ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

BENZOXAZINE MODIFIED TRIGLYCERIDE OILS AS A COATING MATERIAL

M.Sc. THESIS

Can YILDIRIM

Department of Chemical Engineering

Chemical Engineering Programme

Thesis Advisor: Prof. Dr. Ahmet Tuncer ERCİYES

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KAPLAMA MALZEMESİ OLARAK BENZOKSAZİN İLE MODİFİYE EDİLMİŞ TRİGLİSERİD YAĞLAR

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To my parents and wife,

FOREWORD

I would like to thank all the people who supported me and made this study possible. I would like to express my appreciation to my advisor Prof. Dr. Ahmet Tuncer Erciyes for his help and deep interest in my research. I am also grateful to Prof. Yusuf Yağcı for his crucial support and suggestions.
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December 2011 Can YILDIRIM
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ABBREVIATIONS

^{1}H NMR	**:** Nuclear Magnetic Resonance Spectra
ASTM	**:** American Society for Testing and Materials
Bz-OH	**:** Hydroxyl Containing Benzoxazine Monomer
Bz-PG	**:** Benzoxazine Modified Oil Sample
Bz-PGE	**:** Benzoxazine Modified Oil Sample (Enriched)
DIN	**:** German Institute for Standardization
DSC	**:** Differential Scanning Calorimetry
FT-IR	**:** Fourier Transforms Infrared Spectroscopy
PG	**:** Partial Glycerides
PGE	**:** Enriched Partial Glycerides
PG-U	**:** Classical Urethane Oil
POSS	**:** Polyhedral Oligomeric Silsesquioxane
TDI	**:** Toluene Diisocyanate
TGA	**:** Thermal Gravimetric Analysis

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BENZOXAZINE MODIFIED TRIGLYCERIDE OILS AS A COATING MATERIAL

SUMMARY

Triglyceride oils are among the most widely used renewable energy sources. Besides the feeding purposes of triglycerides, these natural products are also used in polymer synthesis and the most used field of application of triglycerides is coating industry. Since their film properties show deficiency, it needs to be modified. In this context, they were previously modified with various polymers such as polystyrene and in this study, polybenzoxazine which is a class of thermosetting resin was used for the modification of triglyceride oil. Polybenzoxazines have been got the interest of the search area of researchers due to their significant characteristics.

For this purpose, firstly, hydroxyl containing benzoxazine monomer was prepared by condensation reaction of phenol with paraformaldehyde in the presence of 6-amino-1-hexanol. In the next step, benzoxazine monomers were linked to hydroxyl groups of partial glycerides by means of toluene diisocyanate. At the final step, benzoxazine modified triglyceride samples were cured and the properties of the benzoxazine modified samples were analyzed. After curing process, the transparent film samples showed good film properties with excellent flexibility and adhesion. The characterization of the samples were identified by FT-IR and ^{1}H NMR. The film properties of the samples were determined by ASTM and DIN procedures and the thermal stability of these samples were analyzed by TGA.

KAPLAMA MALZEMESİ OLARAK BENZOKSAZİN İLE MODİFİYE EDİLMİŞ TRİGLİSERİD YAĞLAR

ÖZET

Polimerler kovalent bağlı ve tekrarlanan ünitelerden oluşan makromoleküllerdir. Doğal olarak oluşan selüloz ve kauçuk gibi makromoleküller insanların günlük ihtiyaçlari için kullanılmaktaydı. Sentetik kauçuk, polietilen, polistiren, polivinilklorür vs. gibi sentetik polimerik malzemeler son ikiyüz yıldan beri üretilip kullanılmaktadir. Bu sentetik polimerler insan hayatı için vazgeçilemez malzemelerdir, fakat, bu malzemeler uzun zaman için insan hayatı ve ekosistem için dezavantaj oluşturmaktadır. Zira, bunların kimyasal olarak bozunması ve tekrar kullanımı zordur. Gelişen dünyada, hükümetler yenilenebilir kaynaklardan bu tür makromoleküllerin üretimini gerçekleştirebilmek için bir takım kararlar almaktadır. Doğal bitki kaynaklarından elde edilen trigliseridler bu amaç için kullanılmaktadır ve yenilenebilir kaynaklardan polimerik malzeme üretiminde önemli bir yere sahiptir.

Trigliseridler sentetik olarak bir gliserol ve üç yağ asiti molekülünün kondenzasyon reaksiyonu sonucu oluşur. Suda çözünmeyen ve uçucu olmayan bu ürünler hem hayvanlarda hem de bitkilerde bulunabilir. Trigliseridlerde bulunan yağ asitlerinin karbon atomları arasındaki bağların hepsi tek bağ olduğunda doymuş, en az bir tane çift bağ var ise doymamış olarak adlandırılırlar.

Trigliseridler kuruma özelliklerine göre kuruyan, yarı-kuruyan ve kurumayan yağlar olarak sınıflandırılır. Bu sınıflandırma doymamışlık derecesine göre yapılır ve doymamışlık derecesi de iyot değeri ile hesaplanır. Bir yağın iyot değeri 100 g yağ veya yağ asitiyle reaksiyona giren iyot miktarıdır. İyot değeri 170’den büyük olanlar kuruyan, 170 ile 100 arasında olanlar yarı-kuruyan, 100’den küçük olanlar kurumayan yağ olarak adlandırılır.

Trigliseridler hem yenilenebilir enerji kaynağı hem de beslenme amaçlı olarak kullanılan doğal ürünlerdir. Beslenme amaçlarının dışında, bu doğal ürünler polimer sentezinde kullanılmaktadır ve en çok kullanılan trigliseridler ayçiçek, hint, keten tohumu, oitika, hurma, soya ve kolza yağlarından elde edilir. Yağ bazlı polimerler çok farklı uygulama alanına sahiptir ve bu polimerlerden bazıları oksipolimerize yağlar, yağ bazlı poliamidler, epoksidize yağlar, yağ bazlı polyesterler ve yağ bazlı poliüretanlardir.

Bu çalışmada üretan yağların film özelliklerini güçlendirmek için termoset yapıda olan polibenzoksazin kullanılmıştır. Polibenzoksazinler benzoxazine monomerlerinin ısı veya katalizör varlığı altında polimerleşmesiyle oluşur. Benzoksazin monomeri fenol türevleri, primer amin ve formaldehitin kondenzasyon reaksiyonu sonucu oluşan oksazin halkası içeren üründür ve bu reaksiyonun yan ürünü olarak su açığa çıkar. Benzoksazinlerin bünyesindeki oksazin halkası ısı veya katalizör yardımıyla açılarak benzoksazin monomerlerinin birbiriyle bağlanıp polimerleşmesini sağlar. Polibenzoksazinlerin yüksek termal stabilite, yüksek kuru ağırlık, sıfır çekme, düşük su absorpsiyonu, katalizör kullanmadan üretim ve kürleme, ve kürleme prosesi sırasında yan ürün açığa çıkarmama gibi çok önemli özellikleri vardır.

Polibenzoksazinlerin bu önemli özelliklerini yağ bazlı polimere entegre etmek amacıyla ilk olarak 6-amino-1-hekzanol ve paraformaldehit ile fenolün kondenzasyon reaksiyonu sonucu ucunda hidroksil bulunan benzoksazin monomeri sentez edildi. Daha sonra, yemeklik yağ olan ayçiçek yağının gliserol ile alkoliz reaksiyonu sonucu kısmi gliseridler elde edildi.

Ucunda hidroksil bulunan benzoksazin monomeri ve kısmi gliseridler toluen diizosiyanat varlığında reaksiyona sokuldu. Önce, kısmi gliseridler toluen diizosiyanatın para kısmı ile ile reaksiyona sokulup, ardından benzoksazin monomeri eklendi ve toluen diizosiyanatın orto kısmı ile reaksiyona girmesi sağlandı. Elde edilen benzoksazinle modifiye edilmiş yağ bazlı ürün camda ve metalde film oluşturduğunda yüzeyinde yağlı bir tabakanın olduğu gözlendi. Bu yağlı tabaka film performansı açısından kötü bir özellik oluşturmaktaydı ve film olarak uygulanmasını engellemekteydi. Bu durumun kısmi gliseridlerde bulunan ve reaksiyona girmemiş trigliseridlerden ileri geldiği düşünülerek, trigliseridler alkollü su ile ekstrakte edildi ve elde edilen zenginleştirilmiş kısmi gliseridler yukarıda bahsedilen sıra ile tekrar

reaksiyona sokulup benzoksazinle modifiye yağ bazlı ürün elde edildi. Bu ürün cama, metale ve tahtaya sürülüp 180 °C'de kürlenerek film elde edildi ve bu filmlerin özellikleri ASTM ve DIN prosedürüne göre belirlendi. Kürleme işleminden sonra, elde edilen saydam filmlerin sert olduğu, yüksek yapışma ve esneklik özelliği gösterdiği ve elde edilen ürünün asite, baza ve suya dayanımının çok iyi performans gösterdiği gözlendi. Hazirlanan örneklerin karakterizasyonu FT-IR ve ^{1}H NMR ile saptandi.

Sonuç olarak, hazırlanan benzoksazinle modifiye yağ bazlı örneğin organik kaplama malzemesi olarak kullanılabileceği yorumuna varıldı.

1. INTRODUCTION

Polymers are macromolecules that are formed by covalently bounded repeating units. These macromolecules which are naturally occuring polymers such as cellulose and rubber were used for daily needs of people. Since two centuries, there have been produced and used synthetic polymeric materials such as synthetic rubber, polystyrene, polyethylene, polivinylchloride and so forth. These synthetic polymers are the undeniable materials for human life, however, they have some negative effects on life in a long period. In the developing world, governments take some decisions to produce these macromolecules from renewable sources. Triglycerides obtained directly from the natural plants have been used for this purpose and they have a crucial position for manufacturing products from renewable sources [1].

Triglyceride oils are the widely used renewable energy sources. Besides the feeding purposes of triglycerides, these natural products are also used in polymer synthesis and the most application area of triglycerides is coating. Since their film properties show deficiency, it needs to be modified. One of the most frequently applied processes is the modification with vinyl monomers such as styrene. In the traditional styrenation process, there can occur homopolystyrene and when the sample of this process is maden a film, it shows poor film properties. In order to make good films, styrenation of the triglyceride oil was studied from the standpoint of preventing the formation of homopolystyrene [2-8]. In continuation to these studies, the present study is based on using the benzoxazine for the modification of triglyceride oil. Polybenzoxazines have been got the importance of the search area of researchers due to their significant characteristics since last decade.

It is well-known that polybenzoxazines have several considerable properties such as high thermal stability, high char yield [9], no shrinkage, low water absorption, no need of catalysts for production and curing, and no by-product during curing [10]. However, they have some undesirable characteristics like brittleness, high curing temperature and difficult processability [11].

In the present study, it is expected that advantages of polybenzoxazines could be incorporated to the film samples of benzoxazine modified triglyceride oil. For this purpose, polybenzoxazine was used as an organic coating material. However, its brittleness makes it inferior for this purpose. In order to give flexibility, partial glycerides were combined to the polybenzoxazine chain.

Benzoxazine monomer was prepared by condensation of phenol with paraformaldehyde in the presence of 6-amino-1-hexanol which forms a free hydroxyl group on the molecule. In the next step, benzoxazine monomers were linked to hydroxyl groups of partial glycerides by means of toluene diisocyanate. After curing, transparent film samples showed good film properties with excellent flexibility and adhesion.

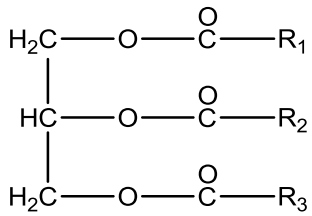
2. THEORETICAL PART

2.1 Triglycerides

Naturally occuring triglycerides are among the renewable sources and can be used at the stage of manufacture of the biodegredable polymers [12]. Linseed and tung oils can be used as a polymer source owing to the double bounds and functional groups [13]. C=C double bound and non-conjugated vinyl groups are present in the structure of triglycerides, and these double bonds are used to form polymerizable plastics [14, 15]. Comparing with petroleum sources, production of triglycerides and their derivatives have low cost and they are biodegradable [1].

2.1.1 Structure of triglycerides

Triglycerides are composed of a glycerol molecule and three fatty acid molecules which form an ester bound (Figure 2.1). They are water-insoluble and non-volatile products that can be found both in vegetable and animal sources [16]. They are synthetically formed from the condensation reaction between glycerol and three fatty acids molecules and the products of this reaction are one molecule triglycerides and three molecules water (Figure 2.2).



R_1 , R_2 , R_3 ; fatty acid chain

Figure 2.1 : A triglyceride molecule.

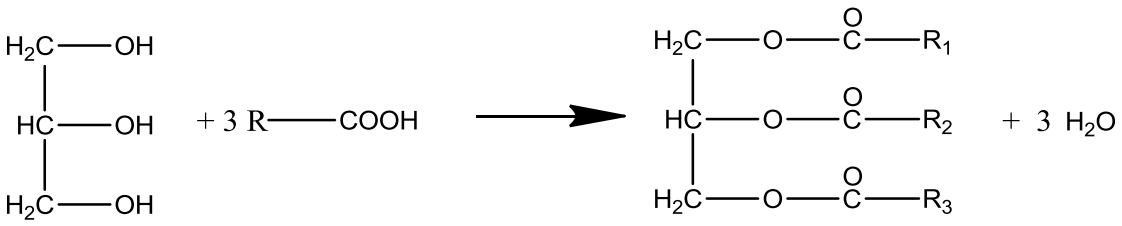


Figure 2.2 : Formation of triglyceride molecule.

When all bonds between the carbon atoms of fatty acids are single, it is called as saturated compound. When there is at least one double bond between the carbon atoms of fatty acids, it is called as unsaturated compound. The carbon numbers of the natural fatty acids are generally between 12 and 22 with an even number. Fatty acid composition of some oils are given in Table 2.1 [17, 18].

Table 2.1 : Fatty acid distribution of some oils.

Fatty acid	Castor oil (%)	Linseed oil (%)	Oiticica oil (%)	Palm oil (%)	Rapeseed oil (%)	Refined tall oil (%)	Soybean oil (%)	Sunflower oil (%)
Palmitic acid	1.5	5	6	39	4	4	12	6
Stearic acid	0.5	4	4	5	2	3	4	4
Oleic Acid	5	22	8	45	56	46	24	42
Linoleic acid	4	17	8	9	26	35	53	47
Linolenic acid	0.5	52	-	-	10	12	7	1
Ricinoleic acid	87.5	-	-	-	-	-	-	-
Licanic acid	-	-	74	-	-	-	-	-
Other acids	-	-	-	2	2	-	-	-

2.1.2 Classification of triglycerides

Oils are commonly classified according to their drying specification which is related to unsaturation degree. Unsaturation degree is determined by iodine value. Iodine value is the amount of g iodine that reacts with 100 g oil or fatty acid [19]. The greater iodine value, the more rapid drying oil. Also, the conjugated unsaturated bonds increase the speed of drying time [18, 20]. The oils with iodine values greater than 170, between 100 and 170, smaller than 100 are called as drying oils, semi-

drying oils and non-drying oils, respectively. There is given iodine values of some fatty acids and triglycerides in Table 2.2 [19].

Drying oils: When they are maden film on the non-absorbtive substrates like glass, they make hard films in 2-4 days. These type of oils consist of fatty acids that contains 2 or more than 2 double bonds abundantly.

Semi-drying oils: When they are maden film on the non-absorbtive substrates like glass, they do not form hard films because they make soft and elastic films in a greater time. These type of oils consist of fatty acids that contains only 1 or 2 double bonds abundantly.

Non-drying oils: When they are maden film on the non-absorbtive substrates like glass, they can not show any film properties in a long time. These type of oils consist of fatty acids that contains only a few amount of 1 double bond.

Table 2.2 : Iodine values of unsaturated fatty acids and triglycerides of them.

Fatty acid	Number of carbon atoms	Number of double bonds	Iodine value of acid	Iodine value of triglyceride
Palmitoleic acid	16	1	99.8	95
Oleic acid	18	1	89.9	86
Linoleic acid	18	2	181.0	173.2
Linolenic acid and α-Elestearic acid	18	3	273.5	261.6
Ricinoleic acid	18	1	85.1	81.6
Licanic acid	18	3	261.0	258.6

2.1.3 Polymers from triglycerides

Most commonly used triglyceride oils in the synthesis of polymers are sunflower, castor, linseed, oiticia, palm, soybean, tall and rapseed oils. Polymers based on triglycerides have been widely used in several applications and some of them can be listed as polyurethanes, oxypolymerized oils, polyesters, polyamides, acrylic resins, epoxy resins and polyesteramides [1]. Triglycerides can be functionalized by the glycerolysis reaction. By means of this reaction triglycerides can be hydroxylated and these hydroxylated triglycerides can be reacted with epoxies, carboxylic acids, anhydrides and isocyanates.

In this part, some oil based polymers are mentioned.

When triglycerides are heated up to elevated temperatures, it leads to autooxidation process with oxypolymerization and thermal-oxidative degradation [21]. Beside by heat, autooxidation can be initiated by light catalyst with forming triglyceride free

radical. Then, this radical reacts with the oxygen to produce peroxy free radical and this peroxy radical that makes reaction with another triglyceride in order to form hydroperoxide and a triglyceride free radical. This process is terminated when two peroxy free radicals meet. A representative autooxidation process is shown in Figure 2.3. The fatty acid type on triglycerides is crucial for oxypolymerization due to double bonds [22]. In an research, oxypolymerizable tendency of some oils are defined [23]. In an another study, it is explained that the increase in temperature accelerates the oxidation process [22].

Viscosity, density, refractive index, iodine and peroxide values are the important properties of oxidized oils and they were all determined during the oxypolymerization reaction [24].

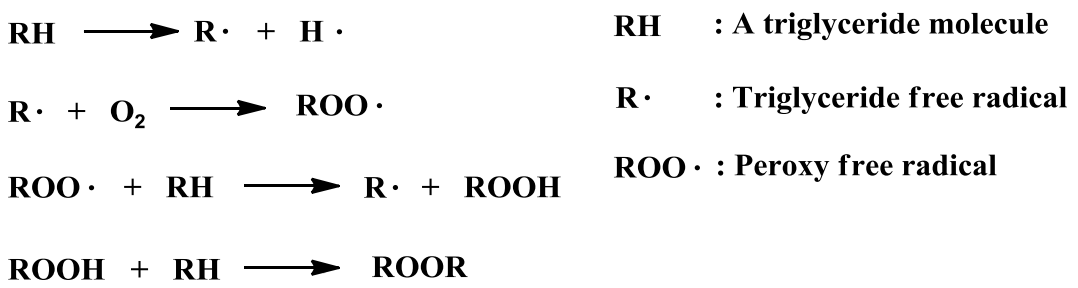


Figure 2.3 : Autooxidation of triglyceride molecule.

Polyesters are one of the most widely used polymers that can basicly be produced by the polycondensation reaction of dibasic acids and diols and their derivatives [25]. The polycondensation of hydroxyl acids and the ring opening of lactones are two other ways of producing polyesters [1].

The most known and applied type of oil based polyesters are the alkyd resins whose productions are relatively economic to other type of resins. They are formed through the reaction of polybasic acids and polyols. Monoglyceride (Figure 2.4) [tuncer hocalari referans ver] and fatty acid methods are the common production routes of alkyd resin [18]. Since the various international legislations limit the use of solvent based alkyd resins, water based alkyd resin was produced. While water borne alkyd resins are environmentally friendly, they show poorer properties than solvent based ones, therefore, their properties have been tried to pull the level of the properties of solvent based alkyd resins.

Oil based polyamides are mostly used in paint industry since they make paint application easier and enhance the film appearance [1]. Nylon 11 is a commercial oil

based polyamide which is synthesized from castor oil [26, 27]. In order to develop the flow of paints thixotropes can be produced through the condensation reaction of dimer acids of tall or soybean oils with amines [28]. Thixotrope materials have a higher viscosity when they are rest and have a smaller viscosity when they are exposed to a constant shear stress [29].

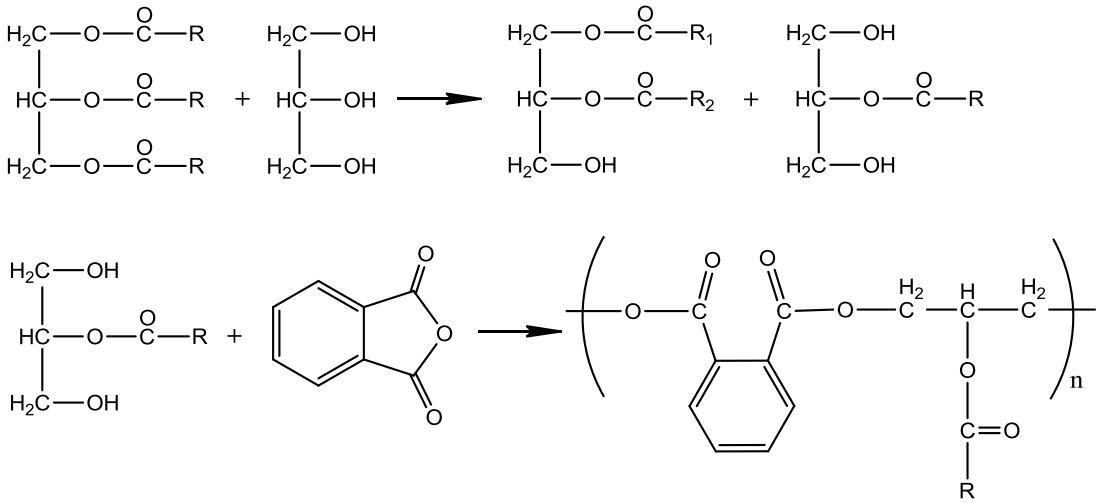


Figure 2.4 : Preparation of alkyd resin by monoglyceride method.

Epoxidation of oils that is widely used in plasticizers and stabilizers for polyvinyl chloride is another application method of oil based compounds. Vegetable oils can be epoxidized with the double bonds present in fatty acids such as oleic, linoleic and linolenic acids [30]. Epoxidation of oleic acid with peracetic acid is shown in Figure 2.5. Epoxidation is based on the formation of peracid which is produced by the reaction of acetic or formic acid with hydrogen peroxide by means of strong mineral acids [31]. When epoxidized oils are reacted with the alcohol, amine and carboxylic acids that have active hydrogen, hydroxylated products are formed [1].

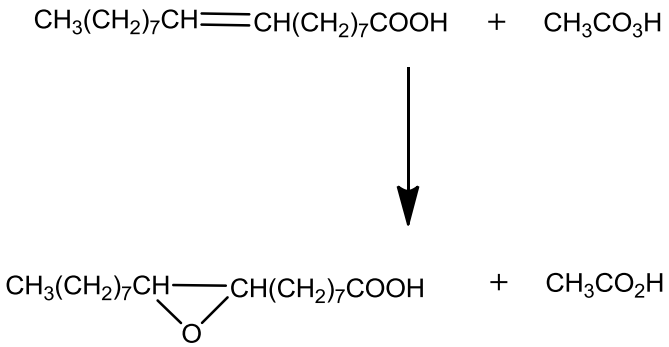


Figure 2.5 : Epoxidation of oleic acid.

Polyurethane oils are the polyaddition product of polyisocyanates and polyols (monoglycerides and diglycerides) in the presence of catalyst. The generalized reaction is shown in Figure 2.6. Polyurethane oils contains both soft and hard segments. The soft segment comes from the long linear chains of glycerides which give flexibility to polyurethane and the hard segment comes from the polyisocyanates. By changing the isocyanate/polyol ratio, the polymer in desired properties can be obtained.

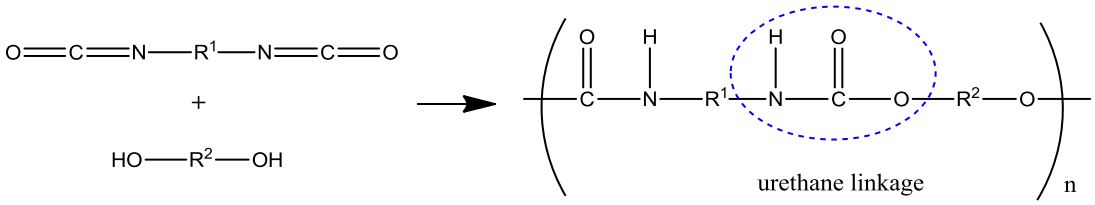


Figure 2.6 : The generalized polyurethane reaction.

There is a very wide application area of polyurethanes that can be listed as coatings, medicine, engineering, automotive, hard and soft plastics, elastomers, varnishes and adhesives [32]. In this part, some vegetable oil derived polyurethane researches were mentioned.

It is mentioned that hydroxylated castor oil can be used instead of hydroxyl containing chemicals based on petroelum sources in order to synthesize polyurethane foams [33]. Also, castor oil is a good material against corrosion [34]. Biodegradable samples based on rapeseed-oil were prepared by Lu and coworkers [35]. In an another study, fatty acid based diisocyanate was produced and used as petroleum based diisocyanate, and similar properties were obtained [32].

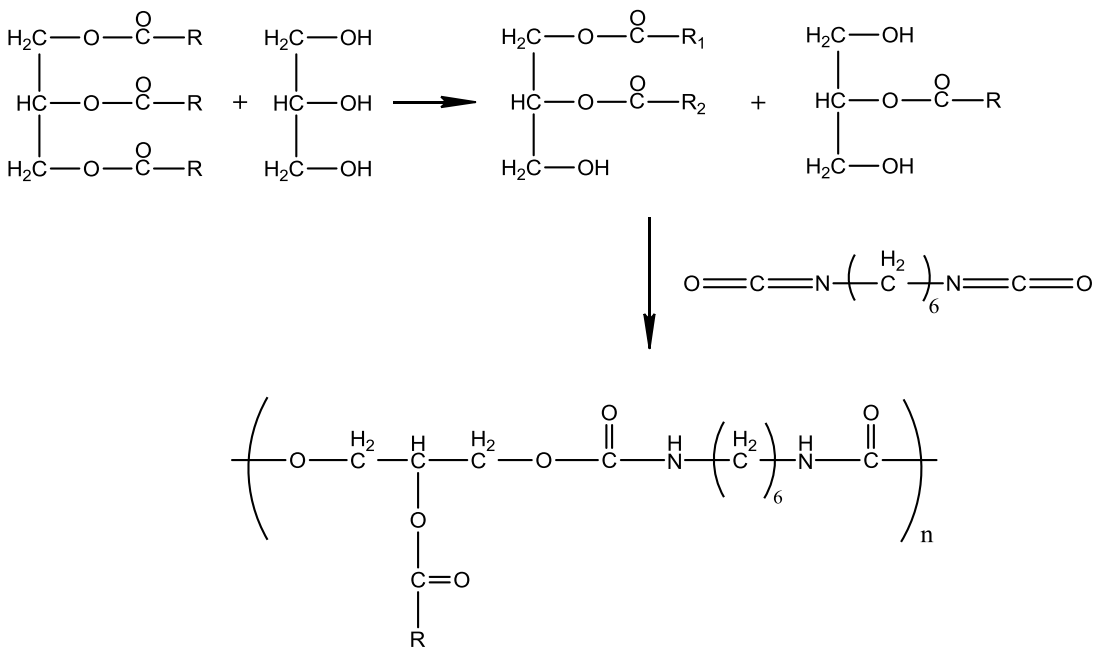


Figure 2.7 : Preparation of partial glycerides based polyurethanes.

Oil based polyurethanes can also be obtained through the reaction of isocyanates and triglyceride derivatives such as monoglycerides and diglycerides which are formed through the glycerolysis reaction (Figure 2.7). The most widely used isocyanates are shown in Figure 2.8.

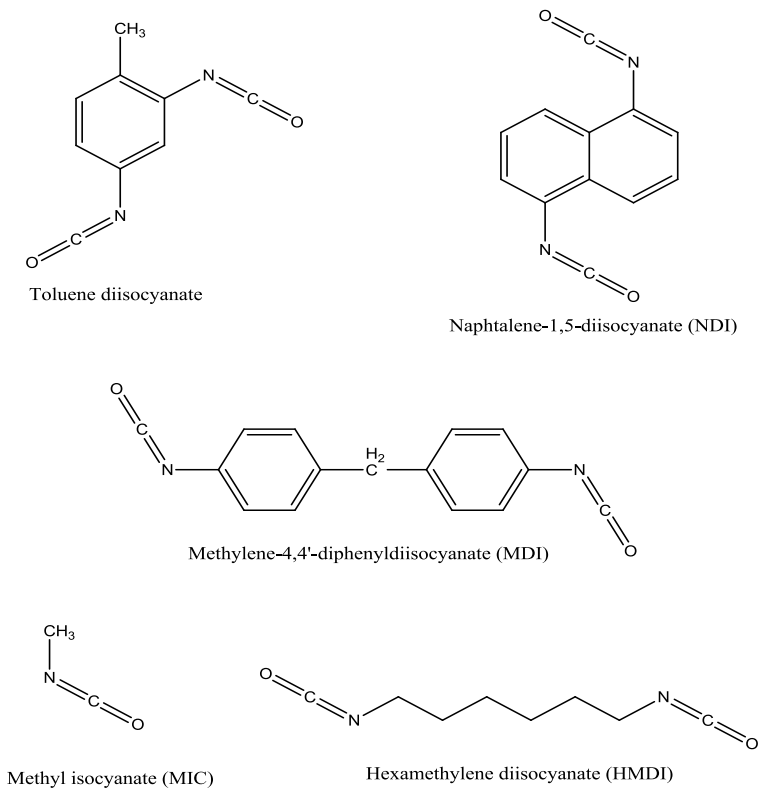


Figure 2.8 : Most widely used isocyanates.

Mono and diglycerides, which are two significant derivatives of the triglycerides, have been used in paint technology due to their good film properties. In a study, the effect of different type of diisocyanates that was reacted with partial glycerides of sunflower oil were determined [36]. The films formed with aromatic diisocyanates showed good water resistance and the films with higher content of diisocyanates showed rapid drying property.

2.2 Polybenzoxazines

Benzoxazines can be synthesized through the condensation reaction of phenolic compounds, formaldehyde and primary amines which form a Mannich bridge [37, 38]. It was first synthesized with phenolic compounds and primary amines by Holly and Cope [39, 40]. Lately, difunctional phenolic compounds and amines were also used in order to obtain a resin with desired properties [41]. The aromatic oxazine ring present in benzoxazine monomers undergoes ring-opening polymerization by heating [42].

2.2.1 Synthesis of Benzoxazine Monomers and Polybenzoxazines

Monofunctional benzoxazines were first synthesized by Holly and Cope as mentioned above. They obtained this monomer in a two-step method with a solvent. Chosen amine and formaldehyde are added and mixed with a solvent in a flask in order to make N,N-dihydroxymethylamine derivative that will react with the hydroxyl group and the ortho position of the chosen phenolic compound and form benzoxazine monomer. An illustrative formula is given in Figure 2.9.

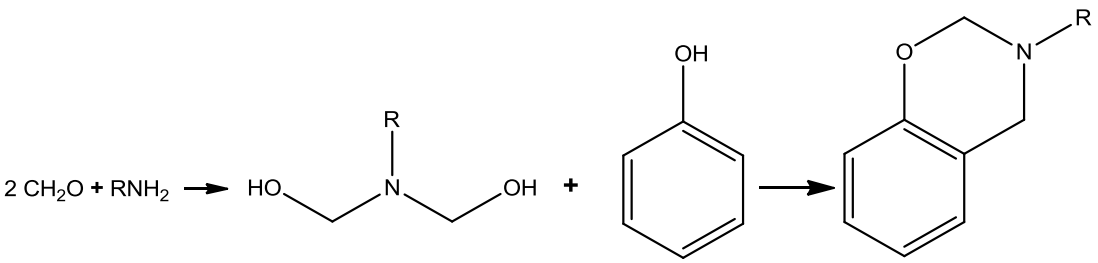


Figure 2.9 : Synthesis of benzoxazine monomer.

When monofunctional benzoxazines were cured, they form only oligomeric structures with nearly 1000 Da average molecular weight. In order to obtain higher

molecular weight polybenzoxazines, multifunctional benzoxazine monomers have been synthesized. By using difunctional phenolic compounds or amines, difunctional benzoxazine monomers are obtained [9]. As it is stated in literature, if both difunctional phenolic compounds and difunctional primary amines are used, long chain benzoxazine monomers are formed [41, 43].

The suitable solvents for formation of benzoxazine monomer are the solvents with relatively low dielectric constants such as chloroform, dioxane, toluene and xylene. When dimethylsulfoxide with higher dielectric constant was used, the yield of the reaction was low and the oligomer formation was high [9]. Morever, it is asserted that carrying out a higher reaction temperature decreases the dielectricity of solvent. As an example to this, Ishida applied the reaction at 150 °C in xylene and obtained a higher yield comparing with the yield of other low reaction temperatures [9]. Besides oligomer formation occurs due to the solvent type, oligomeric structures can occur during the reaction process because of active hydrogen groups such as naphtol, indoles, carbazole, imides and aliphatic nitro compounds [44]. The products of monofunctional benzoxazine reaction is shown in Figure 2.10.

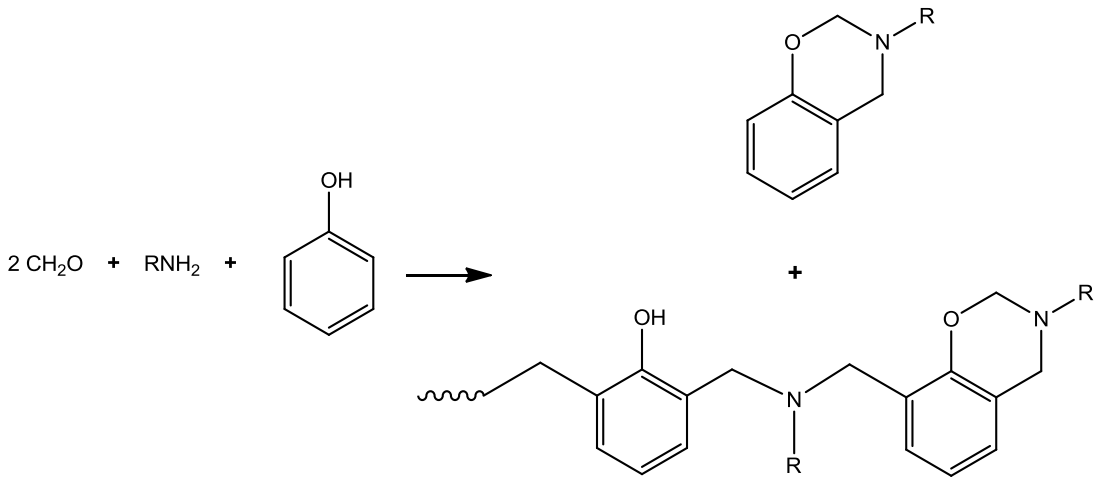


Figure 2.10 : Products of benzoxazine reaction.

A simple figure of ring-opened structure of monofunctional and difunctional benzoxazine monomers are shown in Figure 2.11.

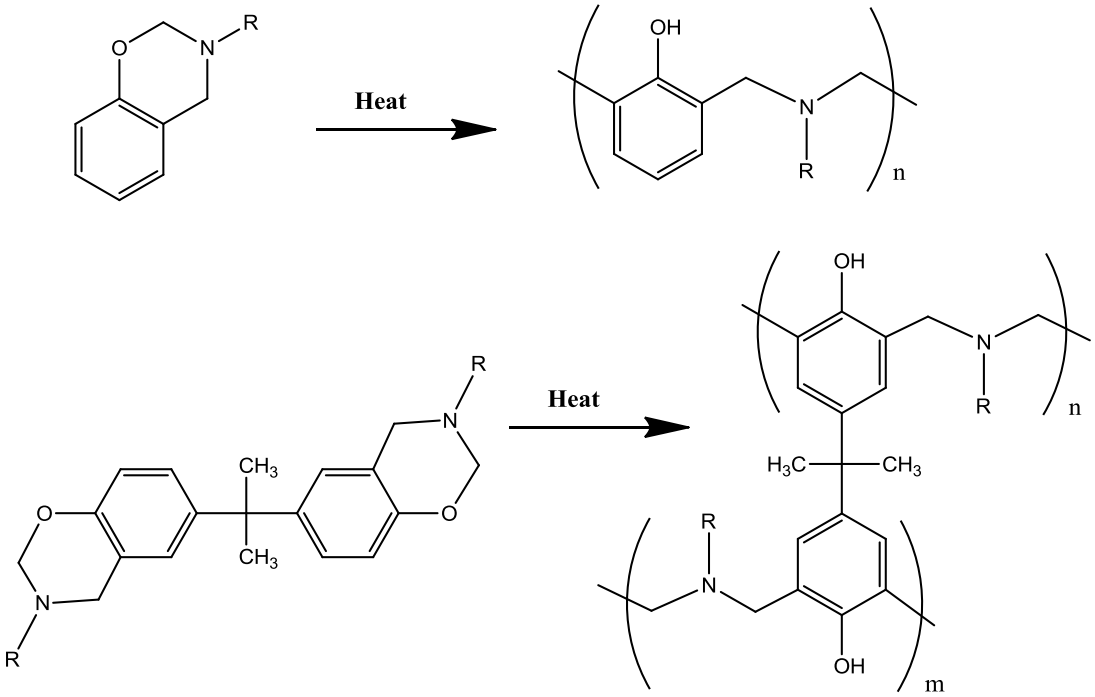


Figure 2.11 : Ring opening of monofunctional and difunctional benzoxazines.

Ishida introduced an another synthesize technique in which no-solvent is used and it is called as solventless method. The advantages of this method are the decreased reaction time and higher yield when it is compared with the solvent-used traditional method [45].

When benzoxazine monomers are heated to elevated temperatures, the oxazine ring present in benzoxazine monomer is opened and chain propagation starts to form. There are several proposed ring-opening mechanisms during the curing process where a carbocation ion and an imminium ion are formed [46]. Electrophilic substitution of the carbocation to the benzene ring of the phenol advances the polymerization step.

2.2.2 Recent advancements of polybenzoxazines

The polybenzoxazines are superior to the phenolic resins such as novolacs and resoles due to both maintaining their properties and having new properties. The most noteworthy features of polybenzoxazines can be listed as high thermal stability, high char yield [9], no shrinkage, low water absorption, no need of catalysts for production and curing, and no by product during curing [10]. These significant features can be improved with convenient primary amines and phenolic compounds. For instance, when difunctional phenolic compound was used the thermal stability

was enhanced comparing with phenol [9]. While they have good properties, they have some undesirable characteristics like brittleness, high curing temperature and difficult processability [11].

In order to improve the properties of polybenzoxazines, several applications were actualized like blending with other polymers such as epoxy resin [47], polyimide [48, 49], polyamide [49], polycaprolactone, polycarbonate [50] and copolymerization with polyurethane [51], polycaprolactone, maleimide benzoxazine with styrene [50].

In recent years, there has been a lot of crucial investigations on the development of the flexibility of benzoxazine based macromolecules to eliminate the disadvantages of brittlenes. For instance, Takeichi and co-workers studied the viscoelasticity of polybenzoxazines with amines having different long chain [43] and, they also prepared polyurethane copolymer [51], polyamide and polyimide blends [49]. Chang et al. studied viscoelastic properties of polybenzoxazines-polyhedral oligomeric silsesquioxane (POSS) hybrid films [52]. Rimdusit et al. prepared anacardic acid-benzoxazine matrice and determined the flexibility [53]. Ishida et al. prepared polybenzoxazine by using polyether diamines having different long chain and obtained flexible thermoset end-products [54].

In addition to developing the flexibility of polybenzoxazines, the cure temperature could be decreased in the presence of urethanes [55] and catalysts such as para-toluenesulfonic acid [56].

Thermal degradation of polybenzoxazines comes true in a three-stage process: cleavage of chain end, evaporation of the amine compound, concurrently cleavage of the Mannich base and phenolic bonds [57].

3. EXPERIMENTAL WORK

3.1 Materials

Refined sunflower oil purchased from the market was used as received. Chloroform, sulfuric acid, glycerol, phenol, paraformaldehyde, sodium sulphate, sodium hydroxide, toluene-diisocyanate (80% 2,4, 20% 2,6 isomers), calcium hydroxide and calcium hydride were bought from Merck. All of them were used without any purification. Toluene was obtained from Merck and it was dried with calcium hydride before use. Diethyl ether and 1-4 dioxane obtained from Riedel de Haen were used as received. 6-amino-1-hexanol bought from Fluka was used without purification. Lead naphthenate was prepared as a 24 wt. % solution in white spirit.

3.2 Equipments

3.2.1 Fourier transform infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer.

3.2.2 Nuclear magnetic resonance spectroscopy (^{1}H NMR)

Chemical structure of the polymers were also determined by using Bruker 250 MHz spectrometer. $CDCl_3$ was used as a solvent.

3.2.3 Differential scanning calorimeter (DSC)

Thermal analyses were done by differential scanning calorimetry (DSC) using Perkin Elmer DSC 4000 at a heating rate of 10°C/min under nitrogen flow.

3.2.4 Thermal gravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were recorded on a Perkin Elmer Diamond TG/DTA instrument at a heating rate of 10°C/min under nitrogen flow.

3.3 Preparation Methods

3.3.1 Preparation of hydroxyl containing benzoxazine monomer (Bz-OH)

In a three-neckled flask, 120 mmol paraformaldehyde and 60 mmol 6-amino-1-hexanol and 100 ml dioxane were mixed in about 20 minutes at room temperature. Then, 60 mmol phenol dissolved in 50 ml dioxane was added into the flask, and the mixture was refluxed with strirring for 5 h. After cooling to room temperature, the dioxane was evaporated with rotary evaporator, then, crude product was taken into chloroform and washed with 0.2 N NaOH, followed by washing with distilled water several times. The washed product in chloroform was dried overnight over sodium sulfate. The chloroform was removed by rotary evaporator, and the residual solvent was removed in vacuum oven at 40 °C for 24 h to obtain a yellow viscous fluid (Yield:65%). FT-IR and ^{1}H NMR spectra were taken.

3.3.2 Synthesis of partial glycerides (PG)

In a three-neckled flask, 13 g glycerol and 100g sunflower oil were mixed with and heated to 218 °C under nitrogen flow. At this temperature, $Ca(OH)_2$ (0.1wt.% of oil content) were added and the flask was heated to 230 °C for 1 h. Then, the mixture was cooled to room temperature and dissolved in diethyl ether, subsequent to this, washed with 0.2 N sulfuric acid and distilled water to eliminate the catalyst and unreacted glycerol. The washed organic layer was dried over sodium sulfate, filtered and diethyl ether was removed by using rotary evaporator. Hydroxyl and acid values were 112 mg KOH/g and 2 mg KOH/g [58].

3.3.3 Enrichment of partial glycerides (PGE)

It is well-known that aqueous alcohol was extensively used in the extraction of partial glycerides [59-61]. In the present study, the enrichment procedure was applied according to explanation given in US Patent [61]. Hydroxyl and acid values are determined as 235 mg KOH/g and 2 mg KOH/g [58].

3.3.4 Combining of benzoxazine to the partial glycerides (Bz-PG)

In a three-neckled flask, to partial glycerides (hydroxyl value: 108 mg KOH) in dry toluene, TDI was added in 5 minutes under nitrogen atmosphere in ice bath. After adding TDI, lead naphtanate (0.02wt.% of partial glycerides content) was added and

temperature was adjusted to 45 °C for 40 minutes. To this reaction mixture, Bz-OH, equivalent to partial glycerides mole, in dry toluene was dropped in 10 minutes and temperature was adjusted to 95 °C for 3 h. At the end of the reaction, there was no isocyanate peak near 2260 cm^{-1} and the toluene was removed by rotary evaporator. Representative reaction scheme is given in Figure 3.1.

Benzoxazine was also combined to the PGE by the same process as explained above (Bz-PGE).

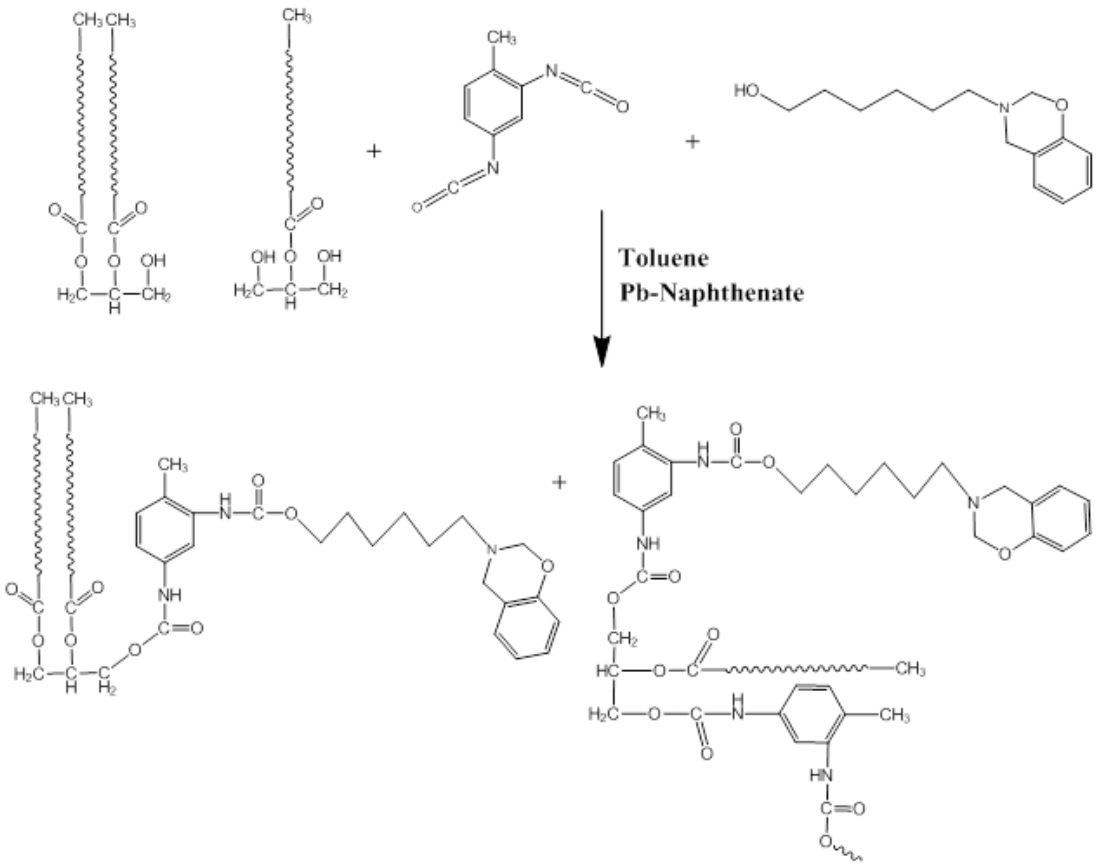


Figure 3.1 : Combining of benzoxazine monomer to partial glycerides.

3.3.5 Classical urethane oil synthesis (PG-U)

Classical urethane oil was prepared as a comparative sample. Partial glycerides to be used in the urethane oil reaction were prepared with a 0.08667 ratio of glycerol/triglyceride. Hydroxyl value obtained by this ratio was 110 mg KOH/g [58]. PG was dissolved in dry toluene and an equimolar amount of TDI was added slowly over 10 minutes. After lead naphthenate was added in the amount of 0.02% of the oil portion, temperature was adjusted to 45 °C for 40 minutes. Then, temperature was adjusted to 95 °C for 3 hours under nitrogen athmosphere.

4. RESULTS AND DISCUSSION

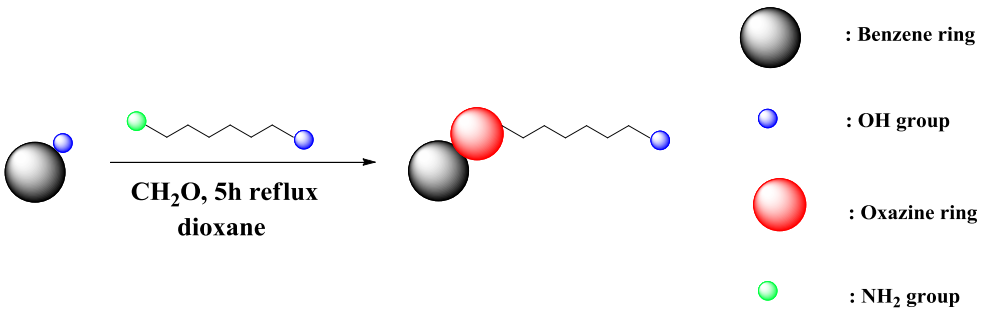


Figure 4.1 : Benzoxazine preparation.

Bz-OH: As mentioned before, Bz-OH monomer was synthesized according to the reaction shown in Figure 4.1. The structure of Bz-OH was confirmed by ^{1}H NMR and FT-IR spectra as well. In the ^{1}H NMR spectra (Figure 4.1), the characteristic resonances of oxazine ring at 3.97, 4.84 and 4.24 ppm are due to the $–CH_2$-N-, O-CH_2-N- and -OH protons, respectively. The aromatic protons of benzoxazine monomer appeared from 6.7 to 7.1 ppm, and the other peaks at 3.62 and 2.73 ppm are assigned to the C-CH_2-OH and N-CH_2-C, respectively. The remaining peaks at 1.56 and 1,36 ppm are assigned to the remaining C-CH_2-C protons. A small signal at 3.69 ppm that is attributed to the methylene of opened ring of oxazine was observed [55, 62].

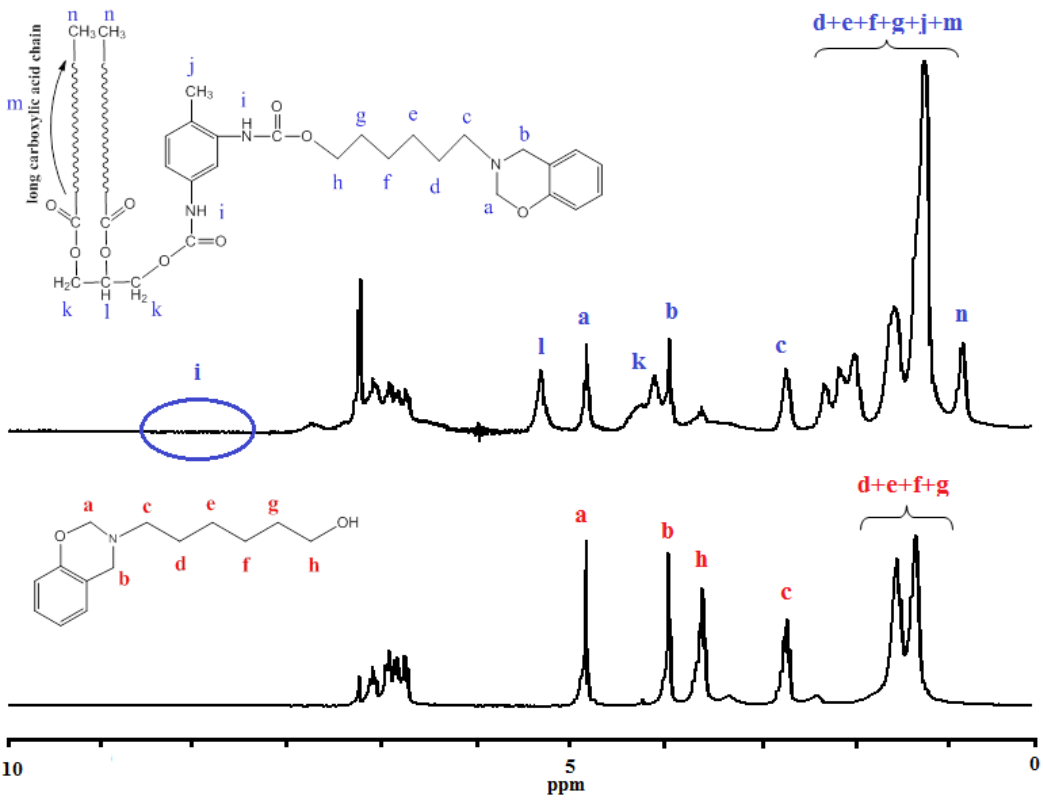


Figure 4.2 : ^{1}H NMR spectrum of Bz-OH and Bz-PGE.

In FT-IR spectra (Figure 4.3), absorbances at 1223 cm^{-1} and 1035 cm^{-1} are assigned to the asymmetric stretching of Ar-O-C and symmetric stretching of Ar-O-C, respectively [63]. The characteristic absorbance of the benzoxazine ring appeared at 922 cm^{-1} is assigned to the out-of-plane bending vibration of the benzene ring that is attached to the oxazine ring [64].

Moreover, the absorption at 752 cm^{-1} shows the ortho-disubstitued benzene [65] and the peaks at 1132 cm^{-1} and 1106 cm^{-1} are due to the asymmetric C-N-C [66]. A broad band from near 3500 cm^{-1} to 3000 cm^{-1} illustrates the formation of hydroxyl group of benzoxazine monomer [67].

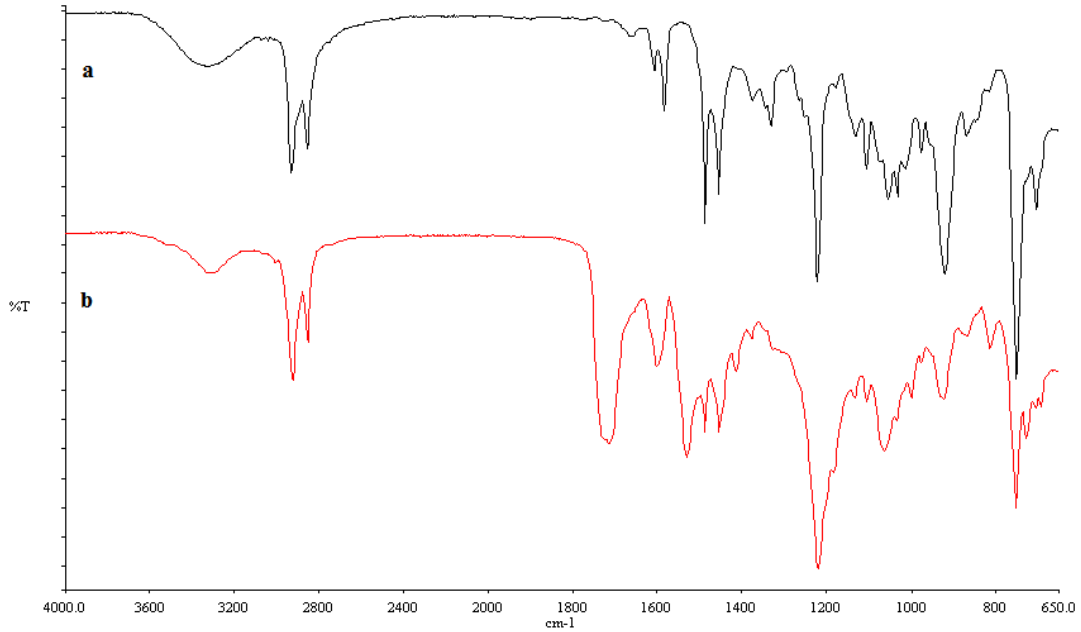


Figure 4.3 : Infrared spectra of pure a) Bz-OH monomer and b) Bz-PGE monomer.

Bz-PGE: The structure of Bz-PGE as shown in Figure 4.4 was confirmed by ^{1}H NMR and FT-IR spectra as well. In the ^{1}H NMR spectrum (Figure 4.1) of Bz-PGE, the oxazine ring resonances appeared at 4.85 and 3.97 ppm which are owing to the the $–CH_2$-N-, O-CH_2-N- protons. The weak absorbances between 8.3 and 9.6 ppm were assigned to –NH of urethane linkage [68]. The reason of the weakness was explained by Mirau as the existence of hydrogen bonding between C=O and N–H groups in the polymer chains [69].

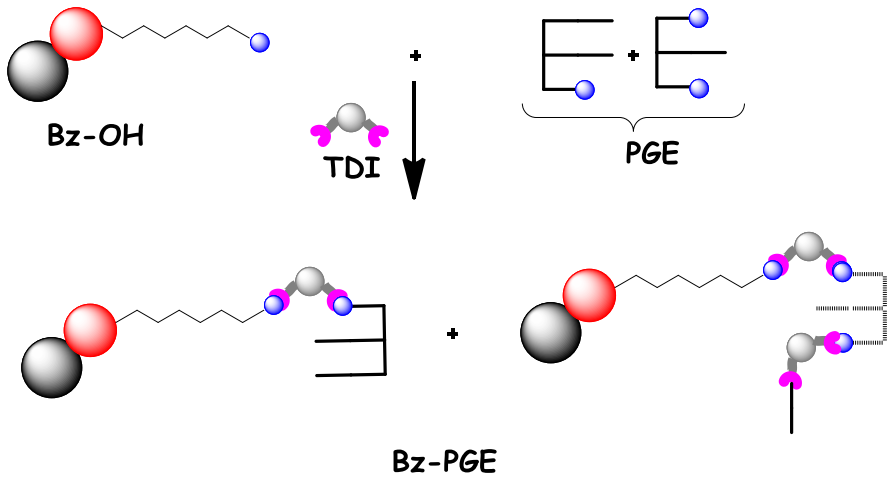


Figure 4.4 : Representative structure of benzoxazine modified oil.

The resonances between 1.28 and 2.34 ppm (long chains of PGE (-CH_2-)), at 0.87 ppm (methyl groups of PGE), at 5.32 ppm (olefinic CH of fatty acids (–CH=CH–)

and CH of glycerol (–CH–O–C(O)–)) were observed [70]. Also, the peak at 4.14 ppm was attributed to the methylene group of PGE (–CH_2–O–C(O)–).

The existence of oxazine ring was also affirmed by FT-IR spectrum. In the FT-IR spectrum of Bz-PGE (Figure 4.3), the absorbances at 1035 cm^{-1} and 1221 cm^{-1} which are assigned to the symmetric and asymmetric stretching of Ar-O-C was observed as in the Bz-OH monomer. Moreover, the characteristic peak of oxazine ring at 924 cm^{-1} displays the out-of-plane bending vibration of the benzene ring that is attached to the oxazine ring.

The formation of Bz-PGE was monitored by FT-IR spectrum as depicted in Figure 4.5. The bands at 1416 cm^{-1}, 1531 cm^{-1} and 1740 cm^{-1} display the C-NH secondary urethane amide [51], C-N stretching combined with N-H bending [64] and the carbonyl absorbance of urethane bond, respectively in Figure 4.5. Moreover, the N-H streching was observed at 3311 cm^{-1} in Figure 4.6.

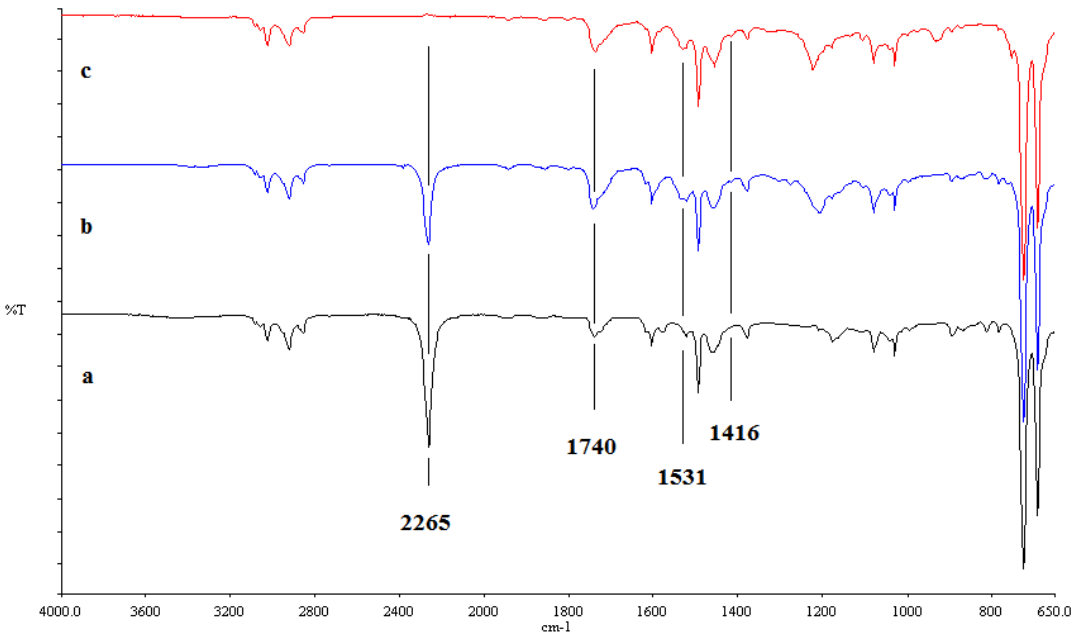


Figure 4.5 : Monitoring of the Bz-PGE formation by FT-IR: a) at the beginning of the reaction b) after 45 min. (before Bz-OH was added) c) after 3 h reaction.

The results obtained from ^{1}H NMR and FT-IR showed that partial glycerides were successfully combined to the benzoxazine monomer through the reaction of hydroxyl groups with TDI. These results are in consistence with those given by literature [68].

The curing of Bz-PGE was carried out at 180 °C for 3 h. Since polyurethane groups start to decompose about at 180 °C [68, 71] the temperature in curing process was not exceeded 180 °C.

Curing behavior of Bz-PGE is followed by FT-IR spectrum and the related spectra were given in Figure 4.6. After 3 h curing period at 180 °C, the characteristic peak of oxazine ring at 924 cm^{-1} and the peak of C-O-C symmetric stretching at 1035 cm^{-1} disappeared. The absorbances at 1489 cm^{-1} and 753 cm^{-1} (disubstituted benzene ring) [65], at 1221 cm^{-1} (C–O–C asymmetric stretching) decreased. These explanations indicate that ring opening and polymerization of Bz-PGE were realized and the curing products of Bz-PGE were given in Figure 4.7.

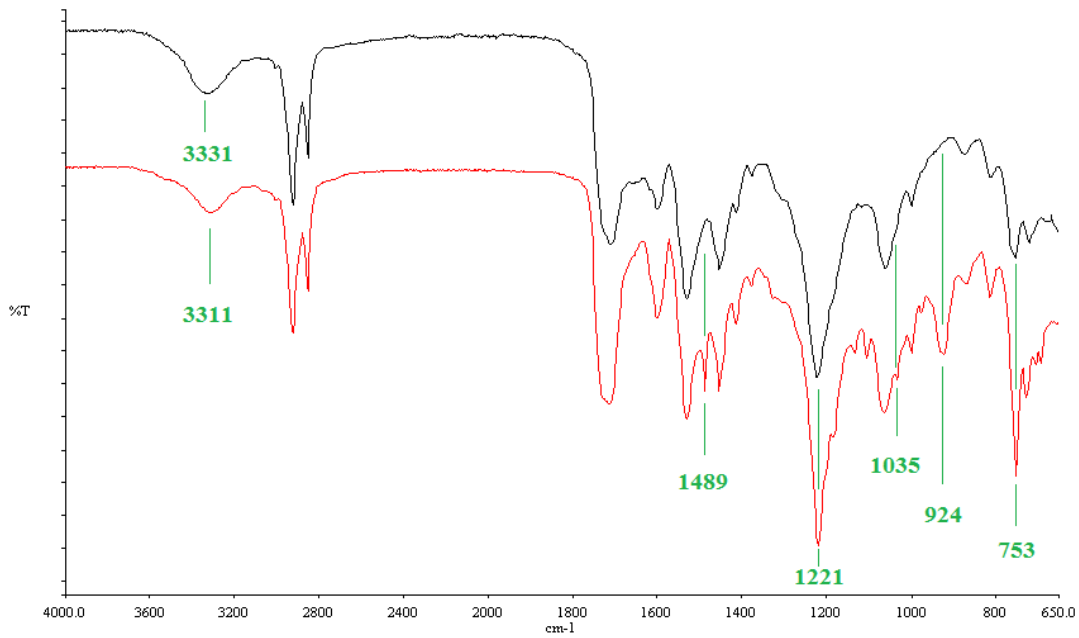


Figure 4.6 : Curing behavior of Bz-PGE: a) pure monomer at room temperature b) after 3 h at 180 °C.

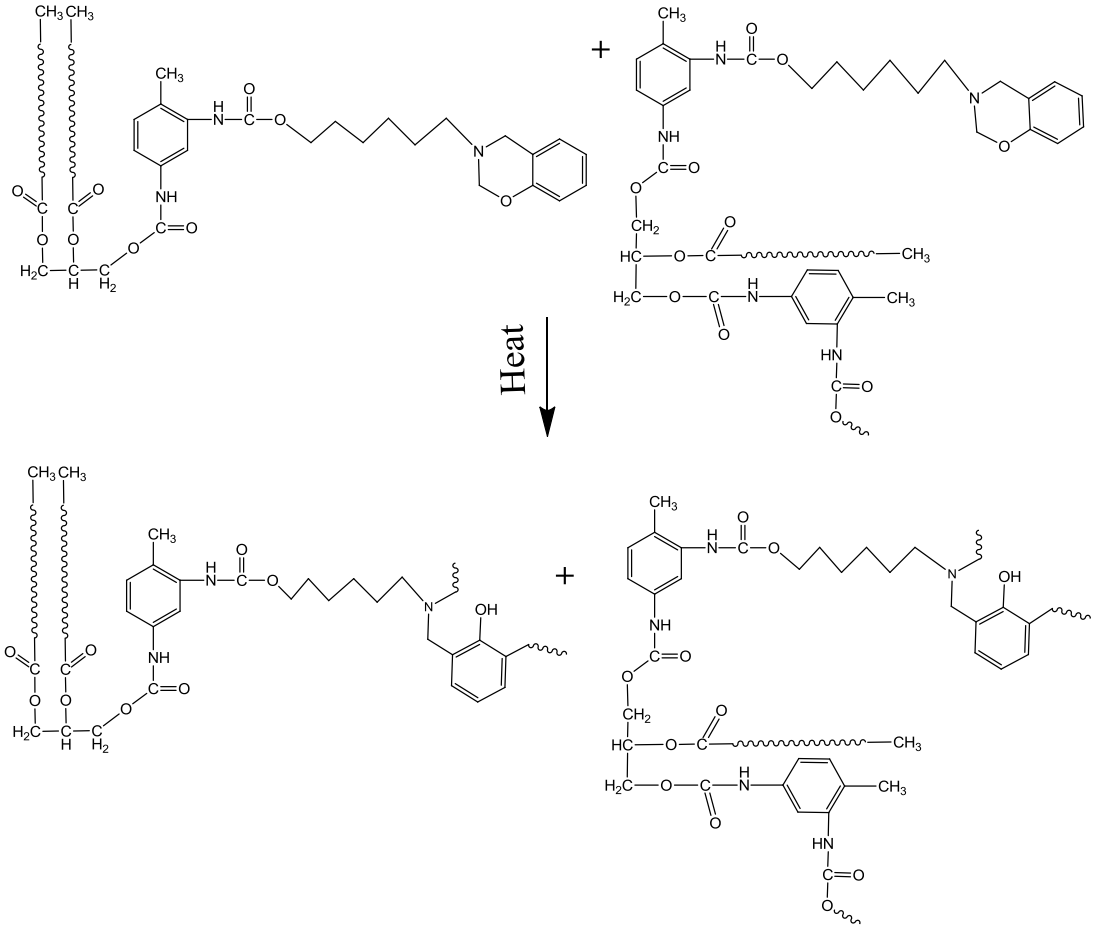


Figure 4.7 : Curing products of Bz-PGE.

Thermal analysis of Bz-OH and Bz-PGE were analysed with DSC in nitrogen atmosphere. Figure 4.8 and Figure 4.9 show the DSC diagrams of both cured film and uncured Bz-OH and Bz-PGE, respectively. In Figure 4.8 an exothermic peak with a maximum at 202 °C illustrating the ring opening of uncured Bz-OH was observed. In the same thermogram, the onset temperature for the opening of the oxazine ring was 175 °C and the degradation process starts after 247 °C.

While the Bz-OH sample gave an exothermic peak with a maximum at 202 °C, the Bz-PGE sample showed this exothermic peak at 236 °C. This difference is due to the existence of urethane groups in the latter sample. Ishida found the same kind of thermal behaviour with the samples containing urethane groups [68]. The onset temperature for the opening of the oxazine ring in Bz-PGE sample was 182 °C. In the case of Bz-OH, a degredation process starts after 247 °C due to the condensation between hydroxyl groups to produce water [68, 72]. This degradation was not observed for the Bz-PGE sample, since, as explained before, the hydroxyl groups were reacted with TDI to combine the partial glycerides to benzoxazine monomer.

After thermal treatment at 180 °C for 3 h, there was no considerable residual exotherm illustrating that the ring opening almost completely took place as seen in Figure 4.9.

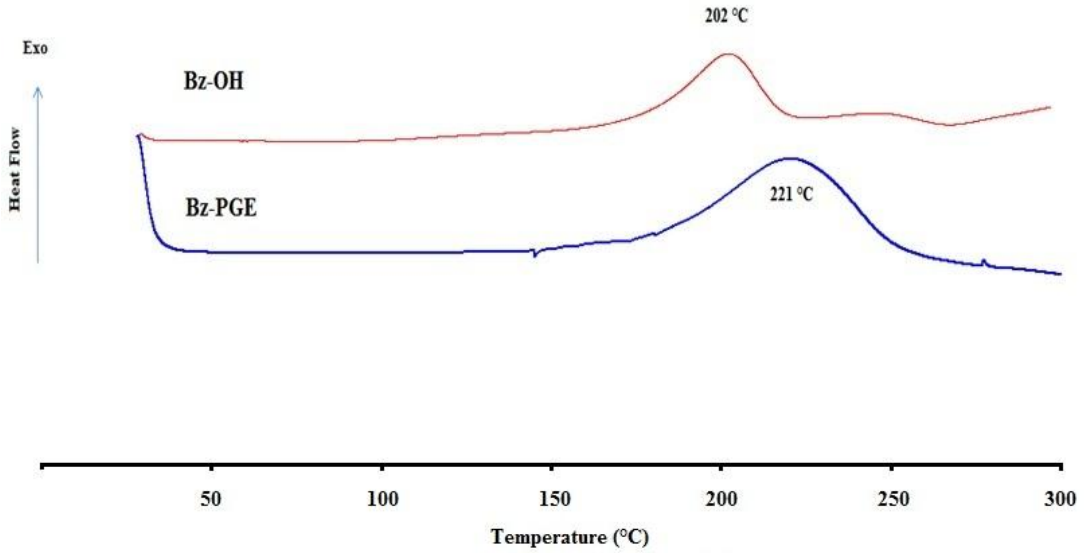


Figure 4.8 : DSC thermograms of Bz-OH and Bz-PGE monomers.

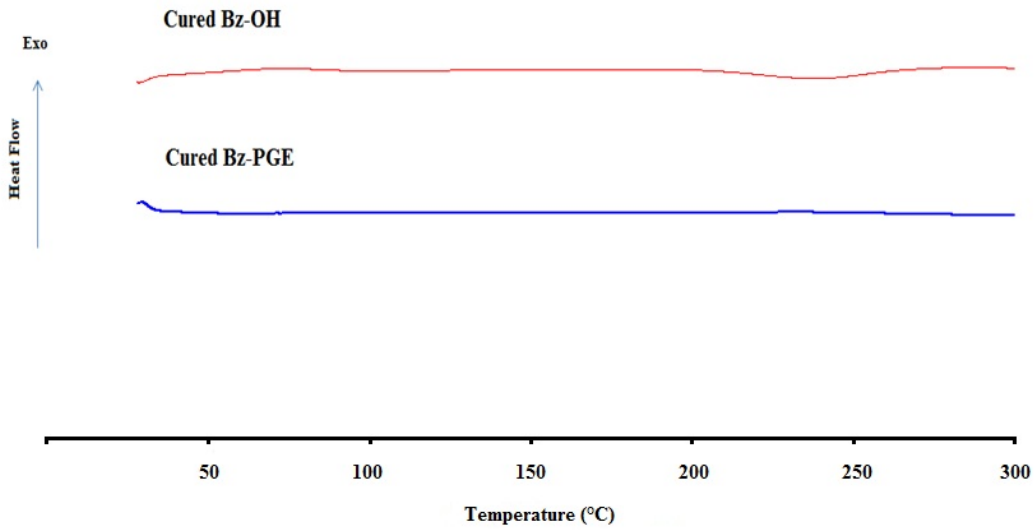


Figure 4.9 : DSC thermograms of cured Bz-OH and Bz-PGE films.

The thermal stability of the Bz-OH and Bz-PGE were evaluated by TGA in a nitrogen atmosphere. Figure 4.10 depicts that temperatures at 5% and 10% weight loss of Bz-PGE are higher than those of Bz-OH. However, this condition is valid

until 282 °C. Over this temperature, decomposition of Bz-PGE goes up drastically which is most probably due to the degredation of urethane linkage [73], although the char yield of Bz-OH is much higher than that of Bz-PGE due to its high aromatic ring content.

Table 4.1 : Thermal gravimetric properties of Bz-OH, Bz-PGE and PG-U

Sample	$T_{5\%}$ (°C)[a]	$T_{10\%}$ (°C)[b]	T_{max} (°C)[c]	Y_{500} (%)[d]
Bz-OH	259.5	285.8	449	26
Bz-PGE	267.4	284	321	13.5
PG-U	180	241	411	11

a: Temperature of 5% of weight loss.

b: Temperature of 10% of weight loss.

c: Temperature of the maximum weight loss rate.

d: Char yield at 500 °C.

The reason of the low char yield of Bz-PGE is most likely due to the partial glycerides and low aromatic content which comes from benzoxazine. There are some studies which had high char yield than our benzoxazine sample with difunctional phenol or amine derivatives [9, 66] If a difunctional phenol such as bisphenol A or bisphenol B is used instead of phenol, the char yield might be higher than the sample based on phenol.

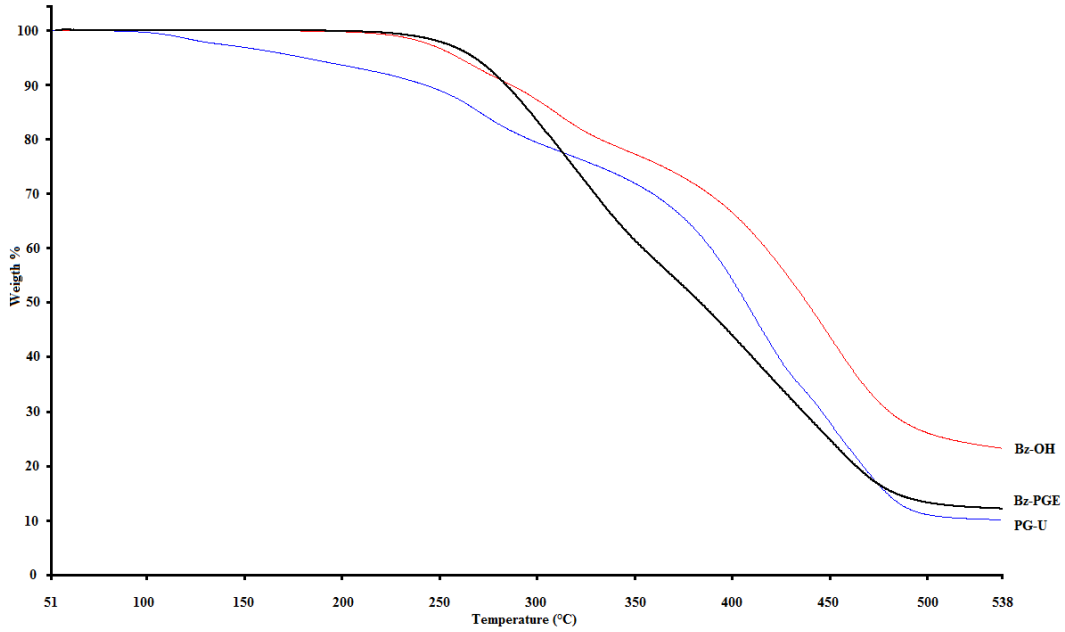


Figure 4.10 : TGA thermograms of cured Bz-OH, Bz-PGE and PG-U films.

The partial glycerides obtained from the glycerolysis reaction was used without enrichment to obtain benzoxazine modified oil sample by apllying the same process as explained before. When this sample (Bz-PG) was applied as a film, it gave a tacky property. In order to overcome this shortcoming additional benzoxazine was added and the film was cured. This film sample also showed tacky property as well. The reason for this tackiness is because of triglycerides present in the crude partial glyceride mixture. In the next step of the study, triglycerides was removed from the mixture by solvent extraction as described in experimental section to obtain enriched partial glycerides (PGE). By this way as shown in Figure 4.11 triglyceride fraction of the crude partial glycerides were removed to a great extent. The benzoxazine modified oil (Bz-PGE) prepared with these enriched partial glycerides were used in the determination of film properties. The samples based on PGE showed non-tacky and transparent films and the film properties of the Bz-OH and Bz-PGE were given in Table 4.1.

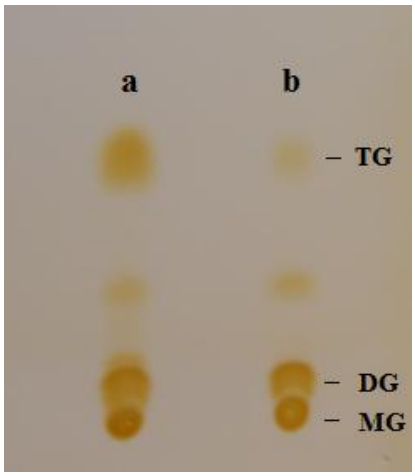


Figure 4.11 : Thin Layer Chromotographam of a) PG and b) PGE

(TG, DG and MG depict triglycerides, diglycerides and monoglycerides, respectively.)

The expected results of flexibility, adhesion, hardness and resistance to water, alkali and acid tests were observed. Both Bz-OH and Bz-PGE samples displayed excellent resistance to water, alkali and acid by showing no visible effect both in solution and on the film in a 24 h period.

While the flexibility of Bz-OH had a poor performance when it was bended over the 16mm-diameter-cylinder, Bz-PGE showed excellent flexibility by linking the PGE to the Bz-OH. Bz-PGE did not show any crack even it was bended over the 2mm-diameter-cylinder.

The difference between hardness of Bz-OH and Bz-PGE explains that partial glycerides softened the polybenzoxazine (Bz-OH).

The adhesion of Bz-OH and Bz-PGE to wood and metal surface is excellent as shown in Table 4.2. However, Bz-PGE sample did not adhere to the glass surface.

Table 4.2 : Film properties of Bz-OH and Bz-PGE

Film properties	Bz-OH	Bz-PGE	PG-U[a]
Flexibility[b]	12 mm[c]	1 mm[d]	1 mm[e]
Adhesion[f]	5B	5B	5B
Rocker hardness	84	56	8
Acid resistance	nc	nc	nc
Alkali resistance	nc	nc	20 min.
Water resistance	nc	nc	30 min.

nc: no change (this states that the film did not undergo any deformation or corrosion).

a: Standard urethane oil was cured with air for 3 days at room temperature.

b: The diameter of the cylinder that caused crack on the film.

c: The avergae dry film thickness was 44 μm.

d: The average dry film thickness was 45 μm.

e: The average dry film thickness was 49 μm.

f: Test method B was applied on wood and tin plates.

5. CONCLUSION

In conclusion, synthesis of benzoxazine modified triglyceride oil and their films were succesfully achieved. Firstly, hydroxyl containing benzoxazine monomer and partial glycerides were prepared, and then, these two compounds were linked by means of toluene diisocyanate. FT-IR and ^{1}H NMR results indicated that benzoxazine molecules were incorporated into the triglyceride oils.

The benzoxazine modified oil sample was made film by film applicator and cured by heating. After curing, benzoxazine modified sample showed good film properties such as flexibility, adhesion, hardness, resistance to alkali, acid and water. Therefore, this obtained material can be considered as a coating material when it is applied on metal and wood surfaces.

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