

New Soybean Oil–Styrene–Divinylbenzene Thermosetting Copolymers. V. Shape Memory Effect

FENGKUI LI, RICHARD C. LAROCK

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received 12 March 2001; accepted 23 August 2001

ABSTRACT: A series of new shape memory polymers are synthesized by the cationic copolymerization of regular soybean oil, low saturation soybean oil (LoSatSoy oil), and/or conjugated LoSatSoy oil with styrene and divinylbenzene, norbornadiene, or dicyclopentadiene initiated by boron trifluoride diethyl etherate or related modified initiators. The shape memory properties of the soybean oil polymers are characterized by the deformability (D) of the materials at temperatures higher than their glass-transition temperatures (T_g), the degree to which the deformation is subsequently fixed at ambient temperature (FD), and the final shape recovery (R) upon being reheated. It is found that a T_g well above ambient temperature and a stable crosslinked network are two prerequisites for these soybean oil polymers to exhibit shape memory effects. Good shape memory materials with high D , FD , and R values are prepared by controlling the crosslink densities and the rigidity of the polymer backbones. The advantage of the soybean oil polymers lies in the high degree of chemical control over the shape memory characteristics. This makes these materials particularly promising in applications where shape memory properties are desirable. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1533–1543, 2002; DOI 10.1002/app.10493

Key words: soybean oil; cationic copolymerization; shape memory effect

INTRODUCTION

Shape memory refers to the ability of some materials to remember a specific shape on demand, even after very severe deformations. In recent years, new shape memory polymers have received attention because of their low cost, low density, high shape recoverability, and easy processibility compared to conventional shape memory metals (alloys).¹ Shape memory polymers basically consist of two phases: a reversible phase and a fixed phase. The reversible phase refers to the polymer

matrix, which has a glass-transition temperature (T_g , amorphous polymer) or a melting temperature (T_m , crystalline polymer) well above the application temperature, which is usually the ambient temperature for most practical applications. The fixed phase is composed of either chemical or physical crosslinks that are relatively stable at temperatures higher than the T_g or T_m of the reversible phase. Typically, at a temperature above the T_g or T_m the shape memory polymer achieves a rubbery elastic state in which it can be easily deformed by an external force. When the polymer is cooled to room temperature, the deformation is fixed because of the frozen micro-Brownian motion of the reversible phase. The hardened reversible phase effectively resists the elastic recovery resulting from the tendency of the

Correspondence to: R. C. Larock (larock@iastate.edu).

Contract grant sponsor: Iowa Soybean Promotion Board.

Journal of Applied Polymer Science, Vol. 84, 1533–1543 (2002)
© 2002 Wiley Periodicals, Inc.

ordered chains to return to a more random state, and thus the fixed deformation is regarded as a "permanent deformation" at room temperature. The deformed shape readily returns to its original shape upon being reheated. The driving force for the shape recovery is primarily entropy, specifically the strong relaxations of the oriented polymer chains between crosslinks.

The first shape memory polymeric material of commercial importance was a polyethylene that was chemically crosslinked by using ionizing radiation during processing.² However, high capital expenditure and complicated techniques are both required in the preparation and the use of high-energy radiation is limited to the preparation of articles with a thin cross section. Therefore, various routes have been developed to prepare new shape memory polymers, especially those with physical crosslinks. This new class of thermoplastic shape memory polymers consists of a number of segmented block copolymers,³⁻¹¹ grafted copolymers,¹² and hybrid copolymers¹³ with deliberately designed segmental structures. Most of the thermoplastic shape memory materials are segmented block copolymers, such as segmented polyurethanes³⁻¹⁰ and polyether-esters.¹¹ In these copolymers the soft segments constitute the polymer matrix (the reversible phase) with a T_g or T_m higher than room temperature, and the hard segments form a physically crosslinked network (the fixed phase) resulting from microphase segregation of the incompatible hard and soft segments. Introducing a chemically crosslinked structure not only facilitates full recovery of the deformation but also renders better shape memory behavior under complex deformations.⁹ In addition to the segmented block copolymers, some grafted copolymers (polyethylene/polyamide-6 grafted copolymers) have been found to show typical shape memory effects.¹² These grafted copolymers are prepared by a melt-blending process. The crystalline polyethylene matrix acts as the reversible phase whereas the polyamide-6 grafts aggregate and form physical crosslinks (fixed phase). Jeon et al.¹³ recently reported a number of norbornyl-polyhedral oligomeric silsesquioxane hybrid copolymers with chain entanglements as the fixed phase. They claim that their new hybrid copolymers have fairly high shape recovery and, more importantly, POSS reinforcement in the copolymer leads to significant enhancement of the thermal stability.¹³

We recently reported a series of new random copolymers prepared by the cationic copolymerization of regular soybean oil (SOY), low saturation soybean oil [LoSatSoy oil (LSS)], or conjugated LoSatSoy oil (CLS) with various alkene comonomers, including styrene (St), divinylbenzene (DVB), norbornadiene (NBD), and dicyclopentadiene (DCP).¹⁴⁻¹⁸ A wide variety of viable chemically crosslinked polymeric materials were obtained, ranging from elastomers through tough to relatively brittle plastics. These new soybean oil polymers not only exhibit competitive thermo-physical and mechanical properties¹⁴⁻¹⁷ but also possess very good damping properties over wide temperature and frequency ranges.¹⁸ By deliberately designing the structures, the soybean oil polymers possess stable crosslinked networks, as well as high T_g values, well above the ambient temperature. Thus, a study of the shape memory effects of these new materials was particularly attractive. In this study we systematically investigated the shape memory properties of these new soybean oil polymers. The effect on the shape memory behavior of the chemical stoichiometry and types of soybean oils and alkene comonomers employed is discussed in detail.

EXPERIMENTAL

Materials

The soybean oils used in this study are SOY and LSS; both are commercially available in supermarkets and were used without further purification. The CLS was prepared by rhodium-catalyzed isomerization of LSS in our laboratory.¹⁹ The percentage of conjugation of the CLS was calculated to be approximately 100%. The compositions of the three different soybean oils used in this study are listed in Table I. The St, DVB (80% DVB plus 20% ethylvinylbenzene), NBD, and DCP were purchased from Aldrich Chemical Company and used as received. The distilled grade boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$, BFE) used to initiate cationic polymerization of the various soybean oils was also supplied by Aldrich. Norway Pronova fish oil ethyl ester (EPAX 5500 EE, NFO) was used to modify the original BFE initiator.

Polymer Preparation

The polymeric materials were prepared by the cationic copolymerization of SOY, LSS, or CLS

Table I Compositions of Triglyceride Soybean Oils

Entry	Soybean Oil	C=C		Fatty Acids ^b (%)				
		Type	No. ^a	C16 : 0	C18 : 0	C18 : 1	C18 : 2	C18 : 3
1	SOY	Nonconjugated	4.5	10.5	3.2	22.3	54.4	8.3
2	LSS	Nonconjugated	5.1	4.5	3.0	20.0	63.5	9.0
3	CLS	Conjugated	5.1	4.5	3.0	20.0	63.5	9.0

SOY, Soybean oil; LSS, LoSatSoy oil; CLS, conjugated LoSatSoy oil.

^a The average number of carbon-carbon double bonds per triglyceride was calculated by ¹H-NMR spectral analysis.

^b For example, C18 : 2 represents the fatty acid (ester) that possesses 18 carbons and 2 C=C bonds.

with St (comonomer) and DVB, NBD, or DCP (comonomers used as crosslinking agents) initiated by BFE or related modified initiators. The detailed reaction procedures are described elsewhere.¹⁵ Briefly, a polymer sample prepared from 45 wt % LSS, 32 wt % St, 15 wt % DVB, and 8 wt % NFO-modified BFE initiator (5 wt % NFO plus 3 wt % BFE) is designated as LSS45-St32-DVB15-(NFO5-BFE3). Because the amount of ethylvinylbenzene present in the DVB is minimal, we omitted it from our nomenclature to avoid confusion.

Characterizations

The dynamic mechanical properties of the bulk polymers were obtained by using a Perkin-Elmer dynamic mechanical analysis (DMA) instrument (Pyris-7e) in a three-point bending mode. A rectangular specimen was made by injecting the reactants into an appropriate mold. Thin sheet specimens of 2-mm thickness and 5-mm depth were used, and the span to depth ratio was maintained at approximately 2. Each specimen was first cooled to about -35°C and then heated at 3°C/min and a frequency of 1 Hz under helium. The viscoelastic properties [storage modulus (E') and mechanical loss factor (damping, $\tan \delta$)] were recorded as a function of temperature. The T_g of the polymer was obtained from the peak of the loss factor curve. The crosslink density (ν_e) was calculated from the high temperature elastic modulus of the DMA results, based on the theory of rubber elasticity.¹⁶

The shape memory behavior of the soybean oil polymers was examined by a bending test.⁹ Figure 1 shows that the specimen (80 × 12 × 3 mm) was first deformed to a maximum angle (θ_{\max}) at the T_g plus 50°C by an external force. (The specimen tended to break at angles > θ_{\max} .) The de-

formed specimen was quenched in a water bath at ambient temperature while still under the external force. When the external force was released at room temperature, minor shape recovery could occur and the deformed angle changed from θ_{\max} to θ_{fixed} . (The deformed angle θ_{fixed} that was fixed at room temperature was typically a little smaller than the originally deformed angle θ_{\max} .) Finally, the deformed specimen was heated to various temperatures at a heating rate of approximately 50°C/min, and the remaining angle (θ_{final}) was recorded after 10 min at each temperature. The following definitions are used to quantitatively characterize the shape memory properties of the polymers: the deformability (D) of the specimen at the T_g plus 50°C is defined as $D = \theta_{\max}/180 \times 100\%$. The fixed deformation (FD) at room temperature, which depicts the ability of the specimen to fix its deformation at ambient temperature, is defined as $\text{FD} = \theta_{\text{fixed}}/\theta_{\max} \times 100\%$. The shape recovery (R) is defined as $R = (\theta_{\text{fixed}} - \theta_{\text{final}})/\theta_{\text{fixed}} \times 100\%$.

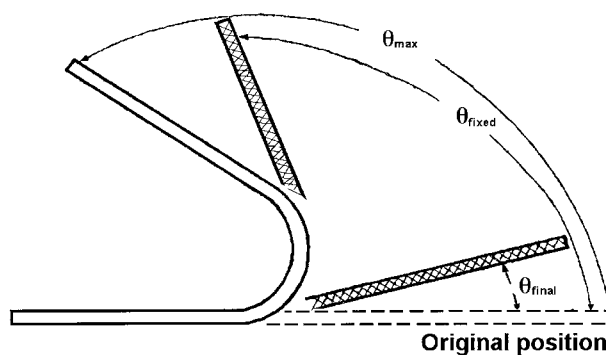


Figure 1 A schematic illustration of the shape memory test.

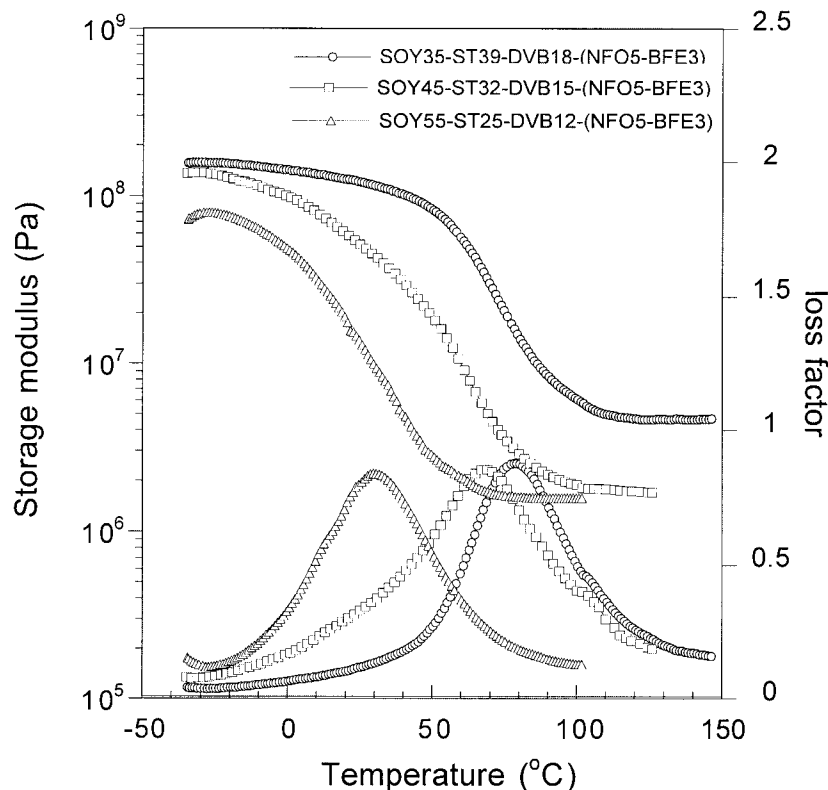


Figure 2 The dynamic mechanical behavior of the SOY polymers prepared by varying the SOY concentration.

RESULTS AND DISCUSSION

A shape memory polymer exhibits mechanical behavior that includes fixing the deformation of the plastic at room temperature and recovering the deformation as an elastomer at relatively high temperatures.^{5–8} Thus, a T_g well above ambient temperature and the formation of stable crosslinks are necessary for a soybean oil polymer to show the shape memory effect. Figure 2 shows the dynamic mechanical behavior of three SOY polymers prepared by varying the SOY concentration with a constant ratio of $\sim 2:1$ for the St/DVB comonomers. The storage moduli of the SOY polymers initially remain constant at low temperatures. As the temperature increases, the storage moduli exhibit large and sharp drops in the temperature region between 20 and 100°C, which correspond to the glass transitions of the SOY polymers as determined by the corresponding loss factor peaks. At temperatures above their T_g values the moduli appear to be on the order of magnitude of rubbery materials (10^6 Pa),²⁰ and the

rubbery modulus plateaus indicate the existence of stable crosslinks in the bulk SOY polymers.

Table II (entries 1–3) gives the T_g and ν_e values of the three SOY polymers illustrated in Figure 2. These SOY polymers possess T_g values higher than room temperature, and various degrees of crosslinking are obtained. As expected, the SOY polymers exhibit a shape memory effect. Table II (entry 1) shows that the polymer SOY35-St39-DVB18-(NFO5-BFE3) exhibits a deformability of 83% at the T_g plus 50°C. Upon releasing the applied force, the deformation of the specimen can be fixed effectively with an FD of 98% at room temperature. No further recoverable strain is found until it is reheated to high temperatures. As the SOY concentration increases, the resulting polymer shows an improved deformability ($D = 100\%$) at the T_g plus 50°C, but its ability to fix the deformation at room temperature is reduced to an FD of 80% (entry 2). When the SOY concentration exceeds 50%, the resulting polymer actually behaves like an elastomer with an FD of 11% (entry 3). The above results indicate that the T_g

Table II Shape Memory Properties of SOY Polymers

Entry	Polymer	T_g (°C)	ν_c (mol/m ³)	Shape Memory Results (%)		
				D	FD	R
1	SOY35-St39-DVB18-(NFO5-BFE3)	79	4.7×10^2	83	98	100
2	SOY45-St32-DVB15-(NFO5-BFE3)	68	1.8×10^2	100	80	100
3	SOY55-St25-DVB12-(NFO5-BFE3)	30	1.0×10^2	100	11	100
4	SOY45-St42-DVB5-(NFO5-BFE3)	36	3.3×10	100	23	100
5	SOY45-St37-DVB10-(NFO5-BFE3)	44	1.4×10^2	100	64	100
6	SOY45-St32-DVB15-(NFO5-BFE3)	68	1.8×10^2	100	80	100
7	SOY45-St30-DVB17-(NFO5-BFE3)	72	5.4×10^2	94	90	100
8	SOY45-St27-DVB20-(NFO5-BFE3)	80	6.0×10^2	92	97	100
9	SOY45-St22-DVB25-(NFO5-BFE3)	96	9.4×10^2	69	93	100
10	SOY45-St17-DVB30-(NFO5-BFE3)	107	1.5×10^3	50	99	100
11	SOY45-St12-DVB35-(NFO5-BFE3)	100	2.9×10^3	33	100	100
12	SOY45-St07-DVB40-(NFO5-BFE3)	86	4.8×10^3	17	100	100
13	SOY45-St00-DVB47-(NFO5-BFE3)	72	5.7×10^3	8	100	100

and crosslinking density play very important roles in determining the shape memory properties. An increase in the SOY concentration results in a decreased rubbery modulus at the T_g plus 50°C (Fig. 2), which is inherently associated with the decreased crosslink density. A lower degree of crosslinking leads to a greater number of conformations that the polymer can adopt upon being loaded and deformed,²¹ thus enhancing the deformability as an elastomer at the higher temperatures. An increase in the SOY concentration also reduces the T_g due to the decreased rigidity of the polymer chains and crosslink density. Thus, the micro-Brownian motion of the polymer chains cannot be effectively frozen, which leads to a low percentage of fixed deformation at room temperature. As the T_g is reduced to the vicinity of room temperature, the room temperature modulus is equivalent to that of a rubbery material (10^6 Pa) and the polymer actually behaves like an elastomer with a very small amount of stable deformation fixed at ambient temperature (entry 3). For a typical shape memory material, the frozen Brownian motion is released upon being reheated and the extended polymer chain segments relax and return to the original random state. Lin and Chen found that less crosslinks lead to incomplete recovery of the deformed specimen.⁹ Note that the three polymers show 100% recovery of the fixed deformation upon reheating to the T_g plus 50°C, indicating that the crosslink density is high enough to effectively store and release the elastic energy in the shape memory process.

Unlike the flexible soybean oil molecule, the crosslinking agent DVB is a very rigid aromatic molecule with more reactive C—C bonds (Fig. 3). An increase in the DVB concentration increases the degree of crosslinking and the T_g values of the resulting polymers. Thus, contrary to the SOY concentration discussed above, an increase in the DVB concentration gradually reduces the deformability of the materials from 100 to 8% at the T_g plus 50°C and evidently enhances the ability of the polymers to subsequently fix their deformations as the FD increases from 23 to 100% at ambient temperature (Table II, entries 4–13). Complete shape recovery was obtained for all of these specimens. Optimal combinations of the shape memory properties are found in the two SOY polymers SOY45-St30-DVB17-(NFO5-BFE3) and SOY45-St27-DVB20-(NFO5-BFE3), which possess D , FD, and R values over 90% (entries 7, 8).

Aside from the chemical stoichiometry, the type of soybean oil employed also greatly affects the shape memory properties of the resulting polymers (Table III, entries 1–3). The three soybean oils used in this study (SOY, LSS, and CLS) have a similar triglyceride structure, but the compositions of the fatty acid side chains are varied (Table I). Specifically, the SOY has approximately 4.5 nonconjugated C=C bonds per triglyceride whereas the LSS has approximately 5.1 nonconjugated C=C bonds per triglyceride. Conjugation of the LSS does not change its triglyceride structure or the degree of unsaturation, but approximately 100% of the C=C bonds that can be con-

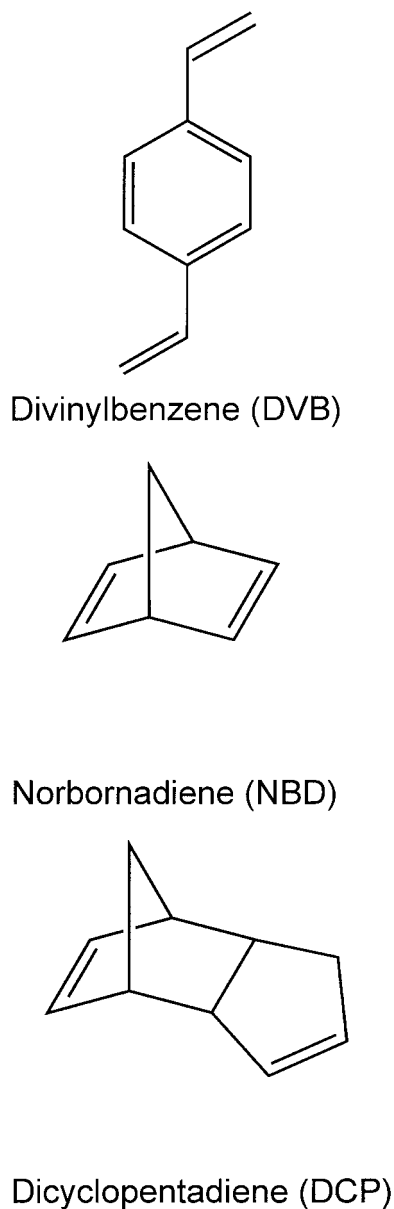


Figure 3 The molecular structures of the crosslinking agents divinylbenzene (DVB), norbornadiene (NBD), and dicyclopentadiene (DCP).

jugated are conjugated in the CLS. Thus, the reactivity toward cationic polymerization is SOY < LSS < CLS. Due to the triglyceride structure and multiple C=C bonds, the soybean oils also contribute to crosslinking like the crosslinking agent DVB. As a result, the CLS polymer possesses a higher degree of crosslinking and T_g than the corresponding SOY and LSS polymers.¹⁶ As expected, the more reactive soybean oil results in

a polymer with a higher FD value and a lower D value. Complete shape recovery is also obtained for the above three soybean oil polymers.

Despite the fact that 100% R is obtained for all of these materials, good shape memory polymers should also possess high D and FD results. It is known that the D and FD results are determined presumably by the crosslink densities and T_g values of the materials. A low crosslink density gives rise to a high D value but it significantly reduces the R whereas a high crosslink density greatly reduces the D value. In addition, a T_g well above ambient temperature is necessary to afford a high FD value. Thus, good shape memory materials should simultaneously possess appropriate combinations of T_g values and crosslink densities, which are high T_g values well above ambient temperature and moderate crosslink densities. Apparently, appropriate combinations of these properties cannot be readily achieved by employing different soybean oils or simply varying the chemical stoichiometries as previously mentioned. In the above cases the T_g values are enhanced to well above room temperature, which is usually accompanied by a significant increase in the crosslink densities. As a result, the D and FD values cannot be improved simultaneously. However, it is noted that, in addition to crosslinking, increasing the rigidity of the polymer backbones can also be an effective means to enhance the T_g . Thus, less reactive and more rigid crosslinking agents have to be employed so that the T_g values can be increased to well above the ambient temperature without significantly increasing the crosslink densities.

Figure 3 shows the molecular structures of the three crosslinking agents (DVB, NBD, and DCP) that we studied. It was found that DVB is the most reactive crosslinking agent whereas DCP is the least reactive crosslinking agent.¹⁵⁻¹⁷ However, the rigidity of the three comonomers in the resulting polymer chains appears to be DVB < NBD < DCP. We found that simple replacement of DVB with either NBD or DCP does not result in viable materials. Thus, mixed crosslinking agents were employed in our copolymerizations. Table III shows that, as expected, mixed crosslinking agents result in a polymer with a lower crosslink density (entry 4) than the corresponding pure DVB-based SOY polymer (entry 1). Although the increased rigidity of the polymer chains tends to enhance the T_g , the polymers are not apparently rigid enough to compensate for the

Table III Shape Memory Properties of Soybean Oil Polymers

Entry	Polymer	T_g (°C)	ν_e (mol/m ³)	Shape Memory Results (%)		
				<i>D</i>	FD	<i>R</i>
1	SOY45-St32-DVB15-(NFO5-BFE3)	68	1.8×10^2	100	80	100
2	LSS45-St32-DVB15-(NFO5-BFE3)	61	5.3×10^2	86	96	100
3	CLS45-St32-DVB15-(NFO5-BFE3)	76	2.2×10^3	77	98	100
4	SOY45-St32-(DVB5-NBD5-DCP5)-(NFO5-BFE3)	42	9.8×10	100	63	100
5	(SOY22.5-LSS22.5)-St32-(DVB5-NBD5-DCP5)-(NFO5-BFE3)	43	1.3×10^2	100	74	100
6	(SOY15-LSS15-CLS15)-St32-(DVB5-NBD5-DCP5)-(NFO5-BFE3)	44	2.7×10^2	100	75	100
7	SOY45-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	68	3.1×10^2	100	97	100
8	(SOY22.5-LSS22.5)-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	70	3.7×10^2	100	98	100
9	(SOY15-LSS15-CLS15)-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	74	5.2×10^2	100	99	100

T_g depression resulting from the decreased crosslink density. Thus, a high *D* value is observed, but a very low FD value is obtained. It was also found that the addition of more reactive soybean oils, such as LSS and CLS, does not apparently increase the T_g values and the shape memory results (entries 5, 6). Further increasing

the rigidity of the polymer chains appears to be necessary to achieve good shape memory results. Based on the above results, moderate crosslink densities and high T_g values, which were well above ambient temperature, were simultaneously obtained by appropriately increasing the concentration of the rigid crosslinking agents. Thus, the

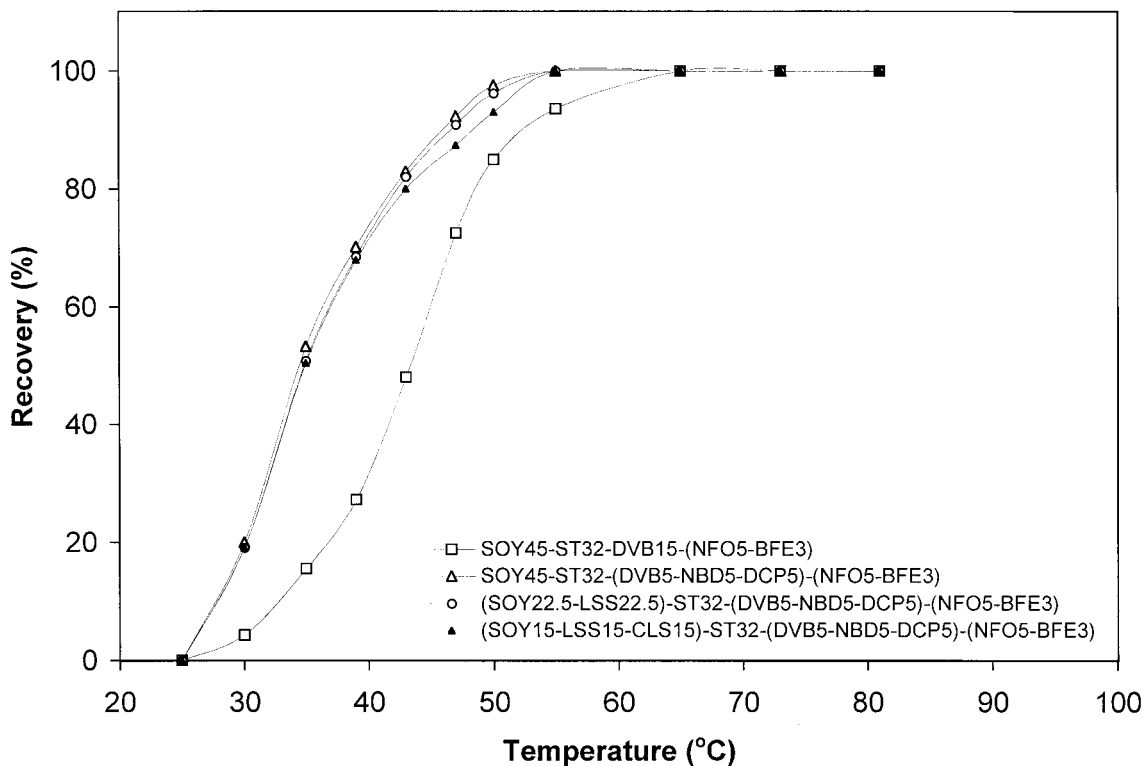


Figure 4 The shape recovery results for the polymers of entries 1 and 4–6 in Table III as a function of temperature.

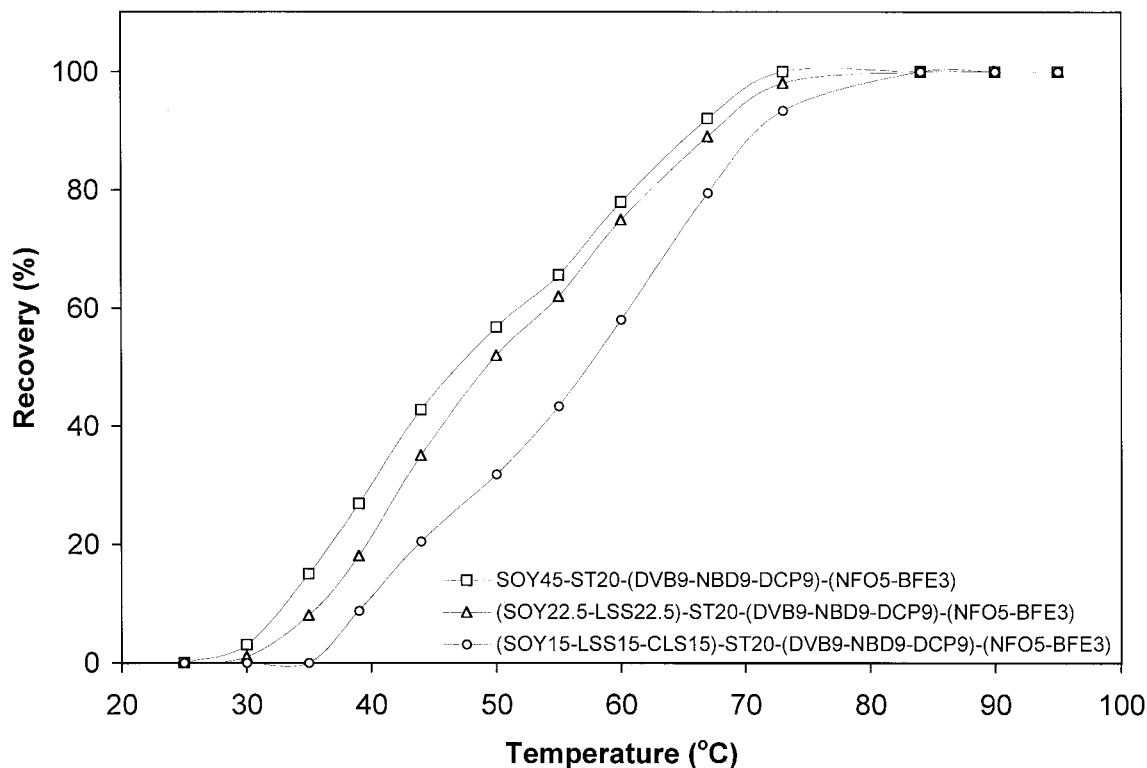


Figure 5 The shape recovery results for the polymers of entries 7–9 in Table III as a function of temperature.

resulting polymers show D , FD , and R values of over 97% and are apparently good shape memory materials (entries 7–9).

Figure 4 gives the shape recovery results at various temperatures for the soybean oil polymers of entries 4–6 in Table III. All of the polymers appear to show shape recovery behavior similar to one another. The SOY45-St32-DVB15-(NFO5-BFE3) polymer exhibits shape recovery at a relatively high temperature, and 100% shape recovery is reached at about 65°C. The other three specimens based on mixed crosslinking agents show shape recovery results that essentially overlap, and complete shape recovery is reached at about 55°C. Note that the onset of shape recovery is observed at temperatures slightly higher than ambient temperature, making the fixed deformations relatively unstable at room temperature. Thus, the polymers afford FD values of 63–75% (Table III, entries 4–6), which make these materials inferior shape memory materials. As previously discussed, by increasing the concentration of the mixed crosslinking agents, the resulting plastics possess appropriate combi-

nations of T_g values and crosslink densities, thus improving their shape memory properties. Figure 5 shows that the polymers of entries 7–9 in Table III not only possess high D and FD values (>97%) but also exhibit much better shape recovery processes. No significant shape recovery is observed at temperatures slightly higher than ambient temperature, making the fixed deformations relatively stable at room temperature. Upon being reheated, complete shape recovery is achieved at approximately 85°C. Thus, the materials appear to be more suitable for applications at room temperature. Figure 6 shows the dynamic mechanical behavior of the soybean oil polymers shown in Figure 5. Apparently, the wide temperature region for the shape recovery process is ascribed primarily to the broad glass transitions of the materials. The initial shape recovery processes are inherently related to the onset of segmental motion (glass transition) of the soybean oil polymers. Because the shape recovery was measured in steps at different temperatures but the DMA was carried out by heating the samples continuously, the shape recovery processes do not cover

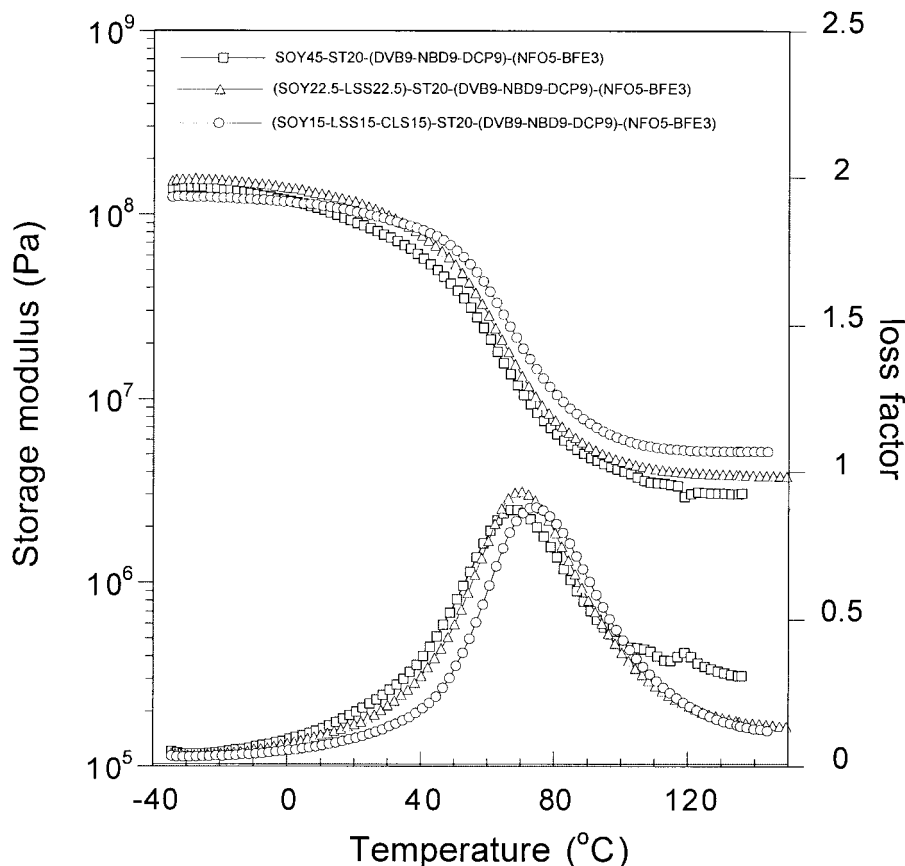


Figure 6 The dynamic mechanical behavior of the soybean oil polymers in Figure 5

exactly the same temperature regions as the corresponding glass transitions.

The shape recovery process of the materials at each temperature may be modeled by the viscoelastic behavior of the polymers. In the deformation of a linear viscoelastic polymer, the total strain (ϵ_T) can be described by a series combination of the Maxwell and Kelvin–Voigt models,^{21,22} which is used to predict the creep and recovery behavior of viscoelastic materials:

$$\begin{aligned} \epsilon_T &= \epsilon_1 + \epsilon_2 + \epsilon_3 \\ &= \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \left[1 - \exp\left(-\frac{E_2 t}{\eta_2}\right) \right] + \frac{\sigma t}{\eta_3} \quad (1) \end{aligned}$$

Here ϵ_1 is the instantaneous elastic deformation resulting from covalent bond stretching and the distortion of bond angles; ϵ_2 is the delayed elastic deformation resulting from micro-Brownian motion of the polymer chains; and ϵ_3 is the irreversible strain resulting from Newtonian flow, which

is identical to the deformation of a viscous liquid obeying Newton's law of viscosity. For the shape memory soybean oil polymers, the deformation and shape recovery are conducted in a rubbery state, and the final recovery of the fixed deformation was found to be essentially 100%. Thus, $\epsilon_1 \ll \epsilon_2$ and $\epsilon_3 = 0$. The total strain can be defined as in eq. (2):

$$\begin{aligned} \epsilon_T &= \frac{\sigma}{E_2} \left[1 - \exp\left(-\frac{E_2 t}{\eta_2}\right) \right] \\ &= \frac{\sigma}{E_2} \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (2) \end{aligned}$$

where τ is the retardation time and $\tau = \eta_2/E_2$. Because of the heterogeneity of the copolymer chains, a single retardation time is not sufficient to describe the deformation and shape recovery of the viscoelastic polymers. In fact, a viscoelastic polymer involves a spectrum of retardation times

Table IV Repeatability of Shape Memory Behavior of Soybean Oil Polymers

Shape Memory Polymer	Shape Memory Results (%)	Shape Memory						
		1st	2nd	3rd	4th	5th	6th	7th
SOY45-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	<i>D</i>	100	100	100	100	100	100	100
	FD	97	95	94	93	90	90	89
	<i>R</i>	100	100	100	100	100	100	100
(SOY22.5-LSS22.5)-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	<i>D</i>	100	100	100	100	100	100	100
	FD	98	96	93	93	90	90	89
	<i>R</i>	100	100	100	100	100	100	100
(SOY15-LSS15-CLS15)-St20-(DVB9-NBD9-DCP9)-(NFO5-BFE3)	<i>D</i>	100	100	100	100	100	100	100
	FD	99	97	93	93	89	90	90
	<i>R</i>	100	100	100	100	100	100	100

following a Gaussian distribution. Thus, the deformation is rewritten as follows.

$$\varepsilon_T(t) = \sum_{i=1}^n \varepsilon_i(\infty) \left[1 - \exp\left(-\frac{t}{\tau_i}\right) \right] \quad (3)$$

Here the $\varepsilon_i(\infty)$ is the equilibrium strain when time is infinity. Therefore, the shape recovery at a certain temperature is actually described by a number (n) of Voigt–Kelvin models joined in series. At a temperature below the glass transition polymer segmental motions are frozen and all of the retardation times (τ_1 to τ_n) are equal to infinity. Thus, no shape recovery is observed. At a temperature within the glass-transition region the retardation times of some segments become measurable whereas others approach infinity. The elastic response is retarded by the viscous resistance of the material, and only partial shape recovery is observed. At a temperature well above the glass transition complete shape recovery is achieved because of the shortening of all of the retardation times (τ_1 to τ_n).

Table IV shows the relationship between the shape memory properties and the number of times the three polymers in Figure 5 were tested. The FD values of the polymers slowly decrease and reach steady values after about five tests. The *D* and *R* values approach 100% and are not evidently affected by the number of tests. Apparently, each of the three polymers show very good reusability as a shape memory material.

CONCLUSIONS

A series of new polymers were prepared by the cationic copolymerization of SOY, LSS, and/or CLS with St and DVB, NBD, or DCP initiated by the BFE initiator or related modified initiators. The shape memory properties of the soybean oil polymers were investigated in relation to the chemical stoichiometry and the type of oil and comonomers employed. The shape memory properties are closely related to the crosslinking densities and glass-transition temperatures. By achieving appropriate combinations of crosslink densities and glass-transition temperatures through structural design of the polymer chain rigidity, soybean oil polymers exhibiting good shape memory effects with high deformability, degree of fixed deformation, and final shape recovery results can be prepared. In addition, these new shape memory polymers also showed good reusability.

The authors are grateful to the Iowa Soybean Promotion Board for financial support. We also thank Dr. J. Jane of the Food Science & Human Nutrition Department and Dr. V. Sheares of the Chemistry Department at Iowa State University for use of their equipment.

REFERENCES

1. Wei, Z. G.; Sanstrom, R.; Miyazaki, S. *J Mater Sci* 1998, 33, 3743.
2. Ota, S. *Radiat Phys Chem* 1981, 18, 81.

3. Tobushi, H.; Hayashi, S.; Kojima, S. *JSME Int J* 1992, 35, 296.
4. Takahashi, T.; Hayashi, N.; Hayashi, S. *J Appl Polym Sci* 1996, 60, 1061.
5. Li, F.; Hou, J.; Zhu, W.; Zhang, X.; Xu, M.; Luo, X.; Ma, D.; Kim, B. K. *J Appl Polym Sci* 1996, 62, 631.
6. Kim, B. K.; Lee, S. Y.; Xu, M. *Polymer* 1996, 37, 5781.
7. Li, F.; Zhang, X.; Hou, J.; Xu, M.; Luo, X.; Ma, D.; Kim, B. K. *J Appl Polym Sci* 1997, 64, 1511.
8. Kim, B. K.; Lee, S. Y.; Lee, J. S.; Baek, S. H.; Choi, Y. J.; Xu, M. *Polymer* 1998, 39, 2803.
9. (a) Lin, J. R.; Chen, L. W. *J Appl Polym Sci* 1998, 69, 1563; (b) Lin, J. R.; Chen, L. W. *J Appl Polym Sci* 1998, 69, 1575; (c) Lin, J. R.; Chen, L. W. *J Appl Polym Sci* 1999, 73, 1305.
10. Kim, B. K.; Young, J. S.; Seong, M. C.; Han, M. J. *J Polym Sci Part B Polym Phys* 2000, 38, 2652.
11. Luo, X.; Zhang, X.; Wang, M.; Ma, D.; Xu, M.; Li, F. *J Appl Polym Sci* 1997, 64, 2433.
12. Li, F.; Chen, Y.; Zhu, W.; Zhang, X.; Xu, M. *Polymer* 1998, 39, 6929.
13. Jeon, H. G.; Mather, P. T.; Haddad, T. S. *Polym Int* 2000, 49, 453.
14. Li, F.; Hanson, M. V.; Larock, R. C. *Polymer* 2001, 42, 1567.
15. Li, F.; Larock, R. C. *J Appl Polym Sci* 2001, 80, 658.
16. Li, F.; Larock, R. C. *J Polym Sci Part B Polym Phys* 2000, 38, 2721.
17. Li, F.; Larock, R. C. *J Polym Sci Part B Polym Phys* 2001, 39, 60.
18. Li, F.; Larock, R. C. *Polym Adv Technol*, to appear.
19. Larock, R. C.; Dong, X.; Chung, S.; Reddy, Ch. K.; Ehlers, L. E. *J Am Oil Chem Soc* 2001, 78, 447.
20. Kinloch, A. J.; Young, R. J. *Fracture Behavior of Polymers*; Applied Science Publishers: New York, 1983; p 25.
21. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994.
22. Vard, I. M.; Hadley, D. W. *An Introduction to the Mechanical Properties of Solid Polymers*; Wiley: New York, 1993.