

# Synthesis and Characterization of Triglyceride-Based Polyols and Tack-Free Coatings via the Air Oxidation of Soy Oil

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**ABSTRACT:** The effect of time and temperature on the air oxidation of soybean oil in the absence of catalysts or added initiators was investigated. It was possible to divide the air oxidation of soybean oil into three regimes. The first regime of air oxidation resulted in insignificant change in the hydroxyl number. During this regime, it was proposed that natural antioxidants, which are present in raw soybean oil, were consumed and peroxide formation occurred. A drastic increase in hydroxyl number due to the formation and subsequent decomposition of peroxides marked the second regime of air oxidation. In the third regime of air oxidation, free radical crosslinking of the soybean oil occurred, and an insoluble gel was formed. The three regimes of air oxidation

were used as a guide for the preparation of soy-based polyols and crosslinked polymers. Crosslinked, tack-free coatings were prepared from a metal catalyzed oxidation of soybean oil, where soybean oil and ambient oxygen were the only reactants. Higher temperatures (125°C) were more efficient than lower (50°C) for obtaining high gel fractions and tack-free coatings. Cure of the coatings was expedited with exposure of the coating to UV irradiation after initial heating. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 690–697, 2006

**Key words:** oxidation; renewable resources; coatings

## INTRODUCTION

Renewable resources have received increased attention as potential alternatives to traditional petroleum-based monomer feedstocks.<sup>1,2</sup> Synthetic approaches that range broadly from incorporating various triglycerides into polyurethane networks to use enzymes as catalysts for polycondensations were targeted for the use of renewable resources as replacements for traditional feedstocks.<sup>3,4</sup> Soybean oil is an abundant and inexpensive vegetable oil, and these agriculture-based triglycerides are considered green feedstocks. Multiple sites of chemical reactivity are intrinsic in soybean-based triglycerides, which makes this renewable resource particularly attractive as a potential alternative to petroleum-based monomers.<sup>5–7</sup> Previous investigations of soybean oil as a potential monomer have used well-established synthetic organic methodologies to modify the internal unsaturated sites.<sup>8</sup> Various synthetic strategies for the introduction of specific reactive functionalities including epoxide,<sup>9</sup> hydroxyl,<sup>10</sup> and aldehyde<sup>11</sup> groups were developed.<sup>11–15</sup> The ap-

plications for soy-based monomers have included rigid polyurethane foams and photo-crosslinkable monomers for adhesives.<sup>9,16–18</sup> Polymers with shape memory attributes were synthesized via the cationic polymerization of soybean oil and crosslinked with divinylbenzene.<sup>19</sup> Halogenated soy-based polyols derived from epoxidized soybean oil were used in the synthesis of polyurethanes, and the effects of pendant halogens that are adjacent to the reactive hydroxyls were investigated.<sup>10</sup>

While the synthesis of monomer feedstocks was primarily explored with traditional synthetic approaches, oxidation of lipids and fats has also gained significant interest because of its important role in several areas including human health with its implications for aging, cancer, and heart disease as well as in food spoilage and monomer feedstocks.<sup>20–23</sup> Because of this broad applicability, lipid oxidation has received significant interest in the literature. Extensive studies of the mechanism of autoxidation of lipids elucidated the initiation and subsequent steps of this free radical reaction. Air oxidation involves free radical intermediates due to the abstraction of allylic hydrogens and the subsequent formation of a delocalized free radical. These free radicals react with ambient oxygen and other triglycerides to form polyols and a host of other products. Multiple products were re-

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ported earlier from the catalyzed autoxidation of soybean oil, including hydroxyl-containing compounds.<sup>24</sup> Several kinetic stages of autoxidation were described for fats under constant pressure.<sup>25</sup> The extent of oil oxidation is frequently assessed using a variety of techniques, which include iodine value, color, refractive index, percentage of free fatty acids, total polar compounds, and hydroxyl number, which is the milligrams of potassium hydroxide equivalent to the hydroxyl groups of one gram of sample.<sup>26–30</sup> These time-consuming techniques require large amounts of organic solvents and precise measurements for reproducible results. Changes in the longitudinal and transverse relaxation times from <sup>1</sup>H NMR were compared with the increase in free fatty acid percentage and total polar materials of oxidized soybean oil.<sup>31</sup>

Renewable resources have received notable attention as important components of coatings, especially as drying oils in alkyd and other resins.<sup>32–34</sup> Moreover, the synthesis of novel coatings from derivatized renewable resources was highlighted in a recent review.<sup>14,35</sup> Coatings used for a variety of applications including anticorrosion and waterborne coatings have successfully incorporated modified soybean oil as a component.<sup>32,36</sup>

The air oxidation in the absence of catalyst, which represents the simplest reaction in term of reactants, i.e., air and soybean oil, has not received significant attention for the synthesis of monomer feedstocks. These reactions also produce polyols, which are suitable for subsequent polymer synthesis. The focus of this research was to investigate the free radical air oxidation of soybean oil and subsequent polyol formation. Synthetic strategies for preparing high hydroxyl number soy polyol monomer feedstocks were developed as a function of time and temperature. In this study, air at a constant flow rate was distributed to the soybean oil. For the first time in this work, three regimes of air oxidation were identified using <sup>1</sup>H NMR spectroscopy, viscosity, and hydroxyl number determination as complementary characterization techniques to monitor the oxidation of soybean oil. In this article, the relationship between hydroxyl number, an analytical technique that requires several titrations, and the doubly allylic resonance in the <sup>1</sup>H NMR spectrum was determined for oxidized soybean oil. The use of <sup>1</sup>H NMR spectroscopy for determination of the extent of oxidation provided a straightforward analysis of oxidized soybean oil.

Emergence of the three regimes of soybean oil air oxidation provided a framework for the more well-defined synthesis of renewable resource-based raw materials. Soy polyols with high hydroxyl number were produced for use in the synthesis of polyesters, polyurethanes, and multifunctional acrylates when the second regime of air oxidation was targeted. The third regime of air oxidation, which includes signifi-

cant branching and crosslinking, produced interesting polymeric networks. Crosslinked coatings synthesized from raw soybean oil were also investigated in this work.

## EXPERIMENTAL

### Statistical design of experiments

A central composite statistical design of experiments (DOE) was developed for the investigation of the air oxidation of soybean oil. The factors assigned for this DOE were temperature, time, and air flow rate. Temperatures ranging from 77 to 110°C, reaction times ranging from 1 to 6 days, and air flow rates from 10 to 40 L min<sup>-1</sup> were investigated. The responses modeled for this DOE were hydroxyl number, viscosity, and doubly allylic and singly allylic <sup>1</sup>H NMR resonances with Stat-Ease software. The Design-Expert version 6.0.1 was used and the central composite design was chosen to model these experiments.

### Air oxidation

The soybean oil was heated to the appropriate temperature in a 250-mL, round-bottomed flask, which was stirred with a magnetic stir bar, and equipped with a dispersion tube that delivered air for the allotted time. The air used in the soybean oil oxidation was kept at ambient temperature prior to entering the reaction flask. For example, 100 mL of raw soybean oil in a 250-mL, two-neck, round-bottomed flask was heated to 110°C while air was delivered to the sample via a dispersion tube at 25 L min<sup>-1</sup> for 3 days. For the high pressure reactions, a Parr reactor charged with 100 mL of raw soybean oil was held at constant temperature and pressure. The reaction was vigorously stirred with the mechanical stirrer in the reactor. The sample was allowed to cool to room temperature after the reaction was completed and analyzed with <sup>1</sup>H NMR spectroscopy, hydroxyl number determination, and viscosity measurements. The allylic protons were found at 2.01 ppm and the doubly allylic protons were found at 2.79 ppm using a Varian Unity 400 MHz NMR at ambient conditions with *d*-chloroform as the NMR solvent. The normalized doubly allylic resonance was calculated from division of the integration of the doubly allylic resonance for the oxidized sample by the integration of the raw soybean oil. The statistical DOE software (Stat-Ease) was used to model the system. Thermogravimetric analysis (TGA) was conducted on a TA Instruments High Res TGA 2950 thermogravimetric analyzer under an oxygen flow rate of 60 mL min<sup>-1</sup>. An ASI ReactIR 1000 (Mettler-Toledo, Columbus, OH) was used for the *in situ* FTIR spectroscopic investigations. Size exclusion chromatography (SEC) was performed at 40°C in tetrahydrofuran at 1

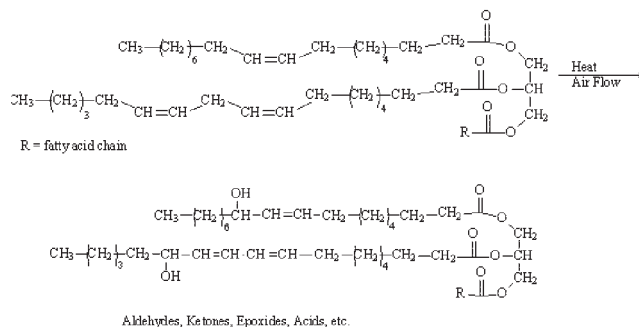
mL min<sup>-1</sup> with three 5- $\mu$ m PLgel columns in series and using a Waters 717 autosampler and Waters 2410 refractive index detector. UV-vis spectra were collected with an Analytical Instrument Systems, spectrometer equipped with fiber optics light guides, a DT1000CE light source, and an Ocean Optics USB2000 UV-vis detector. Viscosity measurements of 100% soybean oil were performed with a TA Instruments AR 1000 rheometer. The geometry used was a 40 mm cone (1.59°) and plate at a gap of 44  $\mu$ m in rotational mode at 25°C.

### Hydroxyl number determination

Hydroxyl number is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl groups of one gram of sample. The hydroxyl number was determined using the procedure outlined in American Oil Chemists' Society (AOCS) Tx 1a-66. The procedure includes the use of pyridine and *n*-butyl alcohol as solvents. Acetic anhydride was reacted with the hydroxyl groups of the soy polyol. Excess acetic anhydride was quenched with water and back titrated with 1.0N KOH in ethanol with phenolphthalein as the indicator. The acid number was determined using the acid value procedure according to AOCS Cd 3d-63. Isopropyl alcohol and toluene were used to dissolve the soy polyol, and the acid was immediately titrated with 0.1N KOH in ethanol using phenolphthalein to indicate the endpoint.

### Film formation

Thin films were formed from a 5 wt %/vol % mixture of raw soybean oil and cobalt(II) ethyl hexanoate (65 wt % solution in mineral oil). The low viscosity mixture was thoroughly blended and drawn in a controlled manner with a doctor blade across a glass microscope slide to create a 100- $\mu$ m layer. These films were heated in an oven for a given period of time at 50, 100, or 125°C. Some films were also exposed to UV irradiation from an Oriel UV reactor. A TA.XT2i Texture Analyzer (Texture Technologies, Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK) was used to perform the tack tests according to ASTM D 2979. The parameters included a probe speed of 10 mm s<sup>-1</sup>, 1.42 psi applied pressure, and a residence time of 0.1 s. Gel fractions were determined after soxhlet extraction in refluxing tetrahydrofuran for 24 h. The soxhlets were dried under vacuum for 48 h prior to the determination of gel fraction. Glass transition temperatures were determined under nitrogen on a Perkin-Elmer Pyris 1 cryogenic instrument at a heating rate of 10°C min<sup>-1</sup>. The  $T_g$  was reported as the transition midpoint during the second heat. The TGA was performed on a TA Instruments High Res TGA 2950 thermogravimetric analyzer under nitrogen at a



**Scheme 1** Air oxidation of triglyceride yields hydroxyl groups replacing allylic protons.

heating rate of 10°C min<sup>-1</sup> to a maximum temperature of 600°C.

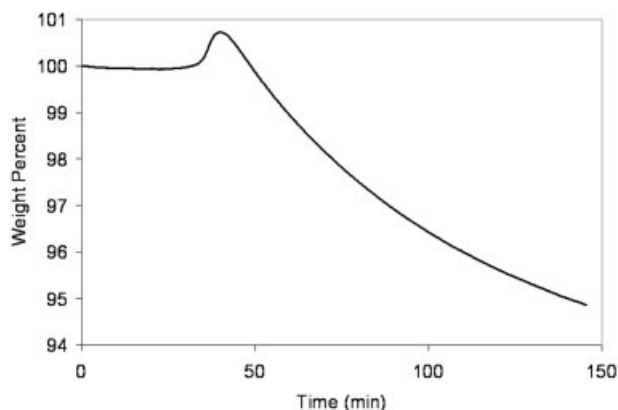
## RESULTS AND DISCUSSION

Soybean oil is widely used in a variety of well-known applications such as drying oils.<sup>34,37-39</sup> Soybean oil is an abundant and inexpensive vegetable oil with multiple sites of reactivity including ester and olefinic sites. In this work, the interest lies in exploiting air oxidation, which is the most inexpensive and simple reaction in terms of reactants (air and soybean oil), as a method for the production of high hydroxyl number soy polyols. Significant work previously investigated the impact of metal catalysts and added initiators on the synthesis of polyols derived from vegetable oils.<sup>40-42</sup> This is the first systematic study of triglyceride air oxidation in the absence of catalysts.<sup>43</sup> The three regimes of air oxidation of soybean oil, which differ significantly in content and application from the kinetic stages previously determined,<sup>25,43</sup> are defined through this work. The knowledge gained from these experiments was used to produce tack-free films with soybean oil and atmospheric oxygen.

### High molecular weight polyols

Initiation of the autoxidation of unsaturated triglycerides occurs via the abstraction of an allylic hydrogen. The free radical process that follows is uncontrolled and propagation occurs simultaneously with termination reactions such as radical coupling. Multiple products are formed from this free radical reaction (Scheme 1).

Several trends were observed during the investigation of soybean oil oxidation, which were used to define three regimes of oxidation. Isothermal TGA of the soybean oil under oxygen atmosphere at 150°C indicated a long period of inactivity or an "induction" period followed with an increase in mass and rapid degradation of the soybean oil (Fig. 1). Mikula et al. have shown similar behavior for bleached and de-



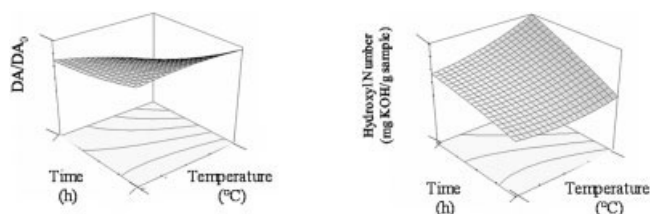
**Figure 1** Isothermal TGA of raw soybean oil at 150°C under oxygen.

odorized soybean oil at high temperatures (>195°C).<sup>44</sup> The temperature of oxidation was found as a crucial parameter for balancing the time required to overcome the induction period and avoiding the subsequent, rapid degradation of the soybean oil. Thus, both time and temperature were important variables for the synthesis of high hydroxyl number soy polyols.

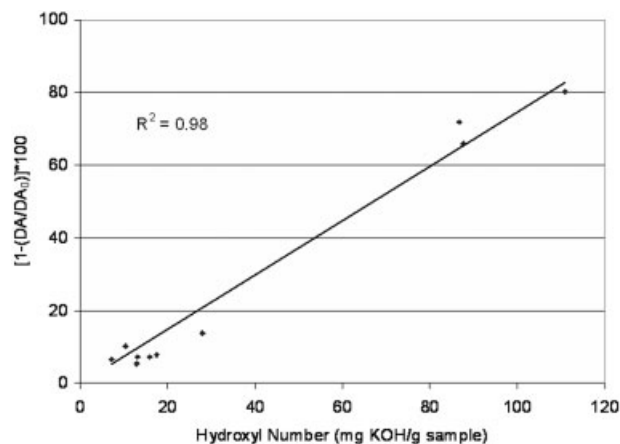
The first regime was defined as the period when insignificant change in the hydroxyl number of the soybean oil occurred. Initiation and consumption of natural antioxidants that are present in the raw soybean oil (e.g., vitamin E) occurred during this time.<sup>43</sup> The first regime of air oxidation was modeled with a statistical DOE, which was performed with Stat-Ease software. The disappearance of allylic and doubly allylic hydrogens, which are abstracted during the initiation of air oxidation, was monitored with <sup>1</sup>H NMR spectroscopy (2.01 and 2.79 ppm, respectively). An increase in reaction time and temperature lead to a decrease in the normalized doubly allylic resonance [(eq. (1))] and an increase in the hydroxyl number (Fig. 2).

$$\text{NDA} = \text{DA}/\text{DA}_0 \quad (1)$$

where NDA, normalized doubly allylic resonance; DA, the integration of the doubly allylic <sup>1</sup>H NMR



**Figure 2** 3D plots of temperature and time dependence of first regime of oxidation for normalized doubly allylic resonance integration and hydroxyl number.

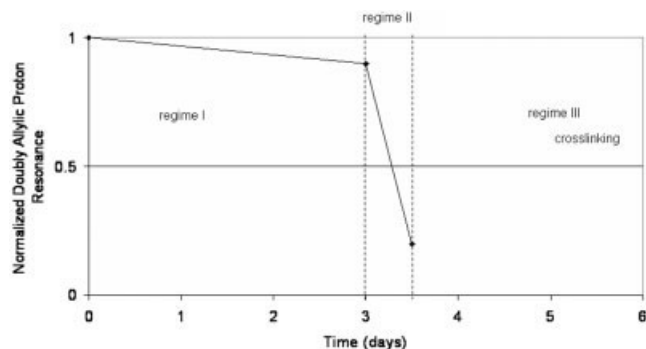


**Figure 3** Significant relationship between the normalized integration of the doubly allylic resonance and hydroxyl number.

resonance of an oxidized soy polyol; and  $\text{DA}_0$ , the integration of the same resonance for the control or unoxidized soybean oil. The doubly and singly allylic resonances followed a similar decreasing trend with oxidation. The doubly allylic resonance was chosen for comparison with the hydroxyl number, because the resolution of the doubly allylic resonance was better when compared to other resonances in the <sup>1</sup>H NMR spectrum. A significant, linear relationship between hydroxyl number and normalized doubly allylic resonance was found ( $r^2 = 0.98$ ) (Fig. 3). From this relationship, an indication of the degree of oxidation was provided without performing multiple titrations that are required for hydroxyl number determination. The integration of the doubly allylic resonance from <sup>1</sup>H NMR was successfully used as an indicator of hydroxyl functionality for these soy polyols. While the increase in hydroxyl number is directly related to the decrease in the normalized doubly allylic resonance, it was not assumed that each abstracted doubly allylic hydrogen resulted in the formation of a hydroxyl group. Rather the relationship between the hydroxyl number and doubly allylic resonance was determined as potentially useful for fast analysis of the extent of oxidation.

Rapid oxidation of the soybean oil occurred in the second regime of air oxidation. This corresponded to the increase in mass or uptake of oxygen in the TGA (Fig. 1). A significant and rapid increase in the hydroxyl number was a feature of the second regime of air oxidation and was accompanied with a decrease in the normalized doubly allylic resonance in the <sup>1</sup>H NMR spectrum (Fig. 4 and Table I). Radical–radical coupling, which indicated that propagation was occurring in this regime, was shown through the broadening of the polydispersity from 1.01 to 15.9 after 3.5 days at 110°C (Table I). As radical–radical coupling occurred and the dispersity broadened, there was also





**Figure 4** Decrease in normalized doubly allylic resonance from  $^1\text{H}$  NMR spectra, indicating an increase in hydroxyl number of soy polyols.

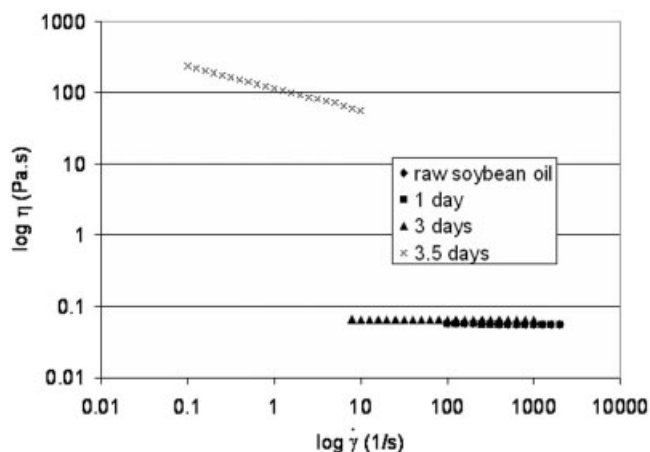
an increase in the weight average molecular weight of the soy polyol (Table I). This rapid increase in polydispersity over a relatively short period of time indicated the swift nature of the propagation. This narrow window for the synthesis of soluble, high functionality ( $>75$  mg KOH/g) soy polyols highlights the usefulness of the accurate definition of this regime. An increase in the high molar mass fractions of the soy polyol produced an increase in the melt viscosity as well during this regime of air oxidation. Viscosity is quite sensitive to the higher molar mass fractions of polymers and oligomers (Fig. 5).<sup>45</sup> The increase in viscosity was undesirable from a processing standpoint, but it was unavoidable with the air oxidation route for the production of soy polyols. Continued reaction at high temperatures resulted in crosslinking of the soybean oil. A network is a product of the termination step and an indication of the third regime of air oxidation. The resulting insolubility of the crosslinked soybean oil prohibited many common characterization techniques. The definition of regime two was critical when targeting the synthesis of more well-defined soy polyols.

To determine the impact of increased air pressure on the oxidation of soybean oil, the reaction was performed in a Parr reactor at elevated pressure. Several reactions were performed to determine the effect of pressure on the oxidation of soybean oil. Reactions

**TABLE I**  
Molecular Weight and Hydroxyl Number Data for Soybean Oil Oxidized at  $110^\circ\text{C}$

Sample	Time (days)	$M_w^a$ (g mol $^{-1}$ )	$M_w/M_n^a$	Hydroxyl number (mg KOH/g)
1	0	1,100	1.01	N/A
2	1	1,300	1.02	$7 \pm 2.4$
3	3	1,400	1.02	$10 \pm 2.5$
4	3.5	44,000	15.3	$110 \pm 2.4$

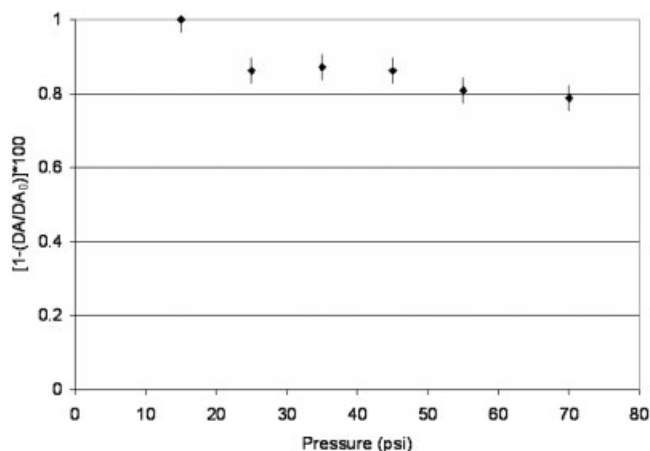
<sup>a</sup> From RI, versus polystyrene standards.



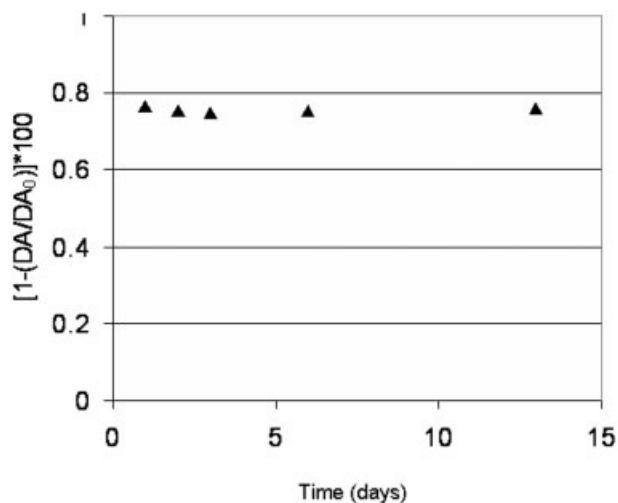
**Figure 5** Increase in viscosity observed with time at  $100^\circ\text{C}$ ,  $25 \text{ L min}^{-1}$ . Raw soybean oil and 1 day are superimposable lowest viscosity.

were allowed to proceed for 1 day at  $110^\circ\text{C}$  at pressures ranging from 15 to 75 psi. An increase from atmospheric pressure to 25 psi lead to an initial drop in normalized doubly allylic resonance, indicating greater oxidation at this modest increase in pressure. However, for the rest of the series, little difference was observed for the increase in pressure (Fig. 6). When the normalized doubly allylic resonances were compared for 1 day at 60 psi versus 1 day in a round-bottomed flask with a constant air flow rate of  $25 \text{ L min}^{-1}$ , it was found that the soybean oil under pressure was only slightly more oxidized than the soybean oil subjected to air flow (NDA: 0.83, 0.93, respectively).

Several high pressure reactions that ranged in length from 1 to 15 days were performed at 75 psi of air pressure. However, an insignificant difference of the normalized doubly allylic resonance was observed after 1 day of heating (Fig. 7). As described in Henry's law, there is a relationship between the vapor pressure



**Figure 6** Effect of pressure on soybean oil oxidation at  $110^\circ\text{C}$  for 1 day.



**Figure 7** Change in normalized doubly allylic resonance with time at 110°C under 75 psi charged air pressure.

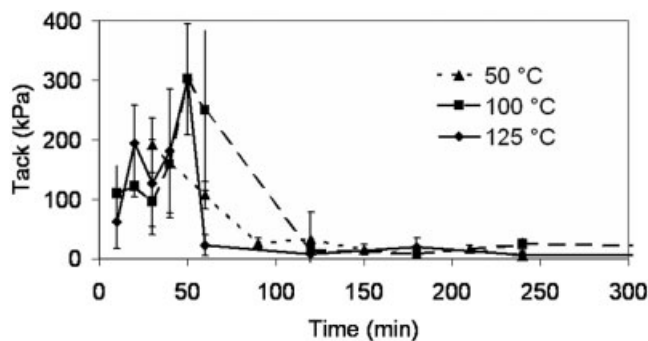
and the mole fraction of the solute. In these high pressure reactions, a specific pressure was charged and remained unchanged for the duration of the experiment. Equilibrium between the gas and liquid was most likely reached, and the extent of oxidation was limited. When the reaction was continued for 3–4 days, the reaction with air flow through the sample was significantly more oxidized than that under a constant pressure (NDA: 0.20, 0.83, respectively) for the same reaction temperature and time. Thus, the technique of passing air through the soybean oil with a dispersion tube was used for the efficient production of high hydroxyl number soy polyols.

Incorporation of the high hydroxyl number soy polyols into crosslinked polyurethane networks was discussed elsewhere.<sup>46</sup> The regimes of air oxidation established herein were used as a guide for the synthesis of either high hydroxyl number polyols or polymeric networks. The third regime of air oxidation for the synthesis of soybean oil-based coatings provides a unique opportunity to exploit the third regime of air oxidation for network formation.

### Crosslinked coatings

Coatings that use soybean oil derivatives and other renewable resources have garnered interest in recent years.<sup>14</sup> When renewable resources are used in coatings, they typically comprise only one component of the formulation.<sup>32</sup> However, from the definition of the three regimes of air oxidation, coatings that consisted of 100% soybean oil were generated through exploiting the crosslinking that occurs during termination in the free radical reactions.

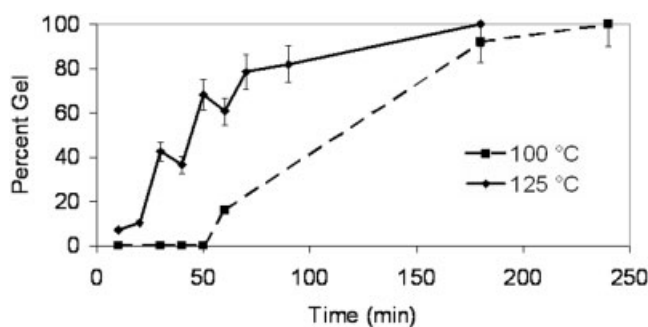
Cobalt catalysts are widely used in the oxidation of unsaturated compounds due to their activity with hy-



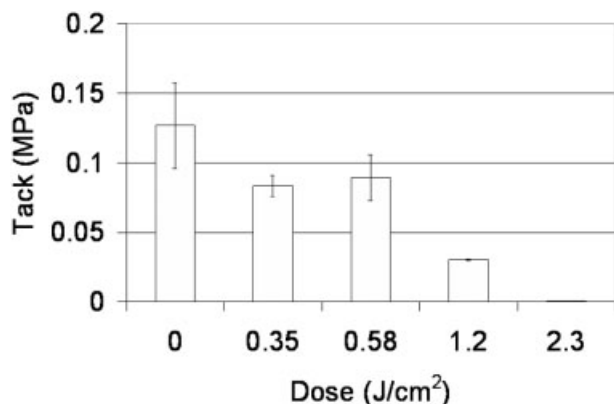
**Figure 8** Decrease in tack of films over time at elevated temperatures.

droperoxides.<sup>47–49</sup> To expedite the onset of the third regime of oxidation, cobalt(II) ethyl hexanoate (65 wt % in mineral oil) was used as a catalyst in a 5 wt %/vol % mixture with raw soybean oil. Thin layers (~100 μm) of this homogeneous solution were uniformly coated on glass slides and placed in an oven at elevated temperature. The effect of reaction time, temperature, and irradiation on the soybean oil-based coatings was investigated. Tack tests and gel fraction measurements were used to gain insight into the degree of crosslinking and tackiness of the coating. To obtain tack-free films, a highly crosslinked coating was desired.

A gradual increase in gel fraction was observed for the lower reaction temperatures (50 and 100°C). As depicted in Figure 8, a longer reaction time was required for the formation of a tack-free coating at the lower reaction temperatures when compared to the coating formed at the highest reaction temperature (125°C). All reaction temperatures resulted in tack-free coatings after 2 h at elevated temperature. Figure 9 shows that a very high gel fraction, nearly 100%, from the coatings was achieved after several hours under the higher reaction temperatures (100 and 125°C). The increase in tack observed during the first hour of reaction was attributed to the soybean oil behaving at first as a low viscosity liquid. As oxidation and crosslinking occurred, the soybean oil became more



**Figure 9** Percent gel of soybean oil coatings.



**Figure 10** Decrease in tack observed with increasing UV irradiation for coatings cured at 100°C for 60 min.

viscous. This phenomenon was observed in regime two for the air oxidation of soybean oil. The tack increased with an increase in the viscosity of the soy-based coating. As regime three was reached and the soybean triglycerides were chemically integrated into the network, a tack-free film was formed. Thermal analysis with differential scanning calorimetry of the films cured for 1 h at 50 and 125°C showed similar behavior, where there was a significant reduction in the number and intensity of endotherms. Oxidation of the soybean oil resulted in a reduction in crystallizable triglycerides.<sup>50</sup> The TGA of a coating that was cured at 125°C for 1 h indicated the onset of weight loss was at 100°C.

To decrease the reaction time for the formation of a tack-free coating, UV irradiation of the films was used. In the absence of heating, UV irradiation with a dose of 2.3 J cm<sup>-2</sup> of UVA did not result in a measurable gel fraction. When the soybean oil film was first heated and then irradiated with the same dose as before, the reaction time to achieve a high gel fraction decreased. The gel fraction was determined at 10-min intervals for the irradiated samples. After 60 min at 100°C followed by UV irradiation, a gel fraction of 80.2% was achieved. Prior to one hour, a gel fraction was not observed for the heated and irradiated films. The gel fraction from the coating that was heated and irradiated is more than four times greater than for the coating that was heated for 1 h at 100°C alone (18% gel). It was also found that the tack of the irradiated and heated coating decreased with increased irradiation (Fig. 10).

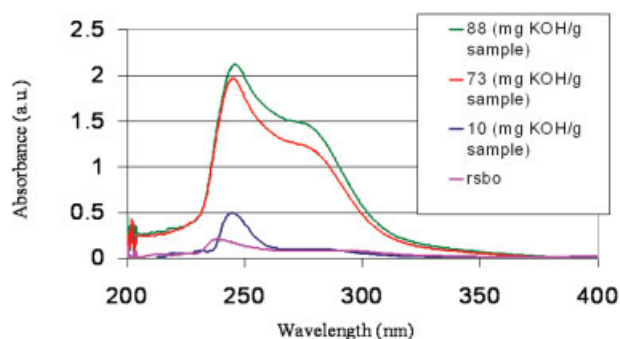
One can speculate on the influence of irradiation on the soy-based coatings. It was proposed that after some heating, conjugated hydroperoxides were formed and excited with irradiation, providing crosslinking sites for network formation (Fig. 11). This explanation accounts for the absence of a gel fraction for those samples that were only irradiated and not heated, because without the hydroperoxides, the soy-

bean oil was only mildly affected with the irradiation.<sup>51</sup> This also accounts for the gel fraction observed after irradiation and heating.

## CONCLUSIONS

The air oxidation of soybean oil, a renewable resource, without the use of catalysts or added initiators was explored. A linear relationship between the hydroxyl number and the normalized integration of the doubly allylic resonance was found for soy polyols. This relationship was used to estimate the degree of oxidation that occurred in a soy polyol sample with the relatively simple technique of <sup>1</sup>H NMR spectroscopy rather than performing several titrations to determine the hydroxyl number. The application of <sup>1</sup>H NMR for an indication of the degree of oxidation provided a rapid, easy alternative technique to hydroxyl number determination. The three regimes of air oxidation were defined. The first regime consisted of insignificant oxidation of the triglycerides, where natural antioxidants were consumed and initiation occurred. Rapid oxidation and reaction occurred during the second regime of oxidation, and high hydroxyl number (>75 mg KOH/g) soy polyols were produced. During this second regime of oxidation, an increase in polydispersity from 1.01 for the raw soybean oil to 15.9 for soy polyol was observed. The increase in polydispersity was attributed to radical-radical coupling during the oxidation. In the third regime of air oxidation, crosslinking and termination of the free radical reaction ensued.

Observation of the third regime of air oxidation, where crosslinking occurs, inspired the synthesis of crosslinked, soybean oil coatings with the aid of a metal catalyst. The effect of reaction time, temperature, and UV irradiation on the formation of tack-free, soy-based coatings was determined. It was found that elevated temperatures decreased the time required for the synthesis of tack-free coatings. UV irradiation of



**Figure 11** Increase in absorbance at 240 nm observed with an increase in hydroxyl number. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

coatings exposed to elevated temperatures decreased the cure time for the production of tack-free films.

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