

Conjugated Low-Saturation Soybean Oil Thermosets: Free-Radical Copolymerization with Dicyclopentadiene and Divinylbenzene

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ABSTRACT: The free-radical copolymerization of 40–85 wt % of conjugated low-saturation soybean oil (CLS), and a 9 : 1 ratio of acrylonitrile (AN) and either divinylbenzene (DVB) or dicyclopentadiene (DCP) using AIBN as the initiator affords transparent yellow samples, which range from hard to slightly rubbery. DMA analysis indicates that the samples containing DCP have $\tan \delta$ values ranging from 0.32 to 0.49, while the damping properties of the DVB samples are slightly lower. Extraction analysis shows that complete chemical incorporation of the CLS into the polymeric network is achieved when the original CLS content ranges from 40 to 65 wt %. Lower incorporation of the CLS into the polymer network occurs when the oil content exceeds 70 wt %. In this

case, up to 30% of the CLS remains unreacted. These observations are supported by ^1H NMR and solid-state NMR. Thermogravimetric analysis indicates a just one important stage of degradation, implying that the polymer network is highly homogeneous in composition. The temperatures of 10% weight loss for the DCP system range from 402 to 428°C, and from 370 to 391°C for the DVB system. The temperature of maximum degradation ranges from 458 to 518°C for the DCP polymers, and 406 to 422°C for the DVB system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 423–430, 2008

Key words: conjugated low saturation soybean oil; bio-based polymers; free-radical copolymerization

INTRODUCTION

In recent years, there has been a growing demand for new starting materials for the fabrication of plastics and rubbers.¹ Until now, plastics have been primarily petroleum-based, which results in economic and environmental problems. Economic problems arise because petroleum is a finite resource and environmental issues result because the decomposition of these materials in nature is lengthy and sometimes generates byproducts that are public hazards.^{1,2} Recently, a growing number of bio-based substances have been shown under the proper reaction conditions to be viable alternatives to petroleum-based monomers. The most widely used are carbohydrates, like cellulose or chitin, and proteins, such as soy or cheese protein.^{3–5}

Materials made with these new bio-based monomers face a number of important challenges; particularly important is that their mechanical properties are better or at least comparable to those present in today's plastics and rubbers but more so, the poten-

tial capability of being biodegradable and/or biocompatible.^{5,6} In the search for more and better options, the fatty acids present in vegetable oils are quite attractive, since they have been successfully introduced in the printing industry as part of fast drying inks,⁷ and as a glue for wood materials,⁸ but the synthesis of high molecular weight polymers has thus far been mostly unproductive.⁹

Particularly promising as bio-based monomers are a wide variety of naturally occurring vegetable oils,¹⁰ which consist of triglycerides differing primarily in their chain lengths and the number of carbon-carbon double bonds present in the triglyceride unit.¹¹ The presence of the double bonds makes these oils suitable for polymerization, either by cationic¹² or free-radical polymerization^{13,14} processes. The reactivity of the oils towards different polymerization techniques depends on the number and nature of the double bonds. Conjugated double bonds are known to be more reactive towards these types of polymerizations.¹⁵

The advantages of vegetable oils as polymeric starting materials include their low cost, ready availability, and annual renewability, as well as the possible biodegradability of the resulting polymeric materials after the targeted use.¹⁵ The triglycerides have relatively high molecular weights before polymerization, plus a branched structure, so when polymerization does take place, viable crosslinked structures

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with considerable molecular weight are fairly easily attained.

Soybean oil is a biodegradable vegetable oil dominating today's food oil market. About 80% of the soybean oil produced each year is used for human food. Another 6% is used for animal feed, while the remainder (14%) serves nonfood uses (soaps, fatty acids, lubricants, coatings, etc.).¹⁵ The polyunsaturation of soybean oil and low-saturation soybean oil (LSS) with still higher polyunsaturated fatty acid content¹⁶ makes it possible to polymerize or copolymerize these natural oils into useful new materials.^{9,15,16}

The Larock research group has recently prepared and characterized a wide variety of plastic, elastomeric, adhesive, and rubbery materials by the copolymerization of regular soybean oil, LSS, and conjugated soybean oil.^{17,18} These materials have been produced by cationic copolymerization of the oils with styrene and/or divinylbenzene (DVB) catalyzed by boron trifluoride diethyl etherate.^{9,17,19} These materials have room temperature moduli ranging from 6×10^6 to 2×10^9 Pa, and glass transition temperatures (T_g) ranging from 0 to 105°C.^{18,20}

More recently, the thermal polymerization of highly reactive tung oil^{21,22} and the free-radical copolymerization of epoxidized acrylated soybean oil (Ebecryl[®] 860) have been reported.²³ The free-radical polymerization technique has always been appealing to industry, since it is a robust and generally cheap process that permits the use of a wide variety of monomers with or without relatively sensitive functionality due to the less-rigorous reaction conditions it requires compared with other chain growth processes.²⁴

The C=C bonds of the LSS (averaging 5.1 per triglyceride unit¹⁷) are slightly more nucleophilic than those of ethylene and propylene and are susceptible to free-radical polymerization. Upon conjugation of the C=C bonds by rhodium-catalyzed isomerization,^{25,26} conjugated LSS (CLS) is produced. These conjugated C=C bonds are even more reactive toward free-radical polymerization. Thus, thermodynamically, the LSS and CLS oils should be radically polymerizable monomers. The free-radical polymerization of soybean oils should afford high molecular weight polymers with crosslinked polymer networks,²⁷ since these oils themselves possess relatively high molecular weights with each of the unsaturated sidechains of the triglyceride able to participate in free-radical polymerization resulting in crosslinking. It should be noted that the allylic free-radical intermediates produced by polymerization of the conjugated dienes in CLS are also considerably more stable than simple alkyl radicals.²⁸

Recently, our research group has also been successful in synthesizing polymers by the free-radical

copolymerization of conjugated linseed oil, acrylonitrile (AN), and DVB.¹³ Although the chemical approach involved in this project is very similar, the properties of the materials are quite different. In this article, we wish to report our recent results on the free-radical copolymerization of CLS, AN, and either dicyclopentadiene (DCP) or DVB. A variety of light yellow, transparent polymeric materials ranging from elastomers to tough and rigid plastics have been prepared by varying the stoichiometry. The synthesis, structure, and thermophysical properties of these new materials are reported herein.

EXPERIMENTAL

Materials

The LSS (Select Oil[®]) oil used in this study is a food-grade oil supplied by Zeeland Food Service (Zeeland, MI), and purchased in the local supermarket. The CLS has been prepared by rhodium-catalyzed isomerization of the LSS oil.^{25,26} The percent conjugation is calculated to be $\sim 100\%$. The DVB comonomer was purchased from Aldrich Chemical (St. Louis, MO) as a mixture of 80% DVB and 20% ethylvinylbenzene, and used as received. The AN and DCP comonomers were purchased from Aldrich Chemical, and used as received.

Polymer preparation and nomenclature

Varying amounts of CLS, AN, and DCP or DVB were mixed in a cylindrical glass vial with 1 wt % 2,2'-azobis(isobutyronitrile) (AIBN). The amount of CLS oil has been varied from 40 to 85 wt %. The ratio of the AN to DVB or DCP was held at 9 to 1. The vial was heated first at 60°C for 12 h, then at 70°C for 12 h, 80°C for 12 h, 90°C for 12 h, and finally 110°C for 12 h. This prolonged heating sequence was necessary to avoid substantial cracking and shrinking. The nomenclature adopted in this work for the polymer samples is as follows; a polymer sample prepared from 50 wt % CLS, 45 wt % AN, 5 wt % DVB, and 1 wt % AIBN is designated as CLS50-AN45-DVB5-AIBN1.

Soxhlet extraction

A 2 g sample of the bulk polymer was extracted for 24 h with 100 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances were characterized further by ¹H NMR spectroscopy. The insoluble materials remaining after extraction were dried under vacuum for several

hours before weighing and subsequent characterization by ^{13}C NMR spectroscopy.

Gel permeation chromatography

All molecular weights (relative to narrow polystyrene standards) were measured using a Waters Breeze GPC system equipped with a Waters 1515 pump, Waters 717-plus autosampler, and Waters 2414 RI detector. HPLC grade THF was used as the mobile phase at a flow rate of 1 mL/min with a sample injection volume of 200 μL . HPLC analyses were carried out using a set of two columns (PL-Gel Mixed C 5 μm ; Polymer Lab, Amherst, MA) heated at 40°C. Prior to analysis, each polymer sample was dissolved in THF (~ 2.0 mg/mL) and passed through a Teflon 0.2-mm filter into a sample vial.

^1H NMR spectroscopic characterization

The ^1H NMR spectra of the extracted soluble substances were obtained in CDCl_3 using a Varian Unity spectrometer at 300 MHz.

GC analysis

An HP6890 series gas chromatograph (Hewlett Packard, Wilmington, DE) equipped with an autosampler and flame ionization detector was used for analysis of the LSS and CLS oils. A SUPELCOWAXTM-10 capillary column (30 m \times 0.25 mm \times 0.25 μm film thickness; Supelco, Bellefonte, PA) was used for separation.

Dynamic mechanical analysis

All dynamic mechanical analysis (DMA) data were obtained using a Perkin-Elmer dynamic mechanical analyzer DMA Pyris-7e in a three-point bending mode. Rectangular specimens were made by copolymerizing the reactants in a cylindrical mold and then cutting and sanding them down to the appropriate sample shape. Thin sheet specimens of 1 mm thickness and 5 mm depth were used, and the width to depth ratio was maintained at ~ 2 . The measurements were performed at a heating rate of 3°C/min from -40 to 250°C and a frequency of 1 Hz in helium (20 mL/min). The crosslink densities were determined from the storage modulus curves utilizing the moduli at $T_g + 40^\circ\text{C}$, based on the theory of rubber elasticity.²⁹

Thermogravimetric analysis

A Perkin-Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the polymeric materi-

als in air (20 mL/min). The samples were heated from 50 to 650°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The LSS oil is a triglyceride oil composed of esters comprising $\sim 19\%$ oleic acid (one C=C), 63% linoleic acid (two C=C), 9% linolenic acid (three C=C) with ~ 5.1 C=C per triglyceride unit.¹⁷ By conjugating the carbon-carbon double bonds in the triglyceride side chains of the natural oil, their reactivity can be significantly improved. The LSS oil has been conjugated using a published procedure^{25,26} to produce the CLS oil.

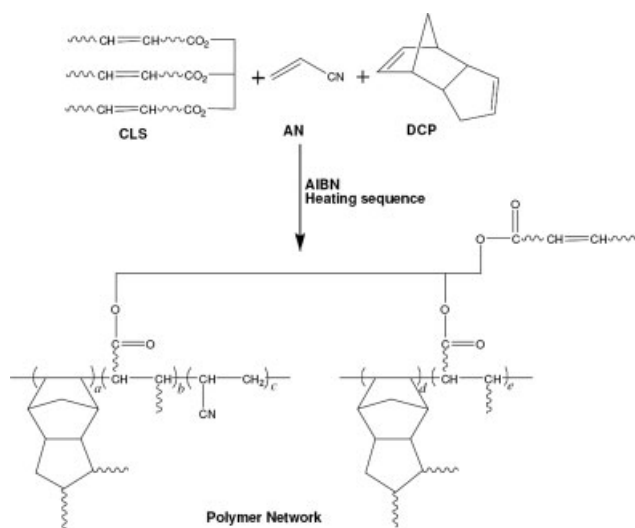
GC analyses of the LSS and CLS oils indicate that the conjugation process affords primarily two conjugated linoleic acid (CLA) isomers. *Cis-9,trans-11* CLA and *trans-10,cis-12* CLA are the predominant isomers present after conjugation (Table I), indicating that during conjugation only one double bond moves and it ends up trans. The amounts of the different CLA isomers indicate that the two different double bonds of the linoleic acid have an equal tendency to move towards the other double bond, since both isomers are present in $\sim 27\%$ in the CLS oil. These findings are in agreement with work recently reported by us on the conjugation of several different vegetable oils.²⁶

Rigid, hard, and transparent yellow plastics have been produced by the free-radical copolymerization of the CLS oil with AN, and either DVB or DCP. The latter three olefins are all monomers suitable for free-radical polymerization. The DVB molecule has two carbon-carbon double bonds that are in conjugation with a benzene ring, making this comonomer quite reactive towards free-radical polymerization. On the other hand, DCP possesses two double bonds in a bicyclic skeleton, which are not in conjugation, but their reactivity towards free-radical polymerization is still considerable due to the strain present in the bicyclic system. The copolymerization of mixtures of AN and DVB or DCP with the CLS oil results in hard plastic materials when as little as 1.5–6 wt % DVB or DCP are employed.

The preparation of the samples is very simple. All of the reagents are mixed in a glass vial along with the free-radical initiator. Polymerization is initiated when the samples are placed in an oil bath at 60°C,

TABLE I
GC Analysis of the Fatty Acid Content of LSS Before and After Conjugation (CLS)^{2,4}

Fatty acid	LSS (%)	CLS (%)
Linoleic acid (C18:2)	63.2	0.5
<i>cis-9,trans-11</i> CLA	–	26.1
<i>trans-10,cis-12</i> CLA	–	28.0



Scheme 1 Polymerization of CLS, AN, and DCP.

a temperature appropriate for AIBN decomposition to free radicals. To avoid any formation of bubbles or cracks and to avoid major shrinkage of the samples during the heating sequence, a lengthy cure time is required and only very gradual increases in the cure temperature have been employed. The samples have been cured by heating them successively in 12-h periods at 60, 70, 80, 90, and 110°C. Scheme 1 illustrates the random polymer network formed upon the copolymerization of CLS, AN, and DCP.

Soxhlet extraction of the samples has been performed to determine the amount of CLS and other comonomers that are not incorporated into the polymer network as crosslinked materials. The results of the Soxhlet extraction for both the DVB and DCP systems are shown in Tables II and III, respectively. As the amount of CLS increases from 40 to 85 wt %, the amount of soluble material increases as well, increasing from 5 to 34% in the case of the DVB samples, and from 1 to 33% for the DCP samples. This increase in soluble materials when adding more CLS oil suggests that this soluble material is mainly unreacted CLS oil. Indeed, ^1H NMR spectroscopic

analysis of the soluble materials indicate that only CLS oil is present; we were unable to find any peaks belonging to AN, DVB, or DCP, either because they simply are not present or because their concentration is so low that the peaks due to the CLS oil overlap them completely.

Soxhlet extraction separated the insoluble materials from the soluble, unreacted CLS oil. These insoluble materials are the crosslinked polymer networks, which must be composed of CLS oil, AN, and DVB or DCP. The insoluble portions have been analyzed by solid-state ^{13}C NMR spectroscopy. As shown in Figure 1 for the sample CLS70-AN27-DCP3-AIBN1, there is evidence at 30–50 ppm for C–H bonds. The peak between 100 and 150 ppm corresponds to C=C carbons apparently left unreacted in the starting materials. The peaks between 150 to 175 ppm correspond to nitrile groups arising from the AN, and the peaks above 200 ppm correspond to the ester moieties present in the backbone of the triglyceride unit.

GPC analyses performed on some of the soluble samples show that the soluble portions removed during Soxhlet extraction constitute mainly three different kinds of molecules. Figure 2 presents the GPC chromatogram of four samples and the original CLS oil. Three major peaks are present. Peak A corresponds to molecules that have a relatively low molecular weight. Since this analysis was performed utilizing polystyrene standards, the molecular weight values calculated by the instrument are only an approximation. These low molecular weight molecules are not present in the pure CLS oil, which indicates that these smaller molecules appear as a consequence of the free-radical polymerization process itself. It is possible that the triglycerides present in the oil undergo some kind of degradation that liberates fatty acids or fractions of the fatty ester chains or these peaks may be due to oligomerization of the various starting monomers. The peak labeled as B corresponds to the largest portion of molecules present in the extracts and it is also present in the CLS oil, suggesting that this peak corresponds to the triglycerides that make up this vegetable oil, further

TABLE II
Extraction and Dynamic Mechanical Analysis Data for Samples Prepared from DVB

Sample	T_g (°C)	$\tan \delta$	Temp. range ^a (°C)	v_e (10^3 mol/m ³)	Sol %	Insol %
CLS40-AN54-DVB6-AIBN1	104	0.35	80–130	109	4.9	96.6
CLS50-AN45-DVB5-AIBN1	101	0.32	75–115	73	4.9	95.1
CLS55-AN40-DVB4.5-AIBN1	85	0.33	65–100	72	5.1	95.1
CLS60-AN36-DVB4-AIBN1	74	0.38	70–90	74	5.9	94.0
CLS65-AN31.5-DVB3.5-AIBN1	56	0.36	40–77	68	7.4	93.1
CLS70-AN27-DVB3-AIBN1	48	0.38	15–50	57	9.9	91.0
CLS75-AN22.5-DVB2.5-AIBN1	25	0.38	0–35	43	15.5	85.5
CLS80-AN18-DVB2-AIBN1	2	0.41	–35 to 27	31	20.1	80.8
CLS85-AN13.5-DVB1.5-AIBN1	–30	0.49	–40 to 0	20	33.8	66.8

^a Temperature range in which the $\tan \delta$ values are above 0.3.

TABLE III
Extraction and Dynamic Mechanical Analysis Data for Samples Prepared from DCP

Sample	T_g (°C)	$\tan \delta$	Temp. range ^a (°C)	v_e (10^3 mol/m ³)	Sol %	Insol %
CLS40-AN54-DCP6-AIBN1	107	0.49	82–140	59	0.9	99.1
CLS50-AN45-DCP5-AIBN1	84	0.45	75–125	60	1.8	98.2
CLS55-AN40-DCP4.5-AIBN1	67	0.44	60–110	31	2.9	97.1
CLS60-AN36-DCP4-AIBN1	65	0.46	50–90	31	2.7	97.3
CLS65-AN31.5-DCP3.5-AIBN1	48	0.48	17–71	23	4.6	95.4
CLS70-AN27-DCP3-AIBN1	32	0.47	0–50	19	7.5	92.5
CLS75-AN22.5-DCP2.5-AIBN1	20	0.53	–8 to 40	20	12.4	87.6
CLS80-AN18-DCP2.0-AIBN1	–7	0.51	–40 to 10	20	19.9	80.1
CLS85-AN13.5-DCP1.5-AIBN1	–32	0.52	–40 to 5	18	32.5	71.3

^a Temperature range in which the $\tan \delta$ values are above 0.3.

establishing that the soluble portions of the samples in this study are composed mainly of unreacted vegetable oil. Finally, a third peak appears (peak C), having essentially twice the molecular weight of peak B, suggesting that this peak is due to triglyceride dimers, which are also present in the pure CLS oil. This dimer is apparently not a result of the polymerization process itself.

The glass transition temperatures of the samples prepared using DVB (Table II) and DCP (Table III) decrease steadily as the amount of CLS oil increases. As explained earlier, the amount of unreacted oil within the polymer network increases as the amount of CLS oil in the original composition increases. This unreacted oil can act as a plasticizer for the materials. Therefore, the samples with a higher concentration of the CLS oil show lower T_g 's. The plasticizer allows more segmental movement of the incorporated comonomers. This increment in segmental movement shows up as a decrease in the T_g value, which for the DVB samples range from 104°C to –30°C, and for the DCP samples range from 107°C to –32°C. This means that the DVB or DCP does not have much influence on the T_g 's, since the values for both systems are fairly similar when comparing samples with identical compositions.

The viscoelastic properties of these thermosets make them suitable for use as damping materials,²⁹ because of their ability to dissipate mechanical energy. The $\tan \delta$ (δ) values for the DVB and DCP systems are reported in Tables II and III, respectively. The higher $\tan \delta$ values are obtained for the DCP-derived materials; they range from 0.43 to 0.53. The DVB system affords $\tan \delta$ values between 0.32 and 0.49. Thus, the DCP materials have a higher capability for absorbing vibrations and dissipating energy inside the polymer network. It is generally accepted that materials with $\tan \delta$ values above 0.3 are considered good damping materials.²⁹ Both the DCP and DVB systems exceed this limit, but the DCP system affords slightly higher values using identical compositions. Thus, DCP has several advantages, since it is much less expensive, and also affords better damping properties. It is also worth noting that the highest values of $\tan \delta$ for both systems were obtained for the samples with higher amounts of the CLS oil (85 wt %), which is also an advantage from a biorenewable point of view. This finding is very important, because these plastics with a high content of the inexpensive vegetable oil show characteristics comparable to those of petroleum-based plastics.

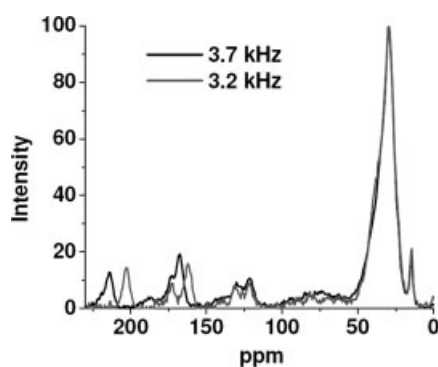


Figure 1 ¹³C NMR spectra of the insoluble materials from CLS70-AN27-DCP3-AIBN1.

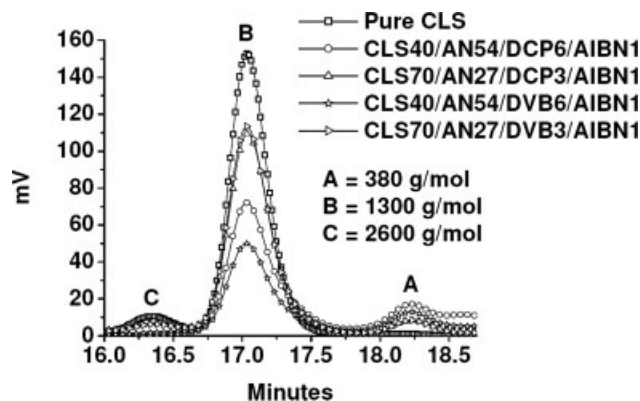


Figure 2 GPC analysis of the soluble extracts.

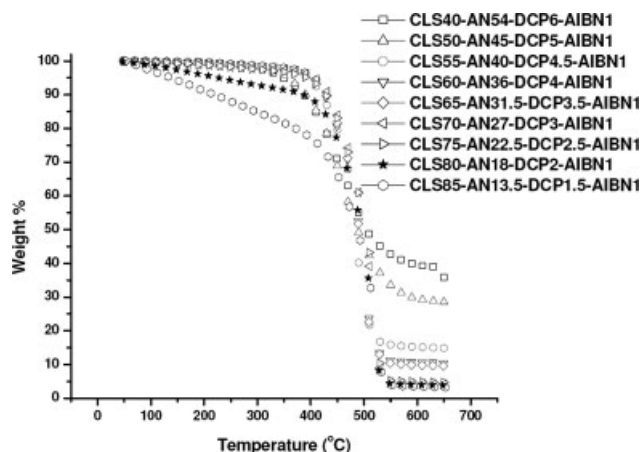


Figure 3 TGA curves for the DCP samples.

In Tables II and III, the temperature ranges at which the samples have a $\tan \delta$ value above 0.3 are reported. As the content of the CLS oil increases, the temperature range for good damping decreases, presumably because the CLS oil acts as a plasticizer, which lowers the T_g (taken at the highest point of the $\tan \delta$ curve) of the material, making it softer as the temperature range falls below room temperature.

Another parameter that varies with the content of the CLS oil is the crosslink density. The DVB system (Table II) has crosslink densities that vary from 109×10^3 to 20×10^3 mol/m³. The higher values correspond to the samples with less CLS oil or with more AN and DVB, which are better crosslinkers compared with the CLS oil. Since the triglyceride CLS oil has ~ 5.1 total carbon-carbon double bonds and possesses a considerably higher molecular weight than either the AN (one double bond) or DVB (two double bonds that can act as crosslinking units), it has a lower crosslinking ability per molecular weight unit compared with the two other comonomers. The crosslink densities of the samples prepared from DCP range between 18×10^3 to 60×10^3 mol/m³. The values decrease as the amount of CLS oil increases for both systems, since the amount of AN and DCP or DVB has to be lowered to keep the 9 to

1 AN-crosslinker ratio constant. It is also observed that the DCP samples have crosslink densities lower than those of the DVB samples; thus, DCP is not as good a crosslinker as DVB.

All of the samples described here are relatively thermally stable below 200°C. They all undergo a three-stage degradation process (Fig. 3), which was previously observed in materials made with vegetable oils utilizing the cationic polymerization technique.¹⁸ The first stage from 30 to $\sim 350^\circ\text{C}$ represents the loss of loosely bound molecules, such as the unreacted CLS oil or small oligomers. The second stage involves degradation of the bulk polymer network, and the third stage involves degradation of the char residue. Thermogravimetric analysis (TGA) data indicates that these thermosets lose $\sim 10\%$ of their original mass below 400°C for the DCP system (Table IV), and at a slightly lower temperature for the DVB system (Table V). The 10% weight loss of these samples corresponds to the loss of volatile, relatively low molecular weight materials, mostly unreacted CLS oil or lower molecular weight oligomers.

For the DCP system, the values of 50% weight loss, which as stated earlier correspond to degradation of the bulk polymer network of the materials, are somewhat higher than those of the DVB system. One reason for this difference could be the amount of energy that needs to be applied to the polymer network to degrade it. The degradation process is understood as the breakage or failure of bonds between atoms that hold together a material and, as consequence of this, small molecules escape the matrix giving rise to the loss of mass.

The temperature of maximum degradation follows the same trend as the temperature of 50% degradation; the DCP-containing systems exhibit higher temperatures, which are opposite to what one would expect, since the crosslink densities are lower than those of the corresponding DVB samples.

It is also important to point out that the quantity of material (char) left after the heating process diminishes as the amount of CLS oil increases in the

TABLE IV
Thermogravimetric Analysis of the DCP Samples

Sample	Temp. of 10% degradation (°C)	Temp. of 50% degradation (°C)	Temp. interval (°C)	Temp. of maximum degradation rate (°C)
CLS40-AN54-DCP6-AIBN1	402	490	88	460
CLS50-AN45-DCP5-AIBN1	419	484	65	490
CLS55-AN40-DCP4.5-AIBN1	421	490	69	496
CLS60-AN36-DCP4-AIBN1	426	491	65	499
CLS65-AN31.5-DCP3.5-AIBN1	428	490	62	499
CLS70-AN27-DCP3-AIBN1	411	463	52	458
CLS75-AN22.5-DCP2.5-AIBN1	413	464	51	461
CLS80-AN18-DCP2-AIBN1	427	502	75	518
CLS85-AN13.5-DCP1.5-AIBN1	210	488	278	462

TABLE V
Thermogravimetric Analysis of the DVB Samples

Sample	Temp. of 10% degradation (°C)	Temp. of 50% degradation (°C)	Temp. interval (°C)	Temp. of maximum degradation rate (°C)
CLS40-AN54-DVB6-AIBN1	376	463	87	406
CLS50-AN45-DVB5-AIBN1	370	471	101	458
CLS55-AN40.5-DVB4.5/AIBN1	373	462	89	453
CLS60-AN36-DVB4-AIBN1	380	462	82	456
CLS65-AN31.5-DVB3.5/AIBN1	378	470	92	465
CLS70-AN27-DVB3.0-AIBN1	382	450	68	424
CLS75-AN22.5-DVB2.5-AIBN1	390	469	79	432
CLS80-AN18-DCV2-AIBN1	391	464	73	454
CLS85-AN13.5-DVB1.5-AIBN1	407	466	59	457

original composition. This phenomenon can be observed in both the DVB and the DCP systems; see Figures 3 and 4. The most logical reason for this is that the char residue is composed mainly of AN, DVB, and/or DCP, which are the components that decrease as the CLS oil content is increased.

In general, the samples prepared using DCP appear to be more rubbery than the DVB samples. This physical observation correlates well with the values found for the crosslink densities. It appears that DVB is a better crosslinker. As the amount of CLS oil increases in the composition of the sample, the softer the material appears. This characteristic is mainly due to two features. First, the higher CLS oil content results in less of the AN, and the more reactive crosslinker DVB or DCP. Therefore, there is less chance to form crosslinks. Secondly, as the amount of CLS oil increases, the amount of unreacted oil increases as well. This unreacted oil acts as a plasticizer, lowering the T_g from above 100°C to around -30°C for both systems. These two features result in the DCP samples having higher $\tan \delta$ values, suggesting that these new vibration-absorbing, bio-based polymeric materials have potential industrial applications as damping materials. For example, they might be used in automobile parts, like door panels,

to isolate the interior from the vibration-producing exterior. Due to the softness of the DCP samples, it is easier to process them and produce samples in a desired shape.

The samples prepared from DVB are more rigid than the ones prepared from DCP. Other than this difference, both systems have similar transparency, coloration, and odor. None of the samples are oily; all samples are glossy and smooth to the touch.

Since the free-radical initiator AIBN releases nitrogen gas upon decomposition, some samples contain voids or bubbles trapped within the samples. To prevent formation of these bubbles, the volume of the glass mold (vial) in which the samples were prepared had to be increased, so the N_2 released had more space to escape from the curing resin. Another problem found during the synthesis of these materials was the development of cracks, particularly when the samples were prepared in plate-like glass molds. The formation of cracks is presumably due to the presence of AN. When AN polymerizes, it shrinks, causing contraction of the resin inside a confined space, which gives rise to cracks. This problem was not observed in cylindrical samples, so all the work reported here was performed on this shape sample.

One of the major advantages of using DCP is that it is a substantially cheaper starting material—\$0.29 per pound compared to \$3.00 per pound for DVB.³⁰ One disadvantage of employing DCP is the resulting lower crosslink density. On the other hand, it appears that the reactivity of both the CLS and DCP is very similar. Overall there is better chemical incorporation of the CLS oil when using DCP compared with DVB.

CONCLUSIONS

Promising new bio-based plastics have been prepared from CLS, AN, and either DCP or DVB. Chemical incorporation of the CLS oil into the polymeric network reaches almost 100% when the oil content is between 40 and 65 wt %, especially for the DCP samples. Lower percentages of oil incorporation into the network are achieved when the oil con-

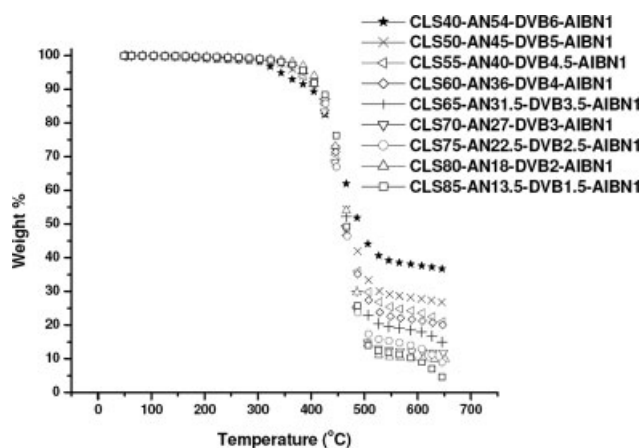


Figure 4 TGA curves for the DVB samples.

tent is 85 wt %. In this case, 20–30% of the original oil remains soluble. DCP gives higher $\tan \delta$ values than the DVB thermosets when comparing the same sample composition. The DCP samples have higher chemical incorporation of the CLS oil in the polymer network, which improves vibrational damping, since the longer triglyceride molecules dissipate vibrations better. The comparable T_g values found for the DCP and DVB systems suggest that DVB and DCP comonomers do not have much influence on the behavior of the T_g 's when comparing the same sample compositions.

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