POLYMERIZATION OF PLANT OILS WITH *p*-DINITROSOBENZENE

by

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To my Family

and

Abidin

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ABSTRACT

POLYMERIZATION OF PLANT OILS WITH *p*-DINITROSOBENZENE

In this study, tacky, black coloured thermoset polymers were synthesized from polymerization of the soybean oil (SO) with polymeric *p*-dinitrosobenzene (PDNB) via an *ene* reaction. The crosslinking agent, polymeric dinitrosobenzene was synthesized using *p*-quinone dioxime and characterized by IR spectroscopy. Two different methods were used for the polymerization: solventless and solvent mediated. In the first method SO/PDNB polymers were synthesized by a two stage polymerization. During the reaction different parameters such as mole ratio of SO and PDNB, pre-heating temperature of SO, polymerization time and temperature were examined. The crosslinking reactions were followed by IR spectroscopy, and the polymers obtained were characterized by dynamic mechanical analyzer, thermo gravimetric analyzer and differential scanning calorimetry. The crosslinked network structure of the polymers was investigated by swelling behavior and surface hardness test. The second method of polymerization used an emulsion polymerization in which hot water was used as continuous phase. However as the water acted as inhibitor the polymers obtained were not suitable for mechanical analysis, only the examination of the polymerization by IR spectroscopy was feasible. Methyl oleate was used as a model compound to examine the details of the chemical structure of the products, however the samples synthesized were highly crosslinked. Thus only IR spectroscopy characterization was possible.

ÖZET

BİTKİSEL YAĞLARIN *p*-DİNİTROZOBENZEN İLE POLİMERİZASYONU

Bu çalışmada, soya yağı (SO) ve polimerik *p*-dinitrozobenzenin (PDNB) ene reaksiyonu sonucu yapışkan, siyah renkli, termoset polimerler sentezlenmiştir. Çapraz bağlayıcı olarak kullanılan polimerik *p*-dinitrozobenzen, *p*-kinon dioksim kullanılarak sentezlenmiş ve karakterizasyonu IR spektroskopisi ile yapılmıştır. Polimerizasyon reaksiyonu iki farklı teknik kullanılarak yapıldı. Birinci teknikte, SO/PDNB polimerleri iki aşamalı polimerleştirme yöntemi ile sentezlenmiştir. Araştırma süresince farklı parametreler kullanılmış ve değiştirilmiştir. Bunlar SO ve PDNB mol konsantrasyonu, SO'ın reaksiyon öncesi ısıtma sıcaklığı ve polimerleştirme sıcaklık-zaman parametreleridir. Çapraz bağlanma reaksiyonu infrared spektroskopisi kullanılarak takip edilmiştir. Sentezlenen polimerlerin analizi ise dinamik mekanik analiz, termal gravimetrik analiz ve diferansiyel taramalı kalorimetre yöntemleri ile yapılmıştır. Çapraz bağların yoğunuğu ise çözücüde şişme ve yüzey sertliği yöntemleri ile incelenmistir. Emülsiyon polimerizasyon tekniği ikinci yöntem olarak kullanılmıştır. Bu teknikte sabit faz olarak kullanılan sıcak su engelleyici (inhibitör) özellikte olup elde edilen polimerlerin mekaniksel özellik tayini için uygun olmadığı gözlenmiştir. Sentezlenen örneklerin polimerleşme reaksiyonları infrared spektroskopisi ile incelenmiştir. Bu iki tekniğin yanı sıra polimerlerin kimyasal yapı tayinini yapabilmek amacıyla model bileşik polimerleştirme yöntemi kullanılmıştır. Metil oleatın model bileşik olarak kullanıldığı teknik sonucu oldukça yüksek oranda çapraz bağlı ürünler elde edilmiştir. Dolayısıyla ürünlerin ancak infrared analizi yapılabilmiştir.

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LIST OF SYMBOLS / ABBREVIATIONS

ASTM	American Society for Testing and Metarials
ATR	Attenuated Total Reflectance
DBQDO	*p*-Quinone Dioxime Dibenzoate
DMA	Dynamic Mechanical Analysis
DNB	*p*-Dinitrosobenzene
DSC	Differential Scanning Calorimetry
DTGA	Differential Thermogravimetric Analysis
E′	Storage Modulus
FT	Fourier Transform
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
MO	Methyl Oleate
MPa	Mega Pascal
NMR	Nuclear Magnetic Resonance
QDO	*p*-Quinone Dioxime
PDNB	Polymeric *p*-Dinitrosobenzene
SO	Soybean Oil
T_g	Glass TransitionTmperature
TGA	Thermal Gravimetric Analysis
Triton X	Octyl Phenol Ethoxylate

1. INTRODUCTION

1.1. Renewable Resources

The growing worldwide demand for petroleum-based polymeric materials has raised environmental concerns about the non-biodegradable, indestructible products and also increased our dependence of crude oil. The rapid growth of demand in the industrial world has placed increased pressures on the finite petroleum reserves and forced us to look for alternative resources. Bio - renewable resources represent a promising new alternative, but they require new approaches and developments in order to be successfully utilized.

Biopolymers produced from the renewable and inexpensive natural resources have drawn considerable attention over the past decade, due to their low cost, ready availability, environmental compatibility, and their biodegradability [1].

Natural oils and fats represent the most promising renewable resources for the chemical industry because of their availability, low cost and biodegradability. Versatile applications in plastics, cosmetics, pharmaceuticals, explosives, lacquers, varnishes, lather and paper industries, mineral oil additives, alkyd resins, high tech and load bearing plastics have been demonstrated [2].

1.2. Vegetable Oils

1.2.1. Composition of Vegetable Oil

Vegetable oils and fats form part of a large family of chemical compounds known as lipids. Chemically all vegetable oils are triglycerides or esters of glycerol and fatty acid, which have the three-armed star structure shown in Figure 1.1. There are over 1000 naturally occurring fatty acids although only about 50 are commonly found. Most of the common oils contain fatty acids with carbon chain lengths between 4 and 24 carbon atoms with zero to three double bonds.

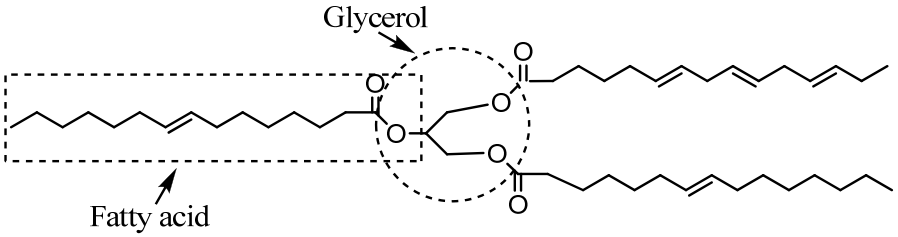


Figure 1.1. Triglyceride molecule

Table 1.1 shows the typical fatty acid composition of some common plant oils. This table lists the name of the plant oil and gives its length in carbon atoms (the number before the colon) and the number of unsaturation sites (the number after the colon).

Table 1.1. The typical fatty acid composition of common oil sources [3]

Vegetable oil	Fatty Acid Composition, % by weight								
	16:0	18.0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.1	0.00	60.6	0.48
Cottonseed	28.3	0.89	0.00	0.00	0.00	13.2	0.00	57.5	0.00
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.3	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.2	0.00	55.5	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.9	0.00	73.7	0.00

The presence of many types of fatty acids indicates that at the molecular level these oils are composed of many different types of triglycerides with diverse levels of unsaturation. Newly developed genetic engineering techniques are likely to make contributions to the expansion of raw materials available to the chemical industry, such as increasing the content of individual fatty acids or dramatically changing the oil quality by the introduction of a new fatty acid.

1.3. Soybean Oil

1.3.1. Composition of Soybean Oil

Soybean is the leading oilseed crop that provides a high content of oil and protein. It comprises 40 % protein, 30 % carbohydrates and approximately 20% oil [4]. About 32% of soybean oil is produced in the United States, 17% in Brazil, 13.5% in China, 12% in Argentina, 11% in European Union, and 3% in India and Japan [5].

Soybean oil is refined by several methods but the most common is by solvent extraction. As virtually all vegetable oils, soybean oil is mainly composed of the triglycerols of several fatty acids. The five main fatty acids found in soybean oil (palmitic, stearic, oleic, linoleic and linolenic acids) differ in chain length and degree of saturation and unsaturation.

Table 1.2 shows the properties of the fatty acids most abundant in soybean oil [6].

Table 1.2. The properties of soybean oil [6]

Characteristics	
Iodine number	117-140
Saponification number	189-195
Viscosity (cP) at 40 ^{o}C	28
Smoke point	213 ^{o}C
Flash point	317 ^{o}C
Fire point	342 ^{o}C
Density (15 ^{o}C)	0.910-0.934

1.3.2. Chemistry of Soybean Oil

Chemical modification of soybean oil is an important route to obtain industrial products using renewable feedstock. There is a high potential to develop new, efficient and environmentally friendly reaction pathways leading to new products or to find new applications for already existing oleo chemicals.

Multiple sites of chemical reactivity are intrinsic in soybean based triglycerides. Figure 1.2 shows all active sites; ester groups (a), double bonds (b), allylic positions (c) and the α - position to ester groups (d).

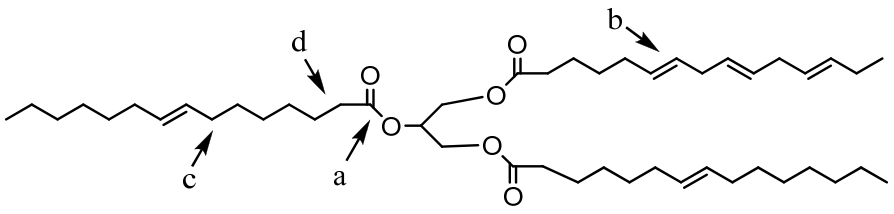


Figure 1.2. Reactive positions in triglycerides

Chemical modification of soybean oil is an important pathway in obtaining useful products from renewable resources. Industrial oleochemistry has concentrated on the carboxylic functionality of fatty acids [7]: the basic oleochemicals are free fatty acids (or their metal salts), methyl esters, fatty alcohols, and fatty amines, with glycerol as a by-product [8], although modern synthesis methods have been recently applied extensively to fatty compounds for the selective fuctionalization of the alkyl chain [9, 10, 11]. Moreover, enzymatic and microbial transformations constitute another branch of chemistry that still needs to be explored [12]. Therefore, there is the potential to develop new, efficient, and environmentally friendly reaction pathways for new products or to find new applications for ones that already exist.

1.3.3. Soybean Oil as a Raw Material for Polymers

The soybean oil based polymers have many advantages over polymers prepared from petroleum-based monomers. In the last decade, a broad range of chemical routes has been developed for using natural or modified vegetable oils especially soybean oil as a basis for polymers, adhesives, and composites with specific properties and applications. The

reactive sites of soybean oil can be used to polymerize triglycerides directly or to modify the triglyceride structure with polymerizable groups using the same synthesis techniques that have been applied in the synthesis of petroleum-based polymers.

The double bonds of triglyceride molecule can be directly polymerized through either by free radical or cationic mechanism [13]. Cationic polymerization has been widely studied by Larock's group and has been applied in the preparation of thermosetting polymers ranging from rubbers to hard plastics [14-24].

In addition, modifications that facilitate the subsequent polymerization of the triglycerides can be applied. These modifications consist of:

a. Introducing reactive groups into the aliphatic chains, which can be easily polymerized (pathway A)
b. The reduction of triglycerides to monoglycerides through a glycerolysis reaction or amidation reaction (pathway B)

In Figure 1.3 the different modification pathways are summarized.

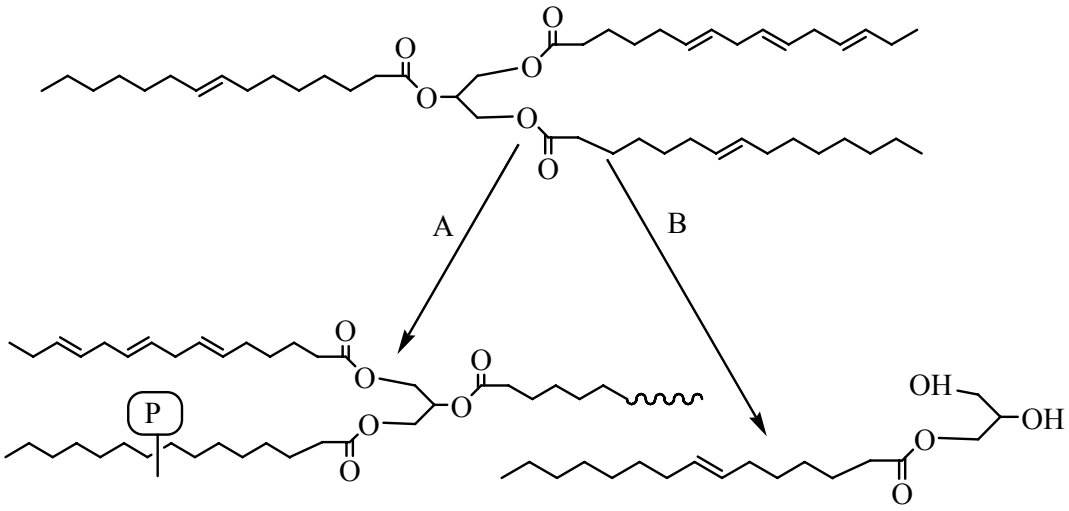


Figure 1.3. General modification pathways: introduction of polymerizable groups into the triglyceride (A) and reduction of the triglycerides to monoglycerides (B)

1.3.3.1. Pathway A. The functionalization of the double bond by attachment of maleates, epoxidation or, introduction of hydroxy function allows the polymerization of triglyceride.

Several triglyceride-based polyols suitable for polyurethane synthesis were synthesized by reacting epoxidized vegetable oils with different chemical reagents.

Polymerizable groups can also be introduced directly into a triglyceride structure by utilizing the –COOH reactivity of carboxylic acid-type reagents toward the oxirane ring. Reacting the epoxy functional triglyceride with acrylic acid incorporates polymerizable acrylate moieties onto the triglyceride. Subsequent to the acrylation reaction, the triglyceride contains residual epoxy groups that are used to further modify the triglyceride by reacting with cyclohexane dicarboxylic anhydride, which contains cyclic groups conducive to stiffening the polymer [25, 26].

Acrylate moieties have also been attached to triglyceride structures by the one-step addition of bromide and acrylate groups to a C=C double bond. Soybean oil has been bromoacrylated in the presence of acrylic acid and N–bromosuccinimide [27].

A very interesting acrylamide derivative of triglycerides has been obtained by the Ritter reaction between soybean and sunflower oils with acrylonitrile in the presence of sulfuric acid [28].

Hydroformylation, using either rhodium or cobalt as a catalyst, and subsequent hydrogenation by Raney nickel, have been used to convert the C=C double bonds ofa vegetable oil to primary alcohols [29].

An ozonolysis reaction has also been applied to different vegetable oils , yielding polyols with terminal primary hydroxyl groups and different functionalities [30].

Reacting soybean oil with paraformaldehyde in the presence of a Lewis acid catalyst has yielded a hydroxymethylated soybean oil derivative [31]. Moreover, hydroxybrominated triglyceride derivatives have also been synthesized in one step, using an NBS/acetone/H_2O mixture [32].

Maleic anhydride can also be attached to unsaturated compounds. Maleinization of vegetable oils, which has been widely used, follows an *ene* reaction path and results in the addition of a succinic anhydride group to the allylic position of the fatty acid. Eren et al. reported the conversion of soybean oil to succinic anhydride-modified soybean oil and subsequent polymerization with different alcohols [33].

Olefin metathesis has also been used as a polymerization reaction. Crossmetathesis has been applied to soybean oil leading to rubbery polymers [34].

1.3.3.2. Pathway B**.** The reduction of triglycerides to monoglycerides via a glycerolysis reaction is another established method for synthesizing monomers from triglycerides. This involves reacting triglycerides with glycerol, giving a product that is generally a mixture of monoglycerides and diglycerides.

Wool's group have explored the synthesis and polymerization of soybean oil monoglyceride maleates to yield rigid thermosetting polymers [35].

Thus, plant-based triglyceride oils have been used to synthesize several different monomers that form polymers with diverse properties, with the results suggesting that these materials will prove useful as alternatives for current petroleum-based plastics in practical applications.

1.4. Vulcanization

Vulcanization, in other words curing or crosslinking, is the key process in the technology of rubbers. Most textbooks have it that Charles Goodyear (1800–1860) invented vulcanization with absolutely no knowledge of chemistry however history of rubber cured by other means goes back to prehistoric times and points out that the Ancient Mesoamericans are the actual inventors.

The vulcanization (cure) of rubbers can be defined as the process by which the reaction between the rubber and the crosslinking agent results in greatly increased elastic properties of the rubber, and the maintenance of these properties over a wide temperature

range. In the case of natural rubber the double bonds on the polymer backbone are used to react with a vulcanizing agent to crosslink the rubber molecule. The vulcanized rubber is harder, more durable, and more resistant to chemicals and other damages. Moreover the surface of rubber becomes smoother and less likely to stick to metal or plastic. In Figure 1.4 are represented the uncured and cured states of rubber molecules.

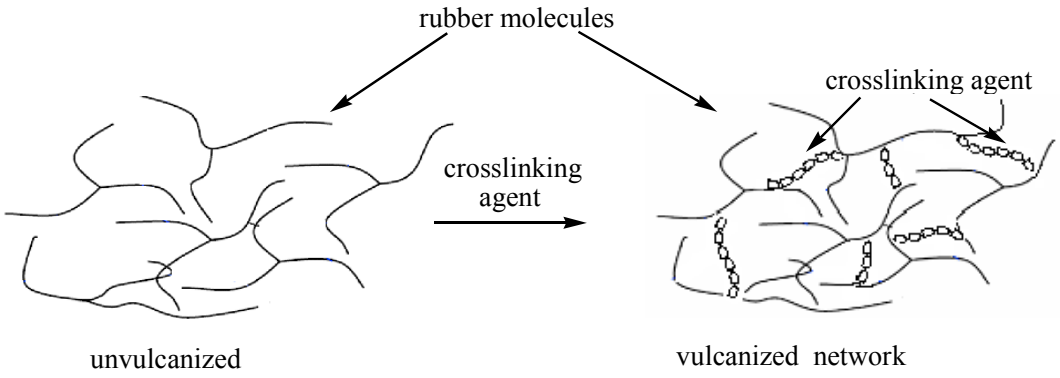


Figure.1.4. Network formation by vulcanization

The reactivity of the internal double bonds of unsaturated triglycerides is similar to that of polyisoprene units of polybutadiene rubbers. Thus the vulcanization methods which have been successful in rubbers are good candidates for polymerization of unsaturated triglycerides.

In fact of sulfur polymerization of oils to factice and peroxide chain extension of oils is known. Therefore following the examples of rubber vulcanization chemistry may lead to new polymerization reactions of plant oil triglyceride.

Also peroxide curing of unsaturated oils leading to soft rubbers and bismaleimide curing leading to rigid polymers have been reported.

The strength and dynamic mechanical properties of the vulcanizate depend on the nature of the crosslinking and on the degree of the crosslinking. Changes observed in the physical properties of a rubber upon vulcanization are summarized in Table 1.3 [36].

Table 1.3. Influence of degree of crosslinking on physical properties of vulcanizate [36]

Property	Change with increase in degree of crosslinking
Dependent only on the degree of crosslinking	
Stiffness (modulus)	Increase
Hardness	Increase
Dependent partly on the degree of crosslinking	
Elongation at break	Decrease
Heat build-up	Decrease
Solvent swelling	Decrease
Creep, stress relaxation	Decrease
Set	Decrease
Resilience	Increase
Abrasion resitance	Increase
Fatigue cracking	Increase
Low temperature crystallization	Decrease in rate
Tensile strength	Increase, then decrease

Vulcanization can occur through various chemical mechanisms such as nucleophilic substitution, endlinking, addition or condensation, free radical coupling and ring opening reactions, among others. The chemically reactive sites available on the polymer and the application area of the final product determine the chemistry employed [37].

1.5. Methods of Vulcanization

The formation of network structure is one of the essential conditions for generating rubbery properties. Thus many vulcanizing systems have been investigated over the last 150 years. Depending on the chemicals used as crosslinking agent these curing systems can be divided into two main groups: sulfur based and non–sulfur based vulcanization systems.

1.5.1. Sulfur Vulcanization

Sulfur is the most commonly used curing agent for elastomers with chemically unsaturated polymer backbones. The sulfur vulcanisation of C=C double bonds containing elastomers leads to the formation of sulfur containing crosslinks between the polymer chains.

Sulfur on its own is not a very good vulcanizing agent thus a typical sulfur vulcanization system is composed of sulfur, a metal oxide, a fatty acid and one or more organic accelerators [38]. Several classes of compounds behave as accelerators in sulfur curing. Table 1.4 shows various commercially available materials either used as accelerators or activators in sulfur vulcanization.

Table 1.4. Classes of vulcanization accelerators in sulfur vulcanization

Class	Acceleration Speed
Amine – aldehyde	Slow
Guanidines	Medium
Benzothiazoles	Semi fast
Sulphenamides and sulphenimides	Fast, delayed action
Dithiophosphates and xanthates	Fast
Thiurams	Very fast
Ditihocarbamates	Very fast

The choice of the accelerator affects the cure rate, the length and the number of crosslinked chains, and also the vulcanization mechanism [39]. Thus specific mechanism for sulfur vulcanization can not be proposed.

Sulfur based vulcanizates provide for tough networks which show excellent tensile, tear and fatigue properties. Some of advantages and disadvantages are listed in Table 1.5.

Table 1.5. Main advantages and disadvantages of sulfur vulcanization

Advantages	Disadvantages
Delayed action	Reversion tendency
Excellent dynamic performance	High compression set

1.5.2. Non-Sulfur Vulcanization

There are many non–sulfur based vulcanization systems including peroxide, phenolic resin, metal oxide, moisture, radiation induced, dynamic and quinoid vulcanization. Non–sulfur cures often show better aging, lower compression set and higher resilience in comparison to sulfur cure.

1.5.2.1. Peroxide Vulcanization. Peroxide crosslinking has been known since the beginning of this century [40]. Typically this type of vulcanization is used for crosslinking of slow reacting saturated rubbers such as some fluorocarbon rubbers, silicone rubbers and ethylene propylene rubbers which can not be crosslinked with other types of vulcanizing agents.

The typical reaction occurring during peroxide vulcanization consists of three steps [41]:

1. Homolytic breakdown of a peroxide into two alkoxy free radicals
2. Abstraction of hydrogen from the polymer
3. Combination of two polymer radicals by coupling to form a carbon-carbon crosslink.

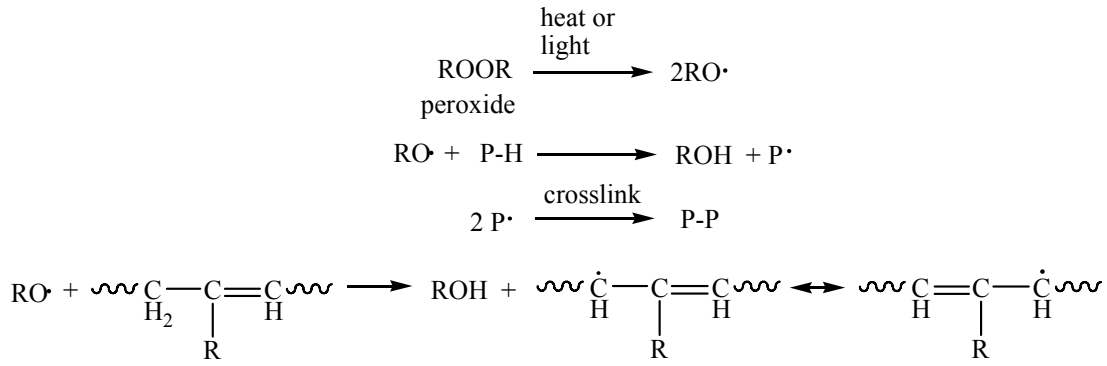


Figure 1.5. Mechanism of peroxide crosslinking (P-H saturated or unsaturated elastomer)

The formation of the carbon-carbon bond is the reason for greater stability of a peroxide vulcanizate. It is important to select a peroxide with a suitable half life in order to obtain optimum cure. A number of different peroxides is available for this type of vulcanization. Of these dicumyl peroxide is one of the most frequently used. Others are benzoyl peroxide, 2,4-chlorobenzoyl peroxide, and tertiary butyl perbenzoate peroxide. In addition to the organic peroxides there are many inorganic peroxides such as Pb, Ba, Mg, Ca and Zn peroxides which can be used to crosslink silicone and polysulfide rubbers. The matallic peroxides can provide crosslinking effects similar to equivalent metallic oxides and carbonates. Table 1.6 summarizes the advantages and disadvantages of peroxide vulcanization [39].

Table 1.6. Advantages and disadvantages of peroxide curing [39]

Advantages	Disadvantages
Simple compounding	Expensive crosslinking agent
Good heat ageing resistance	Low mechanical strength
Low tension set and strain	Higher curing time
No contamination	Difficult hot air cure
Low compression set	Poor resistance to flex fatigue
Transparent rubbers possible	Need secondary cure of high temperature

In addition to the disadvantages described in Table 1.6 there are many limitations to peroxide crosslinking of rubbers. Reaction of the antioxidants with peroxide generated radicals can cause a decrease in the crosslinking efficiency for the peroxide crosslinking reaction and also destruction of the antioxidants. Conversely the presence of such radical scavengers can provide delayed scorch time.

1.5.2.2. Phenolic Resin Vulcanization. The use of resins as curing agents for unsaturated elastomers was first investigated over 70 years ago by Hönel [40]. Since then many crosslinking mechanisms associated with the resin crosslinking have been proposed. The crosslinking of unsaturated elastomers by this method is dependent upon the reactivity of the phenol methylol groups of reactive phenol–formaldehyde resins.

Resin cures are slower than sulfur cures and high temperatures are required. Typically this type of vulcanization is dominated by *ene* reactions in which Lewis acid or higher temperatures are necessary.

Resin vulcanization is used in components where high hardness is essential. Moreover resin cure blends better preserve their properties under long-term storage, do not flow and the vulcanizates have lower elongation set, better gas-tightness, higher thermal stability and etc.

1.5.2.3. Ouinoid Vulcanization. Quinoid compounds such as *para*-dinitrosobenzene (DNB), para-quinone dioxime (QDO) and *para*-quinone dioxime dibenzoate (DBQDO) are known to be able to crosslink unsaturated rubbers [42]. Quinoid cure has been extensively used for rapid curing of butyl stocks requiring heat resistance and excellent electrical properties, thus obtained quinoid cured butyl vulcanizates have been used to fabricate high voltage wire and cable products, molded electrical components, heat resistant seals and tire curing bags.

It is generally believed that DNB is the real crosslinking agent for quinoid vulcanization. DNB can readily be formed during the cure *in situ* from QDO or DBQDO by oxidation according to the Haworth's reaction scheme shown in Figure 1.6 [43], or can be pre-synthesized as polymeric material by different oxidation methods before the vulcanization of the rubber as shown in Figure 1.7 [44-46].

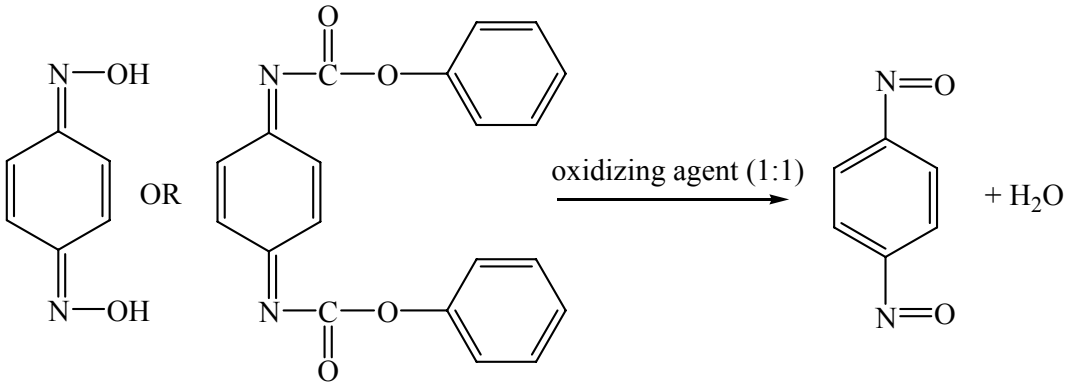


Figure 1.6. *p*-Dinitrosobenzene *in situ* synthesis

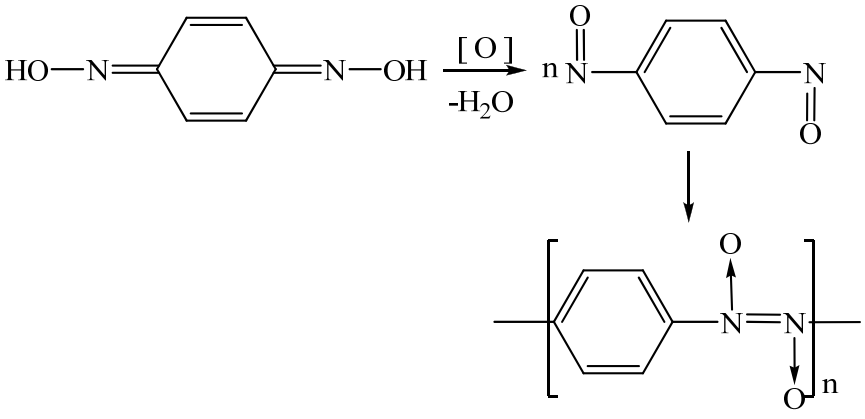


Figure 1.7. Polymeric *p*-DNB synthesis

In the case of *in situ* synthesized DNB vulcanization, the active DNB reacts with the allylic units of the rubber chains via an *ene* addition to form the crosslinking intermediate as shown in Figure 1.8 [42].

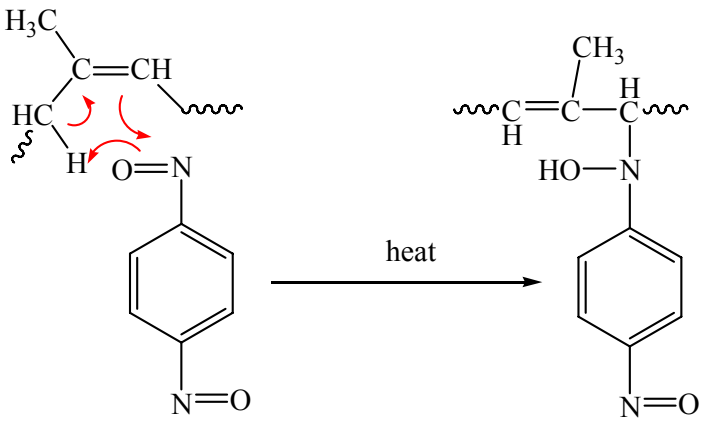


Figure 1.8. *Ene* addition of DNB to allylic position of rubber

The structure of the quinoid crosslink is not yet fully understood. Based on Bruni-Geiger reactions, Rehner and Flory suggested that the quinoid crosslink is of the nitrone type when three molecules of QDO react with two units of isoprene units of butyl rubber [47]. However, Yokose et al. mentioned that only one molecule of QDO was sufficient to form crosslink unit and obtained crosslink is anil type crosslink [42]. In Figure 1.9 the nitrone and anil type crosslinks are shown.

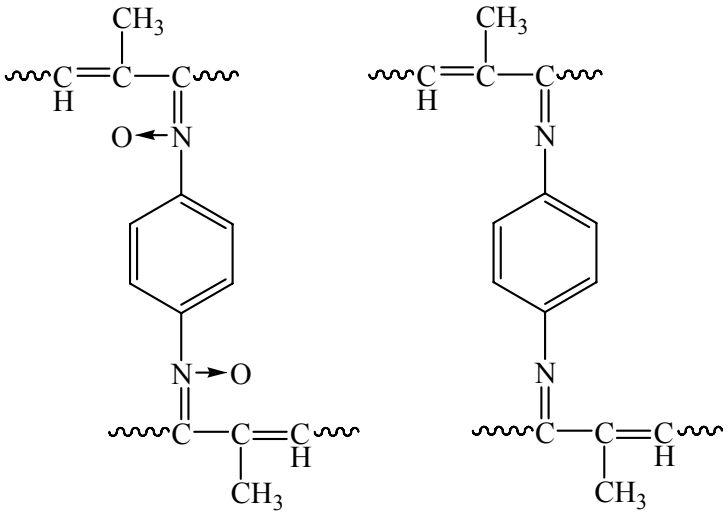


Figure 1.9. Nitrone and anil type quinoid crosslinks, respectively

In 1969 Cain et al. claimed that the suitably substituted aromatic compounds react with the rubber molecule to form the amine type quinoid crosslink [48]. Subsequently Sullivan et al. suggested that the nitroso group underwent an *ene* addition to the olefin to yield an unsaturated hydroxylamine that could then be oxidized by air or unreacted nitroso compound to an alkenyl aryl nitroxide [49]. The proposed mechanism is as in shown in Figure 1.10.

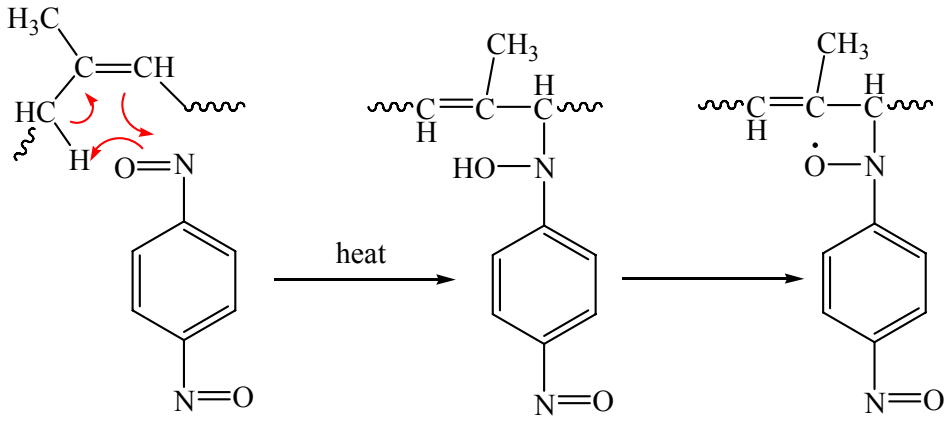


Figure 1.10. Mechansim proffered by Sullivan et al.

After a while, Knight and Pepper asserted that in the case of olefin containing allylic hydrogen atom, the intermediate *N*-alkenyl-*N*-arylhydroxylamine (1) is formed initially via an *ene* addition reaction. Consequently the intermediate may either attack the dinitrosobenzene to form an azoxyrane (2) and a nitrone (3) , decompose thermally to an *N*-alkenylaniline (4) and a nitrone (3), or to undergo dehydration to anil (5) [50]. Figure 1.11 shows the proposed mechanism.

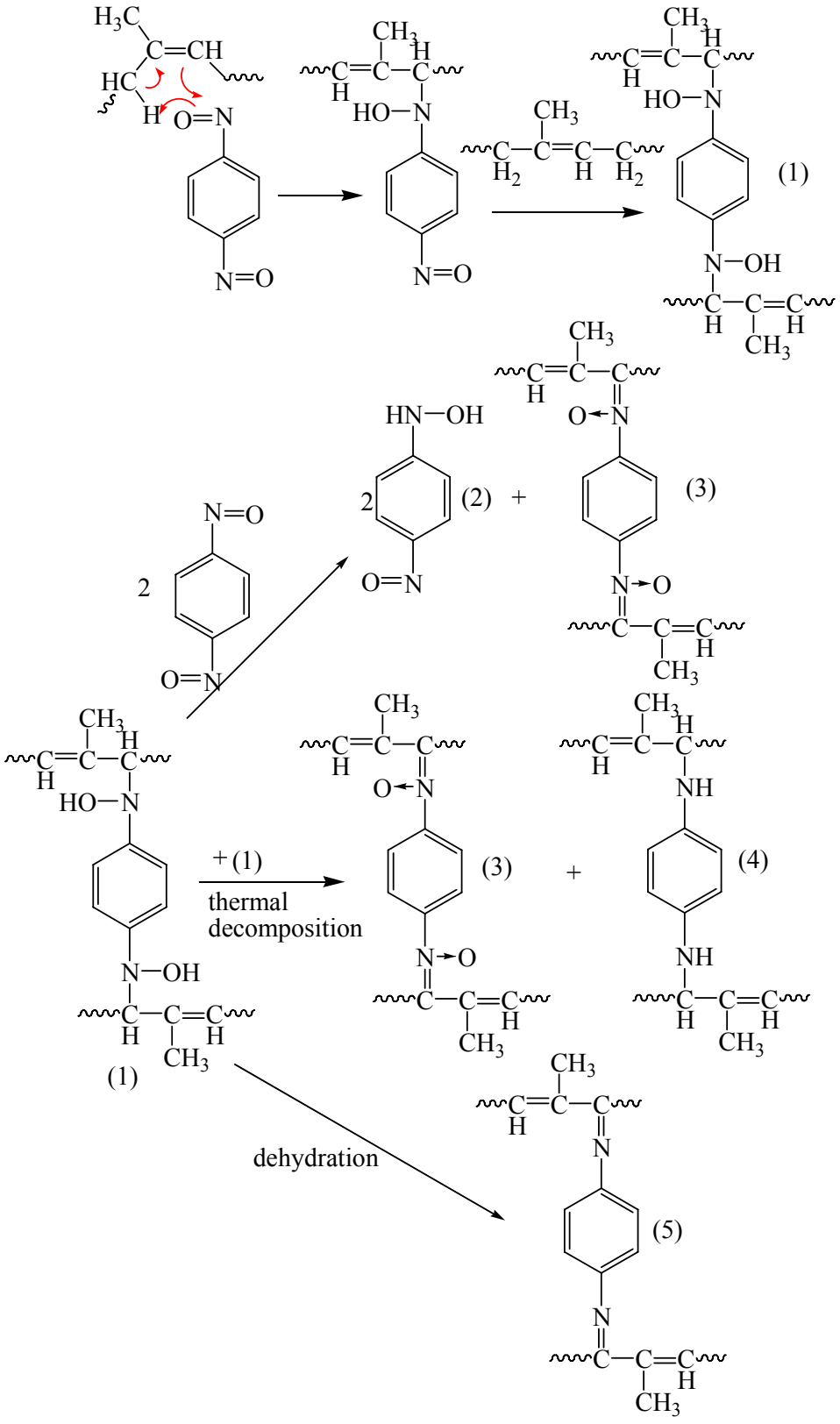


Figure 1.11. Vulcanization mechanism proposed by Knight and Pepper

Klyuchnikov et al. investigations suggested the mechanism shown in Figure 1.12 as the mechanism of depolymerization of polymeric *para*-dinitrosobenzene (PDNB) in the course of vulcanization of unsaturated rubbers [51] in the case of pre-synthesized dinitrosobenzene. In the first step a linear helical molecule of PDNB reacts with an alkene unit of rubber to form a secondary hydroxylamine. The subsequent energetically most favorable step is reversible dissociation of the closest and weakest azoxy bond in the para position relative to hydroxylamine unit formed by addition of the PDNB macromolecule to the rubber.

The free nitroso groups subsequently add to other rubber macromolecules to form crosslinks with further depolymerization of PDNB.

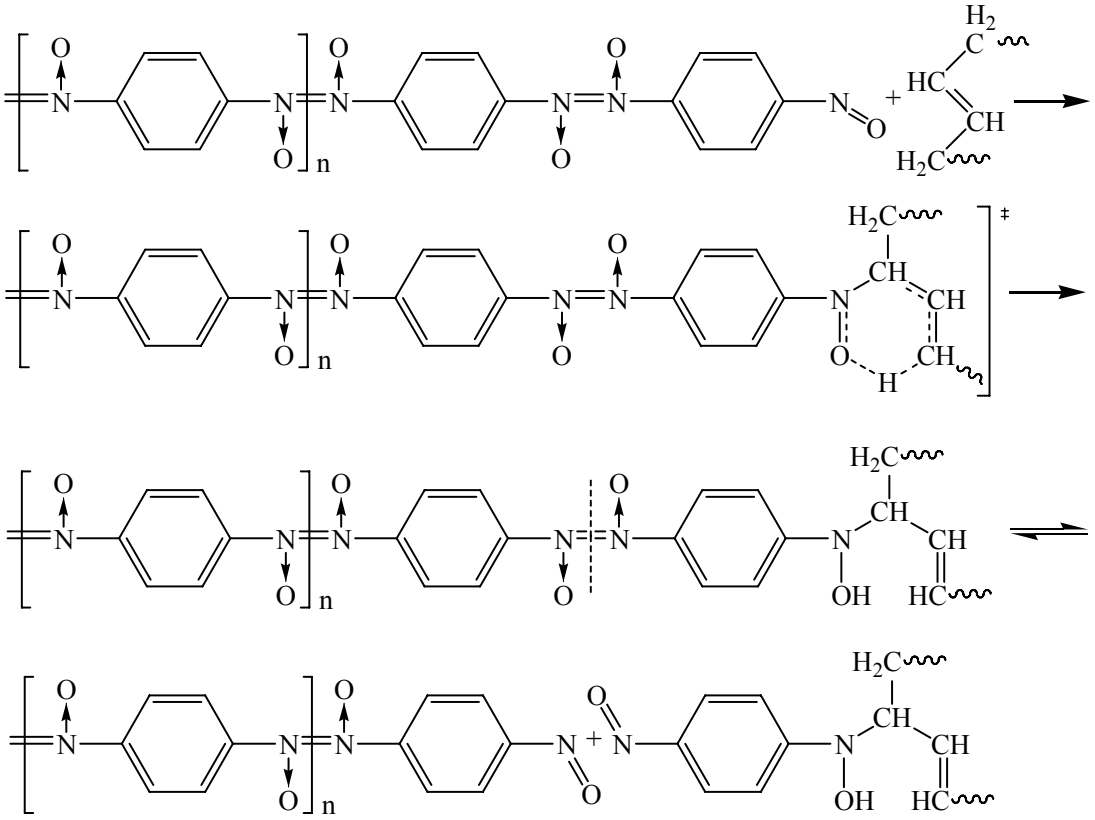
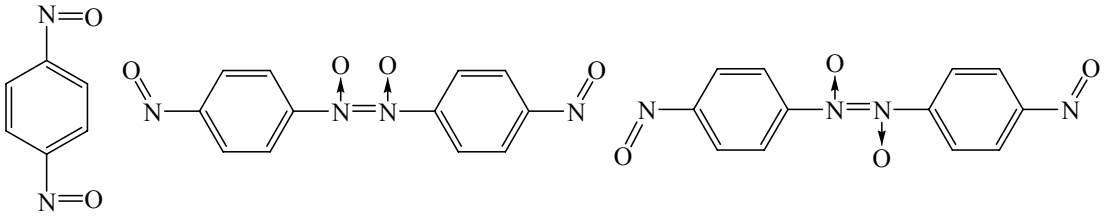


Figure 1.12. Vulcanization mechanism proposed by Klyuchnikov et al.

From these data related to the proposed mechansims of quinoid vulcanization is releaved that no single coherent scheme appears to cover all the known facts or acount for products as diverse as anils, amines, nitrones and azoxyarenes.

1.6. *p*-Dinitrosobenzene

p-Dinitrosobenzene (DNB) is component of rubber substrate adhesion systems and low temperature vulcanizing agent for stocks based on unsaturated rubbers. DNB is finely crystalline, straw green product which is sparingly soluble in dimethyl formamide, alcohol, hot xylene solution and water. This compound exists as an amorphous polymeric solid at room temperature, and the monomeric DNB can be obtained by fast heating in xylene or by sublimation in vacuum upon a surface cooled by liquid nitrogen [51]. The relative stabilities of monomeric, dimeric *cis* and *trans* structures of DNB are dependent upon the physical state, the temperature and the solvent properties. Monomeric, *cis* and *trans* structures of DNB are represented in Figure 1.13.



monomer *cis* dimeric form *trans* dimeric form

Figure 1.13. Monomeric, *cis* and *trans* dimeric forms of DNB, respectively

Polymeric DNB (PDNB) undergoes the following transformation upon heating from cryogenic temperatures shown in Figure 1.14 [52].

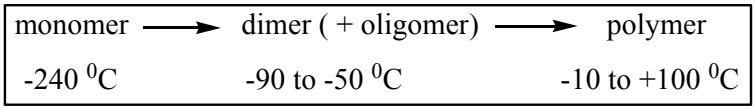
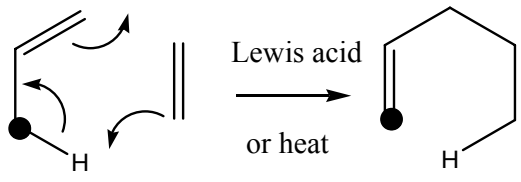


Figure 1.14. Transformations of PDNB upon heating

Dinitrosobenzenes have been known for over a hundred years, first PDNB synthesis was reported by Nietzki and Kehrmann [53]. Hence, different synthesis methods have been proposed and most of these synthesis routes require the preparation of the appropriate QDO followed by simultaneous catalytic or electrochemical oxidation using different oxidizing agents [44-46].

1.7. *Ene* Reaction

The *ene* reaction is a pericyclic reaction that proceeds with activation of an allylic C-H bond and results in allylic transposition of the carbon-carbon double bond with functionalization as shown in Figure 1.15. This process involves an alkene with an allylic hydrogen - the '*ene*' and a compound with electron-deficient multiple bond - the '*enophile*'. As a result of this rearrangement, the *ene* π-bond migrates and two σ-bonds are formed.



Fifure 1.15. Schematic representation of *ene* reaction

Several variations of the *ene* reaction are known. Diversity mostly arises from the enophile used in the reaction. *Ene* reactions involving alkenes-Alder *Ene*, singlet oxygen, azo compounds, carbonyl functionalities-carbonyl *ene*, and nitroso groups have been used in carbon-carbon and carbon-heteroatom transformations with olefins. In the case of the Alder and carbonyl-*ene* reactions, elevated temperatures or Lewis acid activation are often required.

One distinguishing property of the nitroso compounds is high reactivity, a consequence of the low excitation energy due to a very small HOMO-LUMO energy gap. High reactivity leads to complications in handling, as most of nitroso compounds tend to form dimers. In the case of nitroso compounds bearing electron-withdrawing substituents on the nitrogen, they are generated in situ. Dimerization, however, is reversible process, and upon thermolysis it is possible to shift the equilibrium towards the monomeric nitroso compound. Since nitroso compounds are susceptible to air oxidation, an inert atmosphere is required to avoid this complication. One drawback of the nitroso *ene* reaction is the instability of the products of the reaction [54].

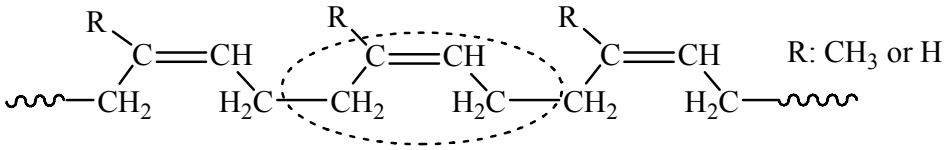
2. RESEARCH OBJECTIVES

The objective of the work is to synthesize and characterize new biodegradable, rubber-like polymers from plant oil triglycerides.

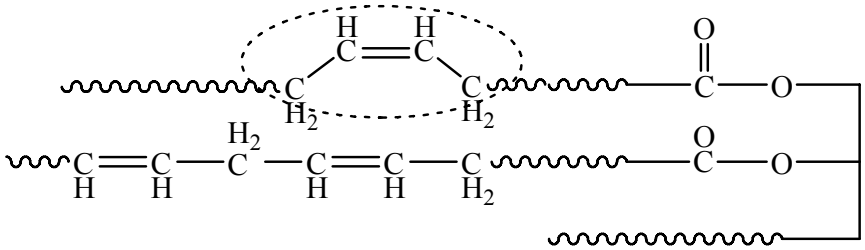
We plan to polymerize soybean oil by using *p*-dinitrosobenzene as a polymerizing crosslinking agent via the *ene* reaction. The resemblence of unsaturated part of triglyceride molecule and polybutadiene rubber is obvious in Figure 2.1. Moreover it is known that the doubly allylic hydrogens observed in the triglyceride molecule are more reactive than allylic ones. Thus the quinoid vulcanization seems to be good candidate for the polymerization of unsaturated triglycerides. Figure 2.2 gives the proposed chemistry for the polymerization of triglyceride molecule with the nitroso unit of polymeric *para*-dinitrosobenzene.

Although there is an extensive literature concerning the vulcanization of different natural plant based oils using sulfur, peroxide and bismaleimide cure, there is no reference about the vulcanization of a plant based oil with polymeric *p*-dinitrosobenzene.

Once the new polymers are obtained we plan to examine their chemical structure by IR and NMR analysis methods, and mechanical and thermal properties using TGA, DMA, DSC, swelling and surface hardness tests.



Polybutadiene Rubber



Soybean Oil

Figure 2.1. The similarity between soybean oil and polybutadiene structures

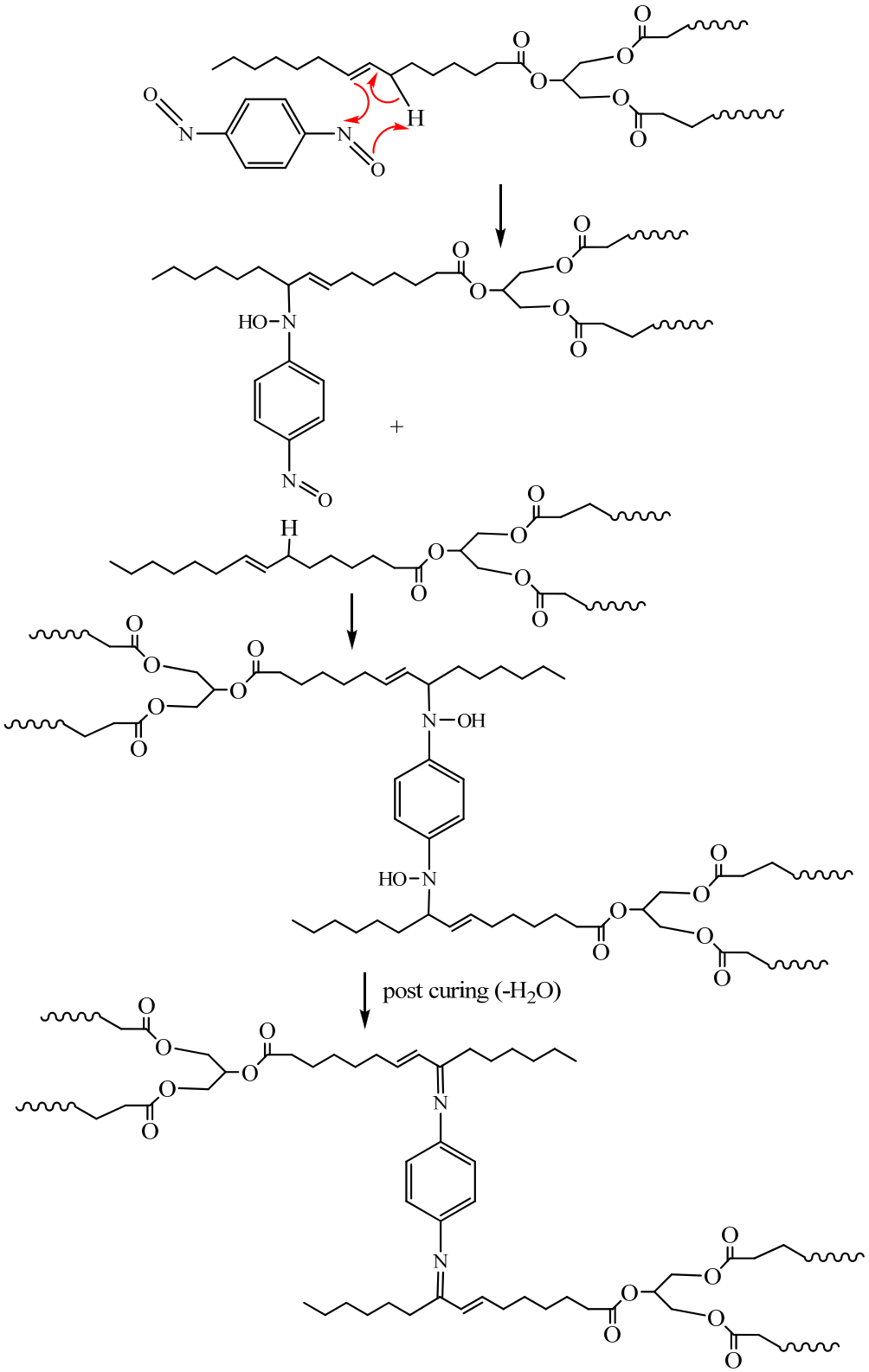


Figure 2.2. Reaction mechanism for polymerization of SO with PDNB

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

1.4-Benzoquinone Dioxime (*p*-quinone dioxime, 97%) was purchased from Aldrich (Steinheim, Germany) and was used as obtained. Hydrogen peroxide (30%) was supplied by Riedel-de Haën Fine Chemicals (Seelze, Germany) and was used as received. Hydrochloric acid (37%) was obtained from Tekkim Lab. Soybean oil (SO) supplied by Marsa (Adana, Turkey) was food grade and used without further purification. Petroleum ether (boiling range 40–60 C) was purchased from Prolabo (Paris, France) and used as obtained. $CDCl_3$ purchased from Aldrich (Milwaukee, WI) was used for ^1H NMR analysis. Dichloromethane was supplied by Çakır Kimya (Istanbul, Turkey). Methyl oleate was synthesized according to procedure described by G.Çaylı [55]. Triton X, commercial emulsifying agent was supplied by Cam Elyaf A.Ş. (Istanbul, Turkey).

3.1.2. Apparatus

The IR analysis was performed on a Perkin Elmer 1600 FT-IR spectrometer using KBr windows and on a Nicolet 380 FT-IR with Smart Diamond ATR. All the ^1H-NMR spectra were recorded on Varian 400-MHz and Varian 60-MHz NMR spectrometer. The spectra were reported as ppm (δ) with TMS as internal standard. The thermal gravimetric analysis (TGA) of polymer samples was done with TA Instrument Q50. Temperature scans were performed from room temperature to 600 ^oC with a heating rate of 10 ^oC/min under nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were performed by a Thermal Analyses Q 100 instrument at a 10 ^{o}C/min heating rate, from -75 ^{o}C to 150 ^{o}C, under nitrogen atmosphere.

Dynamic Mechanical Analysis (DMA) was performed using a TA Instruments Q800 equipped with a liquid-nitrogen cooling apparatus in the single cantilever mode. Themperature scans were run from -70 ^{o}C to 130 ^{o}C at a heating rate of 5 ^{o}C/min with a frequency of 1 Hz and strain of 0.01%. The storage modulus, E', a measure of stiffness, and the loss modulus, E", a measure of energy dissipated, are all measured with the DMA.

The swelling behavior of the polymers were tested in CH_2Cl_2 with a Geartner 7109-46 traveling microscope.

The Zwick/Roell Durometer was used to determine the surface hardness of polymer samples, the test was performed according to ASTM D 2240 standart test.

3.2. Synthesis of Polymeric *p*-Dinitrosobenzene

Polymeric *p*-dinitrosobenzene (PDNB) was synthesized according to Vladykin and Trakhtenberg [56] by oxidation of *p*-quinone dioxime (QDO) in an aqueous suspension wherein hydrogen peroxide is used as an oxidizing agent in the presence of hydrochloric acid as a catalyst.

13.8 g of QDO (0.1 mol) and 52.5 mL of distilled water (2.92 mol) were added to 250 mL three-necked round-bottom flask fitted with a reflux condenser, a internal thermometer, a magnetic stirrer and a drip funnel. The dispersion was heated with continuous stirring at 50-55 ^{o}C for 5 minutes. Subsequently, 18.26 mL of 37 per cent

hydrochloric acid (0.6 mol) was added to the continuously stirred reaction medium. Then, 11.07 mL of 30 per cent hydrogen peroxide (0,36 mol) was added to this mixture dropwise over 30 minutes, in such a way that the temperature of the reaction vessel was constantly between 40 and 50 ^{o}C. Stirring was continued for 30 minutes and the mixture was then filtered and washed with approximately 75 mL distilled water. A yellow-brown solid was obtained which was dried in a vacuum oven at 60 ^{o}C. In order to remove the side products and unreacted QDO, the dried solid was washed with 20 mL acetone. Evaporation of the solvent in the vacuum oven at 60 ^{o}C gave the pure polymeric PDNB as green powder in around 94 per cent yield.

ATR-IR υ (cm $^{-1}$): 3110 (m,), 1485 (s, *trans* –N=N-O, Asym.), 1417 (s, N=N), 1306 (m, $C_{aromatic}$ -N), 1258 (s, *trans* N-O, characteristic for *trans* dimeric structures of aromatic dinitroso compounds), 1104 (s, N-N for aromatic structures), 1012 (s, N-N for aromatic structures), 858 (s, C-H for *para* substituted aromatic structures), 775 (s, C-H), 570 (s, C-H, for aromatic structures out-of-plane ring deformation vibrations), 482 (s, C-H, for aromatic structures out-of-plane ring deformation vibrations)

IR spectrum coincides with the spectrum given in the literature [52].

3.3. Polymerization of Soybean Oil with *p*-Dinitrosobenzene

Two main methods of polymerization of SO and PDNB were investigated in this poject. In the first method the polymerization of SO with PDNB was conducted in two stage polymerization, the first stage being conducted in closed system under nitrogen gas and the second stage performed in an open mold in solventless media under various conditions in which the SO/PDNB mol ratio and pre-heating temperature of SO were the changing parameters. Mechanical test specimens were obtained in this way. The second method was applied using an emulsion polymerization in a solvent media. In addition third

method was performed in a sealed tube and was followed by ^{1}H NMR spectroscopy. Chemical analysis was made in this way.

3.3.1. Polymerization Method I

In a typical sample 0.351 g (0.00258 mol) of PDNB was added to 1.727 g (0.00199 mol) SO pre-heated to 120 ^{o}C in round bottom flask equipped with magnetic stirrer. N_2 gas was passed through the flask to remove any residual moisture. The dispersion was stirred at 90 ^{o}C under N_2 atmosphere for 11 minutes. A temperature increase was observed, the dispersion became milky brown coloured and then dark brown and finally black. During that time increase in the viscosity of dispersion was observed. The dispersion became very thick, viscous and tacky.

The viscous pre-polymer (Stage A) was placed in a silicone mold and the sample was post cured under vacuum (Stage B) for approximately 100 minutes at 120 ^{o}C.

Table 3.1 shows the mol ratios, the reaction temperatures and the reaction times for different samples.

Table 3.1. Changes of variables of polymer synthesis reactions

Sample Code	SO/PDNB mol ratio	Pre-heating Temp. of SO (^{o}C)	Curing Temp. of Stage A (^{o}C)	Curing Time of A stage (min)	Post Curing Temp. (^{o}C)	Curing Time of B stage (min)
SO/PDNB-1/1-120	1/1	120	90	35	120	130
SO/PDNB-1/1-80	1/1	80	90	45	120	180
SO/PDNB-1/1	1/1	Not pre-heated	90	60	120	No curing
SO/PDNB-1/1.3-120	1/1.3	120	90	11	120	100
SO/PDNB-1/1.3-80	1/1.3	80	90	18	120	120
SO/PDNB-1/1.3	1/1.3	Not pre-heated	90	30	120	190
SO/PDNB-1/1.5-120	1/1.5	120	90	4	120	60
SO/PDNB-1/1.5-80	1/1.5	80	90	12	120	80
SO/PDNB-1/1.5	1/1.5	Not pre-heated	90	20	120	120

3.3.2. Polymerization Method II

To 1 g (0.00115 mol) of SO pre-heated to 120 ^{o}C in 100 mL round-bottom flask fitted with stirrer, 10 g (0.56 mol) distilled water and 2 drops of Triton X as emulsifying agent were added. The mixture was heated with continuous strirring up to 90 ^{o}C until homogenuous emulsion was obtained. Then N_2 gas was passed through the flask for approximately 10 minutes, and 0.2047 g (0.00151 mol) PDNB was added. The mixture was heated at 90 ^{o}C approximately for 2 hours until the SO-water emulsion was broken with simultaneous polymer formation. The reaction was kept under N_2 atmosphere to prevent the oxidation of obtained monomeric dinitrosobenzene to dinitrobenzene.

During the polymer formation colour change from milky to black was observed.

The water phase was tried to be removed with filtration, and the polymer was dried under a vacuum for 2 hours to remove the moisture. The polymer obtained was tacky and viscous, and not suitable to be moulded. Characterization was done by FT-IR spectroscopy.

3.3.3. Polymerization in Sealed Tube

The polymers synthesized from method I and II could not be analyzed by ^{1}H NMR, thus 0.0125 g (0.000092 mol) of PDNB was finely dispersed in mixture of 0.06177 g (0.000071 mol) of pre-heated (at 120 ^{o}C) soybean oil and 15 mL $CDCl_3$ in a NMR tube. N_2 gas was purged through the tube. Polymerization was carried out for 100 minutes at 60 ^{o}C to prevent the evaporization of deuterated solvent. Reaction was followed by 60 MHz ^{1}H NMR spectroscopy.

3.4. Model Compound Polymerization

In order to obtain better insight in the curring mechanisms, alternative experimental approaches have to be applied. For that reason methyl oleate was used as a good model for soybean oil molecule.

In a N_2 purged 25 mL round-bottom flask 0.1894 g (0.00139 mol) PDNB and 0.5397 g (0.00181 mol) methyl oleate(MO) were mixed. The curing process was done under N_2 atmosphere to prevent any moisture present in the medium. Polymerization was carried out at 80 ^{o}C for 60 minutes, then at 90 ^{o}C for 60 minutes, and finally at 120 ^{o}C for 2 hours.

Black coloured, sticky, rubber like material was obtained. The reaction was followed by FT-IR spectroscopy.

3.5. Unreacted Soybean Oil Determination

0.5 g of the polymer obtained from method I and 30 mL of petroleum ether were placed in a 50mL weighing bottle. Solution phase was seperated by filtering after 1 hour. This procedure was repeated 3 times. All collected petroleum ether was evaporated by rotary evaporation and subsequent vacuum drying. The soluble substances were isolated for further characterization by NMR, FT-IR and ATR/FT-IR spectrometry. The insoluble solid was dried under a vacuum for several hours under 45 ^{o}C before weighing.

3.6. Surface Hardness Test

Surface hardness curves of polymer samples were obtained by using Zwick/Roell Durometer. For the analysis 1 mm thick samples were prepared by method I polymerization procedure. The samples were protected from any possible mechanical stress before testing.

The specimen was first placed on a hard flat surface. The indentor for the instrument was then pressed into the specimen making sure that it was parallel to the surface. The hardness was read within one second.

3.7. Swelling Test

The cured polymer samples are first subjected to extraction process using petroleum ether for around 3 hours to remove the residual soluble components after curing process. The extracted samples are vacuum dried for several hours under 45 ^{o}C.

Rectangular shaped pieces of polymer samples approximately 9 x 3 x 2 mm were placed in CH_2Cl_2, and the initial lenght was measured with a traveling microscope. The samples were then put in closed containers filled with the solvent. The swollen lenght was measured at definite time intervals until solvent uptake ceased.

4. RESULTS AND DISCUSSION

4.1. Characterization of Soybean Oil

Commercially available soybean oils have a triglyceride structure. The presence of different functional groups makes the soybean oil (SO) ideal monomer of natural origin for the preparation of biodegredable polymers ranging from soft rubbers to tough plastics. Characterization of the crude soybean oil was done by using NMR and FT-IR spectroscopy. Figure 4.1 shows the chemical structure and ^{1}H NMR spectrum of SO. A typical soybean oil molecule reveals nine different proton peaks in the ^{1}H NMR spectrum:

- The peak at the 0.8 ppm belongs to $–CH_3$ protons at the end groups (labeled as 1 in Figure 4.1)
- The peak at the 1.2 ppm belongs to $–CH_2-$ protons of the fatty acid (6)
- The peak at the 1.6 ppm belongs to β protons ($–CH_2-$) of the ester (9)
- The peak at the 2.3 ppm belongs to α protons ($–CH_2-$) of the ester (2)
- The peak around 2 ppm belongs to α protons ($–CH_2-$) of the double bonds (8)
- The peak around 2.7 ppm belongs to the doubly allylic protons(7)
- The peaks around 4.1 and 4.3 ppm belong to $–CH_2-$ protons of glycerol (3)
- The peak at the 5.3 ppm belongs to vinyl protons of the double bond (5)
- The peak at the 5.1 ppm belongs to –CH- proton of the glycerol (4)

Based on our ^{1}H NMR analysis, SO used in this project has an average molecular weight of 870 g/mol.

Figure 4.2 shows the ATR-IR spectrum of unmodified soybean oil. The peak at 1655.05 cm^{-1} represents the carbon-carbon double bond on the backbone of the fatty acid and the peak at 723.14 cm^{-1} shows that these double bonds are in *cis* conformation. The peak at 3009.13 cm^{-1} represents the vibration of hydrogen atoms attched to sp^2 hybridized carbon atoms.

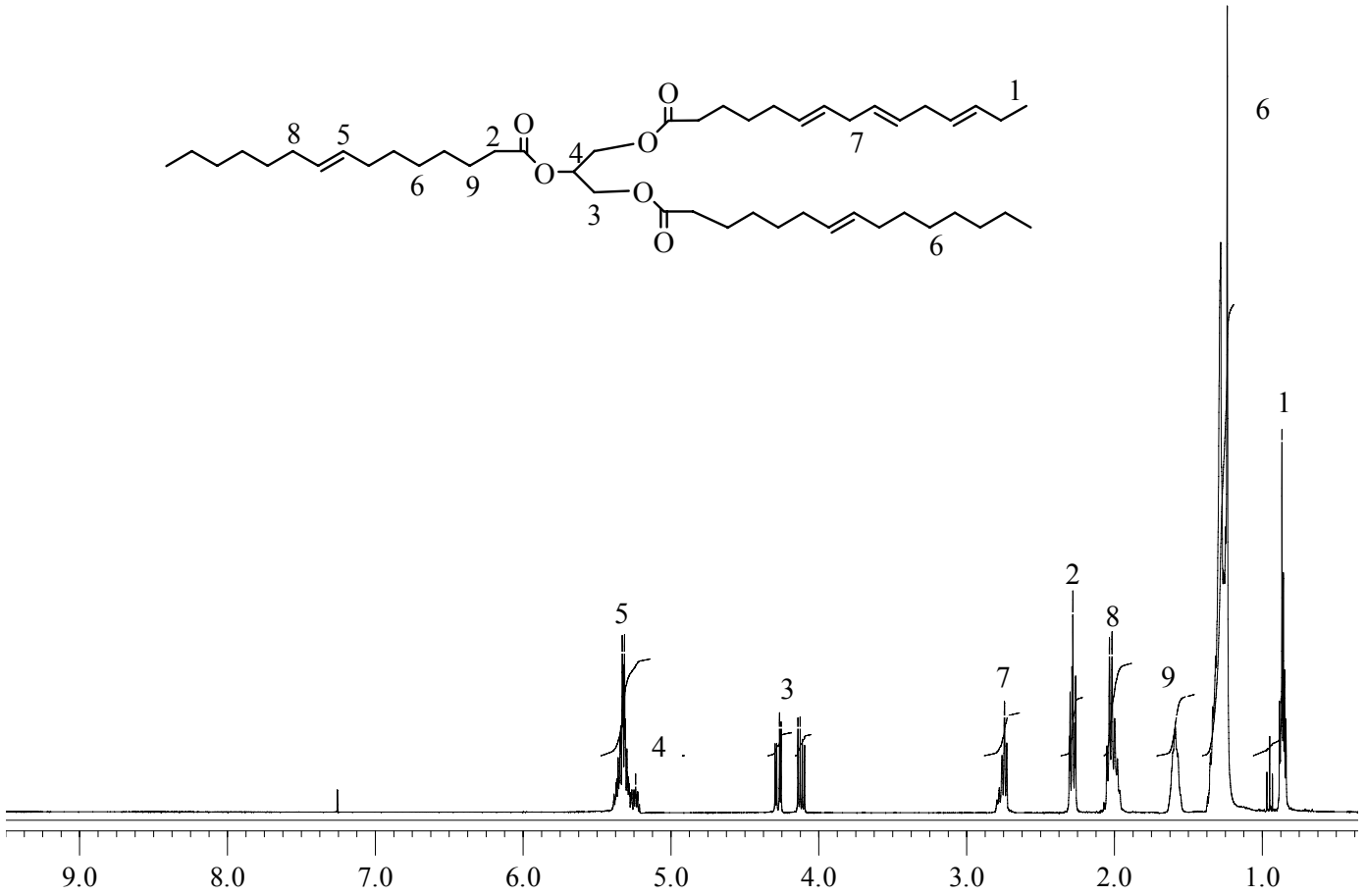


Figure 4.1. ^{1}H NMR spectrum of soybean oil

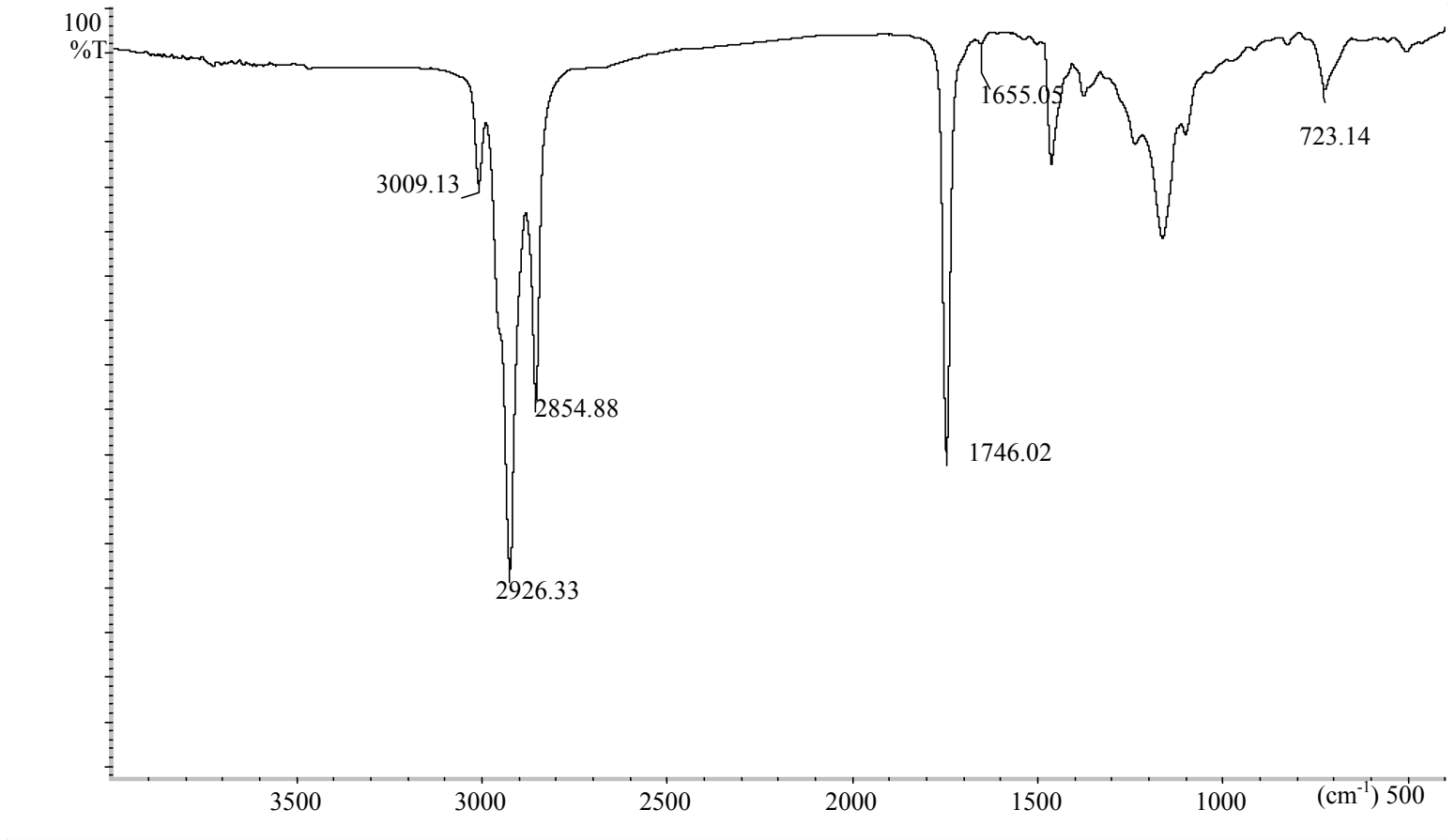


Figure 4.2. ATR-IR spectrum of unmodified soybean oil

4.2. Characterization of Polymeric *p*-Dinitrosobenzene

p-dinitrosobenzene (DNB), an agent for vulcanization of rubbers and rubber-metal adhesives was synthesized using the procedure desribed in chapter 3. PDNB is straw-green finely dispersed polymeric substance with poly (*trans*-azo-*N,N'*-dioxy-1,4-phenylene) structure. As described previously PDNB can not be obtained as a monomer except at very low temperatures.

PDNB is virtually insoluble in organic solvents under ordinary conditions, which complicates elucidiation of its structure. Thus characterization by ^{1}H NMR spectroscopy of PDNB was impossible, only IR spectrum and TGA thermogram have been succesfully recorded.

Figure 4.3 shows the ATR-IR spectrum of PDNB. An intensive band in the area of 1260 cm $^{-1}$ is observed. This peak is characteristic for *trans*-dimers of nitrosoarenes and is atrributed to the N-O stretching vibrations. A striking feature of the infrared spectrum is that the bands vibrations all appear as doublets: 1484, 1416 cm $^{-1}$, N=N-O stretch; 1104, 1011 cm $^{-1}$, C_{ar}- N-N; 858, 775 cm $^{-1}$, C-H para substituted aromatic structures. This infrared spectrum implies that there is no monomeric nitroso group based on the absence of band around 1530 cm $^{-1}$. IR spectrum coincides with the spectrum given in the literature [52].

In Figure 4.4 the TGA thermogram shows the thermal behavior of PDNB. Weigh loss begins at 90 ^{o}C and is rapid between 120 and 160 ^{o}C. This obviously points out that the depolymerization of PDNB starts at 90 ^{o}C and is more rapid as the temperature increases. This is explicable on the basis that, in the absence of the stabilisation afforded by the solid state, the polymer is thermodynamically unstable with respect to the monomer. Thus the preceding result suggests that 90 ^{o}C is a suitable temperature for the

polymerization of PDNB and SO. The synthetic strategy is to depolymerize PDNB *in situ* and use the DNB produced for triglyceride polymerization.

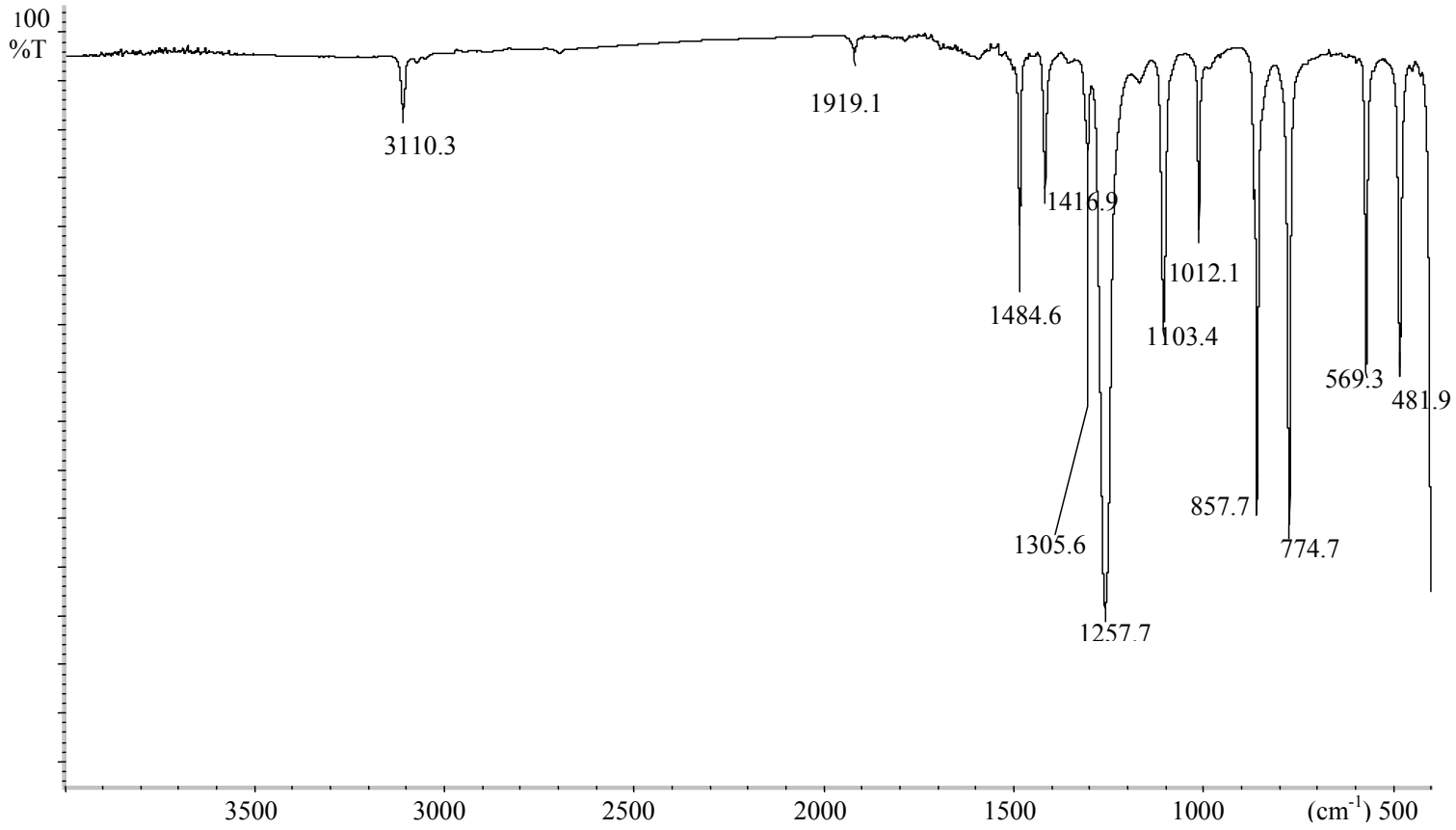


Figure 4.3. ATR-IR spectrum of PDNB

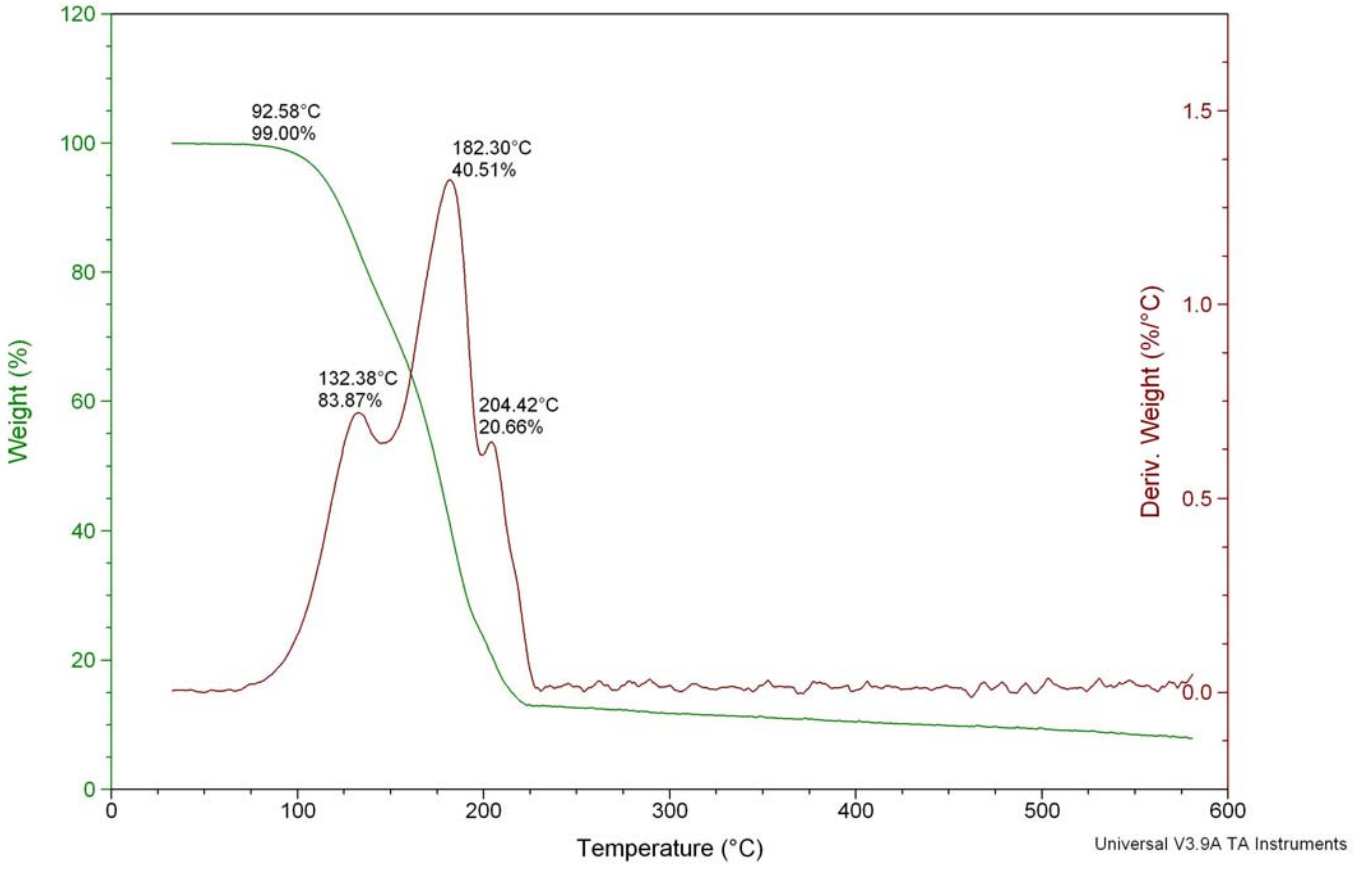


Figure 4.4. TGA trace for PDNB

4.3. Synthesis and Characterization of Polymers

4.3.1. Preliminary Experiments and Characterization

The reaction between PDNB and soybean oil is an *ene* reaction. Although *ene* reactions usually need high temperatures, catalyst and long reaction times, in our work the reactions went in comparatively short time and lower temperatures.

Several attempts were made to rationalize the synthesis of the SO/PDNB polymers. Though the proposed polymerization methods in Chapter 3 seemed to be quite straightforward, there were some factors such as stirring, nitrogen gas and reactor shape which affected the final properties of the products.

The polymerization reactions of SO and PDNB were carried out by mixing the reactants in a certain ratio without solvent. Before curing, the mixture of soybean oil and PDNB had to be purgued with nitrogen gas to prevent any oxygen and moisture residue, because it was reported that the PDNB has potential to behave as a living polymer in the presence of air [57]. Polymeric dinitrosobenzene is difficult material to disperse in any liquid, thus it tends to agglomerate in soybean oil. The mixing of PDNB and SO should be thorough enough to provide a reasonably homogenous mixture. Agglomerated PDNB particles caused heterogenous polymerization and non-homogenous polymer samples were obtained two phased. The fully polymerized and cured solid was at the bottom of either the round bottom flask or silicone mold, and uncured viscous phase was on the surface. Furthermore sometimes PDNB particles clustered together caused sudden expansion. These obstacles were removed by applying continuous stirring during synthesis of the A stage of the polymer. Thus in terms of reactor the polymerization reaction initially had to be performed in a flask suitable for stirring and after a sufficient time the highly viscous pre-polymer had to be poured into a suitable mold for post-curing. If two stage polymerization was not applied the polymer samples tended to cake the round bottom flask

shape, moreover removing the stirrer from the cured sample was impossible, thus the amorphous and formless samples obtained were not suitable for mechanical characterization. Moreover the curing of A stage of the polymer had to be done in closed system under nitrogen atmosphere to suppress the evaporation of the monomeric dinitrosobenzene, since it is fact that during the depolymarization of PDNB the obtained free monomeric nitroso groups are in gaseous state and very labile. The polarization of N-O bond resembling that of C-O bond in carbonyl groups results in a susceptibility of the –N=O group to additions of nucleophiles. On the other hand the free electron pair on nitrogen makes them to acts as nucleophiles. Furthermore they can be easily oxidized to a nitro group or reduced to hydroxylamine or even to an amino group as shown in Figure 4.5 [58].

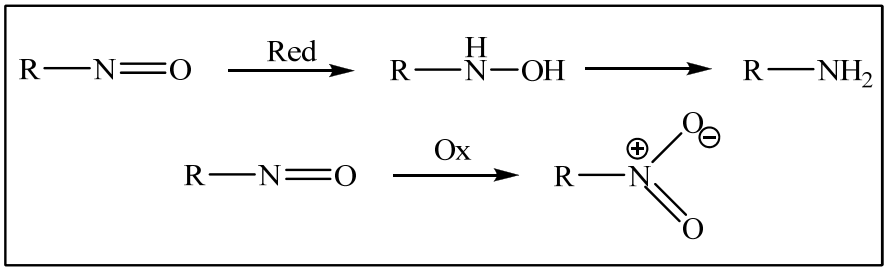


Figure 4.5. Transformations of nitroso group

Based on the preliminary experiments it was observed that the SO/PDNB polymerization begins by the dissociation of *p*-dinitrosobenzene existing as a polymer to the dimer and then consequently to the monomer, and its reaction with the allylic hydrogen in the fatty acid backbone chain. Considering this information and taking into account the TGA trace of PDNB shown in Figure 4.4 which indicates that the depolymerization starts at 90 ^{o}C, the reaction temperature of curing A Stage was adjudged to 90 ^{o}C.

At the end of the reaction tacky, viscous black coloured products (Stage A) are obtained. Characterization of the products was performed by IR spectroscopy. NMR

spectroscopy was not very useful as samples became insoluble in NMR solvents. This suggests that a crosslinked structure is formed. However, the data obtained from the IR spectra were not enough to determine the exact structure of the product of stage A. Considering the references about the vulcanization of rubber with PDNB and the pathway of *ene* reaction, we have proposed the chemical structure in Figure 4.6 as the most favourable structure for the crosslinking of the pre-polymer.

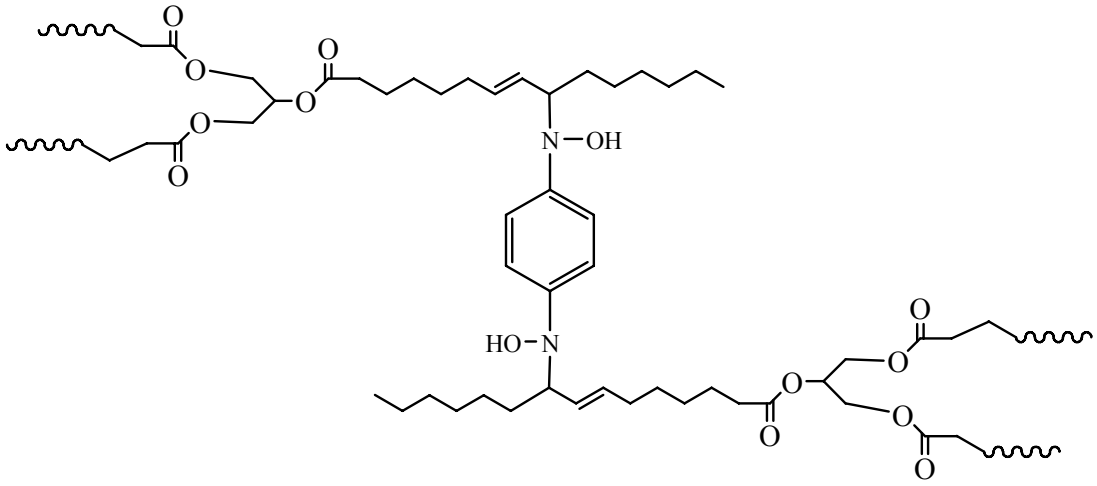


Figure 4.6. Structure of the pre-polymer: *N*-alkenyl-*N*-arylhydroxylamine

Figure 4.7, Figure 4.8 and Figure 4.9 show the ATR-IR and FT-IR spectrums of the unreacted SO/PDNB mixture, SO and PDNB mixture after 5 minutes reaction at 90 ^{o}C and the stage A product of the reaction, respectively.

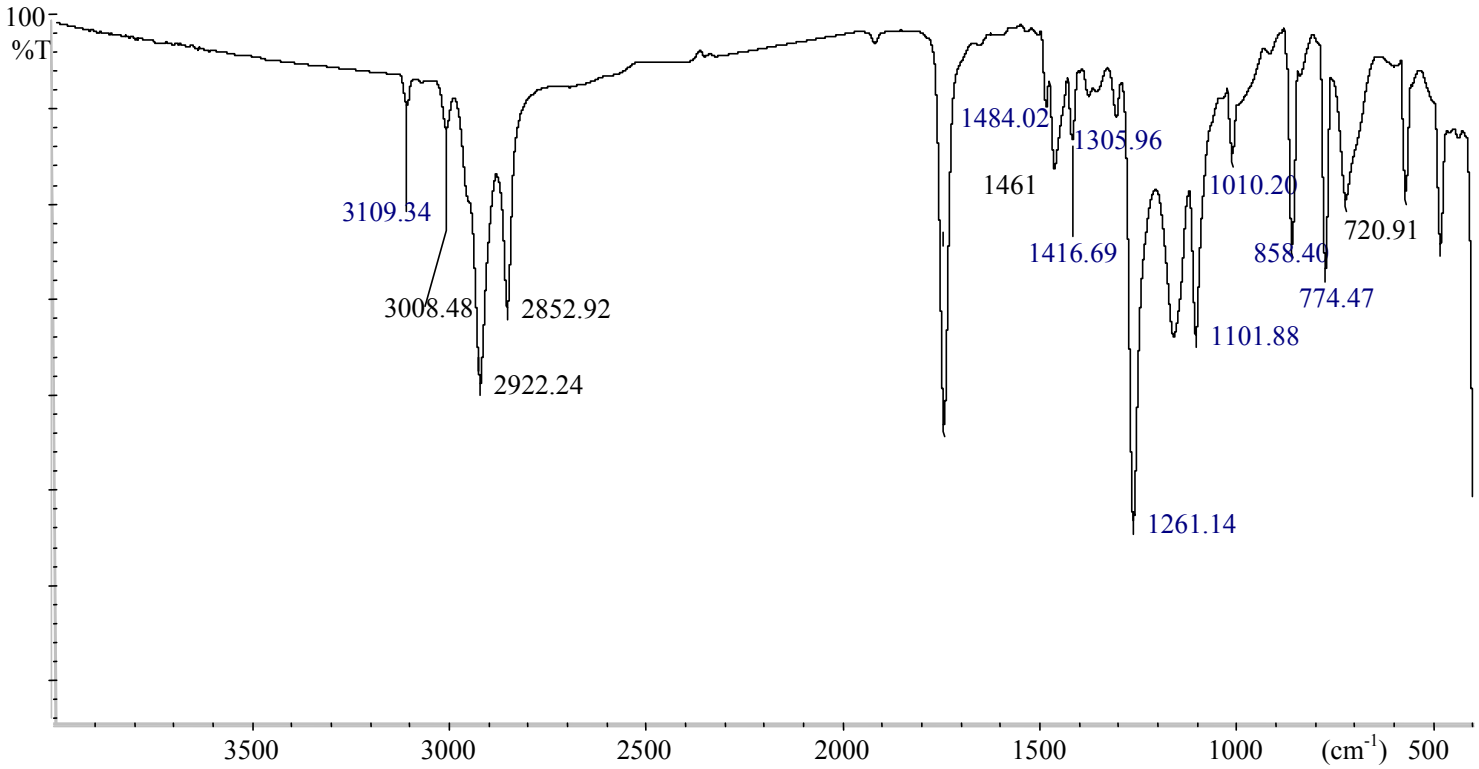


Figure 4.7. ATR-IR spectrum for the unrected SO/PDNB mixture

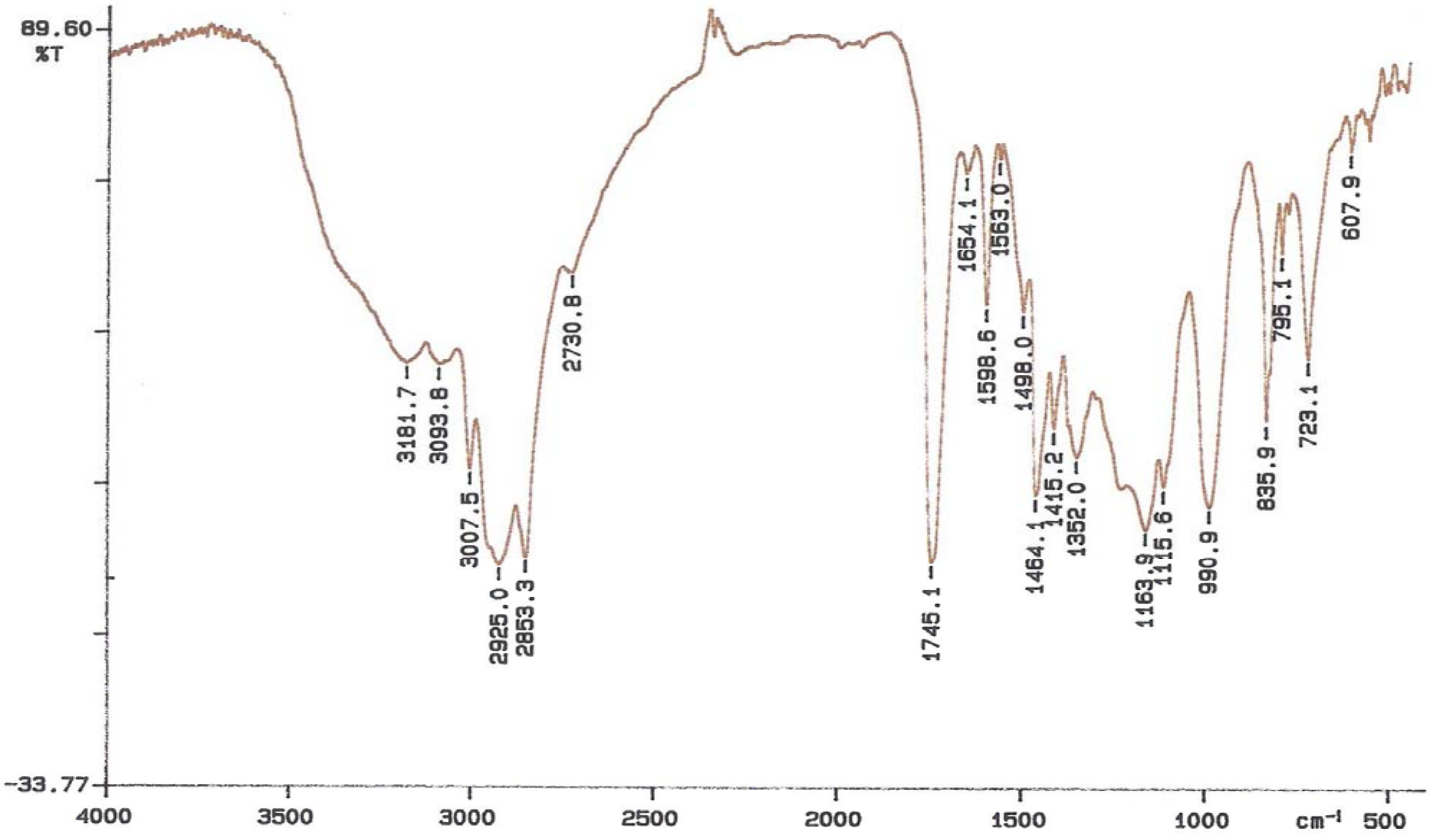


Figure 4.8. IR spectrum of SO and PDNB after 5 minutes reaction at 90 ^{o}C

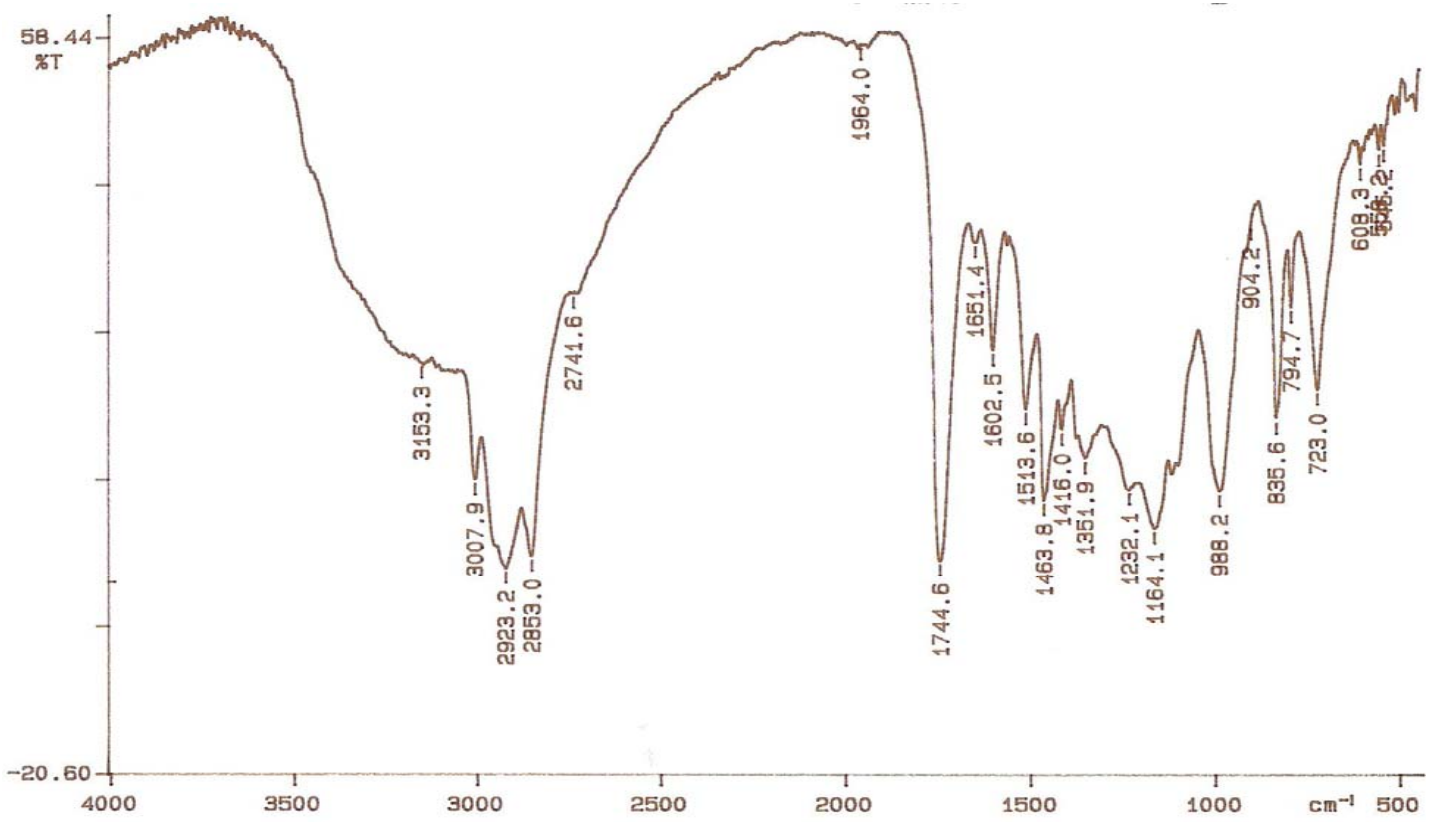


Figure 4.9. IR spectrum of SO and PDNB pre-polymer

In the IR spectrum of the unreacted SO/PDNB mixture, the peaks corresponding to the trygliceride molecule of SO and PDNB are clearly observed. 3109.8, 1484, 1416.6, 1305.9, 1261.1, 1101.8, 1010.2, 858.4 and 774.4 cm $^{-1}$ are attributed to PDNB; 3008.4, 2922.2, 2852.9, 1746, 1461, 1159.1 and 720.9 cm $^{-1}$ belongs to SO, respectively.

The spectrum of the SO and PDNB mixture after 5 minutes reaction at 90 ^{o}C given in Figure 4.8, differs from that of the spectrum of unreacted SO nad PDNB mixture given in Figure 4.7. The disappearance of the peaks corresponding to the polymeric DNB at 3109.8, 1484, 1305.9, 1261.1, 1101.8, 1010.2, 858.4 and 774.4 cm $^{-1}$ can be clearly observed. Since there is no peak related to PDNB, we can assume that at 5. minute of the reaction there is no polymeric DNB. Many new peaks formation is observed. A broad and intense band in the region of 3182-2731 cm^{-1}, is attributed to the O-H vibrations of –N-O-H bond. A new band appeared at 1599 cm^{-1} can be assigned to -C=C- stretching frequency of the aromatic structure. The small band at 1498 cm^{-1} may arise from the nitroso (-N=O) which might be present as a pendant group. The absorption band at 1415 cm^{-1} is most likely to be associated with the N=N stretching of dimeric dinitrosobenzene which suggests the existence of the azoxy type crosslink structure as a side reaction crosslink shown in Figure 4.10.

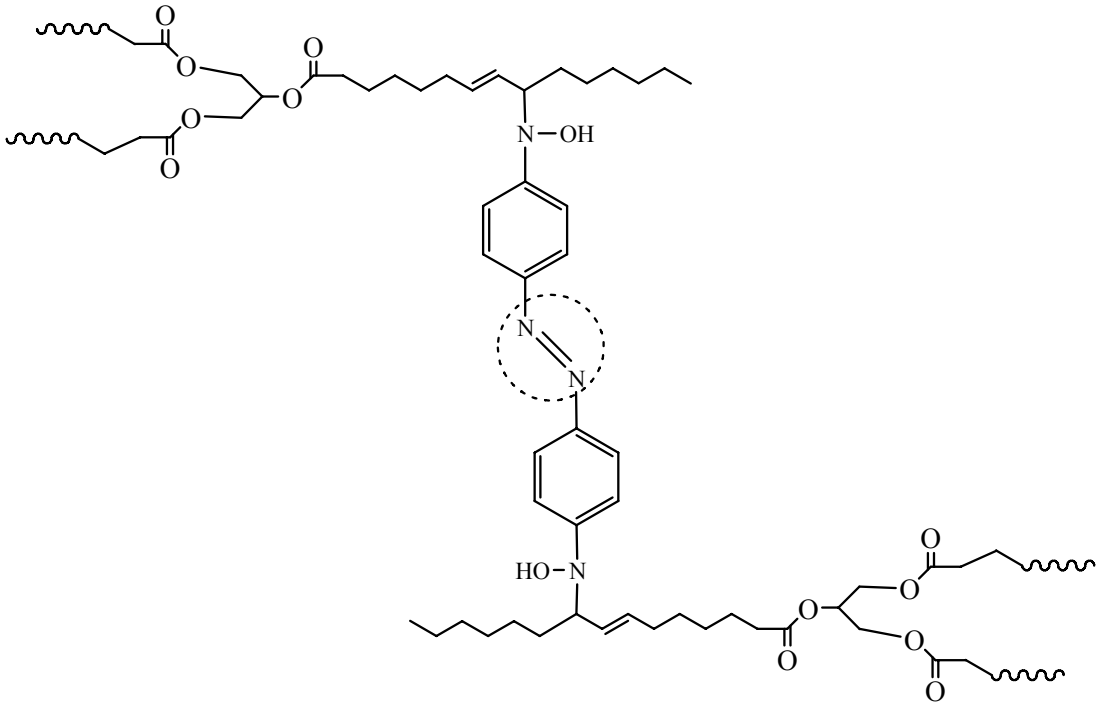


Figure 4.10. Possible crosslink structure of SO/PDNB

The rather strong and diffuse absorption band in around 990 cm^{-1} may be attributed to the N-O vibrations of –N-O-H bond. Peaks at 836–795 cm^{-1} are assigned to to the –C-H- bending of the substituted aromatic groups.

Carefull examination of the IR spectrum of the product of SO/PDNB reaction presented in Figure 4.9. reveals the disappearance of the band at 1499 cm^{-1} and the formation of a new absorption band around 1514 cm^{-1} which can attributed to the conjugation of C=C in the aromatic system and -C=N-. This latter peak suggest that the dehydration process shown in Figure 4.11 is taking place. However this transformation is not thermodynamically favoured in this step of the polymerization. To make it favourable post-curing of the pre polymer (stage A) has to be done.

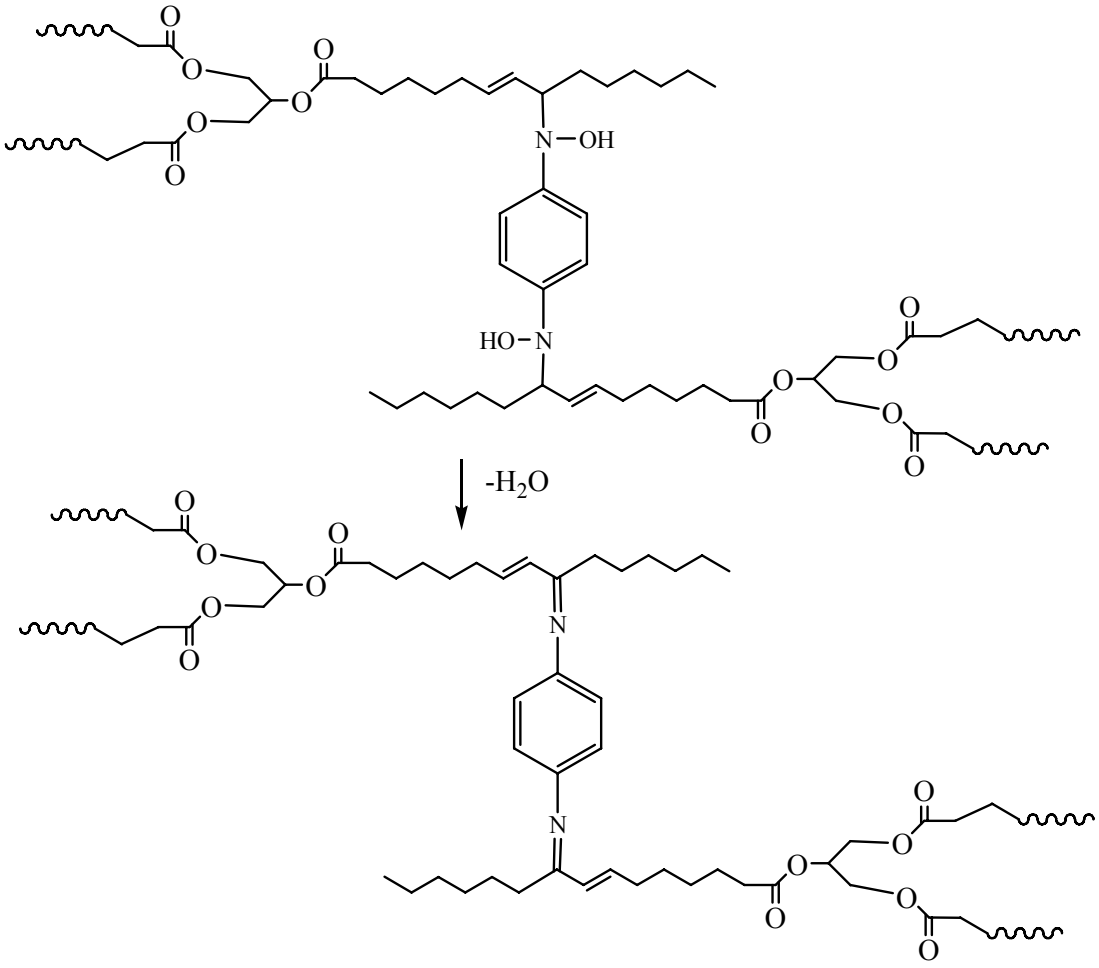


Figure 4.11. Dehydration process of *N*-alkenyl-*N*-arylhydroxylamine to anil

Stage A product is placed in a silicone mold and the sample is post cured under vacuum (Stage B) for a certain time at 120 ^{o}C. The products resulting from the post-curing are black coloured, rubbery, gummy and tacky thermoset polymers. The polymer samples have many rubber-like properties however they can not meet the test of resiliency, extensibility, toughness and resistance to temperature changes shown to be necessary for a general rubber substitue.

The characterization of post-cured polymer was done by IR spectroscopy. Figure 4.12 shows the IR spectra of the final product.

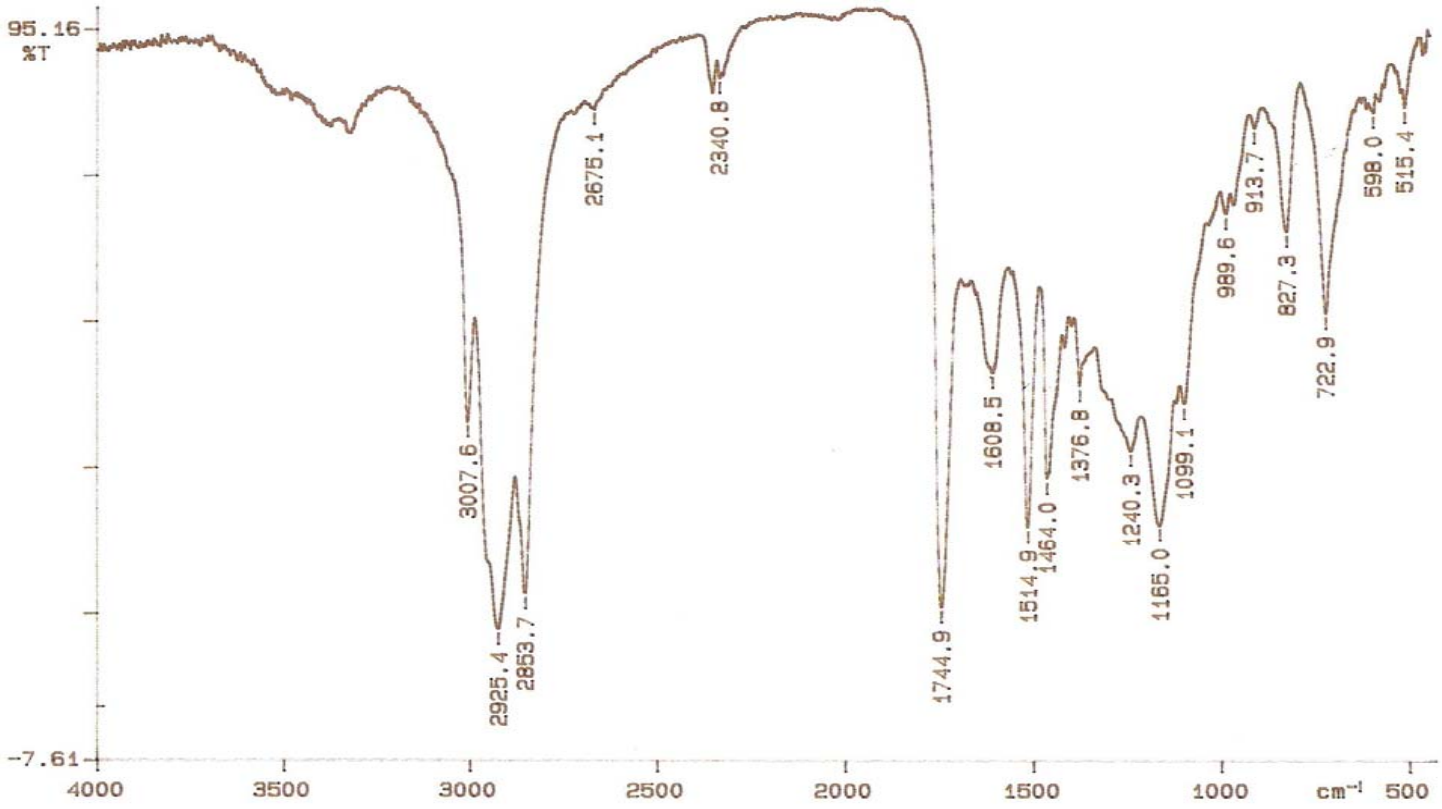


Figure 4.12. IR spectrum of the post-cured SO/PDNB

Striking facts in the spectrum of the post cured polymer in Figure 4.12 are the disappearance of the broad peak around 3182-2731 cm^{-1} , the decrease in the intensity of the peak at 990 cm^{-1} and the increase of the intensity of the peak at 1514 cm^{-1}. By analyzing the three infrared spectrum in Figure 4.8, Figure 4.9 and Figure 4.12 it is evident the shift of absorption band at 1599 to 1608 cm^{-1} which also implies the conjugation of –C=C- aromatic bonds with –C=N- anil bond. The data quoted confirm our assumptions of the proposed structure of the polymer under discussion. An additional argument for the assumed structure seems to be the low solubility of the polymer, symptomatic for polymers with electron conjugations in chain. In spite of all effects for degassing the starting material, the final products still contain voids. This suggests that a volatile by-product is being formed in the B stage of the polymerization. Our conclusion is that the by-product is water.

4.3.2. Effects of SO/PDNB Mol Ratio, Pre-Heating Temperature of Soybean Oil and PDNB Properties on the Polymerization

Raw soybean oil can be cured without any pretreatment, however the process requires a long time and higher concentrations of the curing agent, in that case PDNB.

Polymerization reactions were carried out with at different SO/PDNB mol ratio as shown in Table 3.1, since the exact number of free nitroso groups dissociated during the depolymerization of PDNB is not known, the stochiometry of the reaction can not be predicted. First trial was to react PDNB with excess SO, however the reaction rate was slower and some SO remained unreacted. The isolation of unreacted SO from this reaction medium was impossible. Thus based on the literature related to the vulcanization of butyl rubber with PDNB and the number of allylic positions in triglyceride molecule three different SO/PDNB ratios were chosen.

Moreover pre-heating of soybean oil plays an important role in the polymerization of SO and PDNB. The pre-heated oil facilitates the dispersion and the dissociation of the polymeric curing agent thus provides shorter polymerization time and lower polymerization temperature. It is evident from Table 3.1. that for a given temperature and a definite curing agent soybean oil mol ratio the time of polymer formation depends upon the pre-heating of the oil.

Products synthesized with the soybean oil pre-heated at lower temperature depend on the percentage of the curing agent. These polymers are much more fluid, tacky, sticky and resilient. It was evident from the results and the literature that the particle size and the purity of PDNB change the polymer obtained, as the PDNB content increases the polymer changes from a tacky, sticky, semi-fluid mass to a firmer, less tacky, rubber-like mass. It is obvious also that as the ratio of crosslinking agent is increased, the crosslinking formation sets in before the mixing operation can be completed so the optimum state of cure is reached in a very short time at a relatively low temperature. In such samples the separation of the polymerization into two steps was impossible and samples could not be molded. Furthermore as the ratio of PDNB increseases, the depolymerization rate of the PDNB increases causes formation of unreacted dinitrosobenzene and thus some monomeric DNB escapes. This causes incomplete polymerization based on fast crosslinking and the polymer obtained has more of a crumbly character, and reduced elasticity. Moreover too high PDNB content tends to produce an odor in the finished product.

With regard to the results of the reactions in the Table 3.1 and the preceding approach stated above it was decided that the best SO/PDNB mol ratio is 1/1.3 and most efficient pre-heating temperature of SO is 120 ^{o}C, since this ratio and this temperature give the products with best properties and requires relatively short reaction time.

4.3.3. Effect of Solvent on the Polymerization

Since PDNB is insoluble in soybean oil and slightly soluble in hot water, thermal emulsion polymerization was used as an option. In conventional emulsion polymerization a monomer is polymerized as an aqueous dispersion in presence of a surfactant and initiator. In the reaction of PDNB and SO no initiator is required.

By adopting the thermal polymerization technique, polymerization method II explained in Chapter 3 was applied for the synthesis of SO/PDNB polymers. In polymerization method II, soybean oil and water were mixed in a certain ratio. In order to transfer the highly hydrophobic triglyceride monomer from the monomer droplets to the micelle, non-ionic surfactant such as Triton X was used. The total surface area of the micelles was much greater than the total surface area in the case of the larger triglyceride monomer droplets; therefore the reactive monomeric nitroso groups obtained from the dissociation of PDNB favored to react with the triglyceride molecules in the micelle with regard ro larger triglyceride molecule. Monomer in the micelle quickly polymerized. As the polymer chain grew, phase seperation occured with precipitation of the polymer. The final product was obtained as a dispersion of polymeric particles in water.

Considering the complications in handling the final product and conversion of monomeric nitroso group to hydrated form of nitroso as unstable intermediate as shown in Figure 4.13 [58], this method for polymerization was not applied in the preparation of samples for mechanical characterization.

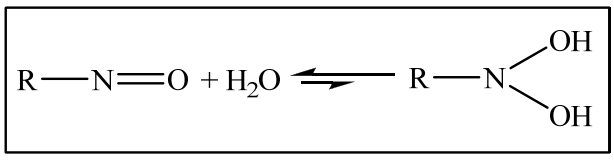


Figure.4.13. Reaction of nitroso group with water.

Moreover the water acts as inhibitor and thermodynamically prevents the dehydration process of *N*-alkenyl-*N*-arylhydroxylamine to anil. Thus synthesis of post cured polymer was impossible. In Figure 4.14 the IR spectrum of dried product is presented. The resemblance between infrared spectrums in Figure 4.8 and in Figure 4.14 is obvious, only that the intensity and broadness of the band in the region of 3182-2731 cm^{-1} are decreased. Moreover the peak around 1009 cm^{-1} specific for N-O bond of hydroxylamine group obviously indicates the presence of arylhydroxylamine structure of the product.

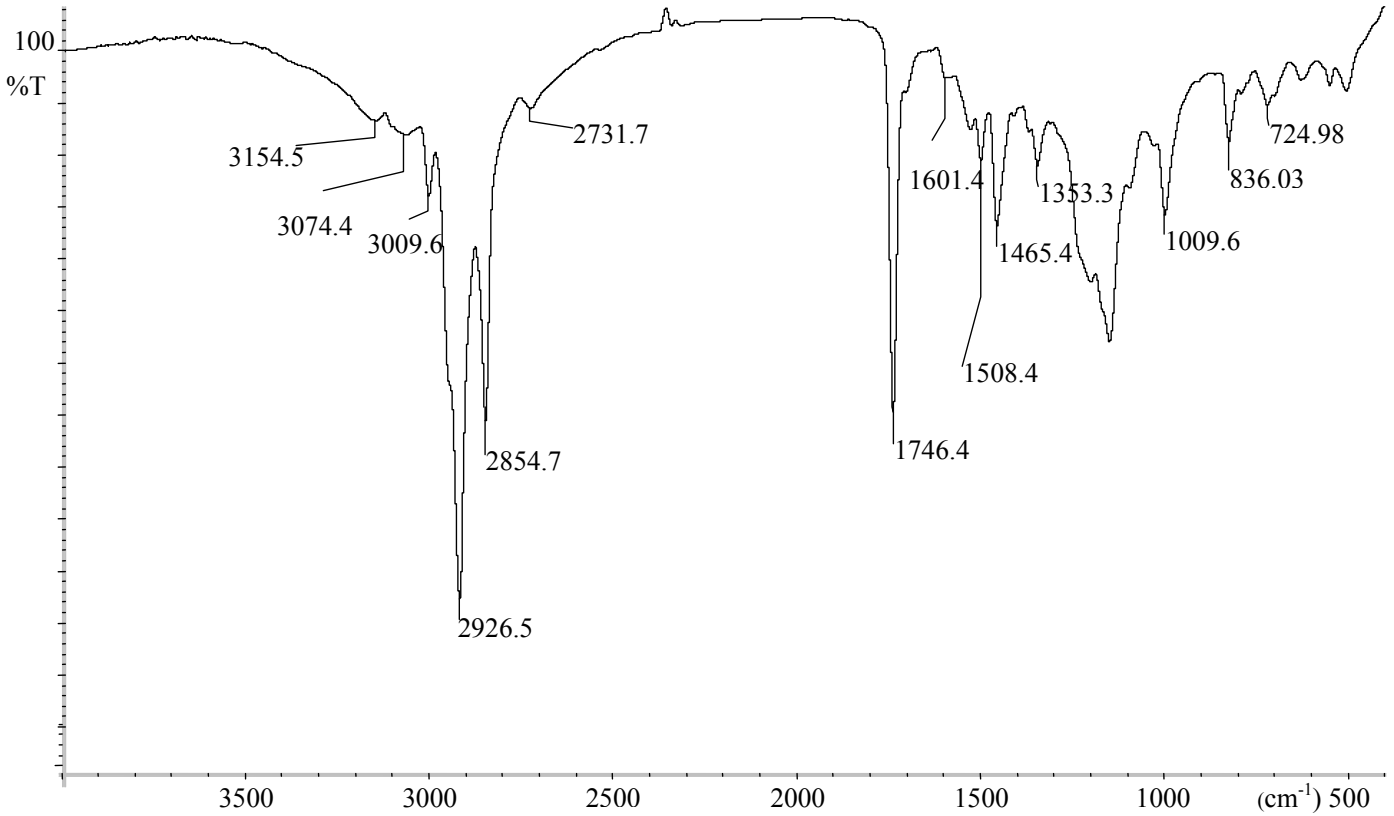


Figure 4.14. ATR-IR spectrum of dried product from emulsion polymerization of SO/PDNB

4.3.4. Polymerization in Sealed Tube

Since the polymers synthesized have crosslinked structure it was impossible to analyze their chemical structures by NMR technique.

A sealed tube test procedure in NMR tube was adopted for the efficient screening of the chemical structure of the polymer.

In the case of sealed-tube polymerizations, the reactants were mixed in a certain ratio as in the polymerization method I, the only difference was the curing temperature. The reaction was performed at 60 ^{o}C to prevent the evaporization of $CDCl_3$ used as solvent. During the reaction at different time intervals ^{1}H NMR spectrum at 60 MHz were recorded. Figure 4.15 shows the overlayed ^{1}H NMR spectrums of the reaction at different time intervals. In the range of phenyl protons a complex multiplet formation is observed with boundaries of 6.5-8.0 ppm during the reaction. This indicates the presence of many different aromatic structures in the polymer.

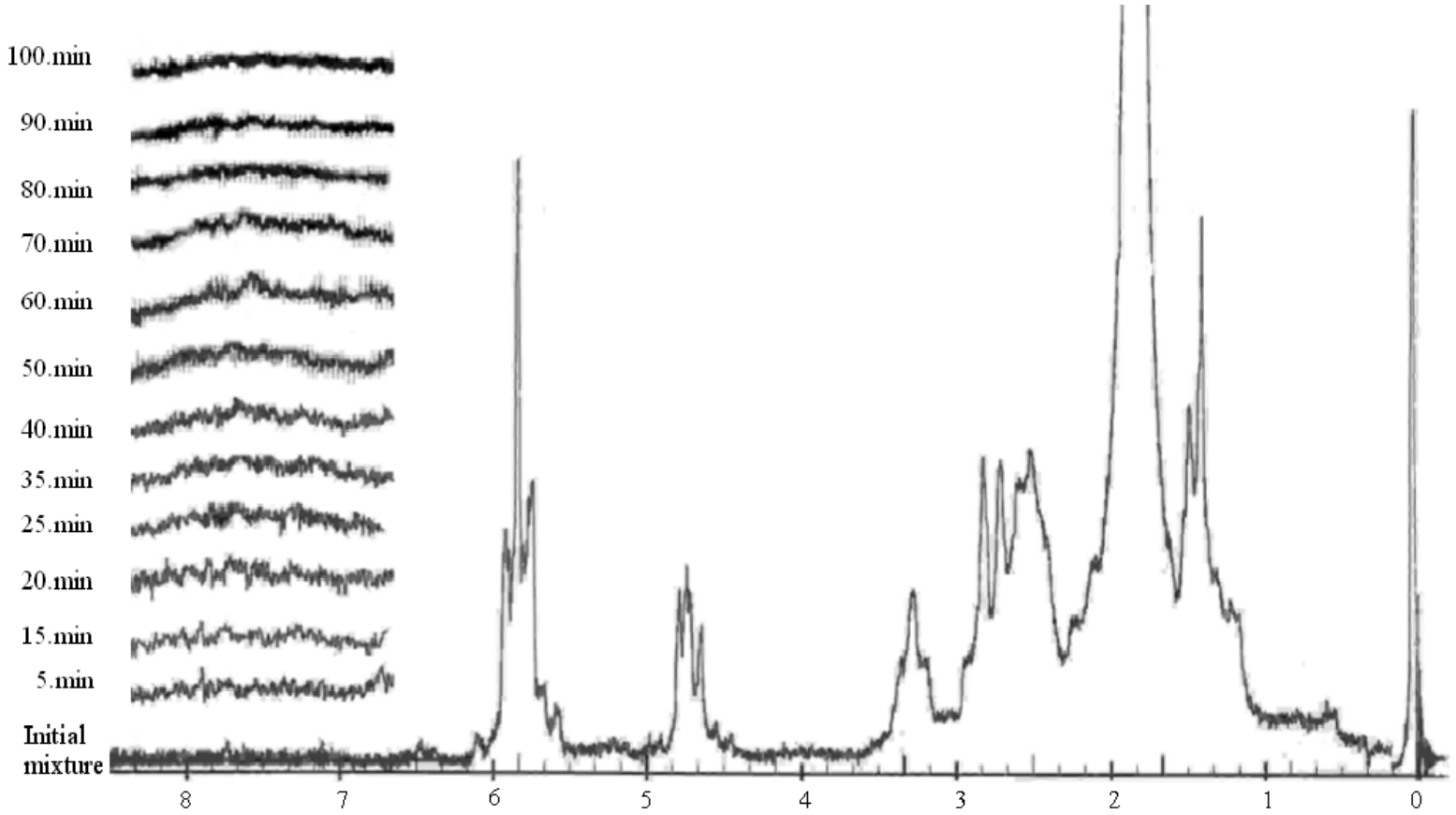


Figure 4.15. Overlayed ^{1}H NMR spectra recorded during the polymerization of SO/PDNB in sealed tube at different reaction times

4.4. Model Compound Polymerization

Standard analytical and chemical techniques are not appropriate to analyse highly crosslinked polymer, because of the insolubility of the three-dimensional network, the low concentrations and the variety of crosslinked structures. Model Compound Polymerization is widely used to gain mechanistic insight in crosllinking, because of its good agreement with real crosslinked material systems and the possibility to use conventional analytical techniques.

The polymerization process is simulated by reactions of monomeric olefin (model for triglyceride moleculer) with curatives. The low molecular weight products are more readily analysed than actual triglyceride molecule.

The choice of a model compound for a specific experiment strongly depends on the aspects to be investigated. The choice of the structure of the model molecules needs to be based on the polymer material under investigation. Moreover the model should resemble the repeating unit of the polymer. Certain aspects must be taken into account:

- Position and configuration of the double bond and allylic hydrogens
- Number of double bonds and allylic hydrogens;
- Additional functional groups;
- Availability of the model;
- Boiling point;
- Solubility.

Using model compounds offers a vital tool for studying the reaction products. However the differences between high-molecular weight triglyceride molecule and low molecular weight model compound should not be neglected when interpreting the results.

Considering the aspects sumerized above methyl oleate was preffered as model compound for the polymerization of soybean oil and polymeric *p*-dinitrosobenzene. Methyl oleate (MO) is an ideal starting material because of its aliphatic carbon backbone and its mono-unsaturation. Methyl oleate was mixed with PDNB in the same manner as soybean oil using the polymerization method I descibed in chapter 3. The polymerization was carried out at 80 ^{o}C, 90 ^{o}C and finaly at 120 ^{o}C. The final products of model polymerization were tacky and viscous liquids. Suprizingly they were also highly crosslinked. The unsaturation in MO presents two allylic positions on either side. Separate reactions of these cites probably gives crosslinked structures. Thus an examination by NMR was impossible, and the characterization of the products were performed only by using IR spectroscopy. Figure 4.16 shows the overlayed ATR-IR spectrum of unreacted MO/PDNB mixture and the final product of MO/PDNB

In the IR spectrum of the unreacted MO /PDNB mixture in Figure 4.16 (a), the peaks corresponding to the trygliceride molecule of MO and PDNB are clearly observed. 3109.8, 1484, 1416.6, 1305.9, 1261.1, 1101.8, 1010.2, 858.4 and 774.4 cm $^{-1}$ are attributed to PDNB; 3011.4, 2922.2, 2852.9, 1741, 1463, 1435, 1168.1 and 722.9 cm $^{-1}$ belongs to MO, respectively. In the spectrum named as (b) in Figure 4.16 the disappearance of the peaks corresponding to the polymeric DNB at 3109.8, 1484, 1305.9, 1261.1, 1101.8, 1010.2, 858.4 and 774.4 cm $^{-1}$ can be clearly observed.

The broad and intense absorption band around 3200 and 2780 cm^{-1} in Figure 4.16 (b) suggest the O-H vibrations of -N-O-H bond. The 1601 cm^{-1} absorption band is assigned to –C=C- stretching frequency of the aromatic structure which is comparable to 1599 cm^{-1} in Figure 4.8. A new absorption band around 1512 cm^{-1} which can attributed to the conjugation of C=C of the aromatic system with -C=N-. The small band at 1408 cm^{-1} is most likely to be associated with the N=N stretching of dimeric dinitrosobenzene. Moreover, a stronger and diffuse absorption band around 990 cm^{-1} may arise due to the -N-O vibrations of –N-O-H bond. Peaks at 836–795 cm^{-1} are assigned to to the –C-H- bending of the substituted aromatic groups. The data quoted suggest the structures shown in Figure 4.17 and Figure 4.18 as products of the MO/PDNB reaction.

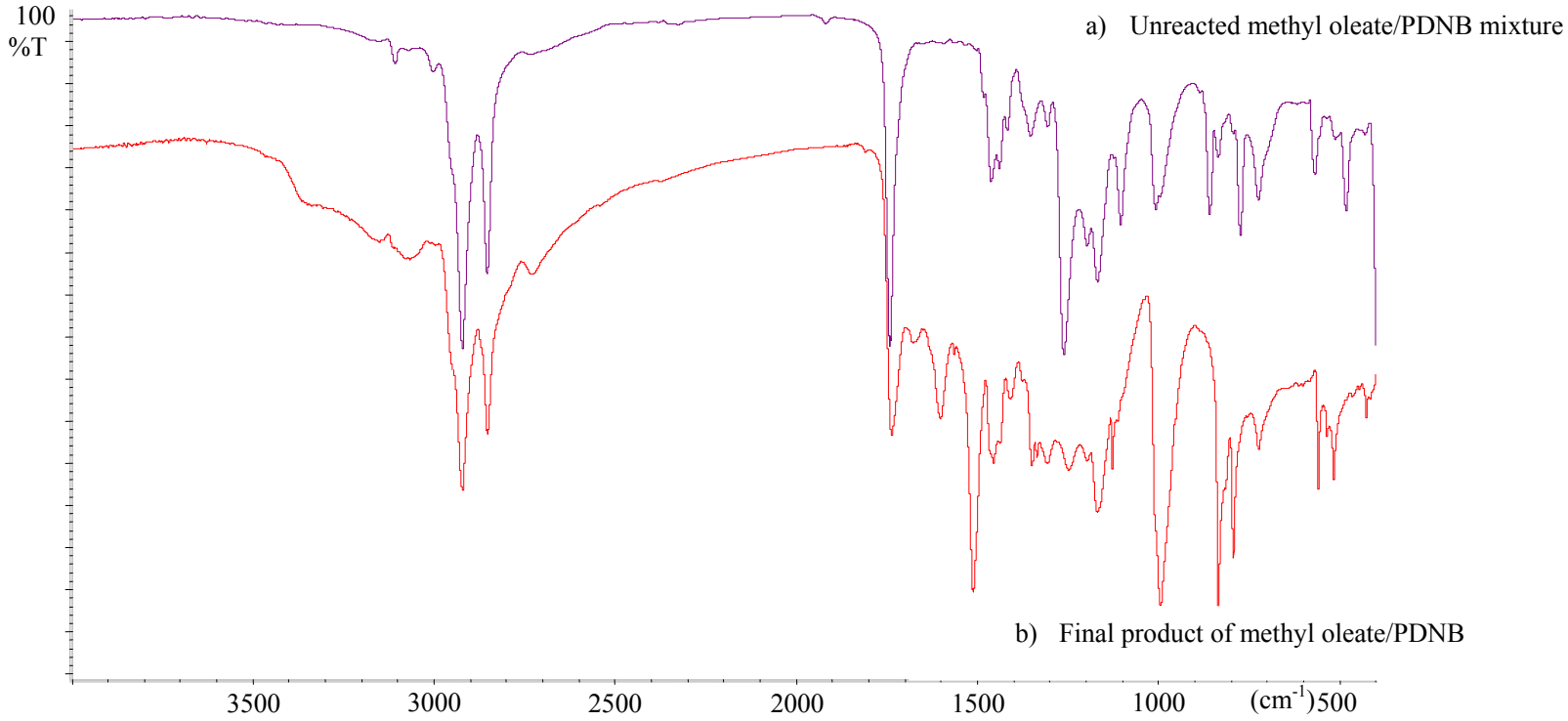


Figure 4.16. Overlayed ATR-IR spectra of a) unreacted methyl oleate/PDNB mixture and b) final product of methyl oleate/PDNB

Insolubility of the material synthesized in common solvents suggests the proposed polymeric structure in Figure 4.17 and Figure 4.18.

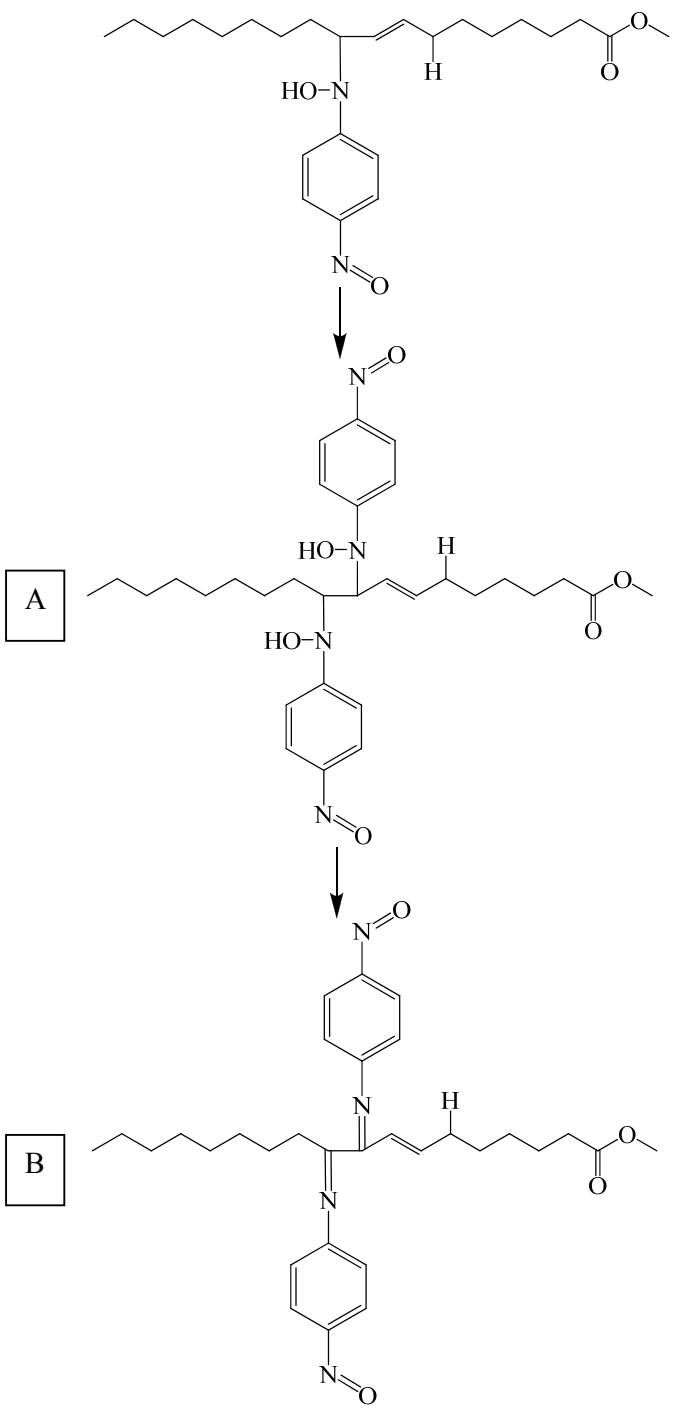


Figure 4.17. MO/PDNB products structures

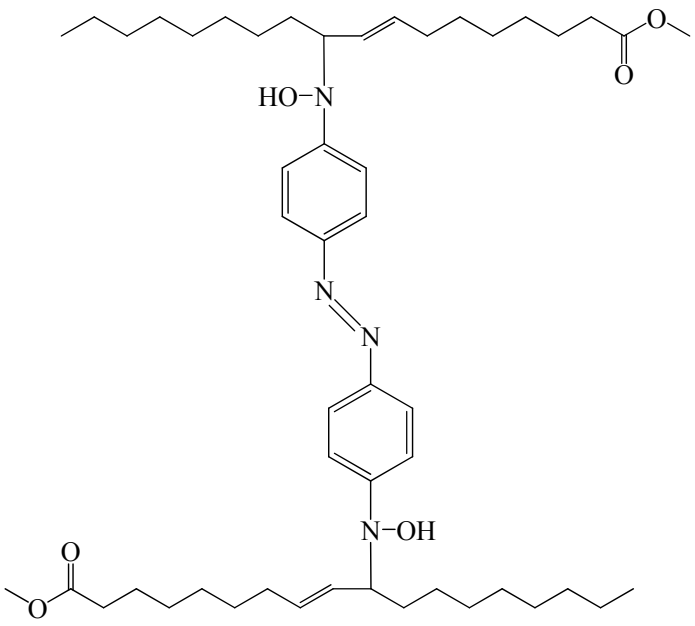


Figure 4.18. MO/PDNB azoxy-type product structure

4.5. Determination of Unreacted Soybean Oil

Unreacted monomers plastify polymer and reduce their rigidity. Therefore determination of the amount of unreacted monomer in the synthesized polymer sample becomes important. Petroleum ether was used to extract the unreacted SO from the polymer samples. Table 4.1 shows the percentages of the soluble portion of different SO/PDNB mol ratio polymers.

Table 4.1. Soluble and insoluble portions (wt%) of the polymers after extraction

Sample Code	Soluble portion (wt%)	Insoluble portion (wt%)
SO/PDNB-1/1-120	25	75
SO/PDNB-1/1-80	29	71
SO/PDNB-1/1.3-120	10	90
SO/PDNB-1/1.3-80	17	83
SO/PDNB-1/1.5-120	17	83
SO/PDNB-1/1.5-80	16	84

The soluble substances of the all samples proned to be unreacted soybean oil as shown in Figure 4.19 of the IR spectrum and Figure 4.20 of the ^{1}H NMR spectrum. No aromatic protons are evident in the ^{1}H NMR spectrum, hence no molecules with DNB reacted only at one end are produced as seen in Figure 4.17 (A). The fact that unreacted triglycerides still exist in the products even when stoechiometricly sufficient PDNB is used indicates that the depolymerization PDNB is not as complete as desired. Structures corresponding to structures in Figure 4.18 are also obtained.

The insoluble substances are crosslinked polymers that are not soluble but are swelleble in common solvents such as THF, CCl_4, DMSO and CH_2Cl_2.

The results in Table 4.1 indicate that 71-90 wt% of insoluble substances were obtained. It is obvious that, in addion to the effect of crosslinking agent concentration, the pre-heating temperature of soybean oil has also effect on the residual monomer content. The polymer of SO (pre-heated at 120 ^{o}C) and PDNB in 1 to1.3 mol ratio, respectively has the lowest ratio as soluble part. This result indicates that pre-heating temperature 120 ^{o}C of soybean oil and SO/PDNB mol ratio is the optimum range to obtain a polymer with the least monomer residue.

As the pre-heating temperature of SO is decreased to 80 ^{o}C, the amount of unreacted free oils present in the polymer network steadily increased.

The preceding results suggest three important points:

- the materials are composed of crosslinked polymer networks plastisized by a about 10 per cent of unreacted free oil
- about 90 per cent of the soybean oil has participated in polymerization and been incorporated into the crosslinked polymer network
- the polymer structure is determined by the pre-heating temperature of soybean oil and the stoechiometry.

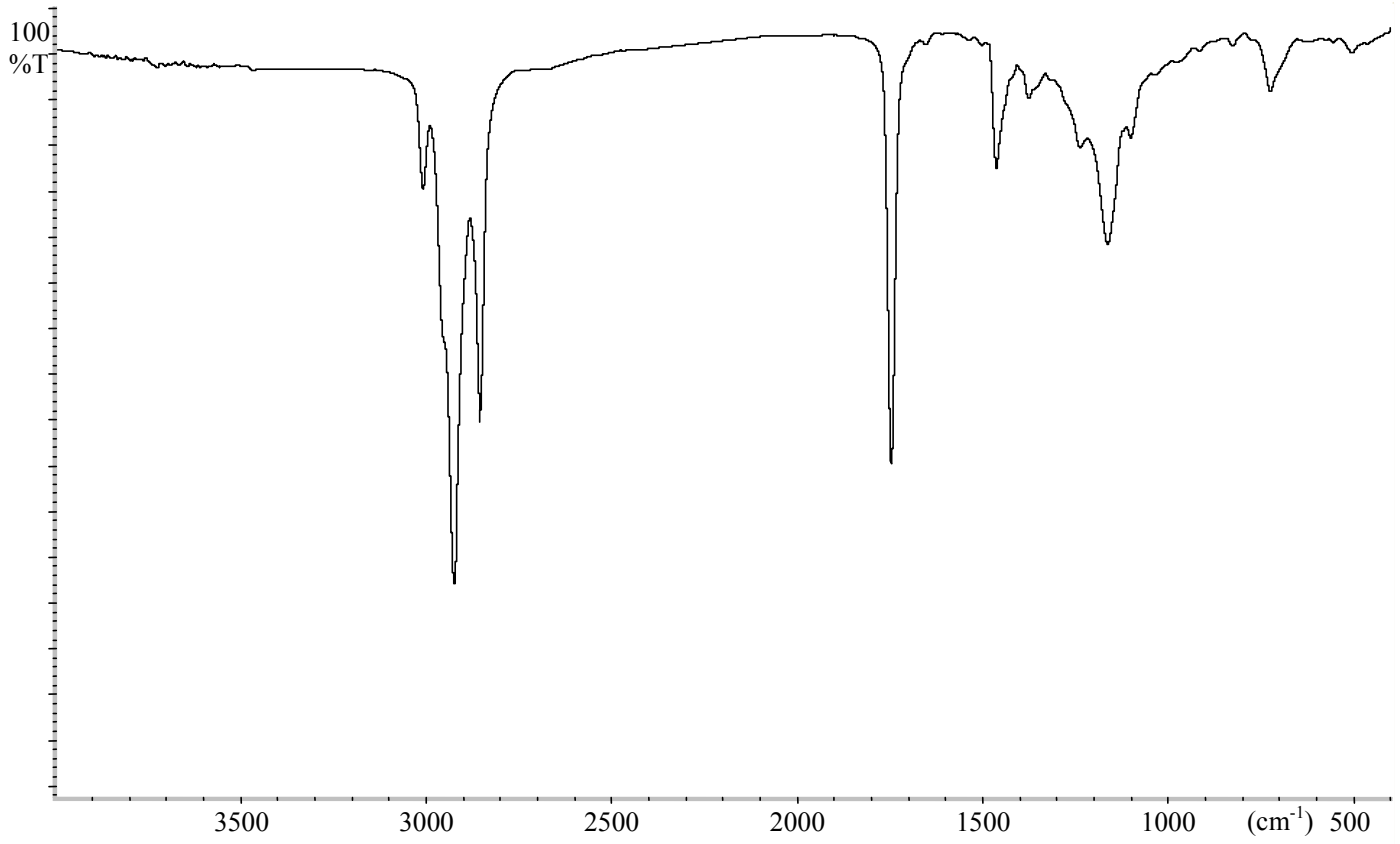


Figure 4.19. ATR-IR spectrum of extracted unreacted soybean oil from polymer

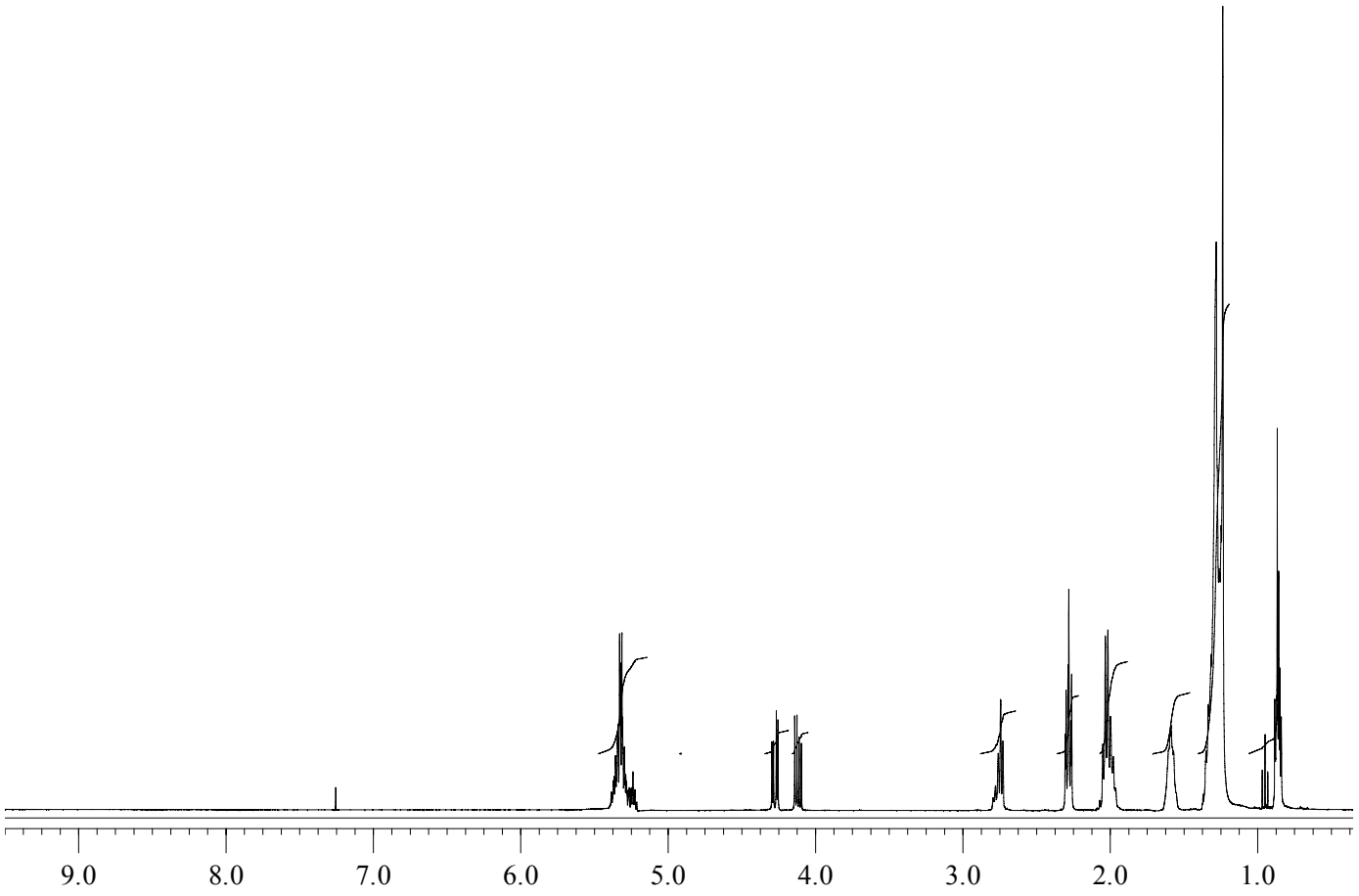


Figure 4.20. ^{1}H NMR spectrum of unreacted soybean oil extracted from polymer

4.6. Mechanical Analysis

A direct approach to study the thermal and mechanical properties of the polymer phase is via the Dynamic Mechanical Analysis (DMA).

DMA Analysis measures the mechanical properties of materials as a function of time, temperature, and vibration frequency. DMA is commonly used to determine quantitative flexural storage and loss moduli, shear storage and loss moduli, tan delta (δ), and the dynamic and complex viscosity of materials.

Typically, a sample is clamped into the DMA apparatus and subjected to an oscillatory deformation while being heated or cooled at some controlled rate. The resonant frequency of the sample and mechanical clamp assembly is continuously monitored as a function of temperature. As the viscoelastic response of the material changes over some temperature range, the electrical energy required to maintain a constant level of sample deformation also changes and is continuously monitored. Quantitative analysis routines are used to calculate the modulus (stiffness) and viscoelastic loss characteristics of a specimen as a function of temperature or time. Transition temperatures (T_g) are readily obtained by determining the peak temperatures of the loss moduli or tan delta profiles.

The polymer samples for dynamic mechanical analysis were prepared to dimensions of 25 x 5 x 0.5 mm. Temperature scans were run from -70 ^{o}C to 130 ^{o}C at a heating rate of 5 ^{o}C/min with a frequency of 1 Hz and strain of 0.01%. Figure 4.21 and Figure 4.22 show the temperature dependence of the storage modulus E' and the loss factor tan δ for the various compositions of SO/PDNB polymers, respectively.

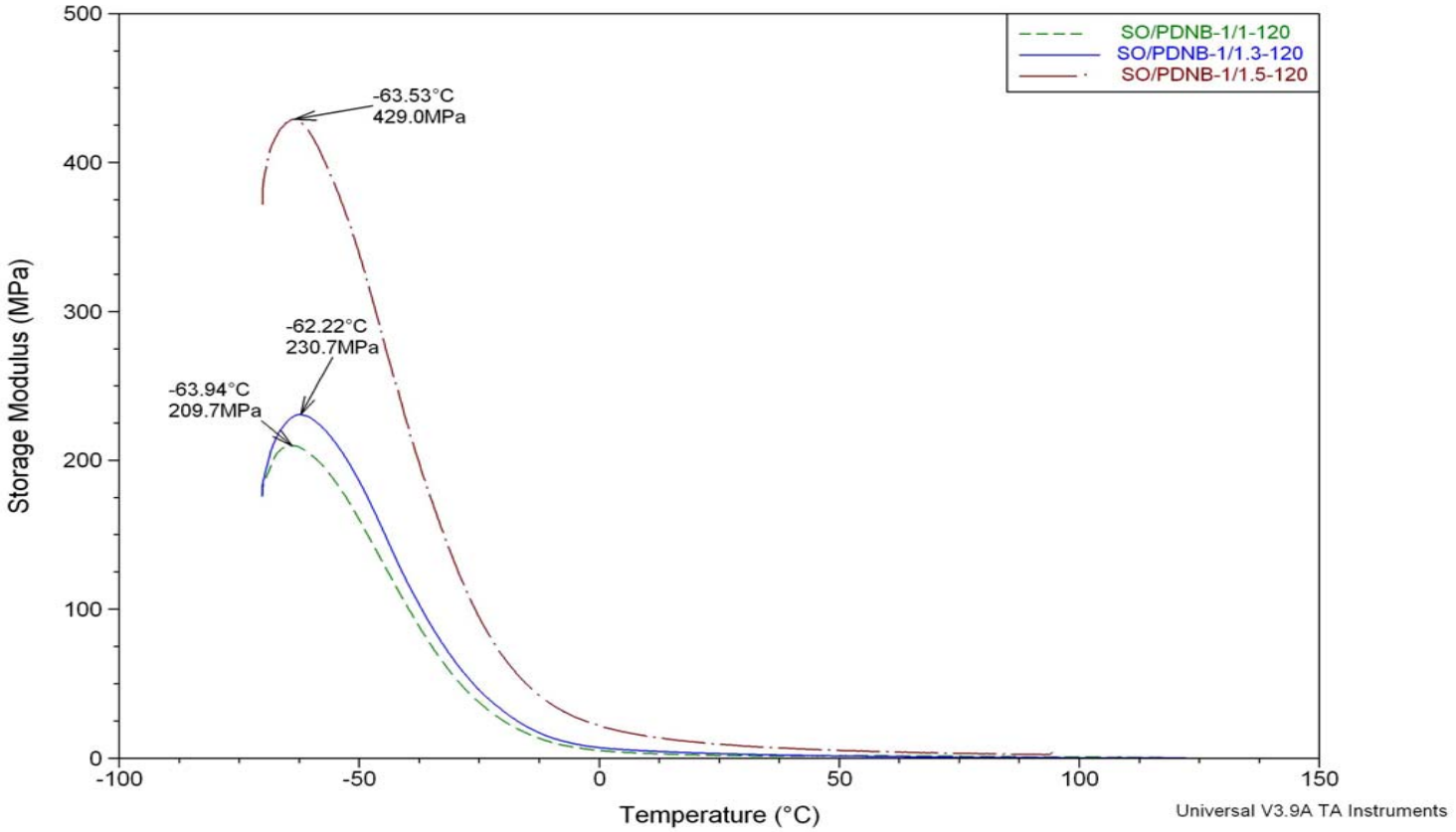


Figure 4.21. Temperature dependence of the storage modulus *E′* for SO/PDNB-1/1-120, SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120, respectively

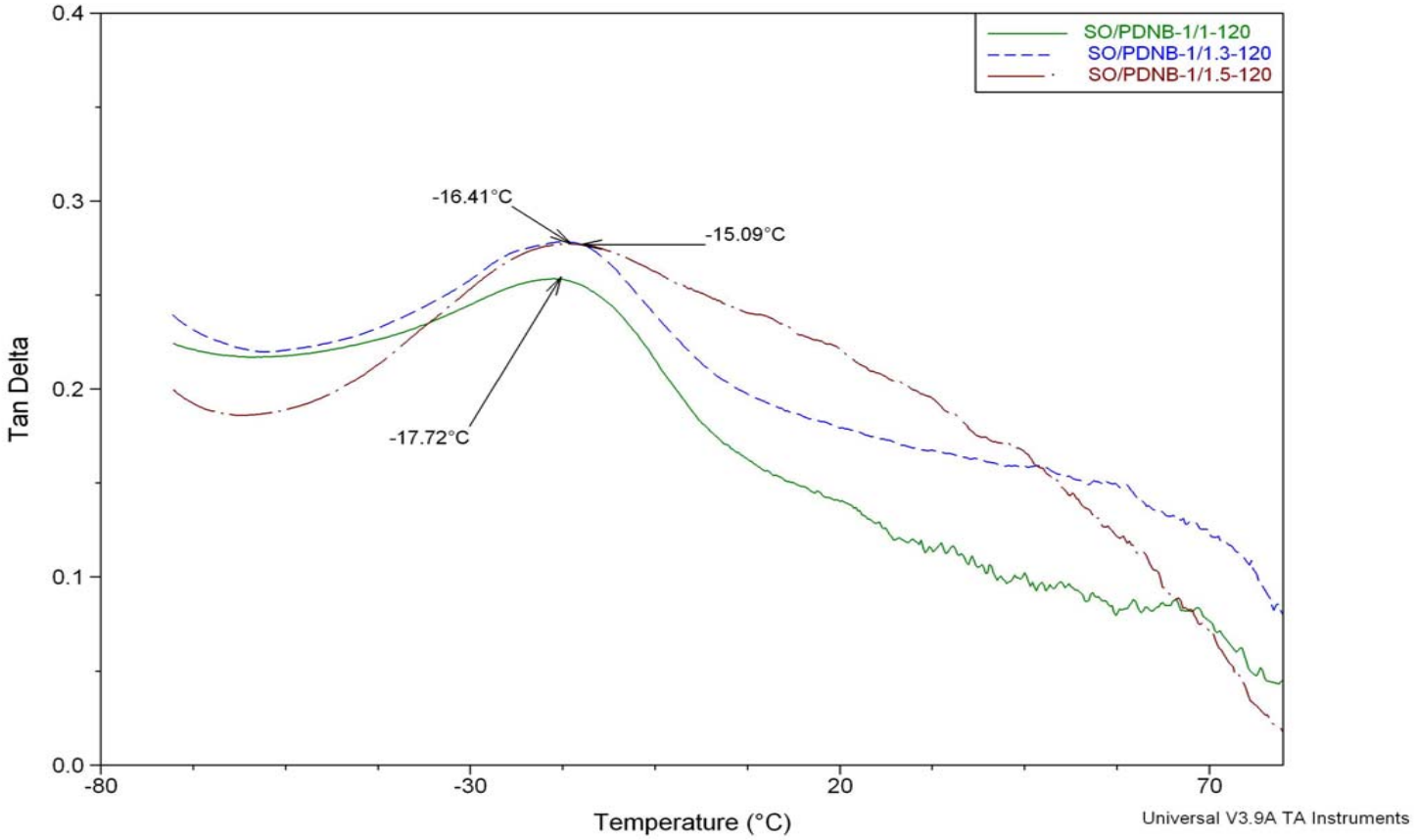


Figure 4.22. Temperature dependence of the loss factor tan δ for SO/PDNB-1/1-120, SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120, respectively

Within the temperature range tested, the storage modulus *E′* for all polymers in Figure 4.21 show a sharp drop followed by a plateau as the temperature increased. Apparently, the sharp drop arises from the extensive motion of chain segments diversified by crosslinking in these polymer samples. The appearance of plateau above the glass transition of the polymers indicates that a stable crosslinked network exist in these polymers. All polymer samples exhibit maximum storage modulus at approximately -63 ^{o}C. The sample with the highest PDNB ratio has the highest storage modulus - approximately 430 MPa over the whole temperature range, while the other two samples exhibit similar behaviour with moduli lower than that of the sample SO/PDNB-1/1.5-120.

In Figure 4.22 the temperature dependence of the loss tangent (tan δ) for the polymer samples is shown. The tan δ, the ratio of the storage modulus over the loss modulus, (*E″/E′*), can be used to measure T_g, and is taken as the temperature corresponding to the maximum of the tan δ peak. The glass transition values are evaluated as -17.8 ^{o}C, -16.4 ^{o}C and -15.1 ^{o}C, for SO/PDNB-1/1-120, SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120, respectively. The T_g regions are fairly broad with the broadest region for the sample with highest ratio of PDNB, and SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120 polymers possess a single tan δ curves, indicating no phase separation. However SO/PDNB-1/1-120 sample shows slightly smaller second maxima, which emphasizes heterogenous phase formation. Despite this the broader peaks indicate that there is a wider distribution of chain lenghts between the crosslink points.

4.7. Thermal Analysis

In order to better understand the thermal behavior of the synthesized polymers, thermogravimetric analysis (TGA), in conjunction with differential scanning calorimetry (DSC), was used to gain a better understanding of the thermal properties of the polymers.

The Thermogravimetric Analyser measures weight changes in a material as a function of temperature or time under a controlled atmosphere. Its principal uses include measurement of a material's thermal stability and composition.

TGA was done to the SO, PDNB, and to the polymers of SO/PDNB with different mol ratios. Figure 4.23, Figure 4.24 and Figure 4.25 reveal the overlayed results for the SO/PDNB-1/1-120, SO/PDNB-1/1.3-120, and SO/PDNB-1/1.5-120, respectively, with thermograms of pure SO and PDNB which are included in these graphs for comparison purposes. All the polymers were extracted and the unreacted soybean oil was removed before TGA analysis.

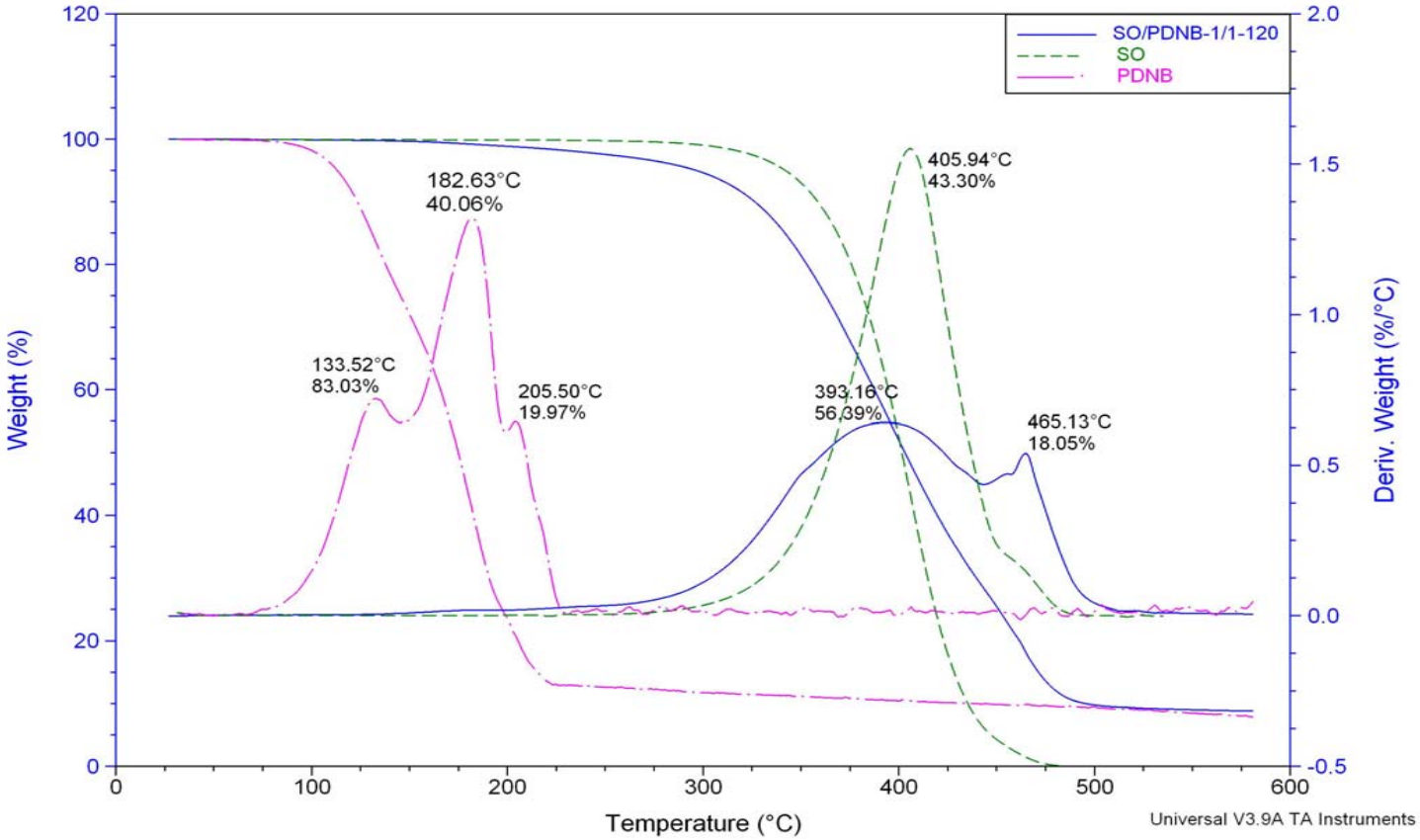


Figure 4.23. TGA and DTGA traces of SO/PDNB-1/1-120, SO and PDNB

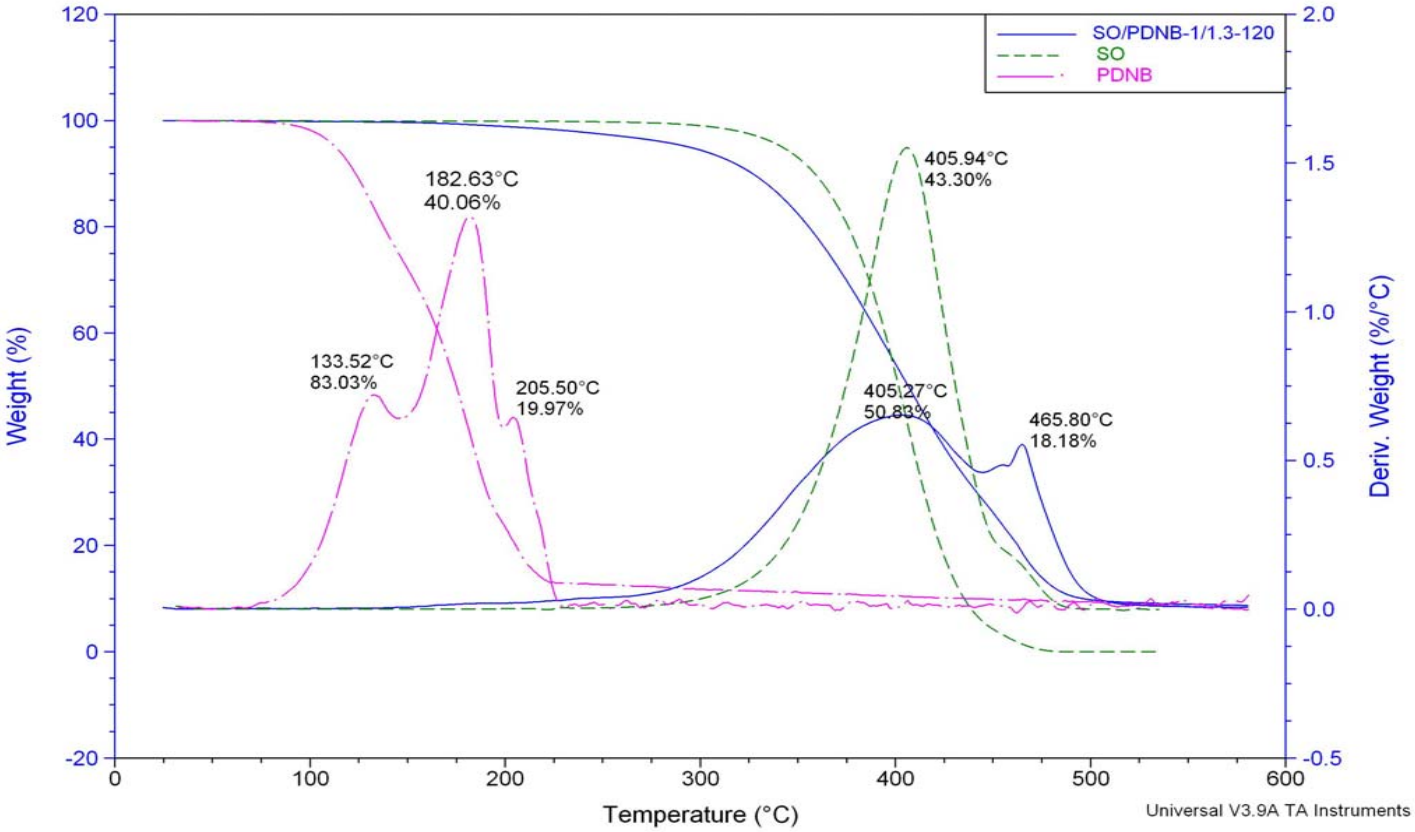


Figure 4.24. TGA and DTGA traces of SO/PDNB-1/1.3-120, SO and PDNB

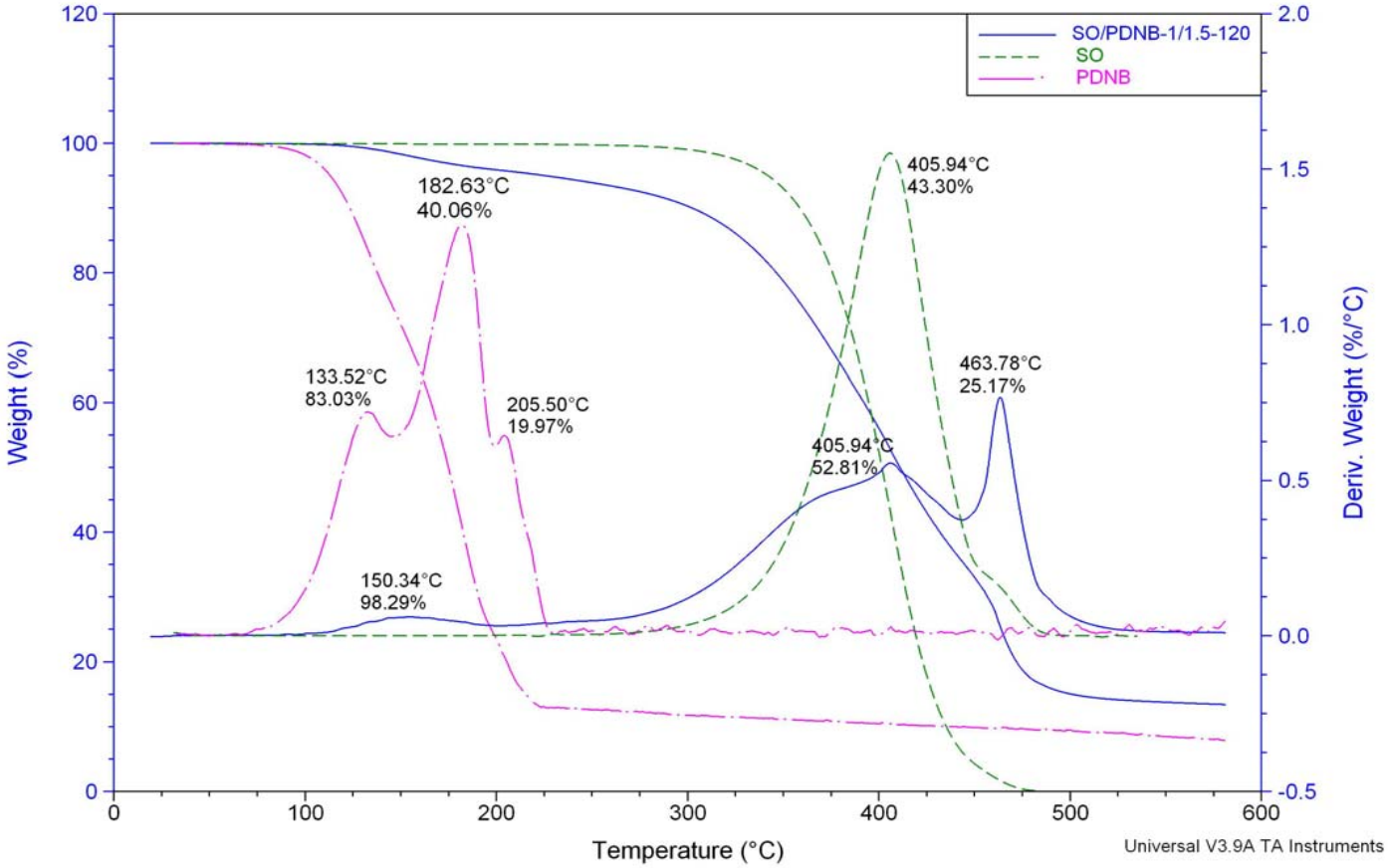


Figure 4.25. TGA and DTGA traces of SO/PDNB-1/1.5-120, SO and PDNB

The TGA and their derivative (DTGA) thermograms together with Table 4.2 which shows the percentages of weigh loss of the polymers at different temperatures, point out that soybean oil based polymers appear to be relatively thermally stable at temperatures lower than 200 ^{o}C under N_2 atmosphere. These thermosetting materials typically show three-stage thermal degradation at 200-300 ^{o}C (Stage I), 300-500 ^{o}C (Stage II) and >500 ^{o}C (Stage III), with the second stage being the fastest. The first stage degradation can be attributed to the evaporation of the water obtained during the dehydration of the residual intermediate *N*-alkenyl-*N*-arylhydroxylamine to the anil. The second step corresponds to degradation and char formation of the crosslinked polymer structure, and also the decomposition of the fatty acid incorporated in the polymer network, while the third stage corresponds to gradual oxidation of the char residue.

Table 4.2. Percentage of weigh loss at various temperatures

Chemical Compound	Percentage of weigh loss (%) at various temperatures(^{o}C)					
	100	200	300	350	400	500
SO/PDNB-1/1-120	0.13	1.14	5.4	18.64	48.18	90.24
SO/PDNB-1/1.3-120	0.13	1.14	5.6	17.62	45.92	90.23
SO/PDNB-1/1.5-120	0.13	4.1	9.7	21.3	44.1	85

However, the thermal degradation behavior of SO/PDNB-1/1.5-120 in Stage I shown in Figure 4.25 reveals to be different. Carefull examination of the TGA measurement showed that there is a higher weigh loss in the Stage I dominated by the decomposition of the unreacted oligomeric DNB, which was confirmed by the thermogram of PDNB. The enhanced char produced from the SO/PDNB-1/1.5-120 polymer is inherently associated with unreacted DNB.

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. The technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in the heat capacity using minimal amounts of sample.

By using DSC method T_g of the polymers were determined. Before analysis the unreacted soybean oil was removed from the samples. Analysis were performed from -75 ^oC to 150 ^oC, under nitrogen flow at a heating rate of 10 ^oC/min. For each sample two runs were done, and approximately the same T_g value was observed in both runs. DSC curves for the polymers are shown in Figure 4.26.

The glass transition temperatures (T_g) of the the soybean oil-PDNB polymers range from -51.45 ^oC to -46.32 ^oC. The kink observed around -10 ^oC in the all DSC curves arises probably due to water obtained during the dehydration of the residual intermediate *N*-alkenyl-*N*-arylhydroxylamine to the anil. It is obvious that all polymers have T_g's which are below ambient temperature and, therefore are in their rubbery state.

The glass transition temperatures of all polymers gradually decrease with increasing amounts of soybean oil in the initial composition. This is mainly due to higher incorporation of the more flexible triglyceride molecules into the crosslinked polymer structure with increasing amounts of oil in the initial polymer composition.

It is noted that the T_g values produced by the DMA are higher than those produced by DSC - this is because the samples are frequency dependant, in other words the higher the frequency used, the higher the T_g.

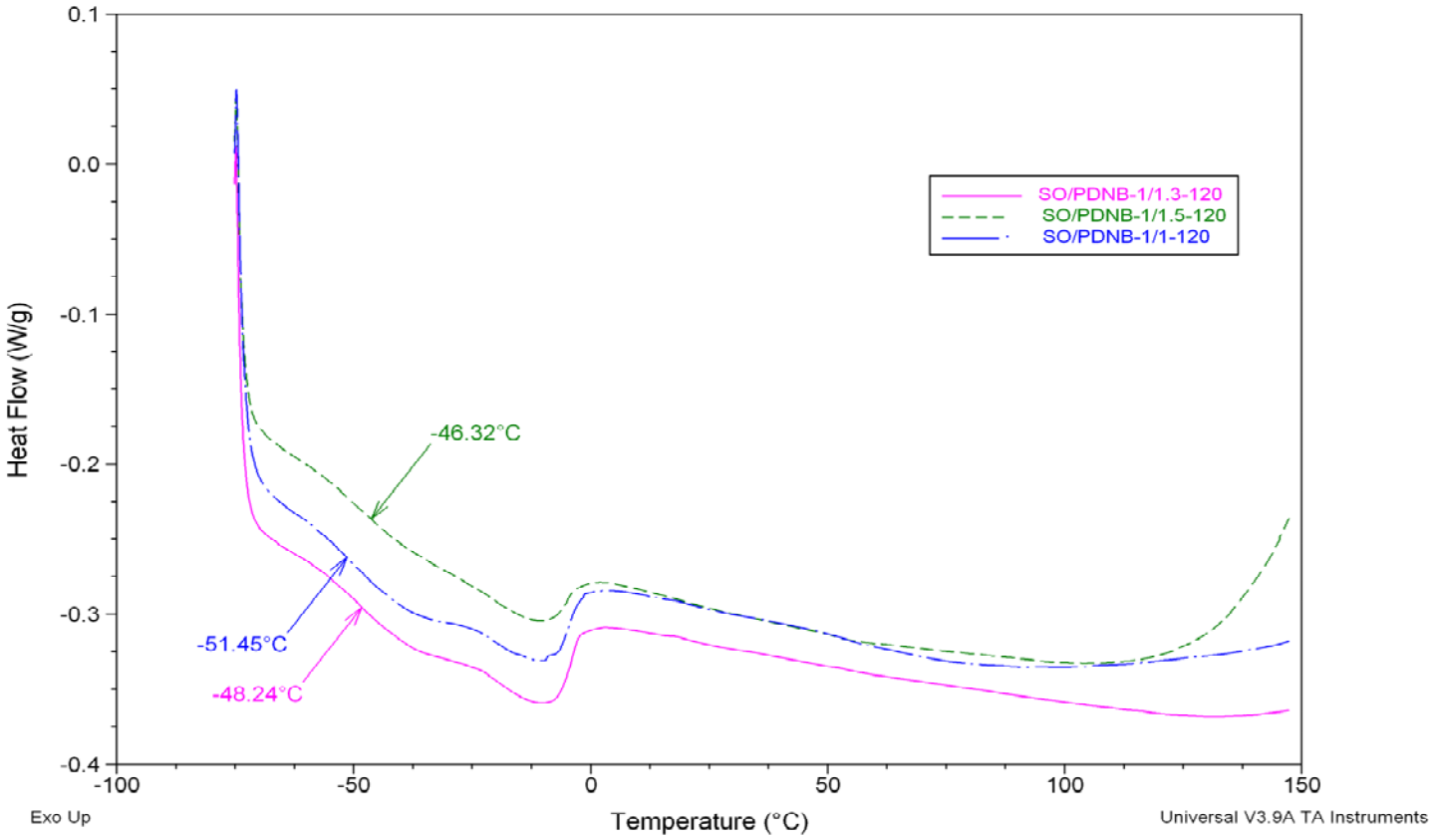


Figure 4.26. DSC traces of SO/PDNB-1/1-120, SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120 polymers

4.8. Swelling Test

One of the methods, to compare the relative crosslink density is swelling behaviour. Crosslinked polymers placed in a good solvent absorb the solvent and swell. As the network is swollen, by absorption of the solvent the chains between network junctions are required to assume elongated configurations.

If the sample is highly crosslinked one, it will absorb less solvent, and by following the change in the length during swelling it is possible to compare the relative crosslink density of different samples. Generally, the smaller the equilibrium swelling ratio, the higher is the crosslink density.

The useful parameter that may be obtained from a swelling test is the linear equilibrium swelling ratio (q), reported as $V/V_o = (L/L_o)^3$ where V_o and V are the volumes of unswollen and swollen polymer samples, respectively; and L_o and L are the unswollen and swollen lengths of the samples, respectively. This ratio depends upon the molar volume of the solvent, the crosslink density and crosslink segment length of the polymer.

If two samples are swollen in the same solvent, the swelling ratio is determined by the crosslink density and crosslink segment length.

The swelling behavior of the polymers in CH_2Cl_2 was examined by using a traveling microscope. The cured polymer samples was first subjected to extraction process using petroleum ether for around 3 hours to remove the residual soluble components after curing process. After that the samples were put in a closed container and the experiment was continued until the solvent uptake ceased.

$q=(L/L_o)^3$ versus a time graph for the polymers is plotted in Figure 4.27. As shown in the Figure 4.27., the polymer with higher concentation of the crosslinking agent swelled less, due to increased crosslink density. Moreover SO/PDNB-1/1.5-120 polymer sample ceases to swell in only 30 minutes while the other two polymer samples with lower PDNB concentration have longer swelling times.

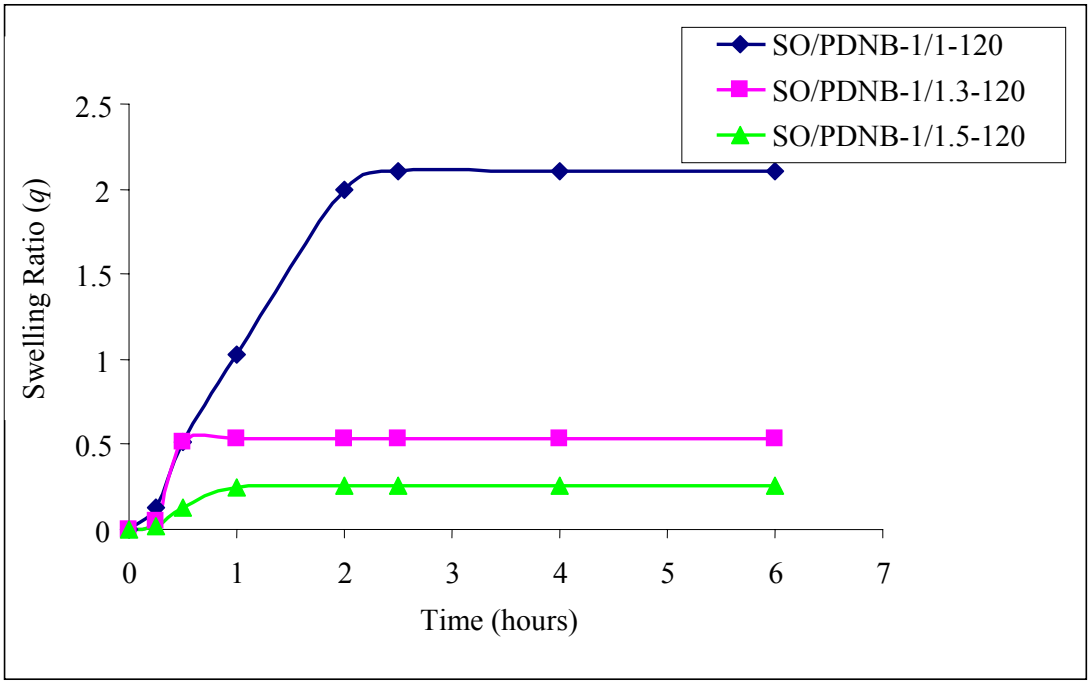


Figure 4.27. Swelling behavior of polymers based on different SO/PDNB mol ratios

Unfortunately, during the determination of swelling behaviour a problem was observed. Samples fragmented into small pieces during the test when placed in solvents. This can be explained by the breakage of regions having low crosslink density. The solvent's polarity breaks the regions of low crosslink density and the regions of high crosslink density remained untouched. This fact is called grain phenomena in literature.

4.9. Surface Hardness Tests

The surface hardness of the polymers was analyzed with a Zwick/Roell Durometer according to ASTM D 2240 standard test. The surface hardness test is a measure of the indentation resistance of elastomeric or soft plastic materials based on the depth of penetration of a conical indentor. Hardness values range from 0 - for full penetration to 100 - for no penetration. Full penetration is between 2.46 and 2.54 mm depending on the apparatus used.

The Shore type instrument is a spring loaded indentation device, in which values are obtained as a function of the viscoelastic property of the material. The truncated cone indentor, extends 2.5 mm and is pressed onto the sample against an spring. The harder the material, the more the deflection, the higher the number.

The polymer samples which were cut as to be 1 mm thick, were protected from any possible mechanical stress before testing. To obtain a reliable analysis data, the samples were tested at least from 10 different points on the same surface. Results from the test are present in the Figure 4.28.

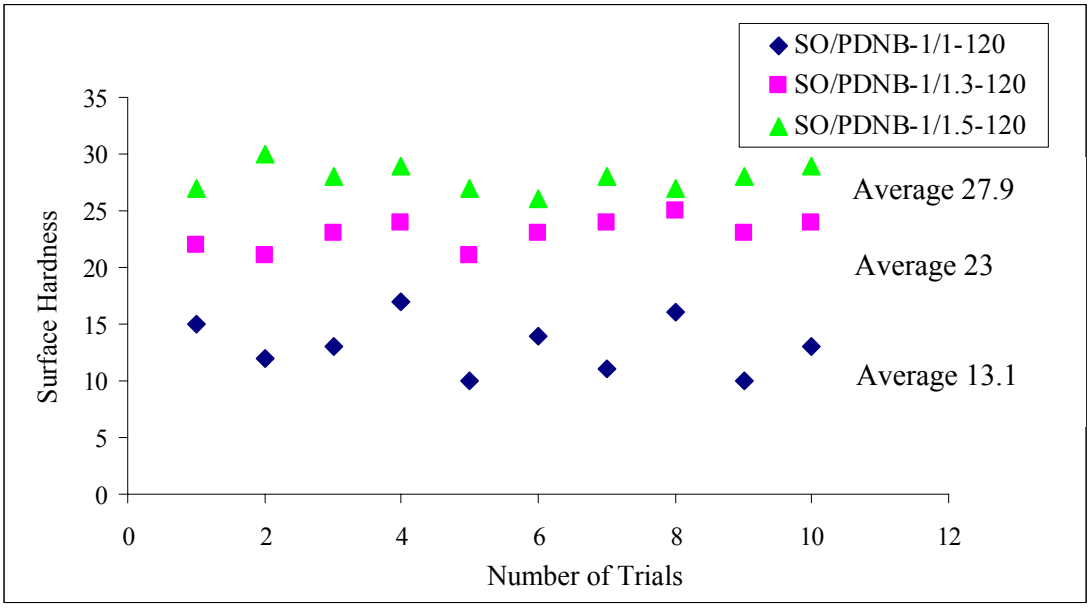


Figure 4.28. Shore test results for different SO/PDNB polymer samples

The surface hardness results reveal that as crosslinking agent ratio increases there is improvement in the surface hardness. It is obvious that SO/PDNB-1/1.5-120 named polymer has higher response to a small surface stress in comparison to the other two samples.

Decreasing the mol ratio of PDNB causes fluctuations on the surface hardness of the polymer samples, which can be attributed to the uneven crosslinking causing soft segments in the polymer network. This result is in agreement with the results of DMA analysis.

5. CONCLUSION

The purpose of this thesis was the design and synthesis of new bio-based thermoset polymers from soybean oil and *para* dinitrosobenzene to replace petroleum based polymers. The SO/PDNB polymers were tacky, highly crosslinked materials.

Polymerization of soybean oil was performed by using *para* dinitrosobenzene which was synthesized by the oxidation of *para* quinine dioxime in acidic medium. Two methods were applied for the polymerization: solventless and solvent mediated. In the first method SO/PDNB polymers were synthesized upon two stage polymerization. In the first stage PDNB was dispersed in soybean oil pre-heated to 120 ^{o}C and was cured with continuous stirring at 90 ^{o}C for specific time. Thus highly viscous pre-polymer called as A stage polymer was synthesized. In the second stage post curing at 120 ^{o}C was applied to synthesis the actual polymer sample. Using this polymerization method varying the mol ratio of SO and PDNB three polymer samples were synthesized and characterized. Qualitative determination was followed by IR spectroscopy, but quantitative determination could not be done because aromatic protons of the crosslinking agent could not be observed by NMR spectroscopy. The IR and NMR spectra of extracted soybean oil show that the extracted oil has a structure similar to that of the native soybean oil. The second method of polymerization involved a thermal emulsion polymerization. However the water involved as solvent in this method caused a hydration of the monomeric nitroso groups which have to act as crosslinking agent. Thus it was noticed that the water inhibited the polymerization and the first method was used to synthesize polymer samples suitable for mechanical characterization.

Many attempts were made to elucidate the chemical composition of polymer samples either by sealed tube polymerization or model compound polymerization, however no satisfactory data were derived, due to highly crosslinked network structure of the samples synthesized.

The effect of increased crosslink density upon the various mol fractions of SO and PDNB on the mechanical properties of the polymer samples was investigated by DMA, DSC, TGA, swelling and surface hardness tests. It was observed that as the crosslinking agent ratio increases an increase in the storage modulus and T_g was observed. However the highly crosslinked materials with the highest ratio of PDNB had a crumbly, factise-like character upon longer post curing times.

In TGA all polymers appeared to be relatively thermally stable at temperatures lower than 200 ^oC under N_2 atmosphere, showing three-stage thermal degradation with the fastest one being in 300-500 ^oC range. Samples were totally decomposed at 500 ^oC yielding approximately 10 per cent char.

The present process and formulation limit the quality of the polymers. Areas of improvements include introducing additives such as carbon black to improve mechanical properties. As an another future project, polymers can be prepared with different plant and vegetable oils such as linseed oil, fish oil etc., and examine their biodegradation.

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