

Preparation and Characterization of Ethylene–Propylene Copolymer Grafted with Acrylamido Tertiary Butyl Sulfonic Acid

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ABSTRACT: Grafting of acrylamido tertiary butyl sulfonic acid (ATBS) onto ethylene–polypropylene copolymer (EPM) was carried out by using a reactive processing method. The grafting copolymer was characterized by means of WAXD, FT-IR, ESCA, and DSC. Improved thermal stability was observed for graft copolymer. Effects of the monomer and the initiator concentrations, reactive temperature, and time on grafting degree were investigated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1299–1302, 1997

INTRODUCTION

Grafting copolymers have been widely used as compatibilizers of immiscible polymer blends as well as for interfacial adhesion in polymeric composites.^{1,2} In comparison with traditional copolymerization processes, the melt grafting process offers not only flexibility in tailoring polymer properties for specific application, but also reduction in equipment.³ Therefore, reactive processing has received increasing attention of polymer scientists and engineers.^{4–10} For example, the grafting reaction of maleic anhydride onto polyethylene⁷ and PP⁸ has been reported. Up to now, the grafting reaction of ATBS onto EPM by means of a melt process has not been found in literature. As is well known, the sulfonic acid can react with some chemical groups of polymers, such as hydroxyl groups of polyesters, etc. Therefore, EPM-*g*-ATBS copolymer perhaps can be used as an effective compatibilizer of polyolefins/polyesters blends and so on.

In the present paper, the melt grafting reaction

of ATBS onto EPM has been investigated. The grafting degree has been determined by means of element analysis. FT-IR, WAXD, DSC, and ESCA have been also applied to characterize the structure of the grafting copolymers.

EXPERIMENTAL

Materials and Preparations

EPM used in this work was brought from PanJin Petrochemicals Corp. Ltd (China). The C₂ content is about 10%, and its melt index is 1.0 g/10 min (230°C and 2.16 kg load). ATBS and dicumyl peroxide (DCP) were commercial reagents, analytically pure.

A Brabender-like apparatus was used to prepare EPM-*g*-ATBS copolymers. Composition of blending mixtures was EPM, 50 g; ATBS, 0–5 wt % of EPM; DCP, 0–1.0 wt % of EPM. The temperature of the mixing chamber was 185–225°C.

Characterization of EPM-*g*-ATBS

Before testing, all samples were molded into very thin films (<50 μm), and then extracted with eth-

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Table I Effects of Concentration of ATBS and DCP on Grafting Degree of ATBS, Melt Flow Index (MFI), and the Critical Surface Tension (γ_c) of EPM-*g*-ATBS Specimens^a

ATBS concentration (wt %)	DCP concentration (wt %)	Grafting degree of ATBS (wt %)	MFI (g/10 min)	γ_c (dyn/cm)
5	0.05	0.26	1.8	29.8
5	0.1	0.34	2.4	27.3
5	0.5	0.78	6.0	24.5
5	1.0	0.89	11.4	22.7
5	0.25	0.57	3.8	25.9
3.5	0.25	0.42	3.6	26.1
2.5	0.25	0.31	3.9	27.0
1.0	0.25	0.19	3.8	30.1
0.5	0.25	0.09	3.8	31.2

^a Tests were carried out at 200°C for 10 min.

anol for 48 h to remove ATBS homopolymer and unreacted ATBS monomer. Finally, the extracted films were kept in a vacuum oven at 80°C to constant weight.

The IR and ESCA spectra of EPM and EPM-*g*-ATBS were recorded with an FTS-7 Fourier-transform infrared spectrometer and an ESCA-LAB-MK2 electron energy spectrometer, respectively.

DSC tests for EPM and EPM-*g*-ATBS specimens were conducted using a Perkin-Elmer 7 calorimeter. Their thermograms were obtained at a constant heating rate of 10°C/min in the temperature range of 25–200°C under a nitrogen atmosphere.

WAXD spectra for both specimens were obtained on an HP1700 X-ray diffractometer with Cu target, $K\alpha$, and Ni-filtered radiation.

The contact angle (θ) of a water drop on EPM

and EPM-*g*-ATBS were measured at 20°C by using a home-made apparatus.

RESULTS AND DISCUSSION

Effects of concentrations of ATBS and DCP on the grafting degree of ATBS are shown in Table I. Here the grafting degree was defined as the content of ATBS in EPM-*g*-ATBS copolymers (wt %). When the reaction processing temperature was fixed at 200°C and the concentration of ATBS was fixed at 5 wt %, the grafting degree of ATBS increased with enhancement of the concentration of DCP. Furthermore, the graft degree of ATBS is proportional to the amount of the addition of ATBS as the same concentration of the initiator (0.25 wt %) is used. As is shown in Table I, the higher the DCP concentration is, the higher the

Table II Effects of the Reaction Time, Temperature, and Half-Life Time of DCP on Grafting Degree of ATBS and MFI of EPM-*g*-ATBS^a

Temperature (°C)	Time (min)	Half-life time of DCP (s)	Grafting degree (wt %)	MFI (g/10 min)
185	10	40	0.23	3.2
195	10	20	0.54	3.6
200	10	15	0.76	3.9
210	10	8	0.69	3.8
225	10	1.5	0.47	4.1
200	5	15	0.28	3.8
200	15	15	0.84	3.9
200	20	15	0.79	4.0

^a 5 wt % ATBS and 0.25 wt % DCP were used in all tests.

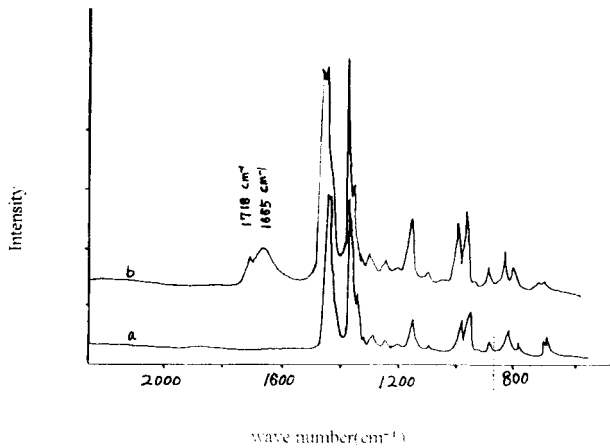


Figure 1 The FTIR spectra of EPM (a) and EPM-*g*-ATBS (b).

melting index of EPM-*g*-ATBS. This feature indicates that the degradation of EPM increases with the concentration of DCP.

The contact angles (θ) of graft copolymer films were measured for different solvents of variable surface tensions. From the results obtained, the critical surface tension (γ_c) values of grafted specimens were calculated by extrapolating the surface tension against $\cos\theta$ plot to $\cos\theta = 1$. The critical surface tensions (γ_c) of the EPM and EPM-*g*-ATBS specimens are listed in Table I. The results suggest that the surface polarity of graft copolymers is augmented by an increase of the content of ATBS in EPM-*g*-ATBS specimens.

The effect of reaction temperature on the grafting degree of ATBS is listed in Table II. The grafting degree increases with increasing the reaction temperature. Its maximum (0.76 wt %) appears at 200°C. Beyond this temperature, the grafting degree decreases. This feature can be tentatively explained as the influence of the half-life time of the used initiator, DCP. As is shown in Table II,

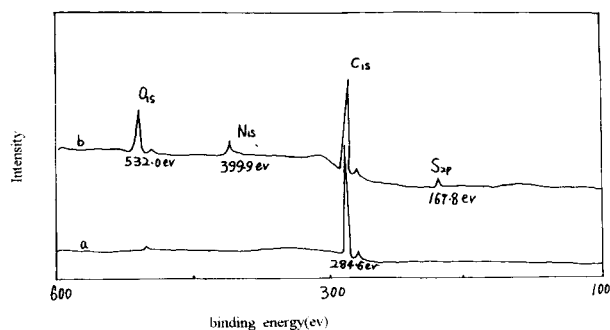


Figure 2 The ESCA spectra of EPM (a) and EPM-*g*-ATBS (b).

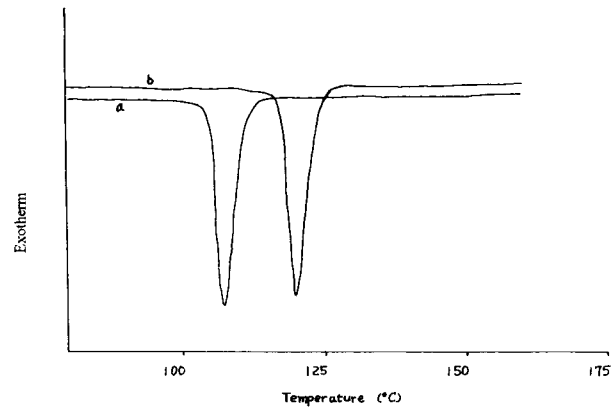


Figure 3 The DSC cooling curves of EPM (a) and EPM-*g*-ATBS (b).

when the temperature is over 200°C, the half-life time of DCP is too short to satisfy the grafting reaction of ATBS. It was also observed that the grafting degree of ATBS increased initially with reaction time and then remained nearly constant when the reaction temperature was kept at 200°C. This could be also explained as the influence of the half-life time of DCP. As is shown in Table II, it is 15 s at 200°C. After several minutes, most of the initiator would be used up.

The FTIR spectra of EPM and EPM-*g*-ATBS are shown in Figure 1. The appearance of two peaks at 1718 cm^{-1} and 1665 cm^{-1} for the grafting sample indicated that amido groups were incorporated into the molecular chains of EPM.

As is shown in Figure 2, O_{1s} , N_{1s} , and S_{2p} peaks appeared for the EPM-*g*-ATBS sample with binding energies of 532.0, 399.9, and 167.8 eV, respectively. This result verified again that the monomer, ATBS, was grafted onto EPM molecular chains.

Thermograms of EPM and EPM-*g*-ATBS are given in Figure 3. It was found that the crystallization temperature (T_c) of EPM is 11°C lower than that of EPM-*g*-ATBS. This feature could be attributed to the nucleating function of ATBS grafted on EPM molecular chains. It reduced the supercooling and enhanced the nucleating rate and crystal growth rate of EPM. The experimental data will be reported later.

The WAXD spectra of EPM and EPM-*g*-ATBS are shown in Figure 4. As indicated by the patterns, grafted ATBS leads to some change of the crystallization structure of EPM. The peak at $2\theta = 15.9^\circ$, which corresponds to the 300 diffraction plane of the form (hexagonal), disappeared after ATBS was grafted onto EPM molecular chains. It

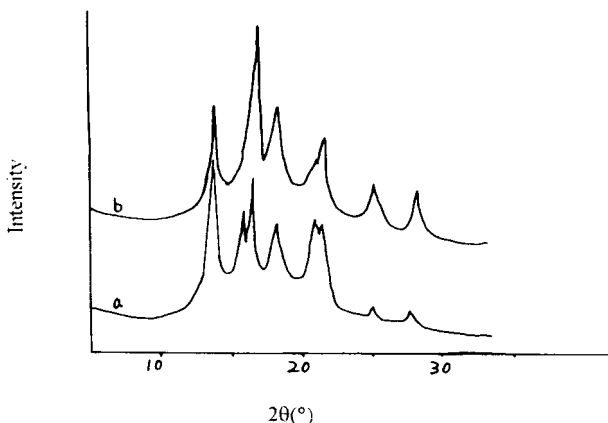


Figure 4 The WAXD spectra of EPM (a) and EPM-g-ATBS (b).

suggests that the mixture of α and β forms of EPM were replaced by the pure α form crystal. The proportion of these two crystal forms usually depends on the preparative process and nucleating mechanism. In this work, the same heat history and crystallization process were adopted for EPM and EPM-g-ATBS. Therefore, it can be concluded that the change of the crystallization structure of EPM-g-ATBS probably originated from a different nucleating mechanism.

CONCLUSION

IR and ESCA spectra verified that ATBS had been grafted onto EPM molecular chains by using the reactive processing method. It was found that the grafted ATBS could act as a nucleating agent for

EPM crystallization and change the crystal form of EPM from the mixture of α and β into the unique α form crystal. There was an obvious effect of the concentration of the initiator on both grafting degree of ATBS and the melt index of EPM-g-ATBS. The concentration of the ATBS monomer also largely influenced the grafting degree of ATBS. Effects of the reaction time and temperature on the grafting degree of ATBS were also discussed. Reasonable explanations could be obtained by considering the relationship of the half-life time of the initiator and the temperature.

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