Novel Rubbers from Cationic Copolymerization of Soybean Oils and Dicyclopentadiene. 1. Synthesis and Characterization

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Novel thermosetting copolymers, ranging from tough and ductile to very soft rubbers, have been prepared by the cationic copolymerization of regular (SOY) and 100% conjugated soybean oils (C_{100}SOY) with dicyclopentadiene (DCP) catalyzed by Norway fish oil (NFO)-modified and SOY- and C_{100}SOY-diluted boron trifluoride diethyl etherate (BFE). The gelation time of the reactions varies from 4 to 991 min at 110 °C. The yields of the bulk copolymers are essentially quantitative, while the yields of the cross-linked copolymers remaining after Soxhlet extraction with methylene chloride range from 69% to 88%, depending on the monomer stoichiometry and the catalyst used. ^{1}H NMR spectroscopy and Soxhlet extraction data indicate that these copolymers consist of a cross-linked soybean oil−DCP network plasticized by certain amounts of methylene chloride-soluble linear or less cross-linked soybean oil−DCP copolymers, unreacted oil, and some low molecular weight hydrolyzed oil. The molecular weights of these soluble fractions are in the range from 400 to 10 000 g/mol based on polystyrene standards. The bulk copolymers have glass transition temperatures ranging from −22.6 to 56.6 °C, while their tan δ peak values range from 0.7 to 1.2. Thermogravimetric analysis (TGA) indicates that these soybean oil−DCP copolymers are thermally stable below 200 °C, with 10% and 50% weight loss temperatures ranging from 280 to 372 °C and 470−554 °C, respectively. These properties suggest that these biobased thermosets may prove useful alternatives to current petroleum-based plastics and find widespread utility.

Introduction

Biomaterials, chemicals, and energy from renewable resources have received considerable interest in recent years.[1−3] The growing demand for petroleum-based products and the resulting negative impact on the environment, plus the scarcity of nonrenewable resources, are just a few of many factors that have encouraged the scientific community to find more sustainable and environmentally responsible solutions for these problems. Considerable interest has focused on the utilization of annually renewable starting materials, such as starch, cellulose, vegetable oils, and proteins for the synthesis of a wide range of bioplastics.[4−8] Deployment of these biodegradable starting materials protects the environment by reducing or completely substituting petroleum-based materials. Furthermore, polymers based on biorenewable resources have often been shown to possess properties comparable or better than those of widely used industrial polymers. As such, they show promise as replacements for petroleum-based plastics, thus reducing waste and preserving our dwindling petroleum reserves.

Soybean oil represents one of the cheapest and most abundant annually renewable natural resources available in large quantities.[9−11] The food market accounts for more than 90% of soy product demand,[12] whereas the remainder accounts for rapidly increasing industrial applications, such as the production of soaps, lubricants, varnishes, coatings, paints,[13,14] and more recently, bioplastics and composites.[1−3] The expansion of industrial applications is mainly fuelled by the growing desire by government and business to reduce their dependence on petroleum imports and the increasing number of price-competitive, soy-based chemicals and materials available. The use of vegetable oils as starting materials offers numerous advantages, such as low toxicity, inherent biodegradability, high purity, and ready availability. For instance, the annual U.S. soybean oil production in 2005/06 is forecast at approximately 20 billion pounds.[15] Like all other vegetable oils, soybean oil is a high molecular weight (MW ∼880 g/mol), unsaturated monomer, which makes it an ideal building block for high MW polymer synthesis. Furthermore, its structure can be altered through genetic engineering in order to improve its reactivity toward polymerization.[16] One such example is production of the genetically modified soybean oil, known as Select Oil.[17] This low saturation soybean oil has 0.5−0.7 C═C bonds more per triglyceride than regular soybean oil.

To further expand nonfood applications of these biorenewable materials, our group has focused on conversion of vegetable oils into industrially useful biopolymers.[18−20] We have recently shown that a variety of promising new polymeric materials, ranging from soft rubbers to hard, tough, and rigid plastics, can be prepared by the cationic copolymerization of readily available soybean oils with styrene (ST) and divinylbenzene (DVB), catalyzed by Norway fish oil (NFO)-modified boron trifluoride diethyl etherate (BFE).[21−23] The resulting polymers exhibit good thermal and mechanical properties, including good damping[24] and shape memory[25] properties, and show promise as replacements for petroleum-based rubbers and conventional plastics. By varying the structure and stoichiometry of the alkene comonomers[21] and the vegetable oils,[26] we have been able to achieve excellent control over the polymer properties. However, to obtain more rigid polymers, high-priced DVB has been required as a cross-linker, reducing the commercial appeal of these materials. Furthermore, the large difference in reactivity between the aromatic comonomers (ST and DVB) and the soybean oils has required us to modify the catalyst by adding NFO in order to produce homogeneous samples.[27]

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Herein, we wish to report the synthesis and initial characterization of a range of novel biobased rubbers prepared by the cationic copolymerization of regular (SOY) and 100% conjugated (C$_{100}$SOY) soybean oils with dicyclopentadiene (DCP). The replacement of DVB (∼\$3.00/lb) with inexpensive DCP (∼\$0.29/lb)[28] as a cross-linker effectively addresses some of the above-mentioned drawbacks and offers a simple route to a range of new and exciting rubbers.

Experimental Section

Materials. Wesson soybean oil (SOY) was purchased in a local supermarket and used without further purification. Conjugated soybean oil (C$_{100}$SOY) was prepared according to our previously published procedure.[29] *endo*-DCP (typically 95% pure) was purchased from VWR chemical company and used as received. Norway fish oil ethyl ester (NFO) (EPAX 5500 EE, Pronova Biocare) was used to modify the original catalyst, boron trifluoride diethyl etherate (BFE) (distilled-grade, Aldrich).

Cationic Copolymerization and Nomenclature. Preweighed amounts of soybean oil and DCP (92 wt % total) were mixed in a beaker and stirred vigorously at ambient temperature until a homogeneous solution was obtained. During this time, 3 wt % of BFE catalyst was diluted with 5 wt % of soybean oil and added slowly to the mixture of soybean oil and DCP. The reaction mixture was stirred vigorously until it became homogeneous, and then it was poured into a glass mold and cured for 12 h at 60 °C and 24 h at 110 °C. Resulting polymers were obtained in essentially quantitative yields. The nomenclature adopted in this paper for the polymer samples is as follows: a polymer sample prepared from 75 wt % SOY, 17 wt % DCP, 8 wt % SOY-diluted BFE catalyst (5 wt % SOY + 3 wt % BFE) is designated as SOY75−DCP17−(SOY5−BFE3).

Soxhlet Extractions. A 3−4 g sample of the bulk polymer was extracted with 100 mL of refluxing methylene chloride for 24 h using a Soxhlet extractor. Following the extraction, the resulting solution was concentrated under reduced pressure and dried in a vacuum oven at 60 °C overnight. The recovered insoluble portion was also dried under a vacuum prior to weighing.

Polymer Characterization. ^{1}H NMR spectroscopic analyses of the soluble substances extracted by methylene chloride were recorded in CDCl$_3$ using a Varian Unity spectrometer at 300 MHz. Cross-polarization magic-angle spinning (CP MAS) ^{13}C NMR analysis of the insoluble materials remaining after Soxhlet extraction of the bulk polymers was performed using a Bruker MSL 300 spectrometer. Samples were examined at two spinning frequencies (3.2 and 3.7 kHz) in order to differentiate between actual signals and spinning sidebands. FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer (KBr pellet). Gelation times were determined as the time elapsed from initial mixing of the reactants at the given temperature to the time when solidification commences, as determined by the complete cessation of flow of the liquid reactants. Measurements were performed in reference to the ASTM standard D2471-99. Gelation times are the average of five individual measurements at a certain temperature. 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. The system was equipped with a set of two columns (PL-Gel Mixed C 5 μm, Polymer Lab., Inc.) and 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. 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 of 2 mm thickness and 5 mm depth were used for the analysis, and the width-to-depth ratio was maintained at approximately 3. The measurements were performed at a heating rate of 3 °C/min and a frequency of 1 Hz in He with a gas flow rate of 20 mL per min and static and dynamic forces applied of 110 and 100 mN, respectively. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Pyris-7 thermogravimeter. The percent weight loss temperatures of the polymeric materials were measured in air with a gas flow rate of 20 mL/min. The samples were heated from 50 to 650 °C at a heating rate of 20 °C/min.

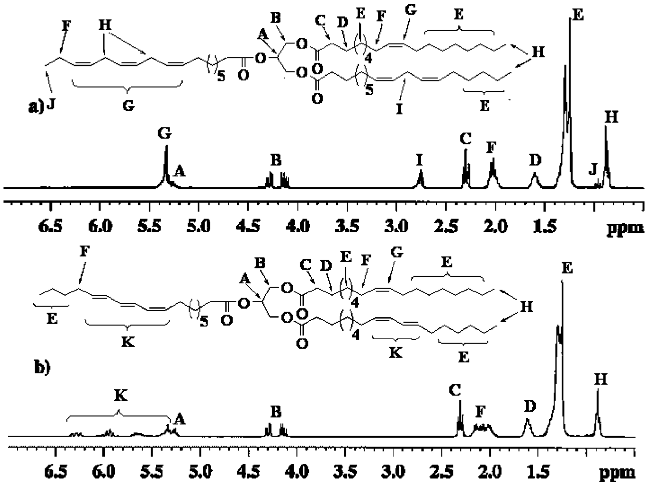


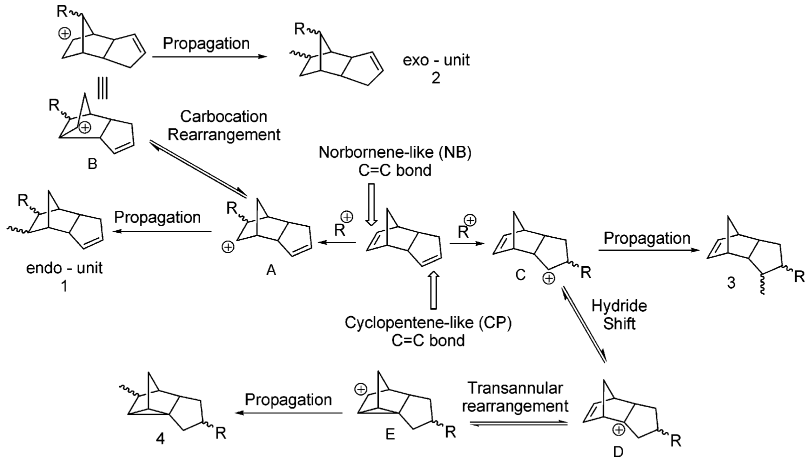
Figure 1. ^{1}H NMR spectra of (a) SOY and (b) C$_{100}$SOY.

Results and Discussion

Chemical Compositions of the Soybean Oils. Commercially available soybean oil employed in this study has a triglyceride structure, consisting of saturated stearic (C16-0) and palmitic (C18-0) acids (15%), as well as unsaturated oleic (C18-1, 23.3%), linoleic (C18-2, 53.7%), and linolenic (C18-3, 7.6%) fatty acids.[9,10] The percent of other saturated and unsaturated fatty acids is negligible. The unsaturated fatty acid content determines the degree of unsaturation of the soybean oil and consequently its reactivity. Figure 1 shows representative ^{1}H NMR spectra for the SOY and C$_{100}$SOY oils. The signals at 4.1−4.4 ppm correspond to the protons on the C-1 and C-3 carbons of the glyceride unit, which indicate that both SOY and C$_{100}$SOY have triglyceride structures. The vinylic hydrogens of SOY are typically detected at 5.2−5.5 ppm, while the bis-allylic protons are observed at 2.7−2.9 ppm, indicating that the C═C bonds in SOY are nonconjugated. Conversely, the vinylic hydrogens of C$_{100}$SOY (Figure 1b) are detected in the 5.2−6.4 ppm range as a group of four multiplets, which indicates the existence of conjugation in the polyene system. Furthermore, complete disappearance of the bis-allylic signal at 2.7−2.8 ppm confirms that C$_{100}$SOY is completely conjugated. Detailed triglyceride peak assignments are well documented in the literature.[30−32] On the basis of our ^{1}H NMR spectral analysis, SOY has 4.3 C═C bonds per triglyceride. C$_{100}$SOY has the same degree of unsaturation, which indicates that hydrogenation of the SOY did not take place during Rh-catalyzed conjugation.[29]

Soybean Oil and Dicyclopentadiene as Cationic Monomers. According to basic thermodynamics, cationic polymerization of SOY is possible only if a negative change in free energy is achieved ($\Delta H - T\Delta S < 0$). During cationic polymerization, the loss of translational degrees of freedom caused by connecting triglyceride units together causes a decrease in entropy. Therefore, the thermodynamic feasibility of the polymerization will depend solely on enthalpic factors, meaning that cationic polymerization must be sufficiently exothermic to compensate for the loss in entropy. This is accomplished through

Scheme 1. Formation of Different DCP Structural Units during the Cationic Polymerization of DCP



conversion of the soybean oil C═C bonds to C−C bonds in the polymer. The C═C bonds in the soybean oil represent sites for electrophilic attack of the reactive species generated by the BFE catalyst. Because of that, electronic effects within the triglyceride monomers will have a crucial effect on their reactivity. SOY, like all other alkene monomers, is expected to polymerize cationically by the addition of monomers to the growing carbocation chain. Thus, the triglyceride monomers must be sufficiently nucleophilic and capable of stabilizing the intermediate carbocation.[33] Since nucleophilicity increases with increasing carbon substitution on the C═C bond, due to the positive inductive effect of alkyl substituents, the C═C bonds of the soybean oils are considered more nucleophilic than those of ethylene and propylene.[34,35] They are, therefore, capable of stabilizing the positive charge to a greater extent and are prone to cationic polymerization. For the same reason, the conjugated C═C bonds in C_{100}SOY are considered even more reactive toward cationic polymerization, since they will generate more stable allylic carbocations as intermediates.[33−35] Thus, both SOY and C_{100}SOY should be cationically polymerizable monomers. Furthermore, unlike ethylene, propylene, isobutylene, or styrene, both SOY and C_{100}SOY are polyfunctional monomers due to the presence of multiple C═C bonds within the triglyceride. Because of their relatively high molecular weights and ability to efficiently stabilize intermediate carbocations, these oils readily afford high molecular weight polymers with cross-linked polymer networks.

DCP is a well-known Diels−Alder dimer of cyclopentadiene, which forms rapidly at room temperature. DCP has been one of the most widely used diene comonomers for the synthesis of ethylene−propylene terpolymers, also known as EPDM elastomers.[36] It has also been used as a diluent for unsaturated polyesters and alkyd resins.[37] DCP provides olefinic sites in EPDM elastomers and in blends with other olefins and diolefins that are readily polymerized to hydrocarbon resins. Such resins are used in a variety of materials, including adhesives, printing inks, rubbers, paints, varnishes, textiles, and floor coverings.[38,39]

Due to the importance of DCP-based petroleum resins, the cationic polymerization of DCP and other bicyclo[2.2.1]alkenes has been studied in great detail in the past.[40−43] Particular attention has been paid to microstructural elucidation of cationic DCP polymers, because of the fact that DCP contains two polymerizable C═C bonds of different reactivities. It is known that the norbornene-like (NB) C═C bond of DCP is more reactive than the cyclopentene-like (CP) C═C bond.[36−43] This dissimilarity means that different structural units can be incorporated into the poly(dicyclopentadiene) (PDCP) backbone. For example, Corner et al. polymerized DCP using $PdCl_2(PhCN)_2$ and BFE as initiators and determined that the resulting polymers incorporated both *endo*-(1) and *exo*-(2) DCP units into their backbones with either 1,2- or 1,3-substitution patterns (Scheme 1).[41] These structural units are generated exclusively by electrophilic attack on the NB C═C bond of the DCP unit, while the CP C═C bond is left intact. Addition of an electrophile (H^+) to the NB C═C bond leads to an *endo*-unit A, which can then rearrange to give an *exo*-unit B. If A acts as a propagating species, then the polymer incorporates unit 1 into its backbone. However, if rearrangement of A occurs before propagation, then B will be the active propagating species and the polymer will incorporate unit 2 into its backbone. It is also important to mention that conversion of *endo*-DCP to *exo*-DCP units proceeds through a Wagner−Meerwein rearrangement and that the reverse reaction has never been observed. This is supported by the fact that *exo*-DCP is energetically favored by 9 kcal/mol over *endo*-DCP. According to Becker and Roth, the heat of combustion of *endo*-DCP is 1377 kcal/mol, while that of *exo*-DCP is 1368 kcal/mol.[44]

More recently, Peng et al. have polymerized DCP using several acid-, Al-, B-, and Ti-based initiators in toluene, CH_2Cl_2, or *n*-hexane as solvents and determined that under specific conditions, besides units 1 and 2, DCP polymers incorporate certain amounts of units 3 and 4 (Scheme 1).[43] In this case, units 3 and 4 are generated by electrophilic attack on the CP C═C bond. Addition of an electrophile (H^+) to the CP C═C bond gives *endo*-unit C, which can undergo simultaneous hydride-shift transannular rearrangement to afford *exo*-unit D. In this case, if C acts as a propagating species then the polymer will incorporate unit 3 into its backbone. However, if rearrangement of C occurs before propagation, then D will be the active propagating species and the polymer will incorporate unit 4 into its backbone. On the basis of their IR and NMR spectral analyses, it has been shown that specific conditions (initiator, solvent, temperature, etc.) favor incorporation of certain structural units over others and that the microstructure of DCP polymers can be controlled to some extent. All DCP polymers synthesized by cationic homopolymerizations have possessed low molecular weights (M_n) ranging from 700 to 4500 g/mol.[40−43]

Cationic Copolymerization of Soybean Oils and DCP. The presence of multiple C═C bonds in soybean oils allows their copolymerization into solid polymeric materials with other alkene comonomers via cationic polymerization. BFE has proved to be a very effective catalyst for cationic polymerizations.[33] However, the homopolymerization of SOY typically results in viscous fluids, which are of limited use.[45] To produce

Scheme 2. Cationic Copolymerization of SOY and C_{100}SOY with DCP

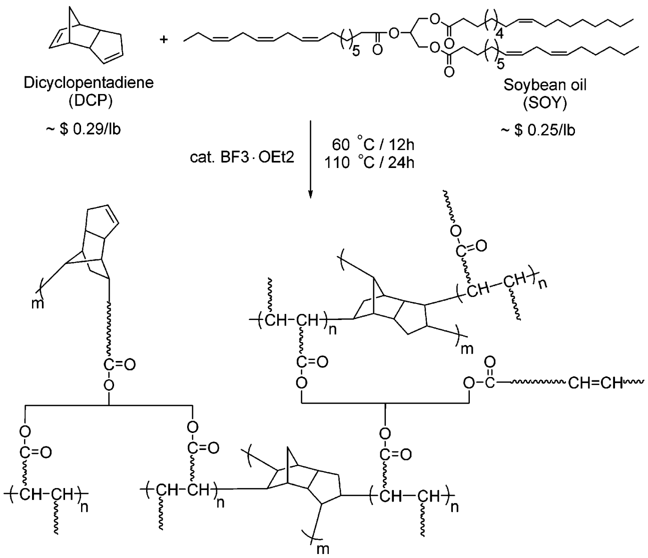


Table 1. Gelation Times and Soxhlet Extraction Data for Soybean−DCP Copolymers

copolymer	gelation times (min)^a	extraction data (%)^a insoluble	soluble
SOY50−DCP42−C8	688 (707)^b	73.7 (70.8)^b	26.3 (29.2)^b
SOY55−DCP37−C8	715 (860)^b	73.2 (70.9)^b	26.8 (29.1)^b
SOY60−DCP32−C8	505 (991)^b	73.0 (70.4)^b	27.0 (29.6)^b
SOY65−DCP27−C8	678 (698)^b	72.5 (70.3)^b	27.5 (29.7)^b
SOY70−DCP22−C8	646 (609)^b	72.0 (70.1)^b	28.0 (29.9)^b
SOY75−DCP17−C8	725 (569)^b	69.7 (70.1)^b	30.3 (29.9)^b
C_{100}SOY55−DCP37−C8	47 (63)^c	84.2 (86.4)^c	15.8 (13.6)^c
C_{100}SOY60−DCP32−C8	5 (72)^c	83.4 (87.4)^c	16.6 (12.6)^c
C_{100}SOY65−DCP27−C8	4 (25)^c	83.0 (87.2)^c	17.0 (12.8)^c
C_{100}SOY70−DCP22−C8	11 (22)^c	82.8 (87.3)^c	17.2 (12.7)^c
C_{100}SOY75−DCP17−C8	6 (28)^c	82.4 (88.1)^c	17.6 (11.9)^c
C_{100}SOY80−DCP12−C8	10 (31)^c	82.4 (88.2)^c	17.6 (11.8)^c

[a] The values outside of the parentheses correspond to samples prepared with the NFO-modified BFE catalyst, C8 = (NFO5−BFE3), while those in parentheses correspond to samples made with a SOY- or C_{100}SOY-modified BFE catalyst. [b] C8 = (SOY5−BFE3). [c] C8 = (C_{100}SOY5−BFE3).

viable harder plastics, SOY has to be copolymerized with more rigid comonomers, such as ST and DVB.[18−20] Utilization of these relatively expensive aromatic comonomers (ST = ∼\$0.75/lb and DVB = ∼\$3.00/lb)[28] considerably improves the polymers' thermal and mechanical properties, but these improvements come at a price. Furthermore, the significant differences in reactivities between SOY and C_{100}SOY on one hand, and ST and DVB on the other, require the use of BFE modifiers, such as NFO, to produce homogeneous polymers,[27] which further complicates the process. In contrast, DCP offers certain advantages over ST and DVB. It is an inexpensive diene (∼\$0.29/lb)[28] with a rigid bicyclic structure. Because of its structure, it can act as a cross-linker in a cationic copolymerization and enhance the polymers' properties. Furthermore, knowing that its cationic polymerization proceeds through the formation of secondary or tertiary carbocation intermediates,[43] it is expected that DCP will exhibit reactivity comparable to that of SOY and C_{100}SOY. This, in turn, might allow one to eliminate the catalyst modifiers previously needed to achieve homogeneity.

SOY and C_{100}SOY have been cationically copolymerized with DCP using both NFO-modified and SOY- or C_{100}SOY-diluted BFE catalysts. Different catalytic systems have been used in order to determine whether NFO is really necessary as a modifier for optimum polymer properties. It is worth mentioning that while completely soluble in NFO, the BFE catalyst has low solubility in both SOY and C_{100}SOY. Because of that, SOY- and C_{100}SOY-diluted BFE catalytic systems are heterogeneous solutions. However, they completely dissolve in bulk soybean oil−DCP solutions giving homogeneous clear brown reaction mixtures. The main reason for dilution of the BFE catalyst with soybean oil is to prevent excessive homopolymerization of the DCP, which can occur at room temperature causing the formation of white flakes of PDCP. Dilution of the BFE catalyst significantly reduces the formation of PDCP flakes and improves solubilization. Scheme 2 shows that soybean oil−DCP copolymerization proceeds through the formation and growth of a cross-linked copolymer network due to the presence of multiple C=C bonds in both the DCP and the soybean oils. The increase in the copolymers' molecular weight through cross-linking results in gelation, which is the irreversible transformation from a viscous liquid to an elastic gel. The gelation times are of great importance in establishing processing parameters. Gelation times for all soybean oil−DCP systems have been determined by measuring the time required for the liquid reactants to reach a certain viscosity at which the cessation of flow is observed. Beyond this point, the material is no longer able to flow easily and has limited processability. All gelation times are measured at 110 °C, since SOY−DCP systems failed to gel at either room temperature or 60 °C even after 48 h. Table 1 summarizes the gelation times for all SOY−DCP and C_{100}SOY−DCP systems prepared with both NFO-modified and SOY- and C_{100}SOY-diluted BFE catalysts. Copolymer systems prepared using the NFO-modified BFE catalyst have shorter gelation times, which is presumably due to slightly better solubilization of the catalyst. The measured gelation times are in the range of 569−991 and 4−72 min for the SOY−DCP and C_{100}SOY−DCP systems, respectively. The much shorter gelation times for the C_{100}SOY−DCP systems are the direct consequence of the higher reactivity of the C_{100}SOY. When compared to the gelation times of the OIL−ST−DVB systems, the SOY−DCP and C_{100}SOY gelation times at room temperature are considerably longer.[21,45] The main reason for this is the much lower reactivity of DCP when compared to that of the ST and DVB comonomers.

Molecular Structure Determination. The fully cured soybean oil−DCP copolymers have been obtained in essentially quantitative yield. Except for SOY50−DCP42−I8, where I8 is either NFO5−BFE3 or SOY5−BFE3, all other copolymers appear as dark-brown rubbery materials at room temperature, which range from tough and ductile to very soft rubbers. The microstructures of these copolymers have been studied by Soxhlet extraction analysis with methylene chloride as a refluxing solvent. Table 1 summarizes the results obtained from these analyses. Typically, after overnight extraction, 70−74 and 82−88 wt % of insoluble materials are retained from the SOY−DCP and C_{100}SOY−DCP bulk materials, respectively. Due to the higher reactivity of the C_{100}SOY, the yield of the cross-linked materials from the C_{100}SOY−DCP systems is noticeably higher than that of the corresponding SOY−DCP systems. Interestingly, all of the values pertaining to a particular series are fairly similar and cover a very small range. For instance, an increase in SOY content from 50 to 75 wt % in the (SOY−DCP)92−(NFO5−BFE3) mixture only lowers the yield of the cross-linked polymer about 4%, whereas an increase in the C_{100}SOY content from 55 to 80 wt % in the (C_{100}SOY−DCP)-92−(NFO5−BFE3) mixture lowers the yield of cross-linked

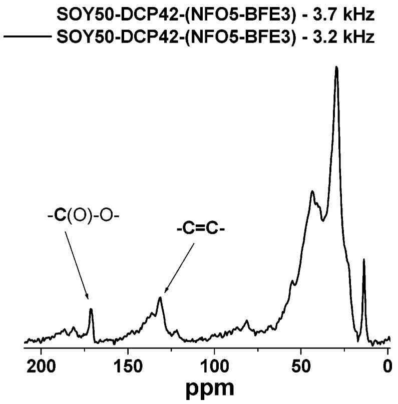


Figure 2. Solid state ^{13}C NMR spectra of insoluble materials remaining after Soxhlet extraction of the SOY50−DCP42−(BFE3−NFO5) bulk copolymer.

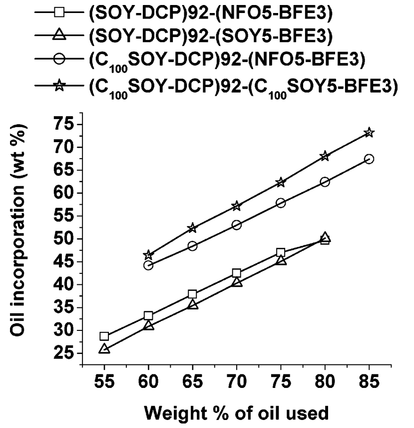


Figure 3. Dependence of the soybean oil incorporation on the wt % of oil in the initial composition.

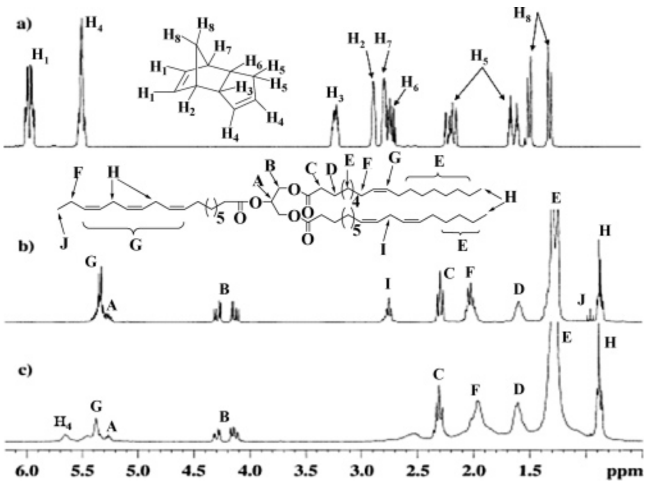


Figure 4. ^{1}H NMR spectra of (a) pure DCP, (b) pure SOY, and (c) soluble extracts of the SOY50−DCP42−(SOY5−BFE3) copolymer.

polymer only 1.8%. We believe that these results are a direct consequence of the similar reactivities of the SOY and C$_{100}$SOY oils and DCP. That is to say that a significant change in the concentration of a slightly more reactive comonomer does not cause a drastic change in the yield of the cross-linked copolymer. The use of NFO as a catalyst modifier offers little advantage for the SOY−DCP system, since it results in only a 1−3% increase in the yield of the cross-linked polymer. On the other hand, its use in the C$_{100}$SOY−DCP system has the opposite effect, causing a decrease in the yield of the cross-linked polymers by 2−4%. Interestingly, when C$_{100}$SOY is used as a catalyst diluent for the preparation of C$_{100}$SOY−DCP copolymers, the yields of the cross-linked copolymers slowly increase with increasing C$_{100}$SOY content in the initial composition. This suggests that in the absence of catalyst modifiers, the cationic initiator (H^{+}) has a preference for C$_{100}$SOY over DCP. Thus, in these systems C$_{100}$SOY is slightly more reactive than DCP. Solid state ^{13}C NMR analyses of the insoluble components remaining after Soxhlet extraction confirm the incorporation of both soybean oil and DCP units into the cross-linked network (Figure 2). This is evidenced by the presence of both C═O and C═C signals at 170 and 130 ppm, respectively. A more detailed discussion will follow later in the text.

It has also been noted that in all copolymers synthesized in this study, the incorporation of soybean oil in the cross-linked copolymer increases with increasing amounts of the oil in the initial composition. Figure 3 reveals an almost linear dependence of oil incorporation with the amount of oil. This is most likely due to the similar reactivities of DCP and both SOY and C$_{100}$SOY. The wt % of oil used in the initial composition is the sum of the oils used both as comonomers and diluents or modifiers. For example, the initial wt % of SOY in both SOY65−DCP27−(NFO5−BFE3) and SOY65−DCP27−(SOY5−BFE3) is taken as 70 wt % (65 wt % of SOY + 5 wt % of NFO modifier or SOY diluent). Also, the calculation is based on the assumption that the soluble components consist solely of unreacted soybean oil. Although not completely correct, this assumption drastically simplifies the calculation and provides a good estimation. The higher C$_{100}$SOY incorporation into the C$_{100}$SOY−DCP copolymer is a direct consequence of its higher reactivity when compared to that of SOY. The use of NFO as a catalyst modifier in the SOY−DCP systems increases the SOY incorporation about 2%, while at the same time, it reduces the C$_{100}$SOY incorporation in the C$_{100}$SOY−DCP system about 5%.

Both the SOY−DCP and C$_{100}$SOY−DCP bulk materials consist of insoluble cross-linked materials plasticized with a certain amount of soluble components. The results summarized in Table 1 show that except in the (C$_{100}$SOY−DCP)92−(C$_{100}$SOY5−BFE3) system, the amount of soluble components increases slowly with increasing soybean oil content in the initial composition. ^{1}H NMR spectral analyses of these soluble materials confirm the presence of both soybean oil and DCP units, as evidenced by signals at 4.1−4.4 ppm and 5.5−5.6 ppm, respectively (Figure 4). The former peaks correspond to the hydrogen atoms of the glycerol unit in the soybean oil, while the latter correspond to the olefinic hydrogens of DCP. The ^{1}H NMR spectra of pure SOY and DCP monomers are included for comparison purposes. It is important to note that the broad peak at 5.45 ppm also corresponds to the DCP unit. Additional proof that the latter two peaks (5.45 and 5.5−5.6 ppm) correspond to DCP is acquired through comparative ^{1}H NMR spectral analysis. Figure 5 shows a series of ^{1}H NMR spectra of soluble extracts of the (SOY−DCP)92−(SOY5−BFE3) copolymers. The results indicate that the intensities of the above-mentioned signals decrease with decreasing amounts of DCP in the initial composition, meaning that they are DCP related. According to Peng et al., these signals correspond to the hydrogen atoms of the unreacted CP C═C bonds in the DCP units.[43] Moreover, the absence of a signal at 5.9 ppm clearly indicates that all of the NB C═C bonds in DCP have reacted. Apparently, the opposite is true for the CP C═C bonds. However, the CP C═C bonds that do react during the cationic copolymerization, along with the NB C═C bonds, form effective cross-links in the bulk materials. Based on ^{1}H NMR spectral

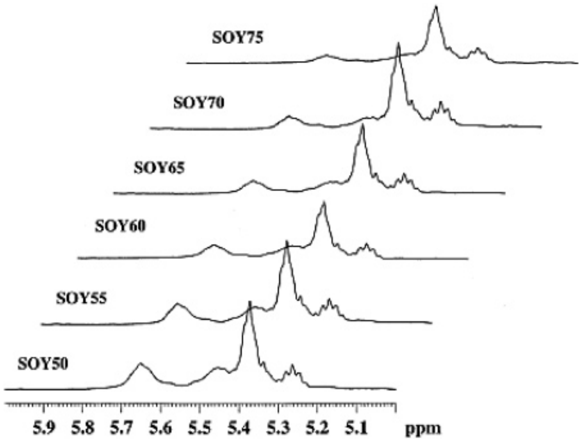


Figure 5. ^{1}H NMR spectra of (SOY−DCP)92−(SOY5−BFE3) extracts in $CHCl_3$.

analyses of the soluble extracts, we believe that the reaction of the NB C═C bonds most likely results in incorporation of *exo*-units 2 (Scheme 1) into the cross-linked copolymer matrix. Unfortunately, ^{1}H NMR spectral analysis does not provide us with enough data to make an analogous judgment about the CP C═C bonds.

To determine the molecular weight distribution of these soluble materials, they have been subjected to GPC analysis. Figure 6 shows a series of chromatographs of soluble extracts from the SOY−DCP copolymers. The results indicate that each extract consists of several components of different molecular weights (MW). For example, peaks A, B, C, D, and E shown in Figure 6, correspond approximately to 420, 750, 1400, 2800, and 5000−10000 g/mol molecular weights, respectively. Comparative GPC analysis of pure SOY reveals that its molecular weight corresponds to that of peak C. Thus, it is not surprising that the intensity of peak C increases with increasing SOY content in the initial (SOY−DCP)92−(NFO5−BFE3) copolymer composition. This molecular weight (∼1400 g/mol) is obviously much higher than the real molecular weight (880 g/mol) obtained by calculation based on the soybean oil fatty acid composition.[26] This deviation is most likely due to the higher hydrodynamic volume of SOY relative to that of a linear polystyrene of the same molecular weight, which is used for calibration.[46] We believe that the lowest molecular weight components (peak A, Figure 6) correspond to NFO (an ethyl ester of Norway fish oil),[47] SOY monoglycerides, SOY diglycerides, or fatty acid fractions formed via acid-catalyzed hydrolysis during the copolymerization process.[48] Peak B, on the other hand, is obviously DCP related since its intensity diminishes with decreasing amounts of DCP in the initial composition. This peak most likely corresponds to soluble DCP oligomers. Peak E represents a higher molecular weight shoulder of peak C in the soluble extracts of the SOY50−DCP42−(NFO5−BFE3) copolymers. However, its intensity tends to increase with increasing SOY content in other (SOY−DCP)-92−(NFO5−BFE3) copolymer samples. We believe that both peaks D and E correspond to either soluble SOY homopolymers or SOY−DCP oligomers. Similar results have been obtained for extracts of the corresponding (C_{100}SOY−DCP)92−(NFO5−BFE3) copolymers (Figure 7). Interestingly, copolymers prepared without the NFO modifier show no evidence of peak B in their chromatograms (the right-hand spectra in both Figures 6 and 7). However, the existence of peak A in each of these chromatograms confirms that the lowest molecular weight components in all other extracts indeed consist of SOY- or C_{100}SOY-related mono- or diglyceride fragments.

Thermal Properties. Table 2 summarizes the glass transition temperatures, cross-link densities, and thermogravimetric data for all soybean oil−DCP copolymers synthesized in this study. The glass transition temperatures (T_g) of the copolymers have been calculated from the peaks of the tan δ curves obtained by DMA analysis. The cross-link densities have been calculated from the storage moduli at temperatures 100 °C above the corresponding T_g temperatures. The calculations are based on rubber elasticity theory, and the detailed procedure has been described in our previous work.[22,26] Thermogravimetric data include 10% and 50% weight loss temperatures (T_{10} and T_{50}) and the temperatures of maximum thermal degradation (T_{max}).

The glass transition temperatures of the soybean oil−DCP copolymers range from −18.4 to 56.6 °C. Except for the samples SOY50−DCP42−I8 (I8 = NFO5−BFE3 and SOY5−BFE3), all other copolymers have T_g's which are below ambient temperature and, therefore, are in their rubbery state. The glass transition temperatures of all copolymers gradually decrease with increasing amounts of soybean oil in the initial composition. This is mainly due to higher incorporation of the more flexible triglyceride molecules into the cross-linked copolymer structure with increasing amounts of oil in the initial copolymer compositions. Also, copolymers prepared with SOY- or C_{100}SOY-diluted catalysts tend to have slightly lower T_g's than those prepared using the NFO-modified catalyst. This is in agreement with the Soxhlet extraction data and percent C_{100}SOY incorporation results (Figure 3) for the C_{100}SOY−DCP copolymers, since the elimination of NFO results in higher C_{100}SOY incorporation into the cross-linked structure and, thus, slightly higher flexibilities and lower T_g values. The same is not true for the SOY−DCP copolymers. At this moment, we are unable to explain this behavior. The cross-link densities, on the other hand, do not show such a regular dependence in all cases. For instance, while the cross-link densities of the SOY−DCP copolymers show a clear tendency to decrease with decreasing amounts of DCP in the initial composition, the cross-link densities of the C_{100}SOY−DCP copolymers do not show any dependence on the DCP amounts in the initial composition. However, they do have slightly higher values than those of the SOY−DCP copolymers, presumably due to the higher reactivity of the C_{100}SOY. The cross-link densities for the SOY−DCP and C_{100}SOY−DCP copolymers are in the range of 119−1034 mol/m^3 and 470−1295 mol/m^3, respectively. These values are much lower than those of the SOY−DVB and SOY−ST−DVB copolymers reported earlier by our group,[22,26,27] which accounts for their rubbery nature. Additionally, our initial results show that the tan δ values of these copolymers are in the range of 0.7−1.2, which suggests that these rubbers might be used as damping materials below ambient temperatures. More detailed dynamic mechanical analysis is underway and will be reported in due time.

Thermogravimetric analysis reveals that all soybean oil−DCP bulk polymers are thermally stable in air below 200 °C and exhibit a three-stage thermal degradation above this temperature (Figures 8 and 9). The first-stage degradation (200−450 °C) is attributed to evaporation and decomposition of the unreacted oil and other soluble components in the bulk material. The second stage (450−550 °C) is the fastest degradation stage and corresponds to degradation and char formation of the cross-linked polymer structure, while the last stage (>550 °C) corresponds to gradual oxidation of the char residue. The second degradation stage is further characterized by T_{max} values determined from the minima of the corresponding derivative percent weight loss curves.[18,26]

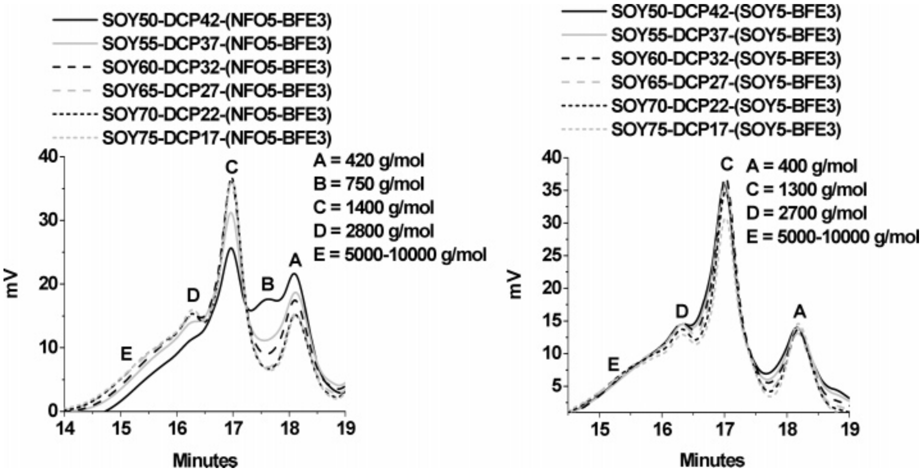


Figure 6. GPC chromatograms of SOY−DCP soluble extracts.

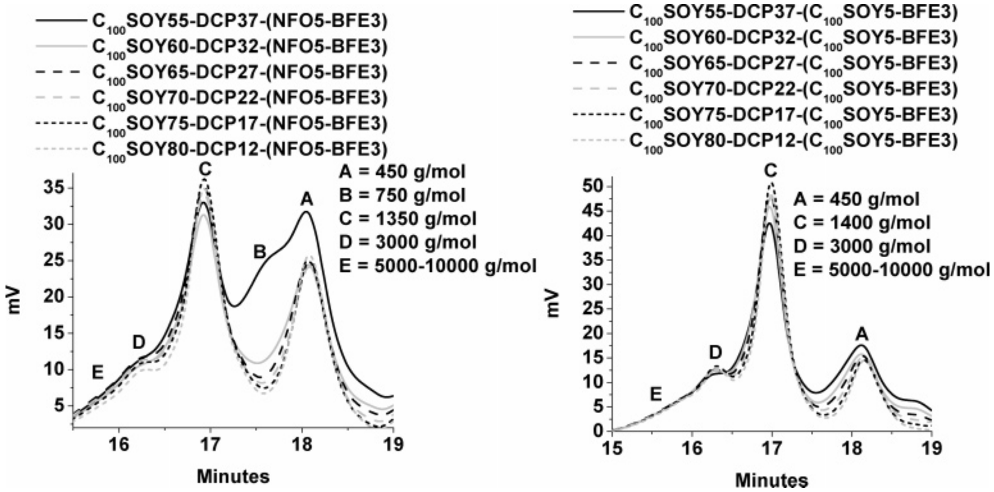


Figure 7. GPC chromatograms of C_{100}SOY−DCP soluble extracts.

Table 2. Thermal Properties of the (SOY−DCP)92−(BFE3−NFO5) Copolymers

copolymer	T_g (°C)[a]	ν_e (mol/m^3)[b]	TGA data (°C) T_{10}[c]	T_{50}[d]	(T_{max})[e]
SOY50−DCP42−C8	39.9 (56.6)[f]	1034 (501)[f]	333 (284)[f]	549 (472)[f]	569 (492)[f]
SOY55−DCP37−C8	16.5 (14.4)[f]	282 (369)[f]	332 (293)[f]	539 (476)[f]	565 (503)[f]
SOY60−DCP32−C8	2.9 (−0.2)[f]	336 (223)[f]	323 (289)[f]	537 (473)[f]	564 (495)[f]
SOY65−DCP27−C8	−6.9 (−8.7)[f]	119 (436)[f]	331 (286)[f]	541 (480)[f]	564 (500)[f]
SOY70−DCP22−C8	−13.0 (−10.8)[f]	154 (339)[f]	334 (289)[f]	535 (474)[f]	560 (479)[f]
SOY75−DCP17−C8	−17.7 (−18.4)[f]	128 (145)[f]	330 (280)[f]	529 (470)[f]	548 (479)[f]
C_{100}SOY55−DCP37−C8	18.7 (16.9)[g]	865 (1295)[g]	337 (364)[g]	548 (542)[g]	581 (549)[g]
C_{100}SOY60−DCP32−C8	1.0 (3.4)[g]	858 (984)[g]	330 (355)[g]	529 (539)[g]	561 (550)[g]
C_{100}SOY65−DCP27−C8	−8.7 (−9.0)[g]	710 (1342)[g]	338 (363)[g]	542 (554)[g]	553 (567)[g]
C_{100}SOY70−DCP22−C8	−9.0 (−11.8)[g]	996 (1340)[g]	325 (349)[g]	511 (528)[g]	537 (542)[g]
C_{100}SOY75−DCP17−C8	−12.8 (−17.0)[g]	470 (974)[g]	340 (366)[g]	530 (544)[g]	550 (562)[g]
C_{100}SOY80−DCP12−C8	−18.5 (−22.6)[g]	745 (1117)[g]	335 (372)[g]	532 (536)[g]	547 (554)[g]

[a] Glass transition temperatures represent the maxima of the tan δ curves obtained by DMA analysis. [b] Cross-link densities have been calculated at temperatures 100 °C above the corresponding T_g. The values outside the parentheses correspond to samples prepared with the NFO-modified BFE catalyst, C8 = (NFO5−BFE3), while those within the parentheses correspond to samples made with the SOY- or C_{100}SOY-modified BFE catalyst. [c] 10% weight loss temperature. [d] 50% weight loss temperature. [e] Temperature of maximum thermal degradation. [f] C8 = (SOY5−BFE3). [g] C8 = (C_{100}SOY5−BFE3).

The thermal degradation behavior of all SOY−DCP and C_{100}SOY−DCP copolymers is shown in Figures 8 and 9, respectively. Thermograms of pure SOY and C_{100}SOY are also included in these graphs for comparison purposes. The TGA data summarized in Table 2 show that the SOY−DCP and C_{100}SOY−DCP copolymers lose 10% of their weight at temperatures ranging from 280 to 334 °C and 325−372 °C, respectively. The higher reactivity of C_{100}SOY over that of SOY is expected to result in higher T_{10} values for the C_{100}SOY−DCP copolymers. Interestingly, the use of NFO as a catalyst modifier seems to diminish this influence, causing all soybean oil copolymers to have similar T_{10} values (see Table 2, T_{10} values outside the parentheses). In contrast, the copolymers prepared with SOY- and C_{100}SOY-diluted catalysts show completely

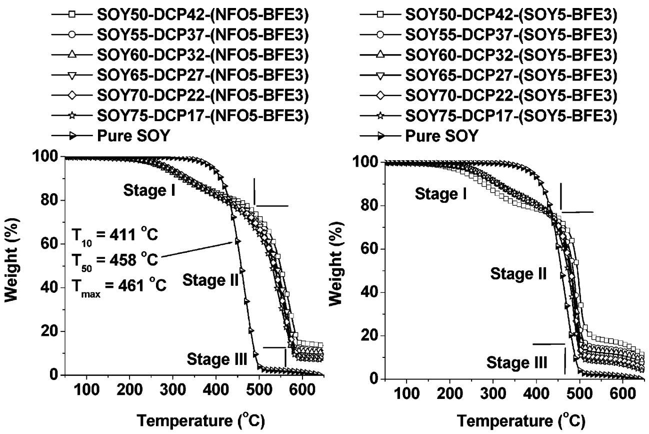


Figure 8. Thermal degradation of the SOY−DCP copolymers in air.

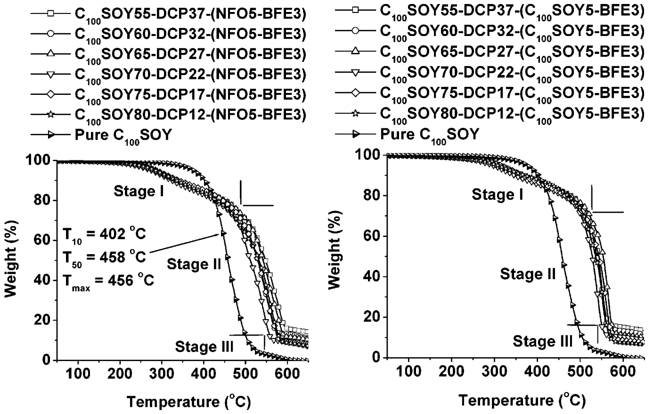


Figure 9. Thermal degradation of the C_{100}SOY−DCP copolymers in air.

opposite thermal properties, with C_{100}SOY−DCP copolymers having 62−92 °C higher T_{10} values from those of the SOY−DCP copolymers (see Table 2, T_{10} values in parentheses). We are inclined to believe that this behavior is due to the enhanced solubility of the modified catalyst in the bulk oil−DCP solution, which in turn causes significant differences in formation of the cross-linked copolymer network. A more detailed explanation of this effect is based on two factors: catalyst homogeneity and differences in reactivities between SOY, C_{100}SOY, and DCP. While the NFO-modified catalyst is completely homogeneous, neither the SOY- nor the C_{100}SOY-diluted BFE catalysts are. Also, when the NFO-modified BFE catalyst is added to the bulk oil−DCP solution, it dissolves instantly giving a dark-brown reaction mixture without the formation of any precipitate. However, when the SOY- or C_{100}SOY-diluted BFE catalysts are added to the bulk solution, we notice formation of white flakes of PDCP, which dissolve in the bulk solution after a couple of minutes. Thus, the addition of 8 wt % of SOY-diluted catalyst to the 92 wt % of bulk SOY−DCP solution initially consumes more DCP due to its higher reactivity over that of SOY. This in turn has two important consequences. First, the cross-linked SOY−DCP copolymer structure is significantly different from that formed with the NFO-modified catalyst, and second, it results in a higher amount of unreacted SOY and other soluble components after Soxhlet extraction (Table 1). This second consequence directly translates to lower T_{10} values for the (SOY−DCP)92−(SOY5−BFE3) copolymers. On the other hand, the addition of 8 wt % of the C_{100}SOY-diluted catalyst to the 92 wt % of bulk C_{100}SOY−DCP solution initially consumes more C_{100}SOY due to its slightly higher reactivity over that of DCP, as previously suggested. This, in turn, reduces the amount of unreacted C_{100}SOY and other soluble components in the bulk copolymers and gives more homogeneous cross-linked copolymer structures. The further consequence is, of course, an increase in T_{10} values for the (C_{100}SOY−DCP)92−(C_{100}SOY5−BFE3) copolymers versus those of the (C_{100}SOY−DCP)92−(NFO5−BFE3) copolymers. As previously mentioned, the 10 wt % loss temperatures correspond to first-stage thermal degradation. Keeping in mind that the initial weight loss of pure SOY and C_{100}SOY occurs at 350 °C and that their T_{10} values are 411 and 402 °C, respectively (Figures 8 and 9), it is obvious that the initial decomposition of the soybean oil−DCP copolymers cannot be ascribed solely to unreacted soybean oil but rather to evaporation and decomposition of the low molecular weight soluble fractions mentioned earlier.

The T_{50} values for the SOY−DCP and C_{100}SOY−DCP copolymers are in the range of 470−549 °C and 511−554 °C, respectively. The use of NFO has the same effect on the T_{50} values as it does on the T_{10} values. When employed as a catalyst modifier, NFO causes all copolymers to have almost the same T_{50} values (see Table 2, T_{50} values outside the parentheses). Quite the contrary, the copolymers prepared with the SOY- and C_{100}SOY-diluted catalyst show just the opposite thermal properties. Thus, the C_{100}SOY−DCP copolymers have 48−81 °C higher T_{50} values (see Table 2, T_{50} values in parentheses). The T_{50} values correspond to the second thermal degradation stage which, as previously suggested, corresponds to degradation and char formation of the cross-linked polymer structure. This hypothesis is supported through a comparison of the second-stage degradations of pure SOY and C_{100}SOY with their corresponding copolymers. It has been experimentally determined that pure SOY and C_{100}SOY have much lower T_{50} values (Figures 8 and 9), which indicates that their decomposition alone cannot account for the high thermal stability of their corresponding copolymers. Evidently, the incorporation of rigid bicyclic DCP units into the copolymer structures considerably increases their thermal stability and thereby proves that the second stage indeed corresponds to degradation of the cross-linked copolymer structure. At the very end of this stage, a certain amount of char is also formed. Our TGA results indicate that the amount of the char formed is directly proportional to the initial amount of DCP (Figures 8 and 9). Thus, copolymers with high initial amounts of DCP have the highest char yields. Besides the T_{50} values, the second-stage degradation is also characterized by T_{max} values, which are in the range of 479−569 °C and 537−581 °C for the SOY−DCP and C_{100}SOY−DCP copolymers, respectively. Similar to our explanations pertaining to the T_{10} and T_{50} values, the T_{max} values show almost the same dependence on both the type of the catalyst and the initial composition of the reaction mixture.

Conclusions

The cationic copolymerizations of SOY and C_{100}SOY with DCP catalyzed by NFO-modified and SOY- and C_{100}SOY-diluted BFE catalysts provide a series of novel thermosetting copolymers ranging from tough and ductile to very soft rubbers. It has been shown that the homogeneity of the catalysts used for the copolymerization have different effects on the copolymer properties. While the NFO-modified BFE catalyst is homogeneous, the SOY- and C_{100}SOY-diluted BFE catalysts are not. The results indicate that NFO can be completely omitted as a catalyst modifier during synthesis of the C_{100}SOY−DCP copolymers, while its use for the synthesis of SOY−DCP copolymers results in a small enhancement of copolymer properties.

Regardless of the catalyst used, all copolymerization reactions appear homogeneous in nature. As opposed to ST and DVB, all monomers used in this study have comparable reactivities, with the order being C_{100}SOY > DCP > SOY. Our analyses show that the nature of the catalyst and the monomers' reactivity have a significant influence on the copolymers' thermal properties.

All copolymers appear as dark-brown polymers with a slight odor. The gelation times of the reactions vary from 4 to 991 min at 110 °C and show no dependence on the initial stoichiometry. The yields of the soybean oil−DCP copolymers are essentially quantitative. On the other hand, the yields of the cross-linked copolymers which remain after Soxhlet extraction range from 69% to 88% and depend on the monomer stoichiometry and the type of catalyst used. ^{1}H NMR spectral and Soxhlet extraction analysis show that the bulk copolymers consist of a cross-linked soybean oil−DCP network interpenetrated with certain amounts of soluble components, such as soybean oil−DCP copolymers, free oil, and some low molecular weight oil fragments, such as mono- and diglycerides or fatty acids. GPC analysis confirms that the molecular weights of these soluble fractions are in the range of 400−10 000 g/mol based on polystyrene standards. The bulk copolymers have T_g's ranging from −22.6 to 56.6 °C. Except for the T_g of SOY50−DCP42−I8, the T_g's of all copolymers are below ambient temperature and are comparable to those of commercially available rubbery materials. Initial DMA analysis reveals that their tan δ values are in the range of 0.7−1.2, suggesting that these materials show promise as damping materials below ambient temperature.[24,49] All soybean oil−DCP copolymers are thermally stable below 200 °C. Their 10% weight loss temperatures are in the range of 280−372 °C, while their 50% weight loss temperatures are in the range of 470−554 °C.

These novel thermosetting copolymers have been prepared using 50−85 wt % of biorenewable materials. Their properties suggest that they may prove useful alternatives for current petroleum-based plastics and find certain utility. In the years to come, biobased polymers will most likely continue to play an important role and help set our society on a more sustainable and environmentally responsible path.

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