New Polymers from Plant Oil Derivatives and Styrene-Maleic Anhydride Copolymers

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ABSTRACT: In this study, styrene maleic anhydride copolymer (SMA2000, Styrene : Maleic Anhydride 2 : 1) is grafted and/or crosslinked with epoxidized methyl oleate, epoxidized soybean oil, methyl ricinoleate (MR), castor oil (CO), and soybean oil diglyceride. Base catalyzed epoxy-anhydride and alcohol-anhydride polyesters were synthesized by using the anhydride on SMA, the epoxy or secondary alcohol groups on the triglyceride based monomers. The characterizations of the products were done by DMA, TGA, and IR spectroscopy. SMA-epoxidized soy oil and SMA-CO polymers are crosslinked rigid infusible polymers. SMA-epoxidized soy oil and SMA-CO showed T_g's at 70 and 66°C, respectively. Dynamic moduli of the two polymers were 11.73 and 3.34 Mpa respectively. SMA-epoxidized methyl oleate, poly[styrene-*co*-(maleic anhydride)]-*graft*-(methyl ricinoleate), and SMA-soy oil diglyceride polymers were soluble and thermoplastic polymers and were characterized by TGA, GPC, DSC, NMR, and IR spectroscopy. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 355–365, 2010

Key words: renewable resources; polyester; crosslinking; mechanical properties

INTRODUCTION

The prevailing raw material used in the synthesis of polymeric materials has been petroleum for the last 50 years. The increasing price and the dwindling reserves of petroleum dictate the use of nonpetroleum raw materials for polymer synthesis. The use of plant oil triglycerides as renewable raw materials in polymer production has many advantages; namely, biodegradability, renewability, CO_2 emission reduction,[1] energy savings, ease of production,[2] low price,[3] and the availability of a variety of chemical transformations on the triglycerides (Fig. 1).[4–6]

US patent 6,121,398 describes the use of acrylated epoxidized soybean oil (ESO) as liquid molding resin to replace commercial unsaturated polyesters.[7] US patent 5,302,670 describes commercially applicable polyurethanes synthesized from fatty amidoalcohols.[8] United Soybean Board (Chesterfield, Missouri) describes a multitude of commercial soybean oil based thermoset polymers in their website.[9]

Polymerization of triglycerides is possible by attaching a polymerizable group to the triglyceride. This strategy has been used by us and by others in many examples.[4,5] Polymers derived from such monomers have low connectivity and low mechanical properties due to the bulky structure of the monomer. This manifests itself in low fracture toughness of the polymers obtained.

In this work, we changed our strategy by starting first with a suitably substituted polymer having a reasonable molecular weight and attaching the triglyceride derivative to it. This strategy is bound to provide molecular weights that are higher and provide the entanglement lengths needed for higher fracture toughness.

The easy reaction of anhydrides with epoxy and hydroxyl groups is well documented. In the literature, soybean oil was maleinated and then was reacted with ESO.[10] Epoxidized linseed oil (ELO) was reacted with different petroleum based anhydrides.[11,12] ELO was found to be a good substitute for petroleum based epoxies.[13] In the US patent 3,321,424 ELO and SMA mixture was used as a metal surface protective coating.[14] SMA1000 (styrene to maleic anhydride ratio 1 : 1) and alcohol and amine containing molecules were reacted to give grafted polymer half esters and half amides, respectively.[15,16] Surface active properties of the half esters and the half amides of SMA1000 and styrene olefin copolymers were investigated.[17,18] Half esters from fatty alcohol and SMA1000 reaction were mentioned in the US Patent 6,719,053.[19,20]

Similarly, we worked on the reactions of two groups of plant oil derivatives with SMA: One group consisted of EMO, MR, and DG, which have only one functional group and should lead to linear,
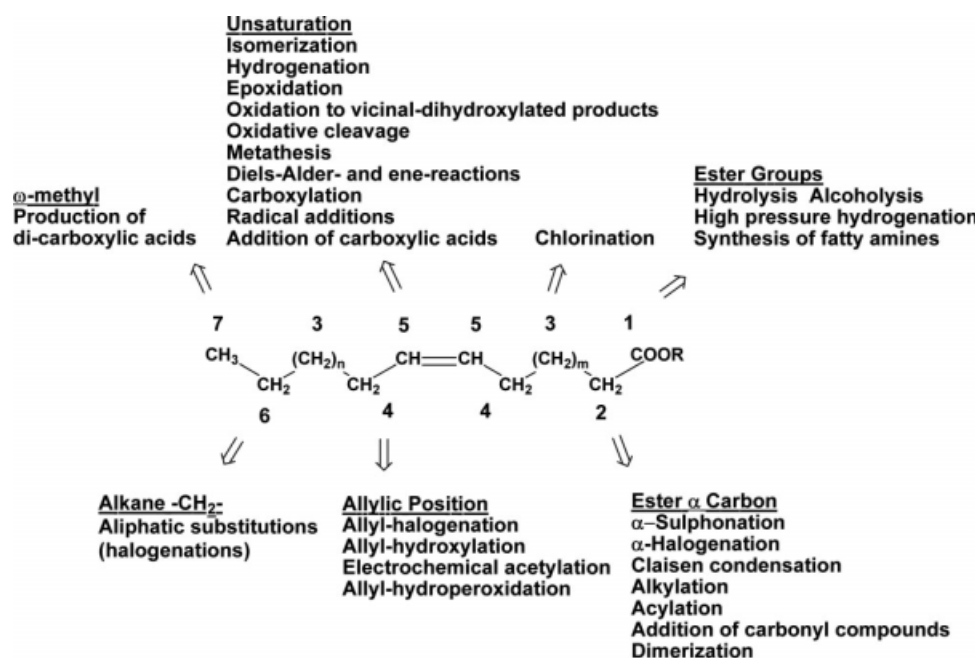
Figure 1 Some possible reactive transformation of the functional groups on a representative fatty ester.[4]

thermoplastic triglyceride-grafted-SMA products. The other group consisted of ESO and CO, which have a multiplicity of functional groups and should lead to thermoset triglyceride-crosslinked-SMA thermoset products. The syntheses we report here are shown in Figure 2. The linear and thermoset polymers are also useful as analytical models for their corresponding crosslinked and thermoset polymers.

EXPERIMENTAL

Materials and methods

ESO (Paraplex G-62) having 4.2 epoxy groups per triglyceride was purchased from C.P. HALL COMPANY (Chicago, IL), SMA2000 (Styrene : Maleic anhydride = 2 : 1) was purchased from Sartomer (Exton, PA) and showed a M_n of 2395 by GPC which corresponds to 7.82 maleic anhydride groups per chain on the average, DABCO, acetone, DMF, methanol, formic acid, diethyl ether, NaOH, and Na_2SO_4 were purchased from Merck (Darmstadt, Germany), THF was purchased from J.T. Baker (Deventer, Holland), soybean oil was supplied by Marsa (Adana, Turkey), olive oil was supplied by Komili (Unilever Turkey, Istanbul, Turkey), phosphoric acid was supplied by Atabay Kimya (Istanbul, Turkey), $CDCl_3$ obtained from Aldrich (Milwaukee, WI) was used for ^{1}H-NMR analysis, castor oil (CO) was supplied by Aklar Kimya (Ankara, Turkey), H_2O_2 and CH_2Cl_2 was supplied by Cakir Kimya (Istanbul, Turkey).

IR characterization of compounds was performed by Perkin Elmer FTIR 1600 series. NMR characteriza-

tion was performed by "Varian" 400 MHz NMR spectrometer. GPC analyses were done using an Agilent 1100 Series GPC-SEC Analysis System with a PL Gel 5 μm MIXED-C Column that was calibrated against polystyrene standarts. DSC characterization was performed by "Thermal Analyses" Q 200 instrument with a 10°C/min heating rate. TGA characterization was performed by "Thermal Analyses" Q 50 instrument with a 10°C/min heating rate. Strain test was performed on a Zwick Model tester with a 2 mm/min strain rate. The dynamic mechanical thermal analysis of the polymer samples were performed by using TA Instrument Q800 Dynamic Mechanical Analyzer (DMA). Temperature scans were run from 35 to 212°C for poly[styrene-co-(maleic anhydride)]-γ-(epoxidized soybean oil), SMA-ESO polymer, and to 175°C for SMA-CO polymer at a heating rate of 3°C/min with a vibration frequency of 1 Hz.

Monomer synthesis

Epoxidized methyl oleate

Methyl oleate was obtained from olive oil following the procedure described in an earlier work[21] and was epoxidized by following the procedure given by Bunker and Wool.[22]

Methyl ricinoleate

Methyl ricinoleate (MR) was synthesized by following the procedure given by Cayli and Kusefoğlu.[21]
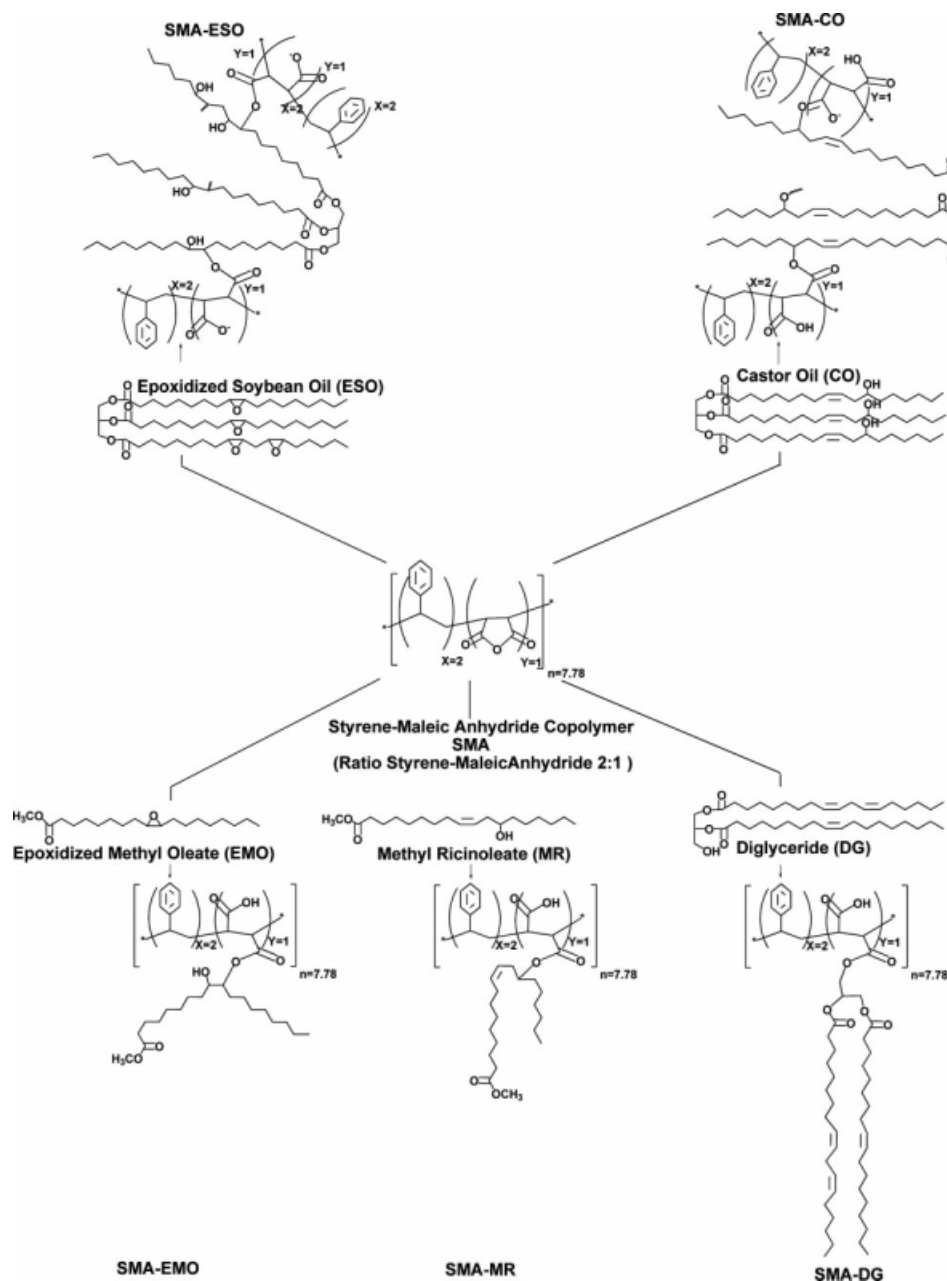
Figure 2 Schematic representation of the new polymers synthesized.

Soy oil diglyceride

MeOH (5 ml) and 0.1 g NaOH were added to 100 g Soybean oil. The solution was stirred for 120 min at 50°C and then allowed to settle for 6 h. Then the diglyceride layer (top) was separated from NaOH catalyst. Diglyceride mixture was washed successively with water, 5% H_3PO_4 (aq) and water. Lower aqueous layers were discarded and the diglyceride layer was dried in a vacuum oven. The product contained both the methyl esters and diglycerides (Fig. 3).

^{1}H NMR (CDCl$_3$, 400 MHz) ppm: 0.9 (—CH$_3$), 1.2–1.6 (—CH$_2$—), 2.0 (—CH$_2$—CH—), 2.3 (—CH$_2$—(C=
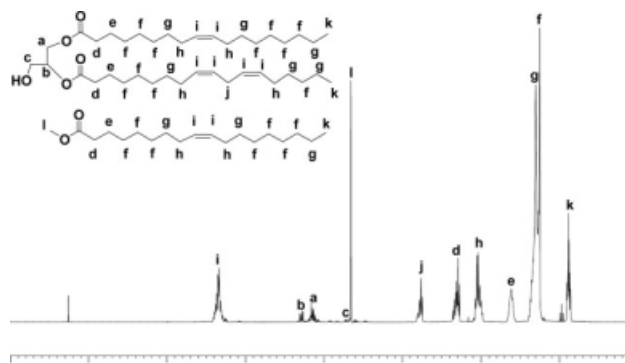

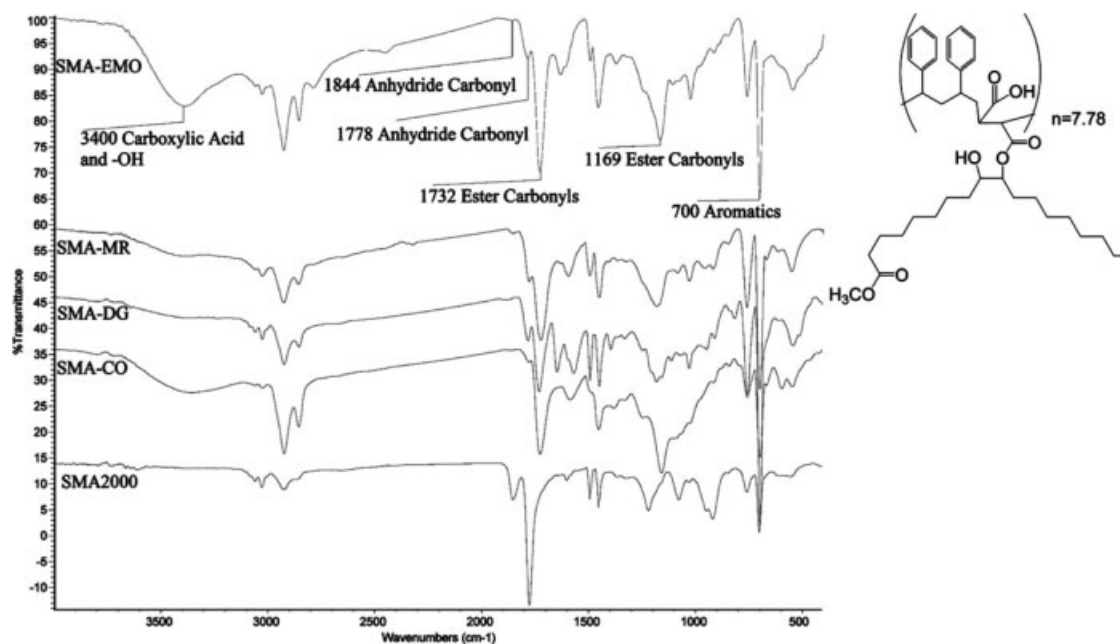**Figure 3** ^{1}H NMR spectrum of soy oil diglyceride.

Figure 4 IR spectrum of SMA-EMO, SMA-MR, SMA-DG, SMA-CO, and SMA2000 polymers.

O)—), 2.8 (=CH—CH$_2$—CH=), 3.7–3.8 (—O—CH$_3$, CH$_2$OH—CH—), 4.1 (—O—CH$_2$—CH—), 4.2 (—CH$_2$—CH(—O—)CH$_2$—), 5.3 (—CH=CH—).

IR (Film) (cm^{-1}): 3466 (w, OH), 3008 (m, =CH), 2924 (s, CH), 2853 (s, CH), 1743 (s, C=O), 1653 (m, —HC=CH—), 1463 (m, CH$_2$, Def.), 1439 (m, CH$_3$O, Def.), 1377 (w, CH$_2$OH), 1242 (m, C—O—C, Def.), 1169 (m, CO, Def.; C—O—C, Def.), 1099 (m, C—O—C, Def.), 723 (m, C—H, Def.).

Polymer synthesis

SMA-EMO poly[styrene-*co*-(maleic anhydride)]-*graft*-(epoxidized methyl oleate)

SMA of 1.0 g (GPC indicated M_n of 2395, 3.27 mmol anhydride groups); 6.4 g EMO (20.5 mmol epoxy, excess) and 1% DABCO were dissolved in 15 mL DMF. The mixture was refluxed at 152°C for 6 h. The polymer was precipitated from the DMF solu-

tion by adding saturated aq. NaCl solution. The product was dissolved in 100 mL CHCl$_3$. The solution was washed three times with 100 mL saturated NaCl in aq. HCl (5%). CHCl$_3$ was evaporated at 90°C. Product was extracted with diethylether in a soxlet apparatus for 6 h to remove residual monomers. The polymer was dried in a vacuum oven at 80°C for 4 h to remove any residual ether. A yellow transparent thermoplastic was obtained (Fig. 2).

IR (Film) (cm^{-1}): 3000–3600 (br, COOH, OH), 3012 (m, ArH), 2927 (s, CH), 2853 (s, CH), 2779 (s, CH$_3$—C=O), 1777 (m, C=O—OH), 1732 (s, C=O), 1629 (m, —HC=CH—), 1486 (m, CH$_2$, Def.), 1453 (m, CH$_3$O, Def.), 1245 (m, C—O—C, Def.), 1169 (m, CO, Def.; C—O—C, Def.), 1097 (m, C—O—C, Def.), 757 (m, Ar), 700 (s, Ar) ^{1}H NMR (CDCl$_3$, 400 MHz) ppm: 0.9 (—CH$_3$), 1.2–1.6 (—CH$_2$—), 1.7 (—ArCH—CH$_2$—CH(CO$_2$H)—), 2.3 (—CH$_2$—(C=O)), 2.7 (—CH(—Ar)—), 3.1 (—CH$_2$—CH(CO$_2$H)—CH$_2$—), 3.4

TABLE I
Results of GPC and DSC Results of Thermoplastic Products

	SMA	SMA-EMO[a]	SMA-MR[b]	SMA-DG[c]
% Maleates reacted	–	83	80	50
Appearance	White solid	Yellow solid	White solid	Yellow solid
T_g (°C) (DSC)	136	146[d]	–[e]	–[e]
M_n (GPC)	2395	4410	4348	4788

[a] EMO M_n : 312.5.
[b] MR M_n: 312.5.
[c] DG (diglyceride) M_n : 618.5.
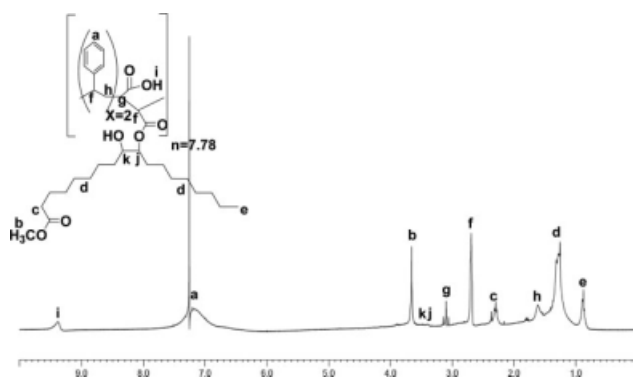[d] Shows some vague transformation.
[e] Shows no T_g.

Figure 5 ^{1}H NMR spectrum of SMA-EMO.

($-CH_2-CHOH-CH(O-)-$), 3.5 ($-CHOH-CH(O-)$ $-CH_2-$), 3.7 ($-OCH_3-$), 7.2 ($-ArH$), 9.4 ($-CO_2H$).

SMA-ESO poly[styrene-*co*-(maleic anhydride)]-γ-(epoxidized soybean oil)

SMA of 1.0 g (GPC indicated M_n of 2395, 3.27 mmol anhydride groups) and 1.56 g ESO (6.54 mmol epoxy groups) were dissolved in 15 mL acetone. The mixture was heated and stirred at 80°C for 2 h in an open reactor, and acetone was allowed to evaporate. Then, the mixture was put in a vacuum oven at 90°C to remove residual acetone for an hour. 1% DABCO was added to the mixture, then the mixture was transferred into a Teflon mold and was heated

in a vacuum oven at 120°C for 4 h. A light yellow transparent thermoset product was obtained (Fig. 2).

IR (Film) (cm^{-1}): 3000–3600 (br, COOH), 2925 (s, CH), 2854 (s, CH), 1844 (w, C—C=O—O—C=O—C), 1778 (m, C—C=O—O—C=O—C, C=O—OH), 1742 (s, C=O), 1653 (m, —HC=CH—), 1490 (m, CH$_2$, Def.), 1457 (m, CH$_3$O, Def.), 1385 (w, CH$_2$OH), 1241 (m, C—O—C, Def.), 1157 (m, CO, Def.; C—O—C, Def.), 1103 (m, C—O—C, Def.), 842 (w, C(—O—)—C(—O)—), 726 (m, C—H, Def.).

SMA-MR poly[styrene-*co*-(maleic anhydride)]-graft-(methyl ricinoleate)

SMA of 1.0 g (GPC indicated M_n of 2395, 3.27 mmol anhydride groups); 5 g MR (16 mmol secondary alcohol groups, excess), and 1% DABCO were dissolved in 15 mL DMF. The mixture was refluxed at 152°C for 6 h. The polymer was precipitated from the DMF solution by adding saturated aq. NaCl solution, then the polymer was dissolved in 100 mL CHCl$_3$. The solution was washed three times with 100 mL saturated NaCl in aq. HCl (5%). CHCl$_3$ was evaporated at 90°C. Product was extracted with diethylether in a soxlet apparatus for 6 h to remove residual monomers. The polymer was dried in vacuum oven at 80°C for 4 h to remove any residual ether. A white thermoplastic was obtained (Fig. 2).

IR (Film) (cm^{-1}): 3000–3600 (br, COOH), 3025 (m, ArH), 2926 (m, CH), 2850 (m, CH), 2763 (m, CH$_3$—C=O), 1852 (m, C—C=O—O—C=O—C), 1774

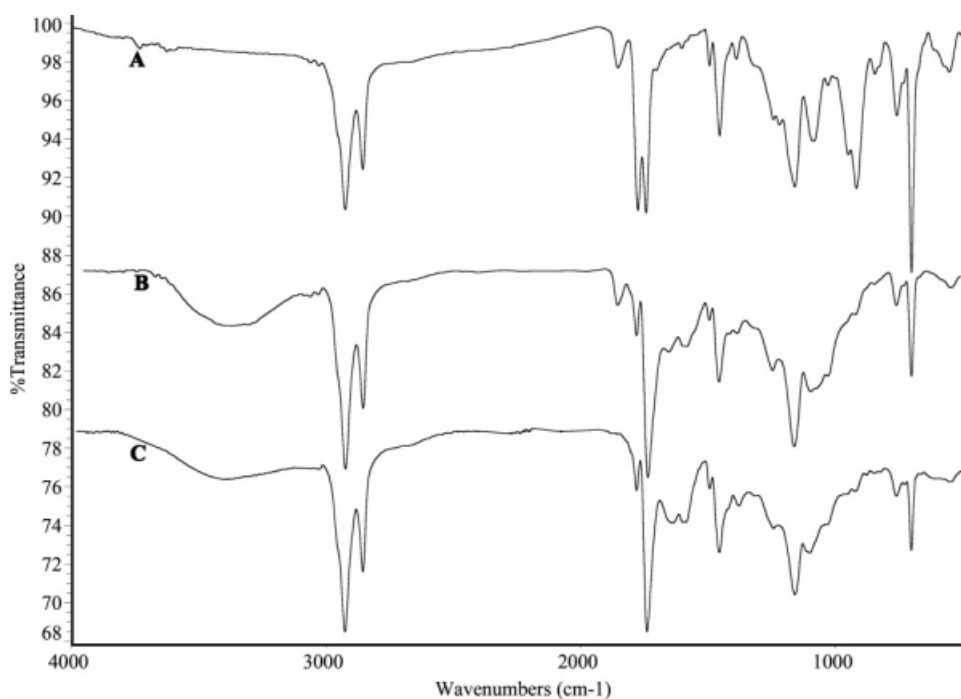**Figure 6** IR spectrum of SMA-ESO; curing after 0 h A, 4 h B, and 12 h C.

Figure 7 TGA analysis of triglyceride based monomers.

Figure 8 TGA analysis of SMA and different graft and crosslinked products with the triglyceride based monomers.
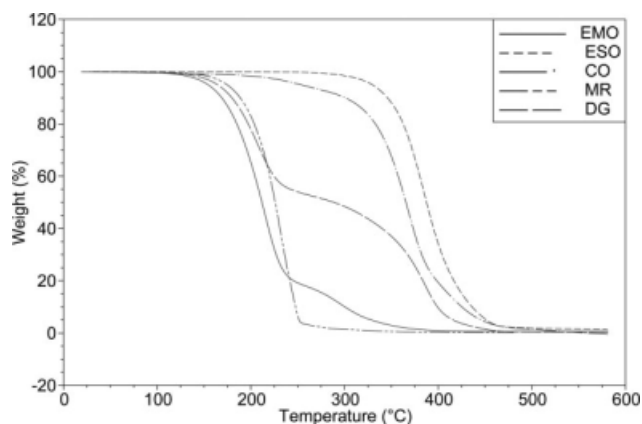
(s, C=O—OH), 1703 (s, C=O), 1595 (m, —HC=CH—), 1491 (m, CH$_2$, Def.), 1450 (s, CH$_3$O, Def.), 1355 (w, CH$_2$OH), 1213 (m, C—O—C, Def.), 1179 (m, CO, Def.; C—O—C, Def.), 1077 (m, C—O—C, Def.), 1028 (m, C—O—C, Def), 913 (m, C=O—OH, Def), 837 (m, =CH$_2$, Def.), (757 (m, Ar), 698 (s, Ar) ^{1}H NMR (CDCl$_3$, 400 MHz) ppm: 0.9 (—CH$_3$), 1.2–1.6 (—CH$_2$—), 1.7 (—ArCH—CH$_2$—CH(CO$_2$H)—), 2.1 (—CH$_2$—CH=), 2.2 (—CH—CH$_2$—CH(O—)—), 2.3 (—CH$_2$—(C=O)), 2.7 (—CH(—Ar)—), 2.9 (—CH$_2$—CH(CO$_2$H)—CH$_2$—), 3.1 (=CH—CH$_2$—CH(O—)—CH$_2$—), 3.6 (—OCH$_3$), 5.5 (—CH=CH—), 7.2 (—ArH), 9.0 (—CO$_2$H).

SMA-CO (poly[styrene-*co*-(maleic anhydride)]-γ-(castor oil))

SMA of 1.0 g (GPC indicated M_n of 2395, 3.27 mmol anhydride groups), 1.04 g CO (3.27 mmol secondary alcohol), and 1% DABCO were dissolved in 20 mL ethyleneglycoldimethyl ether. The mixture was refluxed at 110°C for 4 h. Ethyleneglycoldimethyl ether solvent was removed under vacuum. The mixture was dissolved in a minimum amount of acetone and was cast into a Teflon mold. The mixture in a Teflon mold was heated at 90°C for 4 h to remove acetone. The temperature was then raised to 130°C for 4 h and then 160°C for another 4 h. Transparent light colored thermoset was obtained (Fig. 2).

IR (Film) (cm^{-1}): 3000–3600 (br, COOH), 3061 (s, ArH), 3018 (m, =CH), 2928 (s, CH), 2853 (s, CH), 1854 (m, C—C=O—O—C=O—C), 1780 (s, C=O—OH), 1735 (s, C=O), 1602 (m, —HC=CH—), 1494 (m, CH$_2$, Def.), 1455 (s, CH$_3$O, Def.), 1376 (w, CH$_2$OH), 1220 (m, C—O—C, Def.), 1168 (m, CO, Def.; C—O—C, Def.), 1081 (m, C—O—C, Def.), 914 (m, C=O—OH, Def), (757 (m, Ar), 700 (s, Ar).
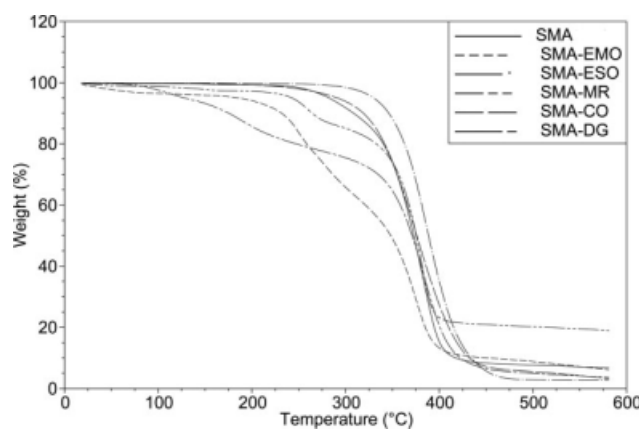
SMA-DG (poly[styrene-*co*-(maleic anhydride)]-graft-(diglyceride))

SMA (1.0 g) (GPC indicated M_n of 2395, 3.27 mmol anhydride groups) and 7 g Soyoil diglycerides (DG) (11.6 mmol primary alcohol, excess) were dissolved in 15 mL DMF. The mixture was refluxed at 152°C for 4 h. The polymer was precipitated from the DMF solution by adding saturated aq. NaCl solution, then the product was dissolved in 100 mL CHCl$_3$. The solution was washed three times with 100 mL saturated NaCl in aq. HCl (5%). CHCl$_3$ was evaporated at 90°C. Product was extracted with diethylether in a soxlet apparatus for 6 h to remove any residual monomers. The polymer was dried in a vacuum oven at 80°C for 4 h to remove any residual ether. A yellow transparent thermoplastic was obtained (Fig. 2).

IR (Film) (cm^{-1}): 3000–3600 (br, COOH), 3026 (m, =CH), 2925 (m, CH), 2854 (m, CH), 1847 (w, C—C=O—O—C=O—C), 1778 (s, C=O—OH), 1734 (s, C=O), 1602 (m, —HC=CH—), 1493 (m, CH$_2$,
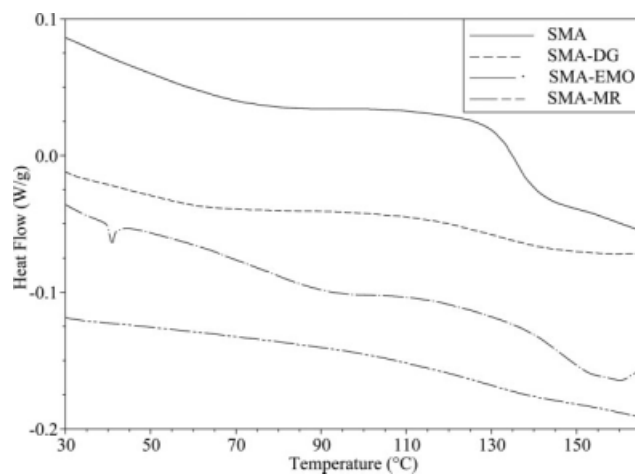

Figure 9 DSC graphs of thermoplastic polymers.

TABLE II
Results of Thermal and Mechanical Analyses of Thermoset Products

Polyester mol : mol	T_g (°C) DMA	Tensile Strength (Mpa)	Elongation at break	Storage Modulus (MPa)[a]
SMA-ESO 1 : 4.3 rxn at 120 °C	71	5.8	16.7	11.73
SMA-ESO 1 : 4.3 postcured at 200°C	74	–	–	20.6
SMA-CO 1 : 3	66 (146 small)	2.6	44.2	3.34
MASO-ESO 1 : 1[10]	16.4	4	46	–
MA-ESO 1 : 1[12]	35	–	–	15.02
MA- ESO 2.4 : 1[10]	47.5	11	34	–
PA- ESO 1.1 [12]	65	–	–	15.89

[a] The storage modulus at elastic region ($T_g + 30°C$).

Def.), 1453 (s, CH$_3$O, Def.), 1219 (br., C—O—C, Def.), 1096 (m, C—O—C, Def.), 1024 (m, C—O—C, Def), 921 (m, C=O—OH, Def), (761 (m, Ar), 701 (s, Ar) ^{1}H NMR (CDCl$_3$, 400 MHz) ppm: 0.9 (—CH$_3$), 1.2–1.6 (—CH$_2$—), 1.7 (—ArCH—CH$_2$—CH(CO$_2$H)—), 2.0 (—CH$_2$—CH=), 2.3 (—CH$_2$—(C=O)), 2.8 (—CH (—Ar)—), 3.1 (—CH$_2$—CH(CO$_2$H)—CH$_2$—), 4.1 (—O—CH$_2$—CH(O—)—), 4.2 (—OCH$_2$—CH(—O—)CH$_2$O—), 5.3 (—CH=CH—), 7.2 (—ArH), 9.8 (—CO$_2$H).

RESULTS AND DISCUSSION

Monomer synthesis

Soy oil diglyceride

Alcoholysis of triglycerides with limited amount of alcohol is known to produce mostly 1° alcohols which are known to react easily with anhydrides. Notable features of the IR spectra include 3466 (w, OH) and 1653 cm^{-1} (m, —HC=CH—). The ratio of diglycerides produced by the partial hydrolysis of triglyceride to the remaining triglycerides was found around 95.5% by measuring the intensity ratio of hydrogens on glyceride residue which are labeled on Figure 3. as a (4.1 ppm (—O—CH$_2$—CH(—O—)—CH$_2$OH), 1.91) to terminal carbon hydro-

gens on the fatty acid residues, which are labeled on the Figure 3. as k (0.9 ppm (—CH$_3$), 9.0) (Fig. 3).

Polymer synthesis and spectral identification

SMA-EMO poly[styrene-co-(maleic anhydride)]-graft-(epoxidized methyl oleate)

In the IR spectra of poly[styrene-co-(maleic anhydride)]-graft-(epoxidized methyl oleate) (SMA-EMO) product anhydride peaks at 1844, 1778 and epoxy peak at 840 cm^{-1} disappear after the reaction. Carboxylic acid and hydroxyl peaks at 3000–3600 cm^{-1}, broad carbonyl peak at 1732 cm^{-1} corresponding to the methyl ester and newly formed ester are observed after the reaction (Fig. 4). When the linear SMA-EMO half-ester is postcured in oven at 180°C for 4 h, a cross linked product is obtained. This is probably due to the esterification of the newly formed carboxylic acid and hydroxyl groups. GPC analysis of the product gives a M_n of 4410 which corresponds to an increase of 2045 over the original M_n of the unsubstituted SMA. This increase indicates an average grafting of 6.55 per SMA polymer. This in turn corresponds grafting of EMO to 84% of the available anhydride sites (7.77) (Table I). The same value was found to be 80.9% by measuring the
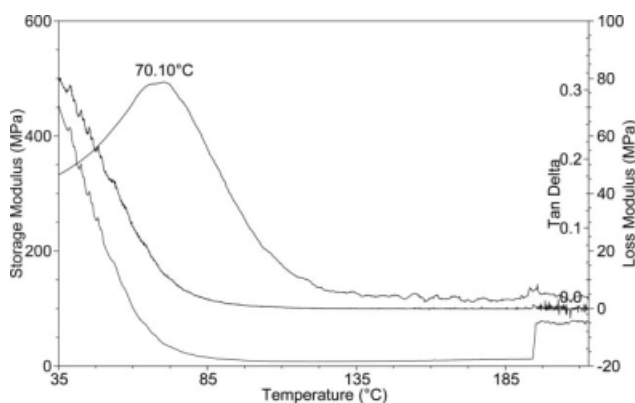

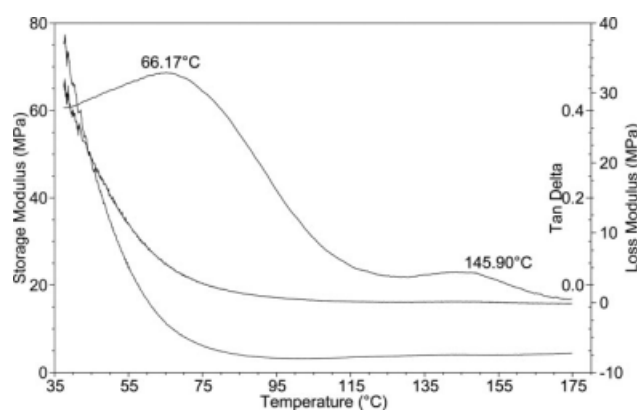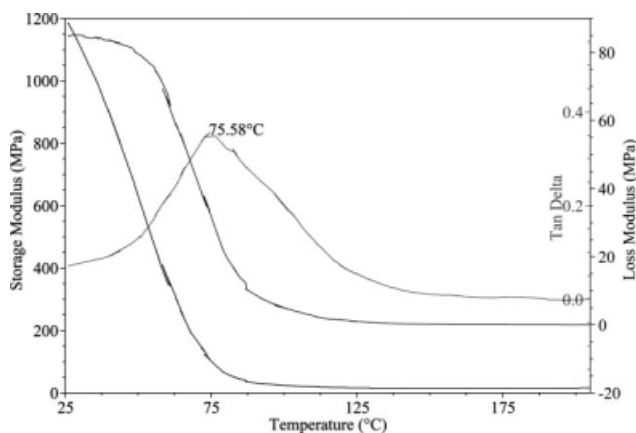**Figure 10** DMA graph of thermoset SMA-ESO polymer synthesized at 120°C.

Figure 11 DMA graph of thermoset SMA-CO polymer.

Figure 12 DMA graph of thermoset SMA-ESO polymer synthesized at 120°C and postcured at 200°C.

intensity ratio of methoxy hydrogens (3.7 ppm (—OCH$_3$), 0.28) to phenyl hydrogens (7.2 ppm (—ArH), 1.0) in ^{1}H NMR (Fig. 5). The two analysis methods gave results that are in good agreement.

SMA-ESO poly[styrene-*co*-(maleic anhydride)]-γ-(epoxidized soybean oil)

Figure 6. A shows the IR spectrum at the beginning of anhydride-epoxide reaction. The anhydride peaks at 1844, 1778, glyceride fatty acid ester at 1742 and epoxy peak at 840 cm^{-1} are present. Figure 6. B shows that after 4 h of curing, the intensity of these peaks are decreased. Yet, the intensity and broadness of 1742 cm^{-1} are increased due to formation of new ester groups in addition to glyceride fatty acid ester. Between 3000 and 3600 cm^{-1} free car-

boxylic acid peak appears. At the end of the reaction, after 12 h of curing, free carboxylic acid, anhydride peaks 1844, 1778 cm^{-1} and epoxy peak 840 cm^{-1} are diminished with further increase in the intensity of the ester peak at 1742 cm^{-1}. These findings prove that anhydride-epoxy reaction is complete (Fig. 6). This product is insoluble in common NMR solvents.

SMA-MR poly[styrene-*co*-(maleic anhydride)]-*graft*-(methyl ricinoleate)

In the IR spectra of poly[styrene-*co*-(maleic anhydride)]-*graft*-(methyl ricinoleate) (SMA-MR), product anhydride peaks at 1844, 1778 cm^{-1} are reduced when compared with SMA. A broad carbonyl peak at 1703 cm^{-1} indicates methyl ester and newly formed ester and the 3000–3600 cm^{-1} peak indicates free carboxylic acid (Fig. 4). In ^{1}H NMR of SMA-MR polymer at 9.0ppm (—CO$_2$H) carboxylic acid hydrogen, at 3.1ppm (=CH—CH$_2$—CH(O—)—CH$_2$—) alpha to newly formed ester, 3.6ppm (—OCH$_3$) methoxy hydrogens on methyl ricinoleate, 7.2ppm (—ArH) aromatic hydrogens on SMA are present, and these peaks show that grafting has occurred. GPC analysis gives a M_n of 4348 which indicates that 80% of the available anhydride groups on SMA polymer have been grafted by MR (Table I).

SMA-CO (poly[styrene-*co*-(maleic anhydride)]-γ-(castor oil))

In the IR spectra of SMA-CO product, anhydride peaks at 1854, 1780 cm^{-1} are reduced when compared to SMA. A broad carbonyl peak at 1735 cm^{-1}
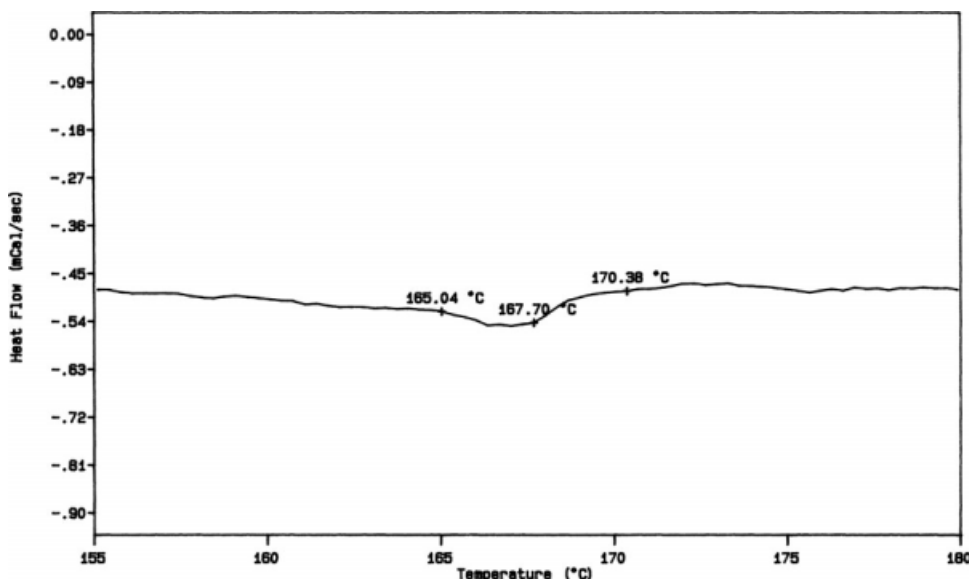
Figure 13 DSC graph of thermoset SMA-ESO polymer.
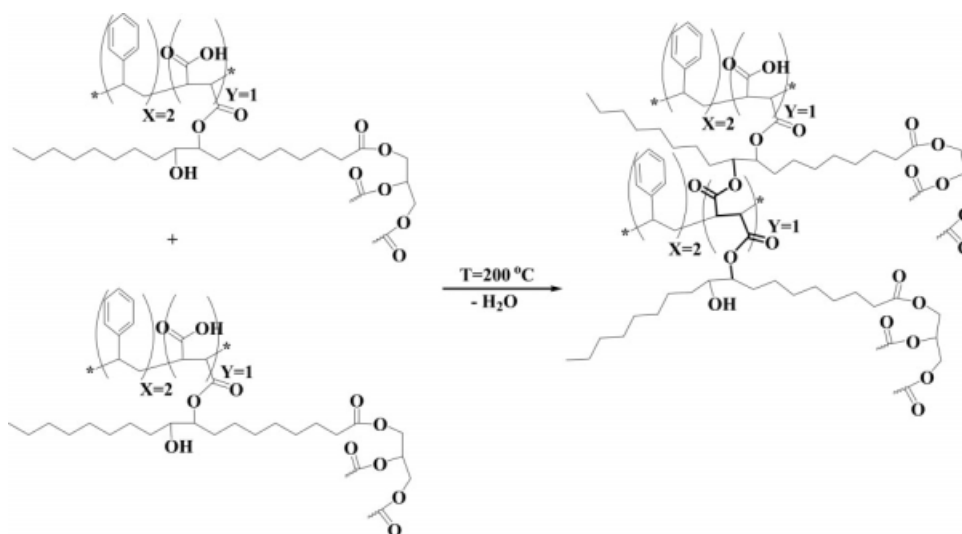
Figure 14 Further esterification and crosslinking reactions in SMA-ESO polymer through the newly created hydroxyl and carboxyl groups.

indicates methyl ester and newly formed ester and the 3000–3600 cm^{-1} peak indicates free carboxylic acid (Fig. 4). This product is insoluble in common NMR solvents.

SMA-DG (poly[styrene-co-(maleic anhydride)]-graft-(diglyceride))

In the IR spectra of SMA-DG product, the anhydride peak at 1847 cm^{-1} is less intense but the carbonyl peak at 1778 cm^{-1} is more intense when compared with SMA, due to formation of free carboxylic acid (Fig. 4). In ^{1}H NMR of SMA-DG polymer, the observed peaks are at 9.8 ppm (—CO$_2$H) carboxylic acid hydrogen, 0.9 ppm (—CH$_3$) terminal carbon hydrogens on the fatty acid residues and at 7.2 ppm (—ArH) aromatic hydrogens on SMA. The ^{1}H NMR of SMA-DG shows that grafting has occurred. GPC analysis gives a M_n of 4788 which indicates that 50% available anhydride groups on SMA polymer have been grafted by DG (Table I).

Thermal properties

TGA analysis of thermoplastic products shows both the characteristics of oil based monomers and SMA. TGA analysis of SMA-EMO shows weight loss between 200 and 300°C which probably corresponds to the loss of EMO. Another weight loss is observed between 300 and 400°C, probably corresponding to SMA ceiling temperature. The 5% Weight loss of SMA-EMO polymer is at 185°C which is higher than monomer EMO yet lover than SMA. At the end of TGA analysis, SMA-EMO gives a char yield of 6.20% which is very close to that of SMA, 6.74%. TGA analysis of SMA-ESO polymer shows mainly

the characteristics of its building blocks which are ESO and SMA since the TGA analysis results of ESO and SMA are almost identical. TGA analysis of SMA-MR shows weight loss between 200 and 300°C which probably corresponds to the loss of MR. Another weight loss is observed between 300 and 400°C, probably corresponding to SMA decomposition temperature.[23,24,25] At the end of TGA analysis SMA-MR gives 18.93% char yield. TGA analysis of SMA-CO polymer shows mainly the characteristics of SMA not the CO. CO has a two step weight loss yet SMA-CO has one just like SMA. At the end of TGA analysis SMA-CO gives 3.31% char yield. In TGA analysis of SMA-DG, weight loss is observed between 200 and 300°C and 300 and 400°C very much like soy oil diglycerides. The char yield is 3.62% (Figs. 7 and 8).

Table I and Figure 9 show the T_g data and DSC analysis of SMA and SMA-EMO, SMA-MR, and
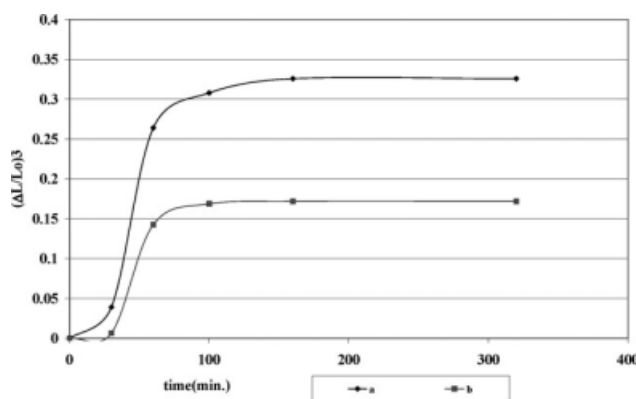
Figure 15 Swelling behavior of SMA-ESO 140°C cured (a) and SMA-ESO 200°C postcured (b) in CH$_2$Cl$_2$ solvent.

SMA-DG grafted thermoplastic soluble polymers. Only SMA showed a distinct T_g at 136°C and SMA-EMO showed some transition at 145°C which can be accepted as T_g. Determination of T_g of the model compounds (SMA-EMO, SMA-MR, and SMA-DG) with DSC was not very successful. Therefore, DMA method was used for the cross linked samples (SMA-ESO and SMA-CO)

Mechanical properties

Mechanical properties of the crosslinked polymers SMA-ESO and SMA-CO were measured by DMA and compared with similar structures reported in the literature such as poly(maleic anhydride-γ-epoxidized soybean oil) (MA-ESO),[10,12] poly(phtallic anhydride-γ- epoxidized soybean oil) (PA-ESO)[12] and poly(maleinated soybean oil-γ-epoxidized soybean oil) (MASO-ESO).[10]

Table II and Figures 10–12. show the relation between the storage modulus of MASO-ESO, MA-ESO, PA-ESO, and the SMA polymers synthesized in this work. T_g of SMA-ESO polyester is the highest and suggests that this material may be useful in structural applications. The storage modulus of ESO based polymer decreases from 15.02 to 11.73 MPa when SMA is used instead of MA (Yet, the storage modulus of SMA-ESO postcured at 200°C is 20.6 MPa, which is higher than both). SMA-CO polyester has a high elongation at break, which suggests that it may be useful as a flexible material.

DMA analysis of SMA-ESO shows a T_g at 70°C (Fig. 10). SMA-CO shows two T_g's one is large at 66°C and probably belongs to the triglyceride segments; the other is small at 146°C and probably belongs to the polymeric backbone (Fig. 11). Both SMA-ESO and SMA-CO have higher T_g's than literature structures MASO-ESO, MA-ESO, and PA-ESO (Table II).

The anhydride-epoxy reaction goes easily at 120°C and creates one secondary hydroxyl and one carboxylic acid group. The direct esterification temperatures of secondary alcohols and carboxylic acids are usually around 200°C. Surprisingly, DMA analysis of SMA-ESO shows a permanent increase in storage modulus from 11.8 to 75 MPa at 194°C (Fig. 10). DSC analysis of SMA-ESO also shows an endotherm at around 168°C (Fig. 13). We believe that this increase in storage modulus is due to further esterification and crosslinking through the newly created hydroxyl and carboxyl groups (Fig. 14). To investigate this possibility, a SMA-ESO sample synthesized at 120°C and another SMA-ESO sample synthesized at 120°C and postcured at 200°C, were subjected to swelling tests and DMA analysis. DMA analysis of 200°C postcured SMA-ESO shows an increase in T_g from 70 to 74°C. Storage modulus at 35°C shows an

increase from 454 to 1012 MPa and storage modulus at T_g+ 30°C (Elastic region) shows an increase from 11.7 to 20.6 MPa (Figs. 10 and 12). The postcured sample (200°C) has considerably higher mechanical properties than the 120°C sample. The increase in modulus observed at 194°C for the 120°C synthesized sample is not observed in the 200°C postcured sample. The 200°C postcured sample swells in CH_2Cl_2 solvent and reaches equilibrium at 160 min, with a volumetric swelling ratio of 0.1718 (Fig. 15). Yet, 120°C synthesized sample swells and reaches an equilibrium swelling in 160 min, with a volumetric swelling ratio of 0.3258. These findings show that 200°C postcured sample has a higher crosslink density than the 120°C sample, and the only plausible reaction is the esterification of the newly created carboxyl and hydroxyl groups as shown in Figure 14.

CONCLUSION

Polymers from SMA and ESO, EMO, CO, MR, DG were prepared. Mechanical and thermal properties of synthesized polymers were compared with plant oil based analogs. Due to the ratio of reactants chosen in the formulation of the polymers, the properties of lipid moiety prevail over those of SMA.

SMA-ESO copolymers showed very interesting and unexpected mechanical behavior. Stiffness of the material decreased with increasing temperature like most of polymers but around 190°C, a dramatic increase of storage modulus was observed. This is probably due to the esterification of residual free carboxylic acid and free OH groups. This behavior is unique to this polymer.

One can envisage a potential use for this polymer in a self healing role. A part manufactured of this material which may be inadvertently over-stressed mechanically and thermally can survive thanks to an increase in modulus when heated above 190°C.

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