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Novel thermosets prepared by cationic copolymerization of various vegetable oils—synthesis and their structure–property relationships

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Abstract

A range of thermoset plastics have been prepared by the cationic copolymerization of olive, peanut, sesame, canola, corn, soybean, grapeseed, sunflower, low saturation soy, safflower, walnut, and linseed oils with divinylbenzene or a combination of styrene and divinylbenzene comonomers catalyzed by boron trifluoride diethyl etherate. The chemical, physical, thermal, and mechanical properties of these new polymers have been investigated as a function of the vegetable oil composition. The vegetable oil reactivity has a direct effect on most of the polymers' properties, which can be reasonably predicted by careful choice of the vegetable oil. Coupled with variations in the comonomer and stoichiometry, the choice of vegetable oil allows one to tailor the polymer's properties for specific applications.

Keywords: Vegetable oil; Cationic copolymerization; Structure–property relationship

1. Introduction

Recent years have witnessed an increasing interest in biomaterials derived from renewable resources. One major initiative has been the synthesis of a wide range of biopolymers from annually renewable and environmentally benign starting materials obtained from agricultural, animal and microbial sources [1–3]. These materials often possess thermal and mechanical properties comparable to or better than those of widely used industrial polymers. As such, they might replace petroleum-based polymers resulting in waste reduction and overall petroleum resource preservation.

Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds [4–6]. In general, the bulk of vegetable oils produced each year is used for human food or animal feed, whereas the remainder finds non-food uses, such as the production of soaps, lubricants, coatings and paints [7]. These oils are generally triglycerides of different fatty acids with varying degrees of unsaturation. The presence of multiple C=C bonds makes biological oils ideal, natural building blocks for the preparation of a range of useful polymeric materials. Their conversion into industrially useful plastics usually proceeds through either fatty acid C=C bond functionalization and subsequent copolymerization or through direct copolymerization of the fatty acid C=C bonds with a variety of alkene comonomers. For instance, Petrovic and coworkers have successfully converted the C=C bonds of soybean oil into polyols by epoxidizing the C=C bonds of the triglyceride oil, followed by oxirane ring-opening of the epoxidized oil [8–12]. The newly synthesized polyols are then reacted with a variety of isocyanates to produce polyurethanes. Wool and coworkers, on the other hand, have prepared rigid thermosets and composites via free-radical copolymerization of soybean oil monoglyceride maleates and styrene [13–15]. The maleate monomers have been obtained by glycerol transesterification of soybean oil, followed by esterification with maleic anhydride [13].

We have successfully prepared a wide range of industrially promising biopolymers by the cationic copolymerization of soybean [16–18], corn [19], tung [20] and fish [21,22] oils without any prior chemical modifications. The copolymerization of soybean oils and divinylbenzene (DVB), for example, results in rigid and relatively brittle plastics with glass transition temperatures (T_g) of approximately 60–80 °C [16]. On the other hand, a variety of viable

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polymeric materials ranging from elastomers to rigid and tough plastics are produced by the cationic copolymerization of soybean oils, styrene (ST) and DVB [17]. Their glass transition temperatures (T_g) vary from 0 to 105 °C, Young's moduli vary from 0.03 to 0.63 GPa, while tensile strengths vary from 0.3 to 21 MPa [23,24]. The resulting thermosets possess excellent thermal and mechanical properties, including damping [25] and shape memory [26] properties, and show promise as replacements for petroleum-based rubbers and conventional plastics.

In addition to soybean, corn, tung and fish oils, there exist many other commercially available vegetable oils with different triglyceride structures. Their compositions mainly differ in their fatty acid content, leading to variations in their degrees of unsaturation and, consequently, their reactivity. Until now, variations in the polymer properties have been the direct result of variations in the polymer composition resulting from changes in the comonomer (ST and DVB) content. Herein, we wish (1) to determine if cationic polymerization, which has been so effective for soybean, corn, tung, and fish oils, can be extended to the polymerization of other readily available vegetable oils, (2) to convert a number of vegetable oils to bulk polymers by varying only the type of the oil while keeping the composition constant, (3) to characterize the materials, and most importantly, (4) to determine their structure–property relationships. This kind of structure–property elucidation is necessary for tailoring the properties of these promising new bioplastics.

2. Experimental

2.1. Materials

The vegetable oils used in this study were Grand olive (OLV), Planters peanut (PNT), Loriva sesame (SES), Wesson canola (CAN), Mazola corn (COR), Wesson soybean (SOY), grapeseed (GRP), Wesson sunflower (SUN), Grand low saturation soy (LSS), Hain safflower (SAF), Loriva walnut (WNT), and Superb linseed (LIN) oils. All of the oils were purchased in the local supermarket, except the Superb linseed oil (supplied by Archer Daniels Midland Co., Decatur, IL), and used without further purification. ST and DVB (80% DVB and 20% ethylvinylbenzene) were purchased from Aldrich Chemical Company and used as received. Norway fish oil ethyl ester (NFO) (EPAX 5500 EE, Pronova Biocare) was used to modify the catalyst, boron trifluoride diethyl etherate (BFE) (distilled grade, Aldrich).

2.2. Cationic copolymerization and nomenclature

The desired amounts of comonomers (DVB or a mixture of ST and DVB) were measured out and added to the vegetable oil and the mixture stirred vigorously in an ice bath, followed by addition of an appropriate amount of the modified BFE catalyst. The modified catalyst was prepared by mixing the NFO with BFE, which was usually required to produce homogeneous polymers [15,16]. The reaction mixture was then injected into a glass mold, sealed by silicon adhesive and heated for 12 h at room temperature, followed by 12 h at 60 °C and 24 h at 110 °C. The resulting thermosets were obtained in essentially quantitative yield. The nomenclature adopted in this paper for the polymer samples is as follows: A polymer sample prepared from 45 wt% LIN, 32 wt% ST, 15 wt% DVB using 8 wt% NFO-modified BFE catalyst (5 wt% NFO + 3 wt% BFE) is designated as LIN45-ST32-DVB15-(NFO5-BFE3).

2.3. Soxhlet extraction

A 2–3 g sample of the bulk polymer was extracted with 100 mL of refluxing methylene chloride for 24 h using a Soxhlet extractor. Following the extraction, the resulting solutions were concentrated under vacuum and the extracts were dried in a vacuum oven overnight. The soluble substances were characterized by ^{1}H NMR spectroscopy. The recovered insoluble portion was dried under a vacuum prior to weighing.

2.4. Characterization

^{1}H NMR spectroscopic analyses of the extracted soluble substances were recorded in $CDCl_3$ using a Varian Unity spectrometer at 300 MHz. Cross-polarization magic angle spinning (CP MAS) ^{13}C NMR analysis of the insoluble materials remaining after Soxhlet extraction of the bulk polymers was performed using a Bruker MSL 300 spectrometer. Samples were examined at two spinning frequencies (3.2 and 3.7 kHz) in order to differentiate between actual signals and spinning side bands. FTIR spectra were recorded on a Nicolet 740 FT-IR spectrometer (KBr pill). Dynamic mechanical analysis (DMA) data were obtained using a Perkin–Elmer dynamic mechanical analyzer DMA Pyris-7e in a three-point bending mode. Rectangular specimens of 2 mm thickness and 5 mm depth were used for the analysis and the width to depth ratio was maintained at approximately 3. The measurements were performed at a heating rate of 3 °C/min and a frequency of 1 Hz in He with a gas flow rate of 20 mL/min and applied static and dynamic forces of 110 and 100 mN, respectively. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris-7 thermogravimeter. The percent weight loss temperatures of the polymeric materials were measured in air with a gas flow rate of 20 mL/min. The samples were heated from 50 to 650 °C at a heating rate of 20 °C/min. The tensile tests were conducted at room temperature according to ASTM-D638M specifications using an Instron universal testing machine (Model-4502) at a cross-head speed of 5 mm/min. The dumbbell-shaped test specimen (type M–I specimen in ASTM D638M) had a gauge section with a length of 50 mm, a width of 10 mm, and a thickness of 3 mm. The gauge section was joined to the wider end sections by two long tapered sections. The dumbbell-shaped specimens were prepared by cutting the material out of a polymer plate, followed by precise machining. At least five identical specimens were tested for each polymer sample. The Young's modulus (E), ultimate strength (σ_b) and elongation at break (ε_b) of the polymers were obtained from the tensile tests and reported as average values. The tensile 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 gelation time is the time elapsed from initial mixing of the reactants at the given temperature to the time when solidification commences, which was determined by the complete cessation of flow of the liquid reactants. Measurements were performed in reference to the ASTM standard D2471-99. The gelation time was averaged from five individual measurements at a specific temperature. Viscosity measurements on the vegetable oils were performed at 23 °C using a Haake RS-150 Rheo Stress Rheometer (Karlsruhe, Germany). Shear stress was applied using a 60 mm 2° titanium cone over the range of 10–2000 s^{-1}. Each sample was tested at least three times and the results reported as average viscosities at maximum shear rate.

3. Results and discussion

3.1. Chemical compositions of the vegetable oils

The commercially available vegetable oils employed in this study are listed in Table 1, along with their fatty acid compositions and corresponding viscosities. These oils are primarily composed of saturated stearic (C16-0) and palmitic (C18-0) acids, as well as unsaturated oleic (C18-1), linoleic (C18-2) and linolenic (C18-3) fatty acids. The content of other saturated and unsaturated fatty acids is negligible. The unsaturated fatty acid content determines the degree of unsaturation of the vegetable oil, and consequently, its reactivity. Fig. 1 shows a representative ^{1}H NMR spectra of Superb linseed oil, along with a detailed peak assignment. The signals at 4.1–4.4 ppm (**A**) correspond to the protons on the C-1 and C-3 atoms of the glyceride unit, which indicate that these vegetable oils have a triglyceride structure. The vinylic hydrogens (**I**) of these oils are typically detected at 5.2–5.5 ppm, while the CH_2 protons positioned between two C=C bonds, also know as bis-allylic protons (**J**), are observed at 2.7–2.9 ppm, indicating that the C=C bonds are non-conjugated. Detailed triglyceride peak assignments are well documented in the literature [27–29].

The oils listed in Table 1 are arranged according to their degrees of unsaturation (d). Degrees of unsaturation, expressed as numbers of C=C bonds per triglyceride, are calculated using the following equation:

$$d = \frac{4A - B}{2B} \tag{1}$$

where A is the integrated area of the convoluted peaks above 5.20 ppm (including the C-2 hydrogen atom of the glycerol group) and B is the integrated area of the peaks at 4.10–4.40 ppm. Calculated d values are shown in Table 1 and compared to the values given in parentheses, which represent the number of C=C bonds per triglyceride calculated from the fatty acid compositions found in the literature [4,5]. It should be noted that the literature values differ slightly from the values obtained by ^{1}H NMR spectral analysis. When comparing the reactivities of the oils in question, one must keep in mind that the composition of the oil may vary significantly and depends on the region where the oil was produced, as well as the methods used for their isolation and processing [4]. Table 1 shows that the d values increase from 2.86 for OLV to 6.07 for LIN, suggesting significant differences in their reactivities. Thus, it is interesting to investigate the effect of the degree of unsaturation on the synthesis, structure, and thermophysical and

Table 1
Fatty acid compositions of various vegetable oils

Entry	Oil	η (cP)	C=C number[a]	% Fatty acids[b]							
				C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1
1	Olive	60.6	2.86 (2.85)	–	9.0	2.7	80.3	6.3	0.7	0.4	–
2	Peanut	59.1	3.27 (3.37)	0.1	11.1	2.4	46.7	32.0	–	1.3	1.6
3	Sesame	53.7	3.81 (3.87)	0.1	8.2	3.6	42.1	43.4	–	1.1	–
4	Canola	55.4	3.97 (3.91)	0.1	4.1	1.8	60.9	21.0	8.8	0.7	1.0
5	Corn	49.9	4.07 (4.45)	0.1	10.9	2.0	25.4	59.6	1.2	0.4	–
6	Soybean	49.3	4.31 (4.61)	0.1	10.6	4.0	23.3	53.7	7.6	0.3	–
7	Grapeseed	48.5	4.49 (4.57)	–	7.0	3.0	27.4	62.5	–	–	–
8	Sunflower	48.8	4.61 (4.69)	0.1	7.0	4.5	18.7	67.5	0.8	0.4	0.1
9	LoSatSoy	47.8	5.03 (5.16)	–	3.0	1.0	31.0	57.0	9.0	–	–
10	Safflower	45.9	5.04 (5.06)	0.1	6.8	2.3	12.0	77.7	0.4	0.3	0.1
11	Walnut	42.5	5.46 (5.24)	–	4.6	0.9	17.8	73.4	3.3	–	–
12	Linseed	38.8	6.07 (6.24)	0.2	5.4	3.5	19.0	24.0	47.0	0.6	–

[a] Calculated by ^{1}H NMR spectral analysis. The values in parentheses are calculated from the oil compositions found in the literature.

[b] Taken from Refs. [4] and [5].

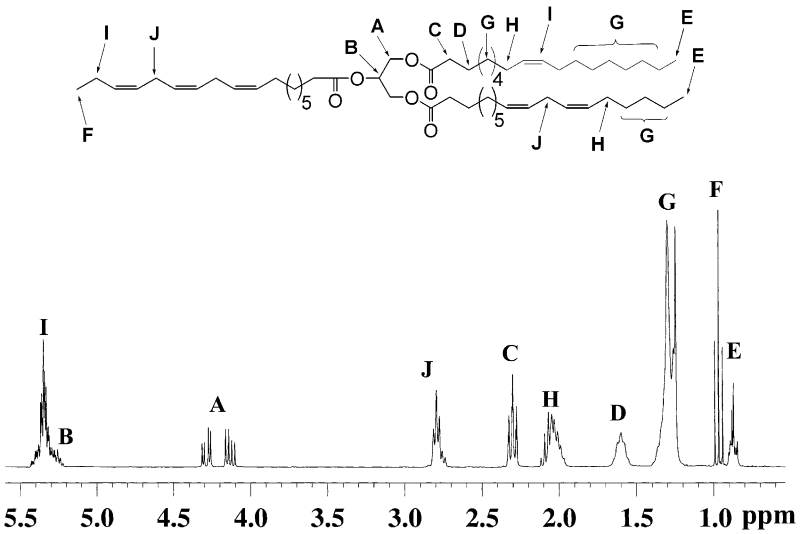

Fig. 1. ^{1}H NMR spectra of LIN with peak assignments.

mechanical properties of the novel bioplastics prepared from these vegetable oils.

3.2. Vegetable oil copolymerization and molecular structure determination

The presence of multiple C=C bonds in vegetable oils allows their copolymerization into solid polymeric materials via cationic polymerization. BFE has proved to be a very effective catalyst in cationic polymerizations [30,31]. However, the homopolymerization of vegetable oils typically results in viscous fluids of limited use [16]. To produce viable hard plastics, vegetable oils have to be copolymerized with more rigid and reactive aromatic comonomers, such as ST and DVB. As in our soybean oil polymerizations [16,17], an NFO-modified BFE catalyst has to be employed in order to produce homogeneous reactions. Basically, 8 wt% NFO-modified BFE catalyst is able to generate homogeneous reactions with all vegetable oils herein employed. The vegetable oils listed in Table 1 were cationically copolymerized with either DVB or a mixture of ST and DVB to give two series of copolymers, namely OIL62-DVB30-(NFO5-BFE3) and OIL45-ST32-DVB15-(NFO5-BFE3). These two compositions have been chosen because they approximate the compositions of maximum oil incorporation into the resulting copolymers as shown in our previous work on soybean oil plastics [16,18].

The gelation times for both the OIL-DVB and OIL-ST-DVB systems were determined by measuring the time required for liquid reactants to reach a certain viscosity at which cessation of flow was observed. The presence of very reactive ST and DVB comonomers facilitates the gelation process and drastically reduces the gelation times when compared to vegetable oil homopolymerization. The gelation times have been determined at three different temperatures (room temperature, 40 and 50 °C) and the data are summarized in Table 2. Room temperature gelation times range from 130 to 348 min for OIL-DVB systems and 80 to 233 min for OIL-ST-DVB systems. The gelation times determined at higher temperatures are naturally substantially shorter. Our results indicate that OIL-ST-DVB mixtures gel faster than the corresponding OIL-DVB mixtures. This can be attributed to the higher concentration of the more reactive comonomers (ST + DVB) in the OIL-ST-DVB compositions. Surprisingly, the gelation times determined at all temperatures appear to be completely independent of the degrees of unsaturation of the vegetable oils. This independence strongly suggests the presence of two opposite effects. The fact that the gelation process involves drastic changes in the viscosity of the reaction mixture leads us to believe that differences in the oil viscosities may be partially responsible for such behavior, especially since the vegetable oil in a given composition accounts for approximately 50 wt% of the whole reaction mixture. In order to examine this phenomenon further, we

Table 2
Gelation times for the OIL-ST-DVB and OIL-DVB copolymers

OIL	OIL45-ST32-DVB15			OIL62-DVB32		
	RT	40 °C	50 °C	*RT*	40 °C	50 °C
OLV	185	19.3	14.0	256	39.7	6.3
PNT	113	15.9	5.1	277	35.0	3.2
SES	80	19.3	3.5	130	34.9	2.4
CAN	118	18.2	4.6	189	33.3	2.7
COR	209	23.2	16	292	37.5	2.7
SOY	130	18.3	12.5	214	29.5	4.1
GRP	233	35.1	14.7	348	78.7	6.7
SUN	156	23.9	9.3	216	34.7	4.1
LSS	163	29.9	9.4	213	50.7	5.4
SAF	84	20.4	7.5	144	29.1	5.4
WNT	184	19.2	7.0	249	37.5	4.2
LIN	185	28.6	19.7	255	54.5	6.6

All gelation times are given in minutes and represent an average value of at least three individual runs.

Table 3
Properties of the OIL-DVB copolymers

Copolymer	T_g (°C)	ν_e[a] (mol/m^3)	TGA data (°C)				Extraction data (%)		E[b] (MPa)	σ_b[c] (MPa)	ε_b[d] (%)	Toughness (MPa)
			T_{10}[e]	T_{50}[f]	ΔT[g]	T_{max}[h]	Insoluble	Soluble				
OLV62-DVB30-(NFO5-BFE3)	0 and 49	7.61×10^3	269	462	193	477.8	64.9	35.1	27.2	1.2	8.4	0.06
PNT62-DVB30-(NFO5-BFE3)	−6 and 48	1.21×10^4	282	461	179	474.6	70.7	29.3	35.9	1.7	9.4	0.09
SES62-DVB30-(NFO5-BFE3)	−8 and 45	1.33×10^4	284	469	179	480.6	75.7	24.3	37.7	2.2	10.4	0.13
CAN62-DVB30-(NFO5-BFE3)	−13 and 45	1.27×10^4	284	463	179	476.6	77.6	22.4	43.9	1.7	7.7	0.07
COR62-DVB30-(NFO5-BFE3)	−12 and 50	1.31×10^4	295	465	171	479.5	80.9	19.1	45.1	2.2	8.2	0.13
SOY62-DVB30-(NFO5-BFE3)	−8 and 50	1.34×10^4	296	470	173	483.6	82.4	17.6	46.6	2.5	8.1	0.12
GRP62-DVB30-(NFO5-BFE3)	−3 and 55	1.97×10^4	312	470	158	483.5	84.1	15.9	50.8	3.0	10.7	0.18
SUN62-DVB30-(NFO5-BFE3)	−10 and 50	2.05×10^4	321	468	147	476.7	84.1	15.9	54.0	3.0	11.2	0.20
LSS62-DVB30-(NFO5-BFE3)	−7 and 50	2.23×10^4	324	468	144	474.0	88.1	11.9	58.4	3.0	10.7	0.23
SAF62-DVB30-(NFO5-BFE3)	−10 and 56	2.26×10^4	332	478	146	490.1	87.5	12.5	62.8	3.1	8.6	0.14
WNT62-DVB30-(NFO5-BFE3)	5 and 58	2.25×10^4	331	472	141	484.7	87.5	12.2	62.4	3.8	11.8	0.26
LIN62-DVB30-(NFO5-BFE3)	11 and 55	2.28×10^4	342	473	130	485.6	87.8	12.2	99.9	5.6	10.5	0.35

[a] Crosslink densities.
[b] Young's modulus.
[c] Ultimate strength.
[d] Elongation at break.
[e] Ten percent weight loss temperature.
[f] Fifty percent weight loss temperature.
[g] $\Delta T = T_{50} - T_{10}$.
[h] Maximum thermal degradation temperature.

have measured and compared viscosities of the vegetable oils employed in this study (Table 1). As expected, all vegetable oils exhibit typical Newtonian behavior with viscosities ranging from 38.8 to 60.6 cP. In general, the greater the degree of unsaturation of the vegetable oil, the lower the viscosity. Higher degrees of unsaturation result in higher oil reactivity during polymerization and, consequently, shorter gelation times. At the same time, higher degrees of unsaturation result in lower oil and initial reaction mixture viscosities, which lead to longer gelation times.

In general, the OIL-DVB copolymers range from soft to hard and brittle plastics, while the OIL-ST-DVB terpolymers range from soft to hard ductile plastics. All copolymers have a dark brown glossy color and a slight odor. The presence of multiple C=C bonds in both the vegetable oils and the DVB results in crosslinked structures for the final copolymers. The yields of crosslinked polymers and soluble fractions have been determined by Soxhlet extraction analysis. Extraction results for OIL-DVB and OIL-ST-DVB copolymers are presented in Tables 3 and 4, respectively. Our results show that the amount of crosslinked polymer increases with increasing degree of unsaturation of the vegetable oil employed in the original composition. For example, the yields of crosslinked OIL-DVB and OIL-ST-DVB polymers increase from 64.9 to 87.8 and 67.5 to 85.9%, respectively, when the *d* values of the corresponding vegetable oils increase gradually from 2.86 (OLV) to 6.07 (LIN). A more detailed analysis, however, reveals that an increase in *d* value of the vegetable oils does not result in a linear dependence of the yield of the crosslinked copolymers. The results indicate that there exists a two-stage dependence as shown in Fig. 2. The first stage represents a rapid increase in the yield of the crosslinked polymer with an increase in *d* value of the vegetable oil. This stage is representative of vegetable oils with *d* values in the range of 3–5 (Table 1, entries 1–10). As *d* increases further ($d > 5$, Table 1, entries 11 and 12), the dependence levels off (stage two) as shown by the flat plateau above $d = 5$. We believe that there exists a certain amount of unreacted fatty acid double bonds left in the crosslinked material after curing. These double bonds are covalently linked to the crosslinked network. Thus, not every double bond in the fatty acid chain of the triglyceride participates actively in crosslinking. Thus, there exists a limit in *d* value of the non-conjugated oils after which a

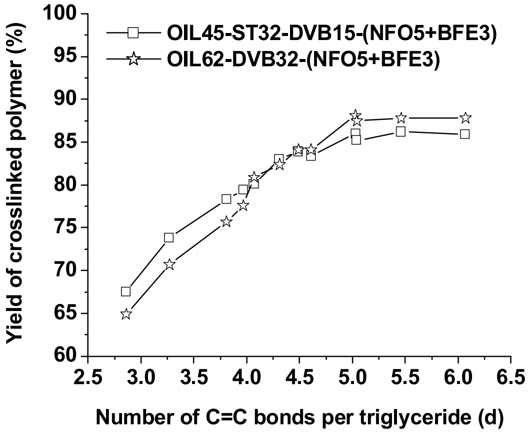

Fig. 2. The effect of the degree of unsaturation on the yield of the crosslinked copolymer.

Table 4
Properties of the OIL-ST-DVB copolymers

Copolymer	T_g (°C)	ν_e[a] (mol/m^3)	TGA data (°C)				Extraction data (%)		E[b] (MPa)	σ_b[c] (MPa)	ε_b[d] (%)	Toughness (MPa)
			T_{10}[e]	T_{50}[f]	ΔT[g]	T_{max}[h]	Insoluble	Soluble				
OLV45-ST32-DVB15-(NFO5-BFE3)	16 and 62	6.03×10^2	276	455	179	465.6	67.5	32.5	13.0	1.9	38.6	0.46
PNT45-ST32-DVB15-(NFO5-BFE3)	19 and 62	7.47×10^2	281	461	178	468.8	73.8	26.2	17.6	3.1	56.3	1.13
SES45-ST32-DVB15-(NFO5-BFE3)	60	8.03×10^2	294	459	167	468.4	78.3	21.7	36.8	3.7	77.3	2.10
CAN45-ST32-DVB15-(NFO5-BFE3)	60	9.38×10^2	295	456	162	468.2	79.4	20.6	37.0	4.2	76.7	2.18
COR45-ST32-DVB15-(NFO5-BFE3)	50	1.34×10^3	294	459	164	465.4	80.1	19.9	38.3	4.7	78.8	2.34
SOY45-ST32-DVB15-(NFO5-BFE3)	53	1.39×10^3	316	463	148	475.2	83.0	17.0	46.3	5.3	86.0	2.56
GRP45-ST32-DVB15-(NFO5-BFE3)	58	1.83×10^3	321	462	141	477.1	83.9	16.1	53.8	5.6	62.8	2.59
SUN45-ST32-DVB15-(NFO5-BFE3)	58	1.85×10^3	309	457	149	462.6	83.4	16.6	54.1	5.7	75.3	3.21
LSS45-ST32-DVB15-(NFO5-BFE3)	66	2.22×10^3	324	462	138	468.8	86.0	14.0	61.9	7.0	77.2	3.94
SAF45-ST32-DVB15-(NFO5-BFE3)	54	2.24×10^3	343	462	119	475.6	85.2	14.8	62.2	7.0	78.1	4.02
WNT45-ST32-DVB15-(NFO5-BFE3)	59	2.24×10^3	332	461	129	477.2	86.2	13.8	63.1	7.5	85.8	4.79
LIN45-ST32-DVB15-(NFO5-BFE3)	56	2.27×10^3	339	465	126	476.6	85.9	14.1	125.6	10.9	69.4	5.83

[a] Crosslink densities.
[b] Young's modulus.
[c] Ultimate strength.
[d] Elongation at break.
[e] Ten percent weight loss temperature.
[f] Fifty percent weight loss temperature.
[g] $\Delta T = T_{50} - T_{10}$.
[h] Maximum thermal degradation temperature.

further increase in the number of double bonds no longer results in an increase in the yield of the crosslinked material.

FT-IR and solid-state ^{13}C NMR spectral analyses have been performed to fully characterize the resulting polymeric materials. A representative solid-state CP MAS ^{13}C NMR spectrum of the LIN45-ST32-DVB15-(NFO5-BFE3) terpolymer after Soxhlet extraction is shown in Fig. 3. The spectrum confirms the presence of ester carbonyl groups ($\delta = 165$–175 ppm), due to incorporation of the LIN into the crosslinked matrix, as well as the presence of C=C bonds ($\delta = 125$–135 ppm). Unfortunately, the broad nature of the latter peak prevents us from distinguishing between the sp^2 carbons of unreacted C=C bonds in the fatty acid side chains and those of the benzene rings in the ST and DVB units. Similar to the CP MAS ^{13}C NMR spectra, the FT-IR spectrum of the insoluble materials obtained from Soxhlet extraction of the LIN45-ST32-DVB15-(NFO5-BFE3) terpolymer (Fig. 4) confirms the presence of carbonyl groups (~ 1750 cm^{-1}) from incorporation of the LIN oil, as well as the presence of C=C bonds, but it does not allow us to clearly distinguish between the C=C bonds of the fatty acids and the benzene rings.

To determine the microstructures of the resulting copolymers, the soluble fractions from the Soxhlet extractions have been subjected to ^{1}H NMR spectral analysis. Representative ^{1}H NMR spectra of the soluble materials from the PNT45-ST32-DVB15-(NFO5-BFE3) and PNT62-DVB32-(NFO5-BFE3) copolymers are shown in Fig. 5. The ^{1}H NMR spectrum of the pure catalyst BFE is also included for comparison purposes. The spectral data confirm that the extract consists of several soluble components. The signals at 4.1–4.2 ppm confirm the presence of residual initiator fragments, while the signals

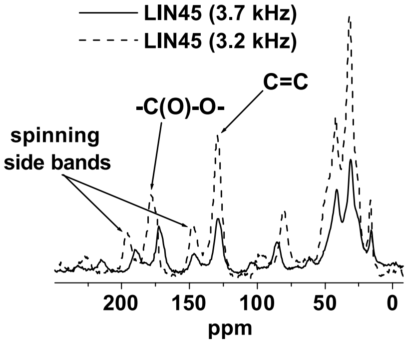

Fig. 3. Solid state ^{13}C NMR spectra of the insoluble materials remaining after Soxhlet extraction of the LIN45-ST32-DVB15-(NFO5-BFE3) bulk copolymer.

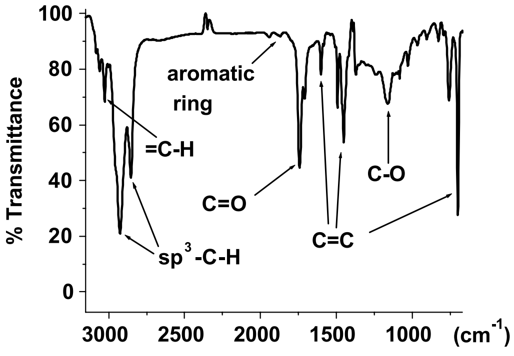

Fig. 4. FT-IR spectra of the insoluble materials remaining after Soxhlet extraction of the LIN45-ST32-DVB15-(NFO5-BFE3) bulk copolymer.

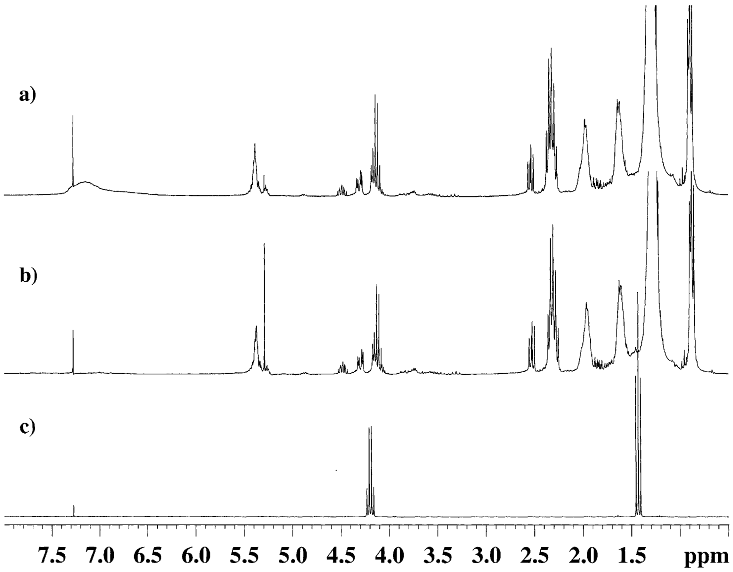

Fig. 5. ^{1}H NMR spectra of (a) soluble materials from PNT45-ST32-DVB15-(NFO5-BFE3), (b) soluble materials from PNT62-DVB32-(NFO5-BFE3), and (c) pure initiator BFE.

at 4.1–4.4 and 5.3–5.5 ppm correspond to glycerol and vinylic protons of the unreacted PNT oil, respectively. Also, the existence of a broad signal in the aromatic region (6.5–7.5 ppm) of the spectrum of the PNT45-ST32-DVB15-(NFO5-BFE3) extract suggests the presence of low molecular weight ST-PNT copolymers. These oligomers are soluble in CH_2Cl_2 and readily extracted during Soxhlet extraction. In contrast, this type of signal was not observed in the spectrum of the PNT62-DVB32-(NFO5-BFE3) extract, suggesting that DVB is completely incorporated into the crosslinked network. Similar results have been obtained during ^{1}H NMR spectral analyses of the soluble extracts from other vegetable oil copolymers.

3.3. Thermogravimetric analysis of the vegetable oil copolymers

Tables 3 and 4 summarize the thermal data for the OIL-DVB and OIL-ST-DVB copolymers, respectively. These include 10 and 50% weight loss temperatures (T_{10} and T_{50}), their differences (ΔT), as well as the temperatures of maximum thermal degradation ($T_{\max}$). Thermogravimetric analysis indicate that the OIL-DVB and OIL-ST-DVB bulk polymers are thermally stable in air below 200 °C and exhibit a three-stage thermal degradation above this temperature (Fig. 6, curve A). The first stage degradation (200–400 °C) is attributed to evaporation and decomposition of unreacted oil and other soluble components in the bulk material. The second stage (400–500 °C) is the fastest and corresponds to degradation and char formation of the crosslinked polymer structure, while the last stage (>500 °C) corresponds to gradual oxidation of the char residue. The second stage is also characterized by a $T_{\max}$ value determined from the minimum of the corresponding derivative % weight loss curve (Fig. 6, curve B). The data in Tables 3 and 4 indicate that the bulk of the OIL-DVB and OIL-ST-DVB copolymers lose 10% of their weight at temperatures ranging from 269 to 342 and 276 to 339 °C, respectively. In general, an increase in d value of the vegetable oil results in higher T_{10} values for both the OIL-DVB and OIL-ST-DVB copolymers. For example, an increase in d value from 2.86 (OLV) to 6.07 (LIN) results in a 73 and 63 °C increase in T_{10} value for the OIL-DVB and OIL-ST-DVB copolymers, respectively. More unsaturated vegetable oils result in polymers with better thermal properties. In spite of the noticeable differences in the T_{10} values, all of the polymers lose half of their weight within a very narrow temperature region, as indicated by the ΔT values. This value is defined as the difference between the T_{10} and T_{50} temperatures and denotes the rate of thermal decomposition in the first and second stages of the

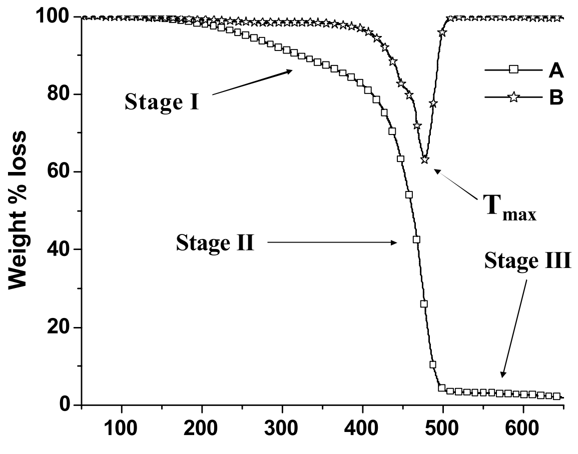

Fig. 6. TGA thermogram of the GRP45-ST32-DVB15-(NFO5-BFE3) copolymer in air (A) and its derivative curve (B).

polymers' thermal decomposition. Our results show that copolymers composed of oils with higher d values have lower ΔT values. This is in agreement with the fact that copolymers of more unsaturated oils contain less unreacted oil. The smaller amount of unreacted oil in the bulk polymer degrades faster and thus results in smaller ΔT values. The results also indicate that the T_{50} values increase as well with increasing d values of the oils. However, unlike the differences for the T_{10} values (73 and 63 °C), these differences are much smaller (11 and 10 °C). The closer these temperatures get to $T_{\max}$, the smaller the differences are. This indicates that the thermal decompositions in the $T_{\max}$ region are almost independent of the d values of the vegetable oils. Fig. 7 represents the TGA thermograms of several OIL-DVB and OIL-ST-DVB copolymers. These thermograms indicate that both systems exhibit quite similar thermal behaviors.

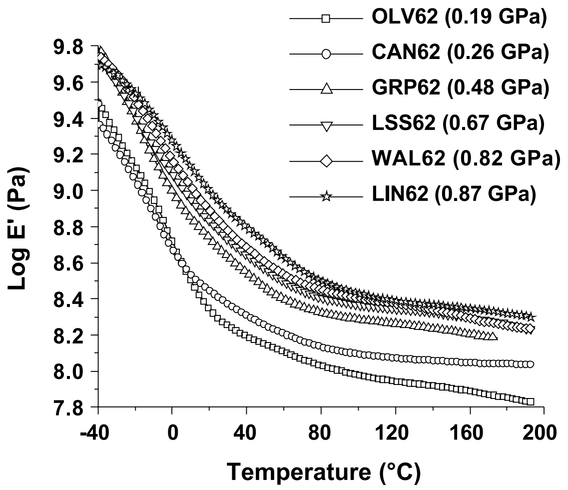

Fig. 8. Temperature dependence of the storage modulus E' for several OIL62-DVB30-(BFE3-NFO5) copolymers with their room temperature E' values given in parentheses.

3.4. *Dynamic mechanical properties of the vegetable oil copolymers*

Figs. 8 and 9 show the temperature dependence of the storage moduli of the OIL-DVB and OIL-ST-DVB copolymers, respectively. Dynamic mechanical analysis (DMA) reveals that all copolymers behave as typical thermosets as evidenced by the presence of rubbery plateaus in their DMA curves. As expected, the storage moduli decrease gradually with increasing temperature until the rubbery plateau region appears above approximately 80 °C. The room temperature storage moduli appear dependent on the degree of unsaturation of the vegetable oils employed for copolymer synthesis. Figs. 8 and 9 show that the storage moduli at room temperature steadily increase from 0.19 (OLV) to 0.87 (LIN) GPa and 0.22 (OLV) to 1.84 (LIN) GPa for the OIL-DVB and OIL-ST-DVB copolymers, respectively. The presence of the rubbery plateau in the DMA curves is evidence for the existence of a crosslinked network in the bulk polymers. According to the kinetic theory of rubber elasticity [32–34], the experimental crosslink densities of all copolymers (ν_e) can be determined

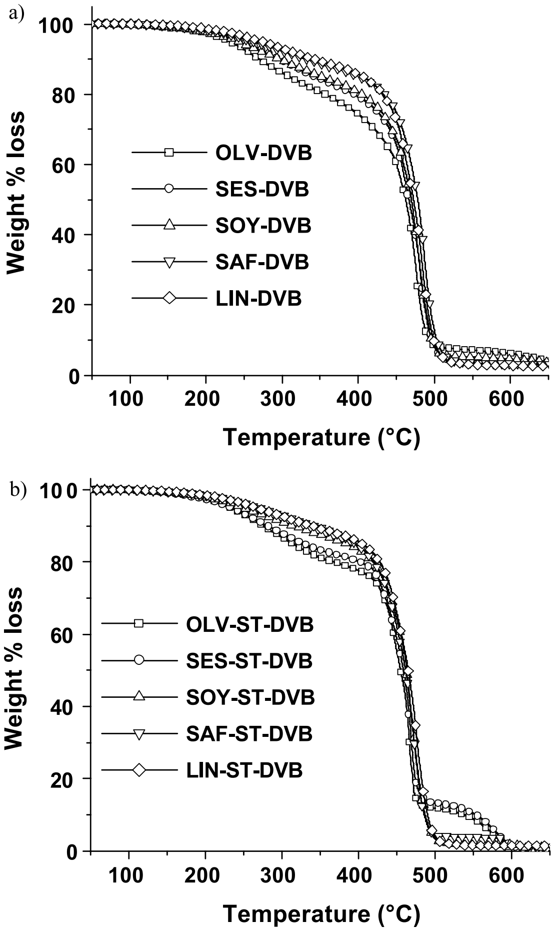

Fig. 7. TGA thermograms of several OIL-DVB (a) and OIL-ST-DVB (b) copolymers acquired in air.

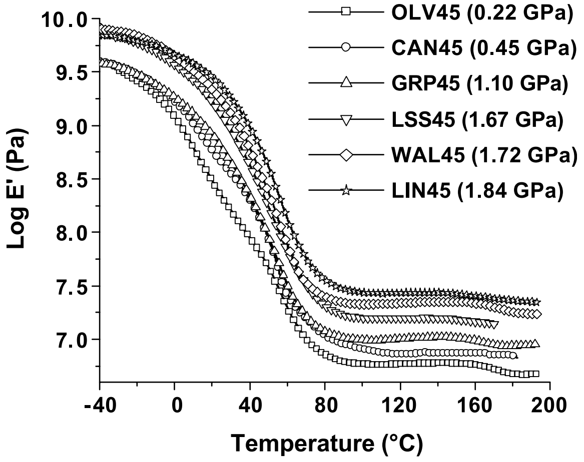

Fig. 9. Temperature dependence of the storage modulus E' for several OIL45-ST32-DVB15-(NFO5-BFE3) copolymers with their room temperature E' values given in parentheses.

from the rubbery moduli using the following equation:

$$E' = 3\nu_e RT$$

where E' represents the storage modulus of the crosslinked copolymer in the rubbery plateau region above the glass transition temperature (T_g), R is the universal gas constant and T is the absolute temperature. The values of the storage moduli E' used for the calculations were taken at approximately 50 °C above the T_g. Typical crosslink densities of the OIL-DVB copolymers are in the range of 7.6×10^3–2.3×10^4 mol/m^3 and are much higher than those of the OIL-ST-DVB copolymers, which are in the range of 6.0×10^2–2.3×10^3 mol/m^3 (Tables 3 and 4). Like regular soybean oil (SOY) [18], all vegetable oils used in this study contribute directly to the crosslink densities of their corresponding copolymers. Keeping in mind that the only variable in both the OIL-DVB and OIL-ST-DVB systems is the vegetable oil employed, it is important to note that copolymers prepared from more unsaturated oils have higher crosslink densities. This means that a careful choice of the vegetable oil employed as the comonomer may also be used as a tool for tuning the polymer properties.

Tables 3 and 4 also summarize the glass transition temperatures (T_g) obtained from DMA analysis of the OIL-DVB and OIL-ST-DVB copolymers, respectively. All OIL-DVB copolymers have two glass transition temperatures, which merge into a very broad transition. The OIL-DVB copolymer matrixes appear as complex heterogeneous systems composed of 'DVB-rich' phases and 'OIL-rich' phases with their own individual glass transitions (Fig. 10). At the very beginning of the reaction, DVB, as the much more reactive monomer, starts to homopolymerize and forms the core of the DVB-rich phase (hard domain). This is evidenced by the formation of white flakes, which correspond to polydivinylbenzene. As the DVB concentration drops, the DVB starts to copolymerize with the OIL, which is present in far greater concentration, until the DVB is completely consumed. During that stage of the reaction, a certain amount of the OIL is incorporated into the copolymer structure. The amount of the oil incorporated is directly related to the reactivity of the oil, which is expressed through its d value. At the end of the reaction, a certain amount of OIL is left unreacted, as evidenced by our extraction data. This oil acts as a plasticizer in the bulk copolymer. The insoluble crosslinked materials are, therefore, composed of 'DVB-rich' domains (formed in the early stages of the reaction) and 'OIL-rich' domains (formed in the later stages of the reaction). The glass transition temperatures we observe from the tan delta curves are considerably lower than expected for the glass transition temperatures of these two domains minus any plasticizer. The low glass transition temperatures are presumably due to plasticization by the soluble components, which are statistically distributed throughout the bulk polymer. Thus, the high temperature transitions (α_1) (from 45 to 58 °C) represent the glass transitions of the plasticized 'DVB-rich' phases, while the low temperature transitions (α_2) (from −13 to 11 °C) correspond to the glass transitions of the plasticized 'OIL-rich' phases. In contrast, most of the OIL-ST-DVB terpolymers (with the exception of the OLV and PNT oil terpolymers) possess a single glass transition (Fig. 11). The glass transition temperatures of the OIL-ST-DVB terpolymers are in the 50–66 °C range, which is slightly higher than the range of the OIL-DVB copolymers. In general, the glass transition temperatures for both the OIL-DVB and OIL-ST-DVB systems show no dependence on the degree of unsaturation of the oils employed in their synthesis. The existence of the dual thermal transitions in the OLV45-ST32-DVB15-(NFO5-BFE3) and PNT45-ST32-DVB15-(NFO5-BFE3) terpolymers is a consequence of the low degrees of unsaturation of these two oils. Their lower reactivities result in formation of heterogeneous systems as opposed to those of the other OIL-ST-DVB terpolymers. Similar to our explanation regarding the OIL-DVB systems, the high glass transitions correspond

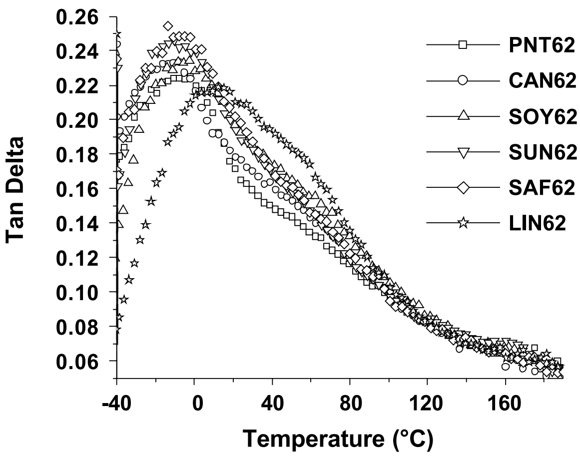

Fig. 10. Temperature dependence of the loss factor tan δ for several OIL62-DVB30-(NFO5-BFE3) copolymers.

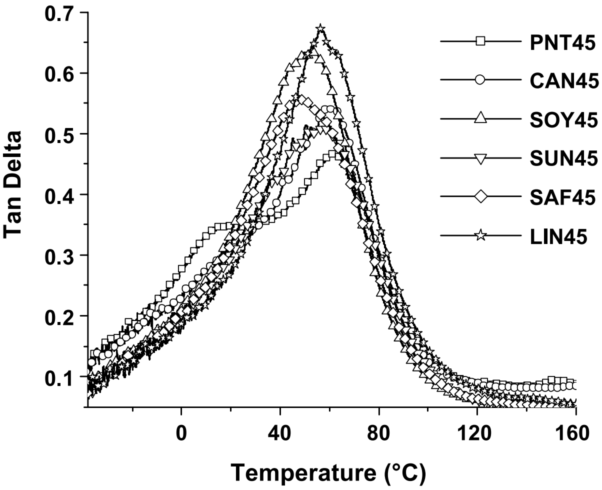

Fig. 11. Temperature dependence of the loss factor tan δ for several OIL45-ST32-DVB15-(NFO5-BFE3) copolymers.

to plasticized ‘ST-DVB-rich’ phases, while the low glass transitions correspond to plasticized ‘OIL-rich’ phases (Fig. 11). Furthermore, when compared to the α_2 transitions in the corresponding OIL-DVB copolymers, the α_2 transitions of the OLV-ST-DVB (16 °C) and PNT-ST-DVB (19 °C) terpolymers are considerably higher. This is a consequence of the lower amounts of OLV and PNT oils and greater amounts of aromatic comonomers incorporated into the ‘OIL-rich’ phases of the OLV-ST-DVB and PNT-ST-DVB terpolymers, respectively. This is not a surprise, since the initial amounts of individual vegetable oils in the OIL-ST-DVB systems (45 wt%) are lower than those in the corresponding OIL-DVB systems (62 wt%). Of course, the opposite is true for the initial amounts of aromatic comonomers.

3.5. Tensile stress–strain performance of the vegetable oil copolymers

Figs. 12 and 13 show the tensile stress–strain behavior of several OIL-DVB and OIL-ST-DVB copolymers, respectively. The OIL-DVB copolymers exhibit a variety of stress–strain behaviors depending on the oil used in their synthesis. In general, all of these copolymers are brittle in nature. Their Young’s moduli are in the range of 27.2–99.9 MPa and show clear dependence on the *d* values of the vegetable oils employed for their synthesis (Table 3). For example, the initial slopes of the LIN, WNT and SAF copolymers are rather steep, indicating the high elastic moduli of these materials. Quite the opposite is observed for the OLV, PNT and SES copolymers, which have significantly lower Young’s moduli and are very soft in nature. The stress–strain curves of all OIL-DVB copolymers show a constant increase in stress with strain until rupture occurs. Elongation-at-break values of these materials are fairly small and similar for all copolymers. They are in the range of 7.7–11.8% and show no dependence on the reactivity of the vegetable oil. The brittle nature of the OIL-DVB copolymers is mainly due to the relatively high crosslink densities of these copolymers, which drastically reduce the copolymers’ flexibilities and elongations at break (Table 3).

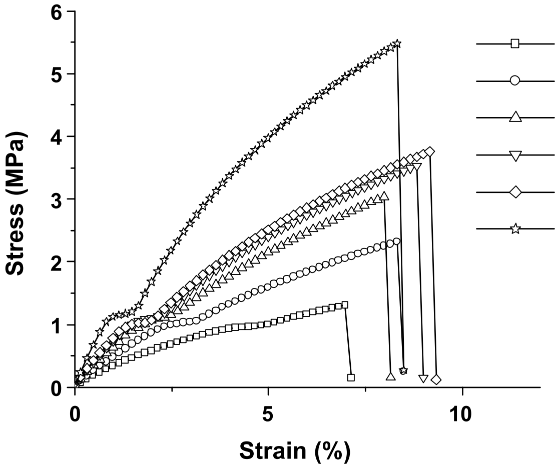

Fig. 12. Tensile stress–strain curves for several OIL62-DVB30-(NFO5-BFE3) copolymers.

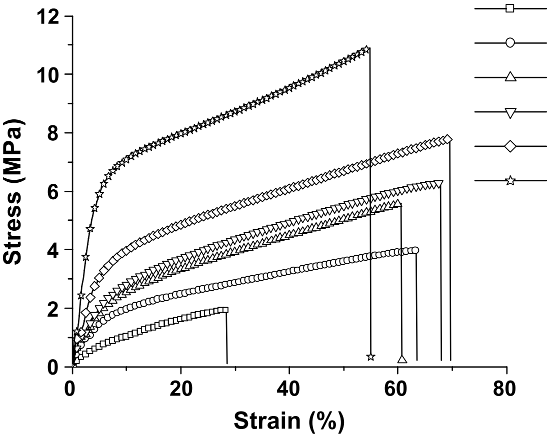

Fig. 13. Tensile stress–strain curves for several OIL45-ST32-DVB15-(NFO5-BFE3) copolymers.

The increase in the crosslink densities of the OIL-DVB copolymers with increasing oil reactivity substantially reduces the mobility of polymer chains between the junctions and, therefore, the number of conformations which they can adopt. On the other hand, the stiffness of these polymers, as well as the energy required for crack propagation during the tensile deformation, progressively increases. Because of that, the ultimate strengths of the OIL-DVB copolymers follow the same trend. These values increase gradually with increasing oil reactivity and are in the range of 1.2–5.6 MPa.

In addition to the Young’s modulus and ultimate strength data, tensile tests also provide information about the polymers’ tensile toughness. Tensile toughness is measured by the area under the stress–strain curve and represents the work expended in deforming the material [35]. Both tensile strength and the elongation-at-break contribute to tensile toughness. In general, brittle materials have low tensile toughness, while ductile materials have high. The tensile toughness of the OIL-DVB copolymers is in the range of 0.06–0.35 MPa. In spite of the independent nature of the elongation-at-break values of the OIL-DVB copolymers and the reactivity of the corresponding oil, Table 3 indicates that the tensile toughness of most of the OIL-DVB copolymers increases gradually with the increasing reactivity of the oil. The only exceptions are the CAN62-DVB30-(NFO5-BFE3), SOY62-DVB30-(NFO5-BFE3) and SAF62-DVB30-(NFO5-BFE3) copolymers, whose values deviate from the expected trend. At this moment we are unable to account for these discrepancies.

The OIL-ST-DVB terpolymers, on the other hand, exhibit stress–strain behavior typical of ductile plastics. They have Young’s moduli ranging from 13.0 to 125.6 MPa and cover a much wider range than those of the OIL-DVB copolymers (Table 4). The deformation of all OIL-ST-DVB terpolymers under the applied load appears closely related to the vegetable oil used in their synthesis. Typically, these materials exhibit tensile yielding behavior with two characteristic regions of deformation in their stress–strain curves (Fig. 13). The first region ($\varepsilon < 10\%$) is characterized by a rapid increase in stress with strain until the yield point. The initial slopes of the curves for the copolymers prepared from the highly unsaturated oils (LSS, SAF, WNT and LIN) are steep, indicating the high Young's moduli of these materials. Conversely, the slopes for the OIL-ST-DVB terpolymers made from the least reactive oils (OLV and PNT) have the lowest Young's moduli of all vegetable oil copolymers prepared in this study. After the yield point ($\varepsilon > 10\%$), the OIL-ST-DVB terpolymers show a slow increase in stress with strain until fracture occurs. Their ultimate strengths are in the range from 1.9 to 10.9 MPa and exhibit a gradual increase with increasing reactivity of the corresponding vegetable oil. Their elongation-at-break values are substantially higher than those of the OIL-DVB copolymers and are in the range from 38.6 to 86.0%. Similar to the values for the OIL-DVB copolymers, these values show no clear dependence on the reactivity of the vegetable oil. Presumably, an increase in the degree of unsaturation of the oil creates two opposite effects, namely an increase in the crosslink density and an increase in vegetable oil incorporation, which may be responsible for this independence. The latter effect contributes to the materials' overall softness and flexibility by increasing incorporation of the flexible triglyceride monomers, while the former effect increases the polymers' stiffness and brittle nature by increasing the polymers' crosslink density. Conversely, the toughness values for the OIL-ST-DVB copolymers range from 0.46 to 5.83 MPa and clearly increase with the increasing reactivity of the vegetable oil.

4. Conclusions

A range of thermosets have been prepared by the cationic copolymerization of olive, peanut, sesame, canola, corn, soybean, grapeseed, sunflower, low saturation soy, safflower, walnut and linseed oils with DVB or a combination of ST and DVB initiated by an NFO-modified BFE catalyst. The physical, thermal and mechanical properties of these new polymers have been investigated as a function of the vegetable oil reactivity.

The gelation times of these copolymers are independent of the degree of unsaturation of the vegetable oil. Thermogravimetric analysis shows that both the OIL-DVB and OIL-ST-DVB copolymers are thermally stable below 200 °C with 10% weight loss temperatures in air of 276 – 339 and 269–342 °C, respectively. The T_{10} and T_{50} values of both copolymer series gradually increase with the increasing reactivity of the corresponding vegetable oil. According to Soxhlet extraction analysis, higher yields of crosslinked polymers have been obtained by employing more unsaturated oils. Dynamic mechanical analysis (DMA) shows that the resulting products are typical thermosets with densely crosslinked structures. Their crosslink densities vary from 7.6×10^3 to 2.3×10^4 and 6.0×10^2 to 2.3×10^3 mol/m^3 for the OIL-DVB and OIL-ST-DVB copolymers, respectively, and show a gradual increase with the increasing reactivity of the vegetable oil used in their synthesis. Most of the OIL-ST-DVB terpolymers have single glass transition temperatures ranging from 50 to 66 °C. Conversely, all of the OIL-DVB copolymers have two glass transition temperatures due to extensive microphase separation caused by thermodynamic immiscibility between the crosslinked matrix and the unreacted oil. The thermal transitions of both the OIL-DVB and OIL-ST-DVB systems show no observable dependence on the reactivity of the vegetable oil.

The tensile-stress strain behavior of these new vegetable oil-based materials demonstrates properties characteristic of polymers ranging from hard and brittle to relatively soft and ductile plastics. Typically, polymers prepared from the more unsaturated vegetable oils possess better mechanical properties. The room temperature Young's moduli, ultimate strengths and toughness of all polymers are ultimately related to the reactivity of the corresponding vegetable oil. All of these parameters show a gradual increase with increasing oil reactivity.

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