ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

AN EASY WAY TO MODIFY TRIGLYCERIDE OILS FOR OIL-BASED BINDER PREPARATION

M.Sc. THESIS

Didem AYCAN

Department of Chemical Engineering

Chemical Engineering Programme

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Thesis Advisor: Prof. Dr. A. Tuncer ERCİYES

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YAĞ TEMELLİ BAĞLAYICI ÜRETİMİ İÇİN TRİGLİSERİD YAĞLARIN MODİFİKASYONUNDA KOLAY BİR YÖNTEM

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To my dearest family,

FOREWORD

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ABBREVIATIONS

APTES : 3-aminopropyltriethoxysilane
ASTM : American Society for Testing and Materials
Bz-Si : Benzoxazine functional silane
Bz-Si/PGE : Benzoxazine functional silane modified oil sample
CF(Bz-Si)/PGE : Cured benzoxazine silane modified oil film
DIN : German Institute for Standardization
DSC : Differential scanning calorimetry
FT-IR : Fourier transform infrared spectroscopy
HMDI : Hexamethylene diisocyanate
IV : Iodine value
NMRP : Nitroxide mediated radical polymerization
PBTDI : Poly(1,4-butandiol)toluene-2,4-diisocyanate
PG : Partial glyceride
PGE : Enhanced partial glyceride
RAFT : Reversible addition-fragmentation chain transfer polymerization
TDI : Toluene-2,4-diisocyanate
TGA : Thermal gravimetric analysis
w/w : Weight per weight ratio
wt% : Weight percent

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LIST OF SYMBOLS

$M(OR)_n$ **:** Metal alkoxide
T_g **:** Glass transition temperature

AN EASY WAY TO MODIFY TRIGLYCERIDE OILS FOR OIL-BASED BINDER PREPARATION

SUMMARY

Triglyceride oils, which are the ester products, formed from one molecule of glycerol and three molecules of fatty acids. They are able to undergo chemical reactions through their functional sites. As being natural and renewable resources they have a great importance for industrial applications such as coatings, soap, surface active materials, chemical intermediates and oleoresinous binders. On the other hand, since their film properties have some deficiencies in organic coating applications, they need to be improved with this respect.

In this context, a number of studies on the modification of triglyceride oils were performed. In these studies macromer and macroinitiator methods have been developed to enhance the film properties. Macromer method was performed by inserting a vinyl functionality to the oil moiety and final macromer were copolymerized with vinyl monomers such as styrene. In the macroinitiator method an initiator molecule such as functionalized azo initiator was inserted into the oil moiety. The polymerization in the presence of macromer or macroinitiator was carried out both free and controlled/living radical polymerization such as nitroxide mediated radical polymerization (NMRP), reversible addition-fragmentation chain transfer polymerization (RAFT). In addition to vinyl monomers, non-vinyl monomers such as methylolated abietic acid, diisocyanates, alkoxysilane and benzoxazine were used for triglyceride oils modifications as well in previous studies.

In the present study, benzoxazine and 3-aminopropyltriethoxysilane were used together to develop an easier way for modification of triglyceride oils. Benzoxazines are preferred for a wide range of applications due to their unique properties such as high char yield, relatively high T_g, low water absorption, no by-products during curing, low flammability, molecular design flexibility and no requirement for curing strong acid catalysts or additives. On the other hand, polybenzoxazines have some disadvantages such as high curing temperature, brittleness and processing conditions. By combining benzoxazine structures with additional functionality, polymers, inorganic materials and nanostructures is the most common method to overcome these disadvantages. In this context, silane coupling agents are extensively used due to be commercially available, highly reactive to the hydroxyl functional surfaces and to have wide variety of functional groups which brings design flexibility. In this way, by establishing chemical bonds between the soft organic and the hard inorganic species properties can be improved**.**

The steps of the process as follows; (i) preparation of partial glyceride (PG), (ii) preparation of enhanced partial glyceride (PGE) (iii) synthesis of benzoxazine functional silane (Bz-Si), (iv) preparation of film samples by the mixing (ii) and (iii) (Bz-Si/PGE), (iv) curing of the films through thermal and sol-gel reaction, v) determination of film properties.

As mentioned above, preparation of film samples is done by using benzoxazine functional silane and enriched partial glyceride. Because producing mono- and diglyceride with high yield by glycerolysis or esterification reactions is impossible due to limited solubility of triglyceride and fatty acids. Final product is obtained as the mixture of mono-, di- and triglycerides. Therefore, by using solvent extraction method enhanced partial glyceride is obtained to increase the yield of individual partial glyceride.

The characterization of the samples were identified by fourier transform infrared spectroscopy (FT-IR). Synthesis of Bz-Si, combining to Bz-Si with PGE, crosslinking reaction and thermally activated curing of Bz-Si/PGE via ring-opening polymerization of benzoxazine moiety were confirmed with respect to FT-IR results.

Thermal analyses of the samples were done by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Cured Bz-Si/PGE film samples (CF(Bz-Si/PGE) gave higher decomposition temperature at both 5% and 10% weight loss compared to Bz-Si and also classical urethane oil and benzoxazine modified oil which were used in previous study. Additionally, no melting behavior of cured Bz-Si/PGE at DSC results indicates that sol-gel reaction between oil moiety and silane group occurred and high degree of crosslinking restricts the molecular motion and also gives high thermal stability to the final product.

In the end, samples with acceptable film properties (with respect to American Society for Testing and Materials (ASTM) and German Institute for Standardization (DIN) procedures) , which are highly important for an organic coating material,were achieved by this modification.

YAĞ TEMELLİ BAĞLAYICI ÜRETİMİ İÇİN TRİGLİSERİD YAĞLARIN MODİFİKASYONUNDA KOLAY BİR YÖNTEM

ÖZET

Polimerik bağlayıcılar, organik kaplamaların en önemli ve tamamlayıcı bileşenleridir. Çünkü kaplamanın kullanım alanına uygun olarak üretilen son ürünün özellikleri, uygulanan bağlayıcının türüne ve yapısına bağlı olarak değiştirilebilmekte ve aynı zamanda geliştirilebilmektedir. Poliesterler, poliüretanlar, akrilikler, vinil asetatlar, silikonlar, polivinil klorürler, fenolikler, silikatlar, poliüreler ve emülsiyon reçineleri gibi pek çok polimer türü organik kaplama malzemeleri için bağlayıcı olarak kullanılmaktadırlar. Fakat bu polimerler genellikle petrokimyasal hammaddelerden üretilmektedirler. Petrokimyasal maddelerin tekrar kullanımlarının zor olması, kimyasal olarak kolaylıkla bozunmaları, fosil kaynakların hızla tükenmeye devam ediyor olması ve bunlarla bağlantılı olarak çevresel ve ekonomik bazı durumlar göz önüne alındığında, bu maddelere alternatif olarak yenilenebilir kaynakların kullanılması son zamanlarda büyük önem kazanmıştır.

Bitkisel yağlar en önemli yenilenebilir kaynaklar olarak kabul edilmektedirler. Yenilenebilirlik özelliklerinin yanısıra, diğer kaynaklarla kıyaslandıklarındaki düşük fiyatları, kolaylıkla elde edilebilir olmaları ve istenilen özellikte ürün elde etmede kolaylıkla modifiye edilebilmeleri bu kaynakları daha çok tercih edilebilir kılmaktadır.

Doğal bitki kaynaklarından elde edilen trigliseridler, bilinen en eski bağlayıcılardır ve yenilenebilir kaynaklardan malzeme üretiminde çok önemli bir yere sahiptirler. Trigliseridler bir molekül gliserol ile üç molekül yağ asitinin, her yağ asidi ve gliserol molekülü arasında ester bağı oluşturmasına dayanan kondenzasyon reaksiyonu sonucu oluşurlar. Bu reaksiyon sonucunda trigliserid molekülü ile beraber 3 molekül su da açığa çıkmaktadır.

Trigliseridlerin sınıflandırılmalarındaki temel etkenler ise yağ asidi zincirindeki çiftli bağların sterokimyası ve doymamışlık derecesidir. Doymamışlık derecesi, 100 g yağın çiftli bağlarının doyurulması için gerekli olan iyot miktarı olarak tanımlanan iyot değerine bağlıdır. Bu parametreye göre iyot değeri 100'den küçük olanlar kurumayan yağ, 170'den büyük olanlar kuruyan yağ, 100 ile 170 arasında olanlar ise yarı-kuruyan yağ olarak sınıflandırılmaktadırlar.

Yaygın olarak kullanılan trigliseridler keten tohumu, Ayçiçek, soya, hint, hurma, hindistan cevizi, kolza ve oitika yağlarından elde edilirler. Triglseridler kullanılarak üretilen polimerik malzemelerin başında ise oksipolimerize yağlar, poliesterler, poliüretanlar, poliamidler, akrilik reçineler, epoksi reçineler ve poliester amidler gelmektedir. Başta kaplama, yüzey aktif madde, plastikleştirici, biyo-yenilenebilir yakıt, yağlayıcı ve mürekkep uygulamaları olmak üzere çok yaygın bir kullanım alanına sahiptirler. Ancak bağlayıcı olarak doğrudan kullanımlarında; kuruma süresi, sertlik, yapışma ve sağlamlık gibi özellikler açısından yetersiz bir film oluştururlar. Bu yüzden trigliserid yağlar, kaplama uygulamalarındaki performanslarını artırmak adına modifiye edilmektedirler.

Bu çalışmanın amacı, trigliserid yağlar kullanılarak yağ bazlı bağlayıcı üretmede kolay bir yöntem geliştirebilmek ve bunun sonucu olarak da film özellikleri iyileştirilmiş son ürünü elde edebilmektir. Bu amaç doğrultusunda trigliserid yağın modifikasyonunda benzoksazin ve 3-aminopropiltrietoksisilan (APTES) kullanılmıştır.

Benzoksazin, bir oksijen ve bir azot atomu içeren altı üyeli heterosiklik bir bileşik olan oksazin halkasına bağlanmış benzen molekülünden oluşmaktadır. Yapıları, heteroatomların pozisyonlarına bağlı olarak değişebilmektedir. Fenolik bileşikler, formaldehit ve primer aminlerin Mannich kondenzasyon reaksiyonları sonucunda oluşurlar. Benzoksazin monomerlerinin yüksek sıcaklıklara ısıtılmasıyla da yapıda bulunan oksazin halkasının açılması başlar ve zincir büyümesi gerçekleşerek polibenzoksazin elde edilir. Termal polimerizasyona ek olarak, asit katalizli ya da foto-başlatıcı mekanizmasıyla katyonik polimerizasyon sonucunda da benzoksazinin polimerleşmesi gerçekleşebilir. Ancak bu yöntemle elde edilen polimer ağı, yapıda kalan katalizör varlığından dolayı düşük termal dayanıklılığa ve kırılgan bir yapıya sahip olur.

Son zamamnlarda benzoksazinler üzerindeki çalışmalara olan ilgide büyük bir artış olsa da, bu alandaki ilk çalışma 1944 yılında Holly ve Cope tarafından gerçekleştirilmiştir. Yüksek yanma ürünü yüzdesi, yüksek camsı geçiş sıcaklığı, düşük su absorplama, kürlenme sırasında yan ürün oluşturmama, tutuşmaya karşı olan yüksek direnç, kürlenme sırasında kuvvetli asit katalizörü ya da katkı maddesi gibi herhangibir maddeye ihtiyaç duymama, yüksek kimyasal dayanıklılık ve moleküler tasarım esnekliği gibi pek çok alanda avantaj sağlayan özelliklere sahiptirler. Ancak diğer taraftan, polibenzoksazinler yüksek kürlenme sıcaklığı, kırılganlık ve proses koşulları gibi bazı dezavantajlara da sahiptirler. Bu sebeple, bu dezavantajların önüne geçebilmek adına benzoksazin yapısının ek fonksiyonalite, polimerler, inorganik maddeler ve nanoyapılar ile kombinasyonları ile ilgili birçok çalışma yapılmaktadır. Böylelikle özellikle kaplama, yapıştırıcı, elektronik ve uçak malzemeleri gibi uygulamalarda istenen özelliklere sahip malzemelerin üretiminde yaygın olarak kullanılmaktadırlar.

Bu tezde ilk olarak, ayçiçek yağının gliserol ile alkoliz reaksiyonu sonucunda kısmi gliserid elde edildi. Kısmi gliseridin bireysel verimini artırmak amacıyla, çözücü ekstraksiyonu yöntemi kullanılarak zenginleştirme işlemi gerçekleştirildi. Daha sonra paraformaldehit, APTES ve fenol kullanılarak Bz-Si sentezlendi. Elde edilen Bz-Si ile zenginleştirilmiş kısmi gliserid karıştırıldı ve ekstra bir reaksiyona gerek olmaksızın Bz-Si ile modifiye edilen yağ bazlı ürün hazırlanmış oldu.

Hazırlanan ürün cama ve metale sürüldü ve 180 °C' de kürlenme işlemi sonucunda da filmler elde edildi. Kürlenme işlemi sırasında hem benzoksazin kısmının halka açılması reaksiyonunun hem de alkoksisilan gruplarından kaynaklanan sol-jel reaksiyonunun gerçekleşmesi sağlandı. Sol-jel prosesi sırasında oluşan çapraz bağlı ağ yapılarının ürüne sağlamlık ve termal kararlılık gibi avantajlar sunması beklenmiştir.

Karakterizasyon FT-IR kullanılarak yapılmıştır. Bz-Si sentezi, bu maddenin zenginleştirilmiş kısmi gliserid ile birleşimi, çapraz bağlanma ve benzoksazin halka açılması reaksiyonu FT-IR sonuçları ile de doğrulanmıştır. Termal özellikler ise DSC ve TGA teknikleri kullanılarak incelenmiştir. Kürlenmiş filmlerin klasik üretan yağı, önceki çalışmalarda incelenen benzoksazin ile modifiye edilmiş yağ ve Bz-Si ile kıyaslandığında % 5 ve % 10 kütle kayıplarının gözlendiği sıcaklıklardan daha yüksek bozunma sıcaklığına sahip olduğu ve erime davranışı göstermediği gözlenmiştir. Yine

bu sonuçtan yola çıkılarak, yağ ve silan grupları arasındaki sol-jel reaksiyonunun yüksek derece çapraz bağlanmayı sağladığı ve bunun da ürüne yüksek termal dayanıklılık verdiği gözlenmiştir.

Film özellikleri ise ASTM ve DIN standartlarına göre belirlenmiştir. Kürlenme işleminden sonra elde edilen filmlerin yüksek yapışma ve esneklik özelliklerine sahip olduğu, asit, baz ve suya karşı dayanımının yüksek olduğu ve sağlam yapıda olduğu gözlenmiştir.

Sonuç olarak, Bz-Si kullanılarak hazırlanan yağ-temelli bağlayıcının istenilen özelliklere sahip film oluşumunu sağladığı gözlenmiştir. Yapıda benzoksazinin bulunması ve sol-jel reaksiyonu sonucu poliester zincirleri arasında çapraz bağlanmanın olmasının termal kararlılık ve dayanıklılığı artırdığı görülmüştür. Tüm sonuçlar göz önüne alındığında Bz-Si kullanılarak kolaylıkla hazırlanan yağ-temelli bağlayıcının kaplama malzemesi olarak kullanılmaya uygun olduğu anlaşılmıştır.

1. INTRODUCTION

Polymeric binders are the most important and complementary component of the organic coatings. Because properties of the final product, which is produced with respect to usage area of the coatings, can be changed or developed depends on the type and nature of the binders [1,2]. A wide range of polymers such as polyesters, polyurethanes and emulsion resins are used as binders for organic coatings [3]. However, they are produced from petrochemical raw materials. In this context, producing macromolecules from renewable sources have great importance due to economic and environmental issues.

As being natural and renewable resources, triglyceride oils are widely used for this purpose in coatings, soap, surface active materials, chemical intermediates applications. They are the ester products, formed from one molecule of glycerol and three molecules of fatty acids. They are able to undergo chemical reactions through their functional sites. On the other hand, since their film properties have some deficiencies in direct usage of them as a binder in organic coating applications, they need to be improved with this respect [4].

In this context, a number of studies on the modification of triglyceride oils were performed to enhance the film properties by using macromere and macroinitiator method. Free and controlled/living radical polymerization were carried out for polymerization process [5]. Both vinyl and non-vinyl monomers were used for triglyceride oil modifications in previous studies. In continuation to these studies, in the present study benzoxazine and APTES were used together to develop an easier way for modification of triglyceride oils.

Benzoxazines have unique properties such as high char yield, relatively high T_g, low water absorption, no by-products during curing, low flammability, molecular design flexibility and no requirement for curing strong acid catalysts or additives [6]. Therefore, they are commonly preferred for a wide range of applications. On the other hand, polybenzoxazines have some disadvantages such as high curing temperature, brittleness and processing conditions.

To eliminate these disadvantages additional functionality, polymers, inorganic materials and nanostructures are combined with benzoxazine structure [7–10]. In this context, silane coupling agents are extensively used due to be commercially available, highly reactive to the hydroxyl functional surfaces and to have wide variety of functional groups which brings design flexibility. And PG was used for giving flexibility to the structure.

Synthesis of Bz-Si, preparation of film samples by the mixing Bz-Si and PGE, curing of the films through thermal and sol-gel reaction and determination of film properties were carried out respectively. In the end, samples with acceptable film properties were obtained.

2. THEORETICAL STUDY

2.1 Triglyceride Oils

Triglycerides, which is defined as naturally occurring oils, are the triesters of glycerols and fatty acids (Figure 2.1.) [11]. In other words, they are composed from a single molecule of glycerol, combined with three molecules of fatty acids by forming ester bond between each fatty acid and glycerol molecule. Three molecules of water are the other product of this condensation reaction (Figure 2.2.) [12,13].

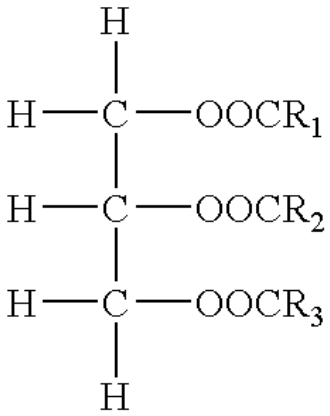

Figure 2.1: A triglyceride molecule.

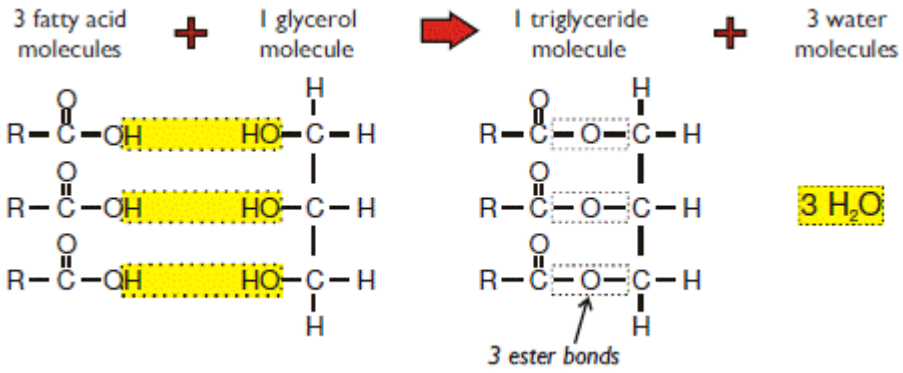

Figure 2.2 : Formation of triglyceride molecule.

They can also be found in vegetable oils but with varying composition of the fatty acids because of the some parameters like type of the plant, growing conditions and climate [14]. Typical fatty acid contents of vegetable oils are summarized in Table 2.1.

Table 2.1 : Typical fatty acid compositions of selected oils [11].

Vegetable Oil	Fatty Acids (%)			
	Saturated[a]	Oleic	Linoleic	Linolenic
Lindseed	10	22	16	52
Soybean	15	25	51	9
Sunflower	11	51	38	trace
Castor	3	7	3	-
Coconut	91	7	2	-

[a]Saturated fatty acids are mainly mixtures of stearic (C_{18}) and palmitic (C_{16}) acids; coconut oil also contains C_8, C_{10}, C_{12}, and C_{14} saturated fatty acids.

2.1.1 Classification of triglyceride oils

Physical and chemical properties of vegetable oils are affected from stereochemistry of the double bonds of the fatty acid chains and their degree of unsaturation. The degree of unsaturation is defined based on iodine value (IV) which is the required amount of iodine in grams for saturation of the double bonds of 100 g oil. And iodine value is used as a parameter to classify oils: drying (IV>170), semi-drying (100<IV<170) and non-drying (IV<100). Iodine values of common vegetable oils are given in Table 2.2 [14]. Also, unsaturation degree is a term related to speed of drying. If an oil has greater iodine value, it means that drying occurs more rapidly. Therefore drying oils form hard films as a result of autoxidation. But semi-drying oils cannot form hard films because of their soft and elastic nature, in other words they harden partially. Non-drying oils cannot harden in a long time, therefore during this time period they cannot show any film properties. Because of that they are used in applications where oxidation is undesirable like lubricants applications [7,15–17].

Table 2.2: Iodine values of common vegetable oils [14].

Vegetable Oil	Iodine value[a]/mg per 100 g
Palm	44-58
Olive	75-94
Groundnut	80-106
Rapeseed	94-120
Sesame	103-116
Cottonseed	90-119
Corn	102-130
Soybean	117-143
Sunflower	110-143
Linseed	168-204

2.1.2 Triglycerides as polymer resources

Since the polymers exhibit some specific properties such as thermal stability, biocompatibility, biodegradability, flexibility, non-flammability, electrical conductivity, adhesion and chemical resistance, they are most useful products in the chemistry industry. Main origin of the polymers is the fossil materials. However, the use of renewable sources for various industrial applications come into prominence due to environmental concerns and depletion of fossil resources. Plant oils are considered to be most essential renewable sources due to offer many advantages apart from their renewability properties [18]. Economic issues such as low prices by comparison with other sources, easily modification to obtain desired product with desired property and also availability make them more preferable.

The main constituents of the plant oils are triglycerides. Because of naturally occurring functional groups present in their structure (ester groups, double bonds, allylic positions and the α-position of ester groups) and easiness of modification triglyceride oils have been widely used in the preparation of polymers with the purpose of enhancing end-product properties [19]. Oxypolymerized oils, polyesters, polyurethanes, polyamides, acrylic resins, epoxy resins and polyesteramides are the some polymers prepared from triglyceride oils. They have been widely used especially

for coatings, lubricants, surfactants, inks, plasticizers and also bio-renewable fuels applications.

In this part, oil-based polymers and their obtaining mechanism are mentioned.

Oxypolymerization is commonly used for the modification of triglyceride oils. The reaction which occurs in this polymerization mechanism is based on oxidative degradation. Oxypolymers are produced through mostly free radical addition and sometimes cycloaddition reactions [20]. A representative oxypolymerization reaction process is shown in Figure 2.3. Oxidizied oils give the end products with high viscosity and better film properties.

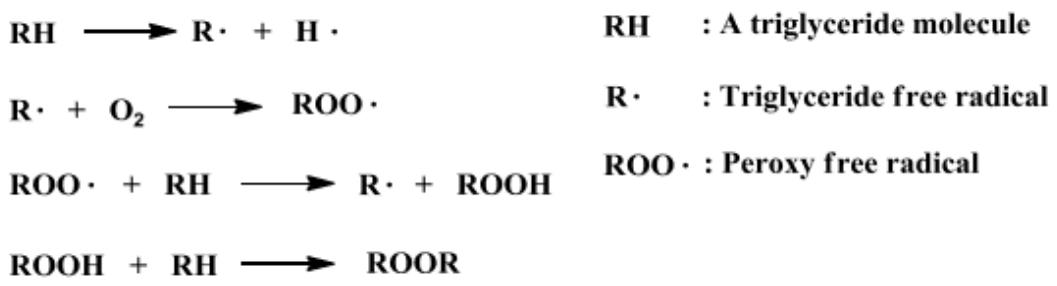

Figure 2.3 : Oxidation of triglyceride molecule.

Alkyd resins, which are produced by the esterification of polyhydroxy alcohols with polybasic acids and fatty acids, are one of the most widely used polymers because of economic and environmental issues [21]. Two different methods as monoglyceride (alcoholysis) and fatty acid methods are used for alkyd resin production [22]. Alcoholysis of the oil with polyol and esterification of free hydroxyls of the alcoholysis product with polyacid are the steps of the monoglyceride method. The related reactions are schematically represented in Figure 2.4.

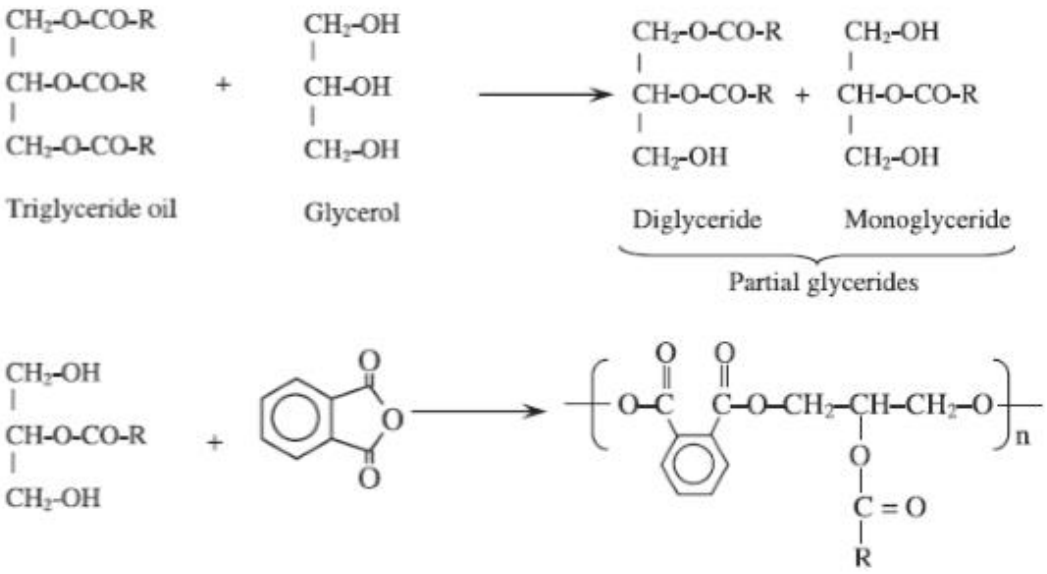

Figure 2.4 : Preparation of alkyd resins.

In fatty acid methods, polyacid, polyalcohol and fatty acid are added together at the beginning of the reaction and than heated. This method is more favoured since there is no need an intermediate step (alcoholysis step) and the final resin have higher viscosity and better drying and hardness properties in comperison with the resin which is produced by other method [4].

Epoxidation of oil is based on the chemical oxidation of fatty acids and their esters resulted converting them to epoxy derivatives [23]. Fatty acids such as oleic, linoleic and linolenic acids can be epoxidized easily due to the presence of double bonds in their structure. Epoxidation of oleic acid is given in Figure 2.5.

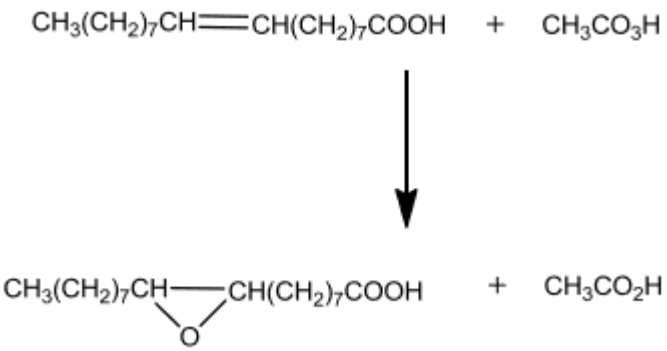

Figure 2.5 : Epoxidation of oleic acid [4].

Epoxidized oils are used as plasticizers and stabilizers for polyvinylchloride and also they can be used for obtaining various type of polymers (hydroxylated products) due

to the reaction of the active hydrogen which is presence in alcohol, amine and carboxylic acids [4].

Polyurethanes are obtained from the reaction of aromatic or aliphatic diisocyanates and hydroxyl-containing materials as shown in Figure 2.6 [4,24]. Triglycerides provide the hydroxyl-containing material part by epoxidation, ring opening, ozonolysis, alcoholysis and hydration reactions [25–27]. In other words, they are used as polyol component for the polyurethane reaction. They give elastomeric properties to the end product because of having low glass transition temperature (T_g). Therefore polyols are considered as the soft part of the urethanes. On the other hand, isocyanates are considered as hard part of the urethanes because of having high glass transition temperature [28].

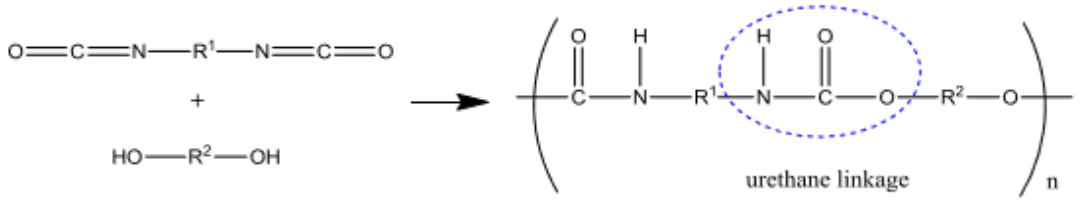

Figure 2.6 : Preparation of polyurethane.

Polyurethanes are used in wide range of applications such as coatings, construction, insulation, fibres, automotive and adhesives [29]. Erciyes et al.studied urethane oils for coating applications. In a study, polymers were prepared by using three kind of diisocyanates, toluene-2,4-diisocyanate (TDI), hexamethylene diisocyanate (HMDI) and poly(1,4-butandiol) toluene-2,4-diisocyanate (PBTDI) as shown in Figure 2.7. and effects of the amount and type of diisocyanate on film properties were investigated. As a result, shorter drying time was achieved by increasing of the diisocyanate amount and in addition, it was observed that aromatic diisocyanate based polymers showed better water resistance [5].

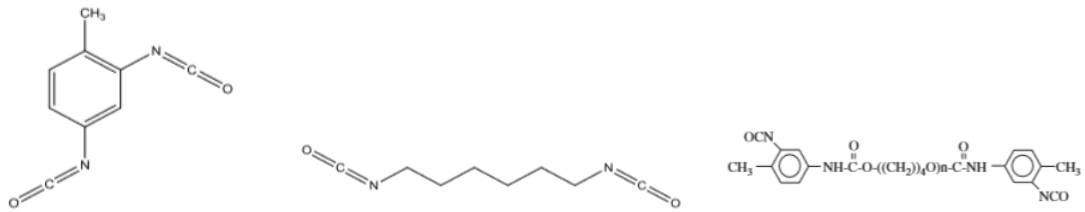

Figure 2.7 : Used isocyanates in the mentioned study; TDI, HMDI and PBTDI respectively.

In another study, effects of monomer structure on the flow properties were investigated. Polymers were prepared by using two different diisocyanates at three different monomer concentrations. As a result, it was observed that despite of having the same structure the samples which contain 2 aromatic rings per a molecule had higher viscosity than the samples which contain 1 aromatic ring per a molecule [26].

2.2 Benzoxazines

Benzoxazine comprises of attaching an oxazine ring, which is a hetero-cyclic six-membered ring with oxygen and nitrogen atom, to a benzene ring [30]. Their structure can be changed depending on the position of the heteroatoms.

The first contribution related to synthesis of benzoxazine is reported in 1944 by Holly and Cope [31]. There are a lot of studies about multifunctional benzoxazines during following years. But the study on the polybenzoxazine properties was firstly reported in 1994 by Ning and Ishida [32].

Benzoxazines have recently great interest due to their unique properties such as high char yield, relatively high T_g, low water absorption, no by-products during curing, low flammability, molecular design flexibility and no requirement for curing strong acid catalysts or additives [6].

On the other hand, polybenzoxazines have some disadvantages such as high curing temperature, brittleness and processing conditions. Therefore, a lot of studies have been done which combined benzoxazine structures with additional functionality [33–35], polymers [36], inorganic materials [37] and nanostructures [38] to overcome these disadvantages.

2.2.1 Synthesis of benzoxazine monomers and polybenzoxazine

Benzoxazine monomers can be synthesized by using phenolic compounds, formaldehyde and primary amines via Mannich condensation reactions as shown in the Figıre 2.8. [39, 40].

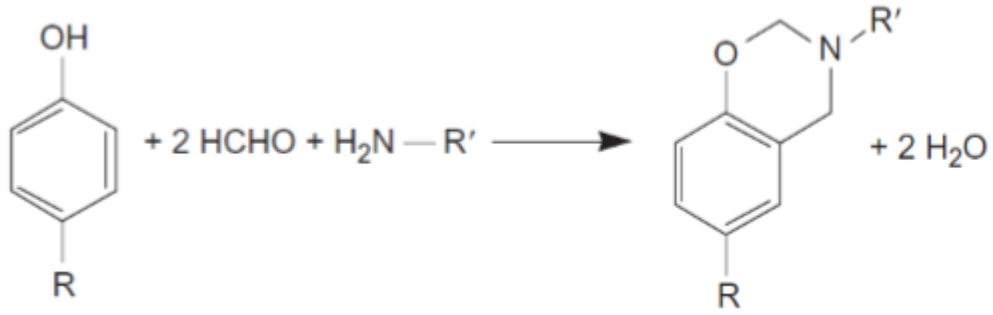

Figure 2.8 : Synthesis of benzoxazine monomers [31].

By heating benzoxazine monomers (both monofunctional and difunctional) to elevated temperatures, the oxazine ring present in benzoxazine monomer is opened (ring opening mechanism) as shown in Figure 2.9. and chain propagation starts.

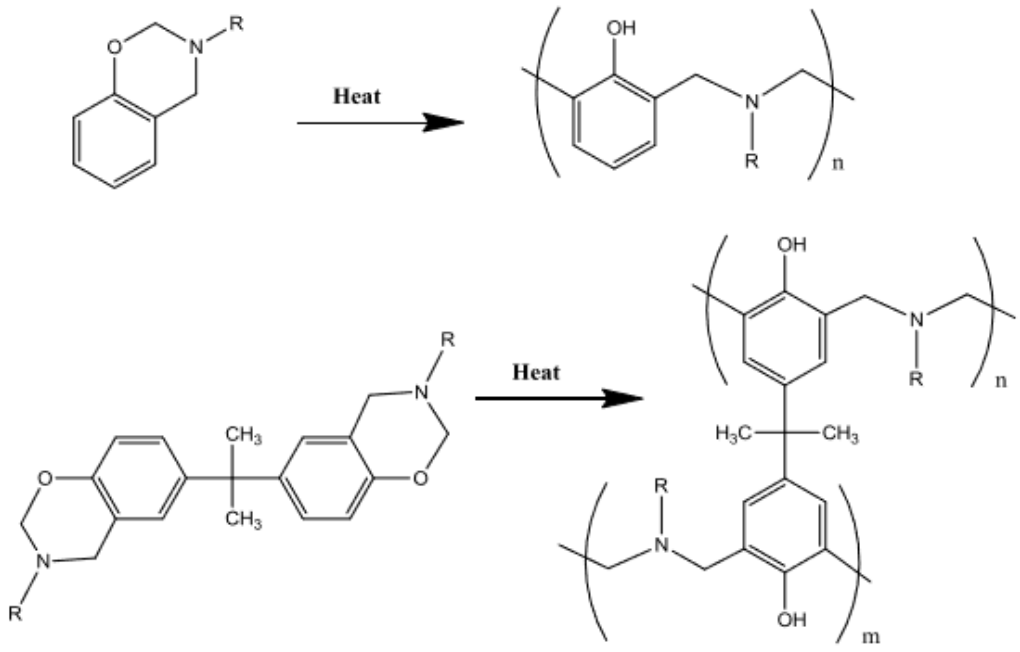

Figure 2.9 : Ring opening mechanism of monofunctional and difunctional benzoxazines [25].

In addition to thermal polymerization, benzoxazine can be polymerize by cationic polymerization (acid catalyzed or photo-initiated mechanism). However, by cationic polymerization polymer networks are obtained with lower thermal stability and more brittle structure due to presence of residual catalyst in polymer network [41].

2.2.2 Polybenzoxazine characteristics and applications

Polybenzoxazines or in other words benzoxazine resins have been developed as a new class of thermoset polymers with unique properties such as near-zero volume changes, low water absorption, high T_g, fast physical and mechanical property development, high char yield and high thermal stability.

However, the most important superiority of polybenzoxazines over the other polymer classes is molecular design flexibility as required monomers can be obtained from commercially available and inexpensive phenols, primary amines and formaldehydes [42].

Consequently, researches about benzoxazines are developing rapidly because of both their excellent properties and many potential applications of the materials and these materials are preferred for various applications such as adhesives, coatings, electronics and aerospace composites [30].

2.3 Sol-Gel Process

2.3.1 Introduction

A sol is defined as a stable (no settling or agglomeration of the particles) dispersion of (discrete, collodial) particles in a liquid [43,44]. A gel is defined as a continuous solid or semi-solid skeleton made of collodial particles/polymers enclosing a continuous liguid phase [45]. When the sol passes through the gelation point, which is the moment when the sol loses its fluidity, a sol becomes a gel [46].

Sol-gel process has recently gained more scientific and technological interest due to provide a lot of advantages such as the final product with higher purity and homogeneity comparing the products which are produced by traditional glass melting or ceramic powder methods, lower processing temperature, easiness of controlling the chemical reactions during the process and nucleation and growth of the primary collodial particles in order to obtain desired size or shape [47–49].

Starting materials for the sol-gel process is a colloid which is formed via surrounding a metal or metalloid element by ligands. Metal alkoxides ($M(OR)_n$) are commonly used in this context due to react with water easily. Process involves two steps. First step contains hydrolysis reaction and second step contains condensation reaction with

the elimination of water or alcohol. The chemical reactions which take place in the process are [43]:

$$Si\text{-}(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + ROH \quad (2.1)$$

$$(OR)_3Si\text{-}OH + HO\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O \quad (2.2)$$

$$(OR)_3Si\text{-}OR + HO\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \quad (2.3)$$

The reaction steps of the process is presented in Figure 2.10.

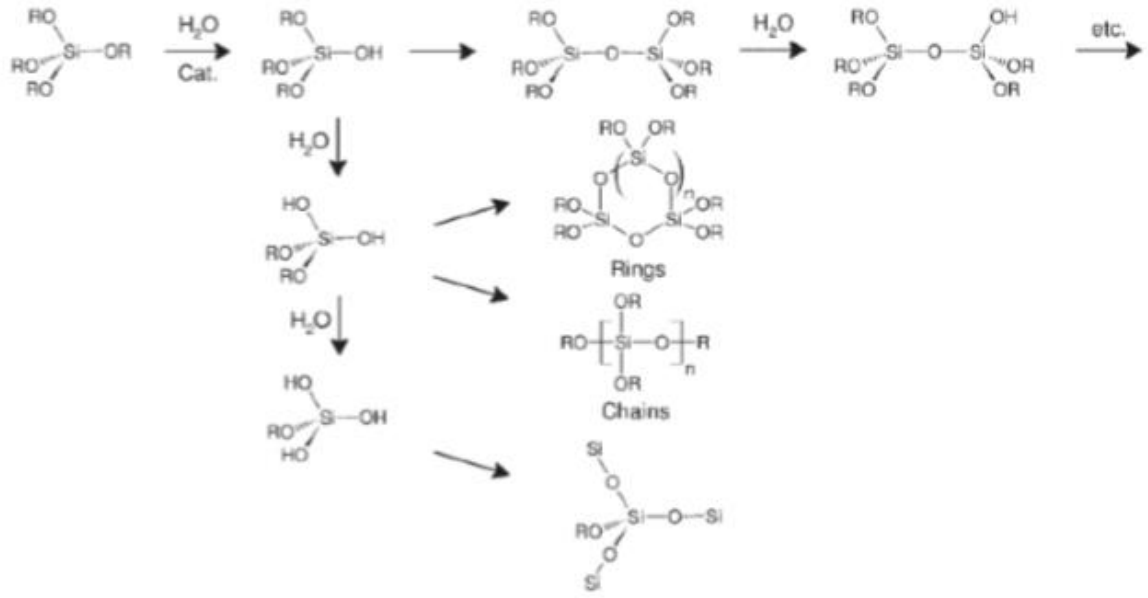

Figure 2.10 : Reaction steps for the tetrialalkoxysilanes in the sol-gel process [3].

2.3.2 Application of sol-gel process

The sol-gel process is commonly used in many domains of applications due to form materials with different configurations such as monoliths, thin films, fibers and powders. In addition, as being versatile, simply, inexpensive, ecologically and energy and resource saving process, the sol-gel technology has a great potential to modificate materials to meet the required properties (mechanical, thermal, chemical, optical or electrical) [47]. Products are formed by this process for a wide range of areas such as gas separations [50], elastomers [51], coatings [28,52–54] and laminates [55].

Preparation of coating materials is the most common application of the sol-gel process due to eliminate shrinkage problem in the preparation of the materials by sol-gel process and adhesion problems.

In this context, silane coupling agents are extensively used due to be commercially available, highly reactive to the hydroxyl functional surfaces and to have wide variety of functional groups which brings design flexibility. In this way, by establishing chemical bonds between the soft organic and the hard inorganic species properties such as mechanical toughness, flexibility, hardness and thermal stability properties can be improved and also can be provided all these properties from one material.

3. MATERIALS AND METHODS

3.1 Materials

Refined sunflower oil purchased from market was used as received. Chloroform, phenol, diethyl ether, 3-Aminopropyltriethoxysilane (APTES, 99%) and ethanol were purchased from Sigma-Aldrich and they were used as received. Sulfuric acid (95-98%), glycerol, paraformaldehyde, sodium sulphate, sodium hydroxide, calcium hydroxide, toluene, acetic anhydride, pridin and potassium hydroxide were purchased from Merck and they were used without any further purification. Methanol (≥99.8%) obtained from VWR was used as received.

3.2 Methods

3.2.1 Preparation of the partial glyceride (PG)

Partial glyceride was prepared through the glycerolysis reaction between triglyceride oil and glycerol in a three-necked flask. Sunflower oil and glycerol (glycerol/oil, w/w: 0.085) were mixed and heated to 218 °C under nitrogen flow through an inlet and a reflux condenser. At this temperature, $Ca(OH)_2$ (0.1 wt% of oil content) was added as catalyst. Then, temperature was set at 230 °C, and the reaction continued for 1h under nitrogen atmosphere. Termination of transesterification was determined by pouring samples, which were taken from the reaction mixture at determined time intervals, into a three-fold amount of ethanol. Then, the mixture was cooled to room temperature and dissolved in diethyl ether, washed firstly with 0.2 N sulfuric acid and than with distilled water in order to eliminate the catalyst and free glycerol, respectively. The ethereal solution was dried over anhydrous Na_2SO_4 and the solvent was removed. The hydroxyl and acid values of PG were determined as 114 and 3 mg KOH/g, respectively [56].

3.2.2 Preparation of enhanced PG (PGE)

PG were enhanced by extraction with aqueous methyl alcohol containing %9 water according to the given procedure for enhancement technique in the US Patent [57].

The hydroxyl and acid values of PGE were determined as 229 and 3 mg KOH/g, respectively [56].

3.2.3 Synthesis of benzoxazine functional silane (Bz-Si)

In a three-necked reaction flask equipped with 85 °C preheated oil bath and purged with nitrogen flow for several minutes, 0.02 mol paraformaldehyde was added in 3 mL of chloroform with continuous stirring. 0.01 mol APTES in 2 mL of chloroform was added to paraformaldehyde solution and mixed for 10 min. Then, 0.01 mol phenol in 4 mL of chloroform was added into the flask and heated. After heating for 3 hours, the solvent was removed in rotary evaporator and Bz-Si was obtained [58].

3.2.4 Preparation of crosslinking film samples of Bz-Si and PGE (CF(Bz-Si/PGE))

Bz-Si and PGE were added into flask in given amounts and mixed to obtain a homogenous mixture at room temperature. Bz-Si/PGE samples were applied as thin film on the glass and tin plates substrates according to standard procedures [59]. The prepared film samples were placed in a cabin of 97% relative humidity at room temperature for 48 h [60]. Then, the samples were cured in an oven at 180 ° C for 48 hours.

3.2.5 Determination of film properties

Film properties of cured samples such as flexibility [59], adhesion [61], water resistance [62], acid resistance [62] and alkali resistance [62] were determined. Adhesion test was investigated by applying film samples on both glass and tin plates with a Bird film applicator with 60 μm aperture. Flexibility and water resistance tests were performed with tin plates. For alkali and acid resistance tests, glass tubes which prepared via dipping method were used.

3.3 Characterization Techniques

3.3.1 Fourier transform infrared spectroscopy (FT-IR)

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

3.3.2 Thermal gravimetric analysis (TGA)

Perkin Elmer Diamond TG/DTA was used for TGA analysis. The measurements were done from 50 °C to 550 °C with a heating rate of 10°C/min under nitrogen flow.

3.3.3 Differential scanning calorimetry (DSC)

DSC thermograms were determined using a Perkin Elmer (DSC 4000) instrument with a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

4. RESULTS AND DISCUSSION

4.1 Synthesis of Bz-Si

Bz-Si monomer was synthesized by using an amino-functional silane (APTES) as the primary amine according to the reaction shown in Figure 4.1 [58]. The structure of Bz-Si was confirmed by FT-IR spectrum in Figure 4.2.

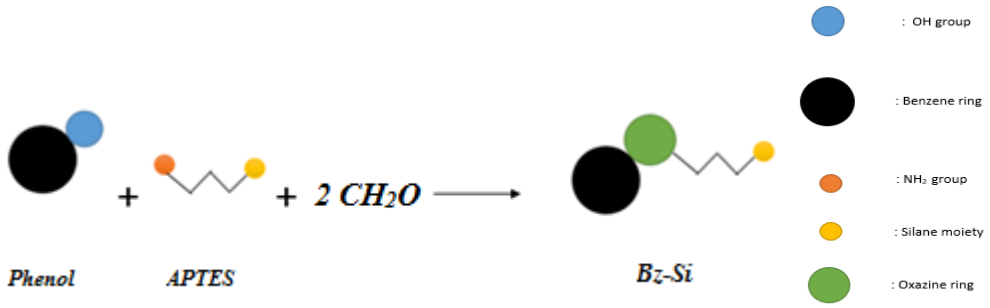

Figure 4.1 : Synthesis of benzoxazine functional silane.

In FT-IR spectrum, the peaks at 1226 and 1164 cm^{-1} are attributed to the asymmetric stretching of Ar-O-C and symmetric stretching of Ar-O-C, respectively [63]. The characteristic peaks belonging to benzoxazine ring is located at 929 cm^{-1}. It shows that out-of-plane bending vibration of the benzene ring is attached to oxazine ring [64]. Absorbances at 750, 1488 and 1585 cm^{-1} correspond to the ortho-disubstitued benzene [63,65]. The presence of the peak at 1073 cm^{-1} corresponds to the Si-O-C of the silane moiety [66]. Absorbances at 2973, 2928 and 2886 cm^{-1} are assigned to the asymmetric stretching of C=C-H.

In addition, there is no peaks at around 3600 and 3400 cm^{-1} indicating that the alkoxy groups were not hydrolyzed during the synthesis [58].

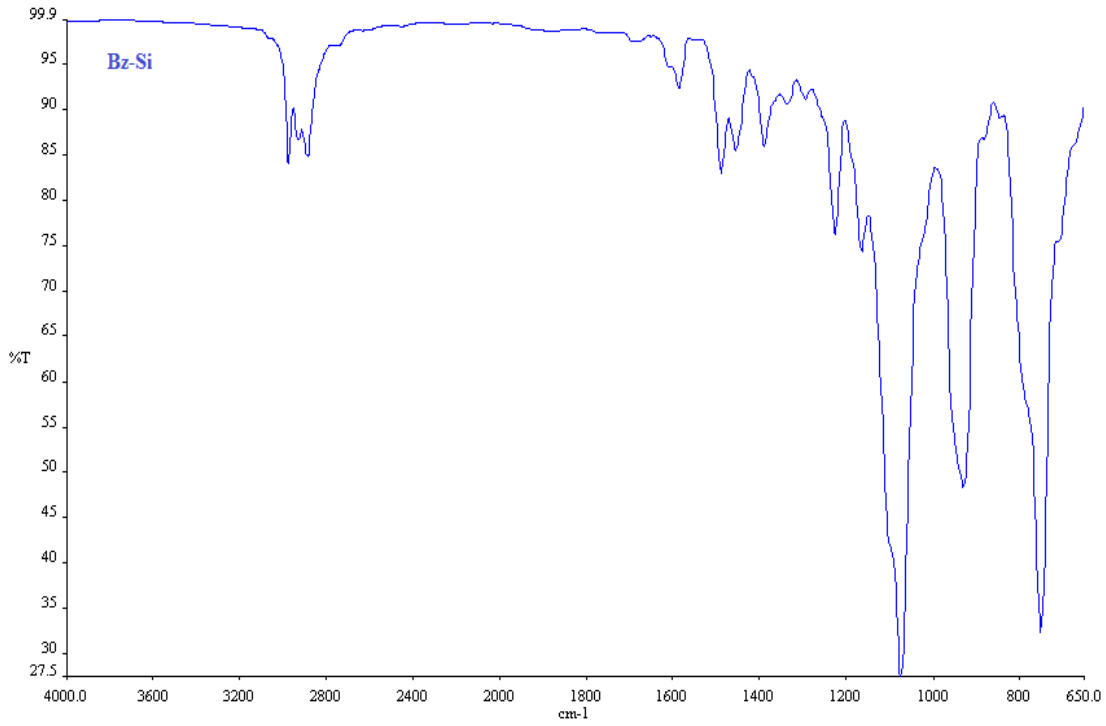

Figure 4.2 : FT-IR spectrum of Bz-Si.

4.2 Preparation of Bz-Si/PGE Film Samples

The structure of Bz-Si/PGE was confirmed by FT-IR spectral analysis. The characteristic peaks, which were detected in the FT-IR spectrum of Bz-Si monomer, were observed in the FT-IR spectrum of Bz-Si/PGE (Figure 4.3) .

Additionally, the presence of the peaks at 1750 cm^{-1} and 3425 cm^{-1} corresponds to the ester carbonyl and hydroxyl groups, respectively [67,68].

The explained results showed that PGE was successfully combined to the Bz-Si monomer.

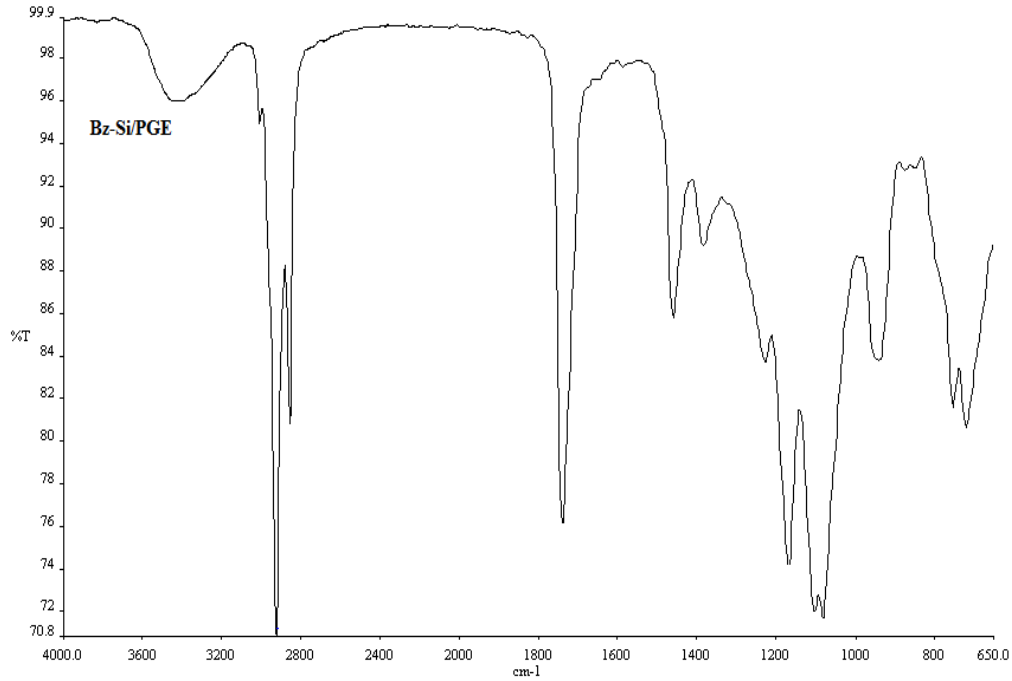

Figure 4.3 : FT-IR spectrum of Bz-Si/PGE.

Thermal curing of Bz-Si/PGE was carried out 180 °C for 48 h. The temperarure in curing process was not exceeded 180 °C. Because APTES start to decompose about at 190 °C [69]. FT-IR spectrum of CF(Bz-Si/PGE) is given in Figure 4.4.

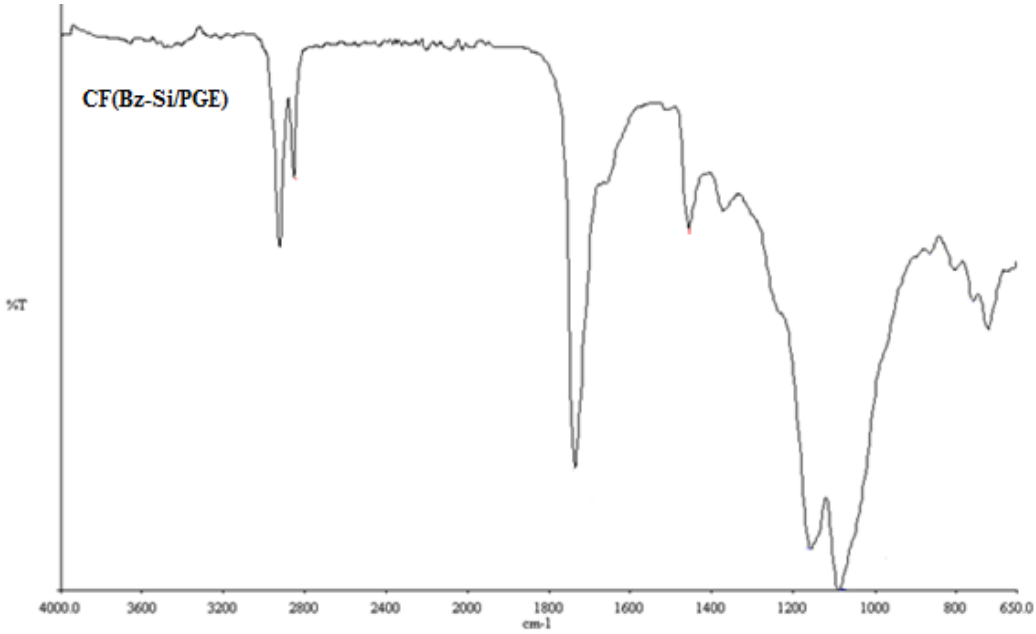

Figure 4.4 : FT-IR spectrum of cured Bz-Si/PGE.

After curing, the characteristic peak of oxazine ring at 939 cm^{-1} disappeared and the peaks of ortho-disubstitued benzene at 1459 and 752 cm^{-1} were decreased. The

disappearance of the peak at 3425 cm^{-1} confirms that hydroxyl groups which comes from partial glyceride reacts with silane moiety. Moreover, the peaks at 1080 and 1170 cm^{-1} decreased after curing.

All these observations indicate that the crosslinking by ring opening and sol-gel reaction of Bz-Si/PGE were performed successfully.

The network structure of final product is shown Figure 4.5.

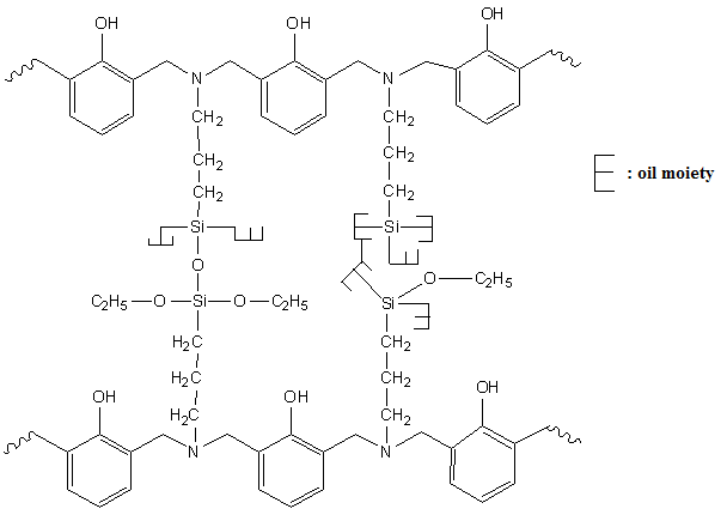

Figure 4.5 : The representative structure of final product.

4.3 Thermogravimetric Analysis (TGA)

The thermal stability of the Bz-Si and cured Bz-Si/PGE were evaluated by TGA under nitrogen atmosphere and compared as seen in Figure 4.6.

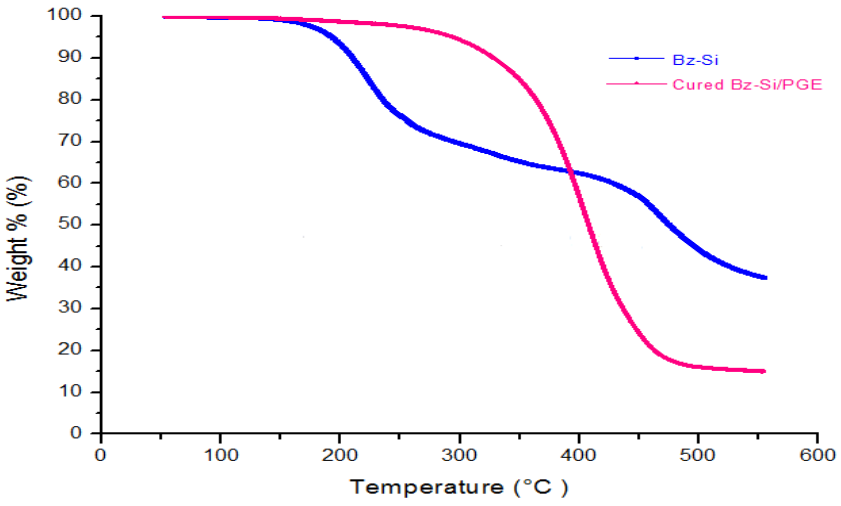

Figure 4.6 : TGA thermograms of Bz-Si and cured Bz-Si/PGE film.

As seen from the Figure 4.6, the char yield of Bz-Si is higher than the char yield of cured Bz-Si/PGE due to the dilution effect of PGE. As shown in Table 4.1 both temperatures at 5% and 10% weight loss of cured Bz-Si/PGE are appreciably higher than those of the Bz-Si. Because incorporation of inorganic silane domains into the structure causes the retarding effect of siloxane bridges [70,71].

In addition, cured Bz-Si/PGE sample exhibit better thermal stability than Bz-Si due to its pre-crosslinked structure. However, at high temperatures Bz-Si/PGE becomes thermally less stable due to presence of ester groups decomposition.

Table 4.1: Thermal properties of samples.

Film sample	$T_{5\%}$ **(°C)**[a]	$T_{10\%}$ **(°C)**[b]	Y_{500} **(%)**[c]
Bz-Si	193	210.3	37.6
Bz-Si/PGE	293.8	327.5	15.2
Bz-PGE[d]	267.4	284	13.5
CUO[d]	180	241	11

[a] Temperature at 5% weight loss
[b] Temperature at 10% weight loss
[c] Char yield at 500 °C
[d] Benzoxazine-modified oil and classical urethane oil (CUO) results from previous study [72]

4.4 Differential Scanning Calorimeter (DSC)

Bz-Si and CF(Bz-Si/PGE) samples were analyzed using DSC with nitrogen purging. Figure 4.7 displays the DSC thermogram of Bz-Si.

Bz-Si exhibits an exothermic peak at about 240 °C in DSC thermogram. This exothermic behavior corresponds to the thermo-induced ring-opening reaction of benzoxazine groups of Bz-Si. The broad exothermic peak from 250 °C to 400 °C is due to the alkoxy group decomposition and the condensation of the silanols.

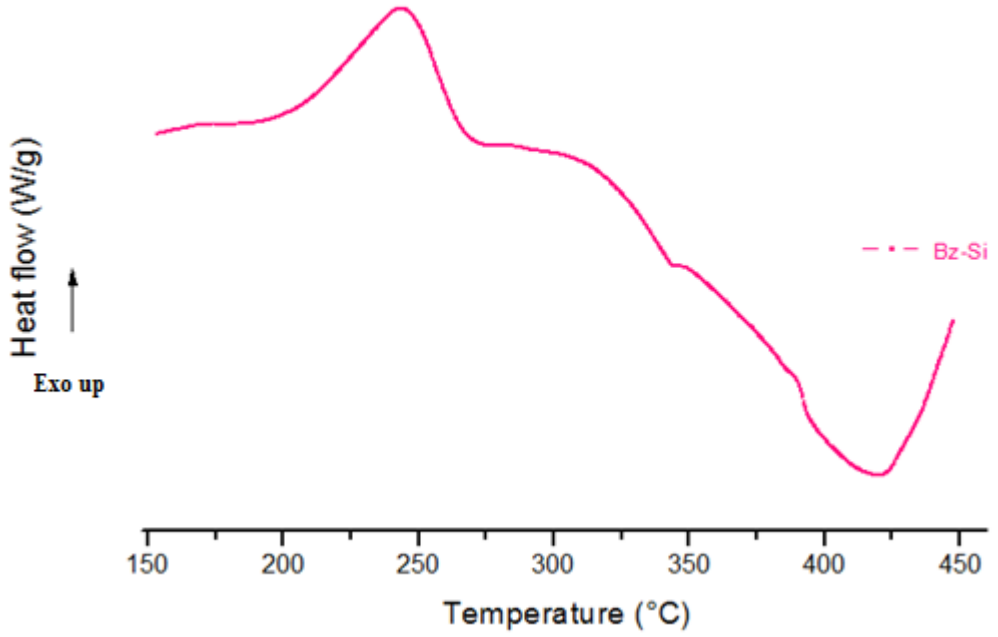

Figure 4.7 : DSC thermogram of Bz-Si.

Figure 4.8 displays the DSC thermogram of cured Bz-Si/PGE.

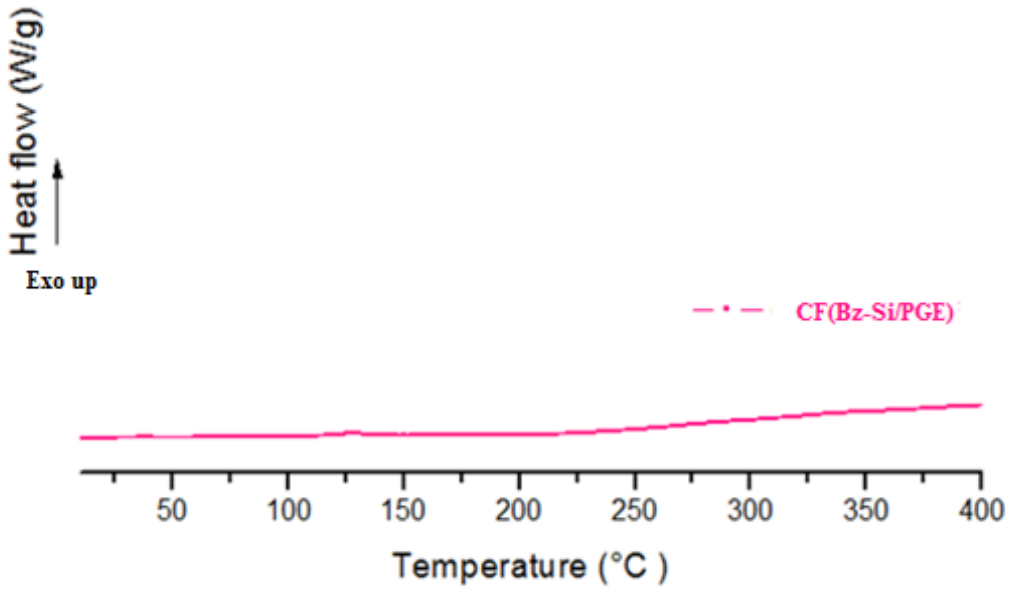

Figure 4.8 : DSC thermogram of CF(Bz-Si/PGE).

As seen from the Figure 4.8, CF(Bz-Si/PGE) sample exhibits no melting behavior. This result proves that sol-gel reaction between oil moiety and silane group occurred

and high degree of crosslinking restricts the molecular motion corresponds high thermal stability.

4.5 Film Properties

The film properties of the obtained samples need to be investigated due to potential use in organic coating applications. Therefore, the film properties were determined and summarized in Table 4.2.

Table 4.2 : Film properties of CF(Bz-Si/PGE).

Film Properties	Film Sample
Flexibility[a]	2 mm
Adhesion on a glass[b]	5B
Adhesion on a tin[c]	5B
Acid resistance[d]	No change
Alkali resistance[e]	No change
Water resistance[f]	No change

[a] The diameter of the cylinder that did not cause a crack on the film.
[b] Test method B was applied on glass plate.
[c] Test method B was applied on tin plates.
[d] Test was performed with 9% H2SO4 for 48 h.
[e] Test was performed with 3% NaOH for 48 h.
[f] Test was performed at 25 °C for 48 h.

As seen from the Table 4.2, film sample displayed excellent resistanced to water, alkali and acid during 48 h period. Adhesive charactheristics were determined on glass and tin surfaces and it was founded good results for both substrates. Moreover, film sample could be bent over a cylinder with a 2 mm diameter without showing any crack.

5. CONCLUSION AND RECOMMENDATIONS

In this study, we investigated the preparation of oil-based binder for coating applications by modification of triglyceride oils via an easy way. Benzoxazine and APTES were used for the modification. Firstly, partial glyceride was prepared and enhanced by using solvent extraction method. Then, Bz-Si was synthesized and mixed with enhanced partial glyceride. After that, obtained film samples were cured at 180 °C for 48 h.

The results indicated that Bz-Si was synthesized and was combined with triglyceride oil successfully. And also the results showed that the crosslinking reaction was performed successfully.

The obtained final product showed good film properties such as high water, alkali and acid resistances, good adhesion and flexibility.

The thermal analysis revealed that the decomposition temperatures both 5 % and 10 % weight loss of cured film samples were approximately two times higher than Bz-Si samples, classical urethane oil and also benzoxazine modified oil which were prepared in previous study. Additionally, crosslinking between polyester chains and silane moiety increased the thermal stability of the final product.

In conclusion, it was understood that the synthesized final product could be used as a coating material.

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