

Synthesis, Structure, and Thermophysical and Mechanical Properties of New Polymers Prepared by the Cationic Copolymerization of Corn Oil, Styrene, and Divinylbenzene

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ABSTRACT: New thermosetting polymeric materials were prepared by the cationic copolymerization of corn oil or conjugated corn oil with styrene and divinylbenzene initiated by boron trifluoride diethyl etherate or related modified initiators. The gel times ranged from a few minutes to hours or even days depending on the stoichiometry and curing temperatures. These polymeric materials possessed crosslink densities of 50 to 1.5×10^4 mol/m³ and glass-transition temperatures of 30–99°C. The materials range from soft rubbers to tough and rigid plastics. The Young's moduli of these materials varied from 0.6 to 474 MPa, the ultimate tensile strengths varied from 0.5 to 17.6 MPa, the

elongation at break percentages varied from 2 to 198%, the flexural strengths varied from 0.2 to 36 MPa, and the compressive strengths varied from 4.8 to 63.8 MPa. In addition to having commercially viable thermophysical and mechanical properties, these new materials also possessed good damping and shape-memory properties, suggesting numerous, promising applications for these novel corn oil-based polymeric materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1830–1838, 2003

Key words: gelation; mechanical properties; cationic polymerization; thermosets

INTRODUCTION

Polymeric materials prepared from renewable natural resources, such as carbohydrates, starch, and proteins, have recently become increasingly important.¹ The advantages of these polymers are their low cost, ready availability of starting materials, and biodegradability.

Corn oil (COR), one of the cheapest commercially available vegetable oils, is a biodegradable, renewable natural resource with a fairly high degree of unsaturation. The majority of COR has thus far been used for human food, such as cooking oil and margarine, and livestock feed.² With the increasing use of corn-derived ethanol for fuel purposes, more and more COR will be produced in the coming years. Thus, it is imperative to find new applications for COR, especially in nonfood uses, such as soaps, paints, inks, varnishes, and polymers.

COR has a triglyceride structure with approximately 4.1 C=C double bonds per molecule on average in the fatty-acid side chains. The fairly high degree of unsaturation present in COR should make it possible to polymerize or copolymerize this oil or the corresponding fatty acids into useful polymers. Typically,

the three fatty-acid side chains of COR are composed of oleic acid (one C=C bond), linoleic acid (two C=C bonds), and linolenic acid (three C=C bonds), just like those of soybean oils.³ Recently, we investigated the cationic copolymerization of regular soybean oil, low-saturation soybean oil (LSS), and conjugated low-saturation soybean oil (CLS) with styrene (ST) and divinylbenzene (DVB) initiated by boron trifluoride diethyl etherate (BFE).^{4–10} By varying the stoichiometry, type of oil, and alkene comonomers, we obtained a wide variety of interesting polymeric materials, ranging from elastomers to tough and rigid plastics. These new soybean-oil polymers exhibited thermophysical and mechanical properties that were comparable to those of commercially available elastomers and conventional plastics and may serve as replacements for petroleum-based polymer materials in many applications. Compared with soybean oil, COR is only slightly less unsaturated and is presently cheaper in price. Thus, it was particularly interesting to investigate the cationic polymerization and copolymerization of COR and the resulting polymer materials.

In this study, we synthesized a variety of different polymeric materials by the cationic copolymerization of regular COR or conjugated corn oil (CCOR) with ST and DVB initiated by BFE or related modified BFE initiators. The synthesis, structure, and thermophysical and mechanical properties and their relationships were investigated.

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EXPERIMENTAL

Materials

We used HyVee 100% pure COR in this study. The CCOR was prepared by a photochemical technique developed in the Verkade group at Iowa State University. The degree of conjugation was calculated to be about 100%. ST, DVB (80 mol % DVB and 20 mol % ethylvinylbenzene), and distilled-grade BFE were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used as received. Norway Pronova fish oil ethyl ester EPAX 5500 EE (NFO) was used to modify the original initiator.

Polymer preparation and nomenclature

The polymeric materials were prepared by the cationic copolymerization of COR or CCOR with ST and DVB initiated by modified BFE initiators with procedures previously used on soybean oils.^{4,5} The desired amounts of ST and DVB were added to the COR. The total amount of reactants was around 50 g. The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of modified BFE initiator. A modified initiator, which was prepared by the mixture of a small amount of NFO with the BFE, was generally required to produce homogeneous reactions and homogeneous polymers. The reaction mixture was then injected into a glass mold, which was subsequently sealed by silicon adhesive and heated for a given time at the appropriate temperatures, usually 4 h at room temperature, followed by 24 h at 60°C, and then 24 h at 110°C. The yields of the resulting bulk polymers were essentially quantitative. The nomenclature adopted in this study for the polymer samples was based on the original composition of the reactants. For example, COR45-ST32-DVB15-(NFO5-BFE3) represents a polymer prepared from 45 wt % COR, 32 wt % ST, 15 wt % DVB and 8 wt % modified initiator (5 wt % NFO + 3 wt % BFE). Because the amount of ethylvinylbenzene present in the DVB was minimal, we omitted it from our nomenclature to avoid confusion.

Characterization

Soxhlet extraction was used to characterize the structures of the COR bulk polymers. A 2.0-g sample of the bulk polymer was extracted for 24 h with 100 mL of refluxing methylene chloride with a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum-drying. The soluble substances were isolated for further characterization. The insoluble solid was dried *in vacuo* for several hours before it was weighed.

The dynamic mechanical properties of the bulk polymers were obtained with a PerkinElmer dynamic

mechanical analyzer (Pyris-7e) (Perkin Elmer, Norwalk, CT) in the three-point bending mode. The rectangular specimen was made by the copolymerization of the reactants in an appropriate mold. Thin sheet specimens 2 mm in thickness and 5 mm in depth were used, and the span-to-depth ratio was maintained at approximately 2. Each specimen was first cooled to about -35°C, and was then heated at 3°C/min and a frequency of 1 Hz under helium. The viscoelastic properties, the storage modulus (E') and mechanical loss tangent ($\tan \delta$; damping), or loss factor, were recorded as a function of temperature. The glass-transition temperature (T_g) of the polymer was obtained from the peak of the $\tan \delta$ curve.

The damping properties were evaluated by the loss tangent maximum [$(\tan \delta)_{\max}$], the temperature range (ΔT) for efficient damping ($\tan \delta > 0.3$), and the integral under the linear $\tan \delta$ -temperature curve [loss tangent area (TA)]. We determined the TA values by first subtracting out the background and then cutting and weighing the paper portions representing the TA under consideration.^{11,12}

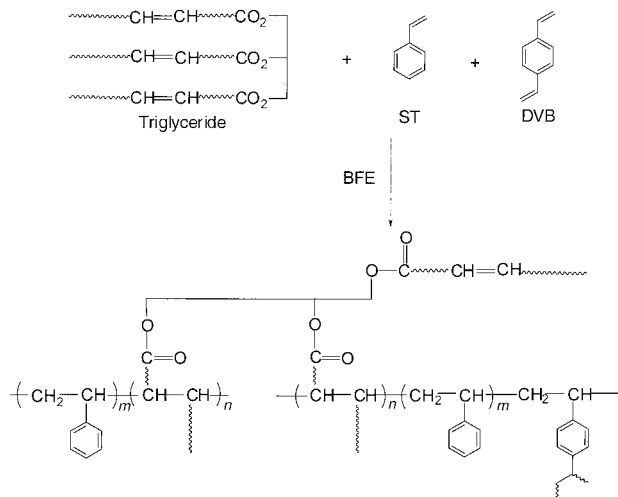
The tensile mechanical tests were conducted according to ASTM D 638M specification (Type I specimen) with an Instron universal testing machine (model 4502) (Canton, MA) at a crosshead speed of 5 mm/min. The Young's modulus (E), ultimate tensile strength (σ_b), and elongation at break (ϵ_b) of the polymers were obtained from the tensile tests. The toughness of the polymer, which is the fracture energy per unit volume of the specimen, was obtained from the area under the corresponding tensile stress-strain curve. The compressive and flexural tests were conducted on the same Instron universal testing machine according to ASTM D 695M-91 and ASTM D 790M-92, respectively.

RESULTS AND DISCUSSION

Structures of COR and CCOR and their cationic copolymerization

COR had a triglyceride structure with a fairly high degree of unsaturation. The three fatty-acid side chains were composed of approximately 27% oleic acid, 59% linoleic acid, and 1% linolenic acid.² ¹H-NMR indicated that the COR had about 4.1 C=C bonds on average per triglyceride, which was close to the 4.5 C=C bonds in the soybean oils used in our previous work.⁴⁻¹⁰ The CCOR had the same degree of unsaturation as the COR, but essentially all of the C=C bonds that could be conjugated in the COR were conjugated in the CCOR.

The nonconjugated and conjugated C=C bonds of the fatty-acid triglyceride side chains were sufficiently nucleophilic so that the COR and CCOR were cationically polymerizable monomers.^{13,14} However, the



Scheme 1

simple homopolymerization of the COR or CCOR usually resulted in low-molecular-weight viscous oils or very weak rubbery materials with no real utility. To produce viable materials, some aromatic rigid monomers had to be used, such as ST and DVB. Scheme 1 shows that the curing process of these COR-ST-DVB systems was characterized by the formation and linear growth of chains that soon began to branch and then crosslink because of the multiple C=C bonds in the COR, CCOR, and DVB. A network of infinite molecular weight was thus obtained, which corresponded to the gelation point, the irreversible transformation from a viscous liquid to an elastic gel.

The time for gelation is a very important factor in the evaluation of the processing of a thermosetting polymer because beyond the gelation point, the curing material is no longer able to flow easily and has limited processability. Figure 1 shows the effect of the COR content (wt %) on the gel time of the reactants at room temperature. The gel time was determined by the time at which the cessation of flow occurred in the material being cured according to ASTM D 2471-88,

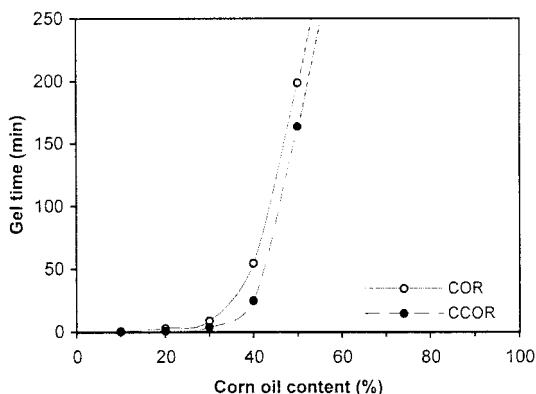


Figure 1 Effect of COR content on the gel time at room temperature.

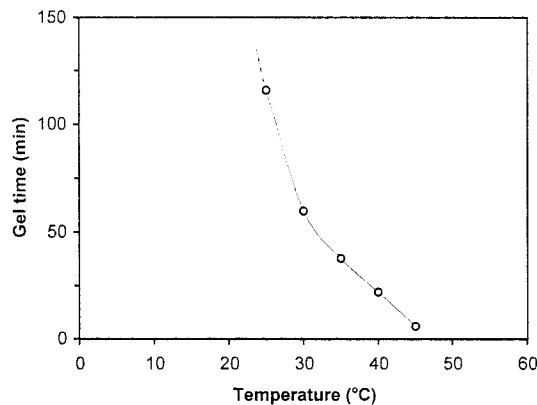


Figure 2 Effect of cure temperature on the gel time of COR45-ST32-DVB15-(NFO5-BFE3).

and the value was averaged from five individual measurements at the specified temperature.¹⁰ In this study, the ratio of ST to DVB was held constant at 3:2. Without any COR, the reactants (ST + DVB) reacted instantly when the initiator was added at room temperature. The gel time gradually increased with increasing COR content. When the COR content exceeded 40%, the gel time increased exponentially. With the same composition, the CCOR reactants gelled faster than the corresponding COR reactants, indicating that CCOR was more reactive than COR. Figure 2 shows that the gel time was also very sensitive to the cure temperatures. The COR45-ST32-DVB15-(NFO5-BFE3) reactants typically gelled in approximately 116 min at room temperature. At a temperature of about 10°C below room temperature, the reactants did not gel within 24 h. As expected, the gel time of the reactants was significantly shortened as the cure temperature increased from room temperature. The same reactants gelled within a few minutes at 45°C.

Gelation does not necessarily inhibit further reaction. Generally, after gelation, the yield of a crosslinked polymer continues to increase until the system vitrifies. In a typical cationic polymerization, vitrification is represented by the cure time at which the yield of crosslinked polymer remains relatively unchanged.¹⁰ Figure 3 shows the dependence of crosslinked polymer yields on the cure time at 35 and 40°C. Apparently, the system underwent a continuing slow increase in the crosslinked polymer yield after gelation. A constant crosslinked polymer yield did not appear, indicating that vitrification could not be determined by the technique used in this study. Figure 3 also shows that with the same cure time only a 5°C increase in the cure temperature made an obvious difference in the crosslinked polymer yields. Thus, increasing the cure temperature was a very effective way to effect crosslinking. In other words, to obtain fully cured networks, the materials had to be post-

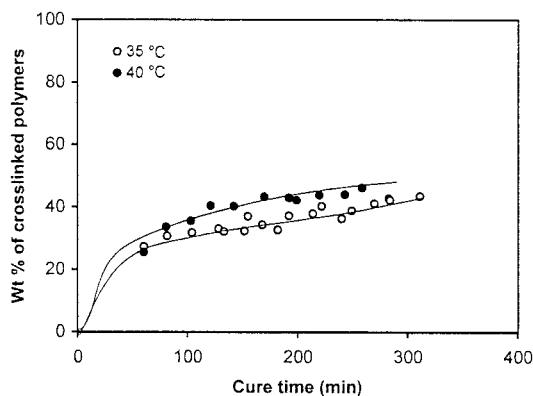


Figure 3 Yields of crosslinked polymers as a function of cure time at 35 and 40 °C for COR45-ST32-DVB15-(NFO5-BFE3).

cured at elevated temperatures. Typically in this study, the final bulk polymers were prepared under the following curing conditions: 4 h at room temperature, followed by 24 h at 60 °C, and then 24 h at 110 °C.

Microstructure of the COR polymers

The fully cured thermosets appeared to be viable polymeric materials ranging from soft rubbers to tough and rigid plastics. The yields of the bulk polymers were essentially quantitative. Like the soybean-oil polymers previously studied,⁴⁻¹⁰ these COR bulk materials were also composed primarily of crosslinked polymers that were compatibilized by a small amount of low-molecular-weight polymers and unreacted COR.

The crosslinked polymers in the bulk materials were primarily COR-ST-DVB copolymers, as determined by Fourier transform IR spectroscopy and ¹H-NMR and ¹³C-NMR techniques. Figure 4 shows that crosslinked polymers constituted the majority of the bulk polymers. When the COR constituted 40–50 wt % of the reactants, the percentages of crosslinked poly-

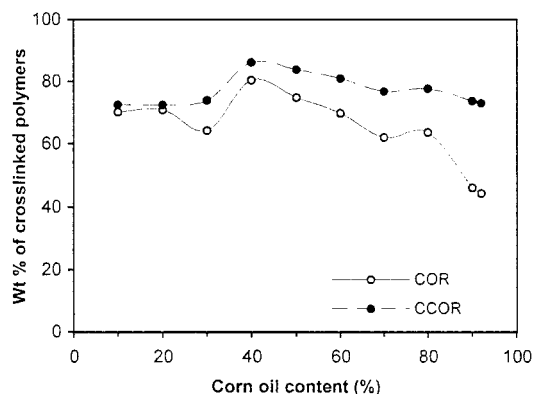


Figure 4 Percentages of crosslinked polymers present in the COR and CCOR bulk materials.

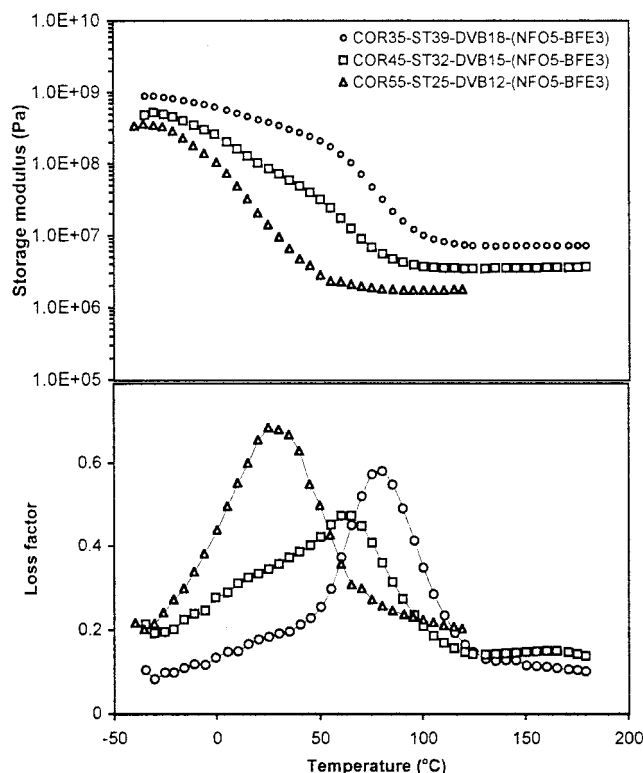


Figure 5 Dynamic mechanical behavior of the COR polymers prepared by the variation of the COR concentration with the ST/DVB ratio constant at 3:2.

mers in the bulk materials reached their maxima. As expected, the CCOR bulk materials contained a greater amount of crosslinked polymers than the COR materials because of the high reactivity of CCOR. On the basis of ¹H-NMR spectroscopic analysis of the extracted soluble substances from the bulk materials and the fact that all of the aromatic monomers were incorporated in the crosslinked polymer networks, we determined that the majority (60–90%) of the COR in the reactants actually participated in the copolymerization and were covalently incorporated into the crosslinked polymer network.

Dynamic mechanical properties

Figure 5 shows the dynamic mechanical behavior of the COR polymers prepared by the variation of the COR concentration when the ratio of ST to DVB was kept constant at 3:2. Typically, E' initially remained almost constant at lower temperatures. As the temperature increased, E' exhibited a sharp drop, followed by a modulus plateau at higher temperatures, where the polymer behaved like a rubber. Apparently, the modulus drop corresponded to the onset of the glass transition in the crosslinked polymer networks, as shown by the corresponding $\tan \delta$ peak. The appearance of a relatively constant modulus at higher temperatures indicated that stable crosslinked networks

TABLE I
Characteristics of COR Polymers

Entry	Polymer	T_g (°C)	ν_e (mol/m ³)	(tan δ) _{max}	ΔT (°C)	TA
1	COR35-ST39-DVB18-(NFO5-BFE3)	79	7.0×10^2	0.6	49 (55–104)	28
2	COR45-ST32-DVB15-(NFO5-BFE3)	63	3.5×10^2	0.47	80 (7–87)	24
3	COR55-ST25-DVB12-(NFO5-BFE3)	30	1.9×10^2	0.68	86 (–16 to 70)	29
4	COR45-ST42-DVB05-(NFO5-BFE3)	37	5.0×10	1.4	83 (–6 to 77)	55
5	COR45-ST37-DVB10-(NFO5-BFE3)	49	1.1×10^2	0.82	82 (–3 to 79)	39
6	COR45-ST32-DVB15-(NFO5-BFE3)	63	3.5×10^2	0.47	80 (7–87)	24
7	COR45-ST27-DVB20-(NFO5-BFE3)	79	8.1×10^2	0.34	33 (63–96)	19
8	COR45-ST22-DVB25-(NFO5-BFE3)	89	1.1×10^3	0.25	—	16
9	COR45-ST17-DVB30-(NFO5-BFE3)	99	2.3×10^3	0.20	—	10
10	COR45-ST12-DVB35-(NFO5-BFE3)	87	4.9×10^3	0.16	—	7
11	COR45-ST07-DVB40-(NFO5-BFE3)	87	5.8×10^3	0.16	—	5
12	COR45-ST00-DVB47-(NFO5-BFE3)	77	1.5×10^4	0.13	—	3

existed in the bulk polymer. As expected, when the COR content increased, the resulting polymers possessed decreased T_g 's and E' values over most of the ΔT studied. The crosslink densities (ν_e 's), calculated on the basis of rubber elasticity theory,^{11,12,15,16} also decreased from 7.0×10^2 to 3.5×10^2 to 1.9×10^2 mol/m³ (Table I, entries 1–3). The gradual decrease in the ν_e was presumably because of the decreased amounts of crosslinking agent DVB in their compositions.

Figure 6 shows the temperature dependence of E' and tan δ for the COR polymers prepared by the

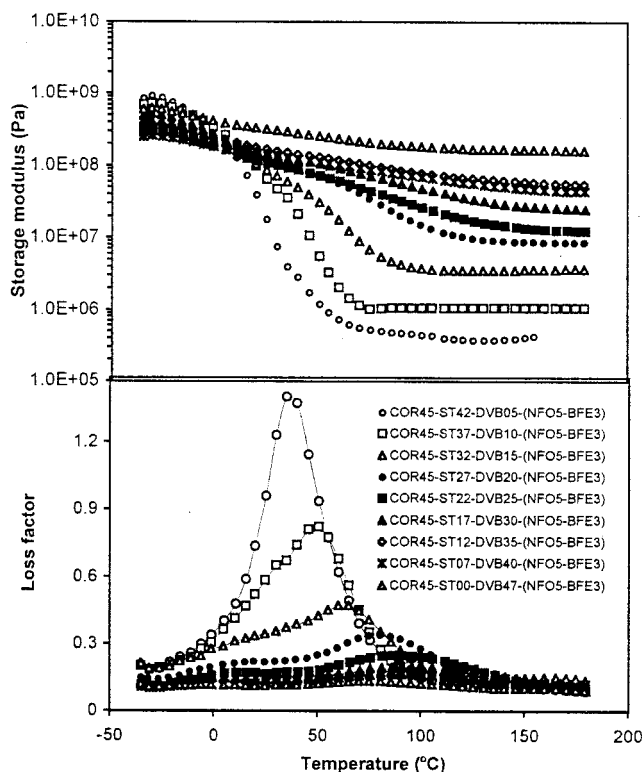


Figure 6 Dynamic mechanical behavior of the COR polymers prepared by the variation of the DVB concentration with the ST + DVB content constant at 47%.

variation of the DVB concentration when the total concentration of the comonomers ST and DVB was kept constant at 47 wt %. The COR45-ST42-DVB05-(NFO5-BFE3) polymer exhibited very low moduli, especially at high temperatures, and its tan δ showed a very sharp peak at about 37°C. An increase in the DVB concentration did not greatly affect the low-temperature moduli of the resulting polymers, but their high-temperature moduli exhibited a dramatic increase. Such behavior was expected because increasing the DVB concentration increased the degree of crosslinking. As the DVB concentration increased further, the molecular motions became more and more restricted, and thus, the amount of energy that could be dissipated throughout the polymer specimen decreased dramatically. Therefore, the tan δ peak positions of the polymers shifted to higher temperatures, and the tan δ intensities diminished accordingly. As a result of crosslinking, a significant broadening of the glass-transition region was also observed. The broadening of the glass-to-rubber transition region is often assumed to be due to a broader distribution in molecular weight between crosslinks or some other kinds of heterogeneities in the network structure.^{12,16} Figure 7 shows that the CCOR polymers exhibited the same dynamic mechanical behavior as the COR polymers illustrated in Figure 6. Because of their high reactivity toward cationic copolymerization, the resulting CCOR polymers possessed higher degrees of crosslinking than the corresponding COR polymers.

Good damping and shape-memory properties

Good damping materials should exhibit a high tan δ (tan $\delta > 0.3$) over a ΔT of at least 60–80°C.¹⁷ It was known that the ester groups attached to the polymer backbones in our bulk polymers were able to greatly contribute to their damping intensities.^{17,18} Crosslinking increased the segmental heterogeneities of the polymer backbone and, thus, was able to effectively broaden the glass-transition (damping) regions of the

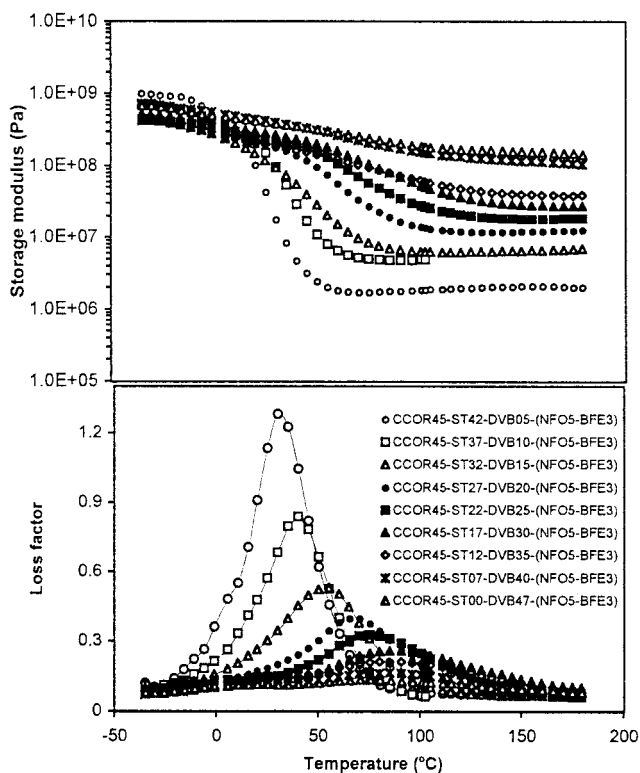


Figure 7 Dynamic mechanical behavior of the CCOR polymers prepared by the variation of the DVB concentration with the content of ST + DVB constant at 47%.

COR polymers. At the same time, however, crosslinking restricted segmental motion and, thus, reduced the polymer's ability to dissipate mechanical energy; that is, it reduced the damping intensities to some extent. Thus, within appropriate compositions and crosslinking densities, these COR polymeric materials were capable of showing efficient damping over a wide ΔT .

The $\tan \delta$, which indicates the damping ability of the material, is the ratio of the mechanical dissipation energy to the storage energy. Thus, a high $\tan \delta$ value is essential for good damping materials. Entries 1–3 in Table I show that as the COR concentration increased,

$(\tan \delta)_{\max}$ of the resulting COR polymers varied from 0.47 to 0.68, and ΔT for efficient damping varied from 49 to 86°C, indicating good damping characteristics for these COR materials.

Entries 4–12 in Table I summarize the effect of DVB content on the damping properties of the resulting COR polymers. The COR45–ST42–DVB05–(NFO5–BFE3) polymer exhibited a $(\tan \delta)_{\max}$ value as high as 1.4, a ΔT of 83°C at $\tan \delta > 0.3$, and a high TA value of 55 K (entry 4). As the DVB concentration increased (entries 4–6), the $(\tan \delta)_{\max}$ and TA values of the resulting polymers gradually decreased. The ΔT value remained almost constant at approximately 80–83°C. Thus, these polymers appeared to be good damping materials. However, as the DVB concentration further increased up to 20% or more, the resulting polymers exhibited $(\tan \delta)_{\max}$ values in the vicinity of or much lower than 0.3 and were no longer good damping materials (entries 7–12).

The damping results for the CCOR polymers appeared to be similar to the COR polymers. However, the high reactivity of the CCOR resulted in a high ν_e , and the reduction of damping intensity by crosslinking became pronounced. As a result, the damping properties of the CCOR polymers appeared to be inferior to those of the corresponding COR polymers, as shown by the ΔT values in Table II.

In addition to good damping properties, the COR polymers could also be tailored to show typical shape-memory behavior. A shape-memory polymer basically possesses a certain degree of crosslinking and a T_g higher than room temperature.⁹ Typically, at temperatures above the T_g , a shape-memory polymer achieves a rubbery elastic state where it can easily be deformed by an external force. When the polymer is cooled to room temperature, the deformation is fixed because of frozen micro-Brownian motion. The deformed shape readily returns to its original shape when it is reheated because of the tendency of the ordered chains to return to a more random state.

TABLE II
Characteristics of CCOR Polymers

Entry	Polymer	T_g (°C)	ν_e (mol/m ³)	$(\tan \delta)_{\max}$	ΔT (°C)	TA
1	CCOR35–ST39–DVB18–(NFO5–BFE3)	76	8.8×10^2	0.60	46 (52–98)	27
2	CCOR45–ST32–DVB15–(NFO5–BFE3)	54	6.6×10^2	0.53	51 (25–76)	27
3	CCOR55–ST25–DVB12–(NFO5–BFE3)	31	6.6×10^2	0.6	62 (0–62)	27
4	CCOR45–ST42–DVB05–(NFO5–BFE3)	31.5	2.2×10^2	1.3	66 (–4 to 62)	50
5	CCOR45–ST37–DVB10–(NFO5–BFE3)	40	5.6×10^2	0.84	57 (8–65)	34
6	CCOR45–ST32–DVB15–(NFO5–BFE3)	54	6.6×10^2	0.53	51 (25–76)	27
7	CCOR45–ST27–DVB20–(NFO5–BFE3)	68	1.1×10^3	0.4	37 (50–87)	21
8	CCOR45–ST22–DVB25–(NFO5–BFE3)	75	1.6×10^3	0.33	25 (64–89)	20
9	CCOR45–ST17–DVB30–(NFO5–BFE3)	88	2.4×10^3	0.26	—	16
10	CCOR45–ST12–DVB35–(NFO5–BFE3)	85	3.4×10^3	0.21	—	14
11	CCOR45–ST07–DVB40–(NFO5–BFE3)	85	9.8×10^3	0.16	—	10
12	CCOR45–ST00–DVB47–(NFO5–BFE3)	75	1.4×10^4	0.14	—	7

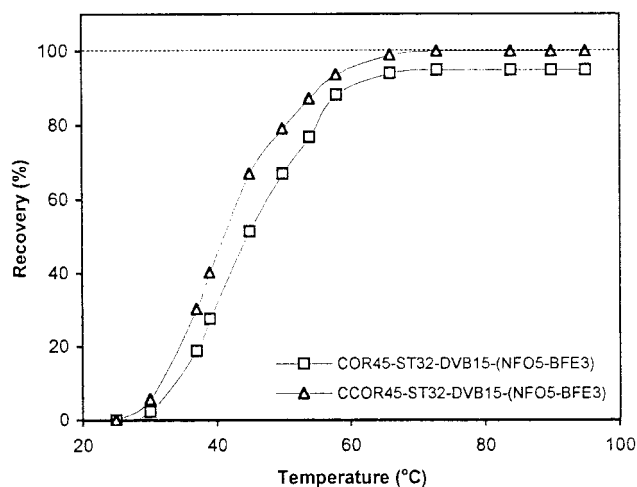


Figure 8 Shape recovery results at various temperature for the COR45-ST32-DVB15-(NFO5-BFE3) and CCOR45-ST32-DVB15-(NFO5-BFE3) polymers.

The COR polymers were typical thermosets with various degrees of crosslinking. Their T_g 's varied from 30 to 99°C. Thus, the thermosets with T_g 's higher than room temperature were expected to exhibit shape-memory behavior. For example, the COR45-ST32-DVB15-(NFO5-BFE3) and CCOR45-ST32-DVB15-(NFO5-BFE3) polymers had T_g values of 63 and 54°C and ν_e 's of 3.5×10^2 and 6.6×10^2 mol/m³, respectively. These two polymers had very good flexibility at $T_g + 50^\circ\text{C}$ with deformability (D) = 100%, as defined in our previous article.⁹ They retained 90% of their deformations when they were cooled to room temperature. Figure 8 shows the subsequent shape-recovery process at various temperatures for these two bulk polymers. No significant shape recovery was observed at temperatures slightly higher than ambient temperature. The 50% recovery of their deformations was reached at 42°C for CCOR45-ST32-DVB15-(NFO5-BFE3) and at 44°C for COR45-ST32-DVB15-(NFO5-BFE3). The CCOR45-ST32-DVB15-(NFO5-BFE3)

polymer completely returned to its original shape at approximately 75°C. The COR45-ST32-DVB15-(NFO5-BFE3) polymer recovered approximately 96% of its original shape at temperatures higher than 75°C primarily because of its relatively low degree of crosslinking.

Mechanical properties

The tensile mechanical properties of the COR polymers were highly dependent on the COR concentration. For example, the COR35-ST39-DVB18-(NFO5-BFE3) polymer contained considerable amounts of rigid aromatic comonomers. This polymer showed the typical tensile behavior of a plastic with $E = 282$ MPa and $\sigma_b = 11.9$ MPa (Table III, entry 1). As the amount of COR became equivalent to the ST + DVB comonomers in weight, the resulting COR45-ST32-DVB15-(NFO5-BFE3) polymer showed a big decrease in E and σ_b but a moderate increase in its ductility and toughness (Table III, entry 2). As the COR concentration exceeded that of the ST/DVB comonomers, the resulting COR55-ST25-DVB12-(NFO5-BFE3) polymer exhibited tensile behavior similar to a very soft rubbery material (Table III, entry 3).

Entries 4–12 in Table III show that the tensile mechanical properties of the COR polymers were also greatly affected by the DVB concentration. The COR45-ST42-DVB05-(NFO5-BFE3) polymer exhibited a modulus of a typical rubber, a viable σ_b , and an ϵ_b of approximately 200% (entry 4). Even though its T_g (37°C) was a little higher than room temperature, this polymer exhibited tensile-test behavior similar to a vulcanized rubber. When the amount of DVB was increased, the E and σ_b of the resulting polymers increased, but their ϵ_b values gradually decreased (entries 4–12). When DVB completely replaced the ST, the COR45-ST00-DVB47-(NFO5-BFE3) polymer possessed the highest elastic modulus, but its ϵ_b and toughness were considerably reduced (entry 12). The

TABLE III
Mechanical Properties of the COR Polymers

Entry	Sample	Tensile tests				Flexural strength (MPa)	Compressive strength (MPa)
		E (MPa)	σ_b (MPa)	ϵ_b (%)	Toughness		
1	COR35-ST39-DVB18-(NFO5-BFE3)	282	11.9	17	1.60	18.0	13.2
2	COR45-ST32-DVB15-(NFO5-BFE3)	46	4.6	53	1.68	2.8	63.1
3	COR55-ST25-DVB12-(NFO5-BFE3)	2.7	1.0	54	0.27	0.2	28.2
4	COR45-ST42-DVB05-(NFO5-BFE3)	0.6	0.5	198	0.56	—	13.9
5	COR45-ST37-DVB10-(NFO5-BFE3)	9	2.3	108	1.46	0.6	44.9
6	COR45-ST32-DVB15-(NFO5-BFE3)	46	4.6	53	1.68	2.8	63.1
7	COR45-ST27-DVB20-(NFO5-BFE3)	93	7.1	28	1.42	7.8	52.1
8	COR45-ST22-DVB25-(NFO5-BFE3)	147	8.5	16	0.90	10.4	56.0
9	COR45-ST17-DVB30-(NFO5-BFE3)	204	9.3	9	0.48	13.8	51.4
10	COR45-ST12-DVB35-(NFO5-BFE3)	229	8.1	5	0.21	17.3	53.8
11	COR45-ST07-DVB40-(NFO5-BFE3)	275	8.1	4	0.15	21.0	—
12	COR45-ST00-DVB47-(NFO5-BFE3)	317	6.6	3	0.09	19.1	32.4

TABLE IV
Mechanical Properties of the CCOR Polymers

Entry	Sample	Tensile tests				Flexural strength (MPa)	Compressive strength (MPa)
		E (MPa)	σ_b (MPa)	ϵ_b (%)	Toughness		
1	CCOR35-ST39-DVB18-(NFO5-BFE3)	568	17.2	4	0.34	36.0	26.4
2	CCOR45-ST32-DVB15-(NFO5-BFE3)	73	7.0	48	2.39	8.1	31.6
3	CCOR55-ST25-DVB12-(NFO5-BFE3)	8.8	2.5	53	0.75	0.7	21.9
4	CCOR45-ST42-DVB05-(NFO5-BFE3)	2.4	1.4	130	1.07	—	5.7
5	CCOR45-ST37-DVB10-(NFO5-BFE3)	11	3.9	104	2.37	0.7	8.4
6	CCOR45-ST32-DVB15-(NFO5-BFE3)	73	7.0	46	2.39	8.1	31.6
7	CCOR45-ST27-DVB20-(NFO5-BFE3)	198	9.8	17	1.25	13.9	4.8
8	CCOR45-ST22-DVB25-(NFO5-BFE3)	299	12.7	8	0.60	21.3	14.7
9	CCOR45-ST17-DVB30-(NFO5-BFE3)	378	11.3	4	0.23	27.7	37.6
10	CCOR45-ST12-DVB35-(NFO5-BFE3)	426	9.7	3	0.14	32.9	54.9
11	CCOR45-ST07-DVB40-(NFO5-BFE3)	463	8.4	3	0.10	32.9	62.8
12	CCOR45-ST00-DVB47-(NFO5-BFE3)	474	7.0	2	0.07	31.3	63.8

toughness of the COR polymers first increased with increasing DVB concentration. Eventually, it reached a maximum at 15 wt % DVB (entry 6), and then, it gradually decreased. Similar results were obtained for soybean-oil-based polymers.⁷

Table IV shows that the CCOR and DVB contents affected the tensile mechanical properties of the CCOR polymers in a manner similar to the COR polymers. Because of the high reactivity of CCOR, the CCOR polymers possessed higher E values and tensile strengths than the corresponding COR polymers (Table III).

As expected, the flexural strengths of the CCOR polymers were higher than the corresponding COR polymers, as shown in Tables III and IV. When the stoichiometries were varied, the flexural strengths of the COR and CCOR polymers ranged from 0.2 to 36 MPa. The compressive strengths of these materials also varied from 4.8 to 63.8 MPa. However, the precise effect of the stoichiometry on the compressive strengths could not be clearly identified at this time.

Figure 9 shows a comparison of the mechanical

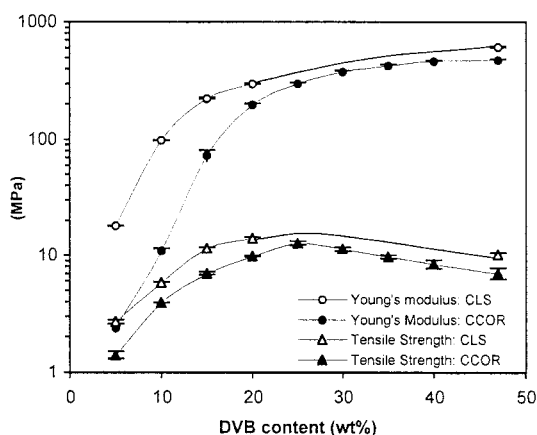


Figure 9 E and σ_b values for the CLS and CCOR polymers at room temperature.

properties of COR and soybean-oil polymers. Both oils had similar triglyceride structures. COR had approximately 4.1 C=C bonds on average per triglyceride, whereas soybean oil had approximately 4.5 C=C bonds, and LSS had approximately 5.1 C=C bonds per triglyceride. As a result, CLS was more reactive than the CCOR toward cationic polymerization. Thus, the CCOR polymers had lower mechanical properties (E values and tensile strengths) than the corresponding CLS polymers.

CONCLUSIONS

COR and CCOR were effectively copolymerized with ST and DVB to form various thermosets by cationic polymerization initiated by BFE. The gelation process of the reactants was significantly affected by the stoichiometry and curing temperatures. The resulting thermosetting polymers possessed ν_e 's ranging from 5.0×10 to 1.5×10^4 mol/m³ and T_g 's ranging from 30 to 99°C. These materials possessed a wide variety of mechanical properties (tensile, flexural, and compressive strengths), ranging from elastomers to tough and rigid plastics. The mechanical properties of the COR polymers were a little lower than the corresponding soybean-oil polymers we investigated previously because COR had a lower degree of unsaturation than soybean oil.⁴⁻¹⁰ In addition to competitive mechanical properties, the new COR polymers with appropriate compositions exhibited good damping properties and typical shape-memory effects. These new, more promising properties will make it possible to fabricate novel, value-added polymer products from COR.

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References

1. Kaplan, D. L. *Biopolymers from Renewable Resources*; Springer: New York, 1998.
2. Watson, S. A.; Ramstad, P. E. *Corn: Chemistry and Technology*; American Association of Cereal Chemistry: St. Paul, MN, 1987.
3. Gunstone, F. D. *Industrial Uses of Soybean Oil for Tomorrow: Special Report '96*; Iowa State University and the Iowa Soybean Promotion Board: Ames, IA, 1995.
4. Li, F.; Hanson, M. V.; Larock, R. C. *Polymer* 2001, 42, 1567.
5. Li, F.; Larock, R. C. *J Appl Polym Sci* 2001, 80, 658.
6. Li, F.; Larock, R. C. *J Polym Sci Part B: Polym Phys* 2000, 38, 2721.
7. Li, F.; Larock, R. C. *J Polym Sci Part B: Polym Phys* 2001, 39, 60.
8. Li, F.; Larock, R. C. *Polym Adv Technol* 2002, 13, 436.
9. Li, F.; Larock, R. C. *J Appl Polym Sci* 2002, 84, 1533.
10. Li, F.; Larock, R. C. *Polym Int* 2003, 52, 126.
11. *Cationic Polymerizations: Mechanisms, Synthesis and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.
12. Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley: New York, 1982.
13. Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 6.
14. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994; Chapter 4.
15. Muruyama, T. *Dynamic Mechanical Analysis of Polymeric Materials*; Elsevier: Amsterdam, 1978.
16. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1961.
17. Corsaro, R. D.; Sperling, L. H. *Sound and Vibration Damping with Polymers*; ACS Symposium Series 424; American Chemical Society: Washington, DC, 1990.
18. Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. *J Polym Sci Part B: Polym Phys* 1988, 26, 1627.