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Synthesis and photopolymerization of norbornyl epoxidized linseed oil

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Abstract

Norbornyl epoxidized linseed oil was synthesized via Diels–Alder reaction of cyclopentadiene with linseed oil at high pressure (~200 psi) and high temperature (240 °C), followed by an epoxidation using hydrogen peroxide with a quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) epoxidation catalyst. The products were characterized using ^{1}H and ^{13}C NMR, FT-IR, and electrospray ionization mass spectroscopy. Photo-induced curing kinetics of norbornyl epoxidized linseed oil coatings was investigated using real-time FT-IR spectroscopy with a fiber optic UV-curing system. The norbornyl epoxidized linseed oil was formulated with three different divinyl ether reactive diluent. The effect of divinyl ether concentration and types of divinyl ether on the curing reaction was investigated. It was found that the curing rate of norbornyl epoxidized linseed oil was lower than that of cycloaliphatic epoxide, but higher than epoxidized linseed oil. The incorporation of divinyl ethers increased the curing rate and overall conversion of the epoxide groups. Of the three divinyl ethers used, coating with triethyleneglycol divinyl ether showed the highest curing rate and coating with cyclohexane dimethanol divinyl ether showed the lowest curing rate. © 2002 Published by Elsevier Science Ltd.

Keywords: Epoxide; FT-IR spectroscopy; Linseed oil

1. Introduction

Seed oils have traditionally been used as drying oils and raw materials for uralkyds and alkyd resin [1]. Naturally occurring seed oils are triglycerides consisting of a mixture of saturated, oleic, linoleic, and linolenic fatty acid. Scheme 1 shows an example of a triglyceride containing an oleic, linoleic, and linolenic fatty acid. Seed oils are classified according to the linoleic and linolenic acid content. A convenient method of classification is drying index [1,2]. Linseed oil has one of the highest drying indexes of the most common drying oils conventionally used in paint and varnish industry.

The carbon–carbon double bond on oleic, linoleic and linolenic fatty acid can be epoxidized by reaction with peroxyacids, dioxirane, or hydrogen peroxide [3]. These epoxides can be polymerized by the reaction with amine-containing monomers through the epoxy-amine cross-linking reaction. Epoxidized seed oils are used extensively as an HCl scavenger for polyvinyl ether [4]. Epoxidized oils are also used as inks, however, epoxidized seed oils have found only modest application in specialty coating systems [5].

One factor that prevents the extensive application of the epoxidized oil is the relative low reactivity of internal epoxide groups. At ambient temperature, the curing times on the order of a week are common for reactions of these oils with aliphatic amines. Epoxidized seed oils are used as reactive dilulents [6] and as toughening materials for commercial epoxy resins [7,8]. Recently, Crivello and Narayan [9] demonstrated that epoxidized oils can be photopolymerized and have been used as cationic UV-curable coatings. The coatings that obtained possess good adhesion and mechanical properties. However, epoxidized seed oils were associated with slow cure rate.

Diels–Alder reaction is the most widely employed synthetic method for the production of cyclic ring systems [10]. A major limitation of the Diels–Alder reaction is the intrinsic slowness and inefficiency of reactions of electronically neutral addends. This has resulted in considerable interest in developing methods for both activated and unactivated Diels–Alder reactions. Lewis acids catalyzed reactions of dienophiles activated by carbonyl or nitrile groups, or electron-transfer catalyzed reactions occurring via cation-radicals [11,12], have been previously reported.

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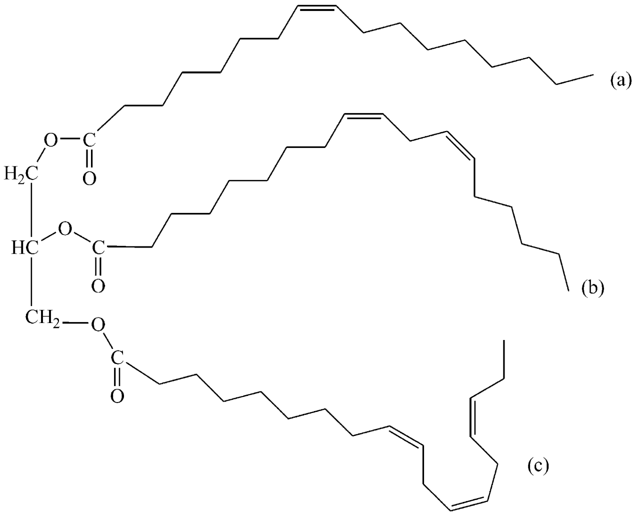


Scheme 1. (a) Oleic fatty acid; (b) linoleic fatty acid; and (c) linolenic fatty acid.

Other approaches for Diels–Alder catalysis include proton-catalyzed reactions involving allylic cations [13–15], and transition-metal catalyzed reactions have also been reported [16]. Recently linseed oil was modified by reacting with cyclopentadiene through Diels–Alder reaction at high temperatures to form a partially norbornylized commercial product known as Dilulin® [17]. Dilulin® has 0–3 norbornyl groups per triglyceride.

Many methods have been developed for the epoxidation of carbon–carbon double bonds, such as methods using peracids [18,19], dioxiranes [20,21], and hydrogen peroxide as epoxidation agents [22]. As reported in our previous study with Dilulin [3], of the three methods, the reaction with hydrogen peroxide using quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) as epoxidation catalyst (PTC) was found to be the most favorable. It had the highest yield, was relatively independent of pH, and had no discernible ring opening reaction. In addition, the reaction with hydrogen peroxide did not require use of solvent, and no byproduct except water was formed during the reaction. This made the product purification process extremely simple.

It is known that the photopolymerization of epoxides is strongly dependent on the structure of the monomer [23]. Glycidyl esters are less reactive than glycidyl ethers, which are less reactive than epoxidized seed oil. The most reactive monomers are cycloaliphatic epoxide due to their larger ring strain as compared to the other epoxides [24]. Based on the previously reported reactivity, it is proposed that epoxy norbornyl group would show higher photopolymerization rate than epoxidized seed oils. As previously stated, partially norbornylized linseed oil (Dilulin) was commercially available, however, it only has an average of one norbornyl group per triglyceride.

The objective of this paper is to norbornylize linseed oil with a higher substitution than the commercially available product. Then, epoxidize the norbornyl linseed oil as previously reported by hydrogen peroxide/quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) system [3]. The norbornyl linseed oil and epoxide of the norbornyl linseed oil were characterized NMR (^{1}H, ^{13}C), IR, and mass (electrochemical spray) spectroscopy. Elemental analysis (C, H, O) was also used for characterization. One of three divinyl ethers, diethyleneglycol divinyl ether (DEGDE), cyclohexane dimethanol divinyl ether (CHDMDE), or triethylene glycol divinyl ether (TEGDE), was formulated with the epoxide of the norbornyl linseed oil. The UV-curing kinetics of this norbornyl epoxidized linseed oil with and without the three divinyl ethers was investigated using real-time FT-IR spectroscopy.

2. Experimental

2.1. Materials

Tungstic acid (99%), tricaprylmethylammonium chloride (Aliquat 336), phosphoric acid (85%), hydrogen peroxide (32%), dicyclopentadiene, 2,6-di-*tert*-butyl-4-methylphenol (BHT), hexane, $CDCl_3$, NMR grade tetramethylsilane, reagent grade acetone, dichloromethane (99%), and dichloroethane (99%) were purchased from Aldrich Chemical Co. Diethyleneglycol divinyl ether (DEGDE), cyclohexane dimethanol divinyl ether (CHDMDE), and triethyleneglycol divinyl ether (TEGDE) were obtained from BASF Corporation. Cycloaliphatic epoxides, 3,4-epoxycyclohexylmethyl-3,4 epoxycyclohexane carboxylate (UVR-6110), and photoinitiator, triarysulfonium hexafluoroantimonate salts (UVI-6974) as a 50% solution, epoxidized linseed oil were supplied by Union Carbide Chemicals and Plastics Company Inc. (Dow Chemical). Wetting agent (Silwet L-7604) was provided by Witco Corporation. Linseed oil was obtained from Cargill as the Supreme grade. All the materials were used as received. The epoxidation catalyst, quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −), was prepared as previously described [3]

2.2. Characterization

All ^{1}H and ^{13}C NMR spectra were obtained on a VARIAN 300 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as a standard. Transmission FT-IR spectra were collected on a Nicolet Magna-IR® 850 spectrometer. The spectrometer was continuously purged with dry air supplied from a Balston Type 75–60 air purification system. Each spectrum was collected at a 4 cm^{-1} resolution and represents 200 co-added scans. Data acquisitions were performed using Omnic FT-IR software (Nicolet) and spectral analysis was performed on Grams 32 software (Galactic Ind.).

Direct ESI-MS spectra were obtained on a 3 T Finnigan

FT/MS Mewstar system (Bremen, Germany). The samples were dissolved in tetrahydrofuran (THF) to concentrations of approximately 50 μg/ml. The electrospray ionization assembly consisted of an Analytical ESI source (Branford, CT) which was fitted with a triple-sheath needle configuration and interface to the Finnigan FT/MS Newstar system. The cationization reagent, sodium or silver iodide (50 μM in methanol) was added to the THF/analyte solution as a sheath liquid flow. The analyte and cation solution were both delivered to the ESI needle tip by a Cole-Parmer 74900 series syringe pump operated at 2 μl/min for a combined flow rate of 4 μl/min. ESI capillary voltage was set to 3000 V for all experiments and all ions were observed as their mono-sodiated adducts, $[M]Na^+$ or $[M]Ag^+$. For the mass spectra, 128K data points per spectrum were collected every second for masses above $m/z = 300$ Da. The MS data was processed on a Finnigan Odyssey (Version 4.2) data system. For each analysis, 20 spectra were summed, and one zero-fill was performed.

Real-time FT-IR spectroscopic measurements were performed on a Nicolet Magna-IR® 850 spectrometer equipped with a LESCO Super Spot MK II UV-curing system. The relative humidity was controlled by a humidity chamber with the aid of $LiI\cdot 3H_2O$ constant humidity solution [25]. The humidity chamber was fitted into the FT-IR spectrometer sample chamber. The UV-radiation from a 100 W DC mercury vapor short-arc lamp was introduced into the humidity chamber by a flexible optical fiber. The end of the optical fiber was positioned at a distance of 5 mm from the KBr crystal to insure the full crystal was irradiated by the UV-light. An UVX digital radiometer was used to measure the radiation intensity and was 10.8 mW/cm^2. The coating was coated on the KBr crystal. Data acquisitions and spectra calculations were performed using Omnic FT-IR software (Nicolet). The UV-curing was conducted at temperature 23 ± 2 °C and 20% relative humidity. Spectra were collected at resolution 4 cm^{-1} and at the rate of 2 spectra/s. In all the cases, triplicate experiments were performed with an accuracy of ± 1%.

2.3. Cracking of dicyclopentadiene

Dicyclopentadiene (100 ml) was charged into a 500 ml flask connected with a fractional distillation system and an ice-cold receiver. The dimer was heated with a flask heater until it refluxes briskly and at such a rate that the cyclopentadiene began to distill in about 5 min and soon reached a steady boiling point in the range 40–42 °C.

2.4. Norbornylization of linseed oil

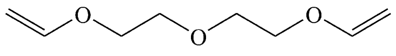
Cyclopentadiene (30 g) and BHT (0.8 g) were charged into a Parr reactor and mixed at room temperature until all the BHT dissolved. Linseed oil (58 g) was added to the mixture and mixed for 20 min. The mixture was then heated to 240 °C and the pressure increased to ~200 psi. The temperature was kept at 240 °C until the pressure dropped to 50 psi. The pressure drop indicates reaction of the cyclopentadiene. After the reaction was completed, 300 ml hexane was added to the product and stirred for 15 min. The precipitated solids were removed using a filter. The solvent was removed using a rotary evaporator at 50–55 °C: IR ν (cm^{-1}) 3052 (C–H stretching of norbornylene C=C–H); ^{1}H NMR ($Me_4Si/CDCl_3$) δ (ppm) 6.08–5.95 (H_2 and H_3), 2.50 (H_1 and H_4), 1.82 (H_5 and H_6), and 1.05–1.20 (H_{7syn} and H_{7anti}); C, H, and O analysis: carbon 81.28 wt%, hydrogen 10.78 wt%, and oxygen 9.47 wt%. Calculated C, H, O content: carbon 80.85 wt% hydrogen 10.64 wt%, and oxygen 8.51 wt%.

2.5. Epoxidation with hydrogen peroxide/quaternary ammonium tetrakis-(diperoxotungsto) phosphate(3 −) system

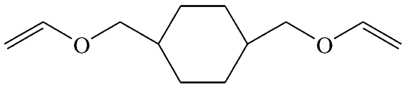
The quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) epoxidation catalyst was prepared as previously described [3]. Norbornylized linseed oil (40 g) was charged into a 500 ml three-necked round-bottom flask equipped with a thermometer, a reflux condenser, and a mechanical stirrer. The norbornylized linseed oil was heated and maintained at 60 °C with the aid of a constant temperature water bath. The quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) (1.4×10^{-3} M) was introduced, followed by the addition of 105 g of 16% hydrogen peroxide. The resulting biphase reaction mixture was vigorously stirred for 4 h. After the completion of the reaction, the water and organic layers were separated: IR ν (cm^{-1}) 851 (epoxy ring deformation); ^{1}H NMR ($Me_4Si/CDCl_3$) δ (ppm) 2.97–3.13 (H'_2, H'_3, H'_9 and H'_{10}), 2.62 (H'_1 and H'_4), 2.00 (H'_5 and H'_6), and 1.06 (H'_{7syn} and H'_{7anti}); ^{13}C NMR ($Me_4Si/CDCl_3$) δ (ppm) 49–51 (C'_2 and C'_3) 56–58 (C'_9 and C'_{10}); C, H, and O analysis: carbon 71.27%, hydrogen 9.60%, and oxygen 14.29%. Calculated C, H, O content: carbon 74.51 wt% hydrogen 9.81 wt%, and oxygen 15.68 wt%.

2.6. Formulations

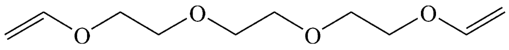
In general, the formulation consists of epoxide resin (norbornyl epoxidized linseed oil, epoxidized linseed oil, or cycloaliphatic diepoxide), divinyl ether, cationic photoinitiator, and Silwet L-7604 wetting agent. The structures of the three divinyl ethers are shown in Scheme 2. For a typical formulation, the desired amounts of divinyl ether were added to epoxide resin with 4.0 wt% of photoinitiator (UVI-6974) of the 50% solution, and 0.5 wt% of Silwet L-7604. The mixture was thoroughly mixed on a roller mill for 10 h. The coating was then cast onto a KBr crystal for the kinetics study. Formulations for the studies of the effect of concentration of DEGDE and types of divinyl ether were shown in Tables 1 and 2, respectively.



Diethyleneglycol divinyl ether



1,4-cyclohexane dimethanol divinyl ether



Triethyleneglycol divinyl ether

Scheme 2. Structures of divinyl ether.

3. Results and discussion

During the formulation of UV-curable coating, especially when the epoxide resin has high viscosity, reactive diluents are often used. Reactive diluents have two requirements: one is to reduce the overall viscosity of the coating formulations and the second is to co-react with monomer of oligomers to form homogeneous films [26]. Vinyl ethers, such as triethylene glycol divinyl ether and 1,4-cyclohexane dimethanol divinyl ether, are often used as such reactive diluents [27,28]. Generally, vinyl ethers are compatible with sulfonium salt photoinitiators and make excellent reactive diluents for epoxy resins. In addition, substituting a vinyl ether for a cycloaliphatic epoxy in a coating formulation may greatly increase the cure speed to a tack-free state.

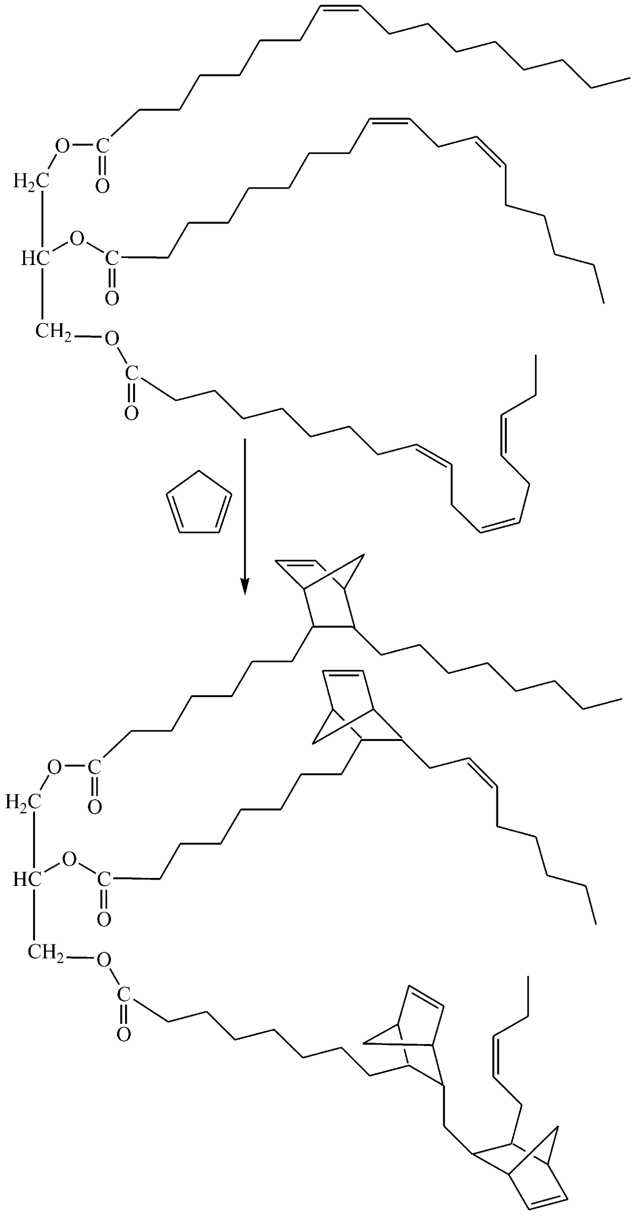
3.1. Norbornylization of linseed oil

Although several previously reported methods [16] have been developed for unactivated Diels–Alder reactions, these methods are not useful for the reaction of linseed oil with cyclopentadiene due to the substantial difference in reactivity between the dienophile (linseed oil) and the diene (cyclopentadiene). The carbon–carbon double bonds on linseed oil are extremely unreactive. However, the conjugated doubles on cyclopentadiene are very reactive. Any method that can activate the carbon–carbon double bonds on linseed oil can also catalyze the dimerization or polymerization of cyclopentadiene resulting in oligomer or homopolymer of cyclopentadiene. The method described in this paper, which combines both high pressure and temperature with BHT (as a free radical retarder) proved to be an efficient pathway for norbornylization (Scheme 3). The high temperature facilitated the activation of carbon–carbon double bond on linseed oil, however, lowered the

Table 1
Formulations for the study of the effect of concentration of DEGDE on the curing speed

Formulation	Norbornyl epoxidized linseed oil (g)	DEGDE (g)	DEGDE (wt%)
A	9.55	0	0
B	8.55	1	10.0
C	7.55	2	20.0

Photoinitator UVI-6974 (4.0 g) and Silwet L-7604 (0.5 g) was used for all the formulations.



Scheme 3. Norbornylization reaction.

Table 2
Formulations for the study of the effect of types of divinyl ether on the curing speed

Formualtion	Norbornyl epoxidized linseed oil (g)	Divinyl ether (g)		
		DEGDE	TEGDE	CHDMDE
D	8.55	1	–	–
E	8.55	–	1	–
F	8.55	–	–	1

Photoinitator UVI-6974 (4.0 g) and Silwet L-7604 (0.5 g) was used for all formulations. ‘–’ means none of this component.

solubility of cyclopentadiene in the linseed oil. The high pressure enhanced the solubility of cyclopentadiene in linseed oil. The BHT was used to inhibit the homopolymerization of cyclopentadiene.

In addition to the temperature and pressure, the yield of norbornylized linseed oil was also proportional to the ratio of cyclopentadiene to linseed oil. However, when the conversion of double bonds to norbornyl groups were $>40\%$, a highly viscous product (>1000 cp) was obtained. When the conversion was $>70\%$, the product obtained was a soft solid. Due to the viscosity limit, the conversion of the double bond was controlled at $\sim 30\%$.

The norbornylized linseed oil was characterized by FT-IR, ^{1}H and ^{13}C NMR, ESI-MS spectroscopy, carbon, hydrogen and oxygen analysis. Fig. 1 shows the FT-IR spectra of linseed oil (Fig. 1a) and norbornylized linseed oil (Fig. 1b). The band assignments of the characteristic bands are shown in Table 3. In the FT-IR spectrum of the linseed oil (Fig. 1a), the band at 3007 cm^{-1} was attributed to the C–H stretching of linseed oil C=C–H. The intensity of 3007 cm^{-1} band decreased after the norbornylization (Fig. 1b). A new band at 3052 cm^{-1} appeared in the spectra of norbornylized linseed oil. The 3052 cm^{-1} band was attributed to C–H stretching of norbornylene C=C–H.

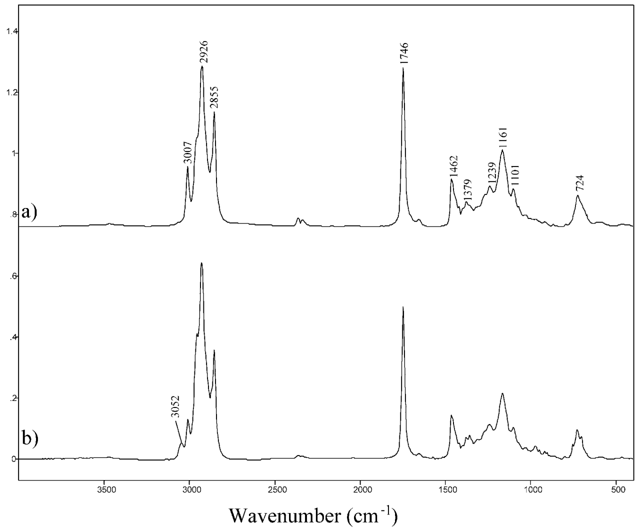


Fig. 1. FT-IR spectra of (a) linseed oil and (b) norbornylized linseed oil.

Fig. 2 compares the ^{1}H NMR spectra of linseed oil (Fig. 2a) and norbornylized linseed oil (Fig. 2b). In the ^{1}H NMR spectrum of linseed oil, resonances at $\delta = 5.34$ ppm (H_9 and H_{10}) were observed. After norbornylization the intensity of the resonances at $\delta = 5.34$ ppm decreased and new resonances at $\delta = 6.08–5.95$ ppm (H_2 and H_3), $\delta = 2.50$ ppm (H_1 and H_4), $\delta = 1.82$ ppm (H_5 and H_6), and $\delta = 1.05–1.20$ ppm (H_{7syn} and H_{7anti}) were observed. The corresponding ^{13}C NMR spectra are shown in Fig. 3. After norbornylization resonances at $\delta = 127–133$ ppm (C_9 and C_{10}) decreased, and new resonances at $\delta = 135–138$ ppm (C_2 and C_3) were observed.

Fig. 4 shows the ESI-MS spectra of linseed oil (Fig. 4a)

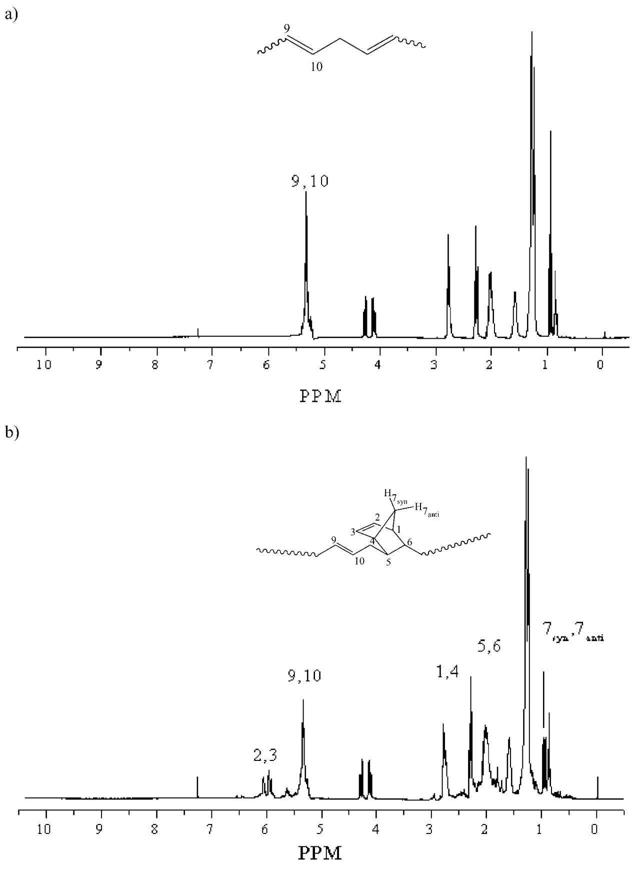


Fig. 2. ^{1}H NMR spectra of (a) linseed oil and (b) norbornylized linseed oil.

Table 3
FT-IR band assignments of linseed oil and partially norbornylized linseed oil

Band (cm^{-1})	Linseed oil	Partially norbornylized linseed oil
3052		C–H stretching of norbornylene =CH
3007	C–H stretching of linseed oil =CH	C–H stretching of linseed oil =CH
2926	Asymmetric C–H stretching of CH_2, CH_3	Asymmetric C–H stretching of CH_2, CH_3
2855	Symmetric C–H stretching of CH_2, CH_3	Symmetric C–H stretching of CH_2, CH_3
1746	C=O stretching	C=O stretching
1651	CH=CH stretching	
1462	Scissoring of CH_2, asymmetric bending of CH_3	Scissoring of CH_2, asymmetric bending of CH_3
1379	Symmetric bending of CH_3	Symmetric bending of CH_3
1161	C–O stretching of $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—O}$	C–O stretching of $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—O}$
1100	C–O stretching of O–CH_2	C–O stretching of O–CH_2
724	In-phase rock of $(CH_2)_n$, $n > 3$	In-phase rock of $(CH_2)_n$, $n > 3$

and norbornylized linseed oil (Fig. 4b). The mass assignments of each peak are shown in Table 4. The data shows that norbornylized linseed oil has 1–6 norbornylene groups on each molecule and molecules that have more than six norbornylene groups are minimal. The carbon, hydrogen, and oxygen analysis data are consistent with the expected structure. The carbon content of norbornylized linseed oil was (81.28 wt%) higher than that of linseed oil (78.14 wt%), but the hydrogen and oxygen content of norbornylized linseed oil (H: 10.78 wt%, O: 9.47 wt%) were lower than that of linseed oil (H: 11.31 wt%, O: 12.12 wt%). Calculated C, H, O content of the norbornylized linseed oil is carbon 80.85 wt% hydrogen 10.64 wt%, and oxygen 8.51 wt%.

4. Epoxidation of the norbornylized linseed oil

The epoxidation of norbornylized linseed oil was carried-out as previously described using hydrogen peroxide as epoxidation reagent with quaternary ammonium tetrakis(diperoxotungsto) phosphate(3 −) as

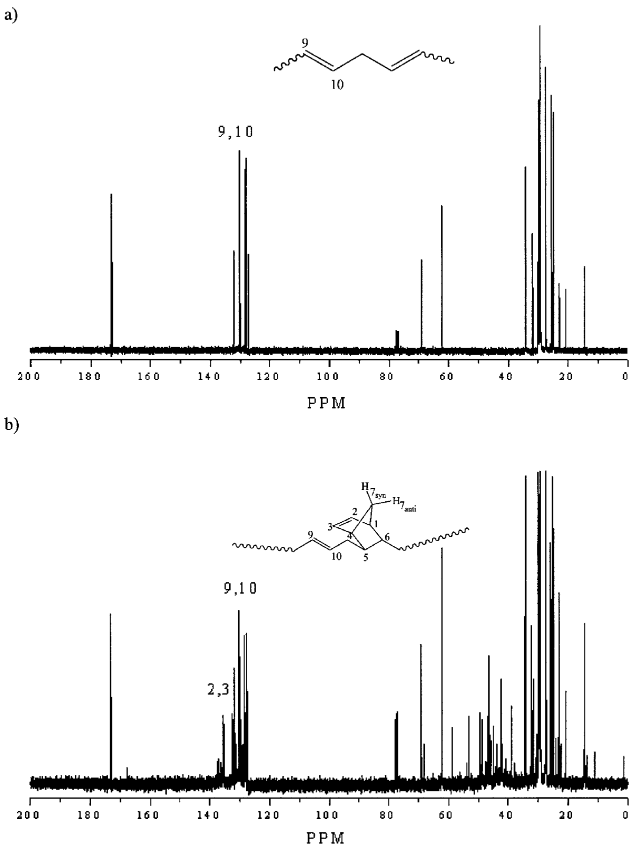


Fig. 3. ^{13}C NMR spectra of (a) linseed oil and (b) norbornylized linseed oil.

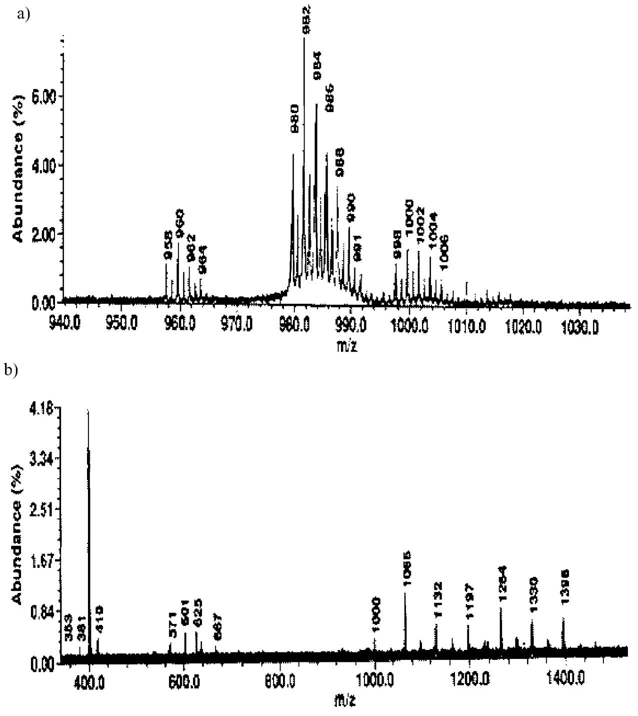
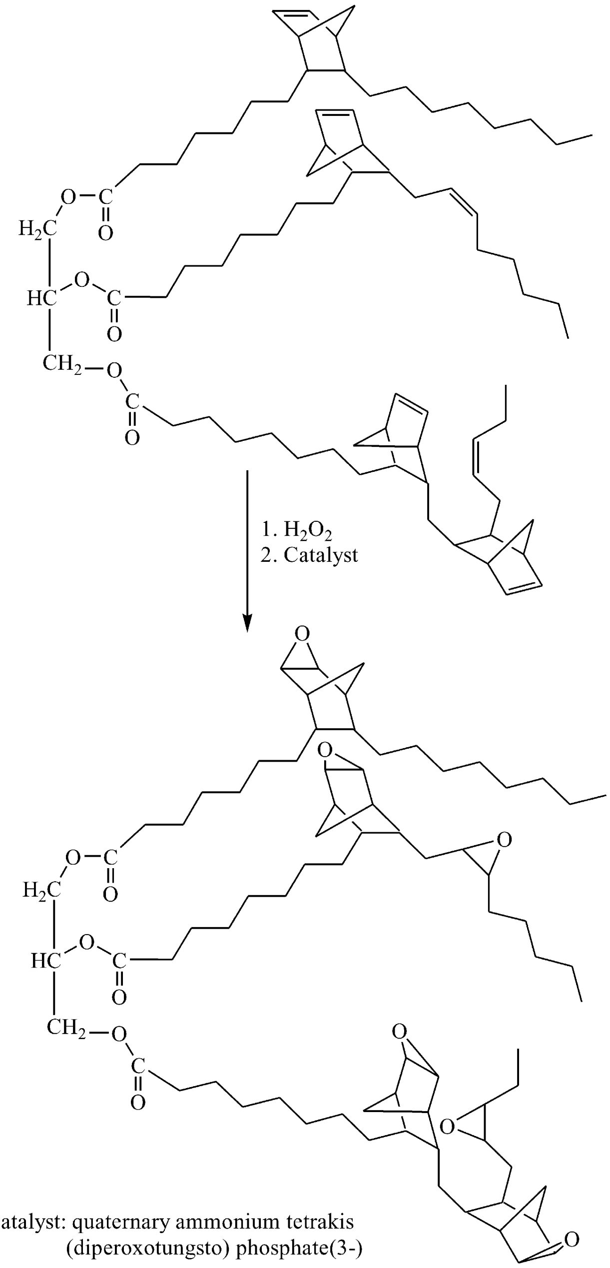


Fig. 4. ESI-MS spectra of (a) linseed oil and (b) norbornylized linseed oil.

Table 4
Band assignments of ESI-mass spectra of linseed oil and norbornylized linseed oil

	[Linseed oil] Ag^+ or [norbornylized linseed oil] $Ag^+ + 1H_2O$						
	Linseed oil	1 norbornyl group	2 norbornyl groups	3 norbornyl groups	4 norbornyl groups	5 norbornyl groups	6 norbornyl groups
Saturated	998	–	–	–	–	–	–
1 Unsaturation	996	1080	–	–	–	–	–
2 Unsaturation	994	1078	1144	–	–	–	–
3 Unsaturation	992	1076	1142	1128	–	–	–
4 Unsaturation	990	1074	1140	1126	1272	–	–
5 Unsaturation	988	1072	1138	1124	1270	1336	–
6 Unsaturation	986	1070	1136	1122	1268	1334	1340
7 Unsaturation	984	1068	1134	1120	1266	1332	1398
8 Unsaturation	982	1066	1132	1198	1264	1330	1396
9 Unsaturation	980	1064	1130	1196	1262	1328	1394



Catalyst: quaternary ammonium tetrakis
(diperoxotungsto) phosphate(3-)

Scheme 4. Epoxidation reaction.

the epoxidation catalyst (Scheme 4) [3]. The product was also characterized by FT-IR, ^1H and ^{13}C NMR, ESI-MS spectroscopy, carbon, hydrogen and oxygen analysis. Fig. 5 shows the FT-IR spectra of norbornylized linseed oil (Fig. 5a) and norbornyl epoxidized linseed oil (Fig. 5b). The band assignments of the characteristic bands are shown in Table 5. The intensity of 3052 and 3007 cm^{-1} bands (C–H stretching of C=C–H) decreased after epoxidation (Fig. 5b). A new band at 851 cm^{-1} appeared in the spectra of norbornyl epoxidized linseed oil. The 851 cm^{-1} band was attributed to ring deformation of epoxy group.

Figs. 6 and 7 represent the ^1H and ^{13}C NMR spectra of norbornylized linseed oil (Figs. 6a and 7a) and norbornyl epoxidized linseed oil (Figs. 6b and 7b), respectively. After epoxidation, the intensity of the resonances at $\delta = 6.08–5.95$ ppm (H_2 and H_3), $\delta = 5.34$ ppm (H_9 and H_{10}) decreased and new resonances at $\delta = 2.97–3.13$ ppm was detected, which was attributed to H_2', H_3', H_9' and H_{10}'. The

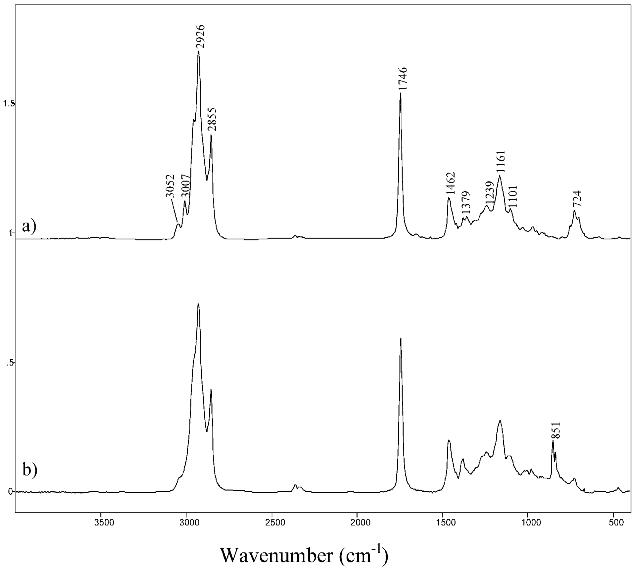
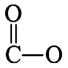


Fig. 5. FT-IR spectra of spectra of (a) norbornylized linseed oil and (b) norbornyl epoxidized linseed oil.

Table 5
FT-IR band assignments of norbornyl epoxidized linseed oil

Band (cm^{-1})	Norbornyl epoxidized linseed oil
2926	Asymmetric C–H stretching of CH_2, CH_3
2855	Symmetric C–H stretching of CH_2, CH_3
1746	C=O stretching
1462	Scissoring of CH_2, asymmetric bending of CH_3
1379	Symmetric bending of CH_3
1161	C–O stretching of  $\overset{\overset{\displaystyle O}{\|}}{C}—O$
1100	C–O stretching of O–CH_2
851	Ring deformation of norbornyl epoxy groups
724	In-phase rock of $(CH_2)_n$, $n > 3$

resonances of H'_2 and H'_3 were partially overlapped with the resonances of H'_9 and H'_{10}. The resonances at $\delta = 2.78$ ppm (H_1 and H_4), $\delta = 1.82$ ppm (H_5 and H_6), and $\delta = 1.05–1.20$ ppm (H_{7syn} and H_{7anti}) in ^1H NMR spectrum of norbornylized linseed oil shifted to $\delta = 2.62$ ppm (H'_1 and H'_4), $\delta = 2.00$ ppm (H'_5 and H'_6), and $\delta = 1.06$ ppm (H'_{7syn} and H'_{7anti}) in the ^1H NMR spectrum of norbornyl epoxidized linseed oil. The ^{13}C NMR spectra show that that resonances at $\delta = 135–138$ ppm (C_2 and C_3) and $\delta = 127–133$ ppm (C_9 and C_{10}) decreased after epoxidation. Concurrently, resonances at $\delta = 49–52$ ppm (C'_2 and C'_3) and $\delta = 56–58$ ppm (C'_9 and C'_{10}) increased.

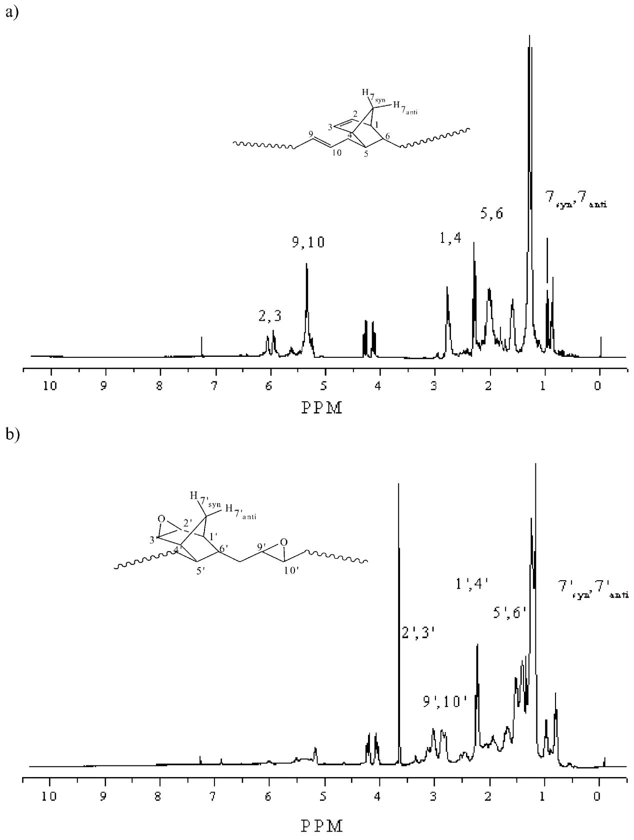


Fig. 6. ^1H NMR spectra of (a) norbornylized linseed oil and (b) norbornyl epoxidized linseed oil.

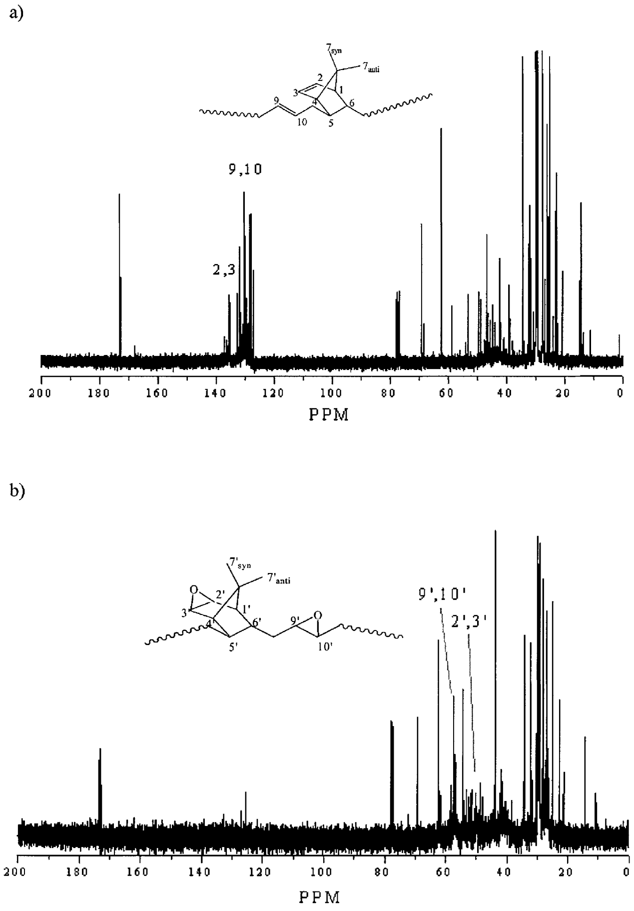


Fig. 7. ^{13}C NMR spectra of (a) norbornylized linseed oil and (b) norbornyl epoxidized linseed oil.

Fig. 8 shows the ESI-MS spectra of norbornyl linseed oil (Fig. 8a) and norbornyl epoxidized linseed oil (Fig. 8b). The ESI-MS spectrum of norbornyl epoxidized linseed oil clearly shows that the double bonds were epoxidized, and almost no ring-opening reactions were observed. The carbon, hydrogen, and oxygen analysis data are consistent with the expected chemical structures. The oxygen content of norbornyl epoxidized linseed oil (14.29 wt%) was higher than that of norbornylized linseed oil (9.47 wt%), but the carbon and hydrogen content of norbornyl epoxidized linseed oil (H: 71.27 wt%, O: 9.60 wt%) are lower than that of norbornylized linseed oil (H: 81.28 wt%, O: 10.78 wt%). Calculated C, H, O content of the norbornyl epoxidized linseed oil is carbon 74.51 wt% hydrogen 9.81 wt%, and oxygen 15.68 wt%.

Even with the characterization presented, there is the possibility that other structure than the idealized structure exists. Isomerization of the linseed oil double bonds is possibility. Typically, isomerization leads to conjugation and homopolymerization of the linseed oil via an alternate Diels–Alder reaction. In the GPC data, some oligomerization

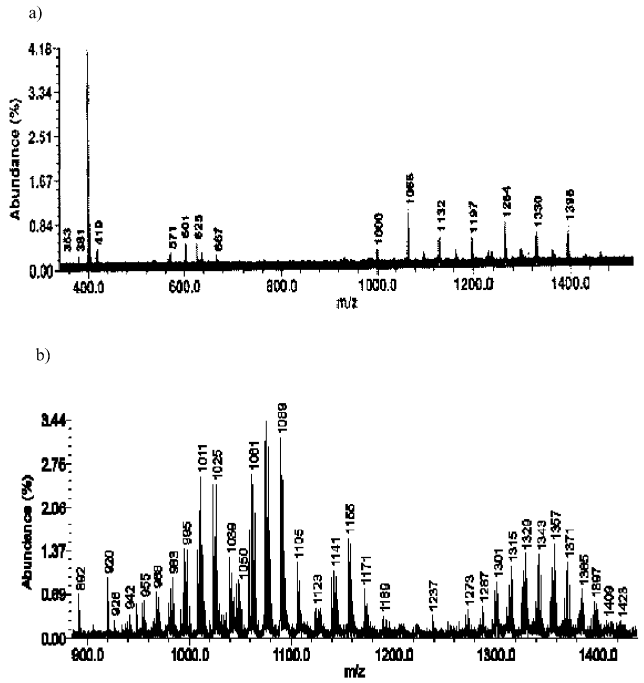


Fig. 8. ESI-MS spectra of norbornylized linseed oil (a) and norbornyl epoxidized linseed oil (b).

of linseed oil is also observed. Conjugation of linseed oil could also lead to reaction with cyclopentadiene. What is not seen, however, is oligomerization of the cyclopentadiene.

5. UV-curing kinetics of the norbornyl epoxidized linseed oil

A comparison of the UV-curing kinetics of the epoxidized linseed oil, norbornyl epoxidized linseed oil, and cycloaliphatic epoxide (UVR-6110) is shown in Fig. 9. Norbornyl epoxidized linseed oil showed higher UV-curing rate and overall epoxide conversion than epoxidized linseed oil due to the higher ring strain. However, norbornyl epoxidized linseed oil has lower curing speed and overall conversion than UVR-6110. For example, at 600 s after UV-irradiation, the overall epoxide consumption for UVR-6110 is 76.6% but for the norbornyl epoxidized linseed oil is only 60.5%. The higher curing speed of UVR-6110 was attributed to the less steric hindrance of the cycloaliphatic oxirane ring [29] and the lower viscosity in comparison with norbornyl epoxidized linseed oil. The lower viscosity increased the mobility of both the monomer and the growing polymer chain, which led to the higher curing speed and overall epoxide conversion.

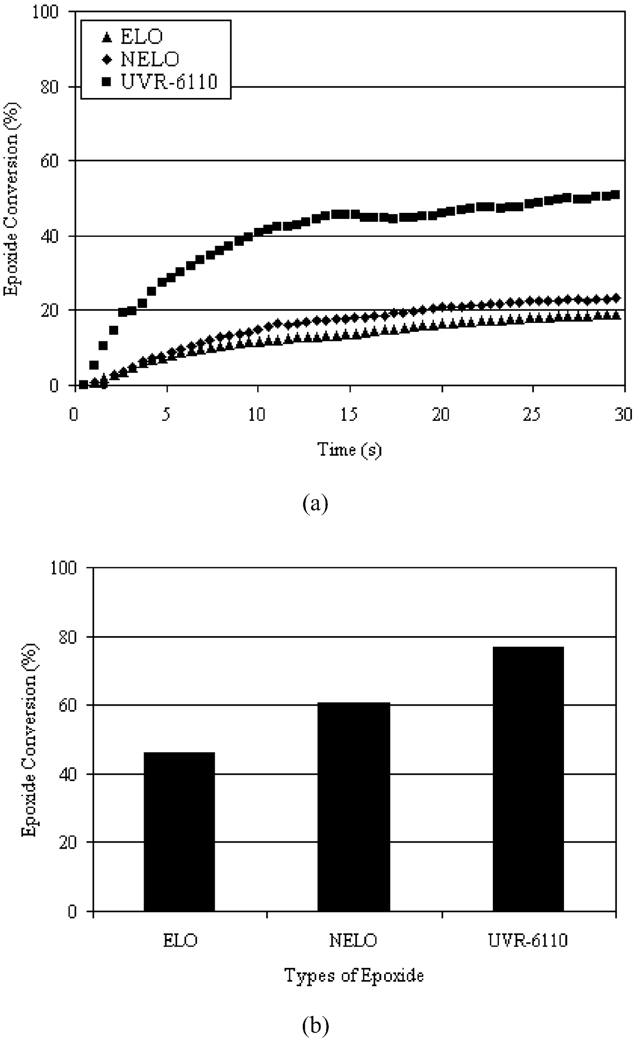
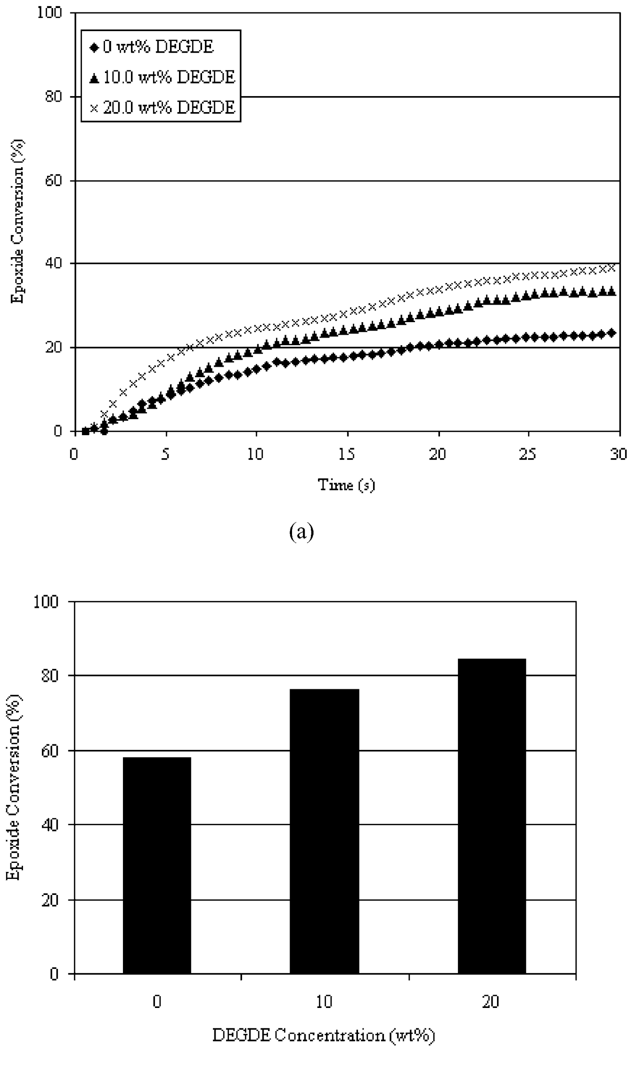


Fig. 9. Effect of types of epoxide on curing reaction of formulation UVI-6974 (4.0 wt%)/epoxide, with a 3.5 s exposure and a 20% relative humidity: (a) $t = 0$–30 s, (b) overall conversion at $t = 600$ s. (NELO and ELO represent norbornyl epoxidized linseed oil and epoxidized linseed oil, respectively).

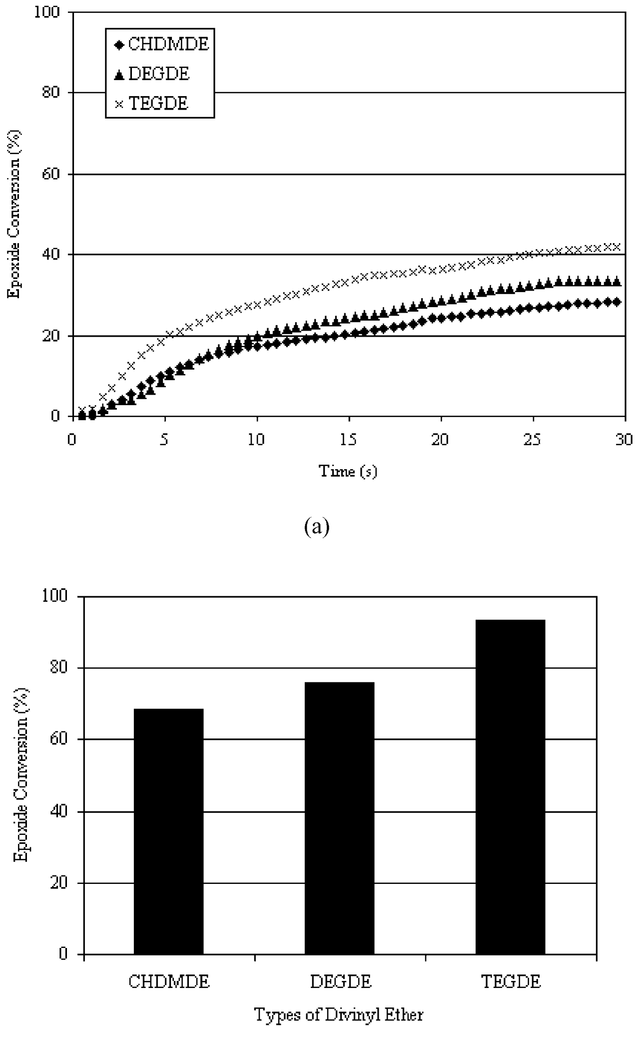
Figs. 10 and 11 shows the effect of divinyl ether (DEGDE) concentration on the curing rate of norbornyl epoxidized linseed oil, and the curing rate of norbornyl epoxidized linseed oil as a function of divinyl ether type, respectively. As shown, the overall epoxide consumption increase from 60.5 to 84.4% when the concentration of DEGDE increased from 0 to 20.0 wt%. The addition of DEGDE lowered the viscosity of the formulation and lowered the T_g of the coating that formed. Both factors attributed to the observed result. The curing rate and overall epoxide consumption were also highly dependent on the structure of the divinyl ether. When 10 wt% of divinyl ether were added into the formulation, the epoxide consumption at 600 s after UV-irradiation was the highest for the formulation with TEGDE (93.3%), and lowest for the formulation with CHDMDE (68.6%). The addition of divinyl ether could affect the T_g of the coating. For coatings with these three divinyl ethers, the one with CHDMDE will have the highest T_g due to the cyclohexane group and the one with TEGDE will show the lowest T_g due to the flexible triethyleneglycol group. For coatings with lower T_g, the onset of both gelation and vitrification are



(a)

(b)

Fig. 10. Effect of concentration of DEGDE on the curing reaction of formulation norbornyl epoxidized linseed oil/UVI-6974 (4.0 wt%)/DEGDE with a 3.5 s exposure and a 20% relative humidity: (a) $t = 0–30$ s, (b) overall conversion at $t = 600$ s. (DEGDE represents diethyleneglycol divinyl ether).



(a)

(b)

Fig. 11. Effect of types of divinyl ether on the curing reaction of formulation norbornyl epoxidized linseed oil/UVI-6974 (4.0 wt%)/divinyl ether (10 wt%), with a 3.5 s exposure and a 20% relative humidity: (a) $t = 0–30$ s, (b) overall conversion at $t = 600$ s. (CHDMDE represents cyclohexane dimethanol divinyl ether, TEGDE represents triethyleneglycol divinyl ether, and DEGDE represents diethyleneglycol divinyl ether).

delayed, and thus the curing rate and overall conversion were enhanced [30].

In comparison with Dilulin, the norbornylized linseed oil obtained through high pressure and high temperature has much higher number of norbornylene groups on each linseed oil molecule (Fig. 12). The kinetic study showed that the UV-curing rate of the norbornyl epoxidized linseed oil was higher than that of the epoxidized linseed oil. The difference in the reactivity between these two types of oxiranes was ascribed to the higher ring strain in the former monomer. However, the curing rate of the norbornyl epoxidized linseed oil was lower than that of the cyclohexene epoxide. This result is consistent with Crivello and coworker's previous study on a series epoxynorbornane monomers [29]. The lower reactivity of norbornyl epoxidized linseed oil was attributed to two factors: (1) greater steric hindrance present in the epoxynorbornyl group, (2) higher viscosity of norbornyl epoxidized linseed oil. The UV-curing rate could increase by decreasing the viscosity of coating formulation.

The epoxide of norbornyl linseed oil was synthesized with a ratio of fused norbornyl epoxide groups to linseed oil based epoxide ranging from 70 to 0%. Control of this ratio will lead to the development of a class of sterically strained epoxides based on seed oils. Utilization of more renewable resources is important with respect to environmental issues and the long-term future of petrochemicals. The curing rate of the norbornyl epoxidized linseed oil with divinyl ether was close to the cycloaliphatic epoxide. Thus, the norbornyl epoxidized linseed oil with divinyl ether as reactive diluents

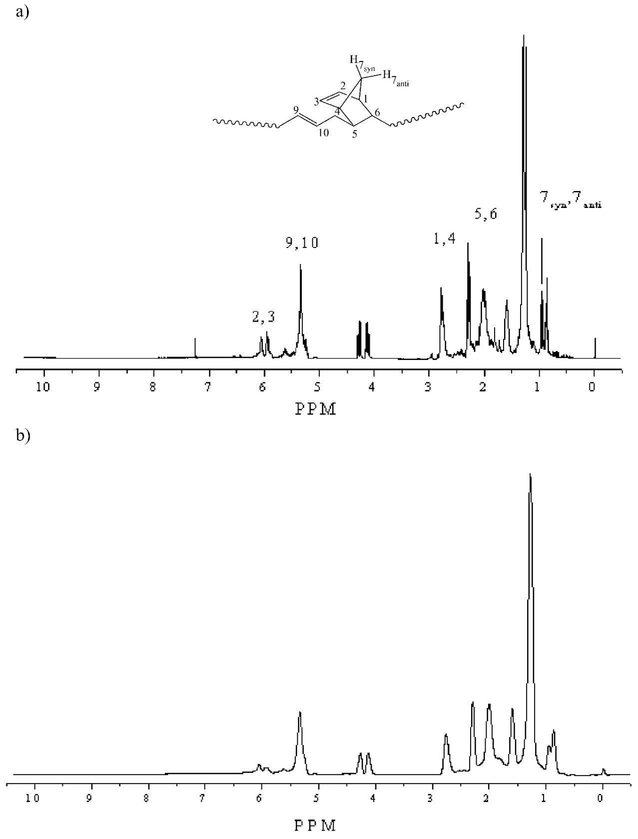


Fig. 12. ^{1}H NMR spectra of norbornylized linseed oil. (a) synthesized in this laboratory, and (b) commercially available.

has potential application in the coatings and adhesives industry.

6. Conclusion

Norbornyl epoxidized linseed oil that has higher number of norbornyl epoxide functional groups on each molecule was synthesized via high pressure and high temperature Diels–Alder reaction, followed by the epoxidation with hydrogen peroxide. The curing rate was significantly improved when divinyl ether was added into the formulation. The extent of the improvement was dependent on the structure of the divinyl ether; the more flexible the divinyl ether, the higher the curing rate.

Acknowledgments

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