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Isosorbide as the structural component of bio-based unsaturated polyesters for use as thermosetting resins

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ABSTRACT

In recent years, the development of renewable bio-based resins has gained interest as potential replacements for petroleum based resins. Modified carbohydrate-based derivatives have favorable structural features such as fused bicyclic rings that offer promising candidates for the development of novel renewable polymers with improved thermomechanical properties when compared to early bio-based resins. Isosorbide is one such compound and has been utilized as the stiffness component for the synthesis of novel unsaturated polyesters (UPE) resins. Resin blends of BioUPE systems with styrene were shown to possess viscosities (120–2200 cP) amenable to a variety of liquid molding techniques, and after cure had T_gs (53–107 °C) and storage moduli (430–1650 MPa) that are in the desired range for composite materials. These investigations show that BioUPEs containing isosorbide can be tailored during synthesis of the prepolymer to meet the needs of different property profiles.

1. Introduction

The development of polymers from renewable resources is a field that is gaining increased interest due to factors such as environmental impact, sustainability and production costs (Noordover et al., 2006a,b; Sablong et al., 2008). Petroleum resins used in conventional thermosetting polymers and composites have enjoyed success when due to their improved performance over traditional materials (Griffiths, 2006; Pilato & Michino, 1994; Potter, 2003; Quilter, 2004) however, their use contributes to the depletion of crude oil reserves and in time their continued use will be prohibitively expensive (Cordesman & Al-Rodhan, 2005; Greenwood et al., 2007). For bio-based materials to be accepted and utilized in place of petrol-based resins, they must demonstrate the ability to be drop-in replacements that possess properties that meet or exceed their petrol-derived brethren. Bio-refining manufacturing processes have produced a number of unique compounds that have structural features not available through petroleum refining processes and should provide unique scaffolds for the development of new monomer resins. One of the most promising structures that has been put forth is isosorbide (1,4;3,6-dianhydro-D-glucitol) due to its fused bicyclic ring structure and its chiral diols giving the molecule a distinctive conformation. Isosorbide is produced commercially through a number of different methods including the enzymatic hydrolysis of starch and the catalytic dehydration of sorbitol, a derivative of glucose, Fig. 1 (Kricheldorf, 1997). Early work on isosorbide based polymers has included the development of thermoplastic polyesters (Jasinska & Koning, 2010; Noordover et al., 2006a,b; Noordover, Duchateau, van Benthem, Ming, & Koning, 2007; Okada, Okada, & Aoi, 1995), polyurethane resins (CognetGeorjon, Mechin, & Pascault, 1996; Noordover et al., 2006a,b), and epoxy thermosetting resins (Feng, East, Hammond, Zhang, & Jaffe, 2011); however, little work has been done in regards to the development of inexpensive thermosetting resins, such as unsaturated polyesters.

2. Background and significance

Composites utilize thermosetting epoxy resins, vinyl ester (VE) or unsaturated polyester (UPE) resins for their polymer matrix with VE and UPE resins being preferred for bulk scale manufacture of general purpose materials due to their low cost and sufficient performance (Goodman, 2000). VE and UPE resins have reduced

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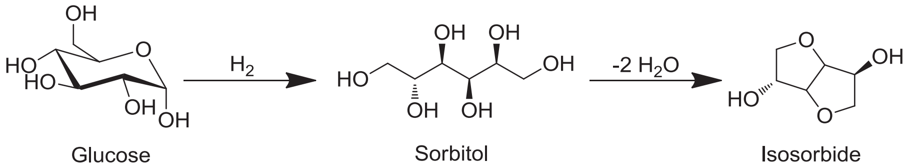

Fig. 1. Synthesis of isosorbide from glucose.

glass transition temperature and fracture toughness but maintain adequate performance for a number of applications. VE and UPE cross-linker monomers typically have extremely high viscosities that necessitate the use of reactive diluents for adequate processing (Pilato & Michino, 1994), but these diluents are designated as hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) (EPA, 2003). The implementation of bio-based materials into thermosetting resins offers a boon of potential to not only improve the properties of current resins, but also for the development of novel renewable resins while driving down production costs by using sustainable materials. Polyesters are among the most economical resins used commercially (Noordover et al., 2006a,b). Early work that focused on isosorbide used it as a constituent for the development of thermoplastic polymers for coatings applications (Noordover et al., 2006a,b). These studies showed that adding isosorbide in increasing concentrations increased the mechanical properties of otherwise poor materials, and isosorbide could increase the T_g of their materials by as much as 73% depending on concentration (Jasinska & Koning, 2010). Subsequent investigations explored solution polymerization of isosorbide based UPEs for coatings applications. These thermoset films were low molecular weight BioUPEs optimized to give T_g of 45 °C and were shown to be thermally stable, indicating that there was the potential for practical applications (Jasinska & Koning, 2010).

Using the successes of previous studies as impetus, this work focuses on the design and synthesis of bio-based UPE resin for use with reactive diluents to produce thermosetting structural polymers for use in composite applications. In this work, isosorbide is investigated as a structural constituent to provide stiffness from the diol component in an unsaturated polyester. Commercial UPE usually rely on gaining stiffness from components with aromatic rings such as terephthalic acid and othophthalic acid. Adding a diol constituent that can provide improvements to mechanical properties will provide a new tool for the development of novel thermosetting UPE resins. BioUPE thermoplastic prepolymers where synthesized through the polycondensation of a mixture of diols and diacids with attention to the effects of isosorbide and maleic anhydride content on the properties. These prepolymer cross-linkers can then be blended with reactive diluents to make a resin system with desirable viscosity characteristics that can undergo thermoset curing. The rheology and thermomechanical properties of these resins and polymers were investigated to understand the mechanical effects of isosorbide incorporation and gauge its utility for UPE composites applications.

3. Experimental procedure

3.1. Materials

Isosorbide (98%, Sigma–Aldrich) and ethylene glycol were used in this study as the diol components of the synthesized BioUPE resin with isosorbide providing stiffness to the thermoset upon free radical curing. Sebacic acid (99%, Sigma–Aldrich), suberic acid (purum ≥98%, Fluka), adipic acid (puriss ≥99%, Fluka), and maleic anhydride (99%, Sigma–Aldrich) were used as the diacid constituents for the synthesis of the BioUPE resin; maleic acid was used in all formulations to provide an unsaturated site that could undergo free radical curing and the straight chain aliphatic diacids were used to modulate the solubility of the synthesized resins. Xylenes (>98.5%, VWR) were used during the reaction as an azeotropic solvent, *p*-toluenesulfonic acid monohydrate (≥95.5%, Sigma–Aldrich) was used to catalyze the esterification and hydroquinone (ACS Reagent Plus ≥ 99.9%, Sigma–Aldrich) was used a free-radical inhibitor at the conclusion of the preparation reaction. Styrene (ACS Reagent Plus 99.9%, Sigma–Aldrich) was used as the reactive diluent for blending the resins. Potassium hydroxide (KOH, ACS reagent grade ≥85% pellets, Sigma–Aldrich) was used to make the titrant solutions for acid number determination that were standardized using potassium hydrogen phthalate (KHP, 99.99%, Alfa Aesar). All chemicals were used as received without further purification.

Viapal 450 commercial UPE resin was provided by Cytec Industries as the cross linking resin free of styrene. Methyl ethyl ketone peroxide (MEKP, Sigma–Aldrich) was used as the free radical polymerization initiator, and cobalt naphthenate (≤6% in mineral spirits, Sigma–Aldrich) was used as a promoter for polymerization.

3.2. General synthesis for BioUPE resins

Isosorbide (0.103–0.308 mol), ethylene glycol (0.103–0.308 mol), maleic anhydride (0.127–0.246 mol) and a diacid (adipic, suberic, or sebacic 0.127–0.246 mol) were suspended in xylenes and melted together at 55 °C before adding *p*-toluenesulfonic acid (5.0 wt%) and refluxed with aid of a Dean-Stark attachment. The progress of the reaction was monitored by acid number (AN) titration, and once the desired AN had been reached, the reaction was fitted with a vacuum distillation adapter and distilled at ambient pressure for 2 h and then under reduced pressure (−680 mbar) for 0.5 h. Hydroquinone was added to the molten resin and allowed to stir for 15 min before placing in a vacuum oven at 55 °C at −30 mbar for 18 h and allowing to cool. Resins appeared as yellow to amber semi-solids with varying stiffness/viscosity.

3.3. Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was used to evaluate the molecular weight and polydispersity index (PDI) of the thermoplastic BioUPE samples before blending the samples with styrene to form thermosetting resins. Samples were processed using a Waters 717 plus Autosampler with a Waters 510 GPC using three columns set in succession, Phenogel 5 μ 10^5 Å, Phenogel 5 μ 10^3 Å, and Phenogel 5 μ 500 Å. The columns were equilibrated at 40 °C before elution with helium purged tetrahydrofuran (THF) at a rate of 1.0 mL/min. The eluent was monitored using dual detectors; the first was a Waters 486 Tunable UV detector set to 230 nm and the second was a Waters 410 Refractive Index Detector both held at 40 °C. Samples were prepared by dissolving 1 mg/mL of polymer in THF and molecular weights were calculated based on retention time of polystyrene standards: 51,000, 10,000, 5050, and 580 amu.

3.4. Formulation and curing package

Resin systems were blended so that their composition consisted of 65 wt% of BioUPE cross-linker and 35 wt% styrene as a reactive

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diluent. All samples were blended to homogeneity using an ARE-250 Thinky planetary mixer at 2000 rpm for 5–10 min. Free radical polymerization of each resin was initiated with 1.5 wt% MEKP using 0.375 wt% CoNap added as a promoter. Resins were cured over night in RTV mold at room temperature and then post-cured at 120 °C for 3 h before any analysis was carried out (Sadler, Nguyen, Greer, Palmese, & La Scala, 2012).

3.5. *Rheology*

A steady state flow procedure was used to obtain viscosity and basic rheology in the formulated BioUPE/styrene blended resins before the initiator and accelerator were added on an AR 2000 Rheometer (TA Instruments). A 40 mm parallel plate geometry (TA Instruments) was utilized in conjunction with a Peltier plate for optimal temperature control over the course of the experiment. The resin samples were placed between the plates and gap spacing (i.e., sample thickness) set at 1000 μm at 25 °C. The shear rate was increased from 0.001 to 100 s^{-1} and then decreased back to 0.001 s^{-1}, and 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points. For low viscosity samples, low shear rates generally produce too little torque for accurate measurement while high shear rates produce too much torque for viscous samples. This was ascertained by torque maps at each shear rate. Viscosity was determined as the average viscosity across the shear rate range where appropriate torque maps were produced.

3.6. *NMR*

The resins were characterized using ^{1}H NMR (250.13 MHz, spectral window of G2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 908 pulse width) on a Bruker (Billerica, MA) AC250 Spectrometer; the resin blends were dissolved in $CDCl_3$ and showed peaks in agreement with the expected chemical shifts for individual constituents of the BioUPEs.

3.7. *Dynamic mechanical analysis (DMA)*

The thermomechanical properties of the polymer samples were measured using TA Instruments Q800 dynamic mechanical analysis (DMA) in 35 mm dual cantilever clamp geometry. Bars were cut into nominal dimensions of 60 mm × 12 mm × 3 mm and were sanded on both sides to ensure uniform cross-sectional area. The samples were tested at 1 Hz with a deflection of 7.5 μm while subjected to a temperature sweep at a rate of 2 °C/min starting at −50 °C and ending at 180 °C. Two temperature ramp experiments were run for each sample. The temperature at the peak of the tan δ was considered as the glass transition temperature of the material (Nielsen & Landel, 1994).

3.8. *FT-IR cure analysis*

Fourier-Transform Infrared Spectroscopy in near IR mode, NIR, was used to calculate the extent of cure for the resin blends based on the consumption of the styrene and unsaturated polyester vinyl groups. The BioUPE resins, before cure and after post-cure, scanned in near IR range of 4000–8000 cm^{-1} wave number with a total of 64 scans, were taken at room temperature for each spectrum. Liquid materials were placed in a glass reservoir having a path length of 3.4 mm and the cured samples were DMA bars with thickness ranging from 4.0 to 5.0 mm. For styrene, the peak at 6135–6136 cm^{-1} corresponding to stretching of vinyl bond was taken as the representative for reactive group and the peak at 4657 cm^{-1}, indicative of the aromatic C=C stretch, was used as the internal reference (Dean, Cook, Rey, Galy, & Sautereau, 2001; Poisson, Lachenal, & Sautereau, 1996; Rey et al., 2000). The peak that appears at 4790 cm^{-1}, the stretching of maleate and fumarate groups in UPE backbone, represents the reactive group of UPE, and the broad peak at 6942 cm^{-1} represents the internal reference of the UPE prepolymer cross-linker (Rey et al., 2000). The total conversion of styrene can be calculated using Eq. (1) and the conversion of the BioUPE resin can be calculated using Eq. (2).

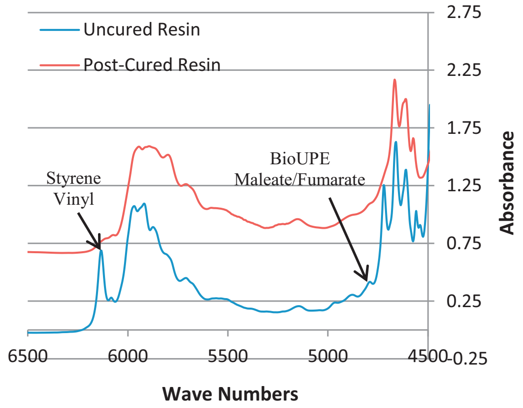

Fig. 2. Representative near IR spectra of uncured and cured resins.

$$\alpha_{\text{styrene}} = \frac{\left[\dfrac{\text{Abs}\ \ 6134\ \ \text{cm}^{-1}}{\text{Abs}\ \ 4657\ \ \text{cm}^{-1}}\right]_{\text{Uncured}} - \left[\dfrac{\text{Abs}\ \ 6134\ \ \text{cm}^{-1}}{\text{Abs}\ \ 4657\ \ \text{cm}^{-1}}\right]_{\text{Cured}}}{\left[\dfrac{\text{Abs}\ \ 6134\ \ \text{cm}^{-1}}{\text{Abs}\ \ 4657\ \ \text{cm}^{-1}}\right]_{\text{Uncured}}} \tag{1}$$

$$\alpha_{\text{UPE}} = \frac{\left[\dfrac{\text{Abs}\ \ 4790\ \ \text{cm}^{-1}}{\text{Abs}\ \ 6942\ \ \text{cm}^{-1}}\right]_{\text{Uncured}} - \left[\dfrac{\text{Abs}\ \ 4790\ \ \text{cm}^{-1}}{\text{Abs}\ \ 6942\ \ \text{cm}^{-1}}\right]_{\text{Cured}}}{\left[\dfrac{\text{Abs}\ \ 4790\ \ \text{cm}^{-1}}{\text{Abs}\ \ 6942\ \ \text{cm}^{-1}}\right]_{\text{Uncured}}} \tag{2}$$

A typical NIR spectrum of the styrenated and BioUPE resin blends can be seen in Fig. 2. The vinyl and maleate bands (6134 and 4790 cm^{-1} respectively) and the reference bands (4657 and 6942 cm^{-1} respectively) consistently exist in similar wave number regions for all of the BioUPE resin blends.

3.9. *Modeling to predict UPE solubility in styrene*

The group contribution method was used produce a calculation model in order to determine the miscibility of the BioUPE resin in reactive diluent using either the Hildebrandt (3) or the Hansen (4) solubility parameter (Krevelen & Nijenhuis, 2009).

$$\delta_1 = \left(\frac{E_{\text{coh}}}{V}\right)^{\frac{1}{2}} \tag{3}$$

$$\delta_2^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

The Hildebrandt equation (3) uses cohesive energy (E_{coh}) and molecular volume (V) to determine the solubility parameter (δ_1) of a given compound. On the other hand, the Hansen equation (4) takes into account molecular forces such as bond dispersion (δ_d), dipole moment (δ_p), and hydrogen bonding (δ_h) to generate its solubility parameter (δ_2). The individual molecular forces can be calculated using Eqs. (5)–(7).

$$\delta_d = \frac{\Sigma F_{di}}{V} \tag{5}$$

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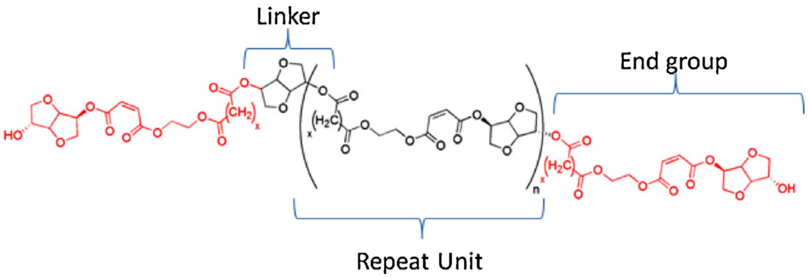

Fig. 3. Model UPE structure.

$$\delta_p = \frac{\sqrt{\Sigma F_{pi}^2}}{V} \quad (6)$$

$$\delta_h = \sqrt{\frac{\Sigma E_{hi}}{V}} \quad (7)$$

For the purpose of these calculations, the average of both solubility parameters (Eqs. (3) and (4)) is used to ensure all possible components are accounted. Using the group contribution method, the sum of the individual constants was plugged into the appropriate equation to derive the desired solubility parameter (Krevelen & Nijenhuis, 2009). A model UPE structure was used to calculate the solubility parameter from three separated pieces of the molecule (Fig. 3): two end groups, a repeat unit, and a linking unit to preserve the correct molecular arrangement. The repeat unit and end groups are arranged so that there is one molecule of each of the four components, and the end groups are terminated with isosorbide due to the reduced reactivity of the endo alcohol group on the structure. Isosorbide was also chosen as the linking group since it would have a more profound effect on the overall solubility over any other diol that would be used for UPE synthesis. When the fragments are put together, the resulting UPE (Fig. 3) can be easily modified to give solubility parameters for any number of repeat units.

After calculating the solubility parameter, the singular value alone does little to explain the solubility of this compound in another. Some suggest that similar solubility parameters indicate high probability of miscibility (Krevelen & Nijenhuis, 2009). However, it is unclear how far apart solubility parameters can be to consider them similar. By using two additional equations, the Hansen solubility parameter (8) and the relative energy difference (RED, 9) a succinct representation of the solute/solvent comparison emerges (Krevelen & Nijenhuis, 2009).

$$(R_a)^2 = 4\left(\delta_{d2} - \delta_{d1}\right)^2 + \left(\delta_{p2} - \delta_{p1}\right)^2 + \left(\delta_{h2} - \delta_{h1}\right)^2 \quad (8)$$

$$RED = \frac{R_a}{R_0} \quad (9)$$

R_a is calculated using the difference of the individual molecular force components (Krevelen & Nijenhuis, 2009) of both the UPE solute and the reactive diluent as the solvent (styrene), and the resulting value is plugged into the RED equation with R_0 being the base solubility parameter of the reactive diluent. The resulting ratio gives a simple numerical value that estimates the solubility of the potential Bio-UPEs in reactive diluent. According to Hansen's solubility parameter, two compounds are more soluble in one another as RED approaches 0 and if the RED value is greater than 1, the two compounds are less similar and are likely to be immiscible (Krevelen & Nijenhuis, 2009).

4. Results and discussion

4.1. Theoretical calculation of UPE solubility

Synthesis of the bio-based unsaturated polyesters (UPE) focused on forming the prepolymer thermoplastic resin from a one pot reaction of diacids (maleic anhydride) with a slight excess of diols (isosorbide, ethylene glycol, etc.). Isosorbide is the key component to the development of these UPE resins; however it is known to be a highly polar molecule and could hinder the solubility of the resin in commonly used reactive diluents (Zhu, Durand, Molinier, & Aubry, 2008; Zhu, Molinier, Durand, Lavergne, & Aubry, 2009). Recognizing this fact, initial formulations included reaction mixtures that contained either a small percentage of ethylene glycol as an auxiliary diol or a straight chain aliphatic diacid in addition to the maleic anhydride. These initial synthetic efforts attempted to maximize both the isosorbide (the component responsible for stiffness) and maleic anhydride (the constituent needed cross-linking the resin into a thermoset). Unfortunately, initial trials were completely insoluble in styrene as well as many common laboratory solvents due to the extremely polar nature of the isosorbide molecule. Without the addition of a hydrophobic component to mitigate the polarity of the isosorbide, the synthesized oligomers were high viscosity semi-solids that were not amenable to blending into resins.

Calculations were completed to show the expected solubility when the chain length (C-0 through C-8) of the auxiliary diacid was varied and the percentage of isosorbide was changed. According to calculations, shorter chain length diacids (oxalic, malonic, and succinic) would not help improve solubility in styrene or other common reactive diluents due to their inability to significantly reduce the RED value. Shorter diacids did not possess enough hydrophobic character (—CH_2— subunits between the carboxylic acids) to mitigate the polarity of the isosorbide ring structure and produce a resin with solubility characteristics that would match the desired reactive diluents. Using the group contribution method in determining the solubility parameter, alcohol and carboxylic acid groups possess a significant influence on the calculated values (Krevelen & Nijenhuis, 2009), whereby increased concentrations of these groups resulted in higher RED values. The esterification reaction converts these groups into a single ester; which itself is a polar group, however not to the same degree as the parent units. This reduces the impact of the polar functionality and allows for the non-polar features to mitigate their effects producing an oligomer that has similar solubility characteristics to the reactive diluents. This effectively dilutes the effect of the polar end groups through higher extents of reaction and increased molecular weight, thus higher molecular weights/repeat units decreased the effects of the polar end groups, reducing the RED value. However, even at very high molecular weights, the RED values never decreased below 1.0 and did not achieve a soluble resin. The diacids with reasonable

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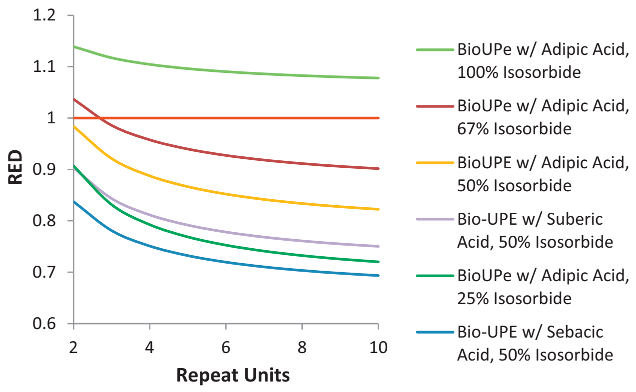

Fig. 4. Predicted structural effects on RED for UPE in styrene.

molecular weight and low cost that would give the greatest probability of producing a soluble resin in styrene were longer chain aliphatic diacids, such as adipic, suberic or sebacic acids, and increasing acid chain length improved solubility, such that UPEs made with sebacic acid had the lowest RED values while adipic acid-based UPEs had the highest RED values, Fig. 4. Furthermore, the results indicated that increased degree of polymerization improved the solubility in styrene, but this effect diminishes with successive increases in the degree of polymerization. Additionally, theoretical calculations also showed that when using isosorbide at more than 75 mol% of the diol content, the probability of producing a BioUPE resin that would be soluble in styrene is low. These calculations were supported by the our first attempts at synthesizing BioUPE resins that used ≥90% isosorbide or shorter aliphatic diacids (oxalic or malonic) that were completely insoluble in styrene.

Using the insight gained from the solubility parameter calculations, we formulated a variety of BioUPE resin compositions to be synthesized. The focus was on a four component system with initial compositions composed of 1.1 mol diol to 1.0 mol diacid. The baseline ratios were established at 50 mol% isosorbide content with an equivalent amount of ethylene glycol as an auxiliary diol and 50 mol% maleic anhydride with matching quantity of the designated diacid. For the purpose of these experiments, chains shorter than adipic acid were abandoned due to poor solubility and only the resins with the highest probability of solubility were pursued. Using this initial composition, component balanced samples were synthesized with adipic acid, suberic acid and sebacic acid to test the strength of the calculated model. Of these samples, the suberic and sebacic acid samples were easily soluble in styrene; however, the adipic acid sample was only partially soluble in styrene and would phase separate when left for any period of time, giving validity to the model. For the rest of our studies on BioUPE resins, sebacic acid was used as a diacid to minimize the solubility effects when studying the other variables in the BioUPE resin characteristics.

4.2. Characterization of BioUPE prepolymers

After completing the synthesis of the BioUPE cross-linkers, the resins were blended with 35 wt% styrene in order to provide resin blends that could be free radically cured to assess their thermomechanical characteristics. However, before these studies were carried out the resin blends were characterized using ^{1}H NMR spectroscopy, which confirmed reaction of the reagents by the upfield shifting of individual component peak (such as the α carbon next to ester carbonyls) and the final composition molar ratios. With the addition of this specified amount of styrene, there was a quantitative peak (vinylic singlet) in each sample that was used as a standard to determine the molar composition of the constituents of each BioUPE sample from the measurement of their peak areas (Fig. 5). The molar amounts of each UPE component were divided by the sum of the molar amount of all of the UPE components to calculate the molar percent of each component in the UPE. Ultimately, these calculated molar ratios did not match the original formulated compositions of the resin that were used during synthesis.

NMR analysis showed that in each of the samples the concentration of ethylene glycol was greatly reduced from the initial formulation (Table 1). This occurrence is most likely due to evaporation of the ethylene glycol during the course of the esterification reaction, causing a stoichiometric imbalance. This discrepancy caused the mole percents of the other constituent to be elevated from their expected values as well; however, in spite of these differences the desired effect in compositional variance was still observed. In the samples where the isosorbide/ethylene glycol ratio differed, there was still a noticeable gradient between the samples that would allow for the investigation of the effect of isosorbide on the thermomechanical properties of the resin. In the samples where other factors were being studied (effect of diacid or maleate content) the mole percent of ethylene glycol were comparable.

Also, observable using NMR was the development of fumarate esters during the esterification process. Fumarate ester is the trans isomer of maleate ester that is formed upon maleic anhydride esterification; which isomerization typically occurs due to heating at moderate temperatures or via catalytic methods (Peters, 1998; Goodman, 2000). Commercially fumarate esters have greater reactivity toward free radical polymerization (Goodman, 2000); however, the parent fumaric acid, the more stable isomer of butenedioic acids, has a poorer reactivity to esterification reaction to form the UPE oligomer when compared to maleic acid and maleic anhydride (Goodman, 2000). For this reason, maleic anhydride is used almost exclusively in commercial UPE preparation. For this same reason, maleic anhydride was chosen as the precursor for polyester synthesis in this work. Nonetheless, we utilized acid catalyzed isomerization to realize the desired fumarate ester subunits to produce crosslinked polymers with higher degrees of cure (Goodman, 2000). This interconversion was easily detected by NMR and the fumaric acid: maleic acid (FA:MA) ratio determined for each resin (Fig. 5 and Table 1).

The acids and anhydride reactants used in the synthesis of UPE can be titrated with a basic solution to determine their concentration. The initial acid number was approximately 500 mg/g for these systems. During the course of BioUPE synthesis, acid number can also be used to measure the concentration of acid that has not been esterified. The extent of reaction (p) is

$$p = \frac{AN - AN_0}{AN_0} \tag{10}$$

where AN is the measured acid number and AN_0 is the initial acid number. Typical UPE resins have molecular weights of ~2000 g/mol (Andrews et al., 2009). Using the compositions obtained by NMR analysis and AN titrations, the extent of reaction (p) could be calculated (Eq. (11)) and used to extrapolate the number average degree of polymerization, $X_{n.}$

$$X_n = \frac{1}{1-p} \tag{11}$$

$$M_n = M_0 X_n \tag{12}$$

In Eq. (12), X_n is used to calculate the number average molecular weight (M_n), where the M_0 is the average molecular weight of the repeat unit to arrive at an estimated M_n for each prepolymer resin. M_0 is calculated from the weighted average of the 4 components (maleate/fumarate, additional acid, ethylene glycol, and isosorbide) in the UPE polymer. Eqs. (11) and (12) can be used to calculate the extent of reaction, p, to achieve the desired molecular weight range of 1500–3000 g/mol. This corresponds to ~90% extent

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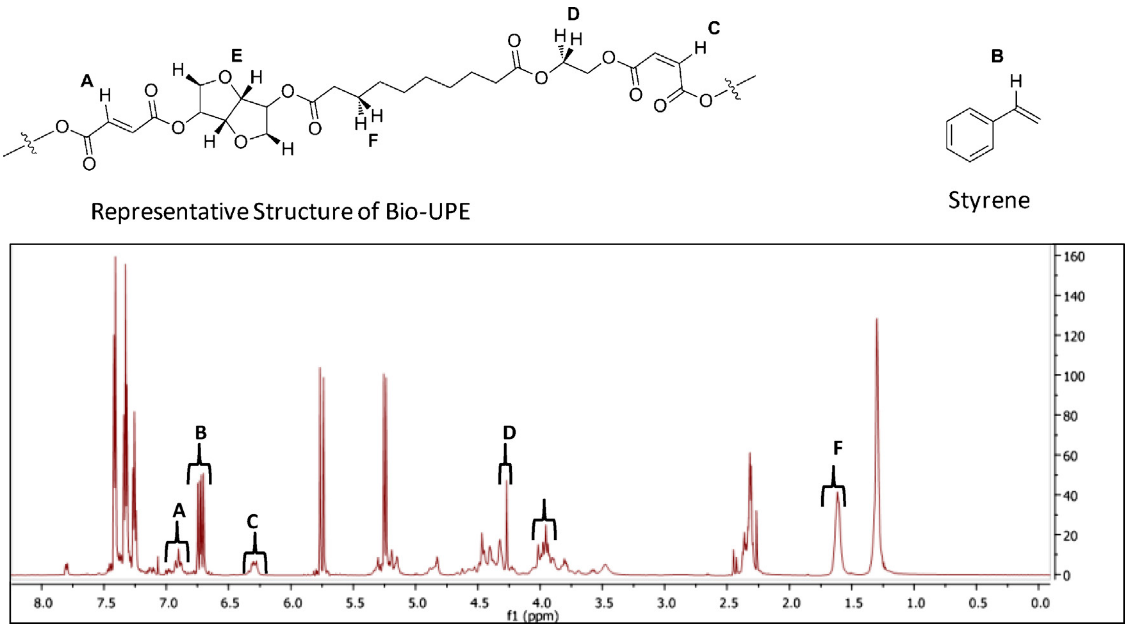

Fig. 5. Representative NMR of BioUPE resin.

Table 1
NMR compositional analysis.

Sample	Mole%									FA/MA ratio
	Isosorbide		Ethylene glycol		2° Diacid		Maleic anhydride			
	Reaction	NMR	Reaction	NMR	Reaction	NMR	Reaction	NMR		
								Maleate	Fumarate	
Suberic acid	26.2	28.7	26.2	9.8	23.8	24.9	23.8	20.5	16.1	0.79
Sebacic acid (baseline sample)	26.2	24.2	26.2	11.0	23.8	25.9	23.8	15.9	20.3	1.27
3:1 EG: isosorbide	13.4	16.2	40.3	17.8	23.1	25.9	23.1	15.0	22.9	1.53
1:1 EG:isosorbide (baseline sample)	26.2	24.2	26.2	11.0	23.8	25.9	23.8	15.9	20.3	1.27
1:2 EG:isosorbide	34.6	33.5	17.8	5.3	23.8	24.4	23.8	16.5	18.0	1.09
1:3 EG:isosorbide	39.3	36.0	13.1	4.4	23.8	22.9	23.8	20.9	15.8	0.76
2:1 Sebacic:MA	26.2	26.8	26.2	16.6	31.4	33.0	16.2	9.8	11.3	1.15
1:1 Sebacic:MA (baseline sample)	26.2	24.2	26.2	11.0	23.8	25.9	23.8	15.9	20.3	1.27
1:2 Sebacic:MA	26.2	23.9	26.2	6.1	16.2	16.8	31.4	19.4	31.0	1.59

of reaction, which required reaction times ranging from 10 to 18 h, based on the quantities of the constituents to reach the desired AN (below 30–40 mg/g). Using this method, we calculated the molecular weights of these samples to range from 1200 to 5700 g/mol, with the accuracy determined by the precision of the final AN titration. The molecular weights of the synthesized prepolymers were also determined by SEC, with the majority of the samples falling within the desired range of $M_n = 1500–3000$, with an average of 4.49–8.77 unsaturated units per molecule. Differences in the molecular weights calculated from NMR/acid number method vs. the SEC method are likely due to error in determining the titration end point and the SEC results are likely to be more accurate.

Using the difference in composition, from 30 to 43 mol% alcohol and 54 to 67 mol% acid, we are able to conclude that the resulting UPE are mostly acid terminated. We thus restructured our modeling work assuming all acid end groups and used the actual measured compositions to calculate the solubility parameter and RED calculations to obtain a more accurate representation of the solubility of the resin in styrene. For the bulk of the samples, as expected, the resins are more soluble as the chain length is increased (Fig. 6). However, in samples possessing elevated isosorbide concentrations, the RED values slowly increased as the chain extends due to the reduced concentrations of aliphatic components that mitigate the polarity of isosorbide. In an effort to understand why samples that were composed of adipic acid were only partially soluble in styrene, calculations were done for adipic acid using the same compositional make up as that of suberic acid. The results show that RED values, while very similar to the initial calculation, were significantly higher than that of the other resin blends (Fig. 6). The

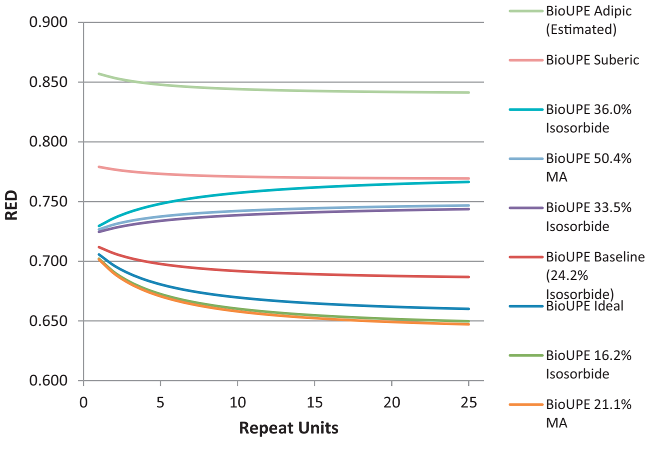

Fig. 6. RED values for actual compositions.

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Table 2
Zero shear viscosities of BioUPE resins.

BioUPE resin blends (with 35% styrene)	Viscosity @ 25 °C (P)	Rheological behavior
Viapal 450 (commercial UPE)	11.11	Shear thinning
Suberic acid	4.65	Newtonian
Sebacic acid (baseline sample)	5.14	Newtonian
3:1 EG: isosorbide	1.20	Newtonian
1:1 EG:Isosorbide (baseline sample)	5.14	Newtonian
1:2 EG:isosorbide	22.8	Shear thinning
2:1 Sebacic:MA	4.52	Newtonian
1:1 Sebacic:MA (baseline sample)	5.14	Newtonian
1:2 Sebacic:MA	14.68	Shear thinning

increasing RED values for high isosorbide content samples and RED values for resins composed of adipic acid indicate, that while theoretically any sample that has a RED value below 1.0 should be soluble, the experimental results indicates that this threshold is closer to 0.75–0.80 for a synthesized prepolymer to be amenable to blending in styrene.

4.3. *Viscosity of thermosetting resin blends*

Liquid molding technique used for composite layups have resin viscosity requirements in the range of 50–2000 centipoise (cP) in order to facilitate the optimal molding and ease of construction (La Scala, Sands, Orlicki, Robinette, & Palmese, 2004; Ziaee & Palmese, 1999). The styrene blended BioUPE samples were evaluated rheologically for comparison with a commercial UPE, the summary of those results can be seen in Table 2. As can be seen, the Viapal 450 sample had viscosity (1100 cP), right in the optimum range for liquid molding. The bulk of the formulated cross-linkers fall within the required viscosity range with the one exception of the sample composed of the highest isosorbide content fell just outside the window at 2200 cP. In general, the resin blends exhibited Newtonian behavior with the higher viscosity resins beginning to show some mild shear thinning behavior as the shear rate increased. The synthesized resins are well distributed through the molding window indicating that the composition can be amended during the cross-linker synthesis to produce a resin with a viscosity tailored for the application requirements.

The viscosity of a concentrated polymeric solution is governed by three factors: the concentration of the solution, molecular weight of the polymer and the topology of the polymeric chain (Hillyer & Leonard, 1973; Krevelen & Nijenhuis, 2009). In these resin systems the solution concentration is fixed at 35 wt% styrene and the molecular weights are all within comparable ranges (10^3); the molecular weight of the prepolymer blends would only become a factor if there was an order of magnitude difference (10^3 versus 10^4) (Hillyer & Leonard, 1973). Variation of the chain length of the auxiliary diacid (from suberic to sebacic) produced almost identical viscosities (460–510 cP) to each other indicating that changing the chain length of the aliphatic diacid ultimately had little effect on the viscosity. This was expected because this change in structure will have little effect on UPE molecular weight or topology.

Changing the maleate content of the resin allowed the viscosity to remained largely unchanged as the concentration increased (450–510 cP) until the concentration exceeded 50% of the diacid content where the viscosity increased dramatically (1450 cP). There were no significant difference in molecular weights among these samples, indicating that the stiff maleate/fumarate unsaturation/carbonyls are the likely contributor to the viscosity increase. Structure effects on viscosity are generally exponential, thus explaining the dramatic increase in viscosity upon the maleate content exceeding 50% of the diacid content.

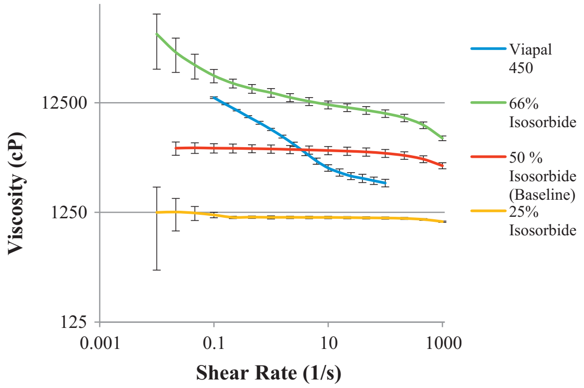

Fig. 7. Isosorbide effect on the viscosity of BioUPE resin blends.

Isosorbide is a large, bent, three dimensional structure that would severely influence the chain topology. This effect can be seen in Fig. 7, where the viscosity versus shear rate of the BioUPE and examined. The samples seen in Fig. 7 possess increasing isosorbide content and their corresponding viscosities very clearly show that isosorbide caused an increase in the viscosity of the resin blends while maintaining a similar range as the commercial Viapal 450. In fact, with higher isosorbide, the fluid became less Newtonian showing some degree of shear thinning. Again, there were no significant differences in molecular weights among these samples, and thus chain topology/composition is the dominant factor in effecting viscosity. These results indicate that BioUPE resin can be tailored in terms of viscosity in order to meet the requirements of thermoset manufacturing processes, with isosorbide being a key factor that influences viscosity of the resin system.

4.4. *FT-IR cure studies*

FT-IR analysis of the resins shows that the extent of cure was high in all of the samples for both the styrene and BioUPE constituents (Table 3). All of the BioUPE resins had a 96.13 ± 0.64% conversion of the styrene after post-cure within the polymer matrix and did not differ significantly from sample to sample. The peaks that corresponded to the BioUPE reactive sites show a slightly lower conversion of 84–91%. The lower conversion rate relative to styrene is expected because the cross-linkable UPEs lose mobility to a higher degree as cure rate increases, while the small molecule styrene is freer to diffuse to free radicals within the system (Brill and Palmese, and Ziaee and Palmese). The UPE conversion rate was related to the ratio of fumarate to maleate found within the prepolymer cross-linker (Table 1) in that a higher ratio of fumarate results in higher cure conversion rates in the thermoset. The only anomaly seen to this trend was the sample that contained increased molar concentrations of unsaturated diacids, which showed an 85% conversion despite a high FA/MA ratio. The higher amount of cross-linking expected to occur would thus reduce the mobility of the UPE polymers, reducing their ability to react. Furthermore, this sample is likely to be styrene deficient relative to the other samples because of the relatively large UPE unsaturation to styrene ratio.

4.5. *Thermomechanical properties*

DMA was used to determine the thermomechanical properties of the cured resin blend to establish the structural effects of the constituents on the properties of the thermoset, a representative plot can be seen in Fig. 8. Resins used in the manufacture of high performance composites ideally have thermomechanical properties in the range of 115–250 °C for T_g and possess moduli in the range of 2–3 GPa at room temperature (La Scala, Sands, Orlicki, Robinette, &

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Table 3
Thermomechanical properties of BioUPE samples.

Sample	tan δ (°C)	E' @ 25 °C (MPa)	E'min (MPa)	Density @ 25 °C	M_c	FA:MA ratio	$\alpha_{styrene}$ %	α_{UPE} %
Viapal 450 (commercial UPE)	116.4 ± 0.56	3315.2 ± 224.7	12.38 ± 2.1	1.23 ± 0.005	1086 ± 26.7	N/A	N/A	N/A
Suberic acid	68.7 ± 1.9	1077.0 ± 73.3	10.42 ± 0.70	1.210 ± 0.001	1119.4 ± 58.2	0.90	96	84
Sebacic acid (baseline)	64.5 ± 1.6	621.5 ± 58.7	10.14 ± 0.61	1.204 ± 0.001	1177.3 ± 48.2	1.3	96	89
16.2% Isosorbide	58.0 ± 2.1	527.0 ± 109.9	13.18 ± 0.65	1.190 0.001	848.8 ± 51.9	1.5	96	91
24.2% Isosorbide (baseline sample)	64.5 ± 1.6	621.5 ± 58.7	10.14 ± 0.61	1.204 ± 0.001	1177.3 ± 48.2	1.3	96	89
33.5% Isosorbide	75.4 ± 0.7	1081.0 ± 41.1	9.50 ± 0.30	1.216 ± 0.001	1219.5 ± 41.6	1.1	95	88
21.1% Maleic anhydride	60.4 ± 4.0	379.7 ± 74.6	3.63 ± 0.41	1.186 ± 0.001	3113.1 ± 768.5	1.1	97	87
26.1% Maleic Anhydride (baseline sample)	64.5 ± 1.6	621.5 ± 58.7	10.14 ± 0.61	1.204 ± 0.001	1177.3 ± 48.2	1.3	96	89
50.4% Maleic anhydride	107.0 ± 8.6	1650.3 ± 121.0	49.15 ± 5.3	1.239 ± 0.001	271.3 ± 31.5	1.6	97	85

Palmese, 2004; Ziaee & Palmese, 1999). In general, UPE resins have a range of properties from fairly low with T_g and modulus ranging from a little slightly above room temperature and 1 GPa to fairly high with T_g of 100 °C and modulus of 3 GPa (Andrews et al., 2009). The commercial UPE resin used for comparison, Viapal 450, fell just within the scope of these parameters: with a T_g of 116 °C and E' of 3.3 GPa. For our studies, the peak of the tan δ (the ratio of the of the loss modulus (E'') to the storage modulus (E')) was used as the indicator of T_g for the BioUPE resin systems. The molecular weight between cross-links (M_C), which is inversely proportional to the crosslink density, of the samples was calculated using the Eq. (13):

$$M_C = \frac{3RT\rho}{E} \tag{13}$$

where the E is the rubber modulus taken from the plateau region of the storage modulus, T is the corresponding absolute temperature of this region (La Scala et al., 2005), R is the universal gas constant, and ρ is the density of the sample, measured using the Archimedes principle (Flory, 1992; La Scala, Logan, Sands, & Palmese, 2008; Palmese & McCullough, 1992). The summary of these results can be seen in Table 3.

The effect of auxiliary diacid on the thermomechanical properties of the resin was the first structural change studied after the field of candidates was narrowed through calculation. DMA analysis of the two resins (suberic and sebacic) show that T_g of the resin was only mildly decreased with an increase in length of the aliphatic diacid: suberic (C-8) at 69 ± 2 °C versus sebacic (C-10) 65 ± 2 °C. The increase in chain length seemed to have a more significant effect on the modulus at room temperature showing a 73% increase in the modulus as the chain length was decreased by two carbons. This structural variation had negligible effect on the M_c of the samples (1120 ± 58 g/mol versus 1180 ± 48 g/mol) as would be expect by interchanging constituents that are only 28 g/mol weight difference into a polymeric systems.

Varying the concentration of isosorbide had a more pronounced effect on the T_g and modulus of the resin, indicating that it was lending structure integrity to the resin system. The baseline resin sample contained 24 mol% of isosorbide based on NMR analysis in the cross-linking prepolymer which resulted in a resin with a T_g of 64 °C. Decreasing the content by as little as 8 mol% as seen in NMR resulted in a reduction in T_g of 6 °C, and increasing the content to 33 mol% of the total resin composition enhanced the T_g to 75 °C. However, increasing the concentration of isosorbide brought the solubility factor back into the picture, as increasing the concentration to as much as 35 mol% isosorbide resulted in a prepolymer that was not soluble in reactive diluent. Isosorbide's effect on the storage modulus was significant: E' increased sharply as the content increased for 24–33 mol%, giving a 74% increase in the E' at 25 °C. The M_C of the samples showed only slight increases as the isosorbide content increased, this is most likely due to the difference in molecular weight of isosorbide (146.14 g/mol) when compared to the ethylene glycol (62.07 g/mol) that it was replacing. Increasing the maleate content in the prepolymer has a significant effect on

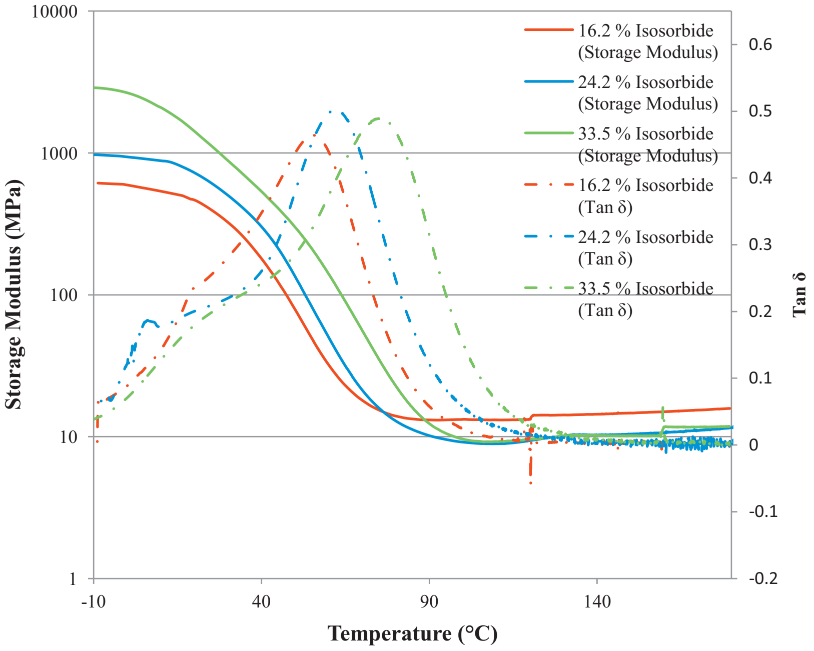

Fig. 8. Storage moduli and tan δ of BioUPE resin systems.

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T_g, storage modulus and cross-link density. The highest observed T_g (107 °C) in the BioUPE systems was a result of a resin synthesized with 50 mol% maleic anhydride of the total molar composition and the same resin had a storage modulus at 25 °C of 1.6 GPa; a significant improvement over baseline resin ($T_g = 64.5 \pm 1.6$ °C, and E'@ 25C = 0.62 ± 0.058 GPa). These BioUPE resin showed a dramatic decrease in the molecular weight between cross-links as the maleate content was increased; which can be explained by the greater number of polymerizable sites can yield a tighter cross-linked network.

Although molecular weight did vary from sample to sample, the thermoset nature of the resulting polymer should mitigate the effect of UPE monomer molecular weight on the thermomechanical properties as long as most UPE monomers have two or more sites of unsaturation per molecule to enable cross-linking. The molecular weight and compositional analysis of the UPE monomers shows that the prepolymers (M_n = 1500–3000 g/mol) had an average of 4.5–8.6 unsaturated units per molecule, indicating that each molecule had sufficient cross-linking character to form a thermoset polymer. Thus, the effects on thermomechanical properties are largely compositional for these UPEs.

5. Conclusions

These results have shown that bio-based UPE resins have the potential to be developed as useful thermosetting resins and that isosorbide can be used as a structural constituent of unsaturated polyester resins from the diol component. Our investigations into BioUPE resins have not identified a formulation using isosorbide that possess solubility in common reactive diluents and having thermomechanical properties that would be amenable to high-performance applications. However, these resins do have viscosities that fall within the necessary ranges for composite application and adequately compare to some commercial UPE resins. These basic BioUPE resins have potential to be leveraged as thermosetting plastics and composites in applications that do not require stricter performance standards. In general, we showed that compositional effects created significant effects in BioUPE viscosity and thermomechanical properties. In particular, our studies have shown that increased isosorbide content does have an effect on viscosity, T_g, and storage modulus but reduced solubility in styrene; and would be an invaluable tool for novel resin development. However, isosorbide has proved to be intractable and in order to produce resins with properties desirable for high-performance applications, it would be necessary to use concentrations of isosorbide that would make the resin insoluble in any potential reactive diluents. Although current formulations are inadequate for high-performance thermosetting applications, in may be possible to use isosorbide in the future to improve current aromatic-based UPEs. Such UPEs would have rigid diacid and diol components, potentially enabling the attainment of properties higher than that of any current UPE.

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