Effects of unsaturation and different ring-opening methods on the properties of vegetable oil-based polyurethane coatings

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Abstract

A variety of vegetable oil-based, waterborne polyurethane dispersions have been successfully synthesized from different vegetable oil polyols exhibiting almost constant hydroxyl functionalities of 2.7 OH groups per molecule. The vegetable oil polyols, which have been prepared from vegetable oils with different fatty acid compositions (peanut, corn, soybean, and linseed oil), range in residual degree of unsaturation from 0.4 to 3.5 carbon–carbon double bonds per triglyceride molecule. The effects of residual unsaturation on the thermal and mechanical properties of the resulting polyurethane films have been investigated by dynamic mechanical analysis, differential scanning calorimetry, and thermal gravimetric analysis. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) has been used to accurately determine the molecular weight and mass distribution of the vegetable oil polyols. Higher residual unsaturation results in polyurethane films with increased break strength, Young's modulus, and toughness. This work has isolated the effect of unsaturation on vegetable oil-based polyurethane films, which has been neglected in previous studies. The effect of different oxirane ring opening methods (methanol, butanol, acetic acid, and hydrochloric acid) on the properties of the coatings has also been examined.

Graphical abstract
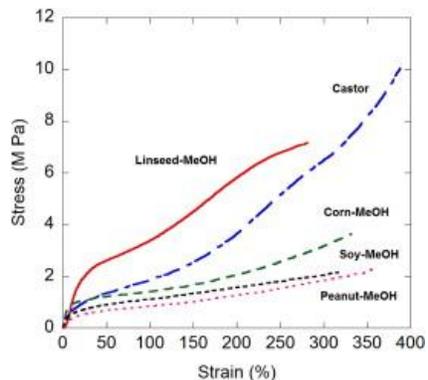
Keywords

- Polyurethanes;
- Renewable resources;
- Mechanical properties

1. Introduction

Polyurethanes are versatile materials with applications ranging from production of rigid plastics to soft foams, films, elastomers, and others [1]. Protective and decorative coatings are particularly important applications. In 2012, the total revenue from paints and coatings manufactured in the United States was $24 billion [2]. While this amount includes all types of coating materials, polyurethanes account for a substantial portion of this market, particularly in high-end applications [3].

Currently, solvent-borne polyurethane raw materials account for 18% of the total value of global consumption of coating materials [3]. The Clean Air Act of 1970, as well as more recent legislation in European countries, greatly affected the entire paints and coatings industry by mandating the reduction and monitoring of the release of volatile organic compounds (VOCs) into the atmosphere [4]. In response to these regulations, manufacturers have sought ways to eliminate organic solvents from paints and coatings. In particular, the focus turned to waterborne polyurethane coatings as an effective means for the reduction of VOC emissions [5]. By switching to waterborne coatings, manufacturers are realizing additional benefits by reducing material costs associated with organic solvents and reducing fire and health risks [6]. As a result, waterborne coatings are gaining market share, especially in the European sector [7].

Currently, coating materials are primarily prepared from petroleum-based materials, linking the supply chain and cost of raw materials to crude oil prices [2]. Serious, long-term supply issues and environmental risks are major concerns as dwindling conventional petroleum reserves lead to the increased exploitation of more expensive and environmentally damaging, unconventional oil resources, such as oil sands or oil shale [8] and [9]. Economic, political, geological, and environmental concerns may also limit the development of untapped petroleum reserves, especially those located in the Arctic regions [10] and [11]. Despite the increase in gas and oil

production in the United States, the connection of domestic gas and oil prices to global markets is expected to intensify, creating greater exposure to global price fluctuations [10]. Consequently, manufacturers will be inclined to develop biobased plastics to hedge against the uncertainty of crude oil price fluctuations and other factors limiting future supplies, such as growing oil consumption in Asian and other emerging markets [12].

Polyurethanes are prepared from two types of reagents: polyols and diisocyanates. More recently, polyurethane coatings made in part from biorenewable sources have been investigated as replacements for petroleum-based feedstocks [13], [14] and [15]. Currently, only polyols can be effectively made from biorenewable materials, such as vegetable oils that can be chemically modified to form polyols and replace petroleum-derived polyether and polyester polyols [15]. In addition to vegetable oils, other biorenewable triglycerides, such as fish oil, have also been used to make polyurethane coatings [16].

The purpose of the present research was to examine the effects of carbon–carbon double bonds in the polyols segment on the physical properties of vegetable oil-based polyurethane dispersions. We believed that residual unsaturation would result in increased chain stiffness of the polyols and be manifest in the resulting physical and mechanical properties of the resulting polyurethanes. Previous research has examined the effect of different hydroxyl numbers using soybean oil-based polyols. However, the hydroxyl value and residual carbon–carbon double bond content changed simultaneously [17]. Other studies have used different vegetable oils and completely reacted all carbon–carbon double bonds, leaving few or no residual carbon–carbon double bonds in the resulting materials [18].

In order to isolate the effects of the extent of unsaturation, several different vegetable oils (peanut oil, corn oil, soybean oil, and linseed oil) were partially epoxidized and subsequently ring-opened to yield vegetable oil polyols with a constant functionality. Vegetable oils from different plant sources vary in triglyceride compositions and unsaturation as summarized in Table 1. The unsaturation of unmodified vegetable oils ranges from 3.37 carbon–carbon double bonds per triglyceride molecule for peanut oil to 6.2 carbon–carbon double bonds for linseed oil. Vegetable oil compositions vary significantly depending on a wide range of factors, including environmental conditions and processing techniques [19]. Additionally, unsaturation measurements based on ^{1}H NMR spectral analysis can differ slightly from values reported based on other analytical techniques [20].

Vegetable oil	Double bonds[a]	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Ricinoleic C18:1
Peanut[b]	3.37	11.1	2.4	46.7	32	–	–
Corn[b]	4.45	10.9	2	25.4	59.6	1.2	–
Soybean[b]	4.61	10.6	4	23.3	53.7	7.6	–
Castor[c]	3.04	1	1	3	4.2	–	89
Linseed[b]	6.24	5.4	3.5	19	24	47	–

[a] Average number of double bonds per triglyceride.

[b] Taken from Ref. [19].

[c] Taken from Ref. [20].

Table 1. Triglyceride composition and unsaturation of selected vegetable oils.

All vegetable oil polyols for this study were prepared with a hydroxyl functionality of approximately 2.7 OH groups per molecule, because this value affords a good range of residual unsaturation in the resulting polyols (0.4–3.5 carbon–carbon double bonds per molecule). In addition, this specific hydroxyl functionality enables a direct comparison with castor oil, which has a natural hydroxyl functionality of 2.7. Castor oil is comprised primarily of ricinoleic acid (>89%), which contains a hydroxyl group at the C-12 position and a carbon–carbon double bond between C-9 and C-10 [21]. The structure of ricinolein, the major triglyceride of castor oil, is shown in Fig. 1.
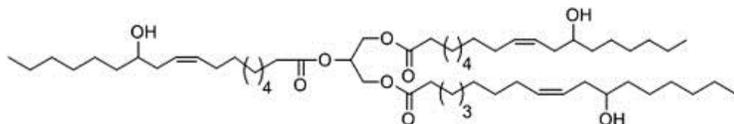

Fig. 1: Ricinolein, major component of castor oil.

Hydroxyl functionality, which is the number of hydroxyl groups per molecule, can be calculated by dividing the molecular weight of the polyol by its equivalent weight as shown in the following equation:

$$\text{Functionality} = \frac{\text{Molecular Weight}}{\text{Equivalent Weight}}$$

Equivalent weight is related to the hydroxyl number as shown in the equation below:

$$\text{Equivalent Weight} = \frac{56,100}{\text{OH Number}}$$

The hydroxyl numbers of polyols are values experimentally determined by acetylating the hydroxyl groups and titrating with potassium hydroxide. [22] Hydroxyl numbers are defined by the mass of KOH in milligrams that is equivalent to the hydroxyl content of 1 g of the polyol [22]. Substituting the expression for equivalent weight into the first equation yields the following relationship for functionality in terms of molecular weight and hydroxyl number:

$$\text{Functionality} = \frac{\text{Molecular Weight} * \text{OH Number}}{56,100}$$

There are two major reasons why the effect of unsaturation has not been isolated in previous studies. First, controlling the partial epoxidation and subsequent ring opening of the oils to achieve the desired hydroxyl functionality with residual unsaturation is difficult. In practice, completely epoxidizing the vegetable oil and partially ring opening the oxirane groups is much easier. This limitation can be overcome by controlling the extent of partial epoxidation by adjusting the molar ratio of hydrogen peroxide to carbon–carbon double bonds [17]. Second, it is difficult to accurately determine molecular weights, especially for low molecular weight polymers. Typically, molecular weights are determined using size exclusion chromatography (SEC), light scattering, osmometry, or viscometry. However, each technique comes with

significant drawbacks. Although SEC is the most common technique for determining the molecular weight of polymers, it is not an absolute method and is often inaccurate without a well characterized calibration standard [23]. There may also be problems with sample aggregation and adsorption onto column materials [24]. Although light scattering is a direct method for determining mass average molecular weight, it is a difficult, expensive, time-consuming procedure and does not provide information about polydispersity [25]. Likewise, osmometry is a direct, but time-consuming method for determining number average molecular weights that does not provide information about polydispersity [25].

In the present study, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) has been used to accurately determine the molecular weight and mass distribution of the vegetable oil polyols. MALDI-TOF is generally used to characterize large biomolecules and synthetic polymers [26] and [27]. MALDI-TOF overcomes two significant challenges encountered with other mass spectrometry techniques used to measure the molecular weight of large molecules: low volatility that makes it difficult to evaporate large molecules and thermal stresses causing large molecules to break apart. MALDI is a soft ionization method and the mass spectra produced have minimal fragment-ion content [28]. With this technique, the sample is first dissolved in a solvent and then mixed with a solution containing small organic molecules that readily absorb UV laser light, called the matrix. This solution is subsequently dried to yield an analyte-doped matrix. Under laser irradiation, the top layer of the matrix undergoes desorption, carrying the analyte with it. The sample is then ionized and subsequently measured with a time-of-flight analyzer [29]. A previous study determined that dihydroxybenzoic acid (DHB) in acetone is the best matrix for vegetable oils [30]. For most biomolecules, the DHB matrix can serve as both a desorption and an ionization vehicle with the best overall performance at the intrinsic pH of the matrix. Thus, for the analysis of biomolecules with a DHB matrix, metal cationization agents are not always needed [23] and [31].

Although MALDI provides accurate, direct molecular weight and weight distribution measurements, it does so only for polymer samples with a polydispersity index (PDI) below 1.1 [32] and [33]. If the PDI is higher (>1.1), molecular weight measurements produce serious errors, because the assumption of constancy of intensity scale calibration is no longer valid [34]. To overcome this problem, polydisperse polymer samples have been grouped into monodisperse fractions using SEC, allowing the utilization of MALDI-TOF to calibrate the SEC curves [35].

Based on our hypothesis that increasing the carbon–carbon double bond content would produce stiffer and stronger polymers, we believed that residual unsaturation in vegetable oil-based polyols was an important, but previously overlooked parameter impacting the physical and mechanical properties of the resulting polyurethane dispersions. Residual unsaturation had not been considered as a variable in previous research when introducing different functionalities (i.e. different OH number) into polyols from a single vegetable oil source. A second purpose of this research was to isolate the effect of different ring opening methods, while keeping the functionality and residual unsaturation constant. A previous study examined the effect of oxirane ring opening using different methods and reagents (hydrogen, methanol, hydrochloric acid, and hydrobromic acid); however, the OH functionality was not held constant, but ranged from 3.5 to 4.1 with minimal residual unsaturation [36]. In the present study, the range of OH functionality is

much smaller (2.6–2.7). In addition, different chemicals (methanol, butanol, acetic acid, and hydrochloric acid) have been used for the oxirane ring opening.

This is the first systematic attempt to isolate the effects of residual unsaturation in vegetable oil polyols on the properties of the resulting polyurethane coatings. While residual unsaturation is often considered undesirable, because it may lead to yellowing of the films, unsaturation from various sources (aromatic diisocyanates, alkyd resins, or castor oil) is fairly common in polyurethane coatings and some yellowing is tolerated in many applications. Residual unsaturation can also act as a site for further chemical modifications. In one previous study, grafted hybrid latexes were prepared by graft copolymerization of acrylic monomers onto polyurethanes made with partially epoxidized and ring-opened soybean oil. The residual carbon–carbon double bonds in the fatty acid chains were used as graft sites [37]. Electron beam irradiation was used to crosslink residual carbon–carbon double bonds in vegetable oil-based polymers [38].

2. Experimental

2.1. Materials

Soybean oil, peanut oil, and corn oil were purchased at the local supermarket and used as received. Linseed oil was provided by Archer Daniels Midland Company (Decatur, IL, USA). Castor oil, dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI), and dibutyltin dilaurate (DBTDL) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Acetone, formic acid, glacial acetic acid, hydrogen peroxide, and methyl ethyl ketone (MEK) were purchased from Fisher Scientific Company (Fair Lawn, NJ, USA). All materials were used as received.

2.2. Synthesis of vegetable oil-based polyols

Various vegetable oils (peanut, corn, soybean, and linseed) were partially epoxidized using hydrogen peroxide and formic acid and subsequently ring opened to form polyols as illustrated in Scheme 1.
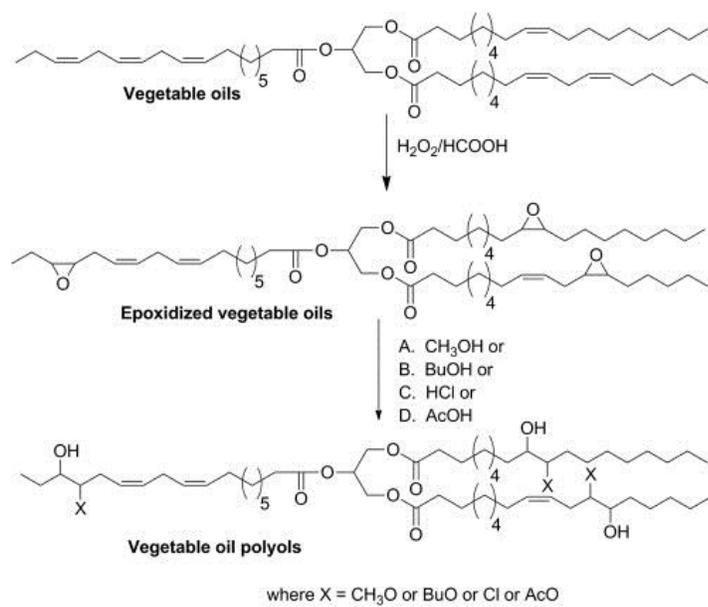
Scheme 1: Synthesis of vegetable oil-based polyols with residual unsaturation.

The procedure used for epoxidation of the vegetable oils followed previously reported protocols [17]. The relative amount of epoxidation was controlled by slightly adjusting the molar ratios of hydrogen peroxide. For more unsaturated oils, such as linseed oil, less hydrogen peroxide was needed. Generally, 250 g of vegetable oil, 85–100 g of hydrogen peroxide (30%) and 38 g of formic acid (88% in water) were added to a round bottom flask with a mechanical stirrer. The mixture was stirred in a water bath at 25 °C for 21 h. For the work-up, the epoxidized vegetable oil was washed with ethyl acetate and aqueous sodium chloride solution. The epoxidized vegetable oil was neutralized to a neutral pH with sodium bicarbonate and dried over anhydrous magnesium sulfate. The epoxidized vegetable oil was vacuum filtered, submitted to rotary evaporation at 38 °C for 1 h and dried in a 70 °C drying oven overnight. The oxirane content of the epoxidized vegetable oils was approximately 2.7 oxirane units per triglyceride, as determined by ^{1}H NMR spectroscopy.

The epoxidized oils were ring opened to prepare polyols with an approximate hydroxyl functionality of 2.7. Two different series of vegetable oil polyols were prepared. In the first series, different methoxylated vegetable oil polyols were synthesized from epoxidized oils. For ring opening with methanol, 246 g of epoxidized vegetable oil, 246 g of methanol, 246 g of isopropanol, and 10 g of fluoroboric acid were added to a 2 L round bottom flask. The mixture was stirred with a mechanical stirrer in a 45 °C mineral oil bath for 2 h. The reaction was quenched with aqueous ammonium hydroxide. For work-up, the sample was washed with ethyl acetate and aqueous sodium chloride solution. The methoxylated polyol was neutralized to a neutral pH with sodium bicarbonate and dried over anhydrous magnesium sulfate. The methoxylated polyol was vacuum filtered, submitted to rotary evaporation at 38 °C for 1 h and dried in a 70 °C drying oven overnight.

In the second series, several chemicals (methanol, butanol, hydrochloric acid, and acetic acid) were used to ring open epoxidized soybean oil (ESO) following previously described procedures [36] and [39]. For ring opening with butanol, 60 g of ESO, 120 g of 1-butanol, and 2.5 g of

fluoroboric acid were added to a round bottom flask. The mixture was stirred with a mechanical stirrer in a 45 °C mineral oil bath for 4 h. The reaction was quenched with aqueous ammonium hydroxide and the work-up followed the same procedures used for methoxylated polyols. For ring opening with hydrochloric acid, 247 g of ESO, 86 g of hydrochloric acid, and 300 mL of acetone were added to a round bottom flask. The mixture was stirred with a mechanical stirrer in a mineral oil bath at 40 °C for 2 h. The work-up followed the same procedures used for methoxylated polyols. Ring opening with acetic acid was achieved using a large excess of acetic acid relative to the ESO. Here, 40 g of ESO and 120 g of acetic acid were added to a two-neck flask with a reflux condenser and mechanical stirrer. The mixture was stirred in an 80 °C mineral oil bath for 8 h. Work-up followed the same procedures used for methoxylated polyols.

2.3. Synthesis of vegetable oil-based dispersions

The synthesis of the vegetable oil-based polyurethane dispersions was carried out as described previously [17]. Briefly, the vegetable oil polyol (10.0 g), IPDI (ranging from 4.15 to 5.5 g based on the OH number of the polyol used), DMPA (ranging from 1.0 to 1.3 g based on the OH number of the polyol used), and one drop of DBTDL were added to a three-neck flask equipped with a mechanical stirrer, condenser, and thermometer. The molar ratios of OH groups from the vegetable oil polyol, NCO groups from the IPDI, and OH groups from the DMPA were kept at 1.0:1.7:0.69. The reaction was carried out at 78 °C for 1 h, and 50 mL of MEK was added to reduce the viscosity of the system. After an additional 2 h of reaction, the reactants were cooled to room temperature and then neutralized by the addition of TEA (2.0 equiv per DMPA), followed by dispersion at high speed with distilled water to produce the polyurethane dispersions with a solid content of ~12 wt% after removal of the MEK under vacuum. The corresponding polyurethane films were obtained by drying the polyurethane dispersions at room temperature in a polytetrafluoroethylene mold. The films were conditioned for one month at room temperature before further testing.

2.4. Characterization

MALDI-TOF spectra were obtained using an Applied Biosystems Voyager DE Pro. The samples were diluted in acetone and a 10 mg/mL solution of 2,5-dihydroxybenzoic acid (DHB) in acetone was used as the matrix. The molecular weights were calculated based on procedures described in ASTM D7134, the standard for determining the molecular weight of atactic polystyrene using MALDI-TOF [34]. Minor modifications to the protocol were necessary to adapt the standard for use with vegetable oil polyols. Instead of all-*trans* retinoic acid, DHB was used for the matrix, which eliminated the use of silver salts. Acetone replaced tetrahydrofuran or toluene as the solvent.

The oxirane content and degree of unsaturation (carbon–carbon double bonds) were determined using ^{1}H NMR spectroscopy with a Varian Unity spectrometer at 300 MHz, as described previously in the literature [20]. The hydroxyl number was determined by following ASTM D1957 [40]. The tensile properties were measured at room temperature using an Instron universal testing machine (Model-4502). The crosshead speed was set at 100 mm/min. The average stress–strain data from five rectangular specimens (50 mm × 10 mm) were used. A dynamic mechanical analyzer (TA Instruments DMA Q800, New Castle, DE) in tensile mode at

1 Hz was used to determine the storage and loss moduli. The samples were heated from −80 to 100 °C at a rate of 5 °C/min. Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (TA Instruments DSC Q20, USA). The samples were heated from 25 to 100 °C at a rate of 20 °C/min to erase their thermal history, cooled to −70 °C, and heated again to 150 °C at a heating rate of 20 °C/min. The sample masses were approximately 5 mg. A thermogravimetric analyzer (TA Instruments TGA Q50, USA) was used to measure the weight loss of the polyurethane films in an air atmosphere. The samples were heated from 30 to 650 °C at a heating rate of 20 °C/min. The mass of the samples used for TGA analysis was approximately 8 mg.

3. Results

3.1. Polyol characterization

The vegetable oil polyols exhibited narrow molecular weight distributions with low PDI values (<1.1), which allowed for quantitative molecular weight characterization by MALDI-TOF. A representative MALDI-TOF spectrum is shown in Fig. 2. The number average, M_n, and mass average, M_w, molecular weights were calculated from the peak intensity and centroid mass results based on methods described in ASTM D7134. Corrections for baseline noise were made based on the recommended signal to noise ratio (S/N) of 3:1.
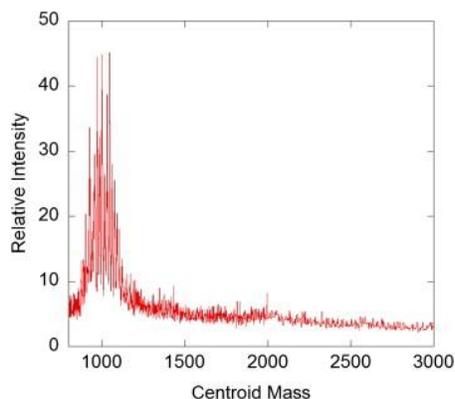

Fig. 2: MALDI-TOF spectrum of methoxylated soybean oil polyol.

The molecular weights for the modified vegetable oil polyols ranged from 1030 to 1226 g/mol. Castor oil, a natural polyol, had a molecular weight of 933 g/mol, which corresponds to the structure of ricinolein, the triglyceride of ricinoleic acid. It should be noted that the higher average molecular weight and slightly higher PDI of the soybean polyol ring opened by acetic acid were likely caused by dimerization of two triglycerides. Dimerization can occur when a hydroxyl group formed during a previous ring opening step is involved in the ring opening of an oxirane group on a second triglyceride molecule. However, the extent of dimerization was minimized by using an excessive amount of acetic acid, as evidenced by the resulting PDI below 1.1.

The results for the residual degree of unsaturation, molecular weight, and OH functionality are listed in Table 2. Based on the ^{1}H NMR spectroscopic results, the residual unsaturation per

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molecule ranged from 0.4 for the peanut oil-based polyol to 3.5 for linseed oil-based polyol. The corn oil-based polyol and the soybean oil-based polyol exhibited similar amounts of residual unsaturation per molecule (1.3 and 1.6, respectively). All polyols under investigation had an approximate hydroxyl functionality of 2.7 OH groups per molecule.

Polyol	OH functionality	Deg. of unsat.[a]	OH number[b]	M_n [c]	PDI[c]
Peanut – MeOH	2.7	0.4	139	1072	1.03
Corn – MeOH	2.6	1.3	143	1030	1.01
Soybean – MeOH	2.7	1.6	142	1067	1.02
Castor	2.7	3.1	163	933	1.01
Linseed – MeOH	2.8	3.5	147	1076	1.02

Polyol	Functionality	Deg. of unsat.	OH number	M_n	PDI
Soybean – MeOH	2.7	1.6	142	1067	1.02
Soybean – AcOH	2.7	1.6	123	1226	1.06
Soybean – HCl	2.6	1.3	136	1054	1.01
Soybean – BuOH	2.7	1.8	139	1092	1.01

[a] As determined from ^{1}H NMR measurements.

[b] As determined from following the ASTM D1957 standard.

[c] As determined from MALDI-TOF measurements.

Table 2: Properties of vegetable oil-based polyols.

3.2. Tensile properties

The stress–strain curves for polyurethane films prepared with different vegetable oils are shown in Fig. 3. The modulus and toughness increase with higher unsaturation, while the % strain decreases. Toughness is a measure of the ability of a material to absorb energy and deform without fracturing; toughness is determined by integrating the area underneath the stress–strain curve. It should also be noted that castor oil behaves differently than the other vegetable oils, which is attributed to the different triglyceride composition found in castor oil. Because castor oil primarily consists of ricinolein, the hydroxyl groups are uniformly positioned at the 12th carbon in the chain. Therefore, castor oil has a very homogenous distribution of hydroxyl functional groups compared to polyols prepared from various other epoxidized vegetable oils (Fig. 4 and Table 3).
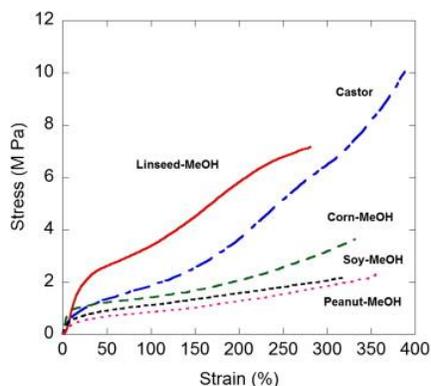

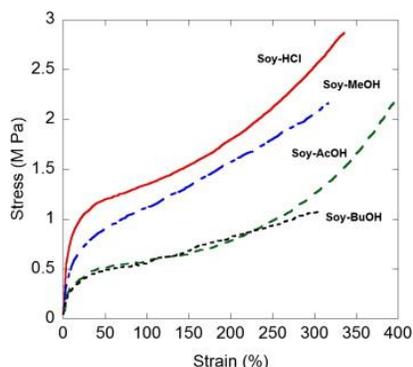Fig. 3: Stress–strain curves for polyurethane films from different vegetable oil polyols.

Fig. 4: Stress–strain curves for polyurethane films from soybean polyols created by different ring opening methods.

3.3. Dynamic mechanical analysis (kinetic transition)

Fig. 5 shows the storage modulus and tan delta curves as a function of temperature for films prepared from different vegetable oils. The drop in storage modulus generally shifted to higher temperatures with higher amounts of residual carbon–carbon double bonds. The sharp tan delta peak for the castor oil-based film to the other films is evidence of the homogeneous distribution of the hydroxyl groups in castor oil compared to the other vegetable oils.
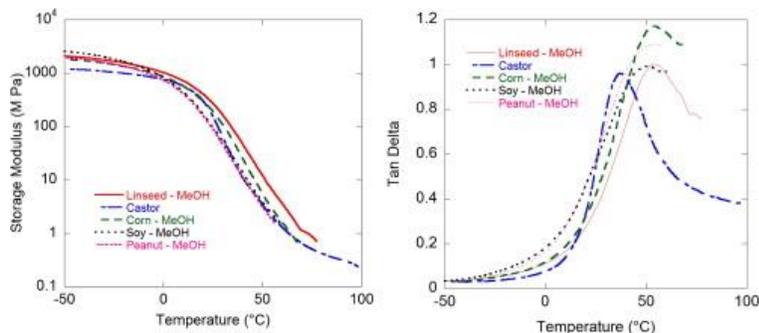

Fig. 5: Storage modulus as a function of temperature for polyurethane films from different vegetable oil polyols.

Fig. 6 shows the storage modulus and tan delta curves as a function of temperature for soybean polyol films with different side groups. Both the storage modulus and the temperature at which the storage modulus dropped increased in the following order of the side groups: 1-butanol < acetic acid, methanol < hydrochloric acid.
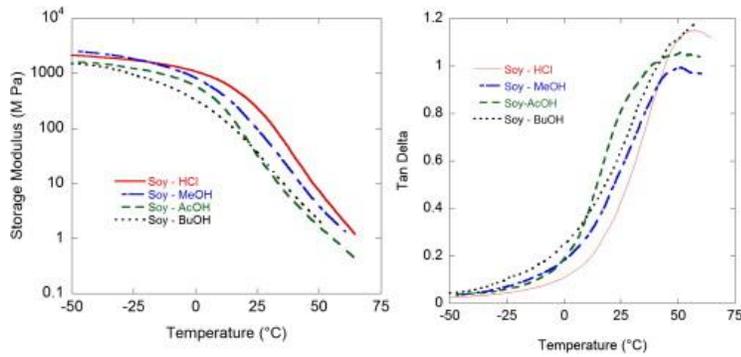
Fig. 6: Storage modulus as a function of temperature for polyurethane films from soybean polyols created by different ring opening methods.

3.4. Differential scanning calorimetry (glass transition temperature)

The glass transition temperatures (T_g) of the polyurethane films were determined by DSC and are listed in Table 4. The T_g of the polyurethane films increased from −9.2 °C to 13.5 °C as the residual carbon–carbon double bond content in the polyol segments increased from 0.4 to 3.5 double bonds per triglyceride. The side chains formed by different ring opening methods have a significant effect on the T_g. Substituting a longer butoxy side chain for the methoxy group lowered the T_g from −7.9 °C to −26.6 °C. Changing the methoxy group to an acetoxy group raised the T_g from −7.9 °C to 3.4 °C, and changing to a chloro group raised the T_g to 2.9 °C.

Polyol	Break strength (MPa)	Young's modulus (MPa)	Toughness (MPa)	% Strain
Peanut – MeOH	2.27 ± 0.03	4.64 ± 1.09	4.25 ± 0.12	343 ± 10
Corn – MeOH	3.40 ± 0.23	12.77 ± 0.83	6.02 ± 0.40	322 ± 12
Soybean – MeOH	2.14 ± 0.06	5.20 ± 0.16	4.11 ± 0.18	312 ± 5
Castor	10.61 ± 1.91	6.29 ± 0.54	15.26 ± 3.54	363 ± 39
Linseed – MeOH	7.55 ± 0.54	16.15 ± 2.13	12.72 ± 1.06	280 ± 14
Soybean – MeOH	2.14 ± 0.06	5.20 ± 0.16	4.11 ± 0.18	312 ± 5
Soybean – AcOH	2.19 ± 0.33	4.81 ± 0.16	3.80 ± 0.49	392 ± 26
Soybean – HCl	2.76 ± 0.28	15.23 ± 2.19	5.60 ± 0.59	338 ± 17
Soybean – BuOH	1.13 ± 0.08	3.54 ± 0.45	2.24 ± 0.13	312 ± 11

Table 3: Summary of engineering stress data.

Polyol	Deg. of unsat. per polyol	T_g (°C)
Peanut – MeOH	0.4	−9.2
Corn – MeOH	1.3	−6.6
Soybean – MeOH	1.6	−7.9
Castor	3.1	6.8
Linseed – MeOH	3.5	13.5
Soybean – MeOH	1.6	−7.9
Soybean – AcOH	1.6	3.4
Soybean – HCl	1.3	2.9
Soybean – BuOH	1.8	−26.6

Table 4: Glass transition temperatures of polyurethane films based on DSC thermograms.

3.5. Thermogravimetric analysis

The thermograms for films prepared from different vegetable oil polyols are shown in Fig. 7: TGA curves Fig. 7. They show that the higher number of residual carbon–carbon double bonds in the linseed polyol decreased the thermal stability at lower temperatures; however, this effect was reversed at higher temperatures.
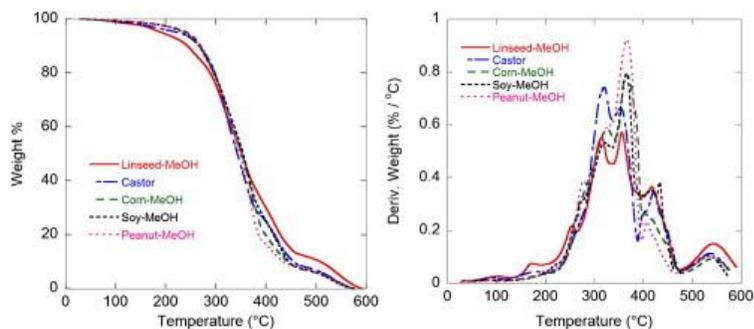

Fig. 7: TGA curves for polyurethane films from different vegetable oil polyols.

The thermograms for films prepared from soybean polyols by different ring opening methods are shown in Fig. 8. The films made from soybean polyols by acid ring opening (acetic and hydrochloric acids) exhibited lower thermal stabilities at temperatures below 350 °C. However, at higher temperatures the film prepared from soybean polyol by hydrochloric acid ring opening was more thermally stable than the other polyols.
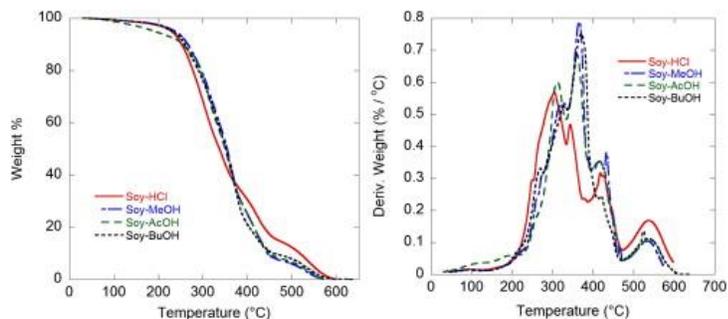

Fig. 8: TGA curves for polyurethane films from soybean polyols created by different ring opening methods.

4. Discussion and conclusions

Residual unsaturation has a strong influence on the mechanical and thermal properties of specific bio-based polyurethane films. Higher amounts of residual unsaturation led to increases in mechanical properties, such as modulus, which increased from 4.64 to 16.15 MPa; the toughness increased from 4.25 to 12.72 MPa; and the break strength increased from 2.27 to 7.55 MPa, when changing from a peanut oil-based polyol to a linseed oil-based polyol. Correspondingly,

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decreases in the % strain at break from 343% to 280% were observed. The glass transition temperatures observed by DSC increased from −9.2 to 13.5 °C.

This investigation indicates that the fatty acid composition also plays an important role. The properties of the castor oil-based polyurethane films cannot be explained entirely by the residual unsaturation of the polyol segments. Specifically, the castor oil-based films exhibit higher break strength (10.61 MPa) and toughness (15.26 MPa) than expected compared to the linseed oil-based films with higher amounts of unsaturation. Furthermore, the castor oil-based polyurethane films exhibit higher percent strain at break (363%) than polyurethane films made with less residual unsaturation (i.e. the peanut oil-based polyurethane film). The differences in physical properties of castor oil-based polyurethane films and other films based on vegetable oil polyols can be attributed to the more homogenous distribution of hydroxyl groups in castor oil caused by its uniform triglyceride composition (>89% ricinoleic acid). The sharp tan delta peak of the castor oil-based polyurethane film is evidence of a more homogenous polymer structure compared to the polyurethane films.

Our study of soybean polyols prepared by different oxirane ring opening methods (methanol, butanol, acetic acid, and hydrochloric acid) indicates that the method of ring opening impacts the resulting properties of the polyurethane films. In particular, increasing the chain length of the alcohol used to prepare the soy polyols reduces the properties of the resulting polyurethane films. The break strength decreases from 2.14 to 1.13 MPa, toughness decreases from 4.11 to 2.24 MPa, and the T_g is lowered from −7.9 to −26.6 °C, when the side chain is changed from a methoxy group to a butoxy group. Polyol prepared by ring opening with hydrochloric acid results in polyurethane films with higher Young's modulus (15.23 MPa) than polyurethane films prepared with polyols made by other ring opening methods. These results, as well as higher T_g for the polyurethanes made with chlorinated polyol compared to the polyurethanes made with methoxylated polyol, were consistent with a previous study into soy-based polyurethanes [41]. In this study, polyurethanes made with acetic-acid ring opened polyols showed the highest T_g, which can be attributed to hydrogen bonding by the acetoxy functional groups.

Acknowledgments

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