POLYOLS MADE FROM VEGETABLE OIL AND THEIR APPLICATIONS

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by

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ABSTRACT

In the course of research, soybean oil was polymerized to form bodied soybean oil (BSBO) also termed heat polymerized soybean oil which was used to derive the epoxy bodied soybean oil – hydroxyl value # 193, BSBO/acetol – hydroxyl value # 72, BSBO/allyl alcohol, SBO/acetol – hydroxyl value # 78, SBO/allyl alcohol polyols. These polyols have reasonable properties in terms of the hydroxyl content, acid value and are produced through inexpensive means. The applications of the above synthesized materials have been studied in part in making of foams, ion exchange materials and resins/composites etc..

Membrane electrode assemblies for the proton exchange membrane fuel cells were developed and tested for their performance in the proton exchange membrane fuel cells. The performance was reasonable based o the amount of catalyst loading at the cathode and the anode.

THESIS FORMAT

The research can be divided into two topics. The first topic is on polyol production from vegetable oil and their applications which are described in detail in Chapters 1-6. The second topic is on making of membrane electrode assemblies for proton exchange membrane fuel cells which is described in detail in chapter-7.

DISCLAIMER

This thesis contains guidelines, procedure and protocols for performing reactions and testing the products synthesized.

The author in no way implies that these procedures are described in complete details or are safe to reproduce. When performing chemical synthesis or analyzing products, there is no substitute for good judgment and thorough background research on hazards and toxicities.

A list of possible hazards and hazardous environments when synthesizing and testing products described in the thesis include, but are not limited to:

Mechanical failure; High pressures; High temperature; High voltage, Chemical toxicity, Chemical reactivity, Chemical explosion, Acid burns and Toxic vapors

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1 CHAPTER 1

Introduction to bio-based materials

1.1 Introduction

In the recent years there has been a growing interest in the development of bio-based products that can reduce the widespread dependence on the petroleum feed stocks. Petroleum is a nonrenewable resource, the inevitable depletion of petroleum resources coupled with the high cost has prompted researchers to develop alternatives to petroleum based products from biomass.

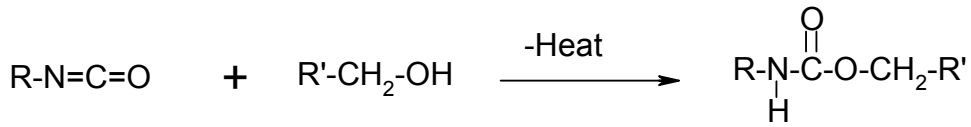
The polyol commodity market is driven by applications such as reacting the hydroxyl moieties of polyols with isocyanate reactive groups to form urethane products. Polyols are usually made from petroleum-based feed stocks and have widespread applications in the making of polyurethane foams, resins, composites, and adhesives. Polyol usage in USA is approximately 3 billion pounds/year, and worldwide polyol usage is approximately 10.2 billion pounds/year. The market potential for bio based polyol in USA is 700–900 million pounds/year, and the global market potential for bio-based polyols is approximately 2.1-2.7 billion pounds/year.

In the above context, modification of the soybean oil was carried out for the production of bodied soybean oil (BSBO), epoxidized bodied soybean oil

(EBSBO), SBO/acetol, SBO/allyl alcohol, BSBO/acetol, and BSBO/allyl alcohol to replace either in part or completely the petroleum based polyols.

1.2 Polyurethanes

Polyurethanes are chemically complex polymeric materials, usually formed by the reactions of liquid isocyanate components with liquid polyol components. The polyurethane polymer-forming reaction occurs as shown by equation 1.



Isocyanate Alcohol Urethane (1)

Polyurethanes, the end products resulting from the reaction of alcohol and isocyanate, have widespread applications in automotive parts, coatings, adhesives and other infrastructure uses. Polyurethanes based on renewable resources can be prepared by reacting the polyol made from plant oil and an isocyanate. Polyurethane production in USA was 6,692.5 million pounds in 2004[1].

1.3 Need for vegetable oil based products

Total vegetable oil production of USA was approximately 11.8 million metric tons in 2003 and is projected to be 12.3 million metric tons in 2008[2]. In 2005 the total oil production as per the forecast is 10 million metric tons of which soybean oil accounts for 8.8 million metric tons. The soybean oil makes up to 80% of the edible oil consumption[3]. Most of the remaining 20% are used in industrial oil products, and about 0.61 million metric tons are exported[4]. The average price of

soybean oil is 22-25 cents/pound

In view of the large volume of soybean oil production in the U.S. and production capacity increases that exceed the rate of growth of the edible oil applications, it was essential to develop alternate uses for soybean oil. Most especially, this is to the benefit of the farmers so as to secure good demands for soybeans and improve the profitability of soybean farming.

1.4 Soybean oil

Vegetable oils are primarily water insoluble, hydrophobic substances that are made up of one mole of glycerin and three moles of fatty acids, so called triglycerides. Fatty acids vary in carbon chain length and the number of unsaturated bonds. Table 1.1 shows the typical fatty acid composition of common oils and Table 1.2 shows the properties and composition of soybean oil.

Table 1.1: The typical fatty acid composition of common oil sources[5]

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
Crambe	2.07	0.70	2.09	0.80	1.12	18.8	58.5	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.3	0.00	31.9	0.93
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

Table 1.2: The properties and composition 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)	0.922-0934
Fatty Acid composition, wt%	
Palmitic acid	2.3-10.6
Stearic acid	2.4-6.0
Oleic acid	23.5-30.8
Linoleic acid	49.0-51.5
Linolenic acid	2.0-10.5

Oil seed and fruits are processed to obtain crude oil. These oils contain free fatty acids, phospholipids, carotenes, sterols, water, odorants and other impurities. Even refined oils contain small amounts of free fatty acids.

Soybean oil is a preferred feed stock for developing new industrial oil product applications due to the overall production quantities and the chemical composition of the vegetable oil. Because soybean oils are relatively unreactive in polymer formulations, they must be functionalized.

The targeted soybean oil moieties for converting to hydroxyl are the carbon-carbon π-bonds of the unsaturated free fatty acids in soybean oil (linoleic and linolenic acids). Several soy-based polyols are already on the market, including SoyOyl^{R} developed by Urethane Soy Systems Company which is a 100% biobased polyol made from renewable, agricultural resources[7].

A common approach for producing currently soy-based polyols includes initially epoxidizing the soybean oil. The epoxidized soybean oil is further reacted in order to convert the epoxy groups to hydroxyl groups, in general by an acid catalyzed ring opening reaction with methanol, yielding methoxilated polyol, or with water.

In addition to applications with urethanes, the epoxidized soybean oil is itself, a commodity chemical used as a plasticizer in the PVC industry.

Current polyols and polyurethanes are produced from petroleum feed stocks. The petroleum crude is currently imported to a great extent from the OPEC countries and this dependence can be greatly reduced through the development of alternatives that are bio-based. The concerns of disposal of the products made from materials of petroleum origin at the end of their useful life have also prompted the researchers and the government to look at alternative materials that are renewable and also biodegradable.

Biobased materials are agricultural products used in a variety of commercial/industrial applications, thereby harnessing the energy of the sun to provide raw materials. Bio-based products include: fuels, energy, chemicals, construction materials, lubricants, oils, automotive supplies, and a host of other products. The government has set the goal of tripling the U.S. use of bioenergy and bio-based products by the year 2010. Meeting this goal could create an additional $15-20 billion a year in new income for farmers and reduce the environmental impact associated with annual greenhouse gas emission by an amount equal to as much as 100 million metric tons of carbon[8].

The biopolymers or bio-based products are biodegradable indicating these products degrade over a period of time through the action of enzymes and or chemical decomposition associated with living organisms (bacteria, fungi, etc.) and their secretion products and thereby eliminating solid waste disposal problems associated with traditional petroleum-derived products.

1.5 Challenges involved in industrialization of soybean-derived products

Raw material availability, product economics and its functionality will be the critical factors in determining the successful commercialization of new uses for soybean oil. Currently, many of the soybean derived products target replacement/substitution of petroleum based products, such as fuels and polymers. The 2005 global production of petroleum is estimated at approximately 4.2 billion metric tons[9] compared to global vegetable oil production is 114 million metric tons of which soybean oil accounts for 34 million metric

tons[10]. It is obvious that at the current production levels, soybean derived products could at best, only supply a few percent of existing petroleum products.

1.6 Background literature

U.S. Patent Application # 20040230009 describes a process a making a vegetable oil based polyol wherein two steps are involved: 1) SBO is epoxidized as per the conventional methods through reacting the SBO with organic Peracids. 2) The epoxy soybean oil thus obtained is reacted with carbon dioxide to form carbonated vegetable oil through the conversion of epoxide ring to a five membered cyclic carbonate ring. The polyol thus obtained is used in the making of non isocyanate polyurethane foams through reacting the polyol with amine having at least two functionality. In this process essentially two steps and additional reagents are involved which adds to the cost of producing the polyol. To the credit of this approach, the resulting polyurethane foam has good properties as claimed in the patent application.

Soybean oil epoxide has been used as an intermediate in multiple synthesis schemes. Oxirane ring opening of epoxidized soybean oil has been performed hydrochloric acid, hydrobromic acid, methanol, and hydrogen[11]. In Petrovic's group, commercial-grade epoxidized soybean oil having an oxirane oxygen content of 6.9% was used as a starting material. This intermediate was then 1) reacted with HCl in the presence of acetone (solvent) to obtain a soy-HCl polyol having an -OH value of 197, 2) reacted with HBr in the presence of acetone (solvent) to obtain a soy-HBr polyol having an -OH value of 182, 3) reacted

with H_2 in the presence of in the presence of isopropanol (solvent) and raney nickel catalyst to obtain a soy-H_2 polyol having an –OH value of 212, and 4) reacted with a mixture of methanol, water, isopropanol in the presence of a fluoboric acid catalyst to obtain soy-met polyol having an -OH value of 199 were synthesized. In these syntheses there were at least two reaction steps, additional reagents, and solvents. The overall processing costs are high which detracts from the advantage of having good properties judged based on the hydroxyl values reported.

Another product currently on the market is referred to as blown soybean oil. This polyol has application in the making of polyurethanes, flexible foam in particular, and is synthesized by blowing a stream of oxygen through the oil which is heated to a temperature of 135^{o}C. After 3 hours of this reaction, the temperature is reduced to 75^{o}C[12]. Though this procedure of inducing the functionality on to the soybean oil seems economical, there are certain drawbacks to this product. For the same increase in molecular weight the bodied soybean oil has less viscosity compared to the blown soybean oil—for the molecular weights of 4600 the viscosity of blown soybean oil was 1 Pa.s and that of bodied soybean oil was 0.24 Pa.s, as per the observations made in cited literature[12] .

The soybased polyols have also been prepared by a catalytic ozonolysis process wherein the ozone was passed through a solution of soybean oil and ethylene glycol in the presence of an alkaline catalyst. In this process ozonides reacted with hydroxyl group of the glycol to form an ester linkage with a terminal hydroxyl group[13]. In this process the resulting product has a catalyst present which might

not be desired for the urethane reaction resulting in the foam product as it is very sensitive to components involved in the foaming reaction.

U.S. Patent Application # 20030191274 describes a process of making a vegetable-oil-based polyol where in two stages are involved: 1) In the first step glycerin is heated and to this saccharide compounds (fructose or cane sugar) are added slowly until saturated and transesterification occurs between the two. 2) The resulting ester is reacted with blown soybean oil with heating and thus allows for the transesterification between the two resulting in final product with increased hydroxyl functionality. There are a total of 3 steps involved in the process of the preparation of this polyol 3) synthesis of blown soybean oil and the other steps as listed above 1) and 2) respectively. This leads to increased costs.

Hydroformulation is also used in the preparation of polyols. These are prepared by converting the carbon-carbon π-bonds in soybean oil to aldehydes through hydroformylation using either rhodium or cobalt as the catalyst. The aldehydes are hydrogenated by raney nickel to alcohols, forming a triglyceride polyol[14]. Multiple reagents and catalysts are involved in the synthesis which must either be removed or accounted for in the final foam formulation.

1.7 Research emphasis of this thesis

The research emphasis of this thesis is on identifying new soy-based polyol (or B-side) syntheses approaches that add highly functional moieties with a minimum number of reaction steps. During the research, soybean oil was polymerized to form bodied soybean oil (BSBO) which was used to derive the epoxy bodied

soybean oil, BSBO/acetol, BSBO/allylalcohol, soybean oil(SBO)/acetol, and SBO/allyl alcohol polyols. These polyols have reasonable properties in terms of the hydroxyl content and are produced through inexpensive means.

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2 CHAPTER 2

HEAT POLYMERIZED VEGETABLE OIL

2.1 Abstract

Polymerization of soybean oil was carried out primarily to increase the molecular weight. The resulting bodied soybean oil was utilized in the making of polyols. An application would be to body/heat polymerize the soybean oil prior to functionalization in preparing a polyol for use in the making of urethanes. A series of screening reactions indicated that a reaction temperature of 330^{o}C was effective for bodying without undue oxidation in the absence of the catalyst. By varying the duration of the reaction a broad range of viscosities, product darkening, molecular weights and iodine values were achieved. Gel permeation chromatography (GPC) analyses of the products indicated the bodied soybean oil was a polydisperse mixture. Approximately 51.5% of the soybean oil reagent remained as monomer while 48.5% had a molecular weight of about 7800 as a result of heat bodying of soybean oil for duration of 1 hour at 330^{o}C.

KEY WORDS: Polymerization, Polyols, Viscosity, Iodine Values.

2.2 Introduction and background

Petroleum shortages in the 1970s led the way into looking for alternative and renewable materials to replace the petroleum based products. One industry which particularly took note of this is the printing industry which started research on the development of alternative and renewable materials for preparation of printing ink vehicles and ink formulations. The inherent properties of vegetable oils such as being nonvolatile and biodegradable made them a good choice for further product development.

The vegetable oil-based inks vehicles typically are prepared by one of two methods. In the first method, vegetable oils are heat-polymerized at a constant temperature in a nitrogen atmosphere to a desired viscosity. In the second method the heat polymerization is permitted to proceed to gel point, and this gel is mixed with the vegetable oil to get a desired viscosity[1,2,3] .

Detailed studies for the reactions involved in the heat polymerization have not been reported. Major reactions include double bond migration and other isomerizations, transesterifications, ring formation, and polymerization. During heat bodying, conjugated dienes are formed by bond migration in polyunsaturated fatty acids. These can form 6-membered rings by intermolecular reaction with double bonds of other fatty acids. As heating continues, other conjugated groups would add to the previously formed unsaturated ring structure[4] . Triglycerides, consisting of three polyunsaturated fatty acids at which addition may occur, introduce the possibility of forming very complex, highly branched

structures and very large molecules[5].

Soybean oil is used in the current study. Here we discuss the effect of reaction time at the temperature of 330^{o}C on the viscosity, molecular weight and iodine value (measure of unsaturation).

2.3 Experimental methods

2.3.1 Materials

Soybean oil of RBD grade (refined, bleached, deodorized) with an iodine value of 125-130 (Hanus) was obtained from a local supplier. Carbon tetrachloride, sodium thiosulfate solution (0.1N), potassium iodide, starch indicator and Wijs solution (for iodine number titrations) were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade nitrogen was obtained from Praxair (St. Louis).

2.3.2 Experimental setup

All reactions were carried out in a Parr reactor of 2 liter capacity equipped with stirrer, heater, thermocouple and a sample port for liquid sampling. The temperature of the reactor was controlled by Omega controller. The reactor was purged continuously with nitrogen and heated to the desired reaction temperature. Depending on the desired molecular weight and viscosity the reactants are kept at the desired temperature for a known duration of 30min, 45min, or 1hr. The speed of the stirrer was set constant at 550 rpm throughout the reaction. All reactions were conducted at a temperature of 330±3^{o}C.

Preliminary studies were conducted in the glassware which was insulated and the desired temperature was achieved 330±3^{o}C with the aid of the heater/stirrer with continuous mixing carried out with the aid of magnetic stir bar. The products obtained were darkened possibly due to the oxidation reactions occurring due to being in contact with air. As a result the system was later changed to a Parr reactor for further studies.

Table 2.2: Summarized the change in iodine value with time for the bodying reaction.

A flow reactor was used for the continuous production of bodied soybean oil by controlling the flow in order to achieve the desired residence time. It was found during the preliminary runs that the product degraded based on the dark color of the product. It was then decided to have the system equipped with stirring and continuous nitrogen purge to remove the volatiles. The volatiles were thought to promote degradation.

The volatiles were in part comprised of decanoic acid (4.22%), palmitic acid (21.21%), linoleic acid (27.10), oleic acid (24.25), stearic acid (8.7) and cis-9-tricosene(2.91%), where the % is the wt% of the by products collected as per the cited paper .

Once the system was changed to the Parr reactor equipped with stirrer, heater, and continuous nitrogen purge a final product was obtained with a lighter color.

It was presumed that the presence of high concentrations of volatiles consisting of fatty acid components as mentioned above was the cause of darkening of the

product. The presence of free fatty acids is not desired from the view that this would increase the acid number of the final product. Free fatty acids are also counter-productive to the effort to polymerizing the polyol.

2.3.3 Method of analysis

Polymerized soybean oil samples were analyzed for the decrease in the amount of unsaturation present in the soybean oil. In olefinic polymerization, two carbon-carbon π-bonds react to form a molecular linkage and single carbon-carbon π-bond, and so, the extent of reaction can be followed by following the decrease in unsaturation.

The method to determine the iodine value is described as follows: The samples of polymerized soybean oil bodied for different durations were weighed and transferred such that there will be an excess of wijs solution of 125±25% for normal or conjugated oils into the Erlenmeyer flasks of 500ml capacity. To this, 20 ml of carbon tetrachloride solvent (HPLC grade) was added and 25 ml of wijs solution were transferred into each flask. Two blank samples were prepared without the sample oil. The flasks with the contents were stoppered and swirled to ensure an intimate mixture is formed, which were then stored in a dark place for 1hr at a temperature of 25±5^{o}C. The flasks were removed from storage and to this 20ml of KI solution and 100ml of water were added. The contents of the flask were titrated with $Na_2S_2O_3$ solution by adding it gradually with constant and vigorous shaking until the yellow color has almost disappeared. To this 1 to 2 ml of starch indicator solution was added and the titration was continued until the

blue color disappeared.

To determine the molecular weight and other properties the samples were sent to Viscotek corp where the samples were analyzed using triple detector GPC/SEC consisting of concentration detector (usually a refractive index detector), an online dilute solution viscometer, and a molecular weight sensitive (light scattering) detector.

The dynamic viscosity of the samples measured in centipoise (cP) was determined using a Model RS100 Rheometer made by Haake – Thermoelectron (Newington, New Hampshire) equipped with a sensor cone and plate 35mm, and 4 degree cone. The distance between the plates was 0.14 mm, speed of rotation was RPM- 50, and duration was 60 sec. The data were collected through an automated data acquisition system utilizing the software RheoWin Pro 297.

The acid values of the soybean oil heat polymerized for durations of 0.5, 0.75 and 1 hour respectively were determined in accordance with AOCS official method[6].

2.4 Results and discussion

The primary goal of this study was to increase the molecular weight of vegetable oil for use in the making of B-side components (polyols) in urethane formulations. Higher molecular weight B-side components can lead to larger amounts of the B-side component in the urethane formulation. The viscosity was measured as a function of polymerization increases with time at the heat bodying temperature of 330±3^{o}C.

As the duration of heating was increased, the ratio of the polymerized oil to unpolymerized oil increased. These observations are readily shown by the plots in Figure 2.5, Figure 2.6, and Figure 2.7[7].

Figure 2.4shows the plot of polystyrene sample used as control (Sample = RA Control) in the analysis of polymerized soybean oil samples.

Figure 2.5 shows the plot of soybean oil heat polymerized for a duration of 1 hour at a temperature of 330^{o}C (Sample = RA # 1).

Figure 2.6 shows the plot of soybean oil heat polymerized for a duration of 2 hour at a temperature of 330^{o}C (Sample = RA # 2).

Figure 2.7 shows the plot of soybean oil heat polymerized for a duration of 3 hour at a temperature of 330^{o}C (Sample = RA # 3).

In Figure 2.4, Figure 2.5, Figure 2.6, and Figure 2.7 peak 1 represents the polymer portion and peak 2 represents the monomer portion in the given sample. The Refractive index (RI) of the sample is shown as red line in the plot (RI = Red) and gives the percent area of the polymerized part and the monomer part. The right angle light scattering (RALS) detector response is shown as green line in the plot (RALS = Green) and gives the absolute molecular weight of each elution fraction. The online dilute solution viscometer response is shown as blue line in the plot (DP = Blue) and gives the intrinsic viscosity and hydrodynamic radius of each elution fraction.

From the plots it was inferred that as the duration of heat polymerization

increased the percent area of peak 1 increased and also the molecular weight of the samples increased. As the polymer peak (peak 1) grew to higher molecular weights, its effect on peak 2 diminished resulting in quite consistent molecular weight values for peak 2 among samples RA # 1, #2, #3.

In Table 2.1: MW, is absolute molecular weight, IV is the intrinsic viscosity, Rh is the hydrodynamic radius, % Area is the percentage of concentration (or mass) of the injected volume, and dn/dc is the refractive index increment. The table summarizes the properties discussed above for each fraction of every sample.

2.4.1 Effect of reaction duration on viscosity

A plot of the viscosity vs time is shown in Figure 2.1. From the plot it can be observed that the viscosity increases at a slower rate up to 2 hours and then there is a steep increase from 2 to 4hrs. Upon further polymerization the material tends to become solid. In the initial stages of the heat polymerization conjugated dienes are formed by bond migration in polyunsaturated fatty acids. These can form 6-membered rings by intermolecular reaction with double bonds of other fatty acid. During the later stages of the heat polymerization process (i.e. 2 to 4 hour duration) the other conjugated groups can add to the previously formed unsaturated ring structure[5]. This explains why the viscosity is very high as the duration of the reaction was increased from 2 to 4 hours as compared to that at 0 to 2 hour duration.

2.4.2 Effect of viscosity on the molecular weight

A plot of the absolute molecular weight vs viscosity is shown in Figure 2.2. The molecular weight was determined using the triple detector gel permeation chromatography (GPC) by Viscotek Corporation. From the plot it can be observed that the molecular weight variation with viscosity is almost linear. The molecular weight increase with the increase in viscosity can be explained as follows: Triglycerides, consisting of three polyunsaturated fatty acids at which addition may occur, introduce the possibility of forming very complex, highly cross-linked structures and very large molecules.

2.4.3 Effect of reaction duration on iodine value

A plot of iodine value vs time is shown in Figure 2.3 wherein the iodine value was determined per the ASTM standard[8]. From the plot it can be inferred that the iodine value decreases sharply during the first hour of the heat polymerization process and then decreases at a constant slower rate up to 4hrs of the heat polymerization process.

During the first 1 hour of the heat polymerization the volatile byproducts resulting from the process contained no linolenic acid and 24.16-28.31% of linoleic acid in the by-product as determined by Erhan et.al.. These acids comprise 7% and 53% of the free fatty acid content in the soybean oil, respectively. This indicates that the more reactive linolenic and linoleic acids are consumed at an early stage of an heat bodying process there by resulting in drastic decrease in iodine value during the first 1 hour of the heat polymerization process. In the subsequent

hours of the heat polymerization process other free fatty acids (i.e. oleic acid) under go the polymerization reaction to produce polymeric materials in the subsequent hours of the heat polymerization process. These “other” fatty acids have a lower reactivity as a direct or indirect result of multiple carbon-carbon π-bonds—this explains the decrease in the rate of reduction of iodine values during the subsequent hours of polymerization reaction .

2.4.4 Effect of reaction duration on acid value

The acid value of the soybean oil heat polymerized for duration of 0.5, 0.75 and 1 hour were determined to be 4.18, 5.4 and 5.5 mg of potassium hydroxide necessary to neutralize fatty acids in 1gram of above samples respectively. It can be observed that the duration of the polymerization reaction had no effect on the presence of residual fatty acid content in the products obtained indicating that with stirring coupled with nitrogen purge is instrumental in driving away the free fatty acids in the form of volatiles.

2.5 Conclusion

Correlations between the molecular weight, viscosities, and iodine values of heat bodied soybean oil qualitatively were established. These correlations provided a useful tool to monitor the bodying process and provided insight into the mechanisms involved in the bodying of soybean oil.

The quality of the bodied soybean oil was evaluated both by its color and its acidity. Poorer product was darker in color. A nitrogen purge was crucial to minimize contact with oxygen and reduce color. It is hypothesized that the

nitrogen purge and stirring were instrumental in removing volatile components and the removal of these volatile components help to maintain low color.

About 50% reduction in iodine value was achieved during the first hour of the bodying process at 300°C while during the next 3 hours of the bodying process there is only about an additional 15% reduction in iodine value. The change in reactivity was believed to be due to both the 2^{nd}-order nature of the bodying process (2^{nd} order in carbon-carbon π-bonds) and the more reactive nature of some of the carbon-carbon π-bonds in the bound linolenic and linoleic acid groups.

The viscosity of the material heat polymerized for one hour is about 4 times more viscous compared to the starting material. The viscosity after 2, 3, and 4 hours of bodying were 22, 185, and 540 times more viscous than the starting material respectively.

The acid value remained constant at approximately 5 in comparison to approximately 4 in the soybean oil indicating the near absence of free fatty acids which is essential for its usage in synthesizing polyols, as high acid values result in poor quality urethane products.

The molecular weight of the material polymerized for 1 hour is about 5 times more while that of the 3 hour sample is 100 times more compared to the starting material. About 51.5% of the soybean oil remained as monomer after one hour while 19.2% remained as monomer aster 3 hours.

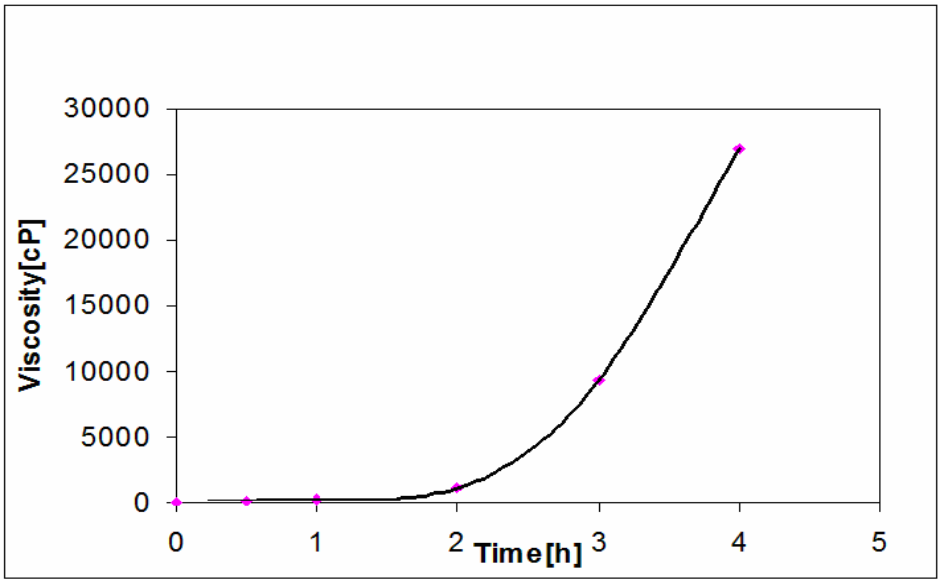

Figure 2.1: The variation of viscosity with the time for which the oil is heat polymerized at 330^{o}C.

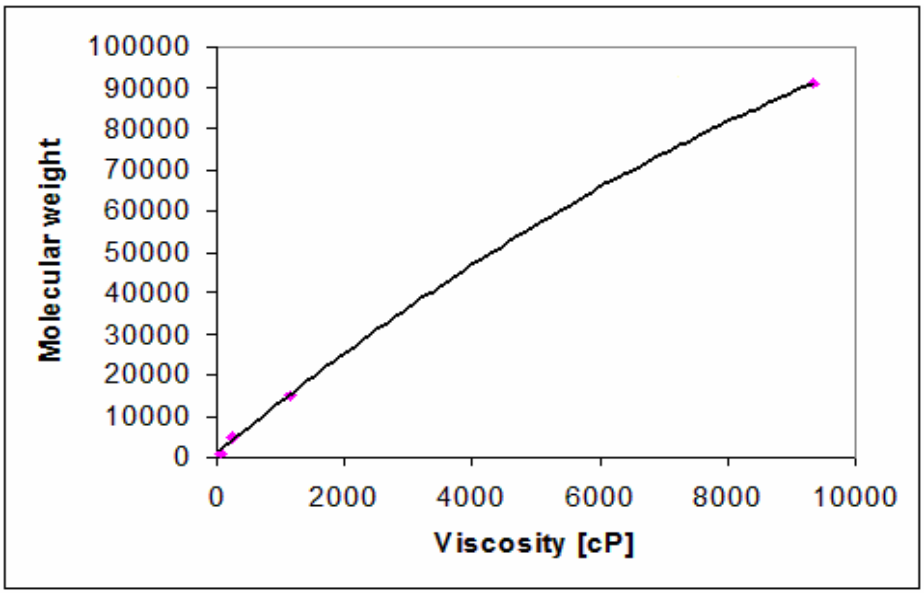

Figure 2.2: The plot of change in molecular weight with viscosity as a result of heat polymerizing the soybean oil at 330^{o}C for varying durations.

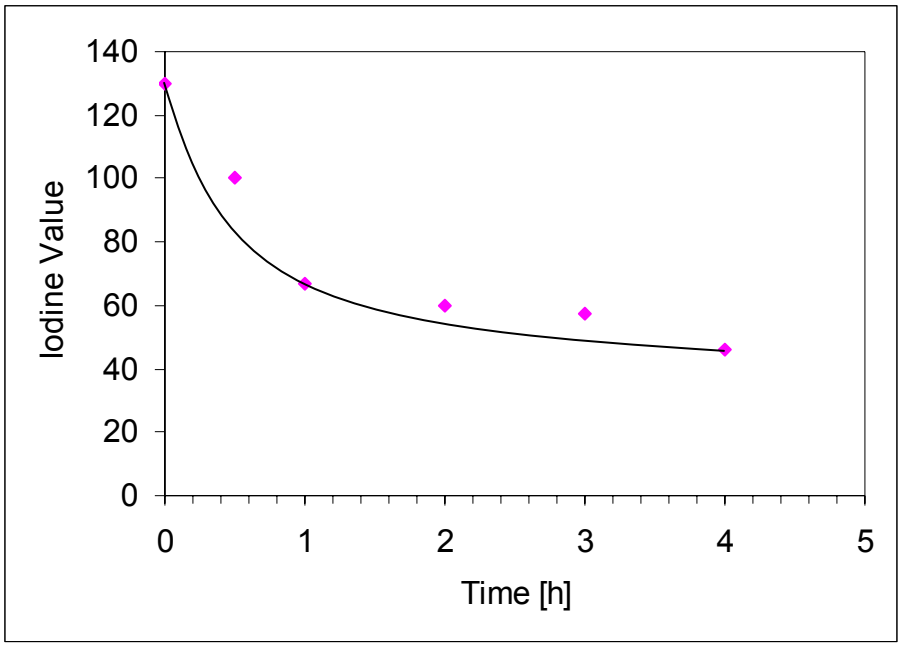

Figure 2.3: The plot of change in iodine value (measure of unsaturation) with time as a result of heat polymerizing the soybean oil at 330^{o}C.

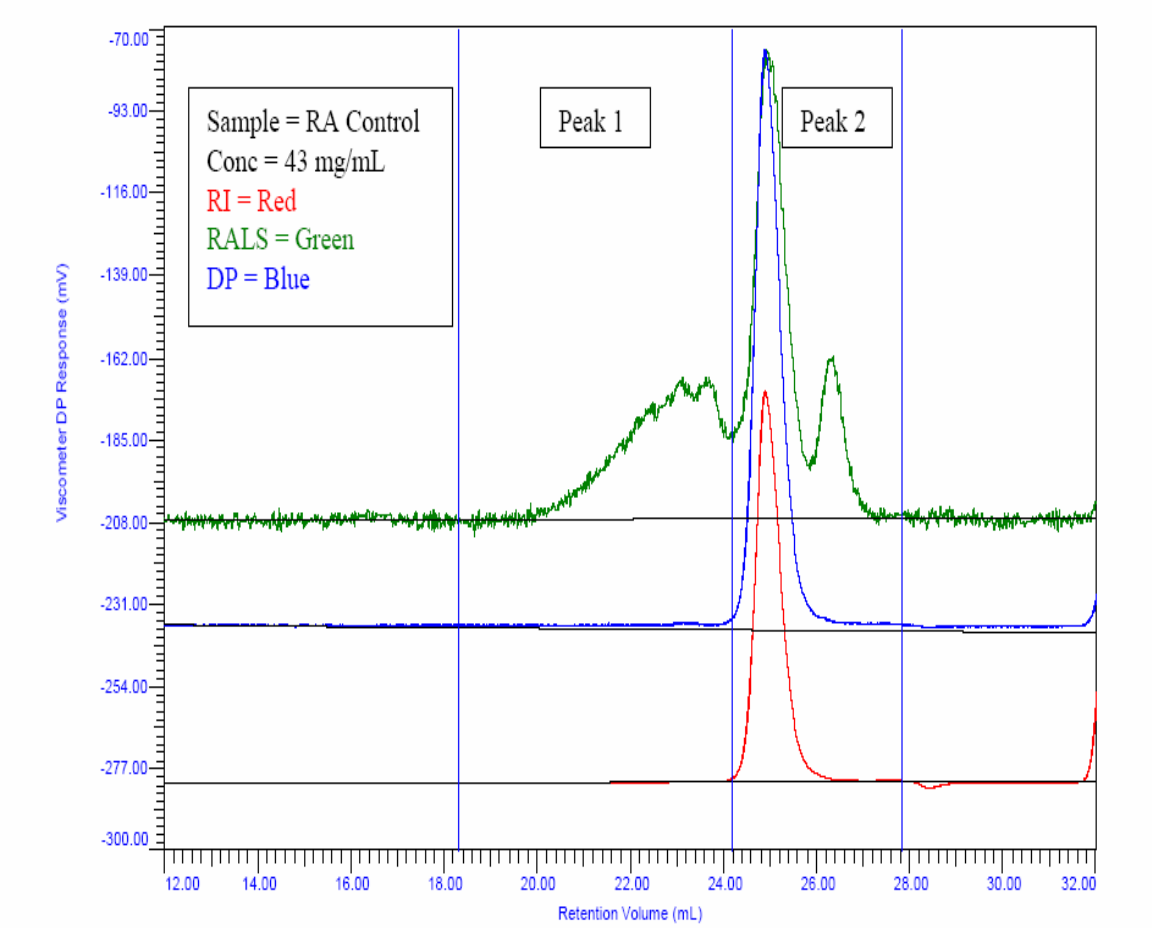

Figure 2.4: The separation of polymer part (peak 1) and the monomer part (peak2) of the polystyrene compound (control).

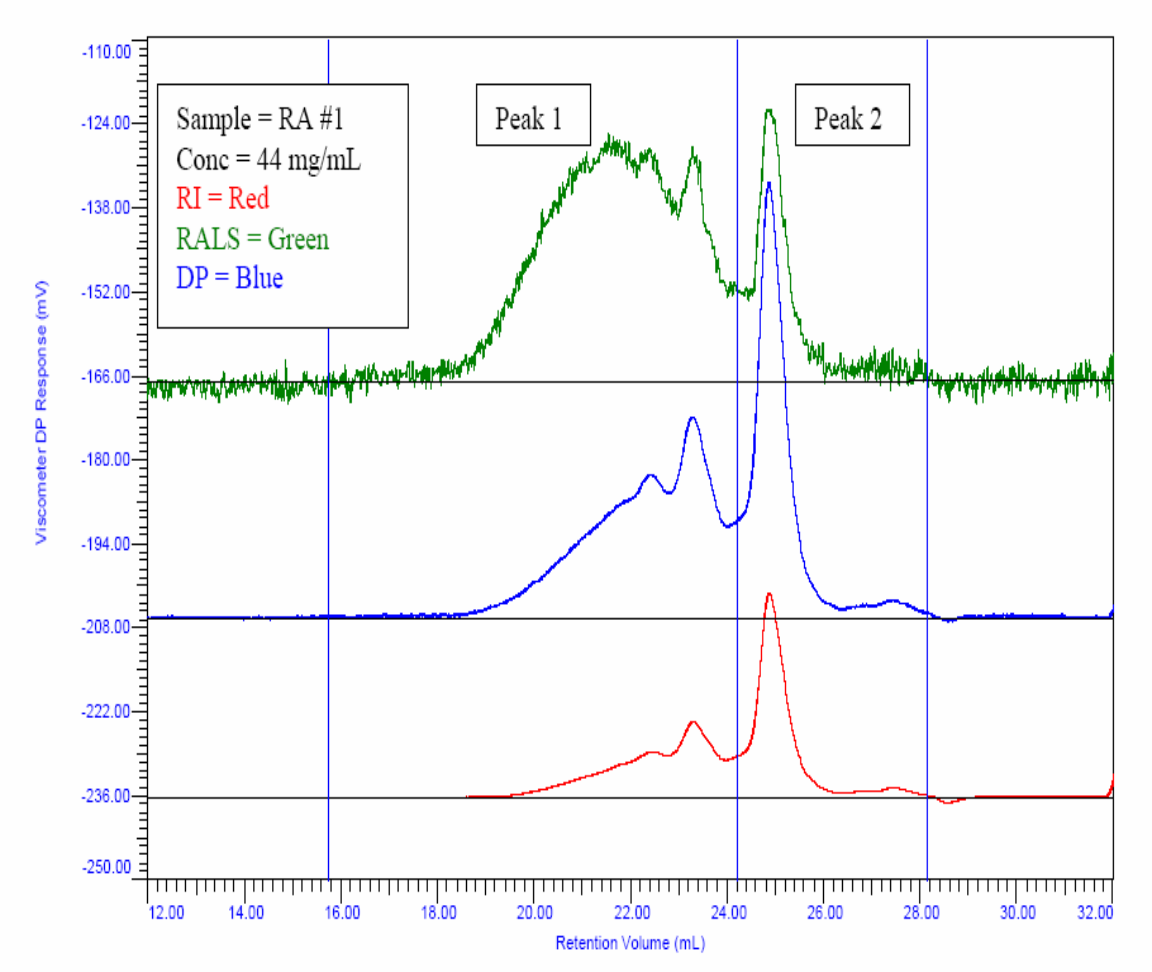

Figure 2.5: The separation of polymer part (peak 1) and the monomer part (peak 2) of the soybean oil heat polymerized for duration of 1hour at 330^{o}C.

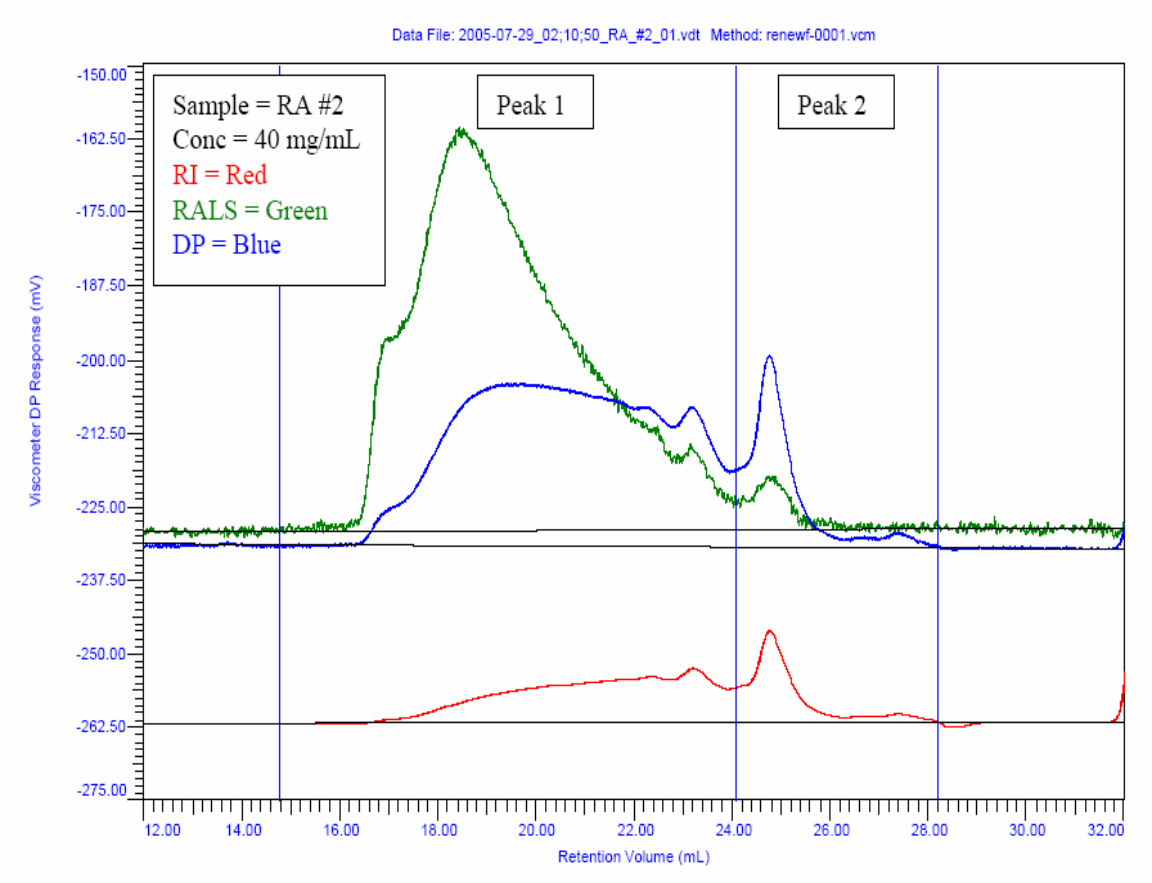

Figure 2.6: The separation of polymer part (peak1) and the monomer part (peak 2) of the soybean oil heat polymerized for duration of 2hour at 330^{o}C.

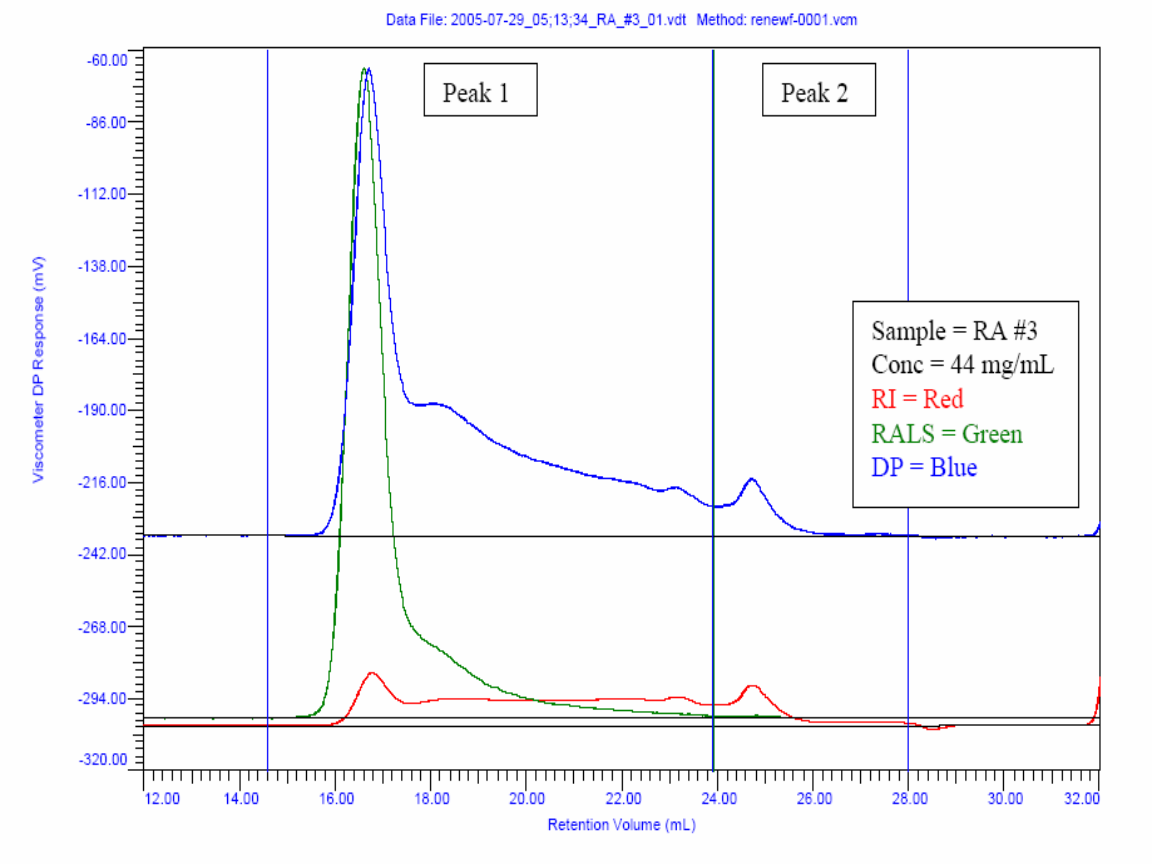

Figure 2.7: The separation of polymer part (peak 1) and the monomer part (peak 2) of the soybean oil heat polymerized for duration of 3hour at 330^{o}C.

Table 2.1: Summary of the properties (Molecular weight, Intrinsic viscosity, Hydrodynamic radius and the concentration of each fraction in a given sample represented as % Area) of the polymerized samples are given below.

	Peak 1				Peak 2				Overall
Sample ID	Mw	IV (dL/g)	Rh (nm)	% Area	Mw	IV (dL/g)	Rh (nm)	% Area	dn/dc
RA Control				0.4	3,725	0.0507	1.44	99.6	0.0621
RA Control				0.3	3,692	0.0491	1.42	99.7	0.0629
RA Control				0.7	3,751	0.0494	1.43	99.3	0.0633
Average	**NA**	**NA**	**NA**	**0.5**	**3,723**	**0.0497**	**1.43**	**99.5**	**0.0628**
RA #1	8,269	0.0807	2.19	48.9	2,041	0.0539	1.20	51.1	0.0660
RA #1	7,899	0.0787	2.14	48.7	1,968	0.0531	1.18	51.3	0.0659
RA #1	7,326	0.0799	2.10	47.9	1,608	0.0539	1.11	52.1	0.0670
Average	**7,831**	**0.0798**	**2.14**	**48.5**	**1,872**	**0.0536**	**1.16**	**51.5**	**0.0663**
RA #2	20,279	0.1097	3.28	71.0	1,805	0.0547	1.16	29.0	0.0694
RA #2	20,784	0.1113	3.32	69.4	1,975	0.0562	1.21	30.6	0.0700
RA #2	20,523	0.1121	3.31	69.7	1,700	0.0565	1.15	30.3	0.0703
Average	**20,529**	**0.1110**	**3.30**	**70.0**	**1,827**	**0.0558**	**1.17**	**30.0**	**0.0699**
RA #3	113,066	0.1840	6.90	81.1	1,935	0.0565	1.20	18.9	0.0714
RA #3	112,754	0.1851	6.91	80.7	2,037	0.0561	1.22	19.3	0.0717
RA #3	110,209	0.1852	6.86	80.5	1,945	0.0567	1.20	19.5	0.0726
Average	**112,010**	**0.1848**	**6.89**	**80.8**	**1,972**	**0.0564**	**1.21**	**19.2**	**0.0719**

Table 2.2: Change in Iodine Value with time during the heat polymerization process carried out in glassware at a temperature of 330±3^{o}C for varied durations.

SI Nos	Time[h]	T [^{o}C]	Iodine Value
1	1.5	330±3	49
2	2.5	330±3	48
3	3.5	330±3	47

Iodine value of Soybean oil is 130

Table 2.3: Acid value as a function of duration of heat polymerization of soybean oil at 330^{o}C

SI Nos	Duration [h]	Temperature (^{o}C)	Acid value
1	0.5	330	4.18
2	0.75	330	5.5
3	1.0	330	5.4

Acid value of SBO ~4

2.6 References

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[4] Powers, P.O., Heat Bodying of Drying Oils, J. Am. Oil Chem. Soc. 27:468-472 (1950).

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[6] ACID Value, AOCS Official Method Te 1a-64 (1997)

[7] W. Wong, and A. Soleymannezhad, Sample Analysis Report, Viscotek Corp. , 1-33 (2005)

[8] Standard Test Method for Iodine Value of Drying Oils and Fatty Acids, ASTM Designation : D 1959 – 97 (1997)

3 CHAPTER 3

EPOXIDATION OF BODIED SOYBEAN OIL

3.1 Abstract

The epoxidation of bodied soybean oil (BSBO) was studied at 40 and 60^{o}C and compared to available data on the epoxidation of soybean oil (SBO). Epoxidation was carried out with in-situ performic acid formation, in the absence of solvent and catalyst. Selectivities decreased at higher temperatures and at higher conversions for both soybean oil and bodied soybean oil. Selectivities for the epoxidation of SBO at 40^{o}C were in the range of 0.65 to 0.75, while those at 60^{o}C were in the range of 0.5 to 0.6. In the case of BSBO, at 40^{o}C the selectivities were in the range of 0.5 to 0.6 and at 60^{o}C were in the range of 0.4 to 0.5. BSBO was more difficult to epoxidize than SBO.

Keywords: Epoxidation, bodied soybean oil, peroxoformic.

3.2 Introduction

The discovery of the reaction of olefins with peracids has been generally credited to the Russian chemist, prileschajew[1]. The preparation and characterization of epoxides were described by Berthelot, Wurtz, and Reboul, as early as 1861**.** The reaction in which an oxygen atom is introduced into a compound containing an unsaturated carbon-carbon bond to form a three-membered ring is termed epoxidation. The carbon-carbon double bonds are reactive due to their relatively high electron density[2]. This property makes the epoxidation of vegetable oils possible.

Epoxidation of vegetable oil is carried out primarily with peroxoacetic and peroxoformic acids on an industrial scale. The product typically is used in the PVC industry as a plasticizer. Epoxidation may be performed to attain maximum epoxy yield which is the case when the product is to be used for further chemical transformations. Alternatively, epoxidation conditions may target maximum conversion rates which necessarily might not correspond to highest conversions.

In the literature numerous references exist concerning the epoxidation of different olefinic substances, only a few have dealt with the kinetics of epoxidation and none have dealt with the kinetics of epoxidation of polymerized vegetable oils (bodied soybean oil, BSBO). The kinetics of the process primarily depends on the reaction conditions. Epoxidation of vegetable oils can be carried out in solution or in bulk, with in situ[3,4,5] formed or preformed peracids [6,7], and with homogeneous or heterogeneous catalysts. A kinetic model for in-situ

epoxidation of anchovy oil with partially preformed peracetic acid in the presence of a resin catalyst was reported[8].

In-situ epoxidation is characterized by two main reactions: (1) formation of peroxoacid and (2) formation of epoxides as summarized by the following two equations:

$$FA + H_2O_2 \quad \leftrightarrow \quad PFA + H_2O \qquad (1)$$

$$DB + PFA \quad \leftrightarrow \quad EO + FA \qquad (2)$$

where FA is formic acid; PFA is peracetic acid, DB is double bond, EO is epoxy group.

Screening studies were conducted to evaluate the various conditions for the effective epoxidation of the bodied soybean oil. These conditions included temperature, amount of hydrogen peroxide, and amount formic acid. In the case of the soybean oil the conditions for effective epoxidation were given in the literature [8,14].

The objective of this work is to find the conditions for a maximum epoxy yield of bodied soybean oil (BSBO)[9,10] and to compare those conditions to epoxidation conditions for soybean oil (SBO). The kinetics of epoxidation was performed with in-situ formed peroxoformic acid in the absence of solvent or auxiliary catalysts. The studies were conducted at the temperatures of 40 and 60^{o}C. The extent of side reactions that may have taken place was determined by

titration and FTIR.

3.3 Experimental methods

3.3.1 Materials

BSBO was made from soybean oil of RBD grade(refined, bleached, deodorized), Formic acid (90%) from Aldrich(Milwaukee, WI, USA) and a 50% (w/w) solution of hydrogen peroxide from sigma (St. Louis, MO, USA) , diethyl ether (HPLC grade), glacial acetic acid (certified A.C.S plus) from fisher scientific (Pittsburgh, PA, USA), and diethyl ether from fisher scientific were used.

3.3.2 Experimental setup

The experiments were carried out in a 500ml three necked round bottom flask equipped with a thermometer, mechanical stirrer and a septum pierced with an injection needle to equalize pressure. The whole apparatus was placed in a water bath to maintain respective temperatures of 40 and 60 ± 0.5^{o}C. The temperature was measured inside the flask and also in the water bath.

BSBO (100g) and formic acid (9.26, 88% in water) were added into the round bottom flask. To this mixture hydrogen peroxide (26g, 50% in water) was added slowly through a seperatory funnel during half an hour.

Epoxidation of SBO was used as a control. SBO (100g) was mixed with formic acid (13.26 g, 88% in water) in a round bottom flask. To this mixture, formic acid (38.3 g, 50% in water) was added slowly through a separator funnel during half an

hour.

The slow addition of hydrogen peroxide was performed to prevent the overheating of the system due the exothermic nature of epoxidation reactions. Samples were taken out of the round bottom flask every hour.

The samples were taken into a separator funnel and washed with distilled water to remove the excess acid present until a pH of 7. Oil phases were extracted by dissolving the washed samples in diethyl ether and then dried with anhydrous sodium sulfate. Solvent was then removed by drying it in the oven.

The purified samples were analyzed using FTIR to qualitatively follow the disappearance of double bonds and formation of epoxy groups. The iodine value, as the measure of concentration of double bonds, was determined using the Hanus titration method [11], and the epoxy oxygen content was measured according to the AOCS standard method[12]. Dimer and trimer formation were evaluated by GPC.

3.3.3 Method of analysis

A FTIR Nicolet (Madison, WI) (model Magna 550 using Omnic 5.1 software) was used to follow the disappearance of carbon-carbon π bonds and the formation of epoxy groups.

GPC was performed with a Hawlett Packard 1100 (Wilmington, DE) Quatpump, Alltech (Deerfield, IL) 500ELSD evaporative light scattering detector, and two Viscotek (Houston, TX) ViscoGel mixed bed columns (covering molecular weights

>20000) in series (each 7.8mm × 30cm). The operating conditions of ELSD are as follows: Drift tube temperature, 90^{o}C; exhaust temperature, 51.5^{o}C; gas flow, 2.93SLPM; gas pressure, 48psig; and solvent pressure, 16.5 psig. Data collection and analysis were performed using Hewlett Packard Chemstation software. The flow rate of tetrahydrofuron eluent was 0.5 ml/min at room temperature with a residence time of about 31 minutes for the smallest compound (SBO).

3.4 Results and discussion

3.4.1 Screening studies

The screening experiments summarized in Table 3.1 were performed to determine the temperature and stoichiometries at which the epoxidation of BSBO can be effectively carried out to obtain maximum epoxy yield. During these screening reactions it was observed that temperatures of 40^{o}C and 60^{o}C are favorable in comparison to the higher temperatures. At higher temperatures the epoxy ring degradation rate is probably higher resulting in the observed decrease in epoxy yields at higher temperatures.

Screening studies as per Table 3.1 were carried out by varying the amount of formic acid in the reaction mixture. The experiments showed that low concentrations of formic acid in (relative to the stoichiometric amount of unsaturation) lead to low epoxy yields. A formic acid concentration of 9.15g per 100g of bodied soybean oil calculated based on the ethlenic unsaturation was identified for further investigation.

Experiments were carried out to determine the impact of the quantity of hydrogen peroxide[13] that is added to the reaction mixture of BSBO and formic acid. The experiments indicate that excess hydrogen peroxide, above about 20% excess, is one of the most important parameters to increase the yield of epoxy moiety (oxirane). An excess of 50% hydrogen peroxide was selected for further studies.

3.4.2 Kinetic studies of the epoxidation of BSBO and SBO

Control experiments on the epoxidation of SBO were performed using the molar ratio of 1: 0.5: 1.5 (carbon-carbon π bonds: organic acid: hydrogen peroxide). BSBO was epoxidized by adding 26.5g of 50% hydrogen peroxide and 9.15g of 90% formic acid per 100g BSBO amounts of hydrogen peroxide and formic acid calculated based on an iodine value of 103 (versus 130 for SBO)—this translates to a stoichiometry similar to that of SBO epoxidation control studies.

The epoxidation reaction mechanism includes peracid reacting with the carbon-carbon π bonds in SBO and BSBO to form the epoxy product with simultaneous regeneration of the organic acid. There is a net generation of one water molecule for each hydrogen peroxide that reacts to form an epoxy group. The excess of 50 mole % relative to the double bonds was considered reasonable based in the screening studies and per Petrovic .et al.

Two series of epoxidations were carried out at two different temperatures (40 and 60 ^{o}C), one with SBO and the other with BSBO. The samples of the first series are designated as SBPFA40 and SBPFA60, where SB stands for soybean, PFA for peroxoacetic acid and the number for the temperature. Samples with BSBO

were designated as BSBPFA40 and BSBPFA60.

The variation of the iodine values (Figure 3.1 & Figure 3.2) and the epoxy oxygen contents (Figure 3.3 & Figure 3.4) were followed as a function of reaction time. The iodine value is directly proportional to the concentration of double bonds present, thus, the iodine value can be used to follow conversion. The combination of iodine value and epoxy oxygen content was used to calculate selectivity.

As conveyed by Figure 3.1 and Figure 3.2, the conversion rate was greater at 60^{o}C than at 40 ^{o}C. At 40^{o}C the iodine value of SBO decreased form 130 to 18 in 7.6 hrs while at 60 ^{0}C the iodine value decreased from 130 to 18 in 3hrs.

In the case of epoxidation of BSBO the conversion rate at 40^{o}C is almost linear and is slower in comparison to the epoxidation at 60^{o}C, where rate is non linear. The iodine value of the BSBO epoxidized at 40^{o}C decreased from 103 to 25 in 10.5 hours while at 60^{o}C the iodine value of BSBO decreased from 103 to 25 in 3 hours.

Temperature had a greater effect on the conversion of double bonds in BSBO as compared that of SBO, at 40^{o}C conversion decreased from 103 to 25 in 10.5 hours while at 60^{o}C the iodine value of BSBO decreased from 103 to 25 in 3 hours. The greater impact on BSBO is likely due to mixing and diffusion issues related to the higher viscosity of BSBO—higher temperatures reduce the viscosity and promote better contact and diffusion within the parameters of this respective experimental system.

The side reactions, such as the epoxy ring opening (reactions with acid or water) followed by the dimerization and trimerization, tend to occur in this system. A range of possible side products is given in Figure 3.11.

Gel permeation chromatography analyses as summarized in Table 3.2 were performed to determine the amount of product polymerized relative to the starting material. All epoxy products of SBO exhibited new, lower retention time peaks indicative of higher molecular weight products being formed. Example GPC chromatograms are presented in the Figure 3.7, Figure 3.8, Figure 3.9, and Figure 3.10. In the case of BSBO the retention times remained the same with an increase in the area of the polymerized component.

For epoxidation of SBO, the percent increase in the polymer area is 4.2% at 10.5 hrs while at 60^{o}C the increase was 14% at the end of 11hrs as given in Table 3.2. This indicates that the temperature has a greater effect on the degradation of epoxy ring to form polymerized side products in the case of epoxidation of SBO. In the case of BSBO, the percent increase in the polymer area is 9.2% at 10.5 hrs while that at 60^{o}C was 12.6% at 11hrs, which shows that temperature has a relatively small effect on the formation of side products (high molecular weight components) in the case of epoxidation of BSBO (a 4.2% increase in polymerized component at 40^{o}C after a duration of 10.5 hrs in comparison to an increase of 14% at 60^{o}C after a duration of 11hrs).

In certain applications like urethane production, polymerization of the B-side components can be advantageous as this can lead to a greater amount of B-side

in the final product (relate to the A-side, polyisocyanate). In the first step, the proton attacks the epoxy group leading to the formation of hydroxyl and formyl groups. If the reaction stops at this stage a polyol is formed which is desirable in urethane pre-polymers. The hydroxyl group may further react with an epoxy group to give internal ethers or oligomeric ethers (dimers, and higher order molecules) as shown in Figure 3.12

Selectivity (S) is a measure of the amount of side reactions occurring during epoxidation, it gives the relative yield of epoxides and was calculated as:

$S = (EO/EO_m)/[IV_o - IV]/IV_o)$ [14]

Where EO is the experimentally determined percent of epoxy oxygen in 100g of oil, IV is the iodine value, IV_o is the initial iodine value and EO_m is the percent of epoxy oxygen in 100 g of oil at complete conversion, calculated as:

$EO_m = [(IV_o/2A_j)/100 + (IV_0/2A_j).A_o].A_o .100$

Where $A_j = 126.9045$ and $A_o = 16.0$. For $IV_o = 130$ is $EO_m = 7.5$

Plots of selectivity vs. time for epoxidations with peroxoformic acid are depicted in Figure 3.5 and Figure 3.6. Higher selectivities are observed at lower temperatures and at the beginning of epoxidation. Selectivities of 0.75 are obtained in the case of SBO at lower temperatures (40^oC) while for BSBO the maximum selectivity was 0.6 at the same temperature. At higher temperatures the selectivity of both SBO & BSBO were low at 0.6 and 0.5, respectively.

Relative yield of epoxides, are calculated as

$Yield\% = 100 * EO/EO_m$

where EO is the experimentally determined percent of epoxy oxygen in 100g of oil, EO_m is the content of epoxy oxygen in 100 g of oil at complete conversion.

During the epoxidation IR spectroscopy was used to follow the disappearance of double bonds at 3009 cm^{-1} and the formation of epoxy groups (doublet at 822 cm^{-1} and 833 cm^{-1}) with time. The presence of OH (3470 cm^{-1}) or C═O groups which would indicate the formation of side reaction products were also followed. From the selectivities that are obtained both in the case of SBO and BSBO and the IR analysis it was concluded that the lower selectivity's are a result of the side reactions occurring involving the opening of the epoxy ring. The presence of OH functionality in the epoxy product obtained based on the IR analysis is acceptable in urethane applications as it enhances the reactivity of the polyol with isocyanate. At this time no attempt was made to distinguish between alcohol groups on polymerized versus non-polymerized product of the SBO and BSBO reactions.

3.5 Conclusions

The epoxidation of SBO and BSBO was carried out with insitu formed peroxoformic acid (oxidizing agent) in order to study the kinetics and the extent of side reactions. Longer reaction times and greater excesses in hydrogen peroxide were required to epoxidize BSBO with maximum yields and selectivities of 40% and 60% respectively.

Reactions at 60^{o}C reduced reaction times by 60-70% for similar conversions relative to reactions at 40^{o}C. Temperature had a greater impact on the BSBO epoxidation due to the higher viscosity of BSBO. The 40^{o}C reactions exhibited about a 20% increase in selectivity to epoxy moieties. This is likely due to the increased stability of epoxy groups at lower temperatures.

Prominent by-products of epoxidation are dimers and trimers of the epoxy product. Up to 14% oligomers formed for SBO epoxidation while only up to 6% formed with BSBO.

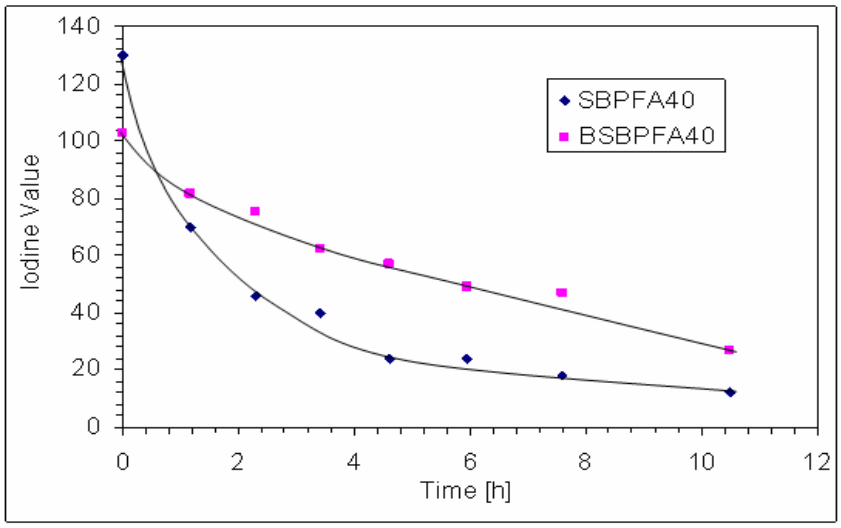

Figure 3.1: Comparison of iodine value vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 40°C.

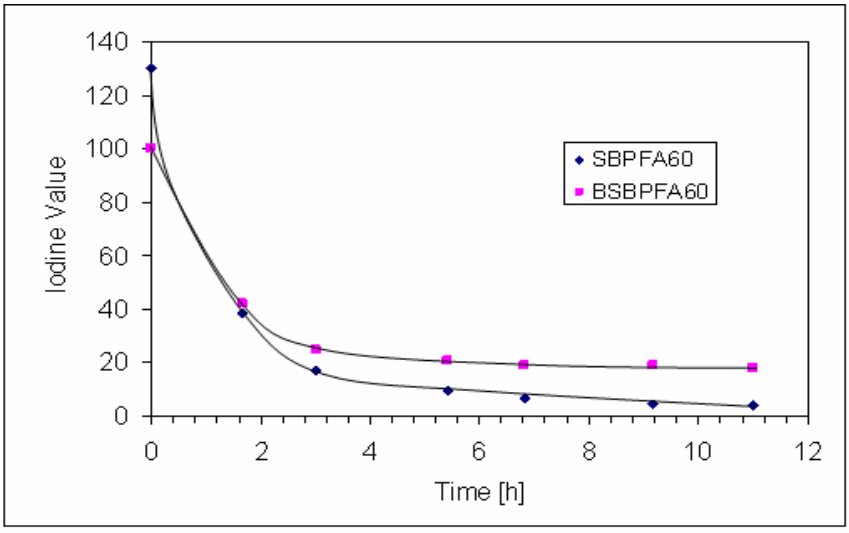

Figure 3.2: Comparison of iodine value vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 60°C.

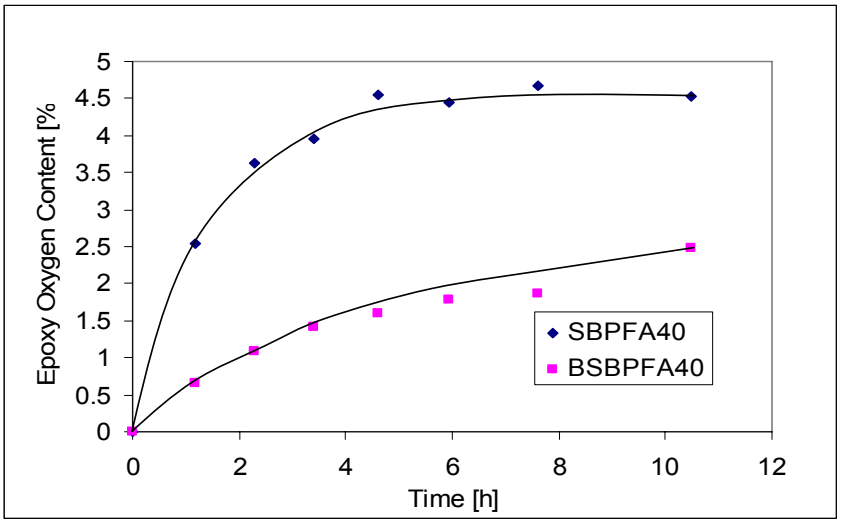

Figure 3.3: Comparison of epoxy oxygen content vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 40°C.

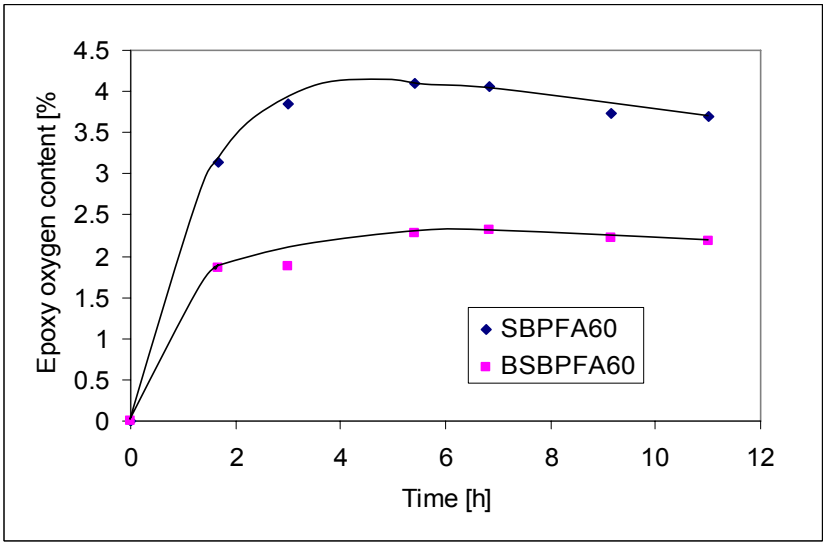

Figure 3.4: Comparison of epoxy oxygen content vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 60°C.

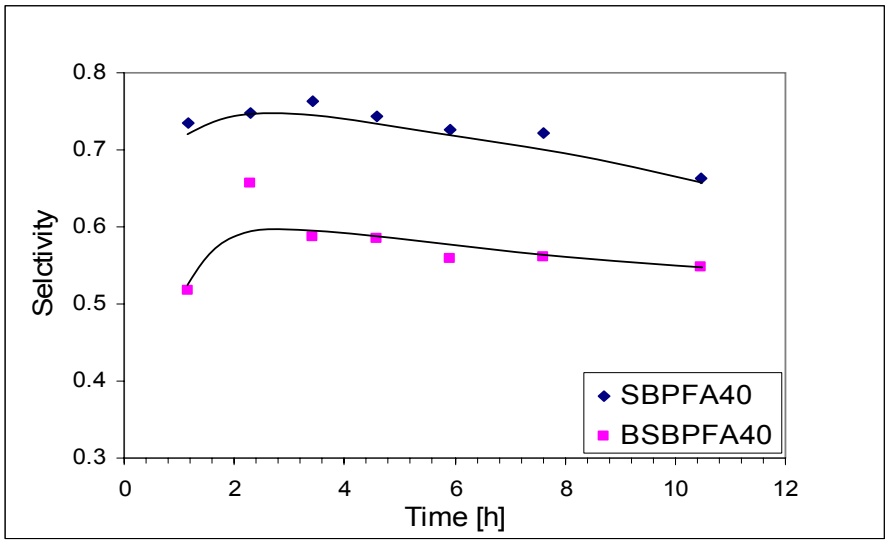

Figure 3.5: Comparison of selectivity vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 40°C.

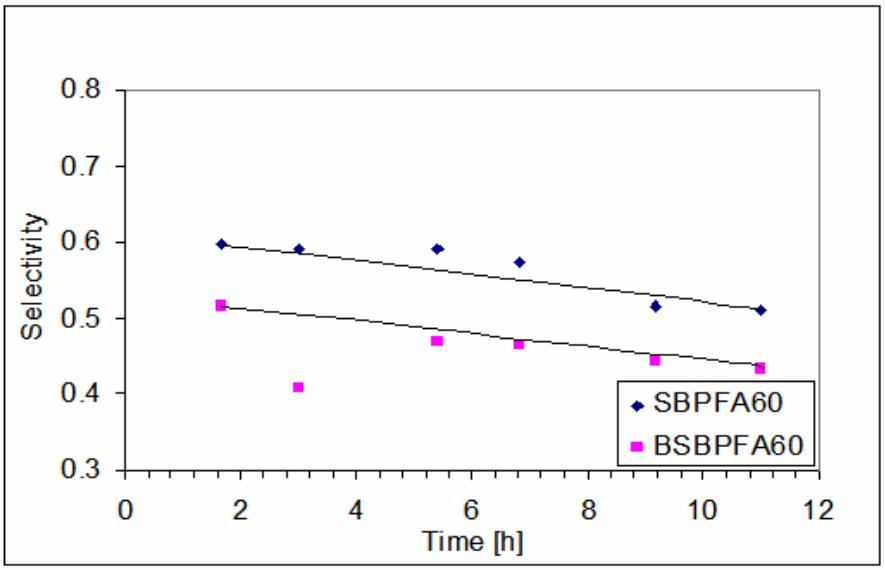

Figure 3.6: Comparison of selectivity vs. time for the epoxidation of soybean oil and bodied soybean oil with peroxoformic acid at 60°C.

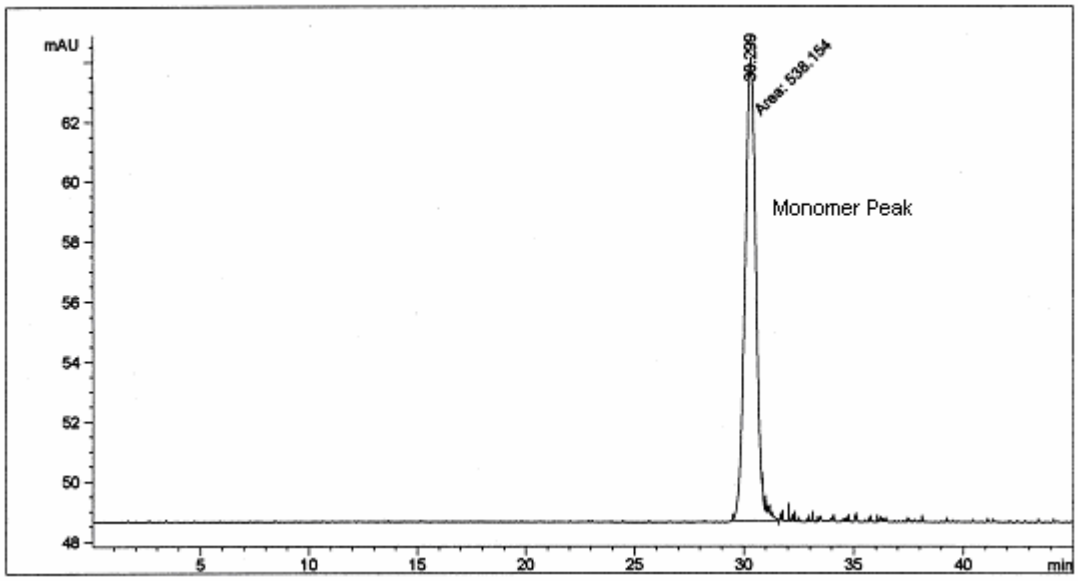

Figure 3.7: GPC chromatogram of SBO (control)

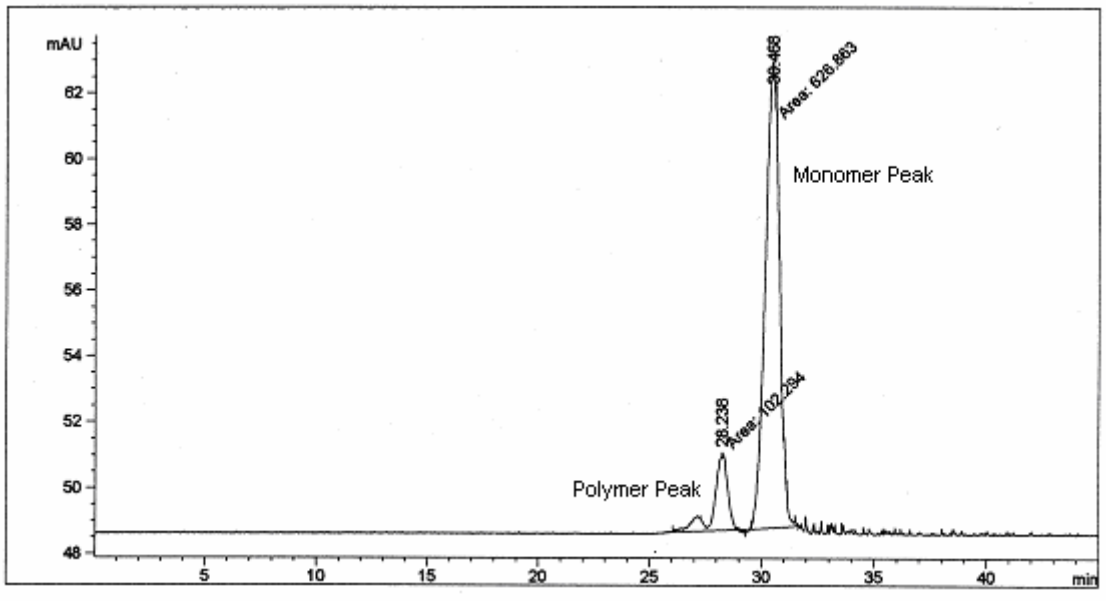

Figure 3.8: GPC chromatogram of SBPFA60 after duration of 11hours

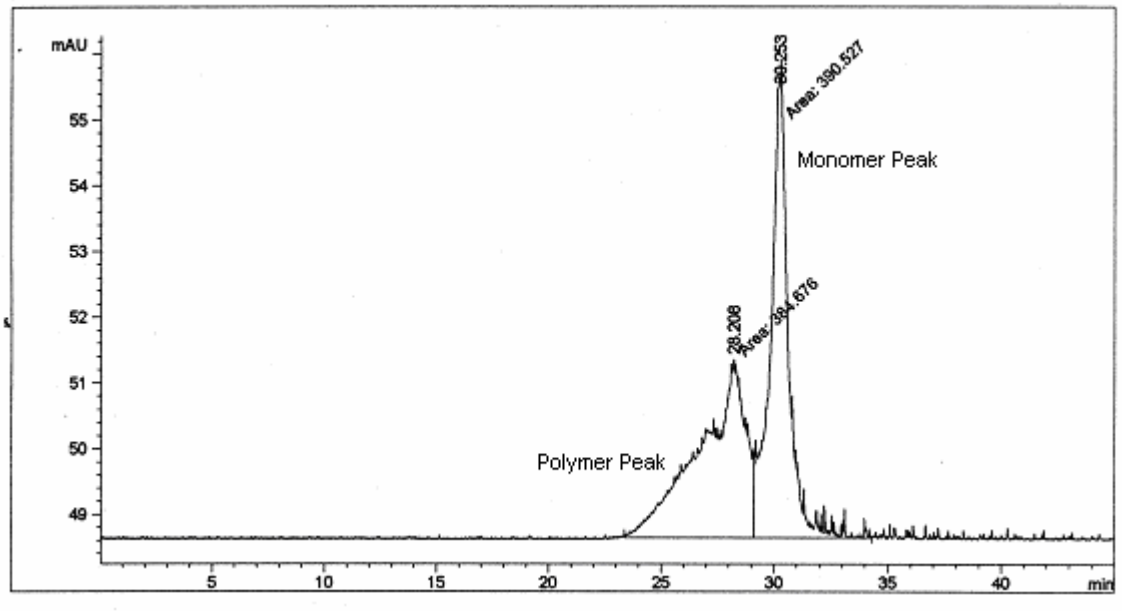

Figure 3.9: GPC chromatogram of BSBO (Starting material)

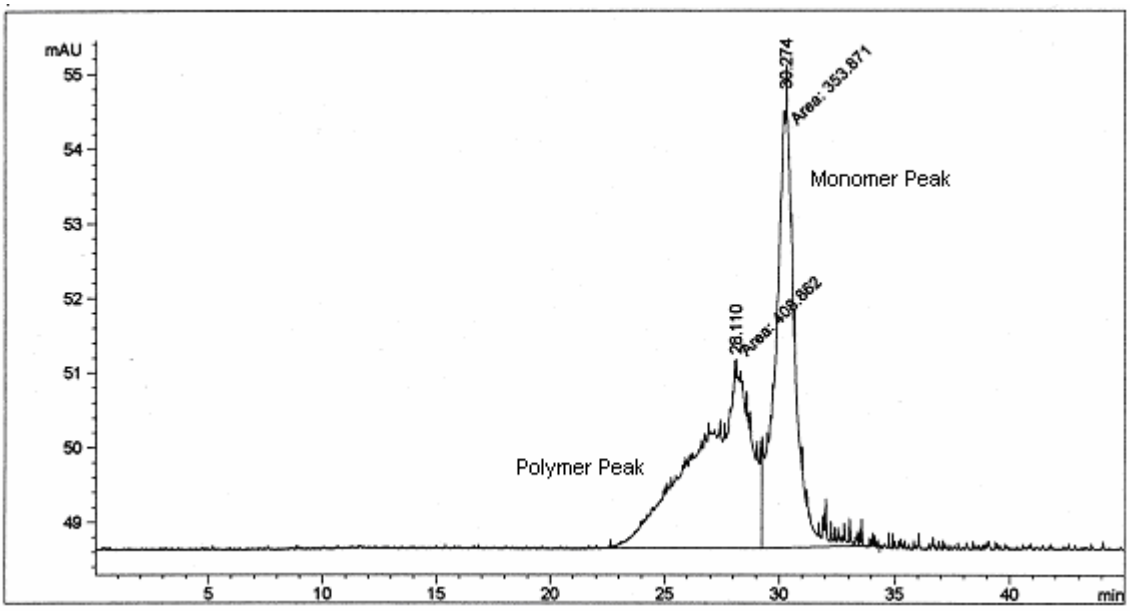

Figure 3.10: GPC chromatogram of BSBPFA40 after duration of 4.5 hours

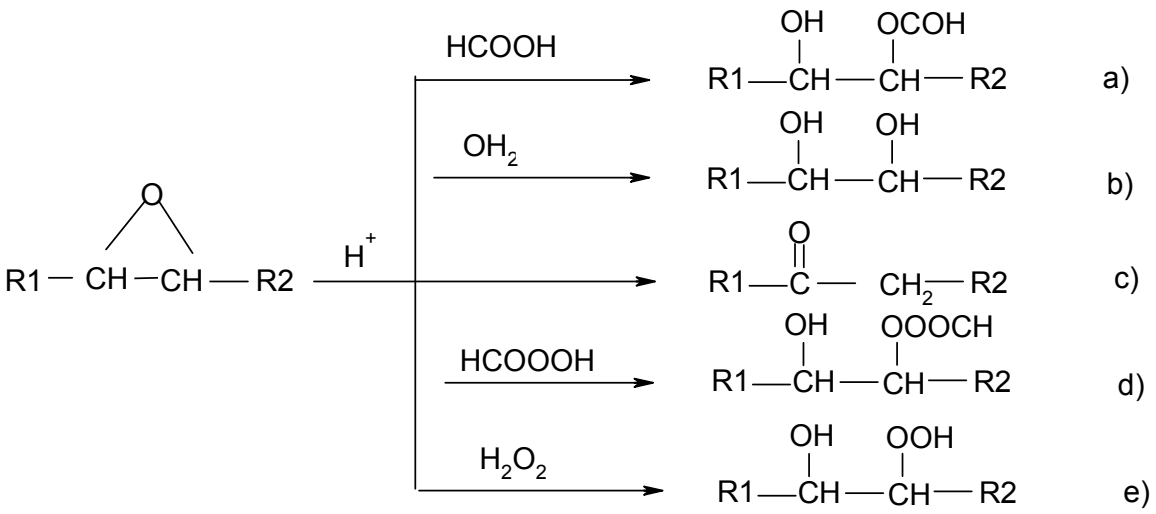

Figure 3.11: Possible side reactions of epoxy group.

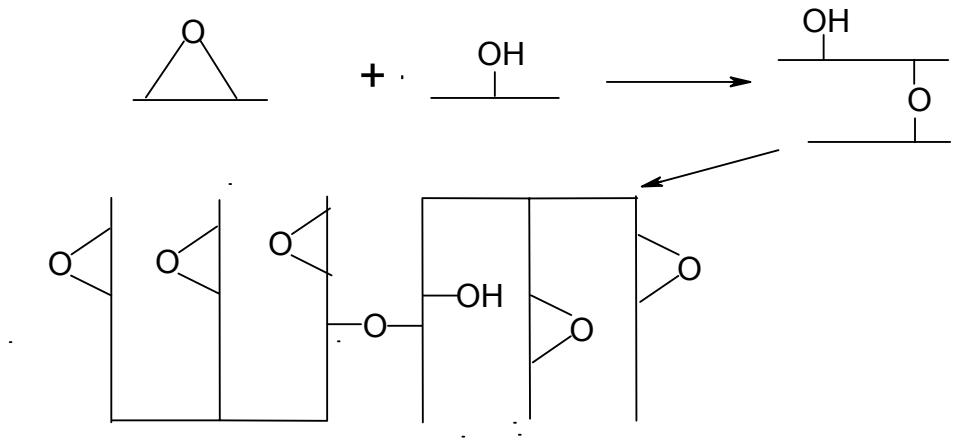

Figure 3.12: Schematic representation of dimmer formation.

Table 3.1: Screening studies on the epoxidation of bodied soybean oil

Sl Nos	Bodied SBO(g)	HCOOH (g)	H2O2 (50%) (g)	Time of Rxn(hrs)	T(^{o}C)	% oxirane Oxygen
1	130	6.57	15	8.5	60	1.41
2	130	6.57	15	11	60	1.37
3	130	6.57	20	5	68	0.59
4	130	6.57	20	8.5	68	0.61
5	130	6.57	20	11	68	0.63
6	100	4.75	20	4	67	0.62
7	100	4.75	20	7.5	67	0.51
8	100	4.75	20	11.5	67	0.48
9	100	4.75	15	4	60	1.74
10	100	4.75	15	7.5	60	1.71
11	100	4.75	15	11.5	60	1.61
12	100	9.15	26.5	4.5	40	1.6
13	100	9.15	26.5	7.5	40	1.85
14	100	9.15	26.5	10.5	40	2.48
15	100	9.15	26.5	3	60	1.88
16	100	9.15	26.5	7	60	2.3
17	100	9.15	26.5	11	60	2.2
con	ESBO					6.5

Table 3.2: Analysis of the GPC results of epoxidized soybean oil and bodied epoxidized soybean oil with peroxoformic acid.

Sample	T [^{o}C]	Time [h]	Area of Monomer[%]	Area of Polymer [%]	Increase in polymer area [%]
SBO	-	-	100.0	0.0	0.0
SBPFA40	40	4.5	98.0	2.0	2.0
		10.5	95.8	4.2	4.2
SBPFA60	60	5.5	92.4	7.6	7.6
		11.0	86.0	14.0	14.0
BSBO	-	-	50.4	49.6	0.0
BSBPFA40	40	4.5	46.4	53.6	4.0
		10.5	45.9	54.1	4.5
BSBPFA60	60	5.5	45.8	54.2	4.6
		11.0	44.1	55.9	6.3

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4 CHAPTER 4

PRODUCTION OF SOY-BASED POLYOLS

4.1 Abstract

Four polyols intended for application in polyurethanes were synthesized by reacting both soybean oil and bodied soybean oil with allyl alcohol and acetol. A temperature of 300^{o}C and reaction duration of 2hrs was essential in attaching the –OH functionality while reacting allyl alcohol with both soybean oil and bodied soybean oil (BSBO). In the case of reaction of acetol with soybean oil and bodied soybean oil, a temperature of 180^{o}C and a reaction duration of 9hrs was essential in attaching the –OH functionality. In both conversions, up to 30% of the carbon-carbon π-bonds in the soybean oil/BSBO reacted with the acetol or allyl alcohol to append the –OH functionality.

KEY WORDS: polyols, soybean oil, bodied soybean oil, functionality

4.2 Introduction and background

The preparation of polymers from renewable resources is of significant economic and scientific interest. Polyurethanes prepared from vegetable oils have a number of excellent properties derived from the hydrophobic nature of triglycerides[1,2,3]. Hydroxyl groups can be introduced in the oils by many means, including attack of the carbon-carbon π–bond to form different polyol structures. A limitation of the majority of the soy-based polyol syntheses methods is they cannot be easily converted to high molecular weight products (MW > 1500) without the introduction of and further reaction of functional groups such as hydroxyl, epoxy and other groups[4,5,6].

The methods of this work were identified as a means to introduce alcohol functionality with only one reaction step and as a means to synthesize higher MW polyols with a minimum of steps. Soybean oil was the triglyceride vegetable oil selected for study due to its abundance and presence of two dominant fatty acids, linoleic acid (50%) and oleic acid (25%) with an average of 4.6 carbon-carbon π–bonds per molecule. The soybean oil molecule is depicted in Figure 4.1.

The average molecular weight of soybean oil is 874, and despite variations in composition from molecule to molecule, it is substantially mono disperse. Polyols from the soybean oil have been prepared by the ring opening of the oxirane groups from epoxidized soybean oil (ESBO) as wells as by hydroformylation of the oil itself and the subsequent reduction of the aldehyde to hydroxyls. In this work, new approaches are evaluated by directly reacting

acetol and allyl alcohol with the soybean oil and the bodied soybean oil. The objective is to attach these alcohols using olefin chemistry while preserving the alcohol functionality.

The polyols resulting per the above procedure have varied properties in terms of the structures, density, viscosity and the molecular weights. These varying properties present a means to prepared B-side monomers for a number of different applications.

Figure 4.1 illustrates the heterogeneity of the soybean oil triglycerides; heterogeneity is the variation of fatty acid type from molecule to molecule. About one in three triglyceride molecules has one saturated acid and one acid with three double bonds (linolenic acid). When double bonds are converted to hydroxyls they are located in the middle of the fatty acid chains of the triglycerides. When these polyols are crosslinked with isocyanates, part of the chain is pendant. For saturated acids, the whole acid becomes a pendant chain in the crosslinked network. Pendant chains do not support stress when the sample is under load and may act as plasticizers.

The objective of this study was to develop polyols using soybean oil and bodied soybean oil. No external catalyst was used which greatly minimizes the down stream processing. After reaction, the presence of unreacted allyl alcohol and acetol was removed through repeated washings with water as both these compounds are very much soluble in water. Also in the current study various parameters such as temperature, duration of the reaction, and percent of allyl

alcohol and acetol added relative to that of the oil are studied. The resulting polyols are characterized by chemical moiety titration and spectroscopic techniques (IR).

4.3 Experimental methods

4.3.1 Materials

Soybean oil of RBD grade (refined, bleached, deodorized) with an iodine value of 125-130 (Hanus) was obtained from local supplier. Acetol, allyl alcohol, carbon tetrachloride, sodium thiosulfate solution (0.1N), potassium iodide, starch indicator, and Wijs solution were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade nitrogen was obtained from Praxair (St.Louis).

4.3.2 Experimental setup

Screening studies of all the reactions were carried out in Swagelok stainless steel reactors, each with a capacity of 9 ml. The desired temperature of the reactor was maintained through controlling the temperature of the muffle furnace. The reactors were first charged with ~7g of reaction mixture which was comprised of 6g of oil and the rest being either acetol or allyl alcohol. Control reactions were performed by using soybean oil and bodied soybean oil. The controls were at the same conditions as those of the reactions involving allyl alcohol and acetol.

Production of liter quantity samples was done in a Parr reactor of 2 liter capacity equipped with stirrer, heater, and thermocouple. The temperature of the Parr reactor was controlled using an omega controller. The system was purged

several times with nitrogen to ensure the presence of inert atmosphere. Then the system was closed and heated to the desired temperature. The speed of the stirrer was set constant at 600 rpm through out the reaction.

4.3.3 Method of analysis

A FTIR Nicolet (Madison, WI) (model Magna 550 using Omnic 5.1 software) was used to follow the formation of hydroxyl groups (3470 cm^{-1}). The iodine values of the polyols were determined according to the ASTM standard titration method[7].

4.4 Results and discussions

4.4.1 Parametric studies

The effect of reaction temperature and concentration of acetol and allyl alcohol (wt% in oil) were studied to determine the optimal conditions for attaching the alcohol functionality.

4.4.2 Effect of reaction temperature

The reaction of allyl alcohol with bodied soybean oil and soybean oil was studied at temperatures of 200, 275, 300 and 330 ^{o}C. A temperature of 300^{o}C provided the best result in terms of attaching the –OH functionality to the soybean oil which was confirmed through FTIR analysis as illustrated by Figure 4.4 and Figure 4.5. At temperatures below 300^{o}C it is likely that the polymerization/attaching reaction did not proceed sufficiently fast. While at temperatures above 300^{o}C a lower –OH functionality can be attributed to the further reaction of –OH group.

In the case of reaction of acetol with bodied soybean oil, a temperature of 180^{o}C was selected for the study as the temperatures above 180 ^{o}C tends to result in the self polymerization of acetol. It was found that at 180 ^{o}C there was reaction between acetol and bodied soybean oil which was confirmed through FTIR analysis Figure 4.6. Products were washed several times to confirm that the alchol functionalities were on the triglycerides rather than on acetol polymers—acetol is water soluble and all polymers are projected to also be water soluble.

In the case of reaction of acetol with soybean oil, temperatures of 150 and 180^{o}C were studied. The temperature of 180^{o}C resulted in reaction between the acetol and soybean oil which was confirmed through FTIR analysis Figure 4.7.

4.4.3 Effect of concentration of acetol & allyl alcohol

Table 4.1 and Table 4.2 summarizes the various ratios of acetol and allyl alcohol taken respectively in terms of weight % of the oil taken. From the analysis of the products obtained it can be concluded that the reaction either reaches equilibrium or completion after a certain point and does not proceed any further in spite of having a larger concentration of the acetol and allyl alcohol in the oil.

One possible explanation for this is that there might be stearic hindrance after a point which does not allow the further interaction between the double bonds of the oil and the double bond present in both allyl alcohol and acetol. This possibly explains why the conversion, as represented by a decrease in iodine value (measure of unsaturation), reached a maximum after about 25% conversion for all

reactions.

Another explanation recognizes the different types of and reactivities of carbon-carbon π–bonds in soybean oil. It is possible that the allyl alcohol and acetol are more reactive with conjugated carbon-carbon π-bonds.

4.4.4 Effect of duration of reaction

Table 4.3 summarizes the reactions for acetol reacting with soybean oil and bodied soybean oil. Table 4.4 summarizes the various reaction times evaluated in the case of allyl alcohol reacting with soybean oil and bodied soybean oil.

The –OH number of bodied soybean oil is 11.2 and SBO is 6.2. At maximum conversions the –OH numbers of the products were as follows: epoxidized bodied soybean oil, 193; BSBO/acetol, 71.2; and SBO/acetol, 75, wherein the hydroxyl number represents amount of reactive hydroxyl groups available for reaction measured as milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of sample.

In the case of reaction of acetol with soybean oil, 9 hrs was required to achieve maximum yields of –OH functionality to the oil.

In the case of reaction of allyl alcohol with soybean oil, 2 hrs at a temperature of 300^{o}C was essential to attach the –OH functionality to the oil. At temperatures above 300^{o}C the –OH functionality may further react to give side products and that below 300^{o}C the reaction possibly proceeds at a very slow rate.

4.5 Conclusions

Polyols were successfully synthesized from soybean oil and BSBO by reacting them with acetol and allyl alcohol. The reactions of the carbon-carbon π-bonds proceeded to a maximum of 30% conversion. Higher stoichiometries of the alcohols were unable to promote further conversion. This limit in conversion is likely due to reactions being limited to conjugated carbon-carbon π-bonds in the soybean oil and BSBO. Functionality was effectively imparted to oil in the absence of catalyst. The functionality was verified qualitatively by FTIR analysis through the presence of the –OH functionality at 3470 cm^{-1}.

Table 4.1: Summary of favorable conditions for the reaction of allyl alcohol with soybean oil and bodied soybean oil

Sl Nos	SBO (g)	BSBO (g)	Allyl alcohol(g)	Duration (hrs)	T [^{o}C]	Iodine Value
1	6.0			2	300	118
2	6.0	-	0.9	2	300	100
3	6.1	-	1.35	2	300	97
4	6.03	-	1.62	2	300	99
5		6.01			300	87
6		6.02	0.35	2	300	66
7		6.03	0.74	2	300	68
8		6.02	1.1	2	300	65

Table 4.2: Summary of favorable conditions for the reaction of acetol with soybean oil and bodied soybean oil

Sl Nos	SBO (g)	BSBO (g)	Acetol(g)	Duration (hrs)	T [^{o}C]	Iodine Value
1	6.1			9	180	125
2	6.0	-	0.45	9	180	101
3	6.1	-	0.91	9	180	97.5
4	6.03	-	1.39	9	180	95
5		6.05		9	180	97
6		6.02	0.45	9	180	63.5
7		6.03	0.91	9	180	65.3
8		6.02	1.39	9	180	66

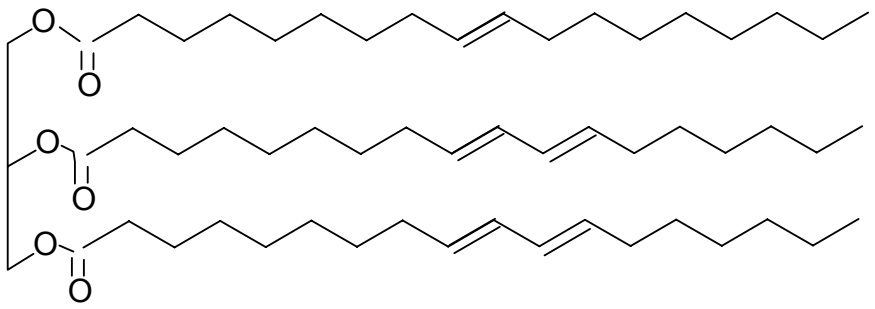
Iodine Value of SBO – 130, Iodine Value of BSBO - 100

Table 4.3: Summary of conditions evaluated for the reaction of allyl alcohol with soybean oil and bodied soybean oil (200^{o}C, 275^{o}C for 2hrs; 330^{o}C for 0.5,0.75,1, 1.5 hrs; 300^{o}C for 2hrs were evaluated keeping the quantities of SBO, BSBO, Allyl alcohol constant)

Sl Nos	SBO (g)	BSBO (g)	Allyl alcohol(g)
1	6.0		
2	6.0	-	0.9
3	6.1	-	1.35
4	6.03	-	1.62
5		6.01	
6		6.02	0.35
7		6.03	0.74
8		6.02	1.1

Table 4.4: Summary of conditions evaluated for the reaction of allyl alcohol with soybean oil and bodied soybean oil (1.5, 3, 4.5, 6, 9 hrs are evaluated at 180^{o}C)

Sl Nos	SBO (g)	BSBO (g)	Acetol(g)	T[^{o}C]
1	6.1			180
2	6.0	-	0.45	180
3	6.1	-	0.91	180
4	6.03	-	1.39	180
5		6.05		180
6		6.02	0.45	180
7		6.03	0.91	180
8		6.02	1.39	180



Average functionality = 4.6

(Iodine Value = 120-140)

$-OOC(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$ Linoleic -51%

$-OOC(CH_2)_7CH=CH(CH_2)_7CH_3$ Oleic - 25%

$-OOC(CH_2)_{14}CH_3$ Palmitic - 11%

$-OOC(CH_2)_7CH=CHCH_2CH=CHCH_2CH=CHCH_2CH_3$ Linolenic - 9%

$-OOC(CH_2)_{16}CH_3$ Stearic - 4%

Figure 4.1: Schematic representation of the soybean oil molecule

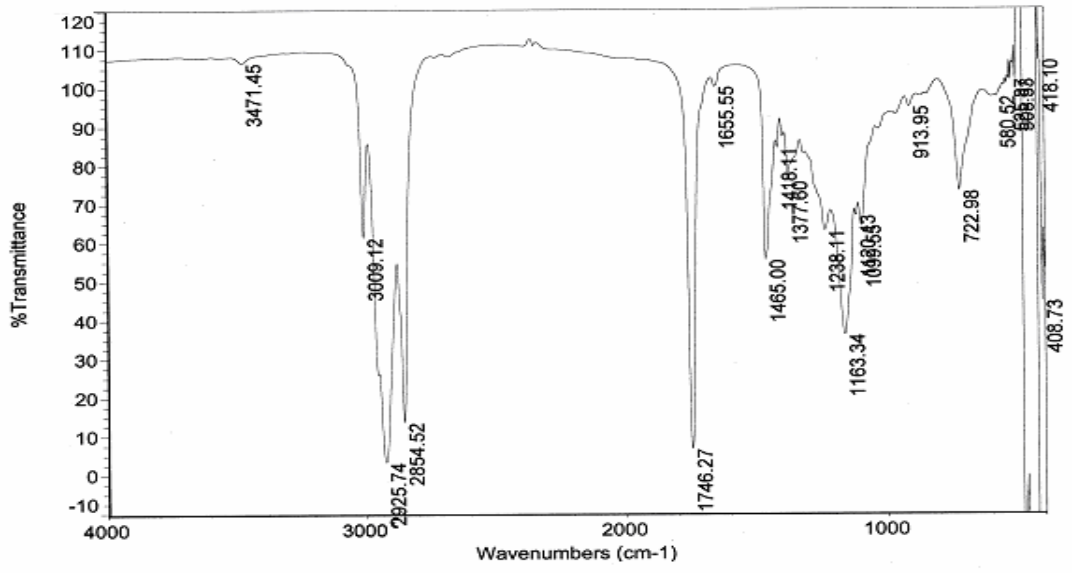


Figure 4.2: FTIR spectra of SBO (-OH functionality 3470 cm^{-1})

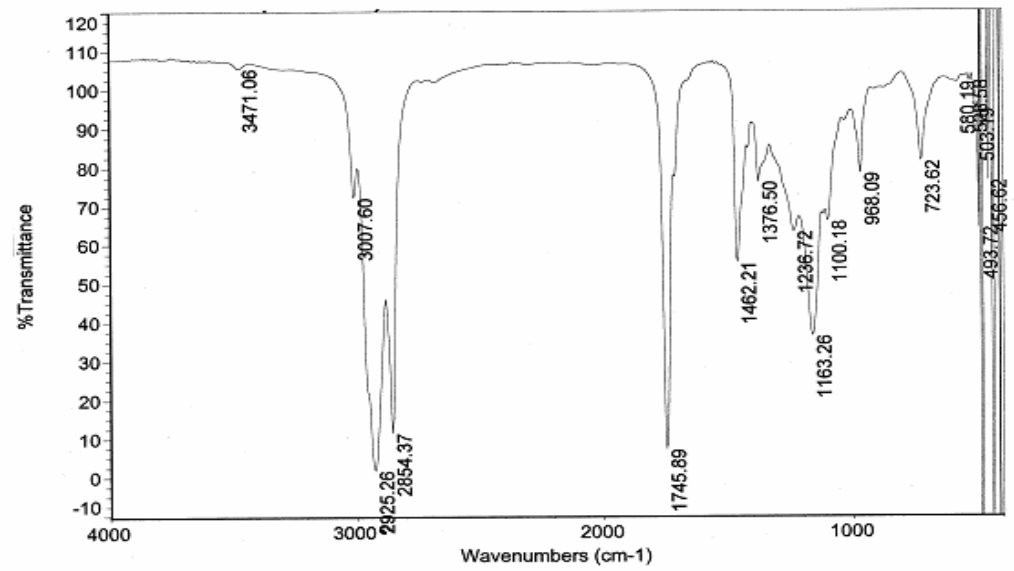


Figure 4.3: FTIR spectra of BSBO (-OH functionality 3470 cm^{-1})

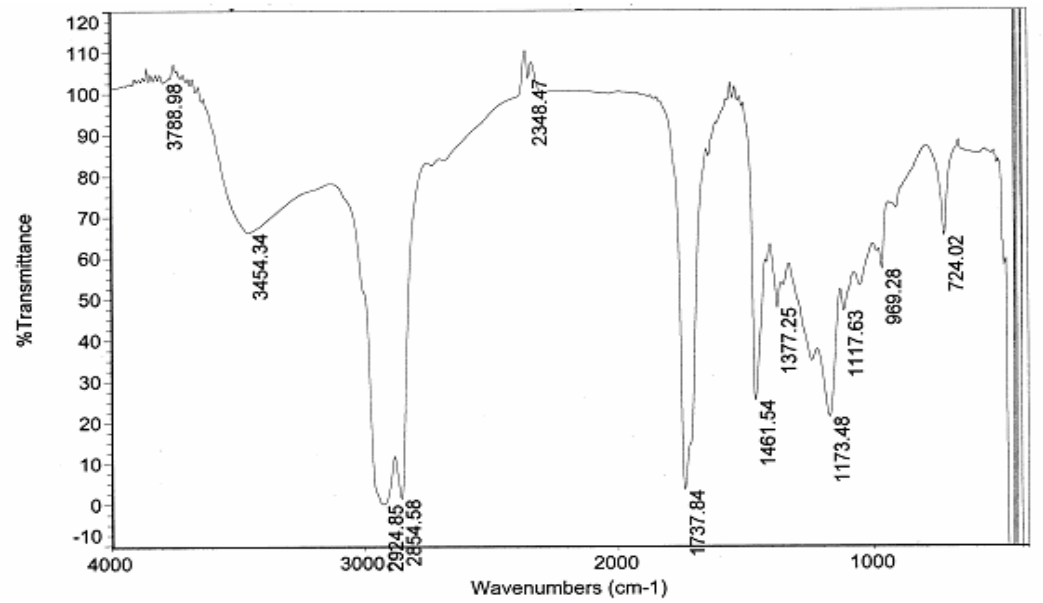


Figure 4.4: FTIR spectra of soybean oil reacted with allyl alcohol at a temperature of 300^{o}C for a duration of 2hrs (-OH functionality 3454.34 cm^{-1})

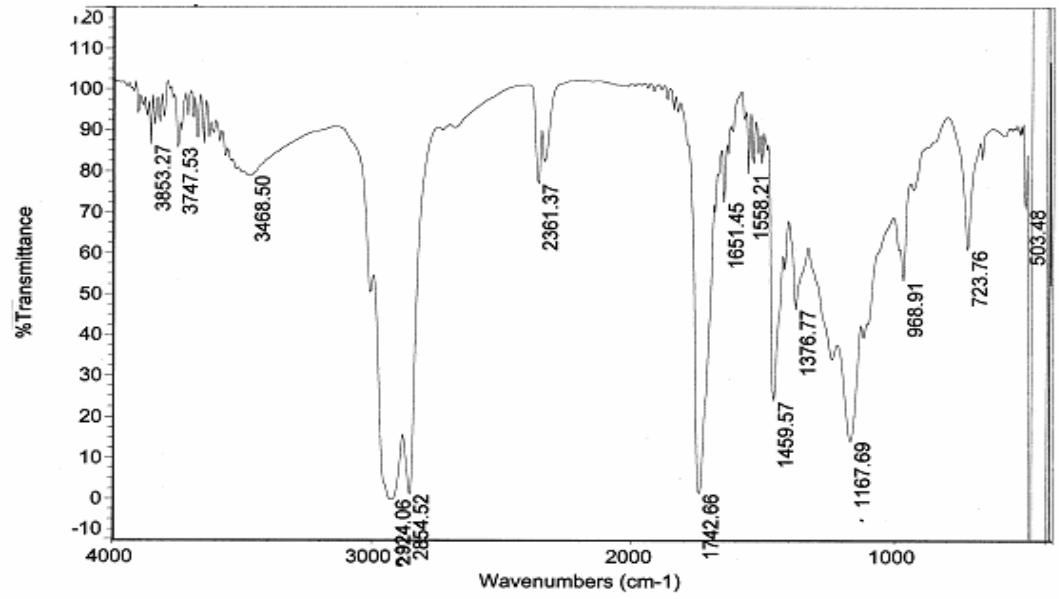


Figure 4.5: FTIR spectra of bodied soybean oil reacted with allyl alcohol at a temperature of 300^{o}C for a duration of 2hrs (-OH functionality 3468.50 cm^{-1})

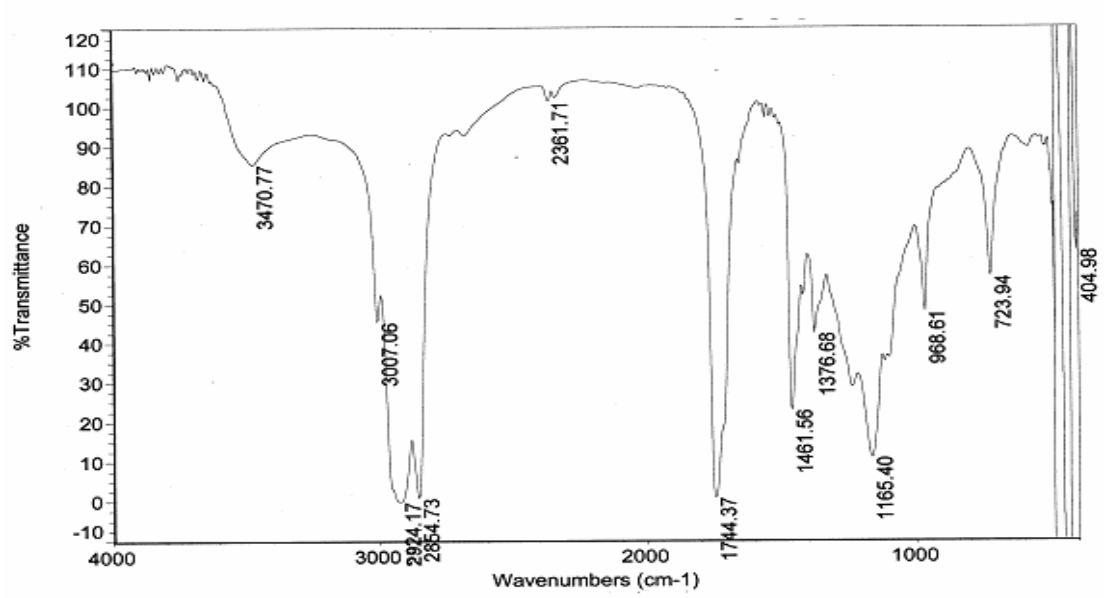


Figure 4.6: FTIR spectra of soybean oil reacted with acetol at a temperature of 180^{o}C for a duration of 9hrs (-OH functionality 3470.92 cm^{-1})

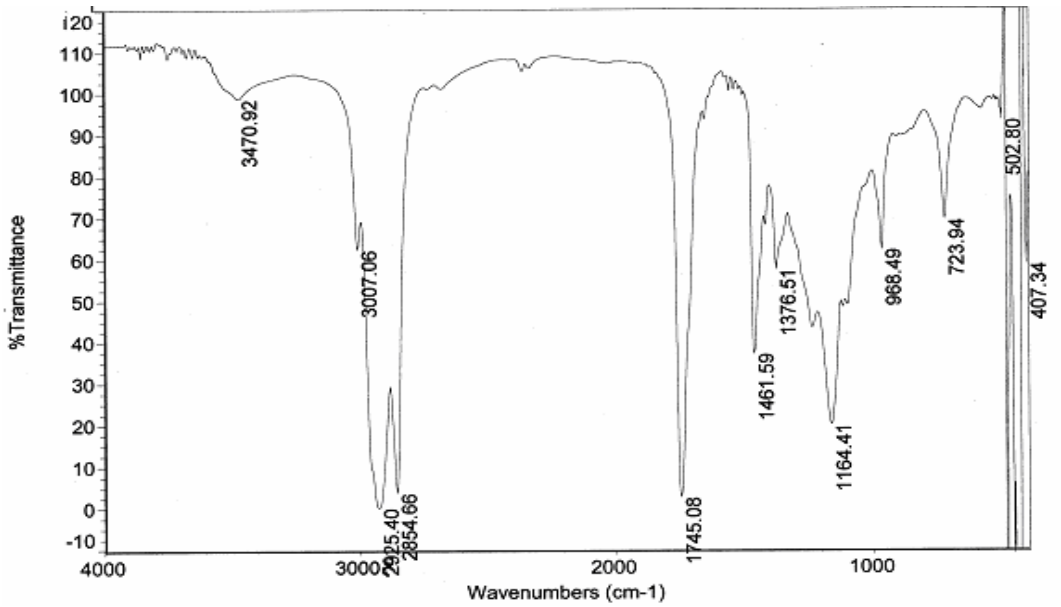


Figure 4.7: FTIR spectra of bodied soybean oil reacted with acetol at a temperature of 180^{o}C for a duration of 9hrs (-OH functionality 3470.77 cm^{-1})

4.6 References

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5 CHAPTER 5

POLYOLS IN THE MAKING ION EXCHANGE MATERIALS, RESIN/COMPOSITES AND POLYURETHANE FOAMS THEIR CHARACTERIZATION

5.1 Abstract

An ion-exchange material containing carboxylic groups was prepared by the acid hydrolysis of polyurethane foam made using a polyol comprised of a mixture of vegetable oil (castor oil) and the commercial polyol, Voranol 490. The ion exchange capacity of the polyol is the result of presence of triglyceride groups in the foam. Removal of the triglyceride's glycerol in an acidic environment produces acid sites available for ion exchange. The maximum amount of foam that was hydrolyzed was 43% conversion based on the triglyceride content oil in the foam formulation.

Bodied epoxidized soybean oil (BESBO) was investigated for its cross-linking reaction with triethylene tetraamine. The BESBO polymer cured by the aliphatic amine, triethylene tetramine (TETA), was semi rigid with an average Tg of 23^{o}C**.** The effect of different BESBO/amine ratios on the thermal properties of the final product was studied.

A third component of the polyol utilization was the screening of the polyols on their reactivity in a urethane rigid foam formulation performed with <2 g of polyol. The reactivity was characterized based on density of the cured foam, qualitative characterization of the type of foam (flexible, hard, or brittle) and the porosity (voids) in the foam. The screening method proved effective for identifying those polyols that had the greatest propensity to produce quality polymers.

5.2 Introduction

The importance of natural products for industrial applications becomes very clear with increasing social emphasis on the issues of environment, waste disposal, and the depletion of nonrenewable resources. The United States agriculture produces over 18 billion pounds of soybean oil annually[1] and frequently the yearly carryover exceeds one billion pounds[2]. Currently only 300 million pounds of soybean oil are used in industrial applications[3]. The development of new economically feasible industrial products from vegetable oils or commercial processes is the objective of continued research in both the public and private sector. Vegetable oils are currently used in the various applications such as printing inks,[4,5] biodiesel,[6,7] and lubricants.

Little to no research has been performed on preparing soy-based polyurethane foams for ion exchange material. Carboxylic functionality groups are a natural ion-exchange material. Alginic acid (giant carbohydrate built from mannuronic acid units) an extract from sea weeds is used as a thickening and emulsifying agent[3].

In this study the ion exchange capacity of the urethane foam is measured in terms of availability of acid sites upon its hydrolysis and castor oil is used in this study in conjunction with VORANOL-490. Polyols such as castor oil and soy-based polyols have a great potential for usage as ion exchange materials due to their molecular structure which primarily consists of glycerin backbone. The polyol used in the making of polyurethane foam is a mixture of glycerol-based polyols

and non-glycerol based polyols such as VORANOL-490. The non-glycerol based polyols provide the rigid structure upon reaction with isocyanate and its subsequent hydrolysis, while the glycerol based polyols result in the formation of free fatty acids upon hydrolysis of the urethane resulting from it. These free fatty acid sites act as ion exchangers, which are held within the rigid structure resulting from the non-glycerol based polyols.

Urethane chemistry was selected to provide the rigid polymer network for foam formation since many people have tried to make polymers with soybean oil by using the free radical olefinic polymerizations with little success[8].. The B-side functionality of soybean oil was improved by imparting the oxirane functionality to the soybean oil through reacting the double bonds in soybean oil with hydrogen peroxide and organic acid[9,10,11]. This makes epoxy soybean oil attractive for its use in industrial applications but its application has been restricted to use as stabilizers in the PVC industry. Researchers have studied the potential of adding the epoxy soybean oil to the coating formulations [12] and adhesives [13] to improve properties of original formulations. Improved formulations were used in the current study.

In the current study, bodied epoxidized soybean oil was used in the making of epoxy resin by reacting BESBO with aliphatic amine.

Soybean oil triglycerides contain both saturated and unsaturated fatty acids. The unsaturated fatty acid composition exceeds 80% depending on the variety and climatic conditions of the harvest[14]. Polyurethanes prepared from vegetable oils

have a number of excellent properties derived from the hydrophobic nature of triglycerides[15]. The structure of triglyceride molecule (type of fatty acids in the triglycerides of the same oil) differ from molecule to molecule. This causes a variation in the chain length between crosslinks in polyurethanes obtained from oil based polyols, despite these variations it has been found that the glass transition of polyurethanes prepared from different oils varies fairly consistently with the hydroxyl content[16].

In the current study various polyols made from vegetable oils such as blown soybean oil, oxidized epoxidized diglyceride, Epoxidized diglyceride, diglyceride with –OH, peroxidized diglyceride etc. are tested for their reactivity which was measured as a function of presence of oxygen based functionality in the molecules. Also the polyols are characterized based on volume of the polyurethane foam resulting from the reaction of polyol with the isocyanate, type of resulting foam (soft, flexible, rigid, brittle etc) and the porosity of the foam as qualitatively interpreted.

It was found that blown soybean oil and oxidized epoxidized diglyceride resulted in about 60cc volume of foam. Also polyol reactivity was evaluated qualitatively based on reaction time and the number of oxygen based functional groups. It was found that castor oil, methoxylated epoxy soybean oil and peroxidized diglyceride had reaction times of 4 seconds.

5.3 Experimental methods

5.3.1 Materials

Bodied epoxidized soybean oil was prepared having an epoxy oxygen content of 3%prepared from bodied soybean oil measured as per AOCS standard method[17]. Polycat 5 and Polycat 8 catalysts were obtained from Air Products inc, sodium hydroxide solution (0.1N), triethylene tetramine (TETA) (60% tech), and potassium chloride solution (4M saturated with silver chloride) were purchased from Sigma-Aldrich (Milwaukee, WI), Castor oil was purchased from Alnor Oil Company, Inc,(Valley Stream, NY) and VORANOL-490 was purchased from Dow Chemicals (Midland, MI).

5.3.2 Experimental setup

In the making of ion exchange material using polyurethane foam, firstly, the foam was synthesized with a B-side consisting of 50% castor oil and 50% Voranol-490. This B-side was mixed with isocyanate in the ratio of 1:1 by weight of polyol to that of the isocyanate along with water and catalyst, each at 2% by weight in the B-side (40% polycat5 and 60% polycat8 of the total catalyst added). The foam was allowed to rise and stabilize before being hydrolyzed to generate bound carboxylic acid groups.

Acid hydrolysis of the foam was performed in order to induce the ion exchange capability. The following sample reaction is given for elucidation. Polyurethane foam (2g) was weighed into a 250ml 3-necked flask equipped with a thermometer

and a magnetic stir bar. To this, 100 ml sulfuric acid (10% conc. by volume) prepared by diluting the concentrated acid with distilled water was added and the contents were maintained at a temperature of 100^{o}C for a duration of 15 hrs with constant stirring. At the end of this duration the foam material was filtered and washed with warm distilled water until the pH was neutral. The resulting material was dried in the oven at 110^{o}C for 12 hours to remove water. The dried foam was then titrated with known concentration of NaOH base to determine the acid sites present measured as ion exchange capacity of the material.

The resin/composite was prepared by reaction of bodied epoxidized soybean oil prepared from bodied soybean oil bodied for duration of 1hr at 330^{o}C. The BESBO was reacted with TETA by preparing a mixture of BESBO (6g) and TETA in varied amounts (from 0.32g to 1.26g). The mixture was stirred at room temperature for 1hr. Then, the solution was poured into 20cc weighing cups. The mixture in the mold was cured over night at 100^{o}C and then at 140^{o}C for 48hrs. The resulting solid was analyzed for various properties.

In determining the reaction time of the each polyol (B-side) as shown in Table 5.3, the B-side was mixed with isocyanate in the ratio of 1:1 by weight of polyol to that of the isocyanate along with water and catalyst, each at 2% by weight in the B-side (40% polycat5 and 60% polycat8 of the total catalyst added). The time when the bubbles start to rise was noted (cream time) down along with the theoretically estimated oxygen based functional groups.

Polyurethane foam characterizations were performed as shown in Table 5.4.

Here, the B-side(polyol) was mixed with isocyanate in the ratio of 1:1 by weight of polyol to that of the isocyanate along with water and catalyst each at 2% by weight in the B-side (40% polycat5 and 60% polycat8 of the total catalyst added). The foam was allowed to rise and stabilize before being characterized both quantitatively through measurement of volume of the foam and qualitatively based on the texture of the foam and voids present in the foam.

5.3.3 Method of analysis

A 758 KFD (Karl Fisher Titrator), 703 Ti stand of Ω Metrochem was used to measure the acid sites in the acid hydrolyzed foam, the glass transition temperature (T_g) of the resin/polymer samples was measured using TA instruments (Newcastle, DE) Q100 Differential scanning calorimeter (DSC) capable of auto sampler operation from -90^{o}C to 600^{o}C. The percent weight loss of the resin/polymer samples was determined using TA Instruments (Newcastle, DE) Q50 Thermogravimetric Analyzer (TGA).

5.4 Results and discussion

5.4.1 Preparing soy-based ion exchange materials

As was evident from the EXPT NO 8, 9, 10, 11 given in Table 5.1 for a given acid concentration and duration of the reaction the percent hydrolyzed foam greatly depended on the temperature. As the temperature increased from 90 to 99^{o}C the percent hydrolyzed foam increased from 17 to 29%. This is consistent with the reaction rate doubling for every 10^{o}C increase in temperature.

For a given temperature and duration of the reaction the percent hydrolyzed foam tends to increase with increasing acid concentration as evident from the EXPT NO 12, 13, 15 given in Table 5.1 The acid is the catalyst that promotes hydrolysis.

The longer the duration of the reaction the greater the percent hydrolysis of the foam. This is evident from the EXPT NOs 1, 8, 14, 17 as given in Table 5.1

It has been observed that the product degradation occurred when using high concentrations of acid (>12%), temperatures > ~105^{o}C, and longer reaction times (>22 hours). Degradation produced a dark-colored, hard solid.

The optimum hydrolysis conditions are 8% acid, temperatures of 100-103^{o}C and reaction duration of about 17 hrs.

5.4.2 TETA formulations

As described in the experimental design summarized in Table 5.2, different weight ratios of BESBO/TETA were prepared to study the properties of the cured resin/polymer. The appropriate BESBO/TETA weight ratio ranged from 0.13:1 to 0.2:1. In screening studies, samples prepared outside/above this ratio range were found to process either similar or lower glass transition temperatures as evident from the DSC thermograms of Figure 5.1, Figure 5.2, Figure 5.3, and Figure 5.4.

One possible explanation might be that the BESBO has secondary (not primary) epoxy moiety, the secondary amine was believed to be difficult to react with the

secondary epoxy. Also, the complicated ring structure resulting from the usage of heat polymerized soybean oil might cause some amount of hindrance in terms of allowing for the reaction of epoxy group with the amine resulting in cross linkage. As a result, in spite of increasing the amine content relative to the amount of BESBO, the glass transition temperature tends to remain same.

From the DSC thermograms of Figure 5.1 and Figure 5.2 it can be seen that the samples give out heat as the temperature is increased from -20 to 50 ^{o}C. This can be attributed to the change in morphology of the components in the resin. In the case of the DSC thermograms of Figure 5.3 and Figure 5.4, the samples are absorbing heat with the increase in temperature in spite of going though the glass transition. This could possibly be due to the presence of some unreacted components in the resin contributing towards the absorption of heat. This was confirmed by a weight loss of 4.69 and 4.99% respectively as shown by the thermograms Figure 5.7 and Figure 5.8 in TGA analysis of these samples.

In the TGA thermograms the weight loss at the temperature of 267.28^{o}C was measured as this was the boiling point temperature of TETA. It can be seen from the thermograms of Figure 5.7 and Figure 5.8 that the weight loss is more comparable to that of the thermograms of Figure 5.5 and Figure 5.6. This to some extent suggests the presence of greater amount of unreacted TETA in the products resulting from the experiments Sl no 3, 4 as per the Table 5.2.

5.4.3 Development of polyol screening method

From Table 5.3 it is observed that the reactivity of polyol is proportional to the

oxygen based functionality except for the polyols consisting of epoxy groups which can be attributed to lower reactivity of epoxy groups in comparison to that of the hydroxyl and peroxy functionality. This is evident from the reported reaction times where in the reaction time of epoxy soybean oil having 4.6 epoxy groups has a reaction time of 60 sec while that of castor oil having 2.7 –OH functionality has a reaction time of 4 s and that of oxidized triglyceride (Blown) is 6 s estimated to have 3 oxygen based functionality (mixture of –OH and –OOH functionalities). From Table 5.4 it was observed that volume of the foam is proportional to oxygen based functionalities (-OH, -OOH) present in the compound except for the polyols consisting of epoxy groups reason same as cited above. This is evident from the obtained volume of the foams, in the case of blown soybean oil it resulted in the foam volume of 60cc while that of epoxy soybean oil having 4.6 epoxy groups resulted in the volume of 15cc.

5.5 Conclusion

Polyurethane foams containing triglyceride moieties can be converted to ion exchange materials through hydrolysis. In these studies, up to 43% of the vegetable oil based polyurethane foam can be hydrolyzed

In the case of reacting epoxidized soybean oil with TETA to form an epoxy resin, the final resin was found to have a glass transition temperature of 15^{o}C. The resin of the bodied epoxidized soybean oil with TETA had a glass transition temperature of ~23.5 ^{o}C.. The lower glass transition materials are considered particularly useful in the electrical encapsulation and potting formulations.

A method was successfully developed to screen soy-based polyols. The polyols containing secondary epoxy groups are less reactive (60 s reaction time) than polyols consisting of hydroxyl and peroxide functionalities (4 to 25 s reaction times, depending on the functionality of the polyol). The foam volume resulting from the reaction of the polyol with isocyanate was least for the epoxy soybean oil at 15 cc, indicating lower reactivity with isocyanate. The foam resulting from the use of blown soybean oil and oxidized epoxidized diglyceride were 60cc.

Table 5.1: Summary of experimental results of the acid hydrolysis of foam

Expt No	T(^{o}C)	%H2So4	Duration (hours)	% Hydrolyzed
1	90	11	16	33.6
2	90	4	16	10
3	73	3	26	5.1
4	101	15	22	Product degraded
5	77	15	12	9.7
6	100	15	9	24
7	94	15	14	25
8	99	15	12	28.86
9	96	15	12	20.7
10	90	15	12	18.54
11	90	15	12	17.3
12	105	1.5	10	13.2
13	105	3.5	10	21.8
14	105	8	16	40.1
15	105	5	10	27
16	90	3	8	9.2
17	103	8	17	43.084

Table 5.2: Summary of experiments carried out in the making of resin

SI No	BESBO [g]	TETA [g]	T [^{o}C]	Time [hrs]	T [^{o}C]	Time [hrs]
1	5	0.32	100	12	140	48
2	5	0.64	100	12	140	48
3	5	0.96	100	12	140	48
4	5	1.28	100	12	140	48

Table 5.3: Summary of Polyol reaction time and oxygen based groups in it

Polyol	RX(sec)	Qualitative Index	Oxy based func groups
Soybean oil	90	1	0
5o% Soybean oil + 50% Diglyceride	50	2	0.5
Diglyceride	25	3	1
Oxidized Diglyceride	8	4	3
Epoxy Soybean oil	60	2	4.6
50% Castor oil + 50% Diglyceride	6	5	1.9
Castor oil	4	5	2.7
Oxidized Triglyceride	6	5	3
Oxidized Epoxy Soybean oil	50	2	2.6
Epoxy Soybean oil with –OH func	4	5	4.6
Peroxidized Diglyceride	4	5	3

Table 5.4: Polyurethane foam characterization

Polyol	Volume(cc)	Type of foam	Porosity (voids)
Blown Soybean oil	61	Flexible (soft)	Very Less
Oxidized Epoxidized Diglyceride	60	Less Flexible	Very Less
Epoxidized Diglyceride	54	Hard (rigid)	Less
50% Diglyceride with –OH + 50% Epoxy Diglyceride	31	Hard (rigid)	Less
Diglyceride with -OH	34	Brittle	Less
Acetol + 0.2% H_2SO_4+ Epoxy Soybean oil	45	Brittle	Very High
Acetol + 1% H_2SO_4+ Epoxy Soybean oil	34	Brittle	Very High
Acetol + Epoxy Soybean oil	22	Brittle	Less
N_2 + Epoxidized Soybean oil	20	Brittle	Very Less
Air + Epoxidized Soybean oil	20	Brittle	Negligible
Epoxidized Soybean oil	15	Very Hard	Almost None (Solid)

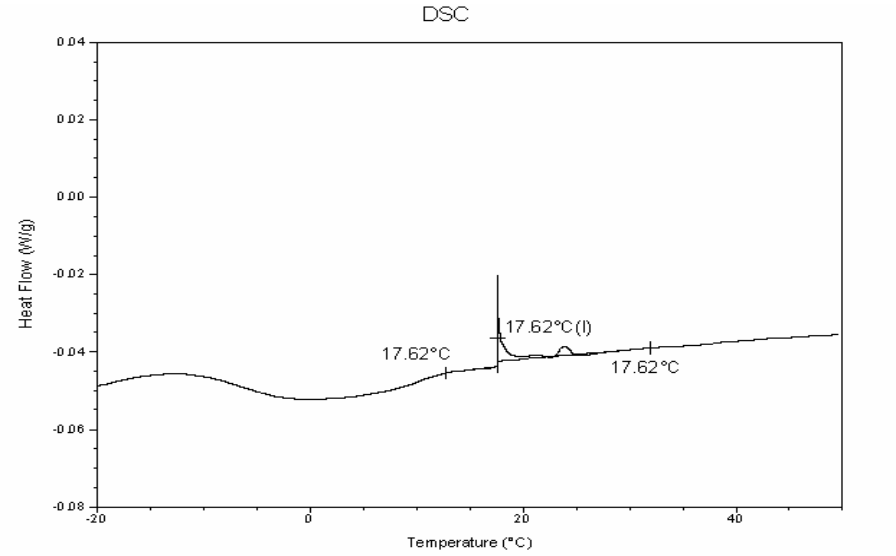

Figure 5.1: DSC thermogram showing the T_g (17.62^oC) of the cured BESBO (5g) by TETA (0.32g)

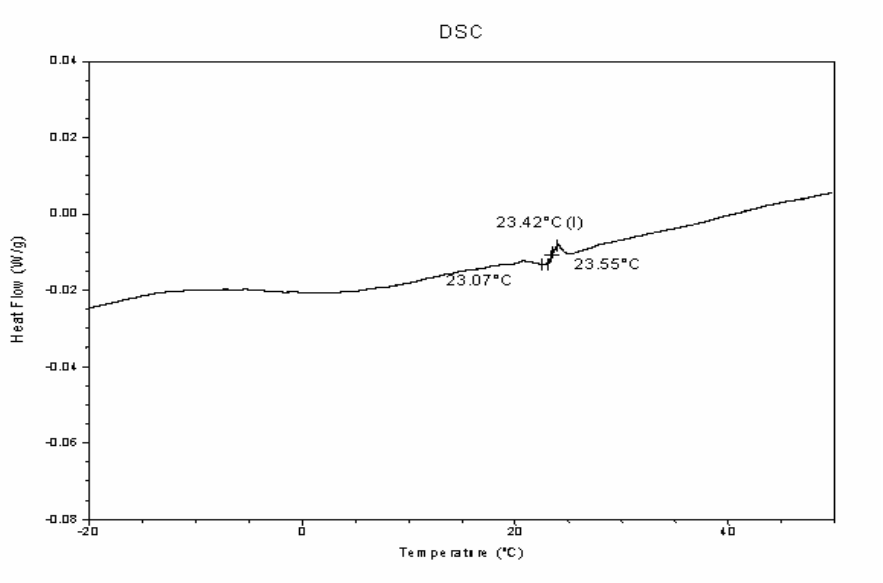

Figure 5.2: DSC thermogram showing the T_g (23.42^oC) of the cured BESBO (5g) by TETA (0.64g)

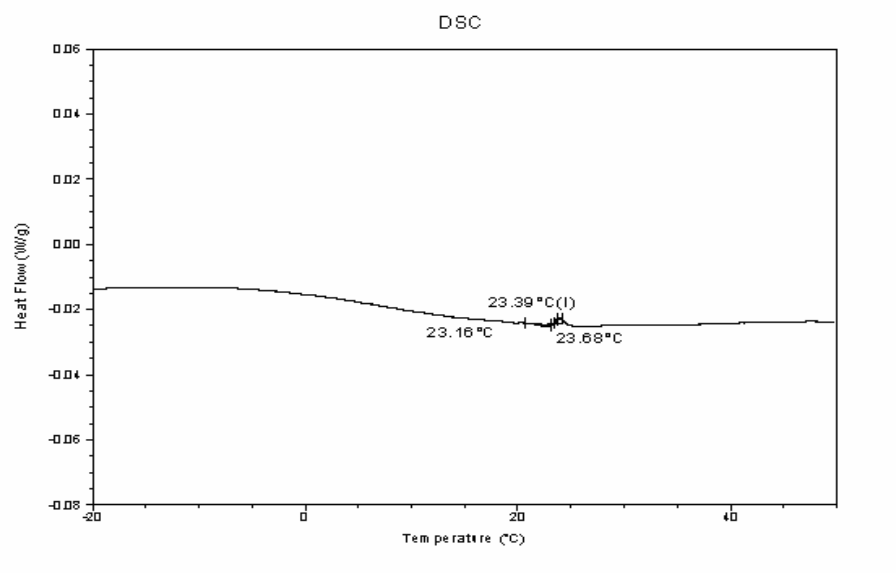

Figure 5.3: DSC thermogram showing the T_g (23.39^oC) of the cured BESBO (5g) by TETA (0.96g)

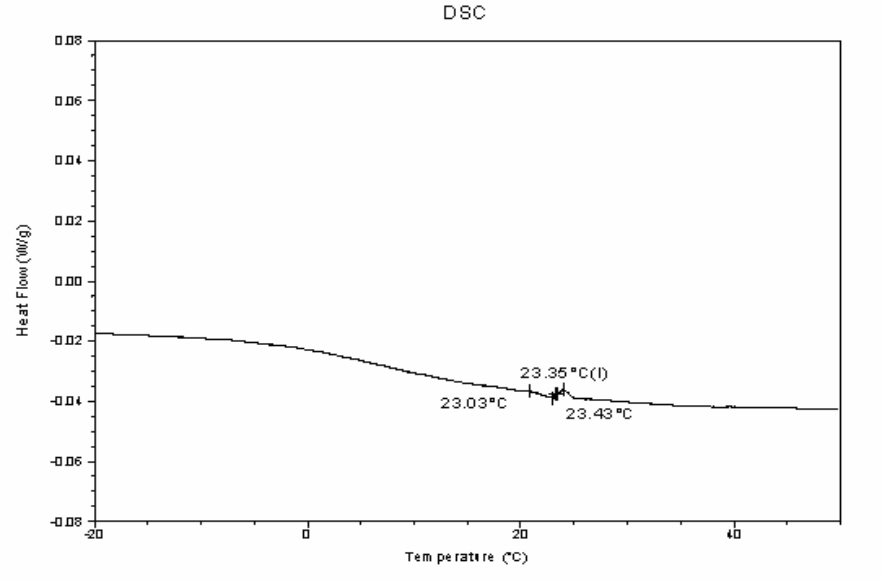

Figure 5.4: DSC thermogram showing the T_g (23.35^oC) of the cured BESBO (5g) by TETA (1.28g)

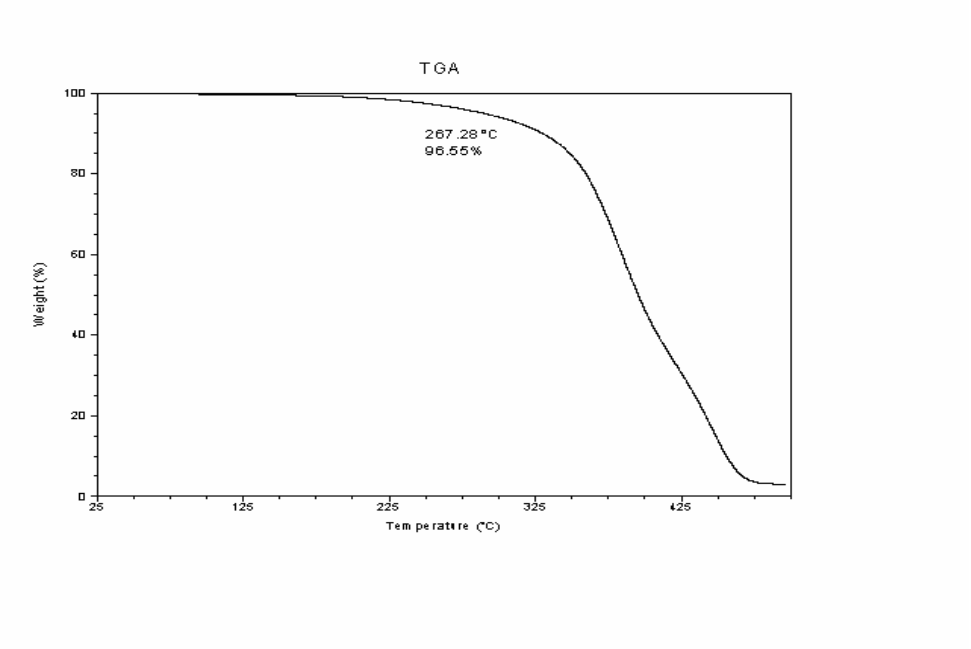

Figure 5.5: TGA thermogram showing the weight loss (3.45%) at 267.28 ^{o}C of the cured BESBO (5g) by TETA (0.32g)

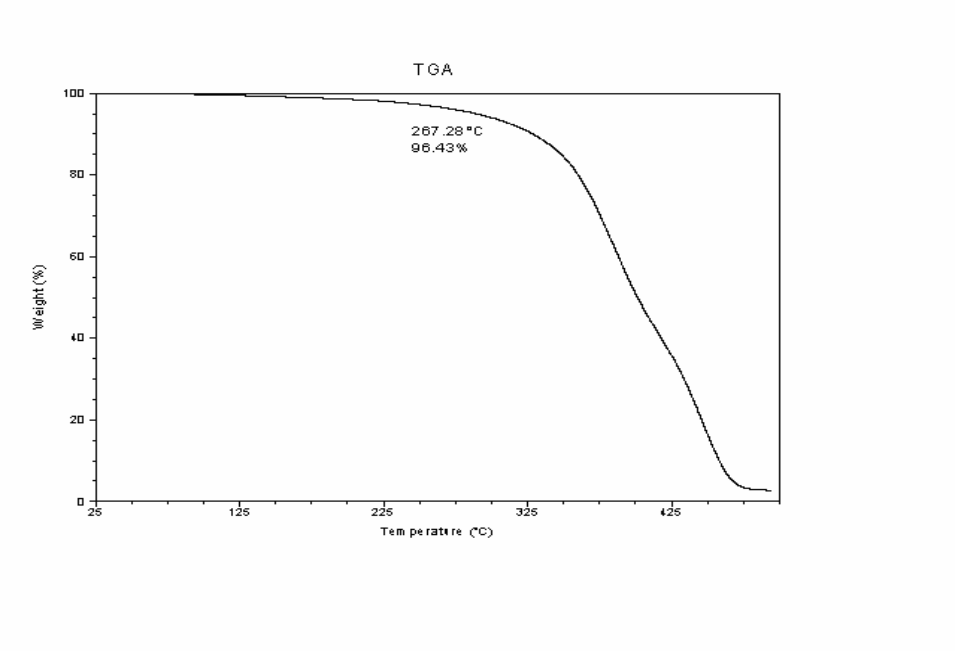

Figure 5.6: TGA thermogram showing the weight loss (3.57%) at 267.28 ^{o}C of the cured BESBO (5g) by TETA (0.64g)

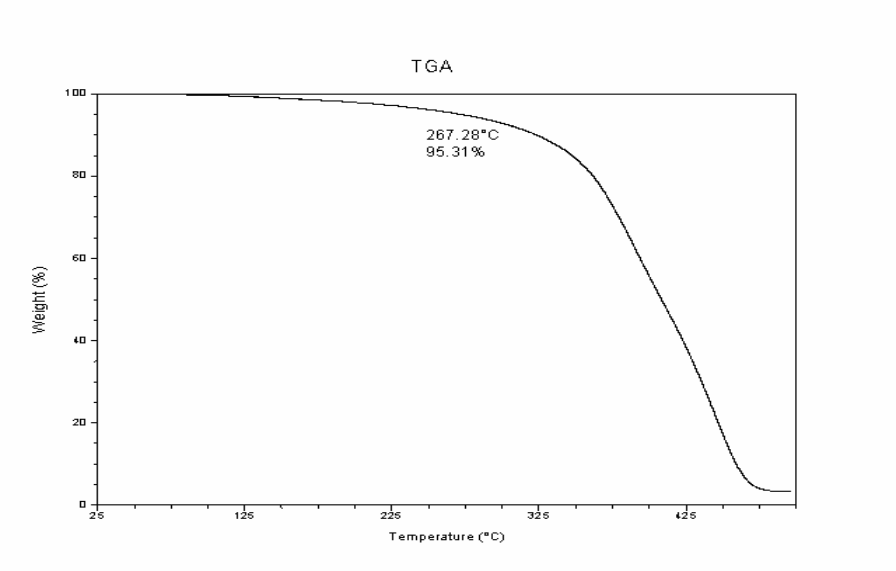

Figure 5.7: TGA thermogram showing the weight loss (4.69%) at 267.28 ^{o}C of the cured BESBO (5g) by TETA (0.96g)

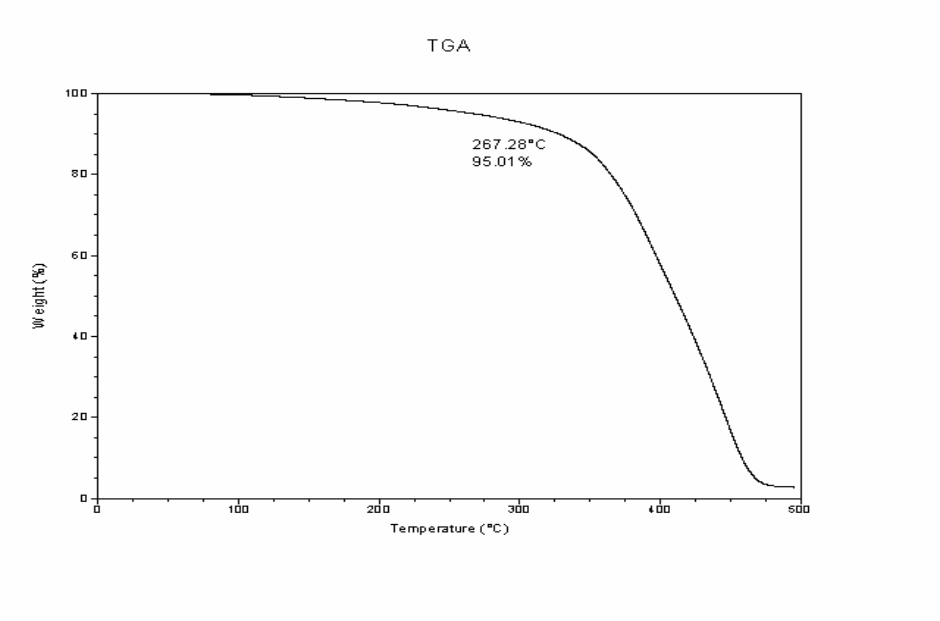

Figure 5.8: TGA thermogram showing the weight loss (4.99%) at 267.28 ^{o}C of the cured BESBO (5g) by TETA (1.28g)

5.6 References

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6 CHAPTER 6

SUMMARY AND AREAS OF FUTURE RESEARCH

6.1 Summary

Naturally occurring triglycerides essentially vegetable oils have the capability to be modified into polyols for use in the making of polyurethanes. Castor oil is a naturally occurring triglyceride having –OH functionality of 2.7 while soybean oil has the chemical structure that enables it to be suitably modified to obtain polyols.

6.2 Areas of future research

The research presented in this thesis demonstrates base case example of how vegetable oils can be converted to polyols through simple but effective processing. Future investigation can target to achieve the following: -

- GPC techniques to better-characterize molecular weights and related properties of the monomer products.
- Catalysts to reduce the bodying temperature and the duration of bodying to obtain product of desired viscosity and molecular weight.
- Designed experiments to better understand the reasons behind a near constant decrease in iodine value 30% of the starting material in polyols

made utilizing acetol and allyl alcohol upon reaction with SBO and BSBO respectively.

- Catalysts to increase attachment of acetol and allyl alcohol to soybean oil in order to obtain polyols with high hydroxyl content.
- Applications of the BESBO in the making of resins/composites with varying properties such as T_g, conductivity, and tensile strength. and
- Suitable foam formulations of the above polyols .

7 CHAPTER 7

CONSTRUCTION OF MEA FOR THE PEM FUEL CELLS

7.1 Abstract

A method of making a membrane-electrode-assembly (MEA) for the proton exchange membrane fuel cell comprises applying an electrode-forming material directly onto a membrane-electrode film. In this chapter preliminary experimental methods were developed to fabricate MEAs from commercially available materials.

The slurry comprised of a liquid vehicle carrying catalyst particles and a binder (5 wt% Nafion solution) for the catalyst particles was applied to a Nafion membrane. The Nafion membrane electrolyte was preswollen by contact with ethylene glycol before the electrode-forming slurry is applied to the membrane-electrolyte. When drying, the swollen membrane-electrolyte was constrained against shrinking in the “X” and “Y” directions during drying. The MEA thus obtained was hydrated and assembled in the fuel cell. The performance of the MEA was measured based on the amount of current that is being generated and also the voltage obtained

KEY WORDS: MEA, Fuel Cell, Nafion, Ethylene Glycol.

7.2 Introduction and Background

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 7.1.

In a fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode); the electrochemical reactions take place at the electrodes to produce an electric current Figure 7.2. A fuel cell, although having components and characteristics similar to those of a typical battery, differs in many aspects. The battery is an energy storage device. The maximum energy available is determined by the amount of chemical reactant stored within the battery itself. The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e., discharged). In a rechargeable battery, the reactants are regenerated by recharging, which involves putting energy into the battery from an external source. The fuel cell, on the other hand, is an energy conversion device that theoretically has the capability of producing electrical energy for as long as fuel and oxidant are supplied to the electrodes. In reality, degradation, primarily corrosion, or malfunction of components limits the practical operating life of fuel cells.

Figure 7.1 shows that an ion specie and its transport direction can differ, influencing the site of water production and removal. The ion can be either a positive or a negative ion, meaning that the ion carries either a positive or negative charge (surplus or deficit of electrons). The fuel or oxidant gases flow past the surface of the anode or cathode opposite the electrolyte and generate electrical energy by the electrochemical oxidation of fuel, usually hydrogen, and the electrochemical reduction of the oxidant, usually oxygen. In theory, any substance capable of chemical oxidation that can be supplied continuously (as a fluid) can be burned galvanically as fuel at the anode of a fuel cell[1]. Similarly, the oxidant can be any fluid that can be reduced at a sufficient rate. Gaseous hydrogen has become the fuel of choice, because of its high reactivity when suitable catalysts are used, its ability to be produced from hydrocarbons. Similarly, the most common oxidant is gaseous oxygen, which is readily and economically available from air, and can be easily stored. A three-phase interface is established among the reactants, electrolyte, and catalyst in the region of the porous electrode. The nature of this interface plays a critical role in the electrochemical performance of a fuel cell, particularly in those fuel cells with liquid electrolytes. In such fuel cells, the reactant gases diffuse through a thin electrolyte film that wets portions of the porous electrode and react electrochemically on their respective electrode surface. If the porous electrode contains an excessive amount of electrolyte, the electrode may "flood" and restrict the transport of gaseous species in the electrolyte phase to the reaction sites. The consequence is a reduction in the electrochemical performance of the porous electrode. Thus,

a balance must be maintained among the electrode, electrolyte, and gaseous phases in the porous electrode structure.

Much of the recent effort in development of fuel cell technology has been devoted to reducing the thickness of cell components while refining and improving the electrode structure and the electrolyte phase, with the aim of obtaining a higher and more stable electrochemical performance while lowering cost[2].

The electrolyte not only transports dissolved reactants to the electrode, but also conducts ionic charge between the electrodes and thereby completes the cell electric circuit, as illustrated in Figure 7.1. It also provides a physical barrier to prevent the fuel and oxidant gas streams from directly mixing.

The functions of porous electrodes in fuel cells are: 1) to provide a surface site where gas/liquid ionization or de-ionization reactions can take place, 2) to conduct ions away from or into the three phase interface once they are formed (so an electrode must be made of materials that have good electrical conductance), and 3) to provide a physical barrier that separates the bulk gas phase and the electrolyte. In order to increase the rates of reactions, the electrode material should be catalytic as well as conductive, porous rather than solid. The catalytic function of electrodes is more important in lower temperature fuel cells and less so in high temperature fuel cells because ionization reaction rates increase with temperature. It is also essential that the porous electrodes must be permeable to both electrolyte and gases, but not such that the media can be easily "flooded" by the electrolyte or "dried" by the gases.

Typical cell components within a PEFC/PEMFC stack include: 1) the ion exchange membrane; 2) an electrically conductive porous backing layer; 3) a catalyst layer (the electrodes) sandwiched between the backing layer and the membrane, and 4) cell plate hardware shown in a double sided (bi-polar) configuration that delivers the fuel and oxidant to the reactive sites via flow channels, as shown in Figure 7.3, Figure 7.4.

Membrane: Organic-based cation exchange membranes in fuel cells were originally made by W. T. Grubb in 1959[3]. This eventually led to development of the perfluorosulfonic acid polymer used in today's systems. The function of the ion exchange membrane is to provide a conductive path while at the same time separating the reactant gases. The material is an electrical insulator. As a result, ion conduction takes place via ionic groups within the polymer structure. Ion transport at such sites is highly dependent on the bound and free water associated with those sites[4].

A commonly used material, Nafion®10 is a polymer that falls within the perfluorosulfonic acid family. It is characterized by a backbone structure that is Teflon®-like, i.e., polytetrafluoroethylene, and which has bonded to it a perfluorinated side chain that has a terminal sulfonic acid group (SO_3-). It is through the regular repeating of the sulfonic acid sites on the side chains that ionic transport characteristics are attained. For the most part, the number of sulfonic acid sites dictates the ionic conductivity of such systems. Even though the bulk of the polymer is fluorinated, imparting a highly hydrophobic character to the bulk of the membrane, the sulfonic acid sites are hydrophyllic. The degree of

water content a membrane can attain is proportional to the ionic sites and, as a result, the significant properties of the membrane (conductivity, gas permeability, and mechanical properties) are dictated by water content.

Porous backing layer: The polymer membrane is sandwiched between two sheets of porous backing media. The function of the backing layer is to: 1) act as a gas diffuser; 2) provide mechanical support, and 3) provide an electrical pathway for electrons. The backing layer is typically carbon-based, and may be in cloth form, a non-woven pressed carbon fiber configuration, or simply a felt-like material. The layer incorporates a hydrophobic material, such as polytetrafluoroethylene. The function of polytetrafluoroethylene is to prevent water from accumulating within the pore volume of the backing layer so that gases freely contact the catalyst sites. Furthermore, it facilitates product water removal on the cathode as it creates a non-wetting surface within the passages of the backing material.

Electrode-catalyst layer: In intimate contact with the membrane and the backing layer is a catalyst layer. This catalyst layer, integral with its binder, forms the electrode. The catalyst and binder electrode structure is either applied to the membrane or else applied to the backing layer. In either case, the degree of intimacy of the catalyst particles and the membrane is critical for optimal proton mobility. The binder helps in binding the catalyst particles within the layered structure and thereby contributes to the overall architecture of the electrode. This architecture has a direct bearing on performance through the enhanced membrane/catalyst contact which helps to minimize the platinum loading

requirements[5].

The catalyst is platinum-based for both the anode and cathode. To promote hydrogen oxidation, the anode uses either pure platinum metal catalyst or a supported platinum catalyst, typically on carbon or graphite for pure hydrogen feed streams.

Typically, the electrodes can be cast as thin films that can be either transferred to the membrane or applied directly to the membrane[6]. Alternatively, the catalyst electrode layer may be deposited onto the backing layer, then bonded to the membrane.

The electrolyte in proton exchange membrane (PEM) fuel cell is an ion exchange

membrane (fluorinated sulfonic acid polymer or other similar polymer) that is an excellent proton conductor. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Water management in the membrane is critical for efficient performance; the fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated. Because of the limitation on the operating temperature imposed by the polymer, usually less than 120°C, and because of problems with water balance, a H2-rich fuel is used.

The actual cell potential is decreased from its equilibrium potential because of irreversible losses, as shown in

Figure 7.5. Multiple phenomena contribute to irreversible losses in an actual fuel cell. The losses, which are called polarization, overpotential, or overvoltage (η), originate primarily from three sources: 1) activation polarization, 2) ohmic polarization, and 3) concentration polarization. These losses result in a cell voltage (V) that is less than its ideal potential, E (V = E - Losses).

From

Figure 7.5 it can be observed that the activation polarization loss is dominant at low current density. At this point, electronic barriers must be overcome prior to current and ion flow. Activation losses increase as current increases. Ohmic polarization (loss) varies directly with current, increasing over the entire range of current because cell resistance remains essentially constant. Gas transport losses occur over the entire range of current density, but these losses become prominent at high limiting currents where it becomes difficult to provide enough reactant flow to the cell reaction sites.

Activation Polarization: Activation polarization is present when the rate of an electrochemical reaction at an electrode surface is controlled by slow electrode kinetics. In other words, activation polarization is directly related to the rates of electrochemical reactions. There is a close similarity between electrochemical and chemical reactions in that both involve an activation energy that must be overcome by the reacting species.

Ohmic Polarization: Ohmic losses occur because of resistance to the flow of ions in the electrolyte and resistance to flow of electrons through the electrode. The

dominant ohmic losses through the electrolyte are reduced by decreasing the electrode separation and enhancing the ionic conductivity of the electrolyte.

Concentration Polarization: As a reactant is consumed at the electrode by electrochemical reaction, there is a loss of potential due to the inability of the surrounding material to maintain the initial concentration of the bulk fluid. That is, a concentration gradient is formed. Several processes may contribute to concentration polarization: slow diffusion in the gas phase in the electrode pores, solution/dissolution of reactants and products into and out of the electrolyte, or diffusion of reactants and products through the electrolyte to and from the electrochemical reaction site. At practical current densities, slow transport of reactants and products to and from the electrochemical reaction site is a major contributor to concentration polarization.

Screening studied were conducted to determine the concentration of vehicle that needs to be used for the pretreatment of the membrane to study the swelling in the X,Y and Z directions, before the catalyst layers (electrodes) are applied onto the membrane and also to use it as the vehicle in the making of catalyst slurry consisting of the catalyst, binder and the vehicle. This is primarily done in order to attain a better adhesion of the catalyst to the polymer electrolyte. The pretreatment of the membrane is done with the swelling agent that has the same composition as the vehicle used in the making of the electrode forming slurry. The choice of the vehicle in the case of polymer electrolyte (membrane) consisting of sulfonic acid cation exchange groups is preferably made from the group consisting of water and glycols in order to minimize the swelling of the

membrane-electrolyte.

The objective of the current study was to make membrane electrode assemblies (MEA'S) in-house using the membrane and the catalysts available off the shelves. To optimize the conditions in order to obtain a better bonding of the electrode to the membrane. The MEA'S thus prepared were tested for their performance.

7.3 Experimental methods

7.3.1 Materials

Nafion membrane N-112^R was procured from fuelcell store. Nafion solutions (5 wt% dispersion in liquid) were procured from Alfa Aesar. 5 wt% platinum on carbon catalyst was procured from Degussa corporation. Ethlene glycol HPLC grade from Sigma Aldrich was obtained.

7.3.2 Experimental procedure

The Nafion 112 membranes were pretreated by soaking it in a 30 mole% ethylene glycol solution in water for about 4 minutes. The membrane was then taken out of the solution and the excess solution was wiped off. The membrane was then constrained from shrinkage by clamping it in the X and Y directions. Catalyst paste was then prepared by mixing 0.1 mg of platinum per cm^2 (using 5 wt% platinum on carbon catalyst having about 60% water as moisture) and 0.9mg of nafion loading per cm^2 (using 5 wt% nafion dispersed in aliphatic alcohol solution) of the area over which it is to be applied with 30 mol% ethylene glycol solution in water. The slurry was added to the ethylene glycol-water to achieve 52% by

weight slurry. The mixture thus prepared was placed in the oven at 80^{o}C for 4 minutes to remove the alcohol present in the nafion solution and then applied to membrane surface. The resulting MEA was heated in the oven at 80^{o}C for about 30 minutes to remove the ethylene glycol present followed by heating in the oven at 130^{o}C for about 10 minutes in order to cure the binder (i.e. Nafion).

7.3.3 Method of testing

As per the above experimental procedure, the MEA's were prepared and were tested for their performance in the fuel cell assembly. Measurements of current and voltage were taken for different load resistances for a given flow rate of hydrogen and oxygen and at a given temperature of the cell (80^{o}C).

7.4 Results and discussion

From the screening studies as summarized in

Table 7.1 it was determined that a 30 mol% solution of ethylene glycol solution in water was the optimal choice. This mixture maintained minimal swelling of the membrane while allowing for a paste of reasonable viscosity for application.

From the plots Figure 7.6, Figure 7.7 it can be seen that the performance of the MEA reduces rapidly and almost linearly with increasing amperage. This is possibly a result of ohmic resistance as a result of improper contact between various components of the fuel cells. The linear nature is characteristic of ohmic losses as summarized by Figure 7.5 One possible reason for the low performance of the MEA in the fuel cell is the usage of 5wt% pt on carbon catalyst, as it introduces lot of carbon and reduces the availability of active sites on the

surface of the electrode.

7.5 Conclusion

The objective of the project in the making of in-house membrane electrode assemblies for the fuel cells was successfully achieved. Further investigations with a higher percent of platinum on carbon catalyst need to be carried out to get better insight about the performance of the MEA'S in the fuel cells.

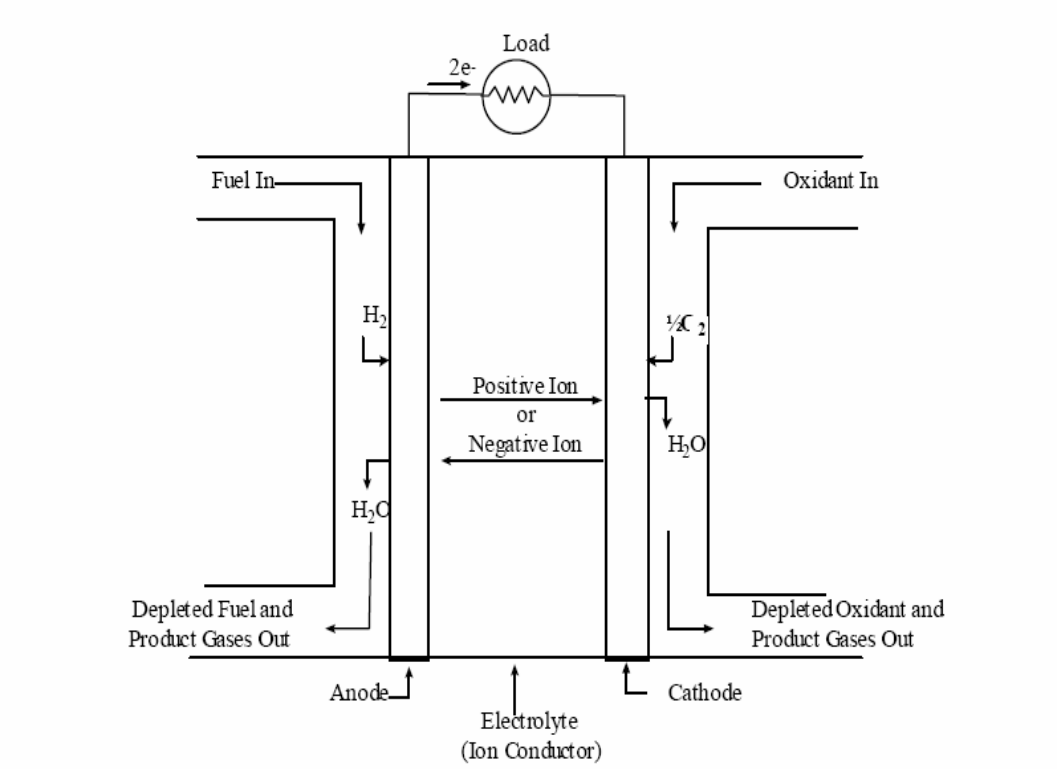

Figure 7.1: The schematic of an individual fuel cell operation

Anode Reaction:

$$H_2 \rightarrow 2H^+ + 2e^-$$

Cathode Reaction:

$$\tfrac{1}{2}\, O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Figure 7.2: Electrochemical reaction in proton exchange membrane fuel cell

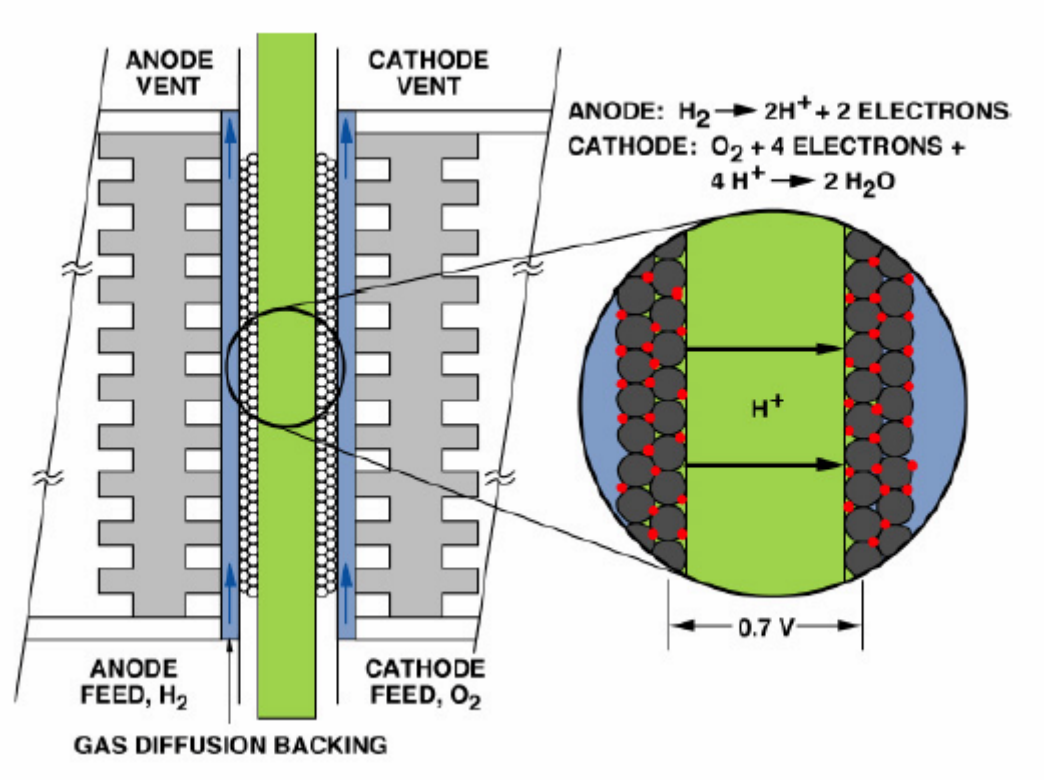

Figure 7.3: Schematic of representative proton exchange membrane fuel cell

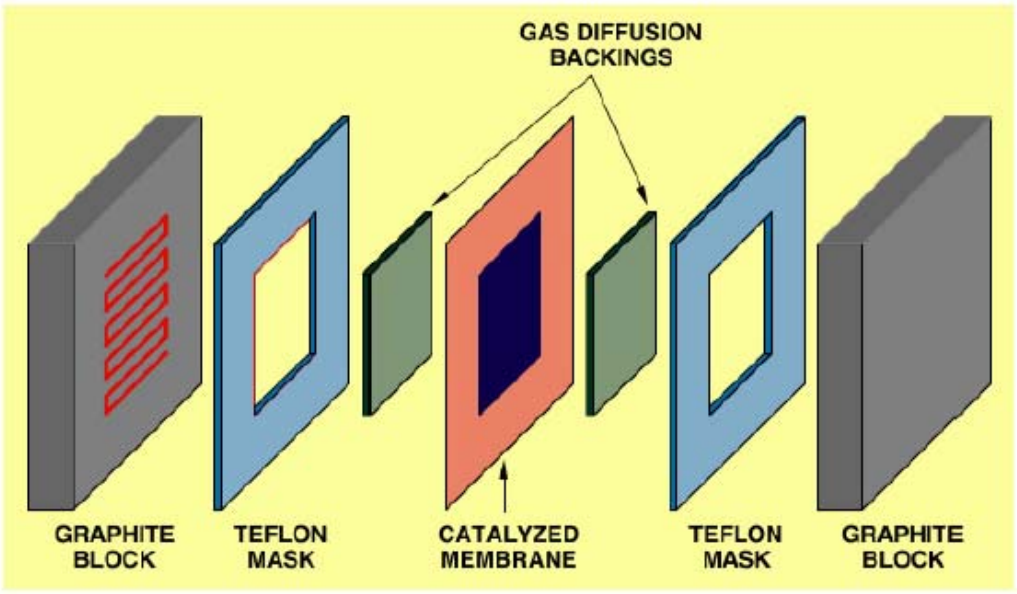

Figure 7.4: Components of single cell proton exchange membrane fuel cell

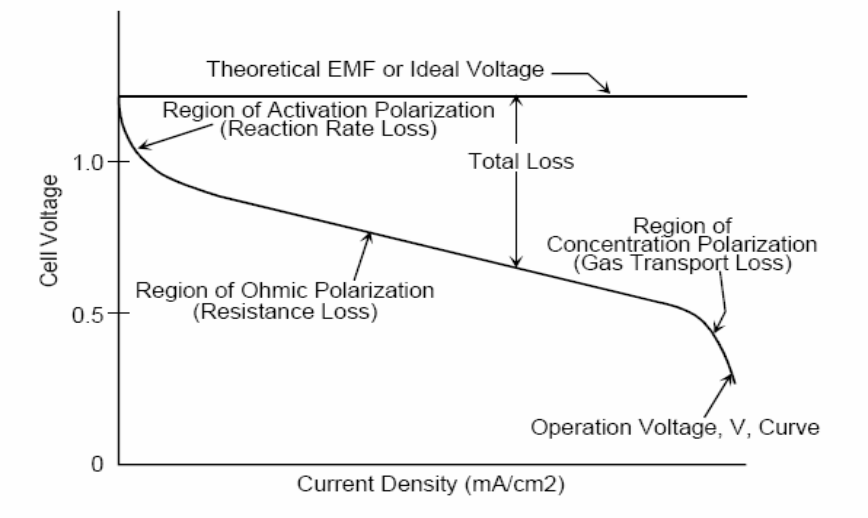

Figure 7.5: Ideal and actual fuel cell voltage/current characteristic

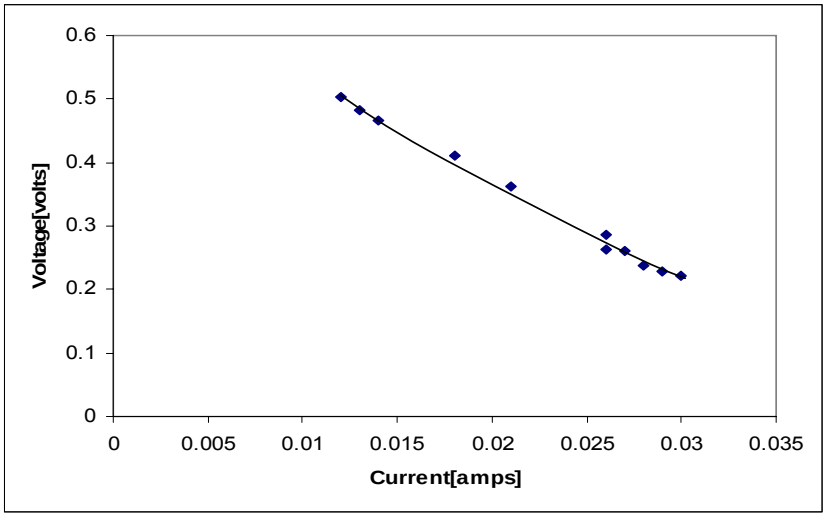

Figure 7.6: The voltage/current characteristic for an MEA having an electrode surface area of 1cm^2 with 0.1mg/cm^2 of platinum loading

Flow rates:

Hydrogen: 16.7cc/sec

Oxygen: 44.44cc/sec

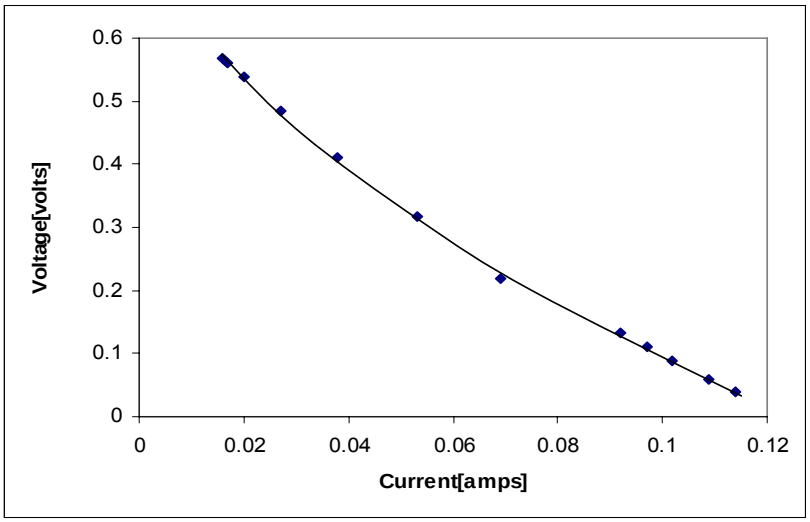

Figure 7.7: The voltage/current characteristic for an MEA having an electrode surface area of 4cm^2 with 0.1mg/cm^2 of platinum loading

Flow rates:

Hydrogen: 16.7cc/sec

Oxygen: 44.44cc/sec

Table 7.1: Screening studies conducted to determine the swelling occurring in each direction in the membrane

SI Nos	Mol% ethylene glycol in water	Duration of soaking (min)	Dimensions of the membrane (X xY xZ) 2x2x 0.0051cm
1	10	4	2.3 x2.33 x0.0057
2	20	4	2.32 x2.35 x0.0057
3	30	4	2.33x2.38 x0.0058
4	40	4	2.38x2.4x0.0060
5	50	4	2.4x2.4 x0.006
6	60	4	2.43x2.42 x0.0062
7	70	4	2.45x2.47 x0.0061
8	80	4	2.5x2.48 x0.0063
9	90	4	2.53x2.51x0.0062
10	100	4	2.52x 2.54x0.0063

7.6 References

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