

Chemical Modification of Metallocene-Based Polyethylene–Octene Elastomer Through Solution Grafting of Acrylic Acid and its Effect on the Physico-Mechanical Properties

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ABSTRACT: In the present work, the metallocene-based polyethylene–octene elastomer (POE) was chemically modified by solution grafting of acrylic acid in presence of benzoyl peroxide. The relative proportions of graft and gel formation were optimized through %weight gain, Fourier Transform infrared spectroscopy, elemental analysis and proton nuclear magnetic resonance spectroscopy. The gel formation in the POE matrix was found to be the prime competitor. The effect of

grafting at its maximum level on various physicochemical properties was thoroughly investigated, using X-ray diffraction analysis, differential scanning calorimetry, mechanical, dynamic mechanical, and thermogravimetric analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3409–3417, 2007

Key words: grafting; acrylic acid; polyethylene–octene elastomer; carboxylated polymer; chemical modification

INTRODUCTION

Free-radical grafting of unsaturated carboxylic acids or their derivatives onto polyolefins is an effective method to impart certain degree of functionality in polyolefins.¹ Chemical modifications of different diene elastomers are well reported.^{2–11} Naqvi and Reddy¹² have investigated grafting of acrylic acid (AA) and ethyl methacrylate (EMA) on low-density polyethylene (LDPE) under melt processing conditions. They have showed that it could be a highly effective way of diversifying the properties of LDPE. Ghosh et al.¹³ have modified LDPE by graft copolymerization with AA, ethyl acrylate (EA), and butyl acrylate (BA), using dicumyl peroxide as the initiator and finally showed that the grafting efficiency has been highest with AA. For the development of biodegradable plastic from the combination of linear LLDPE and starch, grafting of maleic anhydride (MAH) or AA on LLDPE effectively improves the compatibility between LLDPE and starch.¹⁴ The effect of solvents on the benzoyl peroxide initiated graft

copolymerization of poly(ethylene terephthalate) fibers with AA have been studied by Sacak and Oflaz.¹⁵ In addition to the method of free-radical graft copolymerization, the reactive extrusion method and the vapor phase photografting method have also been investigated. Park et al.¹⁶ have employed preirradiation method of grafting of AA on polypropylene fabric, using Cobalt ray and the resultant fabric displays stronger biocidal effect upon all bacteria. Wu et al. investigated graft reaction of AA onto polyethylene–octene elastomer (POE) in a mixer at $(85 \pm 2)^\circ\text{C}$ at 60 rpm rotor speed,¹⁷ although several questions remain unanswered and there is scope for further work.

Recently, the metallocene-based POE, has received much attention because of its several advantages over other polyolefins because of its unique uniform distribution of comonomer content and narrow molecular weight distribution.¹⁸ Due to its nonpolar nature, there is also an opportunity to increase the property spectrum of POE by modifying it with polar group, for better compatibility with polar materials (like polar fillers, etc.) and also for better adhesion property towards polar substrate. In this respect, the POE-g-MAH (MAH grafted POE) has been used as the compatibiliser in the nylon 6/POE system and the impact strength of nylon 6 has been enhanced quite considerably.^{19,20} Keeping this in view, we have studied the graft reaction of AA on POE in solution system and observed its impact on thermal and mechanical properties (both in static and dynamic condition) of the

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TABLE I
Composition of all the Samples

Sample designation	Concentration of monomer (AA) (wt %)	Concentration of BPO (wt %)	Temp. (°C)	Time (h)	Grafting (%)	Gel yield (%)
POE 8150	Unmodified POE					
POE 8150-g-AA	Acrylic acid grafted POE					
POE 8150-g-2.5% AA	2.5	0.3	70	06	0.98	4.10
POE 8150-g-5% AA	5.0	0.3	70	06	2.28	3.82
POE 8150-g-10% AA	10.0	0.3	70	06	6.27	3.10
POE 8150-g-15% AA	15.0	0.3	70	06	6.30	3.09
POE 8150-g-20% AA	20.0	0.3	70	06	6.41	3.08
POE 8150-0.1% BPO _{Crosslinking}	0.0	0.1	70	06	–	2.98
POE 8150-0.2% BPO _{Crosslinking}	0.0	0.2	70	06	–	4.20
POE 8150-0.3% BPO _{Crosslinking}	0.0	0.3	70	06	–	5.12
POE 8150-0.4% BPO _{Crosslinking}	0.0	0.4	70	06	–	5.22
POE 8150-0.5% BPO _{Crosslinking}	0.0	0.5	70	06	–	5.30
POE 8150-g-0.1% BPO	10.0	0.1	70	06	2.32	1.62
POE 8150-g-0.2% BPO	10.0	0.2	70	06	3.52	2.83
POE 8150-g-0.4% BPO	10.0	0.4	70	06	6.39	3.18
POE 8150-g-0.5% BPO	10.0	0.5	70	06	6.35	3.21
POE 8150-g-60°C	10.0	0.3	60	06	2.10	1.96
POE 8150-g-80°C	10.0	0.3	80	06	5.85	3.83
POE 8150-g-90°C	10.0	0.3	90	06	4.81	4.32
POE 8150-g-1H	10.0	0.3	70	01	1.60	0.96
POE 8150-g-2H	10.0	0.3	70	02	2.37	1.52
POE 8150-g-3H	10.0	0.3	70	03	3.82	2.62
POE 8150-g-4H	10.0	0.3	70	04	4.91	3.06
POE 8150-g-5H	10.0	0.3	70	05	5.85	3.08
POE 8150-g-7H	10.0	0.3	70	07	6.30	3.13

The figures in bold indicates variation of that particular parameter under the specified condition.

base material for the first time. As the reactivity of the polyolefins arises from their hydrogen atoms along the hydrocarbon skeleton that is subjected to free-radical attack, crosslinking may occur simultaneously apart from the desired grafting.^{12–14} There is still limited literature discussing extensively both the graft reaction and the gel formation of POE and also on the detailed physicomechanical properties of POE_g.

In this investigation, we have described the variation of different reaction parameters to optimize the extent of grafting as well as gelation in the grafting reaction of AA on POE. We have also studied the detailed physicomechanical properties of the AA grafted POE and tried to correlate the experimental results with their structure.

EXPERIMENTAL

Materials

Polyolefin elastomer, designated as POE, with 39% comonomer content (Engage 8150) obtained from DuPont Dow Chemical (Wilmington, DE), was used as the elastomer matrix. AA (density 1050 kg/m³), a commercial product of Aldrich (Milwaukee, WI), was used after removing the inhibitors by vacuum distillation. Benzoyl peroxide (BPO, 98% purity) procured from Aldrich (Milwaukee, WI), was used as the free

radical initiator for the grafting reaction. The solvents, xylene (E. Merck, Mumbai, India) and toluene (E. Merck, Mumbai, India), all of laboratory grade, were used as received.

Grafting of AA onto POE

A solution of POE (5%, w/v) in toluene was prepared by dissolving 10 g of POE in 200 mL toluene in a three-necked round bottom flask and was stirred for 1 h. Nitrogen was passed through the polymer solution to drive out the dissolved oxygen present in the solvent and also in the reaction flask. Once the mixture was homogenized, the required amount of AA was added drop wise to the reaction mixture. After adding AA, when the mixture was again homogenized, the required amount of BPO was added as initiator to the reaction mixture. The reaction was carried out in nitrogen atmosphere. The grafting reaction was optimized with respect to AA concentration, BPO dose, reaction temperature and time of the reaction. Finally, the samples were collected and were dried under vacuum for 48 h at 40°C for complete removal of the solvent. Percent weight variation, infrared spectroscopy, gel content, and C.H.O analysis were used to characterize grafted POE. Details of the composition of the samples are enlisted in Table I.

Percentage grafting and gel content measurement

The solution grafted samples were taken in a filter paper and placed in the Soxhlet apparatus for extraction. Each extraction was carried out for 24 h, using water as the extracting medium for complete removal of unreacted AA and any homopolymer of AA, if at all formed, during the reaction. After the extraction, the samples within filter paper were dried under vacuum for 72 h at 70°C till they showed no weight variation (W_g). The extent of grafting was calculated from the weight gain by the samples using the following equation

$$\% \text{ Grafting} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

where, W_g = weight of grafted POE and W_0 = weight of POE before grafting.

The residue was further extracted for another 24 h in a Soxhlet apparatus using xylene as solvent. Xylene was used to remove the grafted POE (POE_g) from the mixture of POE_g and POE-gel. The xylene unextracted product, which was the crosslinked POE fragments referred to as "gel yield" of the grafting reaction in this article and was expressed in the form of percentage ratio of the dry xylene-insoluble product to the water-extracted product.²¹

CHARACTERIZATION

Fourier transform infrared spectroscopic studies

Fourier transform infrared (FTIR) studies were carried out in dispersive mode on Soxhlet extracted thin film samples (~ 100 μm) using Perkin-Elmer FTIR-spectrophotometer (model spectrum RX I), within a range of 400–4400 cm^{-1} using a resolution of 4 cm^{-1} . An average of 16 scans has been reported for each sample.

NMR studies

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in a 200-MHz Bruker NMR spectrophotometer at 60°C. All the scans were taken after dissolution of the samples in CDCl_3 .

Elemental analysis

"C, H, and O" analysis was carried out using Perkin-Elmer CHNS/O Analyser (Series-II 2400). The results were expressed in the form of % of the elements present within the samples.

X-ray diffraction studies

The X-ray diffraction patterns of the samples were recorded in a Philips X-ray diffractometer (model PW-1710), using crystal monochromated Co $K\alpha$ radiation

in the angular range 10°–70° (2θ) and at 40 kV operating voltage and 20 mA current. The areas under the crystalline and amorphous portions were determined in arbitrary unit and the percentage of crystallinity (χ_c) was measured using the relation:

$$\chi_c = [I_c/(I_c + I_a)] \times 100 \quad (2)$$

where I_a and I_c are the integrated intensity corresponding to the amorphous and crystalline phases, respectively.

Differential scanning calorimetry analysis

DSC studies were carried out in TA instruments (model Q100 V 8.1), at a heating rate of 10°C/min under nitrogen in the temperature range of –100 to 100°C. The data were analyzed by TA Universal analysis software on a TA computer attached to the machine. Transitions were detected in such curves from the occurrence of discontinuity in the curves. The minimal from the melting endotherm was considered as the melting point (T_m).

Dynamic mechanical thermal analysis

The dynamic mechanical spectra of the samples were obtained by using a DMTA of TA instruments (model 2980 V1.7B). The sample specimens were analyzed in tensile mode at a constant frequency of 1 Hz, a strain of 0.01% and a temperature range from –100 to 20°C at a heating rate of 2°C/min. The data were analyzed by TA Universal analysis software on a TA computer attached to the machine. Storage modulus (E') and loss tangent ($\tan \delta$) were measured as a function of temperature for all the samples under identical conditions. The temperature corresponding to the peak in $\tan \delta$ versus temperature plot was taken as the glass-rubber transition temperature (T_g).

Mechanical properties

Tensile specimens were punched out from the molded sheets using ASTM Die-C. The tests were carried out as per the ASTM D 412 method in a Universal Testing Machine (Hounsfield-H10KS) at a crosshead speed of 500 mm/min at $(25 \pm 2)^\circ\text{C}$. The average of three tests is reported here.

Thermogravimetric analysis

The TGA analysis were carried out in TA instruments (model Q50), at the heating rate of 10°C/min under nitrogen atmosphere up to 600°C. The data were analyzed by TA Universal analysis software on a TA computer attached to the machine. A small amount of material (around 5 mg) was used for TGA study.

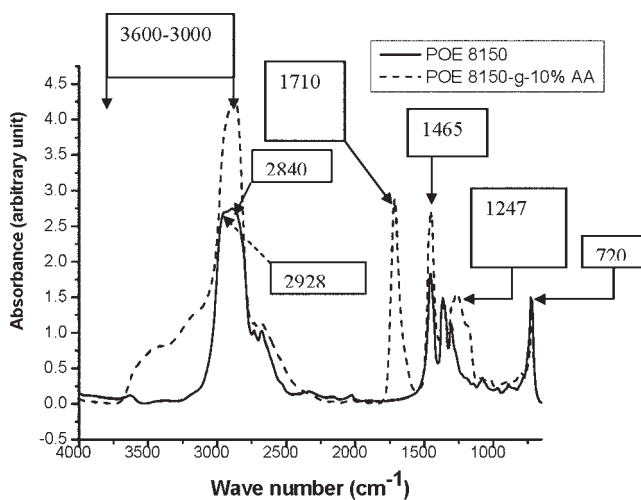


Figure 1 Representative normalized FTIR spectra for the virgin and the 10 wt % AA modified POE.

RESULTS AND DISCUSSION

Optimization of the solution grafting process

Effect of AA loading

Table I illustrates the effect of AA concentration on the grafting percentage and the gel yield at a constant BPO concentration (0.3 wt % with respect to POE). All the reactions have been performed at 70°C for 6 h. Grafting shows an increase on increasing the AA concentration up to 10 wt % (with respect to POE), beyond which these level off. The gel content, however, exhibits a reverse trend, i.e., it decreases as the AA loading is increased. Moreover, the absolute value of grafting yield is distinctively higher when compared with those of the gel yield from 10 wt % of AA onwards, as observed from Table I. In the presence of BPO, grafting reaction of AA on to POE and gel formation among the POE molecules become competitive because of the formation of free radicals on AA and POE. At low AA concentration, the diffusion of monomer molecules toward the free radical sites on the POE backbone governs the grafting extent, whereas at higher concentrations of the monomer, the percentage grafting may remain almost constant as the number of free-radical sites available on the POE backbone becomes a limiting factor, which also results in formation of homopolymer of AA, as indicated by the conversion of reaction medium from clear transparent condition to opaque whitish solution. The gel yield, on the other hand is maximum in the absence of AA (5.12% for “POE 8150-0.3% BPO_{Crosslinking}” sample in Table I) and gradually decreases with the increasing concentration of AA, which indicates greater mobility of the monomeric AA towards polymeric POE macroradicals. The equilibration of the gel yield process is again due to the saturation of the free radical sites on the POE macromolecules.

This “grafting-profile” of AA on to POE could also be reconfirmed from the infrared spectroscopy and

the elemental analysis results. Figure 1 displays the arbitrarily stacked, representative FTIR spectra of virgin POE and 10% AA containing POE samples. All the

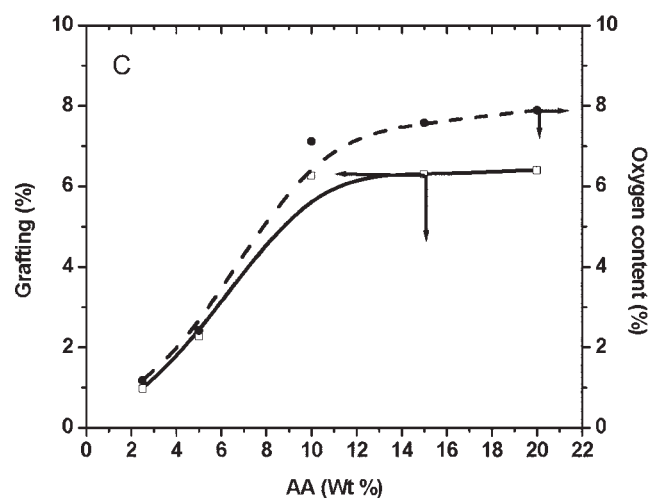
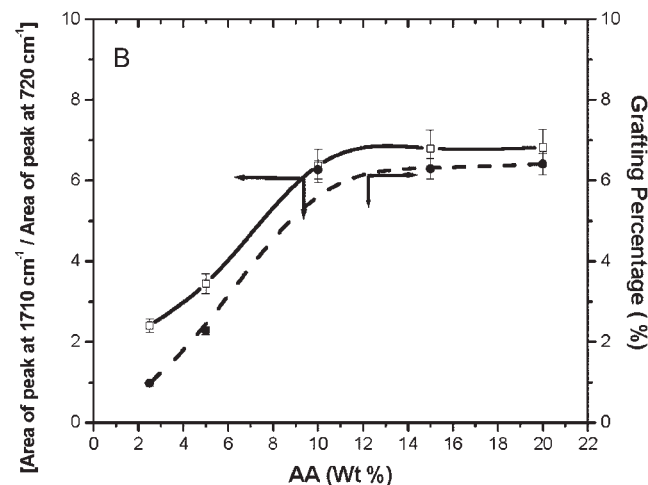
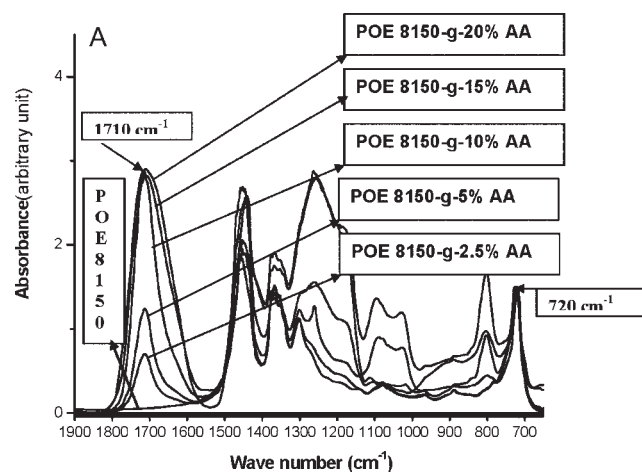


Figure 2 (a) Comparative plots FTIR spectra of the samples at different AA concentrations, highlighting the change in C=O peak at 710 cm^{-1} . (b) Comparative plots of FTIR spectroscopic C=O peak normalized value and grafting percentage at different AA concentrations. (c) Comparative plots of grafting percentage and oxygen content (%) at different AA concentrations.

TABLE II
CHNO Analysis Results of "POE 8150" and "POE 8150-g-AA" Samples

Sample	Grafting (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
POE 8150	Nil	85.06	14.94	Nil	Nil
POE 8150-g-2.5% AA	0.98	84.39	14.43	Nil	1.18
POE 8150-g-5% AA	2.28	83.31	14.27	Nil	2.42
POE 8150-g-10% AA	6.27	79.10	13.78	Nil	7.12
POE 8150-g-15% AA	6.30	78.89	13.53	Nil	7.58
POE 8150-g-20% AA	6.41	78.77	13.34	Nil	7.89

characteristic groups of the POE²² at 2840–2928, 1465, and 720 cm^{-1} are found to be present in the AA modified POE. There are also three additional peaks at 3600–3000 (more of a band than the peak), 1710 and 1247 cm^{-1} , which are due to O–H, C=O, and C–O stretching vibration, respectively.²³ Presence of these groups in the AA modified sample even after extraction with water reconfirms the grafting of the acid on to the rubber matrix. Figure 2(a) displays the plot of normalized carbonyl absorption band at 1710 (normalized against the constant peak absorption at 720 cm^{-1} of POE) against the different AA concentrations and shows an excellent correlation with the grafting percentage values, replotted in Figure 2(b) for comparison.

The elemental analysis data (CHNO), recorded in Table II, and plotted in Figure 2(c) for comparison with that of the grafting percentage values against the different AA concentrations are also in accord with the observations made in Figure 2(a,b). Virgin POE

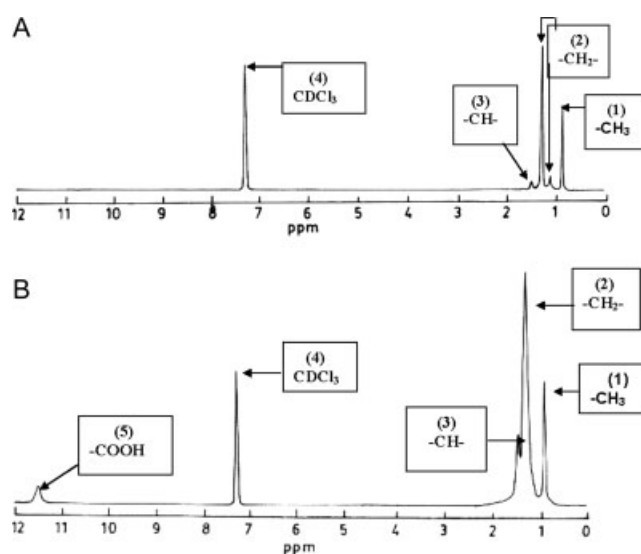


Figure 3 (a) ^1H NMR spectra of unmodified "POE 8150." (b) ^1H NMR spectra of "POE 8150-g-10% AA."

does not show the presence of oxygen, which indicates that the material did not get oxidized before the experiment (POE has got tertiary H and hence tends to oxidize). The oxygen concentration increases steadily on increasing the grafting percentage as observed from Table II, because of the insertion of AA moieties.

Figure 3(a,b) gives the ^1H NMR spectrum of the unmodified "POE 8150" and the "POE 8150-g-10% AA," respectively. For the unmodified POE, it can be observed that only the functional groups of POE, i.e., 1° ($-\text{CH}_3$), 2° ($-\text{CH}_2-$), and 3° ($-\text{CH}-$) appear at 0.8–1.0, 1.1–1.3, and 1.4–1.6 ppm, respectively.²⁴ Figure 3(b) shows the ^1H NMR spectrum of "POE 8150-g-10% AA," which has an extra peak at 11.49 ppm, in addition to the original $-\text{CH}_3$, $-\text{CH}_2-$, and $-\text{CH}$ peaks of the unmodified POE, giving clear indication of presence of $-\text{COOH}$ group in grafted-POE moiety.^{23,25,26} Therefore, it indicates that AA is grafted on POE moiety.

Effect of BPO loading

Table I shows the effect of BPO loading on the grafting percentage and the gel yield for the POE at a constant AA concentration of 10 wt % (the reaction temperature and time have been kept constant at 70°C and 6 h, respectively). The table shows that both the parameters, i.e., the percent grafting and the gel yield increases steadily on increasing the initiator concentration up to 0.3 wt %, beyond which, both the reactions almost level off. Interestingly, there has been always less gel formation when compared with the grafting in the entire experimental range.

As mentioned earlier, both these reactions are fairly competitive (apart from the homopolymerization of AA) and therefore increases simultaneously on increasing the BPO concentration because of availability

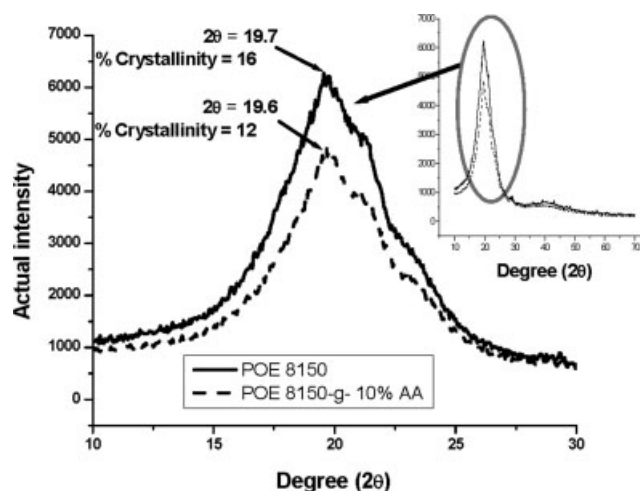


Figure 4 Comparative wide angle XRD spectra of the "POE 8150" and "POE 8150-g-10% AA."

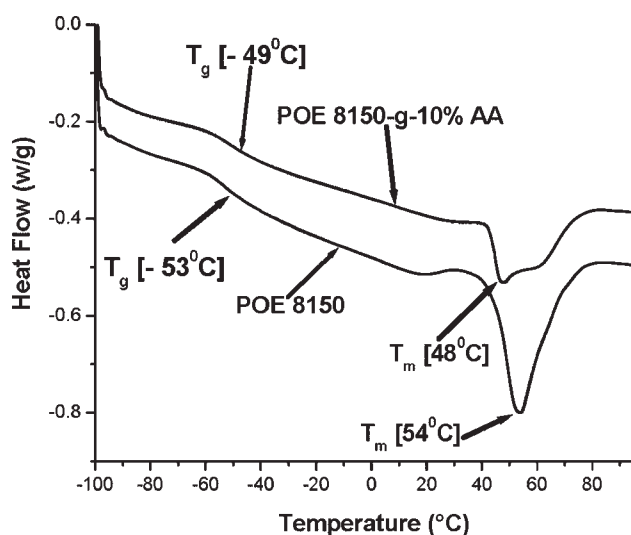


Figure 5 DSC second heating scans for the “POE 8150” and “POE 8150-g-10% AA.”

of these free radicals. In fact, the gel yield is distinctively low in presence of AA. For example, gel yield with 0.2% BPO only is 4.2%, whereas the result is 2.8% in presence of 10 wt % AA (Table I). This indicates greater mobility of the monomeric AA towards polymeric POE macroradicals.

Effect of reaction temperature

The grafting of AA onto POE has been carried out at four different temperatures namely 60, 70, 80, and 90°C to explore the efficiency of grafting reaction and the results are displayed in Table I. In all the cases, 0.3 wt % BPO has been used in presence of 10 wt % AA and the reactions have been allowed for 6 h. The grafting percentage data show an interesting behavior. It increases initially and reaches maxima on raising the reaction temperature from 60 to 70°C, beyond which it exhibits a decreasing trend. The gel yield, on the other hand, shows a steady increase on increasing the temperature from 60 to 90°C. At 60°C, the initiator may not have decomposed completely when compared with the cases at other elevated temperatures (generally the half-life of BPO is calculated at 70°C^{27,28}). Therefore, lower concentration of the initiator radicals obtained from BPO virtually lowers the extent of both

the reactions. Moreover, at 60°C, the rate of diffusion of AA is also lower than that at higher temperature. At 70°C, the rate of diffusion of AA towards POE as well as the decomposition of BPO increase and hence enhance the grafting percentage and the gel yield values. Beyond 70°C, there has been more of thermal polymerization of AA to “polyAA,” which forms a whitish emulsion type batch when compared with other transparent reaction batches. This has reduced the grafting percentage significantly beyond 70°C. The rate of crosslinking reaction, on the other hand, increases on increasing the temperature as usual and therefore there is a steady increase of gel yield.

Effect of reaction time

The time of any chemical reaction is significant and the effect of reaction time at the optimized initiator and monomer concentrations (0.3 and 10 wt %, respectively) at 70°C (optimized reaction temperature) has been studied. Table I summarizes the effect of reaction time on the grafting percentage and gel yield results for the POE-AA system. Although free radically controlled, both these reactions increase steadily with the reaction time and finally level off. The gel formation reaction equilibrates much faster (after 4 h) than the later. A similar argument, as given earlier, can explain all the results.

Physico-mechanical properties of AA grafted POE

In the previous section, optimization of the AA grafting onto the POE matrix has been discussed in detail with reference to all the process parameters. The present part of the article deals with the physico-mechanical effects of AA grafting on POE at the optimized condition. All the studies are concentrated on two samples, the virgin POE and the POE modified with 10 wt % AA (POE-g-10% AA). The modification has been carried out using 0.3 wt % BPO at 70°C for 6 h (optimized condition).

Effect on crystallinity of POE: X-ray diffraction analysis

The relative crystallinity of POE depends on the percentage of the comonomer present in the POE. In the

TABLE III
DSC, DMTA, and TGA Analysis Data of “POE 8150” and “POE 8150-g-10% AA”

Sample	DSC		DMTA			TGA	DTG	
	T_g (°C)	T_m (°C)	E' at -60°C (MPa)	E' at -20°C (MPa)	$\tan \delta_{\max}$ (°C)	T_i (°C)	T_{\max} (°C)	Rate of degradation (%/°C)
Unmodified POE 8150	-53	54	1125	50	-41	437	461	2.7
POE 8150-g-10% AA	-49	48	1610	85	-39	442	466	2.6

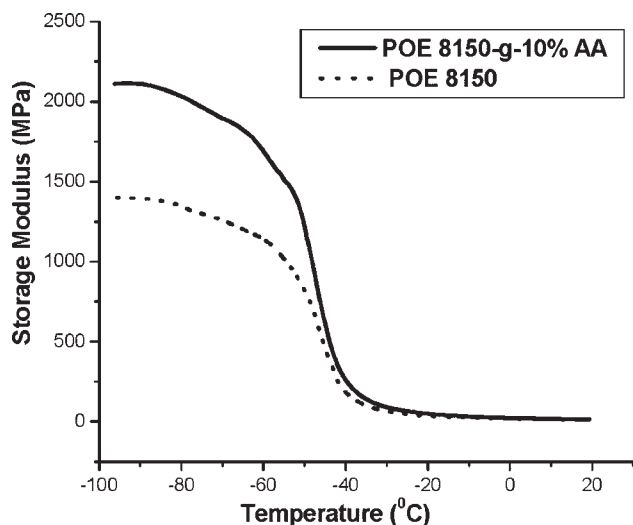


Figure 6 Plots of dynamic storage modulus against temperature for the “POE 8150” and “POE 8150-g-10% AA.”

present investigation, crystallinity of the virgin POE is 16%, calculated using eq. (2) and Figure 4 (plots of actual diffraction intensity against double the angle of diffraction, 2θ). I_c and I_a parameters in eq. (2) have been obtained by deconvoluting the XRD spectra and the corresponding data are reported in Figure 4. Grafting of AA onto POE reduces the crystallinity. The area of the XRD peaks in Figure 4 for the “POE 8150-g-10% AA” is found to reduce significantly ($\sim 25\%$) resulting in a decrease of crystallinity to 12%.

Polyolefins are highly crystalline in nature. In POE the insertion of a comonomer affects the architectural and recurrence symmetry of the polyolefins and reduces the crystallinity. Grafting of AA onto POE disturbs the remnant symmetry of the POE and hence records further drop in the crystallinity value. This fact also confirms the attachment of AA takes place in the polyolefin block of the main chain in POE.

Effects on thermal transition behavior: Differential scanning calorimetry and dynamic mechanical analysis

The effects of AA grafting on the thermal transition behaviors of POE have been investigated. Figure 5 illustrates the second heating DSC scans for the virgin POE and “POE 8150-g-10% AA.” The glass transition temperature (T_g) as determined from the change in slope of the curves is found to increase by a magnitude of 4°C on account of grafting of AA onto POE. On the other hand, the crystalline melting point (T_m) appears 6°C early and also displays low and slightly complex natured crystalline melting endotherm for the same sample as compared with the virgin POE (the transition temperatures are recorded in Table III). T_g , which signifies the segmental mobility, is delayed in the modified sample because of insertion of polar-

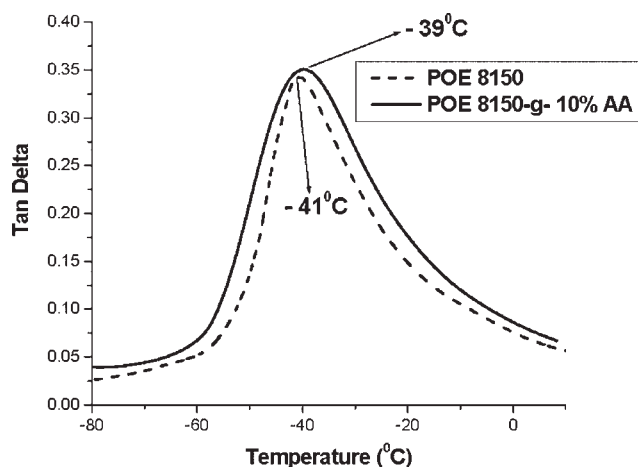


Figure 7 Tan δ versus temperature plots for the “POE 8150” and “POE 8150-g-10% AA.”

ity, resulting in weak dipole–dipole interaction. The early melting transition and low melting enthalpy could directly be correlated with the loss in crystallinity in the virgin POE due to grafting. The complex melting endotherm has resulted probably due to grafted portions in the elastomer.

Figures 6 and 7 elucidate the variation in storage modulus (E') and tan δ against temperature. “POE 8150-g-10% AA” displays comprehensively higher low-temperature dynamic modulus than that of the virgin POE, indicating mechanical reinforcement due to grafting (Table III). At higher temperature of measurement (-20°C), the grafted sample still exhibits higher value, although all these values are significantly lower than that at -60°C (Table III). The T_g of the POE determined from the dynamic mode is higher than that obtained from the static mode (DSC experi-

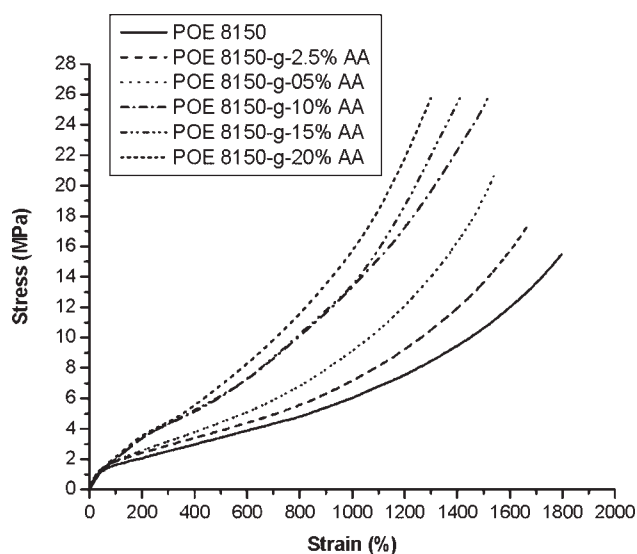


Figure 8 Comparative tensile stress–strain plots of the virgin and AA grafted POE at different AA concentrations.

TABLE IV
Mechanical Properties of "POE 8150" and "POE 8150-g-AA"

Sample name	Tensile strength (MPa)	Elongation at break (%)	Stress at 100% elongation (MPa)	Stress at 200% elongation (MPa)	Stress at 300% elongation (MPa)
POE 8150	15.48 ± 0.01	1796 ± 3	1.61 ± 0.01	2.05 ± 0.02	2.53 ± 0.02
POE 8150-g-2.5% AA	17.53 ± 0.02	1672 ± 2	1.84 ± 0.04	2.43 ± 0.02	2.91 ± 0.03
POE 8150-g-5% AA	20.63 ± 0.06	1539 ± 4	1.89 ± 0.02	2.57 ± 0.01	3.18 ± 0.02
POE 8150-g-10% AA	25.73 ± 0.01	1515 ± 3	1.95 ± 0.02	3.51 ± 0.03	4.32 ± 0.01
POE 8150-g-15% AA	25.76 ± 0.01	1410 ± 3	1.96 ± 0.01	3.52 ± 0.01	4.34 ± 0.02
POE 8150-g-20% AA	25.81 ± 0.01	1300 ± 4	2.09 ± 0.03	3.68 ± 0.02	4.38 ± 0.04

ment) due to wide difference in these modes of experiments. The T_g values obtained from the dynamic mode are reported in Table III. There is a marginal shift in T_g ($\tan \delta_{\max}$) towards higher temperature (around 2°C) in the $\tan \delta$ versus temperature traces in Figure 7. Dipolar interactions, as explained earlier, being weak in nature, are most effective at sub ambient conditions rather than at the room temperature or even higher and are responsible for this delayed response of the macrochains of POE by enhancing the damping behavior at the glass–rubber transition zone, in spite of loss in crystallinity of the virgin POE. This is also responsible for significantly higher low temperature modulus for the grafted sample as well. The broadening in peak area of the loss tangent curves is probably due to wider molecular weight distribution of the POE due to grafting.

Studies on mechanical properties

Figure 8 compares the tensile stress–strain properties of the ungrafted as well as the POE_g samples at all AA concentrations. The corresponding tensile stresses at 100, 200, and 300% elongations, tensile strength and elongation at break (%) values are reported in Table IV. The tensile stresses and tensile strength show a steady increase on increasing the grafting percentage of AA

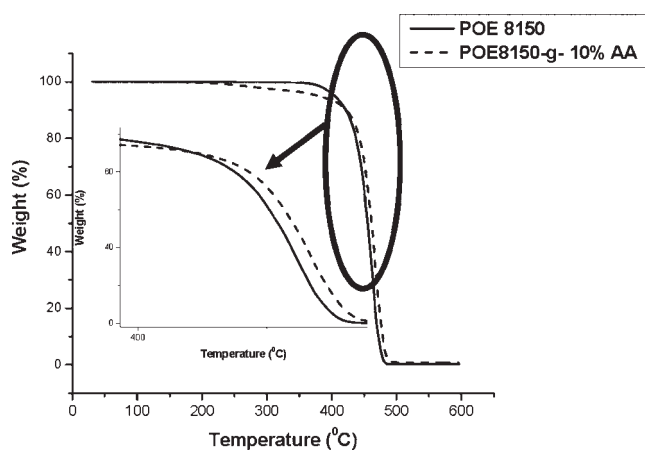


Figure 9 TGA plots of "POE 8150" and "POE 8150-g-10% AA."

onto POE. The elongation at break (%) values, on the other hand, follow the reverse trend. The increase in stress (and strength) is the effect of increasing interchain interaction due to AA grafting and gel yield. This effect comprehensively counter-balances the expected loss in mechanical properties due to the loss of crystallinity.

Effect on thermal stability: Thermogravimetric analysis

The thermogravimetry (TG) and differential thermogravimetric (DTG) plots for POE and "POE 8150-g-10% AA" are compared in Figures 9 and 10, respectively. The temperatures corresponding to the onset of degradation (T_i) and maximum degradation (T_{\max}) for these systems are reported in Table III. The "POE 8150-g-10% AA" shows some early weight losses probably due to the loss of smaller components from the grafted portions. In spite of this, it shows slight improvement in thermal stability as the T_i value is approximately 5°C higher than that of the virgin sample. This improved thermal stability possibly results from the simultaneous effects of the loss of small grafted components and the thermal crosslinking among the POE macromolecules by virtue of combination of the radi-

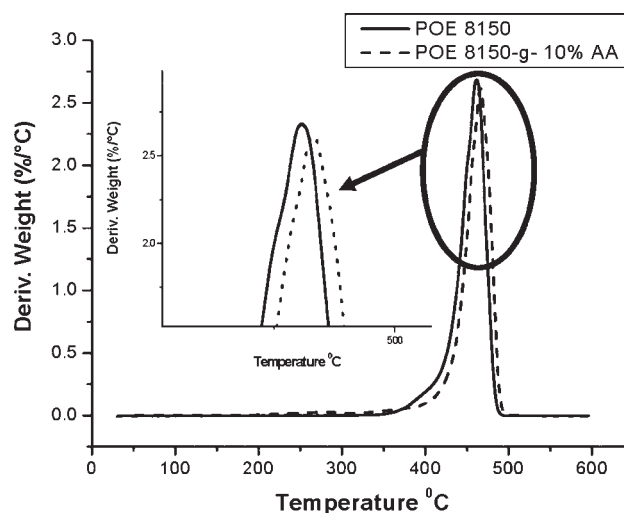


Figure 10 DTG plots of "POE 8150" and "POE 8150-g-10% AA."

cals formed due to side component loss in the previous stage. As a consequence, the T_{\max} is also shifted to slightly higher temperatures for the AA modified sample (DTG plots in Fig. 10 and Table III). The rate of degradation is also reduced at the maximum degradation zone as compared with their virgin component (Table III).

CONCLUSIONS

Chemical modification of POE has been successfully carried out by AA through solution grafting process. The graft reaction has been investigated by % weight gain, % gel yield, infrared spectroscopy, elemental analysis, and NMR studies. The optimum grafting is obtained with 10 wt % AA using 0.3 wt % BPO at 70°C for 6 h of the reaction. The level of grafting at optimized condition has been determined to be 6.27%. There has been a simultaneous gelation of the POE under all circumstances. The gel yield is less than that of the grafting percentage in optimized condition.

Insertion of the AA moiety in POE strongly affects the crystallinity of the base elastomer as it has shown almost 4% drop in crystallinity at its optimized grafting level. This has caused early and slightly complex melting pattern of the modified sample when compared with the virgin, while the reverse trend has been reflected in the glass transition behavior, possibly due to insertion of polarity, resulting in weak dipole-dipole interaction. The modified samples exhibit better mechanical and dynamic mechanical properties than the unmodified elastomer. The thermal stability has been found to be improved slightly despite some early weight losses.

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