Vernonia Oil–Based Acrylate and Methacrylate Polymers and Interpenetrating Polymer Networks with Epoxy Resins

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ABSTRACT: Acrylate and methacrylate monomers were obtained by reacting vernonia oil, a naturally epoxidized oil, with acrylic or methacrylic acid. The highest conversion (85–98%) of epoxy groups was obtained when the reaction was performed with an excess of the carboxylic acid at 100–120°C. The acrylate and methacrylate monomers of vernonia oil were characterized by IR and NMR spectroscopy. These monomers were then cured by sunlight in the presence of benzophenone to produce transparent films. In addition, interpenetrating polymer neworks (IPNs) were prepared in a two-step technique from the sunlight-cured methacrylate of vernonia oil, as the elastomeric component, in combination with a cured epoxy resin (a bisphenol A–type resin). Dynamic mechanical analysis showed good compatibility between the networks of the two cured polymers. An IPN with a 1 : 1 composition of the two polymer components exhibited the properties of a reinforced elastomer. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3835–3843, 2004

Key words: vernonia oil; acrylate and methacrylate monomers; photopolymerization; interpenetrating networks (IPNs); resins

INTRODUCTION

Vegetable oils constitute a renewable resource that can form the basis for new polymers with a wide range of industrial applications. Such polymers would have obvious environmental advantages over conventional petroleum-based polymers. An important class of reactive monomers that can be easily photopolymerized by ultraviolet (UV) radiation are multifunctional acrylates (MFAs).[1–3] These compounds are usually prepared from petroleum, but alternative sources are acrylate derivatives of vegetable oils. Such natural multifunctional acrylated monomers polymerize readily to form highly crosslinked polymer networks. A wide range of polyfunctional acrylate monomers and oligomers of vegetable oils [e.g., poly(ester acrylates), poly(epoxy acrylates), and poly(urethane acrylates)] have already been prepared from epoxidized soybean, castor, lesquerella, palm, and vernonia oils.[4–11] The ecological advantages of polyfunctional acrylate monomers are further enhanced by the fact that sunlight may be used as the curing agent in the production of highly crosslinked polymers.[12] This green curing technology is particularly cost effective and is unique in that it facilitates the polymerization of large items. Many such highly crosslinked polyacrylates based on vegetable oils have found application in a wide range of coatings and adhesives.[4–7]

A vegetable oil with remarkable commercial potential that is currently receiving attention as a basis for new monomers and polymers is vernonia oil, which is obtained from the seeds of *Vernonia galamensis*. The presence of naturally occurring epoxide rings, double bonds, and carboxylic esters groups confers high reactivity on this unique starting material. The oil is composed of triglycerides that contain about 70–80% of an epoxy acid, which is commonly known as vernolic acid, and 20–30% of nonfunctional acid residues.[13,14]

$$CH_3—(CH_2)_4—CH\overset{\displaystyle O}{\overset{\diagup\diagdown}{—CH}}—CH_2—CH{=}$$
$$CH—(CH_2)_7—COOH$$
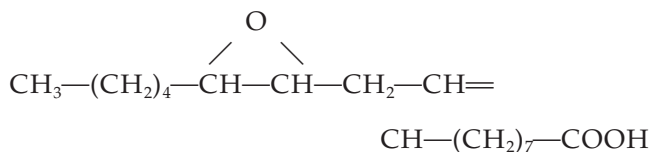
The triepoxy functionality of vernonia oil has been exploited to form crosslinked polymers with difunctional reagents, such as dibasic acids,[15,16] and aliphatic and aromatic diamines.[17] The resulting polymers are soft elastomers with low glass-transition temperatures. Interpenetrating polymer networks (IPNs) prepared by a combination of such elastomers with plastics exhibit properties ranging from reinforced elastomers to toughened plastics, depending on the overall composition of the polymer.[15,18] IPNs have also been prepared from UV-cured triacrylates of other vegetable oils,[7] for example, the photoinitiated

urethane–acrylate of castor oil was used in the generation of co-networks and semi- and full IPNs with various poly(methyl methacrylate)s.

Preliminary results of a study on the synthesis of the acrylate (and methacrylate) of vernonia oil were previously reported.[10,11] The present work describes the synthesis of the acrylate and methacrylate monomers obtained by reacting vernonia oil with acrylic or methacrylic acid, with high conversion of the epoxy groups. The obtained monomers were photopolymerized by sunlight. Thereafter, IPNs were prepared from the sunlight-cured methacrylate of vernonia oil as the elastomeric component in combination with a cured bisphenol A–type epoxy resin. Dynamic mechanical analysis (DMA) of the IPNs was performed and mechanical properties were studied.

EXPERIMENTAL

Materials

Vernonia oil (Ver-Tech, Inc., Bethesda, MD) contained an average of 2.1 epoxy functionalities per molecule. The bisphenol A–type resin, Epicote 828 (Shell Chemical Co., Akron, OH) had an equivalent weight per epoxy group of 190 ± 5 (average molecular weight 380). 2,4,6-Tris(dimethylaminomethyl) phenol (DMP-30), used as the accelerator in the curing of the epoxy resin, was purchased from Aldrich (Milwaukee, WI). Reagent-grade tetraethylammonium bromide (TEAB), tetrabutylammonium bromide (TBABr), benzyltriethylammonium chloride (BzTEAC), hydroquinone, and benzophenone were purchased from Aldrich.

Synthesis of the acrylic or methacrylic monomer of vernonia oil

Acrylate of vernonia oil

A mixture of vernonia oil (13.23 g, 0.01 mol as trivernolin) and acrylic acid (3.61 g, 0.05 mol), containing 0.5 wt % of hydroquinone, was stirred for 8 h at 100°C. An additional amount of acrylic acid (1.44 g, 0.02 mol) was then added, and the reaction mixture was heated for a further 4 h. The progress of the reaction was monitored by titration of the epoxy groups. After cooling to room temperature, chloroform was added to the reaction mixture. The organic layer was separated off, washed with a 5% sodium bicarbonate and then with water, and dried over sodium sulfate. The solvent was removed under reduced pressure. The viscous liquid (14.6 g; 95%) obtained contained 0.4% of epoxy groups.

Methacrylate of vernonia oil

A mixture of vernonia oil (13.23 g, 0.01 mol as trivernolin) and methacrylic acid (4.3 g, 0.050 mol), containing 0.25 wt % of hydroquinone, was stirred for 8 h at 120°C. An additional amount of methacrylic acid (1.72 g, 0.02 mol) was added, and the reaction mixture was heated for 4 h at the same temperature. The remainder of the workup of the reaction mixture was the same as that described for the triacrylate of vernonia oil. A viscous liquid (15.33 g; 97%), containing 0.5% of epoxy groups, was obtained.

Photochemical curing of the acrylate and methacrylate monomers of vernonia oil
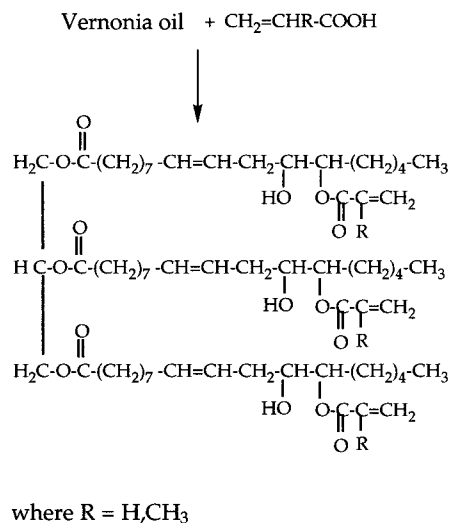
The acrylate or methacrylate of vernonia oil, containing 1–10 wt % of benzophenone as the photoinitiator, was cast onto a glass plate and subjected to UV-irradiation (sunlight) for 60 min. Films with a thickness of about 0.05 mm were obtained. The gel fraction of the cured polymer was determined as the insoluble part of the polymer (%) that remains after extraction with chloroform for 24 h at room temperature.

Preparation of IPNs from the methacrylate of vernonia oil and an epoxy resin

The methacrylate of vernonia oil, containing 5 wt % of benzophenone as the UV photoinitiator, was added to Epicote 828, containing 4 wt % of DMP-30 as the accelerator. The components were gently mixed at room temperature for a few minutes to give a homogeneous mixture, which was then degassed with a vacuum pump at room temperature until frothing ceased. The mixture was poured into a casting Teflon mold (35 × 5 × 1.5). To obtain the IPNs, *in situ* UV-radiation polymerization was carried out in sunlight for 2 h (step 1), followed by heating at 80°C for 2 h and then at 160°C for 4 h (step 2). IPNs containing 25 or 50% of the epoxy resin were prepared. The casting from the polymethacrylate of vernonia oil was obtained in step 1, and that of the cured epoxy resin in step 2.

Characterization

Epoxy groups were determined by potentiometric titration.[19] FTIR analysis was carried out on a Nicolet spectrometer (Nicolet Analytical Instruments, Madison, WI). ^{1}H- and ^{13}C-NMR spectra were obtained with a Bruker WP-200 SY spectrometer (Bruker Instruments, Billerica, MA) in CDCl$_3$ solution with TMS as the internal standard. DMA and tensile tests of the polymers were performed at the Casali Institute for Applied Research, The Hebrew University of Jerusalem. The DMA was conducted under liquid nitrogen with a DMA 983 (TA Instruments, New Castle, DE). All the samples were tested in the temperature range from −120 to 180°C, at a heating rate of 5°C/min, and a fixed frequency of 1 Hz. The glass-transition temper-

Vernonia oil + CH₂=CHR-COOH

$$CH_2=CHR\text{-}COOH$$

Vernonia oil + CH₂=CHR-COOH

H₂C-O-C-(CH₂)₇ -CH=CH-CH₂-CH-CH-(CH₂)₄-CH₃
HO   O-C-C=CH₂
O R

H C-O-C-(CH₂)₇ -CH=CH-CH₂-CH-CH-(CH₂)₄-CH₃
HO   O-C-C=CH₂
O R

H₂C-O-C-(CH₂)₇ -CH=CH-CH₂-CH-CH-(CH₂)₄-CH₃
HO   O-C-C=CH₂
O R

where R = H,CH₃

Scheme 1

ature was taken as the peak maximum of the loss modulus (E'') curves measured at 1 Hz. Tensile testing was carried out on an Instron universal testing machine (model 4502; Instron, Canton, MA) with a loading gauge of 15–20 mm at room temperature. The loading rate was 10 mm/min.

RESULTS AND DISCUSSION

The acrylate and methacrylate monomers of vernonia oil were synthesized by reacting vernonia oil with an α,β-unsaturated carboxylic acid, either acrylic or methacrylic acid (**Scheme 1**).

The mechanism of this type of reaction of an epoxy group with a carboxylic acid has been extensively described in the literature.[20,21] The main reaction is an addition esterification obtained by the nucleophilic attack of the carboxylic group on the epoxy moiety. This reaction generally requires a catalyst such as a tertiary amine,[20,22,23] a quaternary ammonium or phosphonium salt,[22,24,25] or a transition metal chelate.[22,24] Brisler et al.[5] used this type of synthesis to prepare the methacrylate of vernonia oil, with a tertiary amine as the catalyst. Our group previously reported some preliminary results on the synthesis of the acrylate and the methacrylate of vernonia oil.[10,11] In the present work on the synthesis of these monomers, we investigated the effect on the conversion of the epoxy groups of the quaternary ammonium salts TEAB, TBAB, and BzTEAC; the molar ratio of the reactants (epoxy to carboxylic groups); and the reaction temperature and time.

Acrylate of vernonia oil

In the first set of experiments, vernonia oil was reacted with acrylic acid in an equimolar ratio of epoxy to carboxylic groups. Table I shows that, without catalyst, low conversion of epoxy groups (17%, run 1) was obtained after 17 h. With TEAB as the catalyst (0.74 or 5 mol %; runs 2 and 4, respectively), the conversion of the epoxy groups was increased by only a very slight extent (26%). Increasing the reaction time led to gel formation (runs 3 and 5). BzTEAC (5 mol %) gave a 45% conversion of the epoxy groups, and TBAB (5 mol %) gave 60% conversion (a higher amount of TBAB produced a gel; run 8). The catalytic efficiency of the quaternary ammonium salts in the reaction of vernonia oil with acrylic acid was of the following order: TBAB > BzTEAC > TEAB. By using 5 mol % of TBAB as the catalyst, the conversion of epoxy groups was increased from 17 to 60% (Table I).

In the next set of experiments, the esterification of vernonia oil was performed at 100°C with a $1.7M$ excess of acrylic acid without catalyst and with TBAB (5 mol %) as the catalyst. The finding that the conversion of epoxy groups both with and without catalyst was about 70% (Fig. 1) showed that optimal conversion of epoxy groups was obtained with an excess of acrylic acid without the need for a catalyst. Therefore, further investigations of this reaction were carried out with an excess of acrylic acid and without catalyst.

The attempts to enhance the conversion of epoxy groups (>70%) by increasing the reaction time led to gel formation (i.e., to thermal polymerization of the triacrylate of vernonia oil). To prevent gel formation, hydroquinone was introduced as an inhibitor. In the presence of hydroquinone, the reaction time could be increased to 15–17 h, although the conversion of the epoxy groups did not change. We realized that by 8–10 h of reaction at 100°C, the molar ratio of carboxylic to epoxy groups had decreased from the initial 1.7 : 1 to 1.2 : 1–1 : 1. An additional amount of acrylic acid was thus introduced after 8–10 h to maintain the molar ratio of reactive groups at 1.7 : 1 and the reaction mixture was heated for an additional 4–5 h. In this way, the conversion of epoxy groups increased from 68–70 to 94–96%.

TABLE I
Reaction of Equimolar Amounts of Vernonia Oil and Acrylic Acid at 100°C

Run no.	Catalyst (mol %)[a]	Time (h)	Conversion of epoxy groups (%)
1	—	17	17
2	TEAB (0.74)	9	26
3	TEAB (0.74)	22	—[b]
4	TEAB (5.0)	10	24
5	TEAB (5.0)	17	—[b]
6	BzTEAC (5.0)	8	45
7	TBAB (5.0)	8	60
8	TBAB (10.0)	4	—[b]

[a] mol % of acrylic acid.
[b] A gel was obtained.
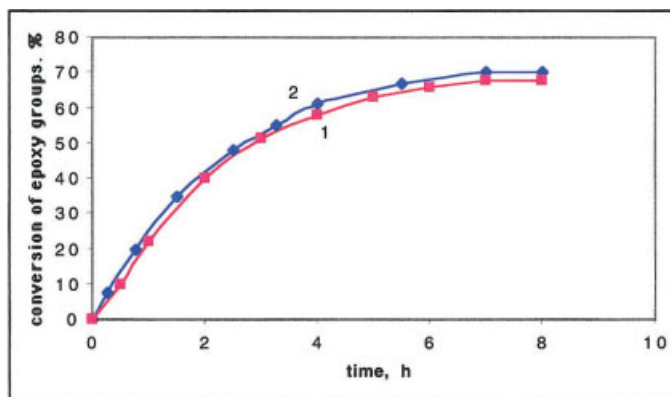
Figure 1 Conversion of epoxy groups as a function of time in the reaction of vernonia oil with excess acrylic acid at 100°C: (1) without catalyst; (2) with 5 mol % TBAB.

Methacrylate of vernonia oil

The reaction of vernonia oil with methacrylic acid was carried out under conditions similar to those used for acrylic acid (i.e., excess of methacrylic acid and the presence of hydroquinone). Figure 2 shows that the conversion of epoxy groups for the reaction of vernonia oil with methacrylic acid at 100°C was lower than that with acrylic acid (40 versus 70%). These results are in accordance with literature data[26] that acrylic acid is more reactive than methacrylic acid ($pK_{a\,met} < pK_{a\,ac}$). When the reaction of vernonia oil with methacrylic acid was carried out at 120°C for 8–10 h, conversion of the epoxy groups was increased to 68%. By analogy with the reaction of acrylic acid, the introduction of an additional amount of methacrylic acid after 8–10 h increased the conversion of the epoxy groups from 68 to 98%.

Spectral characterization

In the IR spectra of acrylated (Fig. 3) and methacrylated (not shown) vernonia oil, the absorption bands of the epoxide group at 840 and 820 cm^{-1} disappeared, and new absorption bands appeared, that is, a doublet at 1640 and 1620 cm^{-1} for the acrylate (or a band at 1630 cm^{-1} for the methacrylate) and a band at 810 cm^{-1} characteristic of the terminal double bond. The absorption band at 3450 cm^{-1} is characteristic of the hydroxyl group.

In the ^{1}H-NMR spectra of the acrylated and methacrylated [Fig. 4(A)] vernonia oil, the shift at 2.97 ppm, characteristic of the epoxy groups, disappeared. New chemical shifts appeared for the protons of the acrylate or methacrylate ester group (–CH—OCO–) at 4.8–4.9 ppm and for the proton of the methine group (–CH—OH) at 3.57–3.65 ppm. New ethylene protons were observed at 5.8, 6.2, and 6.5 ppm in the acrylate and at 5.50 and 6.05 ppm in the methacrylate, and the methyl proton at 1.95 in the methacrylate confirmed the presence of terminal double bonds.

In the ^{13}C-NMR spectra of acrylated and methacrylated [Fig. 4(B)] vernonia oil, the disappearance of the chemical shifts at 57.5 and 58.2 ppm, characteristic of the epoxy groups, was observed together with the
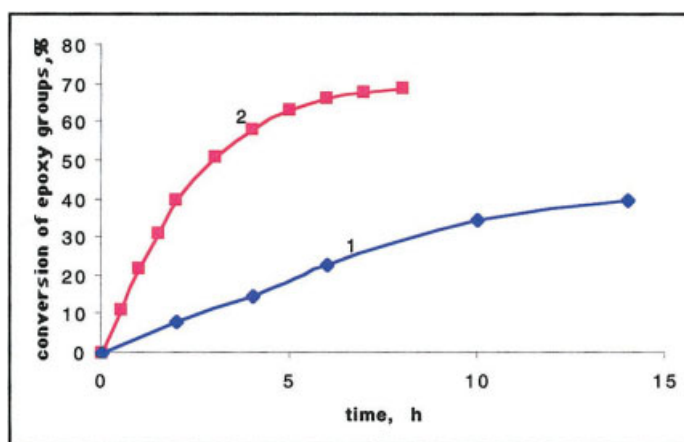
Figure 2 Conversion of epoxy groups at 100°C as a function of time in the reaction of vernonia oil with a 1.7M excess of (1) acrylic acid and (2) methacrylic acid.
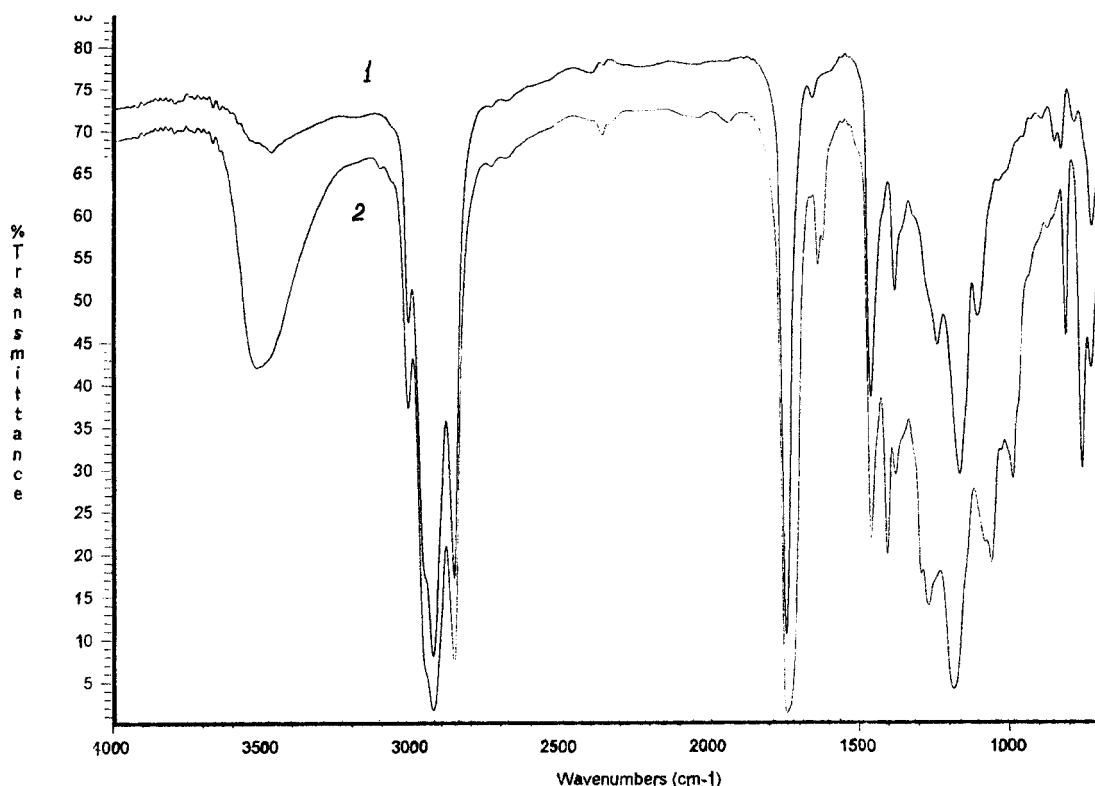
Figure 3 IR spectra of (1) vernonia oil and (2) acrylated vernonia oil.

appearance of new chemical shifts characteristic of the terminal double bond carbons at 128.1 and 130.7 ppm for acrylate and 125.6 and 136.0 ppm for methacrylate. The methyl group of the methacrylate was evident at 18.1 ppm. The new shifts at 165.46 ppm in the acrylate and at 166.65 ppm in the methacrylate monomer were attributed to the carbonyl carbon of the acrylate or methacrylate ester group. Figure 4 presents the ^{1}H- and ^{13}C-NMR spectra of the methacrylate vernonia oil.

Photochemical curing of the acrylate and methacrylate vernonia oil

Photochemical curing of the acrylate and the methacrylate of vernonia oil was carried out in sunlight with benzophenone as the photoinitiator. As the initiator concentration in the acrylate of vernonia oil was increased from 1 to 10 wt %, gelation occurred more rapidly (Fig. 5). A similar effect was observed for the methacrylate of vernonia oil. The maximum gel fraction obtained for the cured acrylate or methacrylate was 65–70%. This value is in agreement with the approximately 30% content of the nonepoxidized triglycerides present in the starting vernonia oil that do not contribute to the gel fraction. All the poly(acrylates) and poly(methacrylates) of vernonia oil with about 60–70% gel fraction were transparent films. Polymers with a lower gel fraction were white powders or weak opaque films.

The IR spectra of the acrylate of vernonia oil before and after photocrosslinking (5 wt % benzophenone for 1 h) are shown in Figure 6. The absence in the crosslinked film of the absorption bands at 1640, 1630, and 810 cm^{-1}, which are characteristic of the acrylic double bond $CH{=}CH_2$, confirmed that the terminal double bonds were involved in the polymerization. The band at 3450 cm^{-1}, characteristic of the hydroxyl group, was preserved.

The mechanical properties of the films obtained from the acrylate and methacrylate of vernonia oil containing 5% benzophenone and irradiated by sunlight for 1 h are shown in Table II. The finding that the tensile strength and Young's modulus of polymers were both very low was not surprising: it is obvious that these random polymers do not have a regular structure, given that they contain about 30% of nonfunctional triglycerides that do not participate in polymer formation.

IPNs from methacrylate of vernonia oil and an epoxy resin

The IPNs of the poly(methacrylate) of vernonia oil and a cured epoxy resin (Epicote 828) were prepared by a simultaneous interpenetrating networks (SIN) method, which combines two independent noninterfering curing reactions: UV-initiated polymerization of the methacry-
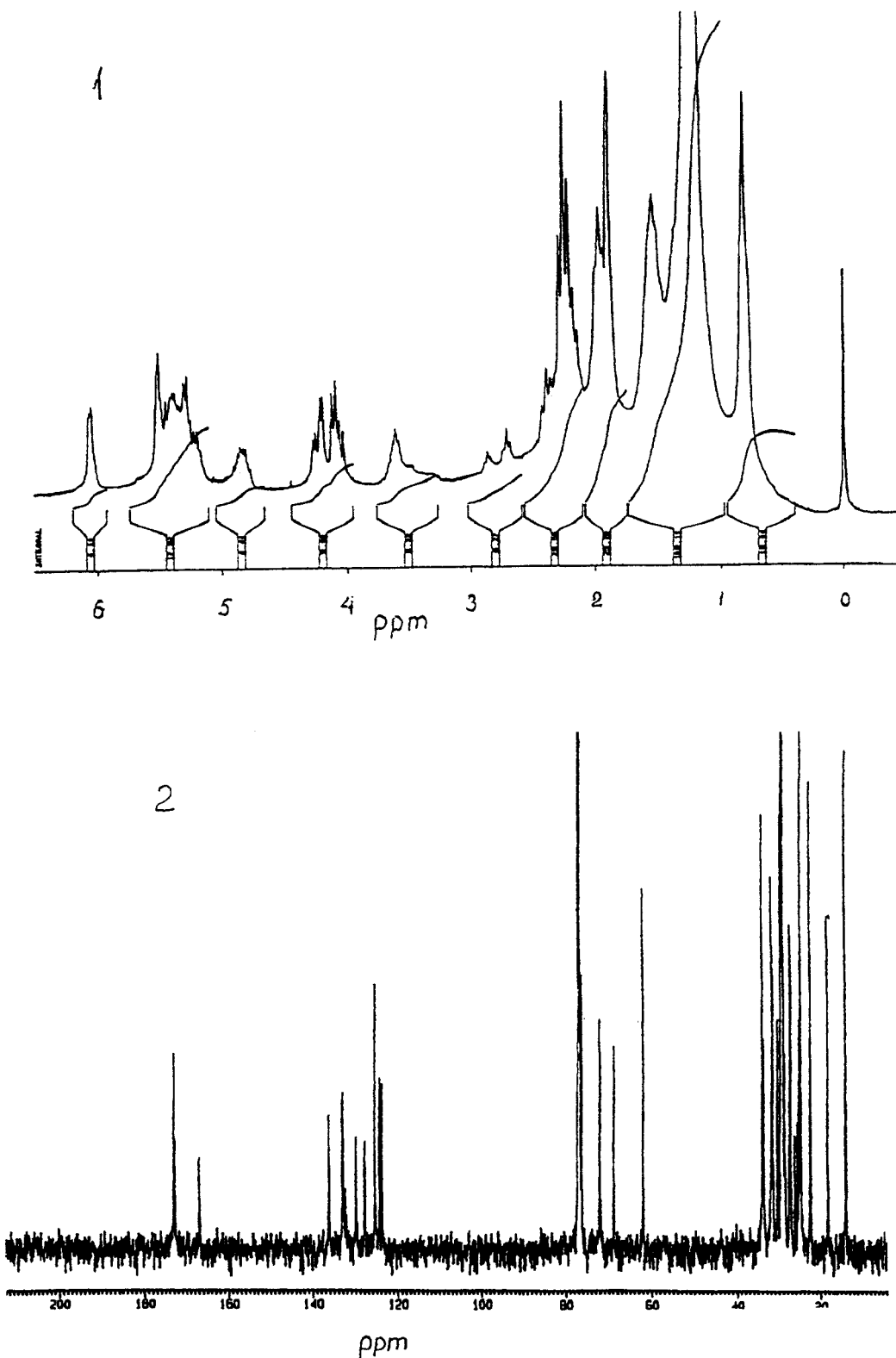
Figure 4 ¹H-NMR (A) and ¹³C-NMR (B) spectra of methacrylated vernonia oil.

late of vernonia oil (step 1) and polymerization of epoxy resin in the presence of a tertiary amine (DMP-30) as the accelerator (step 2).

The temperature dependency of the loss modulus maximum (E'') obtained from DMA for the IPNs con-taining cured epoxy resin and poly(methacrylate) of vernonia oil (25 : 75 and 50 : 50 wt %) is shown in Figure 7. Examination of Figure 7 and Table III shows that the crosslinked poly(methacrylate) of vernonia oil exhibited a low glass-transition temperature ($-19°C$)
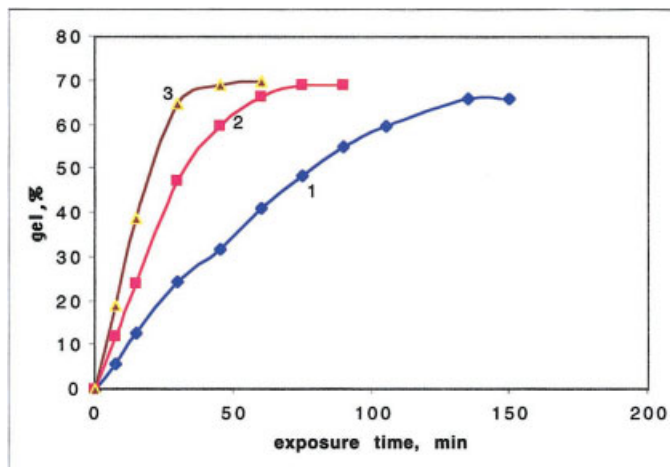
Figure 5 Effect of the concentration of the benzophenone photoinitiator ([(1) 1 wt %; (2) 5 wt %; (3) 10 wt %] on the gelation time of the sunlight-induced polymerization of the acrylate of vernonia oil.

and, analogously with cured polyesters of vernonia oil,[18] it may thus be regarded as an elastomer. Figure 7 and Table III also show that the IPNs with the higher amounts of cured epoxy resin exhibited the higher glass-transition temperatures. Figure 7 shows that each IPN exhibited a single broad peak, whose maximum lay between the maxima of the two component polymers. This finding of a single glass-transition temperature for the IPNs indicated good compatibility between the networks of two cured polymers.

A study of the mechanical properties of the cured homopolymers themselves and of their IPNs showed that the IPN containing 25 wt % of the cured epoxy resin had properties similar to those of the cured poly(methacrylate) of vernonia oil (Table IV). These low mechanical properties of the IPN containing 25 wt % of the cured epoxy resin are attributed to the presence of the relatively large amount of nonfunctional triglycerides exhibiting a significant plasticizing effect.[27] The IPN with 50 wt % of cured epoxy resin
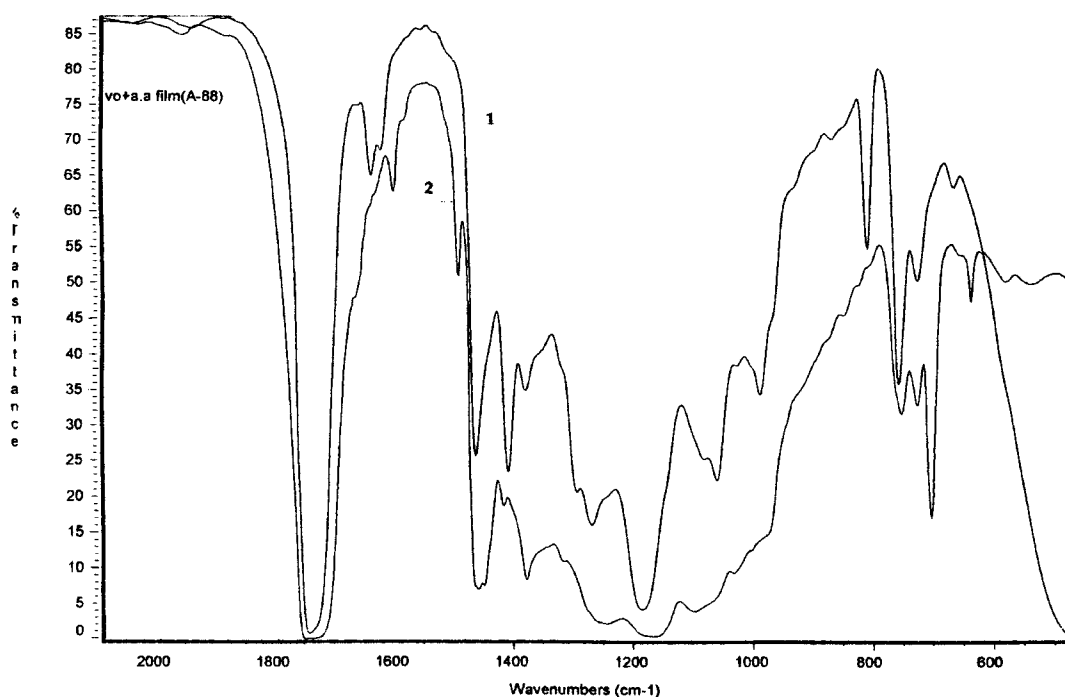
Figure 6 IR spectra of the acrylate of vernonia oil before (1) and after photopolymerization (2).

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TABLE II
Mechanical Properties of Films of Poly(acrylate) and Poly(methacrylate) of Vernonia Oil

Polymer film	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
Poly(acrylate) of vernonia oil	2.6	7.6	105
Poly(methacrylate) of vernonia oil	2.7	11.7	99

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TABLE III
Glass-Transition Temperatures (T_g) of Cured Poly(methacrylate) of Vernonia Oil, Cured Epoxy Resin, and IPNs

Polymer	T_g (°C)
Cured epoxy resin	105
IPN of cured epoxy resin : poly(methacrylate) of vernonia oil 50 : 50 wt %	10
IPN of cured epoxy resin : poly(methacrylate) of vernonia oil 25 : 75 wt %	−4
Poly(methacrylate) of vernonia oil	−19

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exhibited much higher values for tensile strength and Young's modulus. The values of the elongation of the two IPNs were substantially higher than the value for the cured epoxy resin and close to that for the cured poly(methacrylate) of vernonia oil. The IPN containing 50 wt % of cured epoxy resin has the mechanical properties necessary to make it a good candidate for use as a reinforced elastomer.

CONCLUSIONS

Reactive MFAs were prepared by reacting an α,β-unsaturated carboxylic acid (acrylic or methacrylic)

with naturally epoxidized vernonia oil. The highest conversion (90–98%) of epoxy groups was obtained when the reaction was performed with an excess of the carboxylic acid at 100–120°C. The structure of the compounds obtained was confirmed by IR and NMR spectroscopy. The monomers were photopolymerized in sunlight in the presence of benzophenone to give transparent films with a low tensile strength, a low Young's modulus, and rather high elongation. DMA of the polymethacrylate of vernonia oil showed this polymer to be a rubberlike elastomer with a low glass-
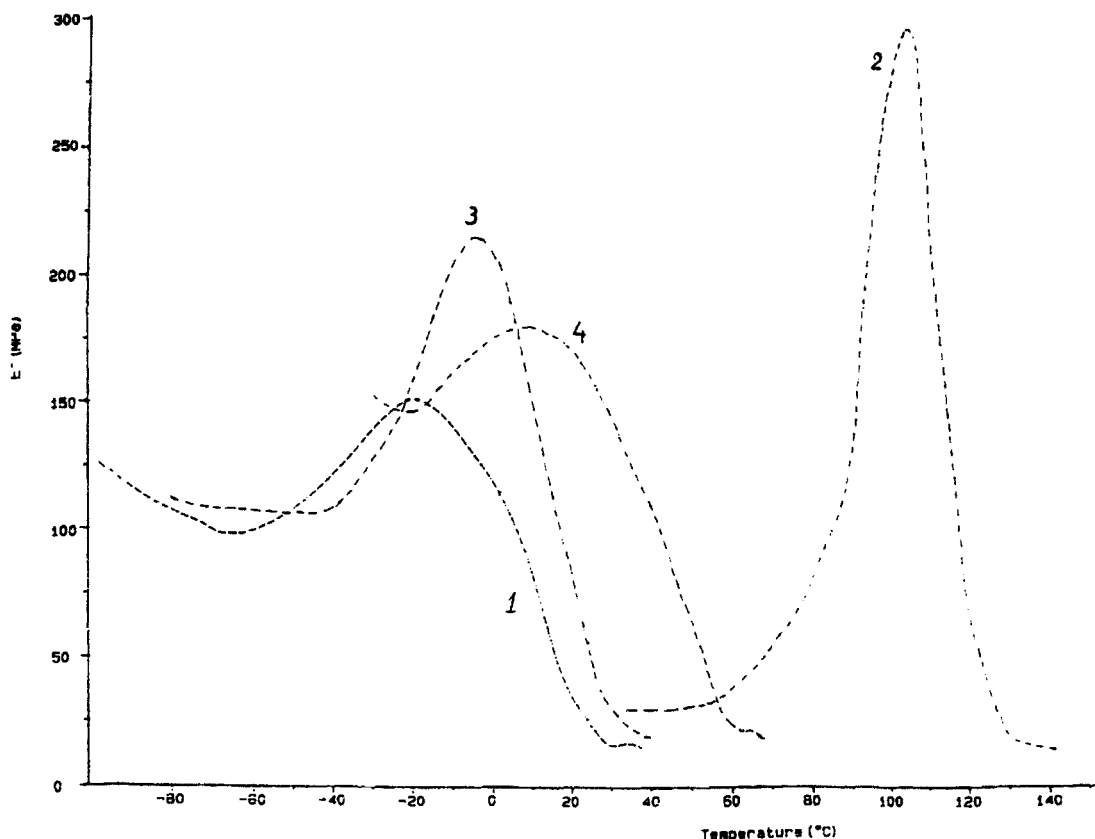
Figure 7 Variation of the loss modulus (E'') with temperature for (1) the cured poly(methacrylate) of vernonia oil, (2) the cured epoxy resin, (3) the IPN of 25/75 cured epoxy resin/poly(methacrylate) of vernonia oil, and (4) the IPN of 50/50 cured epoxy resin/poly(methacrylate) of vernonia oil.

TABLE IV
Mechanical Properties of the Castings

Casting composition of cured epoxy resin : poly(methacrylate) of vernonia oil	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
100 : 0	85	5	2200
50 : 50	16	16	322
25 : 75	2	18	20
0 : 100	1.5	17	13

transition temperature ($T_g = -19°C$). This polymer was used for the modification of commercially available epoxy resins (Epicote 828) to produce IPNs. The finding of single glass-transition temperatures for the IPNs indicated good compatibility between the networks of the two cured polymers. The IPN containing 50 wt % of cured epoxy resin had the mechanical properties necessary to make it a good candidate for use as a reinforced elastomer.

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