

Polymerization of Epoxidized Soybean Oil with Maleinized Polybutadiene

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Received 22 March 2010; accepted 25 July 2010

DOI 10.1002/app.33094

Published online 11 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Epoxidized soybean oil (ESO) triglycerides were reacted with maleinized polybutadiene (MMPBD) to give plant-oil-based thermoset polymers. MMPBD samples were of two different molecular weights [high-molecular-weight maleinized polybutadiene (MMPBD-H), maleate content = 10%, number-average molecular weight (M_n) = 9000, and low-molecular-weight maleinized polybutadiene (MMPBD-L), maleate content = 15%, M_n = 5000]. To increase the crosslink density of the product, a free-radical initiator, benzoyl peroxide, was added to this mixture to further crosslink MMPBD through its double bonds. The characterizations of the products were done by dynamic mechanical analysis, differential scanning calorimetry, thermogravimetric analysis, and IR spectroscopy. The ESO–MMPBD polymers were crosslinked rigid infusible

polymers. ESO–MMPBD-H-1 : 1 and ESO–MMPBD-L-1 : 1 showed glass-transition temperature values at -23 , 78 and -17 , 64°C , respectively, whereas the storage moduli of the two polymers at 25°C were 13 and 16 MPa, respectively. The storage moduli of the polymers remained the same or decreased with the addition of a free-radical initiator. The storage moduli also decreased with increasing ESO concentration above a 1 : 1 epoxy-to-anhydride molar ratio. The surface hardness increased dramatically, and the equilibrium swelling ratio decreased with the addition of free-radical initiator. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 116–123, 2011

Key words: biodegradable; crosslinking; mechanical properties; polyesters; renewable resources

INTRODUCTION

The use of plant oil triglycerides as renewable raw materials in polymer synthesis has many advantages, namely, biodegradability, renewability, CO₂ emission reduction,¹ energy savings, ease of production,² low price,³ and the availability of a variety of chemical transformations on the triglycerides.^{4–6}

The direct polymerization of unsaturated triglycerides is rarely successful. The polymerization of triglycerides is preferably done by the attachment of a polymerizable group to the triglyceride and the polymerization of the triglyceride through this group. We and many others have used this strategy many times.^{4,5} Polymers derived from such monomers have low molecular weights and low mechanical properties because of the bulky structure of the monomers. This manifests itself in a low fracture toughness of the obtained polymers.

To increase the molecular weight, a new strategy was used. The use of a high-molecular-weight polymer with an epoxy reactive functional group with an epoxidized triglyceride to obtain new crosslinked

polymers was the purpose of this study. Maleinized polybutadiene (MMPBD) as the backbone polymer and epoxidized soybean oil (ESO) as the triglyceride component were chosen. ESO, which had 4.2 epoxy groups per triglyceride, acted as a multifunctional crosslinking agent for MMPBD. This strategy works best with a liquid functional polymer that is miscible with the triglyceride. To achieve this, MMPBD, which contained 1,2-polymerized butadiene, was used (1,2 : 1,4 ratio = 20 : 80). This polymer is a viscous liquid at room temperature and is miscible with ESO. Two different MMPBD samples with different molecular weights were used to determine the effect of the molecular weight on the properties of the final products. As an additional feature, in some of the samples, MMPBD was further crosslinked by a free-radical initiator through its vinyl groups. The epoxy–maleate reaction and the radical initiated crosslinking were carried concurrently. The strategy is depicted in Figure 1 and was bound to provide the higher molecular weights and higher crosslinking densities needed for a higher fracture toughness.

The easy reaction of anhydrides with epoxy groups is well documented. Many commercial epoxy adhesives use anhydrides as curing agents. The reaction is catalyzed by metal salts and is believed to proceed through the opening of the epoxide to form metal alkoxide salt followed by the opening of anhydride by the metal alkoxide salt formed. Although there is no argument about the efficacy of the

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Contract grant sponsor: Boğaziçi University Research Fund; contract grant number: 02S101.

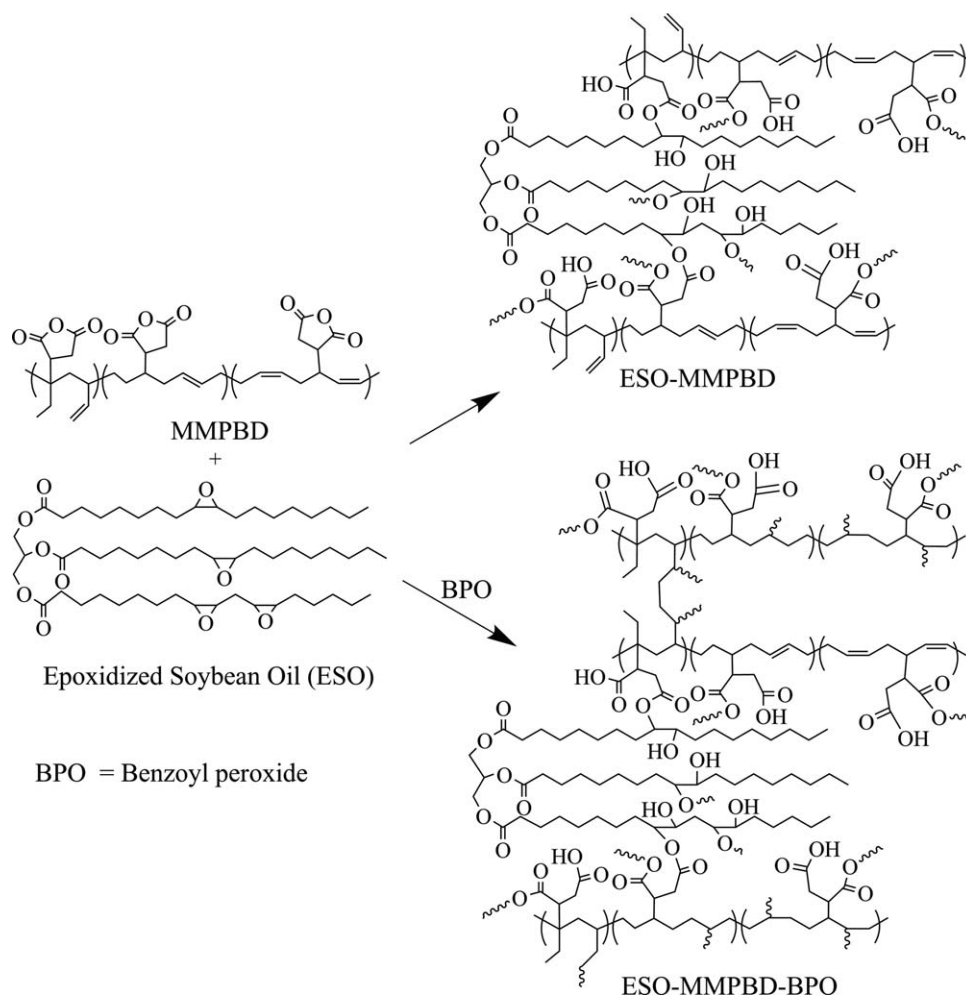


Figure 1 Schematic representation of the newly synthesized polymers.

reaction between an anhydride and an epoxy, different reaction mechanisms have been put forward in different sources.^{7,8} The one we prefer to depict is shown in Figure 2.

The reaction produced a new ester, a carboxylic acid, and a hydroxyl group; the IR signals of these groups could be used to monitor the extent of the reaction. Also, we observed the formation of a new hydroxyl group, which may have also reacted with a second anhydride group. Therefore, the exact stoichiometry between the anhydride and the epoxy groups could not be predicted.

A literature survey showed that maleinized soybean oil and its reaction with ESO is known.⁹ Epoxidized linseed oil has been reacted with different petroleum based anhydrides.^{10,11} A number of Japanese patents, available to us only as their abstracts, describe polymers synthesized from commercial epoxy resins, linseed oil acids, 1,4-polybutadiene, and maleic anhydride to produce a chip-resistant coating on steel.^{12,13} No structural data was given. There are no examples of MMPBD-ESO polymers in the literature.

The aim of this study was to react ESO with two different MMPBD samples with different molecular weights, with and without free-radical initiator, and to monitor the effect of the increasing molecular weight and increasing crosslinking density on the mechanical properties of the resulting polymer. The two different kinds of MMPBD used in this study were commercially available N4-9000-10, with a molecular weight of 9000 and a maleate content of 10%, and N4-5000-15, with a molecular weight of 5000 and a maleate content of 15%.

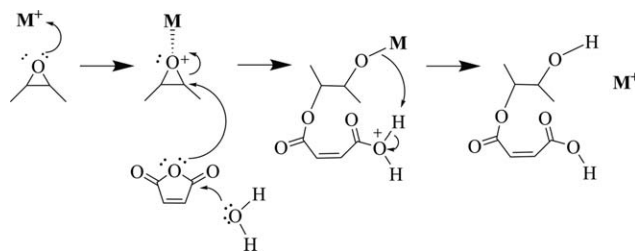


Figure 2 Accepted mechanism of the metal-catalyzed anhydride-epoxy reaction.

EXPERIMENTAL

Materials and methods

ESO (Paraplex G-62), with 4.2 epoxy groups per triglyceride, was purchased from C.P. Hall Co. (Chicago, IL). N4-9000-10 [high-molecular-weight maleinated polybutadiene (MMPBD-H), 10% maleic anhydride grafted, number-average molecular weight (M_n) = 9000] and N4-5000-15 [low-molecular-weight maleinated polybutadiene (MMPBD-L), 15% maleic anhydride grafted, M_n = 5000] were purchased from Synthomer LLC (Powell, OH). AMC-2, a proprietary catalyst containing metal ions, was supplied by Aerojet Fine Chemicals (Rancho Cordova, CA), and benzoyl peroxide (BPO) and diethyl ether were purchased from Merck (Darmstadt, Germany).

IR characterization of the compounds was performed with a Thermo Nicolet, FTIR 380 spectrometer (Thermo Nicolet, Thermo Fisher Scientific, Waltham, MA) with a diamond attenuated total reflection accessory. Differential scanning calorimetry (DSC) characterization was performed with a Thermal Analyses Q 200 instrument (TA Instruments, New Castle, DE) at a 10°C/min heating rate. Thermogravimetric analysis (TGA) characterization was performed with a Thermal Analyses Q 50 instrument (TA Instruments) at a 10°C/min heating rate. The dynamic mechanical thermal analysis of the polymer samples were performed with a TA Instrument Q800 dynamic mechanical analyzer (TA Instruments). Temperature scans were run from -25 to 160–180°C at a heating rate of 3°C/min with a vibration frequency of 1 Hz. A Zwick/Roell durometer (Ulm, Germany) with Shore A was used to determine the surface hardness of the polymer samples. The test was performed according to ASTM D 2240. The swelling behavior of the polymers was tested in CH₂Cl₂ with a Gaertner 7109-46 traveling microscope (Skokie, IL).

Polymer synthesis

MMPBD polymers crosslinked with a free-radical initiator

MMPBD-L (1.0 g) and 1% BPO were stirred at room temperature for 1 h. The mixture was transferred into a Teflon mold and heated in a vacuum oven at 100°C for 4 h. Test samples were extracted with diethyl ether in a Soxhlet apparatus for 6 h and dried in a vacuum oven at 80°C for 4 h. A light orange transparent thermoset product was obtained at 85% yield. The polymer was 100% MMPBD based and was synthesized to serve as an IR model compound.

IR (cm⁻¹): 3000–3600 (br, COOH, OH), 3072 (w, CH), 3004 (m, CH), 2914 (s, CH), 2843 (s, CH), 1770 (m, C=O), 1710 (s, C=O), 1643 (m, C=C, stretch-

TABLE I
Percentages of MMPBD and ESO and Polymer Yields in Different Experiments

ESO (%)	Polymer designation	Yield after extraction (%)	
		With BPO	Without BPO
19.5	ESO-MMPBD-H-1 : 1	91.5	95.7
32.7	ESO-MMPBD-H-2 : 1	84.1	99.6
42.2	ESO-MMPBD-H-3 : 1	86.0	74.6
49.3	ESO-MMPBD-H-4 : 1	74.5	72.4
26.7	ESO-MMPBD-L-1 : 1	87.2	99.9
42.2	ESO-MMPBD-L-2 : 1	84.9	91.1
52.2	ESO-MMPBD-L-3 : 1	75.0	68.8
59.3	ESO-MMPBD-L-4 : 1	71.1	62.0

ing), 1437 (m, CH₂, deformation), 1349 (m, CH₂, wagging), 1268 (w, C—O—C, deformation), 1168 (m, C—O—C, deformation), 1014 (w, C—O—C, deformation), 1072 (w, C=O, stretching vibration), 964 (s, CH₂, rocking), 910 (s, C=CH₂, wagging), 712 (m, C—C, skeletal vibration).

ESO-MMPBD polymers

In a typical procedure, 1.0 g of MMPBD-H (N4-9000-10, gel permeation chromatography indicated an M_n of 9000, 0.102 mmol anhydride groups), 0.24 g of ESO (0.102 mmol epoxy groups), and 1% AMC-2 esterification catalyst (on the basis of the mixture) were mixed (Table I). The viscous product was transferred to a Teflon mold and heated *in vacuo* at 140°C for 4 h. Test samples were extracted with diethyl ether in a Soxhlet apparatus for 6 h and dried in a vacuum oven at 80°C for 4 h. Greenish, transparent, flexible, thermoset products were obtained at typical yields of 82%. The same procedure was used for the free-radical-crosslinked samples, except that 1% BPO (on the basis of the mixture) was also added to the initial mixture. None of the final products dissolved in organic solvents; therefore, NMR data could not be obtained.

To simplify the nomenclature of different samples, the following symbols are used:

1. A:B indicates the epoxy/anhydride molar ratio.
2. MMPBD-H indicates high-molecular-weight MMPBD.
3. MMPBD-L indicates low-molecular-weight MMPBD.
4. BPO indicates added benzoyl peroxide.

Therefore, the label ESO-MMPBD-H-1 : 4-BPO means the following:

1. The ESO-MMPBD mixture had an epoxy/anhydride molar ratio of 1 : 4.

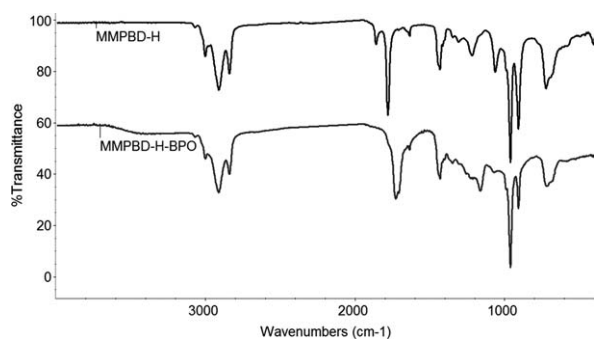


Figure 3 IR spectrum of the MMPBD-H polymer and the crosslinked MMPBD-H-BPO polymer.

2. H-MMPBD ($M_n = 9000$) was used.
3. The free-radical initiator BPO was used.

In subsequent experiments, the amount of MMPBD was kept constant, and the amount of ESO increased in such a way that the epoxy-maleate functional group ratio changed from 1 : 1 to 4 : 1 (Table I).

ESO-MMPBD-L-1 : 1. IR (film, cm^{-1}): 3000–3600 (br, COOH, OH), 2927 (s, CH), 2857 (s, CH), 1729 (s, C=O), 1634 (m, C=C, stretching), 1448 (m, CH_2 , deformation), 1409 (m, C=O–OH, asymmetric stretching), 1373 (m, CH_2 , wagging), 1256 (m, C–O–C, deformation), 1166 (s, C–O–C, deformation), 1095 (m, C–O–C, deformation), 1064 (m, C=O, stretching vibration), 976 (w, CH_2 , rocking), 821 [m, C(–O)–C(–O)–, ring vibration], 727 (w, C–C, skeletal vibration).

RESULTS AND DISCUSSION

Polymer synthesis and spectral identification

Figure 3 shows the IR spectra of the MMPBD-H polymer and its BPO crosslinked product (MMPBD-H-BPO). The intensities of the C–C double bond peaks at 1643 and 910 cm^{-1} decreased upon crosslinking. Curiously, the anhydride peaks at 1862 and

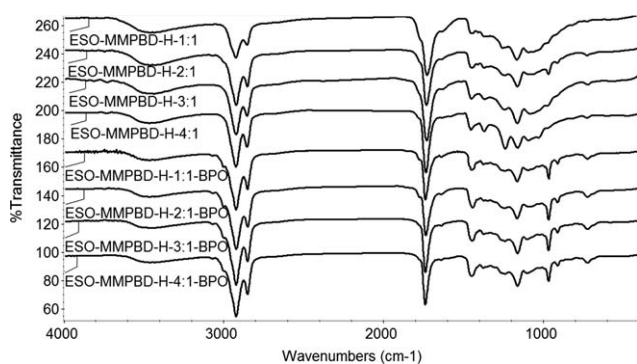


Figure 4 IR spectra of the ESO-MMPBD-H polymers with and without BPO.

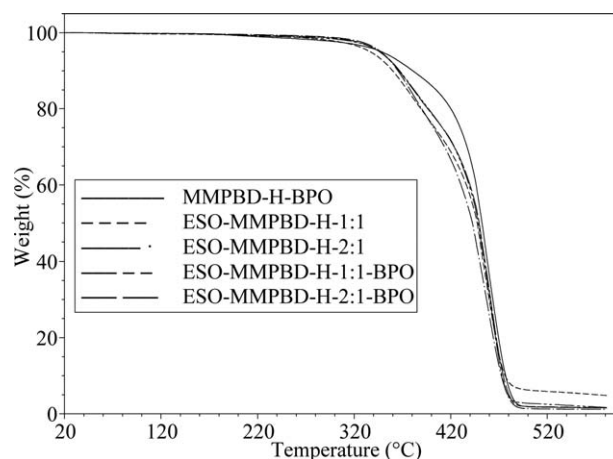


Figure 5 TGA for the MMPBD-H-BPO, ESO-MMPBD-H, and ESO-MMPBD-H-BPO polymers.

1783 cm^{-1} also decreased, and a new carboxylic acid carbonyl peak at 1710 cm^{-1} and a new COOH broad peak at 3000–3500 cm^{-1} were observed. Although the crosslinking reaction was carried out in a dry nitrogen purged vacuum oven, under the crosslinking conditions, some of the anhydride groups were also hydrolyzed. Luckily, the epoxy groups of ESO could also react with carboxylic acids to produce esters, so this artifact did not reduce the reactivity of MMPBD toward ESO.

Figure 4 shows the IR spectra of the ESO-MMPBD-H polymers synthesized with and without free-radical initiator. In all of the spectra, the anhydride peaks at 1862 and 1783 cm^{-1} and the epoxy peak at 840 cm^{-1} decreased. However, the intensity and broadness of the 1738- cm^{-1} peaks increased because of the formation of new ester groups. Between 3000 and 3600 cm^{-1} , free carboxylic acid and hydroxyl peaks appeared. After Soxhlet extraction, the yield of the polymers was between 71 and 91%. These findings proved that the anhydride-epoxy reaction was

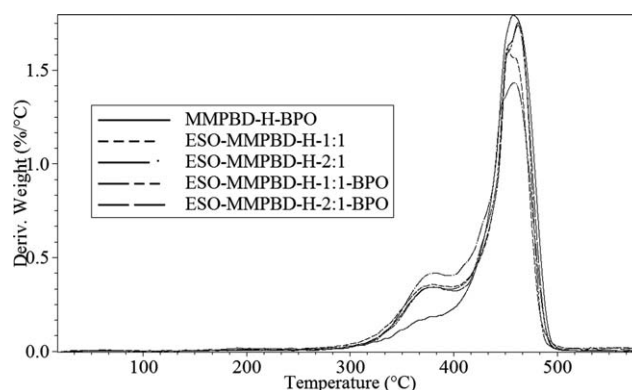


Figure 6 Derivatives of the TGA traces of the MMPBD-H-BPO, ESO-MMPBD-H, and ESO-MMPBD-H-BPO polymers.

TABLE II
TGA Results for All of the Polymers Synthesized in This Study

Polymer	Temperature (°C)				Char (%)
	Weight loss 1	Weight loss 2	50% loss	5% loss	
MMPBD-H-BPO	458	None	452	348	1.54
ESO-MMPBD-H-1 : 1	379	452	447	337	4.86
ESO-MMPBD-H-2 : 1	372	459	443	348	1.17
ESO-MMPBD-H-3 : 1	373	459	438	334	2.19
ESO-MMPBD-H-4 : 1	370	459	434	336	2.07
ESO-MMPBD-H-1 : 1-BPO	371	462	448	347	1.64
ESO-MMPBD-H-2 : 1-BPO	370	462	449	346	1.61
ESO-MMPBD-H-3 : 1-BPO	373	460	447	351	1.07
ESO-MMPBD-H-4 : 1-BPO	375	453	444	349	0.88
MMPBD-L-BPO	457	None	450	326	1.53
ESO-MMPBD-L-1 : 1	370	457	446	351	1.11
ESO-MMPBD-L-2 : 1	375	457	431	320	3.3
ESO-MMPBD-L-3 : 1	375	460	434	334	3.18
ESO-MMPBD-L-4 : 1	378	458	421	336	1.7
ESO-MMPBD-L-1 : 1-BPO	370	460	446	333	2.61
ESO-MMPBD-L-2 : 1-BPO	369	451	443	332	2.21
ESO-MMPBD-L-3 : 1-BPO	377	459	435	343	1.49
ESO-MMPBD-L-4 : 1-BPO	378	457	434	345	1.38

complete (Fig. 4). Identical IR spectra were observed with the ESO-MMPBD-L polymers synthesized with and without the free-radical initiator.

Thermal properties: ESO-MMPBD-H and ESO-MMPBD-L polymers

Because it is very difficult to read the temperature of maximum weight loss from the TGA trace (Fig. 5), derivative TGA (Fig. 6) was used to determine these. Only products having up to 3 : 1 ESO-MMPBD-H ratios were included because the TGA of the MMPBD-H and MMPBD-L polymers were essentially the same. MMPBD, which was crosslinked only with BPO, showed one weight loss with a maximum rate of loss at 458°C; this was due to the decomposition of the MMPBD backbone. The ESO-MMPBD polymers showed two weight losses with maximum rates at 375 and 460°C. The 5% weight loss temperatures of the ESO-MMPBD polymers occurred between 320 and 350°C and was essentially independent of both the molecular weight of MMPBD and the ESO content. Our previous study with triglyceride-containing polymers showed that triglycerides thermally decomposed at these temperatures. The char yields obtained at the end of TGA showed some variation, which was probably associated with the sample geometry and varied between 4.86 and 0.88% (Figs. 5 and 6 and Table II).

The DSC traces did not show any significant transitions. As with most crosslinked polymers, the determination of the glass-transition temperature (T_g) with DSC was not very successful; therefore, the dynamic mechanical analysis (DMA) method was used.

Mechanical properties

The DMA results showed that the storage moduli of the polymers decreased with increasing ESO content. The increasing ESO content should have increased the crosslinking density, but also it introduced long (C_8) unbound alkyl groups, which acted as internal plasticizers.^{14,15} At larger ESO concentrations, the molar ratio of epoxy groups to anhydride groups became more than 1. This left unreacted epoxy groups on ESO, such that the number of ESO molecules that were connected to the PBD backbone only through one (or few) epoxy groups increased. This certainly plasticized the product, and the effect was observed as a reduction in the modulus (Figs. 7 and 8 and Table III).

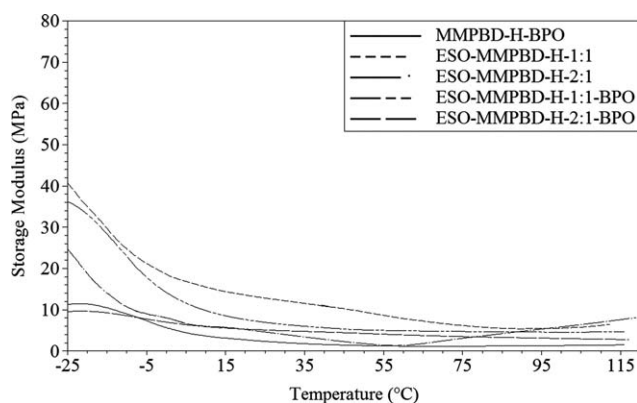


Figure 7 DMA storage modulus graphs for the MMPBD-H-BPO, ESO-MMPBD-H, and ESO-MMPBD-H-BPO polymers.

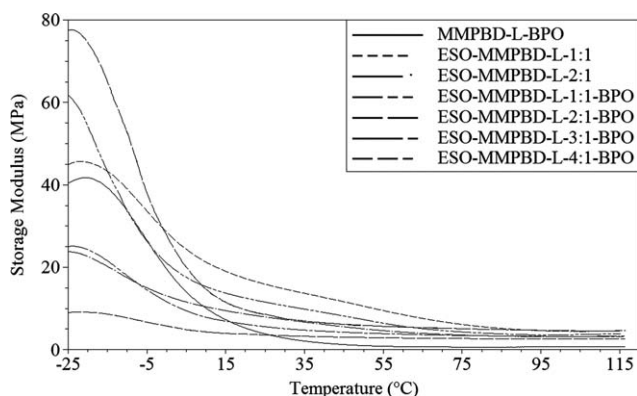


Figure 8 DMA storage modulus graphs for the MMPBD-L-BPO, ESO-MMPBD-L, and ESO-MMPBD-L-BPO polymers.

The additional crosslinking by peroxide did not increase the storage modulus. In fact, in some cases, a reduction in the modulus was observed. The introduction of a free radical may, in addition to crosslinking, have also caused chain scission so that an increase in the crosslinking density was offset by a reduction in the molecular weight of the backbone. In most samples, the amount of extractable material increased when BPO was used. This may have been a result of chain scission (Figs. 7 and 8 and Table III).

The $\tan \delta$ curves of most of the polymers synthesized showed two maxima. This indicated that the triglyceride and polybutadiene segments of the polymers were not completely miscible. The $\tan \delta$ derived T_g 's of the polymers with MMPBD-H and MMPBD-L were essentially the same. An increase in the epoxy-to-maleate ratio to above 1 : 1 generally decreased T_g (Figs. 9 and 10 and Table III).

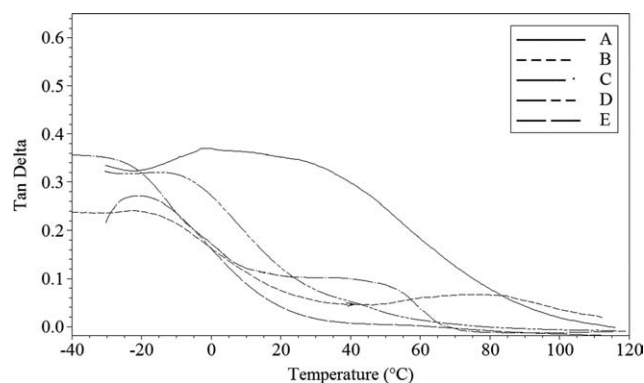


Figure 9 DMA $\tan \delta$ graphs of (A) MMPBD-H-BPO, (B) ESO-MMPBD-H-1 : 1, (C) ESO-MMPBD-H-2 : 1, (D) ESO-MMPBD-H-1 : 1-BPO, and (E) ESO-MMPBD-H-2 : 1-BPO.

The DMA investigations showed that with increasing amounts of ESO crosslinker and also free-radical curing, the intensities of the $\tan \delta$ peak maxima became lower; this indicated greater toughness. Also, the second maxima in the $\tan \delta$ peaks in the ESO-MMPBD polymers shifted to lower temperatures and resembled a shoulder after the addition of the free-radical initiator; this indicated compatibility and homogeneity. These suggest that the addition of free-radical initiator and ESO to the system increased compatibility of the triglyceride and the polybutadiene segments (Figs. 9 and 10 and Table III).

The surface hardness of the crosslinked polymers was also examined. The surface hardness test is a measure of the indentation resistance of elastomeric or soft plastic materials based on the depth of penetration of a conical indenter. Hardness values range from 0 (for full penetration) to 100 (for no penetration). Polymer samples with a thickness of 4 mm

TABLE III
DMA-Obtained T_g Values and 25°C Storage Moduli for Selected Polymers Synthesized in This Study

Polymer	25°C storage modulus (MPa)	25°C loss modulus (MPa)	1st $\tan \delta$ maximum (°C)	2nd $\tan \delta$ maximum (°C)
MMPBD-H-BPO	2	0.83	-1	NA
ESO-MMPBD-H-1 : 1	13	0.81	-23	78
ESO-MMPBD-H-2 : 1	5	0.47	-22	47
ESO-MMPBD-H-1 : 1-BPO	7	0.66	-14	NA
ESO-MMPBD-H-2 : 1-BPO	5	0.13	-22	NA
MMPBD-L-BPO	4	2.30	-6	NA
ESO-MMPBD-L-1 : 1	16	1.62	-17	64
ESO-MMPBD-L-2 : 1	8	0.72	-25	52
ESO-MMPBD-L-1 : 1-BPO	12	1.61	-23	62
ESO-MMPBD-L-2 : 1-BPO	8	1.17	-7	NA
ESO-MMPBD-L-3 : 1-BPO	6	0.66	-25	NA
ESO-MMPBD-L-4 : 1-BPO	4	0.25	-24	NA

NA = not applicable.

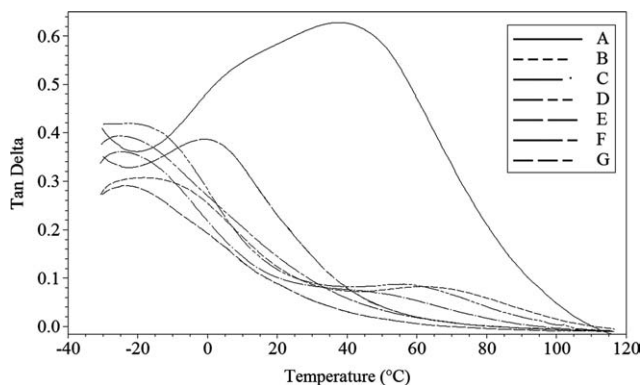


Figure 10 DMA tan δ graphs of (A) MMPBD-L-BPO, (B) ESO-MMPBD-L-1 : 1, (C) ESO-MMPBD-L-2 : 1, (D) ESO-MMPBD-L-1 : 1-BPO, (E) ESO-MMPBD-L-2 : 1-BPO, (F) ESO-MMPBD-L-3 : 1-BPO, and (G) ESO-MMPBD-L-4 : 1-BPO.

were protected from any possible mechanical stress before testing. To obtain reliable analysis data, the samples were tested at least at 10 different points on the same surface. The results of the test are presented in Table IV.

The results reveal that beyond a 1 : 1 epoxy-anhydride ratio, an increase in the ESO content of the polymers decreased the surface hardness. When MMPBD with the higher maleic content was used instead of the one with the low maleic content, the surface hardness increased. The surface hardness result were in a good agreement with the DMA-obtained storage modulus results and also with our original postulate.

The swelling behavior of the polymers in CH_2Cl_2 was examined with a traveling microscope. A useful parameter that could be obtained from a swelling test was the volumetric swelling ratio (q):

$$q = \Delta V/V_0 = (\Delta L/L_0)^3$$

TABLE IV
Surface Hardness of the MMPBD and ESO-MMPBD Series Polymers

Polymer	Surface hardness average of 10 trials	
	BPO	—
MMPBD-H	30	None
ESO-MMPBD-H-1 : 1	65	60
ESO-MMPBD-H-2 : 1	56	48
ESO-MMPBD-H-3 : 1	52	41
ESO-MMPBD-H-4 : 1	49	24
MMPBD-L	41	None
ESO-MMPBD-L-1 : 1	65	61
ESO-MMPBD-L-2 : 1	58	54
ESO-MMPBD-L-3 : 1	55	27
ESO-MMPBD-L-4 : 1	40	12

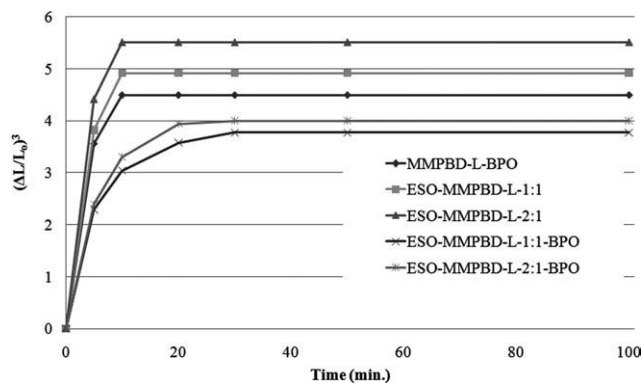


Figure 11 Swelling behavior of some selected MMPBD-L and ESO-MMPBD-L polymers in the solvent CH_2Cl_2 .

A useful parameter that could be obtained from a swelling test was the volumetric swelling ratio (q): where V and V_0 are to the volume and the initial volume and L and L_0 are to the length and the initial length on one side of the sample, respectively. This ratio depends on the molar volume of the solvent, crosslink density, and crosslink segment length of the polymer. The swelling behavior of H-MMPBD and L-MMPBD were identical, and therefore, only the swelling graph of the MPPBD-L polymers is shown (Fig. 11). Increasing the ESO ratio beyond a 1 : 1 epoxy-maleic anhydride ratio increased the swelling due to a plasticizing effect of the partially reacted ESO molecules. The use of the free-radical initiator increased the connectivity across the network; this resulted in lower swelling. The decrease in the volumetric swelling observed with the addition of the free-radical initiator was also in agreement with our expectations (Fig. 11).

CONCLUSIONS

MMPBD was successfully crosslinked with ESO to yield thermosets with up to 70% ESO. The highest modulus was obtained when the epoxy-maleic anhydride molar ratio was 1 : 1. Increasing ESO content did not increase the crosslink density, as the maleic anhydride groups were already depleted. At high ESO contents, ESO molecules attached to the PBD backbone through one (or a few) epoxy groups were formed; these acted as internal plasticizers. This manifested itself in lower moduli and higher swelling ratios.

The 1,2-polymerized butadiene units on MMPBD were used for free-radical crosslinking by the addition of BPO. Surprisingly, BPO crosslinking did not result in an increase in the modulus; this was probably due to the chain scission caused by the free-radical initiator. However, free-radical crosslinking increased the surface hardness and decreased the swelling ratio of the polymer.

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