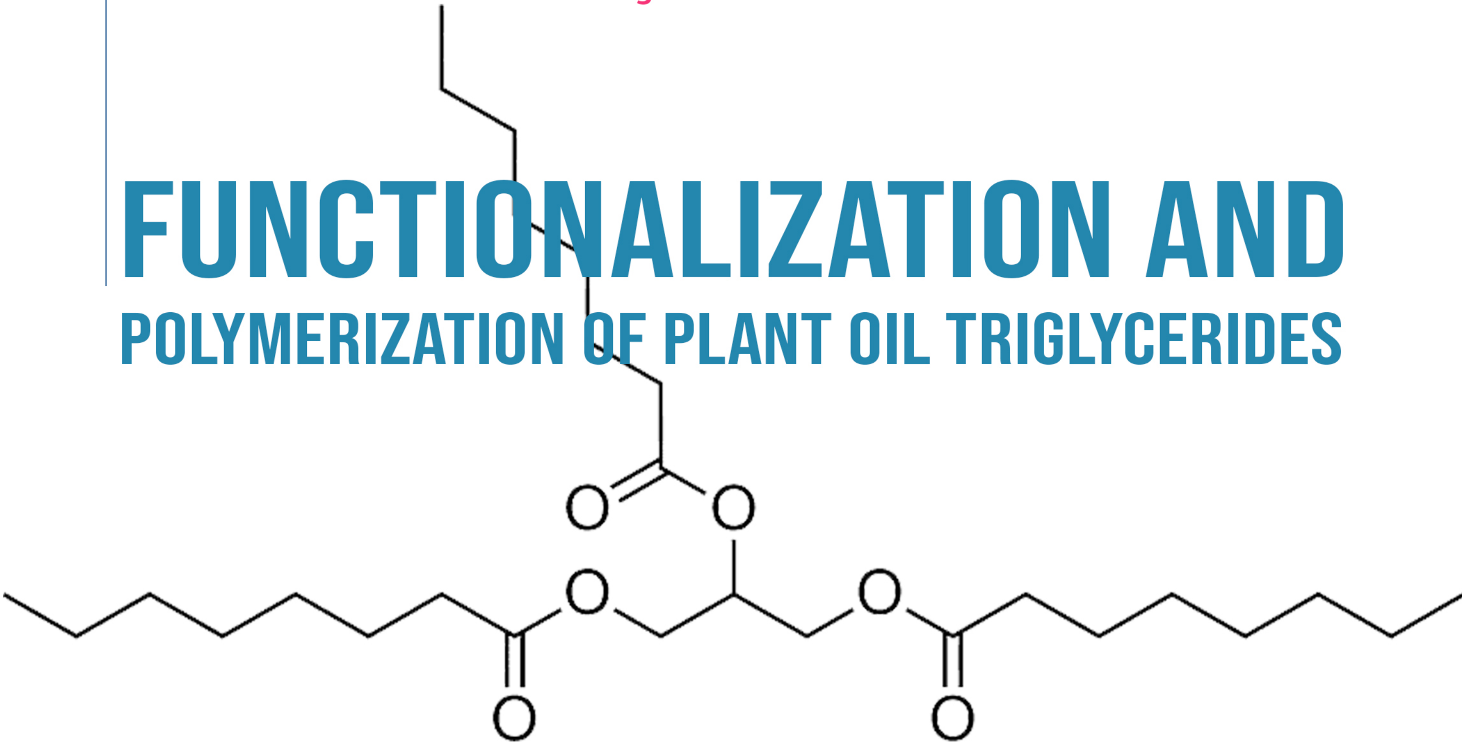
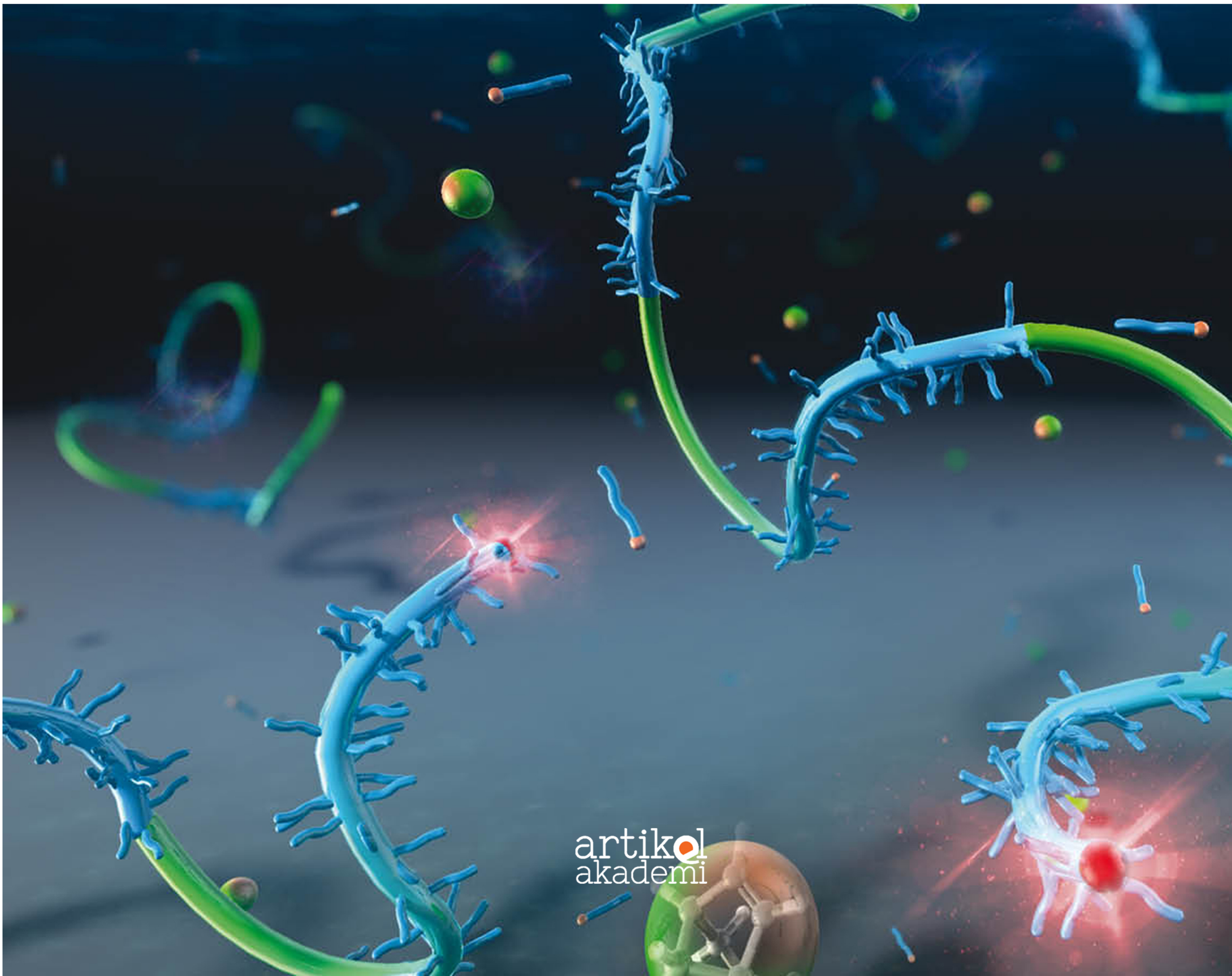
Assoc. Prof. Gökhan ÇAYLI

FUNCTIONALIZATION AND POLYMERIZATION OF PLANT OIL TRIGLYCERIDES





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Gökhan ÇAYLI

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FOREWORD

Mankind has always kept the environment in the second place at the expense of its development and has ignored the negative impacts that face to, but the world resources can no longer support both the increasing human population and the effects resulting from the activities of this population. For this reason, the sustainable development, which considers the needs of the environment and aims to increase the welfare level of people, attracts more and more attention. One of the most important stand point of this model is to use materials that are obtained from renewable resources. One of the most important of those is plant oil triglycerides. In this book, the modification and polymerization of plant oil triglycerides by using allyl positions are explained in detail. I hope this book will clarify many questions in the minds. I wish to thank to all my colleagues who contributed.

Prof. Dr. Gökhan ÇAYLI

March 2022

Dedicated to Beloved One

ACKNOWLEDGEMENT

Too many friends helped and support me while I was writing this book especially two guys Prof. Dr. Selim KÜSEFOĞLU and Dr. Cengiz KAHRAMAN clarify my way with their wisdom and encouragements. I want to thank them separately.

ABSTRACT

FUNCTIONALIZATION AND POLYMERIZATION OF PLANT OIL TRIGLYCERIDES

In this study, new polymers and were synthesized from different plant oil triglycerides by using allylic groups of the triglycerides. Moreover, allylic positions and double bonds of soybean oil were used for preparation of different type of reactive monomers and their polymers.

Soybean, cod liver, and linseed oils were polymerized by oil soluble phenol-formaldehyde resins in one step. Phenols which were used to prepare oil soluble resoles were *p.* ethyl, *p. tertiary* butyl, *p. tertiary* octyl, and *p.* phenyl phenols. Among the triglycerides the best polymerization results were obtained from linseed oil. A series of rubbery polymers were synthesized with linseed oil with 40 per cent phenol formaldehyde resins. For other less unsaturated oils, similar results could be obtained with at least 60 per cent phenolic resin use. Among the oil soluble resoles, the best mechanical and thermal properties were obtained with *p.* ethyl phenol resole. The mechanical properties of *p.* phenyl phenol resole were better than *p. tertiary* butyl and octyl resoles.

In the second part of the study, soybean oil was first converted to allylic brominated soybean oil by NBS (N-bromo succinimide) and then reacted with acrylate and methacrylate salts, $^{-}$OCN, $^{-}$SCN anions and triethyl amine to give allylic acrylate and methacrylate esters of soybean oil, polyisocyanate and polyisothiocyanates of soybean oil and quaternary ammonium salts of soybean oil respectively. Soybean oil was also reacted with iodine isocyanate to give iodo isocyanate addition products of soybean oil. This poly isocyanate was then polymerized with different type of alcohols and amines to give corresponding polyurethanes and polyureas.

Also, similar reactions were performed on methyl oleate as a model compound. Allylic acrylate and methacrylate esters of methyl oleate were obtained by the reaction between allylic brominated methyl oleate and acrylic and methacrylic acid potassium salts. Moreover allylic amine of methyl oleate was prepared by the reaction between allylic brominated methyl oleate and NH_3 and this monomer was polymerized to give AB type unsaturated fatty based polyamides by amide-ester interchange.

In the third, part of this study, acrylated epoxidized soybean oil was polymerized with *p. tertiary* butyl phenol furfural resin via Diels-Alder reaction to give cross linked polymers. When the polymer was heated above 140 ^{o}C, retro Diels-Alder reaction took place with a 60 per cent yields. After cooling of the materials, cross linking was established again. After each heating and cooling cycle the hardness of the polymer increased due to the increasing the cross linking density which was caused from imperfect retro Diels-Alder reaction of furan and acrylate moieties. The chemical, physical and thermal behaviors of the product polymers were characterized.

ÖZET

BİTKİSEL YAĞLARIN FONKSİYONLANDIRILMALARI VE POLİMERİZASYONLARI

Bu çalışmada değişik yağlardan bu yağların alilik gruplarını kullanarak çeşitli polimerler sentezlenmiştir. Ayrıca soya yağının alilik pozisyonları ve çift bağları kullanılarak değişik tipte monomer ve polimerler elde edilmiştir.

Soya yağı, balık karaciğer yağı ve keten tohumu yağı çeşitli türde yağda çözünür fenolik reçinelerle tek basamakta polymerize edildi. Bu çalışmada, *p.* etil, *p. tersiyer* butil, *p. tersiyer* oktil ve *p.* fenil fenolden elde edilen resoller kullanılmıştır. Kullanılan bitkisel yağlar arasında en iyi sonuçları keten tohumu yağından elde edilen polimerler verdi. Yüzde kırktan az miktardaki fenolik reçinelerle değişik özellikte kauçuklar elde edildi. Diğer yağlardan yük taşıyabilen polimerler elde edilebilmesi için en az yüzde altmış oranında fenolik reçineler kullanıldı. Fenolik reçineler arasında ise en iyi sonuçları *p.* etil fenolden elde edile reçineler gösterdi. Para fenil fenolün mekanik ve termal özellikleri etil gibi olmasa da *p. tersiyer* butil ve *p. tersiyer* oktil fenol reçinelerinden daha iyi olmuştur.

Çalışmanın ikinci kısmında ise, soya yağı N-bromo süksinimid kullanılarak alilik brom taşıyan soya yağına dönüştürüldü Daha sonra bu yağ çeşitli nükleofillerle reaksiyona sokularak reaktif monomerler elde edildi. Nükleofil olarak akrilik ve metakrilik asit tuzları, gümüş siyanat, amonyum tiyosiyanat ve trietil amin kullanıldı. Reaksiyonların sonunda, soya yağının alilik akrilat ve metakrilat esterleri, izosiyanat ve izotiyosiyanatları ve kuaterner amonyum tuzları elde edildi. Bunların dışında soya yağı iyot izosiyanatla reaksiyona sokularak soya yağı iyot izosiyanatına çevrildi. Bu monomer daha sonra çeşitli alkol ve aminlerle polimerize edilerek poliuretanlar ve poliüreler sentezlendi.

Benzer reaksiyonlar model bileşik olarak alilik brom taşıyan metal oleatla da gerçekleştirildi. Reaksiyonların sonunda metil oleatın alilik akrilat ve metakrilat esterleri elde edildi. Ayrıca alilik brom taşıyan metil oleat amonyakla da reaksiyona sokularak metil oleatın alil amini sentezlendi. Bu amino ester monomeri daha sonra amid-ester değişimi yardımıyla polimerize edildi.

Çalışmanın üçüncü ve son kısmında ise, akrillenmiş epokside soya yağı *p. tersiyer* butil fenol furfural reçinesi ile polimerize edildi. Elde edile polimer 140 ^{o}C a ısıtılması ve soğutulması sonucunda retro Diels-Alder reaksiyonu ve müteakip Diels-Alder reaksiyonu gerçekleşti. Bu işlemler sonunda polimerin çapraz bağlanma oranının artarak ve polimerin mekanik özelliklerinin kuvvetlendiği gözlendi. Bu polimerin kimyasal, fiziksel ve termal karakterizasyonları da yapıldı.

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LIST OF ABBREVIATIONS

AAMO	Allylic amine of methyl oleate
AASOME	Allylic amines of soy oil methyl esters
ABMO	Allylic brominated methyl oleate
ABSO	Allylic brominated soybean oil
ABSOME	Allylic brominated soy oil methyl esters
ACMO	Allylic acrylate of methyl oleate
ACSO	Allylic acrylate of soybean oil
AESO	Acrylated epoxidized soybean oil
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimeter
E'	Storage modulus
EDA	Ethylene diamine
GLY	Glycerol
HMDA	Hexamethylene diamine
INCO	Iodine isocyanate
IR	Infrared
ISONCO	Soybean oil iodine isocyanate
ITSO	Allylic isothiocyanate of soybean oil
METACSO	Allylic methacrylate of soybean oil
METMO	Allylic methacrylate of methyl oleate
NMR	Nuclear magnetic resonance
PEP	Para ethyl phenol
PPP	Para phenyl phenol
PTB	Para tertiary butyl phenol
PTIOP	Para tertiary octyl phenol
SONCO	Allylic isocyanate of soybean oil
Tan δ	Los factor

TBP-F	Para tertiary butyl phenol furfural resin
TETA	Triethylene tetramine
TGA	Thermo gravimetric analyses

1- INTRODUCTION

1.1. Sustainable Development

Sustainable development is defined as a development that "meets the needs of the present generation without compromising the ability of future generations to meet their own needs." [1-2]. While taking into account the finite sources of our world and endangered ecosystems, sustainable development becomes a key demand today and in the future. The linkage between environment and development was globally recognized in 1980, when the *International Union for the Conservation of Nature* (IUCN) published the *World Conservation Strategy* and used the term "sustainable development." [3-4]. The concept came into general usage following publication of the 1987 report of the Brundtland Commission, formally the World Commission on Environment and Development [4].

The definition of sustainable development is not operational and has created much antagonism and disagreement. Sustainability is often taken to refer to processes that can be maintained indefinitely. This is, of course, not the case for economic growth and development, just as the world's exponential population growth is unsustainable. Development is thus *unsustainable* in this sense [5]. Sustainable development comprises the three components of society, environment, and economy, and its goals can only be achieved if all three components can be satisfied simultaneously [6].

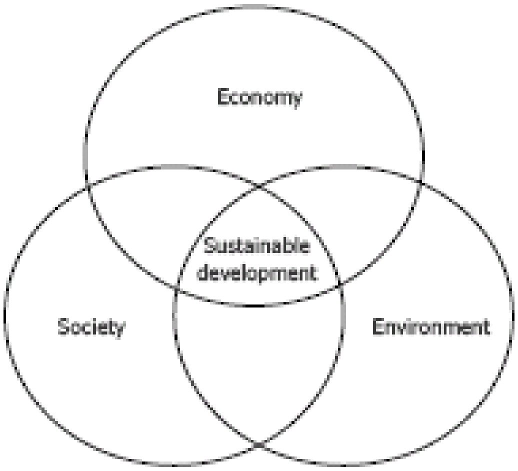


Figure 1. 1. Three components of sustainable development [6].

Agenda 21 published by IUCN clearly identified information, integration, and participation as key building blocks to help countries achieve development. It emphasizes that in sustainable development everyone is a user and provider of information. It stresses the need to change from old sector-centered ways of doing business to new approaches that involve cross-sectoral co-ordination and the integration of environmental and social concerns into all development processes. Furthermore, Agenda 21 emphasizes that broad public participation in decision making is a fundamental prerequisite for achieving sustainable development [7-10].

Until the 19th century, human beings satisfied their needs from environment. At the beginning of industrial revolution, however, the raw materials were not enough for their needs. Coal became a main resource. By the depletion of the coal reserves, petroleum became important at 1950's. Nowadays, petroleum is still the most important natural resource for many industries. Unfortunately, these resources are limited, which means they are non-renewable, and the price of crude mineral oil is also increasing steeply. Moreover, widespread use of petroleum based materials causes environmental problems whose negative impact on the environment will increase day by day. These major concerns explain why chemists must now develop products that can be manufactured in environmentally acceptable ways involving a minimum consumption of energy and petroleum based raw materials, whilst maintaining as favorable an ecological balance as possible [6]. During and at the end of their lifetime these products must be useful to humans without harming them, and must not pollute the environment. From the point of view of the sustainable development, vegetable oils presently offer one of the most important renewable feedstock's for the chemical industry [11]. Therefore, fats and oils can find a large number of possibilities for application. Many chemicals can be synthesized from plant oils. With the reaction of these fine chemicals one can easily synthesize a wide variety of soft, strong on load bearing polymers. The mechanical properties of these polymers can easily adjusted by using different types of plant oil based chemicals together with petroleum based chemicals [12-13].

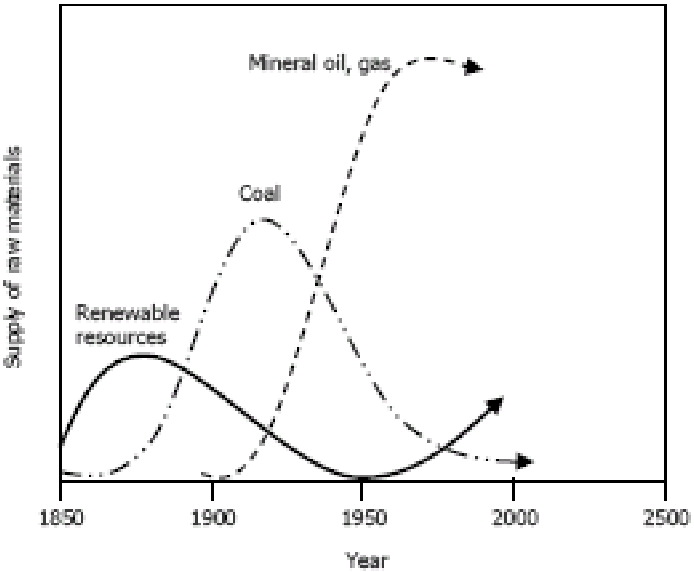


Figure 1. 2. Changing sources of feedstock for the chemical industry [6].

1.2 Properties of Plant Oils

Plant oils are the materials that are water insoluble. Although plant oils contain many different compounds, they are mainly composed of triglycerides. Many different parts of plants may yield oil, but in actual commercial practice oil is extracted primarily from the seeds of oilseed plants.

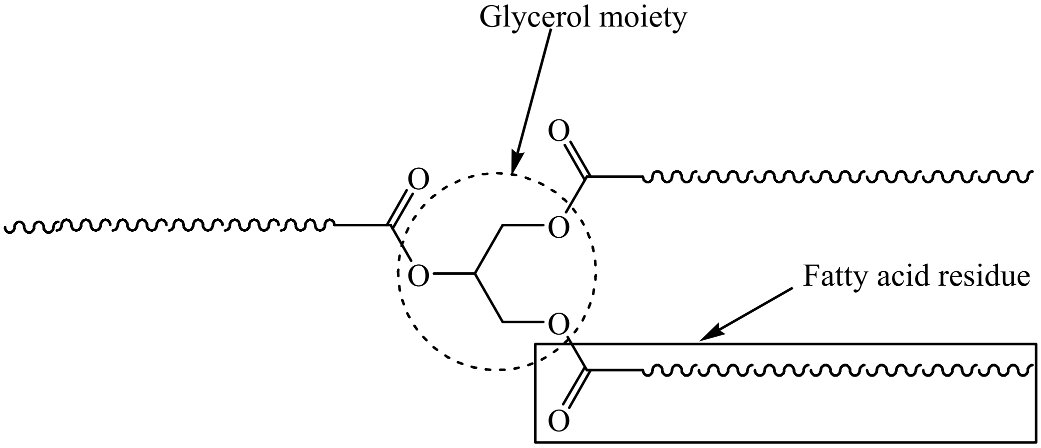
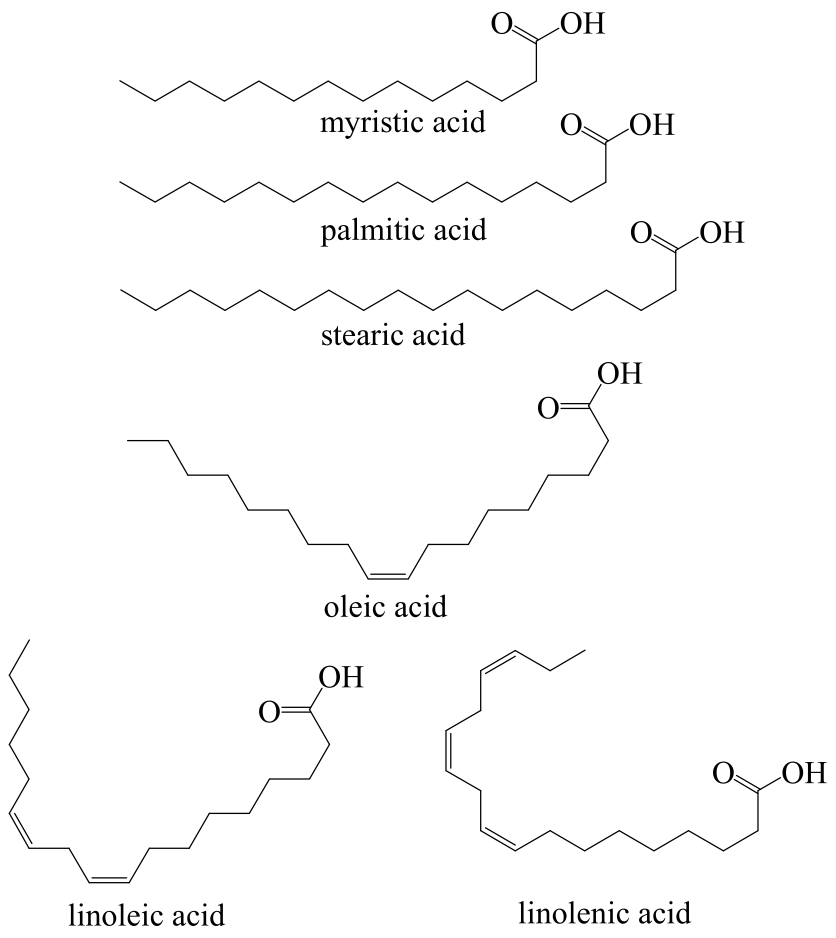


Figure 1. 3. The structure of triglyceride molecule.

Triglycerides are a triesters of glycerol and fatty acids (Figure 1.3.). Fatty acids are aliphatic long chain mono carboxylic acids. In nature, almost all fatty acids are even numbered. Odd numbered fatty acids are rarely found in nature. Even numbered acids are mainly 14-22 carbon chain length [14]. Some of the acids are saturated and some are unsaturated. Saturated ones are called fat are solids at room temperature and usually obtained from animals and the unsaturated ones are liquids and are called oils, and are obtained from plants. Some common fatty acids are presented in Figure 1.4. It should be noted that unsaturated fatty acids exist as cis isomer and that polyunsaturated fatty acids exist as the cis, unconjugated isomer [15-16].



myristic acid

palmitic acid

stearic acid

oleic acid

linoleic acid

linolenic acid

Figure 1. 4. Some common fatty acids in the plant oil triglycerides.

Plant oil triglycerides are mainly consumed as food (Table1.1). Triglyceride vegetable fats and oils can also be used for industrial purposes such as processed linseed oil, tung oil, and castor oil, used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial purposes [17].

Table 1. 1. The usage and the consumption amount of some common plant oil triglycerides [18].

Oil source	World consumption (million tons)	Notes
Soybean	26.0	Accounts for about half of worldwide edible oil production.
Palm	23.3	The most widely produced tropical oil. Also used to make biofuel
Rapeseed	13.1	One of the most widely used cooking oils; Canola is a (trademarked) variety (cultivar) of rapeseed.
Sunflower seed	8.6	A common cooking oil, also used to make biodiesel
Peanut	4.2	Peanut oil Mild-flavored cooking oil
Cottonseed	3.6	A major food oil, also often used in industrial food processing
Palm Kernel	2.7	From the seed of the African palm tree
Olive	2.5	Used in cooking, cosmetics, soaps and as a fuel for traditional oil lamps

Other significant triglyceride oils are Corn oil (one of the most common, and inexpensive cooking oils), Hazelnut oils, Linseed oil, Rice bran oil (from rice grains), Safflower oil (a flavorless and colorless cooking oil), and Sesame oil (used as a cooking oil, and as a massage oil) [19].

1.2.1. Advantages of Plant Oils for Sustainable Development:

Use of the plant oils in chemical industry has two main advantages. Due to their complex nature, plant oil triglycerides can be used as poly reactive monomers (See Figure 1.5.) and they are renewable.

Average annual world plant oil production in the years 1996 to 2000 amounted to 105.0×10^6 t and will increase in the years 2016 to 2020 to 184.7×10^6 t. Eighty to eighty-one percent of the product oils is consumed as human food; 5–6per cent as feed. Approximately 14per cent, 15–17 million tonnes are used by industry [20 -21]. In contrast, the world consumption of fossil mineral oil was approximately 4,000×106 t in the year 2002. The chemical share was about 11per cent in the European Union (EU)[11].

About 80per cent of the triglyceride production is based on vegetable oils and only 20per cent, with declining tendency, is of animal origin. About one quarter of global production came from soybean, followed by palm oil, rapeseed, and sunflower. Coconut and palm kernel oil (laurics) contain a high percentage of saturated C12 and C14 fatty acids and are most important for the production of surfactants [11 and 22].

Among the plant oils soybean oil is the cheapest one. It is vastly produced in USA and price of one barrel soybean oil is nearly 65 $ which is much cheaper than 1 barrel of crude oil that was exceeds 125 $ last month (May 2008) [23]. Properties of plant oils that used in this study is summarized in table 1.2.

Table 1. 2. Typical fatty acid composition of plant oil triglycerides that were used in this study [24]

Name of Oil	Oleic acid (18:1) per cent	Linoleic acid (18:2) per cent	Linolenic acid (18:3) per cent	Stearic acid (18:0) per cent	Palmitic acid (16:0) per cent	Myristic acid (14:0) per cent
Olive oil	78	7	1	2	10	-
Soybean oil	23	53	8	4	11	
Codliver oil	25	-	-	10	4	-
Linseed oil	17	14	60	3	6	-

1.2.2. Properties of Soybean Oil Triglycerides:

To produce soybean oil, the soybeans are cracked, adjusted for moisture content, rolled into flakes and solvent-extracted with hexane. The oil is then refined, blended for different applications, and sometimes hydrogenated. Soybean oils, both liquid and partially hydrogenated, are sold as "vegetable oil," or end up in a wide variety of processed foods. The remaining soybean husks are used mainly as animal feed [25].

The major unsaturated fatty acids in soybean oil triglycerides are 7per cent linolenic acid (C18:3); 51per cent linoleic acid (C-18:2); and 23per cent oleic acid(C-18:1). It also contains the saturated fatty acids 4per centstearic acid and 10per cent palmitic acid [26].

Soybean oil has a relatively high proportion, 7–10per cent, of oxidation prone linolenic acid, which is an undesirable property for food use. In the early nineties, Iowa State University developed soybean oil with 1per cent linolenic acid in the oil. Three companies, Monsanto, DuPont/Bunge, and Asoyia in 2004 introduced low linolenic, (C18:3; cis-9, cis-12, cis-15 octadecatrienoic acid) soybeans through genetic engineering. In the past hydrogenation was used to reduce the unsaturation of linolenic acid, but this produced the unnatural trans-fatty acid trans fat configuration, whereas in nature the configuration is cis [27].

In the 2002–2003 growing season, 30.6 million metric tons of soybean oil were produced worldwide, constituting about half of worldwide edible vegetable oil production, and thirty percent of all fats and oils produced, including animal fats and oils derived from tropical plants [28]. Soybean oil has also been found effective as an insect repellent in some studies [29-30].

1.2.3. Reactive Sites of Plant oil Triglycerides

From the perspective of an organic chemist there are 4 reactive centers may be presented in a plant oil triglycerides. These are allylic positions, α- methylene groups to carbonyl, double bonds, and ester groups (Figure 1.5.)By using these reactive parts on can synthesize different materials. General reactions on the reactive parts of plant oil triglycerides are shown in Figure 1.6. In this study, allylic positions and double bonds of plant oil triglycerides were used to synthesize polymers and reactive monomers [31-32].

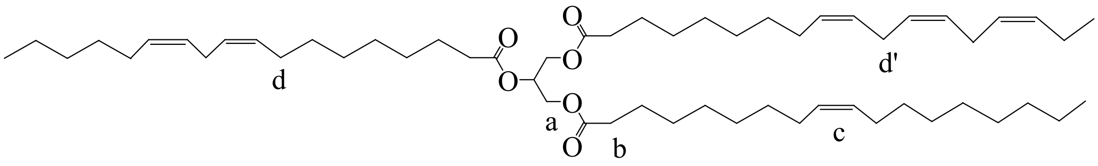


Figure 1. 5. Schematic presentation of reactive groups in a typical plant oil triglycerides a-) ester part b-) α methylene group c-) double bond d-) allylic position d'-) double allylic position.

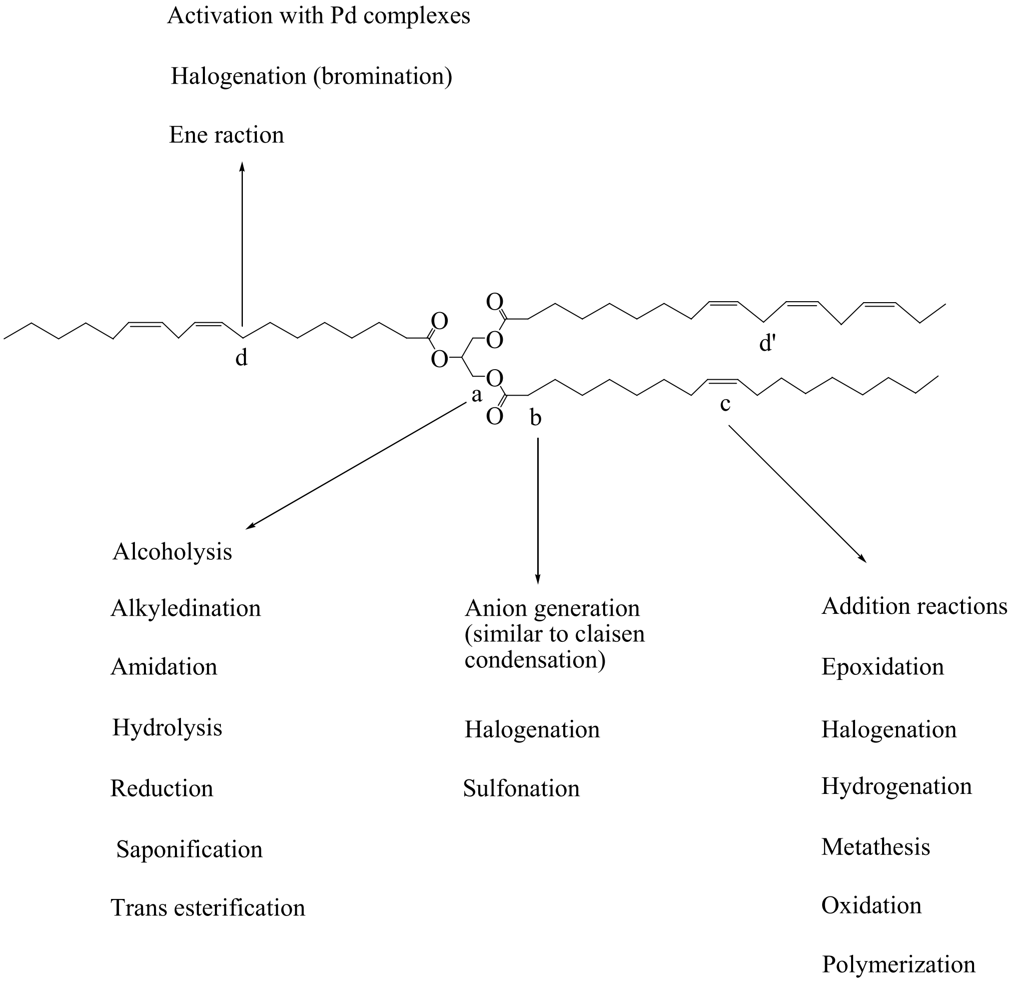


Figure 1. 6. Types of reactions on the reactive parts of plant oil triglycerides.

1.2.3.1. Addition of Iodo Isocyanates: The reaction of iodine isocyanate (INCO) with olefinic compounds has received considerable attention for many years [33] . The pioneering work of Birckenbach and Linhard [34-35] showed that iodine isocyanate adds to olefinic double bonds in a manner typical of pseudo-halogens. Drefahl and Ponsold [36-37] showed that the isocyanate group attaches to the more alkyl or aryl substituted olefinic bonds (Figure 1.7.).

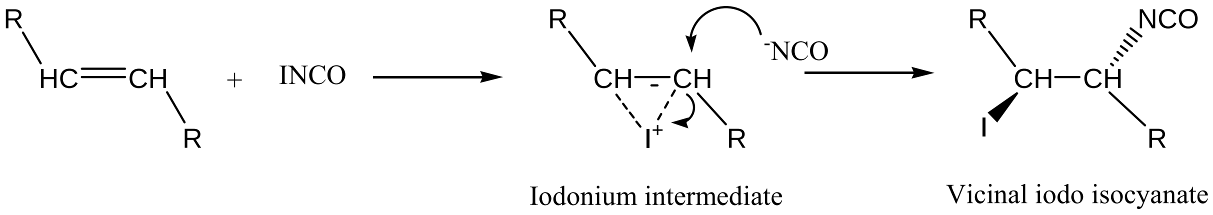


Figure 1. 7. Addition of iodo isocyanate to olefinic double bond

Addition reactions occur in a stereo specific trans manner and it was suggested that an iodonium ion is involved as an intermediate. The diaxially trans positions of iodine and isocyanate groups in the rigid and fused cyclohexane ring was demonstrated by Hassner and Heathcock [38]. The vicinal iodo isocyanates are useful intermediates in the preparation of carbamates, aziridines and ureas, 2-oxazolidines, and β-iodoamines.

Addition of iodo isocyanates to plant oils also gives valuable intermediates. Similar to thiocyanogen addition, just one mole iodo isocyanate can be added to one mol of polyunsaturated fatty acids (Figure 1.8.). This means that one mole unsaturated plant oil triglyceride can bind around three mol iodo isocyanate easily. Many positional isomers are obtained. The product is valuable intermediate to synthesize poly-urethanes and poly ureas. One of the recent literature showed the synthesize aziridine derivatives of the fatty acid methyl esters from iodoisocyanates [39].

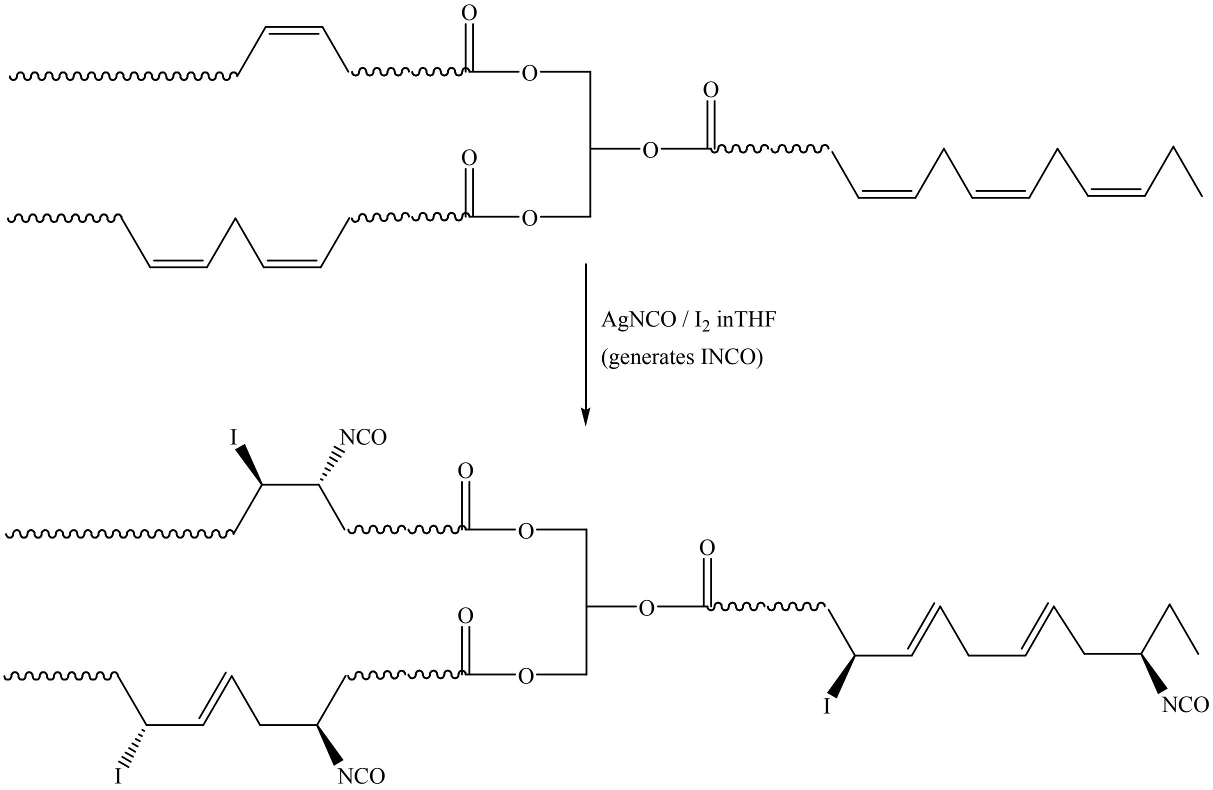


Figure 1. 8. Addition of 3 moles of Iodoisocyanates to plant oil triglycerides.

1.2.3.2. Activation of plant oil triglycerides at allylic positions. Plant oils can be easily modified at allylic positions with different reactions. The one of the most classical example is the production of SOMA (maleinized soybean oil). Soybean oil reacts with maleic anhydride directly by thermal ene reaction to give a fatty based succinic anhydride monomer [40-41]. Due to the similarity of the nature and configuration of the double bons of rubber and plant oil triglycerides, plant oils give ene reactions with vulcanizing agents which give also ene reaction with natural rubbers and at the end of the reactions cross-linked rubbers are obtained. These vulcanizing agents may also polymerize the plant oil triglycerides directly. Depending on the unsaturation degrees of the triglycerides, different type of rubbery materials may be obtained.

One of the other approaches is to activate the allylic positions by using of NBS (N-bromo succinimde) and produce the allylic bromides at the end of the reaction (Wohl-Ziegler reaction) [44-45]. Another approach is to use Pd (II) complexes. Pd(II) salts reacts with double bonds and generate allylic complexes that are susceptible to nucleophilic attacks [46].

The Wohl-Ziegler reaction is a chemical reaction that involves the allylic or benzylic bromination of hydrocarbons using an *N*-bromoimide and a radical initiator. Best yields are achieved with *N*-bromosuccinimide in carbon tetrachloride solvent. Several reviews have been published about the reaction and the mechanism [47]. However, environmental concerns have all but eliminated the use of CCl_4, and its replacement, CH_2Cl_2, is being restricted as well. Many other solvents are reactive toward NBS, and are thus unsuitable, but acetonitrile can be used to good effect [47].

A radical initiator (UV, AIBN) is needed for the homolytic bond cleavage of Br_2. The allylic position is favored for hydrogen abstraction, because the resulting radical intermediate is resonance stabilized (Figure 1.9.). For complex alkenes, bromination is favored to occur at the more highly substituted position, because the corresponding intermediate radicals are better stabilized [47-48].

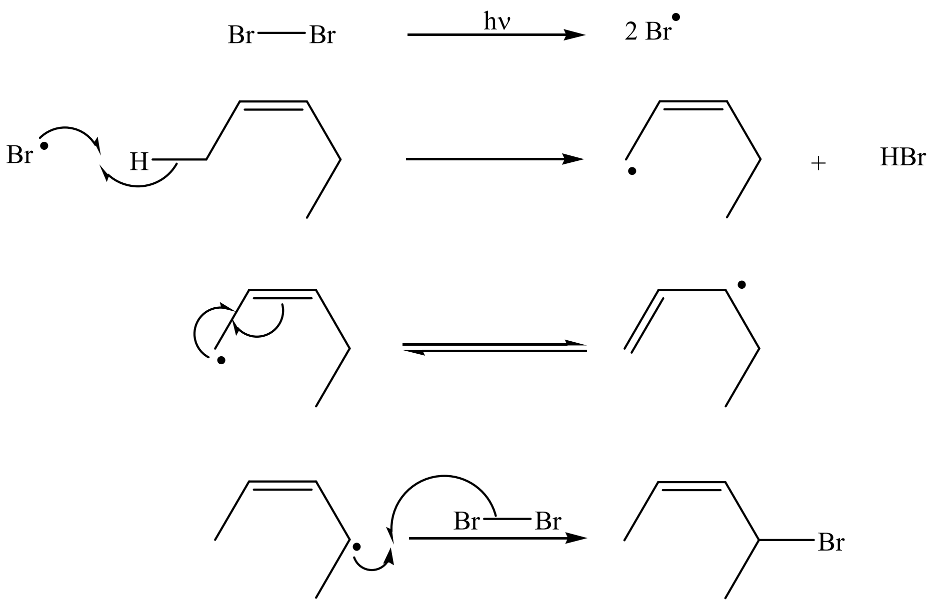
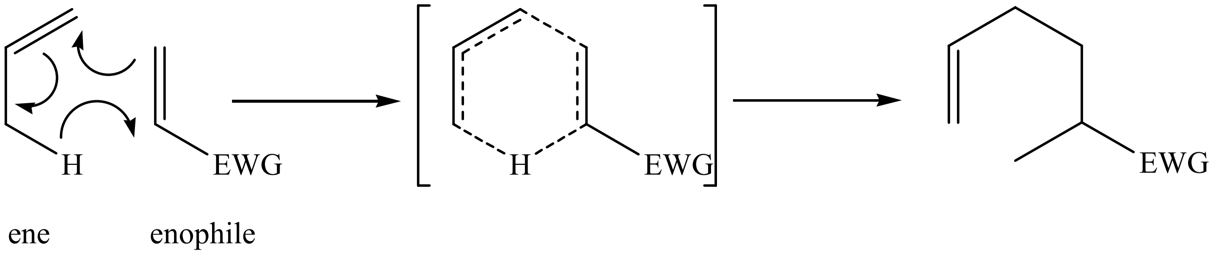


Figure 1. 9. The mechanism of Wohl-Ziegler reaction

It is very important to keep the concentration of Br_2 and HBr low to prevent side reactions derived from simple ionic addition with the alkene. These reagents are therefore generated in situ from NBS. The catalytically active species is Br_2, which is almost always present in NBS samples (red color) [48].

<u>1.2.3.3. Ene reaction.</u> Ene reaction which is also known as Alder-Ene reaction is 6 electrons electro cyclic reaction. The four-electron system including an alkene π-bond and an allylic C-H σ-bond can participate in a pericyclic reaction in which the double bond shifts and new C-H and C-C σ-bonds are formed to the terminal carbon of the allylicgroup. At the reaction 1,5-migration of the allylic hydrogen and change in the position of the allylic double bond occurs [49] (Figure 1.10.). Allylic system reacts similarly to a diene in a Diels-Alder Reaction, while in this case the other partner is called an enophile, analogous to the dienophile in the Diels-Alder reaction. Ene Reaction requires higher temperatures because of the higher activation energy and stereo electronic requirement of breaking the allylic C-H σ-bond.



EWG= electron withdrawing group

Figure 1. 10. Reaction mechanism of ene reaction

Ene compounds are an alkene and the enophile can also be an aldehyde, ketone or imine. For most known ene reactions, the ene is electron-rich, and the enophile is electron-deficient. These compounds may be unstable under the reaction conditions, so that at elevated temperature the reverse reaction takes place - the Retro-Ene Reaction.

The reaction is promoted by heat or Lewis acids such as, $AlCl_3$, $SnCl_4$, and $TiCl_4$. Ene reaction requires highly activated substrates or high temperatures. Reaction products are also often found as unintended byproducts of other chemical reactions.

The concerted mechanism is allowed by the Woodward-Hoffmann rules. The transition state involves the π electrons of the alkene and enophile and the σ electrons of the C-H bond [49-48].

Maleinization of plant oil triglycerides can be considered as a typical example of ene reaction. Another interesting reaction is the vulcanization reaction of the natural rubbers with phenolic resins [50]. At elevated temperatures, resoles which contain reactive methylol groups loose water and produce quinone methide intermediates (Figure 1.11.) which are very reactive species [51-53]. These intermediates react with allylic positions of rubbers and vulcanize the rubbers [54] (Figure 1.12.). The driving force for the reaction is the re-aromatization of the phenol ring during the reaction. Due to the structure and properties of the double bonds of natural rubber and plant oil triglycerides, this research plans to show that plant oil triglycerides can also give the same reactions with oil soluble resoles.

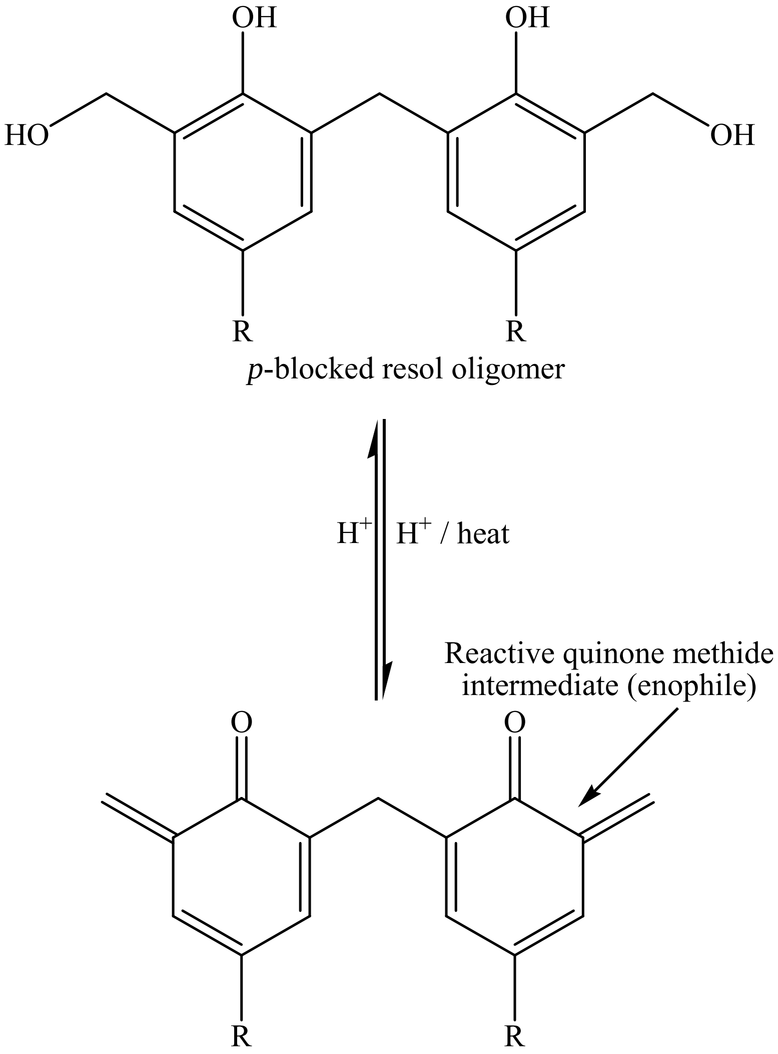


Figure 1. 11. Formation of quinone methide intermediate

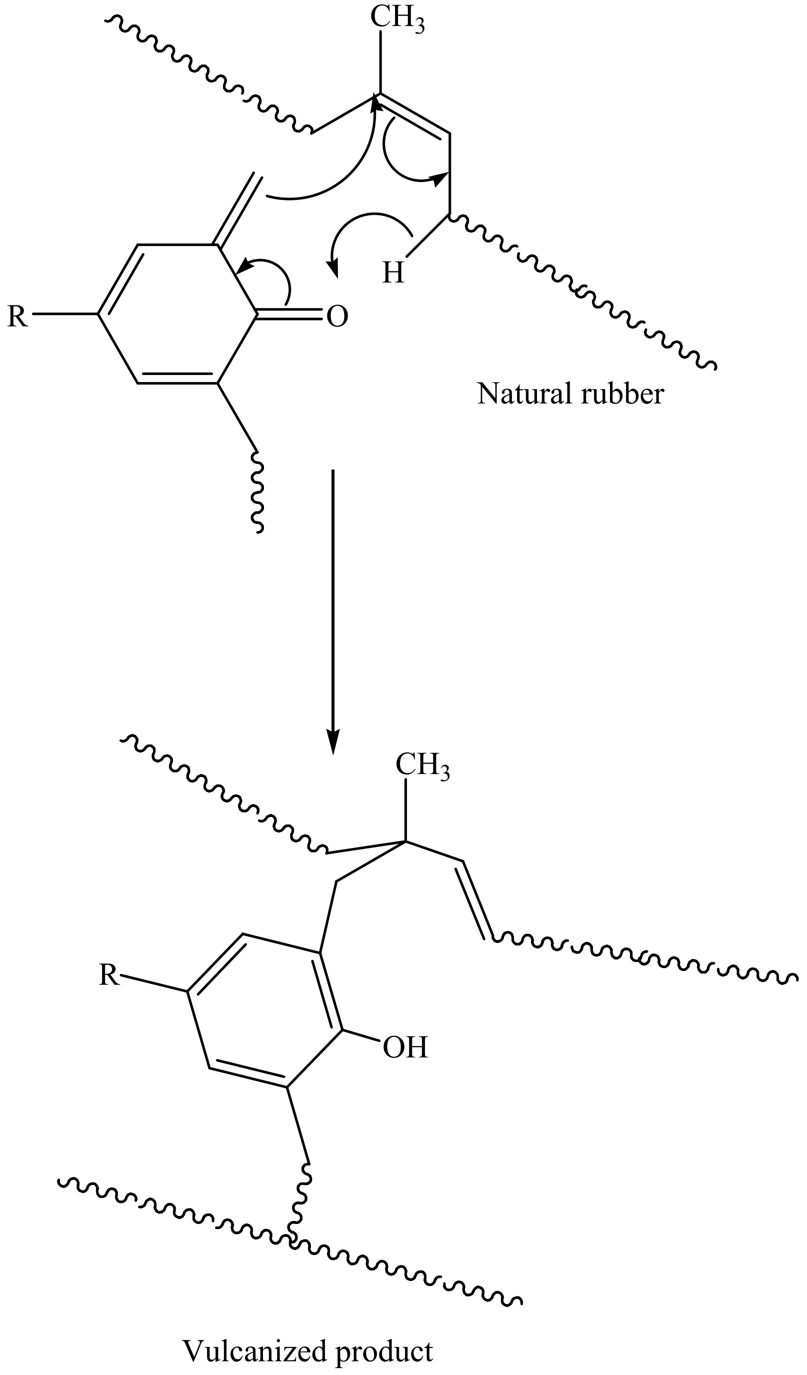


Figure 1. 12. Reaction of quinone methide with natural rubber

Although ene reaction is a 6 electrons pericyclic reaction, above mechanism that is published in books and articles [54-55] is a 8 electron cyclization reaction and such thermally unallowed. This is probably why quite high temperatures are required for the reaction.

1.2.3.4. Reactions of vulcanizing agents with plant oil triglycerides. Because of the resemblance of the structure and electronic properties of natural rubber and plant oil double bonds, the reactivities of the compounds may also be similar. Thus, any chemical reaction or polymerization reaction which is suitable for rubbers should be suitable for plant oil triglycerides.

The reaction between natural rubber and most vulcanizing agent goes by the ene reaction mechanism. Many type of vulcanizing agents were used for rubber vulcanization. These can be classified into 5 groups.

1-) Sulphur containing vulcanizing agents [56]
2-) Oxygen containing vulcanizing agents [57]
3-) Phenolic type vulcanizing agents [55]
4-) Maleimide containing vulcanizing agents [58-59]
5-) Nitroso containing vulcanizing agents [60-61]

Some of the above compounds add to double bonds directly hence different chains are linked. And even the cross-linking amount approximately around 5 per cent, the resulting polymers are the rubbers that show excellent mechanical properties.

The reactions between plant oil triglycerides and some vulcanizing agents were also studied well. For example, reaction of product of sulphur and plant oils is known as “factice” and is used as additives for rubbers. Linoleum is also another reaction product with plant oils and oxygen which acts as vulcanizing agent. Some literature works also published about the rubbers of maleimides and plant oils. Because of the lack of solubility of maleimides in plant oils, this reaction did not find any attention. Thus the chemical literature contains examples of sulfur, peroxide and maleimide polymerization of plant oils while there are no examples of phenolic or nitroso polymerizations.

Among the other two vulcanizing agents, phenolic resins are of great interest due to the low cost of starting materials and excellent mechanical properties. But in the literature, reaction between the plant oils and phenolic resins (resoles) are not found [62-74]. Some information appears in patents but the actual reaction pathways are not disclosed.

1.2.3.5. Diels-Alder Reaction. The Diels- Alder reaction is simply defined as the addition of an alkene to a diene to form a cyclohexane ring. It is called [4+2]-cycloaddition reaction because four π electrons from diene and two π electrons from dienophile form two new σ bond and a new π bond.

Generally, the reaction occur easily just by mixing the components at room temperature or by gentle warming. For many cases, Lewis acids, and some rare cases, high pressures have been used to accelerate the reactions [46].

Some interesting Diels-Alder reactions in which plant oils are used can found in the literature [61]. One of the most important Diels-Alder reaction applications in plant oils is production of dimer acids. The unsaturated fatty acid mixture which is mainly obtained from linseed and soybean oil is heated for several hours at around 300 ^{o}C under inert atmosphere (Figure 1.13). The resulting mixture is then heated under reduced pressure to remove more volatile components. The residue is mainly composed of dimerized acids (60-75 per cent). Other compounds are trimerized fatty acids and higher polymers. This is a commercial process

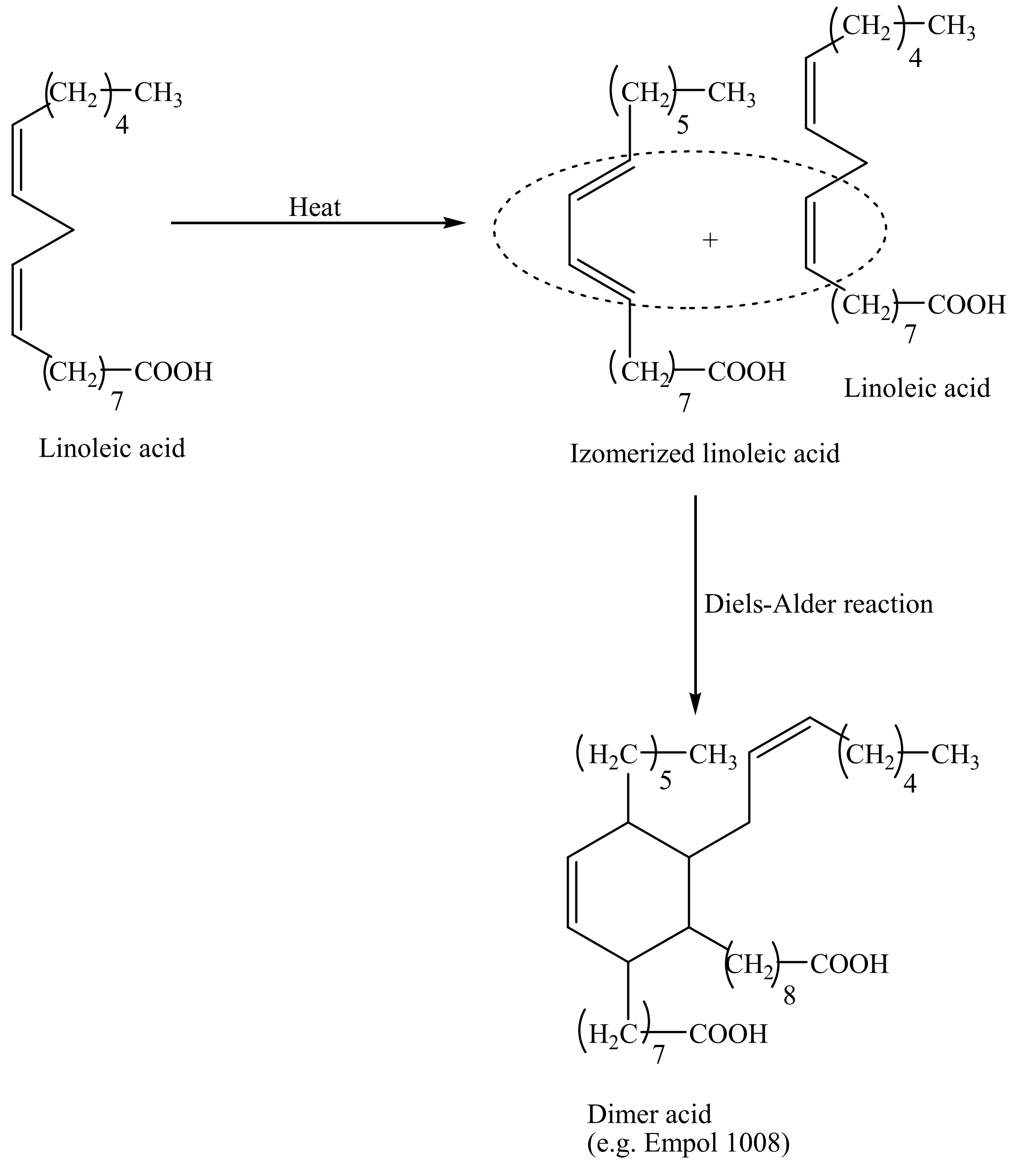


Figure 1. 13. Synthesis of dimer acids from linoleic acid [75].

<u>1.2.3.6. Reactions of Alpha Protons.</u> Although α methylene group is activated by the ester groups, they are not as reactive as double bonds. Like allylic positions, they have to be activated before to give a reaction. Activation may be accomplished by 3 ways.

1-) Halogenation of α carbon atom [76]
2-) Sulfonation of α carbon atom [77]
3-) Generating an anion at α carbon [78]

1.2.3.6. Reactions of Ester groups. Esters are defined as compounds which are condensation products of an acid and alcohol. Due to its nature, esters are polar compounds and they are capable of participating H-bonds as H acceptor. Esters are versatile compounds and can give such interesting reactions. Reaction of unsaturated plant oils with some reactive organic acids such as, maleic and phthalic gives valuable alkyd resins. These resins find waste application areas from polymer industry to coating industry [79-80].

Another interesting reaction of triglycerides is transesterification. Especially transesterification with methanol gives methyl ester which has low viscosity and is used as diesel fuel [81]. Some of the reactions and products are summarized in Figure 1.6.

1.3. Phenolic Resins

1.3.1. Resol Resins:

Resol resins are produced by the reaction of a phenol with an excess amount of formaldehyde (generally accepted amount 1:1.5-2 P/F) under alkaline conditions. This procedure corresponds to Baekeland's original technique.

The reaction of phenol and formaldehyde in alkaline solution results in the formation of o and p methylol groups (Figure 1.14.). The resulting methylol phenols are more reactive towards formaldehyde than the original phenol and rapidly undergo further substitution with the formation of di- and tri methylol derivatives [82].

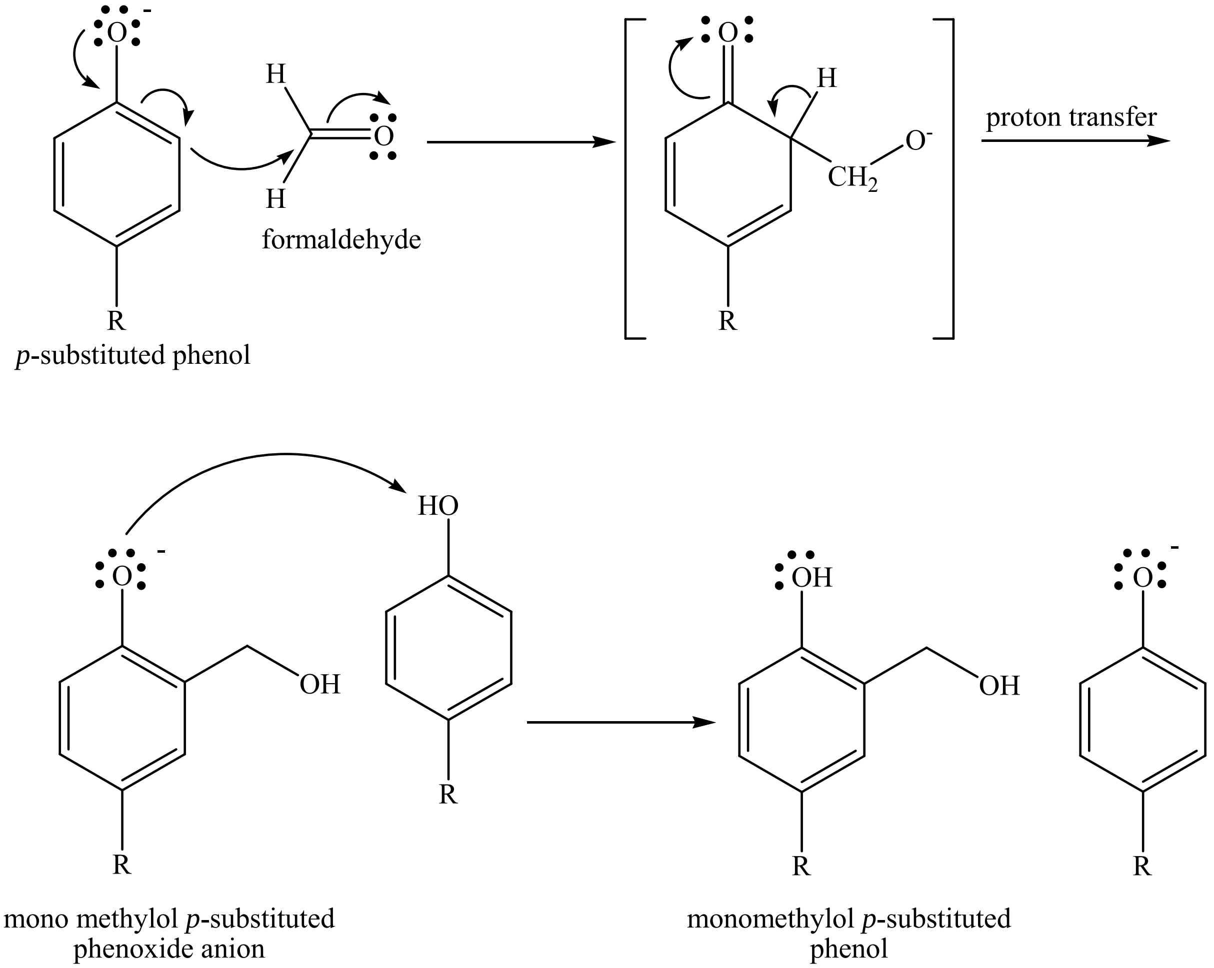


Figure 1. 14. Formation of methylol phenols

Resoles have a molecular weight between 300 and 700. Substitution occurs at ortho and p. positions. With the p. substituted phenols only ortho derivatives are obtained. Moreover no substitution occurs at the m- position (Figure 1.15.).

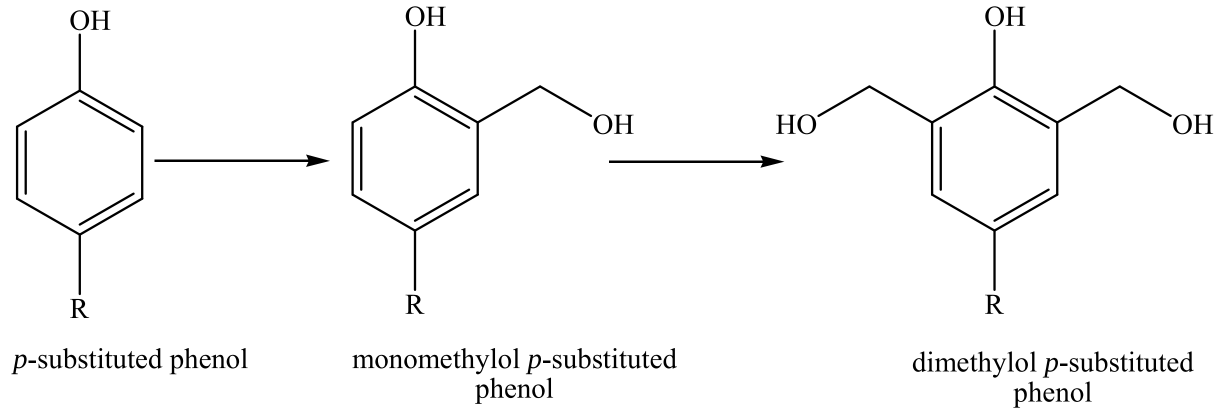


Figure 1. 15. Possible phenolic species at lower temperatures.

1.3.2. Novolac Resins:

Although the versatility of resole resins, they are not stable in neutral and acidic medium. Hence the shelf-life of the resoles is limited (Figure 1.16.). To obtain a stable resin, one should adjust the ratio of phenol and formaldehyde in acidic medium (Figure 1.17.). If the phenol/formaldehyde ratio is greater than unity which generally accepted around 1.25/1, the product resin is called as *Novolac* [75 and 82].

Condensation in acidic medium gives soluble, fusible phenolic resins whose average molecular weight is between 600 and 1,500 and a structure consisting essentially of phenol residues linked by methylene groups in the *ortho* and *p.* positions [75].

Molecular weight (Mw) of the usual novolacs is around 1000. Novolacs can only react further with p.formaldehyde and hexamethylenetetraamine to give considerably cross-linked products that are called cured or thermo hardened.

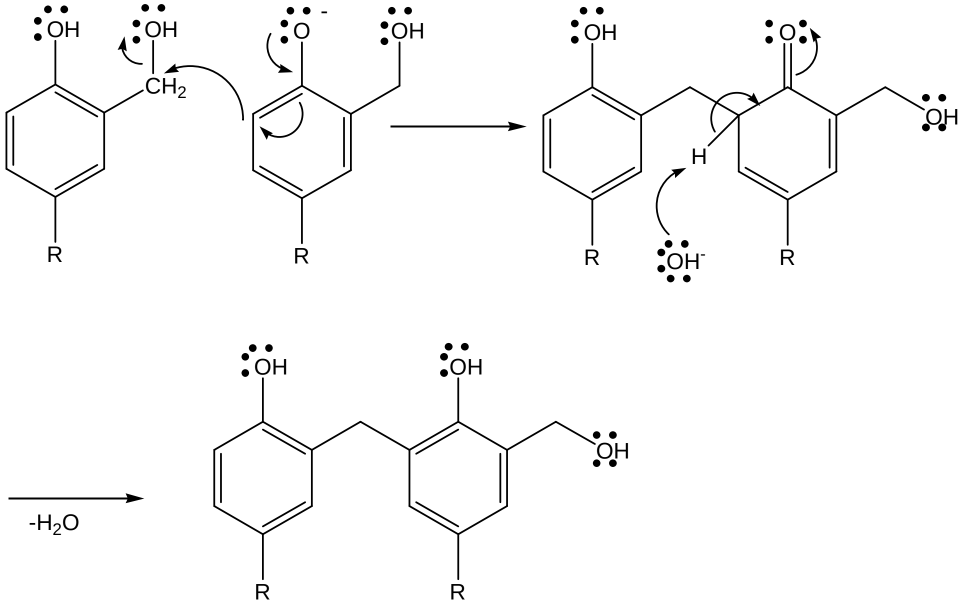


Figure 1. 16. Self condensation reaction of monomethylol phenol resoles.

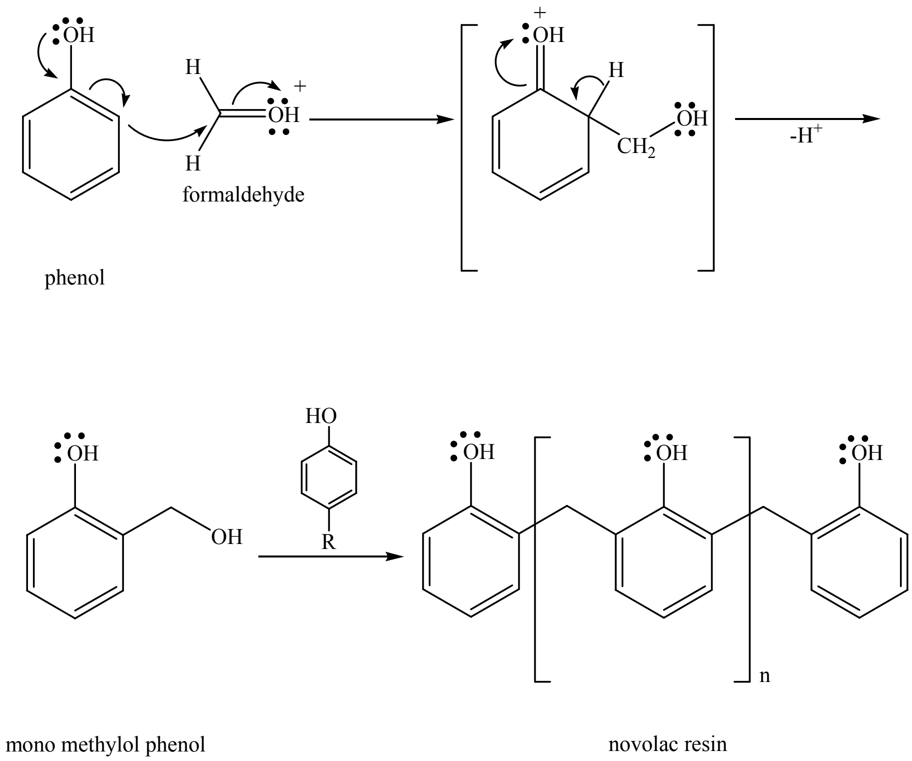
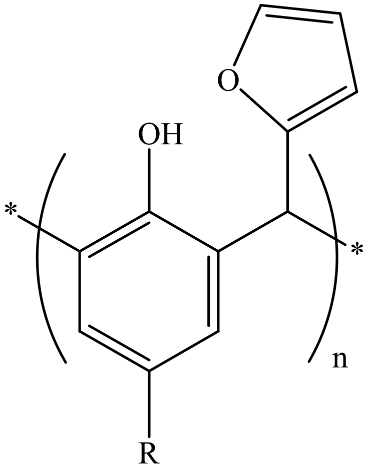


Figure 1. 17. Synthesis of novolacs resins.

1.3.3. Phenol Furfural resins:

Instead of formaldehyde, phenols are also condensed with furfural. Due to the resonance electron density in the furan ring increases at the 2 and 5 positions. This makes the furan ring of furfural unstable in acids. Thus condensation reaction of phenol and furfural can not be carried out by acid catalysts [83].

While using basic catalysts, the ratio of furfural to phenol is generally smaller than 1 thus obtained resin is actually novolac type resin. Although they are made with less than one mol of furfural per mol of phenol, thee resins are not as stable and fusible as novolacs (Figure 1.18.).



repeating unit of phenol furfural resin

n=5

Figure 1. 18. Schematic representation of phenol furfural resin

Phenol-furfural resins are stable under neutral and alkaline medium but not stable in the acidic medium. They readily undergo a thermoset reaction to give a black resin. In this reaction furfurly group takes part in the curing reaction to give in addition furan-type polymers.

In our interest in phenol-furfural resins is based on the fact that furan rings on the polymer chain can give Diels-Alder reaction with different type of dienophiles (1.19.). We are especially interested in acrylated epoxidized soybean oil (AESO) previously synthesized in our group as the dienophile. We are also interested in the possibility of retro Diels-Alder reaction of such polymers.

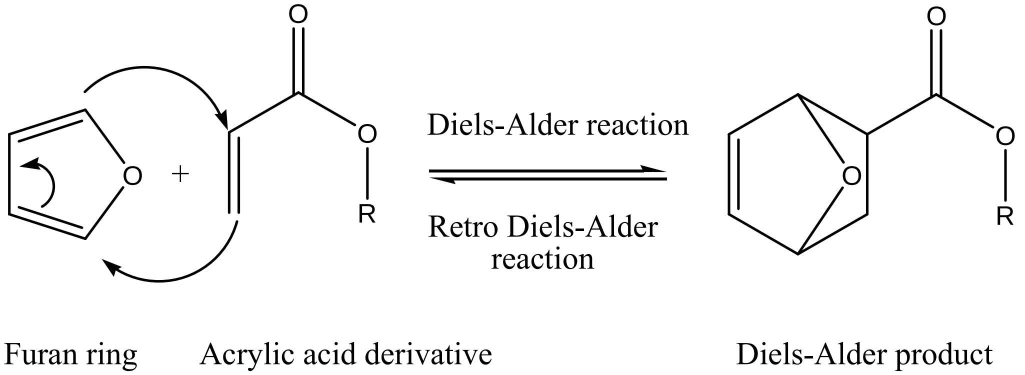


Figure 1. 19. Diels-Alder reaction of furan ring with acrylic acid derivatives.

1.4. Polyurethanes and polyureas and their thio analogs

Polyurethanes are polymer in which the repeating units are coupled with one another through urethane linkages. They are prepared almost exclusively by stepwise addition of di- or polyfunctional hydroxyl compounds to di or polyfunctional isocyanates.

Important isocyanates, used in polyurethane manufacture, are 2, 4-toluene diisocyanate (2,4TDI), 2,6-toluene diisocyanate (2,6TDI), 4, 4'-diphenyl methane diisocyanate (MDI), 1,6 hexamethyl diisocyanate (HMDI), xylene diisocyanate (XDI), and isophorone diisocyanate (IPDI), all of which are petroleum derived [84].

Isocyanates can be synthesized in many ways. The Curtius, Hoffman and Lossen rearrangements, which may involve the nitrene as an intermediate, are not successful for large scale operation. The use of azides is hazardous and the utility of the Hoffman and Lossen rearrangements is limited to preparation of aliphatic isocyanates. Tertiary butyl hypochloride can be used for non aqueous Hoffman rearrangements, but this reagent is expensive. Phosgenation of primary amines and dehydrohalogenation of the resulting carbamoyl chloride are important commercially, in spite of the known toxicity of phosgene [84]

Several kinds of polyurethanes are of commercial significance and are conveniently classified into the following major types-flexible foams; rigid foams; elastomers; fibers and molding compositions; surface coatings; and adhesives.

There have been many attempts to produce polyurethanes from natural sources. Usually plant oil triglycerides are converted to polyols and a commercial petroleum based di isocyanate is used to synthesize the polyurethane. A good example is Drzal's work [85-86]. Drzal and co workers prepared different type of polyols derived from epoxidized soybean oil (ESO) then they polymerize the polyols with different type of petroleum based isocyanates to synthesize rigid and flexible polyurethanes [85]. There are no examples in the literature where the isocyanate is plant oil based.

The thio analogs of polyurethanes and ureas are polythiourethanes and polythioureas. Polythiourethanes can be synthesized from the reaction between isothiocyanates and alcohols. Reaction between di or poly isothiocyanates and di or poly amines give polytioureas Sulfur-containing polythiourethanes have attracted much attention in polymer industry because of their high thermal stability and refractive index (n_d) values. Polymers with high refractive index may be suitable for production of lenses new mercaptan-terminated polythiourethanes were applied as curing agents for epoxy resin. Evaluation of the physico-mechanical and chemical resistance performance shows better results with the increased loading of polythiourethane hardener. Polythiourethane hardeners revealed high reactivity toward curing of epoxy resins at low-temperature conditions (-10 ^{o}C). Polythiourethane-cured epoxy resins stand as an effective surface coating material where high performance is needed in terms of physico-mechanical properties as well as chemical resistance. Moreover polythiourethanes may found a useful material for coating, adhesive, sealing compounds, photo resist and hard coating for ink-jets [87].

Polythioureas as not widely used as polythiourethanes. Polythioureas may be applied to the surfaces in polymn. reactors to inhibit fouling during polymn., esp. in PVC manufacturing Some polytioureas exhibit polarization under electrical fields. Additionally polythioureas may ad to cement to improve workability and bondability [88]

Literature showed that isothiocyanates are mainly synthesized directly by condensation or decomposition reactions. Classically the most widely used method for the preparation of isothiocyanates is the condensation of amines with carbon disulphide in the presence of a base. The second widespread method is the condensation of amines with thiophosgene. Decomposition of mono substituted thioureas also gives corresponding thioisocyanates. Most of these reactions involve toxic reagents.

Another approach to synthesize isothiocyanates is reaction of alkyl halides with thiocyanate anion. Unfortunately, reaction between alkyl halides with thiocyanate anion gives the alkyl thiocyanates as the major product instead of alkyl isothiocyanates (Figure 1.20.).

$$\underset{\text{an akyl halide}}{\mathrm{R{-}X}} + \underset{\substack{\text{thiocyanate}\\ \text{anion}}}{\mathrm{SCN^-}} \xrightarrow[\mathrm{-X^-}]{} \underset{\substack{\text{alkyl thiocyanate}\\ \text{(major product)}}}{\mathrm{R{-}SCN}} + \underset{\substack{\text{akyl isothiocyanate}\\ \text{(minor product)}}}{\mathrm{R{-}NCS}}$$

Figure 1. 20. Reaction of alkyl halides with thiocyanate anion

SCN^- ion attacks with S end instead of N end. However if the substituted halide is an allylic halide, an allylic conversion occurs at refluxing temperature and allylic isothiocyanates are obtained with a shifting of double bonds (See Figure 1.21.) [89]. combined with our knowledge of allylic brominated triglycerides this pattern is a promising entry to plant oil based isothiocyanates.

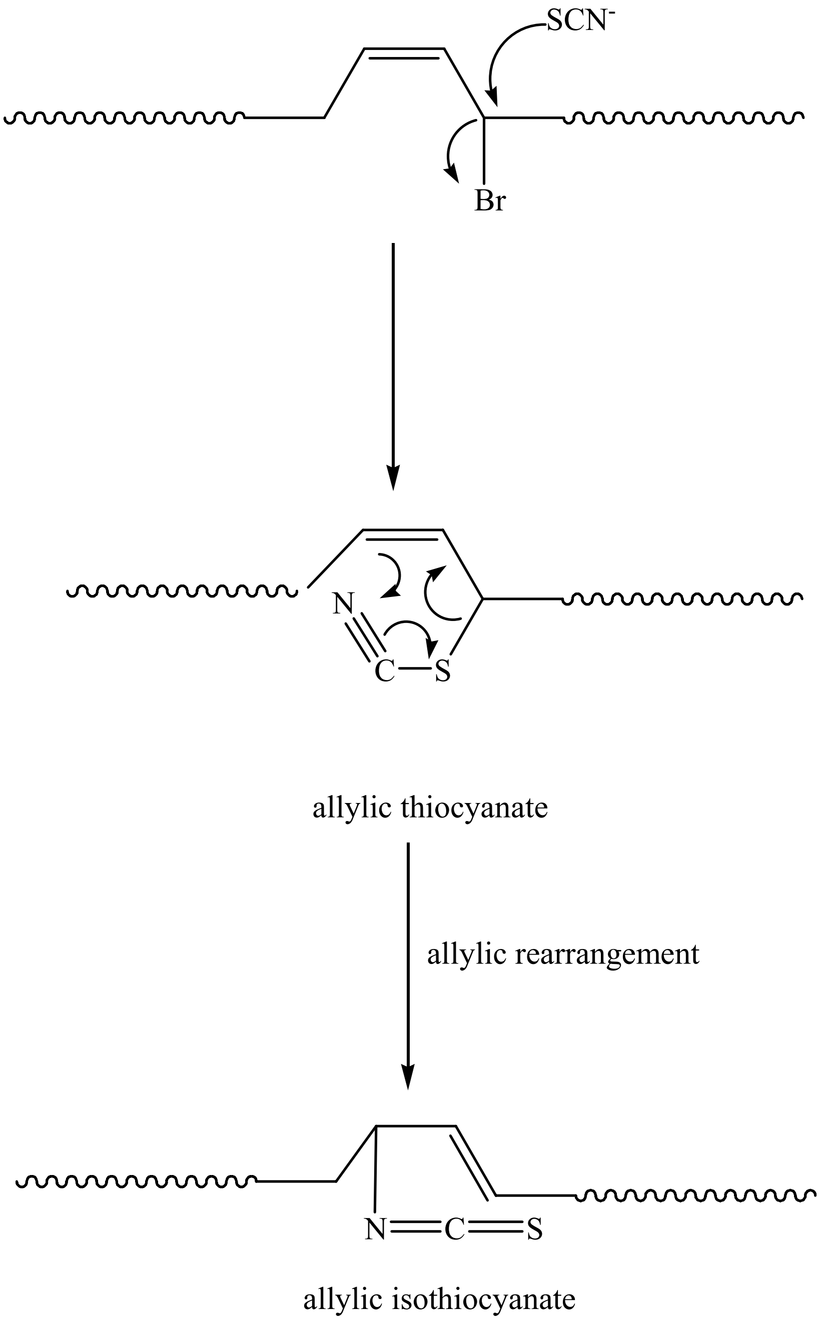


Figure 1. 21. Synthesis of allylic isothiocyanates

Polythioureas are synthesized by the condensation reactions between di or polyisothiocyanates and polyamines. Literature search showed that instead of simple synthesis, the main synthetic route of synthesizing polythiourethanes is the polymerization of diisocyanates with bifunctional dithiol that are derived from the reaction of five-membered dithiocarbonate. This synthetic route can be used to synthesize plant oil based isothiocyanates and polythiourethanes.

Literature also showed that there were no examples of plant oil triglyceride based poly thioisocyanates and related polymers.

1.6. Unsaturated Polyamides

Polyamides are polymers whose repeating units are joined by amide groups. The most important commercial polymers of this type are synthetic linear aliphatic polyamides which are capable of fiber formation. These polymers are generally called as nylons. Such as, Nylon-6 [75 and 82].

Almost all types of polyamides have generally similar physical properties, being characterized by high impact strength, toughness, flexibility, and abrasion resistance. These properties of polyamides are attributable to the formation of hydrogen bonds between the NH and C=O groups of neighboring polymer chains. Due to this special ability, polyamides are not soluble in many organic solvents. They are soluble in H_2SO_4, HCOOH, CH_3COOH, and *meta*-cresol. The melting points of polyamides are higher than the corresponding polyester analogs [75]. The amide groups cause to intermolecular hydrogen bonding which facilitate the crystallization easily.

Polyamides can be synthesized according to these methods:

- polycondensation of amino carboxylic acids. (that lead to AB type polyamides)

- polycondensation of diamines with dicarboxylic acids (that leads to AA-BB type polyamides)

- polycondensation of diamines with derivatives of dicarboxylic acids (acid chlorides or esters). (that leads to AA-BB type polyamides)

- ring-opening polymerization of lactams (i.e.Є-caprolactam). (that leads to AB type polyamides) [90].

Almost all of the above reactions are equilibrium reactions and need to be shifted to the products side, can be accelerated by catalysts. The melt polycondensation technique is not suitable due to the formation of cross linked product by the opening of C=C double bonds present in the polymer backbone. On the other hand, low temperature polycondensation technique may be safely adopted for the synthesis of unsaturated copolyamides and allied polymers. Recently, we reported the synthesis of copolyesters saturated and unsaturated polyamides and polyamideimides from saturated or unsaturated dicarboxylic acids or their sodium salts or the corresponding diacid chloride derivatives and saturated and unsaturated diamines by low temperature polycondensation method [90-91].

Fatty based polyamides are obtained generally by the reaction of di or polyfunctional amines with polybasic acids that are prepared from unsaturated vegetable fatty acids. Dimer acids which obtained from dimerization of poly unsaturated fatty acids can also be used for the preparation of the fatty based unsaturated polyamides. Bio-based polyamides (excluding polypeptides and proteins) are not yet well developed. The unique example of industrially produced 100per cent bio-based polyamide is the AB-type polyamide-11. The monomer, 11-aminoundecanoic acid, is obtained from castor oil after a multistep chemical treatment [92]. Hundred percent bio-based AABB type polyamides are not expected because of the nonavailability of bio-based diamines. Meanwhile, research on new routes or on improvement of the existing ones to obtain di acids from glucose (adipic acid) or vegetable oils (azaleic acid, sebacic acid) for the production of 50per cent bio based polyamides-6,6, -6,9, and -6,10 are under investigation.[92].

The aliphatic unsaturated polyamides are semi-crystalline polymers of high molar mass, relatively flexible at room temperature. The cycloaliphatic unsaturated polyamides are semi-crystalline or amorphous, present higher melting and glass transition temperatures and are much more rigid. The aliphatic and aliphatic–aromatic unsaturated polyamides present lower Tg and Tm as compared to their parent saturated polymers. Some of the unsaturated polyamides seem to have practical merit of such diverse uses-as membrane for reverse osmosis, insulators and an important substitute for unsaturated polymer resins [92].

1.7. Allyl-acrylates

Allylicacrylates are interesting compounds that include two type of C=C double bond. Due to the reactivity difference of acrylic groups and allylicgroups, the homopolymerization of allylic monomers such as allylicacrylates or allylicethers is very unlikely, often problematic. They polymerize at rather low rates [93]. This effect is a result of degradative chain transfer, in which the propagating radical is very reactive. If it is present in the medium the allylic C-H bond in the monomer is quite weak, and chain transfer to the monomer results. The weakness of the allylic C-H bond arises from the high resonance stability of the allylic radical that is formed. This allylic radical is too stable to reinitiate polymerization and undergoes termination by a reaction with another allylic radical or, more likely, with propagating radicals [94].

In the recent years, the synthesis of polymers with a photo- and/or thermo-reactive functional groups has been an active field of research in polymer science. Crosslinking with ultraviolet light has a considerable advantage over thermal curing systems in the conservation of natural resources and energy, environmental preservation, space saving, and productivity. Photosensitive polymers find applications in such fields as integrated circuit and printing technologies, photocurable coatings, photorecorders, photolithography, advanced microelectronics, holographic head-up display, energy exchange materials, liquid crystalline display, and nonlinear optical materials [78]. Acrylic and methacrylic acid allylicesters are one of the most candidate monomers for those applications [78]. Due to the reactivity difference, interesting polymeric materials with allylic pendant groups can be obtained from these monomers via living polymerization techniques. Generally, fatty based allylicacrylates are synthesized by fatty acid chlorides with allylic alcohol at lower temperatures [78].

Another interesting properties of these monomers is the environment of the double bonds of allylic and acrylate groups. Allylic groups are electron rich when compared to acrylic double bonds . Hence under suitable conditions, one can easily modify one of those double bonds. For example with conventional procedure, just allylic double bonds can be epoxidized and acrylic double bonds remain unchanged. Epoxidized acrylates also can find great application areas. Especially fatty based monomer can modify to epoxidized acrylate or methacrylate derivatives. Such as, oleyl acrylates and methacrylates can be produced as difunctional epoxy monomers [78].

2. AIM OF THE STUDY

The goal of this research is to synthesize new polymers from plant oil triglycerides. There are two main strategies to convert plant oil triglycerides to polymers:

1-) Direct polymerization of plant oils without making any change in the structure of plant oil triglycerides.

2-) Functionalization of plant oils and using this functional groups for polymerization. Different synthetic strategies were used to achieve the goals.

In the first part of this study, different oil soluble resoles, synthesized by the reaction between *p*-ethyl, *p tertiary*-butyl, *p tertiary* octyl and *p* phenyl phenol with formaldehyde were prepared and these resoles were polymerized directly with different type of plant oils (Figure 2.1.) such as, cod-liver oil, linseed oil, and soybean oil. The reaction mechanism was investigated by using model compounds and characterization of the polymeric products (Figure 2.2.) by thermal, mechanical and spectroscopic techniques were carried out.

In the second part of this study, allylic positions of the soybean oil were halogenated by reacting of soybean oil with NBS (Figure 2.3.). Then reactive monomers were synthesized by substituting the resulting allylic bromides with different type of nucleophiles such as, acrylates, methacrylates, cyanate, thiocyanate, primary, secondary, and tertiary amines (Figure 2.4). The chemical and physical properties of polymers derived from these functionalized oils were examined.

In the third part of the study, the double bonds of soybean oil were used to make a polymers and foams. For this purpose, soybean oil double bonds were reacted with iodo isocyanate to give valuable vicinal iodo isocyanated soybean oil. Synthesis of different type of polyurethanes and ureas (Figure 2.5.) was achieved using various polyols and polyamines.

Characterization of the monomeric material and thermal and mechanical properties of the produced polymers were also examined. Another valuable monomer that was produced from soybean oil is acrylated epoxidized soybean oil (AESO) (Figure 2.6.). This compound is easily obtained from epoxidized soybean oil and acrylic acid. AESO was reacted with p tertiary butyl phenol furfural resin (Figure 2.6.) to give infusible Diels-Alder polymer (Figure 2.7.). The mechanical and thermal properties of these cross-linked polymers were also determined.

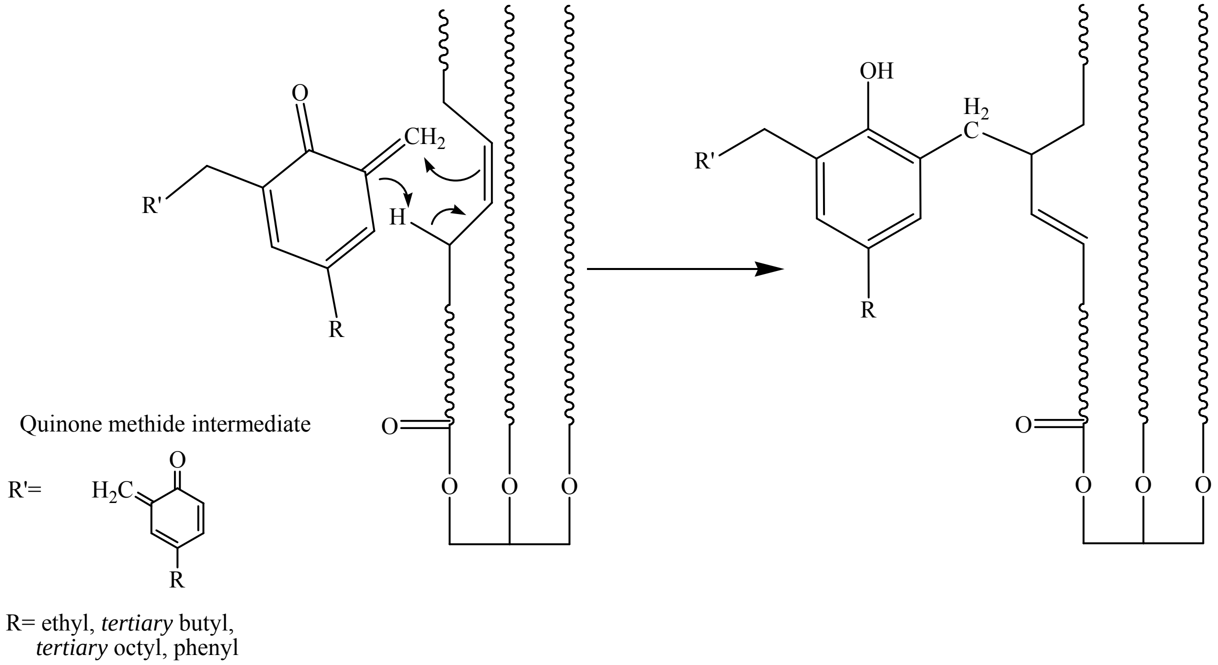


Figure 2.1. Cross-linking of plant oils with phenolic resins via ene mechanism.

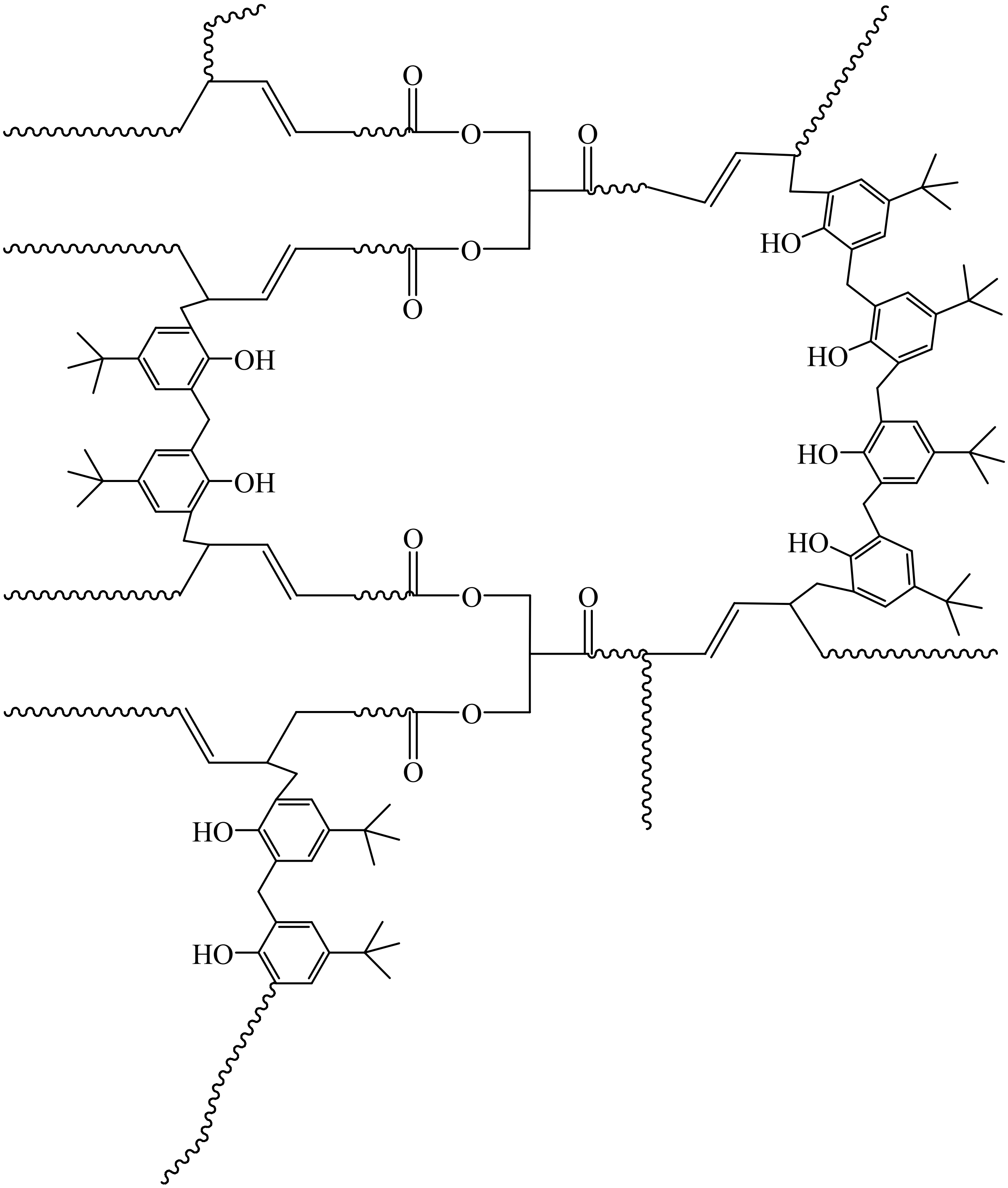


Figure 2.2. Cross linked product of plant oils with oil soluble phenolic resins.

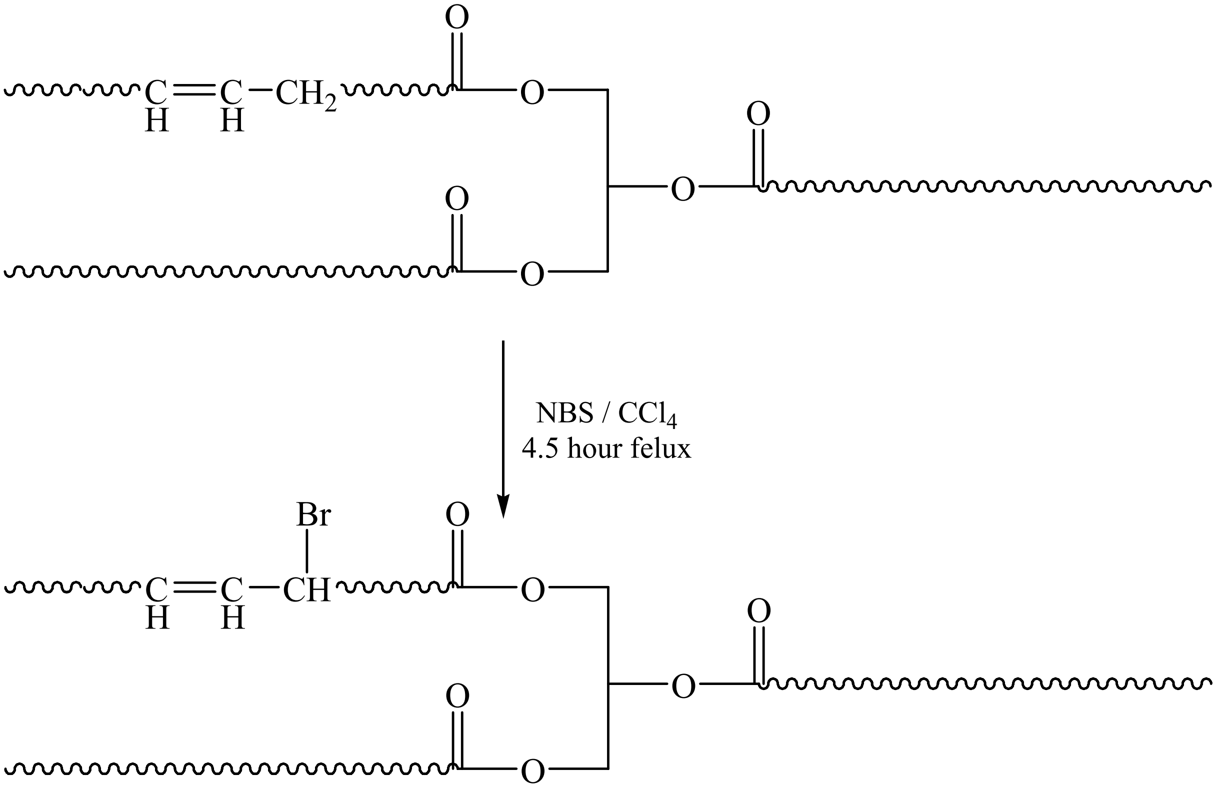


Figure 2.3. Synthesis of ABSO from soybean oil.

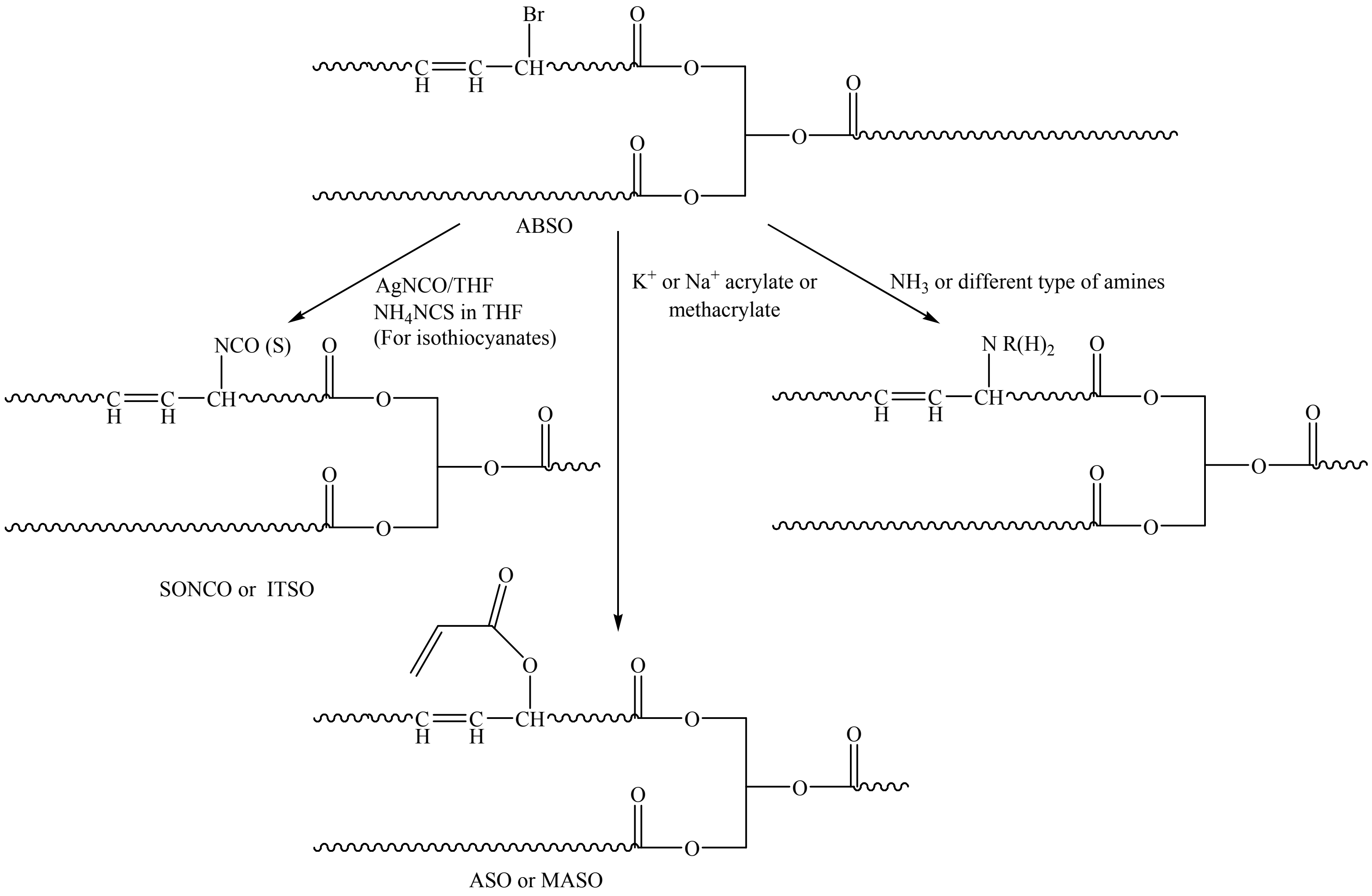


Figure 2.4. Substitution reaction of ABSO with different type of nucleophiles.

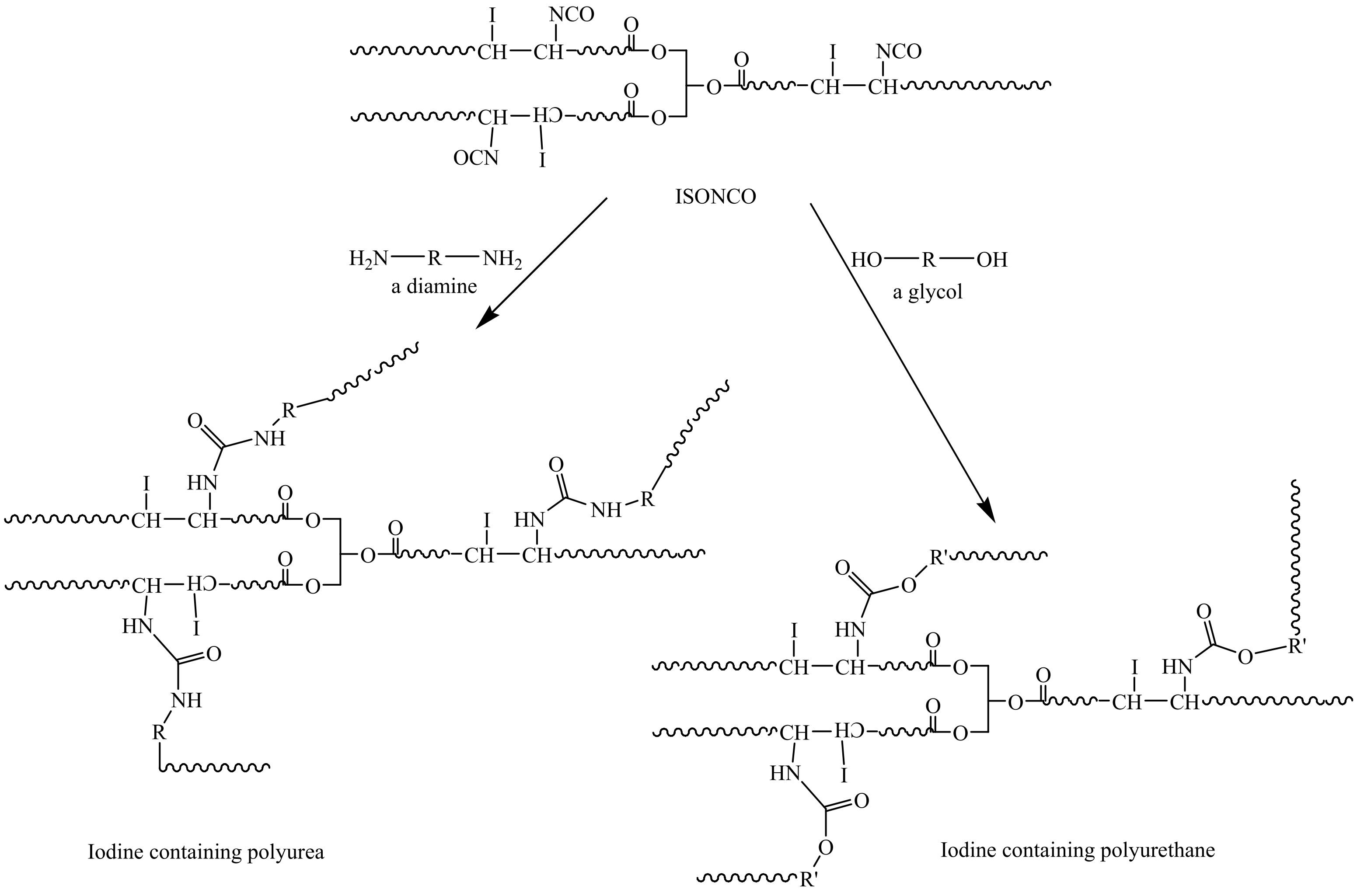
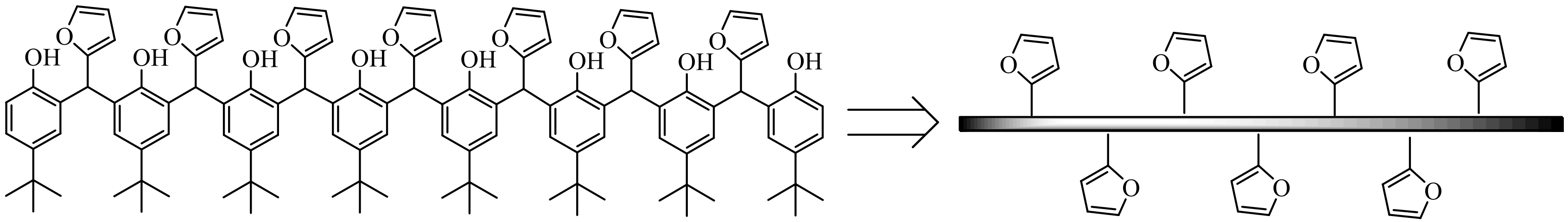


Figure 2.5. Simple presentation of polymerization of ISONCO with di alcohols and di amines.



p teriary phenol furfural resin

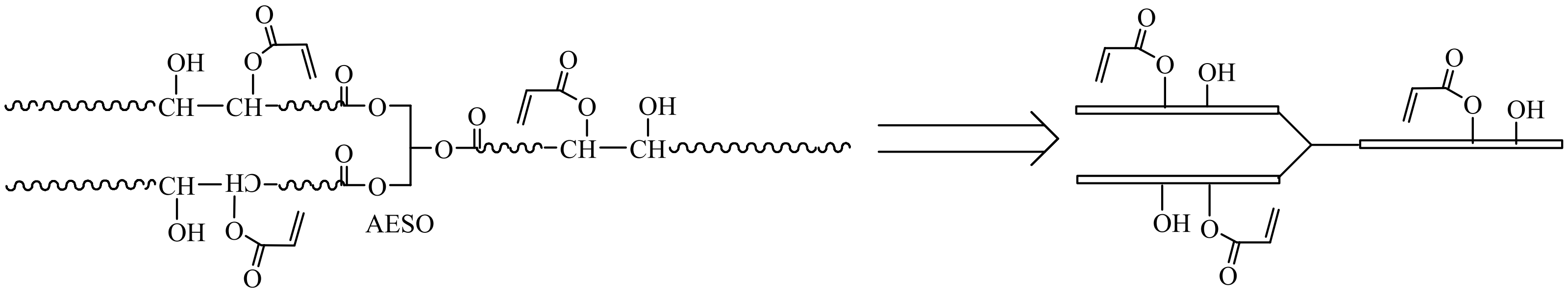


Figure 2.6. Schematic presentation of *p. tertiary* butyl phenol furfural resin and acrylated Epoxidized soybean oil

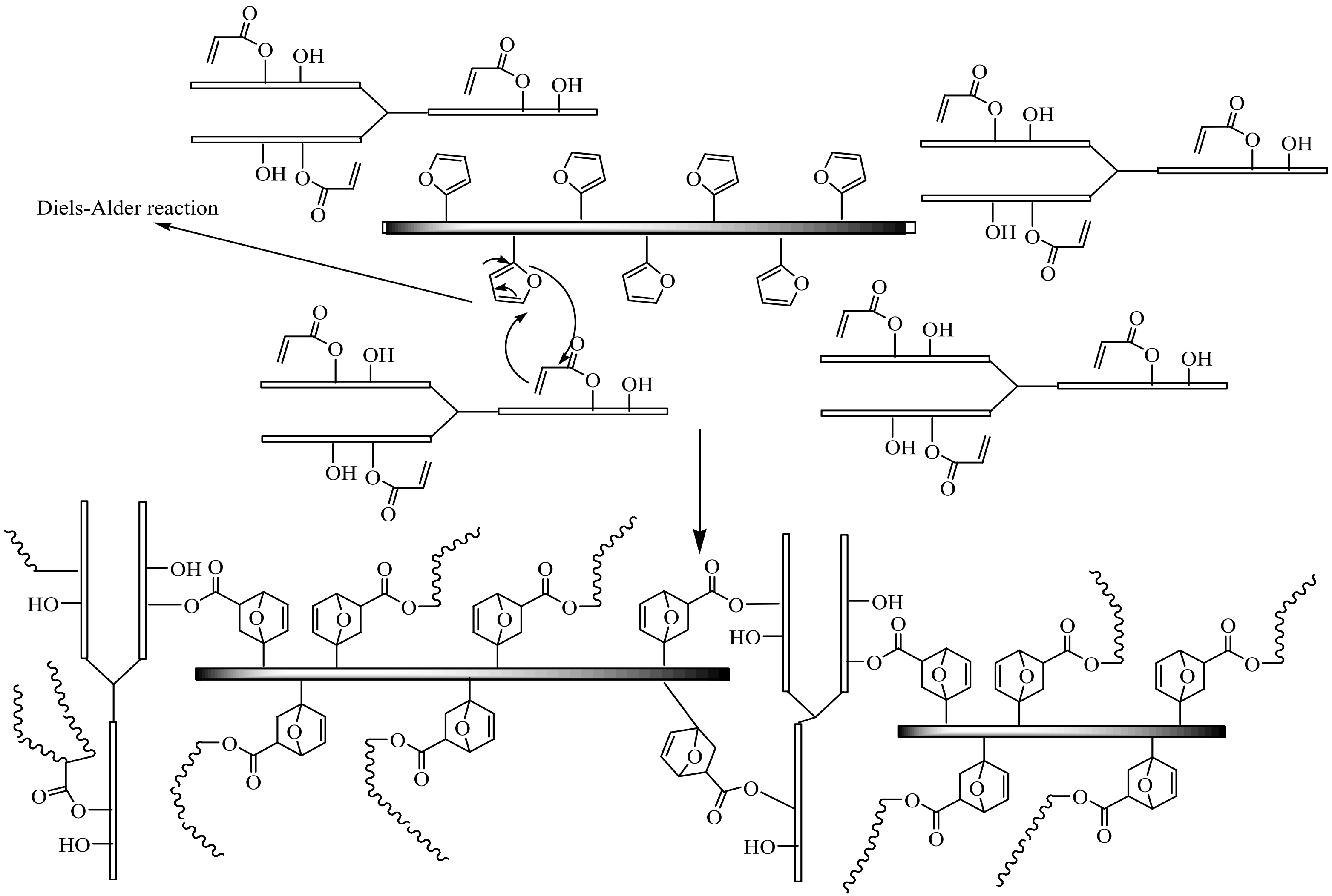


Figure 2.7. Reaction product of PTB-furfural resin and AESO.

3. RESULTS AND DISCUSIONS

3.1. ^{1}HNMR and IR characteristics of plant oil and methyl esters

Plant oil triglycerides are triesters of glycerol and fatty acids. An average plant oil triglyceride may contain approximately 60 C atoms which make the IR and NMR spectra complex. Fortunately, the main reactive sides of the plant oil triglycerides can be easily differentiated by 400 MHz NMR. Four different types of plant oils which have different properties are shown in figure 3.1. In the ^{1}H NMR spectrum, double bond protons appear at 5.2 ppm, Allylic protons appear at 2.0 ppm while doubly allylic protons appear at 2.8-3.0 ppm. There is also a special peak observed at 0.8-1.0 ppm on cod liver oil, soybean oil and linseed oil. This peak is of the last allylic position of the linolenic acid on the carbon. The polyunsaturated C 20 and 22 fatty acids are responsible for this peak.

The other characteristic groups that are found in plant oil triglycerides are α and β methylene groups to ester carbonyl. Alpha protons are observed at 2.25 ppm while beta protons observed at 1.5-.7 ppm. The last characteristic peaks are the peaks of the glycerol protons. Two identical peaks are seen at 4 and 4.2 ppm which belong to outer $-CH_2$- groups. Inner glycerol proton appears at 5.2-5.4 ppm.

IR spectrum of the plant oils are more complicated than the NMR spectrum. But generally these four triglycerides show same peaks for same functionalities (Figure 3.2.). At 3008 cm-^{1} a medium peak is observed due to the =C-H stretching. Aliphatic C-H stretching appears at 2900-2800 cm-1. There is also one ester carbonyl peak is observed at 1742 cm-1. A weak peak can be seen at 1660 cm^{-1} which belongs to C=C stretching. A peak is also observed as a triplet at 1200, 1100 and 1000 cm^{-1} due to the C-O stretching of the tri ester groups of triglyceride. C-H out of plane bending vibration causes a medium peak at 723 cm^{-1} (Figure 3.2.).

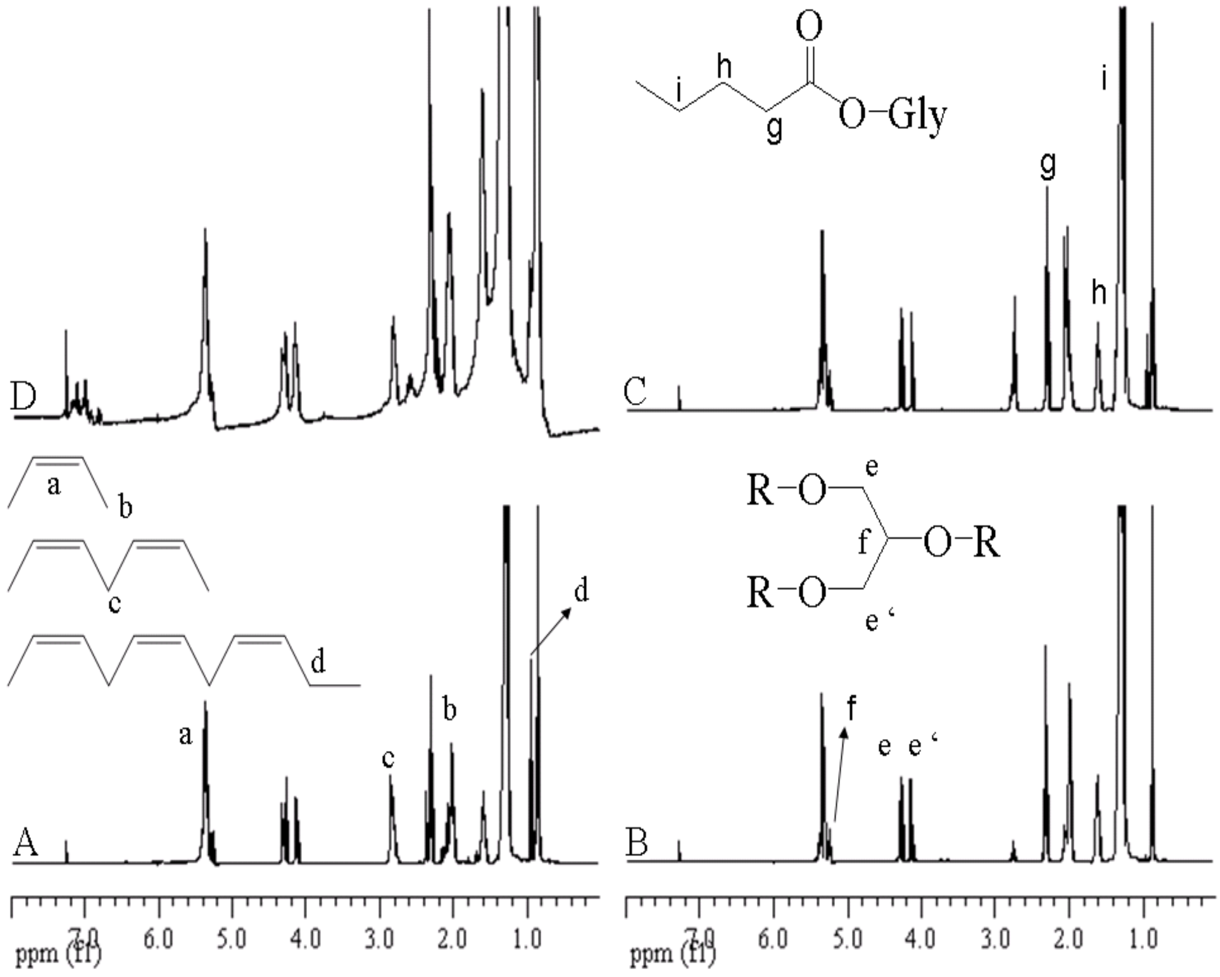


Figure 3.1. ^{1}H NMR's of (A) cod liver oil, (B) olive oil, (C) soybean oil, and (D) linseed oil.

Due to the structure and size of the plant oil triglycerides, it is hard to follow the reactions on them and some times it is impossible to assign the peaks. Moreover, it is generally impossible to separate positional isomers from each other which are formed during reactions. For these reasons, small derivatives such as fatty acid methyl esters, are usually used as model compounds to follow the reaction mechanism.

The ^{1}H NMR and IR spectra of the methyl esters are simpler than plant oils because they contain maximum 19-20 C atoms. In figure 3.3, ^{1}H NMR spectrum of the methyl oleate and soy oil methyl esters are presented. The peaks which belong to the double bond protons, allylic, double allylic, α and β methylene groups appear at the same regions as the plant oil triglycerides. IR spectrum of methyl esters are nearly the same with triglycerides. The only difference is the C-O stretching peaks. Instead of the triplet there are separate peaks that appear at 1245, 1190 and 1170 cm^{-1}respectively (Figure 3.4.).

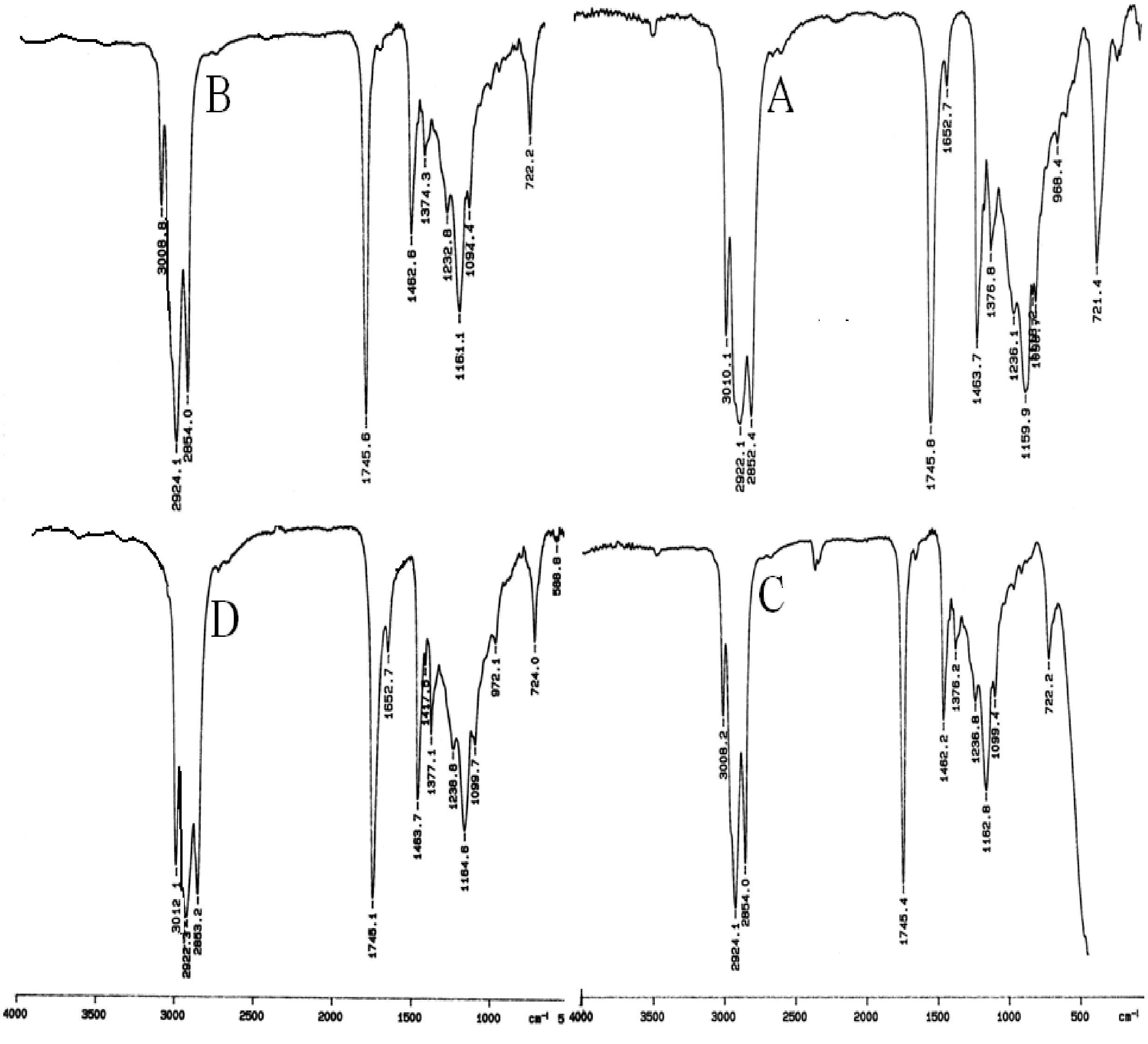


Figure 3.2. IR spectra of (A) cod liver oil, (B) olive oil, (C) soybean oil, and (D) linseed oil.

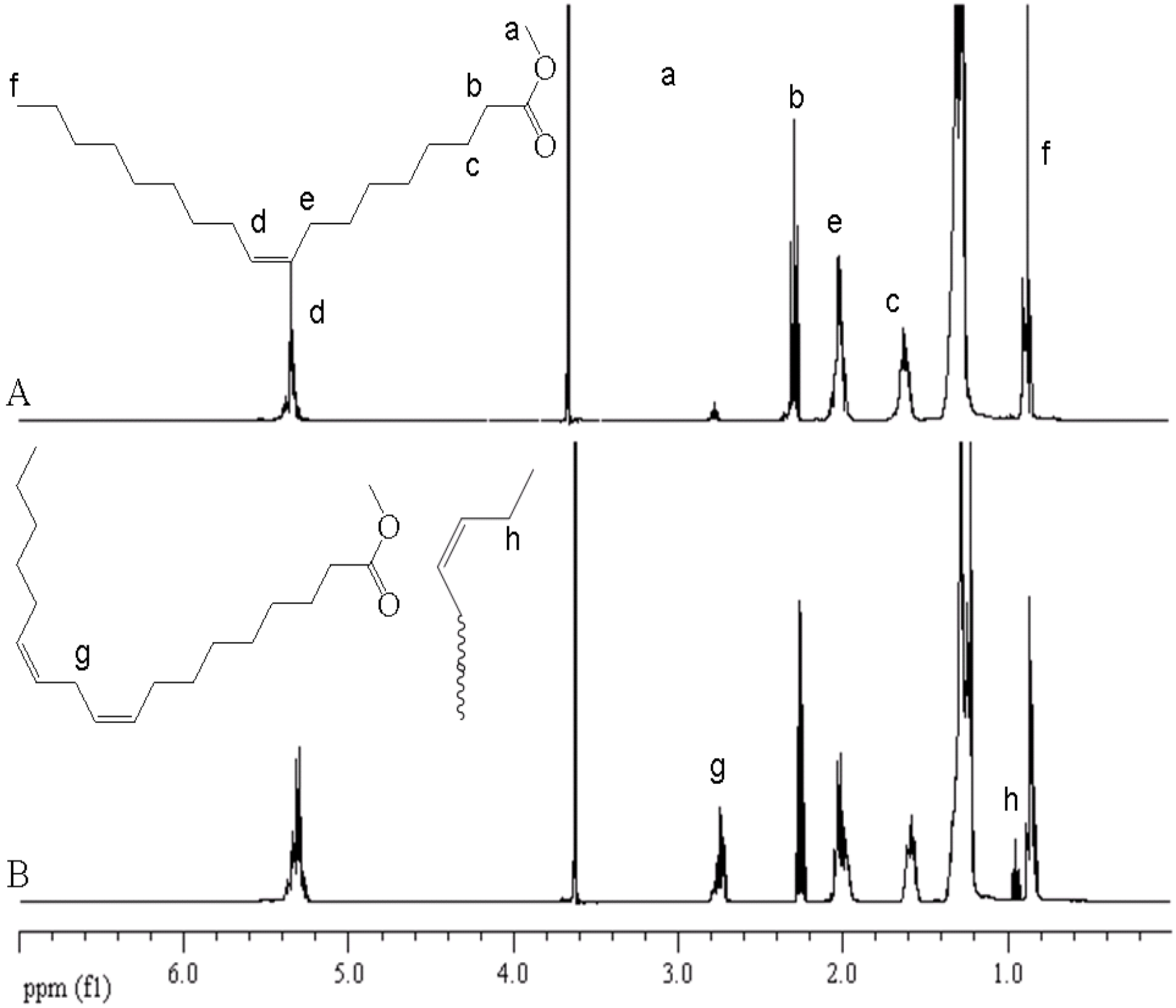


Figure 3.3. ^{1}H NMR's of (A) methyl oleate and (B) soybean oil methyl esters.

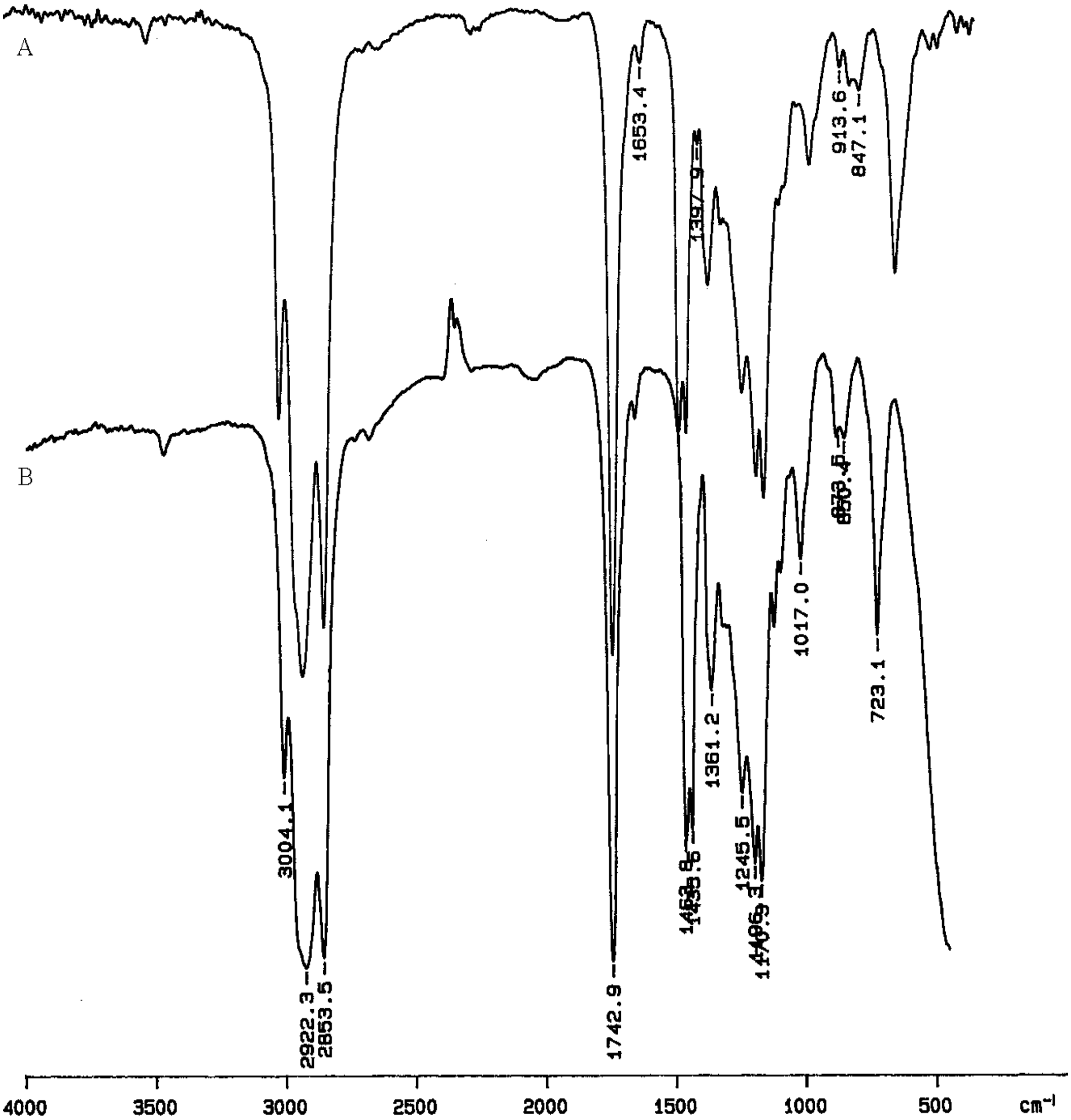


Figure 3. 4. IR Spectra of (A) soy oil methyl esters and (B) methyl oleate.

3.2. Polymerization of plant oil triglycerides with phenolic resins

The known cross linking of natural rubber with phenolic resins and the similarity of the plant oil triglycerides to rubbers led us to examine polymerization of plant oil triglycerides with phenolic resins (Figure 3.5).

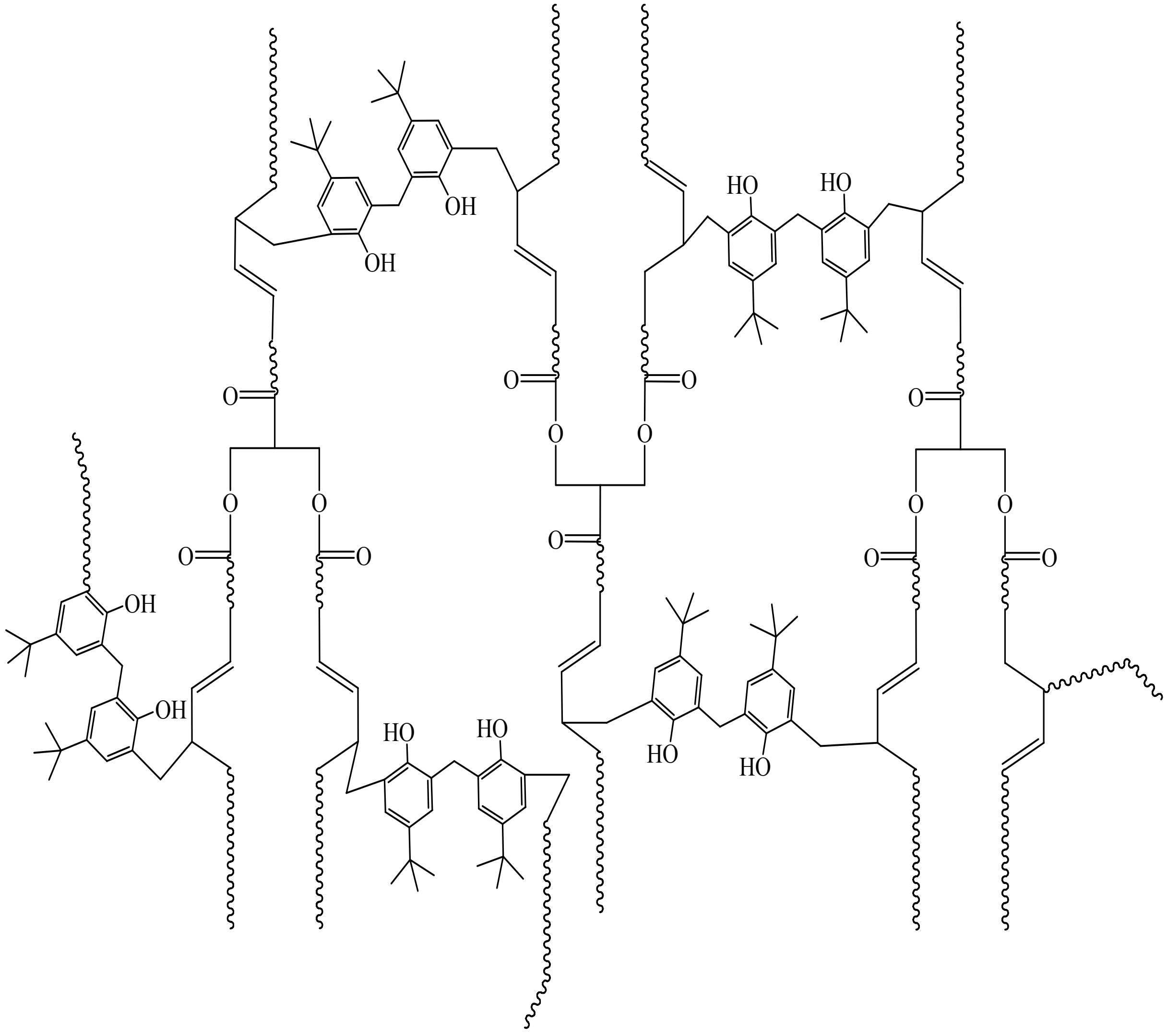


Figure 3. 5. Polymerization of plant oil triglycerides withp.tertiary butyl phenol resin

3.2.1. IR and 1H NMR characterizations of phenolic resins:

IR spectra of the phenols that were used in the synthesis of oil soluble resoles are shown in Figure 3.6. The OH peaks are observed at around 3500 cm^{-1}. At 1610 and 1590 cm^{-1} indicate the C=C stretching. And at 800 cm^{-1}indicates the *p.* substitution. By changing the *p.* substituents, peaks which appear at 1000-1500 cm-1 are also changed. In case of p. phenyl phenol a unique peak is observed at 754 cm-1 probably due to second phenyl ring (Figure 3.9).

Four type of oil soluble resole resin was synthesized in this study by using p. phenyl phenol, p tertiary octyl phenol, p. tertiary butyl phenol (Figure 3.7). The IR spectrum showed that a peak around 3340 cm^{-1} indicates the OH group. A peak which is observed at 1012 cm^{-1} indicates the methylol group. And finally, peaks at 874 and 816 cm-1 are the proof of 1,2,3,5 tetra substitution on the phenyl ring of the resoles (Figure 3.8). The reason why *p.* alkyl substituted phenols were used is that phenol itself gives phenol-formaldehyde resins that are insoluble in plant oils.

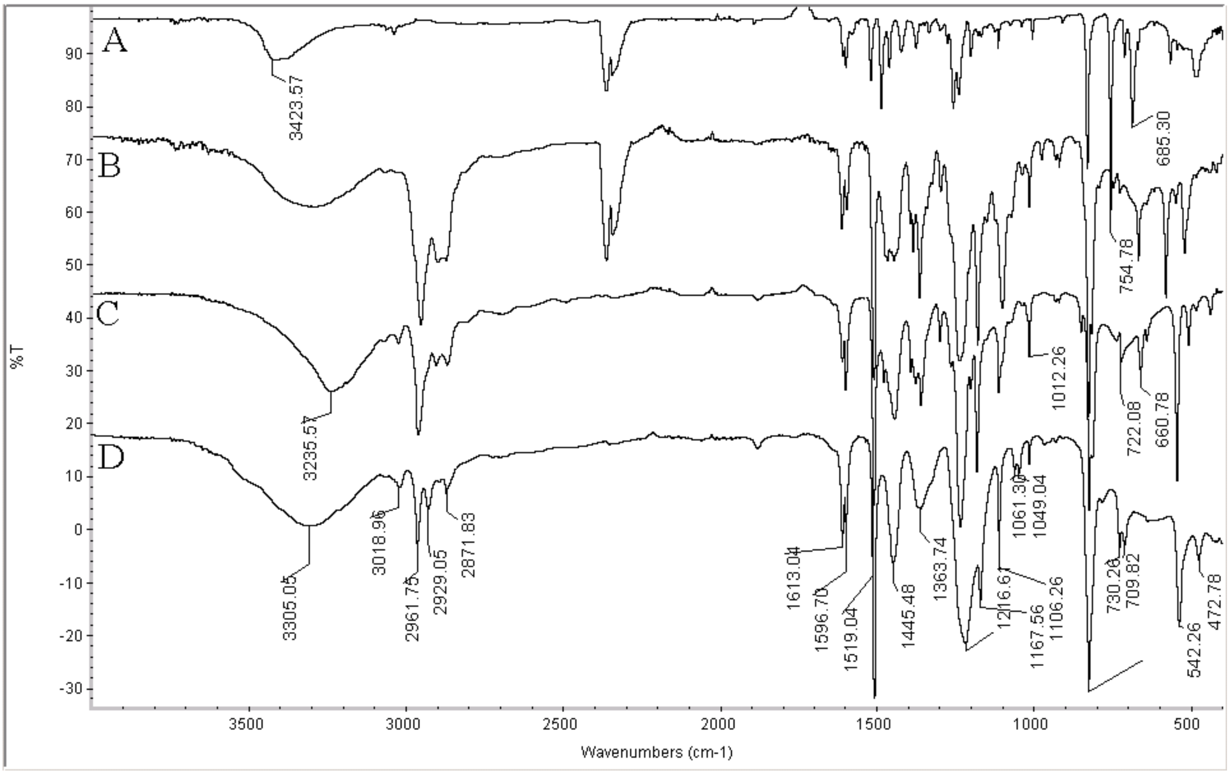
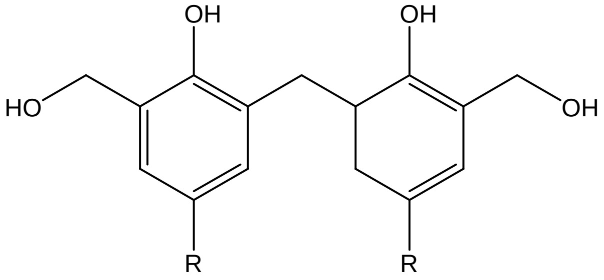


Figure 3.6. IR spectra of (A) *p.* phenyl phenol (B) *p. tertiary* octyl (C) *p. tertiary* butyl (D) *p.* ethyl phenols.



R= ethyl (PEP)

R= *tertiary* butyl (PTBP)

R= *tertiary* octyl (PTOP)

R= phenyl (PPP)

Figure 3.7. General structure of the oil soluble resols.

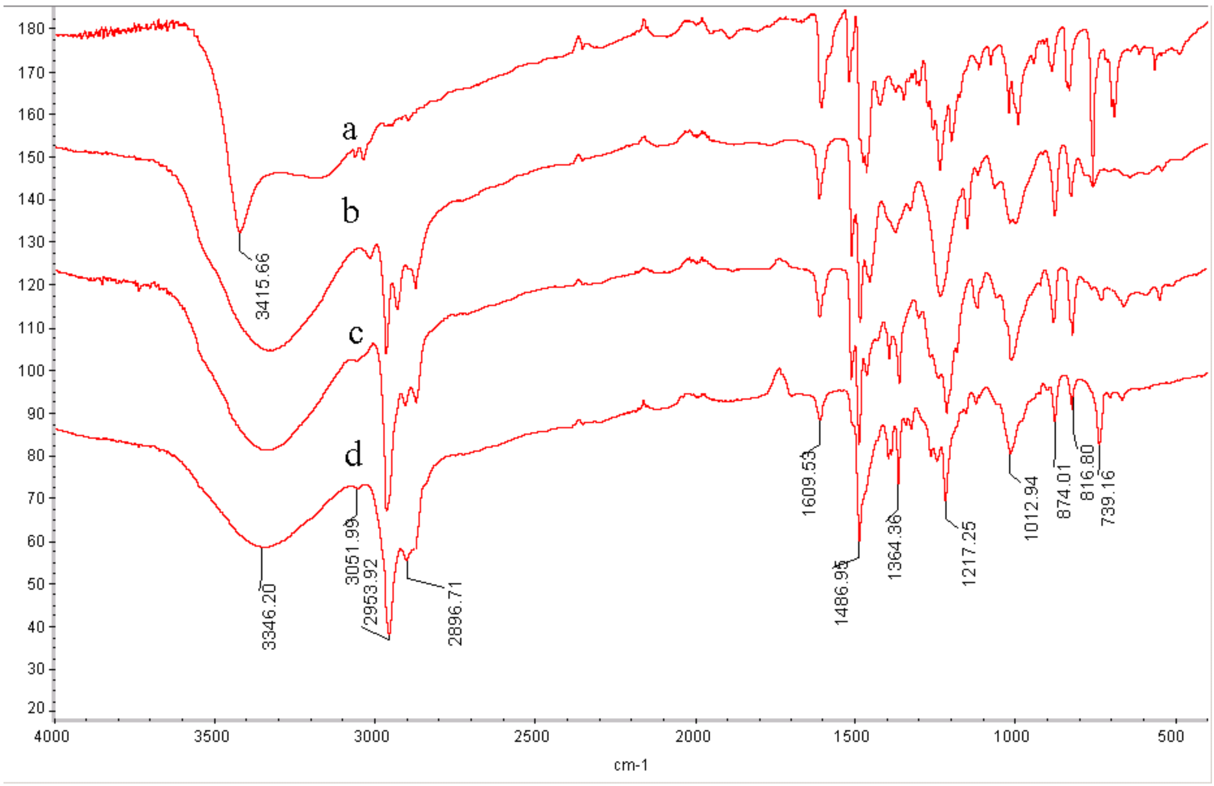


Figure 3.8. IR spectra of (a) *p*. phenyl phenol (b) *p*. ethyl phenol (c) *p* tertiary butyl phenyl (d) *p* tertiary octyl phenol resoles.

The ^{1}H NMR shows an intense peak at 4.7 ppm due to the methylol group (phenyl-C**H$_2$-** OH). At 7 ppm aromatic protons are observed. The OH protons are generally observed at 3.4 ppm abut it changes at p. tertiary octyl phenol resole to 5.0 ppm. There is small amount of double benzylic protons which appears at 4.0 ppm. The ratio of these protons to methylol protons gives the molecular weight of the resoles. The ratio indicates that all resoles were mainly in dimeric forms (Figure 3.9).

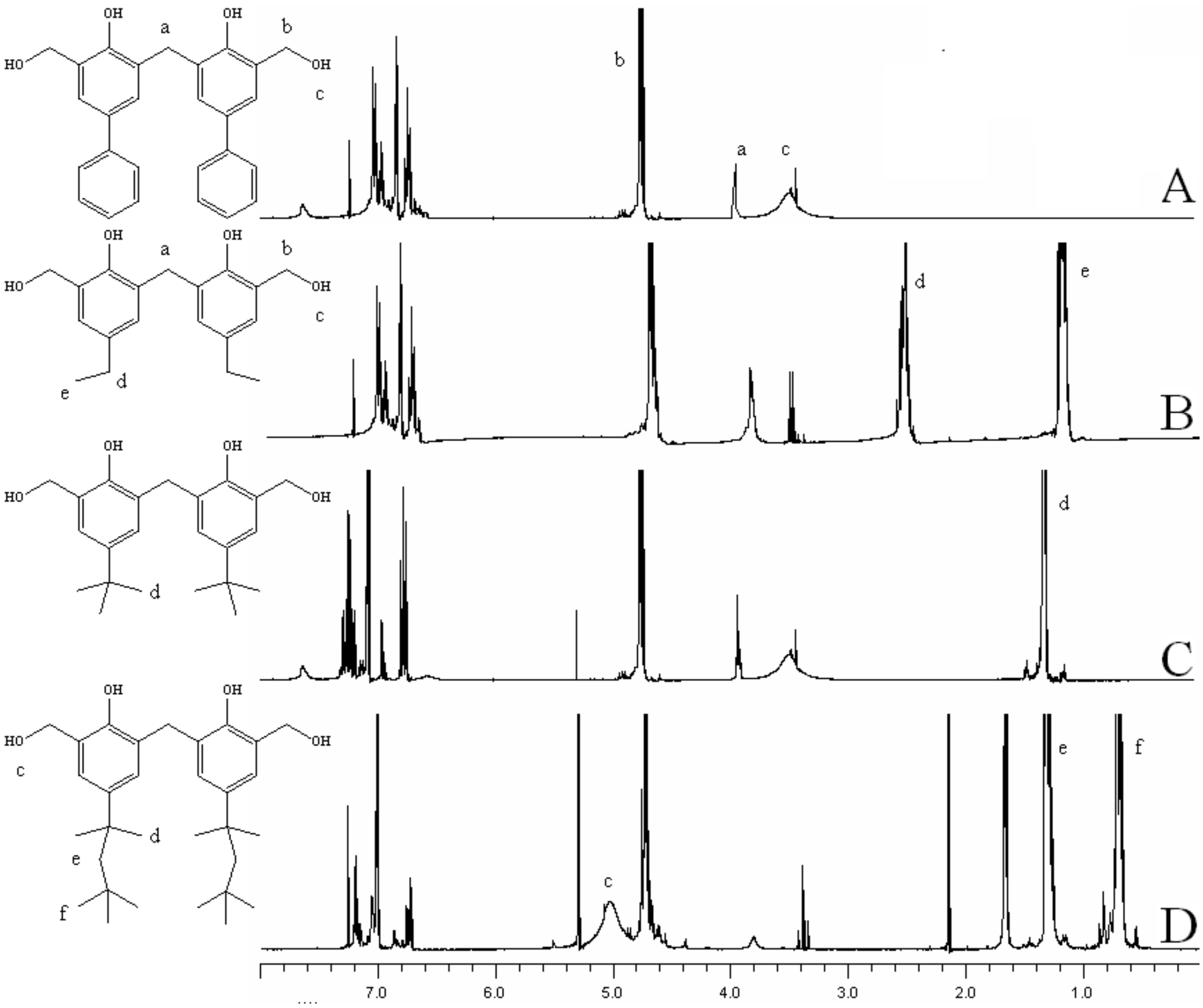


Figure 3.9. ^{1}H NMR spectra of (a) p. Phenyl phenol (b) p. Ethyl phenol (c) p tertiary butyl phenyl (d) p tertiary octyl phenol resoles.

3.2.2 Reaction Mechanism of the polymerization of plant oils with resoles:

Literature shows a lot of information about the reaction of phenolic vulcanizing agents with rubbers. In the literature, three mechanisms are proposed for the vulcanization of rubbers by phenolic resins. Due to the resemblance of the rubber and plant oil triglyceride double bonds, these proposals are also valid for the reaction between phenolic resins and plant oil triglycerides.

In the first hypothesis, reaction is completed by the reaction of rubbers with reactive quinone intermediate. At elevated temperatures dimethylol phenols lost one or two moles of water and quinone methide intermediate is observed. This reactive species react directly with the double bonds via Diels-Alder reaction Pathway (Figure 3.10) or reacts with allylic protons via ene reaction pathway (Figure 3.11). The Ene reaction pathways is 4n+2 type cyclic reaction and thermally allowed. The driving force for the reaction is rearomatization of the benzene ring.

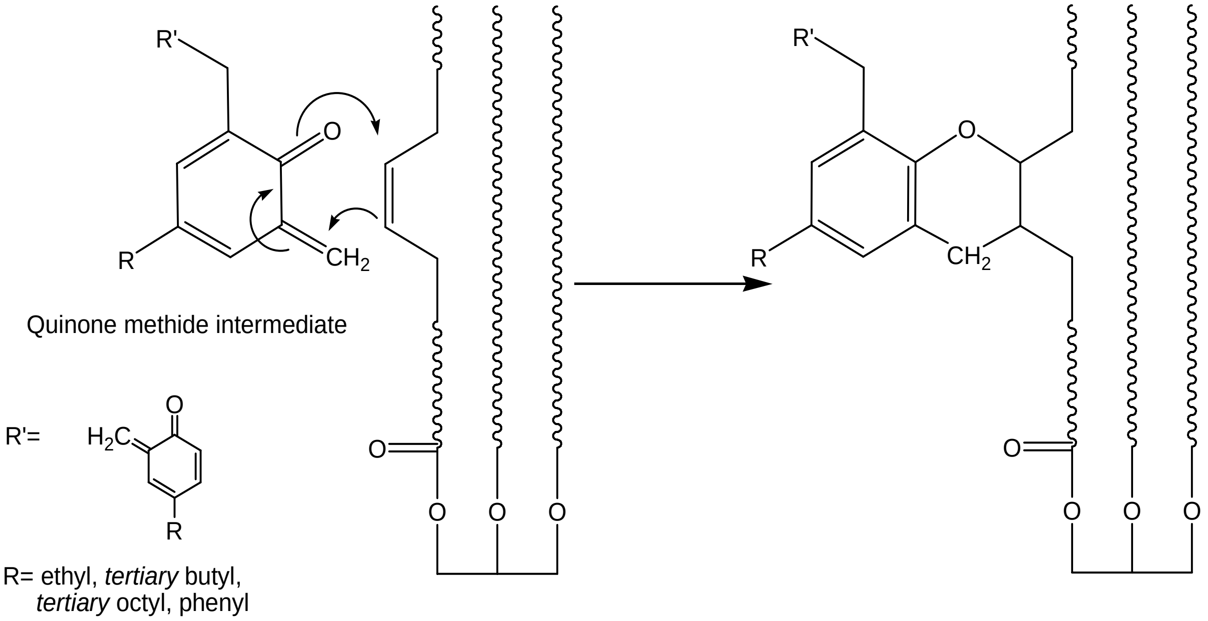


Figure 3.10. Reaction of the quinone methide intermediate with double bonds of plant oil triglycerides wiyh Diels-Alder pathway.

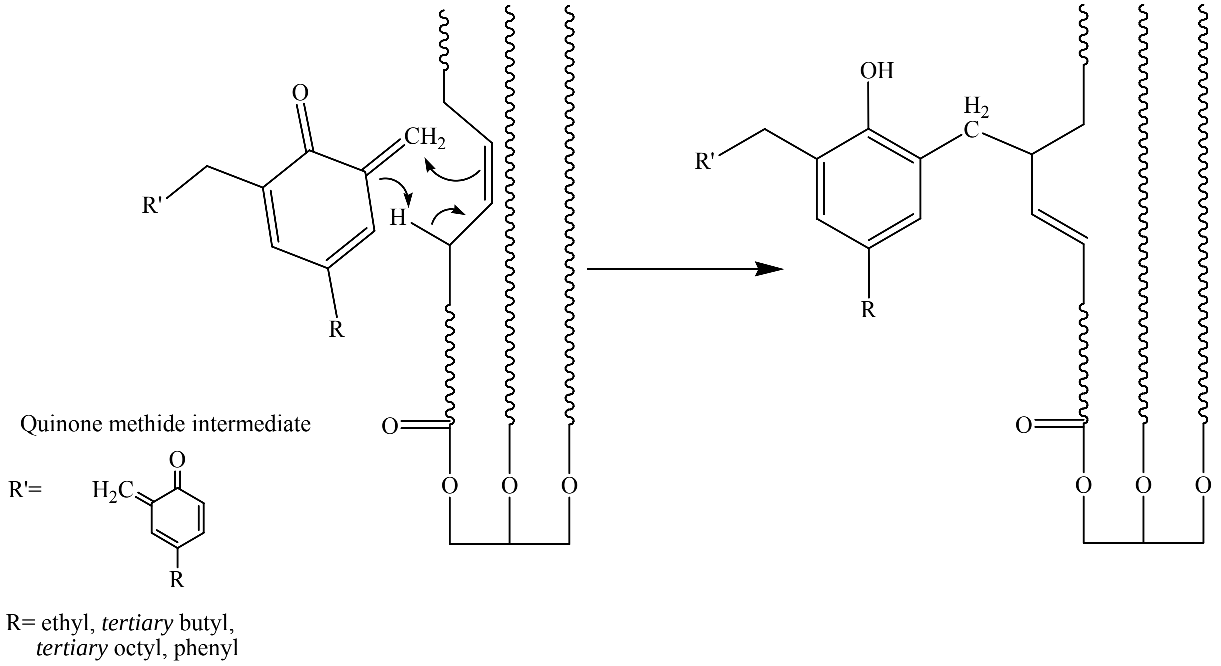


Figure 3. 11. Reaction by Ene pathway.

Methyl oleate and p. tertiary butyl phenol resole was used as model compounds in order to explain the reaction mechanism. Both compounds were heated to 190 °C without any catalyst. After 10 minutes, viscosity of the mixture increased. Gas and formaldehyde evolution was also detected. When PTBP resole was heated itself at 190 °C, it also gave a very brittle solid.

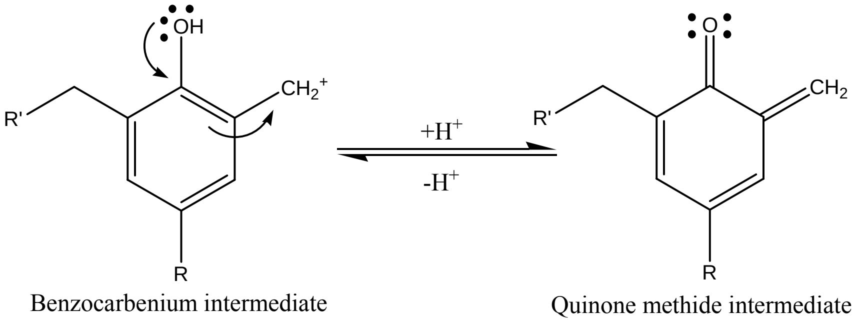


Figure 3.12. Transformation of quinine methide and benzocarbenium intermediates.

^{1}H NMR samples were taken at 10 minutes intervals. After 40 minutes, completion of the reaction was observed. In the ^{1}H NMR spectra, disappearance of the protons of the methylol groups was easily followed. The peak at 4.8 ppm was reduced and disappeared in 60 minutes. During the reaction, there were two new peaks at 4.2 and 4.4 ppm which indicate the double benzylic protons. The amounts of the double benzylic protons are almost 0 at the beginning of the reaction and increase as the reaction progress. The intensity ratio of the aromatic protons to the methoxy group protons or alpha protons of the ester was almost same. Another interesting finding is the intensity of the double bond protons. Only a small amount of decrease was observed in the intensity of the double bond protons (Figure3.14). This proved the Ene reaction mechanism. If the reaction went via Diels-Alder reaction pathway, there would be no double bond protons left in the fatty acids at the end of the reaction. So we conclude that the reaction proceeds through an Ene pathway.

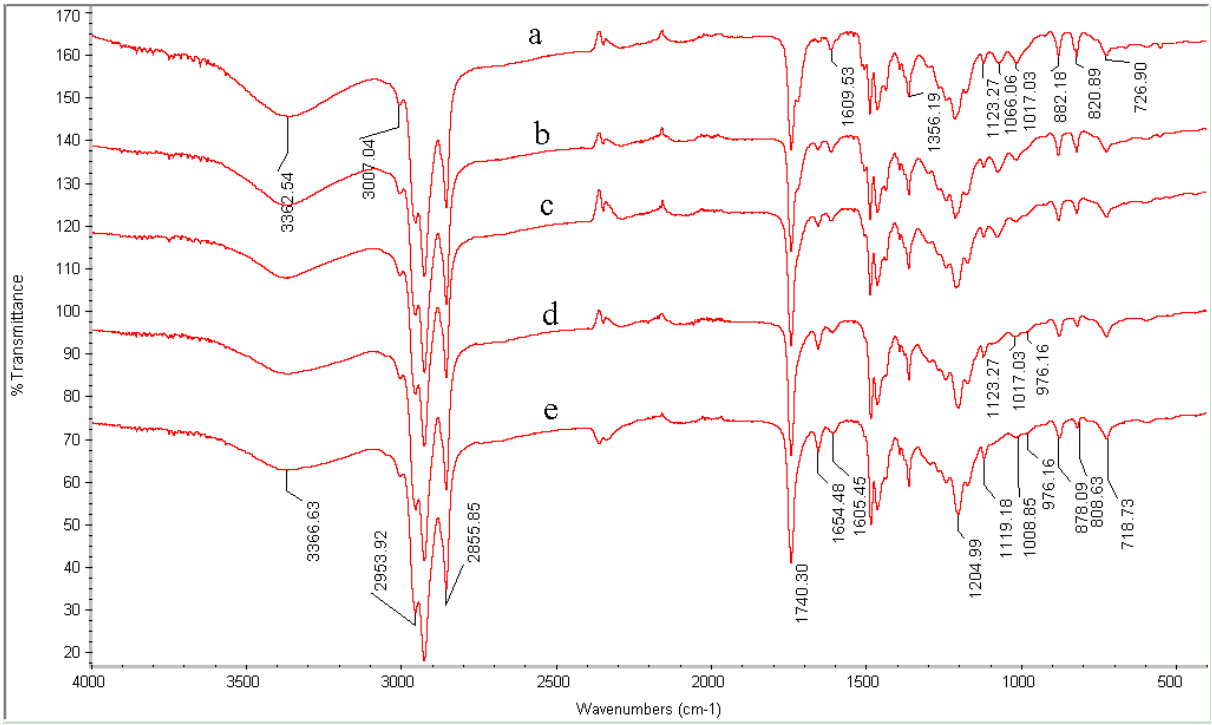


Figure 3. 13. IR spectra of methyl oleate and p. tertiary butyl phenol resoles (a) at starting, after (b) 10 minutes (c) 20 minutes (d) 30minutes and (e) 40 minutes at 190 °C.

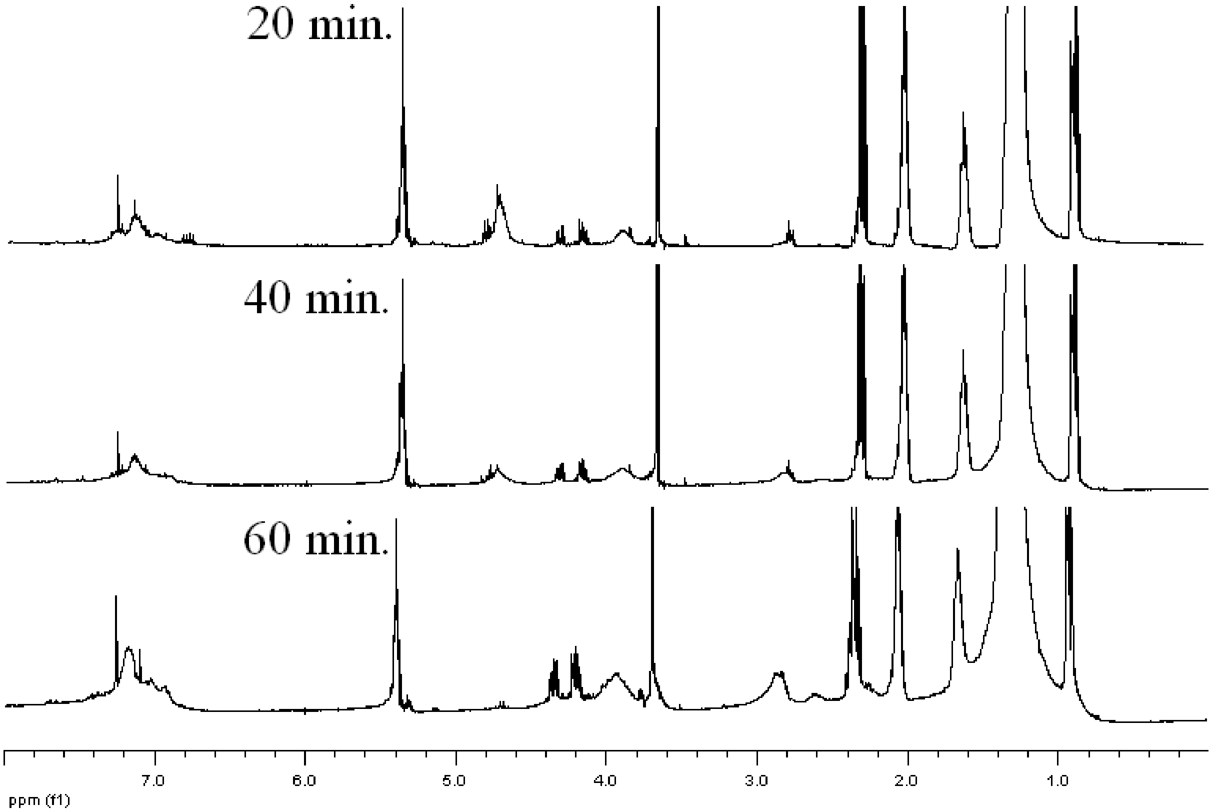


Figure 3.14. ^{1}H NMR s of the reaction mixture of methyl oleate and p. tertiary butyl phenol resole at 195 ^{o}C

3.2.3. Properties of polymers synthesized:

Reaction of phenolic resins with plant oils may be accelerated at higher temperatures but in this case undesirable self condensations of the phenolic resins also take place. Thus, by using maleic acid catalyst, low temperatures were targeted. The lowest optimum temperature for this reaction was found to be 145 ^{o}C. At this temperature materials were kept for 24 hours to complete the polymerization under N_2 gas. After the curing, different type of resol plant oil triglyceride condensates were obtained.

Reaction of oil soluble resoles with linseed oil triglycerides gave orange colored rubbery solids samples containing up to 40 per cent of phenolic resin. At 50 per cent phenolic resin very hard and strong materials were synthesized. Due to its high linoleic acid content linseed oil gave polymers which contain the lowest amount of phenolic resins. On the other hand load bearing hard polymers were obtained when 60 per cent phenolic resin were used with soybean oil and cod liver oil. The mechanical properties of soybean oil polymers were better than cod liver oil polymers.

3.2.3.1. Mechanical properties of the polymers. For the examination of the mechanical properties of the materials produced, there are two test that can be applied. First one is the determination of the stress-strain behaviors and the others is dynamic mechanical analysis. Stress-strain behaviors were determined by the Devotrans DVT G21 machine. DMA properties were followed by the Q-800 type DMAinstrument.

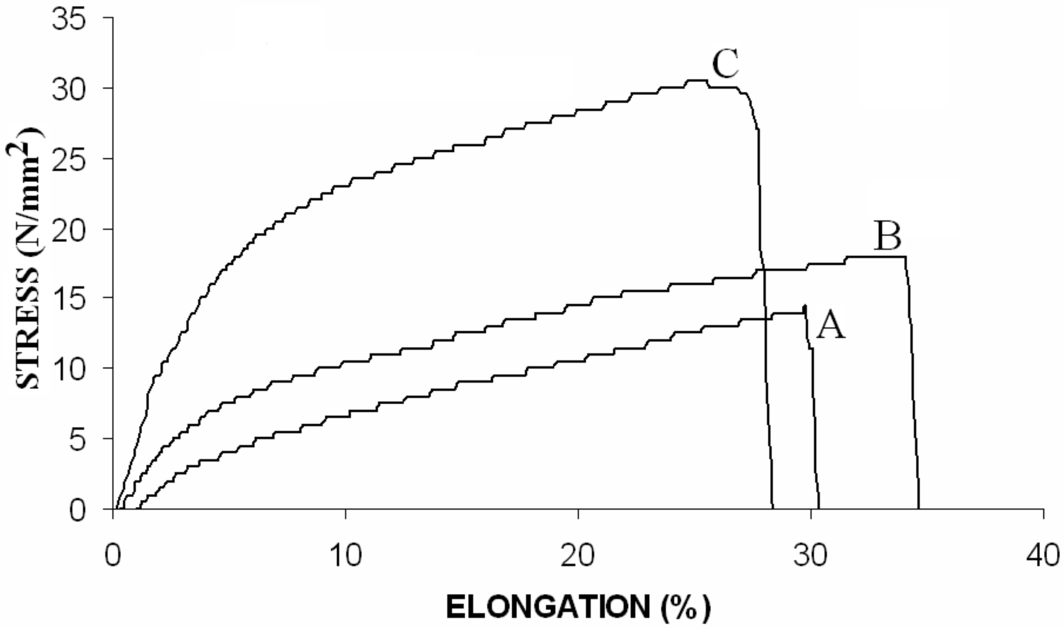


Figure 3.15. . Stress-Elongation curves of the polymers of linseed oil with (A) 10 per cent, (B) 20 per cent, (C) 30 per cent of *p.* phenyl phenol resole after 24 hours curing.

Another interesting effect was observed by changing the p. substitution of the phenolic resins. The highest tensile strength of 40 N/mm^2 were obtained with the *p.* ethyl substitution (Figure 3.16) *p.* phenyl phenol then *tertiary* butyl and finally *p. tertiary* octyl phenyl resoles showed the lower tensile strength (Figure3.17).

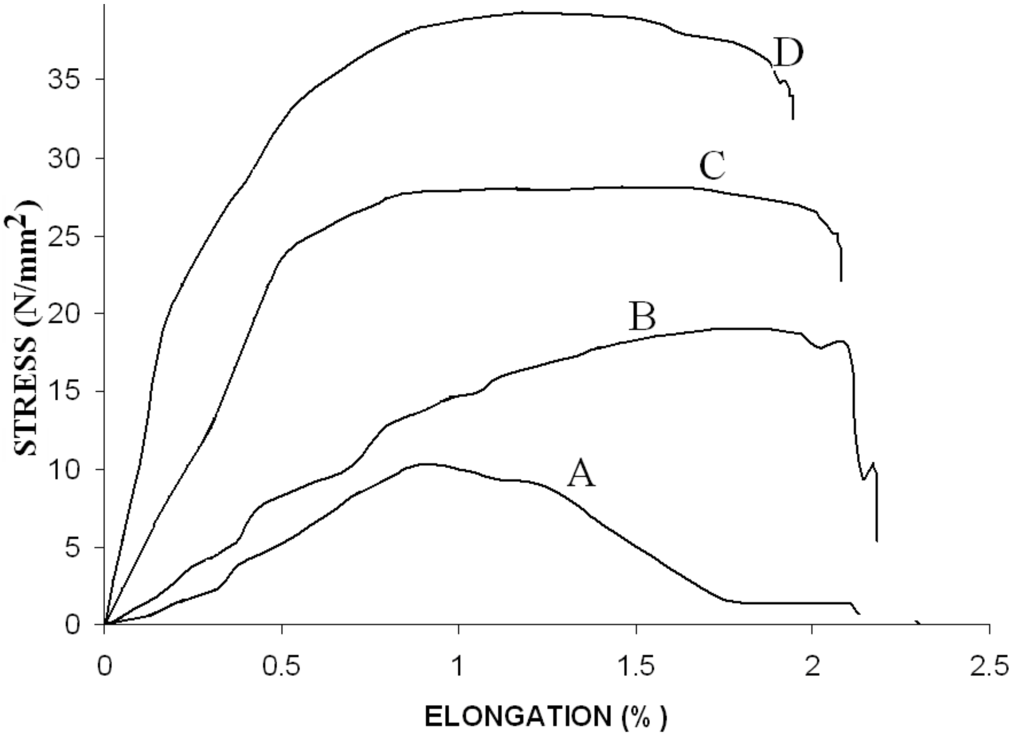


Figure 3.16. Stress-Elongation curves of the polymers of linseed oil with (A) 10 per cent, (B) 20 per cent, (C) 30 per cent, (D) 40 per cent of *p.* ethyl phenol resoles after 24 hours curing.

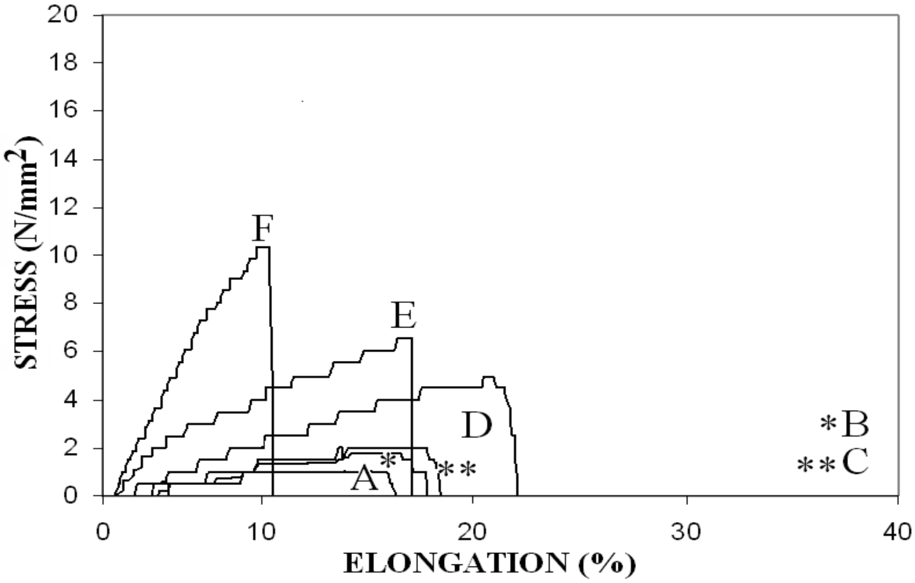


Figure 3.17. Stress-Elongation curves of the polymers of linseed oil with (A) 10 per cent, (B) 20 per cent, (C) 30 per cent, (D) 40 per cent, (E)50 per cent, (F) 60 per cent *p. tertiary* octyl phenol resoles after 24 hours curing

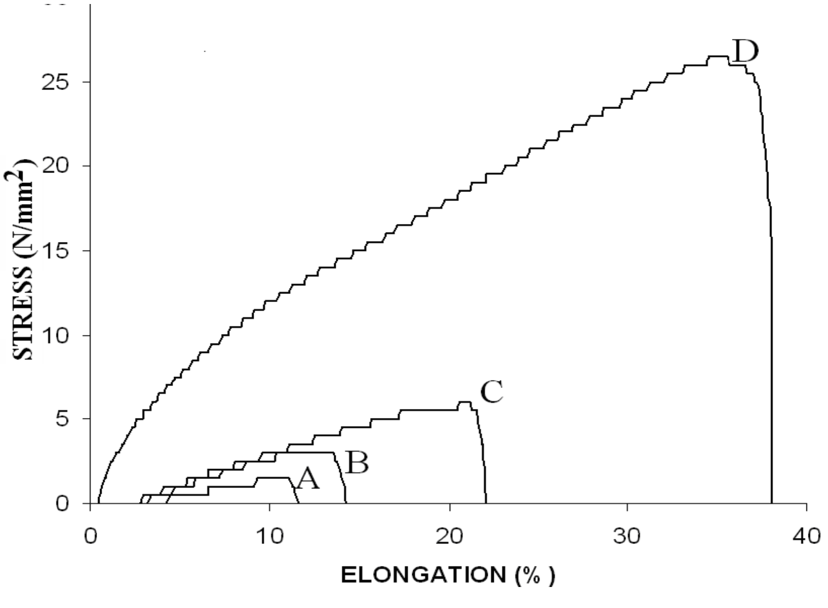


Figure 3.18. Stress-Elongation curves of the polymers of linseed oil with (A) 10 per cent, (B) 20 per cent, (C) 30 per cent, (D) 40 per cent of *p. tertiary* butyl phenol resoles after 24 hours curing.

Dynamic mechanical analysis of the polymers also showed interesting results. By changing the p. substitution from ethyl to tertiary octyl group storage modulus of the materials decreased from 400 MPa to 50 MPa. Similar trend can also be followed at tan δ values (Figure 3.19). With the increasing size of the alkyl substituent, maxima of tan δ peaks increases which implies the viscous character of the material. Another observation is shifting of the peak maxima to lower temperatures with increasing size of alkyl substituents.

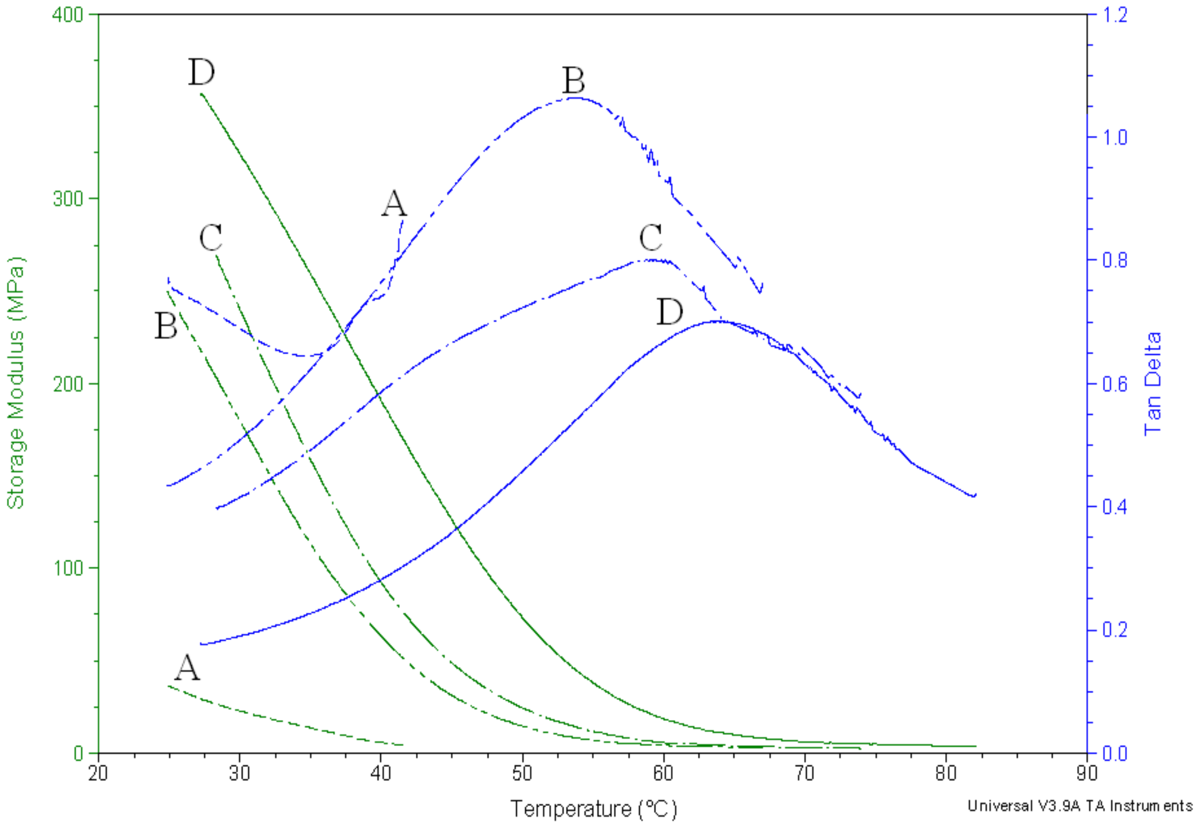


Figure 3.19. Storage modulus and tan δ values of polymers of linseed oil with 40 per cent (A) PTIOP (B) PTBP (C) PPP (D) PEP resoles.

By using p. ethyl phenol with linseed oil a storage modulus of 400 MPa was obtained and the tan δ peak at observed at 65 ^{o}C with a lowest maxima. This result implies the higher elastic nature of the linseed oil and p ethyl phenol resoles polymers.

Another set of experiments were performed with p. ethyl phenol resoles with cod liver and soybean oils. Both of these oils gave load bearable polymers after 60 per cent phenolic resin addition. Soybean oil based polymers showed better storage modulus than cod liver oil based polymers. Storage modulus of the soybean oil based polymers varied from 1.1 GPa to100 MPa (Figure 3.19 and 20).Cod liver oil based polymers showed storage modulus from 300 MPa to 30 MPa. In both case, storage modulus were decreased with the increased amount of triglyceride content. Soy oil based polymers showed tan δ values between 100 °C and 50 °C. Cod liver oil based polymers were showed tan δ values between 60-40 °C.

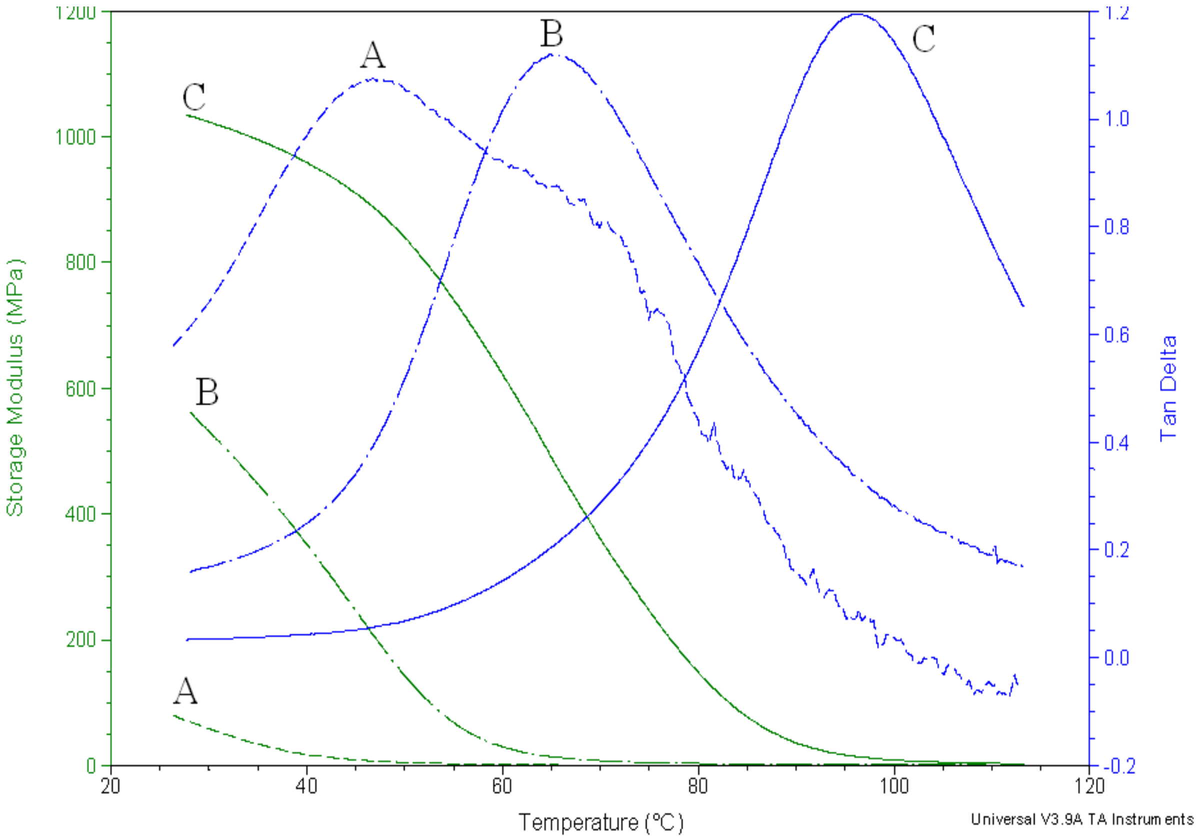


Figure 3.20. Storage modulus and tan δ values of polymers of soybean oil with (A) 60 per cent (B) 70 per cent and (C) 80 per cent p ethyl phenol resole.

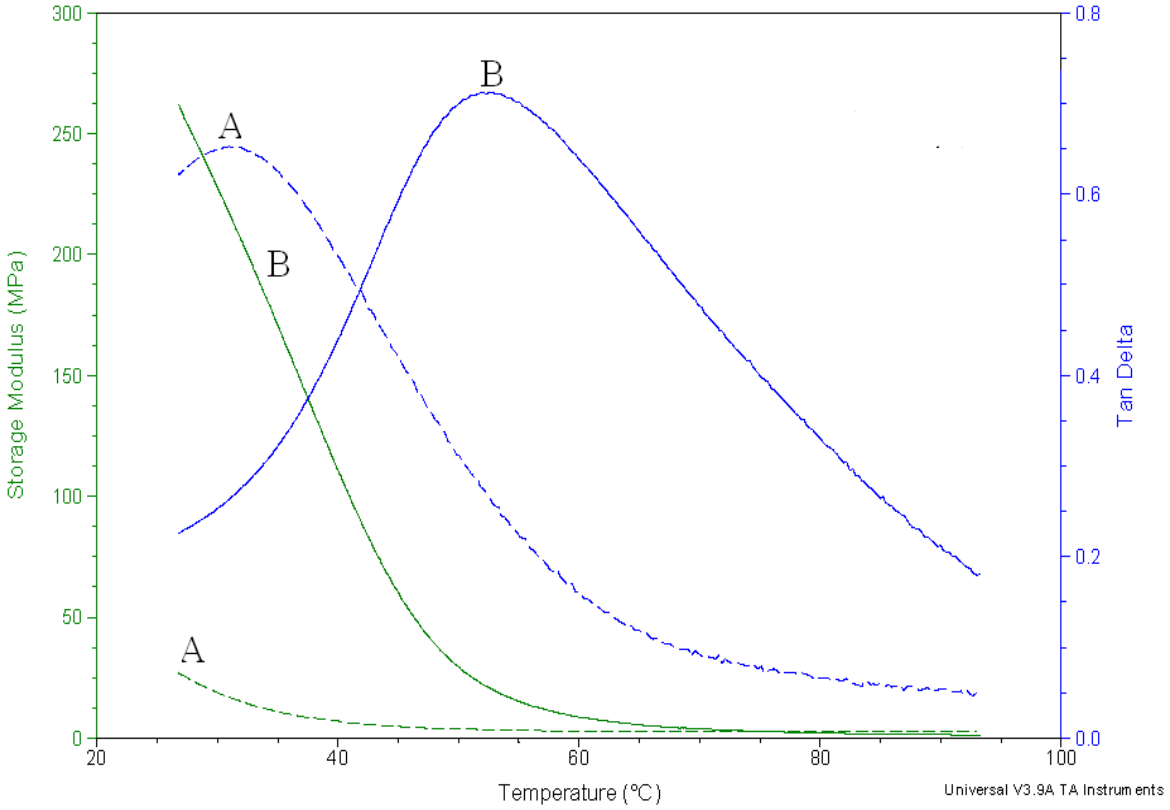


Figure 3.21. Storage modulus and tan δ values of polymers of cod liver oil with (A) 60 per cent and (B) 70 per cent p. ethyl phenol resole.

To prove the cross linked structure of the polymers obtained, swelling ratios were measured in CH_2Cl_2. It was found that when the amounts of the phenolic resin increased to 40 per cent, the swelling ratios of the products were decreased (Figure 3. 22). Another linear relationship was also found between the length of the p. substituent of the phenolic resins and swelling amount. It was found that when the number of the carbon atoms of the alkyl group of the phenolic resin was high, the swelling ratio of the polymer was also high. All polymers reach a plate after 3 hours. And the highest swelling ratio was observed in *p. tertiary* octyl phenyl resole (Figure 3.23).

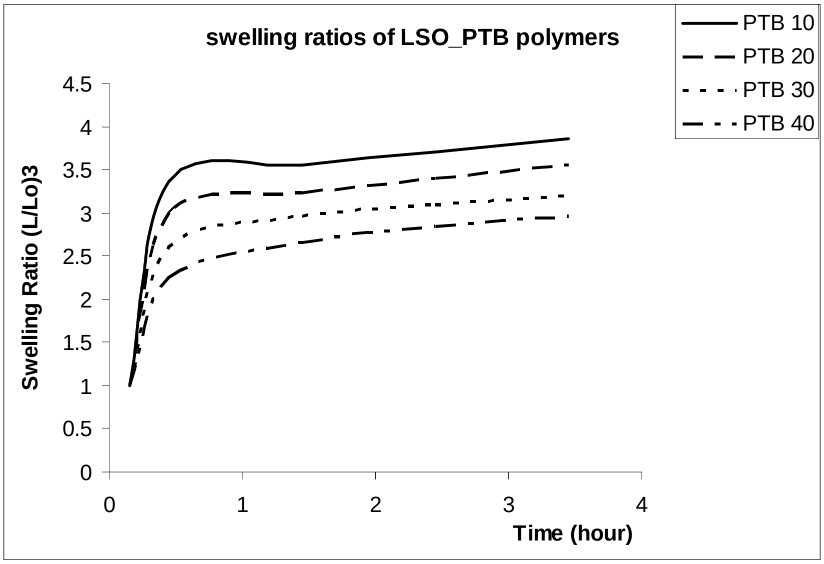


Figure 3.22. Swelling ratios of polymers which composed of linseed oil and different amount of p. tertiary butyl phenol (PTB) resoles

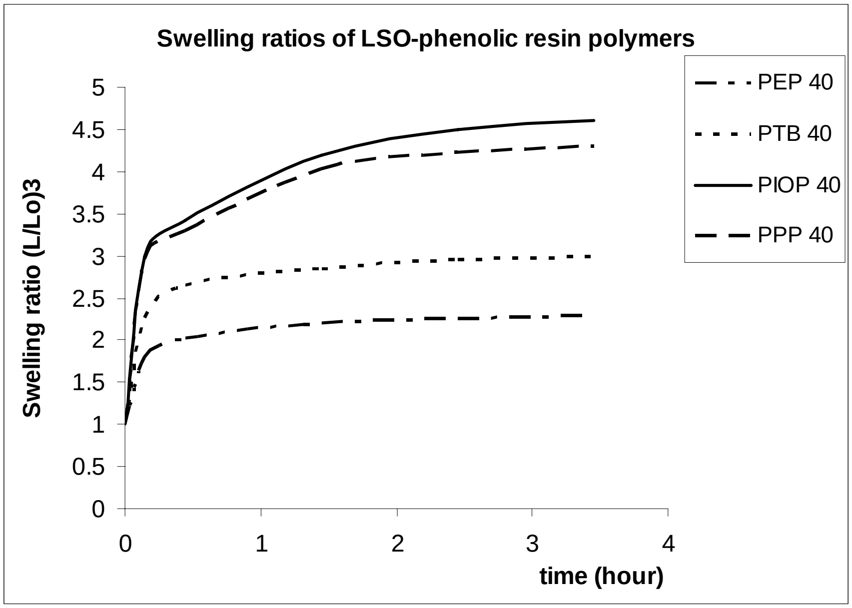


Figure 3.23. Swelling ratios of the polymers which composed of linseed oil and different type of oil soluble resoles.

<u>3.3.3.2. Thermal properties of polymers synthesized.</u> DSC curves of linseed oil polymer made with 60 per cent of the p. tertiary butyl phenol resole showed a melting peak at 50 °C ant a Tg at -50 °C. Pure cured p. tertiary butyl phenol resole showed a very similar melting behavior at 120 °C. The area under curve was smaller than the linseed oil polymer (Figure 3.24).

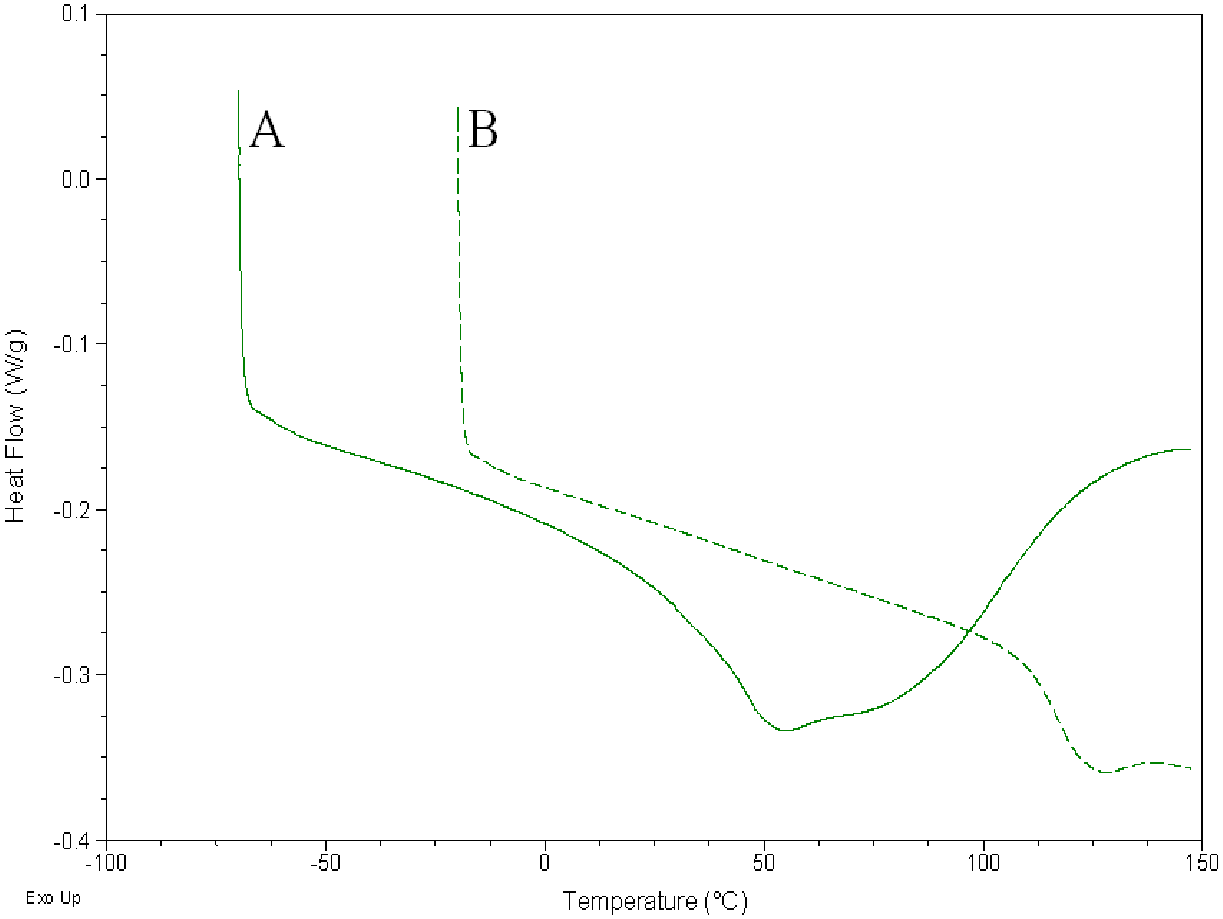


Figure 3. 24. DSC traces of (A) cured 40 per centp. tertiary butyl resole-60per cent linseed oil mixture and (B) pure p. tertiary butyl resole

TGA instrument also gave valuable information about thermal stability of the synthesized polymers. Resoles showed similar degradation curves. The most thermally stable resole was p. phenyl phenol resole. Almost all resoles showed 3 degradation platos in their TGA curve. These platos indicated three segmental lost. When the resoles were polymerized with linseed oil, thermal stability of the resultant polymers were improved. The highest thermal stability was observed at *p.* ethyl phenol resole –linseed polymers. This result was also surprising because thermal stability of the *p.* phenyl phenol resole and linseed oil polymers were expected to be highest due to the heat resistance properties of the aromatic compounds.

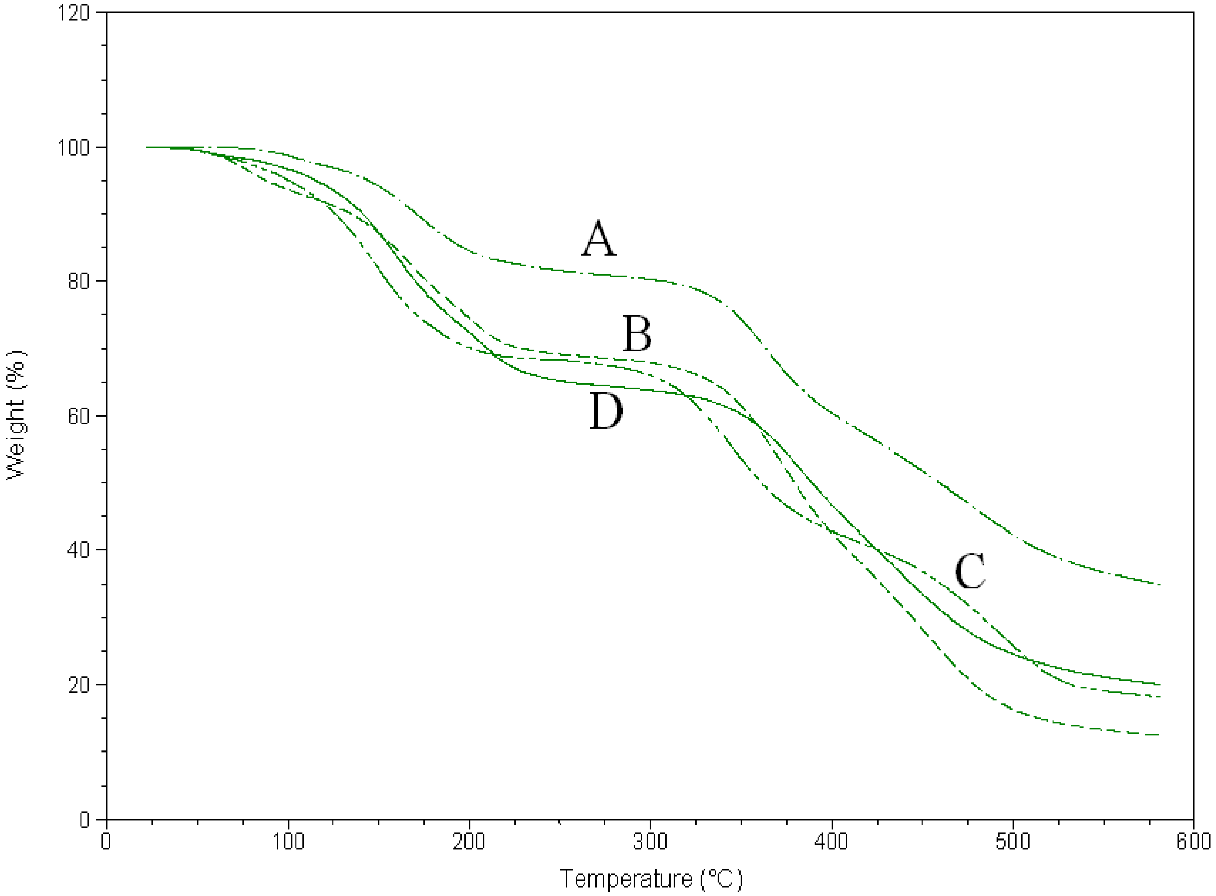


Figure 3.25. TGA curves of the synthesized resoles (A) par phenyl phenol, (B) p tertiary octyl phenol, (C) p. tertiesy butyl phenol, (D) p. ethyl phenol resoles.

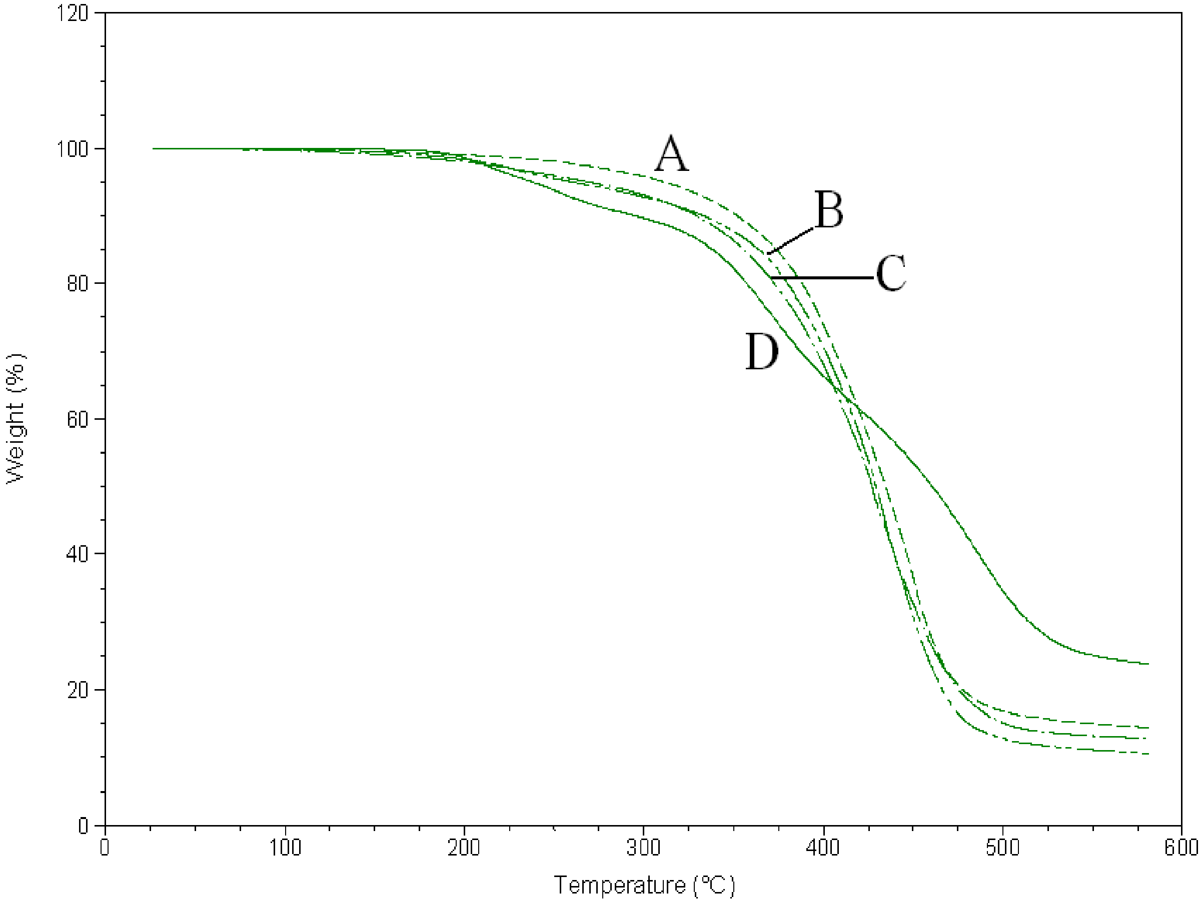


Figure 3.26. TGA curves of linseed oil polymers with (A) p ethyl phenol, (B) p phenyl phenol, (C) p tertiary octyl phenol, (D) p tertiary butyl phenol resoles.

3.3. Synthesis and polymerization *of p. tertiary* butyl furfural resin and AESO

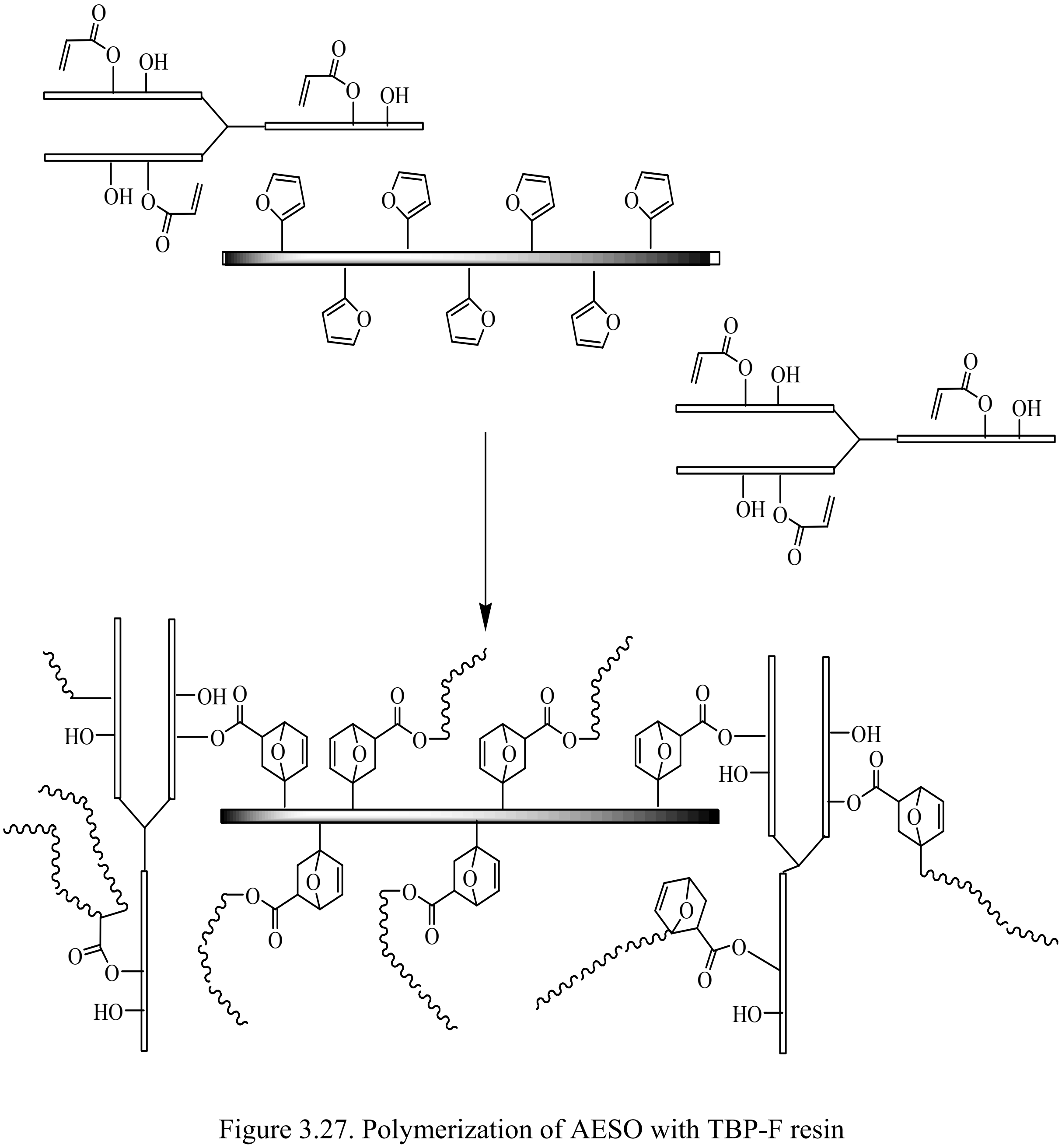


Figure 3.27. Polymerization of AESO with TBP-F resin

3.3.1. Characterization of *p. tertiary* butyl phenol furfural resin and AESO:

Characterization of the TBP-F resins was performed with IR and ^{1} H NMR spectroscopy techniques. IR spectra showed a broad peak at 3370 cm^{-1} due to OH functionality. Peaks at 2960, 2900 and 2860 cm^{-1} was belongs to aliphatic C-H stretching of the butyl group. A triplet was observed at 1270, 1229, and 1180cm^{-1} C-O stretching of the furan ring (Figure 3.28). ^{1}H NMR spectrum showed -CH_3 protons of the p. tertiary butyl group at 1 ppm. OH proton was observed at 4 ppm as a broad peak. Protons of the furan moiety were observed at 5.8, 6.4 and 6.8 ppm. Aromatic protons of the phenyl ring were observed at 7 ppm (Figure 3.29).

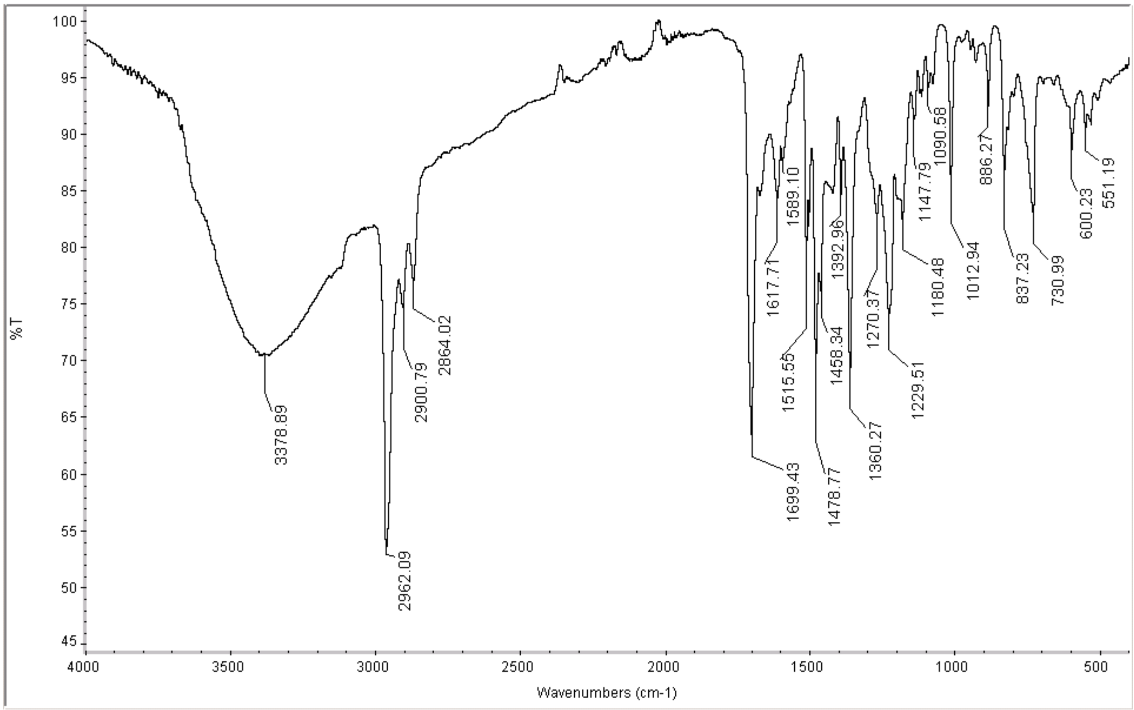


Figure 3.28. IR spectrum of TBP-F resin.

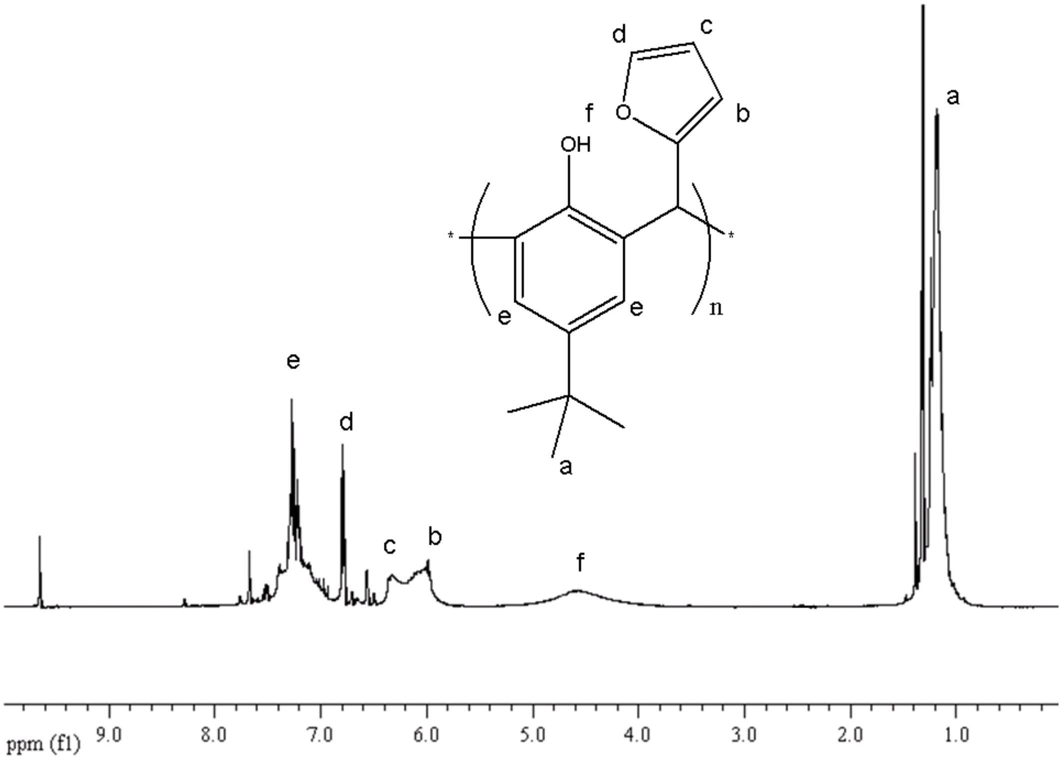


Figure 3.29. ^{1}H NMR spectrum of TBP-F resin.

TBP-F resins synthesized by method A was used in the study. In this method, *p. tertiary* butyl phenol and furfural was polymerized with the presence of NaOH catalyst. Polymerization was performed by azeotropic distillation of toluene for two hours. The GPC results indicated that the number of the repeating unit was 7 and PDI was 1.08. TBP-F resin was a very hard and brittle solid and was not soluble in AESO. Thus, both of the monomers were mixed in the minimum amount of $CHCl_3$ and $FeCl_3$ solution in $CHCl_3$ was added to the mixture. Due to the presence of phenol, color of the mixture turned to greenish-blue. $CHCl_3$ was evaporated at 50-60 ^oC. At low temperature, Diels-Alder reaction was not observed. After solvent evaporation, a black mass obtained. Heating this homogenous mixture at 100 ^oC under N_2 atmosphere gave a rubbery material in 1 hour. When the material was cooled to room temperature, it hardened. The cross linking reaction probably occurred via Diels Alder pathway. The product got harder and harder after repeated heating and cooling cycles and the hardness reached at a plato after ten cycles. If the product was the Ene product, we would not expect reversal of the reaction.

3.3.2. Mechanical properties of the polmers synthesized :

The product is a though and flexible material and had a maximum tensile strength of 60 N/ mm^2 at break. After ten heating cycles maximum tensile strength was reached to 250 N/ mm^2. When the same amount of total heating time was applied to material for one cycle highest tensile strength was measured as 150 N/mm^2 (Figure 3.30). This result suggest that a series of forward and retro Diels-Alder reactions are taking place.

DMA is another technique and gives better information about the mechanical properties of the synthesized material. The DMA plot of the polymers is shown in Figure 3.31. Material that was heated and cooled for 10 times showed a storage modulus at around 1 GPa. This value is close to the values of industrial polymers and is a good result for a plant oil based polymers synthesized by our research groups and by other groups. Neat polymer showed a Tan δ maximum at 35 ^{o}C while the material which was heated 10 times showed a maximum at 54 ^{o}C. This result could be an evidence of the increasing the cross linking and non perfect retro Diels-Alder reaction. Another information was obtained from the heights of the Tan δ peaks. The tan δ values reached maximum values and it could be said that material showed the most viscous character. After ten heating and cooling cycle, the value of maximum of tan δ peak was the lowest and this could be attributed to the increasing elastic character of the polymer.

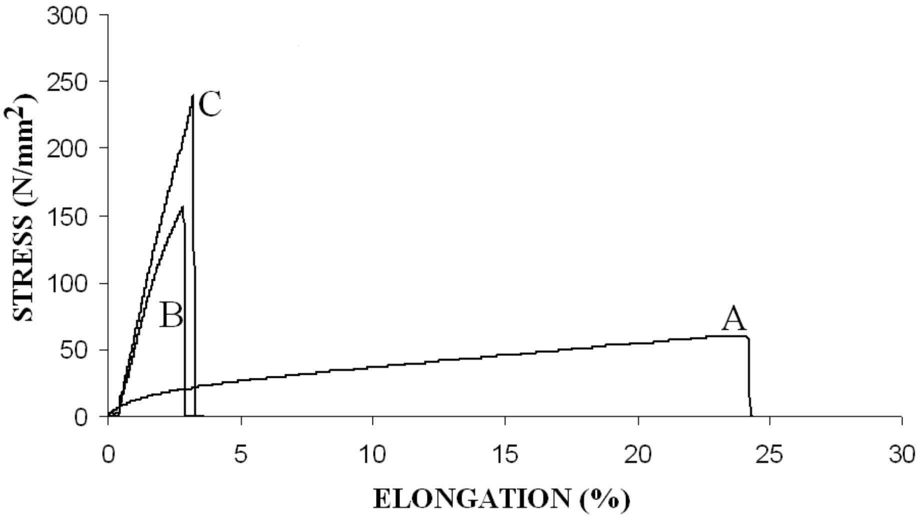


Figure 3.30. Strees-Elongation graphs of (A) TBP-F-AESO polymer (B) TBP-F-AESO after 300 minutes heat treatment at 140 °C (C) TBP-F-AESO resin after ten heating and cooling cycle.

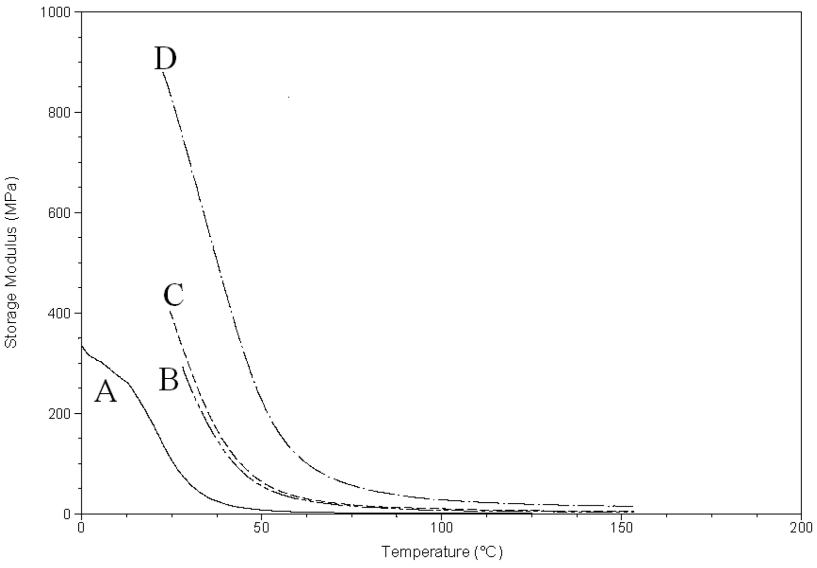


Figure 3.31. Storage modulus of TBP-F-AESO polymers which exposed to different heat treatments (A) thermoset resin without heat treatment (B) thermoset polymer which heated for 300 minutes (C) thermoset resin exposed to 5 heating and re cooling (D) thermoset resin exposed to 10 heating and re cooling.

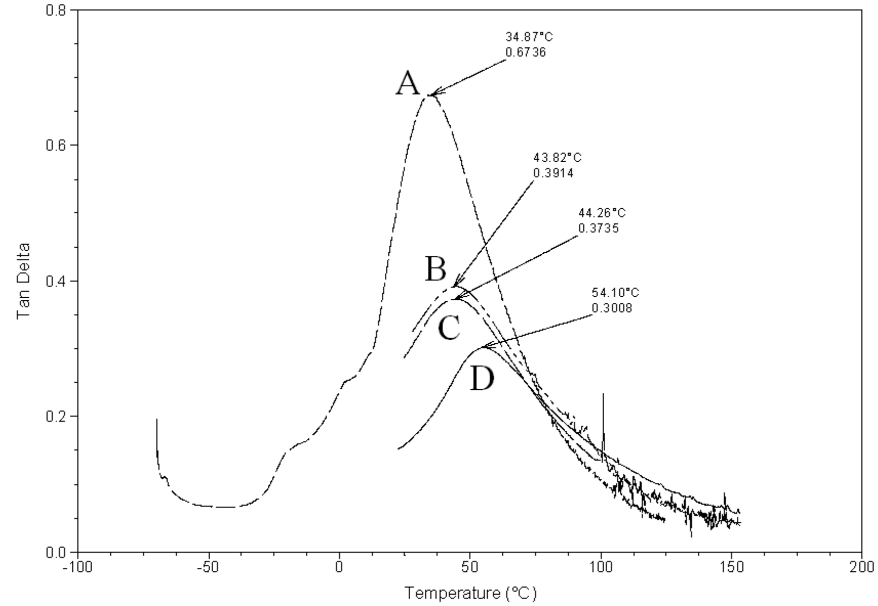


Figure 3.32. Tan δ values of TBP-F-AESO polymers which exposed to different heat treatments (A)thermoset resin without heat treatment (B) thermoset polymer which heated for 300 minutes (C) thermoset resin exposed to 5 heating and re cooling (D) thermoset resin exposed to 10 heating and re cooling.

3.3.3. Thermal properties of the polymers synthesized:

TGA is the one of the most versatile instrument to clarify the thermal behavior of the polymeric materials. In the Figure 3.33 TGA curves show that the *p tertiary* butyl phenol furfural resin showed 3 platos which means that 3 segments were lost when the heat was applied to the material. When the furfural resin was polymerized with acrylated epoxidized soybean oil, the shape of the curves shifted to higher temperatures. There was almost no difference between the curves of E and D (Figures 3.33, and 34). Derivative TGA curves also showed similar result. Curves of the heated and cooled samples showed maxima at higher temperatures which imply the non perfect Diels-Alder reaction. If the retro Diels-Alder reaction went in 100 per cent yield peaks of the resin B should not change.

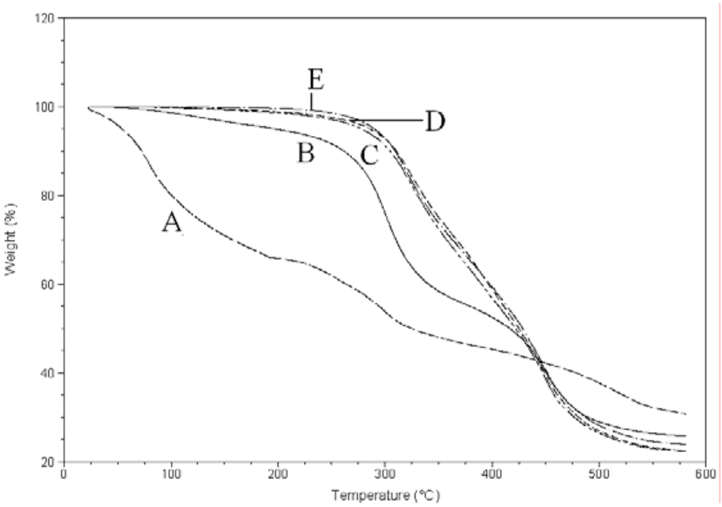


Figure 3.33. TGA graphs of TBP-F-AESO polymers which exposed to different heat treatments (A) TBP-F resin (B)thermoset resin without heat treatment (C) thermoset polymer which heated for 300 minutes (D) thermoset resin exposed to 5 heating and re cooling (E) thermoset resin exposed to 10 heating and re cooling

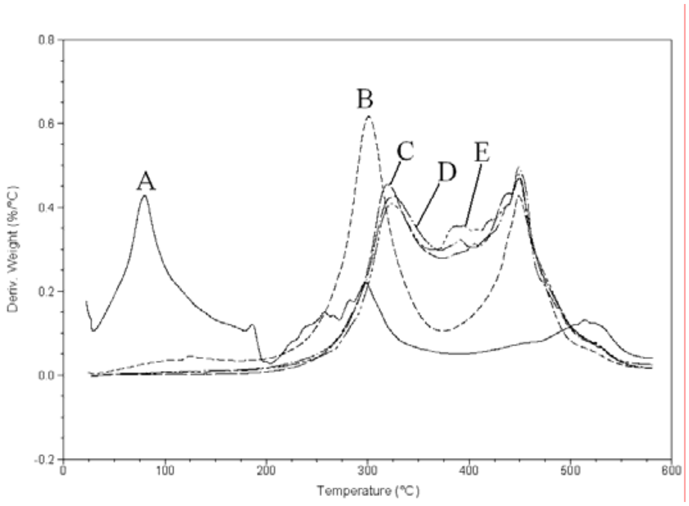


Figure 3.34. Derivative TGA graphs of TBP-F-AESO polymers which exposed to different heat treatments (A) TBP-F resin (B) thermoset resin without heat treatment (C) thermoset polymer which heated for 300 minutes (D) thermoset resin exposed to 5 heating and re cooling (E) thermoset resin exposed to 10 heating and re cooling.

3.4. Synthesis of ABMO and ACSO

3.41.Allylic Bromination of Methyl Oleate (ABMO):

Depending on the purity of the NBS and methyl oleate the infrared and ^{1}H NMR data show the following. IR spectrum: (=CH) 3008 cm^{-1}, (C-H) 2928, 2853 cm^{-1}, (C=C cis) 1659 cm^{-1}, (CH_2 scissoring) 1463, 1435 cm^{-1} (C-O) 1247, 1196, 1170 cm^{-1}, (CH=CH-CHBr) 965 cm^{-1}, (C-H) 723 cm^{-1} (C-Br) 646 cm^{-1} (Figure3.35.). ^{1}H NMR: ($-C\mathbf{H_3}$)0.9 ppm, ($-C\mathbf{H_2}-$) 1.2-1.3 p pm, ($-C\mathbf{H_2}-CH_2-COOCH_3$) 1.6-1.7ppm , ($CH=CH-CHBr-C\mathbf{H_2}$) 1.85 ppm, ($-C\mathbf{H_2}-CHBr-CH=CH-CHBr-C\mathbf{H_2}-$) 1.95 ppm, ($CH=CH-C\mathbf{H_2}-$) 2 ppm, ($CHBr-C\mathbf{H_2}-$) 2.15 ppm, ($-C\mathbf{H_2}-COOCH_3$) a triplet at 2.25-2.3 ppm, ($-OC\mathbf{H_3}$) singlet at 3.65-3.7 ($-C\mathbf{H}Br-$) 4.2 ppm (simple alkyl bromide proton), ($-CH=CH-C\mathbf{H}Br-$) 4.4 ppm (mono allylic bromide proton), ($-C\mathbf{H}Br-CH=CH-C\mathbf{H}Br$) 4.8 ppm (double allylic bromide protons), ($-CH=C\mathbf{H}-CHBr$) 5.4 ppm, ($-C\mathbf{H}=CH-CHBr$) 5.6 ppm, ($-CHBr-C\mathbf{H}=C\mathbf{H}-CHBr$) 5.8 ppm. The results were compatible with literature results. By using ^{1}H NMR, it was found that 80 per cent of methyl oleate was brominated at allylic positions. The rest of the product composed of di allylic bromines, normal aliphatic mono and di bromides (10 per cent) and around 10 per cent of the product was non-reactive saturated methyl stearate and palmytate that were present in the starting material (Figure 3.36). The crude product was purified by column chromatography to give 80 per cent yield of allylicly brominated methyl oleate

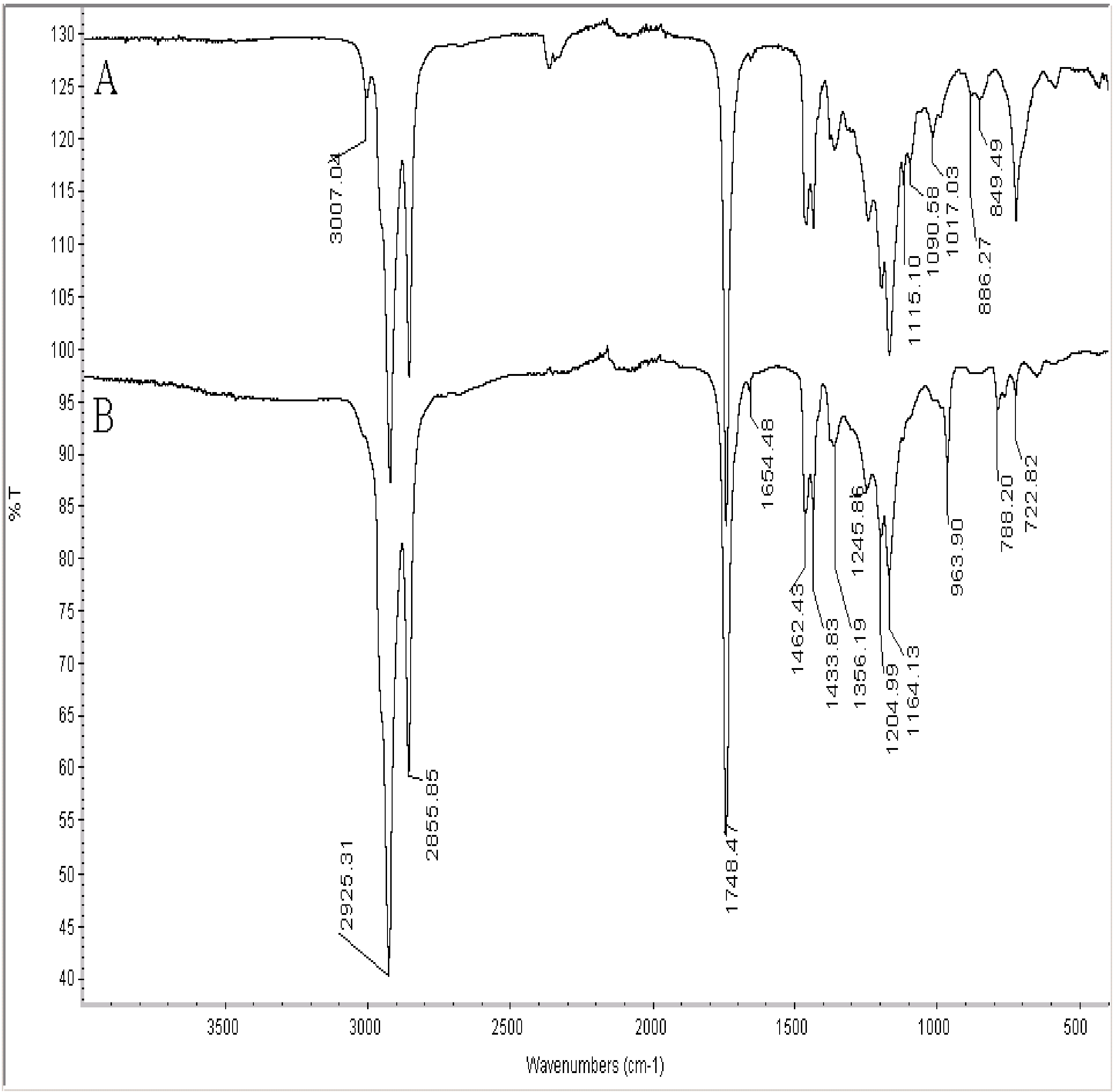


Figure 3.35. IR spectra of (A) methyl oleate and (B) allylic brominated methyl oleate

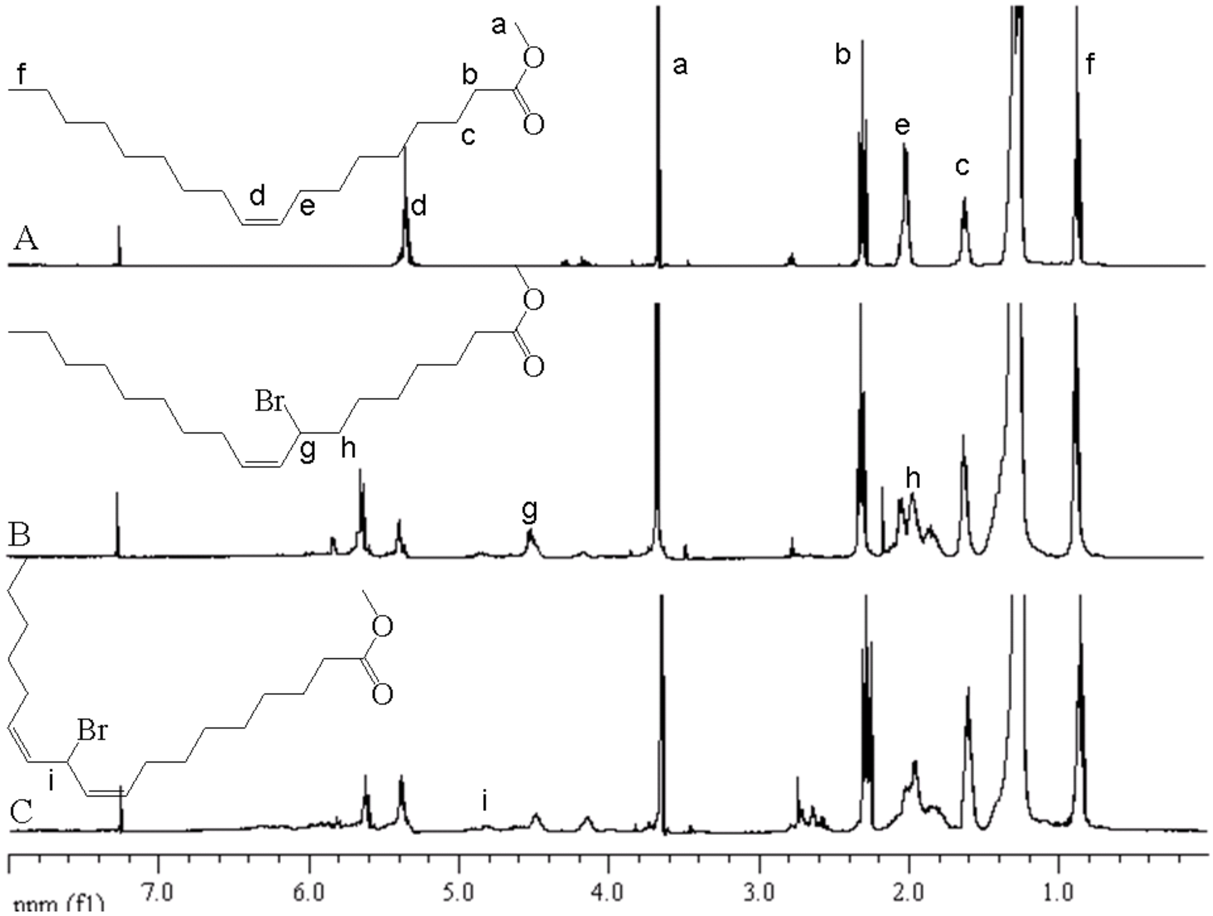


Figure 3.36. ^{1}H NMR's of (A) methyl oleate (B) allylic brominated methyl oleate and (C) allylic brominated soy oil metyl esters (mainly methyl linoleate).

3.4.2. Allylic Bromination of Soybean Oil (ABSO):

The results for the allylic bromination of the soybean oil was the same with the methyl oleate case. IR spectrum showed (=CH) 3010 cm^{-1}, (C-H) 2925,2853 cm^{-1}, (C=O of ester) 1745 cm^{-1}, (C=C cis) 1654 cm^{-1}, (C-O) triplet at 1235,1155,1102 cm^{-1} peaks are characteristic for triglycerides, (CH=CH-CHBr) 967 cm^{-1}, (C-H) 725 cm^{-1} (C-Br)640 cm^{-1} (Figure 3.37.). ^{1}H NMR: $(-C\mathbf{H_3})$ 0.8 ppm,$(-CH=CH-CH_2-C\mathbf{H_3})$ 1 ppm (triplet), $(-CH_2-)$ 1.2-1.4 ppm. $(-C\mathbf{H_2}-CH_2-COOCH_2-)$ 1.6 ppm (β to carbonyl group), $(-CH=CH-C\mathbf{H_2}-)$ 2 ppm, $(-C\mathbf{H_2}-COOCH_2-)$ 2.25 ppm (α to carbonyl group), $(-CH=CH-C\mathbf{H_2}-CH=CH-)$ 2.75 ppm (double allylic position), O-C**H**$_2$- 4.1 and 4.3 as a multiplet (glycerol protons), (-CH=CH-C**H**Br-) 4.5 broad, (-CH=CH-C**H**Br-CH=CH-) 4.8 ppm. (-OCH$_2$-C**H**O-CH$_2$O-) 5.25 ppm (center proton of glycerol), (-C**H**=C**H**-CH$_2$-CH=CH-CHBr-) 5.4 ppm, (-CH=CH-CH$_2$-CH=C**H**-CHBr-) 5.6 ppm, (-CH=C**H**-CHBr-C**H**=CH-) 5.8 ppm. (Figure 3.38)

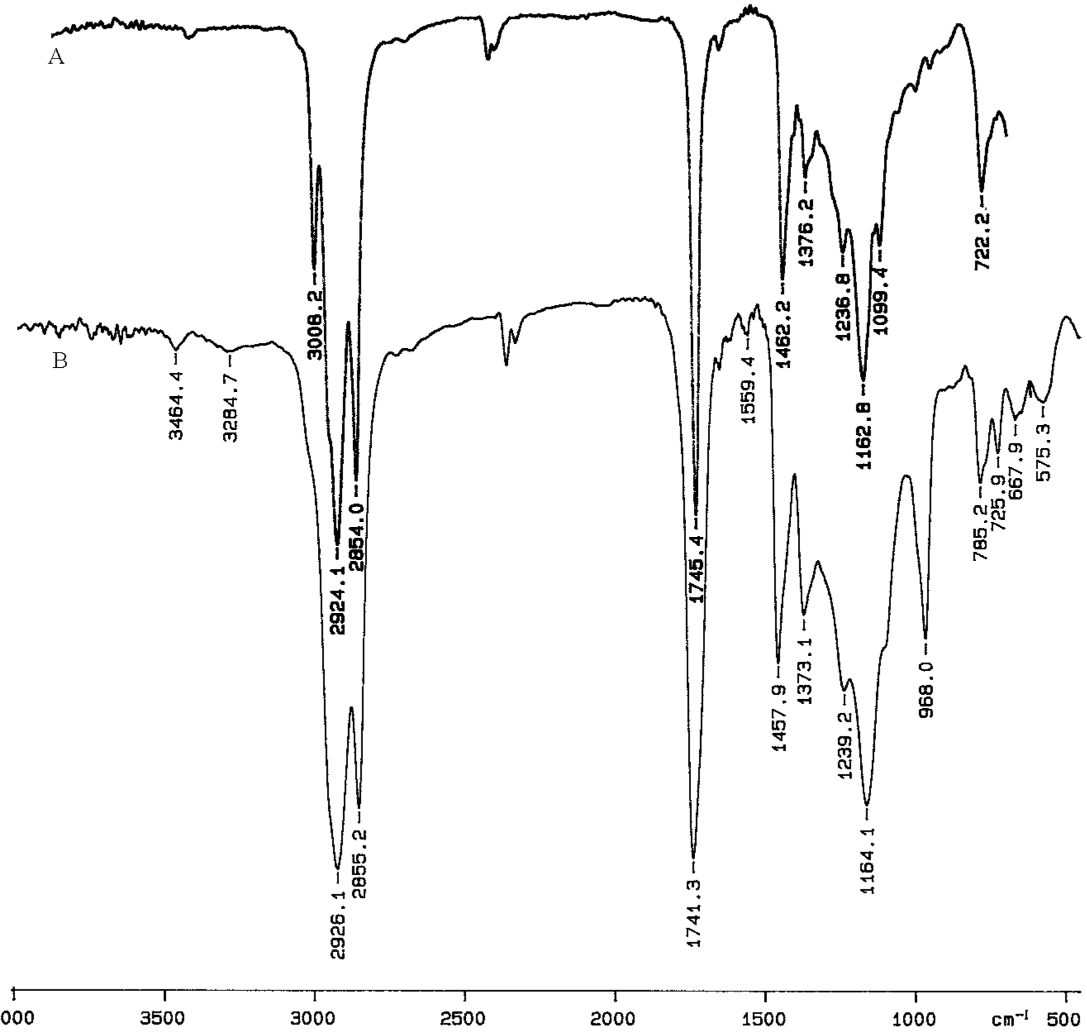


Figure 3. 37. IR Spectra of (A) soybean oil and (B) allylic brominated soybean oil.

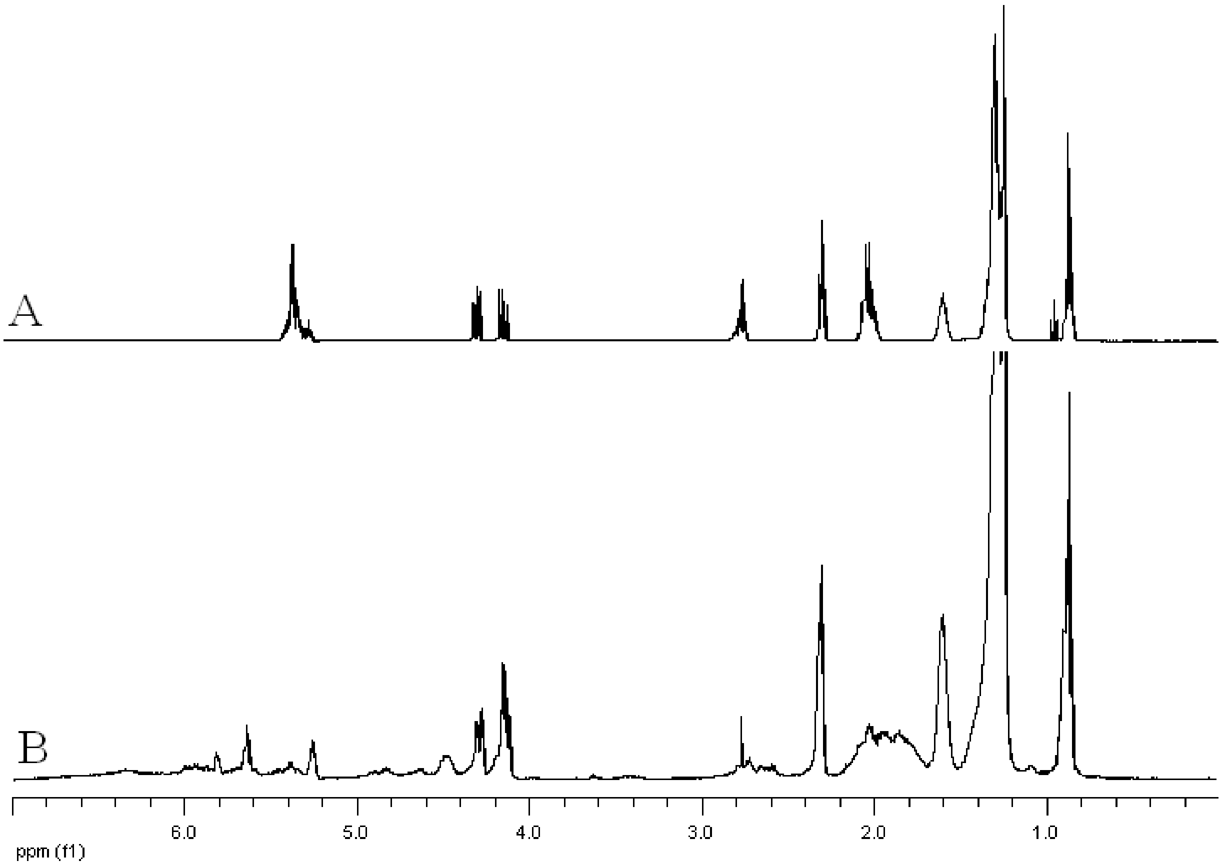


Figure 3.38. ^{1}HNMR Spectra of (A) soybean oil and (B) allylic brominated soybean oil.

3.5. Synthesis and polymerization of soy oil based isocyanates and isothiocyanates

3.5.1. Synthesis of isocyanated soybean oil (SONCO):

In the literature no reference was found on the synthesis of isocyanate containing plant oil triglycerides. Synthesis of iodo isocyanates of fatty acid methyl esters has been reported [95], but no reference was found on the synthesis of the soybean oil based isocyanate In this work allylic isocyanates were synthesized in 60-70 per cent yields (Figure 3.39).

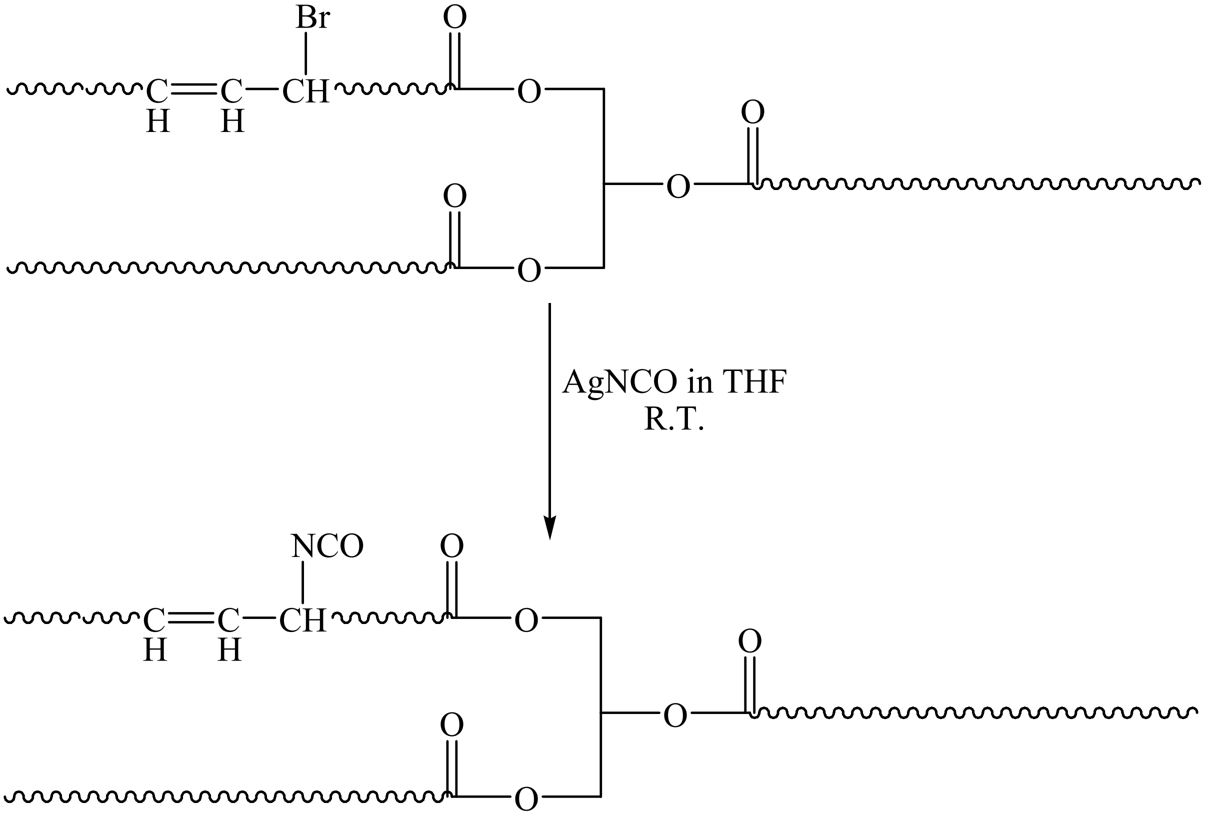


Figure 3.39. Schematic synthesis of isocyanated soybean oil (SONCO)
(positional isomers are not shown).

Yields increased with the increasing amount of AgNCO. This was easily determined by ^{1}H NMR by following the allylic proton signal. When equimolar AgNCO and ABSO were reacted the yield was almost 30 per cent. If 3 equivalent of AgNCO was used, the yield increased to 70 per cent. The yields were calculated by simply measuring the integration ratios between the peaks at 3.9 ppm -C**H**-NCO and peaks at 2.25 ppm (α to carbonyl peaks) in the ^{1}H NMR spectrum of the products (Figure 3.41). Substitution of bromine with isocyanate was easily monitored by observing the changes of the peaks of allylic brominated soybean oil in the IR spectrum. A peak which appeared around 965 cm^{-1} was attributed to allylic -HC=CHC**H**Br stretching and a peak around 640 cm^{-1} is attributed to C-Br deformation. When isocyanate addition occurred, a new peak around 2250 cm^{-1} was observed and the allylic bromine peak at 965 shifted to 970 cm^{-1} (Figure 3.40). Compared with other isocyanate synthesis methods, allylic bromination and the subsequent substitution reactions were simple reactions. Allylic bromination was completed in 4-5 h and the substitution reaction was completed in 4 h. Purification was not required after the synthesis. Although the reactivity ratios were different, the main product and the side products were all alkyl halides and they were readily reacted with AgNCO. The average number of isocyanate groups per triglyceride was found to be 2.1 by measuring the intensity ratio of the geminal H on the same C atom as the NCO group, to the H of carbon α to ester group. Average functionality of typical commercial polyisocyanates is around 2-2.8. The synthesis, however, suffers from the use of an expensive reagent, AgNCO. Unfortunately AgNCO is unique for this reaction because Ag^+ modifies the nature of the intermediate. In the presence of Ag^+ ion OCN^- attacks through the nitrogen end instead of the oxygen end [96]. Isocyanates are sensitive to water. Thus all app.tus should be protected from humidity during the synthesis.

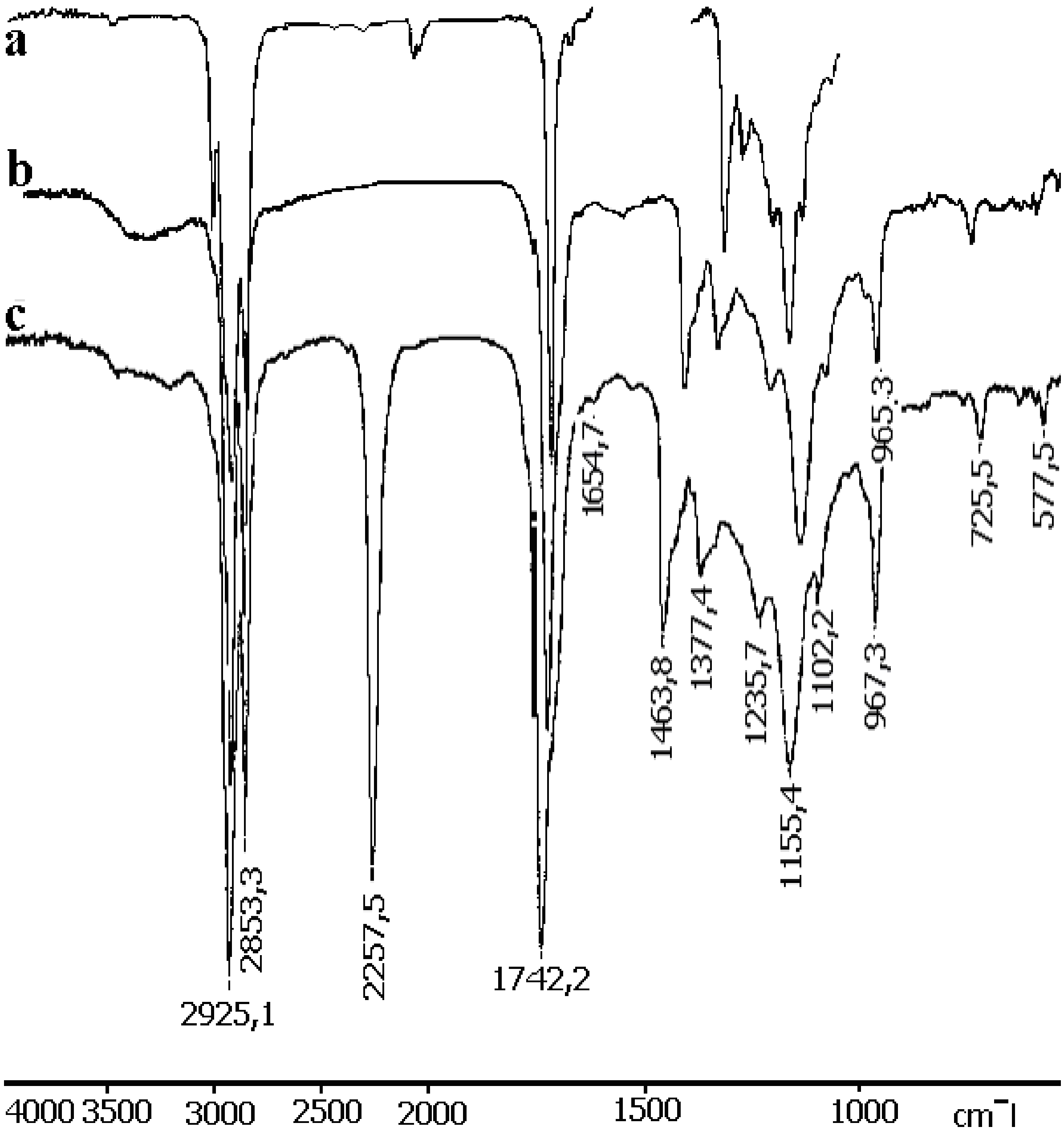


Figure 3.40. IR spectra of a-) Soybean oil,b-) Allylic brominated soybean oil, c-) Isocyanated soybean oil (SONCO).

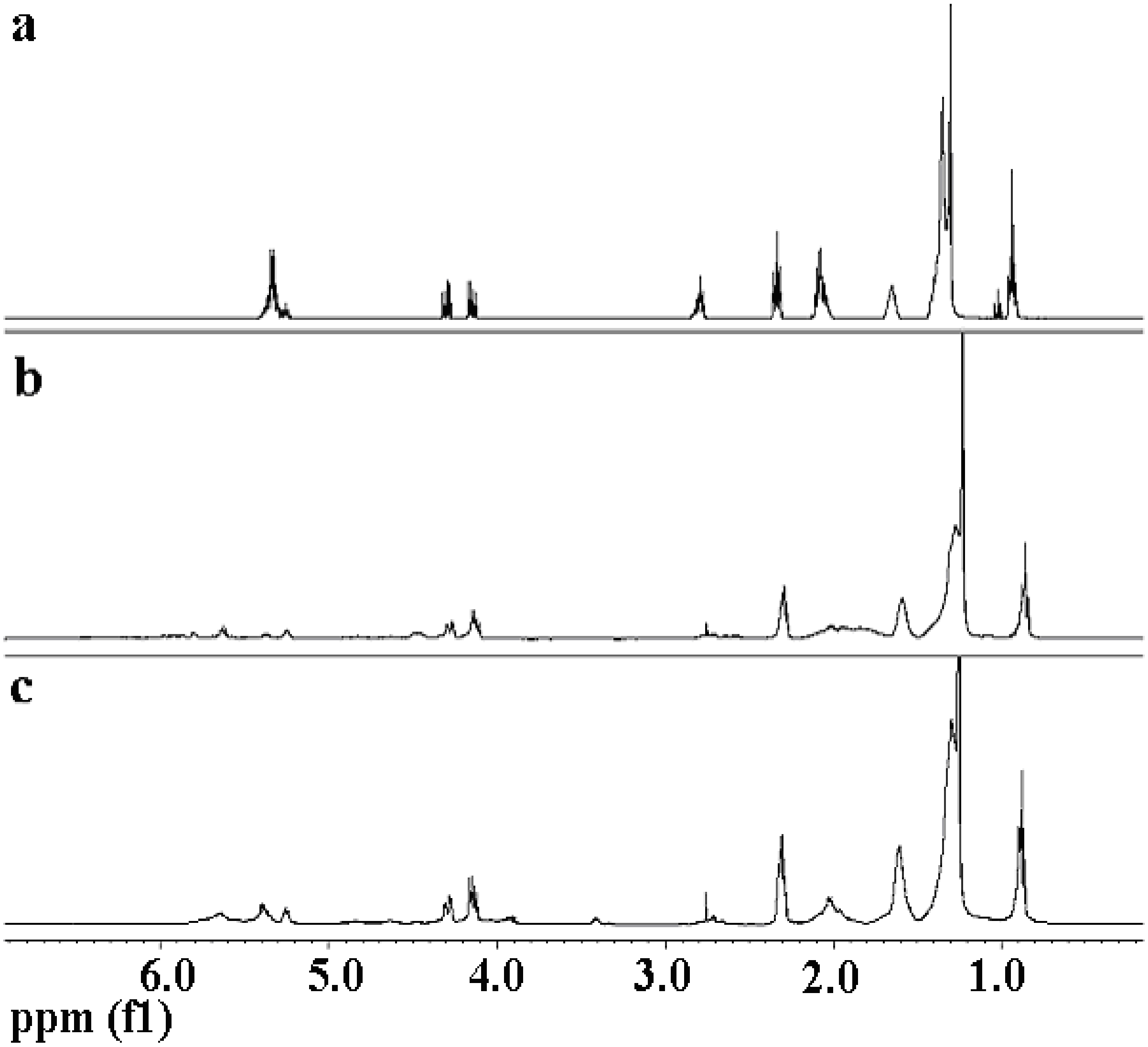


Figure 3.41. 1HNMR spectrum of a-) Soybean oil b-) Allylic brominated soybean oil c-) Isocyanated soybean oil (SONCO)

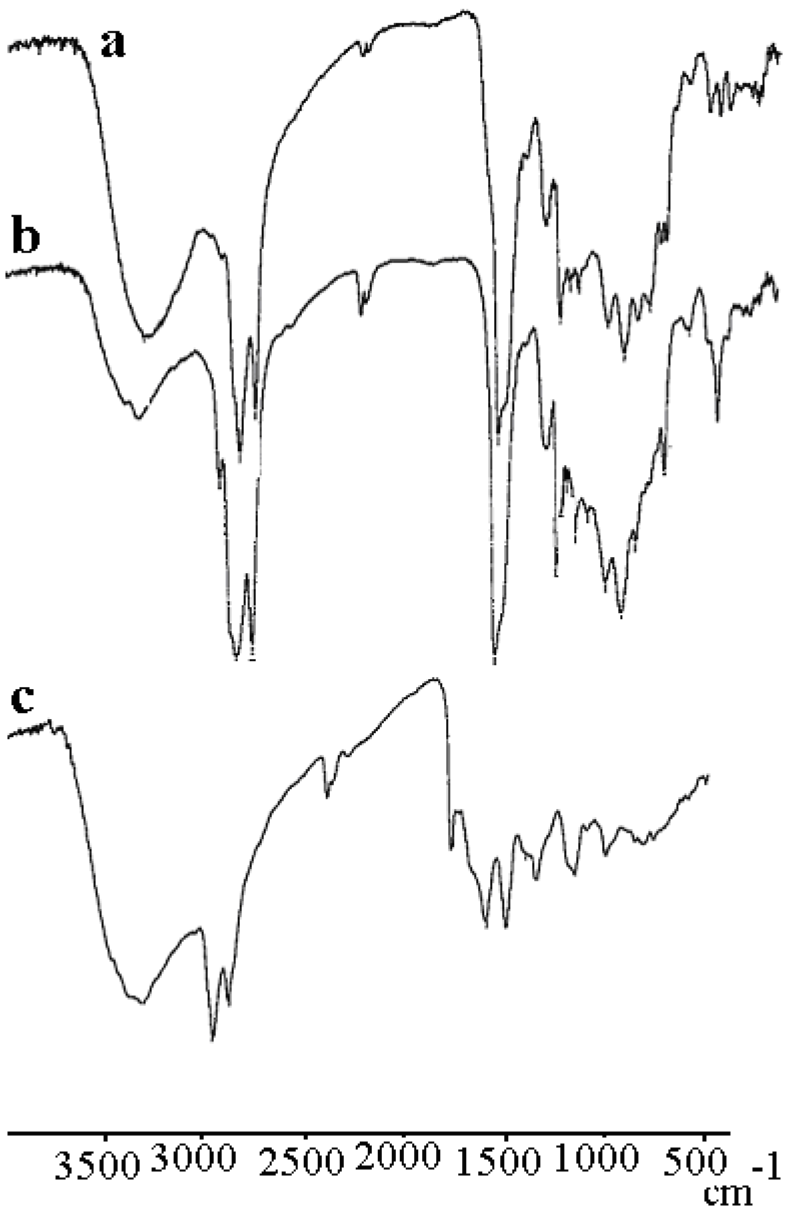


Figure 3.42. IR spectra of a-) glycerol polyurethane b-) castor oil polyurethane c-) TETA polyurea of SONCO.

3.5.1.1 Synthesis and properties of SONCO based polymers. Polymerization of SONCO with glycerol and castor oil was completed in 5 h at 120 °C. SONCO reacted very fast with triethylene tetraamine (TETA) even at room temperature. Thus the gel time of the mixture was too short to allow the production of samples for mechanical testing. The IR spectrum of polyurethanes and TETA polyurea are shown in the Figure 3.42. At 1742 cm $^{-1}$ broad carbonyl peaks are unique for polyurethanes and at 1530 cm^{-1} a urethane N-H deformation is observed. There is a peak observed at 1690 cm^{-1} due to the carbonyl group of the polyurea. The peak at the 1590 cm^{-1} belongs to the C-N stretching vibration of the polyurea.

Physical properties of commercial polyurethanes may vary depending on the application areas. Polyurethanes are generally copolymers of (AB)n type consisting of an alternating block of relatively long, flexible “soft segment” and another block of highly polar, rather stiff chains or "hard segment." The unique physical and mechanical properties of polyurethanes are determined by their two-phase domain structure. The cohesion energy and hydrogen bonds in hard domains are higher than in soft domains. Hence, the role of hard domains is to improve the mechanical properties such as strength and hardness of the polymer. On the other hand, elasticity is provided mainly by soft segments [97]. Polyurethanes that are synthesized in this work have aliphatic and soft segments only. Thus higher elasticity and lower strength is expected.

The polyurethanes synthesized had an E-modulus around 50 kPa and tensile strength around 0.01 N/ mm^2 (100 kPa). The tensile strength of glycerol polyurethane was higher than castor oil polyurethane. Although both materials had low ultimate tensile strength and modulus, they showed excellent elongation and recovery. The elongation of castor oil polyurethane was higher than glycerol polyurethane. Strain at break was about 353 per cent for glycerol polyurethane and 410 per cent for castor oil polyurethane. This is a typical rubbery behavior (Figure 3.43).

The swelling behavior of the products in CH_2Cl_2 was determined by a traveling microscope. The samples were put in a closed container and the experiment was continued until the solvent uptake ceased. The swelling ratio (q) was expressed as:

$$q = (V/V_0) = (L/L_0)^3$$

where V_0 and V are the volumes, and L_0 and L are the lengths of the unswollen and swollen polymer samples, respectively. Figure 11 shows the swelling behavior of the samples. It was very interesting that although glycerol polyurethane had higher modulus than castor oil polyurethane, swelling rate of glycerol polyurethane was higher than castor oil polyurethane in CH_2Cl_2. The equilibrium swelling ratio was maximum for the castor oil polyurethane (Figure 3.44).

Thermal properties of the materials were monitored by DSC. DSC curves showed that glycerol urethane showed a Tg at 19 °C. This polymer may be suitable for rigid foam applications. Castor oil polyurethane showed a Tg at –43 °C and 36 °C which agrees with the rubbery behavior of this polymer. Commercial polyurethanes generally have an average Tg around -20 °C to room temperature [84]. TETA polyurea showed a Tg at 31 °C (Figure 3.45).

For the evaluation of the thermal stability TGA is the most favored technique. Due to the urethane and urea linkages, polyurethanes and polyureas have low thermal stability [84]. The thermal stabilities of the polymers synthesized in this work were monitored by “Thermal Analyses” Q-50 instrument (Figure 3.46 and 47). TETA polyurea started to decompose at temperatures as low as 50 °C. Polyurethanes were relatively more stable: they started to decompose near 200 °C. 5 per cent of weight lost was observed at 56 °C, 149 °C, and 194 °C for TETA polyurea, glycerol polyurethane and castor oil polyurethane respectively. Glycerol polyurethane gave the highest char yield of 30 per cent. TETA polyurea and castor oil polyurethane gave the similar char yields of 10 per cent under N_2. Main weight loss was observed around 300 °C. Generally, aliphatic urethanes ,similar to those synthesized in this study, have thermal stabilities around 250 °C when both substituents on the urethane group are aryl groups thermal stability drops to around 120 °C [84].

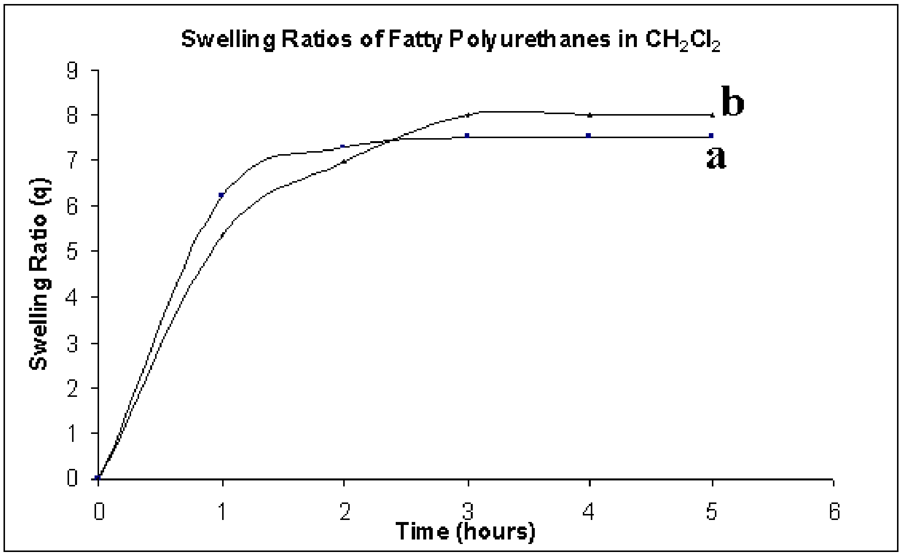


Figure 3.43. Swelling ratios of a-) glycerol polyurethanes and b-) Castor oil Polyurethane

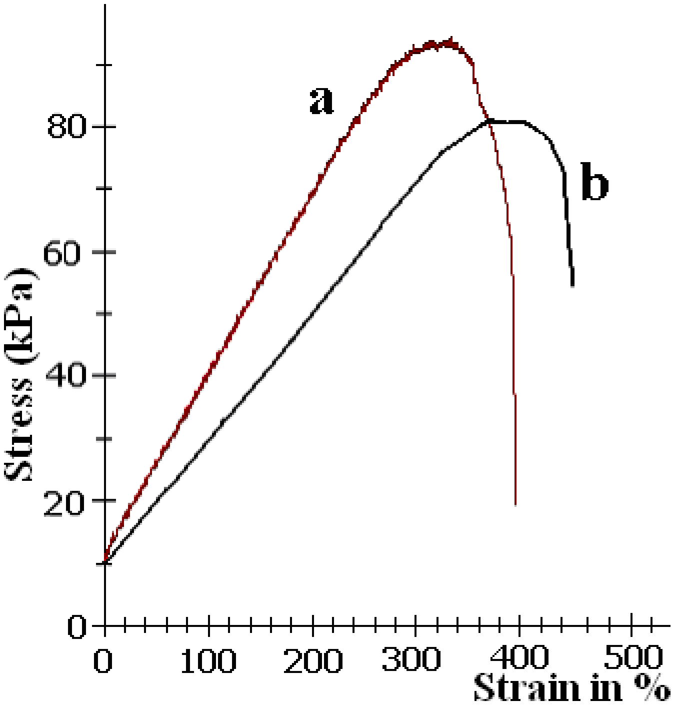


Figure 3.44. Stress-Strain curves of a-) glycerol and b-) castor oil polyurethanes with SONCO.

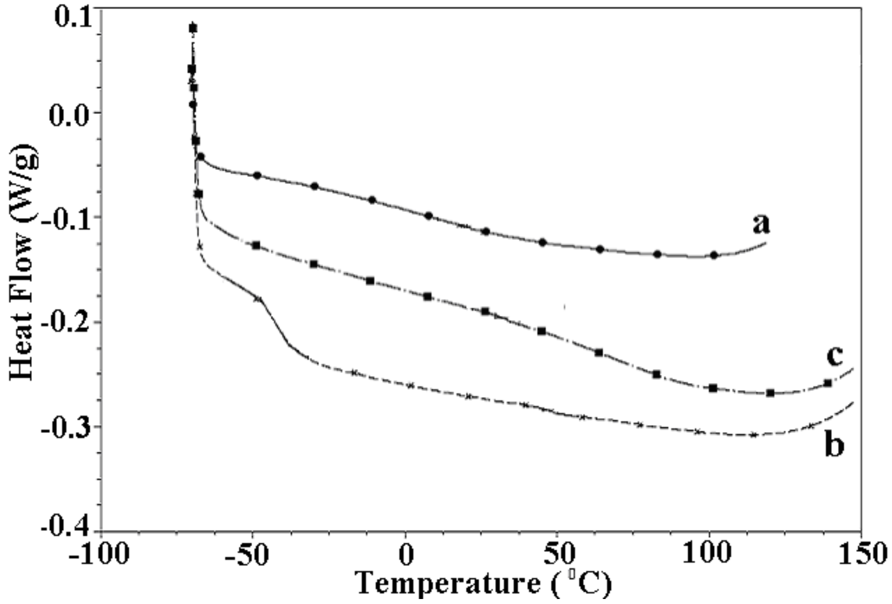


Figure 3.45. DSC traces of a-) glycerol, b-) castor oil polyurethanes and c-) TETA polyurea with SONCO.

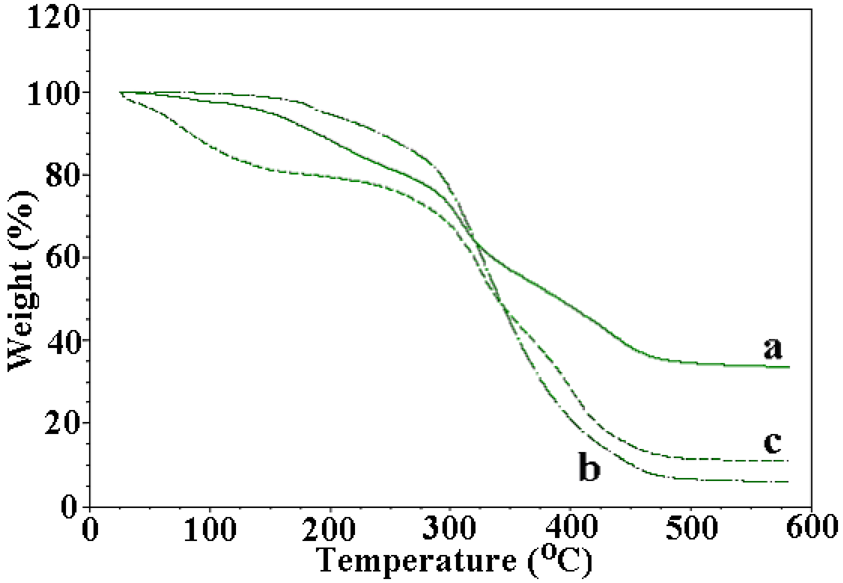


Figure 3.46. TGA traces of a-) glycerol b-) castor oil polyurethanes and c-) TETA polyurea with SONCO.

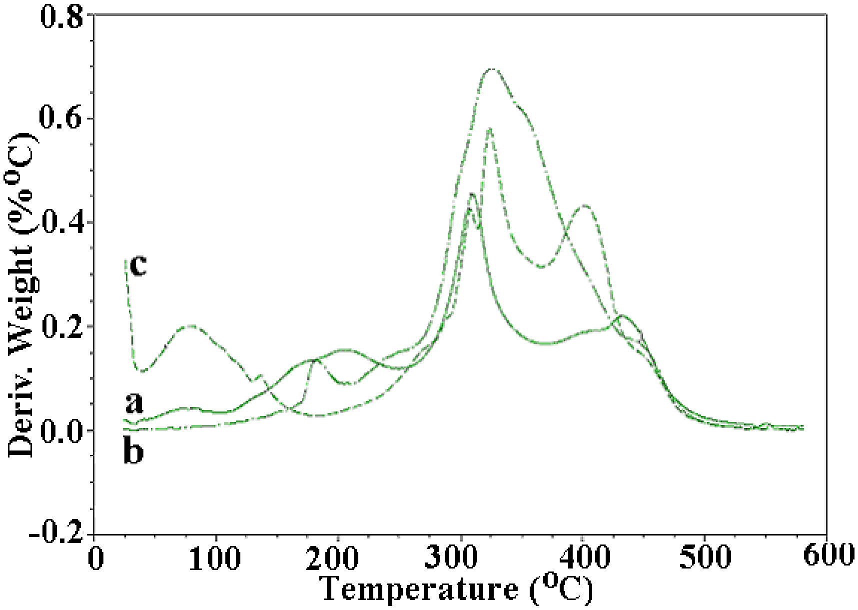


Figure 3.47. Derivative TGA traces of a-) glycerol b-) castor oil polyurethanes and c-) TETA polyurea with SONCO.

3.5.2. Synthesis of soybean oil iodo isocyanate (ISONCO):

Another isocyanate containing compound which was synthesized in this study is soybean oil iodo isocyanate. Synthetic route was simple but required expensive AgOCN reagent.

When an unsaturated compound is reacted with AgOCN and I_2 slurry in THF at -20 °C, corresponding iodo isocyanate is synthesized in one or two hours. Like other unsaturated compounds, soybean oil was reacted with iodine isocyanate complex in THF at 0 °C. Reaction was completed in 2 hours. At the end of the reaction soybean oil iodo isocyanates (ISONCO) was obtained nearly in 100 per cent yield. Isocyanate number per triglyceride was found 3 (Figure 1.8). Theoretically, soybean oil should bind at least 5 mol of iodo isocyanate however it was found that rest of the double bonds were not consumed even by using excess iodine isocyanate reagent. This result is also consistent with literature [98].

Product was characterized by IR and ^{1}H NMR. IR spectrum showed a broad and strong peak at 2258 cm^{-1} due to isocyanate group and a new peak was observed at 577 cm due to C-I bond. Unsaturation of the soybean oil was also observed by peaks at 3006 and 1635 cm^{-1}. When reactions were repeated at excess amount of iodine isocyanate (INCO) reagent, peaks at that region did not disappear (Figure 3.48).

^{1}H NMR spectrum showed a peak at 2.9 ppm due to –CH-NCO proton. And a peak of the geminal H of the I attached carbon appeared at 4-4.2 ppm . Unfortunately this peak conflicted with the glycerol protons (Figure 3.49).

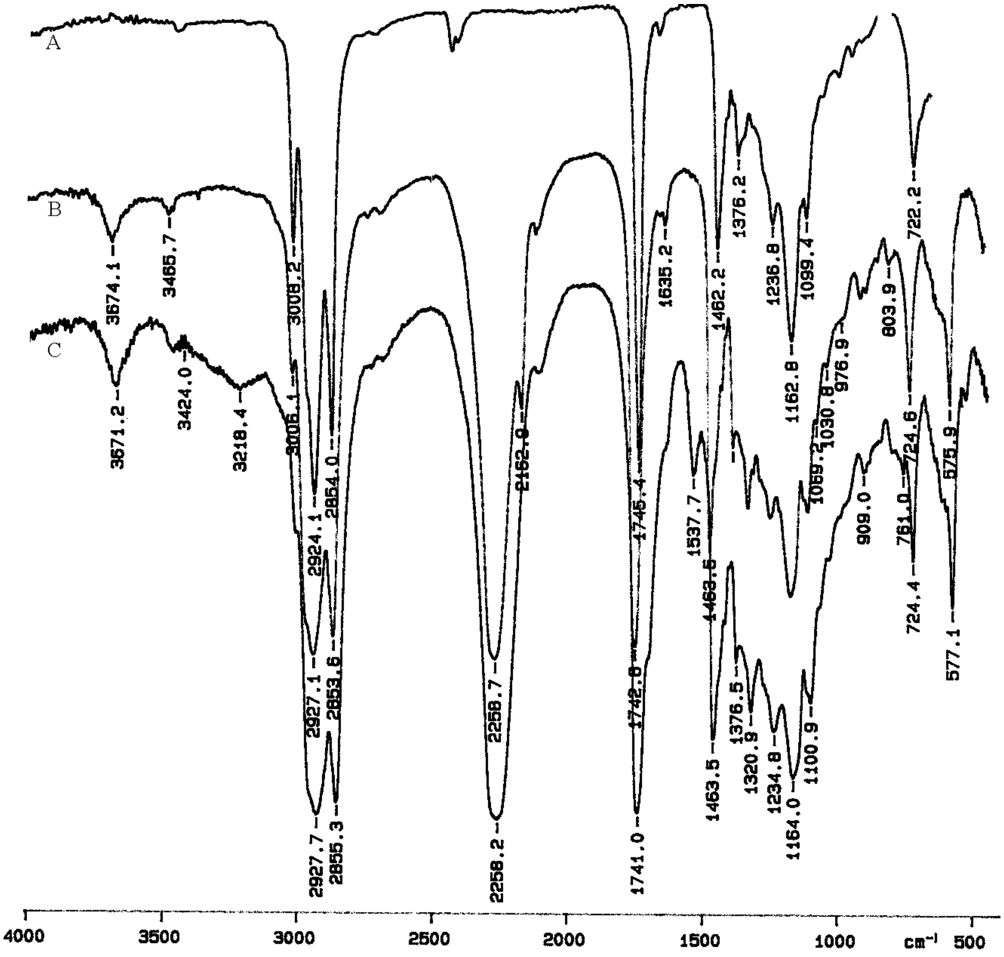


Figure 3.48. IR spectra of (A)Soybean oil (B) ISONCO which synthesized from equal amount of INCO and (C) ISONCO which produced from excess of INCO

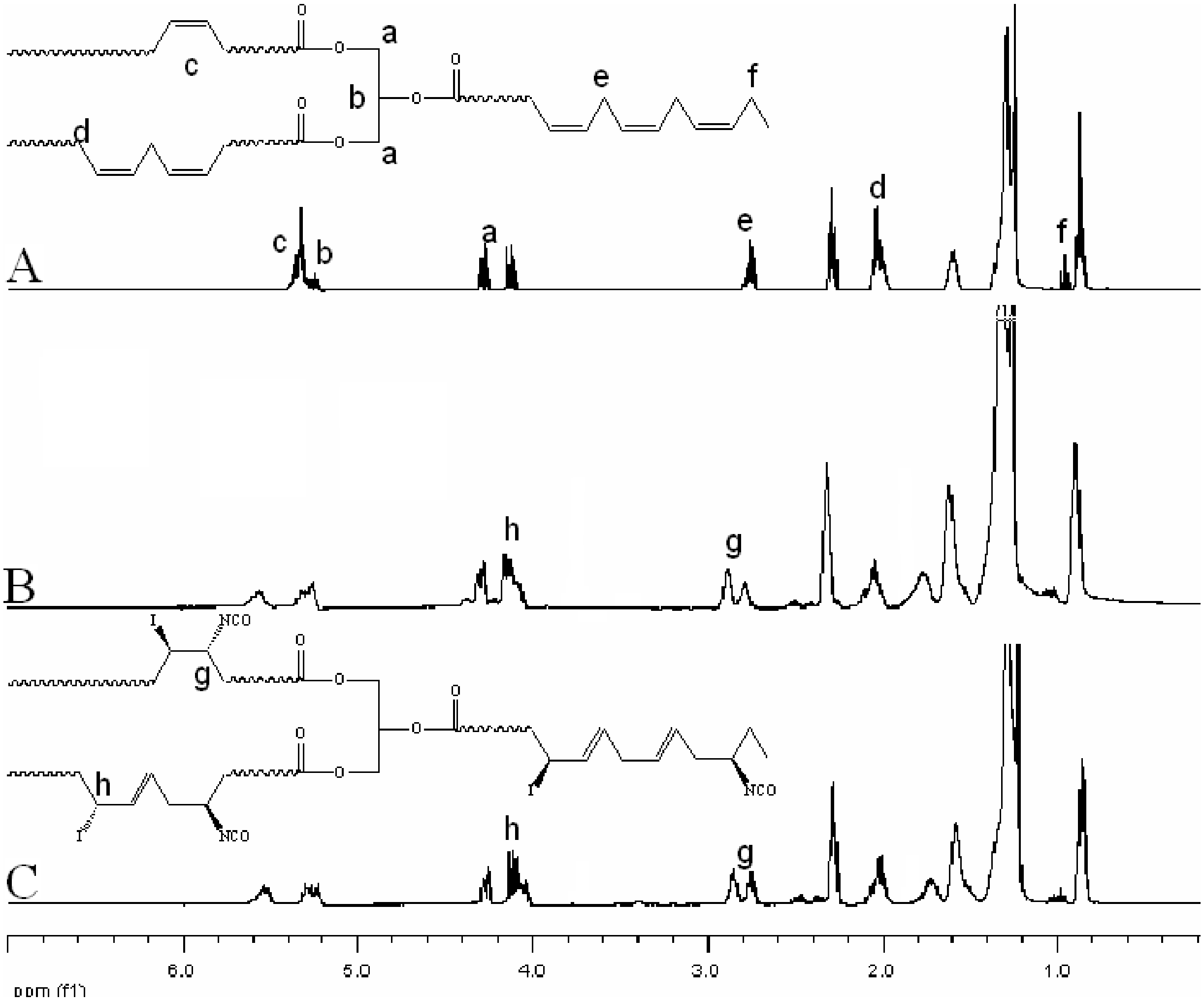


Figure 3.49. ^{1}H NMR's of (A)Soybean oil (B) ISONCO which synthesized from equal amount of INCO and (C) ISONCO which produced from excess of INCO

3.5.2.1 Synthesis and characterization of ISONCO based polymers. ISONCO was reacted with different type of alcohols and amines to give polyurethanes and ureas. IR spectra showed that carbonyl peak at 1742 was broader and in ethylene glycol case another separate peak was observed at 1695 cm^{-1} due to the carbonyl of the urethane group. A new peak was also observed at 1519 cm^{-1} due to C-N stretching of polyurethanes. A new peak was also found at 1042 cm^{-1} region due to C-O stretching of the urethane group (Figure 3.50).

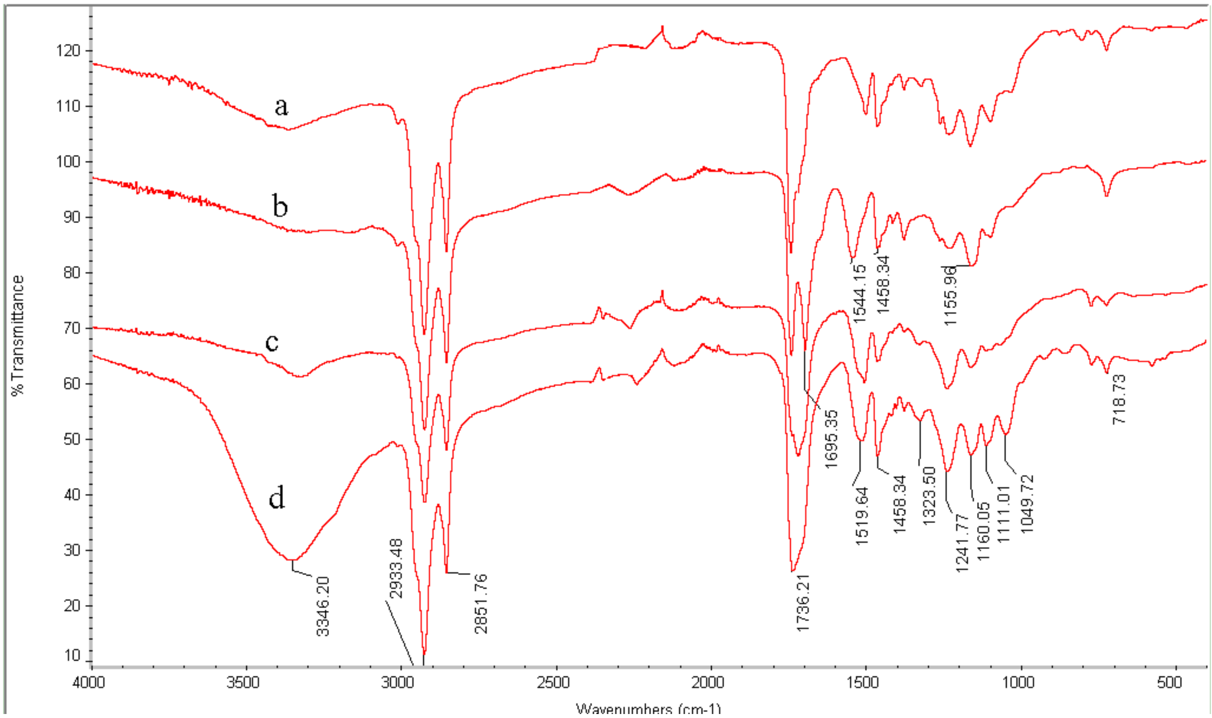


Figure 3.50. IR Spectra of ISONCO polyurethanes with (a) castor oil (b) ethylene glycol(c) pentamethylene glycol and (d) glycerol.

For the polyurea case, peak was observed at 1691 cm^{-1} probably due to carbonyl group of the urea group. Other sets of peaks were defined at 1650 cm^{-1} and 1550 cm^{-1}due to the C-N stretching. Around 3400 cm^{-1} a broad peak was observed probably due to N-H strectching of the urea groups (Figure 3.51).

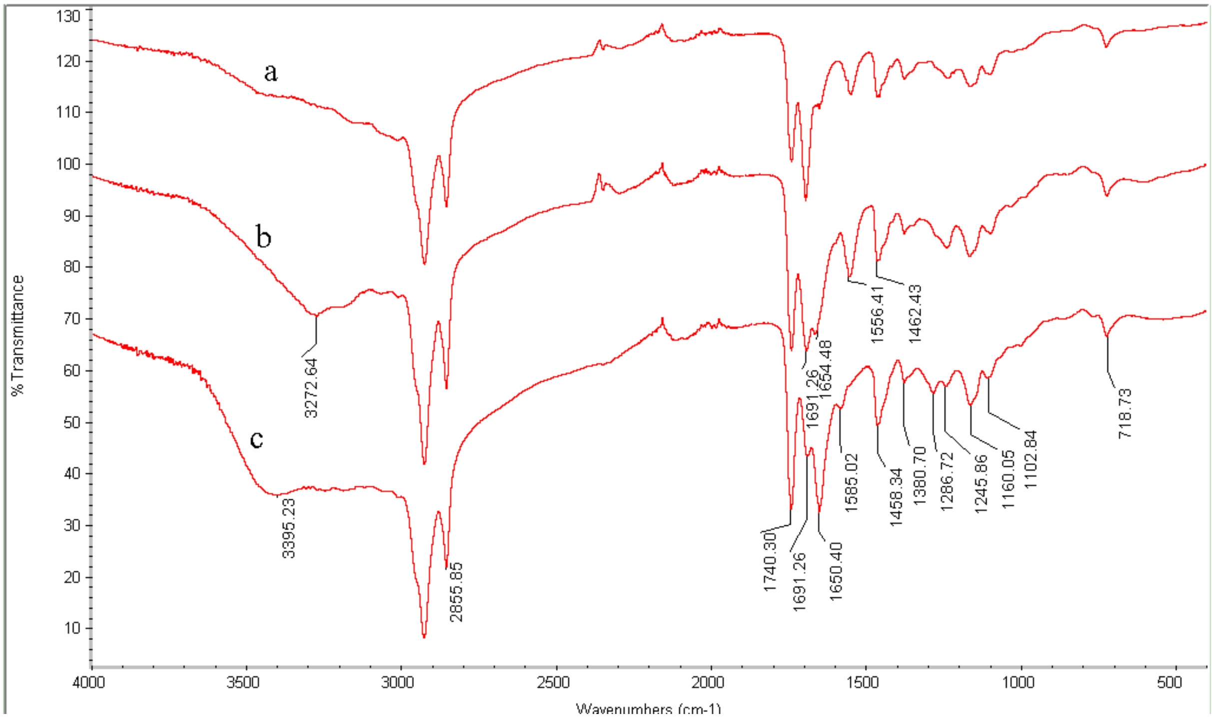


Figure 3.51. IR spectra of ISONCO polyureas with (a) ethylene diamine (b) hexamethylene diamine (c) tetra ethylene diamine.

Mechanical properties of the synthesized polyureas and urethanes were better than the polymers of the SONCO. Among the synthesized polymers castor oil polyurethane showed the highest elongation and the lowest tensile strength of 5 N/mm^2 . The highest tensile strength was observed in the pentamethylene glycol polyurethanes at a value of 30 N/mm^2 (Figure 3.52). The preparation of the shaped articles was hard due to the fast reaction between ISONCO and polyamine. Ethylene diamine sample was prepared and tested. The results was not as high as ISONCO polyurethanes (Figure 3.53).

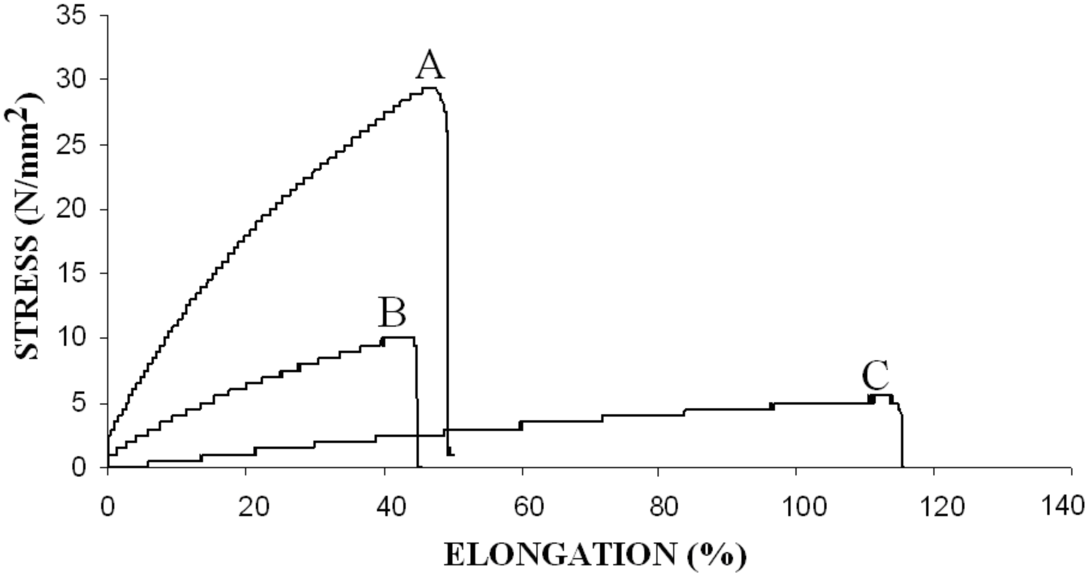


Figure 3.52. Stress-Elongation graphs of ISONCO polyurethanes with (A) pentamethylene glycol (B) glycerol and (C) castor oil

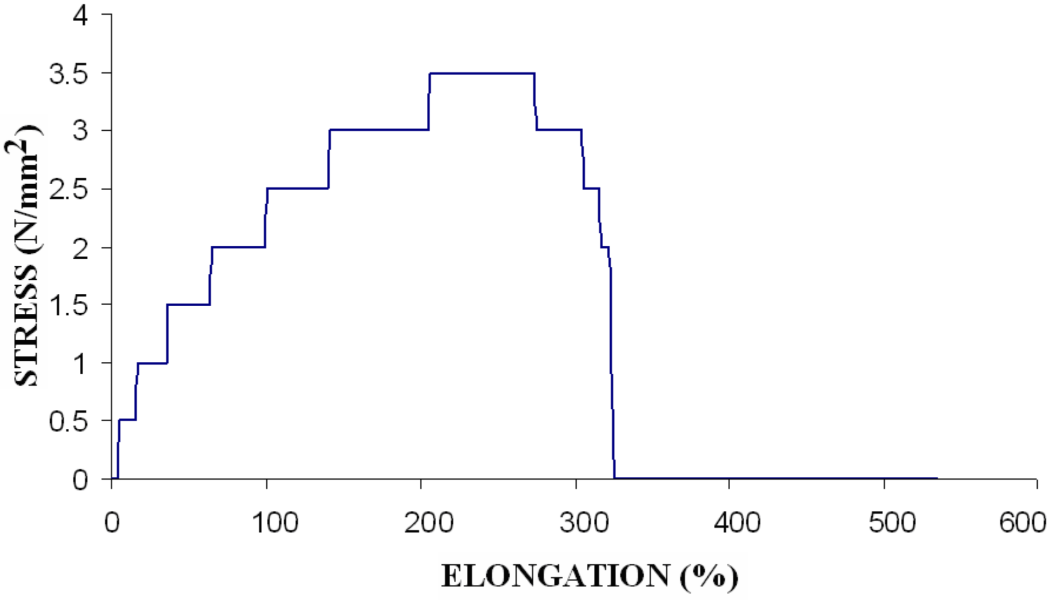


Figure 3.53. Stress-elongation graph of ISONCO with ethylene diamine polyurea

Thermal properties of the materials were interesting. Thermal degradation started at around 150 ^{o}C which was same with SONCO polyurethanes. The highest thermal stability showed by castor oil polyurethane (Figure 3.54.). Stability of the polyureas was higher than polyurethanes. The result is completely different from SONCO polyureas. Hexamethylene diamine polyureas showed the highest thermal stability (Figure 3.55).

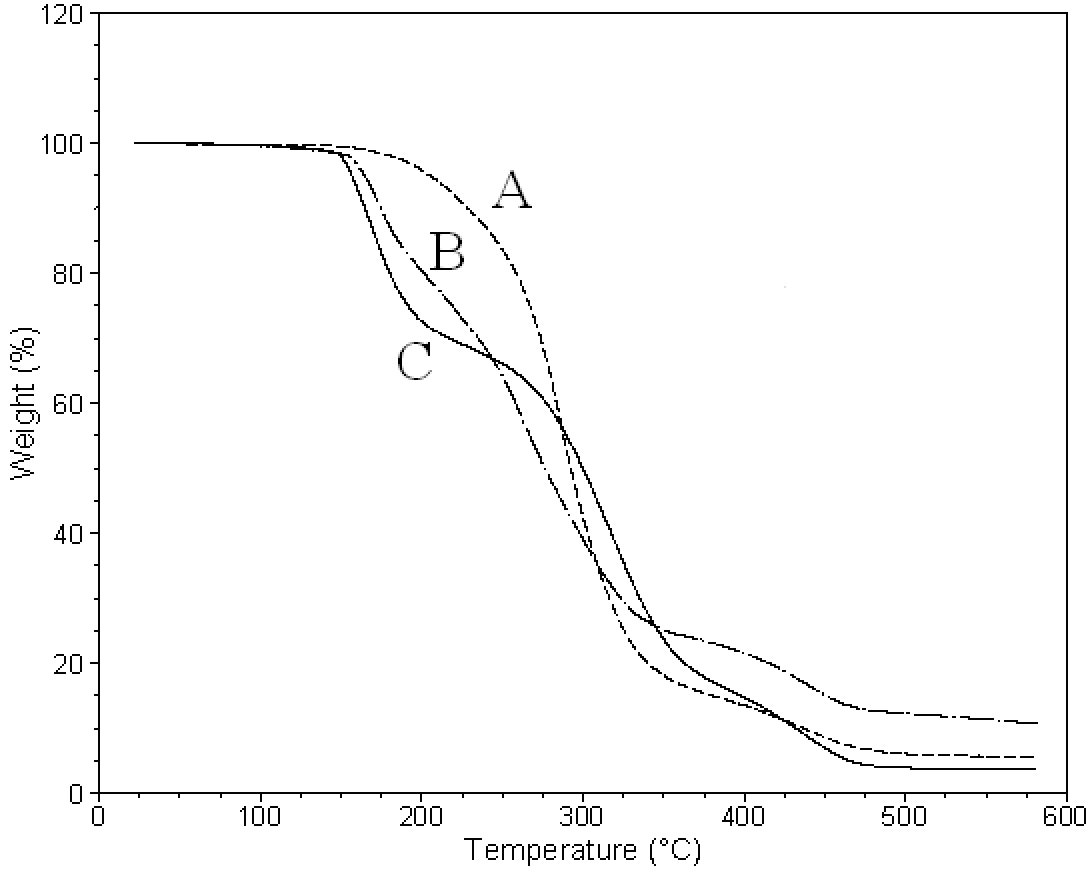


Figure 3.54. TGA curves of polyurethanes of ISONCO with (A) castor oil (B) glycerol (C) pentamethylene glycol

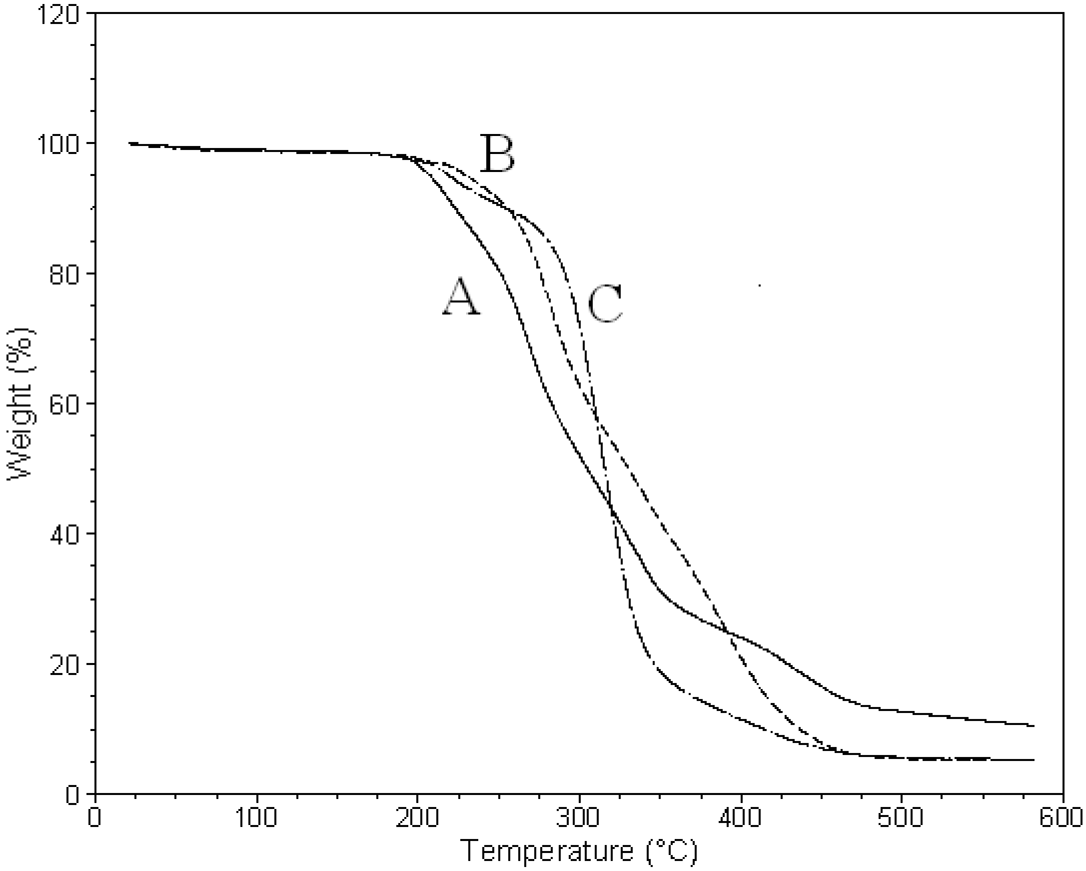


Figure 3.55. TGA curves of polyureas of ISONCO with (A) ethylene diamine (B) hexamethylene diamine (C) triethylene tetraamine.

3.5.4. . Synthesis of allylic isothiocyanate of soybean oil (ITSO):

Allylic isothiocyanates were synthesized directly by the reaction between allylic bromides of soybean oil and ammonium thiocyanate in THF at 60 ^{o}C. Reaction completed in 5 hours (Figure 1.21). Allylic isothiocyanates were obtained in 50-70 per cent yields as a mixture of positional isomers. The yields were calculated by simply weighing the precipitated NH_4Br at the end of the reaction. The yields were confirmed by mixing ITSO with excess n-butyl amine and then titrating the excess n-butyl amine with a standard acid solution [99]. The results of the two methods were consistent with each other. Proton on the carbon bearing the NCS group gave a peak at 4.2 ppm. Peaks of the glyceride moiety also appear in the same region. This unpleasant coincidence made the yield calculation by the help of NMR spectrum impossible. Depending on the reaction time, temperature, and freshness of the allylic brominated soybean oil yields may vary from 50 per cent to 70 per cent. Allylic Bromination and substitution of the bromine with isothiocyanate were easily monitored by observing the changes of the peaks of soybean oil in the IR spectrum. A peak which appeared around 965 cm^{-1} was attributed to allylic -HC=CHC**H**Br stretching and a peak around 640 cm^{-1} is attributed to C-Br deformation. When isothiocyanate addition occurred, a new peak around 2070 cm^{-1} was observed due to NCS group. If the substitution occurred at S side, thiocyanates group gave a peak at around 2150 cm^{-1}. In a separate experiment, benzyl chloride was used as an IR model compound. It was reacted with NH_4SCN and it was observed by IR spectroscopy that the S end was bound to the benzyl group preferentially. In the IR spectrum, a sharp and intense peak at around 2152 cm^{-1} due to SCN group and at 2063 cm^{-1} a small broad peak due to NCS group were observed (Figure3.57). When compared with the other isothiocyanate synthesis methods, allylic bromination and the subsequent substitution reactions were simple reactions. Allylic bromination was completed in 4-5 hours. SCN^- substitution reaction required mild conditions and reaction was nearly completed in 30 minutes at 60 ^oC (Figure 3.56). At room temperature, the substitution reaction was complete in 5 hours. The average number of isthioocyanate groups per triglyceride could not be measured directly but butyl amine titration indicates about 2 thiocyanate groups per triglyceride on the average. The fact that the products do polymerize to thermoset polymers with diols and diamines support this.

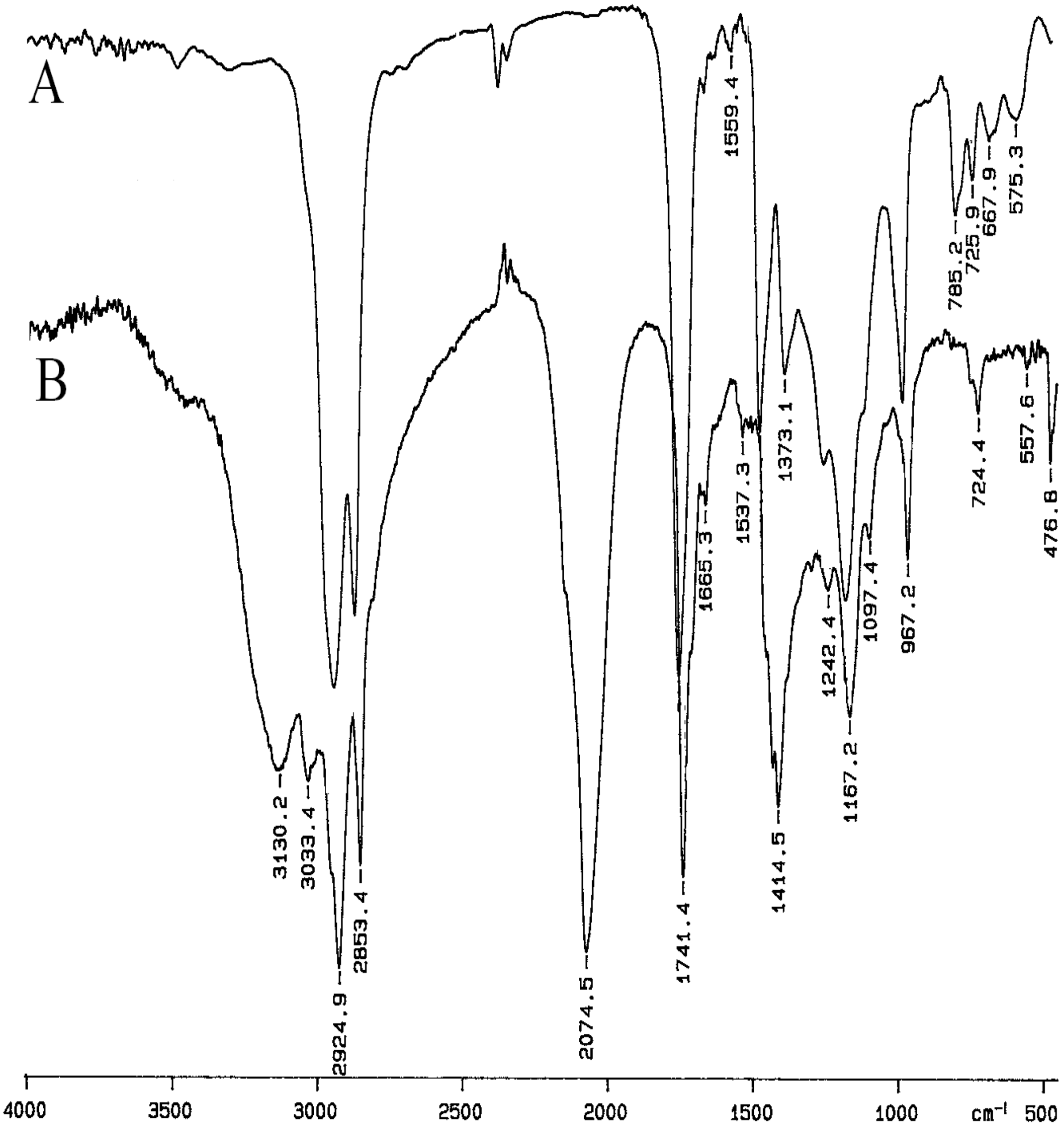


Figure 3.56. IR spectra of (A) allicly brominated soybean oil (B) allylic isothiocyanate of soybean oil.

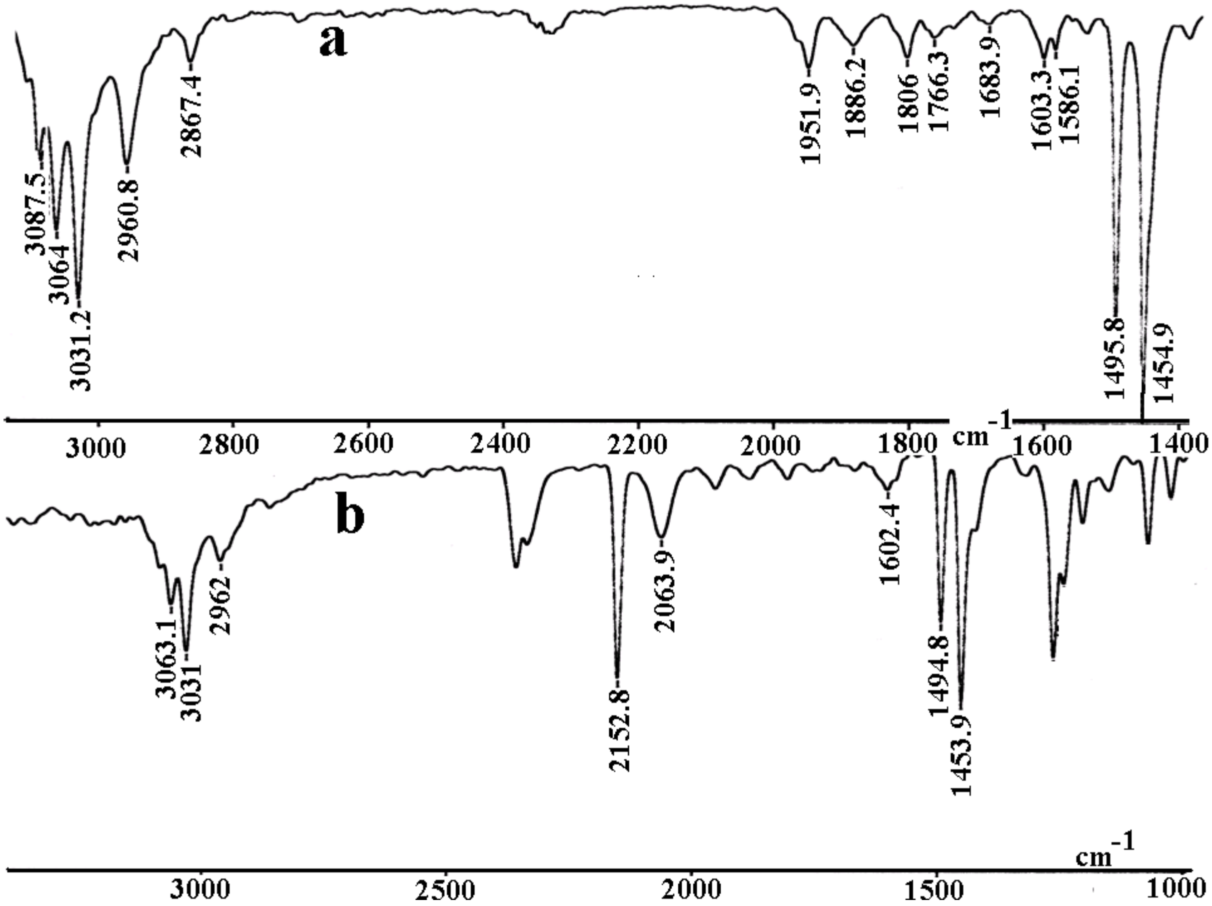


Figure 3.57. The IR Spectra of (a) benzyl chloride and (b) benzyl thiocyanate.

3.5.4.1. Synthesis and properties of ITSO based polymers. Polymerization of ITSO with ethylene glycol, glycerin, and castor oil was completed in 5 hours at 140 °C. ITSO was conveniently miscible with all the other monomers and reacted fast with triethylene tetra amine (TETA) and ethylene diamine even at room temperature. For this reason, ITSO and polyamines were mixed and poured into a teflon mold quickly. Reaction with polyols gave the corresponding polythiourethane and reaction with poly amines also gave the corresponding polythioureas. Polymerization reactions of ITSO were slower than corresponding isocyanated soybean oil. Thus, longer reaction times and temperatures were required [100].

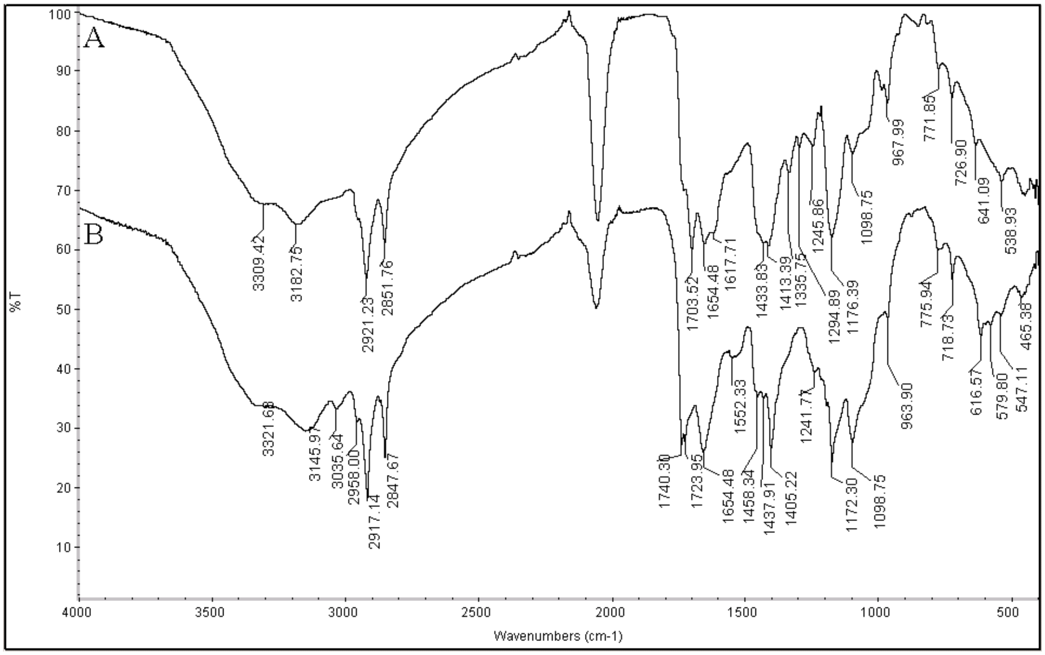


Figure 3.58. IR Spectra of ITSO polythioureas with (A) ethylene glycol and (B) glycerol.

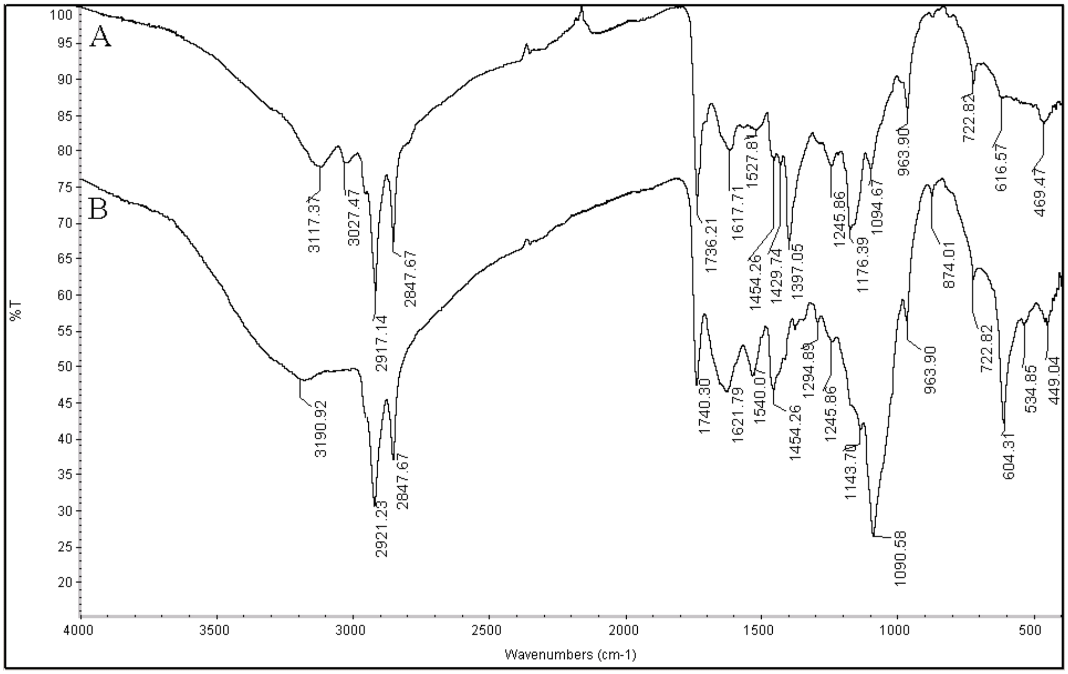


Figure 3.59. IR spectra of ITSO polythioureas with (A) TETA and (B) EDA

Surprisingly, both the thiourethanes and thiourea polymers were not rubbery. They were hard solids. Polythiourethanes were harder than polythioureas. The polythiourethanes synthesized had tensile strength of 70 N/mm^2 (glycerol) and 30 N/mm^2 (ethylene glycol). Not surprisingly, the tensile strength of glycerol polythiourethane was higher than ethylene glycol polythiourethane (Figure 3.60). Elongation at break of the ethylene glycol polythiourethane was smaller than the glycerol one. And the tensile strength of triethylene tetramine polythiourea was higher than the ethylene diamine polythiourea (Figure 3.61). Stress at break values were 60 N/mm^2 and 30 N/mm^2 for TETA and EDA polythioureas respectively. There is a generale trend in the tensile strength that when the functionality of polyols and amines increased the tensile strength of material also increased. All materials also showed low elongation at break. Almost all polythiourea and urethanes showed poor solvent resistance. They swelled and fractured in CH_2Cl_2 in 5 hours.

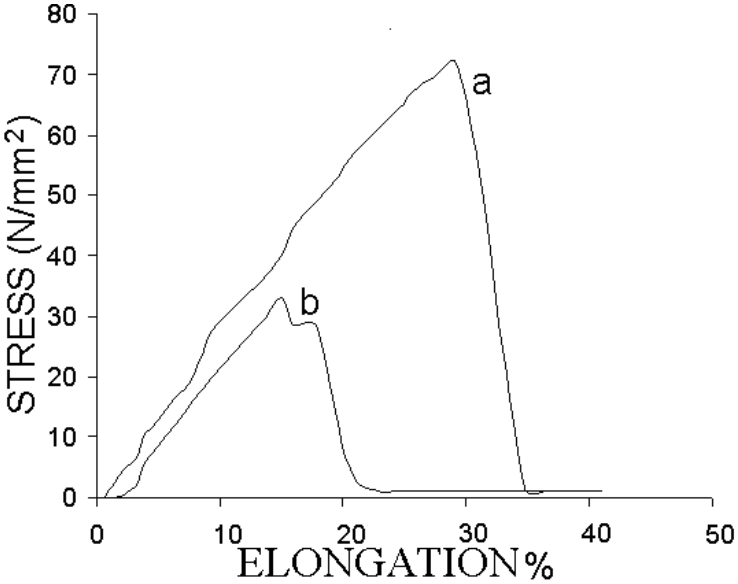


Figure 3.60. Stress strain curves of ITSO a-) glycerol and b-) ethylene glycol polythiourethanes

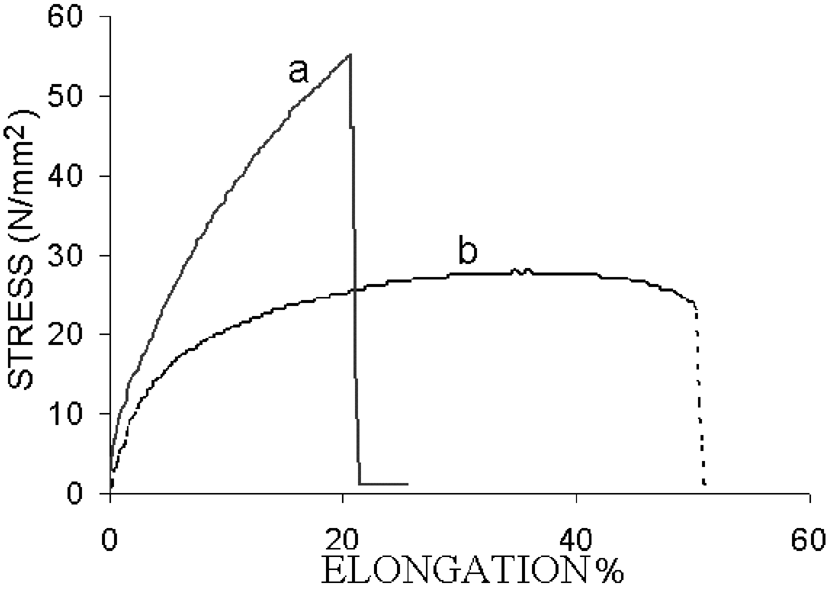


Figure 3.61. Stress strain curves of ITSO a-) Triethylene diamine b-) ethylene diamine polythioureas

Thermal characterizations of the materials were determined by DSC. DSC traces showed Tg's for ethylene glycol polythiourethane at –39 and 58.°C, for glycerol polythiourethane at -38, 9, and 126 °C, for castor oil glycol polythiourethane at -38 and -17 °C, for ethylene diamine polythiourea at -45 °C and triethylene tetramine polythiourea at -39°C respectively. Surprisingly, polythioureas showed heat absorption at around 100 °C (Figures 3.62 and 63). The amount of absorbed heat was around 35 J/g for both polythioureas.

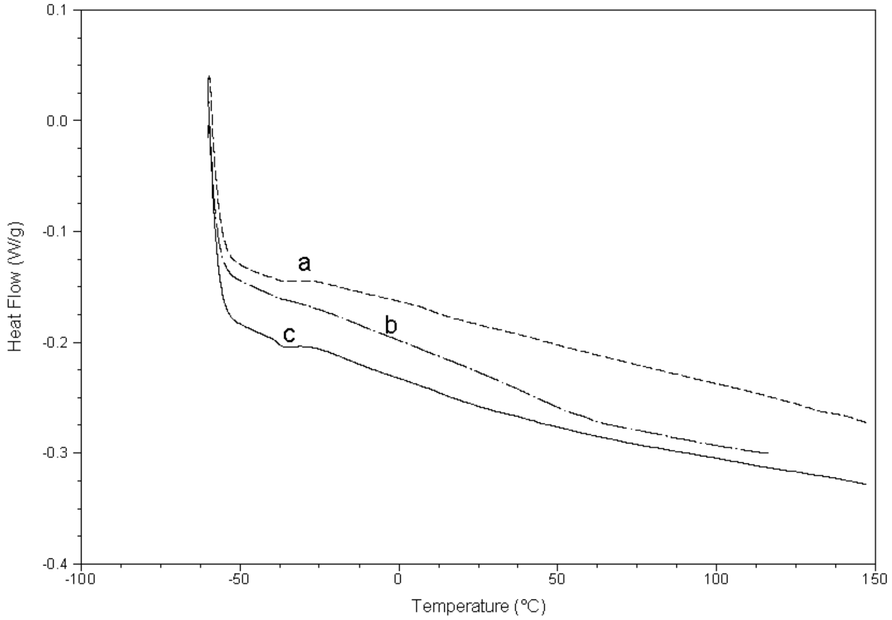


Figure 3.62. DSC traces of a-) ITSO castor oil b-)ITSO glycerol c-) ITSO ethylene glycol polythiourethanes

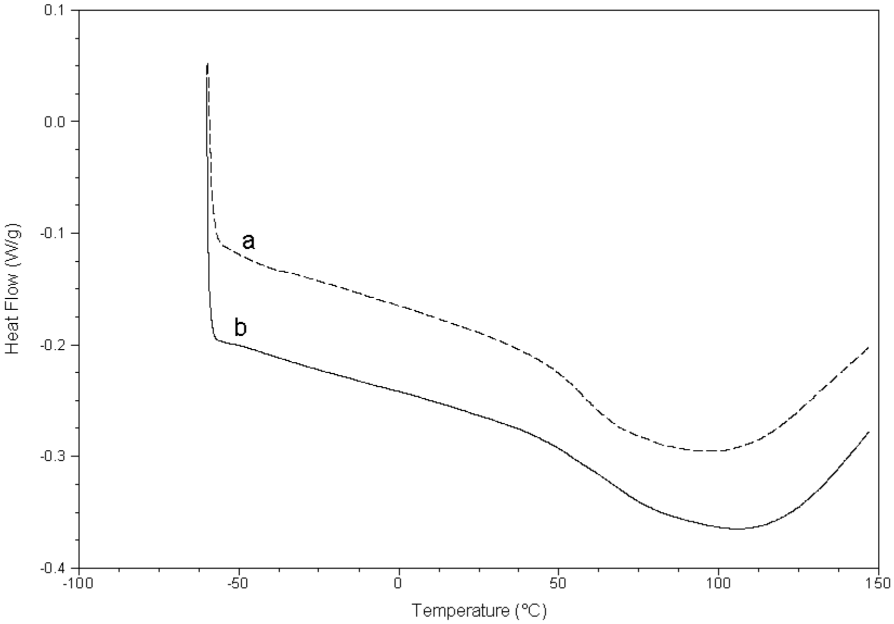


Figure 3. 63. DSC traces of a-)ITSO ethylene glycol polythiourea b-) ITSO triethylene tetramine polythiourea

All polythioureas and polythiourethanes showed 5 per cent wight lost at around 200 ^{o}C (Figures 3.64, and 3.65) during TGA tests. Among polythiourethanes ethylene glycol polymer showed the lowest 5 per cent weight lost temperature at 197 ^{o}C. For polythiourea case, triethylene tetramine polymer gave the lowest result at 194 ^{o}C. Besides 5 per cent weight lost temperature, derivative TGA's (DTGA) gave also valuable information about thermal stability (Figures 3.66. and 67). Ethylene glycol polythiourethane gave the highest peak maxima at 320 ^{o}C. However castor oil and glycerol polythiourethanes gave the same maxima at 300 ^{o}C. Glycerol polythiourethane showed relatively narrow DTGA peak which indicates that almost the entire matrix decomposed at around 300 ^{o}C. But a wide decomposition curve, which indicates that thermal degradation occurred at large temperature range, was observed in ethylene glycol polythiourethane case. This behavior can be attributed to polarity difference between the ITSO and small polyols. Glycerol and ethylene glycol may not be easily diffuse so the reaction can not reach full conversion. Polythioureas also gave also broad degradation peaks at around 300 ^{o}C. This may be explained by the high reaction rate of polyamines. In this case the polyamines reacted fast and the cross linking density increased suddenly which prevent further reactions and maybe some amines are trapped in the matrix. Although solubility and high reactivity seemed a problem, when compared to fatty polyureas and poly urethane analogs of thio polymers, improvement in the thermal stability was observed.

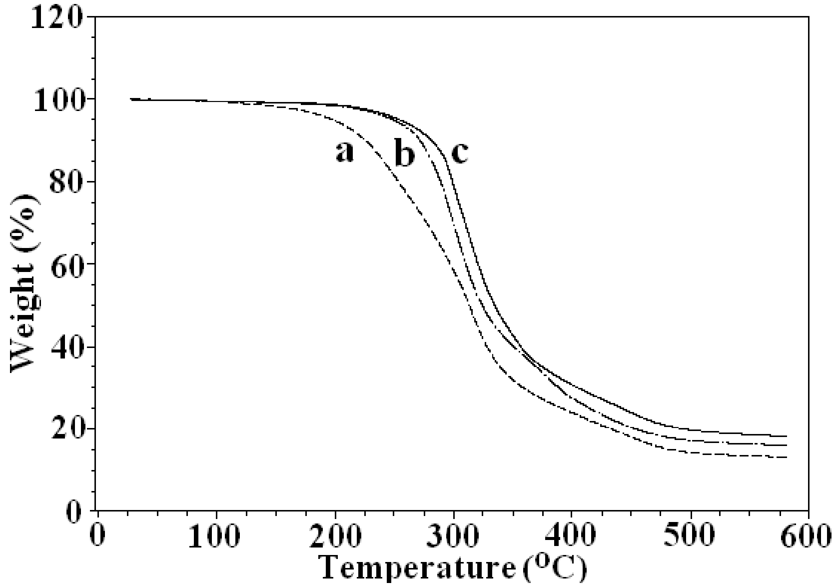


Figure 3.64. TGA traces of a-) ethylene glycol, b-) glycerol, and c-) castor oil polythiourethanes

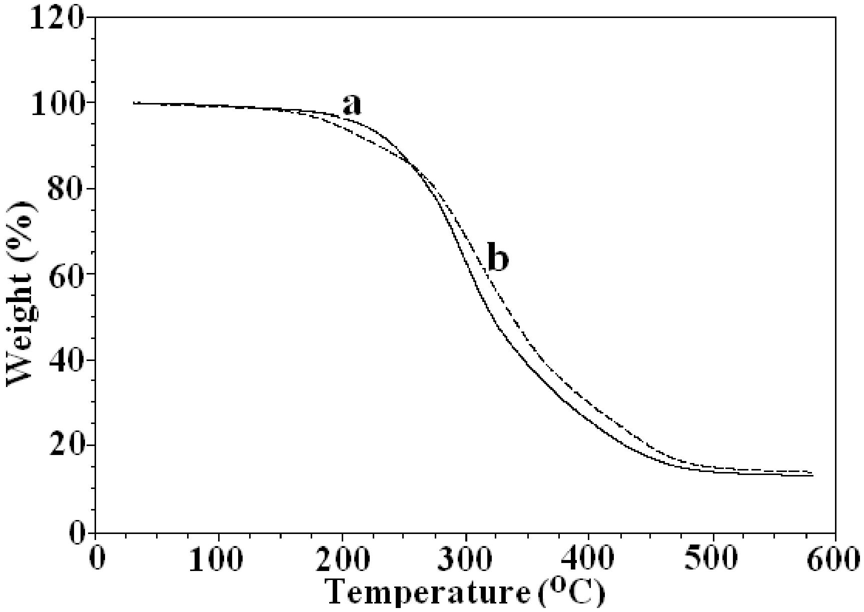


Figure 3.65. TGA Traces of a-) Ethylene diamine and b-) Triethylene tetramine polythioureas.

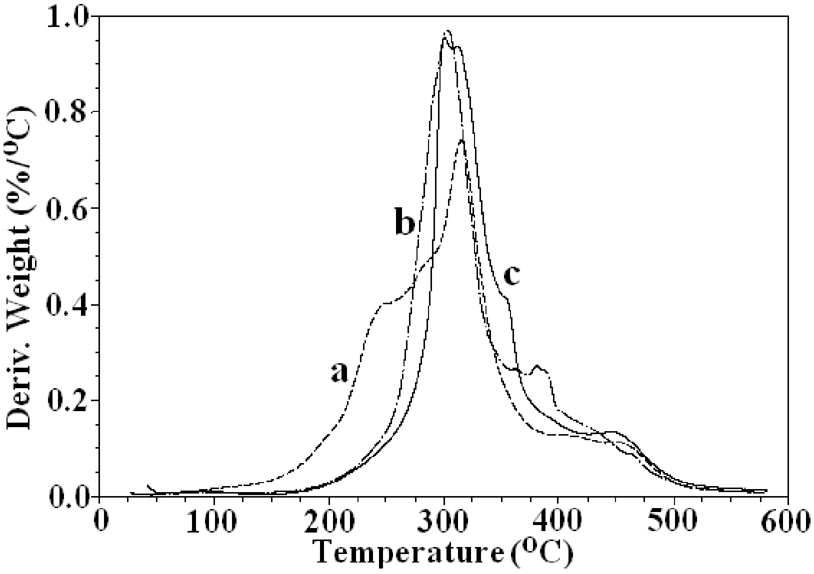


Figure 3.66. DTGA traces of a-) ethylene glycol, b-) glycerol, and c-) castor oil polythiourethane.

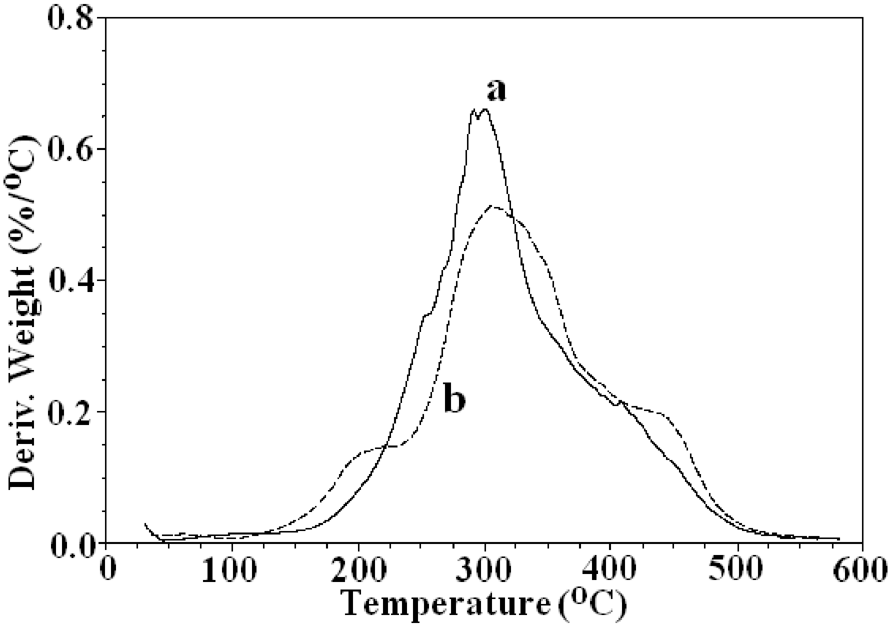


Figure 3.67. DTGA Traces of a-) ethylene diamine, and, b-) triethylene tetramine polythiourea

3.6. Synthesis and polymerization of soy oil based allylic esters

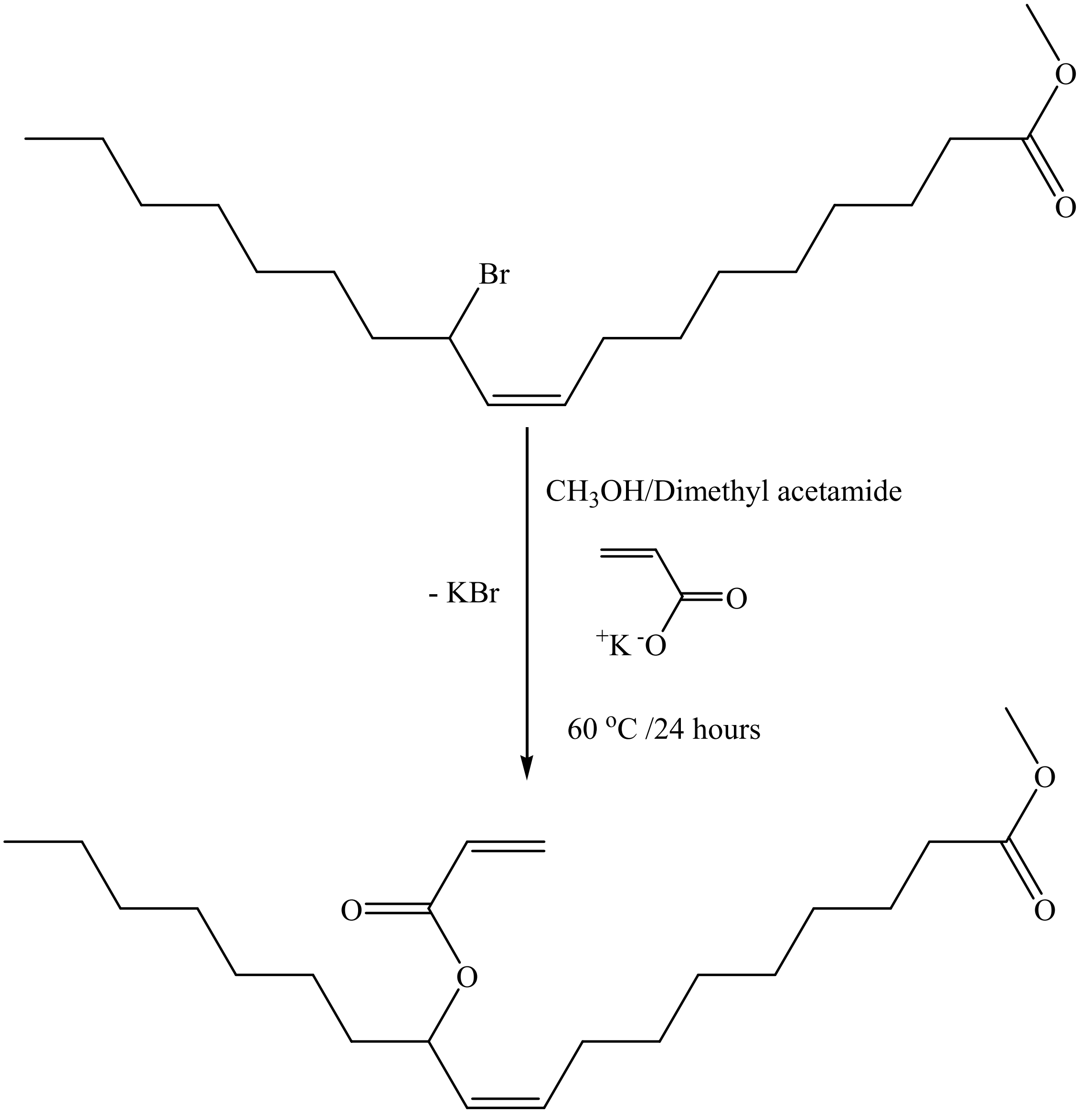


Figure 3.68. Presentation of the synthesis of allylic acrylates from allylic bromides by using methyl oleate as a model compound.

3.6.1. Synthesis of the allylic esters of soybean oil and methyl oleate:

Allylic esters of the soybean oil and methyl oleate were synthesized successfully by substitution reaction of the salts of acrylic and methacrylic acids with allylic brominated of soybean oil.

The products were characterized by IR and ^{1}H NMR techniques. In the IR spectrum all of the monomers showed peaks at 1725-1726 cm-1 due to the ester carbonyl of acrylate and methacrylate groups. Peaks at 1660-1630are getting stronger due to C=C stretching vibration of acrylate and methacrylate groups. A new peak was also observed at 1092 cm^{-1} due to the C-O stretching new ester groups (Figure 3.69 and 3.70).

In the ^{1}HNMR spectrum, the unique peaks of the acrylate groups was observed at 6.2, 6.0, 5.8 ppm. Methacrylate ester gave 2 peaks at 6.1 and 5.5 ppm. In the methyl ester case, there was a new peak observed at 5.2 ppm due to the single protons of allylic esters (Figure 3.71 and 72). This small peak could not be observed in ACSO and METACSO spectra because it coincided with the single proton of the glycerol moiety at 5.2 ppm. The yields were calculated just measuring the ratio between one of the acrylate protons and protons of alpha methylene group.

Depending on the counter ion, temperature, reaction time and solvent polarity different yields were observed. The best yields were obtained by using K salts of the acrylic acids and methacrylic acids at 60 ^{o}C in methanol/dimethyl acetamide solvent system. Due to the weak nucleophilicity of the carboxylates the reaction rate was slow. Thus, 24 hours was needed to complete the reaction. When the reaction proceeded, KBr started precipitate. The amount of the precipitated KBr was also used to calculate the reaction yield. Besides the measurement of the precipitated amount of KBr, ^{1}H NMR was also used. Results of the two methods were consistent with each other.

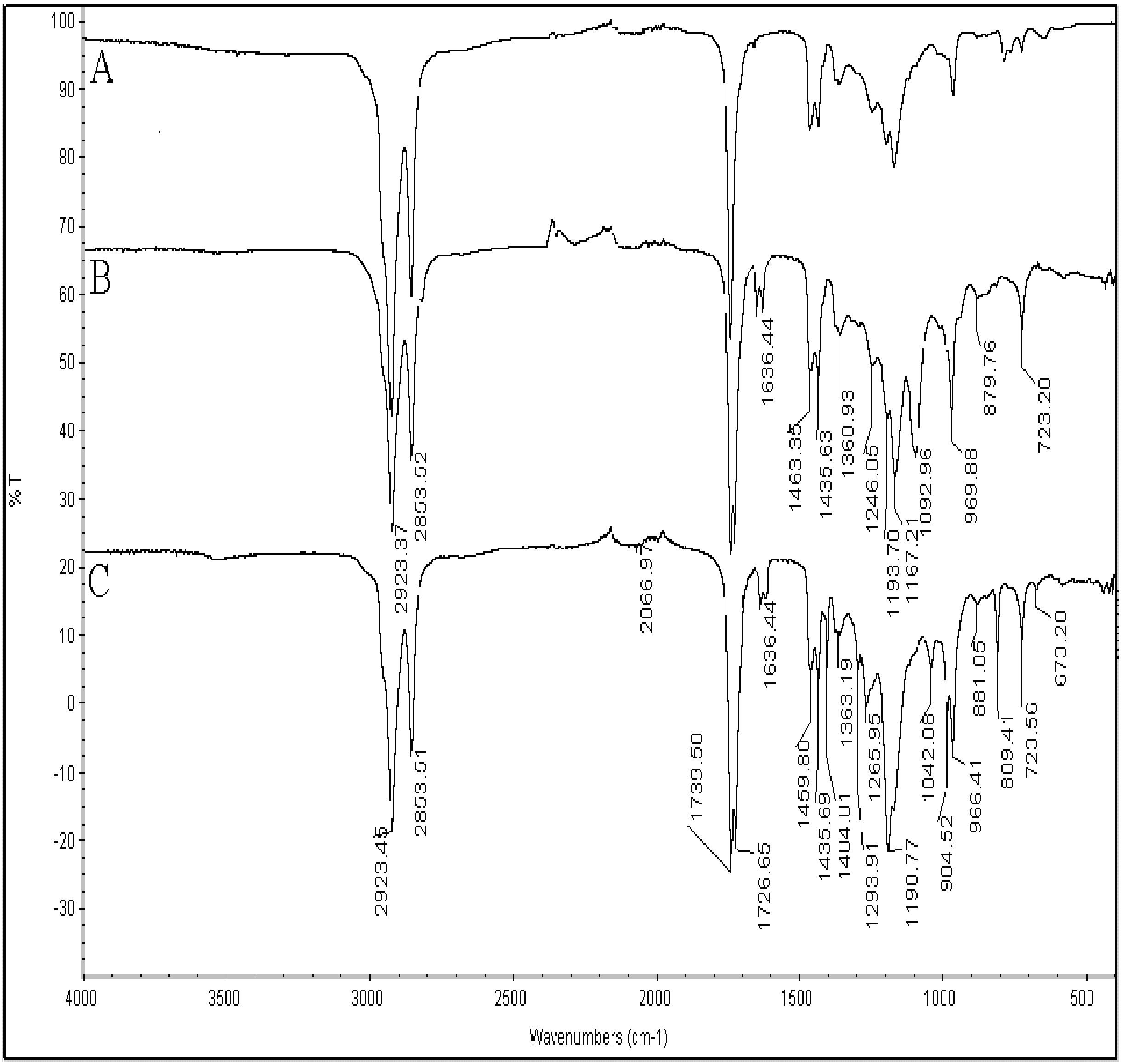


Figure 3.69. IR spectra of (A) ABMO (B) Allylic acrylate of methyl oleate and (C) Allylic methacrylate of methyl oleate.

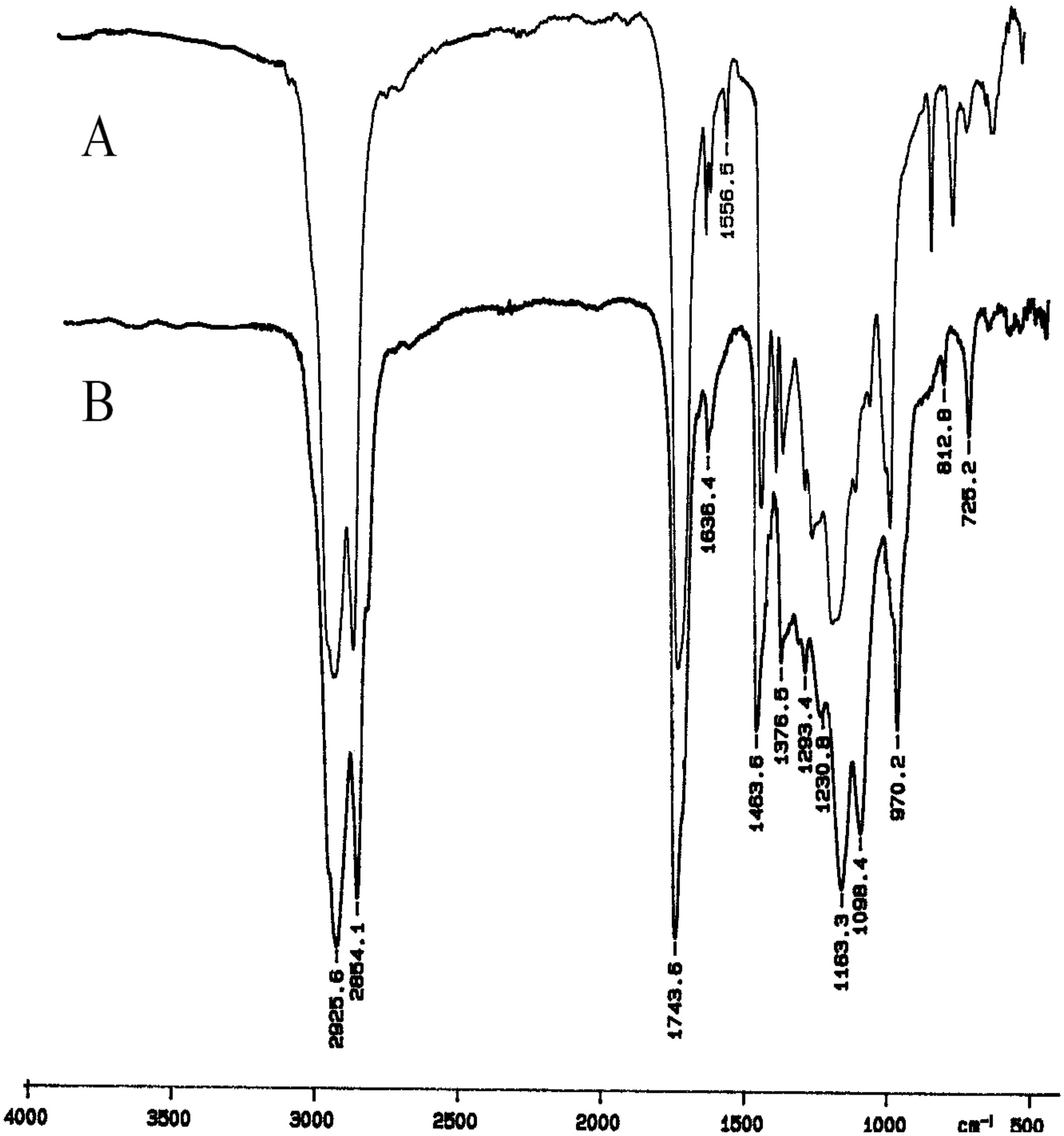


Figure 3.70. . IR spectra of (A)Allylic acrylate of soybean oil (ACSO) and (B)Allylic methacrylate of soybean oil (METACSO)

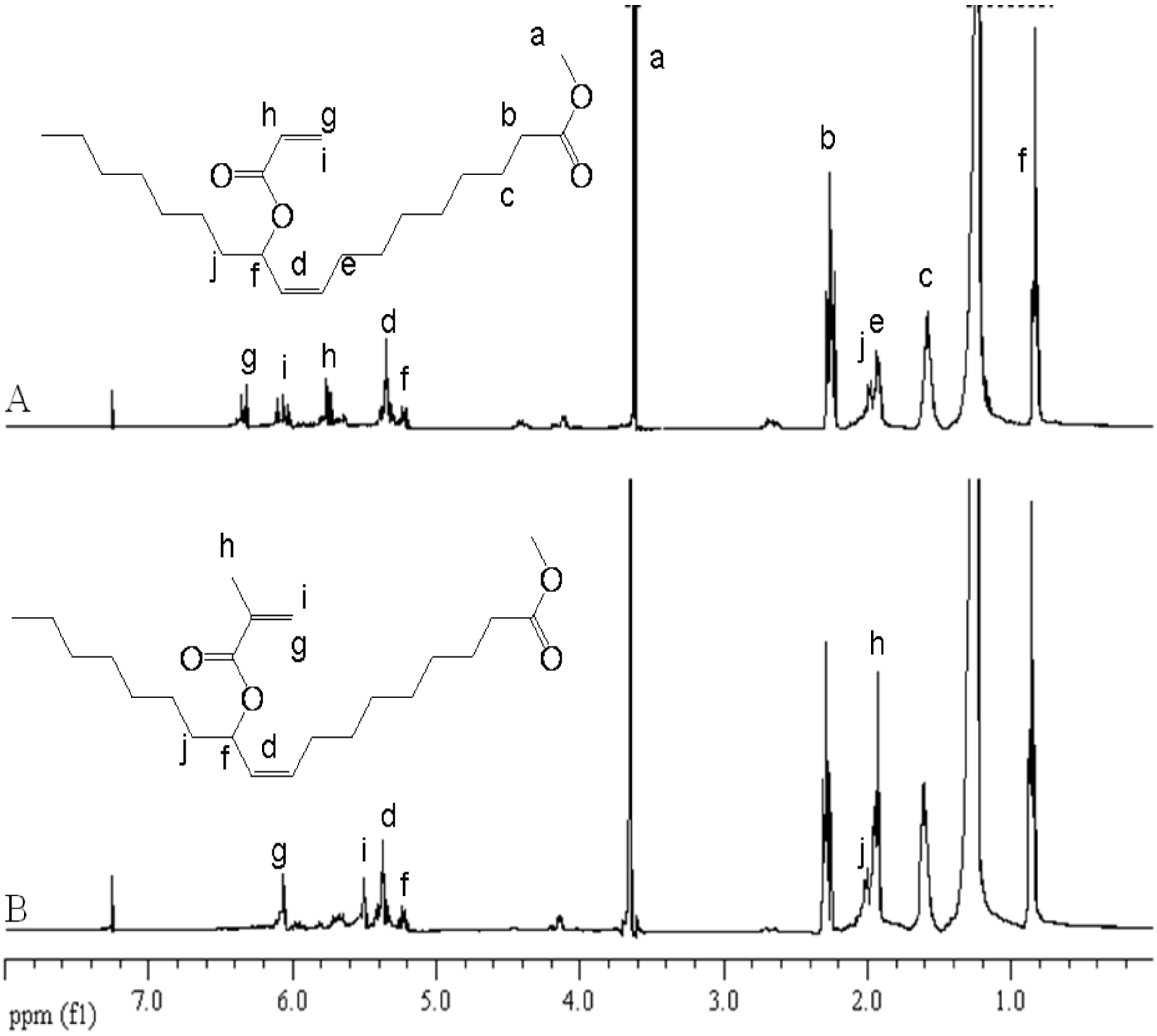


Figure 3.71. ^{1}HNMR of (A) Allylic acrylate of methyl oleate and (B) Allylic methacrylate of methyl oleate

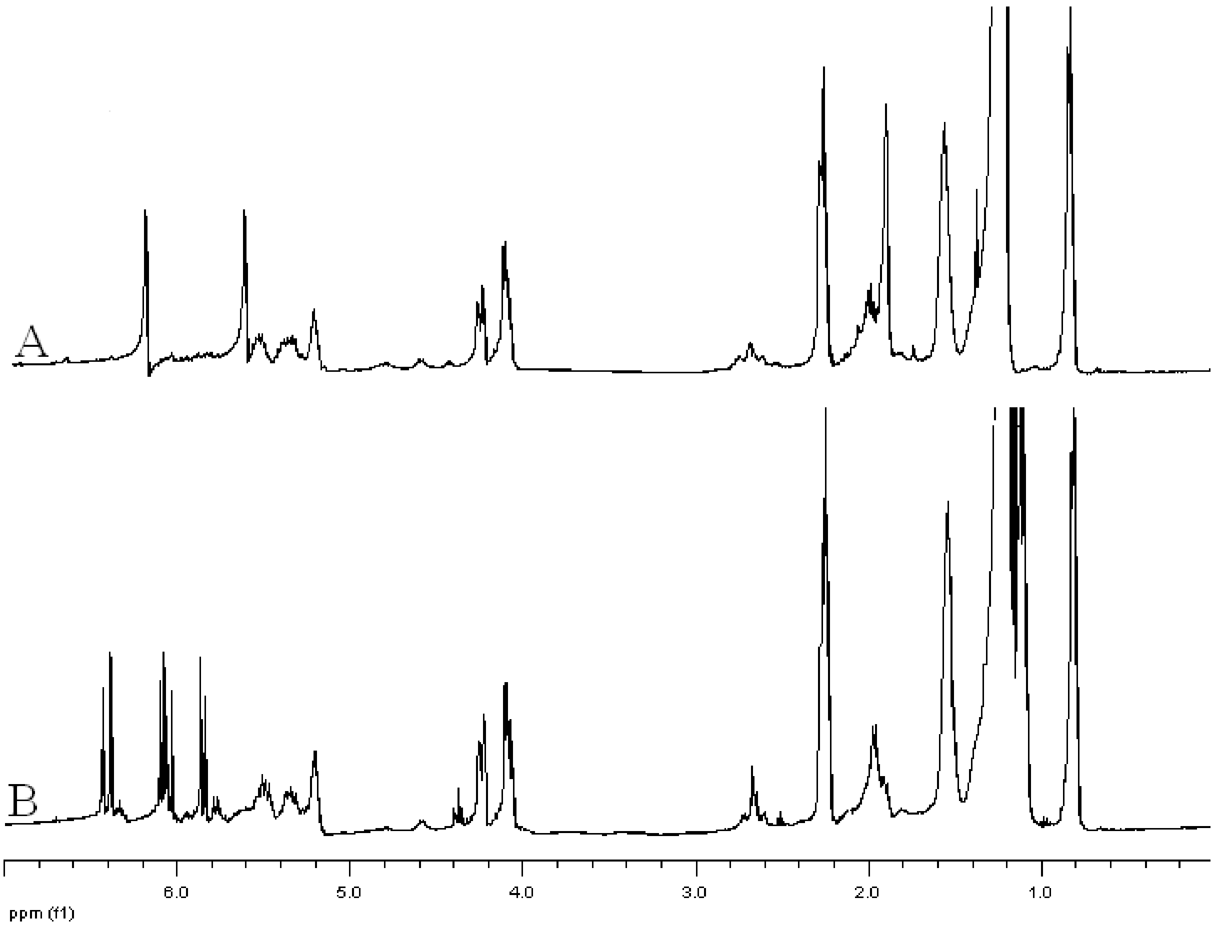


Figure 3.72. ^{1}H NMR spectra of (A) Allylicmethacrylate of soybean oil (MACSO) and (B) Allylicacrylate of soybean oil (ACSO)

3.6.2 Thermal and mechanical properties of the polymers synthesized:

Allylic acrylates contain two different types of double bonds. Reactivities of these double bonds are different. Acrylate double bonds are very reactive when compared to fatty acid double bonds. Polymerization is easily stooped by chain transfer to allylic sites. Thus, allylicmonomers are usually polymerized with more than 1 per cent of initiator. Generally 2-3 per cent initiator is used.

In this study, monomers synthesized were polymerized with 3 per cent initiator. Benzoyl peroxide was chosen as initiator. Polymerization of the acrylated and methacrylated methyl esters and triglycerides gave soft, cross linked, reddish broun polymers. Mechanical properties were not good. Tensile properties of the copolymers of ACSO and METACSO with styrene are shown in the Figure 3.73. Cross linked products showed high elongation at low stress. This behavior is similar with rubbery materials. Copolymers of the acrylated monomers were softer than the copolymers methacrylated monomers. These materials were suitable in the application areas where high tensile strengths are not required.

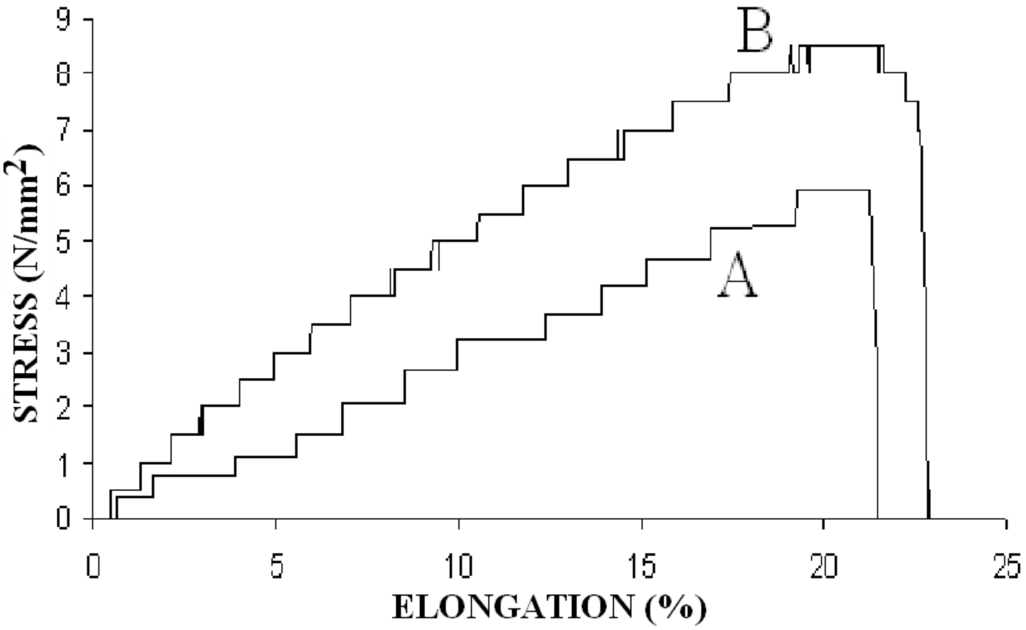


Figure 3.73. Stress-Elongation curve of (A) ABSO and (B) MACSO copolymers with styrene

Thermal properties of the materials were also determined by DSC and TGA analysis. TGA graphs showed that allylicacrylates and methacrylates of the methyl oleate started to degrade around 200 °C (Figure 3.74 and 75).. Similar trend was also observed in the ACSO and MACSO copolymers (Figure 3.76).

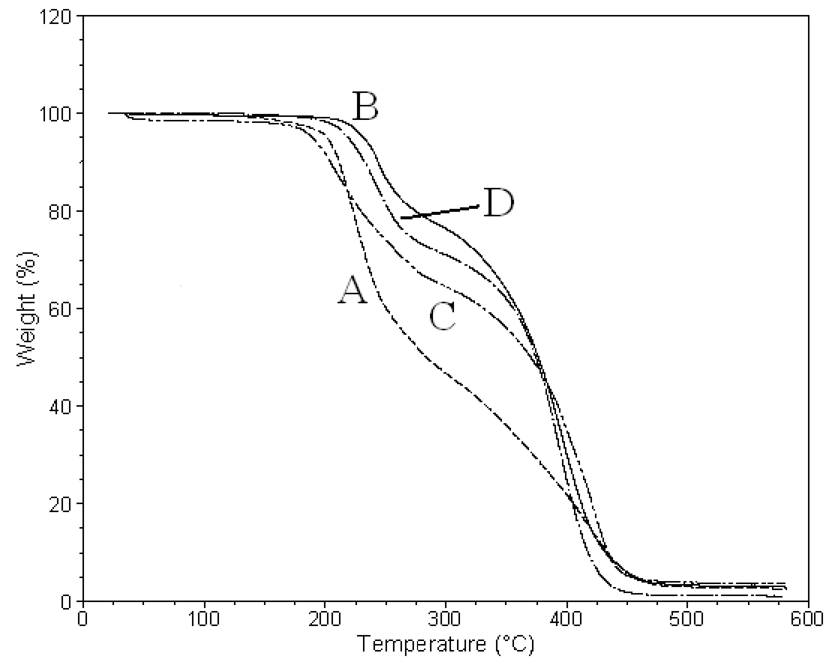


Figure 3.74. TGA traces of (A) homopolymers of allylic methacrylates of methyl oleate (ACMO) and (B) n butyl acrylate (C) methacrylic acid and (D) styrene copolymers

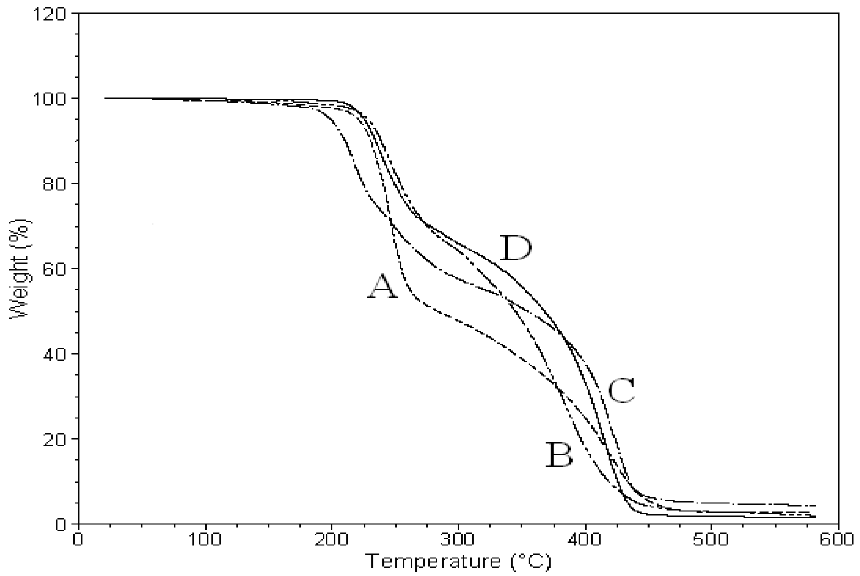


Figure 3.75. TGA curves of (A) homopolymer of allylic methacrylate of methyl oleate (METMO) and (B) n butyl acrylate (C) methacrylic acid and (D) styrene copolymers.

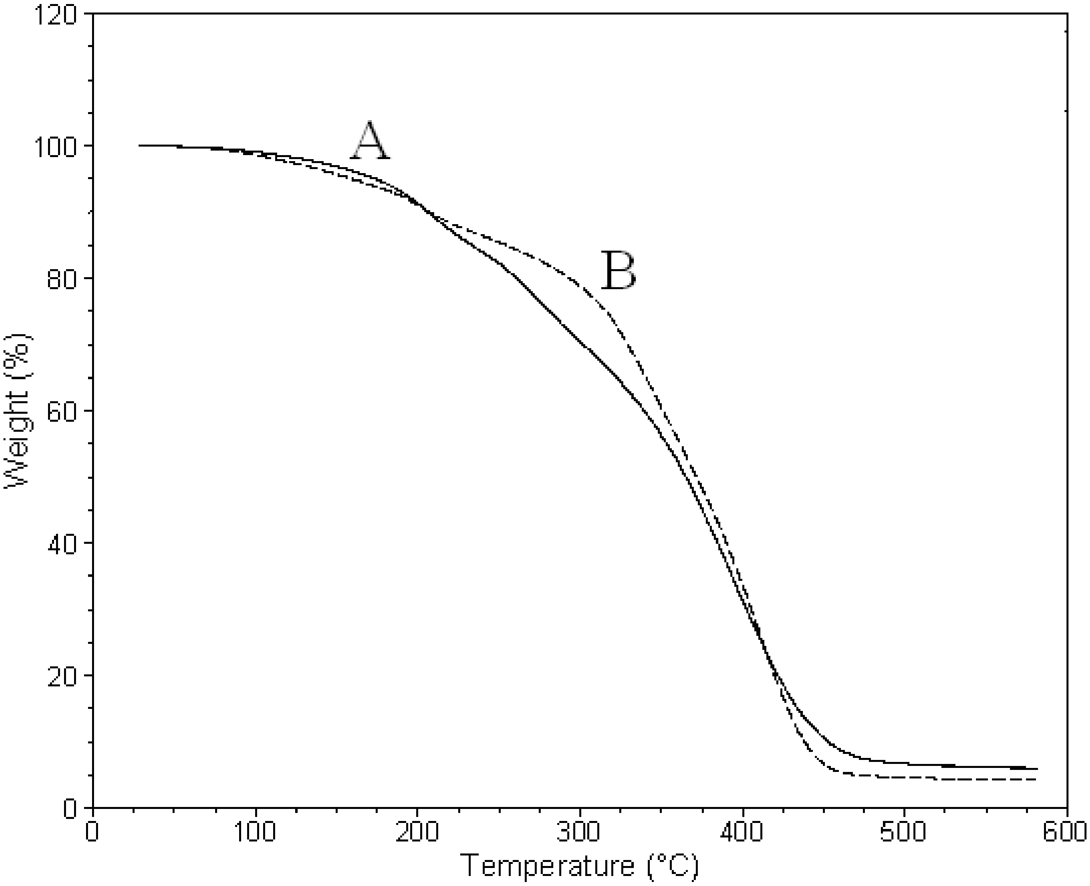


Figure 3.76. . TGA curves of stryrene copolymers of (A) acrylated and (B) methacrylated soybean oil.

DSC curves showed that allylic methacrylate of methyl oleate homopolymer gave a Tg at -40 ^{o}c and a second Tg at 30 ^{o}C. Methacrylic acid copolymer showed the highest Tg at 60 ^{o}C. Styrene copolymer showed two Tg at -3 and 55 ^{o}C (Figure 3.77).

Allylic acrylate of methyl oleate homopolymer showed Tg at 4 ^{o}C. It was very interesting in that methacrylic acid and styrene copolymers of ACMO showed a crystalline melting curve at 65 ^{o}C and -16 ^{o}C respectively (Figure 3.78).

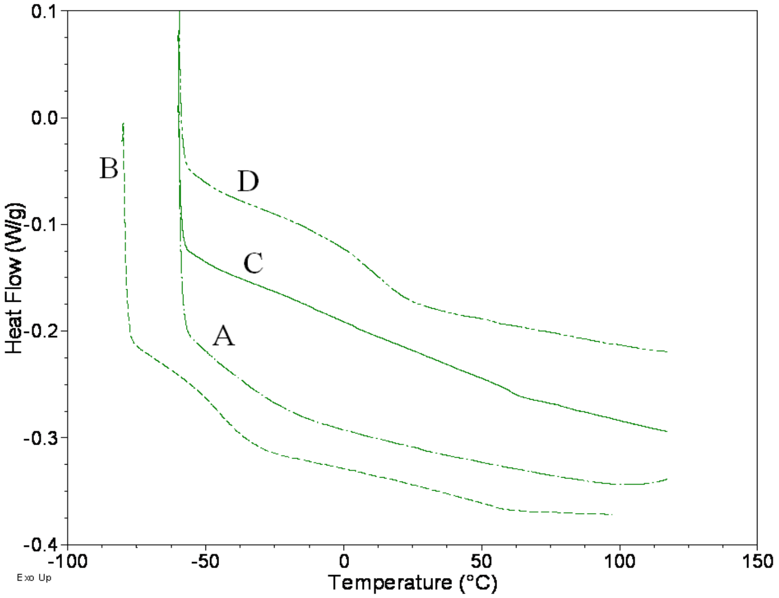


Figure 3.77. DSC curves of (A) homopolymers of allylic methacrylate of methyl oleate (METMO) (B) n butyl acrylate (C) methacrylic acid and (D) styrene copolymers.

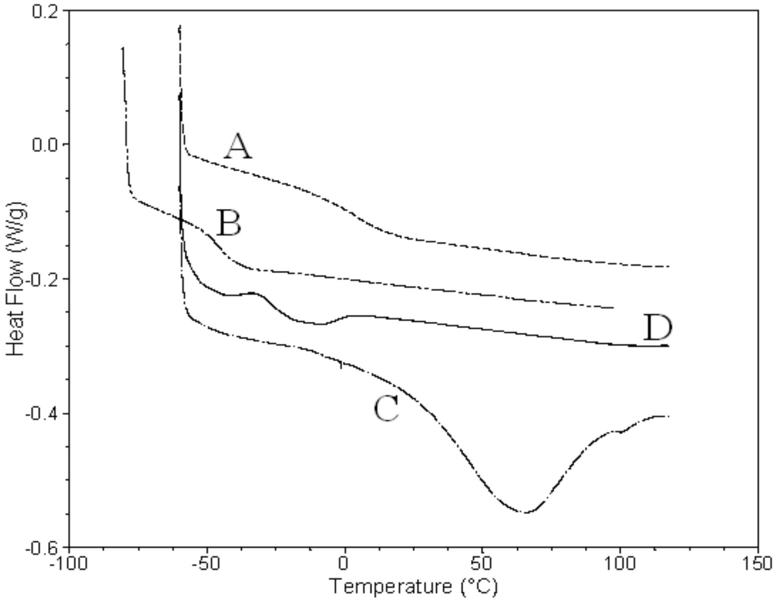


Figure 3.78. DSC curves of (A) homopolymers of allylic acrylate of methyl oleate (ACMO) and (B) n butyl acrylate (C) methacrylic acid and (D) styrene copolymers

3.7. Synthesis of quaternary ammonium salts of plant oil triglycerides and methyl esters

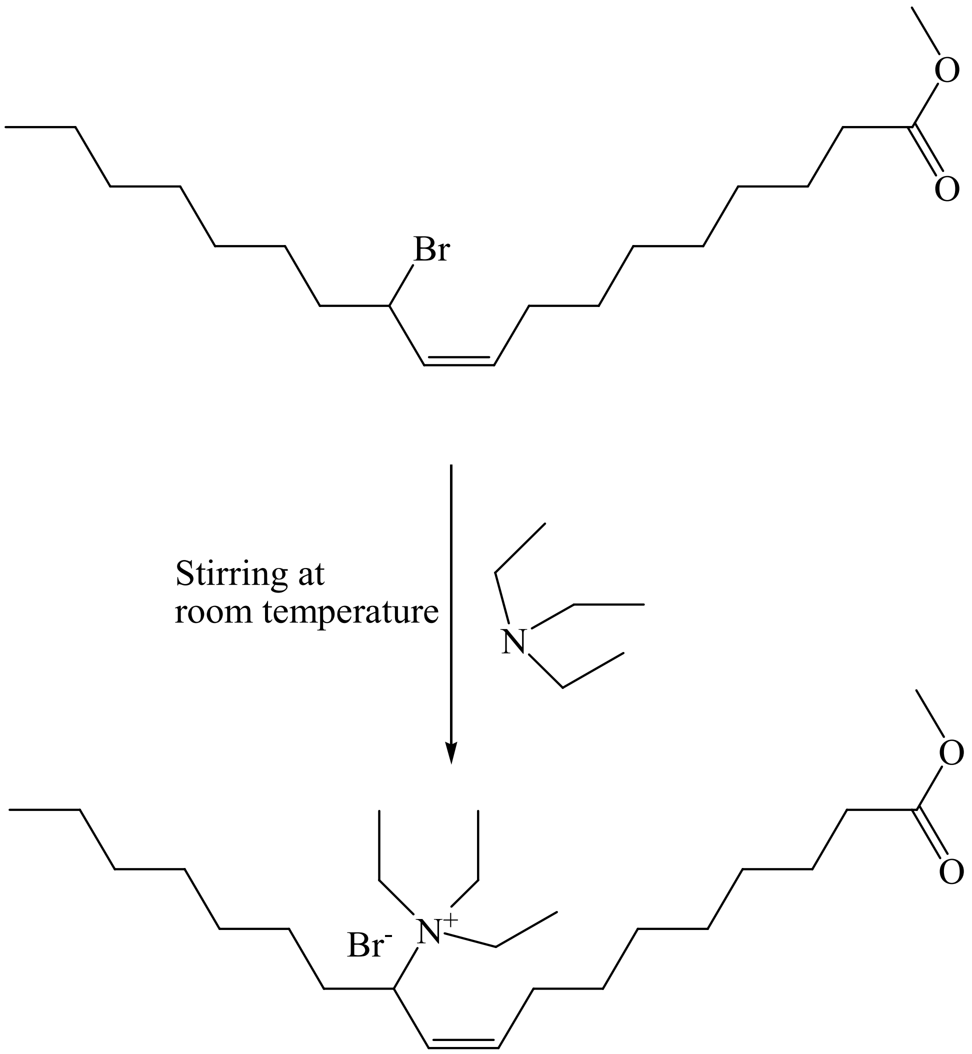


Figure 3.79. presentation of quaternarization of allylic bromines by using methyl oleate as a model compound.

Nitrogen containing compounds especially amines are good nucleophiles than carboxylates. Reaction of the tertiary amines and alkyl halides give quaternary ammonium salts at moderate temperatures. At high temperatures elimination would be favored depending on the basicity of the tertiary amines.

Among the alkyl halides, the ease of the reactivity is high in allylic halides especially allylic bromides [101]. For this reason, ABSO and ABMO were reacted with triethyl amine at 50 °C for one day to give quaternary ammonium salts. Actually, according to IR spectrum the reaction between allylic bromides and triethyl amine, complete in 5 hours. But ACSO and ABMO also contain secondary alkyl bromides. These compounds are not as reactive as allylic bromides. Thus longer reaction times were needed.

After completion substitution reaction, brown colored oily materials were obtained. Characterization of the quaternary ammonium salts were done by IR and ^{1}H NMR techniques. IR spectrum showed same characteristic peaks for both compounds. Peaks were observed at around 2740, 2680, 2490 cm-1, probably due to the C-H stretching of the triethyl ammonium group. Also a medium peak was also observed at at 1397 and at 1035 cm-1 probably due to C-N out of plane bending vibration (Figure 3.80 and 81).

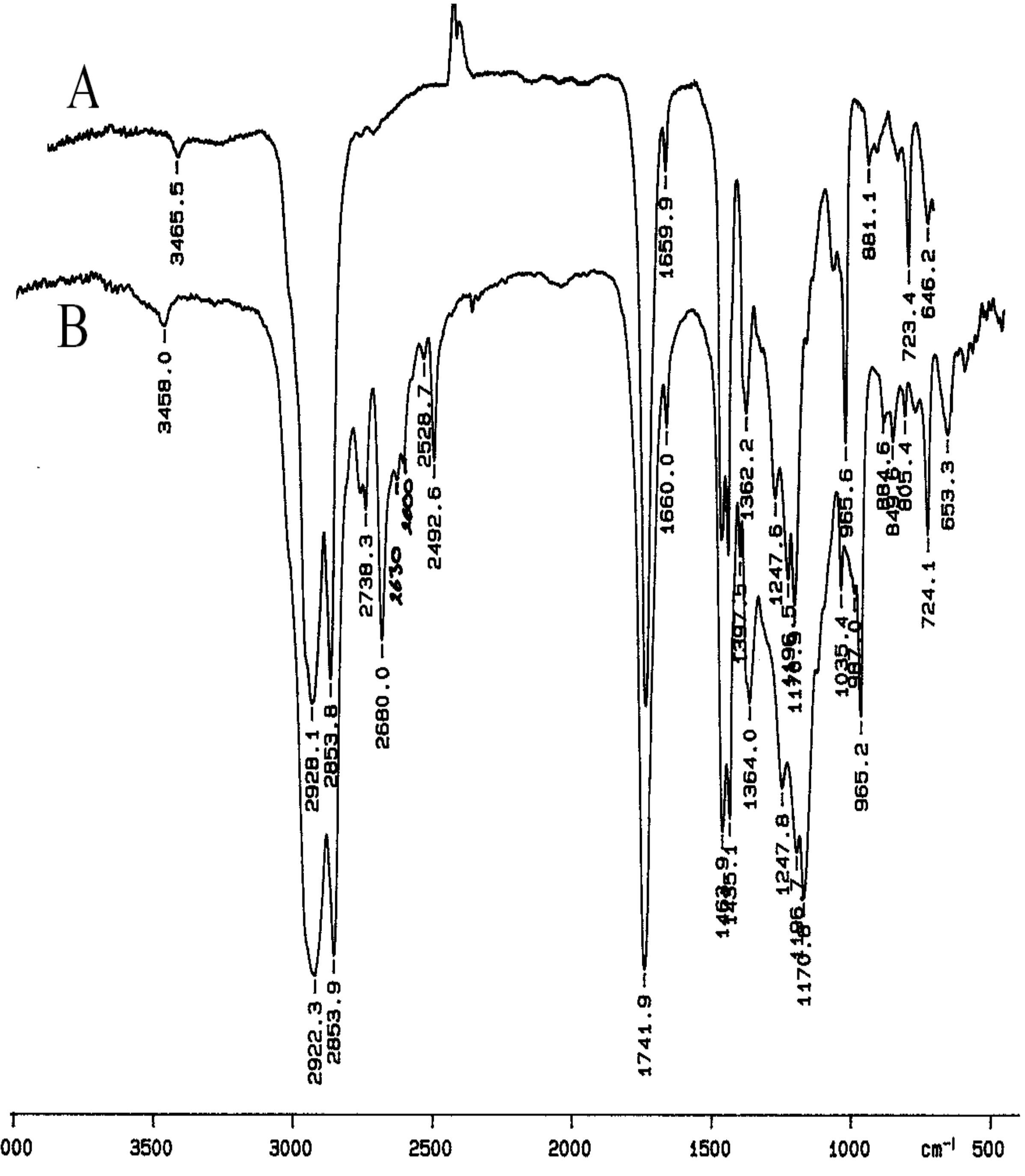


Figure 3.80. IR spectra of (A) ABMO and (B) quarternarized methyl oleate (AQMO).

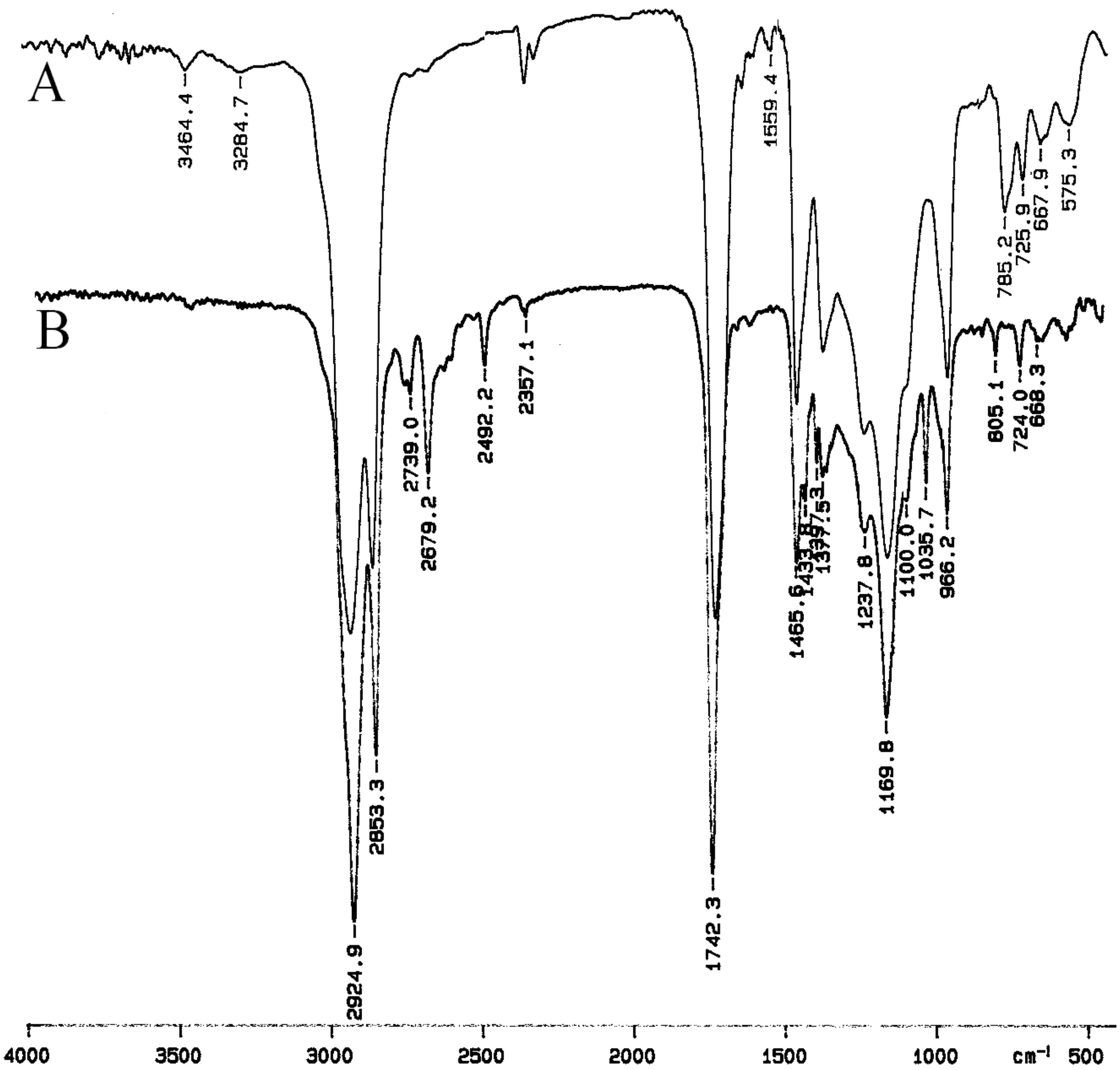


Figure 3.81. IR spectra of (A) ABSO and (B) AQSO

When quaternarization occurred peak at the 4.2 disappeared and a new peak was observed at 4.8 ppm due to the proton which is at the same carbon atom with quaternary ammonium group. ^{1}H NMR spectrum also showed a multiplet at 3.3 ppm due to the $–CH_2$- group of triethyl ammonium group. The integration of this peak was 6 times higher than a peak which appeared at 4.8 (Figure 3.82 and 83). The ratio also proved the structure.

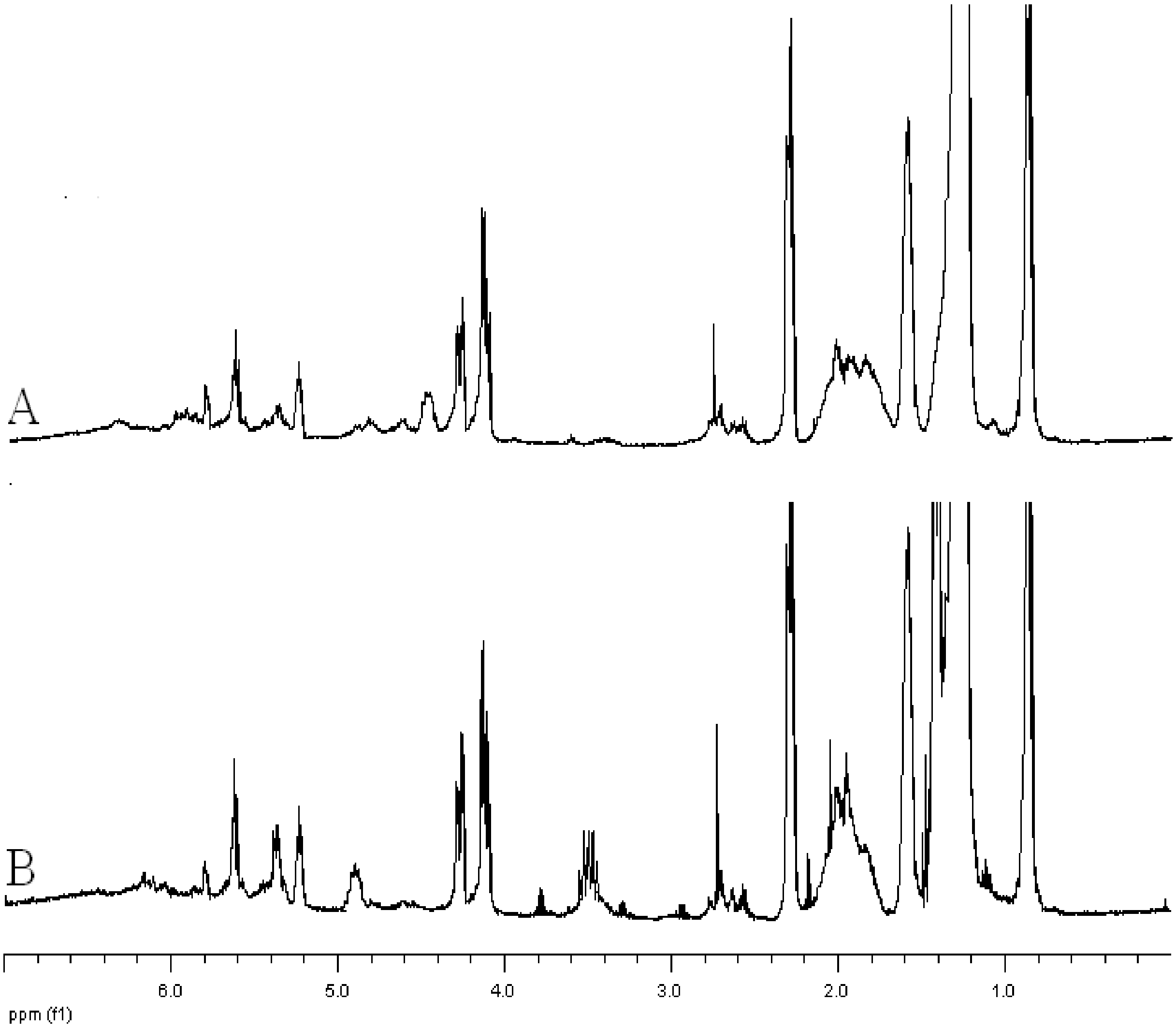


Figure 3. 82. ^{1}H NMR spectra of (A) ABSO and (B) AQSO.

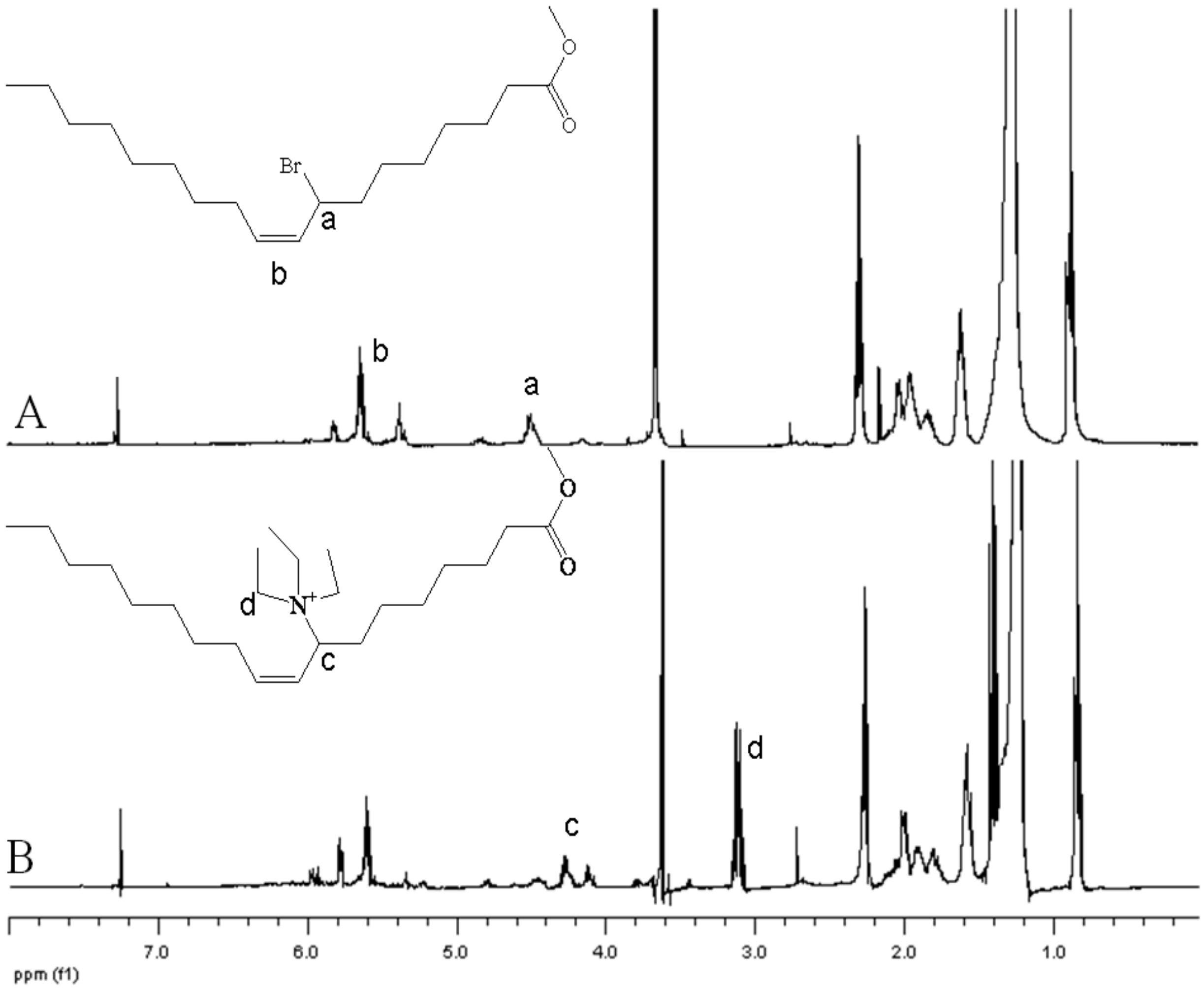


Figure 3.83. ^{1}H NMR spectra of (A) ABMO and (B) AQMO.

Based on ^{1}H NMR results, 70 per cent of the ABMO was converted to quaternary ammonium salts. The yield for the quaternarization of the ABSO approached to 50 per cent which means that 1 equivalent of quaternary ammonium group exists per soybean oil triglyceride. Both of the compounds showed good water solubility and were used as an intercalant for the synthesis of bio-based nano composites [102].

3.8. Synthesis and polymerization of allylic amines of methyl oleate and soy oil methyl esters

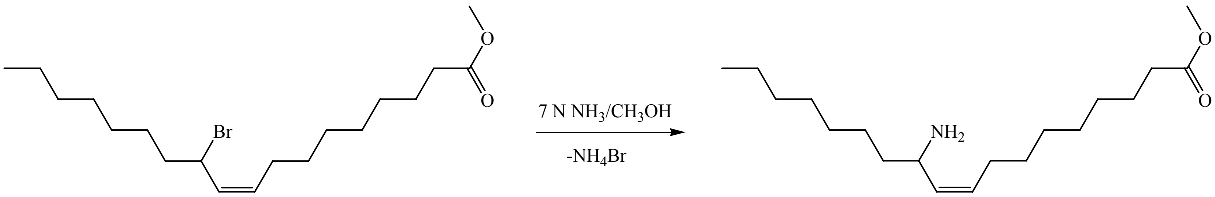


Figure 3.84. Synthesis of allyl amine of methyl oleate

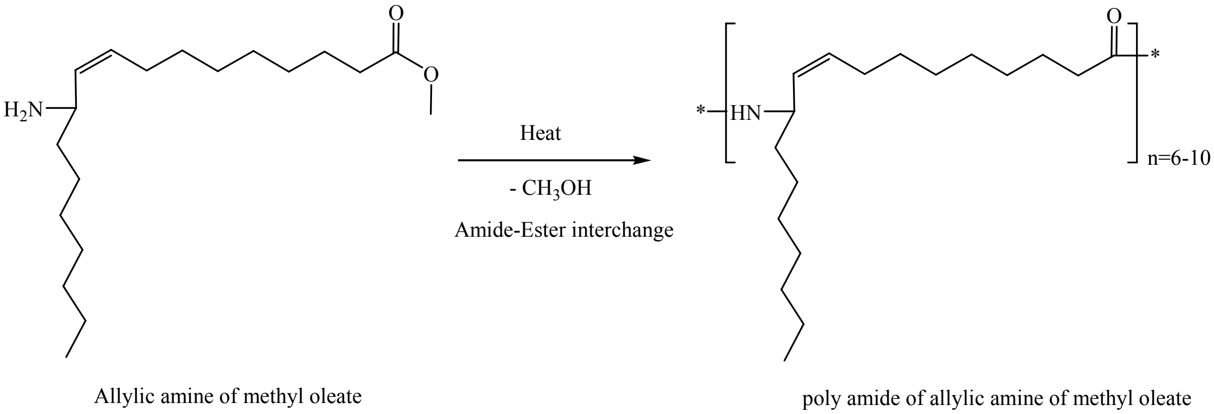


Figure 3.85. Polymerization of allylic amine of methyl oleate.

The simplest amine that one can use in the substitution of a halide is ammonia. Reaction of simple alkyl halides with ammonia often gives a mixture of the primary secondary, and tertiary amines, and quaternary ammonium salts. To prevent obtaining a mixture of amines ammonia should be used as high as 70-100 per cent excess of alkyl halide

Ammoniac solutions unfortunately, can not be used for the preparation of allylic amines of methyl oleate and soy oil methyl esters because of the hydrolysis of the methyl esters in the basic solutions. For this reason, it was preferred to use 7N NH_3 in dry CH_3OH solution. In the literature, it was found that some benzylic halides which contained 12 or more carbon were reacted with this reagent at room temperature for two hours and gave primary amines at 85 percent yields. Rest of the product composed of secondary amines [103].

This procedure was also suitable for the amination of the methyl oleate. Methyl oleate was also soluble in this reagent and this would facilitate the reaction. In the first trial, methyl oleate was stirred with this reagent at room temperature for 24 hours and it was observed that just 5 percent of methyl oleate underwent ester amide exchange and the rest was aminated as desired. In other reactions, ABMO and ABSOME were stirred with 7 N NH_3/CH_3OH different time intervals such as 2, 4, 6, and 24 hours. ^{1}H NMR showed that when the reaction time were increased, yields of the reaction also increased. After 24 hours approximately 100 per cent yields could reach.

Allylic amines of the methyl oleate and soy oil methyl esters were characterized by IR and ^{1}H NMR. In the IR spectrum at 1670 cm^{-1} a weak peak was observed due to the NH deformation vibration. At 1090 a medium peak was observed due to the C-N vibrations of the allylic amines. Peak at 963 cm^{-1} was shifted to 970 cm^{-1} because of the change of the environment of the allylic positions. Peak at 650 cm-1 disappeared due to the lost of bromine atom in the molecule. There is new peak observed at 845 and 880 cm^{-1} probably due to the out of plane bending of the N-H bonds. Peaks at 784 and 767 cm^{-1} disappeared also (Figure 3.86).

In the ^{1}H NMR spectra it was easier to follow the changes. Few changes were observed. Peak at 4.4 ppm disappeared and new peaks were observed at 3.4 ppm ($-C\mathbf{H}-NH_2$) and 3.2 ppm ($-CH2-N\mathbf{H_2}$). The shape of allylic protons in the NMR spectrum also changed. A new peak was observed in the ^{1}H NMR spectrum of the allylic amine of the ABSOME at 4.2 due to the amine at the double allylic position. The ratio of the peak intensities at 3.2 to 3.4 gave 2 which was the proof of the structure (Figure 3.87).

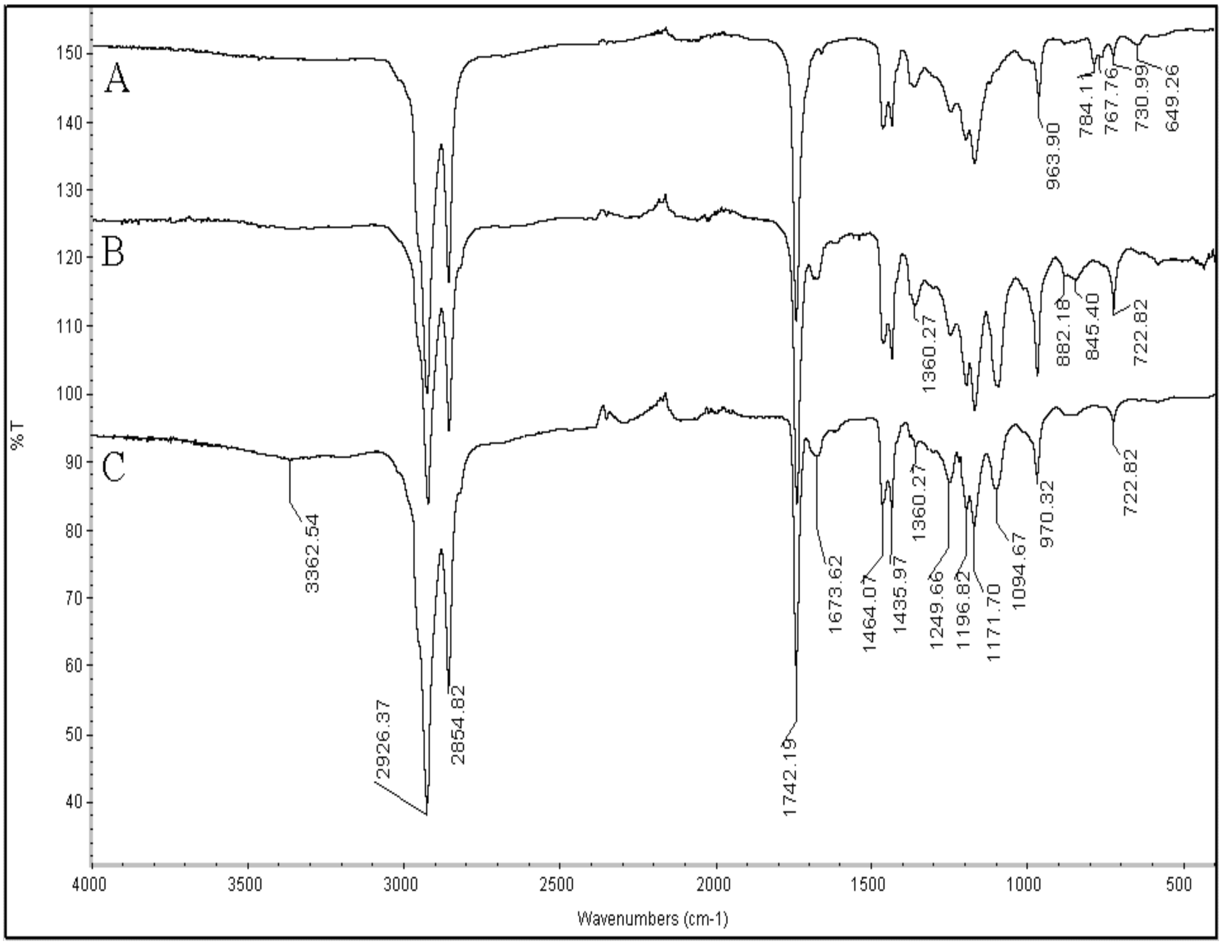


Figure 3.86. IR spectra of (A) allylic brominated methyl oleate, (B) allylic amine of methyl oleate, and (C) allylic amines of soy oil methyl esters.

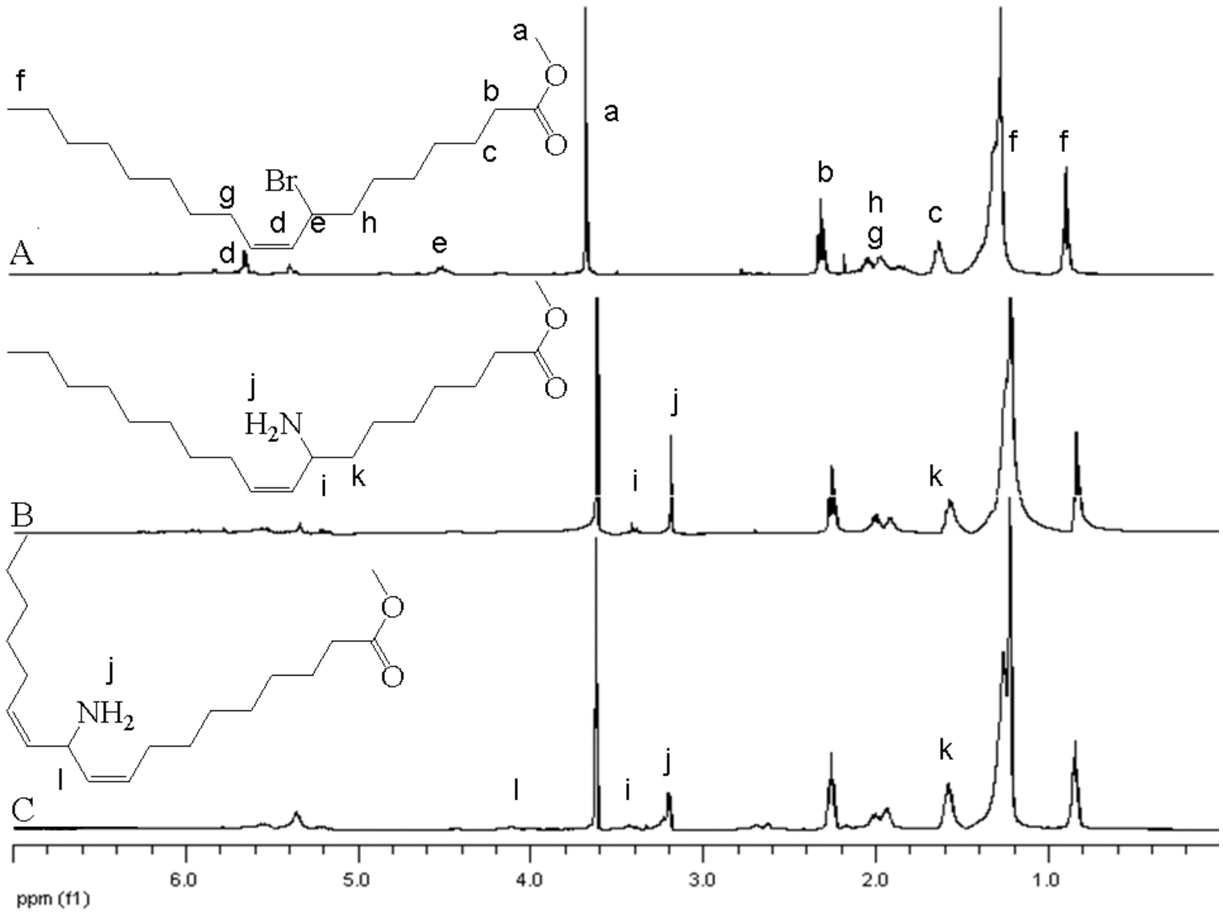


Figure 3.87. ^{1}H NMR's of (A) allylic brominated methyl oleate, (B) allylic amine of methyl oleate, and (C) allylic amines of soy oil methyl esters.

Allylic amines were also polymerized without catalyst. Monomers were heated to 120 under n2 for 4 hours than temperature was raised to 180 °C for 12 hours. Then materials heated to 200 °C. For 10 hours. After the process slightly cross linked polyamides were obtained. TGA of the reaction mixture was also strengthening these findings. In the TGA graphs, the weight lost peaks of the materials shifted to higher temperatures (Figure 3.90). Five per cent weight lost temperatures were also shifted from 137 °C to 187 °C.

In the IR spectra the characteristic peaks for the polyamides were observed. At 3470 cm-1 a peak observed due to the NH stretching. Peaks were detected at 1662 and 1625 cm^{-1} due to the CO absorption (Amide I band). A weak peak was observed at 1535 and 1380 cm^{-1} due to the NH deformation (Amide II band). Peak at 1090 cm^{-1} of the allylic amines disappeared. A new peak was also seen at 1005 cm^{-1} probably due to the NH stretching of secondary amides (Figure 3.89)

The polyamides produced did not show any good mechanical and thermal properties. They are gummy materials which molecular weights around 2000 Dalton with a 2, 5 PDI. This molecular weight indicated that the number of the repeating unit is around 7. although their insufficient thermal and mechanical properties, these materials may have a potential for synthesizing printing inks.

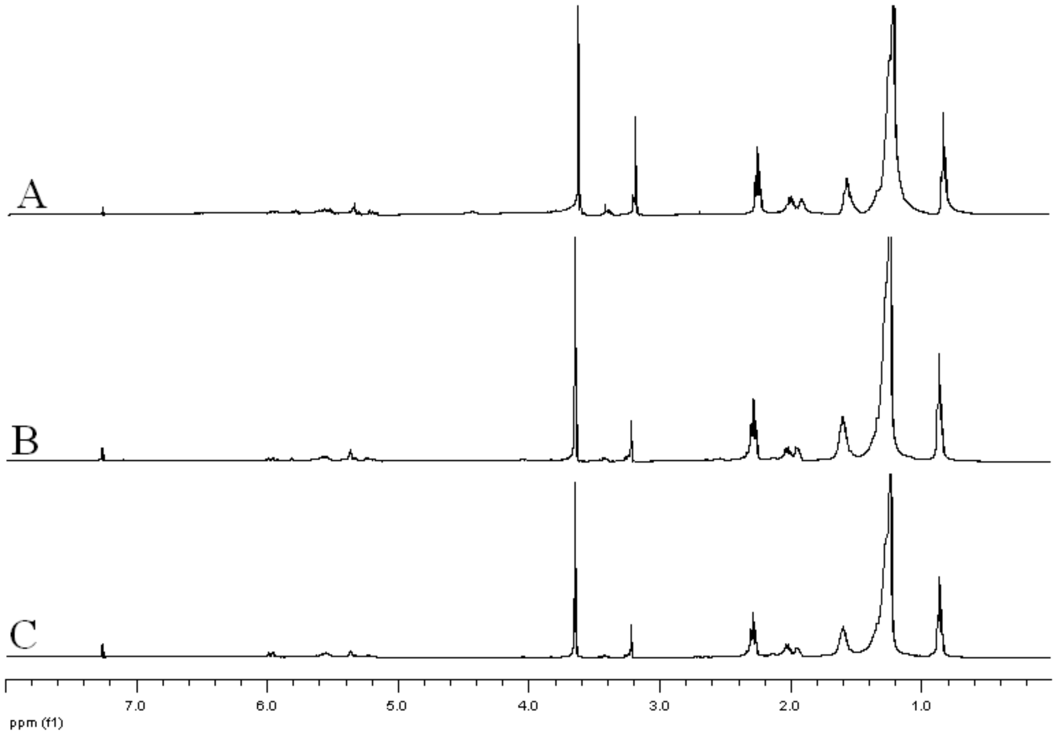


Figure 3.88. ^{1}HNMR spectra of (A) AAMEO and (B) polyamide of AAMO at 180 ^{o}C and (C) at 200 ^{o}C.

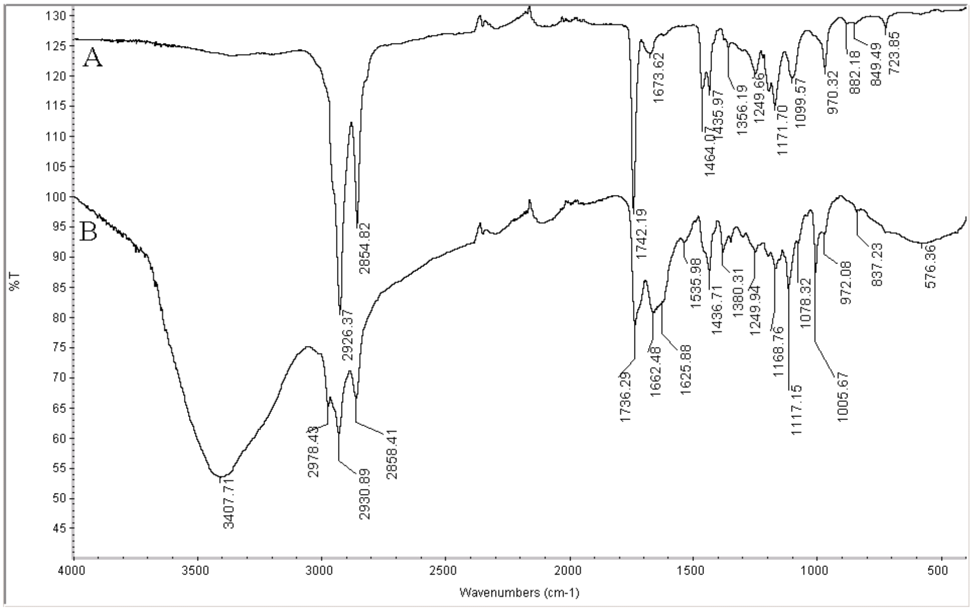


Figure 3.89. IR spectra of (A) Allylic amine of methyl oleate (AAME) and (B) polyamide of AAME

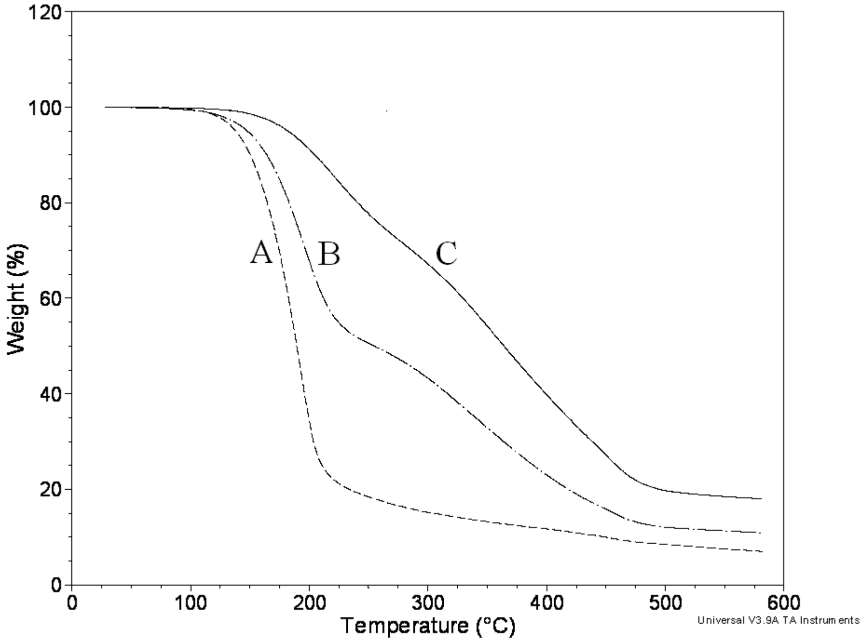


Figure 3.90. TGA traces of (A) AAMO (B) PAAMO at 180 °C and (C) PAAMO at 200 °C.

4. EXPERIMENTAL

4.1. Chemicals and Apparatus

4.1.1. Chemicals:

Soybean oil, cod liver oil and olive oil used were food grade and they were dried in vacuum oven before use. linseed oil was used without any further treatment. NBS (N-bromo succinimide), KOH, acrylic acid, maleic acid, methacrylic acid, styrene, trietyl amine, CCl_4, $CHCl_3$, *p tertiary* butyl, *p tertiary* octyl, *p* phenyl phenol, pyridine, methanol and NaOCN were purchased from Merck and they were used as received. THF was obtained from J.T. Beaker. $AgNO_3$ purchased from Horasan Kimya, Castor oil was purchased from Aklar Kimya. 7 N NH_3 in methanol, and P. ethyl phenol was purchased from Aldrich. Benzoyl peroxide was purchased from Fisher Scientific and was recrystallized from methanol before use. The technical grade azobisizobutyronitrile (AIBN) was supplied from Fluka and was recrystallized from warm methanol before use.

4.1.2. Apparatus:

IR characterization of compounds was performed by Perkin-Elmer FT-IR 1600 series spectrometer using KBr windows. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400-MHz NMR instrument (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. The spectra were recorded as ppm (δ) with $CDCl_3$ as a solvent. DSC characterizations were performed by "Thermal Analyses" Q 200 instrument (New Castle, DE, USA) with a heating rate 10 °C / min under nitrogen atmosphere from -70 to 120 ^{o}C. TGA characterizations were performed by

"Thermal Analyses" Q 50 instrument (New Castle, DE, USA) with a heating rate 10 °C / min under nitrogen atmosphere from room temperature to 600 ^{o}C. The dynamic mechanical properties of the suitable polymers were measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, DE, USA) in the single-cantilever mode at a frequency of 1 Hz and a heating rate of 3 °C/min under nitrogen atmosphere. The samples for the DMA experiments were prepared with a microtome into rectangular shapes having the average dimensions of 12 x 35 x 3 mm^3.The swelling behaviors of the polymers were tested in CH_2Cl_2 by using a Gartner 7109-46 traveling microscope. Strain tests were performed by Zwick Material Prüfung 1446 Model tester with a 20 mm/min elongation rate and Devotrans DVG 32 Model tester with a 20 mm/min elongation rate.

4.2. Dimethylol resols

4.2.4. Synthesis of *p.* ethyl phenol resol:

Para ethyl phenol, 43.65 g, was mixed with 2.21 g of NaOH and 43.54 g of 37 per cent formalin solution. The mixture was then heated to 90-92 ^{o}C for 1 hour. The crude red colored product was dissolved in diethyl ether and washed several times with distilled water then was dried over Na_2SO_4 and the solvent was evaporated at 35 ^{o}C in a rotevaporator.

4.2.5. Synthesis of *p. tertiary* butyl phenol resol:

Para *tertiary* butyl phenol, 54.24 g of, was mixed with 2.21 g of NaOH and 43.54 g of 37 per cent formalin solution. The mixture was heated to 90-92 ^{o}C for 1 hour. Around 40-50 ^{o}C the solution was colorless and homogenous. Then the crude product was dissolved in diethyl ether and washed with distilled water several times and dried over Na_2SO_4. Ether was evaporated in a rotevaporator.

4.2.6. Synthesis of *p. tertiary* octyl phenol resol:

Para *tertiary* octyl phenol, 37.24 g, mixed with 1.105 g of NaOH and 22 g of 37 per cent formalin solution. This mixture was heated to 90-92 °C for 1 hour. The product was dissolved in diethyl ether and washed several times with tap water then dried over Na_2SO_4. Ether was evaporated in a rotevaporator.

4.2.7. Synthesis of *p.* phenyl phenol resol:

Thirty g of (0.176 mol) *p.* phenyl phenol was mixed with 1.056 g of NaOH (0.0264 mol) and 21.5 g of 37 per cent formalin solution (0.264 mol formaldehyde). The mixture was heated to 92 °C for one hour. Crude product was dissolved in diethyl ether and washed with water several times then dried over Na_2SO_4. Ether was evaporated in a rotevaporator.

4.2.8 Polymerization of oil soluble resoles with linseed oil:

Oil soluble resoles were mixed with linseed oil by weight. Mixtures containing 10-50 per cent resoles were prepared. To these mixtures maleic acid (3 per cent of phenolic resin) was added. Mixture was preheated to 80 °C in vacuum oven for half an hour then vacuum was applied to remove any volatile component. Then these mixtures were poured into Teflon molds and the temperature was then raised to 145 °C. All polymerization reactions were performed for 24 hours. for mechanistic experiments, the reaction time was 12 hours.

4.2.9. Polymerization of oil soluble resoles with soybean oil:

Oil soluble resoles were mixed with soybean oil by weight. Mixtures containing 50-70 per cent resoles were prepared. To these mixtures maleic acid (3 per cent of phenolic resin) was added. Mixture was preheated to 80 °C in vacuum oven for half an hour then vacuum was applied to remove any volatile component. Then these mixtures were poured to Teflon molds and the temperature was then raised to 145 ^{o}C. Polymerization reactions were performed for 24 hours.

4.2.10. Polymerization of oil soluble resoles with cod liver oil:

Oil soluble resoles were mixed with cod liver oil to give mixtures containing 60-70 per cent resoles. To these mixtures maleic acid (3 per cent of phenolic resin) was added. Mixture was preheated to 80 ^{o}C in vacuum oven for half an hour then vacuum was applied to remove any volatile component. Then these mixtures were poured to Teflon molds and the temperature was then raised to 145 ^{o}C. Polymerization reactions were performed for 24 hours.

4.2.11. Synthesis of p. tertiary butyl phenol furfural (TBP-F) resin:

Method A: 37.5 g of *p tertiary* butyl phenol mixed with 37.5 g of water. 3.75 g of NaOH and 70 ml of toluene was added to this mixture and heated to 60 ^{o}C. Then 48 g of furfural is added dropwise in 30 minutes. Then the temperature was increased and allowed to reach reflux temperature. Reflux was continued for 2 hours and the mixture was cooled. 100 ml of diethyl ether was added to the mixture and crude product was washed with concentrated salt solution 4 times and washed with tap water until the color of water phase was slightly reddish. Then the residual toluene and water was removed on a rotevaporator at 95 ^{o}C. The GPC result indicated that the MW of the polymer was 1850 which means the average number of repeating units is 7.

Method B: 1 g of K_2CO_3 was dissolved in 50 g of *p tertiary* butyl phenol by heating to 135 ^{o}C in 3 necked flask. 37.5 g of furfural was added dropwise over a period of 30 minutes. Temperature was maintained at 135 ^{o}C for 4 hours. The GPC result indicated that the MW of the polymer was 1500 which indicates that the average number of repeating units is 5.

4.2.12. Polymerization of TBP-F resin with AESO:

TBP-F resin, 15 g, and 20.64 g of AESO (Acrylated Epoxidized soybean oil) were mixed in 50 ml dry $CHCl_3$. To this mixture, 0.3564 g $FeCl_3$ (2 per cent of phenolic resin by weight) solution in 20 ml $CHCl_3$ was added. Stirring was continued until all materials were dissolved. Then this homogenous solution was poured to mold and $CHCl_3$ was removed at 50 ^{o}C in a vacuum oven. Dark red colored creamy mixture was obtained and then this mixture was cured at 110 ^{o}C for 1 hour under N_2 atmosphere. A flexible, though , rubbery polymer was obtained.

4.3. ABMO (Allylic brominated methyl oleate)

4.3.1. Synthesis of ABMO:

Methyl oleate, 29.0 g (0.1 mol) and 17.8 g of NBS (0.1 mol) were mixed in 150 ml of freshly distilled CCl_4. The mixture was refluxed for 4.5 h. The mixture was protected from light and kept overnight at room temperature and then filtered. CCl_4 was evaporated at 30 °C under vacuum. 37.0 g of orange colored oil was obtained. The desired mono allylic bromide was obtained in 80 per cent yield. The crude product was purified by column chromatography (28 cm x 2 cm) on silica gel 60 (*Merck*, 70-230 mesh) with n-pentane/chloroform (8.5:1.5) as eluent to give 29,6 g (80 per cent yield) of allylicly brominated methyl oleate (ABMO)

4.4. ABSOME (allylic brominated soyoil methyl esters)

4.4.1. Synthesis of ABSOME:

Soybean oil methyl esters (SOME), 30 g, were mixed with 30 g of NBS in 150 ml of freshly distilled CCl_4. The mixture was refluxed for 4.5 h. The mixture was protected from light and kept overnight at room temperature and then filtered. CCl_4 was evaporated at 30 °C on a rotevoporator.

4.5. ABSO (Allylic brominated soybean oil)

4.5.1. Synthesis of ABSO:

Soybean oil, 20 g, and 25 g of NBS were mixed in 150 ml of CCl_4. The mixture was refluxed for 4.5 h. At the end of the reflux, the mixture was kept overnight in the dark at room temperature and then filtered. An orange solution was obtained. Solvent was evaporated under reduced pressure at 30 °C. Approximately 30 g of allylic brominated soybean oil was obtained. This compound was used in the next steps without purification because all the products and side products are alkyl halides reactive toward the AgNCO and the sep.tion of all the positional isomers was not possible by any sep.tion technique.

4.4. SONCO (Isocyanated soybean oil)

4.4.1. Synthesis of SONCO :

Crude ABSO, 8 g, was dissolved in 20 ml of dried THF. 6 g of AgNCO slurry in 60 ml THF was added in 3 portions with 1 hour intervals at room temperature. Stirring was continued for 4 more h and the flask was kept overnight at room temperature. During the whole operation the app.tus should be covered with aluminum foil and should be dry.

4.4.2. Polymerization of SONCO with castor oil:

2.5 g of SONCO (1.78 mmol) was mixed well with 2.1 g of castor oil (2.21 mmol, assuming the generally accepted molecular weight of 932 g). Mixture was poured into a Teflon mold and heated to 120 °C for 5 h. A soft very flexible rubbery solid was obtained.

4.4.3. Polymerization of SONCO with glycerol:

SONCO, 2.5 g, (1.78 mmol) was mixed well with 0.2464 g of glycerol (2.678 mmol). Mixture was poured into a Teflon mold and heated to 110 °C for 5 h. At the end of reaction semi soft rubbery polymer was obtained.

4.4.4. Polymerization of SONCO with TETA:

SONCO, 2.5 g, (1.78 mmol) was mixed well with 0.13 g of TETA at room temperature. The mixture started to solidify suddenly and heat released. At the end of the reaction a hard polymer was obtained.

4.5. ITSO (Isothiocyanated Soybean oil)

4.5.1 Synthesis of ITSO:

ABSO, 14 g, (0.01 moles) was dissolved in 20 ml of dried THF. 1.52 grams of NH_4SCN was dissolved in another 20 ml of dry THF. These clear solutions were mixed together and refluxed for 5 hours. Then THF was evaporated in a rotevaporator. The brown oily product was obtained. This product then was centrifuged in order to get rid of excess NH_4NCS.

4.5.2. Polymerization of ITSO with castor oil:

ITSO, 2.5 g, (0.00178 moles) was mixed well with 2.1 grams of castor oil (0.00221 moles). Mixture was poured into a Teflon mold and heated to 140 °C for 5 hours. A soft very flexible rubbery solid was obtained.

4.5.3. Polymerization of ITSO with glycerol:

ITSO, 2.5 g, (0.00178moles) was mixed well with 0.163 grams of glycerol (0.00178 moles). Mixture was poured into a Teflon mold and heated to 140 °C for 5 hours. At the end of the reaction a hard polymer was obtained.

4.5.3. Polymerization of ITSO with ethylene glycol:

ITSO, 2.5 g, (0.00178moles) was mixed well with 0.111 grams of ethylene glycol (0.0018 moles). Mixture was poured into a Teflon mold and heated to 140 °C for 5 hours. At the end of the reaction a hard polymer was obtained.

4.5.4. Polymerization of ITSO with ethylene diamine:

ITSO, 2.5 g, (0.00178moles) was mixed well with 0.108 grams of ethylene diamine (0.0018 moles). This mixture started to solidify even at room temperature. Thus the mixture was poured into a Teflon mold quickly and heated to 140 °C for 5 hours. At the end of the reaction a hard polymer was obtained.

4.5.5. Polymerization of ITSO with triethylene tetra amine:

ITSO, 2.5 g, (0.00178moles) was mixed well with 0.2628 grams of triethylene tetra amine (0.0018 moles). This mixture also started to solidify even at room temperature. Thus the mixture was poured into a Teflon mold quickly and heated to 140 °C for 5 hours. At the end of the reaction a hard polymer was obtained.

4.5. ISONCO (Iodo isocyanated soybean oil)

4.5.1. Synthesis of ISONCO

In a 250 ml round bottom flask, which was covered with aluminum foil, 19.82 g of freshly prepared AgNCO was mixed with 200 ml of THF. This slurry was cooled to – 30 ^{o}C.

To this cold mixture 25.4 g of I_2 was added. Stirring was continued for 2 hours in order to obtain INCO formation. Then to this mixture, 20 g of dry soybean oil was added. Mixture was kept at room temperature for approximately 2 hours. At the end of the reaction, the red color of the solution disappeared. The slurry was filtered and resulting yellow colored solution was evaporated in a rotevaporator. The product was a yellow viscous oil.

4.5.2. Polymerization of ISONCO with ethylene glycol:

ISONCO, 5 g, (0.00357 mol) and 0.332 g of ethylene glycol (0.00535 mol) were mixed in a Teflon mold. 1 drop of pyridine was added as catalyst. This mixture was allowed to stay over night. Very flexible red colored rubber was obtained.

4.5.3. Polymerization of ISONCO with castor oil

ISONCO, 5 g, (0.00357 mol) and 3.32 g of castor oil (0.00357mol) were mixed in a Teflon mold. 1 drop of pyridine was added as catalyst. This mixture was allowed to stay over night. Strong flexible red colored rubber was obtained.

4.5.4. Polymerization of ISONCO with glycerol:

ISONCO, 5 g, (0.00357 mol) and 0.328 g of dry glycerol (0.00357mol) were mixed in a Teflon mold. 1 drop of pyridine was added as catalyst. This mixture was allowed to stay over night. Strong flexible red colored rubber was obtained.

4.5.5. Polymerization of ISONCO with ethylene diamine:

ISONCO, 5 g, (0.00357 mol) and 0.321 g of ethylene diamine (0.00535 mol) were mixed. The reaction between amine and ISONCO was complete in a few seconds. A white flexible solid was obtained at first. The color of the solid turned to reddish-brown with time (approximately after1 day).

4.5.6. Polymerization of ISONCO with hexamethylene diamine:

ISONCO, 5 g, (0.00357 mol) and 0.557 g of hexamethylene diamine (0.00535 mol) were mixed. The reaction was complete in a few seconds. A white flexible solid was obtained at first. The color of the solid turned to reddish-brown with time (approximately after1 day).

4.5.7. Polymerization of ISONCO with triethylene tetra amine:

ISONCO, 5 g, (0.00357 mol) and 0.393 g of triethylene tetra amine (0.00269mol) were mixed. The reaction was complete in a few seconds. A white flexible solid was obtained at first. The color of the solid turned to reddish-brown with time (approximately after1 day).

4.6. ACMO (Allylicly Acrylated Methyl Oleate)

4.6.1. Synthesis of ACMO:

ABMO, 20 g, (0.0533 mol) was mixed with 30 g of acrylic acid which contains (0.0533 mol potassium acrylate). This mixture was heated to 45 ^{o}C and stirred overnight. The crude product was washed with several times with water then washed with 5 per cent $NaHCO_3$ solution until no bubbling was observed. The crude product was purified by column chromatography (28 cm x 2 cm) on silica gel 60 (70-230 mesh) with petroleum ether/chloroform (8.5:1.5). About 75 per cent yield was obtained.

4.6.2. Copolymerization of ACMO with styrene

ACMO, 2 g, was mixed with 1 g of styrene. To this mixture 0.12 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^{o}C overnight. A yellow soft cross-linked material was obtained.

4.6.3. Copolymerization of ACMO with methyl acrylate

ACMO, 2 g, was mixed with 0.5 g of methyl acrylate. To this mixture 0.1 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^{o}C overnight. A red, soft, cross-linked material was obtained

4.6.4. Copolymerization of ACMO with n butyl acrylate:

ACMO, 2 g, was mixed with 1 g of n butyl acrylate. To this mixture 0.12 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^{o}C overnight. A red, soft, cross-linked material was obtained

4.6.5. Copolymerization of ACMO with methacrylic acid:

ACMO, 2 g, was mixed with 0.5 g of methacrylic acid. To this mixture 0.1 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^{o}C overnight. A hard, cross-linked material was obtained

4.7. METACMO (allylic methacrylate of methyl oleate)

4.7.1. Synthesis of METACMO:

ABMO, 20 g, (0.0533 mol) was mixed with 30 g of methacrylic acid in 100 ml CH_3OH/Dimethylacetamide solution which contains (0.0533 mol potassium methacrylate). Then this mixture was heated to 60 ^oC and stirred overnight. The crude product was washed with several times with water then washed with 5 per cent $NaHCO_3$ solution until no bubbling was observed. The crude product was purified by column chromatography (28 cm x 2 cm) on silica gel 60 (70-230 mesh) with petroleum ether/chloroform (8.5:1.5). About 75 per cent yield was obtained.

4.6.2. Copolymerization of METACMO with styrene

METACMO, 2 g, was mixed with 1 g of styrene. To this mixture 0.12 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^oC overnight. A yellow soft cross-linked material was obtained.

4.6.3. Copolymerization of METACMO with methyl acrylate

METACMO, 2 g, was mixed with 0.5 g of methyl acrylate. To this mixture 0.1 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^oC overnight. A red, soft, cross-linked material was obtained

4.6.4. Copolymerization of METACMO with n butyl acrylate:

METACMO, 2 g, was mixed with 1 g of n butyl acrylate. To this mixture 0.12 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^oC overnight. A red, soft, cross-linked material was obtained

4.6.5. Copolymerization of METACMO with methacrylic acid:

METACMO, 2 g, was mixed with 0.5 g of methacrylic acid. To this mixture 0.1 g of benzoyl peroxide was added. N_2 gas was purged for 5 minutes and the test tube was sealed and heated to 85 ^oC overnight. A hard, cross-linked material was obtained

4.8. ACSO (Allyic acrylate of soybean oil)

4.8.1. Synthesis of ACSO:

Acrylic acid (20 g, 0.277 mol) was dissolved in 50 ml dimethyl acetamide. KOH (3 g, 0.0535 mol) was dissolved in 50 ml of methanol. Then this methanol solution was added to methacrylic acid solution. The resulted solution contained 0.0535 mol K acrylate. To this clear solution, 15 g of ABSO was added. The mixture was stirred 24 hours at 60 ^oC. The crude product was washed with water several times then washed with $NaHCO_3$ until no bubbling was observed. The crude product was used without any purification.

4.9.2. Polymerization of ACSO with styrene:

Benzoyl peroxide (0,3 g) was dissolved in 5 g of styrene. To this clear mixture, 5 g of ACSO was added. N_2 was purged for 10 minutes and the tube was sealed and waited at 80 ^oC overnight. A very soft rubbery red colored solid was obtained.

4.9. METACSO (Allylic methacrylate of soybean oil)

4.9.1. Synthesis of METACSO:

Methacrylic acid (20 g, 0.232 mol) was dissolved in 50 ml dimethyl acetamide. KOH (3 g, 0.0535 mol) was dissolved in 50 ml of methanol. Then this methanol solution was added to methacrylic acid solution. The resulted solution contain 0.0535 mol k methacrylate. To this clear solution, 15 g of ABSO was added. The mixture was stirred 24 hours at 60 ^oC. The crude product was washed with water several times then washed with $NaHCO_3$ until no bubbling was observed. The crude product was used without any purification.

4.9.2. Polymerization of METACSO with styrene:

Benzoyl peroxide (0,3 g) was dissolved in 5 g of styrene. To this clear mixture, 5 g of METACSO was added. N_2 was purged for 10 minutes and the tube was sealed and waited at 80 ^oC overnight. A rubbery soft red colored solid was obtained.

4.10. AQMO (Quaternary ammonium salt of methyl oleate)

10 g of ABMO (0.0266 mol) was diluted in 20 ml of THF. To this mixture 10 ml of TEA (0.072 mol) was added. After 30 min solution became turbid. And solution was stirred overnight at 45 ^{o}C. Then THF was evaporated in a rotevaporator. The crude product was used without any purification.

4.11. AQSO (Quaternary ammonium salt of soybean oil)

10 g of soybean oil (0.0071 mol) was diluted in 20 ml of THF. To this mixture 10 ml of TEA was added. After 30 min solution became turbid. And solution was stirred overnight at 45 ^{o}C. Then THF was evaporated in a rotevaporator. The crude product was used without any purification.

5. CONCLUSION

In this study, functionalization and polymerization of plant oil triglycerides were performed by using the allylic positions and double bonds of plant oil triglycerides.

Direct polymerization of the soybean, linseed, and cod-liver oil with different type of oil soluble resoles gave polymers with different physical properties. Linseed oil gave rubbery polymers when it was reacted with less than 40 per cent of resoles. Above 40 per cent, hard insoluble and infusible brown colored polymers were obtained. When the p. substituents of the phenyl ring of the resoles were changed from ethyl to tertiary octyl group, thermal and mechanical properties of the product were lower. Long alkyl chains act as an internal lubricator and this may be responsible for the observation of these changes. Among the plant oil triglycerides, linseed oil gave the polymers which had better mechanical and thermal properties by mixing with minimum amount of resoles. Linseed oil contains about 50 per cent of linolenic acid which would be responsible for the good results obtained with linseed oil polymers. Low resole amount also implied that linseed oil triglycerides were cross linked by resoles. Among the resoles, p. ethyl phenol resoles gave the best results. Small alkyl chains of the resin were too small and did not act as a lubricant.

By using allylic positions and double bonds of the soybean oil triglyceride valuable monomers were synthesized by the end of the study, allylic amine derivative, triethyl ammonium salts, allylic acrylates and methacrylates, isocyanates and isothiocyanates of soybean oil were synthesized. Substitution reactions of allyically brominated methyl oleate and soybean oil with suitable nucleophiles were used. Iodo isocyanates of the soybean oil was also synthesized by reaction between soybean oil and iodine isocyanate reagent.

Allylic amine of the methyl oleate and soy oil methyl esters gave gummy polyamide polymers by ester-amide exchange. These polyamides could be useful for printing ink or coating applications.

Quaternary ammonium salts of methyl oleate and soybean oil were oil soluble compounds. These salts were used as intercalant compounds for clay in the synthesis of bio based nanocomposites. They easily penetrated the interlayer galleries of the sodium montmorillonite which was determined the increase in the distance of interlayers of sodium montmorillonite clay.

Allylic acrylates and methacrylates of the methyl oleate and soybean oil gave rubbery orange colored cross linked materials. Methacrylates esters gave stronger materials than acrylate monomers, while the acrylates were tacky and soft.

Isocyanate containing soybean oil was synthesized in 60-70 per cent yield in two steps from alylicly brominated soybean oil. This isocyanate containing plant oil triglyceride is the first example of a plant based isocyanate. Although expensive AgNCO was used to synthesize isocyanate containing triglycerides, at the end of the reaction AgBr by-product is fully recovered and may then be used for regeneration of AgNCO. On the other hand, soy oil based poly isothiocyanates were synthesized by the reaction between allylic bromides and cheap ammonium thiocynanates in 70 per cent yields. Allylic isocyanates and isothiocyanates of the soybean oil were reacted with different polyols and poly amines to give corresponding polurethanes and polyureas and their thio analogs. Poly urethanes showed good elongation under small forces that is a typical behavior of the polyurethanes. Allylic isocyanates were reacted so fast with amines. Thus, shaped specimens could not be prepared. Thio analogs of the polyurethanes and ureas are tougher and elongations of the materials were much lower than the usual polyurethanes and ureas. Thermal stability of the poly thiourethanes and ureas were also higher than their oxy analogs. Additionally, diamines reacted with plant oil based isothiocyanates fast enough to be suitable for reaction injection molding (RIM) and resin transfer molding (RTM) processes.

Iodo isocyanates of the soybean oil triglycerides were synthesized by direct addition to double bonds. The maximum amount of the attached isocyanate group per triglyceride was three. Reaction of the soybean oil iodo isocyanate with different type of polyols and polyamines gave the corresponding polyurethanes and polyureas. It was interesting that polyols with low polarity such as castor oil mixed well and homogenous materials were obtained. If the polarity of the polyols was high as in glycerol the reaction was not complete even in one day. Curing with polyols should be conducted at low temperatures to minimize isocyanate and allophanate formation. At high temperatures HI evolution occurs and this acid might hydrolyze the polyurethane bonds. Mechanical properties of these polyurethanes were higher than the polyurethanes which were synthesized from allylic isocyanates. The soybean oil iodo isocyanates gave a fast reaction with poly amines even at 0 ^{o}C. Thus shaped specimens could not be prepared. Polyurethane polymers can be synthesized from soybean oil iodo isocyanates and these materials can be used in many practical applications. Polyureas can also be used for similar purposes and can be used as an adhesive.

The last series of reactions was performed with acrylated soybean oil and p. tertiary-phenol furfural resin. Acrylate groups on the soybean oil gave Diels-Alder reaction with furan rings on the phenolic resin. A dark red colored polymer was obtained at 100 ^{o}C in one hour. This polymer had a unique behavior in that it was hardened upon heating and re cooling. This may be due to repeated Diels-Alder and retro Diels-Alder reactions. Polymers with good thermal and mechanical properties were obtained. After 10 times heating and cooling, storage modulus of the polymers approached to one GPa which is close to the storage modulus of many industrial polymers.

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Industrial activities that develop uncontrollably with the increasing world population increase human pressures on limited natural resources and reveal many environmental problems. Especially in the last century, responding to this rapid change, especially global warming and its effects, environmental pollution, deforestation, destruction of agricultural areas, access to healthy food and water, ecological problems, epidemic diseases, etc. Scientific research plays a key role in minimizing the problems. From this point of view, the reuse of recycled materials plays a critical role in ensuring the sustainable use of natural resources. The current Covid-19 pandemic is a powerful reminder of this necessity.

Due to the limited world oil and coal reserves and the negative effects of the use of these resources on the environment, intensive research on renewable resources continues. Materials obtained from renewable resources are also very important substances for sustainable development. Plant oils (plant oil triglycerides) as renewable resources are emerging as a very important resource. In this book, the structures of plant oil triglycerides, their reactive parts, the reactions they give and the different polymers obtained are explained simply and in a language that can be understood by almost everyone. I believe that this work, which also explains the synthesis methods, will be a good reference for researchers on the subject.

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