ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF FULLERENOL URETHANE OIL COMPOSITE AND ITS FILM PROPERTIES

M.Sc. THESIS

Deniz SERTEL

Department of Chemical Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FULLERENOL/ÜRETAN YAĞI KOMPOZİTİN ÜRETİMİ VE ÖZELLİKLERİ

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To my family and fiance,

FOREWORD

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ABBREVIATIONS

ASTM : American Society for Testing and Materials
DSC : Differential Scanning Calorimeter
FT-IR : Fourier Transform Infrared Spectrophotometer
NaOH : Sodium Hydroxide
KOH : Potassium Hydroxide
LUMO : Lowest Unoccupied Molecular Orbital
PEG : Polyethylene glycol
PG : Partial Glyceride
TBAH : Tetrabutylammonium Hydroxide
TDI : Toluene Diisocyanate
TGA : Thermal Gravimetric Analysis
VOBP : Vegetable Oil Based Polymers

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SYNTHESIS OF FULLERENOL URETHANE OIL COMPOSITE AND ITS FILM PROPERTIES

SUMMARY

Fullerenes are members of organic molecules which are formed by carbon allotropes. They proved not only to be new carbon allotrope with esthetic appearance but also a molecule of many talents possessing a wide range of different properties. They are widely used in industrial application due to its physical, chemical and electrochemical properties in recent years. However, the wide application of fullerenes is impeded by their almost complete incompatibility with water and aqueous solution. In early stage of its research, it was embedded into polymeric matrix. Resulting products have been studied for combined properties of fullerene and polymer. However, incompatibility between fullerene and the polymer matrix leads to formation of large fullerene aggregates. These problems are sorted out by modification of the fullerene which retain many of characteristic properties of pristine fullerene but are easier to dissolve in common organic solvents. Several functional groups have been attached exohedrally onto fullerene surface via, hydrogenation, halogenation, radical addition, and hydroxylation and go on. Hydroxyl derivatives have been studied most extensively. These types of fullerene were named as fullerenol. They have attracted great deal of interest because of its easy synthesis, high solubility and stability.

The produce of polymers from renewable resources is recently have much attention and scientist has focused on the use of cheap, biodegradable, and renewable starting materials in order to reduce petroleum dependence and the detrimental affects on the environment. Vegetable oils and fatty acids are one of the cheapest and most abundant biological sources available in large quantities, and their use as starting materials has many advantages, including low toxicity and inherent biodegradability. In recent years, extensive work has been done to develop polymers from triglycerides or fatty acids as the main component.

The ultimate aim of this thesis is to synthesis of fullerenol urethane oil composite and to determine its film properties. For this purpose, first fullerene molecules were converted to fullerenol molecules by the reaction of fullerene with aqueous NaOH in the presence of tetrabutylammonium hydroxide, the most effective catalyst. The structure of prepared fullerenol was investigated by using FT-IR. “OH” groups which attached on the fullerene surface was determined by TGA analysis. Then, partial glyceride was prepared by sun flower oil and glycerol by glycerolysis reaction. After that fullerenol molecules were covalently bounded to partial glyceride. Thermal and structural properties of final products have been systematically investigated using techniques including FT-IR, DSC and TGA. Also, film properties such as flexibility, water resistance, acid resistance, alkali resistance and drying time were determined according to ASTM.

FULLERENOL/ÜRETAN YAĞI KOMPOZİTİN ÜRETİMİ VE ÖZELLİKLERİ

ÖZET

Fullerenler, karbon atomlarından oluşan altıgen ve beşgen yüzleri içeren kapalı kafes yapısındaki moleküllerdir. Genel formülü, n altıgenlerin sayısı olmak üzere, C_{2n+20} ile ifade edilir. Sadece 12 beşgenden oluşan C_{20} fullerenlerin en küçük üyesidir. Karbon atomu sayısı çift ve 20'den büyük olmak üzere her sayıda fulleren molekülü olması mümkündür. Fulleren moleküllerinde karbon atomları birbirine güçlü σ ve π bağlarıyla, kristal içerisindeki fulleren molekülleri ise birbirine zayıf Van Der Walls bağlarıyla bağlıdır. Fulleren molekülleri yapısındaki karbon atom sayısına göre farklılık göstermektedir. C_{60} saf kristali yüzey merkezli kübik yapıda iken C_{70} kristali hekzagonel sıkı paket yapıda olabilmektedir.

Fullerenler genel olarak 3 şekilde sınıflandırılırlar. Bunlardan ilki intercalation olarak adlandırılan yapılardır. Bu yapılarda fulleren molekülü kendine ait moleküler özelliklerini korurken kendisine eklenen atom geniş kafeslerin arasını doldurur. İkincisi ekzohedral fulleren yapılarıdır. Bu yapılar fulleren molekülüne dışardan farklı atom veya atom gruplarının bağlanması ile oluşur. Son fulleren yapısı ise endohedral fullerenlerdir. Bu yapılar, bir ya da birden çok atomun fulleren molekül kafesi içerisinde hapsedilmesiyle oluşur. Kafes içerisindeki atom metal atomu ise bu tür fullerenlere endohedral metallofurenler denilmektedir.

1985 yılında keşfedilen bu yapılar modern bilimdeki en ilginç moleküllerden biri olarak tanımlanabilir. Fulleren sadece estetik görünümlü karbon allotropu olmak dışında sıra dışı özelliklere sahip bir moleküldür. Ancak bu özellikler fullerenin az çözünebilir ve işlenebilir olması dolayısıyla kısıtlanmaktadır. Araştırmaların başında polimerik matrisin içine gömülerek ortaya çıkarılan karışımlar ve bileşikler hem polimer özellikleri açısından (iyi çözünebilirlik ve işlenebilirlik) hem de fulleren özellikleri açısından (optik, manyetik ve iletkenlik) incelenmiştir. Ancak fullerenlerin ve polimerlerin birbirleriyle uyumsuz olması ve birbirlerine yapışmaması polimerik Matris içinde büyük fulleren parçacıklarının birikmesine sebebiyet vermiş ve bu durum oluşan malzemenin kullanım performansının düşük olma riskini ortaya çıkarmıştır. Bu problemlerin çoğu fullerenlerin modifiye edilmesiyle çözülmektedir. Modifiye edilmiş fulleren molekülleri saf fullerenlerin çoğu özelliğini barındırmaya devam etmekle birlikte yaygın olan organik maddelerde çözülmesini kolaylaştırarak ileri çalışmalara daha uygun hale getirmiştir. Fulleren ve polimerin uygun, fonksiyonel gruplarla modifiye edilmesi fulleren ve polimerler arasında güçlü bir etkileşim meydana getirmekte ve fullerenin polimer matrisi içinde iyice yayılmasını ve güçlü bir şekilde yapışmasını sağlamaktadır. Değişik fonksiyon grupları fullerene hidrojenleşme, halojenleşme, oksitlenme, metilasyon, hidroksillenme gibi yollarla bağlanmaktadır. Geçmişten günümüze halojenleşme ve hidroksillenme en çok çalışılan iki yöntemdir.

Fullerenol olarak adlandırılan yapı hidroksillenme yöntemiyle oluşmuş olup, kolay reaksiyona girme özelliğinin yanı sıra yüksek çözünürlülüğe ve kararlılığa sahiptir.

Bu özelliklerinden dolayı modifiye edilmiş fullereni polimer zincirlerine aşılamak malzemenin kullanabilirliğini arttırmak açısından önemli bir yer tutmaktadır. Çünkü fullerenol ve polimer birleştiğinde çözünürlüğünün ve işlenebilirliğinin artması yanı sıra kullanışlı malzemeler oluşumuna da sebebiyet vermektedir.

Polimer malzeme üretimi yaygın olarak petrol bazlı kaynaklardan yapılmaktadır. Ancak petrol kaynaklarının kısıtlı olması, petrol fiyatlarının gün geçtikçe artması ve petrolün yanması sonucu oluşan karbon monoksit gazlarının çevreye vermiş olduğu zararlardan dolayı, bilim insanları yenilenebilir enerji kaynaklarına yönelmeye başlamıştır. Bitkisel yağlar bu yenilenebilir kaynakların en önemli olanlarından biridir. Bitkisel yağların ana bileşeni trigliseritler olup bu yapılar gliserinin ve üç yağ asidinin esterleşmesi ile oluşmaktadır. Trigliseridler kuruma özelliklerine göre kurumayan, yarı kuruyan ve kuruyan yağlar olarak 3 ana sınıfa ayrılır. Bu sınıflandırma doymamışlık derecesine göre yapılır. Yağ asitlerindeki doymamış gruplar, iyot indisi tayini ile belirlenir. İyot indisi 100g yağa katılabilen halojenin, iyot cinsinden gram miktarıdır. İyot indisi yükseldikçe yağın kuruma özelliği artar. İyot değeri 170'den büyük olanlar kuruyan, 170 ile 100 arasında olanlar yarı-kuruyan, 100'den küçük olanlar kurumayan yağ olarak adlandırılır.

Kullanılan yağın içeriğine ve özelliğine göre değişik fiziksel özelliklere sahip polimerler elde edilebilmektedir. Bitkisel yağlarda polimer oluşumu temelde üç farklı yöntem ile gerçekleştirilmektedir: (i) çift bağların direkt polimerizasyonu, (ii) çift bağların kimyasal modifikasyonu (iii) trigliseritlerin indirgenmesiyle monogliseridlerin oluşturulması genel olarak bu üç farklı yöntemi oluşturur. Karbon çift bağların direk polimerizasyonunda bu bağlar bir serbest radikal ya da bir katyonik mekanizma yoluyla polimerize edilir. Modifikasyonlar ise trigliseridlerde bulunan C=C çift bağı, ester grubunun alfa karbonu, allilik karbonlar tarafından sağlanabilmektedir. Son olarak bitkisel yağlardan polimer üretiminde gliseroliz adı verilen bir yöntem kullanılır. Gliseroliz reaksiyonu bir solvent içinde veya emülgatör katalizörü varlığında gerçekleştirilir. Bu reaksiyon sonucunda mono-digliserid ürün karışımı oluşur. Bu ürün karışımı polimer yapımında platform geçiş monomeri olarak kullanılır ve kısmi gliserid olarak adlandırılır. Kısmi gliseridler izosiyanat, diasit, anhidrit ve epoksi gibi komonomerlerle polikondezasyon reaksiyonu verebilmektedir.

Üretan yağlar kısmi gliseridler ile diizosiyanat arasında gerçekleşen reaksiyonlar sonucu oluşur. Diizosiyanatlar alifatik veya aromatik yapıda olabilirler. Kullanılan monomerler doğrudan ürün özelliklerine etki etmektedir. Poliüretan oluşumunda kullanılan yağlardan bazıları ayçiçeği yağı, keten yağı, soya yağıdır.

Bu tezde fullerenol ve ayçiçek yağının gliseroliz reaksiyonu ile oluşturulan kısmi gliserid karışımından kompozit malzeme oluşturulmuş ve bu malzeme yüzey kaplama özellikleri yönünden incelenmiştir. Sözü edilen malzemenin üretiminde ilk aşamada fullerenin kısmi gliserid ile kovalent bağ oluşturmasını sağlayacak bir yüzey modifikasyonu gerçekleştirilmiştir. Bu yüzey modifikasyonunda benzen içinde çözünmüş fulleren molekülü NaOH ile tepkimeye sokulmuştur. Tepkime hava ortamında gerçekleştirilmiş ve tetrabutilamonyum hidroksit katalist olarak kullanılmıştır. Elde edilen fullerenol molekülünün yapısı FT-IR ile incelenmiştir. Tepkimede oluşan OH moleküllerinin sayısını hesaplayabilmek için ise TGA analizi yapılmıştır. Daha sonra ayçiçek yağının gliserol ile alkoliz reaksiyonu sonucunda kısmi gliserid elde edilmiştir. Daha sonraki aşamada ise fullerenol molekülü ve kısmi gliserid kovalent bağla bağlanmış ve yüzey kaplama malzemesi elde edilmiştir.

Hazırlanan fullerenol-üretan yağı kompozit malzemenin kimyasal yapıları FT-IR ile incelenmiştir. Buna ek olarak, numunelerin termal özellikleri TGA ve DSC analizleriyle izlenmiştir. Elde edilen kompozit malzemenin ısıl kararlılığının klasik üretan yapıdan daha az olduğu gözlenmiştir.

Ayrıca elde edilen kaplama malzemesinin film özellikleri ASTM standartlarına uygun şekilde kuruma zamanı, esneklik, su, asit ve baza dayanıklılık testleri ile incelenmiştir.

1. INTRODUCTION

Fullerene is a form of carbon having a large spherical molecule consisting of a hollow cage of sixty or more atoms. They have received much attention in recent years due to its unique chemical and physical properties. However, fullerene has limitation to dissolve in water, which prevents application in industrial area. For easy application, fullerene can be converted to poly hydroxyl fullerene (fullerenol) [1].

Recently, much research is focused on combine polymers with fullerene. Polymer is a large molecule or a macromolecule, composed of repeating structural units. Natural and synthetic polymers are widely used in various industries including coating, adhesive, biomedical, and pharmaceutical. They are generally produced from petroleum resources. With the depletion of fossil fuel reserves, rising price of petroleum and increase environmental problems, there is an urgent need to develop polymeric materials from renewable resources. Vegetable oils are excellent renewable source for manufacturing polymer components. It is well known that vegetable oils are triglycerides of different fatty acids and glycerol. Three different methods are used for the preparation of polymers from vegetable oils (i) direct polymerization of double bonds (ii) chemical modification of double bonds (iii) reduction of triglyceride to monoglyceride [2-4].

In this thesis, polymers which were produced by reduction methods were combined with fullerenol. For this purpose, first partial glycerides were prepared by the glycerolysis reaction between sun flower oil and glycerol. After that fullerenol are covalently bounded to partial glycerides through the reaction of hydroxyl groups with TDI. The chemical structure of the intermediate sample, (fullerenol) and the final products were determined. Thermal characteristic of the resulting product was also determined thermal analysis such as TGA and DSC. The film properties in view of coating purposes were determined.

2. THEORETICAL PART

2.1 Fullerene

Buckimsterfullerenes are members of organic molecules which are formed by carbon allotropes. The name of Buckminsterfullerene comes from architect Buckminster Fuller whose geodesic dome design is similar to the molecular structure of fullerene (Figure 2.1). The first fullerene was discovered in 1985 and its first large scale production was done in 1990 by resistive heating of graphite. Light fullerenes such as C_{60} and C_{70} can be used in different areas of science and engineering, including material science, mechanics, mechanical engineering, construction, electronics, optics, medicine, pharmacology, food and cosmetics [5,6].

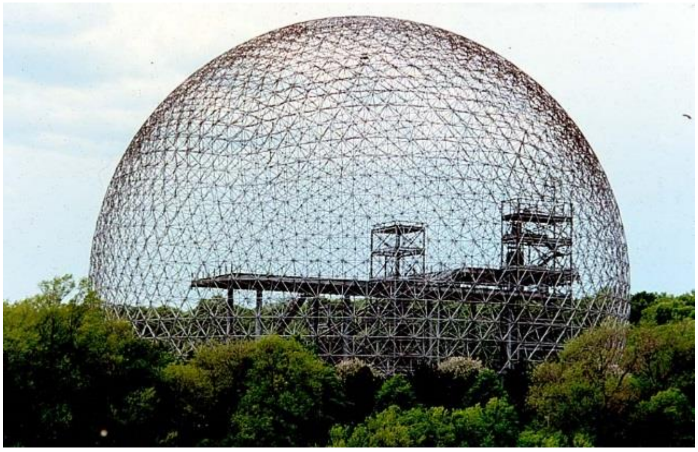

Figure 2.1 : The Montreal Biosphere by Buckminsterfullerene Fuller, Montreal, 1967.

Fullerenes are spherical, caged molecules with carbon atoms located at the corner of the polyhedral structure consisting of pentagons and hexagons. According to the Euler theorem, in order to close a sphere of n hexagons, 12 pentagons are required. As a result, all fullerenes have 12 pentagons independent from their sizes. C_{60} is the smallest and stable fullerene, which obeys this rule. C_{60} is also known as (C_{60}-Ih)fullerene because it has 60 carbon atoms that form a sphere belonging to the icosahedral symmetry group Ih and the numbers in brackets indicate the presence of only pentagons and hexagons. Fullerenes consisting of more carbon atoms are also possible and they can be called as higher fullerenes such as C_{70}, C_{72}, C_{78}, C_{80} [7].

Fullerene can generally be separated into three categories [8]:

(1) Intercalation compounds, in which the fullerene host keeps its molecular properties and additional atoms doped the large interstices in the lattice, such as alkali metal doped C_{60} compounds

(2) Exohedral solids formed from fullerenes to which additional atoms, ions or clusters are covalently bonded on the outside of the fullerene shell. The structure of exohedral fullerene was shown in Figure 2.2 (a).

(3) Endohedral cluster solids formed from non-carbon atoms are encapsulated by fullerene. The structure of endohedral fullerene was shown in Figure 2.2 (b).

X-ray powder and single crystal diffraction techniques have been used to determine crystal structures of the types of fullerene [8].

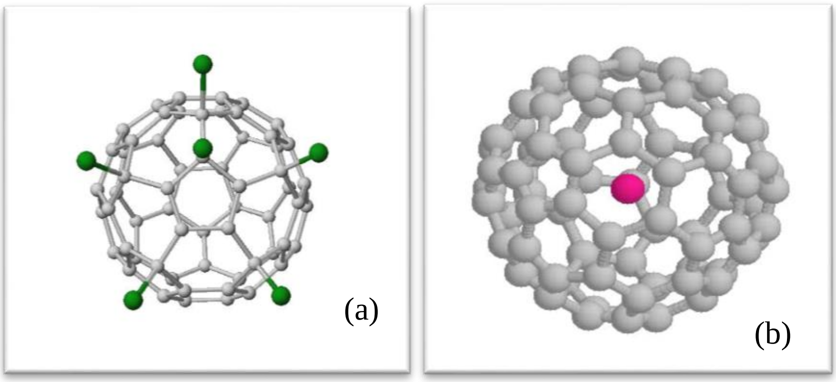

Figure 2.2 : Structures of Exohedral (a) and Endohedral (b) fullerene.

2.2 Properties of Fullerene

2.2.1 Chemical properties of fullerene

Fullerenes are stable but not completely unreactive. The characteristic fullerene reaction is electrophilic addition to hexagon-hexagon double bonds. In the addition the sp^2 –hybridized carbons are changed into sp^3-hybridized ones. C_{60} and C_{70} exhibit the capacity to be reversibly reduced with up to six electrons. This high electron affinity results from the presence of triply-degenerate low-lying LUMOs (lowest unoccupied molecular orbital). Due to their high electron affinity fullerenes are easily reduced. However, their oxidation is difficult due to their higher ionization energy. Oxidation is irreversible. Fullerene has a localized pi-electron system, which prevents molecule from displaying superaromaticity properties [9-10].

2.2.2 Physical and spectroscopic properties of fullerene

The heats of formation of C_{60} and C_{70} have been determined by calorimetry to be 10.16 kcal/mol per C-atom for C_{60}, and 9.65 kcal/mol per C-atom for C_{70}. Since fullerene thermodynamically less stable than either diamond or graphite, the values for which are 0.4 and 0 kcal/mol, respectively.

Fullerenes can be easily modified in the solution state. The solubility plays an important role in extractions or chromatographic separations. The solubility of C_{60} in a different of organic solvents has been given in Table 1.1 [11].

Table 2.1 : Solubility of C_{60} in a various solvent [11].

Solvent	[C_{60}],mg/mL	Mole Fraction (x 10^4)	N
n-pentane	0.005	0.008	1.36
n-hexane	0.043	0.073	1.38
Cyclohexane	0.036	0.059	1.43
n-decane	0.071	0.19	1.41
Decalines	4.6	9.8	1.48
Carbon disulfide	7.9	6.6	1.63
Dicloromethane	0.26	0.27	1.42
Chloroform	0.16	0.22	1.45
Tetracloromethane	0.32	0.40	1.46
Tetrahydrofuran	0.000	0.000	1.41
Benzene	1.7	2.1	1.50
toluene	2.8	4.0	1.50
Tetraline	16	31	1.54
Benzonitrile	0.41	0.71	1.53
Anisole	5.6	8.4	1.52
Chlorobenzene	7.0	9.9	1.52
1,2-dichlorobenzene	27	53	1.55
1-methynaphthalene	33	68	1.62
1-chloronaphthalene	51	97	1.63
Acetone	0.001	0.001	1.36

Fullerene naturally is insoluble in polar and H-bonding solvents like acetone, tetrahydrofuran or methanol. Fullerene is sparingly soluble in alkenes with the solubility increasing with the number of atoms. Fullerene completely dissolves in aromatic solvents and in carbon disulfide. A significant increase of the solubility takes place on going from the benzenes to naphthalenes. Although there are trends for the solution behavior of C_{60}, there is no direct dependence of the solubility on a certain parameter like the index of refraction *n*. When the solubility expressed in mole fraction units it is evidence that C_{60} is not very soluble even in the best solvents listed in Table 1.1. The solubility of C_{70} has the similar trends as C_{60} but it is more soluble. For example, the solubility of C_{60} in water at 25 ^{0}C is equal to 1.3×10^{-13}g.L^{-1} and the solubility of C_{70} is equal to 1.1×10^{-11}g.L^{-1} [11-6].

The melting point of fullerene has not been determined yet and is estimated to be higher than 1000^{o}C. In nitrogen atmosphere the fullerene starts to being degradation at 600^{o}C. The decomposition is much more rapid in the presence of oxygen. On heating in oxygen, C_{60} is gradually oxidized: C-O adducts are formed at 200^{o}C, and at 400 - 500^{o}C decomposition is substantial [11].

Solid C_{60} has a face-centered-cubic (FCC) structure at room temperature as shown Figure 1.2. They have very low density (1,68 g/cm^3) as compared to graphite (2,1-2,3 g/cm^3) or even diamond (3,51 g/cm^3). Four equivalent molecules are contained in a unit cube with edge length a=14.198A^o, at the origin and face centers [11].

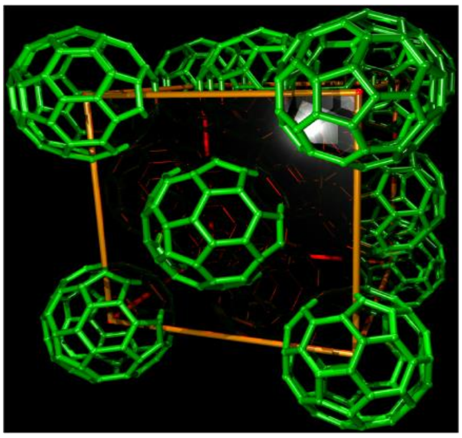

Figure 2.3 : FCC Crystal of C_{60}.

2.3 Fullerenol

Polyhydroxylated fullerenes are a member of fullerenes that has many hydroxyl groups. They are also called as fullerenols or fullerols. Fullerenols can be produced by the chemical modification of covalent C-O bonds, on their spherical surfaces. The chemical formula $C_{60}(OH)_n$ shows structure of the fullerenol and n represents to different number of hydroxyl groups. Fullerenol is representative of fullerene derivatives dissolvable in water because of its abundant hydroxyl groups. The solubility of fullerenol increases with the number of the hydroxyl groups. [12-13].

Fullerenols can be used in many application areas such as solution chemistry, electrochemistry, and biochemistry. Also fullerenols can be used to obtain new fullerene derivatives because they are soluble in water and bear polar hydroxyl groups. Therefore, synthesis of water-soluble fullerene and its derivatives has been an important research field for many years. Scientists have been done many experiments about the synthesis of fullerenol after the discovery of fullerene in 1985. These researches briefly explained at below [13-14]:

Djordjević et al., reported preparation of fullerenol by a procedure of complete substitution of bromine atoms from polybromine derivatives $C_{60}Br_{24}$ in alkaline media. This new fullerene derivative was characterized as consisting of a chemical composition of 22 hydroxyl groups [15].

Li et al., synthesized fullerenol by using a typical two-phase reaction in the presence of tetrabutylammonium hydroxide. This new fullerene derivative was characterized as consisting of a chemical composition of an average of 22-26 hydroxyl groups [16].

Lu et al., improved the synthesis techniques of Li et al., and Na element which was included in fullerenol was removed by using dialysis method [13].

Muradyan et al., synthesized fullerenol by using mechanochemical techniques. Fullerenol C_{60} was prepared by mechanochemical processing of fullerene with KOH in a planetary ball mill. Fullerenol was synthesized with formula of $C_{60}(OH)_{27.6}$ [17].

Zhang et al., synthesized fullerenol by direct reaction of fullerene with aqueous NaOH. Polyethylene glycol (PEG) 400 was used as catalyst in the reaction. Two types of fullerenol were obtained from this synthesis. First fullerenol had 8.5 number of OH groups and second fullerenol had 27 number of OH groups. Difference between numbers of OH groups depended on experimental conditions [18].

Chiang et al., synthesized fullerenol by electrophilic addition of nitronium tetrafluoroborate with arenecarboxylic acid under mild reaction conditions. The structure of these new fullerene derivatives was characterized as consisting of a chemical composition of an average of 13-15 hydroxyl groups. Hydrolysis of these derivatives in alkaline aqueous solution affords the corresponding water-soluble fullerenols consisting of 18-20 hydroxyl groups per $\mathbf{C}_{60}$ molecule on average [19].

Sun et al., synthesized fullerenol by the reaction of fullerene with metal potassium in a refluxing toluene solution [21].

2.4 Vegetable Oils

Vegetable oils are important biorenewable resources extracted from many kinds of seeds and are normally named by their biological source, such as soybean oil and palm kernel oil. Chemically, vegetable oils consist of mainly triglycerides which are produced by esterification of glycerol with three fatty acids [21-22]. A general molecular structure of triglycerides is represented in Figure 2.4.1.

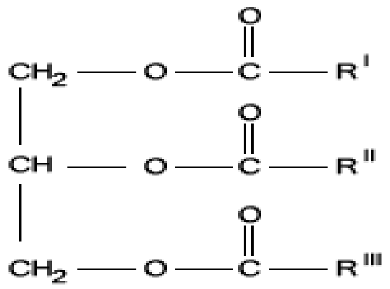

Figure 2.4 : Molecular structure of triglyceride.

The fatty acids account for approximately 95% of the total weight of triglycerides and their content and chemistry are characteristics of each plant oil and geographical condition [23, 24]. Fatty acids are classified as saturated and unsaturated fatty acids. While saturated fatty acids have no double bonds, unsaturated fatty acids contain one or more than double bonds. Double bonds are named as isolated when double bonds between the carbon chain are separated by at least 2 carbon atoms. Double bonds are named as conjugated when single and double bonds alternate between certain carbon atoms [25]. Nature and the distribution of the fatty acids indicate the physical state of vegetable oils. Most vegetable oils are liquid at room temperature. Generally, higher melting point vegetable oils are obtained with more carbons in the fatty acid chain, a lower number of carbon–carbon double bonds, and an E (trans) configuration and conjugation of the carbon–carbon double bonds [21].

Table 2.2 : Fatty acid distribution of some oils.

Acid	Castor oil (%)	Linseed oil (%)	Palm oil (%)	Soybean oil (%)	Sunflower oil (%)
Palmitic acid	1.5	5	39	12	6
Stearic acid	0.5	4	5	4	4
Oleic acid	5	22	45	24	42
Linoleic acid	4	17	9	53	47
Linolenic acid	0.5	52	-	7	1
Ricinoleic acid	87.5	-	-	-	-
Licanic acid	-	-	-	-	-

2.4.1 Classification of triglycerides

Stereochemistry of the double bonds of the fatty acids chains, the degree of unsaturation and the length of fatty acids are important parameters affecting the chemical and physical properties of oils. On the other hand, the degree of unsaturation is the most important parameter that affects the properties of oil. Unsaturation can be determined by iodine value (IV). The IV value represents the amount of iodine (mg) that reacts with the carbon-carbon double bonds in 100 g of the vegetable oil under specific condition; the larger IV value indicates more carbon-carbon double bonds per vegetable oil triglyceride. Triglyceride can be separated into three categories depending on their iodine values; drying (iodine value greater than 170), semi-drying (iodine value between 100 and 170) and non-drying oils (iodine value smaller than 100) [25-26].

Drying oils: These types of oil readily absorb atmospheric oxygen when exposed and form a dry thin elastic film. They are rich in unsaturated fatty acids. Linseed oil, Safflower oil, Poppy oil and Tung oil can be given as example of drying oil [27].

Semi-drying oils: They are between drying and non-drying oils. They absorb atmospheric oxygen slowly and produce a soft film even after long exposure. They have linoleic and saturated acids but do not contain linolenic acid. Cotton seed oil, Sesame oil can be given as example of this category [27].

Non-drying oils: They do not absorb atmospheric oxygen and they do not form elastic films even after long exposure. These oils are rich in saturated acids and oleic acids. Castor oil and olive oil are important examples for this category [27].

2.5 Vegetable Oil Based Polymers

Natural or synthetic polymers have important role in modern life. They are used as daily life materials, commodity to industry and technology in the many fields such as electronics, machinery, communications, transportations, pharmacy, and medicine as highly advanced materials [28]. Generally, petrochemicals are used as main sources of polymer production. However, petroleum sources are limited and prices increase day by day. In addition, fossil fuel combustion expose carbon monoxide gases and it caused global warming. Since petroleum based products creates an environmental problems [29-30], scientists have begun to develop polymers which are produced from biological sources and have focused on the use of cheap, biodegradable, and renewable starting materials such as starch, cellulose, carbohydrates, proteins, and vegetable oils for synthesizing a wide range of biopolymers. The life cycle of these polymers is shown in Figure 2.5 [31].

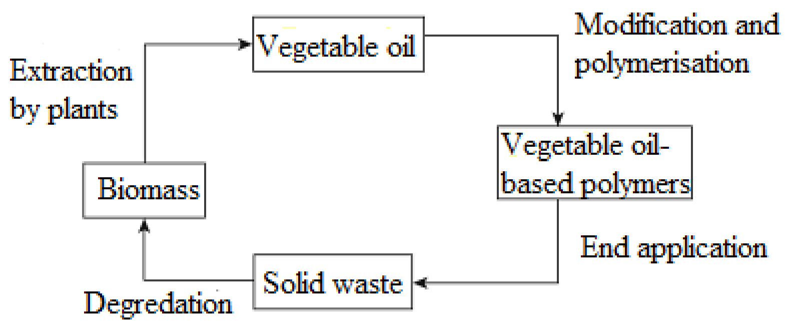

Figure 2.5 : Life cycle of vegetable oil-based polymers.

Vegetable Oil Based Polymers (VOBP) have more advantage when they are compared with other bio-based biopolymers such as starch and proteins. These advantages can be explained as following [32]:

(1) Vegetable oils are precursors for monomer chains that can be used to synthesize various polymers including polyurethane, polyester and polyether.

(2) Vegetable oils are suitable for synthesis of hydrophobic polymers and complement nicely other bioresources like carbohydrates and protein that are naturally hydrophilic [32].

(3) Vegetable oils are suitable for producing monomers with structures similar to petroleum-based monomers. Therefore, petroleum-based biopolymers are possibly substituted by VOBP with identical desired properties [32].

Triglycerides contain several reactive positions that are amenable to chemical reaction: ester groups, double bonds, allylic positions and α-position of ester group (Figure 2.6). These sites can be used to introduce polymerizable groups on the triglyceride using similar techniques applied in the synthesis of petrochemical-based polymers [33].

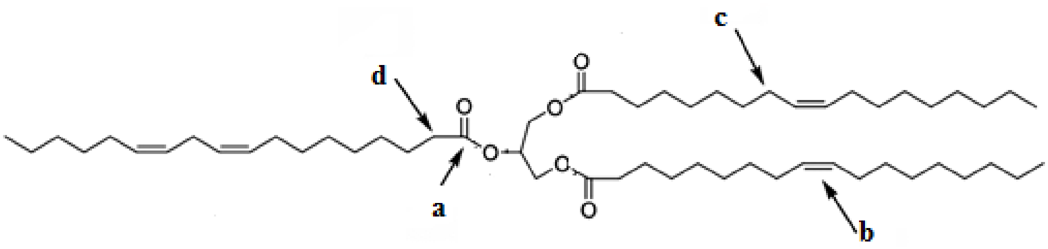

Figure 2.6 : Reactive positions in triglycerides: ester groups (a), double bonds (b),allylic positions (c), and α-position of ester group (d).

There are three ways for the preparation of polymers from vegetable oils (Figure 2.7). The first one is the direct polymerization through the double bonds or other reactive functional groups present in the fatty acid chain. The second route consists of the chemical modification of the double bonds, introducing functional groups which are easier to polymerize, and the third is the chemical transformation of plant oils to produce platform chemicals which can be used to produce monomers for the polymer synthesis [4].

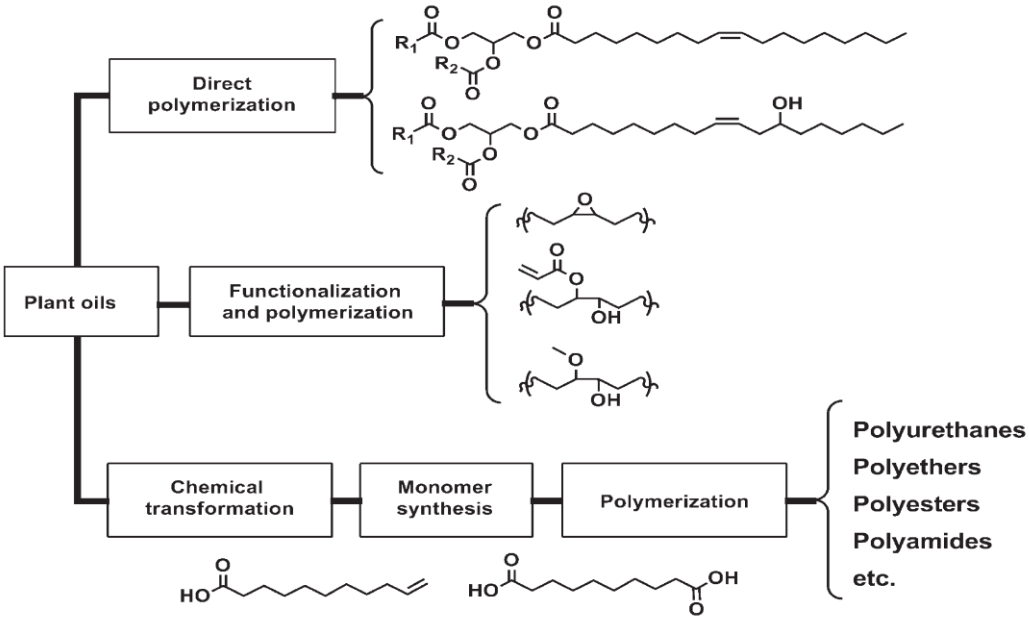

Figure 2.7 : General strategies for the synthesis of plant oil-based polymers.

2.5.1 Direct polymerization of C=C

C=C double bonds in vegetable oils has capacity to being polymerized. These double bonds will be polymerized through a free radical or a cationic mechanism. The free-radical polymerization of triglyceride double bonds has received little consideration due to the existence of chain-transfer processes to the many allylic positions in the molecule [34-35].

2.5.2 Functionalization of C=C and polymerization

Since the internal double bonds in the triglyceride structure are not sufficiently reactive for any viable polymerization process considerable efforts have been devoted to modification of C=C into more reactive functional groups that could facilitate the polymerization of the triglycerides [34].

2.5.3 Conversion of triglycerides into mono/diglycerides

The conversion of the triglycerides into mono/ diglycerides or into simple fatty acids can produce platform chemicals for producing monomers toward polymer synthesis. Mono-diglycerides are produced from the esterification reaction between triglyceride with glycerol [36-37].

3. EXPERIMENTAL WORK

3.1 Materials

Fullerene with purity of (98%) was purchased from Sigma Aldrich and it was used to obtain fullerenol according to method described by Li *et. al*. Commercially purchased sunflower oil was used as received. Benzene, sodium hydroxide, tetrabutylammonium hydroxide (TBAH), methanol, calcium hydroxide, glycerol, sodium sulfate, toluene-diisocyanate (80% 2,4, 20% 2,6 isomers), sulfuric acid, tin(II) 2-ethylhexanoate 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 was received from Riedel de Haen and was used as received.

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 Thermal gravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were recorded on an Exstar SII TG/DTA. The measurements were done from room temperature to 800°C with a heating rate 10°C/min.

3.2.3 Differential scanning calorimeter (DSC)

Thermal analyses were done by differential scanning calorimetry (DSC) using Perkin Elmer DSC 4000. The measurements were done from room temperature to 200°C with a heating rate 10°C/min.

3.3 Preparation Methods

3.3.1 Preparation of fullerenol

Fullerenol was synthesized according to the method described by Li *et al* [32]. A benzene solution of C_{60} (80 mg in 60 ml) was vigorously stirred with aqueous NaOH (2 g in 2 ml water) containing a few drops of TBAH (40% in water) at 50 ^oC under air. Two hours later, the benzene solution, originally deep violet, turned colorless and brown sludge precipitated. Benzene was removed by decantation and sludge was evaporated under pressure. Then the sludge was stirred 10 ml deionized water at 50 ^oC under air for another 10 h. After that the resultant aqueous solution in brown was filtered to remove a trace of water insoluble residue. Then methanol (MeOH:50 ml) was added to produce brown precipitate. The precipitation process was repeated three or four times to ensure complete of removal of TBAH and NaOH. The precipitation process was finished when the pH value of solution was less than 8.

3.3.2 Preparation of partial glyceride (PG)

Partial glyceride was prepared by glycerolysis reaction between sun flower oil and glycerol in a three-necked round-bottom flask equipped with a dry nitrogen flow through inlet and reflux condenser. Sunflower oil and glycerol (8.5 %of oil) were placed into reaction flask. They were mixed and heated to 218 ^oC under nitrogen flow. At this temperature, calcium hydroxide (0.1wt.% of oil content) was added as catalyst. After that, the temperature was set at 232 ^oC and kept constant. The reaction was continued for 1 hour. Then, the mixture was cooled to room temperature and it was mixed with diethyl ether and washed first with 0.2 N sulfuric acid and then 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 calculated as 113 mg KOH/g and 2 mg KOH/g, respectively.

3.3.3 Classical urethane oil synthesis

Classical urethane oil was prepared as a comparative sample. It was synthesized from the reaction of PG with TDI, using solvent methods. The partial glycerides and dry toluene were taken into reaction flask and heated to 40-50^oC, and an equivalent amount of isocyanate component was added slowly over a 10 min period. After that tin(II) 2-ethylhexanoate was added in the mixture. The temperature was set to 90-95^{o}C and maintained until the reaction was completed.

3.3.4 Combination of fullerenol with the partial glyceride

Partial glyceride in dry toluene was stirred with TDI in 5 minutes into flask at the ice bath. Then, reaction was taken on hot plate at 45 °C for 40 minutes. After that, fullerenol equivalent to partial glyceride and tin(II) 2-ethylhexanoate as catalyst was added the mixture and temperature was adjusted to 90-95°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.

3.3.5 Characterization

The structure of fullerenol, urethane oil and final products were characterized by using Fourier-Transform Infrared Spectroscopy (Perkin-Elmer FT-IR Spectrum One B spectrometer). Thermal properties of pure fullerene, fullerenol, urethane oil and final products were investigated by Thermogravimetric Analyzer (Exstar SII TG/DTA 6300).

Film properties such as flexibility, water resistance, alkali resistance, acid resistance and drying time were also determined. Glass tubes were used to determine water, alkali and acid resistance, as explained in the standard methods [38-39].

4. RESULT AND DISCUSSION

Fullerenol was prepared by the reaction of fullerene in benzene with aqueous NaOH in the presence of tetrabutylammonium hydroxide as explained experiment part. Tetrabutylammonium hydroxide was preferred as catalyst, because it is the most effective catalyst under aerobic conditions at room temperature. Possible reaction mechanism for the formation of fullerenols is presented in Figure 4.1. For the reaction using NaOH, the attack of –OH to fullerene followed by the oxidation with molecular oxygen via one electron transfer from the fullerene anion gives the hydroxylated fullerene. The successive attack of –OH and repeated oxidation finally gives the fullerenol. Because the reaction does not occur in the absence of O2, NaOH solution must be in contact with the air [12].

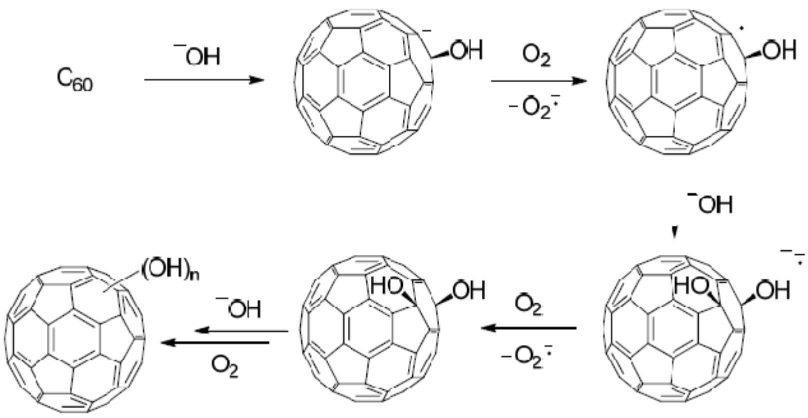

Figure 4.1 : The reaction mechanisms for the formation of fullerenols.

In order to determine whether the “OH” groups were attached on the fullerene surface or not FT-IR analysis was applied. The FT-IR spectrum of the resulting fullerenol sample is presented in Figure 4.2. The fullerenol IR spectrum showed a broad hydroxyl absorption centered at 3351 cm-1, C=C double bond vibration centered at 1640 cm-1, a OH in plane bending vibration centered at 1390 cm-1, and C- O stretching vibration centered at 1020 cm-1. These results showed that the fullerenol was successfully synthesizes by the applied procedure. Actually similar results were also previously given by Li.et al.[9].

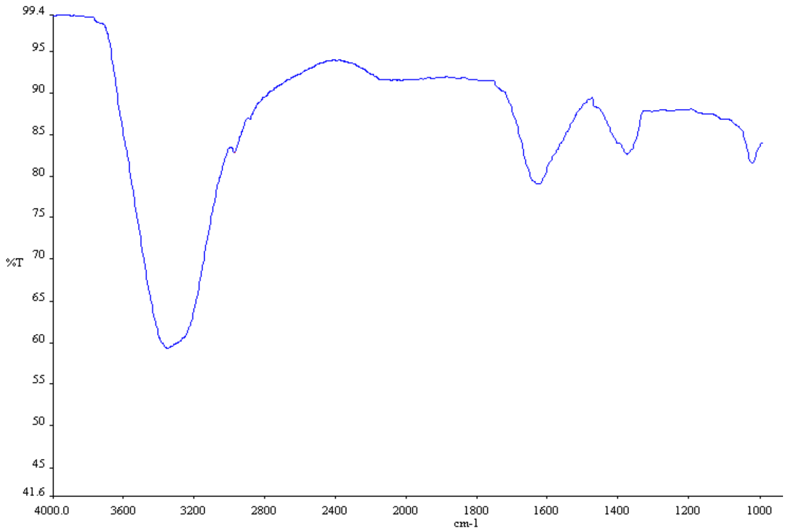

Figure 4.2 : FT-IR spectra of fullerenol.

In order to determine the number of hydroxyl groups attached to surface of fullerene molecule TGA analysis was applied. TGA thermogram was given in Figure 4.3**.** As seen from this thermogram residual moisture which remains after vacuum drying removed below 100^{o}C. The weight loss between 150-570^{o}C represents the remove of OH groups formed on the surface.

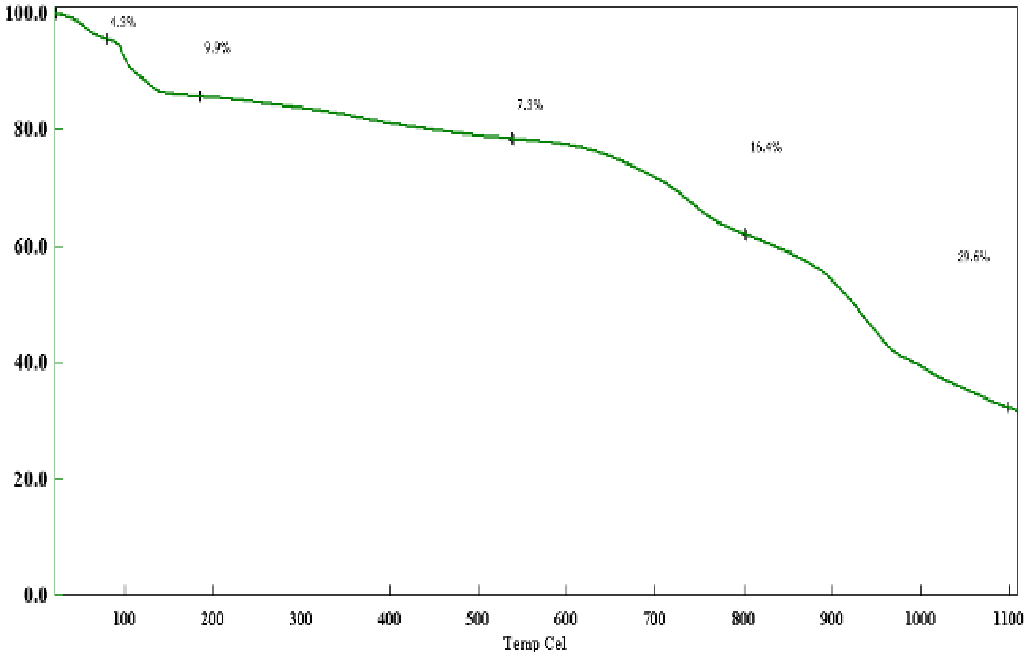

Figure 4.3 : TGA thermograms for fullerenol.

In order to determine how many “OH” groups present on the fullerene surface a calculation explained by Goswami et.al. was performed and found that 16 hydroxyl groups were attached on the surface of prepared sample.

Figure 4.4 shows the thermogravimetric curves of pristine fullerene under N_2. The pure fullerene is thermally stable until 600 °C.

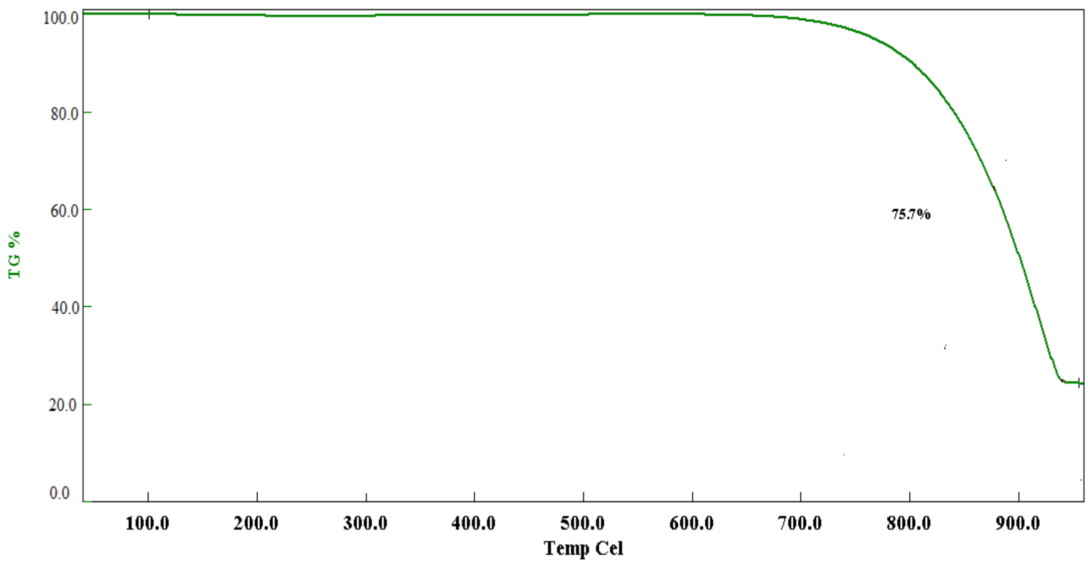

Figure 4.4 : TGA thermograms for pristine fullerene.

In the next step of the study prepared fullerenol was used as alcohol component and combined to the sunflower oil partial glycerides through the reaction with TDI. These studies will be explained in two parts.

First, sunflower oil partial glyceride was prepared by the glycerolysis reaction according to the procedure given in experimental part as shown in Figure 4.5.

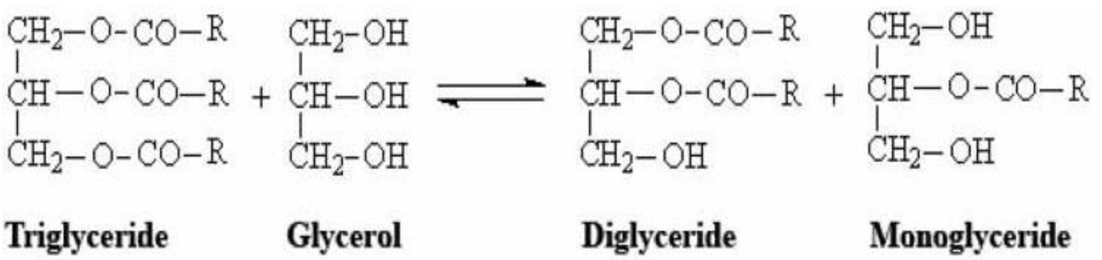

Figure 4.5 : Synthesis of partial glyceride.

The hydroxyl and acid values of partial glyceride were calculated as 113 mg KOH/g and 2 mg KOH/g, respectively.

After that, partial glyceride and fullerenol was combined to each other by the reaction with TDI. No doubt that this product can be considered as a fullerenol- urethane composite. As mentioned in experimental part in order to reach the final composite structure, firstly partial glyceride reacted with TDI at 40°C to allow reactive isocyanates group react with hydroxyl in partial glyceride. After that less reactive isocyanate groups remain after partial glyceride and isocyanate raction as unreacted was reacted with the hydroxyl of added fullerenol in the reaction medium at 90°C. The chemical structure of the final composite sample FT-IR analysis was applied (Figure 4.6). Reaction was monitored by decrease in intensity of the hydroxyl IR absorption band a 3400 cm-1. As predicted, the IR spectrum of the fullerenol and partial glyceride product showed the disappearance of a band around 2272 cm-1 corresponding to the absorption of isocyanate groups.

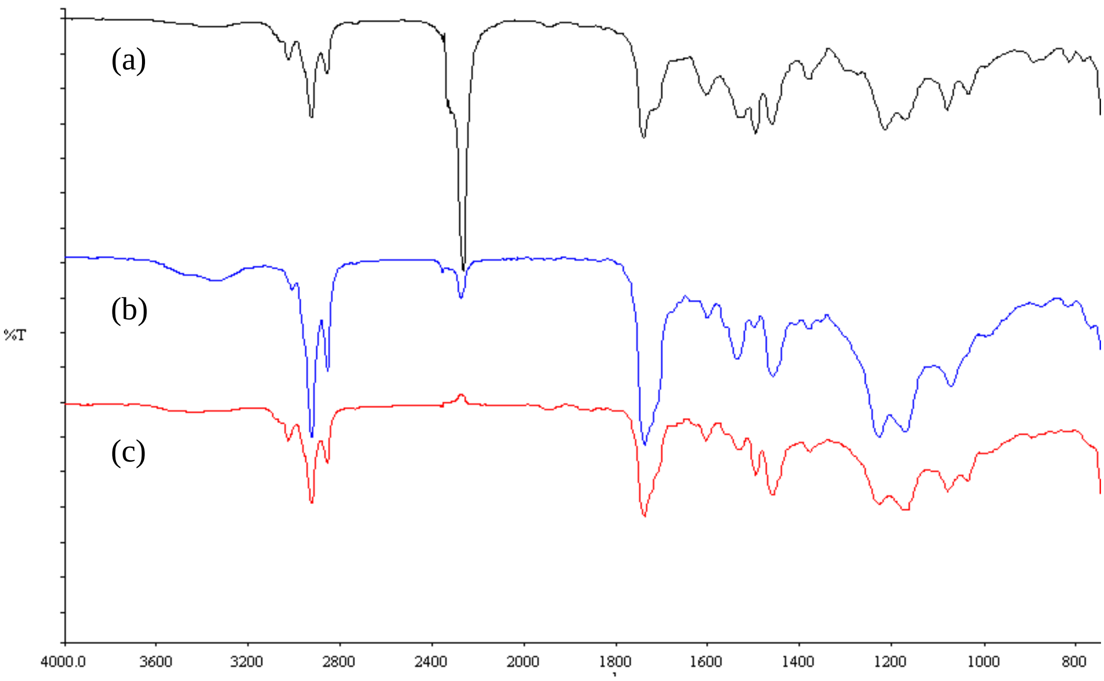

Figure 4.6 : FT-IR spectra of partial glyceride-fullerenol reaction (a) at the beginning of reaction (b) after 45 minute (after adding fullerenol) (c)after 4h later, final product.

Fig. 4.7 shows the TGA curves of classical urethane oil and combination of partial glyceride and fullerenol samples. TGA data indicates that fullerenol urethane oil composite have less thermal stability than classical urethane oil samples because nature of the hydroxyl groups which were attached on the fullerene surface.

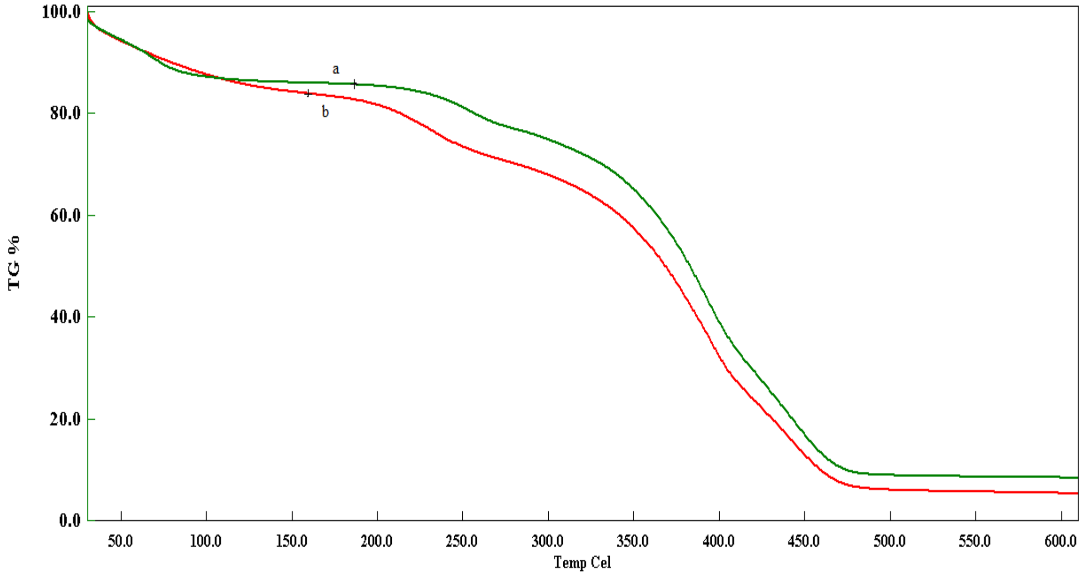

Figure 4.7 : TGA curves of (a) Classical urethane oil, (b) fullerenol urethane oil composite.

The DSC analysis of fullerenol urethane oil composite was given in Figure 4.8. This figure shows that thermal degradation of urethane oil composite occurs in three stages. At the first stage, the dehydroxylation of free OH groups were occurred. In the second stage dehydroxylation of free OH groups on the partial glyceride was occured. Free OH groups which could not attached to the fullerene were dehydroxylation at the final step (Figure 4.8). On the other hand DSC analysis of pure polyurethane shows only one degradation step (Figure 4.9).

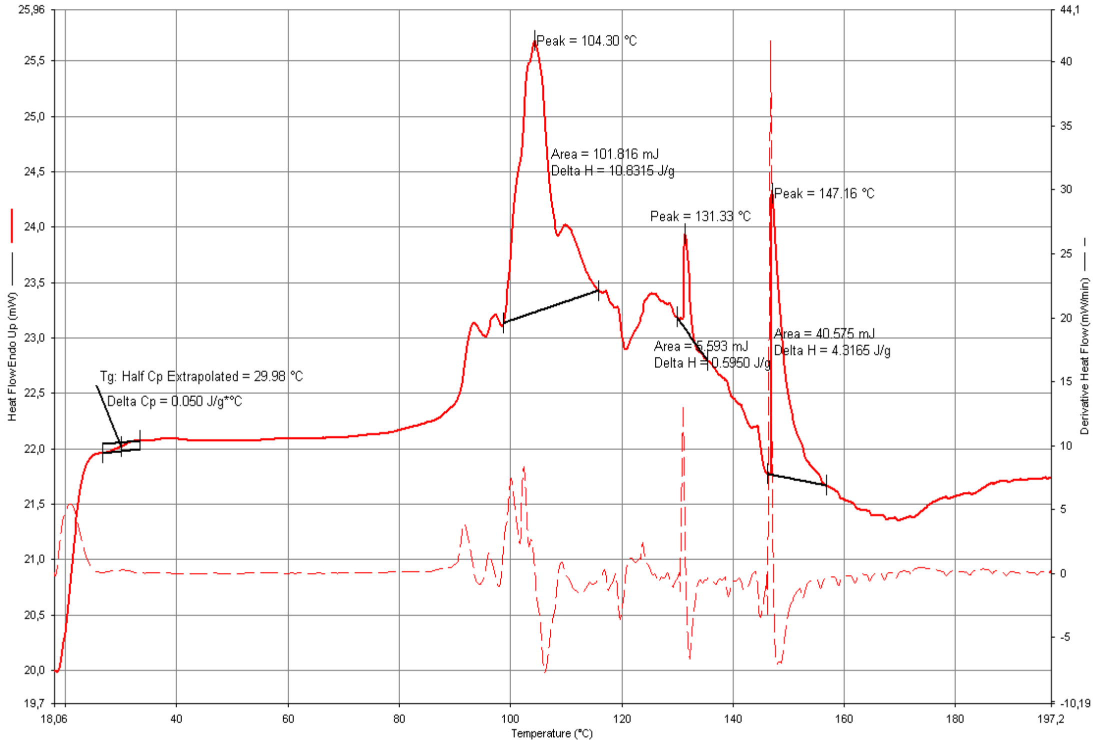

Figure 4.8 : DSC analysis of fullerenol urethane oil composite.

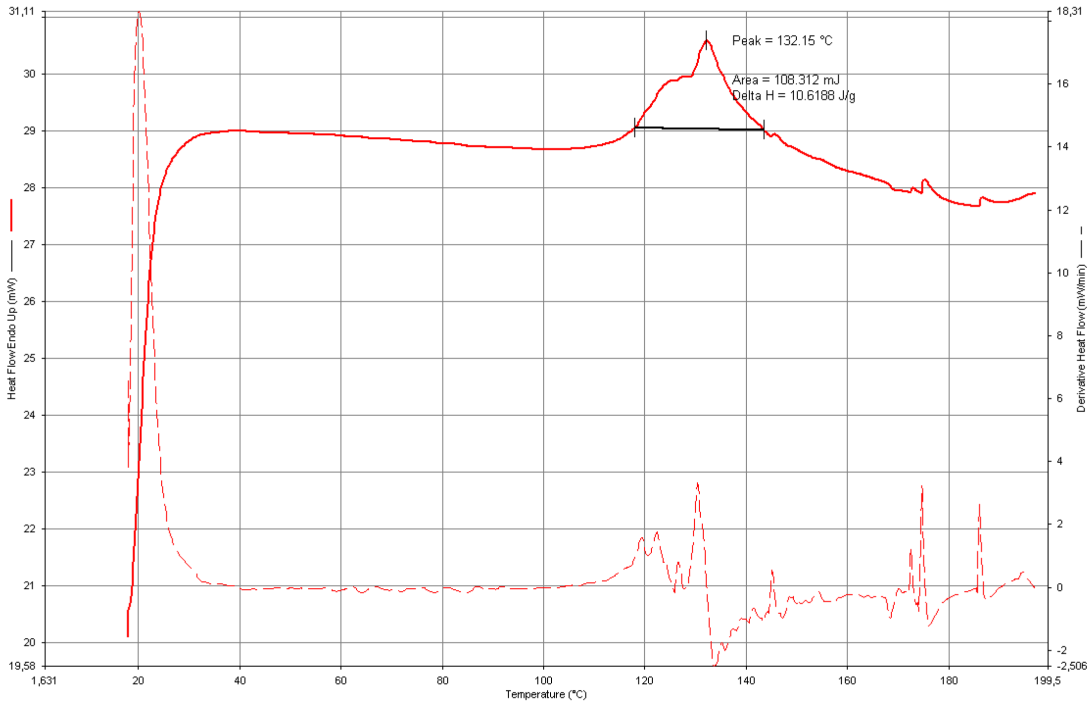

Figure 4.9 : DSC analysis of classical urethane.

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The film properties of fullerenol urethane oil composite was determined to evaluate its potential use terms of organic coatings. Film sample was prepared with 0.5% zirconium napthenate and 0.05% cobalt napthenate and it was dried 20 ˚C for 24 hours. After drying, film properties of final product was investigated by various test methods including flexibility, drying and resistance to water, alkali and acids test. The fullerenol urethane oil composite did not show any crack even it was bended over the 2mm-diameter-cylinder. The fullerenol urethane oil samples displayed excellent resistance to water and acid after 24 h period. In case of exposure to alkali, the film was partially peeling after 48 min later. Drying time was found as 3 minutes.

5. CONCLUSION

In conclusion, synthesis of fullerenol-urethane oil composite was achieved successfully. Firstly, fullerenol was synthesis reaction between NaOH and fullerene by using tetrabutyl ammonium hydroxyl as catalysts. FT-IR analysis was done to understand whether reaction was achieved or not. The results of synthesis of fullerenol were presented as: FTIR spectrum of fullerenol 3351, 1640, 1390, 1020 cm-1. After that, fullerenol and partial glycerides were combined through the reaction of hydroxyl groups and TDI. After this reaction, the characteristic peaks of hydroxyl group at a 3400 cm^{-1} and the peak of isocyanate groups at 2272 cm^{-1} disappeared. This result showed that fullerenol molecules were bounded to the partial glyceride successfully. According to thermal analysis, the decomposition temperatures of fullerenol urethane oil composite were less than classical urethane oil. The fullerenol-urethane oil sample was made film by film applicator and film properties such as flexibility, drying time, and resistance to alkali, acid and water were investigated.

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