

Effect of addition of multifunctional monomers on one-step reactive extrusion of PP/PS blends

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Abstract

One-step reactive compatibilization of PP/PS alloys was studied by using a twin-screw extruder in the presence of dicumyl peroxide (DCP). Compared with mechanical extrusion, reactive extrusion greatly reduced the average dispersed particle size, due to the formation of PP-g-PS graft copolymers, which behave as in situ formed compatibilizers. In order to suppress the degradation of the PP chain during the process, some multifunctional monomers such as GTL, TMPTA, DEGDA, TPGDA were added in combination with DCP. By studying the effect of the monomers on the MFR and the morphology of the resulted blends, it is found that the flexibility of the additive molecules and the reactivity of the double bond of carbon contained in the molecule are crucial for the grafting reaction. The suppression of PP degradation depends on a certain amount of double bonds. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive extrusion; Polypropylene; Polystyrene; Multifunctional monomer

1. Introduction

Recently in situ compatibilization of immiscible polymer blends by reactive extrusion has been widely studied [1–4]. For polyolefins, because of their non-reactive functionalities, there are two commonly used approaches in reactive extrusion. One approach is the ‘two-step’ process, in which polymers are functionalized selectedly in the first step, and then blended in an extruder in the second step. Graft reaction should occur between the functionalized groups during blending, and graft co-polymers are formed in situ. The other approach is a ‘one-step’ process, in which low-MW compounds are added into the melted blends to initiate grafting/coupling reactions at the interface and form graft/block co-polymers during extrusion.

However, the presence of peroxide during reactive extrusion leads to the serious chain-scission of the PP

backbone, which affects the property of the alloys. In the previous study [5–7], the in situ compatibilization of polypropylene/poly(styrene-co-acrylonitrile) (PP/AS) (70:30) blends was carried out by one-step reactive extrusion. A multifunctional monomer Glycol Trilinate (GTL) in combination with dicumyl peroxide (DCP) was added into the blends, and was found to be able to suppress the PP degradation efficiently, and promote the grafting reaction to some extent at the same time. In this study, some multifunctional monomers with double bonds of carbon were added in combination with DCP in PP/PS blends, and the addition effect of multifunctional monomers on PP degradation and the reactive compatibility are well studied.

2. Experimental

2.1. Materials

The polypropylene (PP) used in this study was a

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commercial product of Yanshan Petrochem. Co., type no. 1300. The polystyrene (PS) was a commercial product of BASF Co. The functional monomer, glycerol trilinoleate (GTL), was prepared from glycerol and linoleic acid in our laboratory. Dicumyl peroxide (DCP) was a commercial product from Fushun Chemical Factory (purity 99%). Trimethylolpropane triacrylate (TMPTA), diethylene glycol diacrylate (DEGDA) and tripropylene glycol diacrylate (TPGDA) were commercial products of Beijing Oriental Chemical Engineering Research Center.

2.2. Preparation and testing of blends

70:30:0.3 PP/PS/DCP blends of various multifunctional monomers were prepared on a 30-mm twin-screw extruder (L/D = 25), with the speed of 30 rev./min.

2.3. Characterization

2.3.1. FTIR

The alloy granules were dissolved in boiling xylene to form a transparent solution. Same volume of cold 1,4-dioxane was then poured into the hot xylene solution to anticipate PP. After that, PP was filtered and dried in an oven for 10 h at a temperature of 70°C, and then PP was vacuum-dried and hot pressed into film, which was characterized by FTIR.

2.3.2. Scanning electron microscopy (SEM)

Morphology of the PP/PS blends were observed through SEM, Hitachi S-400. The specimen were cryogenically fractured (in liquid nitrogen), and etched in 1,4-dioxane at a temperature of 70°C for 8 h. After drying, the fracture surface was sputtered with gold before observation.

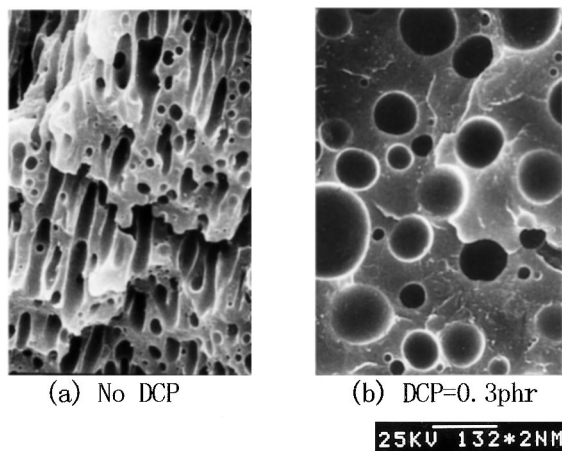


Fig. 1. SEM micrographs of the 70:30 PP/PS blends: (a) No DCP, and (b) DCP = 0.3 phr.

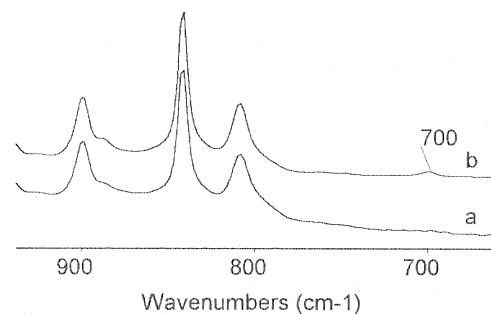


Fig. 2. FTIR spectra of PP separated from resulting blends (PP/PS = 70:30): (a) mechanical extrusion; and (b) DCP = 0.3 phr.

2.3.3. MFR

Alloys were measured at 230°C using a load of 2.16 kg according to the ASTM-1238-86T standard.

3. Results and discussion

Fig. 1 shows SEM micrographs of the 70:30 PP/PS blends obtained from the mechanical extrusion and the reactive extrusion, respectively. Compared with the non-reactive process, reactive extrusion could lead to finer particles of the dispersed phase, and the average particle size decreased.

Fig. 2 illustrates the FTIR spectra of PP separated from the resulting PP/PS (70:30) blend. No absorption band at 700 cm^{-1} was found in the spectra of PP separated from the mechanical extrusion blend. While it was observed that the absorption band at 700 cm^{-1} appeared in the spectra of PP when 0.3 phr DCP was

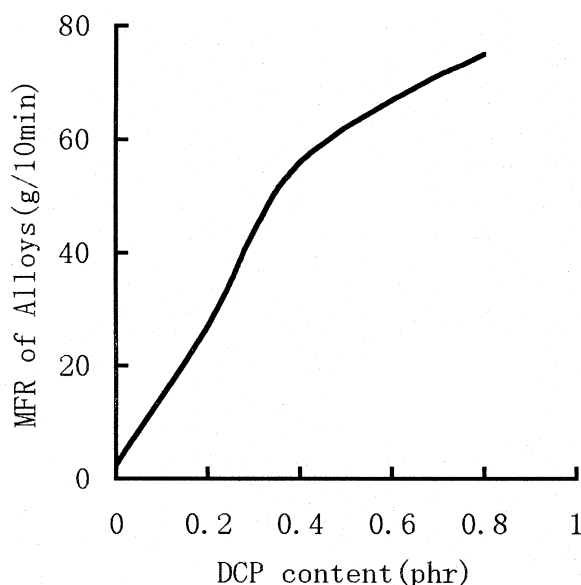
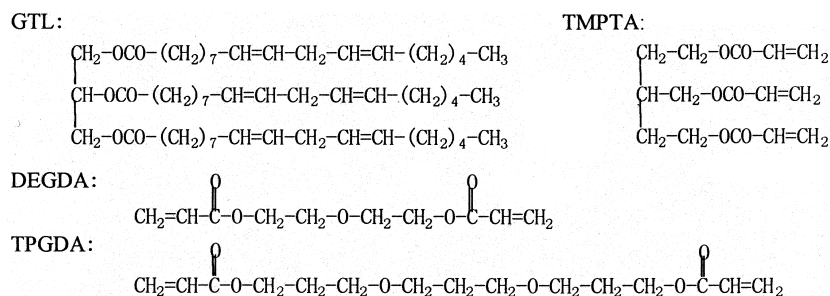


Fig. 3. The MFR of the resulting PP/PS (70:30) alloys vs. DCP content.



added into the blend. The absorption band at 700 cm^{-1} has been assigned to the vibration of the benzene group of PS. It means that PS is grafted on PP during reactive blending, and the in situ formed PP-g-PS graft co-polymers behaved as a compatibilizer.

Fig. 3 shows the variation of the MFR of PP/PS/DCP alloys with a change of DCP concentration. The sharp increase of the MFR was observed for the reactive extrusion sample, indicating serious degradation of the PP chain.

According to the above results, it was found that the addition of DCP in the blends of PP/PS could initiate the grafting reaction of PP and PS chains. The in situ formed PP-g-PS graft co-polymers improved the morphology of alloys and also led to the serious chain-scission of the PP backbone. In order to resolve this contradiction, it is necessary to find a proper co-agent, which not only suppresses the degradation of PP chains, but also further promotes the graft compatibilization of PP/PS blends.

In our previous study, the in situ compatibilization of PP/AS (70:30) blends was carried out by one-step reactive extrusion in the presence of dicumyl peroxide (DCP). A multifunctional monomer GTL was added into the blends in combination with DCP. It was found

that GTL could suppress the PP degradation efficiently, and promote the grafting reaction. This result gave us good enlightenment. We expected that the addition of a multifunctional monomer could really suppress the degradation of PP chains and further promote the graft compatibilization of PP/PS blends.

Four kinds of multifunctional monomers with different molecular structures were studied in the following content. Their molecular structures are shown below:

The four kinds of different multifunctional monomers (2 phr) were added, respectively, in the PP/PS/DCP reactive extrusion process. Then their morphologies were observed through SEM. Fig. 4 shows the SEM micrographs of the 70:30 PP/PS blends. From Fig. 4a–d, the average dispersed particle sizes were decreased gradually. This result shows that the different molecular structures of multifunctional monomers can lead to the different effects for the PP/PS grafting reaction. The flexibility of molecules of the monomers and the reactivity of the double bond contained in the molecule are crucial for the grafting reaction. That is, the longer the chain of the molecules and the nearer the double bonds are located to the ends of the chains, the more easily the grafting reaction is promoted.

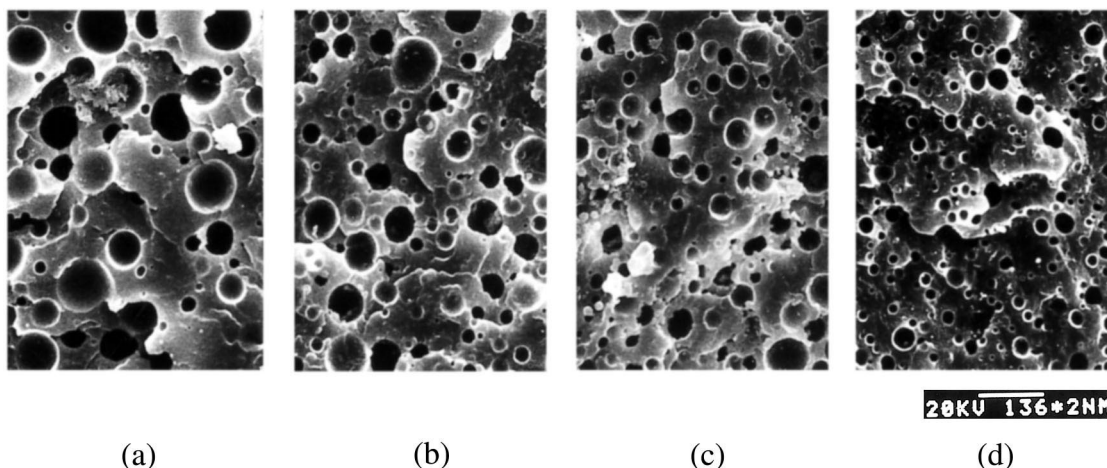


Fig. 4. SEM micrographs of the 70:30 PP/PS blends (DCP = 0.3 phr): (a) GTL = 2 phr; (b) TMPTA = 2 phr; (c) DEGDA = 2 phr; and (d) TPGDA = 2 phr.

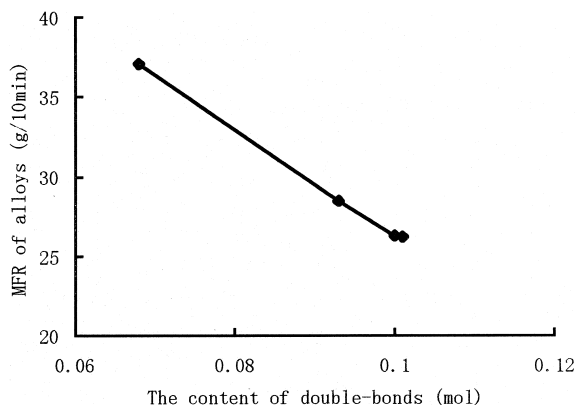


Fig. 5. MFR of the resulting alloy vs. the content of double bonds.

Fig. 5 shows the relationship between the MFR of the resulting alloys and the content of double bonds in the multifunctional monomers for the same amount added. It was observed that the efficiency of suppressing degradation of the PP chain is closely related to the content of double bonds in the system. That is, the greater the content of double bonds, the more effective the suppression of PP degradation.

4. Conclusions

1. The addition of peroxide DCP during the PP/PS

blending process could initiate the grafting reaction of PP and PS. The in situ formed PP-g-PS graft co-polymers, which behaved as a compatibilizer reduced the average dispersed particle size.

2. The effect of multifunctional monomers such as GTL, TMPTA, DEGDA, TPGDA on the MFR and the morphologies of the resulting blends was investigated. It is found that the flexibility of molecules of the monomers and the reactivity of the double bond contained in the molecule are crucial for the grafting reaction. That is, the longer the chain of the molecules and the nearer the double bonds are located to the ends of the chains, the more easily the grafting reaction is promoted. Also, the suppression of PP degradation must depend on a certain number of double bonds.

References

- [1] Peter Van Ballegoole, Rudin A. *Polym Eng Sci* 1988;28(21):1434.
- [2] Peter Van Ballegoole, Rudin A. *J Appl Polym Sci* 1990;39:2097.
- [3] Xanthos M, Dagli SS. *Polym Eng Sci* 1991;31(1):929.
- [4] Crevecoeur JJ., Nelissen L, Van der Sanden MCM et al. *Polymer* 1995;36(1):753.
- [5] Tai X-Y, Xie X-M. *J Synth Resins Plast* 1998;15(1):35.
- [6] Tai X-Y, Xie X-M. *J Funct Polym* 1998;11(2):231.
- [7] Xie X-M, Tai X-Y. *Acta Polymerica Sinica* 1999;4:410.