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Publisher *Taylor & Francis*

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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Yin, Zhihui , Zhang, Yajie , Xiaomin, Zhang and Yin, Jinghua(1997) 'Preparation and Characterization of Melt Grafted Acrylamide Tertiary Butyl Sulfonic Acid onto Polypropylene', International Journal of Polymeric Materials, 36: 1, 1 – 9

To link to this Article: DOI: 10.1080/00914039708044131

URL: <http://dx.doi.org/10.1080/00914039708044131>

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Preparation and Characterization of Melt Grafted Acrylamide Tertiary Butyl Sulfonic Acid onto Polypropylene

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(Received 27 April 1996)

Grafting of acrylamide tertiary butyl sulfonic acid (ATBS) onto polypropylene (precisely, ethylene/propylene random copolymer containing 8% ethylene content) was carried out by melt extruding with addition of dicumyl peroxide (DCP) as an initiator. The structure of graft copolymer was characterized by using WAXS, FT-IR, ESCA and DSC. Improved thermal stability was observed for graft copolymer. The effect of monomer and initiator concentration, reactive temperature and screw speed on degree of grafting efficiency of grafting has been investigated.

Keywords: Acrylamide; butyl sulfonic acid; polypropylene melt grafting

INTRODUCTION

Grafting copolymers have been widely used for the compatibilization of immiscible polymer blend as well as the improvement of interfacial adhesion in polymeric composites [1~2]. In comparison with traditional copolymerization processes, the modification of existing polymer by reactive melt processing offers not only the flexibility in tailoring polymer properties for specific application but also reduction in equipment [3]. Consequently, reactive polymer processing has

received increasing attention polymer scientist and engineers [4~10]. For example, the grafting reaction of maleic anhydride onto molten polyethylene [7] and polypropylene [8] (PP) has been previously studied. However, the graft reaction of acrylamide tertiary butyl sulfonic acid (ATBS) onto PP by means of a melt process has not found to be reported. The sulfonic acid often interact strongly with other functional groups, which leads to miscibility enhancement.

In the present paper, the melt grafting reaction of ATBS onto PP has been investigated. The purpose is to use the functional PP as the effective toughening agent of polyamide and a *in-situ* compatibilizer of polyamide-polypropylene blend. The degree of grafting was determined by means of element analysis. FT-IR, WAXS, DSC and ECSA were also applied to characterize structure of graft copolymer.

EXPERIMENTAL

Materials

The polymers used in this work were a ethylene/propylene random copolymer containing 8% ethylene (PP1330) manufactured by YanShan Petrochemicals Corp. LTD. (China), and with melt index 1.5 g/10 min. Acrylamide tertiary butyl sulfonic acid (ATBS) and dicumyl peroxide (DCP) were reagent grade.

Preparation of PP-g-ATBS

A Brabender single screw extruder was used to prepare PP-g-ATBS. Composition of reaction mixture was 500 g of PP, 0 to 5 wt% of ATBS and 0 to 1.0 wt% of DCP. The screw speed was 30~80 rpm. Temperature of extruding process was 185~225°C. The graft copolymers were compression molded into thin films, and then extracted with alcohol for 48 hours to remove traces ATBS and homopolymer. Finally, films were dried under reduced pressure at 80°C to constant weight.

Characterization of PP-g-ATBS

The IR spectra of purified films were recorded onto a FTS-7 Fourier-transform infrared spectrometer.

The ESCA spectra of purified films were recorded onto an ESCALAB-MK2 electron energy spectrometer.

Differential scanning calorimetric studies were conducted using a Perkin-Elmer 7 thermal analyzer. The analysis was carried out at a constant heating rate of 10°C/min in the temperature range of 25–200°C under nitrogen atmosphere.

The WAXS spectra of purified films were performed on a HP1700 wide angle X-ray diffraction spectrometer with Cu K α , Ni-filtered radiation.

The content of ATBS in graft copolymer was determined by using element analysis instrument.

Contact angle(θ) of a water drop on PP and PP-g-ATBS samples were measured at 20°C by using a home-made apparatus.

Melt flow index were determined using an extrusion plastometer (JiLin University Scientific Instruments Inc., China) standardized according to ASTM D1238-79. The temperature was set at 230°C, and 2.16 kg load.

RESULTS AND DISCUSSION

Characterization of Graft Copolymer

FTIR spectroscopy is an well known method to identify functional groups and to make quantitative analysis. The FTIR spectra of PP and PP-g-ATBS are shown in Figure 1. The appearance of two peaks in the purified graft sample at 1718 and 1665 cm^{-1} indicates the addition of amido groups in PP molecular backbone. It was shown that ATBS monomer has been grafted onto PP molecular chains. Finer differences were observed in the 721 cm^{-1} band which is attributed to the rocking-mode vibration of long ethylene sequences-(CH_2) $_n$ -with n [11]. A lowering of the absorbance with increasing the degree of grafting. This feature suggests that ATBS monomer may be mainly grafted onto the ethylene sequences of the polymer molecular chains. Figure 2 is the ESCA spectra of PP and purified graft copolymer. In the graft sample, the O_{1s} , N_{1s} and S_{2p} peaks appeared at 532eV, 399.9eV and 167.8eV, respectively. The PP spectra has only C_{1s} peak at 284.6eV. This result verified that ATBS has been grafted onto PP molecular chains.

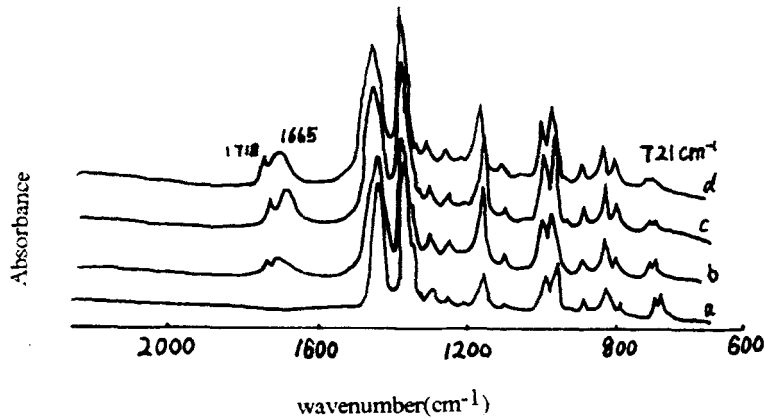


FIGURE 1 The FTIR spectra of PP (a) PP-g-ATBS (b, c, d); (b)-containing ATBS 0.26%; (c)-containing ATBS 0.42% (d)-containing ATBS 0.78%.

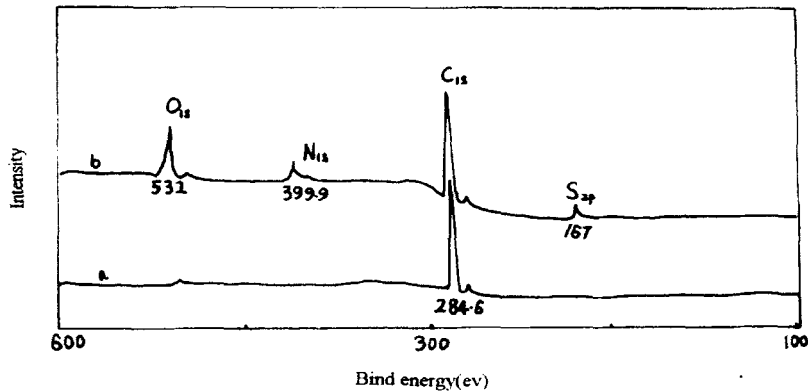


FIGURE 2 The ESCA spectra of PP(a) and PP-g-ATBS (b).

The DSC cooling curves of PP and graft copolymer are given in Figure 3. Plain PP sample shows a broad exotherm, its crystallization temperature of ethylene sequences is closed to that of propylene sequences, the two crystallization peaks overlapped. With the increase of the degree of grafting, the crystallization exothermic peak of ethylene sequences decreased gradually. This indicated that the grafted ATBS damaged the regularity of ethylene sequences. The crystallization temperature of propylene sequences increased with increasing degree of grafting. The observed increase in crystallization temperature can be

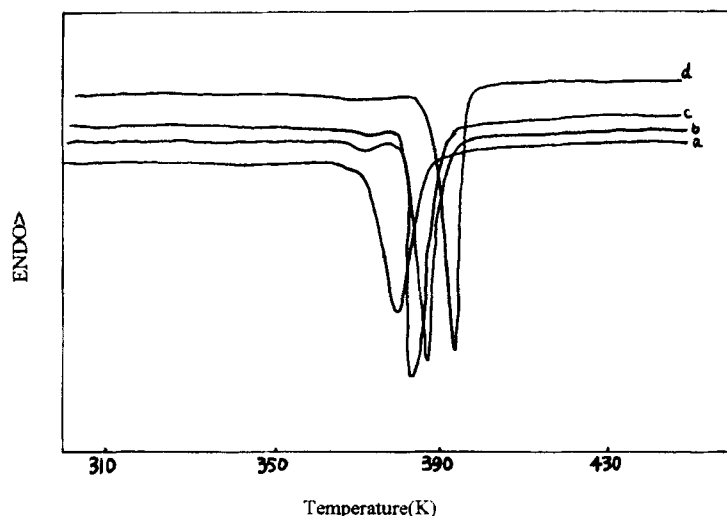


FIGURE 3 The DSC cooling curves of PPM (a) and PP-g-ATBS (b, c, d); (b) containing ATBS 0.19%; (c) containing ATBS 0.47%; (d) containing ATBS 0.88%.

attributed to that ATBS act as a nucleating agent in propylene sequences crystallization process. The WAXS spectra of PP and PP-g-ATBS are shown in Figure 4. As indicated by the patterns, grafting ATBS leads to some change of crystallization structure of PP crystals. The peak at $2\theta = 15.9$ degree, which corresponds to the 300 diffraction plane of the β form (hexagonal), decreased with increase of the degree of grafting of PP-g-ATBS. The relative amount of the β -form is usually described in terms of the K value, which is defined as:

$$K = \frac{H(300)}{H(300) + H(110) + H(040) + H(130)}$$

where $H(110)$, $H(040)$ and $H(130)$ are the heights of three strong equatorial α -form peaks (110), (040) and (130), and $H(300)$ the height of the strong single β -form peak (300). Using this equation, the K value of PP, PP-g-ATBS of ATBS content 0.26%, 0.57% and 0.78% as follows: 28.3%, 17.4%, 12.1% and 0.57%, respectively. It may be concluded that, by grafting of ATBS on PP, the proportions of monoclinic (α -form) and hexagonal (β -form) phases is modified in the PP. The proportion

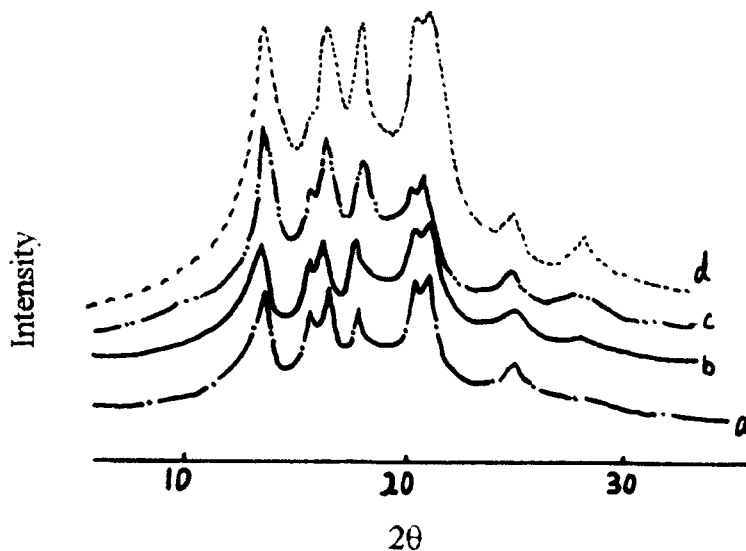


FIGURE 4 The WAXD spectra of PP (a) PP-g-ATBS: (b,c,d); (b) containing ATBS 0.26%; (c) containing ATBS 0.57%; (d) containing ATBS 0.78%.

of these two forms usually depends on preparing conditions of samples and nucleating process. In our work preparing conditions were same for all samples. Therefore, it can be concluded that the change of the crystallization structure of PP-g-ATBS was originated from a different nucleating process.

The contact angle (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 samples were calculated by extrapolating the surface tension against $\cos\theta$ plot to $\cos\theta = 1$. The critical surface tension (γ_c) of the PP and PP-g-ATBS samples is listed in Table I. The result suggested that the surface polarity of graft copolymer is augmented with an increase of the content of ATBS in PP-g-ATBS samples.

Influence of Monomer (ATBS) and Initiator (DCP) Concentration

Table I shows the influence of monomer and initiator concentration on the grafting reaction at a reaction temperature of 200°C. Run 1–5

TABLE I Influence of monomer and initiator concentration on graft reaction

Run	monomer concentration (wt%)	initiator concentration (wt%)	degree of grafting (wt%)	MFI MFI (g/10min)	γ_c γ_c (dyn/cm)
1	5	0.05	0.26	1.8	29.8
2	5	0.1	0.34	2.4	27.3
3	5	0.5	0.78	6.0	24.5
4	5	1.0	0.89	11.4	22.7
5	5	0.25	0.57	3.8	25.9
6	3.5	0.25	0.44	3.6	26.1
7	2.5	0.25	0.31	3.8	30.1
9	0.5	0.25	0.19	3.8	31.2

All runs carried out at 200°C for 60 rpm.

showed the influence of initiator concentration for a fixed monomer concentration of 5 wt%. As the initiator concentration was increased from 0.05 to 1 wt%, the degree of grafting increased sharply. The melt flow index (MFI), which is an indication of the extent of degradation, increased with increasing initiator concentration, indicated a increase in degradation of PP.

Run 5–9 showed the influence of monomer concentration on the grafting reaction for a fixed initiator concentration of 0.25 wt%. As the monomer concentration was decreased from 5 wt% to 0.5 wt%, the degree of grafting decreased marginally, i.e. from 0.57 to 0.19 wt%. The MFI values were unaffected by changing the monomer concentration.

Influence of Screw Speed and Reactive Temperature

Table II exhibits the effect of screw speed on the degree of grafting. It was observed that the degree of grafting increases with speed decreased and then remains constant. With an increase in reaction time, the radicals will have more time for reaction, and as a result, the degree of grafting will increase. After some time all initiator was used up, and no further change in degree of grafting was observed with an increase in reaction time. The effect of reaction temperature on degree of grafting was listed in Table II. With increasing reaction temperature, the degree of grafting increases from 185°C to 200°C, and the degree of grafting reached a maximum value at 200°C. However beyond 200°C, it decreases with increase in temperature. With increasing temperature,

TABLE II Influence of screw speed and temperature on graft reaction

<i>Run</i>	<i>temperature</i> (°C)	<i>screw speed</i> (rpm)	<i>degree of grafting</i> (wt%)	<i>MFI</i> (g/10min)
10	185	60	0.23	3.2
11	195	60	0.42	3.6
12	200	60	0.57	3.8
13	210	60	0.69	3.8
14	225	60	0.47	4.1
15	200	30	0.88	3.8
16	200	45	0.84	3.9
17	200	80	0.79	4.0

All runs are 5 wt% ATBS and 0.25 wt% DCP.

degree of grafting increases due to increase decomposition rate of initiator. Therefore, the number of free radicals and their mobility also increase resulting in a high degree of grafting, high mobility also results in mutual termination of free radicals for copolymerization. Hence, the maximum value of degree of grafting was appeared. From Table II, it was seen that the reaction time and temperature has only a small effect on the MFI.

CONCLUSIONS

The results show that ATBS monomer had been grafted onto PP by melt mechanical mixing. Various reaction condition that affected the degree of grafting were investigated. The initiator concentration largely controlled the degree of grafting and melt flow index, and the screw speed and temperature had a small effect on the MFI. The degree of grafting increased with increasing monomer concentration, but the MFI remained constant. Crystallization temperature of grafting copolymer was higher than that of PP, and the crystal form of grafting sample was different from the PP.

Acknowledgements

The authors would like to acknowledge the financial support of Chinese National Natural Science Foundation Committee: No. 59433010-010.

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