites [96]. The reduced heat of reaction and increased exothermic peak temperature indicated that the boron nitride surface is inhibiting the BZ polymerization reaction [97]. Incorporation of Kenaf fiber in a polybenzoxazine resin matrix to form a unidirectional reinforced composite resulted in systems with enhanced flexural property [98]. Compounding by calcium carbonate leads to good particulate-filled PBZ composite [99].

2.3.6 Degradation of polybenzoxazine

2.3.6.1 Thermal stabilization and degradation

Polybenzoxazines are thermo-oxidatively stable. This is exemplified by the superposition of the thermograms of the cured resin in air and N_2 [100]. It has been shown that the thermal stability of polybenzoxazines is substantially improved further by reactive amines. Various diphenols are found to have some effect on the thermal stability of this series of polybenzoxazines. Nitrogen-containing phenolic resins are also non-flammable polymers [101]. A study on their thermal decomposition revealed that PBZ decompose by loss of amine fragments [102]. Hence, one strategy for thermal stabilization is to introduce cross-linking sites on the amine moieties. Thus, propargylation was an effective means for thermal stabilization. The introduction of ethynyl [68,69,102] and nitrile [69,77] groups in the backbone has been fruitful for conferring thermal stability. It has been seen that thermally stable phenol precursor such as naphthols also ensures thermal stability for the resultant PBZ [64]. The structural modifications and compounding conducive to enhanced resistance to thermal degradations of PBZ have been discussed at different points in the preceding sections. Ishida et al identified the decomposition product of aromatic amine based polybenzoxazines through TGA and GC-MS techniques [103]. Several degradation products were identified, derived from the degradation of the polymer and the recombination of the degradation products. Benzene derivatives, amines, phenolic compounds and Mannich base emergedirectly from the polymer. Benzofuran is derived from further degradation of phenols. Biphenyl compounds are obtained from recombination of phenyl radicals after the loss of substituents form benzene, amine and phenol derivatives. Isoquinoline and phenathridine derivatives result from Mannich base by loss of OH groups and dehydrogenation. The overall degradation pattern is shown in (2.21). This team also investigated the thermal decomposition processes of a model compound containing a Mannich bridge and a series of polybenzoxazine model dimer, with moreor-less similar observations [104]. In this case, the 2,4- dimethylphenol-based BZ dimers degraded into smaller and highly volatile compounds, leaving no char at the end of degradation.



(2.21)

The p-cresol-based BZ dimers also degraded into smaller and highly volatile products. Some of these are able to undergo cross linking and aromatization processes and form char. The major decomposition products for modified, p-cresol-based dimers are amines and ester compounds.

2.3.6.2 Chemical degradation of PBZ

As the network contains basic amine groups, the stability of polybenzoxazines in acid medium is doubtful. The chemical stability of typical polybenzoxazines based on bisphenol-A and primary amines in a carboxylic acid solution has been studied [105]. It was found that the Mannich base is stable. It is proposed that the nature of the primary amine is responsible for the interactions between the carboxylic acid and the Mannich-base model dimers. As a result, the chemical stability of polybenzoxazines may also be related to the nature of the amines, which, in turn, influence the strength of the hydrogen-bonded network structure that develops upon cure. While aniline-based BZ was stable in acidic medium, that based on methylamine disintegrated into small fragments. The strong salt formation between the more basic Mannich bases from the former disrupts the hydrogen-bonding network and triggers the degradation. The rapid degradation of certain BZs in acid medium was attributed to macroscopic stres cracking.

2.3.6.3 UV stability of PBZ

The UV stability of PBZ has also been investigated [106]. Carbonyl-containing species were formed when B-a resin was exposed to ultraviolet radiation (1 .290 nm) in ambient air at room temperature. The isopropylidene linkage was the reactive site of cleavage and oxidation, resulting in the formation of a 2,6-disubstituted benzoquinone. Interestingly, the Mannich bridge was neither cleaved nor oxidized. A comparative UV exposure study has been performed on polybenzoxazines containing the same amine (methylamine), but with phenolic units possessing various substituents on the para-positions of the phenyl rings [107]. B-a is shown to have the highest degree of substituted benzoquinone formation followed by those polymers derived from hydroquinone, 4,40-(hexafluoroisopropylidene) diphenol, 4,40-thiodiphenol, 4,40-dihydroxybenzophenone, p-cresol and phenol. The nature of the para-position in phenolic substituents was found to have an impact on the oxidation process affecting the degrees of substituted benzoquinone formation. Some secondary reactions were also found to occur as a result of photooxidation.

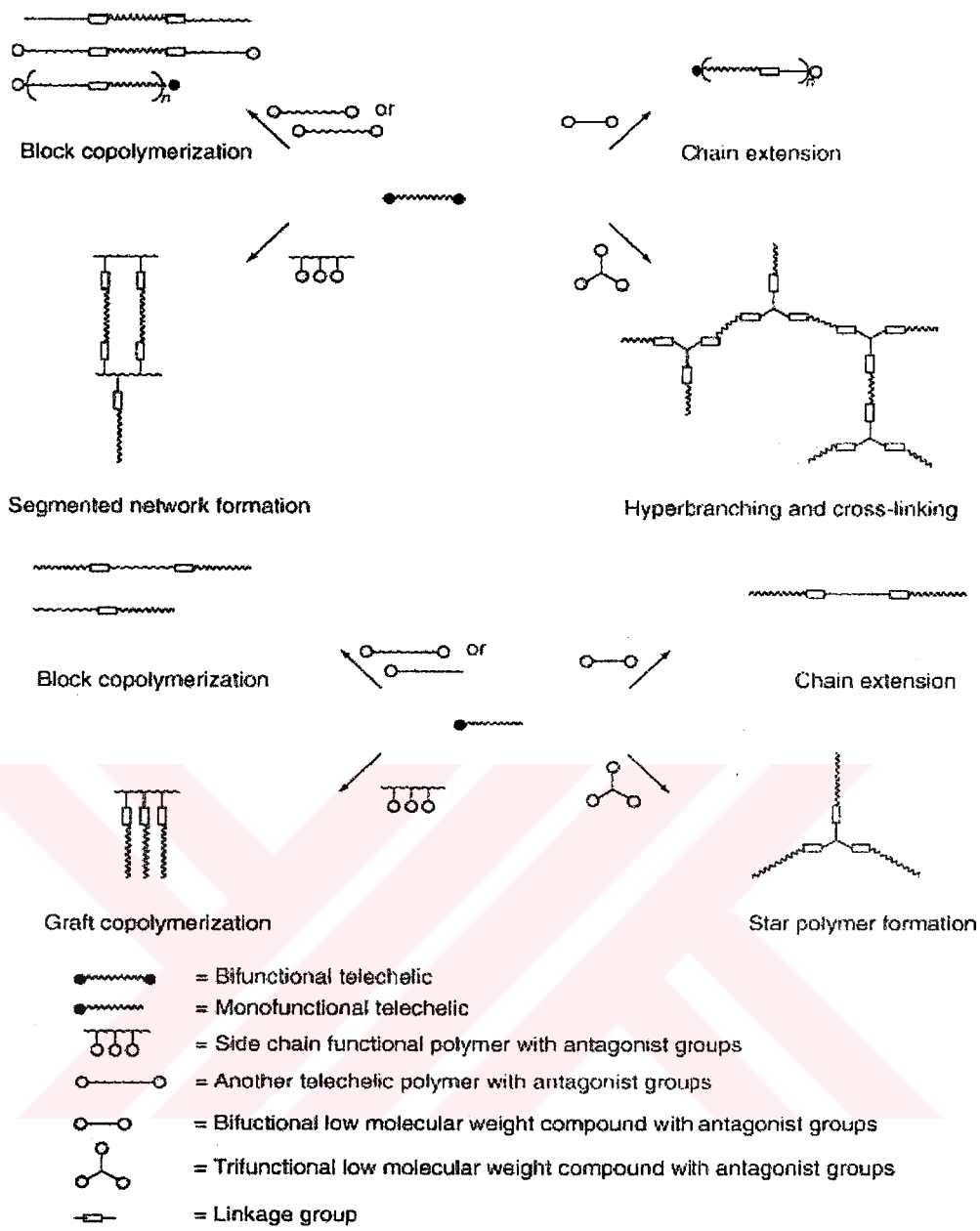
2.4 Telechelic Polymers

2.4.1 Introduction To Telechelic Polymers

Telechelic polymers are defined as macromolecules that contain two reactive end groups. A pioneering work on the synthesis functional polymers and their conversion to the final products with specific properties by reacting with functional groups may be dated back to 1947 [108]. However, the concept was not fully recognized until 1960 [109]. Significant contributions to the development of this class of polymeric materials are still found in the current literature. In the last decade there has been a rapid growth in the development and understanding of new controlled radical polymerizations [110]. Precise control of functionality, molecular weight, and uniformity (molecular weight distribution) can now be made not only by ionic polymerization routes but also by newly developed living radical polymerization (qv) techniques. Another striking development has been achieved in the metathesis polymerization. Many new catalysts have been developed and applied to preparation of advanced materials [111-115] . The range of monomers and functional groups used in the preparation of telechelic polymers has been expanded in recent years as a result of such developments. This article describes the general techniques for the preparation of telechelics. A special emphasis has been placed on controlled radical and metathesis polymerization methods. A polymer can be considered to be telechelic if it contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multifunctional telechelics (polytelechelics) [116]. The functionality is defined as (2.22).

$$f = \frac{\textbf{Number of functional groups}}{\textbf{Number of polymer chains}} \qquad (2.22)$$

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and hyper-branched or dendric polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Various macromolecular architectures obtained by the reactions of telechelics are represented in (2.23) [117].



(2.23)

The functionality of the end group itself is important. When such groups are bifunctional (eg, vinyl groups) they can participate in polymerization reactions, yielding graft copolymers or networks; such telechelic polymers are called macromolecular monomers, macromonomers, or macromers. Industrial interest in telechelics was stimulated by the development of thermoplastic elastomers, which consist of ABA block and multiblock copolymers. Liquid telechelic polymers are the basis for reaction injection molding. Liquid telechelics that can be used for network formation offer processing advantages and may result in materials with improved properties [118].

2.5 Jeffamines

The Jeffamine, polyoxyalkyleneamines contain primary amino groups attached to the terminus of a polyether backbone. Jeffamine Reagents as polymeric precipitants "similar" to the polyethylene glycols. They are thus "polyether amines." The polyether backbone is based either on propylene oxide (PO), ethylene oxide (EO), or mixed EO/PO.

Poly(propyleneoxide) amines, also called as Jeffamines, are used as epoxy curing agents and lead tough, clear, impact-resistant coatings (for decoupage and furniture, reinforced composites, electrical encapsulation, and lamination), castings, and adhesives. They are light in color, low in viscosity and completely miscible with a wide variety of solvents. In addition, the utility of PPOA with Mw up to 2500 as intermediates in preparation of acrylates that are used as ultraviolet light-curible buffer coatings and top coatings for optical fibers[4]. Furthermore, surface moisture absorption ability and, therefore, surface electrical resistivity [119] can easily be adjusted by the segmental length of the Jeffamines. Jeffamines can be in the form of monoamine, diamines, and triamines which are available in variety of molecular weights. Therefore, telechelic poly(propyleneoxide) amines can be used as cross-linkers, chain extenders, and precusors for block and graft copolymers.

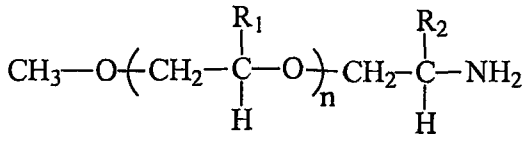
Jeffamines are synthesized as either monoamines (M-series), diamines (D series), or triamines, and are made in a variety of molecular weights, ranging up to 5,000. The ED-series are aliphatic diamines structurally derived from the propylene oxide capped polyethyleneglycol.

The wide range of molecular weights, amine functionality, and oxide type and distribution provides flexibility in synthetic design of compounds made from Jeffamine Reagents. For the most part, Jeffamine Reagent products undergo typical amine reactions and are low viscosity liquids, exhibiting low vapor pressure.

2.5.1 Jeffamine Monoamines

The Jeffamine monoamines are designated as the Jeffamine M series. The M is representative of the fact that they are Monoamines. The number designation after the letter M represents the approximate molecular weight.

Jeffamine M-series products are prepared by reaction of a monohydric alcohol initiator with ethylene and/or propylene oxide, followed by conversion of the resulting terminal hydroxyl group to an amine. M-series products have the structure (2.24).



(2.24)

Table 2.3: Molecular Weights of Jeffamine M Series

Product	Mol. Ratio PO/EO	Approx. Mol. Wt.
XTJ-505 (M-600)	9/1	600
XTJ-506 (M-1000)	3/19	1000
XTJ-507 (M-2005)	29/6	2000
JEFFAMINE M-2070	10/31	2000

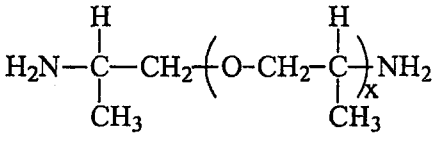
XTJ-505 and XTJ-507 products are predominately PO based, whereas XTJ-506 and Jeffamine M-2070 products are predominately EO based and are therefore more hydrophilic.

2.5.2 Jeffamine Dimines

The Jeffamine diamines are the D series and the ED series.

2.5.2.1 Jeffamine D Series

The D-series products are amine-terminated polyoxypropylene diols. They have the structure (2.25).



(2.25)

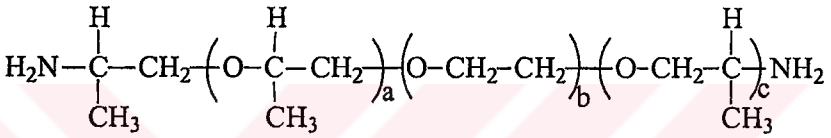
Table 2.4: Molecular Weights of Jeffamine D Series

Jeffamine Product*	X	Approx. Mol. Wt.
D-230	2-3	230
D-400	5-6	400
D-2000	33(Avr.)	2000
D-4000	68(Avr.)	4000

*Calculated by assuming product is all diamine. However, product is a mix of 86/ 14 diamine/ aminoalcohol.

2.5.2.2 Jeffamine ED Series

The Jeffamine ED-series products are polyether diamines based on a predominantly polyethylene oxide backbone. This imparts complete water solubility to each of the members of this series. The Jeffamine ED-series products have the structure (2.26).



(2.26)

Table 2.5: Molecular Weights of Jeffamine ED-series

Product	Approx.Value (a)	Approx.Value (b)	Approx. Mol. Wt.
HK-511(XJT-511)	2.0	2.0	220
XJT-500(ED-600)	9.0	3.6	600
XJT(ED-2003)	38.7	6.0	2000

The added hydrophilicity of the ED-series products has particular utility.

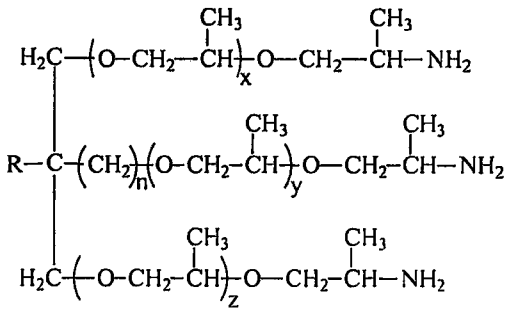
2.5.3 Jeffamine Triamines

Currently there are three Jeffamine T-series products— Jeffamine T- 403, XTJ- 509 (T-3000), and Jeffamine T-5000 triamines.

2.5.3.1 Jeffamine T Series

The T-series products are propylene oxidebased triamines and are prepared by reaction of PO with a triol initiator, followed by amination of the terminal hydroxyl groups. They are exemplified by the following structure (2.27).

TMP:trimethylolpropane; 2,2bis(hydroxymethyl)-1-butanol

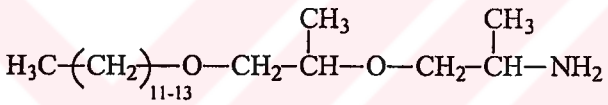


(2.27)

2.5.4 Jeffamine Surfonamine Monoamine Series

The Surfonamine products are monofunctional amines similar to the M-series. They are oleophilic and not water soluble.

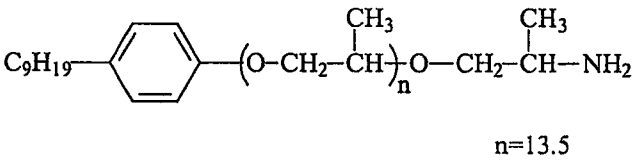
2.5.4.1 Surfonamine S ML-300 Chemical Intermediate



(2.28)

Surfonamine ML-300 is a monoamine derived from a propylene oxide adduct of a C12-14 alcohol. Use of this product is restricted solely to use as a chemical intermediate.

2.5.4.2 Surfonamine MNPA-1000



(2.29)

Surfonamine MNPA-1000 is a 1000 molecular weight, nonylphenol initiated, polyoxypropylene glycol derived monoamine.

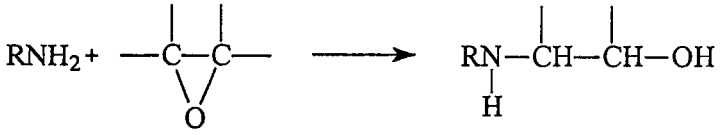
2.5.5 Chemical Reactions

Jeffamine polyoxyalkyleneamines undergo *reactions typical of primary amines*. General reactions which have proven to be useful include those listed below in the form (2.30).

$$\text{JEFFAMINE amine} + \text{Reactant} \longrightarrow \text{Product}$$

$$\text{Reactant} \longrightarrow \text{Product} \tag{2.30}$$

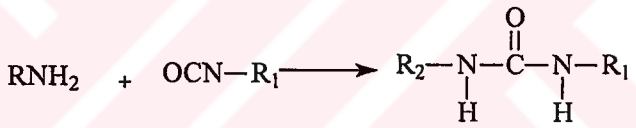
Epoxy reactions occur by the non-catalyzed addition of epoxides to Jeffamine amines. This alkoxylates each NH functionality to produce aminoalcohols.



(2.31)

Epoxides ("epoxy resins") Aminoalcohols

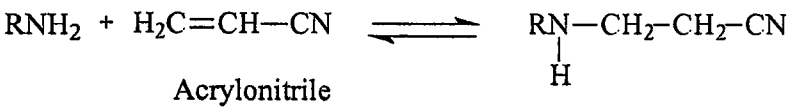
Polyurea linkages are formed from the rapid, uncatalyzed reaction of Jeffamine amines with polyisocyanates. When spray process, this reaction has found great commercial utility in a variety of applications including castings, coatings, and sealants.



(2.32)

Isocyanates Ureas

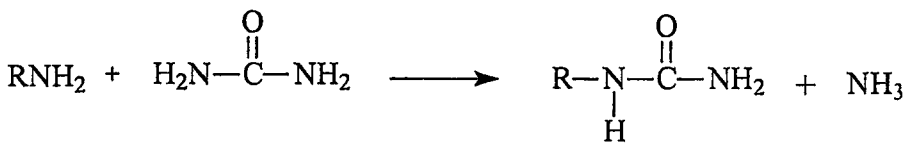
The Michael addition of an activated double bond compound to a Jeffamine amine is a reversible reaction.(Acrylonitrile addition leads to a cyanoethylated product that can be catalytically hydrogenated to a non-reversible and stable aminopropylated polyetheramine.)



(2.33)

Acrylonitrile Cyanoethylated amines

Substituted ureas are formed by heating Jeffamine amines with urea at temperatures of 125-175°C, while removing ammonia. This will result in mono-and di-substituted ureas.



(2.34)

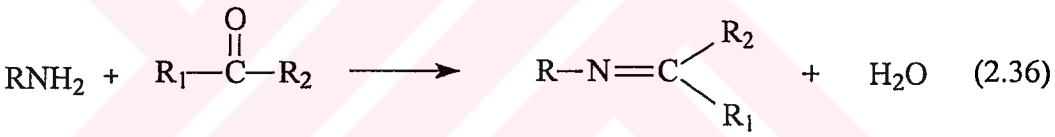
Ureas Substituted ureas

Amides can be formed from the Jeffamine amine by an acid-catalyzed reaction with carboxylic acids, lactams, or anhydrides, or by ester-amide interchange reactions.

(2.35)

Carboxylic acids (or esters, anhydrides, etc.) Amides

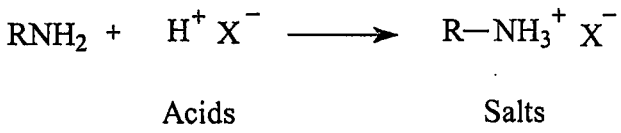
Imines, or Schiff bases, are formed by reacting the Jeffamine amines with aldehydes or ketones, at elevated temperature, while removing water.



(2.36)

Aldehides or ketones Imines

Salts of Jeffamine amines may be readily formed with a variety of organic and inorganic acids.



(2.37)

Acids Salts

3. EXPERIMENTAL

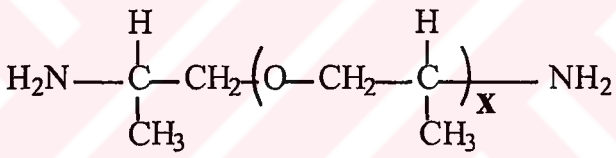
3.1. Materials and Chemicals

3.1.1. Materials

- Jeffamines series: D-230, D-400, D-2000, T-403, T-5000 (with Mw: 230, 400, 2000, 403, 5000, Huntsman)
- *p*-formaldehyde (Merck)
- 2-napthol (Merck)

were purchased and used as received.

3.1.1.1. Diamine Series of Jeffamines

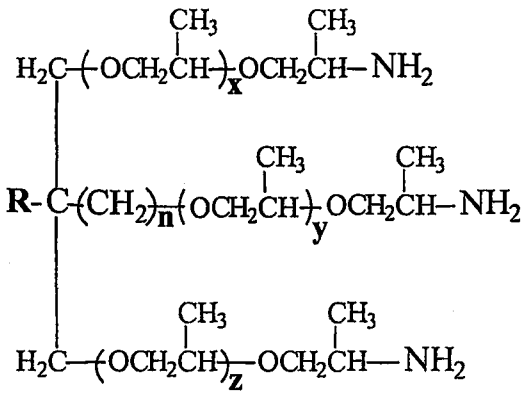


x=2-3 mol, D-230

x=5-6 mol, D-400

x=33 mol , D-2000

3.1.1.2. Triamine Series of Jeffamines



R= $-C_2H_5$, n=1, x+y+z=2-3 mol, T-403

R= -H, n=0, x+y+z=82 mol, T-5000

3.1.2. Solvents

- 1,4-dioxane (Labscan)
- Chloroform (J.T. Baker)

3.2. Equipments

3.2.1. Infrared Spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One B infrared spectrophotometer

3.2.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.3. Differential Scanning Calorimetry (DSC)

A Du Pont modular thermal analyzer system in conjunction with 910 differential scanning calorimeter was used to perform thermal analysis. A constant heating rate of 10 °C/min was using during DSC experiments.

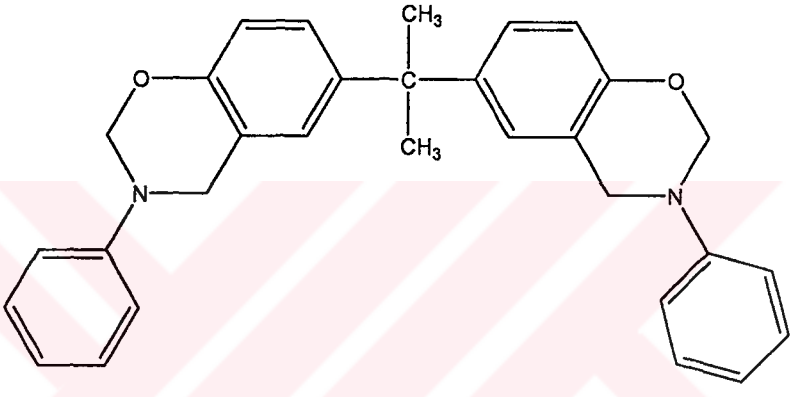
3.3. Preparation Methods

3.3.1. General Procedure for the naphthoxazine-functionalized poly(propyleneoxide) amines

2-naphthol (1g, 0.005 mol) was placed in a 100 ml round bottom flask. *p*-formaldehyde (0.6 g, 0.002 mol) and Jeffamine D-2000 are added to the flask. 20 ml 1,4-dioxane was added into flask which containing a magnetic stirring bar. The yellow solution was heated for 4h at 110 °C by refluxing, cooled to room temperature and solvent was evaporated. The viscous polymer was dissolved in chloroform and washed with 1% NaOH solution five times, and neutralized with distilled water. The polymer solution was dried with sodiumcarbonate, filtered off, and was evaporated. The viscous brown polymer was redried under vacuum before the analysis. The same method was applied for D-230 (1g , 0.0004mol), D-400 (1g, 0.003 mol), T-403 (1g, 0.003 mol), T-5000 (1g, 0.0002 mol).

3.3.3. Preparation of Films for Contact Angle & AFM Measurements

5 mg of each napthtoxazine-functionalized polymer with B-a monomer (3.1) (mol ratio:1/1) were mixed. 5 ml of 1,4-dioxane was added to mixture and it was stirred in ultrasonic water bath until homogen solution was obtained. Two-three drops of mixtures were dropped onto glass plates and the films were prepared by Spin Coating Method. Spin coated films were ~50-60 nm thick. Thicker films were prepared by sandwiching the polymer and the monomer between two glass slides. All films were cured at 160°C about 1-3h. Contact angle measurements and AFM measurements were done at room temperature.



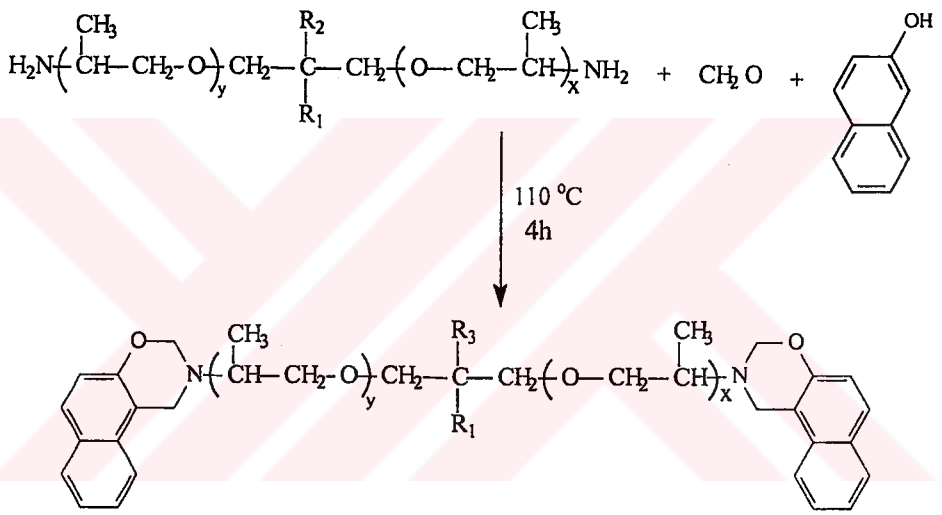
(3.1)

B-a monomer
Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane.
(B-a)

4. RESULTS and DISCUSSION

4.1. Synthesis of the Naphthoxazine-Functionalized Poly(propylene oxide) amines

Diamine and triamine containing telechelic poly(propyleneoxide) amines with various molecular weights are functionalized to naphthoxazine units by using 2-naphthol and *p*-formaldehyde as depicted in (4.1). 1,4-dioxane used as a solvent.



(4.1)

Linear Diamine: $R_1 = CH_3$, $R_2 = -H$, $R_3 = -H$

Branched Triamine: $R_1 = C_2H_5$, $R_2 = H_2C$ $O-CH_2-CH(CH_3)$ NH_2 , $R_3 = H_2C$ $O-CH_2-CH(CH_3)$ N O

4.1.1. Characterization of the Polymers

The structures of naphthoxazine-functionalized polymers were confirmed by ^{1}H-NMR measurements. ^{1}H-NMR spectra of functionalized telechelic Jeffamines exhibit broad signals corresponding to O-CH_2-N and Ar-CH_2- in the oxazine ring at 4.4 ppm and 5.02 ppm (Figure 4.2, 4.3, 4.4, 4.5). Also Figure 4.1(a&b) illustrate the difference

between D-2000 and functionalized-D-2000 as oxazine ring and nafhthol rings signals in the b part .

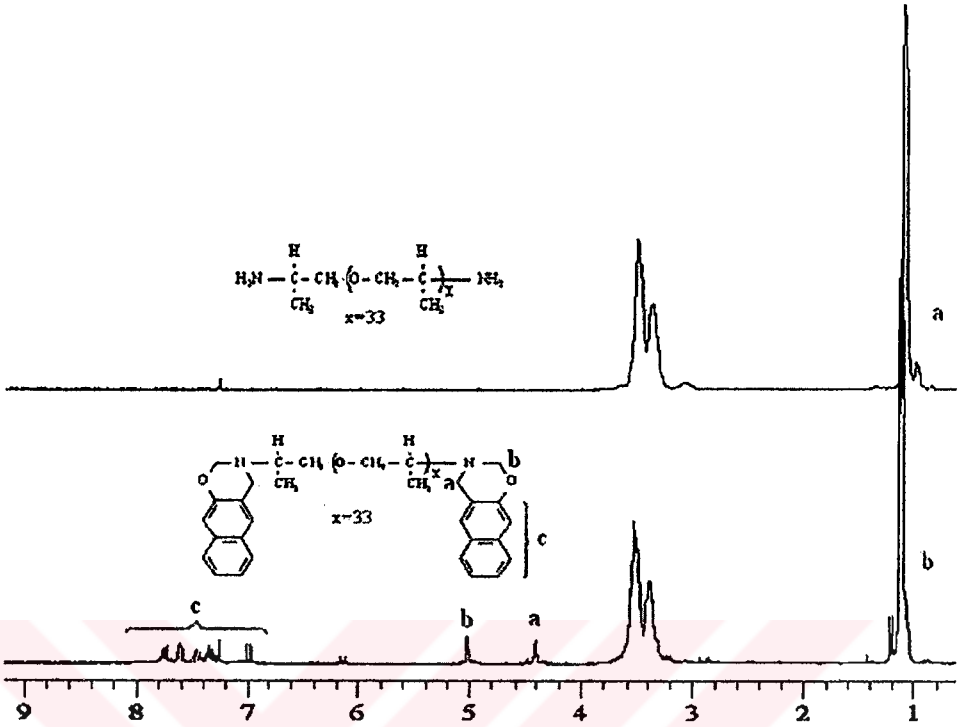


Figure 4.1: ^{1}H-NMR spectra of **a:** D-2000 and **b:** naphthoxazine-functionalized NFD-2000.

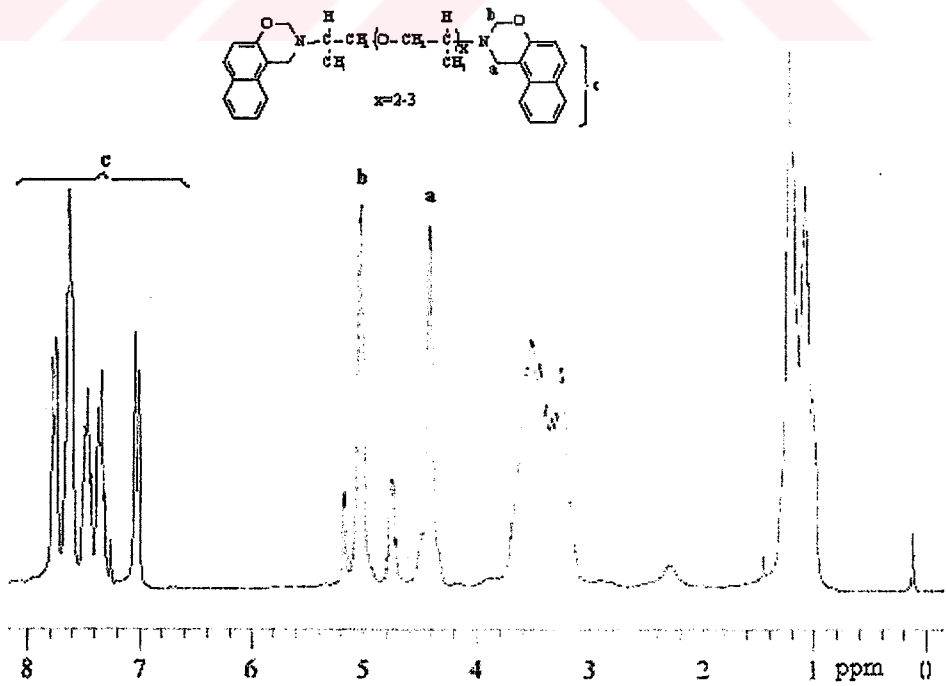


Figure 4.2: ^{1}H-NMR spectrum of naphthoxazine-functionalized D-230 (NFD-230).

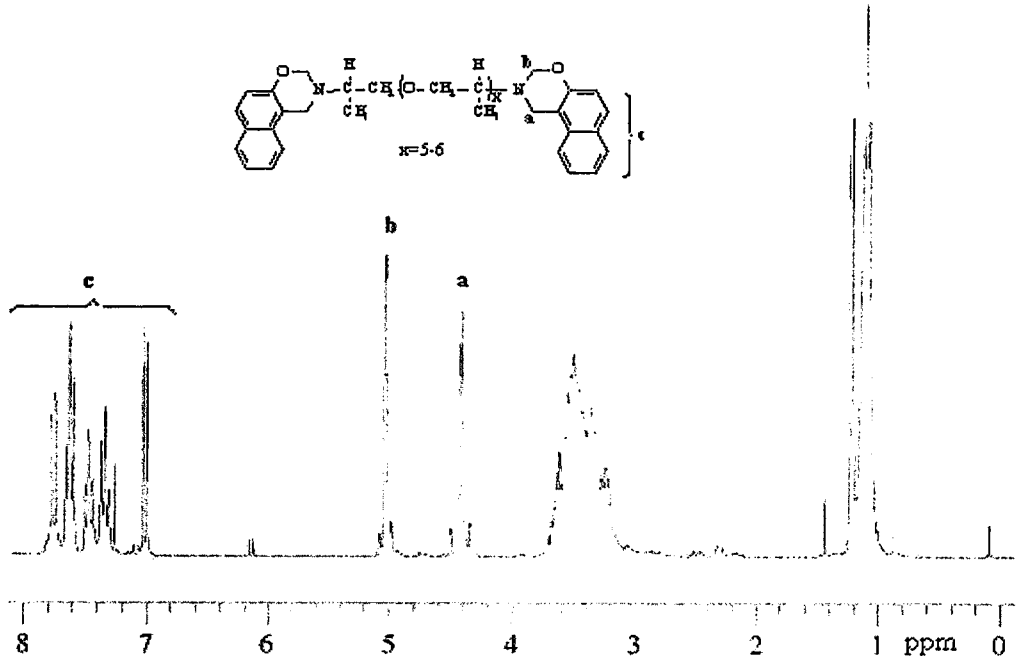


Figure 4.3: ^{1}H-NMR spectrum of naphthoxazine-functionalized D-400 (NFD-400).

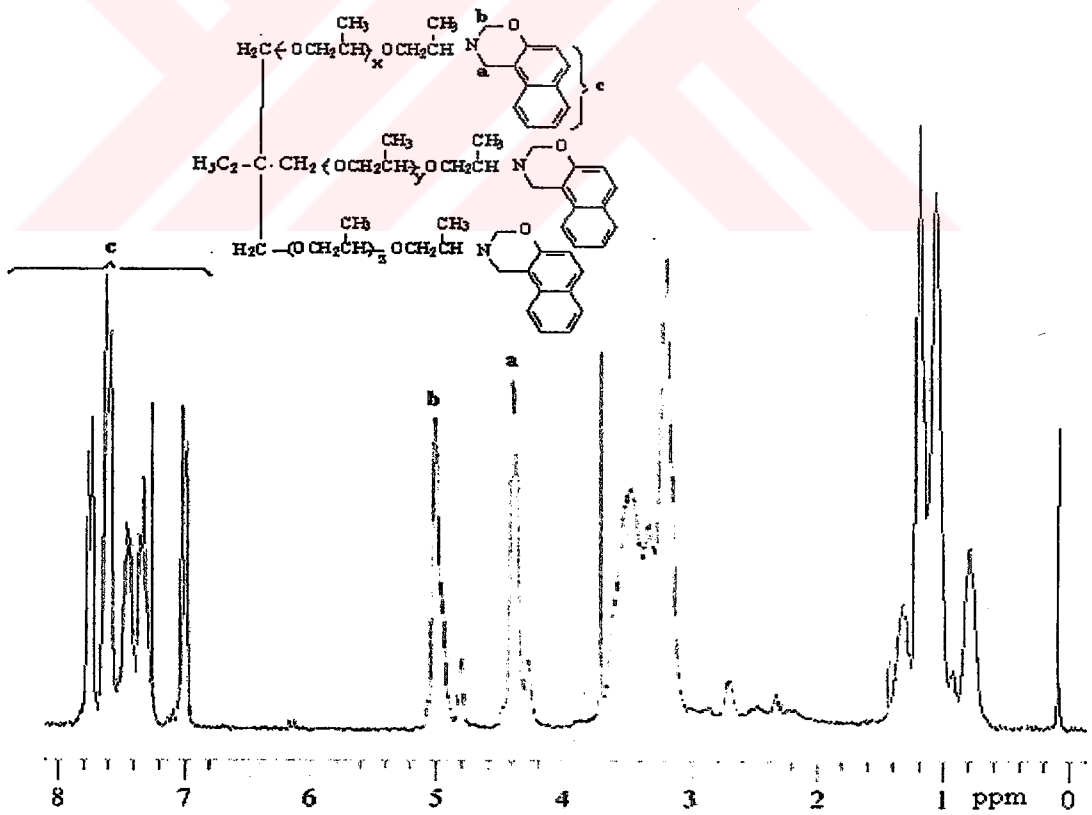


Figure 4.4: ^{1}H-NMR spectrum of naphthoxazine-functionalized T-403 (NFT-403).

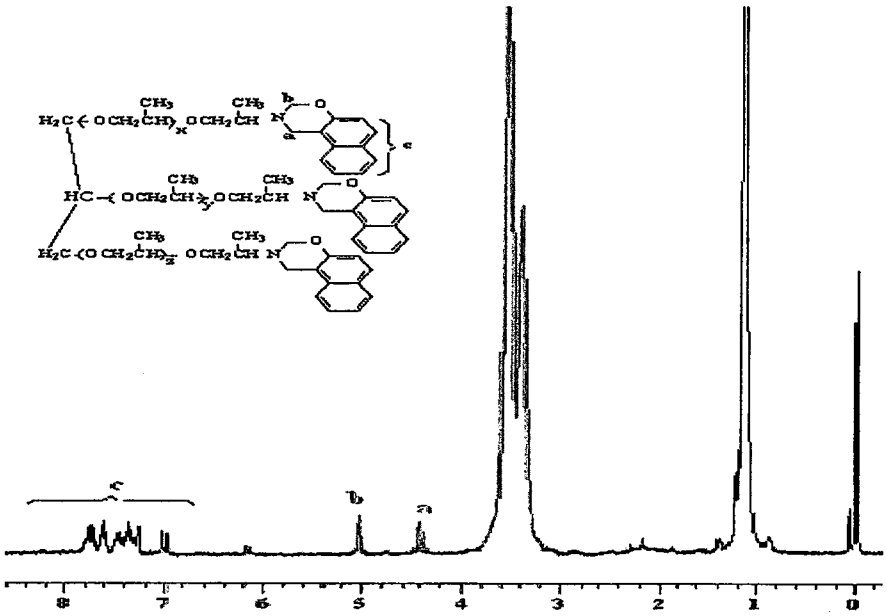


Figure 4.5: ^{1}H-NMR spectrum of naphthoxazine-functionalized T-5000 (NFT-5000).

In the IR spectra of Figure 4.6(a&b), our aim was to observe characteristic absorbtions of naphthoxazine ring in b and amine groups in a. In Figure 4.6a at 3367&3290 cm^{-1} (amine groups) were observed. In Figure 4.6b at 1227 cm^{-1} (asymmetric stretching of C-O-C), at 1016 cm^{-1} (symmetric stretching of C-O-C), at 944 (disubstituted naphthene ring) [120–121]. In addition, Figure 4.7 present IR Spectra of all naphthoxazine-functionalized Jeffamines.

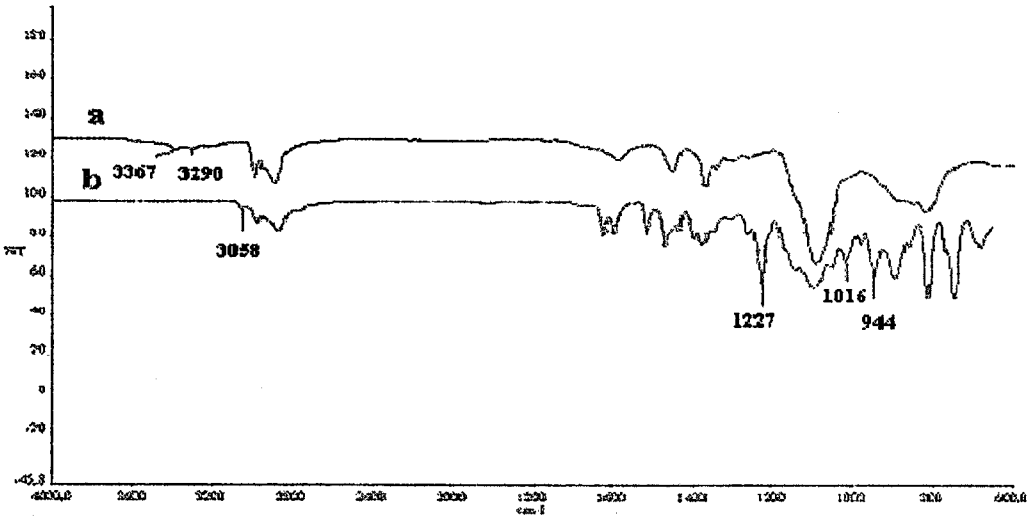


Figure 4.6: IR Spectra of **a:** D-230, **b:** naphthoxazine-functionalized D-230 (NFD-230).

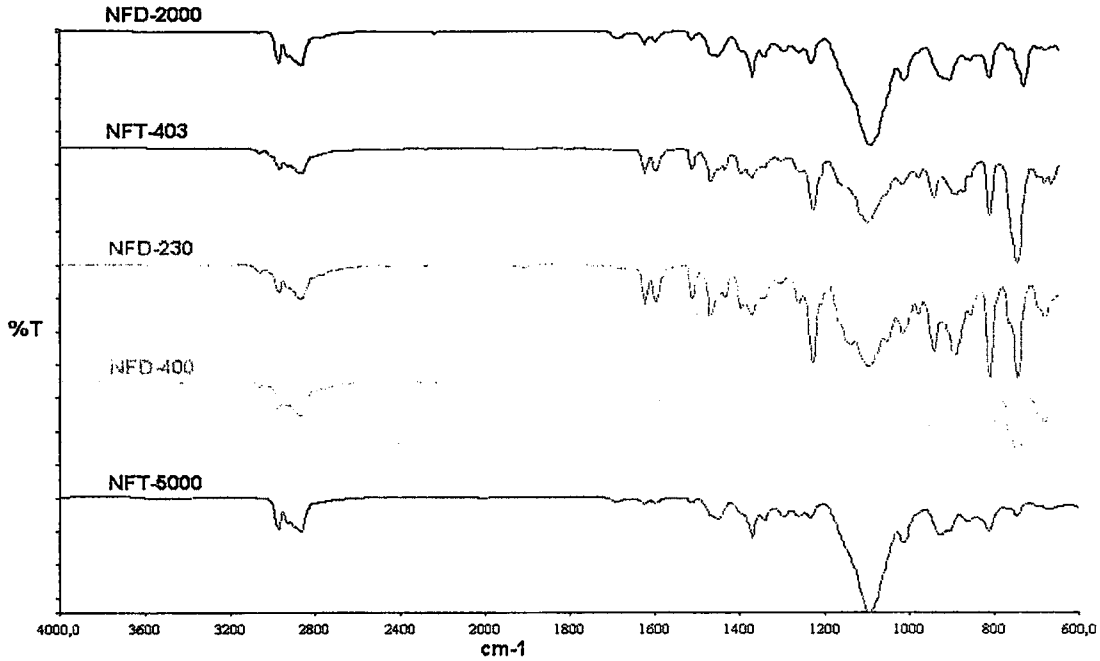
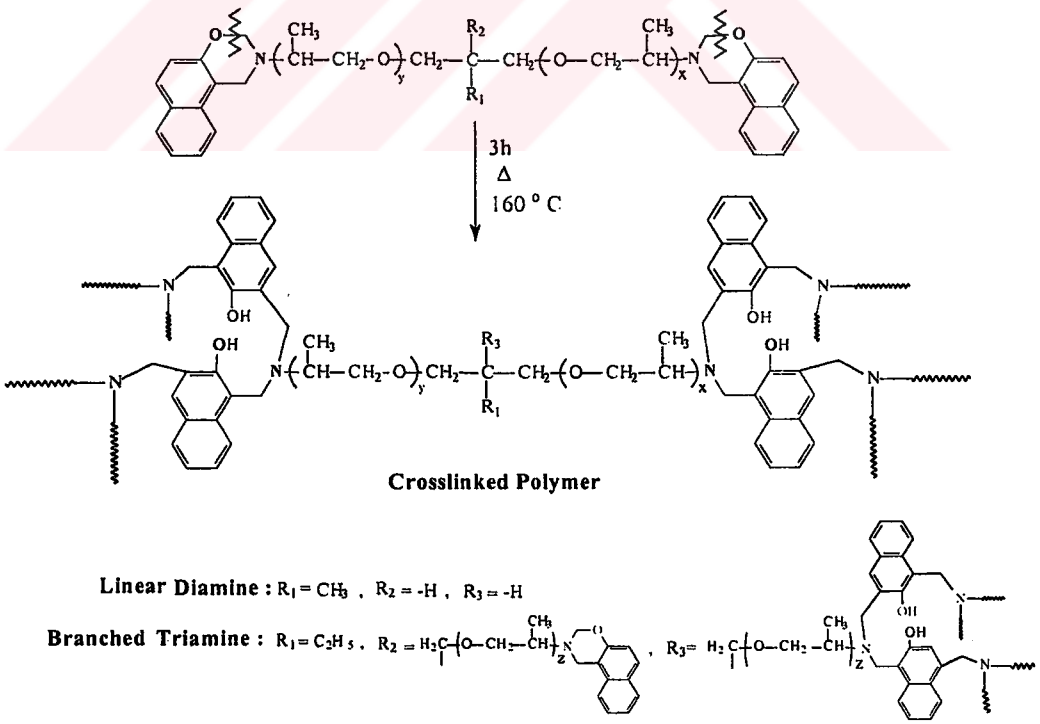


Figure 4.7: IR Spectra of all naphthoxazine-functionalized Jeffamines.

4.1.2. Thermal Behavior

The ring openning polymerization of naphthoxazine-functionalized Jeffamines is shown in (4.2).



(4.2)

The curing behaviour of functionalized polymers are characterized by DSC. In the first run, the endotherms corresponds to solvent evaporation or volatile sample(which

can be caused during the synthesis of Jeffamines) while the exotherm at 229.5, 236.4, 243.9, 251.0, 251.5 °C (belong to NFD-230, NFT-403, NFD-400, NFD-2000, NFT-5000) to ring opening polymerization of naphthoxazine units. Moreover, the exotherms disappeared in the second run, which indicates the ring-openning polymerization, too (Figures 4.8, 4.9, 4.10, 4.11, 4.12). Furthermore, in the first run, there are endotherms which are appeared in the Jeffamines themselves (can belong to the volatile compounds occurred in the synthesis of Jeffamines) shown in Figure 4.8, 4.9, 4.10 and 4.11.

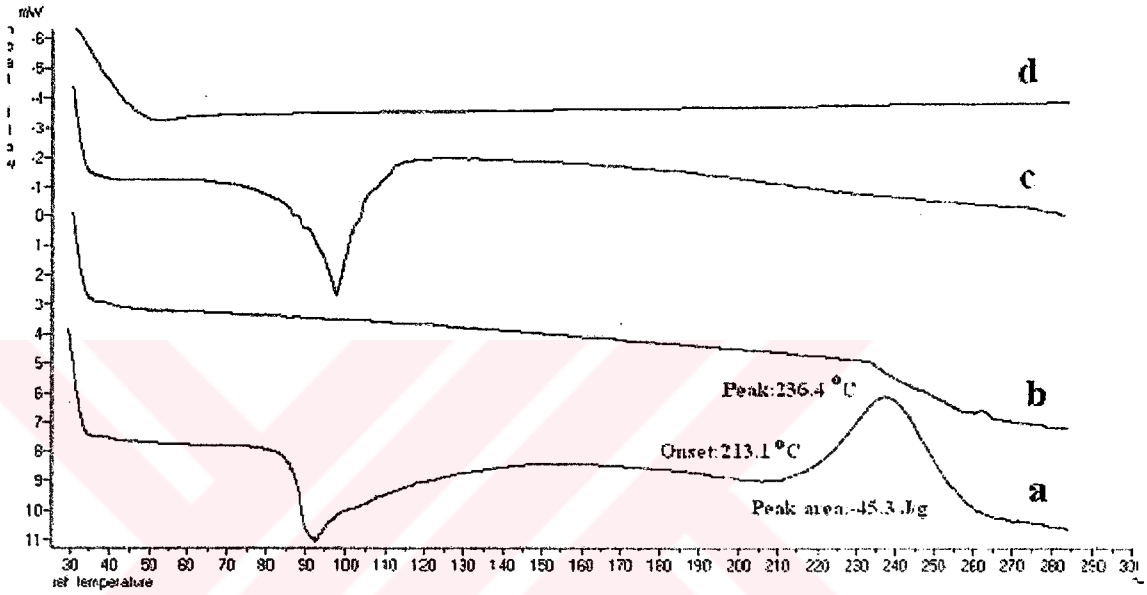


Figure 4.8: DSC curves of a:first run naphthoxazine-functionalized T-403, b:second run NFT-403, c: first run T-403, d: second run T-403 (30-300 °C).

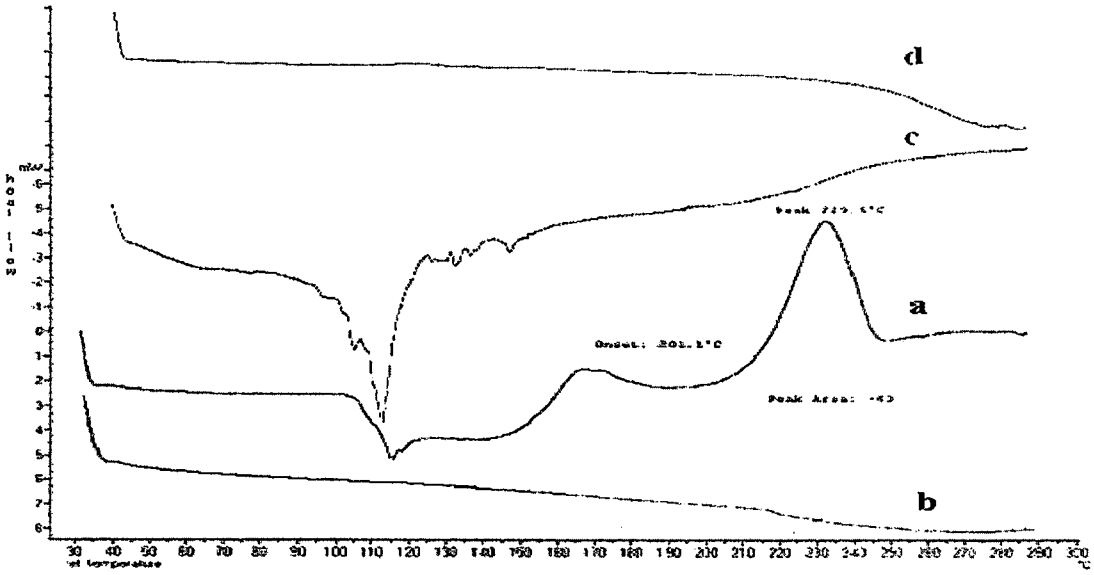


Figure 4.9: DSC curves of a:first run naphthoxazine-functionalized D-230, b:second run NFD-230, c: first run D-230, d: second run D-230 (30-300 °C).

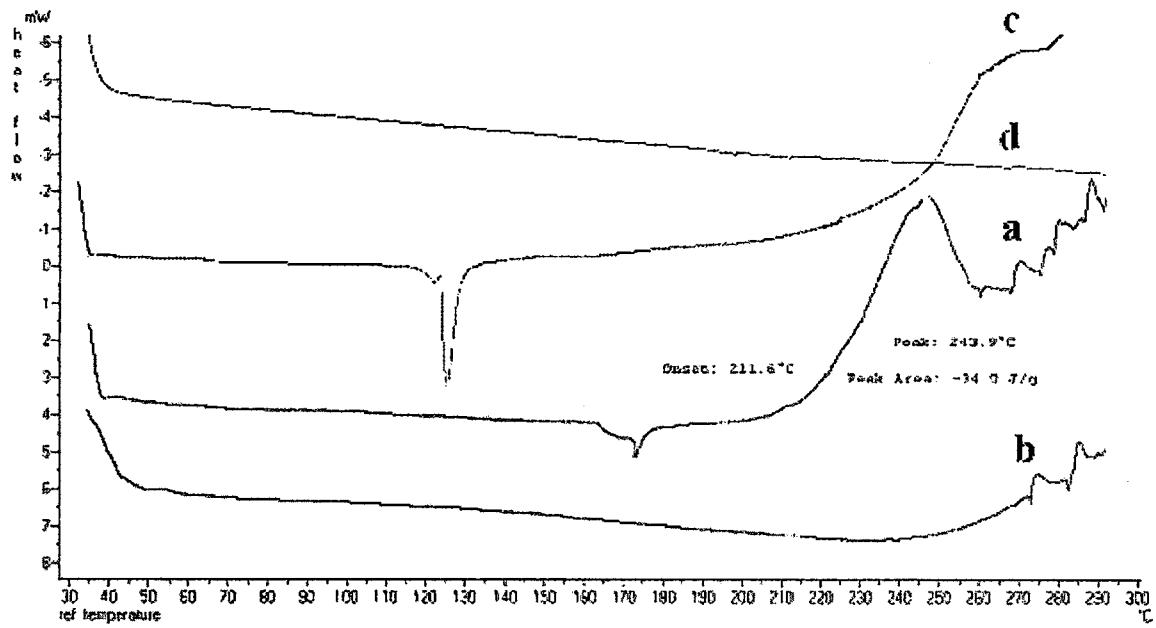


Figure 4.10: DSC curves of a:first run naphthoxazine-functionalized D-400, b:second run NFD-400, c: first run D-400, d: second run D-400 (30-300 °C).

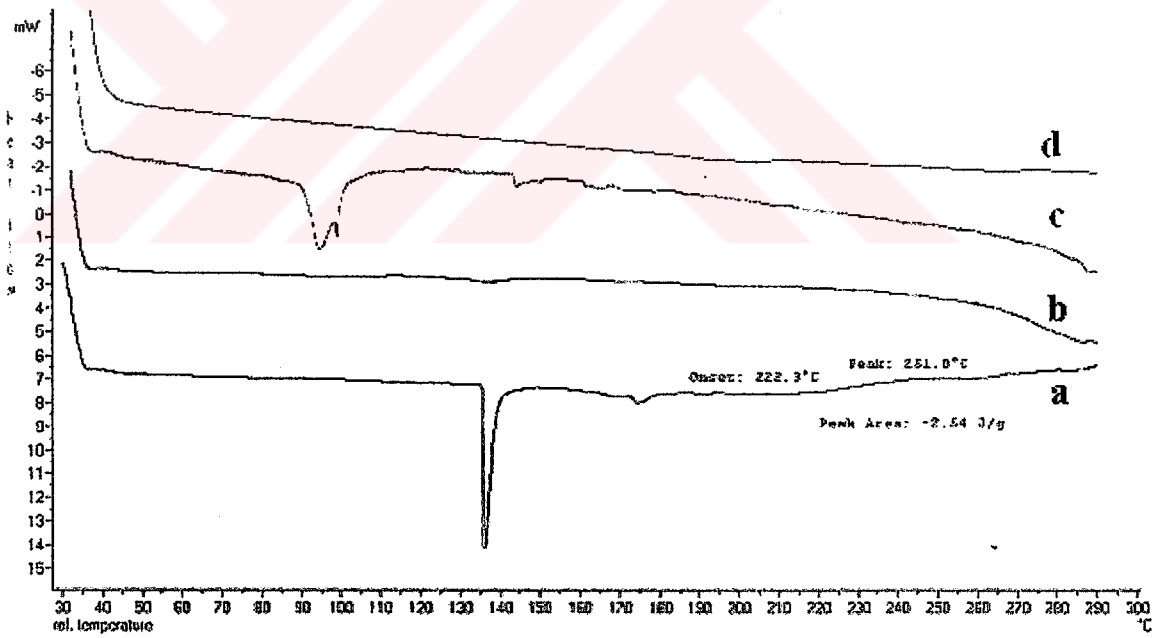


Figure 4.11: DSC curves of a: first run naphthoxazine-functionalized D-2000, b: second run NFD-2000, c:first run D-2000, d:second run D-2000 (30-300 °C).

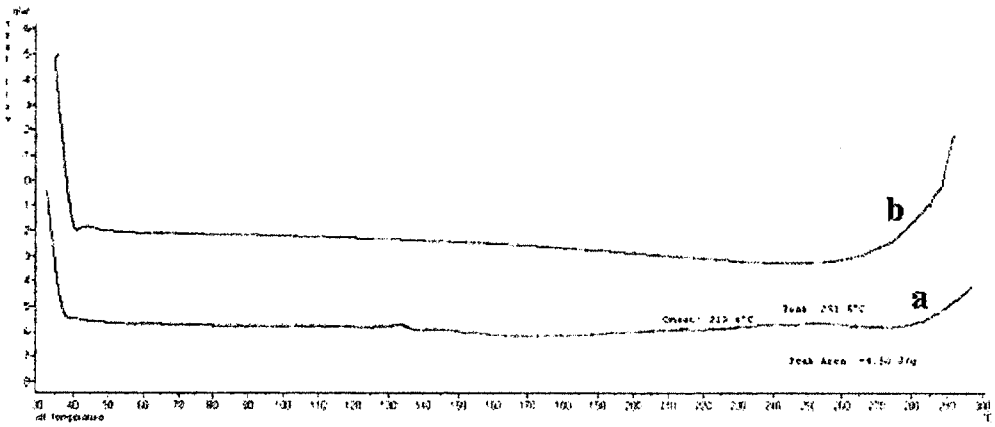


Figure 4.12: DSC curves of a: first run naphthoxazine-functionalized T-5000, b: second run NFT-5000, c: first run T-5000, d:second run T-5000 (30-300 °C).

As can be seen from Table 4.1, the yield of resulting polymers is strongly effected by the chain length of naphthoxazine functional starting PPOA. As the molecular weight of the initial polymer increases the conversion to naphthoxazine is reduced. Additionally, up to the molecular weight of 2000, the number of amine functionality also affects the overall conversion.

Table 4.1: % Yield [a] and DSC characteristics of naphthoxazine-functionalized Jeffamines (NFJ) with various molar masses.

NFJ	% Yield	Onset of curing (°C)	Maximum curing temp.(°C)	Amount of exotherm ($J.g^{-1}$)
NFD-230	78	204.7	229.5	-63.2
NFT-403	64	213.1	236.4	-45.3
NFD-400	62	211.6	243.9	-34.0
NFD-2000	29	212.3	251.0	-2.21
NFT-5000	30	213.4	251.5	-4.50

[a]Conditions: Time: 4h, T: 110 °C, Solvent: 1,4-dioxane

The curing mechanism of NFD-400 polymer was monitored with an IR (Fig. 4.13, 4.14). While the polymer was cured at 160 °C for 1.5h the occurrence of the ring-opening reaction of naphthzoxazine ring was observed with the sharply decrease of intensity of absorption bands at 1230 (shifted to 1265) cm^{-1} (C–O–C asymmetric stretching mode), decrease of intensity of absorption bands at 1016 (shifted to1023)

cm^{-1} (C–O–C symmetric stretching mode) indicate the reaction is not completed. Also, appearance peak at 3300 cm^{-1} (-OH of phenol), the disappearance of absorbtion peak at 943 cm^{-1} of the C-H of the α,β-disubstituted naphthalene ring and appearance of absorbtion peak at 890 cm^{-1} band that is due to C-H of the α,β,γ -trisubstituted naphthalene indicate the performance of the ring opening reaction of the naphthoxazine ring. Although increasing reaction time caused slightly differences in the intensity of absorbtion bands of phenol [122].

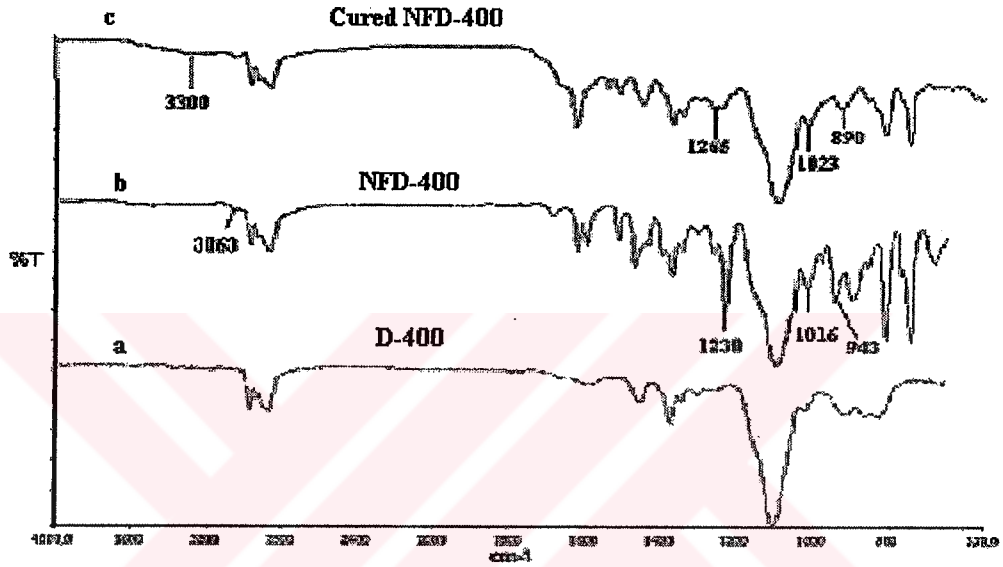


Figure 4.13: IR Spectra of a:D-400, b: naphthoxazine-functionalized D-400, c: crosslinked naphthoxazine-functionalized D-400 after curing (3h, 160 °C).

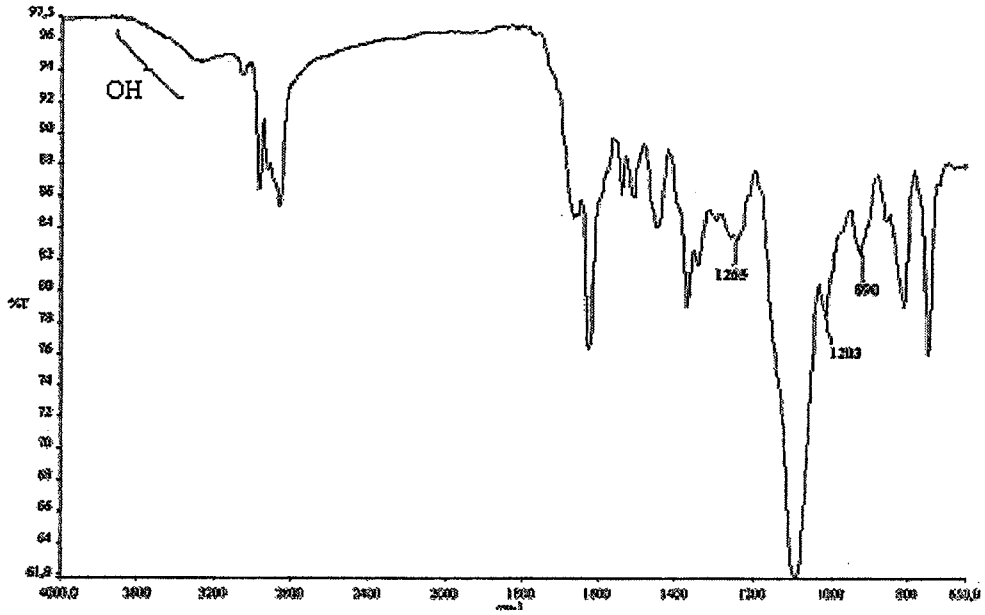


Figure 4.14: IR Spectra of crosslinked naphthoxazine-functionalized D-400 after curing (3h, 160 °C).

4.1.3. Contact Angle Measurements and The Surface Topography

The water contact angles on polymer films were measured both on spin coated thin films (50-60 nm thick) and on thicker films (~ micrometer thick) prepared by sandwiching between two glass slides. The benzoxazine monomer gave a water contact angle of 53° before curing and 67° after curing. When polymer films were prepared at monomer/polymer mol ratio of 3/1 and cured, the water contact angles of all films increased significantly and become very close to that on cured monomer B-a (67°) as shown in Table 4.2. A slight decrease of water contact angle from 66° to 63° was observed for cured naphtoxazine functionalized linear Jeffamines&PB-a as Jeffamine molecular weight increased from 230 to 2000 g/mole. For cured naphtoxazine functionalized branched Jeffamines, the water contact angle stayed nearly constant at 65-66° when the molecular weight of the polymer was increased from 403 to 5000 g/mole.

Table 4.2: Water contact angle measurements of cured [a] naphtoxazine functionalized Jeffamines(NFJ)/PB-a at room temperature.

NFJ/PB-a [b]	Contact Angles (°)
PB-a	67
NFD-230/PB-a	66
NFD-400/PB-a	64
NFD-2000/PB-a	63
NFT-403/PB-a	66
NFT-5000/PB-a	65

[a] Curing Conditions: 160 °C, 3h
[b] mol ratio:1/3

Preparing the polymer films at monomer/polymer mole ratio of less than 3 decreased the water contact angles. In Table 4.3, water contact angles of PB-a/naphtoxazine-functionalized D-2000 are seen at various monomer/polymer mole ratio before and after curing. The water contact angles before (curve a) and after (curve b) curing are plotted as a function of mole ratio in Figure 4.14. The increase in the water contact angle with the mole ratio before curing is due to the increasing probability of finding lower surface energy monomer at the top surface (film/air interface). The increase of water contact angle from 35 to 50° before curing with mole ratio increasing from 1 to 3 is consistent with a homogenous mixture of monomer and polymer initially. The

curing at high temperatures increases the water contact angle for two reasons: i) Opening of the naphtoxazine groups at the ends of the polymers, ii) The diffusion of the lower surface energy benzoxazine monomer to the polymer/air interface and the subsequent curing. Opening of the naphtoxazine groups increases the hydrophobicity. The excess benzoxazine monomer diffuses to the top surface to minimize the total interfacial energy of the system and cures there as a top layer in contact with the underlying polymer film.

Table 4.3: Water contact angle measurements of PB-a/naphtoxazine-functionalized D-2000 (NFD-2000) with different mol ratio.

Mol Ratio(B-a/NFD)	Contact Angles (°C) Before Curing [a]	Contact Angles (°C) After Curing [a]
0/1	31	37
1/4	32	48
2/4	32	49
3/4	35	52
4/4	35	54
6/4	38	56
8/4	42	59
12/4	50	63

[a] Curing Condition:160 °C, 3h

Figure 4.15 shows contact angles of water drops on B-a/NFD-2000 films after curing process with different mol ratio (from the Table 4.3). If a drop is spreaded on a polymer film greatly this film likes water so it shows hydrophilic properties and has low contact angle. The drop in Figure 4.15a which does not have B-a monomer is more spreaded and has lower contact angle than the drop which has B-a monomer with 12/3 ratio(monomer/polymer) in Figure 4.15b because B-a monomer is more hydrophobic than polymer and becomes more hydrophobic with curing process because of the ring openning reaction (occurrance of H-bonding on its crosslinked structure) of it.

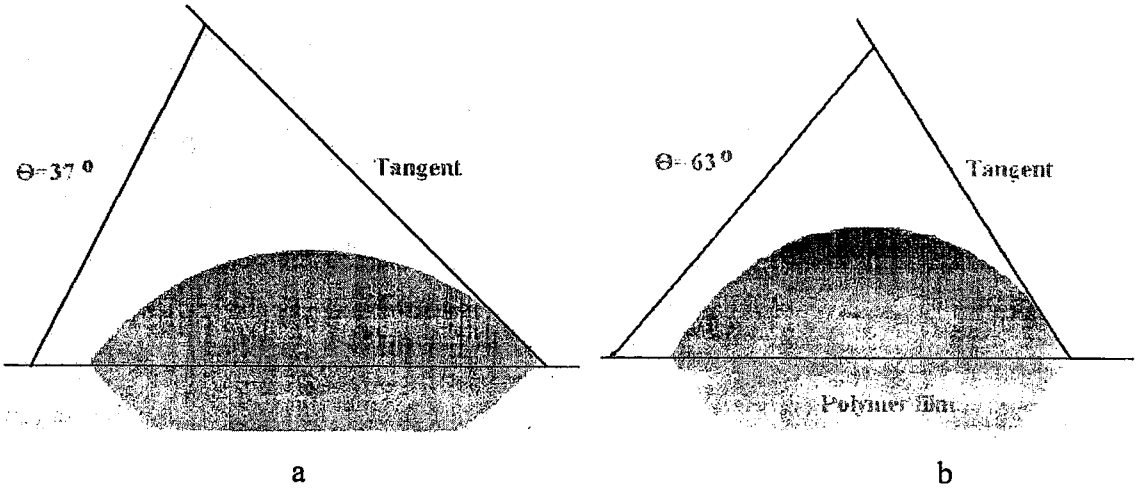


Figure 4.15: Contact Angle of Water Drops on B-a/NFD-2000 after curing a: Mol Ratio: 0/1, b: Mol Ratio: 12/4.(from the Table 4.3).

Figure 4.16(a&b) shows water contact angles of PB-a/naphtoxazine-functionalized D-2000 before and after curing process as a function of mol ratio of B-a monomer. Figure a&b illustrate that the contact angle of water droplet increases when % ratio of B-a monomer increases. In addition, contact angle is increased by curing behavior of benzoxazine&naphtoxazine groups.

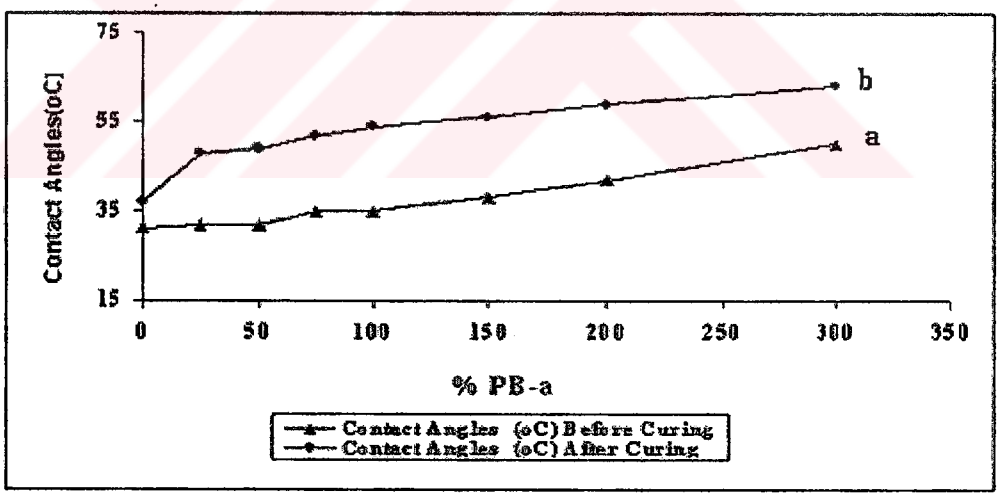
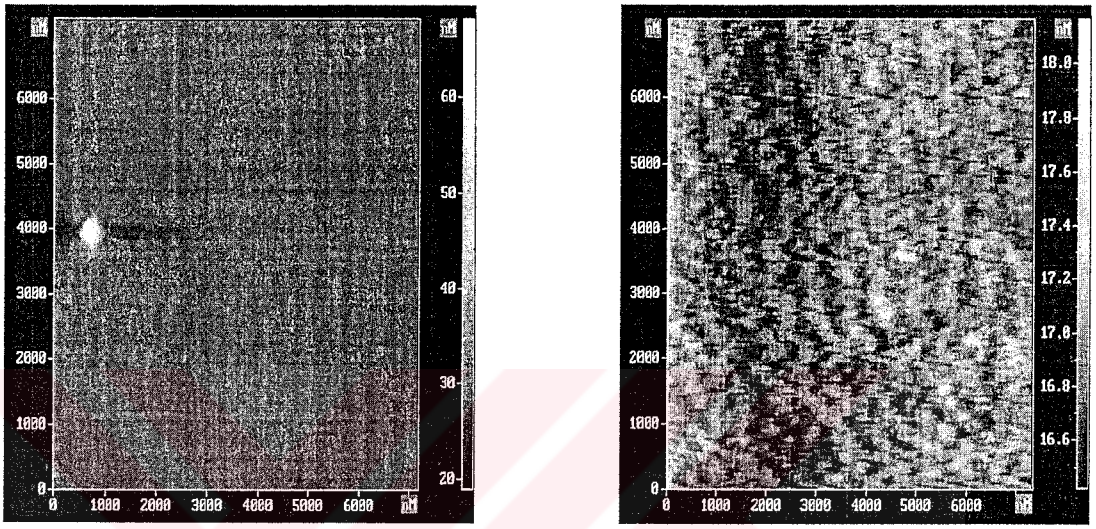


Figure 4.16: Water Contact Angles of B-a/naphtoxazine-functionalized D-2000 a: Before Curing b: After Curing (3h, 160 °C).

These results indicate, apart from the effect of excess monomer, that the naphtoxazine-functionalized end groups dominate in determining the surface hydrophobicity of the cured polymer films. The chain ends of a polymer are known to be more mobile [reference: Jeff Kobberstein] and segregate to the top surface when functionalized with hydrophobic groups. For more branched chains, the effect of chain ends will be more dominant. It is then expected that the effect of the length of polymer

chain (molecular weight) on the surface hydrophobicity will be less. In fact, we observed this for tri-functionalized branced polymers compared to di-functionalized linear polymers.

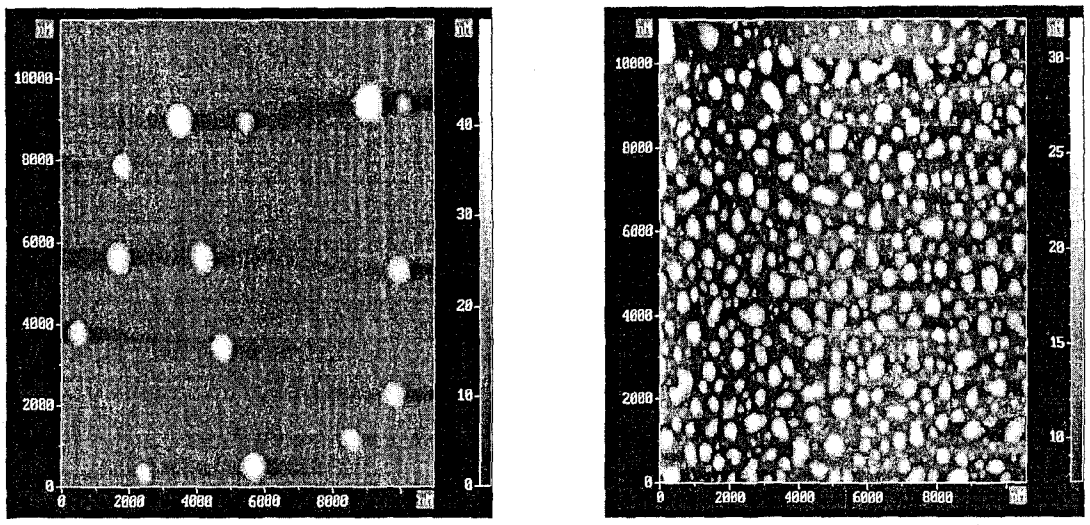
The surface topography and the phase pictures of the monomer and polymer films were determined by AFM. For all polymers, and monomer-polymer mixtures, AFM height pictures showed smooth and featureless surfaces before curing, as the polymers were soft and viscous (Figure 4.17).



(a) (b)

Figure 4.17: AFM Images for a: D-2000&B-a monomer after spin coating before curing, b: monomer after spin coating before curing.

Curing the films at 160 °C for 3 hours resulted in morphological changes on the top surface. Figure 4.18 shows the AFM height pictures of the same films of Figure 4.17 after curing. On both films, 20-40 nm heigh spherical aggregates were observed. Between these aggregates, a smooth film existed. These aggregates are the dewetted droplets of monomer. For D-2000 film, the aggregates also represent the excess monomer that cured and were segregated to the top surfaces and got dewetted on top of the stable polymer film.



(a) (b)

Figure 4.18: AFM Images for a: D-2000&B-a monomer after curing, b: monomer after curing.

The magnified height picture of the D-2000 film in the smooth region between the aggregates is seen in Figure 4.19. The surface is relatively smooth with few nm heigh undulations. These undulations represent the regions of cross-linking between the polymer chains.

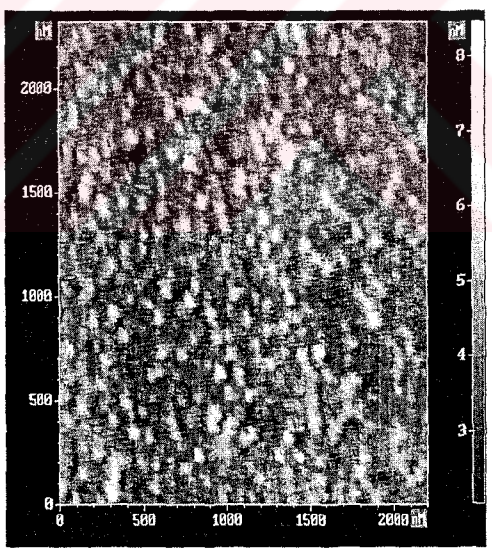


Figure 4.19: for 2 micron x 2 micron AFM picture of D-2000&monomer after curing.

2 micron size AFM pictures of D-230 and D-400 films also showed distinct regions after curing with significant phase contrast. Figure 4.20a and Figure 4.20c show AFM height pictures of D-230 and D-400 films, respectively. In addition to aggregates, 20-30 nm diameter circular regions are clearly seen in D-230 film. The phase picture of Figure 4.20a is seen in Figure 4.20b. These circular regions are seen to have a

brighter phase contrast indicating more elastic materials. We attribute these to dense cross-linking and thus hardening in the films. Such dense cross-linking regions were also observed in T-403 as seen in Figure 4.20d.

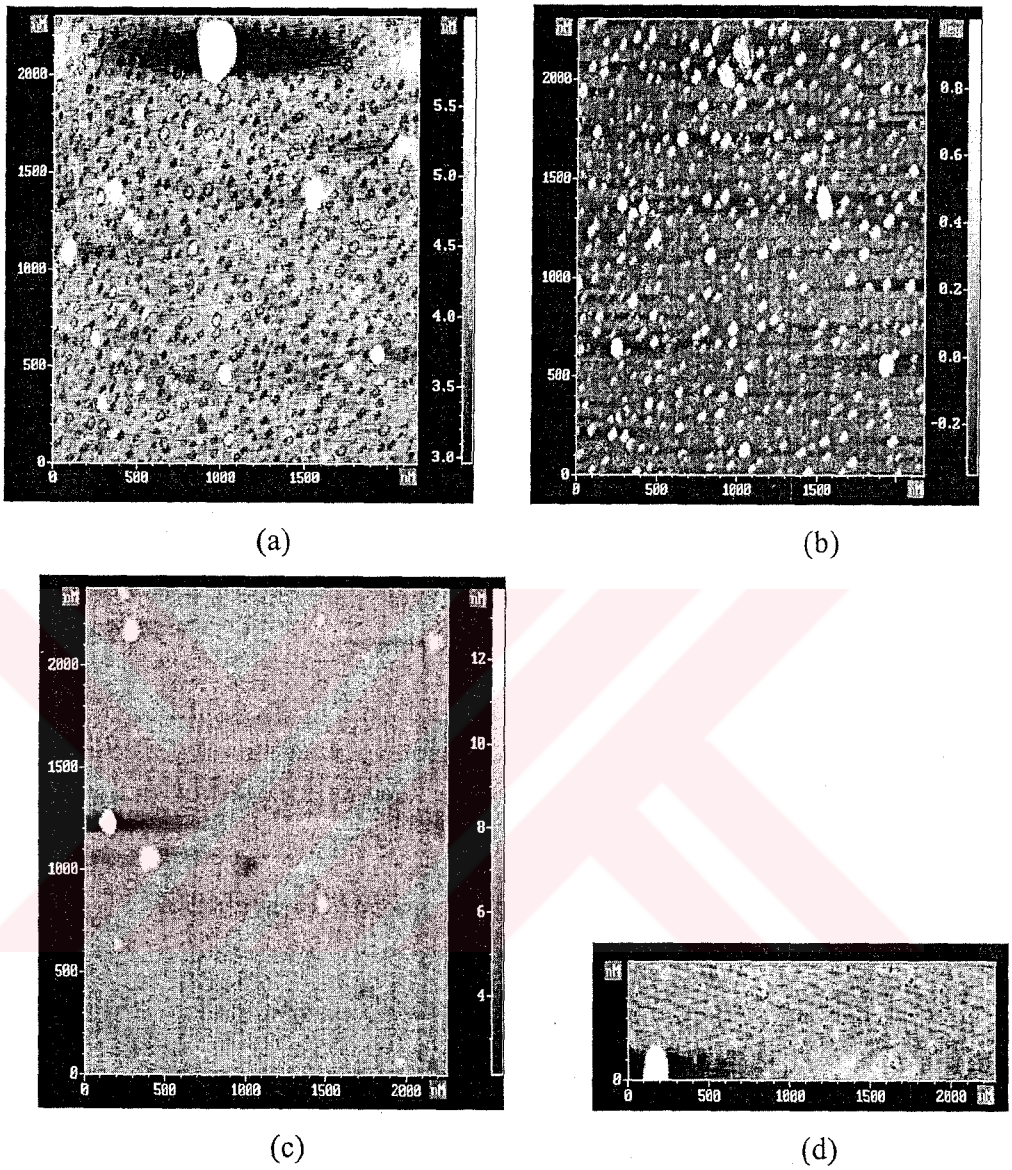


Figure 4.20: 2 micron x 2 micron AFM pictures of a: Height picture of D-230&B-a monomer after curing, b: Phase picture of D-230, c: Height picture of D-400&B-a monomer after curing, d: Height picture of T-403.

Figure 4.21 shows the AFM height picture of T-5000. Apart from aggregates, the surface of largest molecular weight branched polymer T-5000 looked smooth with few nm height undulations similar to that of D-2000 in Figure 4.18. As the molecular weight of the polymer increases, the chain ends are further away from each other. Thus small cross-linking regions are well dispersed in the matrix of the polymer resulting in relatively smooth surfaces.

For low molecular weight polymers, the chain ends are expected to aggregate easily resulting in regions of dense cross-linking as observed by AFM.

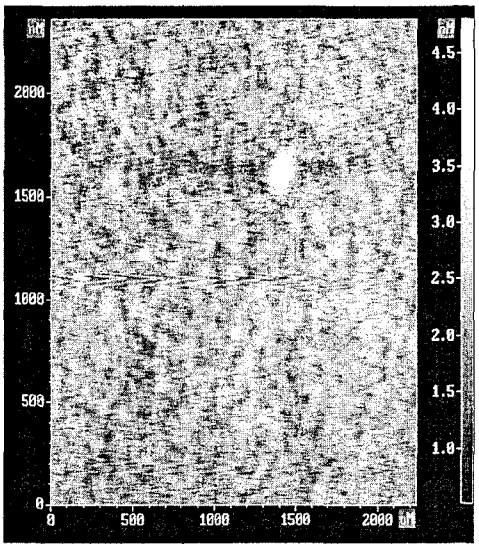


Figure 4.21: 2 micron x 2 micron AFM picture of T-5000&B-a monomer after curing.

5. CONCLUSION

In this thesis, naphtoxazine-functionalized Jeffamines were prepared by the reaction of linear (Diamines: D-230, D-400, D-2000) and branched (Triamines: T-403, T-5000) reactive elastomer Jeffamine series having various molecular weights, with *p*-formaldehyde, and 2-naphthol in order to improve the properties of the trunk polymers. The structures of the resulting polymers were characterized by FTIR and ^{1}H-NMR. In addition, cure behavior of polymers were studied using DSC which indicated a single exothermic curing peak between 230-251 ^{o}C based on benzoxazine functionality. The results showed that % yield and amount of exotherm of synthesized polymers were decreased with increasing of chain length of the linear and branched Jeffamines at the beginning. Also, maximum curing temperature of synthesized polymers were increased with increasing of linear and branched Jeffamines. B-a monomer was added to synthesized polymers because synthesized polymers were soft, viscous and unsuitable in room temperature for preparing their films in order to investigate the contact angle measurements and the surface topography of them. In addition, hydrophilicity of polymers with B-a and effect of naphtoxazine functionality on hydrophilicity of these trunk polymers were investigated by water contact angle measurements before and after curing process. The B-a monomer films showed the highest contact angle and most hydrophobic with curing process because of the ring openning reaction (occurrance of H-bonding on its crosslinked structure) of it. Moreover, contact angle of monomer& polymer mixture films were increased with increasing the % content of B-a monomer so, hydrophilicity of them were decreased. Also, Surface topography of polymers were represented by AFM images and these images indicated the crosslinking of naphthoxazine functions and B-a monomer.

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