

SURFACE MODIFICATION OF POLYVINYL ALCOHOL FILMS BY
FUNCTIONALIZED SOYBEAN OIL TRIGLYCERIDES

by

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SURFACE MODIFICATION OF POLYVINYL ALCOHOL FILMS BY
FUNCTIONALIZED SOYBEAN OIL TRIGLYCERIDES

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*To My Mother
and
My Dearest*

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ABSTRACT

SURFACE MODIFICATION OF POLYVINYL ALCOHOL FILMS BY FUNCTIONALIZED SOYBEAN OIL TRIGLYCERIDES

In this study, maleinized (SOMAP) and isocyanated (SONCO) soybean oil triglycerides have been successfully grafted onto the surface of polyvinyl alcohol (PVA) films. The surface grafting occurred through the reaction of succinic anhydride or isocyanate functionalities of soybean oil and available hydroxyl groups of PVA films in toluene using DMAP as a catalyst. After grafting, the films were rinsed with toluene to remove ungrafted triglycerides from the surface. The reaction on the surface was confirmed by ATR-IR and ^1H NMR spectroscopic techniques. A series of films were prepared by different concentrations of SOMAP or SONCO in toluene. The increase in hydrophobicity with an increase in SOMAP or SONCO concentrations was observed by contact angle measurements and the contact angles reach their maximum value of 88° and 94° for 26 and 2.5 per cent SOMAP and SONCO concentrations in toluene, respectively. Surface morphology and roughness of PVA-g-SOMAP film was investigated by AFM while optical microscopy was used for characterization of PVA-g-SONCO films. The homogeneity of the grafted surfaces was examined by optical microscopy after the colour reaction which gives a blue colour complex with pure PVA films. PVA-g-SONCO films were not dyed meaning that nearly all the surface was completely grafted successfully while there were unreacted regions on the PVA-g-SOMAP films. Quantitative determination of the extent of grafting per surface area (cm^2) was done by titration of the free acid groups produced in esterification reaction. Grafting density was found to be 1.56×10^{-4} mole triglyceride per cm^2 of the PVA film. The grafted films were further characterized by DSC. SOMAP or SONCO grafted PVA films have lower Tg values than pure PVA film which proves the surface grafting. However, the difference between Tg values of the grafted films and pure PVA film is very low due to the fact that grafting occurs only on the top of surface while the rest of the sample remains pure PVA.

ÖZET

POLİVİNİL ALKOL FİMLERİNİN FONKSİYONEL SOYA YAĞI TRİGLİSERİTLERİ İLE YÜZEY MODİFİKASYONU

Bu çalışmada maleinize edilmiş (SOMAP) ve izosiyanatlanmış (SONCO) soya yağı trigliseritleri polivinil alkol (PVA) filmlerinin yüzeyine graft edildi. Soya yağı üzerindeki süksinik anhidrit ve izosiyanat fonksiyonel grupları ile polivinil alkol filmlerinin hidroksil grupları arasındaki graft reaksiyonu DMAP katalizörü kullanılarak toluen içinde gerçekleştirildi. Filmler graft edildikten sonra yüzeyde reaksiyona girmeden kalan trigliseritleri uzaklaştırmak için toluen ile yıkandı. Yüzeydeki bu reaksiyon ATR-IR ve ¹H NMR spektroskopik teknikleri kullanılarak kanıtlandı. Değişik konsantrasyonlarda SOMAP ve SONCO kullanılarak bir dizi film hazırlandı. Temas açısı ölçümleri ile SOMAP ve SONCO konsantrasyonları arttıkça filmlerin hidrofobik özelliğinin arttığı görüldü ve yüzde 26 SOMAP veya yüzde 2.5 SONCO çözeltileri ile graft edilmiş filmlerin maksimum temas açıları 88 ve 94 derece bulundu. SOMAP ile graft edilmiş yüzeyin morfolojisi ve pürüzlülük değerleri AFM ile incelenirken, SONCO ile graft edilmiş PVA filminin yüzey karakterizasyonunda optik mikroskop kullanıldı. Graft edilmiş yüzeylerdeki homojenlik saf PVA yüzeyi ile mavi renkli bir kompleks oluşturan renk reaksiyonu uygulandıktan sonra optik mikroskop ile incelendi. SOMAP graft edilmiş filmlerin bazı bölgeleri reaksiyona girmeden kalırken SONCO graft edilmiş PVA filmlerinin maviye boyanmadığı yani tüm yüzeyin başarıyla graft edildiği görüldü. Birim yüzey alana graft edilmiş trigliserit oranını kantitatif olarak bulmak için esterleşme reaksiyonu sonucu oluşan serbest asit grupları titre edildi. PVA filminin cm² başına graft edilme oranı 1.56 x10⁻⁴ mol trigliserit olarak bulundu. Ayrıca graft edilmiş filmler DSC ile karakterize edildi. SOMAP veya SONCO ile graft edilmiş PVA filmlerinin Tg değerlerinin daha düşük olduğu görüldü. Graft edilmiş ve edilmemiş PVA filmlerin Tg değerleri arasında gözlenen farkın çok az olmasının nedeni yüzeyi graft edilmiş örneğin çok büyük bir kısmının saf PVA olarak kalması ile açıklanabilir.

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LIST OF ABBREVIATIONS

ABSO	Allylic Brominated Soybean Oil
AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
ATR-IR	Attenuated Total Reflectance Infrared
DMAP	Dimethylamino Pyridine
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
IR	Infrared
ISONCO	Isocyanated Soybean Oil
MA	Maleic Anhydride
M_n	Number Average Molecular Weight
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity Index
PVA	Polyvinyl Alcohol
RMS	Root Mean Square
SO	Soybean Oil
SOMAP	Maleinized Soybean Oil
SONCO	Isocyanated Soybean Oil
T _g	Glass Transition Temperature
Trigonox C	tert-butylperoxybenzoate

1. INTRODUCTION

1.1. Renewable Raw Materials for the Chemical Industry

Traditionally, the supply of raw materials for the chemical industry has been satisfied by petroleum feedstock. In recent years due the shortage of the available petroleum reserves and a growing awareness of the environment, people have focused on the use of renewable feedstock to produce a wide range of chemicals and industrial products.

Plant oils and fats are one of the most common renewable resources being used as starting materials to synthesize environmentally friendly polymers which have many advantages compared with polymers derived from petroleum based monomers. They are renewable, biodegradable, widely available and economical raw materials having various applications in paints, coatings, cosmetics, additives, leather, and textile [1].

Among the natural oils soybean oil attracts a great of interest due to its high availability, low cost and environmentally benign property. Moreover, its high degree of unsaturation (iodine number of 140) allows different chemical transformations to obtain usefully functionalized molecules.

1.2. Natural Oils

1.2.1. Structure and Properties of Fatty Acids and Triglycerides

Natural oils are primarily water insoluble, hydrophobic substances which can be derived from both plant and animal sources. These oils are composed of triglyceride molecules, the products of the esterification reaction of glycerol and the fatty acids, as shown in Figure 1.1.

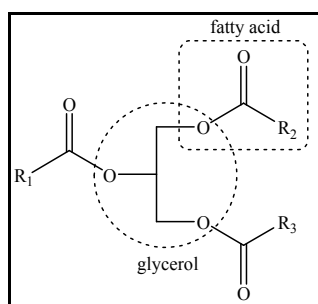


Figure 1.1. A general structure of a triglyceride molecule

Chain lengths of the fatty acids in triglycerides may vary from 2 to 80 carbons, but 12 to 22 are the most common in vegetable oils. The fatty acids usually have 0 to 3 unsaturated sites and commonly appear at the 9, 12, and 15 C position relative to the carboxyl group and in a cis configuration. Although double bonds and carboxyl groups are the main functional groups in fatty acids, some fatty acids have fluoro (fish oil), hydroxy (castor oil), keto and epoxy groups (vernonia oil) [2].

Typical oils contain approximately 10 different fatty acids and each oil has a unique distribution of them which determine the distribution of double bonds. This is very important for further modification of vegetable oils. Table 1.1 shows the fatty acid distribution of some common oils. Nowadays, it is possible to control the fatty acid distribution to some degree and add the necessary functionalities to triglyceride molecules with the newly developed genetic engineering techniques.

Table 1.1. Fatty acid distribution of some common oils

Vegetable Oil	Fatty Acid (%)						
	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acid	Ricinoleic Acid	Other
Castor Oil	1.5	0.5	5	4	0.5	87.5	-
Soybean Oil	10	4	25	55	6	-	-
Linseed Oil	5	4	22	17	52	-	-
Sunflower Oil	6	4	42	47	1	-	-
Palm Oil	39	5	45	9	-	-	2
Rappeseed Oil	4	2	56	26	10	-	2

1.2.1.1. Structure and Properties of Soybean Oil. Soybean oil is a mixture of glycerol esters of unsaturated and saturated long chain fatty acids and has an average of 4.2 double bonds per triglyceride molecule. Figure 1.2 shows the approximate distribution of fatty acids in soybean oil and Table 1.2 shows the general properties of soybean oil.

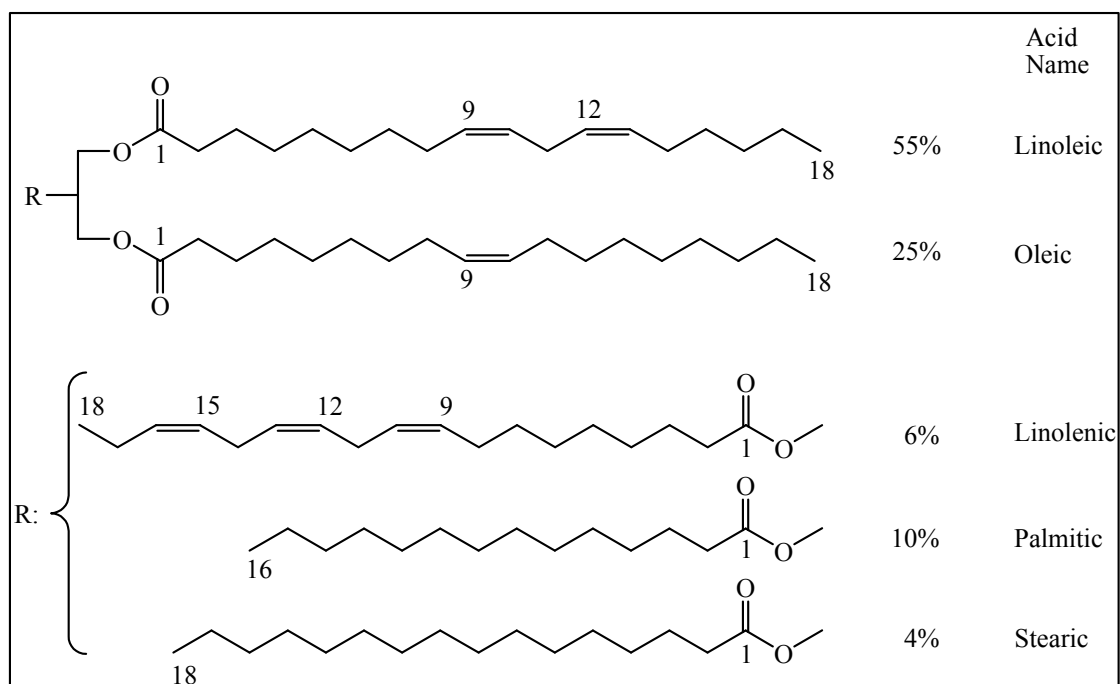


Figure 1.2. Fatty acid distribution of soybean oil

Table 1.2. The general properties of soybean oil [3]

Characteristics of Soybean Oil	
Iodine number	117-140
Saponification number	189-195
Viscosity (cP) at 40°C	28
Smoke point	213°C
Flash point	317°C
Fire point	342°C
Density (15°C)	0.910-0.934
Molecular Weight (g/mole)	850-870

Owing to the overall production quantities and chemical composition especially high level of unsaturation, soybean oil is one of the most preferred feedstock for making industrial oil products. Soybean oil must be functionalized before using it can be used as a monomer in polymer formulations because it is relatively unreactive in its natural form.

1.2.2. Chemistry of Triglycerides

1.2.2.1. Reactive Sites of Triglycerides. A triglyceride molecule has four active sites suitable for chemical reactions. These are the ester group (a), double bonds (b), allylic carbons (c), and the α position of the ester groups (d) as shown in Figure 1.3. These active sites can be used to introduce polymerizable groups on triglycerides using the known synthetic techniques of organic chemistry.

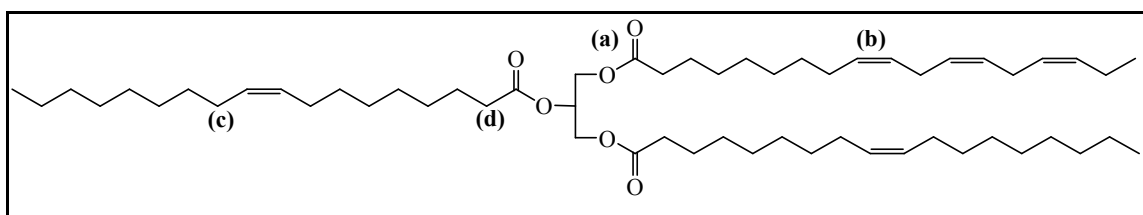


Figure 1.3. Reactive sites in a triglyceride molecule

1.2.2.2. Monomers from Triglycerides. Chemical modification of triglycerides is an important way to obtain renewable industrial products. The reactions of triglycerides can be mainly classified in three groups: reactions on the hydrocarbon chain, reactions on the double bond and the reactions on the carbonyl function. Chemical reactions involving carboxylic/ester groups have been used successfully in an industrial scale in the paint and varnish industry.

While synthesizing monomers from triglycerides, three different methods can be applied. The synthesized monomers are overviewed in Figure 1.4.

The first method is to functionalize the double bonds of triglyceride with polymerizable chemical groups. This way enables to attach maleates (1) or convert the

unsaturation to epoxy (2) and hydroxyl functionalities (3) [4]. It is also possible to attach vinyl functionalities to these epoxy and hydroxyl groups (4). For instance, reaction of acrylic acid with epoxy functional triglyceride results in acrylated triglycerides, while reaction of maleic anhydride results in triglycerides having maleate half esters on their backbone [5, 6]. Furthermore, it is possible to attach acrylate and isocyanate moieties after the bromination of triglycerides at the allylic position in the presence of N-bromosuccinimide [7, 8].

The second method is to convert the triglyceride molecules into monoglycerides through a glycerolysis reaction (8) or an amidation reaction(9) [9].

The third method for synthesizing monomers from triglycerides is to functionalize the unsaturation sites as well as converting the triglyceride into monoglycerides (10, 11). After glycerolysis of an unsaturated triglyceride, hydroxylation or glycerolysis of a hydroxy functionality is done. Maleic anhydride can then be reacted with the final monomer.

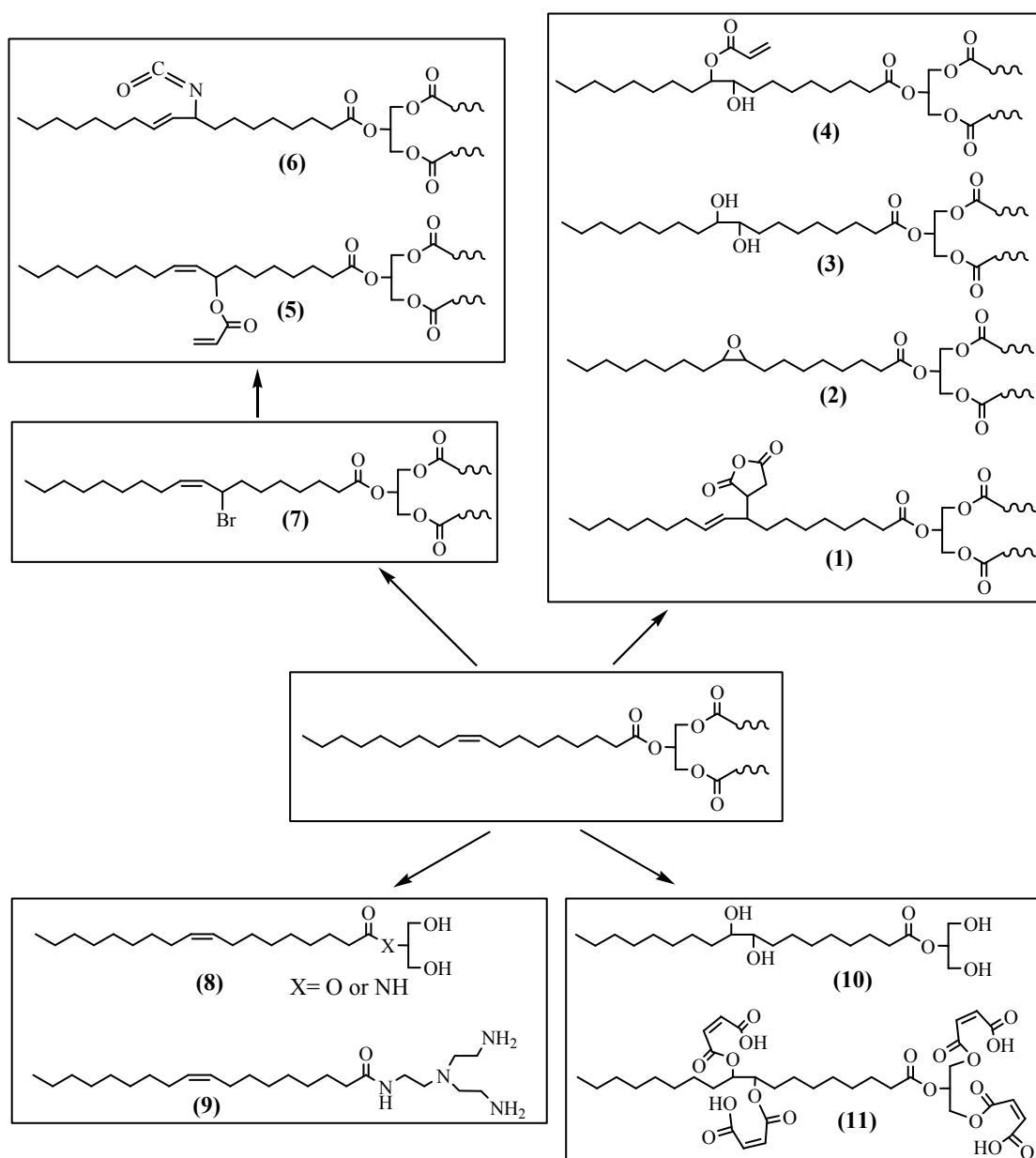


Figure 1.4. Some chemical methods that have been used to synthesize monomers from triglyceride molecules

1.3. Maleinization of Soybean Oil

Maleic anhydride reacts with soybean oil to produce maleinized soybean oil. Maleinization may occur thermally, Lewis acid catalyzed [10] or with a free radical initiator [11].

It is known that fatty acids with conjugated unsaturation react with maleic anhydride by Diels-Alder mechanism. On the other hand, fatty acids containing only one double bond also react with maleic anhydride because they have an allylic position; so, they can undergo the Ene reaction. Both the Diels-Alder and Ene mechanisms are shown in Figure 1.5 and Figure 1.6, respectively.

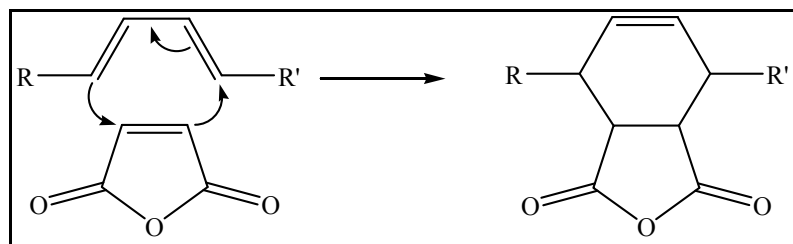


Figure 1.5. Diels-Alder mechanism

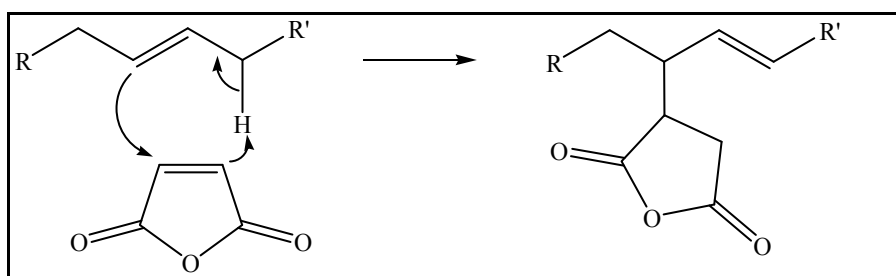


Figure 1.6. Ene mechanism

Soybean oil contains mostly non-conjugated double bonds. Due to the prevalence of non-conjugated double bonds, high temperature or a catalyst is needed to facilitate the reaction. Both reactions attach cyclic anhydrides to the triglyceride which are capable of reacting with polyols to give polyesters.

1.3.1. Thermal Maleinization

The maleinization reaction which occurs at very high temperatures (above 200 °C) follows an Ene type reaction mechanism resulting in the addition of succinic anhydride group to the allylic position of the fatty acids. The mechanism involves an allylic shift of one double bond by transferring the allylic hydrogen to the enophile as shown in Figure 1.7.

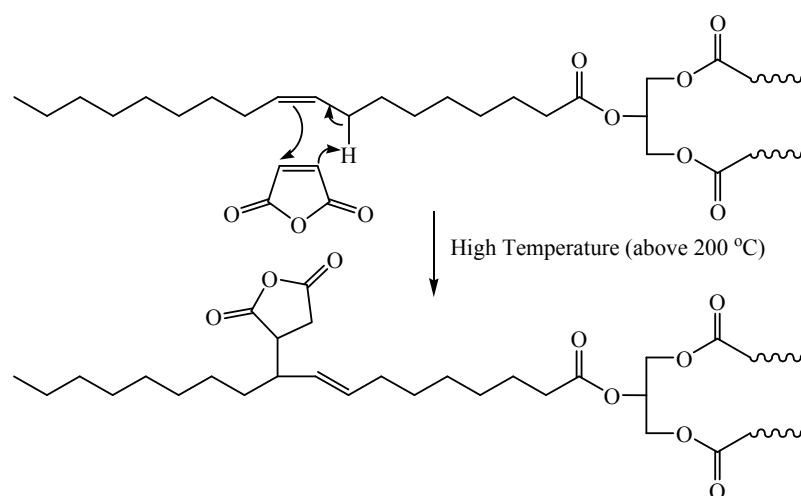


Figure 1.7. Thermally maleinized soybean oil (SOMA)

1.3.2. Lewis Acid Catalyzed Maleinization

The maleinization reaction in the presence of Lewis acids was reported by Eren et al [10]. It was said that Lewis acids help to facilitate the reaction at low temperatures. However, the product is completely different that of the thermally maleinized soybean oil. In addition to the Ene reaction acylation reaction may occur in the presence of Lewis acids. Figure 1.8 shows the acrylated product.

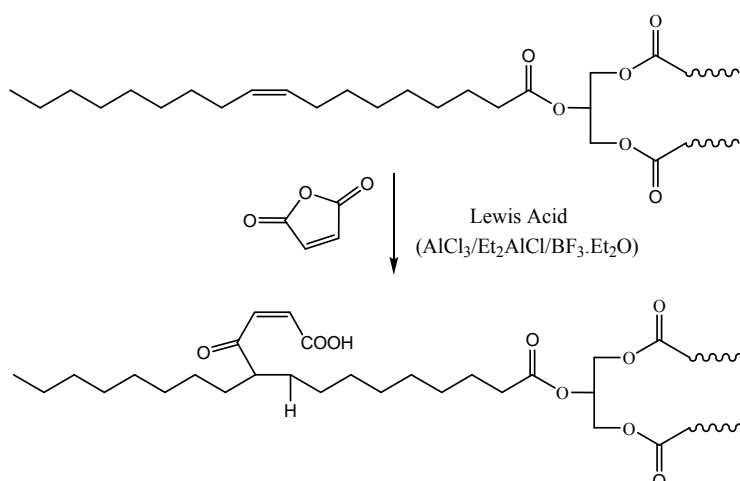


Figure 1.8. Lewis acid catalyzed maleinization of soybean oil (Acylated product)

Second mechanism involves radical addition of maleic anhydride to soybean oil. Free radical abstracts one of allylic hydrogens then the addition of maleic anhydride through this position occurs, as shown in Figure 1.10. Furthermore, another possible mechanism is the copolymerization of maleic anhydride with triglyceride which is also responsible for the increase in viscosity of the reaction product, Figure 1.11.

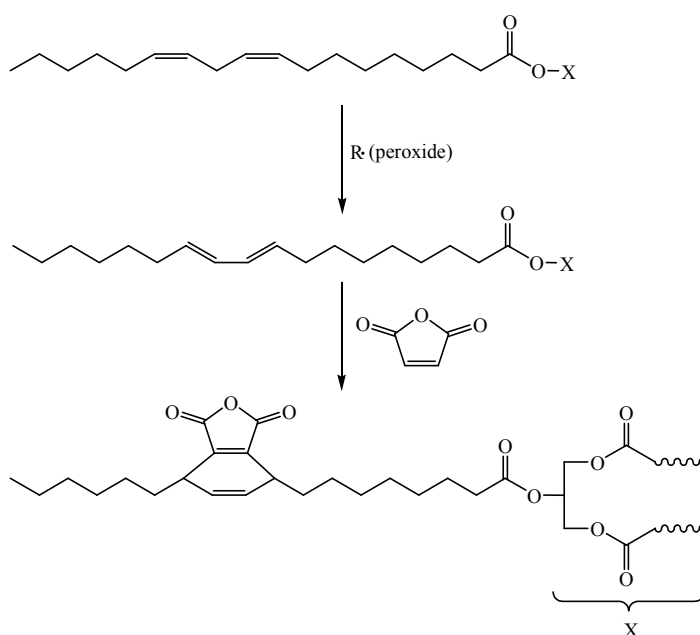


Figure 1.9. Diels-Alder mechanism of free radical maleinized soybean oil

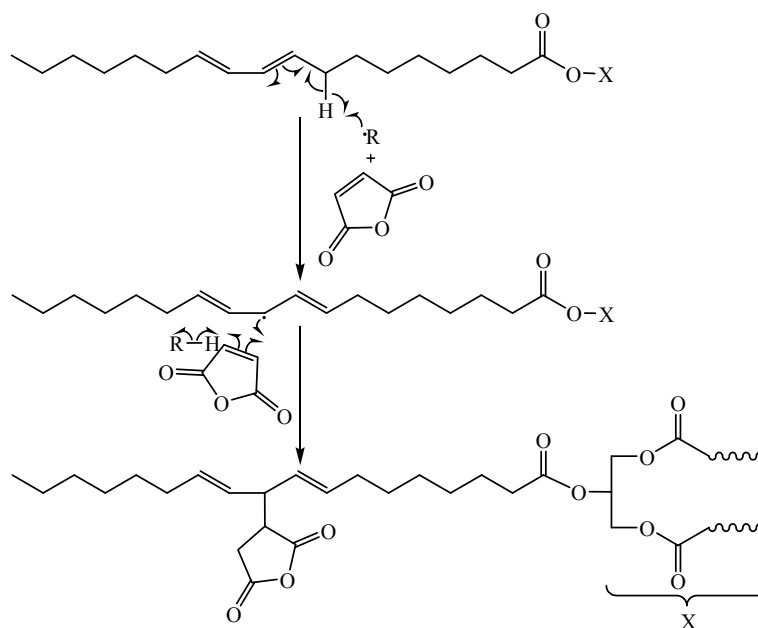


Figure 1.10. Radical addition of maleic anhydride to soybean oil

The degree of maleic anhydride addition was further investigated by Tran et al [11]. According to the acid number of hydrolyzed product only one mole of maleic anhydride can react with soybean oil triglycerides although further maleinization is theoretically possible. It was reported that the steric hindrance prevents further reaction of maleic anhydride.

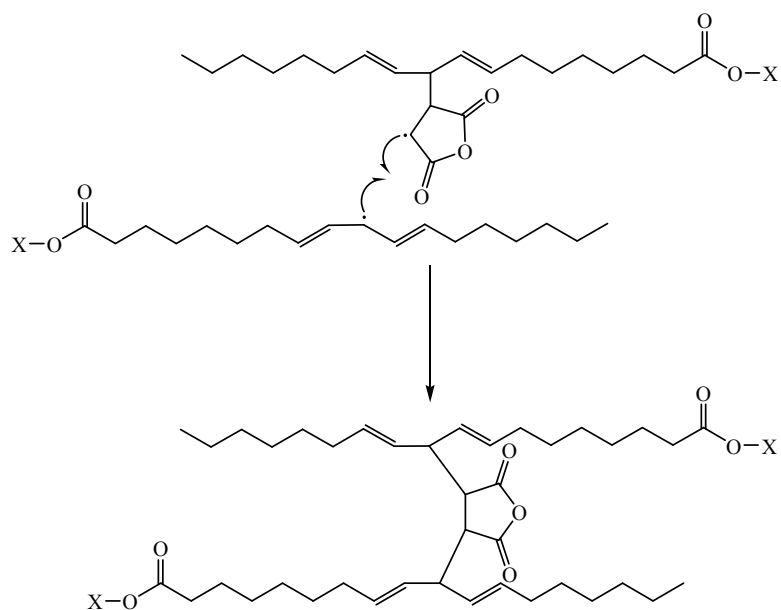


Figure 1.11. Copolymerization mechanism of free radical maleinization

1.4. Reactions of Maleinized Soybean Oil Triglycerides with Alcohols

The alcoholysis reaction of a cyclic anhydride with alcohols is known. The reaction goes to completion in a short time at room temperature in the case of primary alcohols. However, in the case of secondary alcohols higher temperatures, long reaction times, and usually a base catalyst are required. The reaction results in the formation of an ester without any by product. The esterification mechanism of a cyclic anhydride involving dimethylamino pyridine (DMAP) as a base catalyst is shown in Figure 1.12.

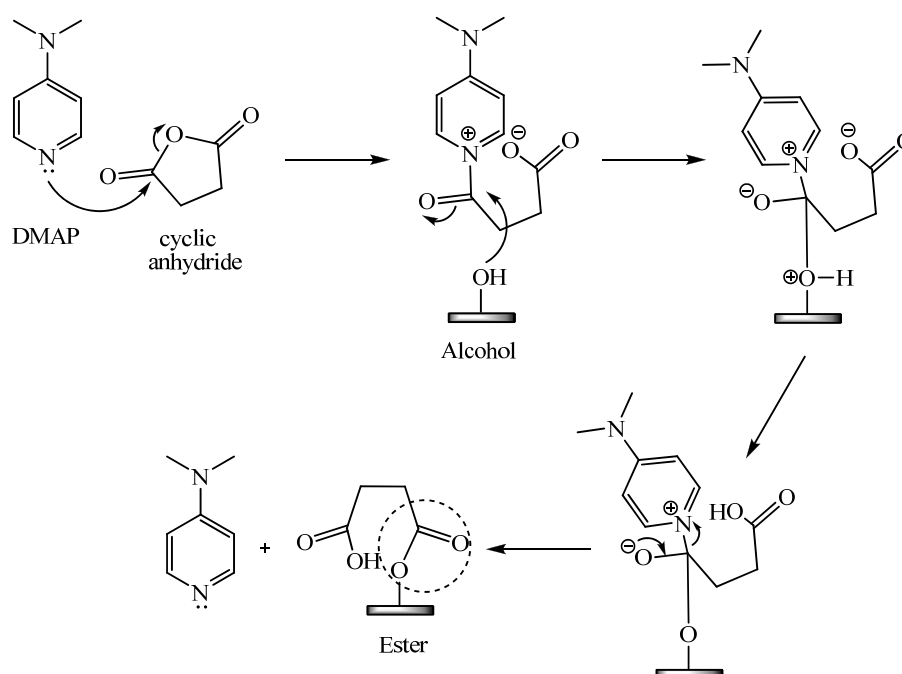


Figure 1.12. The esterification mechanism of a cyclic anhydride in the presence of a base catalyst

Eren et al. [10] also reported the polymerization of maleinized soybean oil triglycerides with diols (1) to the half ester stage. The alcohols used were low molecular weight polyols (ethylene glycol, glycerol, pentaerithritol, etc.) and long chain diols (PEG 160, PEG 600, etc.). Due to the fact that the succinic anhydride on a triglyceride molecule is less reactive than maleic anhydride, different transesterification catalysts (SnCl_4 , p-toluene sulfonic acid, and 2-methylimidazole) were examined and the basic catalysts were found the best for the reaction.

Thames et al. examined the reaction of maleinized soybean oil with functional vinyl monomer including hydroxyethyl acrylate (HEA), hydroxyethyl methacrylate (HEMA) (2) and with a vinyl ether monomer such as hydroxy butyl vinyl ether (3) [13]. The functionalized derivatives have been formulated to be used as latexes, textile finishes and other coating compositions.

Figure 1.13 shows the products of maleinized soybean oil triglycerides with various hydroxyl group containing monomers.

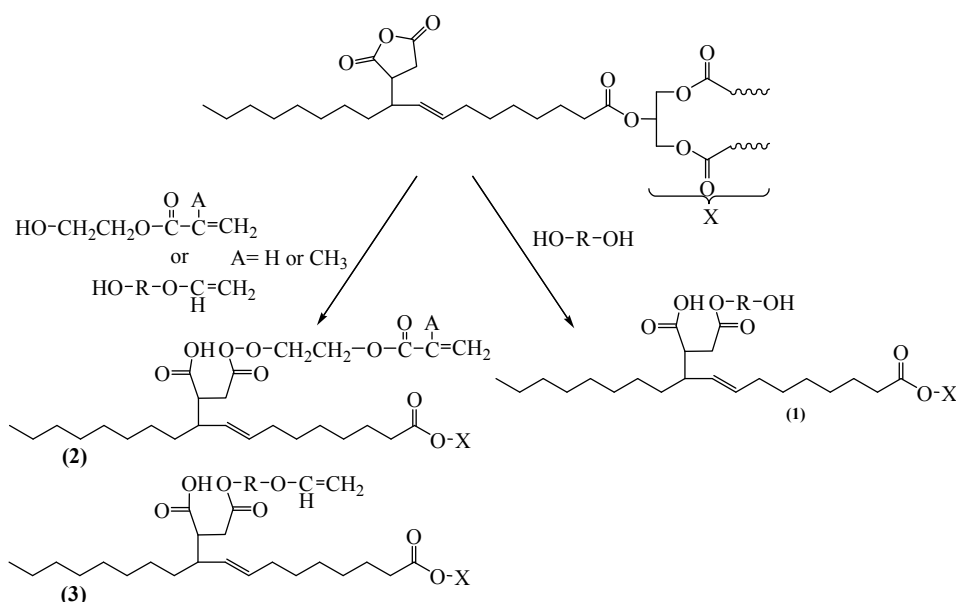


Figure 1.13. Reactions of maleinized soybean oil triglycerides with various alcohols

1.5. Isocyanated Soybean Oil

Two step synthesis of soybean oil based isocyanates has been reported by Çaylı and Küsefoğlu [8]. In the first step, soybean oil triglycerides were brominated with N-bromosuccinimide at the allylic position, then the brominated oil (ABSÖ) was reacted with AgNCO. In this manner the bromine species were replaced by NCO groups without affecting the double bonds of soybean oil triglycerides as shown in Figure 1.14.

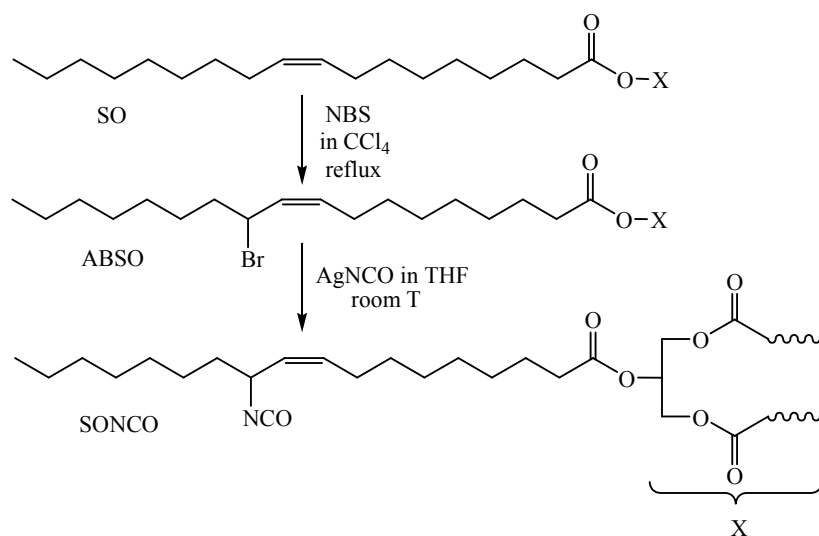


Figure 1.14. Synthesis of isocyanated soybean oil

Moreover, the polymerization of isocyanated soybean oil with glycerol and castor oil in the presence of a base catalyst gives a polyurethane whose isocyanate and polyol monomers are both plant oil based. A general mechanism involving the formation of a polyurethane with DMAP as a base catalyst is depicted in Figure 1.15.

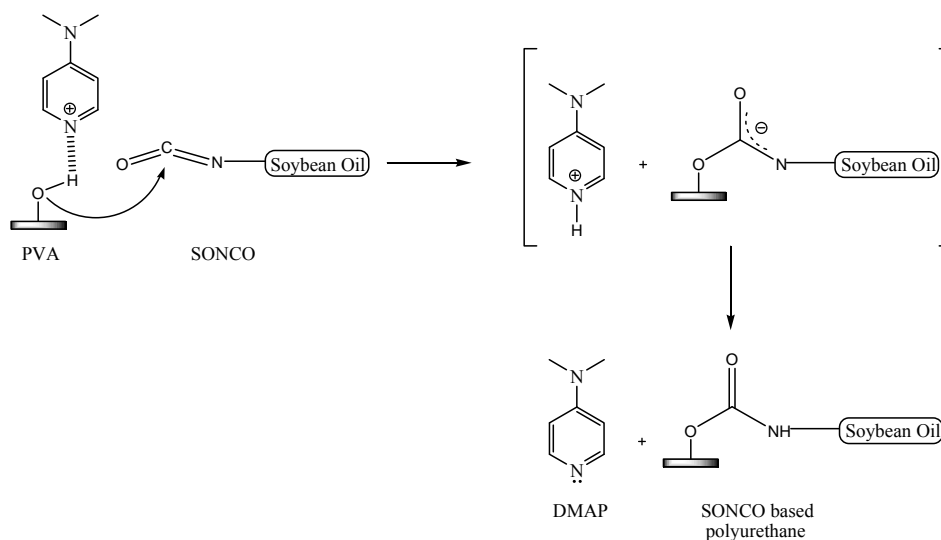


Figure 1.15. The mechanism involving the formation of a polyurethane in the presence of a base catalyst

1.6. Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is highly hydrophilic, nontoxic and biocompatible polymer with excellent film forming property. It is prepared by the polymerization of vinyl acetate, followed by hydrolysis of the ester in the presence of an alkaline catalyst as shown in Figure 1.16.

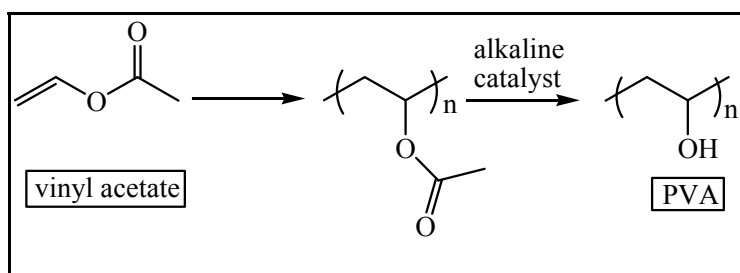


Figure 1.16. Synthesis of polyvinyl alcohol

Depending on the extent of hydrolysis polyvinyl alcohols with varying properties can be produced. The physical properties of PVA such as strength, water solubility, gas permeability, and thermal characteristics vary with the degree of crystallinity which is dependent on the extent of hydrolysis and the degree of polymerization (molecular weight) of the polymer. Partially hydrolyzed grades contain acetate groups, which reduce the overall degree of crystallinity. This also results in lower strength and increased water solubility. Figure 1.17 shows the change of some physical properties of PVA with molecular weight and extent of hydrolysis.

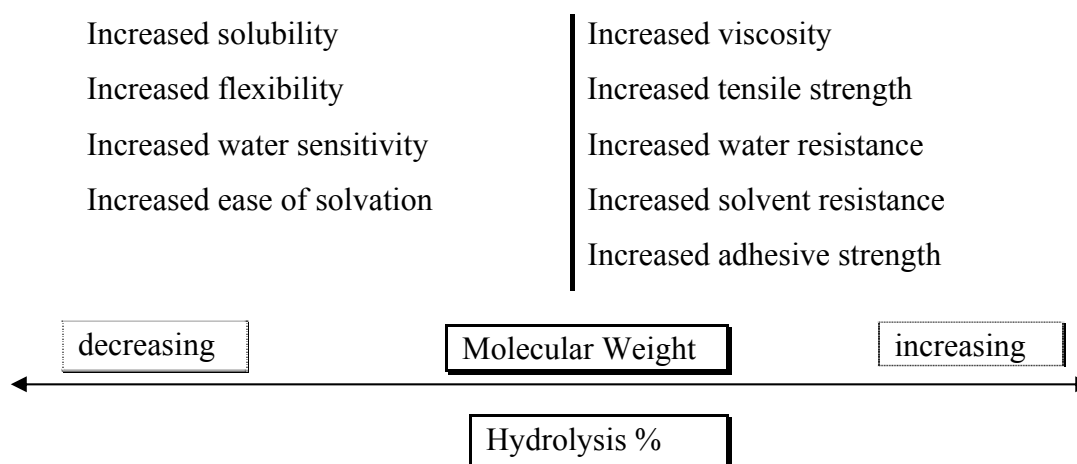


Figure 1.17. The variation of some physical properties of PVA with molecular weight and hydrolysis rate

1.6.1. Chemistry of Polyvinyl Alcohol

The chemical reactivity of PVA comes from the secondary alcohol groups attached to every other carbon on the polymer chain. Although PVA is a secondary alcohol, it is very reactive and gives typical reactions of most alcohols. Alcohol groups are good nucleophiles, readily available to react with electron deficient centers. In a large number of publications formation of organic ethers, urethanes, acetals, sulfur compounds, inorganic esters and chelates has been reported [14]. Grafting reactions of PVA provide a potential route to alter the chemical or physical properties for specific uses.

The reaction of PVA with natural oil C_{18} monocarboxylic acids was reported by Rheineck et.al [15]. It was a simple polyesterification reaction resulting in the polyvinyl esters of linseed, soya, tall oil, and tallow fatty acids to be used as durable clear coatings, as shown in Figure 1.18. Phenol was found as mutual and nonreactive solvent with both components which overcomes hydrogen bonding in the PVA and allows the fatty acids to react with sheltered hydroxyl groups.

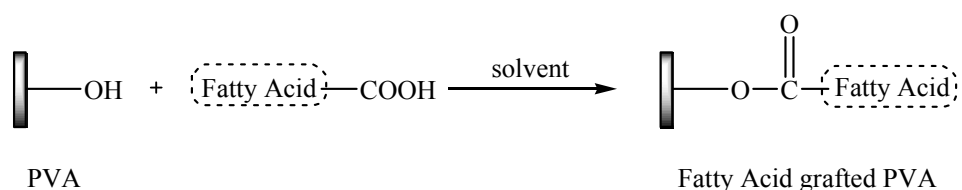


Figure 1.18. Fatty acid esters of polyvinyl alcohol

PVA was grafted with succinic anhydride in solid state in order to be used as an alternative for pH sensitive hydrogels [16]. The reaction shown in Figure 1.19 was completed without crosslinking with grafting degree up to about 6.5 per cent under low reaction temperature, short reaction time and low amount of catalyst.

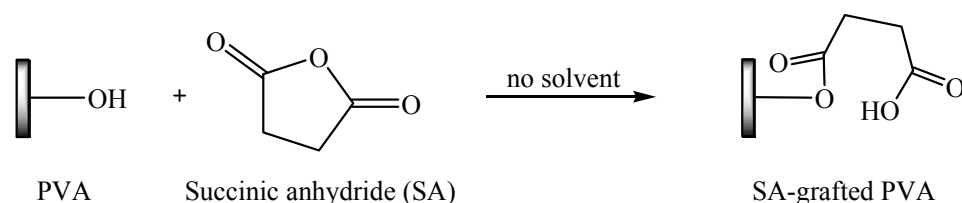


Figure 1.19. Succinic anhydride esters of polyvinyl alcohol

Furthermore, the modification PVA films by grafting of organic reactive monomers and polymers onto their surface impart useful properties without affecting the bulk properties. The synthesized materials may lead to very interesting applications.

Caro et al. [17] obtained primary amine groups on the surface of PVA film with the reaction of hexamethylene diisocyanate in toluene, shown in Figure 1.20. The surface modification of PVA film enables to bind biomolecules such as heparin (anticoagulant) or fibrinolytic enzymes to achieve biocompatible materials.

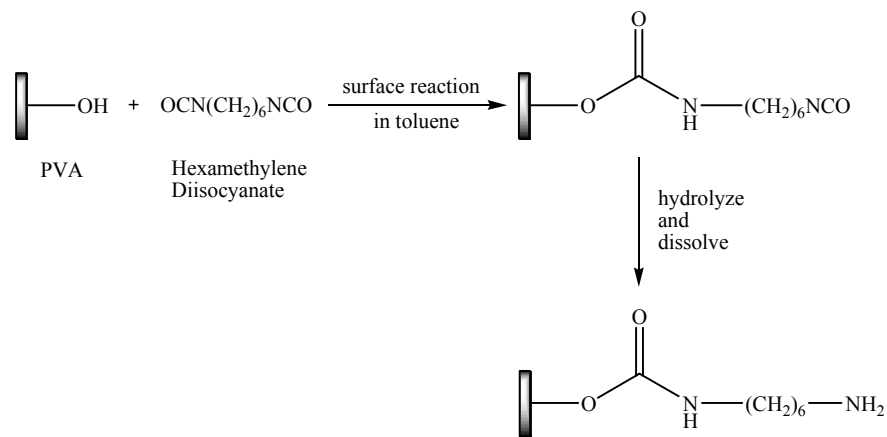


Figure 1.20. The reaction of PVA film with hexamethylene diisocyanate

PVA films are also known with their oxygen barrier performance than other polymers at low humidity levels. However, oxygen barrier property of PVA deteriorates above 60 per cent relative humidity [18]. Therefore, to reduce moisture sensitivity in humid atmosphere hydrophilic PVA films have been grafted with hydrophobic substances. Pemberton et al. has reported the grafting of PVA films with poly(organophosphazene) (POPZ) by benzoyl peroxide initiator [19] or triethoxy silane as a coupling agent [20]. The presence of allylic functions in POPZ enables radical and silane coupling reactions and due to its hydrophobic character, POPZ imparts hydrophobicity on the PVA surface to improve oxygen barrier properties at high humidity. Figure 1.21 depicts the structure of POPZ.

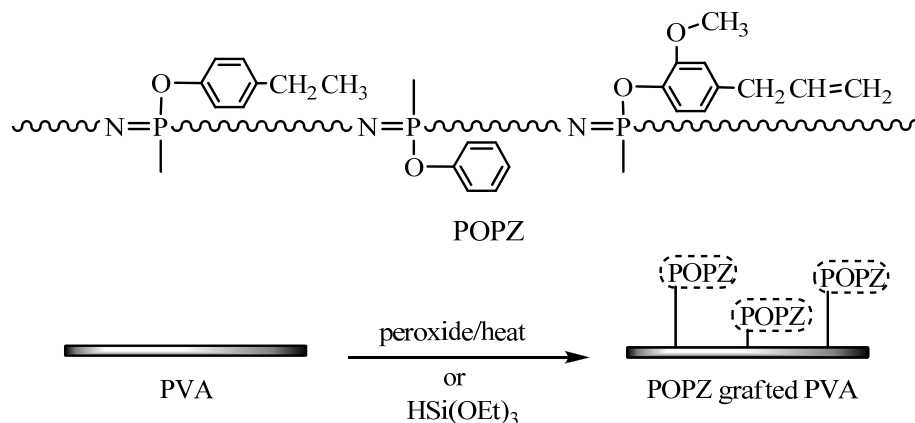


Figure 1.21. POPZ grafted PVA film

2. RESEARCH OBJECTIVES

The aim of the project is to modify hydrophilic PVA films with functionalized soybean oil triglycerides imparting hydrophobicity on their surface.

The soybean oil triglycerides used in this study are maleic anhydride functionalized triglyceride (0.8 succinic anhydride functionality per triglyceride, SOMAP) and isocyanate functionalized triglyceride (2.1 isocyanate per triglyceride, SONCO) both of which were previously synthesized in our group.

The surface grafting of PVA films with SOMAP and SONCO occurs through the reaction of succinic anhydride or isocyanate groups of soybean oil triglycerides with available hydroxyl groups on the film surface in the presence of a base catalyst. The synthesis and structures of SOMAP and SONCO grafted PVA films are shown in Figure 2.1 and Figure 2.2, respectively.

The incorporation of SOMAP and SONCO onto PVA films will be confirmed by ATR-IR and ^1H NMR spectroscopy.

The change in surface properties of the PVA films will be investigated by contact angle measurements, atomic force microscopy and optical microscopy. Thermal properties of PVA-g-SOMAP or SONCO films will be characterized by DSC.

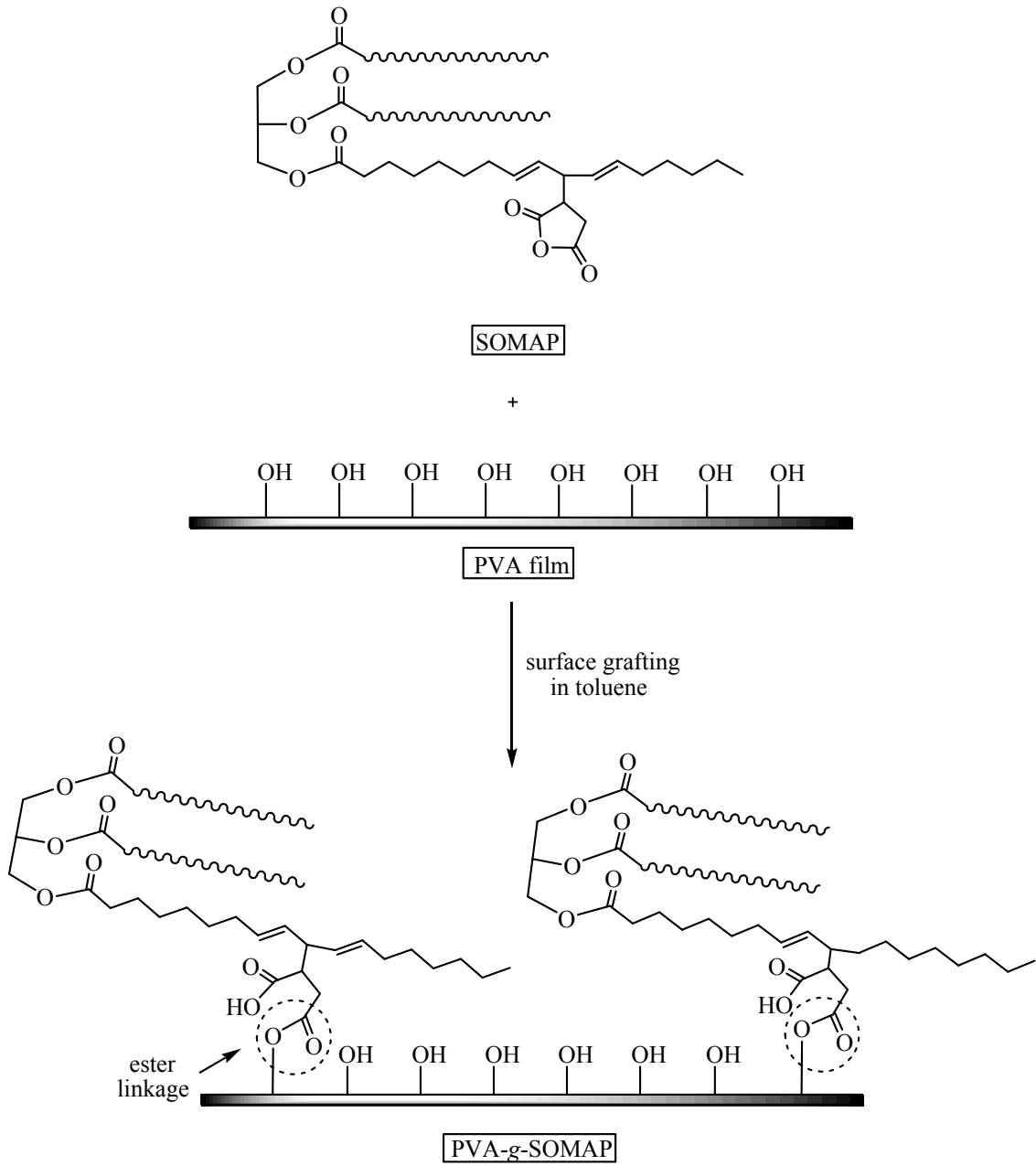


Figure 2.1. Synthesis and structure of PVA-g-SOMAP film

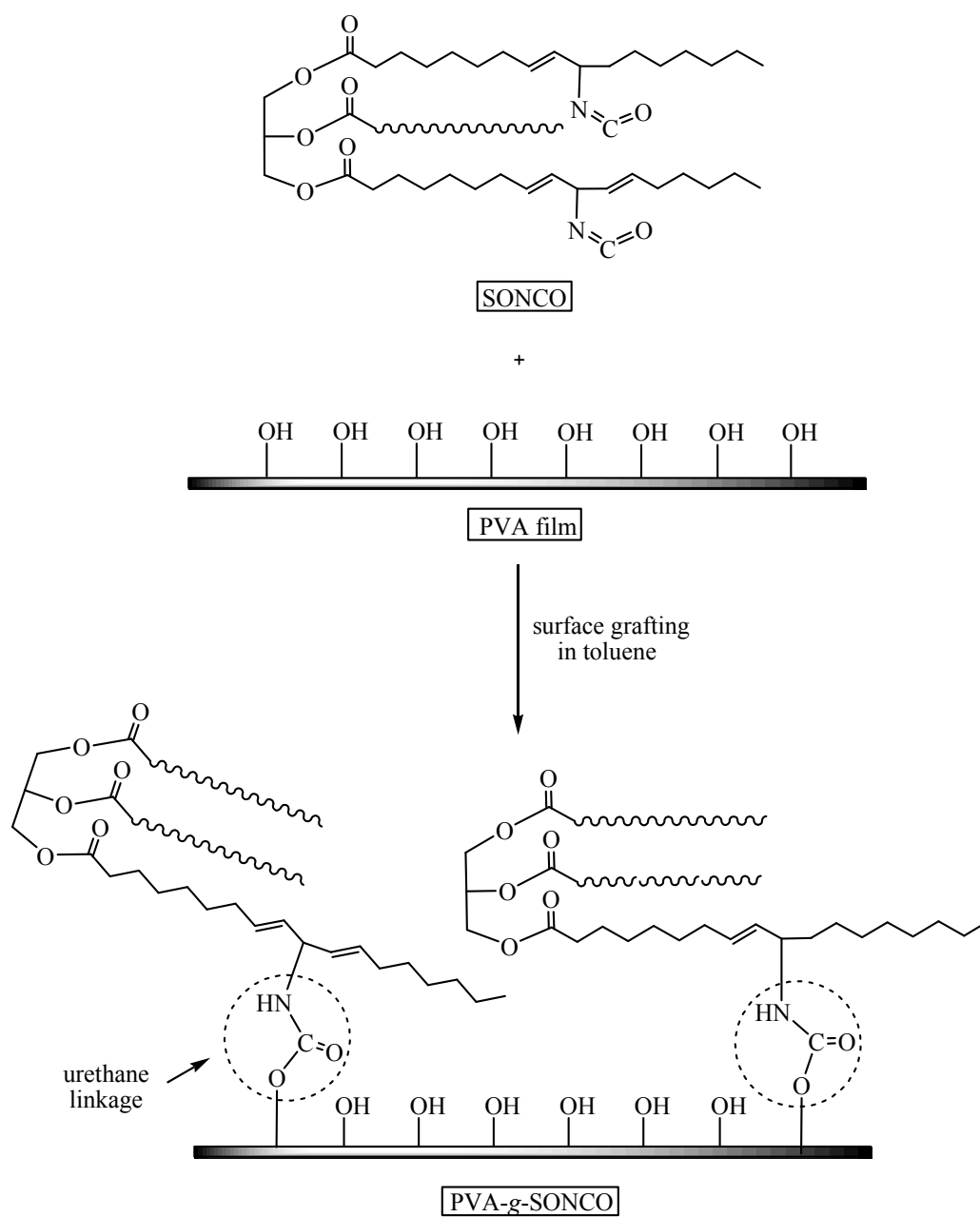


Figure 2.2. Synthesis and structure of PVA-g-SONCO film

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Maleic anhydride and tert-Butylperoxybenzoate (Trigonox C) were obtained from Cam Elyaf A.Ş. (Turkey) and used as received. Soybean Oil (SO) supplied by Marsa (Turkey) was food grade and used without further purification. 98 per cent hydrolyzed Polyvinyl Alcohol (PVA) was purchased from Aldrich (USA) and used as obtained. Dimethylamino pyridine (DMAP) and toluene were supplied by Merck (Germany) and used as received. CDCl_3 and DMSO-d_6 were purchased from Merck (Germany) and BDH Chemicals (England), respectively, and used for ^1H NMR analysis.

3.1.2. Apparatus

The IR analysis was performed on a Perkin Elmer 1600 FT-IR spectrometer using KBr window and Nicolet 380 FT-IR with Smart Diamond ATR. All the ^1H NMR spectra were recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for proton. The spectra were reported as ppm (δ) with TMS as internal standard.

Gel Permeation Chromatography (GPC) analyses were done using an Agilent 1100 Series GPC-SEC Analysis System with a PL Gel 5 μm MIXED-C Column that was calibrated against polystyrene standards.

Contact Angle Measurement was performed using KSV CAM 101 contact angle instrument.

Atomic Force Microscopy (AFM) was performed by using Quesant-Ambios Universal Scanning Probe Microscope (USPM) (Ambios Technology, Santa Cruz, CA). Phase mode imaging was performed using a silicon nitride cantilever probe with a nominal resonance frequency around 170 kHz and a nominal tip radius of 5-10 nm. Optical Microscopy was performed by Olympus BX51 Polarize Microscope equipped with Camedia C7070 7.1 MP camera.

DSC characterization was performed by “Thermal Analyses” Q 200 instrument with a 10 °C/min heating rate.

3.2. Synthesis of Maleinated Soybean Oil (SOMAP)

A N₂ purged flask which was equipped with magnetic stirrer was sealed with rubber septum. 26.14 g (29.64 mmol) soybean oil and 3.21 g (32.77 mmol) maleic anhydride were mixed at 70 °C. Due to the sublimation of maleic anhydride, excess MA was used (1 mole SO:1.1 mole MA). After the temperature was raised to 150 °C 0.52 g (2 per cent by weight based on soybean oil) Trigonox C was added. After one hour another portion of 0.2649 g (1 per cent by weight based on soybean oil) Trigonox C was added. The temperature was reduced to 130 °C after 30 minutes. The reaction was completed after two hours and finally vacuum was applied to remove excess anhydride and initiator. Complete removal was observed when there was no bubble formation in the reaction medium. Final product was yellow, viscous oil. The characterization of the final product was done with ATR-IR. Due to low MA functionality per mole of SO, NMR characterization was difficult. However, NMR showed no unreacted maleic anhydride was left in the product.

ATR-IR (cm⁻¹): 3008.26 (C=C, stretching), 2926.52, 2854.95, and 1461.86 (C-H, stretching), 1858.48, 1781.71 and 921.19 (succinic anhydride peaks), 1744.67 (C=O, stretching), 1220.73, 1164.90, and 1092.74 (C-C(=O)-O, stretching), 722.61 (C=C, bending).

3.3. Hydrolysis of Maleinated Soybean Oil

1.22 g SOMAP was dissolved in 30 ml THF in a two necked flask and refluxed. Excess amount of deionized water, 0.3 g, was added in 5 portions at 70 °C. After a 3-hour reaction, vacuum was applied to remove THF and excess water. IR showed the disappearance of anhydride peaks at 1851, 1749, and 918 cm^{-1} and appearance of carboxylic OH peaks at 3319.6 cm^{-1} .

3.4. Attempted Hydrolysis of Soybean Oil

1.15 g soybean oil was dissolved in 20 ml THF in a two necked flask and refluxed. Excess amount of deionized water, 0.3 g, was added in 5 portions at 70 °C. After a 3-hour reaction vacuum was applied to remove THF and excess water. IR showed that soybean oil did not hydrolyze in this condition. Thus, it was demonstrated that water treatment of SOMAP results in the hydrolysis of the anhydride groups only and that the triglyceride ester groups remain intact.

3.5. Acid Number Determination of SOMAP and SO

Acid number determination was done according to ASTM D 974-64 [21]. 1.22 g hydrolyzed SOMAP was dissolved in 25 ml acetone:toluene (w:w;1:1) mixture in an erlenmeyer flask. It was titrated with 0.5 N KOH, in the presence of 2-3 drops of 1 per cent phenolphthalein. The acid number of SOMAP was found as 90. In a separate experiment SO was used as a blank and determined to have an acid number of 2.42. Acid number of hydrolyzed SOMAP is an accurate determination of the number of succinic anhydride groups on the triglyceride molecule.

3.6. Synthesis of Isocyanated Soybean Oil (SONCO)

Isocyanated soybean oil was synthesized according to the method described by Çaylı and Küsefoğlu [8]. 8 g allylic brominated soybean oil (ABS0) was dissolved in 20 ml of

dry THF. 6 g of AgNCO slurry in 60 ml dry THF was added in 3 portions with 1 hour intervals at room temperature. Stirring was continued for 4 more hours and the flask was kept overnight at room temperature. During the whole operation the flask should be dry and should be covered with aluminum foil. NMR analysis of the product indicates the presence of 2.1 isocyanate groups, on the average, per triglyceride molecule.

ATR-IR (cm^{-1}): 3008.26 (C=C, stretching), 2926.95, 2855.00, and 1461.51 (C-H, stretching), 2258.86 (-N=C=O, stretching), 1742.44 (broad C=O, stretching), 1628.76 (C=C cis, stretching), 1220.73, 1166.08, and 1092.74 (C-C(=O)-O, stretching), 968.28 (-CH=CHCH-Br, stretching). ^1H NMR (ppm): 0.8 (-CH₃), 1 (triplet, -CH=CH-CH₂-CH₃), 1.2-1.4 (-CH₂-), 1.6 (β to carbonyl group, -CH₂-CH₂-C(=O)-OCH₂-), 2.25 (α to carbonyl group, -CH₂-C(=O)-OCH₂-), 2.75 (double allylic position, -CH=CH-CH₂-CH=CH-), 3.9 (CH=CH-CH-NCO), 4.1 and 4.3 (multiplet, glycerin protons, -O-CH₂-), 4.5 (broad, -CH=CH-CH(Br)), 4.8 (-CH=CH-CH(NCO)-CH=CH-), 5.25 (center proton of glycerin, -O-CH₂-CHO-CH₂O-), 5.4 (CH=CH-CH₂-CH=CH-CH(NCO)), 5.8 (-CH=CH-CH(NCO)-CH=CH-).

3.7. Preparation of PVA Films

The 10 per cent PVA solution was prepared by dissolving 4.03 g polymer in 36 ml deionized water at 90 °C with continuous stirring in 3 hours. This solution was cast onto microscope slides by rolling a glass rod over the surface. Extreme care was taken in drying process to ensure complete drying. After two days of open air drying, films were kept at 60 °C in a vacuum oven for two days. IR showed that the water peak at 1650 cm^{-1} was completely eliminated.

3.8. Surface Grafting Reaction of PVA Films

In a general procedure, a 2cmx2cm completely dried PVA film on a microscope slide was placed in a round bottom flask. A solution of SOMAP or SONCO in toluene was added to the flask with weighted amounts of catalyst and the mixture was heated while

stirring. At the end of the reaction the film was rinsed with toluene, dried under vacuum and removed from the microscope slide. The reaction setup is shown in Figure 3.1.

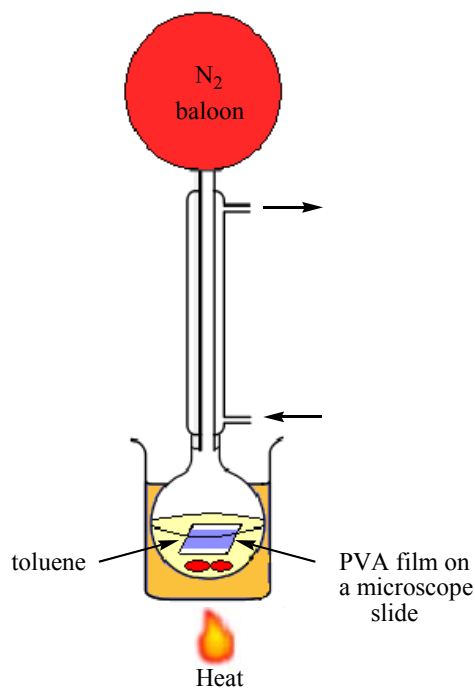


Figure 3.1. Reaction Setup

3.8.1. The Reaction of SOMAP with PVA Films

6, 12, 22, 26 and 33 per cent solutions of SOMAP in dry toluene were prepared in round bottom flasks equipped with a reflux condenser, N₂ inlet and magnetic stirrer. 1 per cent DMAP catalyst by weight based on SOMAP was dissolved in these solutions. The amounts of the reactants for the preparation of PVA-g-SOMAP films are given in Table 3.1. The PVA films were placed in the flasks on microscope slides and reacted at 60 °C, 75 °C, and 90 °C under N₂ in 24 hours. The grafted PVA films were then rinsed with 20 ml toluene several times to remove excess and unreacted SOMAP and finally dried at 60 °C under vacuum for 2 days.

Table 3.1. Amounts of reactants for the preparation of PVA-g-SOMAP films

SOMAP (g)	DMAP (g)	Toluene (mL)	per cent SOMAP in toluene
0.4900	0.0050	9	6
1.0388	0.0104	9	12
1.20712	0.0120	5	22
1.5089	0.0151	5	26
2.1553	0.0221	5	33

ATR-IR (cm^{-1}): 3287.53 (OH, stretching of PVA), 2927.98 and 2853.83 (C-H, stretching of SOMAP), 1774.14 (succinic anhydride stretching of SOMAP), 1740.78 (ester group stretching of SOMAP), 1713.98 (newly formed ester group stretching after the reaction), 1653.83 (C=C, stretching of SOMAP), 1087.55 (C-O, stretching of PVA), 846.16 (C-H, bending of PVA).

In ^1H NMR spectrum except PVA peaks, extra peaks at 0.95 and 1.2 ppm corresponding to $-\text{CH}_3$ and $-\text{CH}_2-$ protons of SOMAP appear.

3.8.1.1. Determination of the grafting ratio through titration. The 2cmx2cm PVA-g-SOMAP film sample was dissolved in 10 ml hot deionized water. 1 ml THF was added in order to be sure that all grafted triglyceride was completely solved. This solution was titrated with 0.5 N KOH and 1 ml KOH was used in the titration of free carboxylic acid groups on the triglyceride. This experiment allows the calculation of surface density of triglycerides on the PVA film.

3.8.2. The Reaction of SONCO with PVA Films

In a typical example a solution of SONCO in dry toluene was prepared and placed in a round bottom flask equipped with a reflux condenser, N_2 inlet and magnetic stirrer. 1 per cent DMAP catalyst by weight based on SONCO was dissolved in the solution. The PVA film on a microscope slide was placed in the flask and allowed to react at 60 °C or 75 °C under N_2 for 18 hours. The grafted PVA film was then rinsed with 20 ml toluene several

times to remove excess and unreacted SONCO and finally dried at 60 °C under vacuum in 2 days. The reaction was repeated with different SONCO concentrations. The amounts of reactants for the preparation of PVA-g-SONCO films are given in Table 3.2.

Table 3.2. Amounts of reactants for the preparation of PVA-g-SONCO films

SONCO (g)	DMAP (g)	Toluene (mL)	Per cent SONCO in toluene
0.082	0.00080	9	1
0.069	0.0007	5	1.5
0.087	0.00087	5	2
0.115	0.00117	5	2.5
0.280	0.00279	5	6

ATR-IR (cm^{-1}): 3298.81 (OH, stretching of PVA), 2939.31 and 2907.09 (C-H, stretching of SONCO), 1758.31 (C(=O)-O-, stretching), 1714.71 (O-C(=O)-NH), 1646.74 (C(=O)-NH-, stretching), 1565.17 (N-H bending), 1087.55 (C-O, stretching of PVA), 846.16 (C-H, bending of PVA).

In ^1H NMR spectrum except PVA peaks, extra peaks at 0.95 and 1.2 ppm corresponding to $-\text{CH}_3$ and $-\text{CH}_2-$ protons of SONCO appear.

3.9. Surface Characterization of Grafted Films

3.9.1. Contact Angle Measurements

Contact angles were measured by the sessile drop method using water at room temperature. Each contact angle reported was the mean value of five measurements taken at different positions on the film. The contact angles were measured on both sides of the drop and averaged.

3.9.2. Atomic Force Microscopy

Due to the fact that the air contact surface of the solution cast PVA film was very rough, PVA solution was spin-coated on a 2cmx2cm microscope slide to get more smooth surface for AFM measurement. First AFM image was taken with blank PVA film after complete drying. Second AFM image was taken after the reaction of SOMAP took place on the same film. The roughness data were compared. Because the roughness of the SONCO coated PVA film was very high, the surface characterization could not be done with AFM instrument.

3.9.3. Colour Reaction of Films

It is generally known that iodine solutions give a blue colour complex with PVA in the presence of boric acid solution [22]. Pure, SOMAP and SONCO grafted PVA films were placed into 5 ml deionized water in a beaker. One drop of iodine test solution containing iodine, KI with diluted HCl and a few drops of boric acid solution (1 in 25) were added on to the wet films. Blank PVA regions on the film were dyed blue while grafted regions did not change colour. The photographs of these films were taken from optical microscopy.

4. RESULTS AND DISCUSSION

4.1. Characterization and Quantative Analysis of SOMAP

Soybean oil triglycerides were maleinized in the presence of a free radical initiator as described in Section 3.2. According to the literature maleic anhydride reacts with soybean oil in three different ways [11].

a) Free radical mechanism: Maleic anhydride attaches to soybean oil through its allylic positions.

b) Diels-Alder mechanism: Due to isomerization in the presence of a free radical initiator, conjugation of double bonds occurs. Conjugated double bonds react with maleic anhydride by Diels-Alder mechanism.

c) Copolymerization mechanism: The copolymerization of maleic anhydride with soybean oil triglycerides occurs which is responsible for the increase in viscosity of the final product.

These mechanisms are impossible to differentiate by ^1H NMR of the product. Owing to high number of H atoms in soybean oil, 3 succinic anhydride protons could not be identified. However, there were no peaks at 7.0 ppm corresponding to maleic anhydride proving that all maleic anhydride was reacted with soybean oil.

Qualitative characterization of SOMAP was performed by ATR-IR. Figure 4.1 shows the ATR-IR spectrum of SOMAP. Peaks at 1858.48, 1781.71, and 921.19 cm^{-1} are characteristic for succinic anhydride. There are no peaks corresponding to $-\text{COOH}$ groups showing that the anhydride was preserved during the reaction.

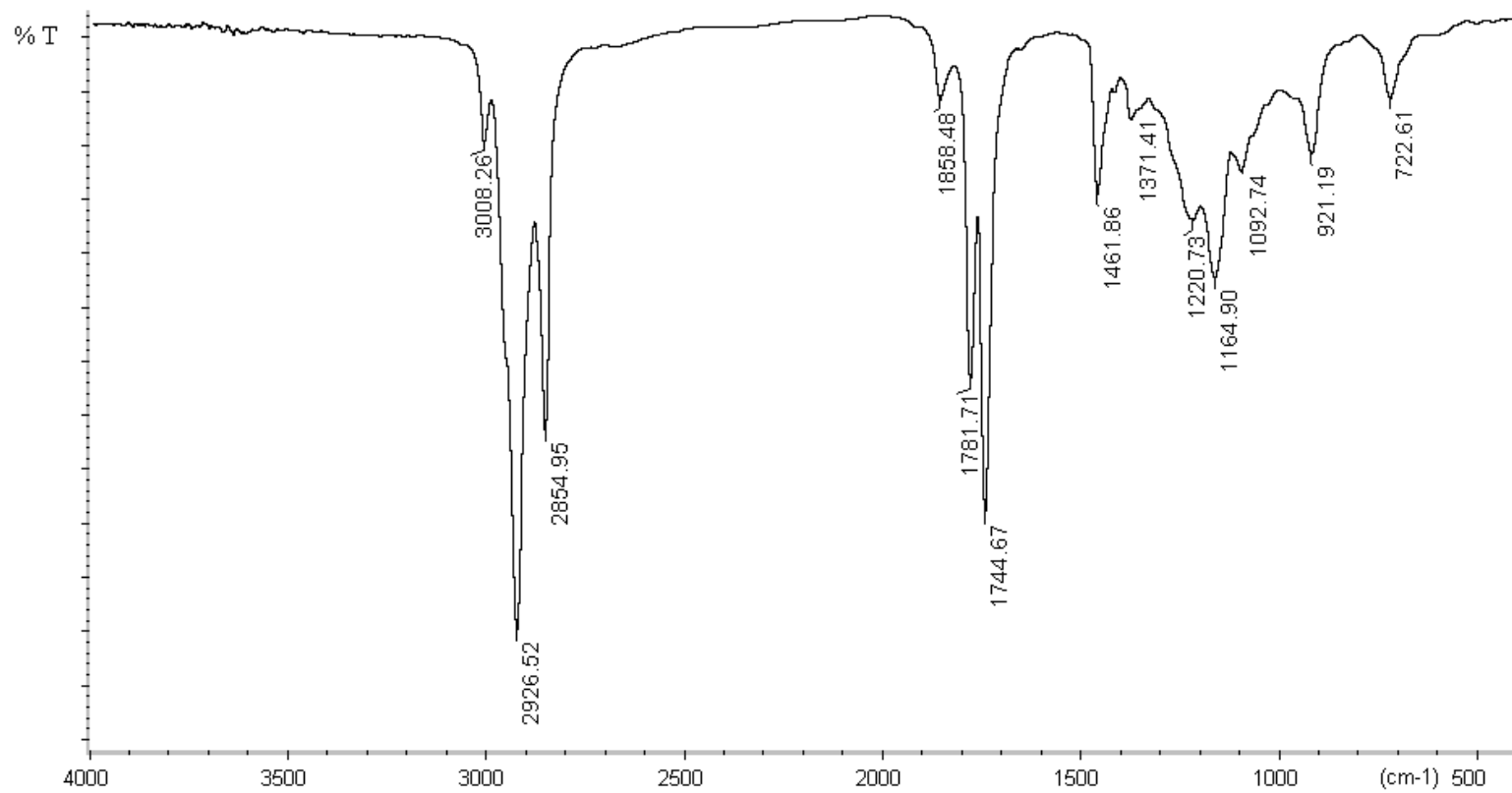


Figure 4.1. ATR-IR spectra of SOMAP

The quantitative determination of available succinic anhydride groups per soybean oil triglyceride was performed by acid number determination. ASTM D 974-64 was the basis for the acid number determination. Maleinized soybean oil was hydrolyzed as described in the section 3.3. The reaction and the IR spectrum of the hydrolyzed product are shown in Figure 4.2 and Figure 4.3, respectively. The reduction in anhydride peaks at 1858.5, 1776.1 and 921.4 cm^{-1} and the appearance of carboxylic acid OH band at 3441.5 cm^{-1} were observed. Free acid groups of SOMAP were then titrated with KOH and acid number was calculated as mg KOH/g sample. An appreciable increase in acid number of SOMAP was observed when compared with that of the soybean oil which was exposed to the hydrolysis reaction in the same conditions as SOMAP. To be certain that triglyceride esters are not hydrolyzed under these conditions acid number of soybean oil was determined and found to unchanged. Table 4.1 shows the acid numbers of soybean oil and SOMAP. The low acid number obtain for soybean oil is due to the free fatty acids naturally found in it.

Table 4.1. Acid numbers of soybean oil and SOMAP

	Acid Number (mg KOH/g sample)
Soybean oil	2.42
SOMAP	90

Calculation using the acid number of SOMAP indicates 1.6 moles acid per mole of triglyceride. Because the hydrolysis reaction results in 2 moles COOH groups per succinic anhydride, the anhydride functionality in SOMAP is therefore 0.8 moles of anhydride per mole of triglyceride. This means that unreacted soybean oil may exist in the samples obtained and these need to be completely removed after surface grafting on PVA films.

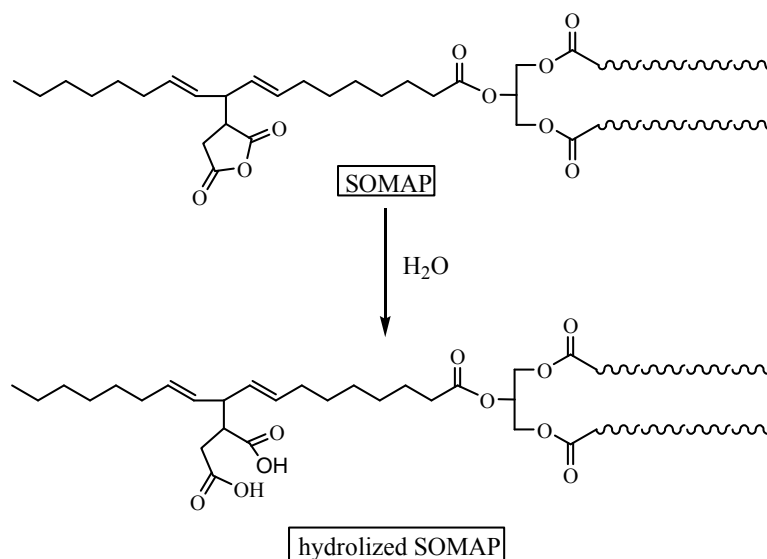


Figure 4.2. Hydrolysis of SOMAP

The average molecular weight of SOMAP was determined by GPC. Table 4.2 shows the average M_n and PDI values.

Table 4.2. M_n and PDI values of SOMAP

	SOMAP
M_n	1680
PDI	2.053

The fact that M_n is higher than expected for a simple addition of maleic anhydride to the triglycerides indicates that some copolymerization is also taking place. These M_n and PDI values are the average of two different regions corresponding to low and high molecular weight SOMAP with low PDI values. According to these results it was concluded that the copolymerization of the triglyceride with maleic anhydride occurs as well as the Diels-Alder and free radical reaction of soybean oil with maleic anhydride. The high molecular weight region stems from the copolymerized product which is also the reason for high viscosity of the final product.

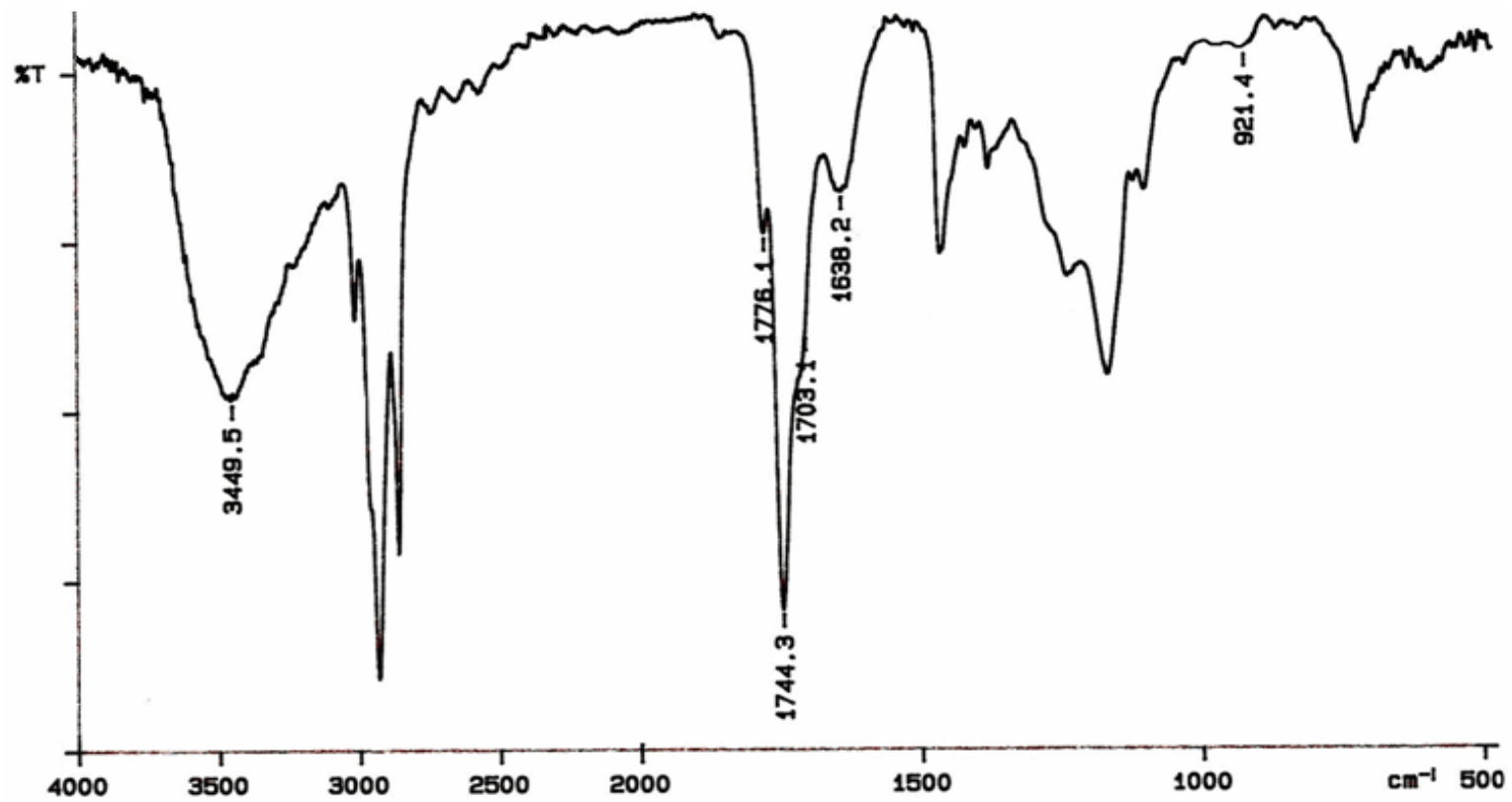


Figure 4.3. IR spectrum of hydrolyzed SOMAP

4.2. Characterization and Quantitative Analysis of SONCO

Allylic brominated soybean oil (ABSO) was reacted with 3 equivalents of AgNCO in THF at room temperature. Approximately 60-70 per cent of the bromine was replaced by NCO groups at the end of the reaction with no consumption of the double bonds of triglyceride molecules. Because there are theoretically up to 10 different allylic positions, SONCO was obtained as a mixture of all possible positional isomers and no attempt was made to separate them.

Figure 4.4 shows the ATR-IR spectrum of SONCO. The peaks at 2258.86 and 968.28 cm^{-1} correspond to isocyanate and allylic bromine, respectively. The ester peak of triglyceride at 1742.44 cm^{-1} is also broadened due to the formation of many different positional isomers.

^1H NMR spectrum in Figure 4.5 shows the appearance of the peaks at 3.9, 4.6, and 4.8 ppm corresponding to the allylic hydrogens where isocyanate addition occurs. The peak at 5.6 ppm corresponds to the hydrogen of (-CH=CH-CH(NCO)).

The average number of isocyanate groups per triglyceride was found to be 2.1 by calculating the ^1H NMR signal intensity ratio of the total geminal protons on the C atom bearing the NCO group (3.9, 4.6, and 4.8 ppm), to the -CH₃ protons of the triglyceride (0.8 ppm).

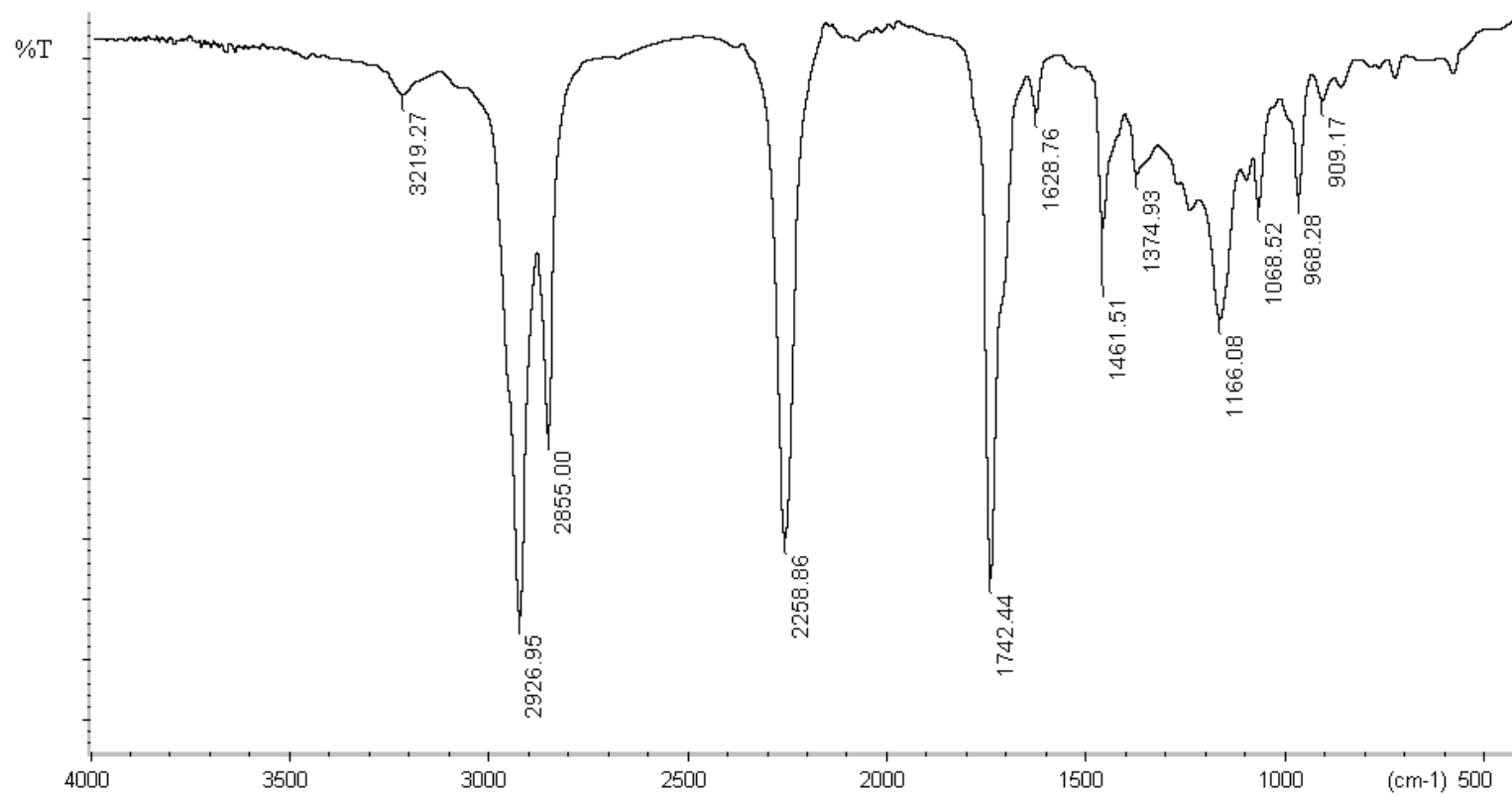


Figure 4.4. ATR-IR spectrum of SONCO

4.3. Characterization of Polyvinyl Alcohol

Since PVA is generally synthesized by hydrolysis of polyvinyl acetate (PVAc), the stereochemical structure of PVA is that of PVAc which is atactic. ^1H NMR spectrum of PVA in DMSO- d_6 is shown in Figure 4.6. Methylene protons of the backbone appear at 1.3-1.5 ppm and the methine protons attached to $-\text{OH}$ and $-\text{OCOCH}_3$ appear at 3.8 and 3.9 ppm, respectively. The $-\text{CH}_3$ protons of the unhydrolyzed acetate group give a characteristic peak at 1.95 ppm. The hydroxyl proton ($-\text{OH}$) of the PVA are separated into triads at 4.25, 4.49 and 4.68 ppm due to the H bonding between $-\text{OH}$ groups of the polymer and DMSO. The solvent peak appears at 2.5 ppm while the water peak coming from DMSO appears at 3.4 ppm.

Figure 4.7 shows the ATR-IR spectrum of unreacted PVA. The broad band at 3265.33 cm^{-1} corresponds to the O-H stretching vibrations of the hydroxyl group of the PVA. The backbone aliphatic C-H stretching vibrations give sharp bands at 2942 and 2907.80 cm^{-1} , while 845.95 and 1092.66 cm^{-1} are attributed to aliphatic C-H bending and C-O stretching vibrations of PVA, respectively. The small band at 1732.12 cm^{-1} is attributed to the carbonyl functional groups due to residual acetate groups remaining after the manufacture of PVA from hydrolysis of PVAc. The peak at 1658.89 cm^{-1} corresponds to water because PVA films are hygroscopic.

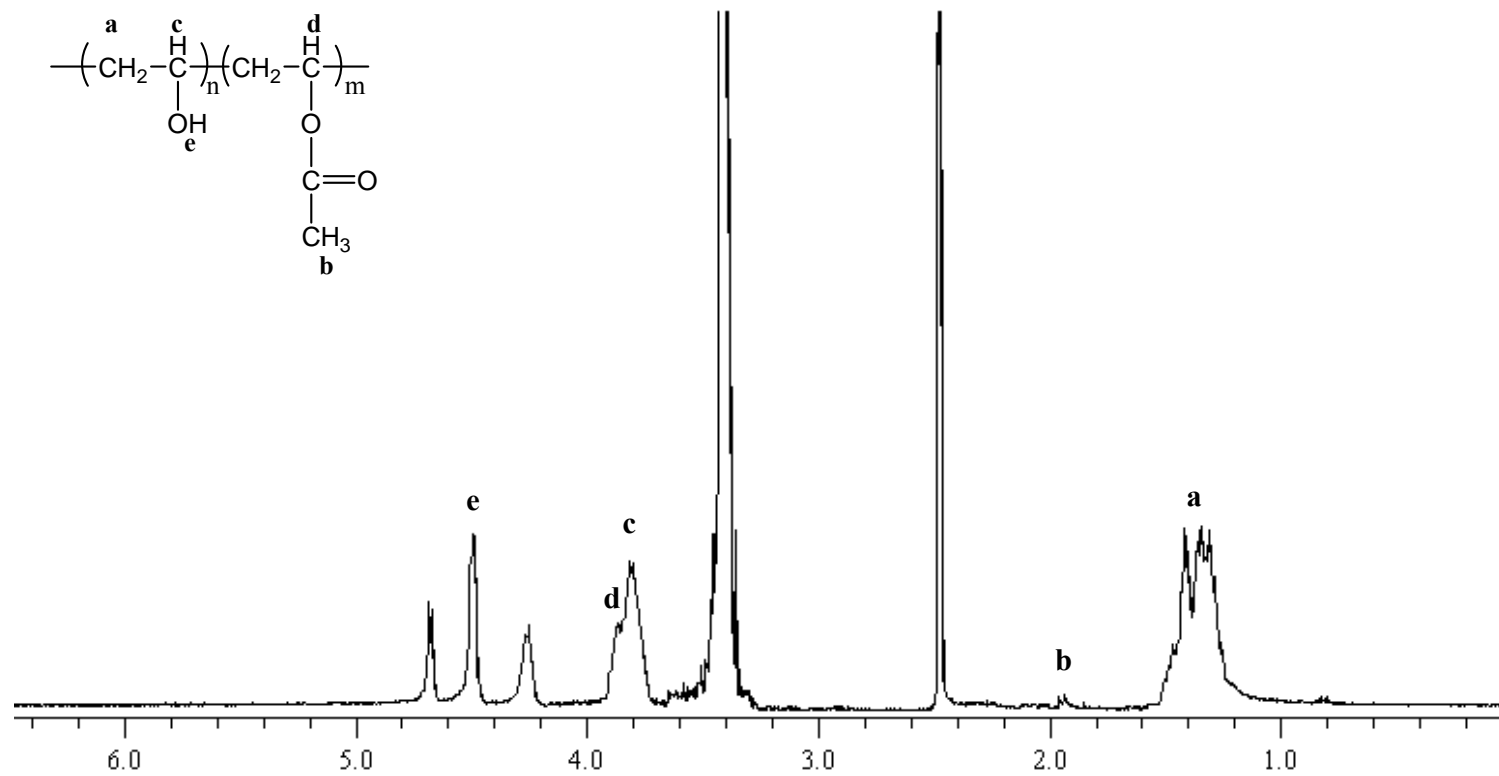


Figure 4.6. ^1H NMR spectrum of PVA

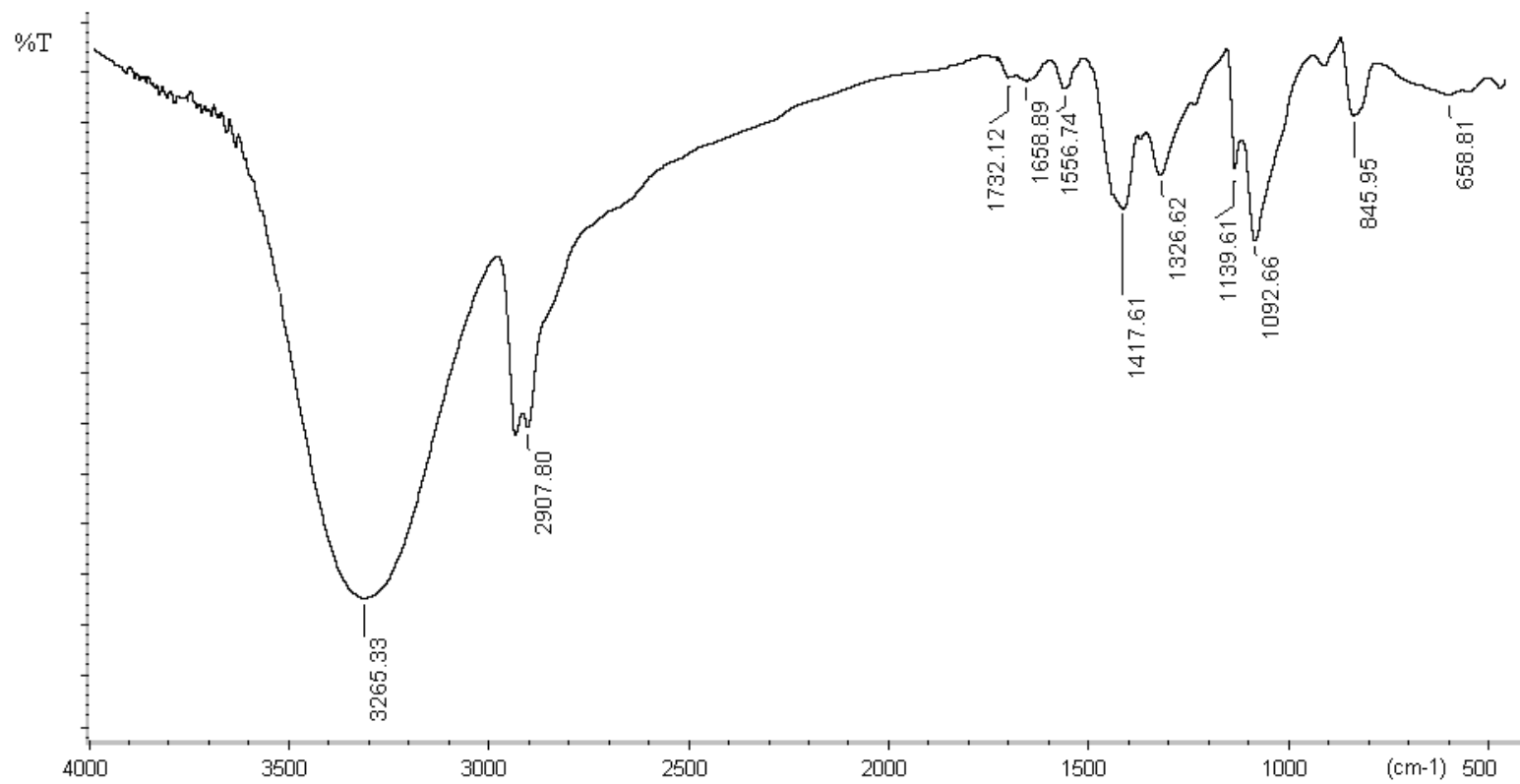


Figure 4.7. ATR-IR spectrum of PVA

4.4. Surface Modification of PVA Films

PVA films were solution cast onto microscope slides and dried at 60 °C in a vacuum oven before the reaction until the water peak at 1658.89 cm^{-1} was completely eliminated. Extreme care was taken in drying process due to the sensitivity of the anhydride and isocyanate moieties to water. ATR-IR spectrum of dried PVA is shown in Figure 4.8.

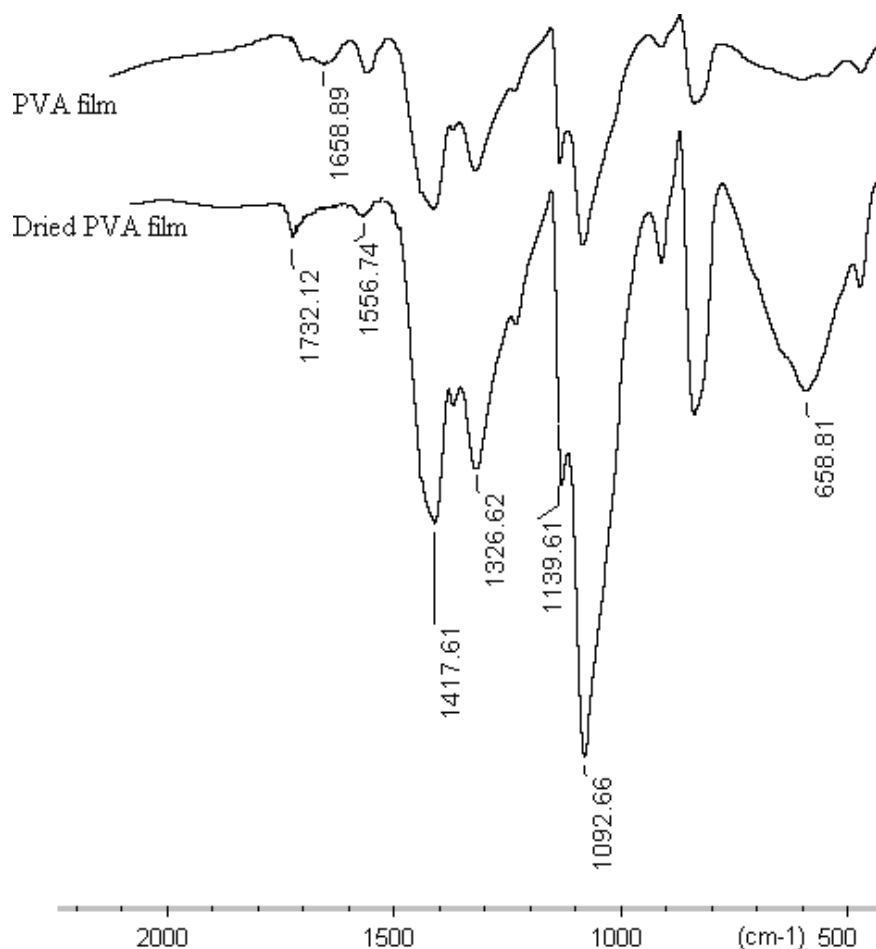


Figure 4.8. ATR-IR spectrum of dried PVA

4.4.1. Surface Grafting Reaction and Characterization of PVA-g-SOMAP Films

The dried PVA film samples were placed in dry toluene solutions of SOMAP containing 1 per cent DMAP as a catalyst and reacted at 75 °C under N_2 atmosphere in 24

hours. Reaction set up is shown in Section 3.8. A base catalyst is needed to facilitate the reaction between succinic anhydride groups of soybean oil and available hydroxyl groups of PVA due to low reactivity of secondary hydroxyl groups towards succinic anhydride functionalities on triglycerides. Since the interaction between toluene and PVA film is very weak (The swelling degree with toluene is less than 1 per cent after 48 h), this reaction occurs only on the film surface [23]. The structure of the final product is shown in Figure 4.9.

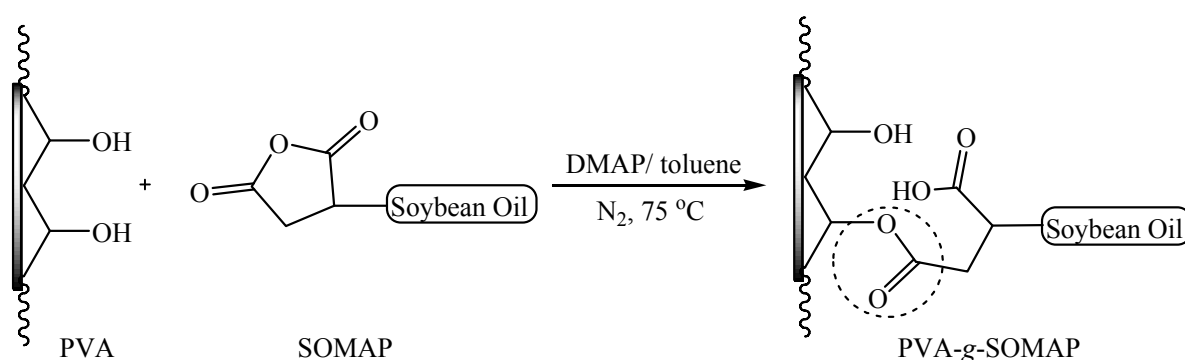


Figure 4.9. Surface grafting reaction of PVA with SOMAP in toluene

After the reaction, films were rinsed with toluene several times in order to remove excess and unreacted SOMAP from the surface and dried. The characterization of SOMAP grafted PVA films was done by ATR-IR and ¹H NMR spectroscopic techniques.

ATR-IR spectrum of SOMAP reacted film with catalyst is shown in Figure 4.10. Since the common peaks of SOMAP overlap with PVA, only carbonyl and alkyl regions are available to confirm the reaction on the surface. The PVA-g-SOMAP film shows a distinct band at 1740.78 cm⁻¹ corresponding to the ester peak of soybean oil. A new band at 1713.98 cm⁻¹ attributed to the new ester peak. The disappearance of the anhydride peaks at 1774.14 and 1858.48 cm⁻¹ is observed. The peaks at 2927.02 and 2856.99 cm⁻¹ most likely correspond to the C-H stretching of SOMAP rather than PVA. The O-H stretching vibrations of the remaining acid group on anhydride cannot be distinguished since they overlap with the O-H stretching vibrations of PVA. When the grafted film was lifted from the microscope glass and the ungrafted side was placed on the ATR-IR, the spectrum obtained was identical to unreacted PVA.

There is a need to prove that SOMAP actually reacts with the PVA surface and the observations above are not caused by some physical adsorption phenomena. The same reaction was done without catalyst. The ATR-IR spectrum of treated film without catalyst is similar to that of the starting PVA. This result shows that only very little adsorption of SOMAP on PVA surface occurs and no esterification takes place. Thus, it was shown that toluene does not solve PVA film and the reaction between SOMAP and PVA film does not occur without DMAP; but, it takes place in the presence of DMAP.

^1H NMR sample of SOMAP-g-PVA film was prepared by washing the reacted side of the film surface with hot DMSO- d_6 .

^1H NMR spectrum of SOMAP-g-PVA film is shown in Figure 4.11. All the peaks, which appear in PVA, also appear in the grafted film with a very little change in the chemical shift values. However, extra peaks at 0.95 and 1.2 ppm appear which correspond to the $-\text{CH}_3$ and $-\text{CH}_2-$ protons of soybean oil triglycerides, respectively. This clearly confirms the reaction of SOMAP with PVA film. As the amount of co-dissolved PVA from lower layers of the film is not known NMR analysis is not suitable for quantitative determination of grafting.

4.4.1.1. Determination of the surface grafting degree with SOMAP. The extent of surface grafting reaction was determined by titration of free carboxylic acid groups resulting from the esterification reaction of succinic anhydride groups on triglyceride with polyvinyl alcohol. After complete removal of unreacted SOMAP from the surface, a PVA film grafted with 22 per cent SOMAP in toluene for 24 hours was dissolved in hot water: THF (1:0.1 by weight) mixture. In general an acid value is determined as mg KOH/g sample. However, because the grafting reaction happens only on the film surface, the calculation using the total weight of the film was unimportant; thus, it was decided to use the total grafted surface area of the film instead of its weight. According to the results after this assumption, it was found that 5×10^{-4} mole KOH was used in titration corresponding to 5×10^{-4} mole $-\text{COOH}$ groups per $2\text{cm} \times 2\text{cm}$ PVA surface. Due to the fact that SOMAP has 0.8 mole succinic anhydride per mole of triglyceride, the extent of grafting was found as 1.56×10^{-4} mole triglyceride per cm^2 of the PVA film.

4.4.2. Surface Grafting Reaction and Characterization of PVA-g-SONCO Films

The dried PVA film samples were reacted with known amounts of SONCO in the presence of DMAP at 75 °C under N₂ atmosphere in 18 hours. Toluene was used as a solvent. DMAP catalyzes the formation of polyurethanes from the reaction of isocyanates with alcohols. Due to the fact that SONCO has 2.1 isocyanate functionalities per triglyceride and that the isocyanate groups are much more reactive with hydroxyl groups, the surface grafting reaction went faster and gave high grafting ratios despite low amounts of SONCO used. The reaction and the final product is shown in Figure 4.12.

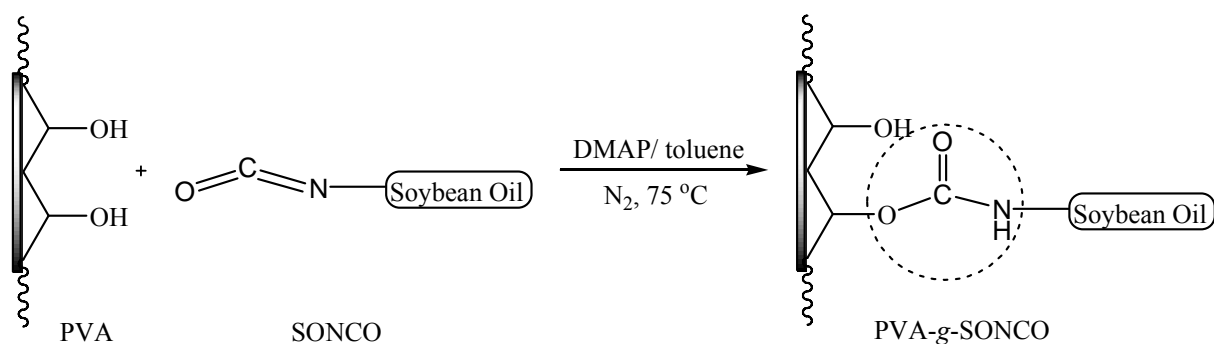


Figure 4.10. Surface grafting reaction of PVA with SONCO in toluene

After the reaction, films were rinsed with toluene several times in order to remove unreacted SONCO from the surface and dried. The characterization of SONCO grafted PVA films was done by ATR-IR and ¹H NMR spectroscopy.

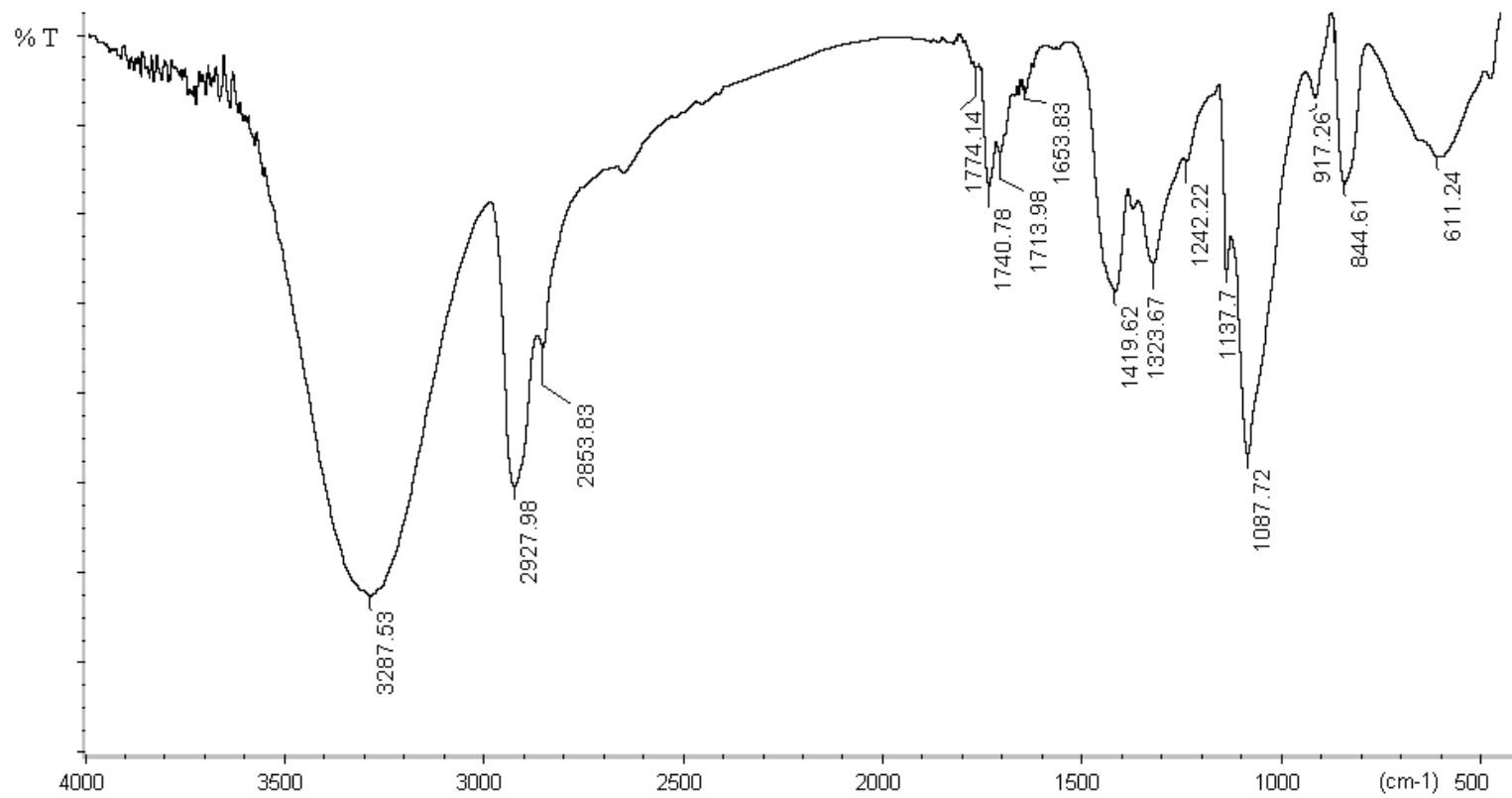


Figure 4.11. ATR-IR spectrum of PVA-g-SOMAP

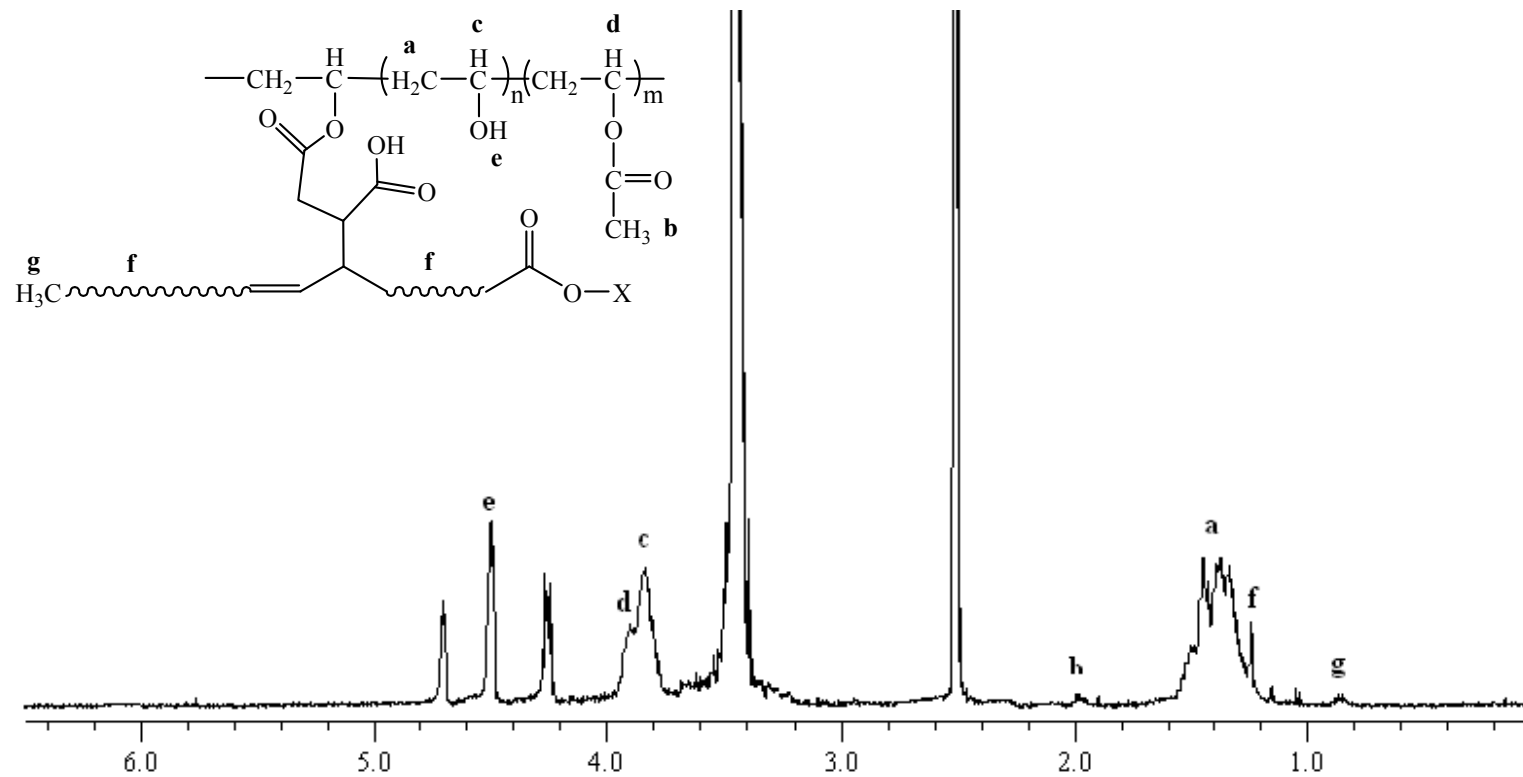


Figure 4.12. ¹H NMR spectrum of PVA-g-SOMAP

ATR-IR spectrum of PVA-g-SONCO film is shown in Figure 4.13. The loss of isocyanate peak at 2259.21 cm^{-1} is observed. The broad peak at 1711.86 is unique for polyurethane linkages. The peaks at 1644 and 1564 cm^{-1} correspond to C=O stretching of the amide group and N-H bending, respectively. However, the N-H stretching vibrations of the amide group around 3500 cm^{-1} cannot be distinguished since the overlap with O-H stretching vibrations.

^1H NMR sample of PVA-g-SONCO film was prepared by washing the reacted side of the film surface with hot DMSO.

^1H NMR spectrum of PVA-g-SONCO film is shown in Figure 4.14. All the peaks appeared in the grafted film with a very little change in the chemical shift values. However, extra peaks at 0.95 and 1.2 ppm appear which correspond to the $-\text{CH}_3$ and $-\text{CH}_2-$ protons of soybean oil triglycerides, respectively. This clearly confirms the reaction of SONCO with PVA film.

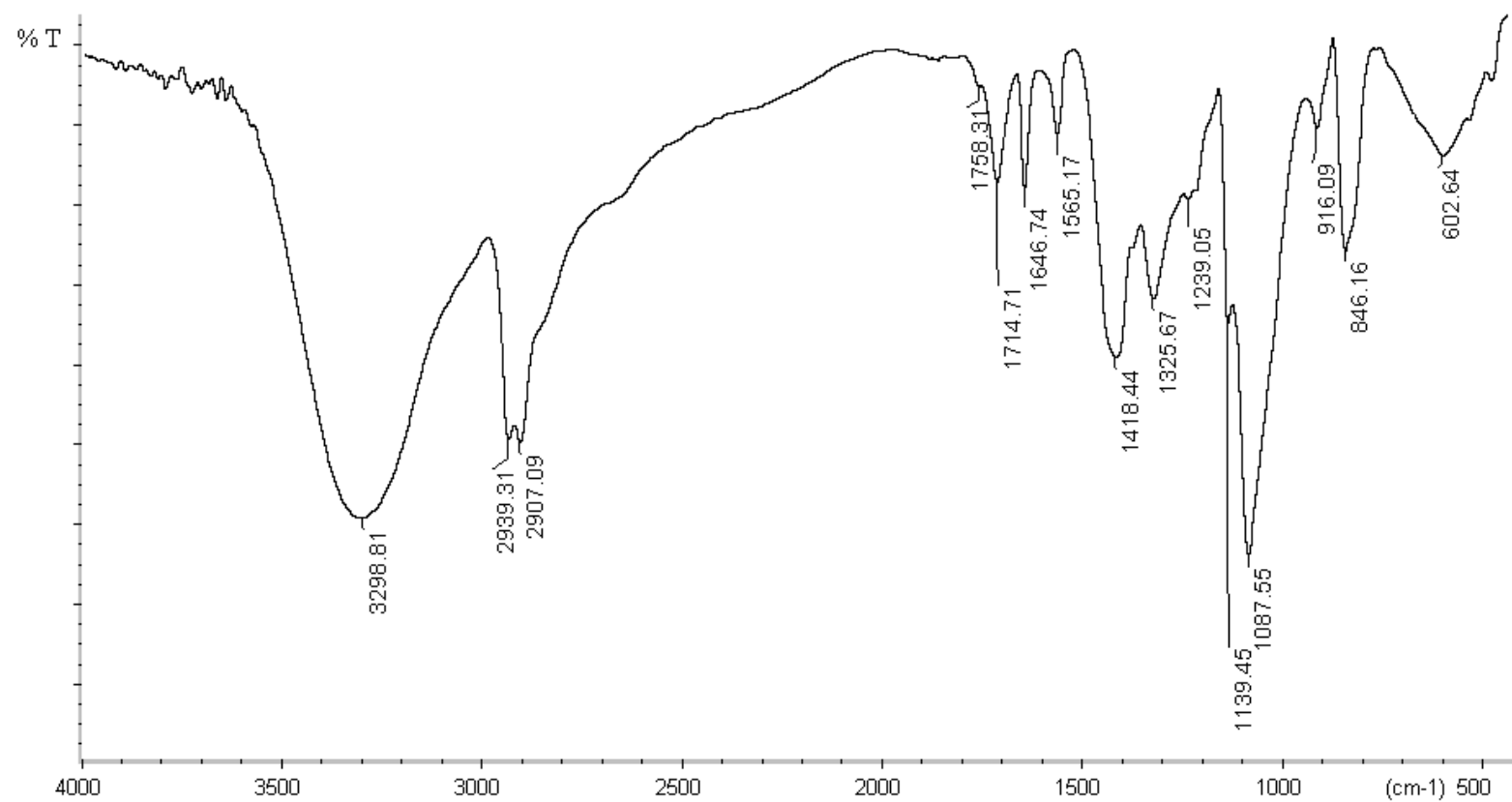


Figure 4.13. ATR-IR spectrum of PVA-g-SONCO

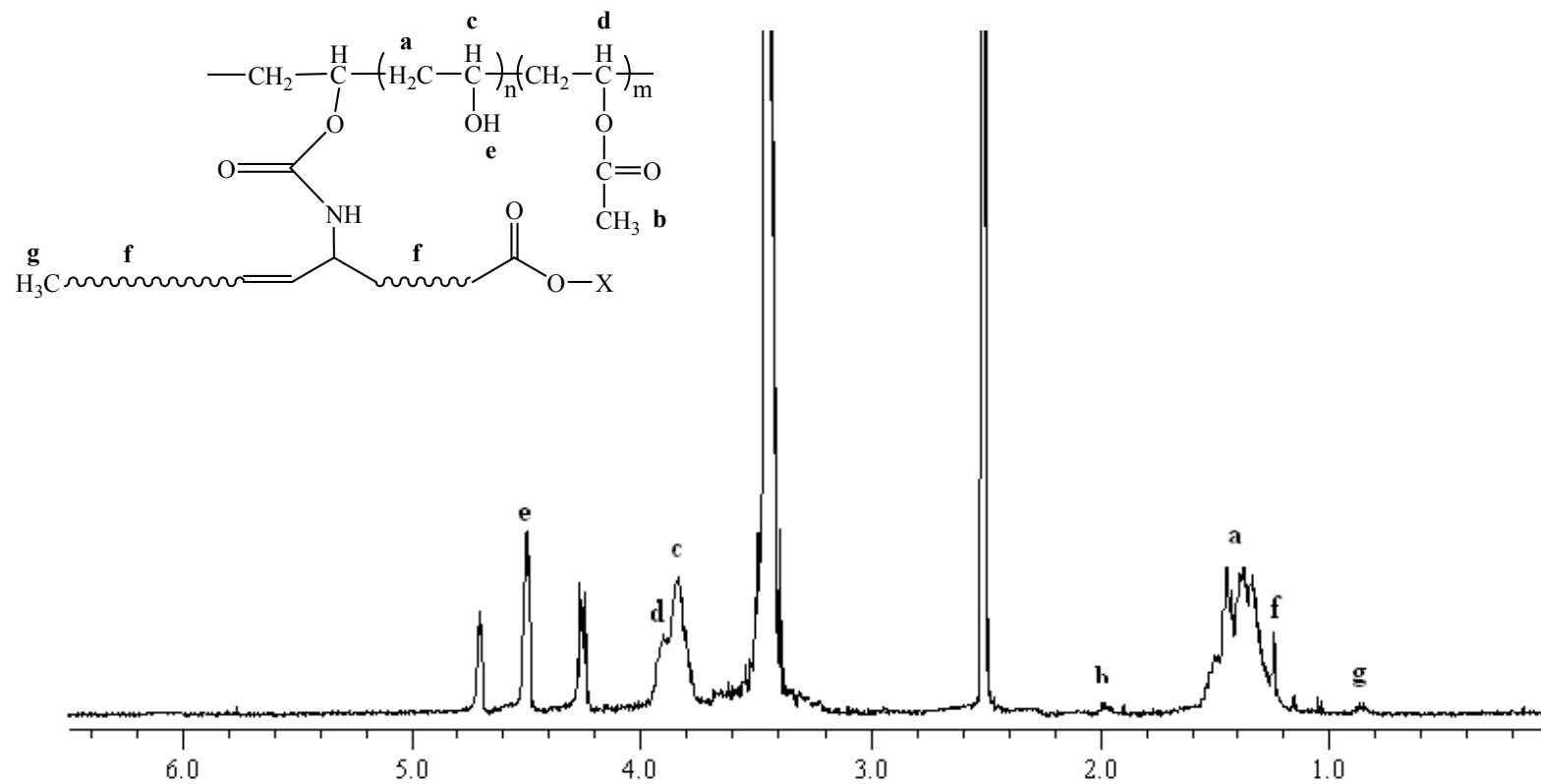


Figure 4.14. ^1H NMR spectrum of SONCO-*g*-PVA

4.5. Contact Angle Measurements

Wetting is the ability of a liquid to remain contact with a solid surface due to the intermolecular interactions between the two. The extent of wetting is determined by a force balance between adhesive and cohesive forces. Adhesive forces cause a liquid droplet to spread over the solid surface while the droplet balls up and avoids contact with the surface due to cohesive forces. Wettability is measured by contact angle.

When a liquid droplet is placed onto a solid substrate, because there are three phases in contact (liquid-solid-air), there will be three surface tensions that have to be considered. Young formulized this phenomenon with a simple mechanical balance, named Young's equation [24]:

$$\cos\theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV}$$

where θ is the contact angle of liquid with solid, and γ_{SV} , γ_{SL} , γ_{LV} are the surface tensions at the interphase of solid-vapor, solid-liquid, and liquid-vapor, respectively (Figure 4.15). The unit of surface tension is $\text{mJ}\cdot\text{m}^{-2}$ or $\text{mN}\cdot\text{m}^{-1}$.

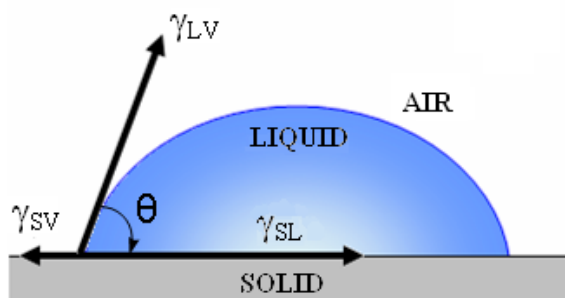


Figure 4.15. Surface tension vectors on a liquid droplet sitting over a solid substrate

A contact angle less than 90° (low contact angle) indicates that wetting of the surface is very favorable. Conversely, contact angles greater than 90° (high contact angle) indicates that wetting of the surface is unfavorable. If the liquid is water, a wettable surface is named hydrophilic, while a non-wettable surface is hydrophobic.

Measuring the contact angles of water on a surface provides information about the hydrophilicity and hydrophobicity; moreover, the polarity and homogeneity of the outermost few angstroms of this surface. Contact angle measurements using Sessile Drop was based on a setup shown in Figure 4.16. A certain volume of water was placed on film samples with a syringe as a droplet. The shape of the droplet was recorded through a camera and the acquired images were analyzed by the image analysis software.

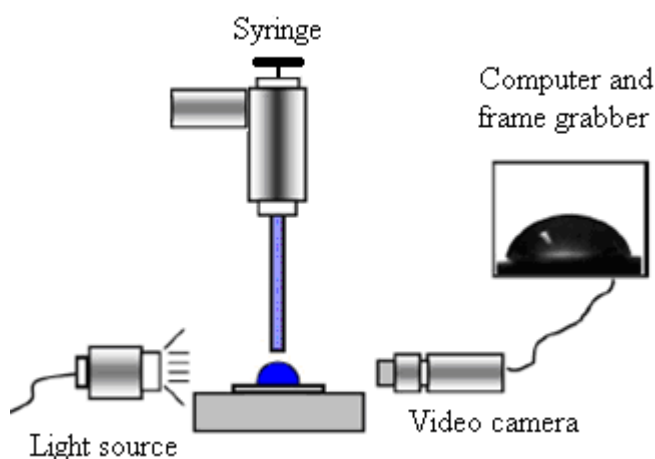


Figure 4.16. Schematic diagram of contact angle measurement with a Sessile drop.

Dried PVA films treated with SOMAP solutions of various concentrations (6, 12, 22, 26, 33 per cent by weight) at different temperatures were studied by water contact angle measurements. The variations of contact angles with SOMAP concentration temperature are represented in Figure 4.17. The curve shows an increase in contact angles from $\theta = 48^\circ$ to 88° . At 75°C and 90°C the increase in water contact angles is higher than that of 60°C . However, there is no considerable change in contact angles at 75°C and 90°C . Therefore, 75°C was found as the best temperature for our reaction.

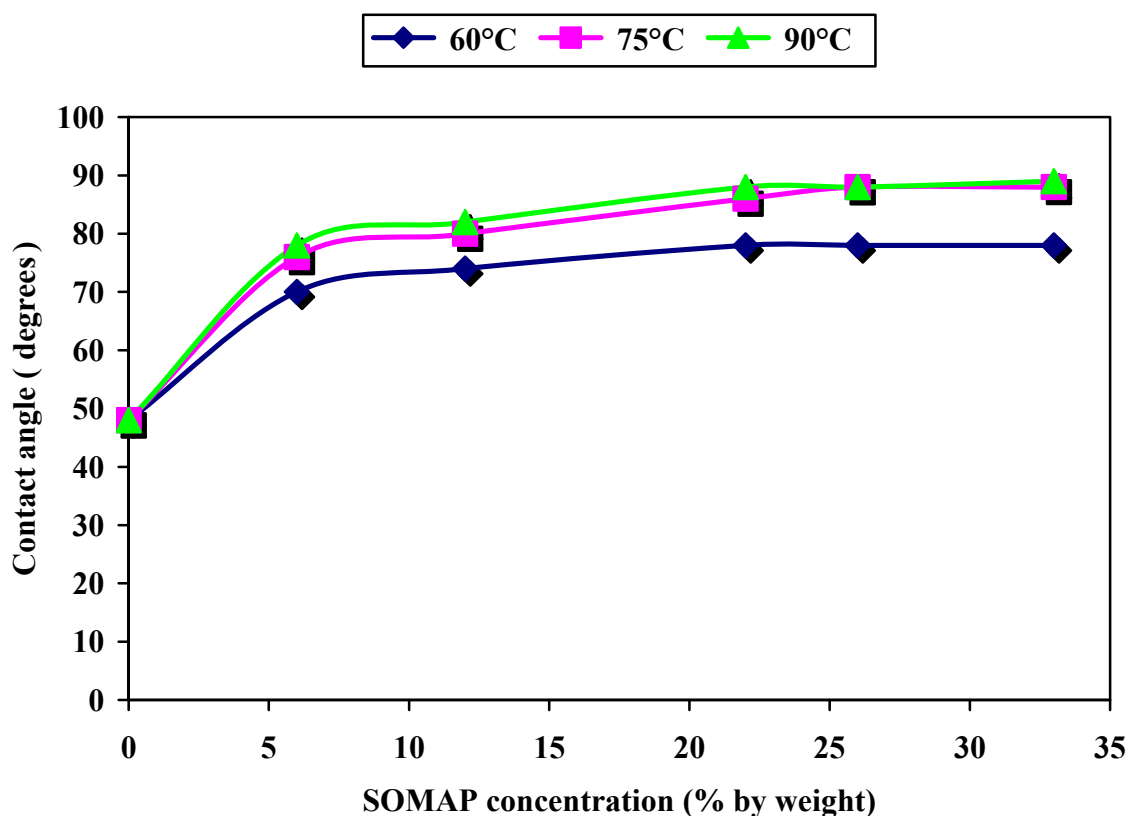


Figure 4.17. Variations of water contact angles versus SOMAP concentration at 60 °C, 75 °C, and 90 °C

To check for the hydrophobicity of used SOMAP itself, a smooth layer was prepared by depositing SOMAP onto a microscope slide by solution casting. This film was dried at 75 °C for 24 hours and its water contact angle was found as $\theta=65^\circ$. This result is not as high as the contact angle values of PVA-g-SOMAP films, because polar succinic anhydride groups on triglyceride molecules imparts hydrophilicity on the pure SOMAP layer and SOMAP does not form a solid layer on the microscope slide in this temperature and time range.

The water contact angle corresponding to the ungrafted side of PVA film does not change and remains at $\theta=48^\circ$ after the grafting process.

The grafting reaction of SOMAP requires that a new $-\text{COOH}$ group is formed for every graft reaction. The presence of this polar and hydrogen bonding group makes the

surface more hydrophilic and detracts from the overall aim of our work. Efforts were made to see if this newly formed -COOH group could be esterified with an available -OH group on the PVA surface. Extended heating of the grafted films at $100\text{ }^\circ\text{C}$ for 24 hours did not show any further increase in contact angles. It is generally known that further esterification of the second acid group of an anhydride requires very high temperatures for esterification. However, such high temperatures could not be applied to the reactions on PVA films due to the danger of degrading the PVA film. Thus, we conclude that the further esterification did not take place. This attempted reaction is shown in Figure 4.18.

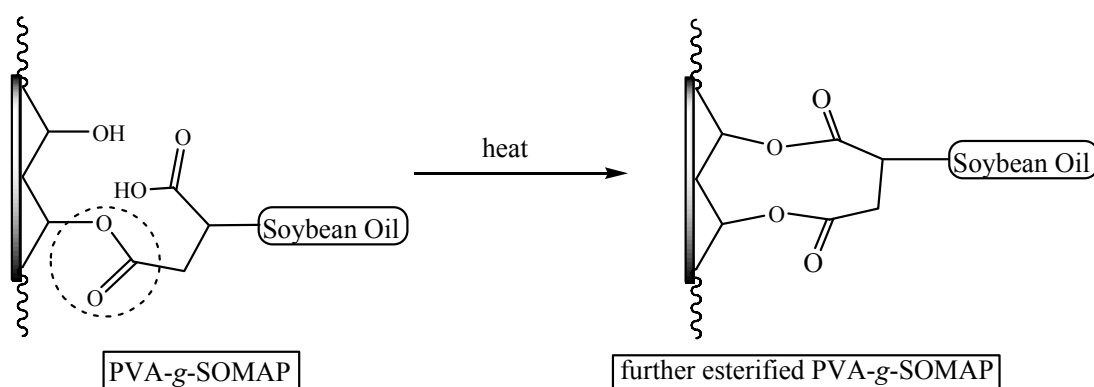


Figure 4.18. Attempted further esterification of SOMAP-g-PVA film

Contact angle measurements were done on the PVA-g-SONCO films which were reacted with different concentrations of SONCO in toluene (1, 1.5, 2, 2.5, and 6 per cent by weight) at $60\text{ }^\circ\text{C}$ and $75\text{ }^\circ\text{C}$. The change in water contact angles with the concentration of SONCO at the mentioned temperatures are shown in Figure 4.19. The increase in water contact angles with the concentration and temperature can be seen. It can be noted that the contact angles increases rapidly and reaches its maximum value of 94° for a 2.5 per cent SONCO concentration.

To find out the maximum water contact angle of SONCO itself, SONCO was solution cast on a microscope slide and dried at $75\text{ }^\circ\text{C}$ for 18 h. It was found as 110° .

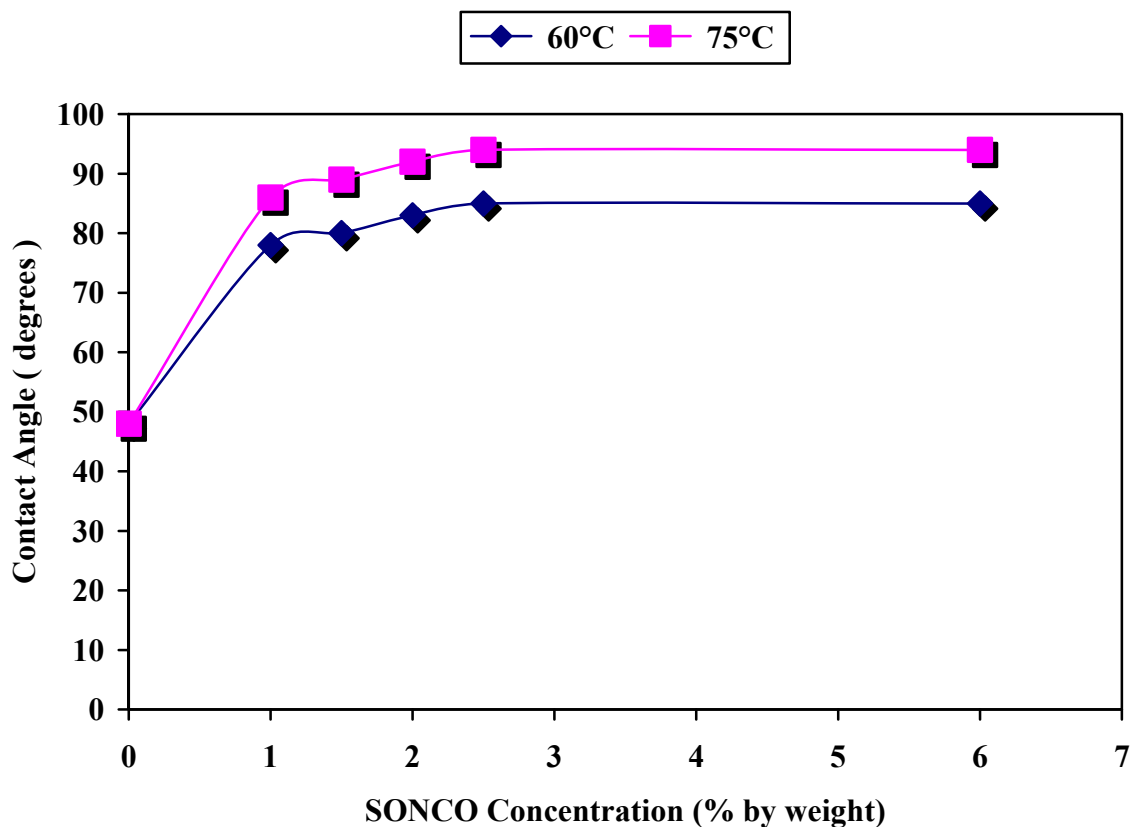


Figure 4.19. Variations of contact angle measurements versus SONCO concentration at 60 °C and 75 °C

According to the contact angle values it was found that the hydrophobicity of PVA film reaches its maximum value when the grafting reaction is carried out in a solution with 26 per cent SOMAP concentration and 2.5 per cent SONCO concentration. Furthermore, the optimum temperature was found as 75 °C for a good surface reaction without the danger of the PVA film swelling in toluene.

4.6. AFM Results

The atomic force microscope (AFM) is a well established and one of the most powerful tools for probing surface topography of various materials. The basic principle of the AFM is scanning the surface of interest with a sharpened probe tip attached to a flexible cantilever while maintaining a constant force between the probe and sample. By

monitoring the motion of cantilever, the topography of the surface of interest can be determined. The scanning process in AFM is shown in Figure 4.20.

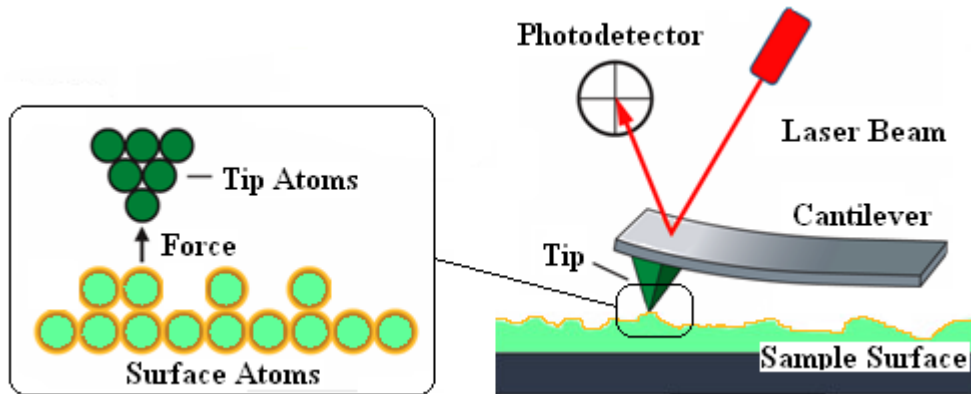


Figure 4.20. The scanning process in AFM

In particular, AFM provides information on surface roughness values at a high resolution level which cannot be achieved by the other techniques [25]. The surface roughness can be presented as the height value of the Z axes of the image, where the peak-to-valley height can be employed to assess the roughness. To obtain more accurate surface roughness analysis, the average surface roughness can be assessed with root mean square (RMS) of peak-to-valley heights which is calculated according to the following equation[26]:

$$RMS = \sqrt{\frac{\sum_i^N (H_i - H_{ave})^2}{N}}$$

where N is the number of measurement of height, H_i is a peak-to-valley height value, H_{ave} the average peak-to-valley height within a given area.

To obtain information involving the change of surface morphology, three dimensional AFM images of pure PVA film and PVA-g-SOMAP film prepared from 26 per cent SOMAP solution are depicted in Figure 4.21. From AFM image of pure PVA film the irregular rolling mountain peaks with different sizes were observed over the surface.

After the grafting reaction of SOMAP in toluene most of the rolling mountains disappeared. To be sure that toluene does not affect the surface morphology, pure PVA film was kept in toluene under the same conditions as the reaction without any reactants. In the three dimensional AFM image of this film, Figure 4.22, the same irregular rolling mountains can be seen as pure PVA film. Thus, it can be said that toluene has very little effect on the surface morphology of the pure PVA film.

The RMS and mean surface roughness values of pure PVA, pure PVA film kept in toluene and PVA-g-SOMAP films are shown in Table 4.3. The surface becomes much rougher with the surface grafting of SOMAP onto pure PVA film and roughness increases from 0.2572 to 3.167 nm. It was seen that toluene is also responsible for the roughness of the pure PVA film. However, the PVA-g-SOMAP film has higher RMS value than that of the film kept in toluene which proves that the surface grafting reaction took place.

Table 4.3. RMS and mean surface roughness values of pure PVA film, pure PVA film in toluene and PVA-g-SOMAP film

	RMS Deviation (Sq)	Mean Deviation (Sa)
Pure PVA film	0.2572 nm	0.1705 nm
Pure PVA film in toluene	2.152 nm	1.365 nm
PVA-g-SOMAP film	3.167 nm	2.167 nm

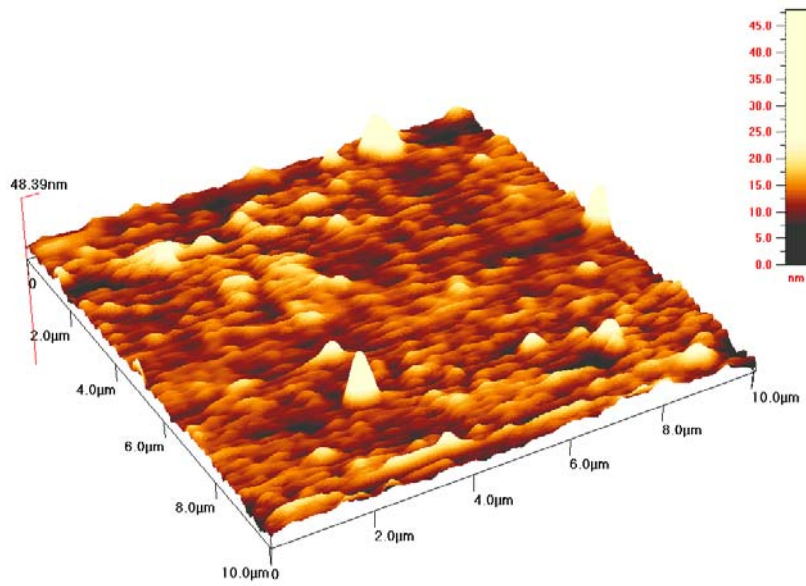
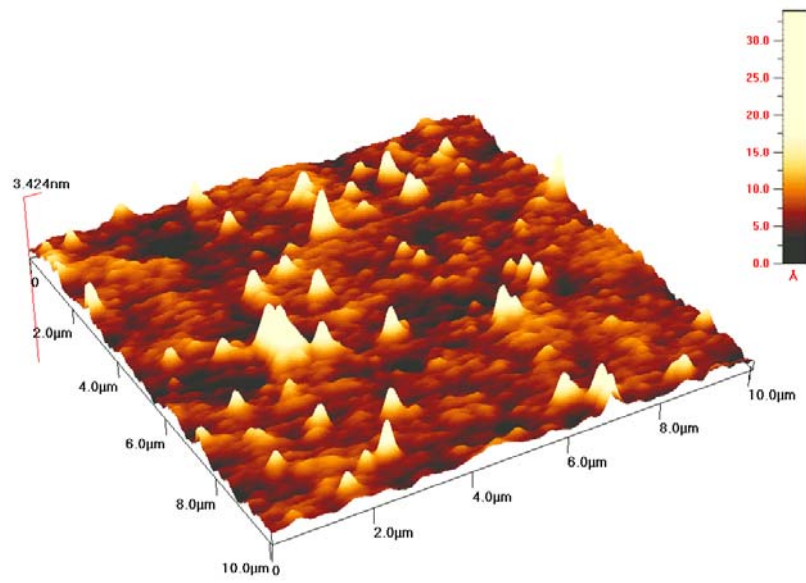


Figure 4.21. AFM images of a) pure PVA film, (b) PVA-g-SOMAP film

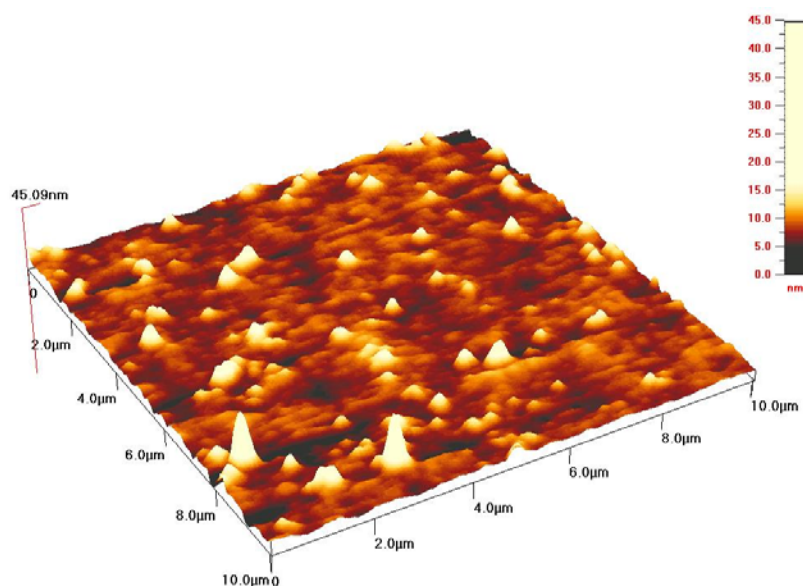


Figure 4.22. AFM image of pure PVA film waited in toluene

4.7. Optical Microscopy Results

PVA-g-SONCO films could not be characterized by AFM due to the fact that their roughness values were too large for the AFM instrument. Thus, obtained films were investigated by optical microscopy with 500 magnification. The images obtained by optical microscopy are shown in Figure 4.23. PVA film has a smooth and non coloured surface while PVA-g-SONCO film has small dark coloured regions resulting from the grafting of SONCO onto the PVA film. Compared to SOMAP, SONCO has a tendency to graft in smaller clusters which are considerably thicker.

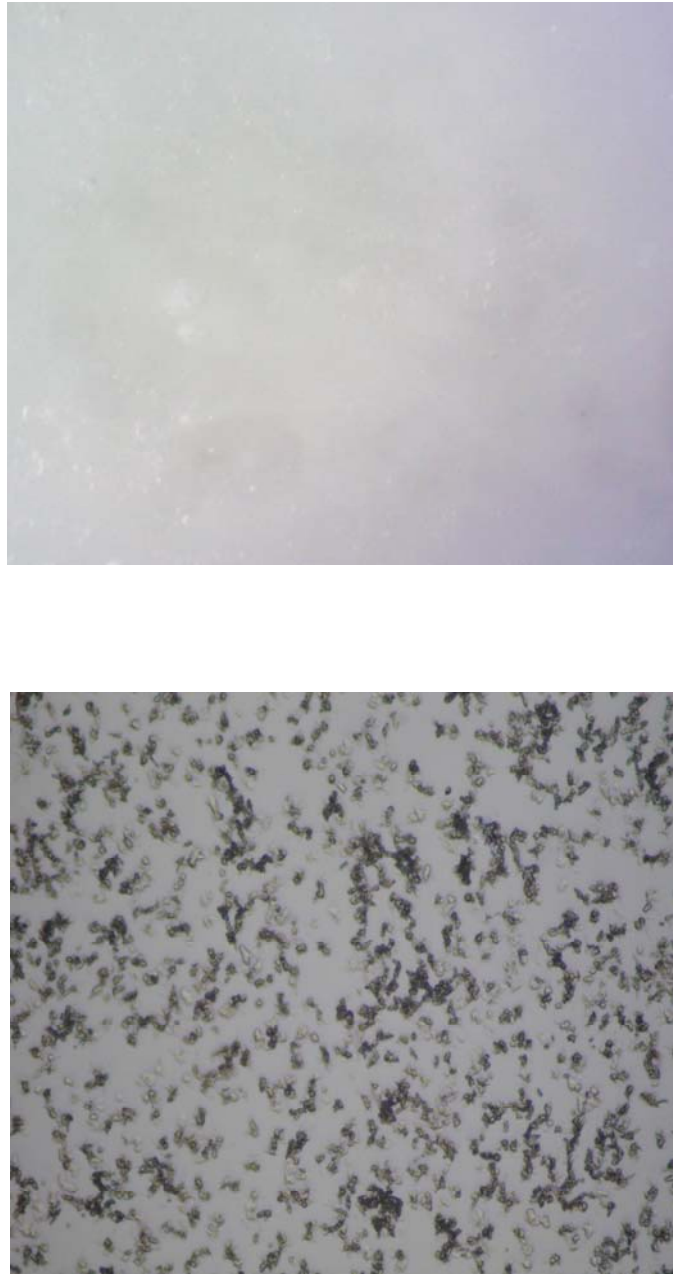


Figure 4.23. Optical microscopy images of a) pure PVA film, (b) PVA-g-SONCO film

4.8. Determination of Homogeneity of Films by a Colour Reaction

To determine the presence of PVA in a chemical formulation qualitatively, a colour reaction of PVA is used with one drop of iodine test solution and a few drops of boric acid solution. This gives a dark blue colour in the presence of PVA. This idea was applied onto PVA films in order to get qualitative information about the extent of grafting. Figure 4.24 (a), (b) and (c) show, respectively, the optical microscopy images of the pure PVA, PVA-g-SOMAP and PVA-g-SONCO film surfaces after the colour reaction. Pure PVA film was completely dyed blue. However, only the ungrafted regions of PVA-g-SOMAP film was dyed blue while the ungrafted regions remained undyed. Furthermore, PVA-g-SONCO film was not dyed at all indicating that essentially all PVA surface was grafted successfully with SONCO.

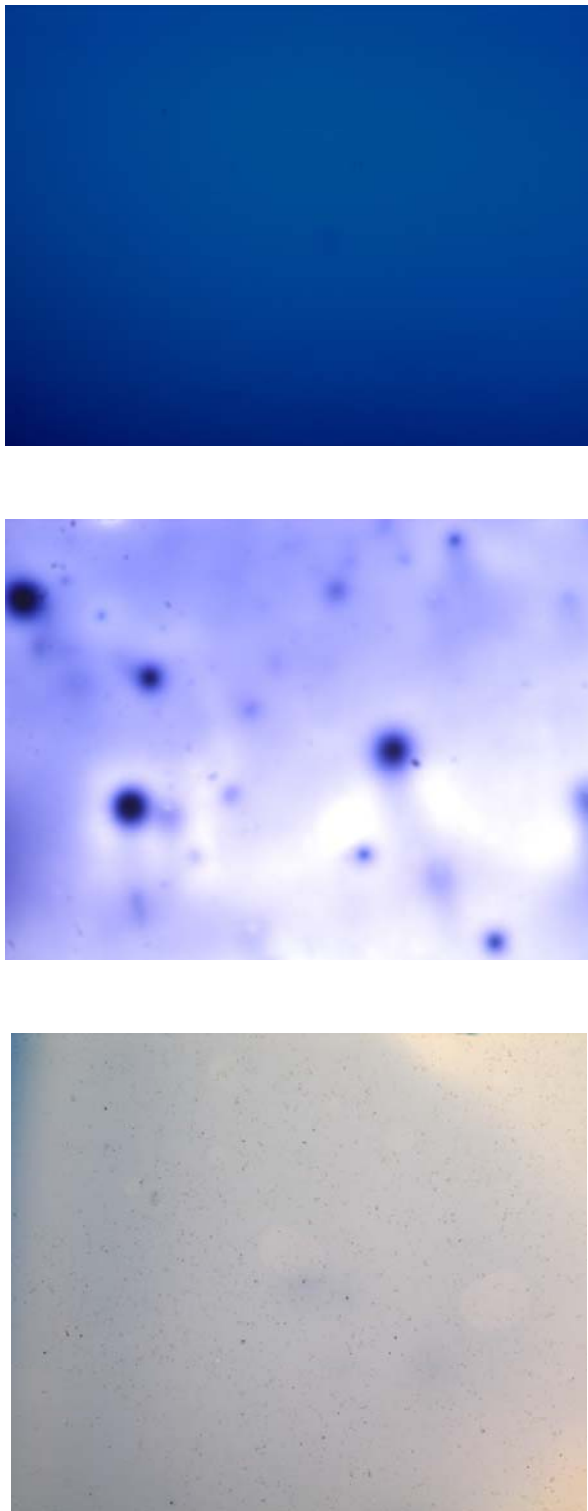


Figure 4.24. Colour reaction results of (a) pure PVA, (b) PVA-g-SOMAP, (c) PVA-g-SONCO

4.9. DSC Results

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. Studying phase transitions, such as melting, glass transitions, or exothermic decompositions is the main application of DSC.

In this study the T_g values of pure PVA and PVA-*g*-SOMAP or SONCO film samples were determined. Temperature scans were run from 0 °C to 160 °C at a heating rate of 10 °C/min. For each sample two runs were done and approximately the same T_g values were observed in both runs.

Figure 4.25 shows the DSC traces of (a) pure PVA, (b) PVA-*g*-SOMAP, and (c) PVA-*g*-SONCO films. The glass transition temperatures (T_g) of the SOMAP and SONCO grafted PVA films are lower than the pure PVA film due to the incorporation of the flexible triglyceride molecules onto PVA films. However, the difference between T_g values of pure PVA film and grafted films are very low because only the top of the surface was grafted while nearly 99 percent of the sample was pure PVA.

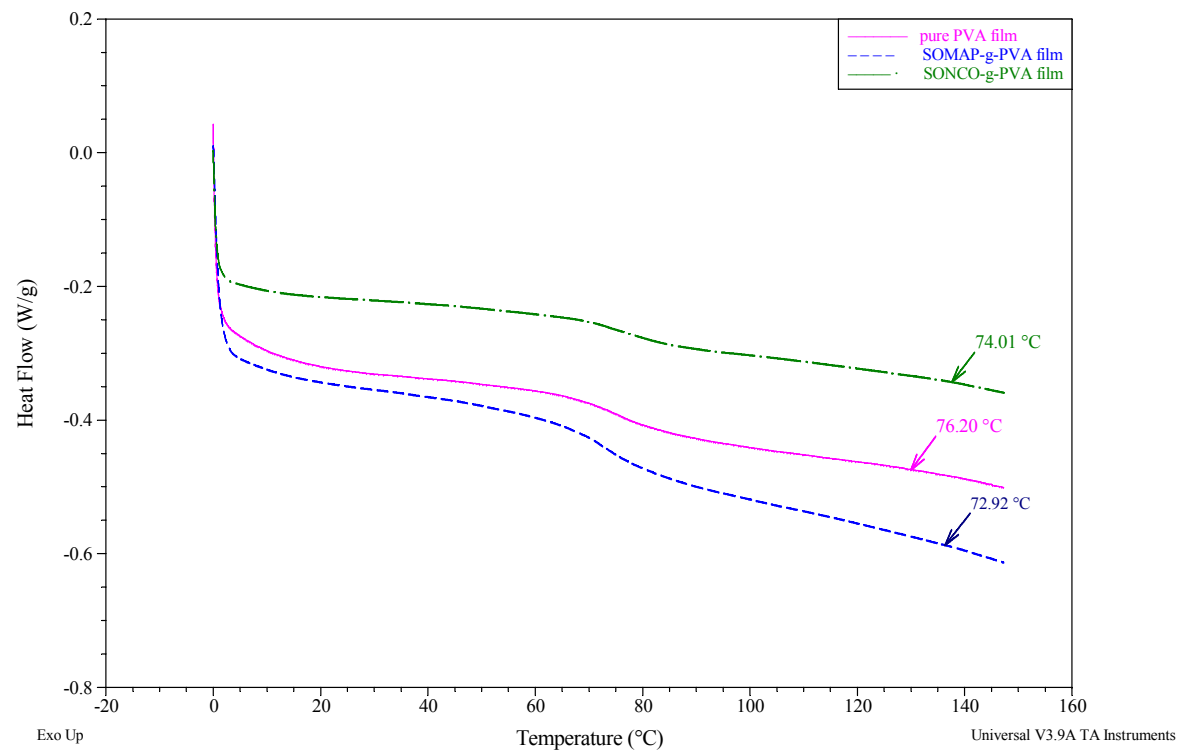


Figure 4.25. DSC traces of (a) pure PVA, (b) PVA-g-SOMAP, and (c) PVA-g-SONCO

5. CONCLUSIONS

Polyvinyl alcohol films were hydrophobically modified by the grafting reaction of maleinized or isocyanated soybean oil triglycerides onto their surfaces. ATR-IR and ^1H NMR confirmed the surface grafting reaction. The hydrophobicity of the surfaces was studied by water contact angle measurements and the surfaces obtained were characterized by AFM and optical microscopy. The grafting homogeneity of the surfaces was examined from the images taken from optical microscopy after colour reaction. Furthermore, the incorporation of soft, flexible soybean oil triglycerides on to the surface leading to the decrease in Tg values was confirmed by DSC.

For future work oxygen and water vapour barrier properties of the films obtained may be investigated.

The potential use of PVA surface grafting is intriguing. Preliminary reactions were carried out on PVA nanofibers using the same strategy which was applied to the PVA films. The PVA nanofibers used were prepared by electro spinning. If high density surface grafting can be achieved, then removal of the inside core of the PVA nanofiber by dissolving in water should produce tubes with extremely thin, nanometer thickness walls that have hydrophilic inner walls. Such devices may have interesting dialysis possibilities. Figure 5.1 shows the scheme.

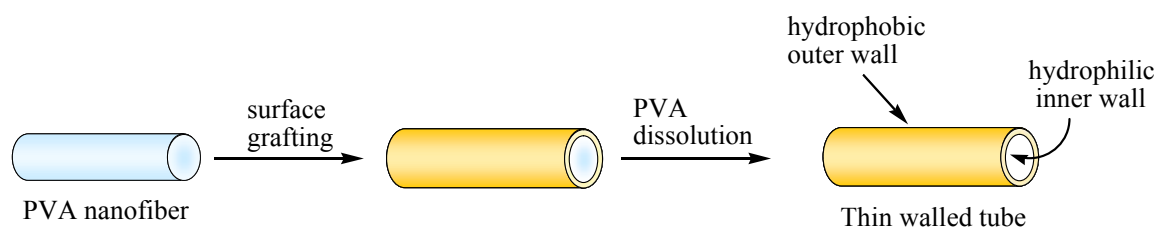


Figure 5.1. Possible application of the surface reaction on PVA nanofiber

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