ELSEVIER

Polymer 42 (2001) 1567–1579

polymer

www.elsevier.nl/locate/polymer

Soybean oil–divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships

F. Li, M.V. Hanson, R.C. Larock*

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

Received 17 February 2000; received in revised form 24 April 2000; accepted 12 July 2000

Abstract

The cationic copolymerization of regular soybean oil, low saturation soybean oil (LoSatSoy) and conjugated LoSatSoy oil with divinylbenzene initiated by boron trifluoride diethyl etherate ($BF_3\cdot OEt_2$) or related modified initiators provides polymers ranging from soft rubbers to hard plastics, depending on the reagents, stoichiometry and initiators used. Nuclear magnetic resonance spectroscopy and dynamic mechanical analysis (DMA) indicate that the resulting polymers are typical thermosets. The structure of the bulk polymer is that of a densely crosslinked polymer network mixed with a certain amount of less saturated free oil. The moduli of the bulk polymers are approximately 4×10^8–1×10^9 Pa at room temperature, which are comparable to those of conventional plastics. Typically, micro-phase separation occurs in soybean oil and LoSatSoy polymers as evidenced by the appearance of two glass transition temperatures α_1 and α_2; α_1 (approximately 80°C) is the glass transition temperature of the crosslinked polymer, and α_2 (approximately 0°C) corresponds to the solid–liquid transition (glass transition) of the oil-rich phase in the bulk polymer. In the conjugated LoSatSoy polymers, the crosslinked polymer network becomes more compatible with the unreacted free oil. Three distinct decomposition temperature regions of the thermosets are observed by thermogravimetric analysis (TGA): 200–400°C, 400–530°C, and above 530°C. These regions correspond to evaporation and decomposition of the unreacted free oil, degradation and char formation of the crosslinked polymer network, and subsequent oxidation of the char residues in air, respectively. The thermal stability of these polymers is found to be largely dependent on the amount of unreacted free oil in the bulk polymer. The conjugated LoSatSoy polymers have the highest moduli and thermal stabilities, since they contain the least unreacted free oil. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Soybean oil; Cationic copolymerization; Thermal analysis

1. Introduction

The environment is being overwhelmed by non-biodegradable, petroleum-based polymeric materials [1,2]. The growing demand for such materials has increased our dependence on crude oil and left our highways, beaches and landfills overflowing with these non-renewable, indestructible materials. The current interest in cheap, biodegradable polymeric materials has recently encouraged the development of such materials from readily available, renewable, inexpensive natural sources, such as carbohydrates, starch and proteins. However, relatively little work has been reported on the conversion of fats and oils to high molecular weight polymers [3,4].

Soybean oil is a biodegradable vegetable oil dominating today's food oil market. About 80% of the soybean oil produced each year is used for human food. Another 6% is used for animal feed, while the remainder (14%) finds nonfood uses (soap, fatty acids, lubricants, coatings, etc.) [5]. The polyunsaturation of soybean oil and low saturation soybean oil (LoSatSoy), with still higher polyunsaturated fatty acid content [6], makes it possible to polymerize or copolymerize these natural oils into useful new materials. Boron trifluoride has been used to initiate polymerization of the methyl esters of the fatty acids of soybean oil [7]. The polymeric oils obtained are dark in color, have high acid numbers and a viscosity of *P* or above on the Gardner scale. Boron trifluoride ether complexes of dimethyl ether, diethyl ether, dioxane and tetrahydrofuran have also been used as initiators. These initiators produce polymeric oils at 120–160°C with improved color. Polymerization of the free fatty acids of soybean oil has also been initiated by boron trifluoride. The products are extremely viscous, but crosslinked gels are not obtained [8]. Soybean oil itself has been directly used as an adhesive in the manufacture of pressboard [9]. However, all reports on the polymerization of soybean oil materials that have appeared in the literature

---

* Corresponding author. Tel.: +1-515-294-6342; fax: +1-515-294-0105.
E-mail address: larock@iastate.edu (R.C. Larock).

PII: S0032-3861(00)00546-2

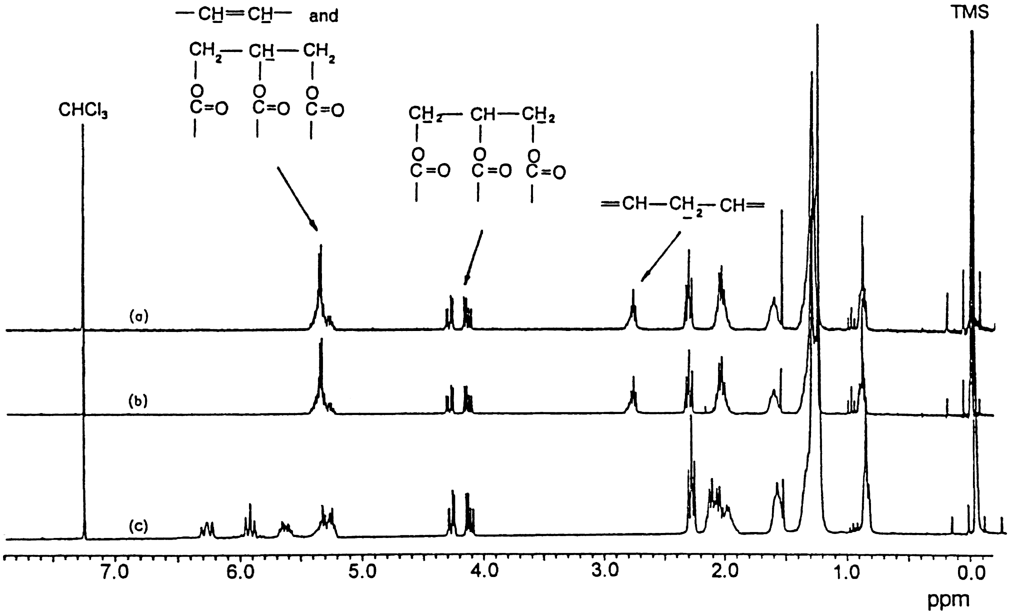

Fig. 1. ^{1}H NMR spectra of: (a) Wesson soybean oil; (b) LoSatSoy oil; and (c) conjugated LoSatSoy oil.

so far have been concerned with the production of viscous oils, produced primarily by the polymerization or copolymerization of the fatty acids obtained from soybean oil.

The present work reports the direct conversion of soybean oils themselves to useful solid polymers. We thus report our progress in understanding the synthesis–structure–property relationships of the thermosetting polymers prepared directly from soybean oil, LoSatSoy oil and conjugated LoSatSoy oil by cationic polymerization initiated by boron trifluoride diethyl etherate and modified initiating systems. The advantages of these polymer materials are their low cost, availability from a renewable natural resource, and their possible biodegradability.

2. Experimental

2.1. Materials

The natural oils used in this study are food-grade soybean oil and LoSatSoy oil commercially available in supermarkets. They have both been used without further purification. The conjugated LoSatSoy oil was prepared by the rhodium-catalyzed isomerization of the regular LoSatSoy oil [10]. The percent conjugation is calculated to be approximately 100%. The 80% divinylbenzene comonomer purchased from Aldrich Chemical Company was a mixture of isomers, and used as received. The distilled grade boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) used to initiate cationic polymerization of the various soybean oils was also supplied by Aldrich. Norway Pronova fish oil ethyl ester (EPAX 5500EE), soybean oil methyl esters (Soygold-1100 and Soygold-2000, AG Environmental Products, L.L.C.) and tetrahydrofuran (THF) (Aldrich) were used to modify the original initiator. The reference polymers used in this study are polystyrene (Grd #210, Huntsman Corp.), low-density polyethylene (Paxon 3205, Viskase Corp.) and an epoxy resin (Perkin–Elmer sample).

2.2. Cationic copolymerization

The following reaction procedure was usually employed, unless otherwise stated in the text. The desired amount of divinylbenzene comonomer was added to the soybean oil. The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of the initiator, and then sealed under air. The total amount of reactants was typically 4 g. The sealed reaction mixture was heated for a given time at the appropriate temperatures, routinely 12 h at room temperature, 12 h at 60°C and then 24 h at 100°C. The nomenclature adopted in this work for the samples is as follows: SOY, LSS and CLS represent regular soybean oil, LoSatSoy oil and conjugated LoSatSoy oil, respectively; DVB is the divinylbenzene comonomer; BFE is boron trifluoride diethyl etherate; NFO, SGI and SGII are the Norway fish oil ethyl ester, Soygold-1100 and Soygold-2000, respectively. For example, LSS50–DVB35–(SGI10-BFE5) corresponds to a polymer sample prepared from 50 wt% LoSatSoy oil, 35 wt% divinylbenzene and 15 wt% SGI-modified BFE initiator (10 wt% Soygold-1100 plus 5 wt% boron trifluoride diethyl etherate).

2.3. Soxhlet extraction by methylene chloride

A 2 g sample of the bulk polymer was extracted with 100 ml of refluxing methylene chloride using a Soxhlet extractor for 24 h. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances were isolated for

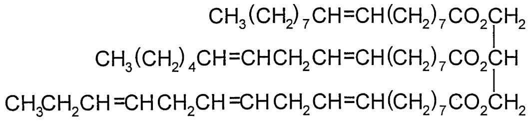

Fig. 2. Typical triglyceride structure for soybean oil.

further characterization. The insoluble solid was dried under vacuum for several hours before weighing.

2.4. Characterizations

Dynamic mechanical analysis data were obtained using a Perkin–Elmer dynamic mechanical analyzer DMA Pyris-7e in a three-point bending mode. The rectangular specimens were made by copolymerizing the reactants in an appropriate mould. Thin sheet specimens of 1 mm thickness and 2.5 mm depth were used, and the width to depth ratio was maintained at approximately 5. The measurements were performed at a heating rate of 3°C/min and a frequency of 1 Hz in helium (20 ml/min).

A Perkin–Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the polymeric materials in air (20 ml/min). The samples were heated from 30 to 650°C at a heating rate of 20°C/min. All ^{1}H NMR spectra were recorded in $CDCl_3$ using a Varian Unity spectrometer at 300 MHz.

3. Results and discussion

3.1. Molecular structures and the homopolymerization of soybean oil, LoSatSoy oil and conjugated LoSatSoy oil

Fig. 1 shows the ^{1}H NMR spectra of (a) soybean oil and (b) LoSatSoy oil. The peaks at 4.1–4.4 ppm originate from the protons in the methylene groups of the triglyceride. The vinylic hydrogens are detected at 5.2–5.5 ppm. The protons in the CH_2 groups between two carbon–carbon double bonds appear at 2.7–2.8 ppm. Soybean oil is calculated from the ^{1}H NMR spectrum to have approximately 4.5 carbon–carbon double bonds per triglyceride, while LoSatSoy has a relatively high degree of unsaturation, approximately 5.1 carbon–carbon double bonds per triglyceride. The molecular structure of soybean oil is illustrated in Fig. 2. The three side chains of the triglyceride are typically composed of esters comprising 20–30% oleic acid (one C=C), 50–58% linoleic acid (two C=C) and 5–10% linolenic acid (3 C=C). The structure of the LoSatSoy oil is similar to that of the soybean oil, but with more carbon–carbon double bonds in the triglyceride side chains. The high degree of unsaturation in these oils makes the cationic polymerization of these natural oils possible [11].

Complexes of boron trifluoride diethyl etherate have proven to be particularly effective initiators for cationic polymerization [11–14]. However, due to the relatively high molecular weight and the multiple chain structures of these natural oils, their reactivity towards cationic homopolymerization using boron trifluoride diethyl etherate as the initiator is rather low. Furthermore, the soybean oils have been found to be immiscible with the initiator employed. Thus, the $BF_3 \cdot OEt_2$ initiated homopolymerization of pure soybean oil or LoSatSoy oil has proven relatively difficult.

By conjugating the carbon–carbon double bonds in the triglyceride side chains of the natural oil, their reactivity can be significantly improved [15]. Fig. 1c is the ^{1}H NMR spectrum of the conjugated LoSatSoy oil. Compared with that of regular LoSatSoy oil in Fig. 1b, the ^{1}H NMR spectrum of the conjugated LoSatSoy oil clearly shows that some of the vinylic hydrogens (5.36 ppm) have moved downfield (5.61–6.33 ppm) upon conjugation. The peak at 2.76 ppm, which corresponds to the protons in the CH_2 groups between two carbon–carbon double bonds, completely disappears. The percent conjugation, which is calculated by integrating the vinylic hydrogens (5.36/5.61–6.33 ppm) in the conjugated LoSatSoy oil and taking into account the known fatty acid composition of this oil, is approximately 100%. Note that conjugation does not change the triglyceride structure. The miscibility of this conjugated oil and the $BF_3 \cdot OEt_2$ initiator is still poor. Although the relatively high reactivity of the conjugated LoSatSoy oil may result in some reaction at the interface, the resulting polymers are rather weak.

3.2. Heterogeneous copolymerization of soybean oil, LoSatSoy oil and conjugated LoSatSoy oil with divinylbenzene

Rigid, hard polymers have been produced by cationic copolymerization of the various soybean oils with the more reactive divinylbenzene, which is a monomer suitable for cationic polymerization [11]. Divinylbenzene has a lower molecular weight and a much higher density of carbon–carbon double bonds per molecule than the various soybean oils. Conjugation of the two double bonds with the phenyl group in this molecule makes this comonomer quite reactive towards cationic polymerization. In fact, addition of 0.1 wt% of the $BF_3 \cdot OEt_2$ initiator to pure divinylbenzene produces a very rapid, almost explosive, reaction. Fortunately, the copolymerization of mixtures of divinylbenzene with the less reactive soybean oil results in moderate reactions and hard plastic materials when 10–40% divinylbenzene is employed.

However, for all of the regular soybean oil compositions examined, the reactions are heterogeneous. It is known that the regular soybean oil is completely miscible with divinylbenzene. As the initiator is added with stirring to the homogeneous soybean oil/divinylbenzene solution, a large number of small, solid, white particles promptly appear and precipitate to the bottom. The higher the divinylbenzene concentration in the original composition, the more white particles observed. The residual solution is at first brown in color. After some time, the brown colored solution gels. The resulting polymer samples are then dark brown, but heterogeneous with a hard bottom. Microscopic studies have shown that these particles are not able to serve as active polymerization centers once they are formed during the reaction, and subsequent copolymerization happens solely in the residual solution. From previous results, it has been shown that the cationic polymerization of soybean oil itself does not produce solid polymers. However, the comonomer divinylbenzene is very reactive. Thus, these white particles are no doubt divinylbenzene homopolymers.

Unfortunately, the heterogeneous reactions have the following disadvantages. First, the properties of the polymers are difficult to control experimentally. Typically, these white solid particles precipitate to the bottom before the residual solution starts to gel. Therefore, the densities are not identical in the resulting bulk polymers, and the mechanical properties of the polymers are different in various parts of the bulk material. This is unfavorable from a material design standpoint. Another disadvantage is the inefficiency in consuming the starting materials. It is well known that thermosetting polymers derive their strength and characteristics through crosslinking [26]. The divinylbenzene comonomer plays an important role in the resulting crosslinked polymer-structure of our materials. In the heterogeneous reactions, some divinylbenzene comonomer is consumed before copolymerization of the matrix occurs. Thus, less divinylbenzene is available for copolymerization with the soybean oil. The resulting polymers are, therefore, relatively soft and weak.

There are two possible reasons for the heterogeneous nature of these copolymerization reactions. One is the big difference in the reactivity of the soybean oil and the divinylbenzene comonomer. Pure divinylbenzene results in very fast reactions. However, the reactivity of the carbon–carbon double bonds in the soybean oil is much lower. In fact, no evidence for homopolymerization of the soybean oil has been obtained after the initiator is added. Thus, in these copolymerization mixtures, divinylbenzene comonomers tend to react first with themselves, which results in the heterogeneous reactions observed above. The other reason for the heterogeneity is the poor miscibility of the initiator and the soybean oil as previously discussed. On the other hand, divinylbenzene is completely miscible with the initiator and very fast homopolymerization can occur. Thus, when the initiator is added to the mixture of the soybean oil and divinylbenzene, the initiator prefers to interact with the divinylbenzene, which is very reactive. Thus, a lot of solid white particles are observed during the early stages of copolymerization.

To better understand what is causing the heterogeneous reactions, we performed the copolymerization of several more reactive oils and divinylbenzene. LoSatSoy oil and conjugated LoSatSoy oil are more reactive cationically than the regular soybean oil [11,14,16]. However, a lot of solid white particles still appear during their copolymerization with divinylbenzene. Tung oil is another much more reactive-triglyceride oil with about 7.5 carbon–carbon double bonds per triglyceride. More than 80% of those double bonds are conjugated, primarily as a conjugated triene [27]. Pure tung oil becomes solid shortly after addition of the initiator. Thus, its reactivity is comparable to that of divinylbenzene. However, reactions involving mixtures of tung oil and divinylbenzene are still not homogeneous.

The reactivity of the regular soybean oil and divinylbenzene may be controlled by the reaction temperature. However, our results indicate that white particles still precipitate during copolymerization with divinylbenzene, even at -20 to 30°C.

The size of the particles formed can be substantially reduced by modifying the reaction procedure. For example, half of the soybean oil was mixed with divinylbenzene (M-I), and the other half of the soybean oil was mixed (even though immiscible) with the initiator (M-II). Mixture M-I was then slowly added to mixture M-II with stirring or vice versa. Much finer particles were observed. However, these experiments do not tell us whether the revised procedure decreases the amount of divinylbenzene available for homopolymerization, or simply decreases the particle size, but the amount of the divinylbenzene consumed as solid white particles remains unchanged.

3.3. Homogeneous copolymerization of soybean oil, LoSatSoy oil and conjugated LoSatSoy oil with divinylbenzene

From the above discussion, it follows that the poor miscibility between the soybean oil and the initiator, rather than the difference in the reactivities between the oils and divinylbenzene, is the main reason for the heterogeneous copolymerization reactions. If so, improvement in the miscibility in this system should solve the heterogeneity problem.

We have previously reported that Norway fish oil ethyl ester (EPAX 5500EE) is miscible with both the initiator and soybean oil [16,17]. Thus, a certain amount of this fish oil should be effective in improving the miscibility in these systems. Our results show that the copolymerization of soybean oil/fish oil mixtures with divinylbenzene results in a homogeneous reaction when the ratio of fish oil to soybean oil reaches 50/50 (w/w). This further confirms our hypothesis that poor miscibility in these systems is the origin of the heterogeneous reactions.

To more effectively use the cheaper, more abundant soybean oil, it is important to understand the mechanism by which this initiation process and subsequent polymerization occurs. The $BF_3 \cdot OEt_2$ initiator is substantially more soluble in the fish oil ethyl ester, and can initiate polymerization of the fish oil [16,17]. Despite rapid initiation, the chain propagation is slow due to the relatively high molecular weight and low reactivity of the fish oil ethyl ester. Thus, the mixture of fish oil and the original initiator provides a cationically active initiating system that is

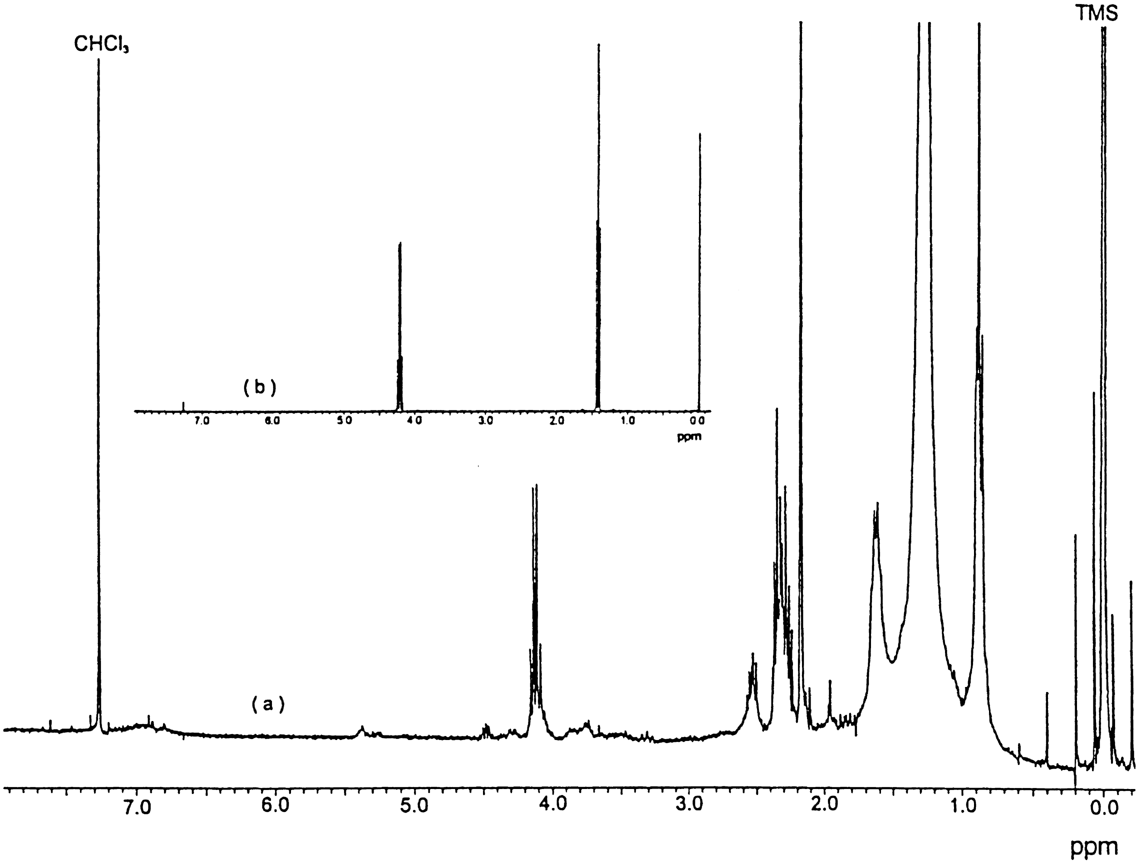

Fig. 3. ^{1}H NMR spectra of: (a) the oil extracted from the sample SOY60–DVB35–BFE5; and (b) original BF_3·OEt_2 initiator.

mutually miscible in the various soybean oils employed in this study and the divinylbenzene comonomer. This modified initiator employing small amounts of fish oil ethyl ester leads to materials that are essentially homogeneous.

The heterogeneity problems have been greatly diminished by using as low as 3 wt% fish oil ethyl ester in the modified initiator. When the fish oil ethyl ester contributes 5 wt% to the modified initiator, the reacting solution becomes homogeneous with very few fine white particles. Completely homogeneous reactions have been obtained when the initiator is modified by 10 wt% fish oil ethyl ester. Apparently, 10 wt% fish oil-modified initiator is also necessary to achieve homogeneous reactions in the LoSatSoy oil and conjugated LoSatSoy oil systems also. In addition to the Norway fish oil ethyl ester, soybean oil methyl esters (Soygold) are also miscible with the triglyceride soybean oils and boron trifluoride diethyl etherate. Thus, they have also been used to modify the initiator in the same way as the fish oil. The results are similar to those of the reactions employing fish oil-modified initiators.

3.4. Microstructures of the thermosetting polymers

The polymers in this study are thermosets due to crosslinking through the multiple carbon–carbon double bonds present in the soybean oils and the comonomer divinylbenzene [20]. Soxhlet extraction results have been used to study the microstructures of the bulk polymers with methylene chloride as the refluxing solvent. The extracted soluble oily substances range from 12 to 31 wt% and appear to be unreacted free oil and initiator fragments. Fig. 3a shows the ^{1}H NMR spectrum of the soluble materials extracted from the bulk polymer SOY60–DVB35–BFE5. The triglyceride protons (4.2–4.5 ppm) of the oil and evidence of initiator fragments (4.1–4.2 ppm) are observed (also refer to Fig. 3b). The weak peaks at 5.2–5.5 ppm indicate that the extracted oils are much less unsaturated than the soybean oils originally employed.

The insoluble substances remaining after Soxhlet extraction, which range from 69 to 88 wt%, are crosslinked polymers. These materials are highly crosslinked and are not soluble in solvents such as THF and CH_2Cl_2. All of the divinylbenzene employed has been incorporated into the crosslinked network as evidenced by the absence of peaks due to divinylbenzene in the ^{1}H NMR spectrum of the extracted oils. Our extraction results suggest that considerable amounts of the soybean oils have participated in the copolymerization and been incorporated into the crosslinked polymer network. The above results suggest that the structure of the bulk polymer is that of a crosslinked polymer network mixed with a certain amount of more saturated free oil.

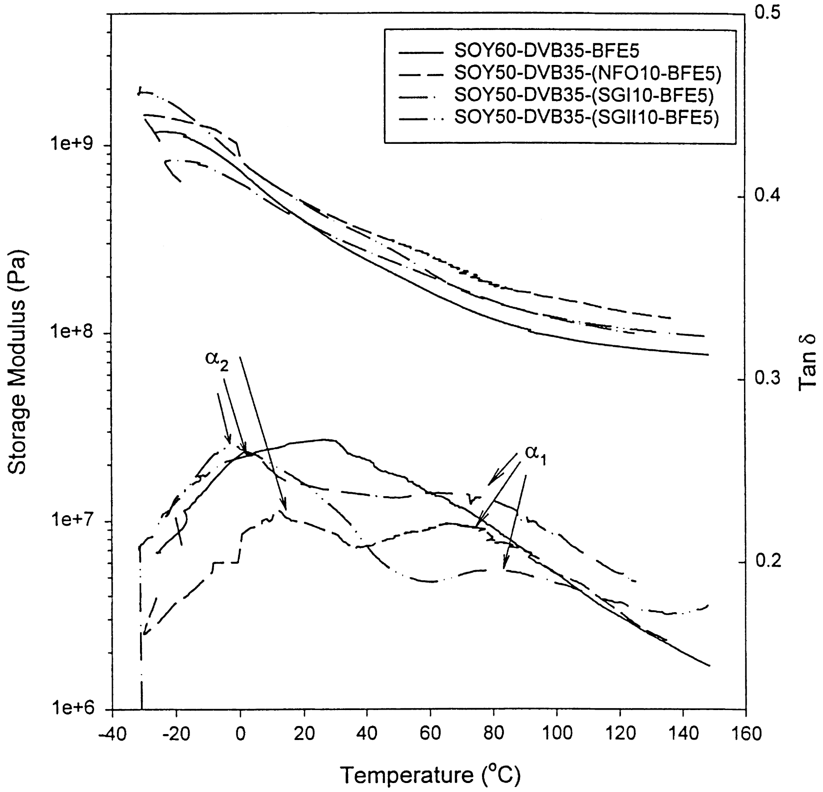

Fig. 4. Temperature dependence of the storage modulus E' and loss factor tan δ for the soybean oil polymers prepared using various modified initiators.

The polymer structure is in fact determined by many factors, including the initiating systems, the soybean oil used, and the stoichiometry. The heterogeneous materials prepared from the original initiator possess a lower amount of crosslinked polymer than the materials produced by using modified initiators with the same stoichiometry. The yield of crosslinked polymers obviously increases with increasing divinylbenzene concentration in the original composition. The conjugated LoSatSoy oil produces higher yields of crosslinked polymers than the regular soybean oil and LoSatSoy oil with the same stoichiometry.

3.5. Dynamic mechanical properties

Fig. 4 shows the temperature dependence of the storage modulus E' and loss factor tan δ for the regular soybean oil polymers. The homogeneous polymers prepared using various modified initiators are compared to the heterogeneous sample SOY60–DVB35–BFE5. The loss factor behavior of all of the polymers prepared from the modified initiators is very similar. The loss factor peak at about 80°C corresponds to the α relaxation, the glass transition of the crosslinked polymer network, which is mainly due to the contribution of segments of soybean oil and divinylbenzene copolymers in the crosslinked network. The broad transition range indicates that the segmental movements in these crosslinked molecules are rather extensive upon crosslinking. Another loss factor peak appears at about 0°C. Although some authors have reported the appearance of β relaxation at the beginning of α relaxation in some other thermosetting polymers [21,22], such β relaxation peaks have generally consisted of only a shoulder or a much less intense tan δ peak in the dynamic mechanical behavior. Thus, the intense tan δ peaks at approximately 0°C in this study cannot be simply ascribed to β relaxation of the thermosetting polymers. As has been previously discussed, the structure of the polymer bulk is mainly composed of two parts: chemically crosslinked polymer molecules and unreacted free oil. In fact, the solid–liquid transition of the soybean oils themselves is about 0–10°C, which is in the same temperature region as the second loss factor peak of our bulk polymers. Thus, the peak at 0°C appears to be due to the glass transition of the unreacted free oil in the bulk polymer. That is to say, two α relaxations appear; α_1 corresponds to the glass transition temperature of the crosslinked polymer molecules at approximately 80°C and α_2 at approximately 0°C is due to the solid–liquid transition (glass transition) of the unreacted free oil present in the polymer. In other words, micro-phase separation occurs during cationic copolymerization initiated by the modified initiators. In the resulting polymers, one phase is the matrix mainly composed of crosslinked polymer molecules, while another phase is the free oil-rich domains statistically distributed throughout the polymer matrix.

Within the temperature range tested, the storage modulus E' shows a gradual drop with increasing temperature

Table 1
DMA, TGA and Soxhlet extraction results

Entries	Polymer sample	E_{room} (Pa)	ν_e (mol/m^3)	T_g (°C)		Structure (wt%)			TGA (°C)	
				α_1	α_2	Crosslinked	Free oil	Inc. oil[a]	T_{10}	T_{50}
1	SOY60–DVB35–BFE5	4.0×10^8	7.60×10^3	27	–	69	31	29	415	490
2	SOY50–DVB35–(NFO10-BFE5)	5.0×10^8	1.16×10^4	70	10	77	23	37	425	491
3	SOY50–DVB35–(SGI10-BFE5)	4.9×10^8	9.52×10^3	83	−5	74	26	34	419	490
4	SOY50–DVB35–(SGII10-BFE5)	4.0×10^8	9.48×10^3	70	5	74	26	34	418	489
5	LSS60–DVB35–BFE5	6.0×10^8	1.04×10^4	37	–	82	18	42	423	485
6	LSS50–DVB35–(NFO10-BFE5)	7.0×10^8	1.30×10^4	70	0	84	16	44	425	486
7	LSS50–DVB35–(SGI10-BFE5)	4.2×10^8	9.71×10^3	65	20	74	26	34	422	487
8	LSS50–DVB35–(SGII10-BFE5)	4.7×10^8	9.70×10^3	70	20	76	24	36	421	486
9	SOY55–DVB30–(NFO10-BFE5)	2.5×10^8	6.51×10^3	15	5	75	25	40	380	475
10	SOY60–DVB25–(NFO10-BFE5)	1.7×10^8	4.18×10^3	20	0	73	27	43	360	470
11	LSS55–DVB30–(NFO10-BFE5)	3.8×10^8	8.35×10^3	30	8	80	20	45	405	486
12	LSS60–DVB25–(NFO10-BFE5)	1.9×10^8	4.18×10^3	17	0	77	23	47	395	485
13	CLS50–DVB35–(NFO10-BFE5)	1.2×10^9	1.89×10^4	90	–	88	12	48	440	485
14	CLS55–DVB30–(NFO10-BFE5)	1.0×10^9	1.14×10^4	80	–	86	14	51	436	486
15	CLS60–DVB25–(NFO10-BFE5)	7.8×10^8	7.21×10^3	68	–	86	14	56	433	483

[a] Wt% of oil incorporated into the crosslinked network.

(Fig. 4). This arises from the extensive segmental movement of crosslinked polymer molecules. The glass transition range of α_1 and α_2, therefore, covers almost the whole temperature region studied. As a result, the storage modulus gradually drops. The appearance of an elastic plateau above the glass transition temperature of the polymer molecules, α_1, indicates that a stable crosslinking structure exists in these polymers. The magnitude of the rubbery modulus indicates that these soybean oil polymers have higher crosslink densities than those of polyester thermosets [18,20,22]. Despite the similarities in the loss factor behavior, the polymers prepared from various modified initiators have differences in their storage moduli. The polymer SOY50–DVB35–(NFO10-BFE5) has the highest storage modulus over the whole temperature range, while the other two specimens SOY50–DVB35–(SGI10-BFE5) and SOY50–DVB35–(SGII10-BFE5) exhibit similar behavior with moduli lower than that of the sample SOY50–DVB35–(NFO10-BFE5).

Table 1 lists the DMA and Soxhlet extraction results for the regular soybean oil polymer samples (entries 2–4). Apparently, the wt% of the unreacted free oil and the incorporated oil varies from one sample to another. The incorporated oil and the free oil in the polymer phase may plasticize the polymer, thus lowering both the glass transition temperature and the modulus of the materials. Table 1 (entries 2–4) shows that the variations in the DMA results are mainly due to the presence of the free oil and the incorporated oil segments in the bulk polymers. However, we are presently unable to determine the amount of free oil in the crosslinked polymer phase and in the oil-rich phase for a specific material.

The specimen SOY60–DVB35–BFE5 prepared using just boron trifluoride diethyl etherate as the initiator affords heterogeneous material, i.e. a macro-phase separated material. Solid particles are observable in the resulting bulk polymer. However, a single relaxation temperature is detected in the loss factor behavior (also see Fig. 4), even though two phases are obvious in the bulk polymer. The temperature at the loss factor peak (approximately 25°C) corresponds to the glass transition temperature of the polymer matrix. It is assumed that the particles formed in the heterogeneous copolymerization are highly crosslinked divinylbenzene homopolymers. The crosslinking density may be high enough to freeze the motions of extensive segments in the polymer backbone, and thus its glass transition becomes too small to be measured by this technique [18,19]. Because the divinylbenzene is consumed during the early stages of this polymerization by formation of solid white particles, the residual solution contains more soybean oil and less comonomer. Eventually, the solution polymerizes to form the matrix of the polymer. This matrix is, of course, composed of crosslinked polymer molecules and unreacted free oil. The crosslinked polymer, in fact, incorporates more soybean oil segments due to the high concentration of soybean oil present in the original composition of the residual solution after formation of the white particles. This crosslinked polymer containing more soybean oil segments in the backbone becomes more compatible with the residual free oil [23,24]. The free oil may significantly influence the molecular motion of the polymer in compatible systems [25]. Thus, the glass transition of this polymer matrix appears at a single low temperature (∼25°C), and the modulus is also lower than those samples prepared using modified initiators. In other words, for the macro-phase separated soybean oil polymer

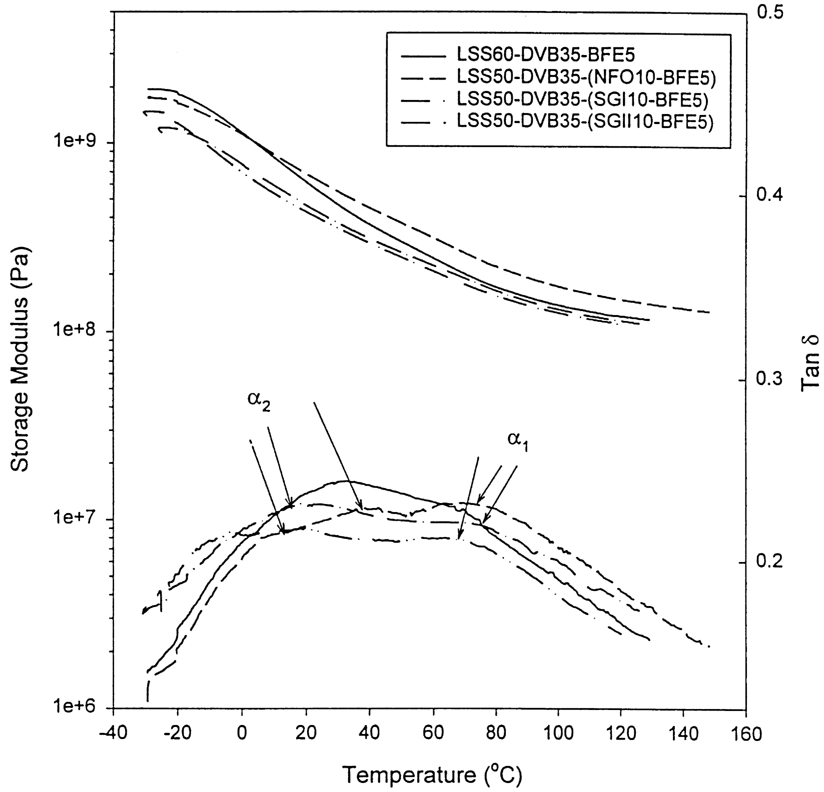

Fig. 5. Temperature dependence of the storage modulus E' and loss factor tan δ for the LoSatSoy oil polymers prepared using various modified initiators.

in Fig. 4, a single glass transition temperature is detected, but the homogeneous specimens exhibit two glass transition temperatures, which indicates that micro-phase separation exists in the bulk polymers.

Fig. 5 shows the dynamic mechanical behavior of the LoSatSoy oil polymers possessing the same composition as the regular soybean oil polymers in Fig. 4. The temperature dependence of the loss factor for the LoSatSoy oil polymers is similar to that of the regular soybean oil polymers in Fig. 4. One single loss factor peak is obtained for the macro-phase separated polymer sample LSS60–DVB35–BFE5. The apparently homogeneous polymers prepared using modified initiators, however, show two glass transition temperatures. The results in

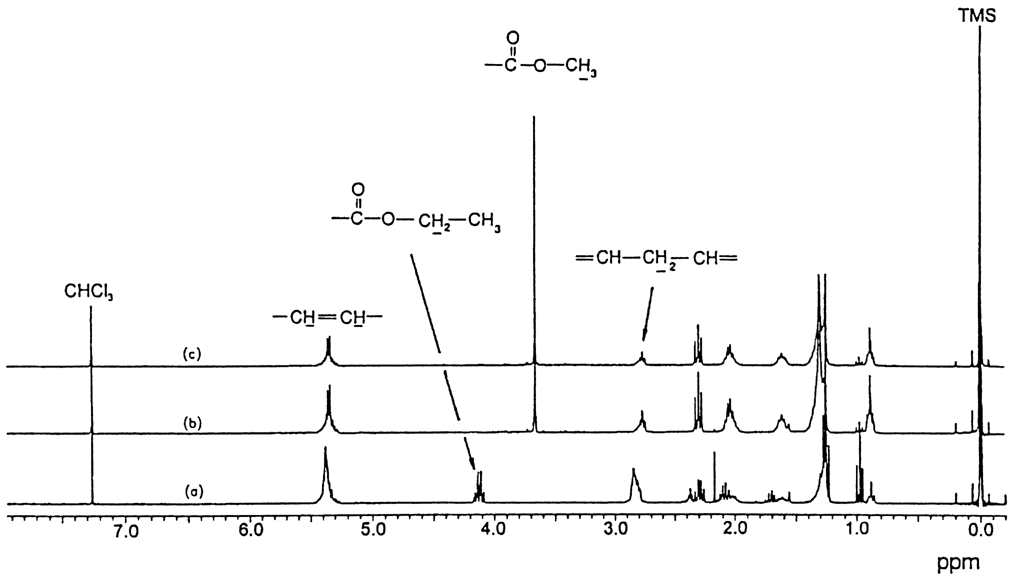

Fig. 6. ^{1}H NMR spectra of: (a) Norway fish oil ethyl ester; (b) Soygold-1100; and (c) Soygold-2000.

Table 2
Average number of carbon–carbon double bonds in the starting materials

Samples	Structure	No. C=C per molecule	No. C=C/three chains
Soybean oil	Triglyceride	4.5	4.5
LoSatSoy oil	Triglyceride	5.1	5.1
Norway fish oil	Ethyl ester	3.6	10.8 (3.6 × 3)
Soygold-1100	Methyl ester	1.7	5.1 (1.7 × 3)
Soygold-2000	Methyl ester	1.5	4.5 (1.5 × 3)

Table 1 indicate that more LoSatSoy oil molecules have been incorporated into the crosslinked polymers than the polymers prepared from regular soybean oil, which inevitably improves the miscibility between the crosslinked polymer molecules and the unreacted free oil in the LoSatSoy oil polymer. Thus, the gap between the α_1 and α_2 peaks in the LoSatSoy oil polymers narrows as a result of the improved miscibility between the unreacted free oil and the crosslinked polymer network. Because of the decreased amounts of unreacted free oil present in the LoSatSoy oil polymers, the moduli of the LoSatSoy oil polymers are higher than those of the regular soybean oil polymers over the whole temperature range. Similarly, the specimen prepared using the fish oil-modified initiator has the highest storage modulus among the LoSatSoy oil polymer samples.

It should be noted that the modified initiating systems employing Soygold-1100 and Soygold-2000 do not result in higher modulus LoSatSoy oil polymers than the sample prepared from the original initiator (Fig. 5), which is quite different from the regular soybean oil polymers shown in Fig. 4. This may be related to the structure of the various additives. Fig. 6 gives the ^{1}H NMR spectra of pure fish oil ethyl ester (6a), Soygold-1100 (6b) and Soygold-2000 (6c), respectively. As previously mentioned, soybean oil and LoSatSoy oil possess a triglyceride structure (see Fig. 1). However, Soygold-1100 and Soygold-2000 are methyl esters, and the Norway fish oil is an ethyl ester. The average number of carbon–carbon double bonds per molecule is listed in Table 2. Soybean oil has approximately 4.5 carbon–carbon double bonds per triglyceride, i.e. 1.5 per side chain. LoSatSoy oil has approximately 5.1 carbon–carbon double bonds per molecule or 1.7 per side chain. The fish oil ethyl ester has 3.4 carbon–carbon double

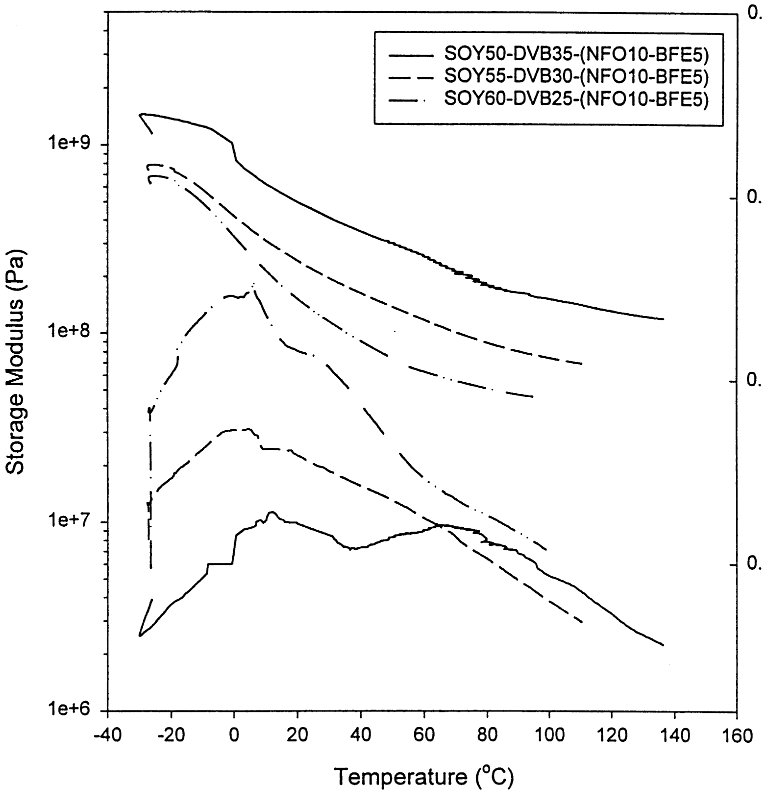

Fig. 7. Temperature dependence of the storage modulus E' and loss factor tan δ for the soybean oil polymers prepared using different comonomer concentrations.

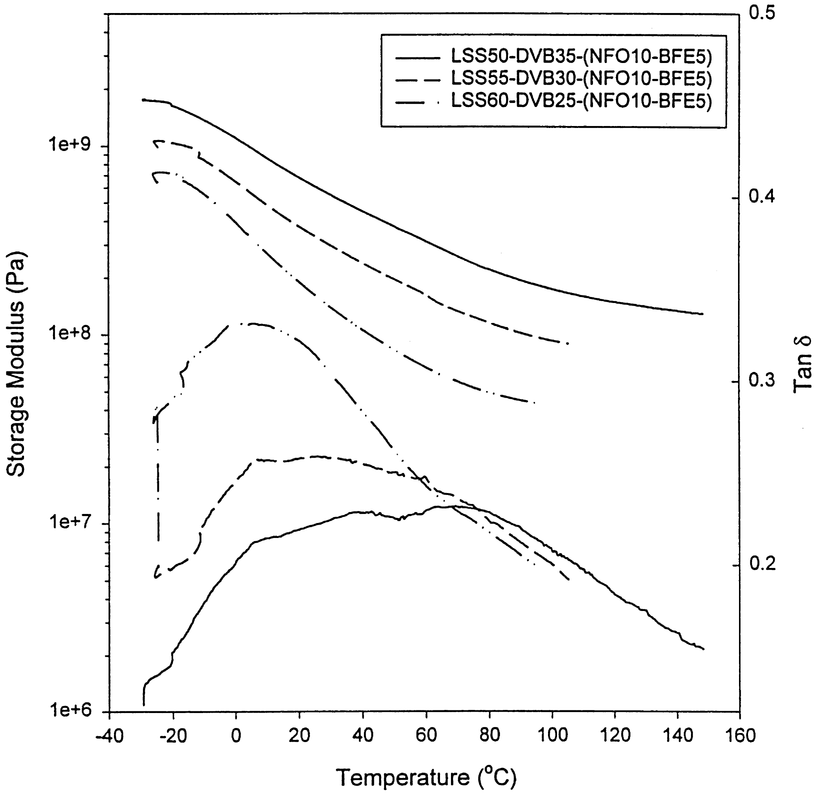

Fig. 8. Temperature dependence of the storage modulus E' and loss factor tan δ for the LoSatSoy polymers prepared using different comonomer concentrations.

bonds per molecule, while Soygold-1100 and Soygold-2000 have only 1.7 and 1.5 carbon–carbon double bonds per molecule, respectively. Fish oil, therefore, is more reactive than the two Soygolds. Thus, in both the regular soybean oil and LoSatSoy oil systems, the best materials have been obtained by using 10 wt% fish oil-modified initiator. In the regular soybean oil reactions, fish oil, Soygold-1100 and Soygold-2000 have as many or more carbon–carbon double bonds per chain on average as the soybean oil itself. So, the modified initiators not only result in homogeneous reactions, but also in higher modulus products. In the LoSatSoy oil systems, however, only the fish oil ethyl ester has more carbon–carbon double bonds per chain than LoSatSoy oil. Soygold-1100 and Soygold-2000 have less or an equal number of carbon–carbon double bonds per chain than the LoSatSoy oil. That is the reason why fish oil-modified initiators result in the highest modulus LoSatSoy oil polymer, while the LoSatSoy oil polymers prepared from Soygold-modified initiators have moduli lower than the polymer prepared from the original initiator.

Fig. 7 gives the temperature dependence of the storage modulus E' and loss factor tan δ for regular soybean oil polymers prepared using a fish oil-modified initiator and different divinylbenzene comonomer concentrations. It shows that the divinylbenzene concentration greatly affects the dynamic mechanical behavior of the resulting polymers. The more divinylbenzene used in the original composition, the higher the modulus of the resulting polymer over the whole temperature range. It is interesting to note, however, that only a 10 wt% increase in the divinylbenzene concentration can increase the modulus of the polymer by 5–6 fold. Another characteristic that is noteworthy is the loss factor behavior of the bulk polymers. Two peaks are observed when 35 wt% divinylbenzene is employed in the original composition. The free oil-rich phase has a glass transition temperature α_2 at about 5°C, while the glass transition temperature α_1 of the resulting crosslinked polymer is approximately 75–80°C. When more soybean oil is employed in the original composition, the modulus of the resulting polymer decreases significantly and the damping behavior also changes. In particular, the peak α_2, which corresponds to the glass transition temperature of the oil-rich phase, appears relatively unchanged, while the peak for the crosslinked polymer, α_1, shifts downward to lower temperatures. Table 1 shows that the oil molecules incorporated into the resulting crosslinked polymer network increase when increasing the soybean oil concentration in the original composition (entries 2,9,10). Thus, the crosslinked polymer becomes more compatible with the unreacted free oil molecules in the bulk polymer. As a result, the temperature α_1 of the crosslinked polymer greatly decreases (Fig. 7). On the other hand, increasing the amount of soybean oil results in higher amounts of free oil in the resulting polymers. Although more of the free oil becomes

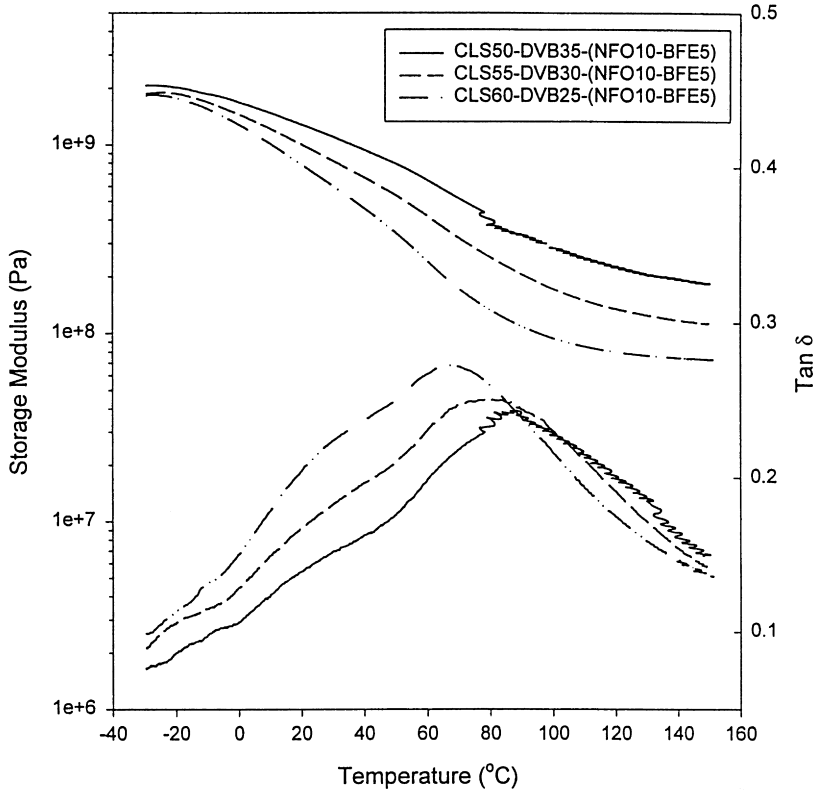

Fig. 9. Temperature dependence of the storage modulus E' and loss factor tan δ for the conjugated LoSatSoy polymers prepared using different comonomer concentrations.

miscible with the crosslinked polymer, the amount of free oil present in a separate phase remains essentially constant. Thus, the loss factor peak for the free oil-rich phase appears relatively unchanged.

Fig. 8 shows the dynamic mechanical behavior of the LoSatSoy oil polymers with different amounts of comonomer in the original composition. The results are similar to those of the regular soybean oil polymers shown in Fig. 7. The moduli of the resulting polymers are proportional to the divinylbenzene concentration in the original composition. By increasing the LoSatSoy oil concentration in the original composition, the peak corresponding to the polymer glass transition temperature shifts to lower and lower temperatures (also see Table 1, entries 6,11,12).

Fig. 9 gives the DMA results for the conjugated LoSatSoy oil polymers with different comonomer concentrations. Compared with those of the regular soybean oil and the LoSatSoy oil polymers (Figs. 7 and 8), the conjugated LoSatSoy oil polymers have higher moduli over the whole temperature region. The glass transition temperatures α_1 of the crosslinked polymer molecules are the same order of magnitude as those of the regular soybean oil and LoSatSoy oil polymers. Unlike the previous regular soybean oil and LoSatSoy oil polymers, however, the conjugated LoSatSoy oil polymers have a single glass transition temperature. The low-temperature shoulders indicate that the unreacted free oils become more compatible with the crosslinked polymers. When the conjugated LoSatSoy oil concentration in the original composition is increased, the glass transition of the resulting polymer slightly shifts to lower temperature (also see Table 1, entries 13–15). It is known that the reactivity of natural oils can be improved by conjugating their carbon–carbon double bonds. Consistent with this expectation is the finding that more LoSatSoy oil molecules are incorporated into the polymer network (Table 1) and the polymer becomes more compatible with the residual free oil in the bulk. A single glass transition, therefore, has been observed in the conjugated LoSatSoy oil bulk polymer.

Fig. 10 provides a comparison of the DMA curves for the conjugated LoSatSoy oil polymer CLS50–DVB35–(NFO10-BFE5) and some conventional polymers. The modulus of the conjugated LoSatSoy oil polymer is approximately 1×10^9 Pa at room temperature, comparable to that of polyethylene. Its glass transition temperature is approximately 90°C, which is similar to that of polystyrene (90–100°C). The crosslinked structure of the conjugated LoSatSoy oil polymer is mainly composed of divinylbenzene polymer segments, analogous to that of polystyrene. Due to the highly crosslinked nature of our polymer, the glass transition temperature should be higher than that of polystyrene. However, the unreacted free oil present in the conjugated LoSatSoy oil polymer decreases its modulus and the corresponding glass transition

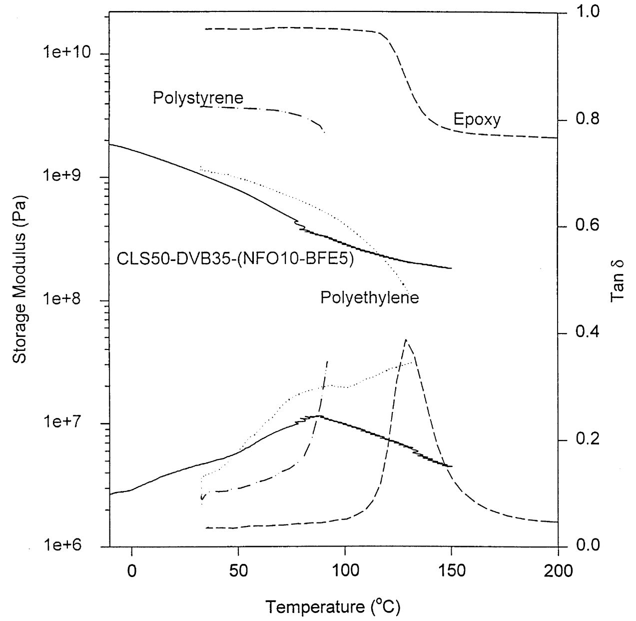

Fig. 10. Temperature dependence of the storage modulus E' and loss factor tan δ for the conjugated LoSatSoy oil polymer CLS50–DVB35–(NFO10-BFE5), commercial polystyrene, polyethylene and an epoxy resin.

temperature. Due to the thermosetting nature of our polymer, the CLS polymer shows a relatively high modulus at higher temperatures. For other linear polymers, however, the materials tend to flow and not much strength is expected as the temperature reaches 100°C and above.

3.6. Thermal stability and structure relationships

Fig. 11 shows the TGA curves for the polymer SOY50–DVB35–(NFO10-BFE5), and the insoluble and soluble substances obtained upon extraction by methylene chloride. Generally, the bulk polymer is thermally stable under 200°C, followed by three decomposition temperature regions, 200–400°C (stage I), 400–530°C (stage-II) and above 530°C (stage-III). The extracted soluble substances, i.e. mostly unreacted free oil, disappear in a temperature region between 200–400°C, the same temperature range as the first decomposition step (stage-I) of the bulk polymer. A careful examination of the TGA experiments shows that decomposition at stage-I is mainly due to evaporation and decomposition of the free oil. On the other hand, the insoluble substance obtained after extraction consists of a highly crosslinked polymer. Its decomposition temperature is above 400°C at the heating rate of 20°C/min, approximately that of stage-II of the decomposition of the bulk polymer. This step corresponds to degradation and char formation of the crosslinking polymer structure. Above 530°C, the char residues gradually oxidize in air. Thus, the origins of the multi-decomposition behavior for the bulk polymer are as follows. The first temperature region (stage-I) is mainly due to evaporation and decomposition of the unreacted free oil in the bulk polymer; the second temperature region (stage-II) is due to decomposition and char formation of the crosslinking polymer network; and the last temperature region (stage-III) is due to oxidation of the char residues.

Table 1 lists the TGA results for the regular soybean oil, LoSatSoy oil and conjugated LoSatSoy oil polymers. T_{10} and T_{50} are the temperatures at 10 and 50% weight loss. T_{10}, which generally lies in stage-I, is used to evaluate the thermal stability of the bulk polymer. T_{50} in stage-II indirectly reflects the consistency of the crosslinking structure of the bulk polymer. Table 1 indicates that T_{10} and T_{50} values increase with increasing divinylbenzene compositions. This once again supports the previous hypothesis that the divinylbenzene predominantly contributes crosslinking to the resulting

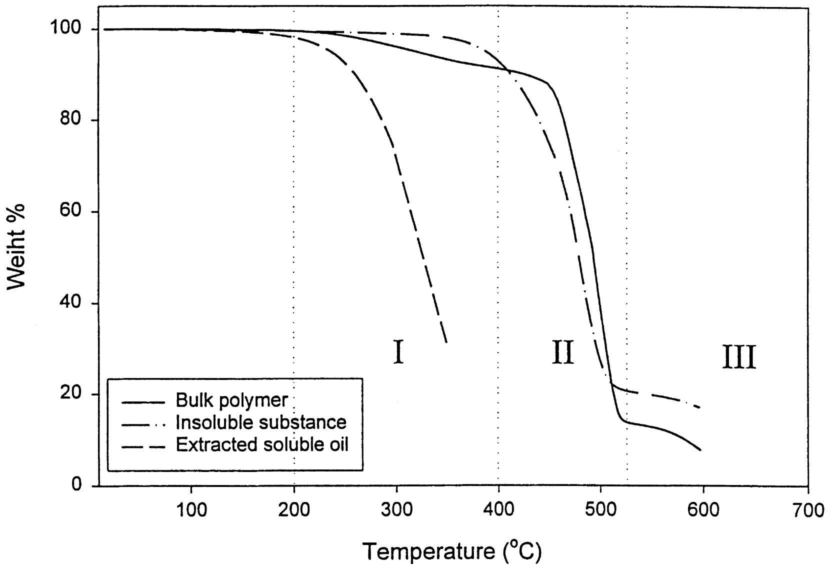

Fig. 11. TGA curves for the soybean oil bulk polymer SOY50–DVB35–(NFO10-BFE5) and the insoluble and soluble materials obtained upon extraction.

thermosetting polymers, and thus increases the thermal stability of the bulk polymers. The nature of the oil employed also influences the thermal stability of the resulting polymers, but not as much as the divinylbenzene comonomer does. Generally, more reactive, more highly unsaturated oils result in more thermally stable polymers. The conjugated LoSatSoy oil polymers have the highest thermal stability among all of our soybean oil polymer samples.

4. Conclusions

(1) The cationic copolymerization of regular soybean oil, LoSatSoy oil or conjugated LoSatSoy oil with divinylbenzene comonomer initiated by boron trifluoride diethyl etherate results in polymers ranging from soft rubbers to hard thermosets, depending on the oil and stoichiometry employed. However, these reactions are found to be heterogeneous and the densities of the resulting polymers, therefore, are different in various parts of the bulk polymer. The heterogeneous nature of these reactions appears to be mainly due to poor miscibility between the oils and the initiator.

(2) Homogeneous copolymerization of the various oils with divinylbenzene has been achieved using initiating systems modified by Norway fish oil ethyl ester, Soygold-1100, Soygold-2000 or THF. The resulting bulk polymers are also homogeneous and exhibit higher conversions of starting materials to crosslinked polymers than those employing boron trifluoride diethyl etherate alone. The fish oil-modified initiators have resulted in the best polymers.

(3) Dynamic mechanical analysis shows that these polymers are typical thermoset plastics. The moduli of the polymers at room temperature are between 4×10^8 and 1×10^9 Pa. Their glass transition temperatures are around 60–80°C. The moduli of the bulk polymers can be enhanced by using conjugated soybean oil or by increasing the divinylbenzene comonomer concentration in the original composition. Generally, micro-phase separation occurs in all of the soybean oil polymers. In the conjugated LoSatSoy oil polymers, the crosslinked polymer molecules become more compatible with the unreacted free oils present in the bulk polymers.

(4) Thermogravimetric analysis shows that three distinct decomposition regions for these polymers exist, which correspond to: (1) evaporation and decomposition of the unreacted free oil present in the bulk polymer; (2) degradation and char formation of the crosslinked polymer; and (3) subsequent oxidation of char residues in air. The thermal stability of the bulk polymers is mainly determined by the unreacted free oil present in the bulk polymer. Conjugated LoSatSoy oil polymers have the highest modulus and thermal stability due to the relatively low amount of unreacted free oil present in the bulk polymer.

Acknowledgements

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

References

[1] Bisio AL, Xanthos M. How to manage plastics wastes: technology and market opportunities. New York: Hanser Publishers, 1995.
[2] Mustafa N. Plastics waste management: disposal, recycling and reuse. New York: Marcel Dekker, 1993.
[3] John LA, Myers DJ. In: Erichson DR, editor. Practical handbook of soybean processing and utilization. St. Louis, MO/Champaign, IL: American Soybean Association/American Oil Chemist's Society, 1995.
[4] Formo MW. In: Swern D, editor. 4th ed. Bailey's industrial oil and fat products, vol. 2. New York: Wiley, 1982. p. 343–405.
[5] Gunstone FD. Industrial uses of soybean oil for tomorrow. Special Report '96, ISU and the Iowa Soybean Promotion Board, 1995.
[6] Hammond EG, Nikolau D. Beneficiaries of modified soybean traits. Special Report '93, ISU and the Iowa Soybean Promotion Board, 1993.
[7] Croston CB, Tubb IL, Cowan JC, Teeter HM. J. Am. Oil Chem. Soc. 1952;29:331.
[8] Bradley JJ. US Patent 3 550 961, 1951.
[9] Hossain SU. US Patent 3 301 744, 1967.
[10] Larock RC, Dong X, Reddy K. In preparation.
[11] Matyjaszewski K, editor. Cationic polymerizations: mechanisms, synthesis and applications. New York: Marcel Dekker, 1996.
[12] Hiamenz PC. Polymer chemistry. New York: Marcel Dekker, 1984.
[13] Vdlmert B. Polymer chemistry. Berlin: Springer, 1973.
[14] Faust R, Timothy DS. Cationic polymerization: fundamentals and applications. ACS symposium series 1997 (p. 665).
[15] Marc LG. Organic chemistry. Reading, MA: Addison-Wesley, 1984.
[16] Li F, Marks DW, Larock RC, Otaigbe JU. Polymer 2000;41:7925–39.
[17] Li F, Larock RC, Otaigbe JU. Polymer 2000;41:4849–62.
[18] Bueche F. Physical properties of polymers. London: Interscience Publishers, 1962.
[19] Ward IM, Hadley DW. An introduction to the mechanical properties of solid polymers. New York: Wiley, 1993.
[20] Flory JP. Principles of polymer chemistry. New York: Cornell University Press, 1953.
[21] Ghorbel I, Valentin D. Polym Compos 1993;14:324.
[22] Valea A, Martinez I, Gonzalez ML, Eceiza A, Mondragon I. J Appl Polym Sci 1998;70:2595.
[23] Folks MJ, Hope PS, editors. 1st ed. Polymer blends and alloys. New York: Blackie Academic and Professional, 1993.
[24] Paul DR, Newman S. Polymer blends. New York: Academic, 1978.
[25] Titow WV. PVC Plastics: properties, processing and applications. New York: Elsevier, 1990.
[26] Stepto RFT. Polymer networks: principles of their formation, structure and properties. New York: Blackie Academic and Professional, 1998.
[27] Planck RW, Pack FC. Tung: chemistry and technology of tung products 1875–1950. USDA, Southern Regional Res. Lab., Louisiana, 1952.