Preparation of Polypropylene/Acrylonitrile–Styrene Copolymer Alloys by One-Step Reactive Blending

XU-MING XIE,[1] YA-YUN LIU,[1] BAO-HUA GUO,[1] JUN FENG,[1] TATSUO ISHIKAWA,[2] TAKASHI MORINAGA[2]

[1] Laboratory of Advanced Materials, Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing, 100084, People's Republic of China

[2] Goi Works, Hitachi Chemicals Co., Ltd., 14 Goi Minami Kaigan, Ichihara-shi, Chiba, 290 Japan

ABSTRACT: The compatibilization of polypropylene/acrylonitrile–styrene (PP/AS) blends through the addition of peroxide (DCP) was investigated in this study. The grafting reaction between PP and AS with the addition of peroxide occurred during the reactive-blending process. The *in situ*-formed grafting copolymers of PP-*g*-AS and AS-*g*-PP were then characterized by FTIR. The optimum concentration of the initiator, DCP, was 0.2 wt %, and the reaction temperature should be above 195°C. It was found that, when AS was the major component of the blends, the grafting of AS onto PP was the main process; conversely, when PP was the major component, PP was grafted onto AS. These results can be explained by the main-chain scission of PP during the reactive-blending process. With increase of the AS component, the total degree of grafting increased at first and then decreased after the composition of the blends reached 50/50. The maximum degree of grafting was found to be 6 wt % for the 50/50 PP/AS/DCP blend. PP was more degradable than was AS in the presence of peroxide at high temperatures. The MFR values of the PP/AS/DCP blends were slightly greater than were those of the simple PP/AS blends, which means that blending is an effective way to protect PP from degradation. SEM micrographs of the cross section of PP/AS/DCP showed a fine dispersion and a smaller domain size of the dispersed-phase particles, implying that the *in situ*-formed grafting copolymers act as a compatibilizer to reduce the interfacial tension between the PP and AS phases. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1284–1290, 2001

Key words: polypropylene; acrylonitrile–styrene copolymer; reactive blending; FTIR; *in situ*-formed compatibilizer

INTRODUCTION

The blending and mixing of polymers is an inexpensive route to the improvement of various polymer properties. The effective property modifications for totally miscible and partially miscible polymer blends were carried out in many cases.[1,2]

However, most polymer blends are immiscible and incompatible. Such an immiscible system has a distinct dispersed phase. Because of the poor interfacial adhesion between the dispersed phase and the matrix, improvement of the mechanical properties of the blends were generally poor. A compatibilizer, such as a block copolymer or a graft copolymer, has been widely used to improve the mechanical properties of immiscible polymer blends, since the block or graft copolymers are very effective in reducing the interfacial tension

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and improving interfacial adhesion by chain entanglement or bridging at the interface. However, in many cases, the compatibilizer had to be synthesized separately for each pair of immiscible polymers.

Recently, *in situ* compatibilization of immiscible polymer blends by reactive extrusion has drawn wide attention.[3–9] The compatibilizer is created during extrusion through interfacial reactions between different reactive constituents. Because there is no reactive functional group in polyolefin chains, it is necessary to functionalize polyolefin before the reactive processes. This approach is often used in polypropylene-containing blends. Another approach is the so-called one-step process, in which low molecular weight compounds are added into the melted blends to initiate grafting/coupling reactions at the interface and form *in situ* graft/block copolymers during the mixing process.[10–17]

In this study, a one-step reactive processing method was used to obtain polypropylene/acrylonitrile–styrene copolymer (PP/AS) alloys. The alloys can be expected to have an improvement of the balancing properties of chemical and solvent resistance, processability, and dimensional stability without increasing cost. The blending of PP/AS through the addition of dicumyl peroxide (DCP) was first studied using a Brabender. The formation of the grafting copolymer between PP and AS, the *in situ*-formed compatibilizer, was investigated during the melt-mixing process, and the degrees of grafting for various blend compositions were determined by Fourier transform infrared (FTIR). The dependence of the melt grafting reaction conditions on the compatibilization of PP/AS/DCP blends was also studied. A scanning electron microscope (SEM) was used to observe the morphologies of the compounded blends.

EXPERIMENTAL

Materials

The PP (type 1300), with a melt flow rate (MFR) = 1.2 g/10 min, was from the Yanshan Petrochemical Corp. (Beijing, China). The AS resin, supplied by the Hitachi Chemical Corp. Ltd. (Chiba, Japan), contained about 24 wt % acrylonitrile. DCP was made by the Fifth Factory of Chemical Engineering of Fushun (China). The solvents, toluene and dioxan, were from the

Chemical Engineering Works of Beijing Tong County (Beijing, China).

Preparation of Blends

Blends of PP and AS were compounded on a Brabender Plasticorder equipped with a 50-cm^3-sample chamber at a given temperature and at a rotor speed of 30 rev min^{-1}. The components were first dry-blended. Next, 50 wt % of the dry-blended resin was put into the Brabender and mixed. Then, the appropriate amount of DCP was added to the resins. Finally, all the remaining dry-blended resin was put into the Brabender. A mixing time greater than 5 min was required to complete the free-radical graft reaction, which led to the dissipation of DCP and dispersion of the blends. All processes were carried out under a nitrogen atmosphere.

Separation of Grafted Copolymers

The *in situ*-formed grafted copolymers in the resulting compounds were separated by applying appropriate solvents using the following procedure: The resulting compounds were first dissolved in toluene at 110°C for 3 h. The homogeneous solutions were then poured into a dioxan solvent to precipitate PP and the PP-*g*-AS terpolymer (sample A), and the precipitates were separated by filtration. Finally, the remaining AS copolymer and AS-*g*-PP copolymer (sample B) remaining in the dioxan was obtained by boiling the solvents. Thus, the resulting compounds, the PP/PP-*g*-AS copolymer (sample A) and AS/AS-*g*-PP (sample B), were both obtained.

FTIR Measurement

The *in situ*-formed PP–AS melt-grafted copolymers were characterized by FTIR. The FTIR spectra were recorded on a Nicolet 20SXC spectrometer. Two hundred scans at a resolution of 4 cm^{-1} were used to obtain spectra from the samples. The degree of grafting for sample A (PP and PP-*g*-AS) and sample B (AS and AS-*g*-PP) were determined using the IR calibration curves which were established by using the simple blends of PP and the AS copolymer.

SEM Observation

The phase morphologies of the PP/AS blends were observed through the SEM. The sections were obtained with an ultramicrotome under a liquid-
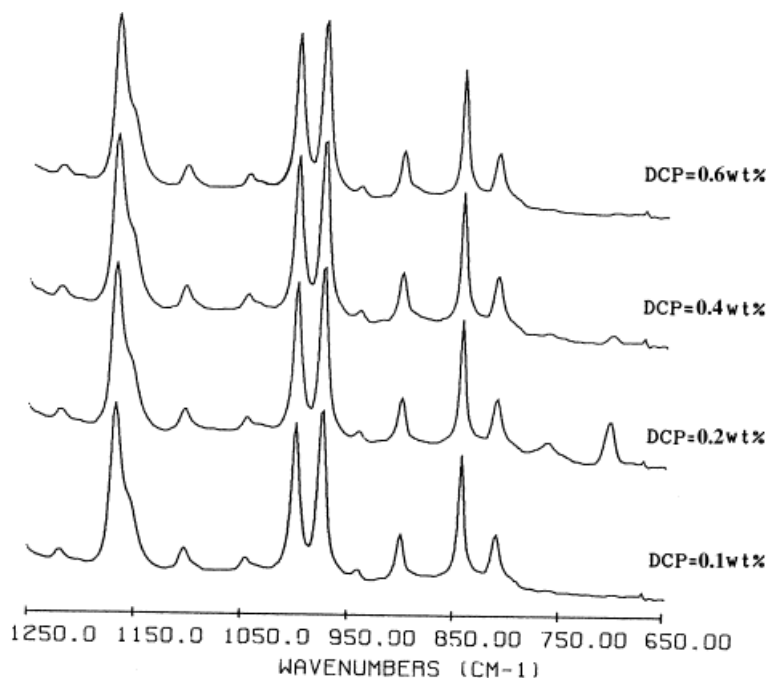
Figure 1   FTIR spectra of samples A separated from the resulting compounds of 88/12 PP/AS reactive-blended at 200°C for various DCP concentrations.

nitrogen atmosphere. Then, these sections were etched by dioxan to remove the AS dispersed phase and, subsequently, gold-plated by evaporation. All observations were carried out using a Hitachi-450 SEM.

Measurement of Flow Properties

The MFRs of pure PP and PP initiated with DCP were measured at 230°C. With a load of 2.16 kg, the MFRs of the AS copolymer and the AS copolymer initiated with DCP were measured at 190°C. Also, the MFRs of the PP/AS and PP/AS/DCP blends were measured at 190°C. Through an XRZ-400-type equipment, MFR measurements of grafted PP were carried out at 230°C with a load of 2.16 kg, which satisfies the ASTM D-1238-86T standard.

RESULTS AND DISCUSSION

The possible reactions of PP/AS blends that occur in the presence of the initiator DCP during melt blending are shown below.
Radical generations:

$$ROOR \rightarrow RO^{\bullet} + RO^{\bullet} \qquad (1)$$

$$RO^{\bullet} + PP \rightarrow ROH + PP^{\bullet} \qquad (2)$$

$$RO^{\bullet} + AS \rightarrow ROH + AS^{\bullet} \qquad (3)$$

Degradation:

$$PP^{\bullet}_{x+y} \rightarrow PP^{\bullet}_{x} + PP_{y}$$
$$AS^{\bullet}_{x+y} \rightarrow AS^{\bullet}_{x} + AS_{y} \qquad (4)$$

Coupling and grafting:

$$PP^{\bullet}_{x} + PP^{\bullet}_{y} \rightarrow PP_{x+y} \qquad (5)$$

$$AS^{\bullet}_{x} + AS^{\bullet}_{y} \rightarrow AS_{x+y} \qquad (6)$$

$$PP^{\bullet} + AS^{\bullet} \rightarrow PP\text{-}g\text{-}AS \quad \text{or} \quad AS\text{-}g\text{-}PP \qquad (7)$$

The grafting or crosslinking reaction between PP and AS that is shown in eq. (7) can be expected to occur.

Figure 1 illustrates FTIR spectra of samples A which were separated from the compounds that resulted from reactive blending 88/12 PP/AS at 200°C with various DCP concentrations. It is seen that the absorption band at 701 cm^{-1} appears in the spectra for the blend samples with 0.2 and 0.4
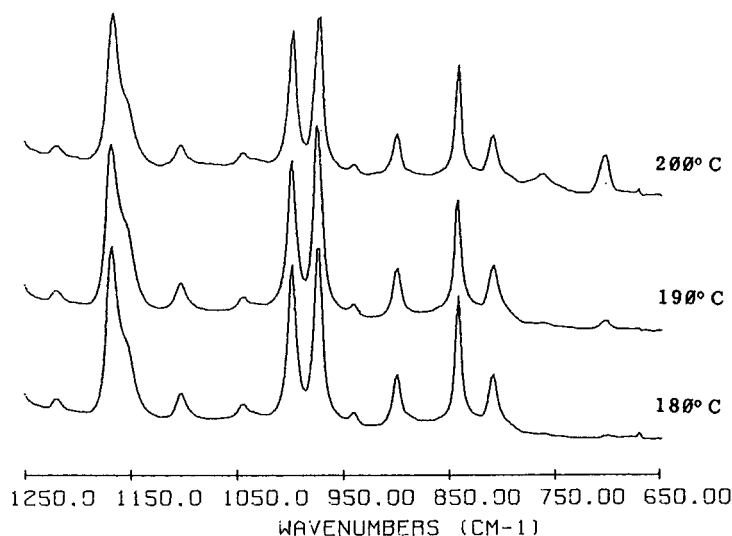
Figure 2 FTIR spectra of samples A separated from the resulting compounds of 88/12 PP/AS reactive-blended at various temperatures, for a given DCP concentration of 0.2 wt %.

wt % DCP contents. The absorption band at 701 cm^{-1} was assigned to the vibration of the benzene group of the AS copolymer, so the result means that AS was grafted onto PP during reactive blending. However, no absorption band at 701 cm^{-1} was found in the spectra of samples A of lower and higher concentrations of DCP. This is reasonable because (1) the excess initiator results in more severe degradation of PP. In other words, the chain scission of PP becomes the main process in the reactive blending, so the grafting reaction is suppressed; and (2) it was difficult for DCP of lower concentration to initiate the grafting reaction. Hence, there should be a balance between the grafting reaction and the content of the initiator.

Figure 2 demonstrates the dependence of temperature on the grafting reaction for the DCP concentration at 0.2 wt %. FTIR spectra of samples A separated from the resulting compounds of 88/12 PP/AS indicate that the intensity of the absorption band at 701 cm^{-1} increased with increasing temperature, as shown in Figure 2.

Based on the results mentioned above, the optimum reaction conditions were obtained. To prevent thermal decomposition, reactive blending should be carried out at 195°C, and the concentration of the initiator DCP should be 0.2 wt %.

Figure 3 shows IR spectra of samples A separated from the resulting compounds for various compositions of PP/AS/DCP blends. As shown in Figure 3, the absorption band at 701 cm^{-1} appeared significantly in the spectrum of sample A, which was separated from the 50/50, 30/70 and 10/90 PP/AS/DCP blends, which implies that a portion of the AS copolymer was melt-grafted onto PP. However, no clear absorption band at 701 cm^{-1} was observed in the spectra of samples A when the PP content was greater than 50 wt % in the blends. It should be noted that the intensity of the band at 701 cm^{-1} decreased with increase of the PP contents in the blends. This result indicates that the grafting reaction of AS onto PP is the main process when the AS component is the majority one, and it may be related to the degra-
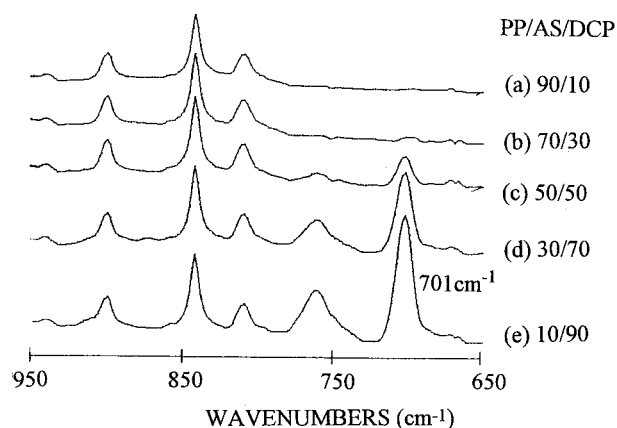
Figure 3 FTIR spectra of samples A separated from the resulting compounds reactive-blended at 195°C for various compositions of PP/AS/DCP blends.
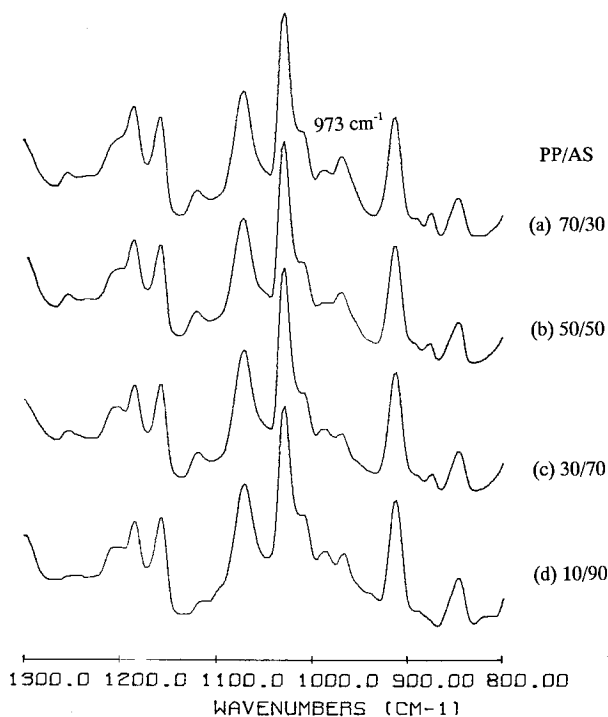
Figure 4 FTIR spectra of samples B separated from PP/AS/DCP blends for various compositions.

dation of PP and AS under the presence of an initiator. The degradation of PP occurs more easily than that of AS in the presence of an initiator at high temperature. So, the main-chain scission of PP is predominant when PP is major component in the blends, and the grafting reaction of AS onto PP should hardly occur. This will be discussed in detail later.

Figure 4 illustrates the spectra of samples B separated from PP/AS/DCP blends of various compositions. The absorption band at 973 cm^{-1} was assigned to be the vibration of the CH$_3$ rocking and C—C stretching of PP, which implies that a portion of PP was grafted onto the AS copolymer. The intensity of the band at 973 cm^{-1} decreased with increase of the AS component in the blends. This result also indicates that the main-chain scission of PP is easy when PP is the major component in the blends; thus, the grafting of PP onto AS becomes the main process during the reactive-blending process. It corresponds to the result shown in Figure 3.

Based on the above results, it is recognized that both the PP-g-AS and AS-g-PP copolymers can be formed in the melt reactive blending process. The degrees of grafting of samples A and B are determined by calculating the peak at a ratio

between A_{701}/A_{809} and A_{973}/A_{1952} and referring to the IR calibration curves obtained from the simple blends of PP and AS. The dependence of the degree of grafting on the contents of the samples A and B is shown in Figure 5. The degree of grafting of samples A increased with increasing AS content in the blends, and, inversely, the degree of grafting of samples B decreased with increasing AS content, namely, the lower the composition of a component in the blends, the higher the degree of grafting for that component. It should be pointed out that the value for the degree of grafting is very high for each component (PP or AS) when it is the minor phase in the blends. These results showed the effects of the main-chain scission of the polymers, which significantly happens when the component is the major phase in the blends.

The total degree of grafting of the resulting compounds can be determined using the following equation:
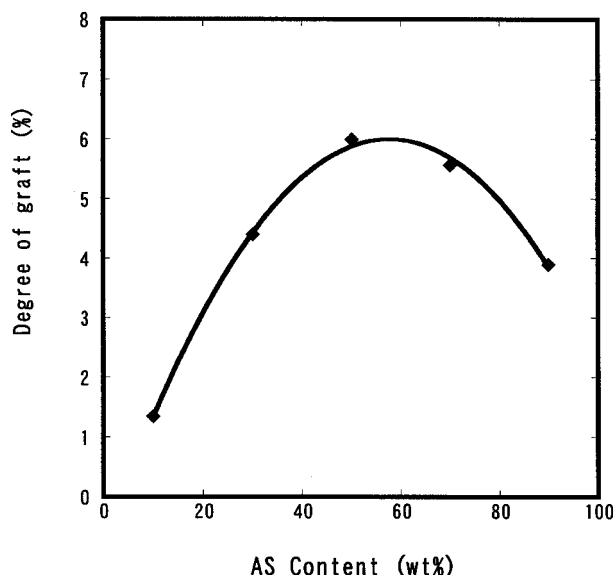
Total degree of grafting

$$= \frac{D.G(A) \times W(A) + D.G(B) \times W(B)}{W(A) + W(B)} \quad (8)$$

$D.G(A)$ is the degree of grafting of sample A; $D.G(B)$, the degree of grafting of sample B; $W(A)$, the weight of the sample A; and $W(B)$, the weight of the sample B.
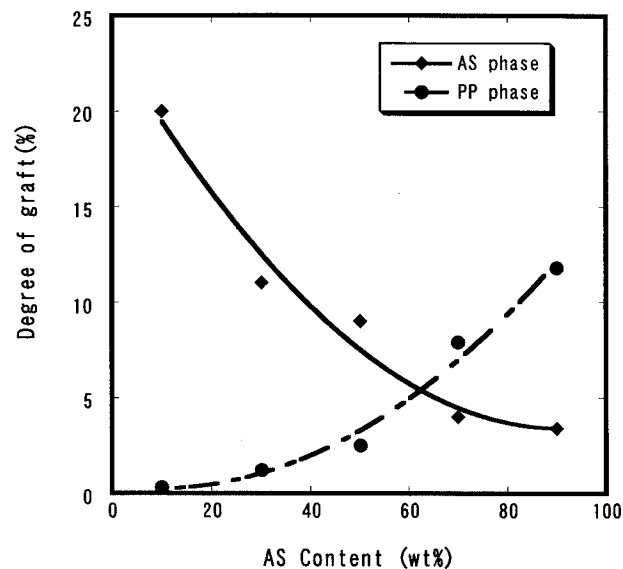
Figure 5 Dependence of the degree of grafting on AS contents in the blends for samples A and B.

Figure 6 Dependence of the total degree of grafting on AS contents in the blends.

The dependence of the total degree of grafting on the AS copolymer content in the blends is shown in Figure 6. With increase of the AS content, the degrees of grafting increased at first, but decreased after the composition reached 50/50 (wt). The maximum degree of grafting was found to be 6 wt % for the 50/50 PP/AS/DCP blend, meaning that the probability of chain contact between PP and the AS copolymer is the highest at the 50/50 composition, and, thus, the polymer chains involved in the grafting reaction were the greatest amount.

During the grafting reaction, degradation of polymers can be expected. The changes of the MFR of the blends of both simple melt-mixed samples and reactive-blended samples were determined. Figure 7 shows the values of the MFR of the PP/AS blends versus the weight percentage of AS. It is seen that the MFR value of PP initiated with DCP is greater than that of PP by about 25 times. Conversely, the MFR value of a single AS copolymer initiated with DCP is slightly greater than that of a pure AS copolymer. These results mean that PP is more degradable than is the AS copolymer in the presence of peroxide at high temperature, and this also concurs with the results of the degree of grafting for PP/AS/DCP blends, which were discussed above. The changes in the MFR values for PP/AS and PP/AS/DCP blends have the same tendency. The MFR values of the blends first increased with increasing AS content and reached a maximum at the PP/AS

composition of 30/70, then decreased. The MFR values of PP/AS/DCP blends were slightly greater than were those of the PP/AS simple blends, meaning that the blending of PP/AS has the effect of protecting PP from degradation.
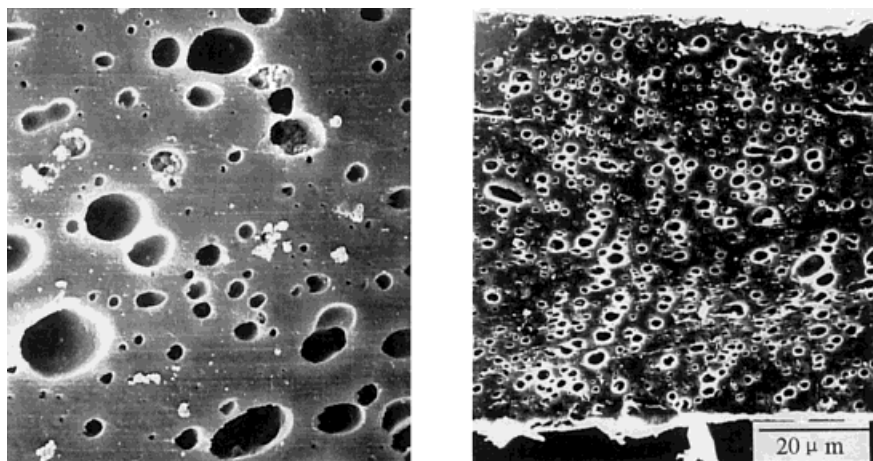
Figure 8 illustrates SEM micrographs of the cross section of the 70/30 PP/AS and PP/AS/DCP blends. The SEM micrographs show better dispersion in the PP/AS/DCP blends than that in the PP/AS blends. The dispersed phase size in the 70/30 PP/AS/DCP blends, which is about 4–6 μm, is smaller than that in the 70/30 PP/AS blends, which is 15–17 μm. This implies that the *in situ*-formed PP–AS grafting copolymer played the role of a compatibilizer in the PP/AS/DCP blends. The *in situ*-formed grafting PP–AS copolymer reduced the interfacial tension between the PP and AS phases.

CONCLUSIONS

1. It was found that the grafting reaction between PP and AS occurred with the addition of peroxide during the blending process. The *in situ*-formed grafting copolymers of PP-*g*-AS and AS-*g*-PP were confirmed using FTIR. The optimum concentration of the initiator, DCP, is 0.2 wt %, and the reaction temperature should be above 195°C.

2. When PP is the major component of the
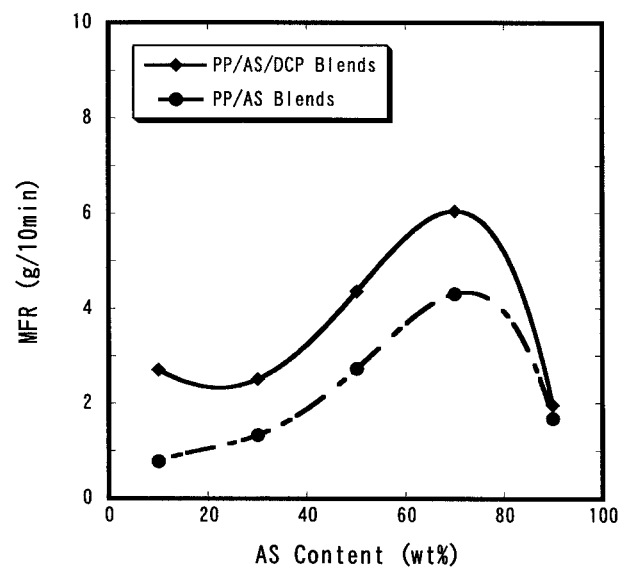
Figure 7 Values of the MFR of the PP/AS blends versus the AS contents.

Figure 8 SEM micrographs of the cross section of the 70/30 PP/AS and PP/AS/DCP blends.

blends, the grafting of AS onto PP was the main process; conversely, when the AS component was the major component, PP was grafted onto AS. These results can be explained by the main-chain scission of PP during the reactive-blending process. With increase of the AS component, the total degree of grafting increased at first and then decreased after the composition of the blends reached 50/50. The maximum degree of grafting was found to be 6 wt % for the 50/50 PP/AS/DCP blend.

3. PP was shown to be more degradable than was the AS copolymer in the presence of peroxide at high temperature. The MFR values of the PP/AS/DCP blends weere slightly greater than were those of the simple PP/AS blends, which means that blending is an effective way to protect PP from degradation.

4. The SEM micrographs of the cross section of PP/AS/DCP and PP/AAS/DCP showed a fine dispersion and a smaller domain size of the dispersed-phase particles. The dispersed—phase size in the 70/30 PP/AS/DCP, which was about 4–6 μm, was much smaller than that in the 70/30 PP/AS blend, which was 15–17 μm. This implies that the *in situ*-formed grafting copolymers play the role of a compatibilizer to reduce the interfacial tension between the PP and AS phases.

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