Unsaturated polyester resins for thermoset applications using renewable isosorbide as a component for property improvement

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ABSTRACT: Unsaturated polyester (UPE) resins are used in a variety of thermosetting applications due to the reduced cost when compared to epoxy resins; however, UPE resins also have reduced thermomechanical performance. Investigating avenues to improve the performance of UPEs has led to the use of bio-based starting materials as structural components of the synthesized prepolymers as a result of their advantageous structural features. Isosorbide, a compound derived from renewable feedstocks, has been utilized to provide additional stiffness from the diol component for novel unsaturated polyesters resins. These resins have been shown to possess T_g's ($32-72°C$) and storage moduli ($540-2200$ MPa) that are in the desired range for composite materials with viscosities ($1.2-25$ Pa s) amenable to a variety of liquid molding techniques. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42315.

INTRODUCTION

Thermosetting polymers and composites are used in an array of applications and have been successful due to their improved performance over traditional materials.[1–4] Composite materials commonly utilize thermosetting epoxy, 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 when compared to epoxy resins; however, this comes at a cost of reduced performance.[5] VE and UPE resins have reduced glass transition temperatures (T_gs) and fracture toughness but maintain adequate performance for a number of applications. VE and UPE cross-linker monomers typically have extremely high viscosities ($2000-80,000$ cP)[6] that necessitate the use of reactive diluents for adequate processing,[1] but these diluents are designated as hazardous air pollutants (HAPs) and volatile organic compounds (VOCs).[7] UPE resins are the preferred cross-linking system for the development of new high performance materials due to cost; however, the thermomechanical properties that can be achieved using this type of resin does not generally fit the requirements for high performance applications.

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.[8,9] Bio-refining manufacturing processes have produced a number of unique compounds that have structural features not available through petroleum refining processes and provide unique scaffolds for the development of new 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. Early work on isosorbide based polymers have included the development of thermoplastic polyesters,[9–12] polyurethane resins,[9,13] and epoxy thermosetting resins.[14] Studies using isosorbide in the synthesis of thermoplastic polymers showed that isosorbide in increasing concentrations enhanced the mechanical properties of otherwise poor performing materials, and isosorbide can raise the T_g of those materials by as much as 73% depending on concentration.[12] Past research in our laboratories has focused on the development of a bio-based UPE resin system using isosorbide as the sole diol monomer in the prepolymeric resin to provide stiffness. Isosorbide was shown to significantly improve T_g and storage modulus using no other monomer for structural integrity.[15]

Since earlier work has proved that isosorbide can be used to successfully improve the thememomechanical properties of polymeric systems, the focus of this work was to design and synthesize UPE resin systems using isosorbide as an additive to provide stiffness in addition to components typically used in commercial resins to provide strength to produce thermosetting polymers for use in composite applications. UPE resins are

prepared by reacting diols with diacids and/or anhydrides. Commercial UPEs usually rely on gaining stiffness from monomers with aromatic rings such as terephthalic acid and othophthalic acid linked together with aliphatic diols such as diethyelene glycol. These components are known low T_g components[5,16] and limit the glass transition temperature of the unsaturated polyester. In this work, isosorbide was investigated as a structural constituent to provide stiffness from the diol component in addition to the aromatic diacids that are found in commercial UPE systems.[5,17] Adding a diol constituent that can provide improvements to mechanical properties is believed to provide a new tool for the development of novel thermosetting UPE resins.

Thermoplastic prepolymers were synthesized through the polycondensation of a mixture of diols and diacids with attention to the effects of increasing isosorbide concentration on the properties. These prepolymer cross-linkers were then blended with reactive diluents to make resin systems with desirable viscosity characteristics that can undergo thermoset curing. The rheological and thermomechanical properties of these uncured resins and thermoset polymers were investigated to understand the effects of isosorbide incorporation and gauge its utility for UPE composites applications.

EXPERIMENTAL

Materials

Isosorbide (98%, Sigma-Aldrich) and diethylene glycol (DEG, 99%, Alfa Aesar) were used in this study as the diol components of the synthesized UPE resin systems with isosorbide being used as a monomer to provide additional stiffness to the thermoset upon free radical curing. Phthalic anhydride (ACS Reagent Plus $\geq$ 99%, Sigma-Aldrich) was used as the aromatic diacid for the synthesis to provide stiffness for the UPE resin. Maleic anhydride (99%, Sigma-Aldrich) was used in all formulations to provide unsaturated sites that could undergo free radical curing. Xylenes (>98.5%, VWR) were used during the reaction as an azeotropic solvent, p-toluenesulfonic acid monohydrate ($\geq$95.5%, Sigma-Aldrich) was used to catalyze the esterification and hydroquinone (ACS Reagent Plus $\geq$ 99.9%, Sigma-Aldrich) was used as 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 $\geq$ 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).[18] All chemicals were used as received without further purification. Methyl ethyl ketone peroxide (MEKP, Syrgis) was used as the free radical polymerization initiator, and cobalt naphthenate (CoNap, $\leq 6.5\%$ Co^{+2} in mineral spirits, Sigma-Aldrich) was used as a promoter for polymerization.

General Synthesis of UPE Resins

Isosorbide (0.0−0.2114 mol), diethylene glycol (DEG, 0.211.1−0.4222 mol), maleic anhydride (0.8464 mol) and phthalic anhydride (0.3376 mol) were suspended in xylenes and melted together at 55°C before adding p-toluenesulfonic acid (5.0 wt %) and refluxed with the aid of a Dean-Stark attach-

ment. The progress of the reaction was monitored by Acid Number (AN) titration. Once the acid number was reduced to 12−23 mg/g, which required 18−96 h, the reaction was fitted with a vacuum distillation adapter and distilled at ambient pressure for 2 h and then under reduced pressure (−68 mbar) for 1.5 h. Hydroquinone was added to the molten resin and allowed to stir and cool for 15 min\ before placing in a vacuum oven at 55°C at −30 mbar for 18 h to remove remaining xylene and was confirmed during the NMR analysis. Resins appeared as yellow to amber semi-solids with varying viscosity, and were blended with the appropriate amounts of styrene before analysis.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to evaluate the molecular weight and dispersity (Đ) of the thermoplastic UPE samples before blending the samples with styrene to form thermosetting resins. Samples were dissolved in tetrahydrofuran (THF), concentration of ∼7−8 mg/mL and processed using a Waters 717 plus Autosampler with a Waters 510 GPC using three columns set in succession, Phenogel 5μ 105 Å, Phenogel 5μ 103 Å, and Phenogel 5μ 500 Å. The columns were equilibrated at 40°C before elution with helium purged 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. Molecular weights of the resins were calculated based on retention time of polystyrene standards: 51,000 amu, 10,000 amu, 5050 amu, and 580 amu.

Formulation and Curing Package

Resin systems were blended so that their composition consisted of 65 wt % UPE cross-linker and 35 wt % styrene as a reactive diluent. Hexion 713–6150 was used as commercial product for comparison purposes. Despite this commercial product only containing 24 wt % styrene, this resin has a similar UPE composition compared to the sample containing 0% isosorbide. As a result, this commercial resin sample was used simply to baseline the properties of a typical product, not for structure−property relationships. All samples were blended to homogeneity using a Resodyne Labram acoustic mixer at 60 Hz and 65% intensity. 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 for 24 h in a silicone mold at 50°C, postcured at 120°C for 3 h and allowed to equilibrate at ambient temperature before any analysis was conducted.

Rheology

The viscosity and basic rheology of the formulated UPE resins were measured using a steady state flow procedure 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 the gap spacing (i.e., sample thickness) was set to 1000 μm at 25°C. The shear rate was increased from 0.1 s^{-1} to 100 s^{-1} and then decreased back to 0.1 s^{-1}; 5 measurements were taken per decade. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were
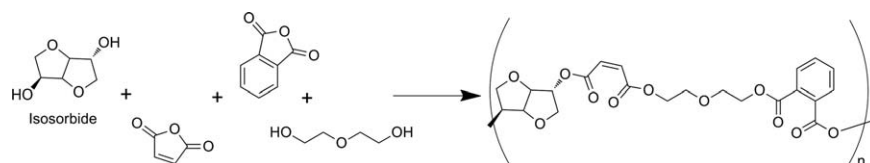
Scheme 1. Synthesis of oligomeric UPE cross-linkers.

recorded when the shear rate stabilized to within 5% tolerance for three consecutive points.

NMR

The resins were characterized by means of ^{1}H NMR spectroscopy (600.18 MHz, spectral window of 12000 Hz, 0.378 Hz/pt digital resolution, 16 scans at 298.3 K, 8.0 pulse width) using a Bruker (Billerica, MA) AC600 Spectrometer. The resin blends were dissolved in $CDCl_3$ and showed peaks in agreement with the expected chemical shifts for individual constituents of the UPE resins.[17] Selected peaks for each constituent were used for quantification of mole percent: δ 7.75 (b, 2H, phthalic acid), 6.93 (bd, 1H, fumarate), 6.77 (dd, 1H, vinylic styrene), 6.32 (bd, 1H, maleate), 4.03 (b, 3H, isosorbide),[19] 3.83 (bs, 2H, diethylene glycol. Molar concentrations for each component were determined by measuring the area of each peak and dividing by the number of protons responsible for each peak.

Extent of Cure

Fourier-Transform Infrared Spectroscopy in near-IR mode (NIR) was used to calculate the extent of cure for the UPE resin blends based on the consumption of the styrene vinylic and polyester unsaturation groups. The UPE resins, before cure and after post-cure, were scanned in NIR range of 4000 cm^{-1} to 8000 cm^{-1} at room temperature with a total of 64 scans per spectrum. Liquid materials (i.e., uncured resin) were placed in a glass reservoir having a path length of 3.4 mm and the cured samples were Dynamic Mechanical Analysis (DMA) bars with thicknesses ranging from 4.0 to 4.5 mm. The peak at 4715−4725 cm^{-1}, corresponding to stretching of maleate and fumarate groups in UPE backbone, represents the reactive group of UPE; the broad peak at 5978 cm^{-1} represents the ethereal methylene groups of the UPE backbone and is used as the internal reference of the UPE prepolymer cross-linker.[20,21] For the styrene conversion, the peak at 6132−6136 cm^{-1}, corresponding to stretching of the vinyl bond, was taken as representative of the reactive group and the peak at 4663 cm^{-1}, indicative of the aromatic C=C stretch, was used as the internal reference.[20–23]

Polymer Properties

Thermo-gravimetric behaviors of the postcured UPE/styrene blends were measured using a Thermogravimetric Analyzer (TGA) Q5000 from TA Instruments. Samples of 11−55 mg were placed in a platinum pan and heated from 25 to 650°C at rate of 20°C min^{-1} under an inert argon atmosphere (40 mL min^{-1} balance gas flow rate and 60 mL min^{-1} sample gas flow rate).

The thermomechanical properties of the polymer samples were measured using TA Instruments Q800 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 and amplitude of 7.5 μm, while subjected to a temperature ramp from −50°C to 200°C at a rate of 2°C/min. DMA can be used to determine T_g of a polymer through three methods. Storage modulus (E') is one method where the inflection point is considered the T_g. A more conservative value for the T_g is derived from the peak of the loss modulus (E'') and is commonly reported. The temperature at the peak of the tan δ (E''/E') is the third method and considered as the glass transition temperature of the material for this study.[24] The data for these UPE resins showed that tan δ was more in line with the inflection point of the storage modulus, while E'' peak was at significantly lower temperatures than the inflection point of the E'.

RESULTS AND DISCUSSION

Synthesis and Characterization of UPE Prepolymers

Synthesis of the UPE systems using isosorbide as a comonomer, Scheme 1, was accomplished in a one pot reaction of the diol and diacid components to form the oligomeric thermoplastic cross-linker. Formulation of these cross-linkers began with the mole ratio of diols slightly elevated over the diacid (9.5% excess diol) to ensure that the resulting oligomer possessed alcohol end groups for solubility purposes. Once this mole ratio was set, the isosorbide/DEG composition or the phthalic anhydride/maleic anhydride ratio was adjusted to elicit different thermomechanical properties in the prepolymeric samples. Hexion 713–6150 was used as the commercial resin baseline for these studies and a baseline sample (0% isosorbide) was synthesized in an effort to match the characteristics. The resulting baseline oligomer was stoichiometrically similar to the commercial Hexion sample that was characterized previously.[25] The progress of the reaction was followed using AN titrations to calculate the extent of reaction in order to ensure that prepolymers with similar molecular weights were synthesized.

When the desired degree of reaction was achieved, the UPE prepolymers were isolated and blended with styrene to form resins that can free radically cure to form thermosets. The blended resins were characterized by ^{1}H NMR spectroscopy to ensure that the relative molar ratios were still in correspondence with their beginning concentrations. Reaction of the reagents was confirmed by the upfield shifting of individual component peaks (such as the α carbon next to ester carbonyls) and the final composition molar ratios. With the addition of the 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 UPE sample from the measurement of their peak areas. The molar amounts of each UPE component were divided by the sum of the molar amounts of all of the UPE components to calculate the molar percent of each component in the UPE, summarized in Table I.

Table I. NMR Analysis of Isosorbide UPE Resins

	Mol %									FA/MA ratio	Reaction time (h)
	Isosorbide		DEG		Phthalic anhydride		Maleic anhydride	NMR			
Sample	Reactants	NMR	Reactants	NMR	Reactants	NMR	Reactants	MA	FA		
0% Isosorbide	0.0	0.0	52.2	49.8	37.3	41.1	10.5	5.5	2.6	0.5	18
10% Isosorbide	10.5	12.4	41.8	37.0	37.3	39.9	10.5	5.6	5.1	0.9	60
15% Isosorbide	15.7	19.3	36.6	31.0	37.3	41.6	10.5	3.6	4.4	1.2	74
25% Isosorbide	26.2	26.5	26.1	22.9	37.3	41.8	10.5	5.2	3.6	0.7	96
15% Isosorbide (low MW)	15.7	17.1	36.7	33.4	37.2	40.0	10.5	5.0	4.5	0.9	60
25% Isosorbide (low MW)	26.2	26.8	26.1	21.6	37.2	43.3	10.5	4.7	3.6	0.8	72
15% Isosorbide, 17.5% MA	15.0	18.2	35.1	31.2	29.1	35.9	17.4	4.9	9.8	2.0	60
15% Isosorbide, 25% MA	16.0	16.4	37.5	33.2	23.9	27.8	22.6	14.4	8.1	0.6	60
Hexion 713–6150[25]		0.0		50.0		39.0		1.0	9.0	15	

Additionally, the analysis by NMR allowed for the quantification of the fumarate esters that developed during the course of the reaction. Fumarate (FA) esters are the trans isomers of maleate esters (MA) that occur as a result of the reaction and isomerization of maleic anhydride with secondary alcohols. Fumarate possesses greater reactivity for use in free radical polymerization; however, the parent fumaric acid is the more stable of the butene-dioic acids and possesses poorer reactivity in the formation of esters.[5] Commercially, maleic anhydride is the preferred reagent for the formation of UPE resins due to its increased reactivity for the esterification reaction, cost, and its propensity to isomerize into the more stable fumarate ester at higher temperatures.[5] This side reaction is also aided by the use of secondary alcohols, in this case isosorbide, which favors isomerization to form the fumarte esters.[5] It is for these reasons that maleic anhydride was chosen as the precursor for our polyester synthesis and the interconversion was easily detected by NMR and the fumaric acid: maleic acid (FA:MA) ratio determined for each resin, Table I. The results show that longer reaction times (60−96 h) needed to account for lower reactivity of the endo-hydroxyl on the isosorbide due to sterics.[26,27] This extended reaction time was necessary to achieve higher molecular weight prepolymers which also resulted in greater conversion to the fumarate ester.

NMR analysis showed the baseline sample synthesized with 0% isosorbide was compositionally similar to the commercial Hexion 713–6150 system. Unfortunately, our prepared sample was not able to replicate the FA/MA ratio that is seen in the commercial product indicating the possibility that it was manufactured starting from fumaric acid in place of maleic anhydride (unlikely), heated to higher temperatures, and/or heated for longer times.

The primary nature of the DEG monomer used in the baseline sample allowed for facile esterification and achieved high molecular weight oligomers in a shorter reaction time (18 h) compared with samples that contained isosorbide (60 h+). Generally, the results of the NMR studies are in agreement with the initial molar ratios of the reaction mixture, with minor variations. All of the synthesized prepolymeric resins showed slight reduction in the molar concentration of FA plus MA versus the initial reaction mixture due to sublimation of the maleic anhydride or degradation of the monomers which is common for UPE synthesis,[5] resulting in slight elevation of the molar concentration of the other monomers. Another factor in this discrepancy is likely caused by different rates of reaction of the monomer components and experimental error in NMR analysis. Regardless, the desired trend of increasing isosorbide concentration in UPE oligomers was enabled by increasing the concentration of isosorbide in the starting reaction mixtures.

Using the NMR analysis to obtain an accurate quantification of the component ratios of the resin systems, we were able to do a theoretical calculation of the M_n of the prepolymeric resin in conjunction with the AN titration to determine the degree of polymerization. The anhydride reactants used in the syntheses of the UPE resins can be titrated with a basic solution to determine their concentration as the reaction progresses. The initial AN for these systems ranged from 410 to 450 mg/g. The extent of reaction can be determined using eq. (1).[28]

$$p = \frac{AN - AN_0}{AN_0} \tag{1}$$

In eq. (1), AN is the measured acid number, AN_0 is the initial acid number, and p is the extent of reaction. An extent of reaction of 95% ($p = 0.95$) was the goal for all the UPE resin

Table II. NMR and GPC Analysis of Molecular Weight

Sample	p^a	NMR analysis		GPC analysis				Average sites of unsaturation per molecule (repeat unit MW)	Reaction time (h)
		M_n	M_w	M_n	M_w	Dispersity (Đ)	p^b		
0% Isosorbide	0.97	4200	8200	3900	6600	1.7	0.97	2.71 (1236)	18
10% Isosorbide	0.96	2600	5000	4000	7000	1.7	0.98	3.19 (1254)	60
15% Isosorbide	0.96	2800	5500	3500	6800	1.9	0.97	2.03 (1722)	74
25% Isosorbide	0.93	1800	3400	2700	4500	1.7	0.96	1.68 (1610)	96
15% Isosorbide (low MW)	0.93	1700	3400	1100	2300	2.0	0.89	0.77 (1436)	60
25% Isosorbide (low MW)	0.93	1400	2800	1500	3500	2.3	0.94	0.87 (1715)	72
15% Isosorbide, 17.5% MA	0.93	1700	3400	1700	4100	2.4	0.93	1.86 (913)	60
15% Isosorbide, 25% MA	0.94	1800	3500	1600	3400	2.2	0.93	2.83 (566)	60
Hexion 713-6150[25]				1100				1.0	

$^a p$ extent of reaction calculated from the AN.
$^b p$ for the GPC analysis was calculated using the modified Carothers equation.

systems, which corresponds to an oligomeric molecular weight of ~2500 g/mol. Using the composition obtained by NMR analysis, and the p obtained from the AN titrations, the number average degree of polymerization (X_n) can be calculated. However, it was determined that there was a stoichiometric imbalance (r) in the concentration of the components and this factor had to be taken into taken into account using eq. (2).

$$r = \frac{N_A^o}{N_B^o} \quad (2)$$

In eq. (2), N_A^o is the initial concentration of the deficient component and N_B^o is the initial concentration of the constituent in excess. The value of r is always less than one. Using these values, the degree of polymerization can be calculated using the modified Carothers equation [eq. (3)], which was used to calculate the number average molecular weight [M_n, eq. (4)], and the weight average molecular weight [M_w, eq. (5)] of the oligomer.[29]

$$X_n = \frac{1+r}{(1+r-2rp)} \quad (3)$$

$$M_n = X_n M_0 \quad (4)$$

$$M_W = M_0((1+p)X_n) \quad (5)$$

In eqs. (4) and (5), the M_0 is the average molecular weight of the repeat unit to arrive at an estimated M_n or M_w for each pre-polymer resin respectively. M_0 is calculated from the weighted average of the four components (maleate/fumarate, phthalic acid, diethylene glycol, and isosorbide) in the UPE polymer. The results of this method are summarized in Table II, and their corresponding molecular weights as determined by GPC using the retention time of polystyrene standards calculated using the Waters Empower GPC Software.[30,31] The accuracy of NMR

method is ultimately determined by the precision of the final AN titration and the interpretation of the NMR spectra for the quantified peak areas. Using this method, the calculated M_n can be drastically affected by end point determination in the AN titration and surplus breadth in the integral range of the quantified peaks. Over or under-titration of the resin can result in an incorrect extent of reaction (p), where at $p > 0.8$ an error as little 0.02 can result in M_n calculations incorrect by hundreds of mass units. Moreover, incorrect integral ranges in the NMR analysis can result in a poor M_0 determination as well as skewed r factors that can result in M_n calculations that can be thousands of mass units in error. Yet, the GPC results are based on the polystyrene standards and may not have the same radius of gyration in THF at 40°C as a UPE for a given molecular weight resulting in a systematic error in molecular weight for UPEs. In all, the results show that the NMR method results in M_n values that are very similar to those that were determined through GPC analysis. The differences in the molecular weights calculated are likely due to the aforementioned sources of error. Dispersity (Đ) can also be calculated from the NMR determination of molecular weight. The Đ is typically M_w/M_n; however, in this case of these calculations that reduces to $Đ = 1 + p$; making the Đ values determined from the NMR calculations appreciably similar to those found by GPC.

The molecular weight of UPE resin systems is affected by a number of factors: reaction stoichiometry, reaction time and structure of the resin components. In the case of this investigation, the reaction stoichiometry was similar for all reactions, even though some slight deviations in stoichiometry occurred because the reaction conditions cause some loss of material or decomposition. With the addition of isosorbide into the system, reaction time became a critical factor due to the structural configuration of the new diol subunit. Table II shows there is a
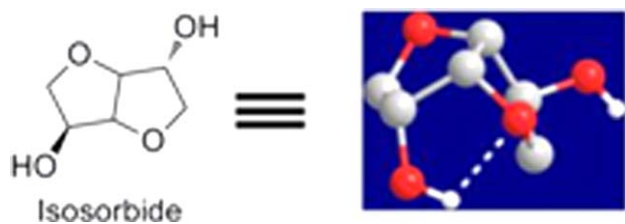
Figure 1. Conformation of isosorbide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

noticeable effect on the time needed to reach similar extents of reaction with increased isosorbide content when compared with straight chain diol systems (Table II). There are two reasons for this. First, diethylene glycol has primary alcohol groups that are more reactive with the diacid/anhydride monomers. Second, the bent structure of isosorbide (Figure 1) causes steric hindrance of one of the hydroxyl groups. The exo hydroxyl group is exposed for polymerization. On the other hand, the endo hydroxyl on the isosorbide fused ring system has been shown to undergo intramolecular hydrogen bonding in addition to being protected by the steric bulk of the rest of the molecule.[26] Thus, the simple addition of the steric hindrance from the secondary alcohols[5] likely retards the reaction. Thus, these combined factors necessitate a significant increase in the amount of time needed to facilitate the formation of larger molecular weight oligomers.

While increasing the isosorbide content resulted in the sluggish accumulation of molecular weight of the oligomer and forcing extended reaction times (Table II) to result in higher molecular weight prepolymers, the protracted length of the reactions did not appreciably change maleate/fumarate ratio (Table I). This indicates that higher temperatures were likely used to make the commercial Hexion resin with high FA/MA ratios.

There is an optimum range of molecular weights for UPE oligomers. High molecular weight UPE oligomers are often desired to enable high cross-link density, thermal, and mechanical properties, but also results in increased viscosity and more difficulty in processing. UPEs with low molecular weights are not desired because these can have significant content of oligomeric chains with no unsaturation functionality, resulting in high plasticizer content in the resulting thermoset. High molecular weight oligomers have the benefit of having a greater number of unsaturated sites per molecule without the need to increase the concentration of maleic anhydride, Table II, but again detrimentally effect viscosity as is presented in the next section. The increased number of unsaturations per molecule with increased molecular weight likely has a direct effect on the properties of the resulting cured materials; having multiple sites for polymerization results in greater frequency to be incorporated in the growing polymeric network. This can also be controlled during UPE synthesis by the addition of higher concentrations of maleic anhydride and will result in an increase in the number of unsaturated sites at lower molecular weight; however, this will often sacrifice stiffness and strength by removing the phthalic acid constituents.

Variation in the concentration of the MA at the beginning of the reaction had no noticeable effect on the development of the molecular weight of the resulting prepolymeric materials. Similarly, the MA/FA ratio was unaffected by the increasing concentration of MA in the initial reaction mixture (Table I).

Rheological Evaluation of Resin Blends

The molding technique employed to make thermosetting composites is dependent on the resin viscosity. Generally, UPE resins have viscosities that range from 4000 to 6000 centipoise (cP) or higher depending on the composition of the resin.[5] Repair resins are often high viscosity materials that are rheologically modified with fillers in order to facilitate resistance to sagging or dripping when applied to vertical surfaces.[25] The isosorbide based UPE samples blended with styrene were evaluated rheologically as a function of composition and were compared with the commercial Hexion 713–6150. The summary of those results can be seen in Table III. The measured viscosity was plotted against the shear rate and the data fit using the Ostwald-de Waele power law equation [eq. (6)].

$$\eta = \kappa \gamma^{n-1} \qquad (6)$$

In eq. (6), κ is the magnitude of viscosity, with higher values indicating more viscous resins and n is the flow behavior index, where lower values indicate greater shear thinning. The formulated cross-linkers displayed high viscosities, relative to typical UPE viscosities. In addition, the resin blends as a group exhibited slight non-Newtonian behavior due to shear thinning behavior, while the commercial UPE resin displayed no shear thinning, likely due to its lower molecular weight.

The viscosity of the resin systems is directly related to the concentration of the isosorbide in the oligomer; increasing the isosorbide concentration increases the magnitude of viscosity (κ, Pa s), and the rate of shear thinning (n). The higher viscosity resins show some mild shear thinning behavior as the shear rate increased. These characteristics are representative of the factors that govern the viscosity of a concentrated polymeric solution: concentration of the solution, molecular weight of the polymer and the topology of the polymeric chain.[16,32,33] In these resin systems, the solution concentration is fixed at 35 wt % styrene so the dominating factors are molecular weight and the topology of oligomeric cross-linkers. Rouse dynamics show that the viscosity increases linearly with the molecular weight of a polymer when it is below the critical molecular weight[34,35]; the beginnings of this phenomenon is seen in the increase in viscosity of the isosorbide-based UPE systems where the molecular weight is varied, and is likely to continue linearly according to the Rouse dynamics model. Because the molecular weight of the resin samples are similar, molecular weight effect on the viscosity is minimal and the predominant character in the differences in viscosity can be attributed to the changes in the topography (structural features and conformation of isosorbide versus DEG) of the polymeric backbone.

Rouse dynamics states viscosity is also influenced by the interaction of segments between molecules and connected segments of the same molecule.[34] The segments are composed of the discrete portions of the polymer backbone that in solution move with the velocity of the solvating liquid.[34] The friction between these segments results in development of viscous forces, and at

Table III. Rheological Behavior

Sample	Average M_n	κ (Pa s)	N	R^2	Thixotropy	Viscosity (cP)
0% Isosorbide	4100	1.2 ± 0.2	0.82 ± 0.07	0.98	Slightly shear thinning, no thixotropy	1200
10% Isosorbide	3300	5.9 ± 0.9	0.65 ± 0.03	0.98	slightly shear thinning, slight thixotropy	5900
15% Isosorbide	3200	12 ± 0.8	0.59 ± 0.05	0.99	shear thinning, thixotropic	12000
25% Isosorbide	2300	18 ± 3.0	0.35 ± 0.05	0.99	shear thinning, slight thixotropy	18000
15% Isosorbide Low MW	1400	7.5 ± 1.0	0.43 ± 0.07	0.98	slightly shear thinning, slight thixotropy	7500
25% Isosorbide Low MW	1500	25 ± 4.3	0.38 ± 0.06	1.00	shear thinning, v. slight thixotropy	25000
15% Isosorbide, 17.5 MA	1700	7.8 ± 2.2	0.55 ± 0.06	0.99	shear thinning, thixotropic	7800
15% Isosorbide, 25% MA	1700	5.0 ± 0.3	0.84 ± 0.07	0.99	shear thinning, slight thixotropy	5000
Hexion 713-6150[25]	1100	0.59			No shear thinning or thixotropy	590

higher polymeric concentrations, the effect of the segmental interaction dominates over the polymer–solvent interaction.[33,34] Chain topography is of utmost importance for the overall flexibility of the segments and their ability to rapidly change conformation in order to relax after stress has been applied.[34] Isosorbide is a bent, three-dimensional molecule with a fused bicyclic furan ring that is conformationally constrained and does not possess the inherent flexibility of most diol compounds that are used for UPE syntheses. Additionally, the oxolane ring in the fused bicyclic ring which has the potential for hydrogen bonding and produces additional chain interactions that increase the viscosity of the resin system. This is evident in the results reported in Table III, and can be seen graphically in Figure 2. The baseline sample, 0% isosorbide UPE, possessed a viscosity of 1.2 Pa s and the viscosity of UPE systems steadily increased as the isosorbide content increased to 18 Pa s for the sample with 25% isosorbide. This follows the expected behavior for the Rouse model of viscosity in that with the addition of segments along the backbone of the polymeric chain with reduced conformational freedom, when compared with DEG, decreases the flexibility of the chain and results in greater friction between the polymeric chains. The effect of this constrained bicyclic ring is further seen in the development of shear thinning character as the concentration of isosorbide increases. When the shear-rate increases, the viscosity decreases, indicating that at higher shear-rates the semi-rigid polymeric chains are aligning. As the resin system is at rest, the polymeric chains possess contact points that occur as a function of overlapping structures, bends in the chain or coiling of the oligomers. Once shear is applied to the system and begins to increase, the overlapping and coiled polymeric chains begin to arrange themselves into a semi-ordered state induced by the shear-stress, facilitating the ability of one chain to flow past another. The aligning of the oligomeric chains and the resulting reduction in friction between them causes the viscosity to decrease.[36]

Similarly, changing the ratio of phthalic anhydride to maleic anhydride has a similar effect on the viscosity of the UPE resin system, but to a lesser extent. Increasing the MA content has the effect of lowering the viscosity while also reducing the shear-thining character (larger n). This occurs due to the removal of the aromatic ring structures that are provided by the phthalic anhydride subunits in the oligomers. This aromatic character provides additional rigidity to the oligomeric chain and $\pi-\pi$ stacking stabilization that requires additional energy to overcome in order to initiate viscous flow. These results indicate that the isosorbide UPE resin can be tailored in terms of viscosity to tune the properties for desired processing methods, with isosorbide being a key factor that influences viscosity of the resin system.

NIR Cure Analysis
NIR analysis of the resins shows that the extent of cure was high in all of the samples for both the styrene and isosorbide
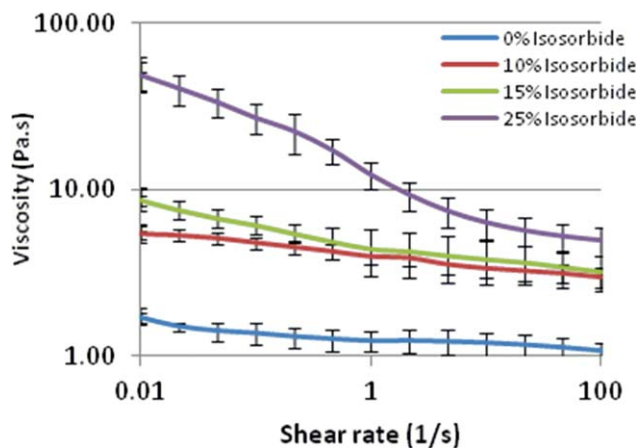

Figure 2. Isosorbide concentration effect on viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Cure and Thermomechanical Properties of UPE Resins

Sample	Thermomechanical			Extent of cure		Decomposition	
	tan δ (°C)	E' @ 25°C (MPa)	M_c	α_{BioUPE} (%)	$\alpha_{Styrene}$ (%)	IDT (°C)	$T_{d\ max}$ (°C)
0% Isosorbide	30 ± 1	500 ± 60	Immeasurable	71 ± 4	95 ± 4	271 ± 2	414 ± 1
10% Isosorbide	60 ± 2	1600 ± 300	4400 ± 800	73 ± 2	91 ± 3	287 ± 7	408 ± 14
15% Isosorbide	71 ± 1	2200 ± 500	3800 ± 300	76 ± 1	87 ± 4	299 ± 17	414 ± 1
25% Isosorbide	68 ± 1	1000 ± 70	21200 ± 4700	83 ± 4	89 ± 1	233 ± 12	414 ± 5
15% Isosorbide (low MW)	32 ± 3	500 ± 20	Immeasurable	97 ± 1	94 ± 1	208 8	405 ± 11
25% Isosorbide (low MW)	60 ± 3	1300 ± 300	Immeasurable	97 ± 1	95 ± 1	243 ± 14	419 ± 2
15% Isosorbide, 17.5% MA	72 ± 1	2200 ± 500	1700 ± 100	95 ± 1	98 ± 1	257 ± 3	419 ± 3
15% Isosorbide, 25% MA	71 ± 2	1700 ± 100	1500 ± 200	87 ± 1	95 ± 1	274 ± 22	416 ± 2
Hexion 713–6150[25]	51	1600				~175	~400

based UPE constituents, Table IV. The conversion of the unsaturated polyester monomers was calculated using eq. (7) and the conversion of styrene was calculated using eq. (8). A typical NIR spectrum of the resin can be seen in Figure 3.

$$\alpha_{UPE} = \frac{\left[\frac{Abs\ 4720\ cm^{-1}}{Abs\ 5978\ cm^{-1}}\right]_{Uncured} - \left[\frac{Abs\ 4720\ cm^{-1}}{Abs\ 5978\ cm^{-1}}\right]_{Post-Cured}}{\left[\frac{Abs\ 4720\ cm^{-1}}{Abs\ 5978\ cm^{-1}}\right]_{Uncured}} \quad (7)$$

$$\alpha_{Styrene} = \frac{\left[\frac{Abs\ 6162\ cm^{-1}}{Abs\ 4663\ cm^{-1}}\right]_{Uncured} - \left[\frac{Abs\ 6162\ cm^{-1}}{Abs\ 4663\ cm^{-1}}\right]_{Post-Cured}}{\left[\frac{Abs\ 6162\ cm^{-1}}{Abs\ 4663\ cm^{-1}}\right]_{Uncured}}. \quad (8)$$

All of the UPE resins had a > 85% conversion of the styrene constituent after post-cure within the polymer matrix and did not differ significantly from sample to sample. Peaks corresponding to the UPE reactive sites showed a lower extent of cure, falling between 70 and 85%, relative to that of styrene. This is expected because the cross-linkable UPEs lose mobility to a higher degree as the extent of cure increases, while the small molecule styrene is free to diffuse to free radicals within the system.[37,38]

Typically, the UPE conversion is related to the ratio of fumarate to maleate found within the prepolymer cross-linker (Table I), with fumarate ester being forty times more reactive than male-

ate esters.[39] This can be seen in the UPE sample synthesized with 17.5% MA. This sample possessed the highest FA/MA ratio of the samples studied in this work and proved to have nearly the highest conversion of the UPE component (95%) and the highest conversion of the styrene component (98%).

The 0% isosorbide UPE sample exhibited the lowest UPE conversion and a 95% conversion of the styrene reactive diluent, while the 25% isosorbide UPE sample displayed the highest percent conversion; however, at the expense of the styrene conversion. The isosorbide-based UPE monomers show increasing extent of cure as the concentration of isosorbide increases. This effect is most likely caused by the electron withdrawing effect on the isosorbide ring system destabilizing the double bond of the neighboring FA or MA group. This would account for the increased extent of cure of the UPE monomers for the series of 4 UPE high MW resins with isosorbide content increasing from 0 to 25 wt %; however, the maximum extent of cure found was ~83%, typical of crosslinking resins for bulk polymerization.[37] This can be indicative of a curing system that has reduced molecular mobility lowering the frequency and opportunity to react which would limit the overall conversion of UPE unsaturated sites. This effect can further be seen in comparing the low molecular weight UPEs to the high molecular weight UPEs with 15% and 25% isosorbide; the lower molecular weight UPEs had elevated extent of cure of 97% versus ≤ 83% for the higher molecular weight UPEs. This indicates that the decreased molecular size has induced enough molecular freedom to drive the polymerization closer to completion.

This phenomenon is also evident in the UPE samples that were synthesized with elevated concentrations of maleic anhydride. These samples possessed a greater potential for a more tightly cross-linked thermoset using a low molecular weight oligomer (~1600 g/mol), and exhibited extents of cure for both the UPE and styrene >85%. Lower MW resins and resins with lower maleate content vitrify at higher extents of cure allowing for greater cross-linking potential. Yet, as the MA content increased from 17.5% to 25%, the UPE monomer extent of cure decreased from 95% to 87% indicating that polymerization becomes inefficient at high UPE unsaturation content.
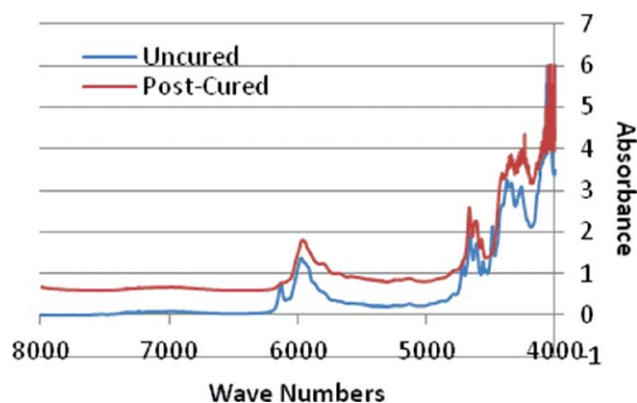

Figure 3. Representative NIR Spectrum (25% Isosorbide UPE in styrene). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
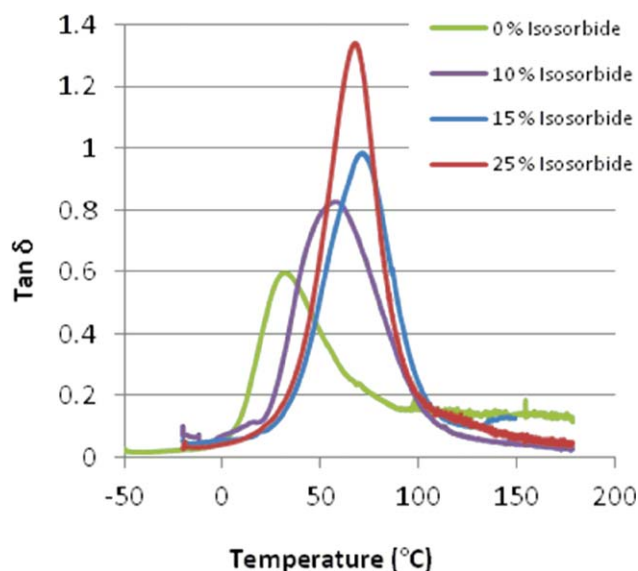
Figure 4. Isosorbide content effect on T_g of high MW UPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermomechanical Properties

After curing, the UPE resin systems became hard, translucent amber thermosets. DMA was used to determine the thermomechanical properties of the cured resin blends and to establish the effect of the increasing isosorbide concentration. Resins used in the manufacture of high performance composites ideally have T_gs in the range of 115−250°C and possess moduli in the range of 2−3 GPa at room temperature.[38,40] In general, UPE resins range in properties from relatively low with T_gs of approximately room temperature and modulus of 1 GPa at RT, to moderate T_gs of 100°C and modulus of 3 GPa at RT.[25] The commercial UPE resin used for comparison, was on the lower end of this scale: with a T_g of 51°C and E' of 1.6 GPa at RT. For our studies, the peak of the tan δ (the ratio of the E'' to the E' was used as the indicator of T_g for the UPE resin systems.
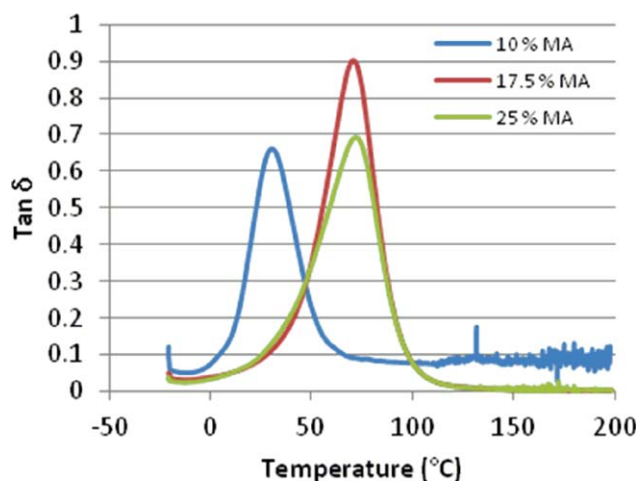

Figure 5. Maleate content effect on T_g for low MW samples with 15% isosorbide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The molecular weights between cross-links (M_c), which is inversely proportional to the crosslink density, of the samples were calculated using eq. (9).

$$M_C = \frac{3RT\rho}{E} \tag{9}$$

In eq. (9), E is the minimum storage modulus in the rubbery plateau region, T is the corresponding absolute temperature,[41] R is the universal gas constant, and ρ is the density of the sample,[42–44] measured using the Archimedes' principle. The summary of the results can be seen in Table IV. Lower M_c values are indicative of systems that have tightly cross-linked structures. This is evident in the resins with higher molecular weight UPE (15−25% isosorbide content) showing increased T_g values at lower extents of cure when compared to the low molecular weight samples of similar composition, indicating that vitrification is occurring due to the formation of a tightly cross-linked networks before the polymerization can reach completion.

As anticipated, introduction of isosorbide into the synthesis of the UPE prepolymer improved the thermomechanical properties of the resulting cured thermosets as seen in Figure 4. Adding as little as 10 mole percent isosorbide to the reaction mixture in place of an equivalent amount of DEG resulted in a significant increase in T_g when compared with the baseline sample. This also resulted in an increase in room temperature storage modulus by a factor of 3, Table IV, mostly as a result of shifting the T_g to higher temperatures and displaying more glassy behavior at room temperature. As the concentration of isosorbide increased in the samples, the T_g increased in relation; however it was noticed that as the concentration of isosorbide increased from 15% to 25% the T_g decreased slightly. This is a result of the 25% isosorbide sample possessing significantly reduced molecular weight between cross-linkers when compared to the other samples due to the sterics of the isosorbide molecule. This reduced M_c results in resins that have fewer average sites of unsaturation per oligomer than the equivalent 10% and 15% isosorbide samples; resulting in lower cross-link density and higher extents of cure while not achieving improvements to the T_g. It should be noted that increasing the isosorbide content results in increased damping as shown by a larger area under the tan δ peak. This again occurs because of the combination of reduced cross-linking and increased extent of cure.

The low molecular weight UPEs possessed lower T_gs and poorer properties despite having higher extents of cure when compared with the high molecular weight UPEs with 15% and 25% isosorbide. The underlying reason for this is the few unsaturation sites per molecule (<1 for the low MW 25% isosorbide sample, Table II) indicating that there is a high amount of nonfunctional oligomers which act as plasticizers that do not react into the polymer network and reduce the properties of the thermoset. For example, the 15% isosorbide sample had a decrease of 38°C in T_g and 1700 MPa in modulus at room temperature as M_n decreased from 3500 g/mol to 1100 g/mol. This indicates that isosorbide based UPE systems can be tailored for properties by varying molecular weight of the oligomer, concentration of isosorbide, degree of unsaturation, and extent of cure.

As seen in Table IV, increasing the concentration of maleate character in the prepolymer has a significant effect on T_g, even

when utilizing lower molecular weight oligomers (Figure 5). The additional MA content allows for greater degrees of unsaturation at lower molecular weights (Table II) and tighter cross-linked networks (lower M_c) than the baseline samples. This translated into cured resins from low molecular weight oligomers (15% isosorbide, 17.5% MA, $M_n = 1700$) that possessed T_g of 71°C, that exceeded similar molecular weight samples with lower MA contents (15% isosorbide, 10% MA, $M_n = 1100$, $T_g = 33$°C). However, as the maleate content increased from 17.5% to 25.0%, there was no significant change in the T_g of the cured material. This was likely due to the lower extent of cure for the sample with 25% MA (87%) relative to the sample with 17.5% MA (95%).

Samples were subjected to thermal analysis to determine thermal stability of the novel material. Thermal stability factors such as initial decomposition temperature (IDT, the temperature at which 5.0% of the sample has decomposed) and the temperature of maximum decomposition rate ($T_{d,\ max}$), peak of the thermogram derivative) were determined. The results of the thermal analysis are summarized in Table IV. The IDT for UPE resins ranged from 210 to 300°C with T_{max} ranging from 405 to 415°C. These values are higher than the comparable Hexion 713–6150 (175°C and 400°C, respectively). Isosorbide concentration seemed to have no discernible effect on the maximum decomposition temperature; however, the IDT slightly increased with the addition of isosorbide to the oligomeric materials. The only exception to this trend was the 25% isosorbide sample. This can be explained by the low extent of cross-linking/high value of M_c that is likely due to the low number of unsaturation sites per UPE monomer for that sample, resulting in increased free end groups that can begin depolymerization at high temperatures.[45] Molecular weight of the oligomer and cross-linking seemed to be the dominant factors when it came to the IDT, the higher molecular weight oligomers and the more densely cross-linked oligomers were capable of withstanding higher temperature before beginning to decompose.

CONCLUSIONS

These results have shown that isosorbide can be utilized as a component of UPE resins to improve properties from the diol constituent. Resins of this nature have the potential to be developed as useful thermosetting material for use in composite materials. Our investigations into UPE resins with isosorbide have shown that increasing concentration of this unique diol compound substantially increases the T_g and moduli of the cured polymers. However, while the viscosities of these uncured resins adequately compare to some commercial UPE resins, increasing the concentration also causes an increase in the viscosity of the uncured resin, which could affect their processing in composite applications. Addition of isosorbide monomer to the reaction system causes increased time to form the desired prepolymer molecular weight due to the reduced reactivity isosorbide hydroxyl groups, especially the endo hydroxyl. Additional formulation and synthesis will be necessary to obtain a resin that fulfills the requirements for high performance materials, but isosorbide shows promise as a component for the development of UPE systems that can meet these needs.

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