

Biobased Thermosets from the Free-Radical Copolymerization of Conjugated Linseed Oil

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ABSTRACT: New polymeric thermosets were prepared through the bulk free-radical copolymerization of 100% conjugated linseed oil, acrylonitrile, and divinylbenzene. Under the appropriate reaction conditions and with the appropriate curing sequence, 61–96 wt % of the oil was incorporated into the crosslinked thermosets. The resulting yellow, transparent thermosets varied from being soft and flexible to being hard

and brittle. Dynamic mechanical analysis and thermogravimetric analysis showed that these thermosets had good mechanical properties and thermal stability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 979–985, 2007

Key words: structure-property relations; radical polymerization; renewable resources; thermosets

INTRODUCTION

The widespread use of nonbiodegradable, petroleum-based polymeric materials has raised many environmental concerns.^{1,2} The demand for these nonrenewable, virtually indestructible materials is increasing, as is our dependence on crude oil. A possible remedy is to use natural, renewable resources as feedstock for the preparation of plastics.

Recently, a shift in interest toward making polymeric materials prepared from readily available, renewable resources, such as cellulose,³ starch,⁴ proteins,⁵ and natural oils,⁶ has been seen. These biopolymers offer the advantages of low cost, ready availability from renewable natural resources, and possible biodegradability. For years, however, modified celluloses have found applications in the plastics industry.^{3,7} Thus, the concept of using renewable resources in plastics is not new.

Much of the work on polymeric materials derived from natural oils has involved functionalized oils. Wool et al.⁸ and Hazer et al.⁹ prepared a copolymer and a grafted copolymer from derivatives of soybean and linseed oils with styrene or methyl methacrylate by free-radical polymerization, respectively. Petrovic and coworkers^{10,11} carried out the oxirane ring opening of epoxidized oils, followed by condensation

polymerization with isocyanates to produce polyurethanes.^{10,11} Our group has primarily focused on developing thermosetting resins from nonfunctionalized natural oils, such as soybean oil,¹² corn oil,¹³ linseed oil,¹⁴ tung oil,¹⁵ fish oil,¹⁶ and a number of other natural oils¹⁷ via cationic, free-radical, and thermal polymerizations.^{6,17}

Linseed oil is used widely as a drying oil for surface coatings.¹⁸ It is a triglyceride oil composed of 4% stearic (C18 : 0), 19% oleic (C18 : 1), 15% linoleic (C18 : 2), and 57% linolenic (C18 : 3) acids with approximately six carbon-carbon double bonds per triglyceride.¹⁷ The high number of linolenic acid double bonds per triglyceride makes linseed oil susceptible to free-radical polymerization. Previously, our group reported the preparation of various thermosets from conjugated linseed oil, styrene, and divinylbenzene (DVB) via thermal polymerization.¹⁴ The resulting materials ranged from soft and rubbery materials to tough and rigid plastics.

We now report that the free-radical copolymerization of 100% conjugated linseed oil (C₁₀₀LIN), acrylonitrile (AN), and DVB, with 2,2'-azobisisobutyronitrile (AIBN) as an initiator, produces transparent and yellow crosslinked thermosets, which range from being slightly flexible to being hard and brittle. These thermosets can be considered biobased because they use a natural, renewable oil as a comonomer.

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EXPERIMENTAL

Materials

Regular linseed oil, provided by Archer Daniels Midland (Decatur, IL), was conjugated in our laboratory

with a previously reported process.¹⁹ The conjugation was determined to be approximately 100%. AN, DVB (technical-grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), and AIBN were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received.

Polymerization

The crosslinked polymers were prepared by bulk free-radical copolymerization. The reported amounts of C₁₀₀LIN, AN, DVB, and AIBN are all weight percentages. The ratio of AN to DVB was kept at 9 : 1 in all cases. C₁₀₀LIN, AN, DVB, and AIBN were all weighed and poured into a glass vial. Normally, 3-g samples were prepared. The amount of oil was varied from 30 to 75%. It was found early on that the most promising materials employed 40–60% oil; thus, these materials were investigated most extensively. The initial oil composition was then varied in 5% increments. Enough headspace was provided between the top of the mixture and the cap of the vial to allow for any expansion or evolution of gases. The reactants were mixed thoroughly until all the AIBN had dissolved. Once the initiator and monomers were added, the system was cured for 12 h each at 60, 70, 80, 90, 110, and 120°C. This lengthy sequence was employed to minimize shrinking and cracking. After the completion of the curing sequence, the vials were broken to remove the samples. The following system of nomenclature has been adopted for simplicity: C₁₀₀LIN50–AN45–DVB5–AIBN1 corresponds to a polymer sample prepared from 50 wt % C₁₀₀LIN, 45 wt % AN, 5 wt % DVB, and 1 wt % AIBN.

Soxhlet-extraction analysis

A 2-g sample of the bulk polymer was extracted for 24 h with 100 mL of refluxing methylene chloride with a Soxhlet extractor. After the extraction was complete, the resulting solution was concentrated on a rotary evaporator with subsequent vacuum drying. The soluble substances were weighed and analyzed by ¹H-NMR spectroscopy. The insoluble materials were dried in a vacuum oven for several hours before weighing.

Characterization

¹H-NMR spectroscopy analysis of the soluble substances was carried out in CDCl₃ with a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz. Cross-polarization/magic-angle-spinning ¹³C-NMR analysis of the insoluble materials remaining after Soxhlet extraction of the bulk polymers was performed with a Bruker MSL 300

spectrometer (Bruker America, Billerica, MA). The samples were examined at two spinning frequencies (3.2 and 3.7 kHz) to differentiate between the actual signals and spinning sidebands.

Gel permeation chromatography (GPC) analysis of the soluble materials was carried out with a Waters Breeze GPC system (Milford, MA) with a Waters 1515 pump, Waters 717 Plus autosampler, and a Waters 2414 refractive-index (RI) detector with polystyrene standards for molecular weight calibration. Each sample was dissolved in tetrahydrofuran (THF; ~ 2 mg/mL) and passed through a Teflon 0.2-mm filter into the sample vial. The selected mobile phase was HPLC-grade THF with a flow rate of 1 mL/min and a sample injection volume of 200 μL. The instrument was equipped with two columns (PLgel mixed-C 5-μ columns, Polymer Laboratories, Inc., Amherst, MA) and heated at 40°C.

The dynamic mechanical properties of the bulk polymers were obtained with a PerkinElmer DMA Pyris 7e dynamic mechanical analyzer (PerkinElmer, Foster City, CA) in a three-point-bending mode. The rectangular specimens made from the thermosets had dimensions of approximately 12 mm × 5 mm × 2 mm. The specimens were first cooled to –40°C and then heated to 200°C at a rate of 3°C/min and a frequency of 1 Hz under helium. The viscoelastic properties, namely, the storage modulus (*E'*) and mechanical loss (damping) factor ($\tan \delta$), were recorded as a function of temperature. Glass-transition temperatures (*T_g's*) for the polymers were obtained from the peaks of the $\tan \delta$ curves. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA Pyris-7. Specimens having masses of approximately 10–15 mg were used. A temperature scan from 50 to 650°C was performed at a heating rate of 20°C/min under air.

RESULTS AND DISCUSSION

¹H-NMR spectroscopy analysis of the oils

Figure 1 shows the ¹H-NMR spectra of both the regular and conjugated linseed oils. The peaks from 4.1 to 4.4 ppm correspond to the four hydrogens of the methylene groups present in the glycerol moiety of the triglyceride. The peak at 2.8 ppm can be observed in the spectrum of the regular linseed oil and corresponds to the methylene hydrogens between the carbon–carbon double bonds, also known as the bisallylic protons. This peak disappears upon conjugation, as shown in the spectrum of C₁₀₀LIN. The conjugation is also evident in the wider range of chemical shifts for the vinylic protons (5.2–6.6 ppm) in the conjugated oil versus 5.2–5.4 ppm for the regular linseed oil. Both the regular and conjugated linseed oils were calculated by ¹H-NMR spectroscopy.

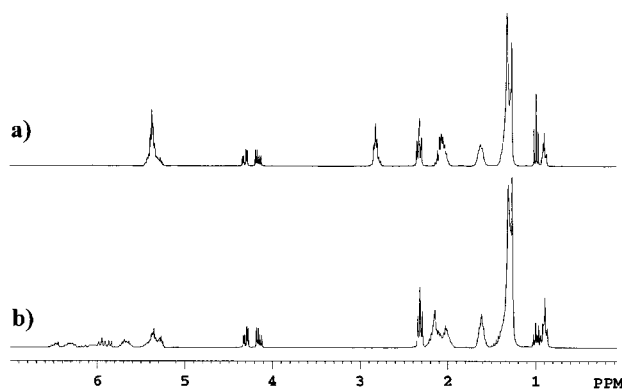


Figure 1 $^1\text{H-NMR}$ spectra of (a) regular linseed oil and (b) C_{100}LIN .

copy analysis to have approximately 5.7 carbon-carbon double bonds per triglyceride. This degree of unsaturation (d) was calculated with the following equation:

$$d = (4A - B)/2B$$

where A is the integrated area of the peaks above 5.20 ppm (including the C-2 hydrogen atom of the glycerol moiety) and B is the integrated area of the peaks at 4.10–4.40 ppm.¹⁷

By the conjugation of the carbon-carbon double bonds in the triglyceride side chains of natural oils, such as linseed oil, their reactivity can be significantly improved.²⁰ Conjugation does not change the number of carbon-carbon double bonds present in the triglyceride structure. However, the double bonds that are moved undergo a change in structure from *cis* to *trans*.²¹ The conjugation percentage, determined by the integration of the vinylic hydrogens in the conjugated oil and taking into account the known fatty acid composition of the oil, is approximately 100%.²¹ The degree of conjugation can also be roughly estimated by the identification of the absence of the bisallylic proton peak at 2.8 ppm.

Analysis of the conjugated oil in the thermosets

The produced polymers are thermosets because of crosslinking between the various carbon-carbon double bonds present in the linseed oil and DVB. They range from hard and rigid materials to soft and flexible materials. They are transparent and yellow and have a slight odor. Shrinking and cracking occurred with some of the samples containing 40 and 45 wt % oil in the feed ratio. The microstructures of the bulk polymers were investigated through Soxhlet extraction with methylene chloride as the refluxing solvent. The extracted soluble portion is an oily substance ranging from 4 to 39 wt % (Table I).

The $^1\text{H-NMR}$ spectra of the soluble portions (Fig. 2) indicate that the oily substance is primarily unreacted oil. However, oligomers or low-molecular-weight components of polyacrylonitrile may also be present. They would probably appear in the same region as the saturated hydrogens of the oil. The weak peaks in the vinylic region (5.2–6.5 ppm) indicate that the extracted oils are more saturated than the original oil. The samples prepared with 40–60% oil range from being hard and rigid to being soft and flexible. The increasing amounts of unreacted oil seen with the systems having the greater oil content appear to act as plasticizers, causing the change in the properties.

Further elucidation of the extracts, carried out by GPC, indicates the presence of three components of various molecular weights (Fig. 3). Thus, peaks A, B, and C correspond to molecular weights of approximately 380, 1300, and 2600 g/mol, respectively. An analysis of C_{100}LIN indicates that peak B corresponds to the molecular weight of the triglyceride. However, the actual molecular weight of linseed oil is around 880 g/mol. Differences in the hydrodynamic volume between the polystyrene standards used for calibration and the oil are responsible for the discrepancy.²² Peak C appears to correspond to a dimer of the triglyceride, whereas peak A represents

TABLE I
Properties of the Various Thermosets

Sample composition	T_g ($^{\circ}\text{C}$) ^a	ν_e (mol/m^3) ^b	E' at 25 $^{\circ}\text{C}$ (Pa)	T_{max} ($^{\circ}\text{C}$) ^c	Soluble (%) ^d	Insoluble (%) ^e
$\text{C}_{100}\text{LIN40-AN54-DVB6-AIBN1}$	101	6879	1.62×10^9	432	4	96
$\text{C}_{100}\text{LIN45-AN49.5-DVB5.5-AIBN1}$	93	4910	1.07×10^9	435	4	96
$\text{C}_{100}\text{LIN50-AN45-DVB5-AIBN1}$	80	3429	7.15×10^8	456	8	92
$\text{C}_{100}\text{LIN55-AN40.5-DVB4.5-AIBN1}$	72	3128	4.28×10^8	464	20	80
$\text{C}_{100}\text{LIN60-AN36-DVB4-AIBN1}$	60	1549	1.60×10^8	476	39	61

^a Obtained from the maxima of the $\tan \delta$ curves.

^b Obtained from the equation $E' = 3\nu_e RT$ with the E' values at $T_g + 40^{\circ}\text{C}$.

^c Temperature of maximum degradation.

^d Any component or material extracted from the crosslinked thermoset.

^e Crosslinked thermoset remaining after extraction.

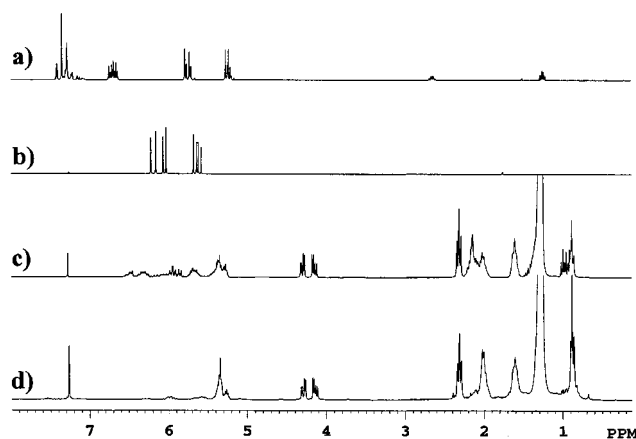


Figure 2 ^1H -NMR spectra of (a) DVB, (b) AN, (c) C_{100}LIN , and (d) the soluble portion of $\text{C}_{100}\text{LIN}50\text{-AN}45\text{-DVB}5\text{-AIBN}1$.

some lower molecular weight component, perhaps oligomers of polyacrylonitrile, because the peak height is proportional to the concentration of the AN monomer in the original composition.

The insoluble crosslinked substances remaining after extraction correspond to 61–96% of the original thermoset material (Table I). These samples are highly crosslinked and are insoluble in THF and CH_2Cl_2 . The absence of DVB peaks in the ^1H -NMR spectrum of the soluble components (Fig. 2) indicates that the DVB crosslinker has been completely incorporated into the crosslinked network. As the amount of DVB is increased in the original composition, an increase in the yield of the crosslinked polymer can also be seen. This is also consistent with the extraction results mentioned previously (Table I).

Solid-state ^{13}C -NMR analysis was carried out for the insoluble crosslinked materials. Figure 4 shows the presence of the triglyceride carbonyl ($\text{C}=\text{O}$) at

170 ppm. Carbon–carbon double bonds ($\text{C}=\text{C}$) from either the oil or DVB can be seen at approximately 135 ppm. The cyano group (CN) carbon associated with AN is buried under the carbon–carbon double-bond signals around 135–140 ppm. The aromatic signal associated with DVB is also buried under the carbon–carbon double-bond signals. Thus, it can be concluded from both the ^1H and solid-state ^{13}C -NMR that the bulk polymer structure is a cross-linked polymer network retaining free (unreacted) oil that is more saturated than the oil employed in the feed. The more saturated free oil may be due to either triglyceride molecules that are dimerized, as evidenced by GPC analysis, or triglyceride molecules that are more highly saturated and therefore cannot be incorporated into the thermoset as easily.

Dynamic mechanical analysis (DMA)

The DMA results in Figure 5 show the temperature dependence of $\tan \delta$ for the various compositions investigated. All the compositions give a single $\tan \delta$ peak, indicating that the $\text{C}_{100}\text{LIN-AN-DVB}$ systems possess a single homogeneous phase at the molecular level. This $\tan \delta$ peak is a primary relaxation peak, which corresponds to T_g , and is a result of the micro-Brownian motion of the amorphous chains of the thermoset.²³ The data in Figure 5 and Table I indicate that as the amount of oil in the original composition increases, along with an increase in the amount of unreacted oil in the thermoset, the T_g values decrease from about 101 to 60°C. As mentioned earlier, the unreacted oil can act as a plasticizer, allowing more flexibility between the chains, which results in the material having lower T_g values.

DMA also shows how the crosslinking density plays a role in T_g . The experimental crosslinking density (ν_e) has been calculated according to the

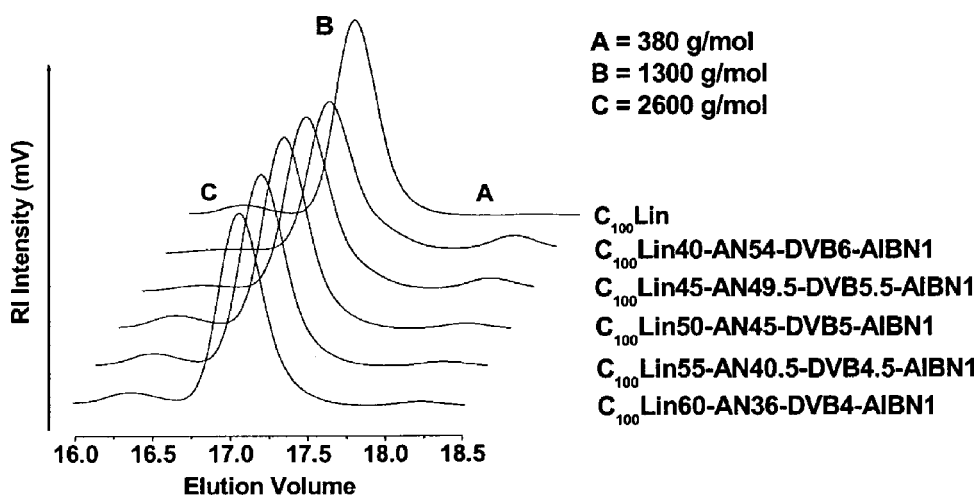


Figure 3 GPC analysis of the soluble extracts.

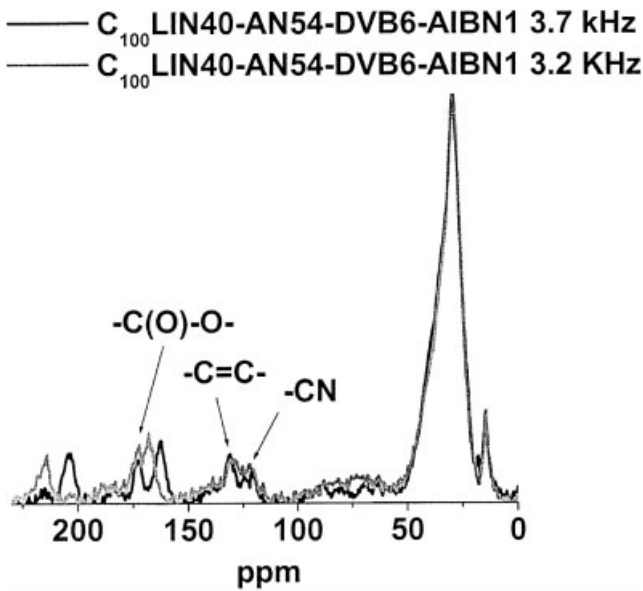


Figure 4 Solid-state ^{13}C -NMR spectra of the insoluble portion after the extraction of $\text{C}_{100}\text{LIN40-AN54-DVB6-AIBN1}$.

kinetic rubber theory of elasticity^{24,25} with the following equation:

$$E' = 3\nu_e RT$$

where E' is the storage modulus at $T_g + 40^\circ\text{C}$ in the rubbery plateau, R is the gas constant, and T is the absolute temperature (K). The data in Table I indi-

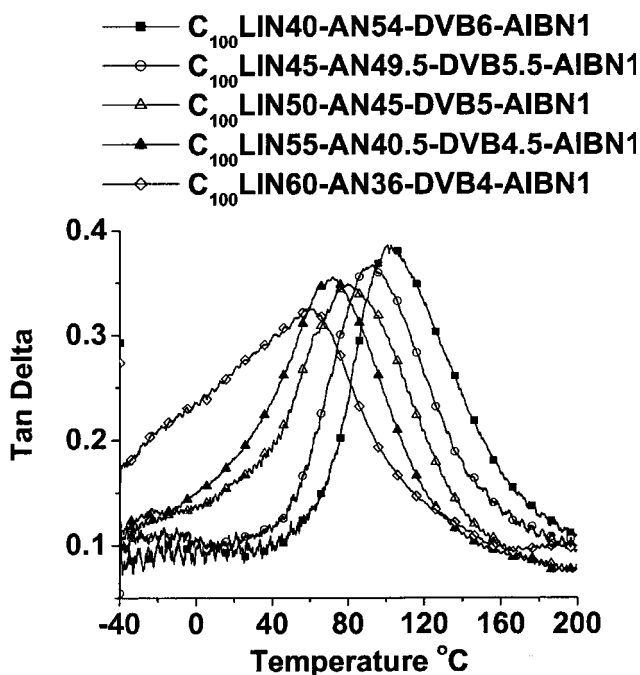


Figure 5 $\text{Tan } \delta$ graphs obtained by DMA for nonextracted samples.

cate that as the amount of DVB is reduced, the crosslinking density also decreases. This decline in T_g is seen because less crosslinking results in greater segmental mobility in comparison with systems with higher crosslinking. This means lower temperatures are needed for the initiation of the segmental motion of the polymer chains.

E' for the different compositions plotted against the temperature is shown in Figure 6; the room-temperature values are given in Table I. The table shows that increasing the amount of oil from 40% in the original composition ($\text{C}_{100}\text{LIN40-AN54-DVB6-AIBN1}$) to 60% ($\text{C}_{100}\text{LIN60-AN36-DVB4-AIBN1}$) results in a decrease in E' . Because E' measures the ability of a material to return or recover from an applied force,²⁶ the data correlate nicely with the samples with higher DVB contents and crosslinking densities (those with 40 and 45% oil in the original composition) having higher E' values than the samples with less DVB and lower crosslinking densities.²⁷

TGA

The TGA data are shown in Figure 7 and Table I. The thermal decomposition of these materials can be divided into three stages. The first stage is from 50 to 400°C and corresponds to the degradation of the soluble components (i.e., oil) in the thermoset. The second stage from 400 to 525°C represents the decomposition of the bulk crosslinked thermoset. This region is where the maximum degradation of

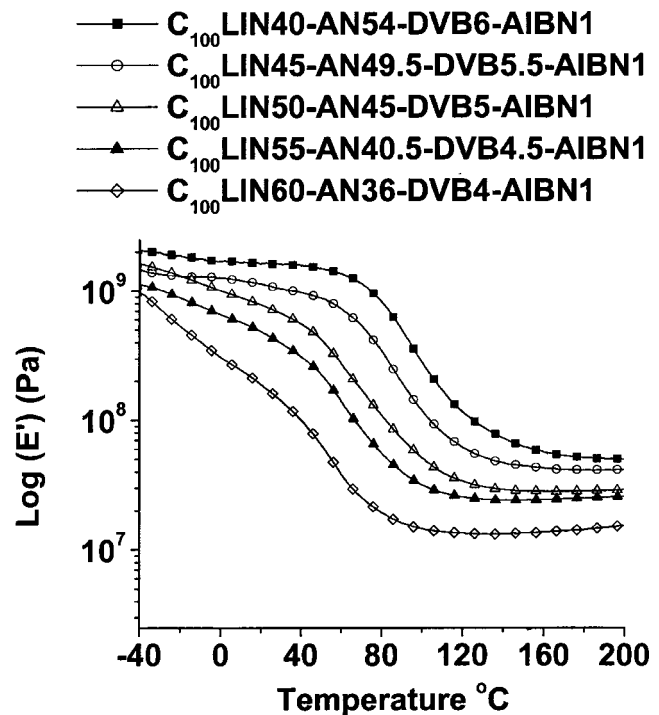


Figure 6 E' from DMA for nonextracted samples.

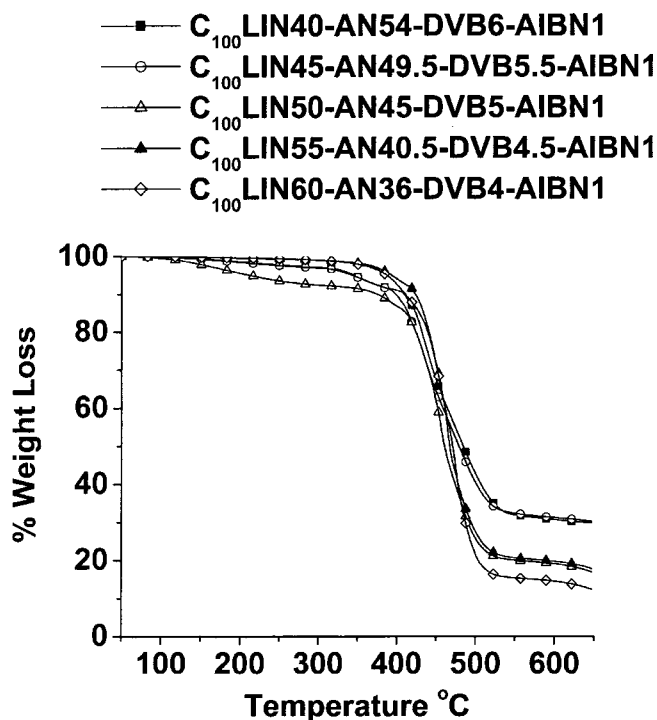


Figure 7 Weight-loss percentages of samples obtained by TGA.

the material occurs. The third stage from 525 to 650°C corresponds to the oxidation of the char.

The temperature of maximum degradation (Table I) in the second stage increases as the oil content goes from 40% in the feed ratio to 60%. This is interesting because the samples with more oil in the feed composition have lower crosslinking densities than those with less oil in the feed composition. This trend is the opposite of that seen in the cationic polymerizations of natural oils carried out by our group previously.²⁸ However, the C₁₀₀LIN55-AN40.5-DVB4.5-AIBN1 and C₁₀₀LIN60-AN36-DVB4-AIBN1 samples may have had so much unreacted oil (Table I) that not all of it may have degraded in the first stage of the thermal degradation. This means that the unreacted oil, which still has unsaturation, as evidenced by the ¹H-NMR spectra of the soluble materials, might undergo further curing during TGA, resulting in enhanced thermal stability.

CONCLUSIONS

The free-radical polymerization of C₁₀₀LIN, AN, and DVB initiated by AIBN gives thermosets that are transparent and yellow and range from hard and brittle materials to soft and rubbery materials. Extraction analysis reveals that not all the oil is incorporated into the thermoset. DMA shows that the unreacted oil and the crosslinking density affect

T_g and E' . TGA shows that these thermosets are thermally stable up to 150°C and that the bulk thermoset does not degrade until temperatures that slightly exceed 400°C. The range of properties attained with these materials makes them suitable for applications in which petroleum-based polymers are currently used. Even though these thermosets contain monomers obtained from petroleum, they represent a significant step toward a more biobased plastic.

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