

# Polymerization of Epoxidized Soybean Oil with Maleinized Soybean Oil and Maleic Anhydride Grafted Polypropylene Mixtures

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**ABSTRACT:** In this study, maleinized soybean oil triglycerides (SOMA) were reacted with epoxidized soybean oil triglycerides (ESO) to give plant oil-based thermoset polymers. To increase fracture toughness of the product, different amounts of SOMA was replaced by maleic anhydride grafted polypropylene (MMPP) (Epolene E43, maleate content 2.9%,  $M_n = 3900$  and Polybond 3200, maleate content 1%,  $M_n = 1,10,000$ ). The improvement in mechanical properties was monitored. The characterizations of the products were done by DMA, DSC, TGA, and IR spectroscopy. ESO-SOMA and ESO-SOMA-MMPP polymers are crosslinked

rigid infusible polymers. ESO-SOMA-MMPP(E43) and ESO-SOMA-MMPP(PB3200) showed a phase change at 146 and 169°C, respectively, probably due to the melting transition of the MMPP backbone. Storage moduli of the two polymers at 35°C were 54.6 and 246.1 MPa, respectively. Storage moduli and the impact strength of the polymers increased with MMPP content and with MMPP molecular weight. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3311–3317, 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<sub>2</sub> emission reduction,<sup>1</sup> energy savings, ease of production,<sup>2</sup> low price,<sup>3</sup> and the availability of a variety of chemical transformations on the triglycerides.<sup>4,6</sup>

Direct polymerization of unsaturated triglycerides is rarely successful. Polymerization of triglycerides is preferably done by attaching a polymerizable group to the triglyceride. This strategy has been used by us and by others in many examples.<sup>4,5</sup> Polymers derived from such monomers have low molecular weights and low mechanical properties due to the bulky structure of the monomers. This manifests itself in low fracture toughness of the polymers obtained.

To increase the molecular weight and to reach the desired entanglement length, we changed our strategy. We included a high molecular weight polymer having the same functional group as one of the monomers in the polymerization mixture. Thus, maleinized soybean oil (SOMA) and maleic-modified polypropylene (MMPP) mixtures were used as the anhydride component of the reaction, and epoxidized soybean oil (ESO) was used as the epoxy component. This strategy, depicted in Figure 1, 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. Many commercial epoxy adhesives use anhydrides as curing agents. The reaction is believed to proceed through hydrolysis of the anhydride to a diacid and reaction of the carboxylic acid groups with the epoxide. Figure 2 shows this reaction.

We note that the reaction produces new ester, carboxylic acid and hydroxyl groups whose IR signal can be used to monitor the extent of the reaction. We also note that the formation of a new hydroxyl group which may also react with of a second anhydride group and, therefore, exact stoichiometry between the anhydride and epoxy groups cannot be predicted.

SOMA is reacted with ESO.<sup>7</sup> Epoxidized linseed oil was reacted with different petroleum-based

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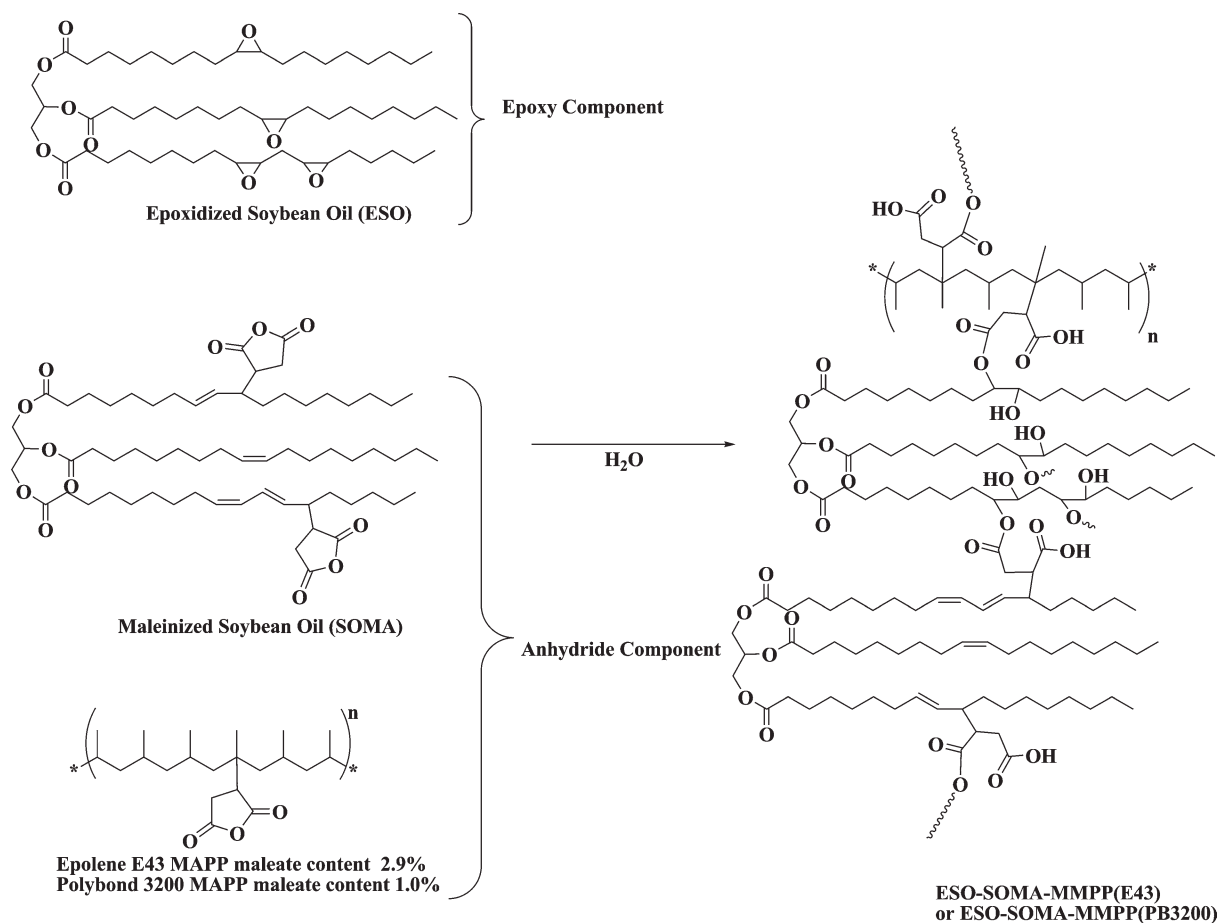


Figure 1 Schematic representation of the new polymers synthesized.

anhydrides.<sup>8,9</sup> US patents 4,548,985 and 4,600,648 describe the use of maleic anhydride graft polypropylene (MMPP) films with ESO to increase adhesion.<sup>10,11</sup> US patents 6,201,066 and 6,482,530 describe the use of MMPP and ESO mixtures to increase adhesion of low density polyethylene to polyesters and metal foils.<sup>13,14</sup>

The aim of this work is to polymerize ESO-SOMA mixtures in the presence of different amounts of MMPP and to monitor the effect of increasing molecular weight on the mechanical properties of the resulting polymer. Two different kinds of MMPP are used in this work. E43 with a molecular weight of

3900 and PB3200 with a molecular weight 110,000 to further demonstrate the effect of molecular weight on the mechanical properties.

## EXPERIMENTAL

### Materials and methods

ESO(Paraplex G-62) having 4.2 epoxy groups per triglyceride was purchased from C.P. Hall Company (Chicago, USA); Epolene E43 (2.9 % maleic anhydride grafted,  $M_n = 3900$ ) was purchased from Westlake Chemical (Longview, TX); Polybond 3200 (1%

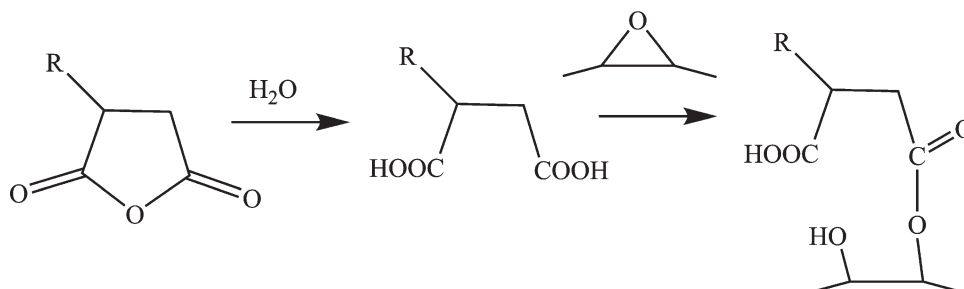


Figure 2 Epoxy-anhydride reaction mechanism.

maleic anhydride grafted,  $M_n = 110,000$ ) was purchased from Crompton Corporation (Middlebury, CT); toluene was purchased from Merck (Darmstadt, Germany); soybean oil was supplied by Marsa (Adana, Turkey); and maleic anhydride (MA) from Fluka (Buchs, Switzerland) was used without purification.

IR characterization of compounds was performed by Thermo Nicolet, FTIR 380 spectrometer, using the diamond ATR accessory. 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. The dynamic mechanical thermal analysis of the polymer samples was performed by using TA Instrument Q800 dynamic mechanical analyzer (DMA). Temperature scans were run from 25°C to 160–180°C at a heating rate of 3°C/min with a vibration frequency of 1 Hz. The swelling behavior of the polymers was tested in CH<sub>2</sub>Cl<sub>2</sub> with a Gaertner 7109-46 traveling microscope (Skokie, IL). The samples were placed in a closed container, and the experiment was continued until the solvent uptake ceased. The Zwick/Roell Durometer (Ulm, Germany) with Shore A was used to determine the surface hardness of polymer samples; the test was performed according to ASTM D 2240 standard test. Izod Impact test specimens were tested with a 453 g (1.0 lb) pendulum according to ASTM D256 standard.

### Monomer synthesis

#### Maleinized soybean Oil

Thermally SOMA was synthesized by following the procedure given by Küsefoğlu and coworkers.<sup>14</sup>

### Polymer synthesis

#### ESO-SOMA polymer

One grams of SOMA (1.8 mmol anhydride groups) and 0.44 g ESO (1.8 mmol epoxy groups) as obtained, without drying, were stirred at room temperature for an hour. The mixture was transferred

into a Teflon mold and was heated in a vacuum oven at 140°C for 4 h. A light orange transparent thermoset product was obtained (Fig. 1).

IR (Film) (cm<sup>-1</sup>): 3000–3600 (br, COOH, OH), 2926 (vs, CH), 2855 (s, CH), 1739 (vs, C=O), 1460 (m, CH<sub>2</sub>, Def.), 1415 (w, CH<sub>3</sub>, Assy. Def.), 1375 (m, CH<sub>3</sub>O, Def.), 1239 (m, C–O–C, Def.), 1165 (s, CO, Def.; C–O–C, Def.), 1101 (m, C–O–C, Def.), 1016 (w, C=O, Str. Vib.), 971 (w, CH<sub>3</sub>, Rock), 920 (w, COOH, Def), 868 (w, C(–O–)–C(–O–), Ring Vib.), 724 (w, C–C, Skel.Vib.)

#### ESO-SOMA-MMPP polymer

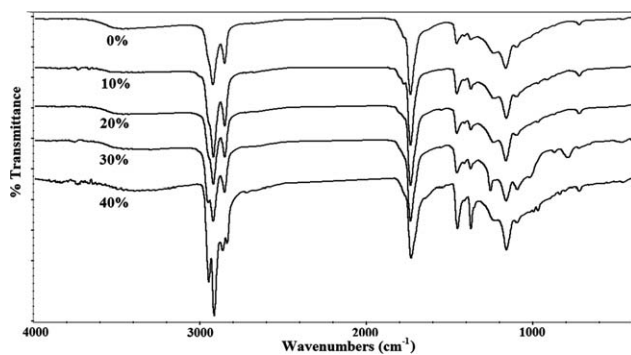
In a typical procedure (for 10% MMPP) 6.20 g SOMA (11.16 mmol anhydride groups), 1 g MMPP (GPC indicated  $M_n$  of 3900, 0.3 mmol anhydride groups) and 2.80 g ESO (11.46 mmol epoxy groups) were dissolved in 15 mL 1 : 1 toluene:xylene mixture (Table I). The mixture was heated under reflux for 2 h. Then, the condenser was set for distillation and the solvent was removed. The viscous product was transferred to a Teflon mold and heated under vacuum at 180°C for 4 h. Test samples were extracted with diethylether in a soxlet apparatus for 6 h to remove any unreacted monomer and dried in a vacuum oven at 80°C for 4 h to remove any residual ether. A yellow transparent, flexible, thermoset product was obtained in 94% yield (Fig. 1).

In the subsequent experiments, a portion of SOMA was removed and replaced by MMPP in such a way that epoxy:maleate functional group ratio is always 1 : 1 (Table I). For example, sample called ESO-SOMA-MMPP(E43)%10 contains 10% MMPP(E43) by weight of the total mixture of reagents.

ESO-SOMA-MMPP(E43)%40. IR (Film) (cm<sup>-1</sup>): 3000–3600 (br, COOH, OH), 2951 (s, CH), 2918 (s, CH), 2867 (s, CH), 2841 (s, CH<sub>2</sub>, Sym. Stretch) 1735 (s, C=O), 1554 (w, C–O, Stretch), 1456 (m, CH<sub>2</sub>, Def.), 1415 (m, CH<sub>3</sub>, Assy. Def.), 1375 (m, CH<sub>3</sub>O, Def.), 1235 (m, C–O–C, Def.), 1162 (s, CO, Def.; C–O–C, Def.), 1098 (m, C–O–C, Def.), 1024 (w, C=O, Str. Vib.), 999 (w, PP, Helix Chain) 972 (w,

TABLE I  
Weights of MMPP, SOMA, and ESO Used in Different Experiments

Polymer	MMPP(E43) % on final product	E43 (g)	SOMA (g)	ESO (g)
ESO-SOMA-MMPP(E43)%10	10	1.00	6.20	2.80
ESO-SOMA-MMPP(E43)%20	20	1.00	2.73	1.27
ESO-SOMA-MMPP(E43)%30	30	1.00	1.57	0.76
ESO-SOMA-MMPP(E43)%40	40	1.00	0.99	0.51
	MMPP(PB3200) % on final product	PB3200 (g)	SOMA (g)	ESO (g)
ESO-SOMA-MMPP(PB3200)%10	10	1.00	6.23	2.77
ESO-SOMA-MMPP(PB3200)%20	20	1.00	2.76	1.24
ESO-SOMA-MMPP(PB3200)%30	30	1.00	1.60	0.73
ESO-SOMA-MMPP(PB3200)%40	40	1.00	1.02	0.48



**Figure 3** IR spectrum of ESO-SOMA-MMPP(E43) polymers with different MMPP(E43) content.

CH<sub>3</sub>, Rock), 810 (m, C(—O—)C(—O—), Ring Vib.), 724 (w, C—C, Skel.Vib.)

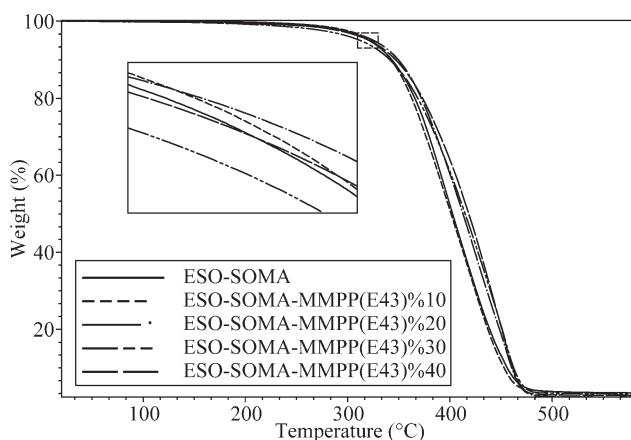
ESO-SOMA-MMPP(PB3200)%40. IR (Film) (cm<sup>-1</sup>): 3000–3600 (br, COOH, OH), 2950 (s, CH), 2922 (s, CH), 2857 (s, CH<sub>2</sub>, Sym. Stretch) 1738 (vs, C=O), 1554 (w, C—O, Stretch), 1459 (m, CH<sub>2</sub>, Def.), 1414 (w, CH<sub>3</sub>, Assy. Def.), 1375 (m, CH<sub>3</sub>O, Def.), 1237 (m, C—O—C, Def.), 1164 (s, CO, Def.; C—O—C, Def. ), 1099 (m, C—O—C, Def.), 1024 (m, C=O, Str. Vib.), 975 (w, CH<sub>3</sub>, Rock), 725 (w, C—C, Skel.Vib.)

## RESULTS AND DISCUSSION

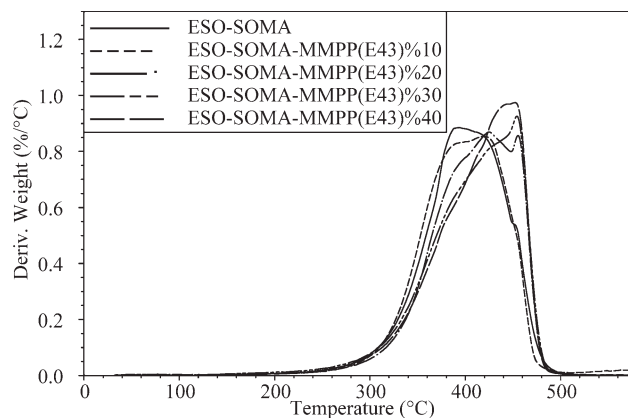
### Polymer synthesis and spectral identification

ESO-SOMA-MMPP(E43) and ESO-SOMA-MMPP(PB3200) polymers

Figure 3 shows IR spectrum of ESO-SOMA-MMPP(E43) polymers at different MMPP content. In all the spectra, anhydride peaks at 1860–1841, 1783–1770, 1712 cm<sup>-1</sup> are diminished. In our previous experience with IR spectra, it was observed that unreacted epoxide peak appears between 800–900 cm<sup>-1</sup>, and its exact position is highly dependent on



**Figure 4** TGA analysis of ESO-SOMA and ESO-SOMA-MMPP(E43) polymers.



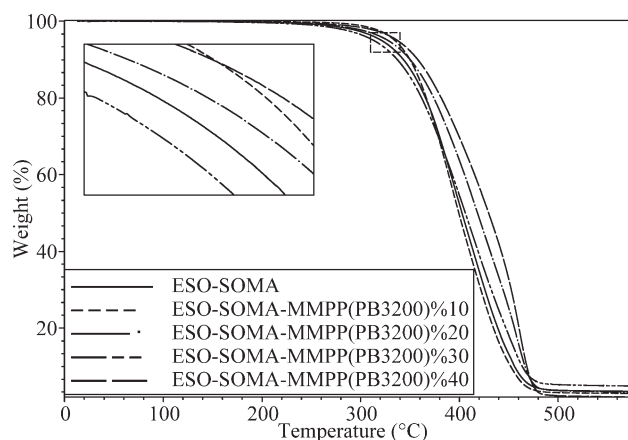
**Figure 5** Derivative of the TGA trace of ESO-SOMA and ESO-SOMA-MMPP(E43) polymers.

the matrix. In Figure 3, the epoxy peaks appearing in 800–900 cm<sup>-1</sup> region are considerably reduced in intensity compared to ESO itself. Yet, the intensity and broadness of 1742 cm<sup>-1</sup> peaks are increased due to formation of new ester groups. Between 3000–3600 cm<sup>-1</sup>, free carboxylic acid and hydroxyl peaks appear. After soxlet extraction, the yield of polymer is between 86–94 %. These findings prove that anhydride–epoxy reaction is complete (Fig. 3). Another observation is that PP backbone CH stretching absorption at 2990 cm<sup>-1</sup>, CH deformation absorptions 1456 and 1415 cm<sup>-1</sup> become more intense compared to ester peak at 1742 cm<sup>-1</sup> with increasing MMPP content. Identical IR spectra are observed with ESO-SOMA-MMPP(PB300) polymers.

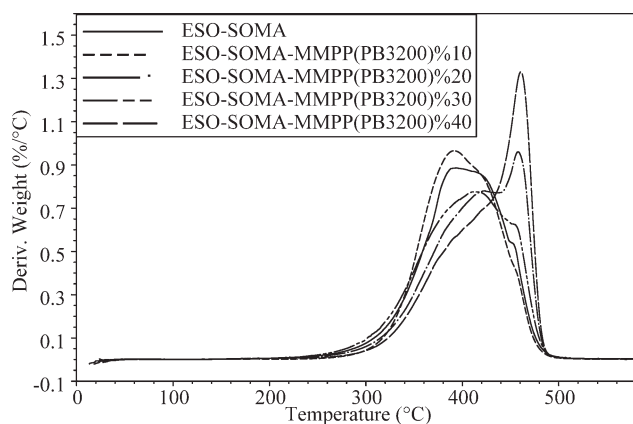
### Thermal properties

ESO-SOMA-MMPP(E43) and ESO-SOMA-MMPP(PB3200) polymers

TGA analysis of SOMA-ESO shows only one weight loss with the maximum rate of loss at 388°C which



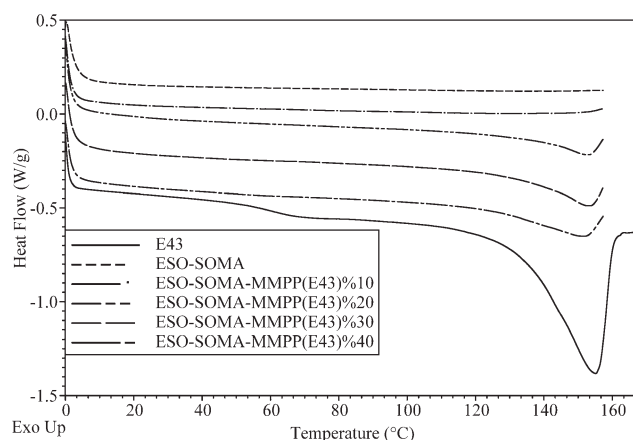
**Figure 6** TGA analysis of ESO-SOMA and ESO-SOMA-MMPP(PB3200) polymers.



**Figure 7** Derivative of the TGA trace of ESO-SOMA and ESO-SOMA-MMPP(PB3200) polymers.

is due to triglyceride loss. MMPP(E43) and MMPP(PB3200) polymers show also only one weight loss but at 445°C and 460°C, respectively. ESO-SOMA-MMPP polymers show two weight losses with maximum rates at 388°C and 445°C as they contain MMPP, SOMA, and ESO. A total of 5% weight loss temperatures show that ESO-SOMA-MMPP(E43) polymers show the highest thermal stability at 20% MMPP content and ESO-SOMA-MMPP(PB3200) polymers show the highest thermal stability at 40% MMPP content. At the end of TGA analysis, ESO-SOMA-MMPP polymers give char yields changing between 2.05% and 4.88% (Figs. 4–7, and Table II).

Table II and DSC traces in Figure 8 show transitions that are probably due to melting of MMPP segments. The melting transition becomes more prevalent at higher MMPP concentration. The highest  $T_m$  belongs to polymer containing 20% MMPP(E43) and the intensity of the  $T_m$  peak progressively increases with MMPP content.



**Figure 8** DSC analysis graphs of ESO-SOMA, E43 and ESO-SOMA-MMPP(E43) polymers.

**TABLE II**  
DSC Derived  $T_m$  Transformations of ESO-SOMA-MMPP Polymers and 5% Weight Loss Temperatures Obtained by TGA

Polymer	$T_m$ (°C)	5% weight loss temperatures (°C)
ESO-SOMA	—	—
E43	155.6	321.3
ESO-SOMA-MMPP(E43)%10	146.9	323.3
ESO-SOMA-MMPP(E43)%20	147.8	325.7
ESO-SOMA-MMPP(E43)%30	143.9	312.6
ESO-SOMA-MMPP(E43)%40	137.5	321.3
ESO-SOMA-MMPP(PB3200)%10	144.7	334.9
ESO-SOMA-MMPP(PB3200)%20	139.1	327.8
ESO-SOMA-MMPP(PB3200)%30	120.6	313.3
ESO-SOMA-MMPP(PB3200)%40	143.7	337.4

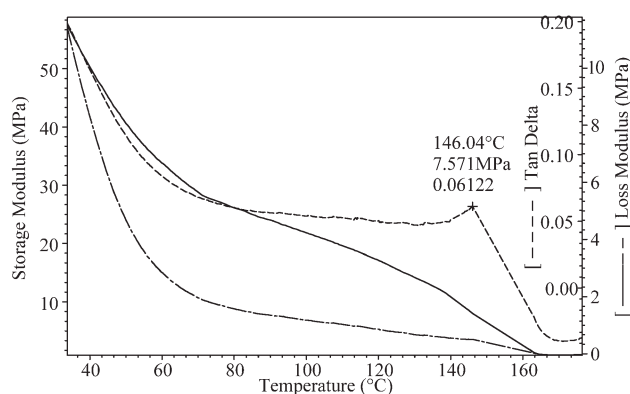
### Mechanical properties

Storage moduli of polymers are expected to increase with the increasing MMPP content and MMPP molecular weight.

DMA analysis of both ESO-SOMA-MMPP(E43) and ESO-SOMA-MMPP(PB3200) polymers shows that the storage modulus increases with increasing MMPP content (Table III). Also, at the same polymer content, increasing MMPP molecular weight increases the storage modulus. The difference in storage modulus due to MMPP molecular weight is highest at 30% which translates to 700% improvements. The 40% samples are the only samples that show  $\tan \delta$  maximas in DMA measurements. The temperatures where  $\tan \delta$  maximas are observed coincide within experimental error with well defined melting endotherms in DSC analysis. They are probably due to the melting transition of the MMPP backbone. This transition appears at 146°C for ESO-SOMA-MMPP(E43)%40 and 169°C for ESO-SOMA-MMPP(PB3200)%40 clearly showing the increase in  $T_m$  of the product polymer with molecular weight of the backbone (Figs. 9 and 10, and Table III). This

**TABLE III**  
Surface Hardness and DMA Storage Modulus of ESO-SOMA and ESO-SOMA-MMPP Polymers at 35°C

Polymer	Surface hardness average of ten trials	Storage modulus at 35°C (MPa)
ESO-SOMA	60	—
ESO-SOMA-MMPP(E43)%10	67	9.6
ESO-SOMA-MMPP(PB3200)%10	65	8.1
ESO-SOMA-MMPP(E43)%20	78	15.1
ESO-SOMA-MMPP(PB3200)%20	85	39.5
ESO-SOMA-MMPP(E43)%30	84	35.7
ESO-SOMA-MMPP(PB3200)%30	90	221.6
ESO-SOMA-MMPP(E43)%40	87	54.6
ESO-SOMA-MMPP(PB3200)%40	94	246.1

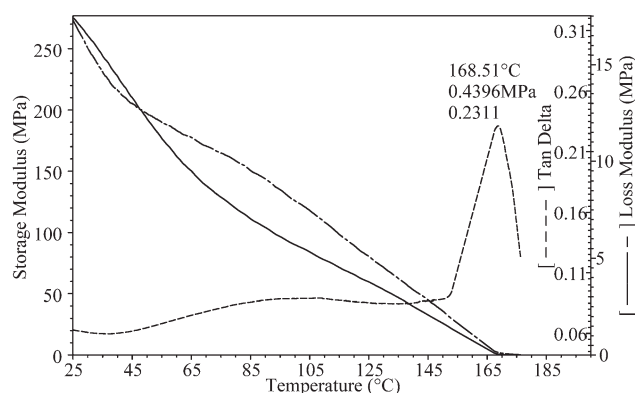


**Figure 9** DMA graph of ESO-SOMA-MMPP(E43)%40 polymer.

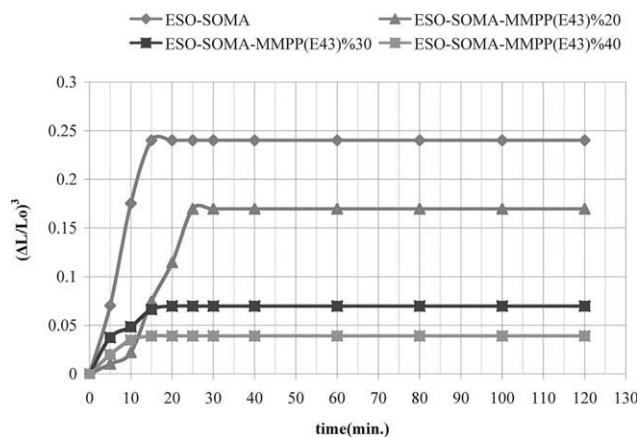
dramatic increase in storage modulus is observed when increasing amounts of MMPP replace SOMA. Similarly, dramatic increases in storage modulus are observed when a high molecular weight MMPP is used instead of a low molecular weight MMPP. These improvements in storage modulus are in perfect agreement with our original postulate.

Samples with higher molecular weight MMPP are expected to have higher impact strengths. In fact, samples containing less than 40% MMPP are too elastic to break. ESO-SOMA-MMPP(E43)%40 and ESO-SOMA-MMPP(PB3200)%40 showed Izod impact strengths at 36.6 J/m and 46.6 J/m, respectively, which shows that higher the molecular weight of the MMPP used, the higher is the impact strength.

The useful parameter that may be obtained from a swelling test is the volumetric swelling ratio ( $q$ ).  $q = \Delta V/V_o = (\Delta L/L_o)^3$  where  $V$  refers to the volume and  $L$  refers to the length on the one side of the sample. This ratio depends upon the molar volume of the solvent, the crosslink density, and crosslink segment length of the polymer. The swelling behavior of the polymers in  $\text{CH}_2\text{Cl}_2$  was examined by using a traveling microscope. MMPP is known to be insoluble in



**Figure 10** DMA graph of ESO-SOMA-MMPP(PB3200)%40 polymer.

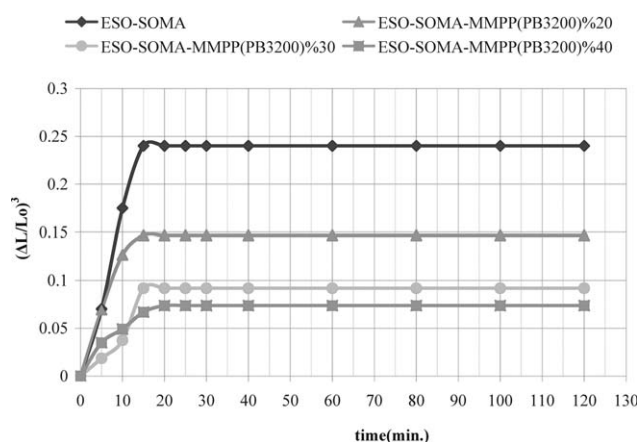


**Figure 11** Swelling behavior of ESO-SOMA and ESO-SOMA-MMPP(E43) polymers in  $\text{CH}_2\text{Cl}_2$  solvent.

our choice of solvent ( $\text{CH}_2\text{Cl}_2$ ) and introduction of MMPP increased connectivity across the network resulting lower swelling. Decrease in volumetric swelling observed with increased MMPP content is also in agreement with our expectation (Figs. 11 and 12).

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 having 1mm thickness were protected from any possible mechanical stress before testing. To obtain a reliable analysis data, the samples were tested at least at 10 different points on the same surface. Results of the test are presented in the Table III.

Results reveal that starting with 10% polymer content, increasing the MMPP content increases the surface hardness. Also, when a higher molecular weight MMPP is used instead of a low molecular weight MMPP, the surface hardness increases. Surface hardness results are in good agreement with DMA obtained storage modulus results and also with our original postulate.



**Figure 12** Swelling behavior of ESO-SOMA and ESO-SOMA-MMPP(PB3200) polymers in  $\text{CH}_2\text{Cl}_2$  solvent.

## CONCLUSIONS

The results show that the thermal properties of the polymers are not dependent of MMPP content or molecular weight. Yet, mechanical properties of polymer increases with increasing MMPP content and increasing MMPP molecular weight.

The increase in mechanical properties with the high molecular weight MMPP is quite dramatic as the high molecular weight MMPP used in this work (PB3200) also has considerably lower maleate content. We conclude that higher molecular weight and therefore higher entanglement is more important than crosslink density.

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