

Synthesis of POE-*graft*-methyl methacrylate and acrylonitrile and its toughening effect on SAN resin

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Abstract POE-*graft*-methyl methacrylate and acrylonitrile (POE-*g*-MAN) was prepared by suspension graft copolymerization of methyl methacrylate (MMA) and acrylonitrile (AN) onto polyethylene-octene copolymers (POE). POE-*g*-MAN/SAN resin blends (AOMS) were prepared by blending POE-*g*-MAN with styrene-acrylonitrile copolymer (SAN resin). The effects of reaction conditions on the graft copolymerization and the toughening effect of POE-*g*-MAN on SAN resin were discussed. The results showed that the optimized reaction conditions were AN/(MMA + AN) ratio of 15 wt%, POE/(POE + MMA – AN) ratio of 60 wt%, BPO/(POE + MMA – AN) ratio of 1 wt%, toluene dosage of 44.4 wt%, PVA dosage of 0.4 wt%, SDS dosage of 0.07 wt%, aqueous phase/oil phase mass ratio of 1.5, at 80 °C for 20 h, and when the POE/AOMS mass ratio was 25 wt% under the optimized reaction conditions, the notched Izod impact strength of AOMS reached 54.0 kJ/m². Fourier transform infrared spectroscopy provided substantial evidence of grafting of MMA and AN onto POE chains, and differential scanning calorimetry showed that the graft branches affected the crystallization of POE chains and made the melt temperature and the fusion heat be lower. Transmission electron microscopy analysis showed that the highest toughness occurred when the size of POE-*g*-MAN particles and the surface to surface interparticle distance were proper. Scanning electron microscopy analysis indicated that the AOMS fracture surface had plastic flow visible which looked like a fibril morphology when POE content was 25 wt% with the AN/(MMA + AN) ratio (f_{AN}) of POE-*g*-MAN of 15 wt%. The toughening mechanism of AOMS was shear yielding of matrix, which endowed AOMS with remarkable toughness. Dynamic mechanical thermal analysis showed

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that the compatibility of the POE phase and SAN phase improved after graft copolymerization of MMA and AN onto POE.

Keywords Polyethylene-octene (POE) · POE-*graft*-methyl methacrylate and acrylonitrile (POE-*g*-MAN) · POE-*g*-MAN/SAN resin blends (AOMS) · Impact strength · Compatibility

Introduction

Styrene-acrylonitrile copolymer (SAN) has excellent properties, such as rigidity, chemical resistance, and high tensile strength. But it has the drawback of notch sensitivity. The fracture toughness of brittle or notch sensitive polymers by the incorporation of rubber toughed SAN has been well known as acrylonitrile butadiene styrene terpolymer (ABS). However, ABS and related blends will suffer yellow discoloration and visibly drop in mechanical properties in outdoor use because of the double bonds in the main chain of butadiene. To overcome these problems, the substitution of ethylene-propylene-diene terpolymer (EPDM) for butadiene-based rubber has been widely investigated [1–4].

Ethylene-octene copolymers (POE) produced by DuPont Dow Elastomers Co. Ltd., using a metallocene catalyst, are a new family of homogeneous polyolefin polymers. They have received much attention due to their narrow molecular weight and unique uniform distribution of comonomer [5]. POE was a kind of elastomer without double bonds in the main chain. So POE can be used to replace butadiene-based rubber because of its better thermal stability.

Bae et al. [6] reported the graft modification of ethylene-propylene-diene terpolymer (EPDM) with MMA–AN and St–AN; they found that the light resistance, weatherability, and thermal stability of AEM(AN–EPDM–MMA graft copolymer) were better than those of the AES(AN–EPDM–St copolymer). MMA is a weak polar monomer and AN is a strong polar monomer [7]. Their ratio could be regulated to change the polarity of the grafting chain (*g*-MAN).

In this paper, POE was modified by grafting MMA and AN onto POE to synthesize POE-*graft*-methyl methacrylate and acrylonitrile (POE-*g*-MAN) through suspension graft copolymerization, and the effects of reaction conditions, such as AN/(MMA + AN) ratio, POE/(POE + MMA – AN) ratio, BPO dosage, and reaction time on the graft copolymerization were discussed. The toughening effect of POE-*g*-MAN on SAN resin was investigated. The structure–property relationship of AOMS, including compatibility of POE-*g*-MAN and SAN resin, phase structure and toughening mechanism of AOMS, were detailed in this article.

Materials and experimental methods

Materials

POE 8130 from Du Pont Dow Elastomers Co. Ltd., USA. SAN 350 resin, with about 30 % acrylonitrile and a density of 1.08 g/cm³, was from Kumho P&B Chemicals,

Inc. Korea. Acrylonitrile (Shanghai Chemical Reagent Corp., Shanghai, China) were purified by distillation before use. Methyl methacrylate (Shanghai Chemical Reagent Corp.) was washed with 5 % aqueous sodium hydroxide solution and then with water until neutral, dried over anhydrous sodium sulfate, and distilled under vacuum before use. Benzoyl peroxide (BPO; Guangzhou Chemical Reagent Factory, Guangzhou, China) was recrystallized from ethanol. Polyvinyl alcohol (PVA 224; Kuraray Co. Ltd., Japan) at a concentration of 2 wt% was dissolved in distilled water before use. Toluene (Guangzhou Chemical Reagent Factory) and sodium dodecyl sulfate (SDS; Guangzhou Chemical Reagent Factory) was of analytical purity.

Synthesis of POE-g-MAN

A given amount of POE was dissolved in toluene in a flask equipped with a stirrer, thermometer, condenser, and nitrogen gas inlet. Then, a mixture of MMA, AN, BPO, and SDS were added to the reactant system. After the monomer was fully dissolved, PVA aqueous solution and distilled water were added dropwise, and during the process the stirring speed increased gradually. Thus, the reactant system changed from a solution system to a suspension system. After charging with nitrogen, the reactions were carried out under various experimental conditions, as shown in Table 1.

(a) Decomposition of the peroxide to primary radicals

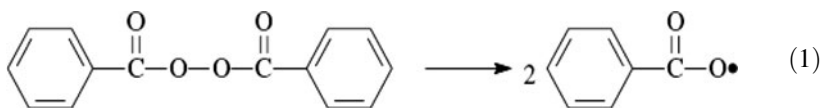


Table 1 Reaction conditions for graft copolymerization

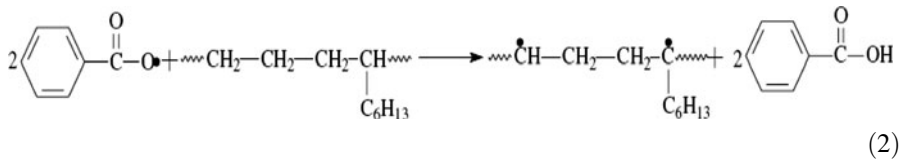
Conditions	Description
AN/(MMA + AN) ratio (wt%)	0, 5, 10, 15, 20, 25, 30, 35
POE/(POE + MMA + AN) ratio (wt%)	45, 50, 55, 60, 65, 70
Initiator dosage (wt%) ^a	0.4, 0.6, 0.8, 1.0, 1.2, 1.4
Aqueous phase/oil phase (w/w) ^b	1.5
Toluene dosage (wt%) ^c	44.4
PVA dosage (wt%) ^c	0.4
SDS dosage (wt%) ^c	0.07
Reaction time (h)	0.5, 1, 2, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5
Reaction temperature (°C)	80

^a The initiator dosage was based on monomers and POE

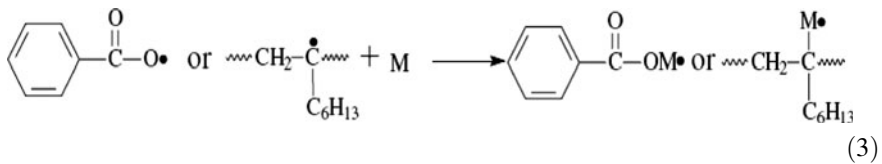
^b Aqueous phase referred to distilled water, oil phase referred to monomers, POE and toluene

^c The toluene, PVA, and SDS dosage were based on oil phase

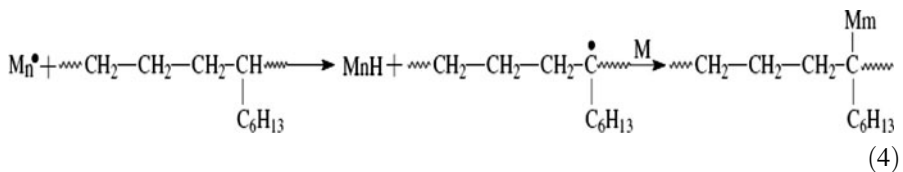
(b) Radical transfer reactions involving the primary radical and POE used



(c) Addition of monomers to primary radical or the POE macroradical



(d) Chain transfer to POE chain



The obtained product was precipitated by excess ethanol under stirring. The precipitate was collected by filtration and then dried to constant weight, and the product was extracted to separate MMA-*co*-AN by using acetone for 48 h in a Soxhlet extractor. The extracted POE-*g*-MAN was dried to constant weight at 80 °C in the vacuum oven. The monomer conversion ratio (CR), grafting ratio (GR), and grafting efficiency (GE) of the copolymerization were estimated using the following equations:

$$\text{CR} = \frac{\text{weight of monomer reacted}}{\text{weight of monomer charged}} \times 100\% = \frac{m_2 - m_2w}{m_1} \times 100\% \quad (5)$$

$$\text{GR} = \frac{\text{weight of monomer grafted onto POE}}{\text{weight of POE}} \times 100\% = \frac{m_3 - m_2w}{m_2w} \times 100\% \quad (6)$$

$$\text{GE} = \frac{\text{weight of monomer grafted onto POE}}{\text{weight of monomer reacted}} \times 100\% = \frac{m_3 - m_2w}{m_2 - m_2w} \times 100\% \quad (7)$$

$$w = \frac{D}{S}$$

where m_1 is the weight of charged monomers, m_2 is the weight of dry sample, m_3 is the weight of extracted dry sample, w is the weight percentage of POE in the obtained product, D is the weight of charged POE, S is the weight of obtained product.

Fourier transform infrared (FTIR) measurements

FTIR spectra were recorded on an FTIR-8300 spectrometer (Shimadzu Corporation, Japan) using compression-molded thin film samples.

DSC analysis

DSC measurements were performed on a DSC instrument (DSC 204, NETZCH, Germany) under N₂ atmosphere. All samples were heated from 30 to 160 °C at a rate of 10 °C/min and maintained 160 °C for 3 min to erase their thermal history. Then, the samples were cooled down to −110 °C at a rate of 20 °C/min, and heated to 150 °C at a rate of 10 °C/min.

Preparing of POE-*g*-MAN/SAN blends

A mixture of POE-*g*-MAN and SAN resin was dried in an oven at 80 °C for at least 12 h. AOMS with different POE contents were prepared by melt blending POE-*g*-MAN and SAN resin with a laboratory two-roll mill at 165 °C for 10 min, followed by compression molding at 170 °C. Test specimens were cut from 0.4-cm-thick plaques for mechanical properties testing. POE content refers to the weight percentage of POE in AOMS.

Mechanical properties

The notched Izod impact strengths were measured by a pendulum impact tester (XJU2.75, Philips, Netherlands) at 25 °C according to GB1843-96. The tensile and flexural properties were measured by a tension tester (AG-1, Shimadzu, Japan) at 25 °C according to GB1040-92 and GB1042-79, respectively.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) measurements were performed on a DMA instrument (DMA 242C, Netzsch, Germany), temperature range: −110 to 160 °C, at a rate of 10 °C/min.

Morphological observation

Ultrathin sections of compression-molded specimens were prepared with an ultramicrotome (LKB Ultratome V, Bromma, Sweden) at −130 °C to achieve a smooth, undeformed surface. Observations of phase structure were carried out with a TEM (JEOL-1230, JEOL, Japan) at an accelerating voltage of 80 kV. Ultrathin sections were stained with RuO₄ for the electron micrograph yielding excellent contrast and definition.

The fractured surfaces of notched impact tests were sputtered with a thin gold layer before viewing with a SEM (XL30E, Philips, Netherlands).

Results and discussion

FTIR spectroscopy

The FTIR spectra of the POE, unextracted POE-*g*-MAN, and extracted POE-*g*-MAN were illustrated in Fig. 1. The characteristic absorption band of MMA appeared at $1,729\text{ cm}^{-1}$ for the carboxylic stretching vibration, and the characteristic absorption band of AN appeared at $2,238\text{ cm}^{-1}$ for the $\text{C}\equiv\text{N}$ stretching vibration in the spectrum of unextracted POE-*g*-MAN and extracted POE-*g*-MAN; they were absent in the spectrum of POE. These results provided substantial evidence of grafting of MMA and AN onto POE chains.

DSC analysis

DSC was used to understand the effects of weight ratios of monomers and GR on the thermal properties of POE-*g*-MAN copolymer. The DSC heating thermograms of POE-*g*-SAN with different GR and AN/(MMA + AN) ratios were shown in Figs. 2 and 3, respectively. Figure 2 showed that there are a glass transition and a melt peak in the DSC heating thermograms of pure POE ranging from -75 to $150\text{ }^{\circ}\text{C}$. However, there were two glass transition and a melt peak in the DSC heating thermograms of POE-*g*-MAN in the same temperature range. It can be considered that the new glass transition of POE-*g*-MAN was due to the segment movement of the graft MAN chains, and the graft MAN chain can be considered to be a long chain. The melting temperatures (T_m) and the heat of fusion (ΔH_f) of POE-*g*-MAN were lower than that of pure POE. Table 2 showed the effect of GR on the value of T_m , ΔH_f , and T_g . It was apparent that T_m and ΔH_f decreased with an increasing of GR, which was due to the grating MAN chains that disrupted the

Fig. 1 FTIR spectra: (a) POE; (b) unextracted POE-*g*-MAN; (c) extracted POE-*g*-MAN

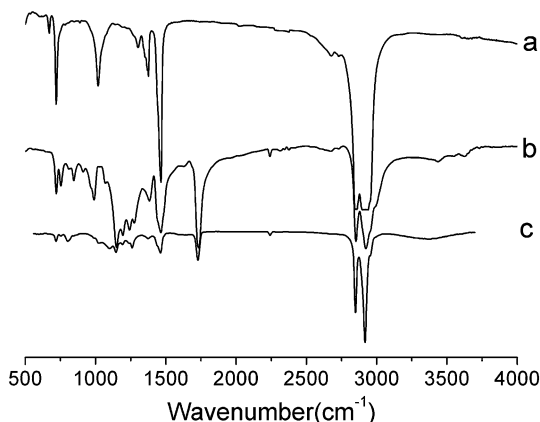


Fig. 2 DSC heating thermograms of POE and POE-g-MAN with different GR: (a) POE; (b) POE-g-MAN with GR of 17.0; (c) POE-g-MAN with GR of 23.7; (d) POE-g-MAN with GR of 30.8

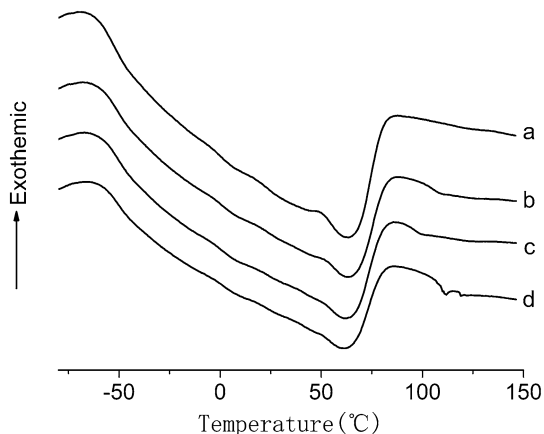
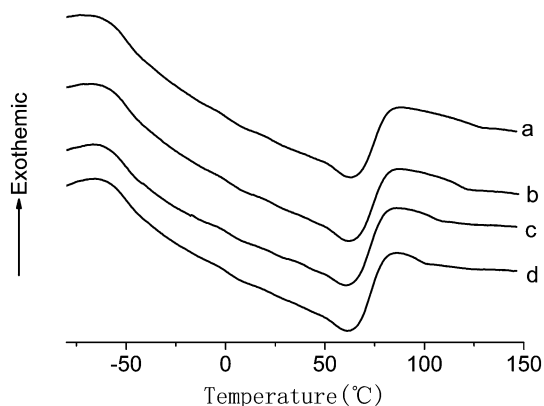


Fig. 3 DSC heating thermograms of POE-g-MAN copolymer with different AN/(MMA + AN) ratio, (a) POE-g-MAN AN/(MMA + AN) = 0; (b) POE-g-MAN AN/(MMA + AN) = 5; (c) POE-g-MAN AN/(MMA + AN) = 15; (d) POE-g-MAN AN/(MMA + AN) = 25



regularity of the chain structures in POE and increased the spacing between the chains [8]. The T_g of POE phase increased with increasing of GR. It was probably caused by the increase in difficulty in polymer chain arrangements as the grafted branch chains prohibited the movements of the polymer segments.

Figure 3 showed T_g of graft MAN chains of POE-g-MAN with different weight ratio of AN/(MMA + An). It was determined that the T_g with increasing An loading was 112.1, 105.0, 95.7, and 90.7 °C.

Table 2 The T_m , ΔH_f , and T_g of POE and POE-g-MAN with different GR

Sample	Grafting ratio (%)	T_g of POE phase (°C)	T_m (°C)	ΔH_f (J/g)
a	0	-60.5	63.2	8.7
b	17.0	-58.3	63.0	8.2
c	23.7	-57.8	62.5	8.0
d	30.8	-55.9	61.1	5.4

Effects of reaction conditions on the copolymerization and impact properties

Effect of AN/(MMA + AN) mass ratio

Figure 4 showed effect of AN/(MMA + AN) mass ratio on the graft copolymerization behavior of POE-*g*-MAN and the notched Izod impact strength of AOMS. The polymerization was performed with the initiator concentration of 1.0 wt%, the dispersant concentration of 0.4 wt%, POE/(POE + MMA – AN) mass ratio of 60 wt%, and at 80 °C for 20 h. With the increasing AN/(MMA + AN) ratio, CR changed little from 0 to 25 wt%, but decreased with the AN content more than 25 wt%. GR and GE decreased gradually with the increasing loading of AN. Figure 4 also demonstrated the effect of AN/(MMA + AN) weight ratio of POE-*g*-MAN on the notched Izod impact strength of AOMS, which contained 25 wt% POE. POE is a type of non-polar polymer, while SAN resin is a typical polar polymer. Homogenous dispersion of the non-polar POE in polar SAN would not be easy. By modifying POE through grafting polar MAN branches, POE-*g*-MAN can be dispersed well in the SAN matrix. The notched Izod impact strength of AOMS increased with the increasing of AN percentage, up to 54.0 kJ/m² at 15 wt%. However, with further increasing of AN percentage, notched Izod impact strength of AOMS decreased. This can be explained by the fact that the polarity of the grafted MAN branches increased with the increasing weight ratio of AN/(MMA + AN). Since polarity of AN is higher than that of MMA [7], when the percentage of AN increased, the polarity of grafted MAN branches was enhanced. When the polarity of the grafted MAN branches matched with the polarity of SAN, POE-*g*-MAN can be dispersed well in the SAN matrix, and can effectively improve the impact resistance of SAN resin. However, too weak or too high polarity of the grafted chain would induce poor compatibility and low toughness. To obtain the highest toughening effect, the most suitable AN/(MMA + AN) mass ratio was 15 wt%.

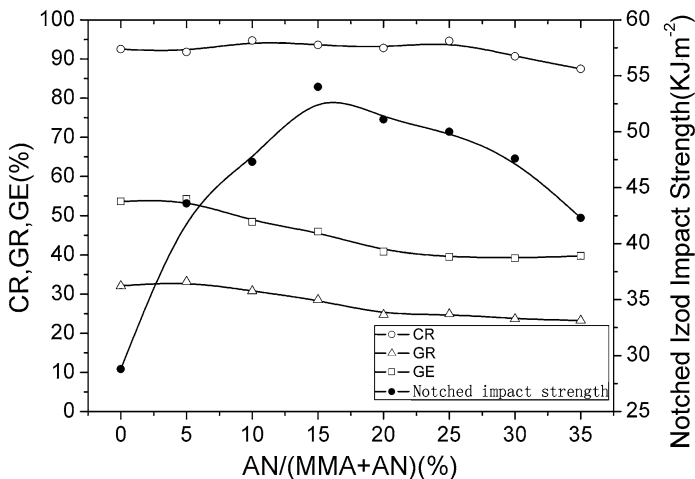


Fig. 4 Effect of AN/(MMA + AN) mass ratio on graft copolymerization behavior and the notched Izod impact strength of AOMS

Effect of POE/(POE + MMA – AN) mass ratio

Figure 5 showed effect of POE/(POE + MMA – AN) mass ratio on the graft copolymerization behavior of POE-*g*-MAN and the notched Izod impact strength of AOMS. The polymerization was performed with the initiator concentration of 0.6 wt%, 15 wt% of AN/(MMA + AN) mass ratio, and at 80 °C for 20 h. CR and GR changed slightly with an increasing loading of POE. It was reasonable to observe that GE increased monotonously with increasing of POE ratio. The result can be explained by the fact that more graft sites were supplied owing to increasing of POE content [9]. As a result, GE increased. From Fig. 5, with increasing POE/(POE + MMA – AN) ratio, the notched Izod impact strength of the blends increased, and reached maximum at 60 wt% then decreased significantly. To obtain the highest toughening effect, the most suitable POE/(POE + MMA – AN) mass ratio was 60 wt%.

Effect of BPO content

Figure 6 demonstrated the effect of initiator (BPO) concentration ranging from 0.4 to 1.4 wt% on the graft copolymerization and the notched Izod impact strength of AOMS. The reaction was performed with the initiator concentration of 0.6, 15 wt% of AN/(MMA + AN) mass ratio, 60 wt% of POE/(POE + MMA – AN) mass ratio, and at 80 °C for 20 h. It was reasonable to observe that CR increased gradually with increasing BPO contents. GR and GE increased with the increasing initiator concentration, up to 28.55 and 45.91 %, respectively, at 1.0 wt%, and then changed slightly. With increasing BPO contents, the free radical concentration in reaction system increased, and the reaction rate accelerated, so that CR increased. The increasing phenomena of GR and GE can be explained by the fact that the

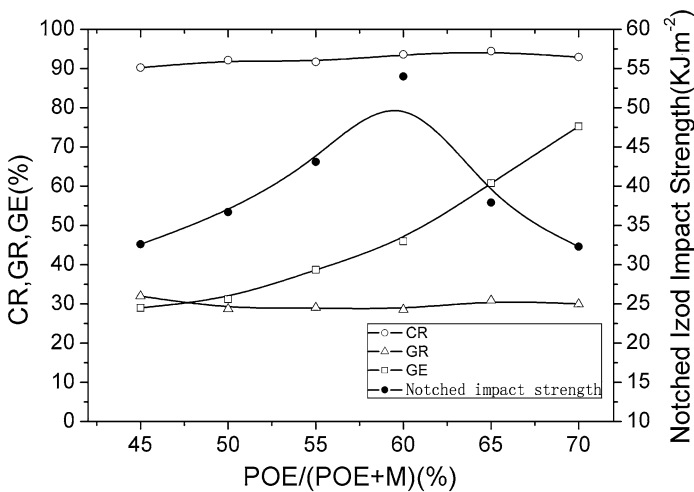


Fig. 5 Effect of POE/(POE + MMA – AN) mass ratio on graft copolymerization behavior and the notched Izod impact strength of AOMS

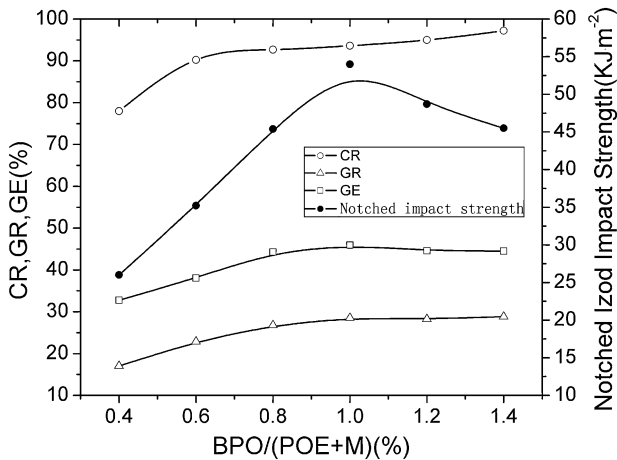


Fig. 6 Effect of BPO content on the graft copolymerization behavior and the notched Izod impact strength of AOMS

amount of monomer radicals, propagating chain radicals and POE macro-radicals increased with an increasing of initiator concentration. The more the amount of the free radicals, the more the monomers grafted onto the POE. As a result, GR and GE increased. However, with a further increasing of BPO content, GR and GE changed slightly. The reasons were followed: although the free radical concentration increased, the numbers of the graft site supplied by the main chain of POE were constant for the constant concentration of POE, so that GR and GE kept almost constant. From Fig. 6, the notched Izod impact strength of SAN/POE-*g*-MAN blends increased with the increasing of BPO dosage, up to 54.0 kJ/m² at 1.0 wt%. However, with further increasing of BPO content, the notched Izod impact strength of AOMS decreased. The reasons were as follows: when the content of BPO was low, the GR of the POE-*g*-MAN was low, which thus had poor compatibility with SAN resin, and the toughening effect was poor. However, when BPO dosage exceeded 1.0 wt%, GR of the POE-*g*-MAN was high but an excess of BPO dosage resulted in slight crosslinking of POE. For elastomer-toughened plastics blends, the crosslinking of the elastomer can increase the strength of rubber particles, which resulted in difficult dispersion in the plastics matrix and a decrease in toughening effect [10]. In order to obtain the highest toughening effect, the most suitable BPO dosage was 1.0 wt%.

Effect of reaction time

Figure 7 showed the effect of reaction time on the graft copolymerization behavior and the notched Izod impact strength of AOMS. CR increased dramatically with increasing of reaction time up to 8 h and then increased slightly. GR increased up to 8 h and then levels off. This result comes from the decreasing concentrations of monomer and initiator with an increase in reaction time. GE increased quickly in the first 1 h, and then decreased with increasing of reaction time up to 5 h. Values of

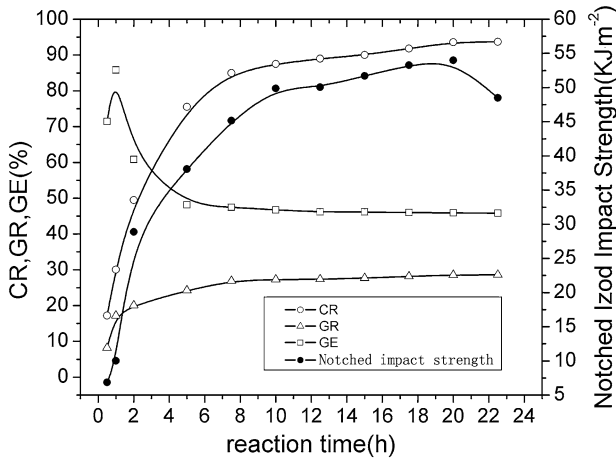
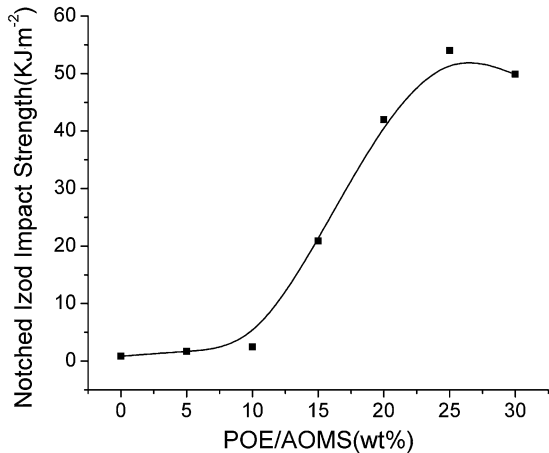


Fig. 7 Effect of reaction time on the graft copolymerization behavior and the notched Izod impact strength of AOMS

Fig. 8 Effect of POE content on notched Izod impact strength of AOMS



GE were higher than 60.0 % with the reaction time from 0.5 to 2 h, which showed that in this period the grafting copolymer was formed rapidly than the copolymer of MMA and An. This can be explained by the fact that at early reaction stage, monomer molecules and radicals were easy to diffuse to POE chains. Whereas, with increasing reaction time up to 2 h, the distribution of branch chains on the chain of POE became saturated. Moreover, the viscosity of the reaction medium increased, the diffusion of monomer molecules into POE chains became difficult, and the monomer tended to copolymerization, so GE decreased. From Fig. 7, with increasing reaction time, the notched Izod impact strength of AOMS increased, and reached the maximum at 20 h then decreased. The reasons were followed: the further increase of reaction time resulted in the excess crosslinking of POE, when reaction time exceeded 20 h, which decreased toughening effect of POE-*g*-MAN on

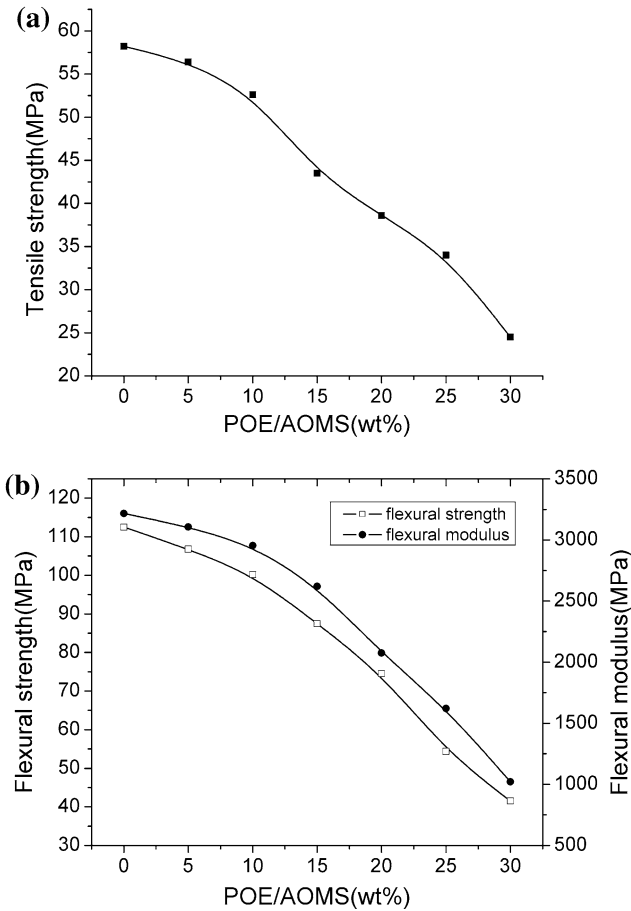


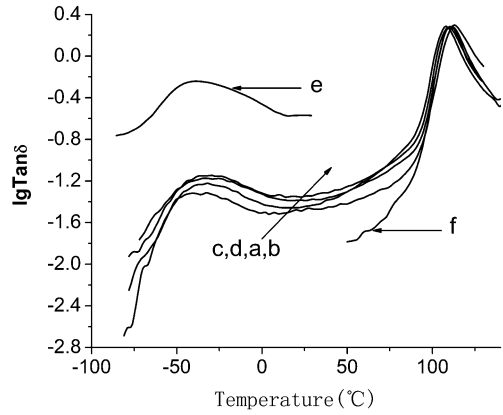
Fig. 9 Effect of POE content on **a** tensile and **b** flexural properties of AOMS

SAN resin significantly. In rubber-toughened plastics blends, increasing the degree of crosslinking of rubber can increase the strength of rubber particle, which can prevent cracking of rubber particle in impact deformation from decreasing impact strength of blends. But rubber particle became too big and rigid owing to excess crosslinking, which resulted in difficult disperse in plastics matrix and decreasing in toughening effect [10]. Therefore, in order to obtain the highest toughening effect, reaction time of 20 h was the most suitable for the graft copolymerization.

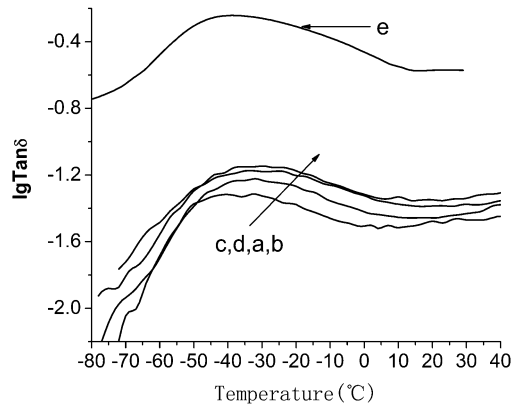
Effect of POE content on tensile and flexural properties of AOMS

Figure 8 showed the effect of POE content on the notched Izod impact strength of AOMS. The notched Izod impact strength of AOMS increased slightly with the increasing of POE contents from 0 to 10 wt%. When the POE content was more

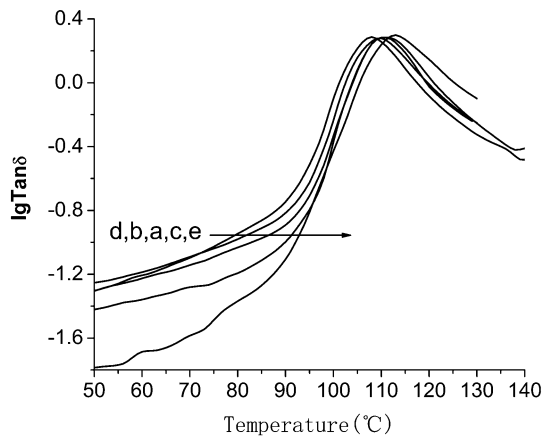
Fig. 10 DMA curves of AOMS: $f_{AN}/wt\%$. (a) 5 wt%; (b) 15 wt%; (c) 25 wt%; (d) 35 wt%; (e) POE; (f) SAN resin



(a) whole curve



(b) tanδ of POE phase



(c) tanδ of SAN phase

Table 3 T_g values of AOMS with different f_{AN}

Sample	f_{AN} (wt%)	T_{g1} (POE phase) (°C)	T_{g2} (SAN phase) (°C)	ΔT_g (temperature difference between T_{g1} and T_{g2}) (°C)	AOMS notched Izod impact strength (kJ/m ²)
POE	–	–38.9	–	151.8	–
SAN	–	–	112.9		0.87
<i>a</i>	5	–33.8	110.8	144.6	43.6
<i>b</i>	15	–29.8	110.6	140.4	54.0
<i>c</i>	25	–32.4	110.6	143.0	47.9
<i>d</i>	35	–32.8	109.9	142.7	42.7

than 10 wt%, the notched Izod impact strength increased dramatically with increasing POE content, up to a maximum at 25 wt%. When the POE content of the blends was between 10 and 15 wt%, a sharp brittle-to-tough transition was observed upon variation of POE content. However, the notched Izod impact strength of the blends decreased slightly with the increasing of POE contents from 25 to 30 wt%.

Figure 9 showed the effect of POE content on the tensile and flexural properties of AOMS. The tensile strength, flexural strength, and modulus decreased linearly with increasing POE content. It showed clearly that the flexibility of AOMS was enhanced and the rigidity was weakened with increasing POE content.

Dynamic mechanical analysis

Figure 10 showed DMA curves of SAN resin, POE, and AOMS that contained 25 wt% POE prepared by POE-*g*-MAN with different f_{AN} , which present two major peaks; the lower temperature peak corresponded to T_g of the POE phase and the higher corresponded to T_g of the SAN phase. As shown in Fig. 10 and Table 3, temperature difference between T_g of POE phase and T_g of SAN phase were smaller than that between POE and SAN resin after graft copolymerization of MMA and AN onto POE, indicating that the compatibility of the POE phase and SAN phase improved. DMA also showed that when AN percentage was 15 wt%, the temperature difference between T_g of POE phase and T_g of SAN phase was the smallest, which illuminated the best compatibility and interfacial adhesion force of POE-*g*-MAN and SAN.

Phase structure of AOMS

TEM micrographs of AOMS containing 5, 15, and 25 wt% POE, respectively, were shown in Fig. 11, where the phase of POE appeared white and the phase of SAN resin matrix appeared dark and gray. All images showed the phase structure of AOMS is “sea-island” structure, where POE was dispersed phase and SAN resin was continuous phase. The vague interface indicated interfacial penetration between POE-*g*-MMA-AN particles and SAN resin matrix because grafting of MAN

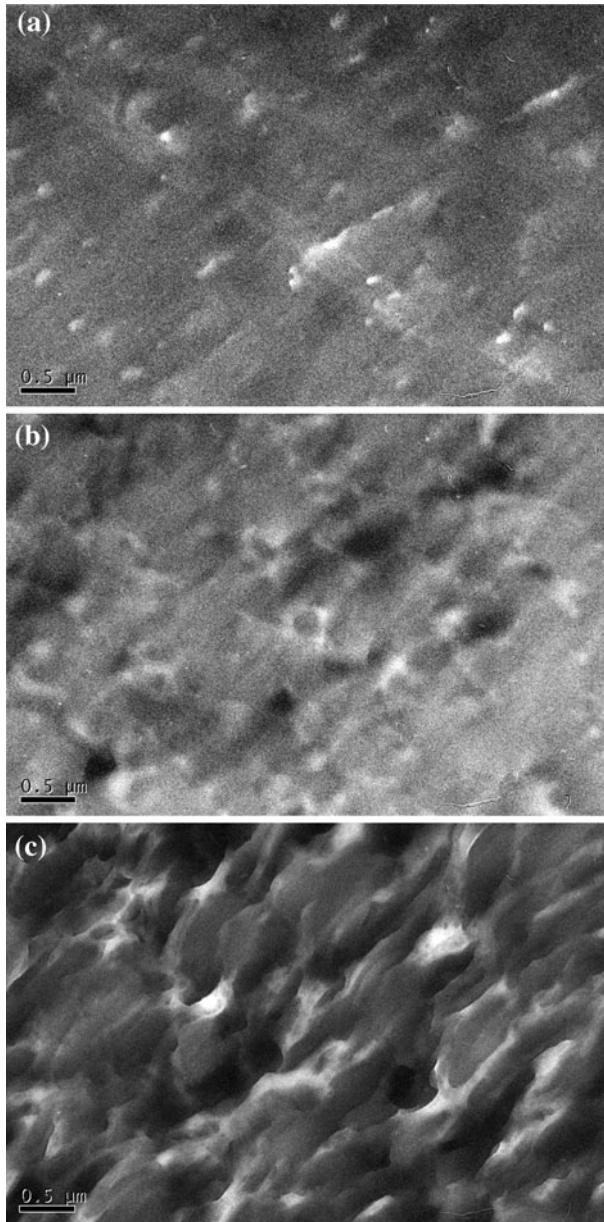


Fig. 11 TEM micrograph of AOMS. POE content is **a** 5 wt%, **b** 15 wt%, and **c** 25 wt% in AOMS

molecular chains onto POE improved the miscibility between the two phases. From Fig. 11a–c, when POE content was 5, 15, and 25 % in AOMS, the average particle diameter of dispersed phase was about 0.1, 0.15, and 0.25 μm , respectively, and the average surface to surface interparticle distance was about 0.6, 0.4, and 0.2 μm , respectively. This result showed the particle diameter increased and the surface to

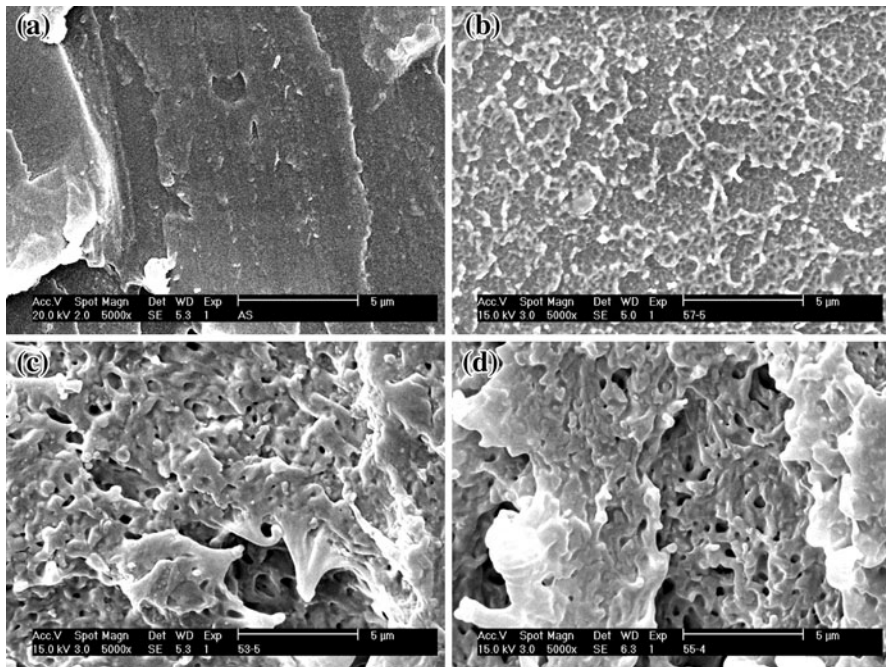


Fig. 12 SEM micrograph of the fracture surface of **a** SAN resin; **b** AOMS containing 5 wt% POE; **c** AOMS containing 15 wt% POE; **d** AOMS containing 25 wt% POE

surface interparticle distance shortened with increasing POE content. When the specimens were applied by impact force, the stress field in the matrix around the particles of dispersed phase will interact considerably, which resulted in the efficiency of inducing the crazing and shear yielding increased obviously [11], so the notched Izod impact strength of AOMS increased gradually.

Toughening mechanism

Figure 12 showed SEM micrographs of the fracture surface of SAN resin and AOMS containing 5, 15, and 25 wt% POE, respectively. In Fig. 12a, the SAN resin fracture surface had a flaky appearance, by crack break-up, which was a typical brittle fracture characteristic, so the impact energy dissipation was small. For AOMS containing 5 wt% POE, in Fig. 12b, the surface was composed of many more fragments than that of SAN resin. The toughening mechanism of the blends was branching and termination of crack. When the POE content of AOMS was 15%, in Fig. 12c, the fracture surface showed a lot of cavitations and features of slight plastic flow, which indicated the occurrence of shear yielding of the SAN resin matrix. The shear yielding can absorb much impact energy, so the notched Izod impact strength of the specimens was high. As shown in Fig. 12d, the surface of AOMS containing 25 wt% POE showed a plastic flow which looked like fibril

morphology and fewer cavitations than that of AOMS containing 15 wt% POE, which illustrated the extent of shear yielding increased, so the notched Izod impact strength of specimens was much higher, i.e., 54.0 kJ/m². Therefore, when the POE content was low, the toughening mechanism of the blends was branching and termination of crack, then changed into cavitations and slight shear yielding, and finally changed into severe shear yielding accompanied by cavitations with POE increasing.

Conclusions

POE-*g*-MAN was synthesized by suspension graft copolymerization of MMA and AN onto POE, and various AOMS were prepared by melt blending POE-*g*-MAN and SAN resin. The effects of reaction conditions on the graft copolymerization and the toughening effect of POE-*g*-MAN on SAN resin were discussed. The results showed that the optimized reaction conditions were AN/MMA – AN ratio of 15 wt%, POE/(POE + MMA – AN) ratio of 60 wt%, BPO/(POE + MMA – AN) ratio of 1 wt%, toluene dosage of 44.4 wt%, PVA dosage of 0.4 wt%, SDS dosage of 0.07 wt%, Aqueous phase/oil phase mass ratio of 1.5, at 80 °C for 20 h, and when the POE/AOMS mass ratio was 25 wt% under the optimized reaction conditions, the notched Izod impact strength of AOMS reached 54.0 kJ/m². According to FT/IR, it was confirmed that St and An is essentially grafted onto POE. From the result of DSC, it was found that the values of T_m and ΔH_f decreased as the graft ratio increasing, and T_g of POE chain increased with an increasing GR. TEM analysis showed that the highest toughness occurred when the average particle diameter of dispersed phase was about 0.25 μm . SEM analysis indicated that the AOMS fracture surface had a plastic flow which looked like fibril morphology when POE content was 25 wt% with the AN/(MMA + AN) ratio (f_{AN}) of POE-*g*-MAN of 15 wt%. The toughening mechanism of AOMS was shear yielding of the matrix, which endowed AOMS with remarkable toughness. DMA showed that the compatibility of POE phase and SAN phase improved after graft copolymerization of MMA and AN onto POE. When the grafting chain polarity was similar to that of SAN, the miscibility between POE-*g*-MAN and SAN resin was best. Therefore, POE-*g*-MAN can be used for toughen agent of SAN resin.

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