Synthesis of a Maleic Anhydride Grafted Polypropylene–Butadiene Copolymer and Its Application in Polypropylene/Styrene–Butadiene–Styrene Triblock Copolymer/Organophilic Montmorillonite Composites as a Compatibilizer

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ABSTRACT: A maleic anhydride grafted propylene–butadiene copolymer (MPPB) was prepared. Fourier transform infrared spectroscopy and ^{1}H-NMR results indicate that the maleic anhydride molecules reacted with the double bond in the butadiene unit of the propylene–butadiene copolymer (PPB), and the grafting percentage increased with the butadiene content in the initial copolymer. The gel permeation chromatography results show that the introduction of butadiene in the copolymer prevented the degradation of PPB. The MPPB was applied in polypropylene (PP)/styrene-butadiene-styrene triblock copolymer (SBS)/organophilic montmorillonite (OMMT) composites as a compatibilizer. In the presence of 10-phr MPPB, the impact strength of the composite was improved by about 20%. X-ray diffraction patterns indicated the formation of the β-phase crystallization of PP in the presence of MPPB, and a significant decrease in the spherulite size was observed. Transmission electron microscopy (TEM) images showed that the OMMT was better dispersed in the matrix upon the inclusion of MPPB. A better distribution of the rubber phase and a rugged fracture surface were observed in the scanning electron microscopy images as the MPPB proportion was increased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1820–1827, 2009

Key words: compatibilization; composites; graft copolymers; poly(propylene) (PP)

INTRODUCTION

Polypropylene (PP) is one of the most important plastics, as it has an excellent balance of mechanical properties, melt flow, color stability, chemical residence, and moisture barrier properties, together with a low cost. However, critical disadvantages for the wider application of this material are its low impact strength and nonpolar and inert nature, which result in difficulties in blending, coating, and inking.[1] The functionalization of PP with polar molecules is the most attractive method for improving the properties of this material.[2] By far, maleic anhydride (MA) is the most important molecule in this context,[3,4] and MA-modified PP has been prepared for commercial purposes and used to improve the polarity,[5] compatibility, and interaction of PP with other materials.[6,7] The grafting reaction is normally carried out by a radical mechanism:[1] a peroxide initiator provides radicals, some of which abstract hydrogen from the PP tertiary carbon to form PP macroradicals. However, because of the inert nature of the PP structure and the difficulty in controlling the free-radical reaction, the grafting reaction is normally accompanied by several undesirable side reactions, such as β scission, chain transfer, and coupling, which result in the degradation of the material.[3] The grafting percentage of MA-g-PP is normally around 5% (w/w).[8,9]

In this study, a propylene–butadiene copolymer (PPB) was used to enhance the reactivity of PP and control the reaction position of the grafting. Fourier transform infrared (FTIR) spectroscopy and ^{1}H-NMR were used to characterize PPB before and after the MA grafting. The maleic anhydride grafted propylene–butadiene copolymer (MPPB) was then applied in a composite of PP/styrene–butadiene–styrene triblock copolymer/organophilic montmorillonite (OMMT) as a compatibilizer. The mechanical properties of the composites were measured. Polarized optical microscopy (POM) and X-ray diffraction (XRD) were used to differentiate the size and type of crystalline PP in the composite with and without MPPB. The dispersability of OMMT in the composites was characterized by transmission electron microscopy (TEM). Scanning electron microscopy (SEM) was used to investigate the compatibility of the PP plastic phase and styrene-butadiene-styrene triblock copolymer (SBS) rubber particles.

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TABLE I
Compositions of the PP/SBS/OMMT/MPPB Composites

PP	SBS	OMMT	Antioxidant 1010	MPPB
100	5	3	1	0
100	5	3	1	3
100	5	3	1	5
100	5	3	1	10

For all components, the unit was parts per hundred parts of PP.

EXPERIMENTAL

Materials

Both the PPB and homopolypropylene (PP) used for grafting were synthesized in a 1-L stainless steel polymerization reactor in a hexane solution. MgCl$_2$-supported Ziegler–Natta was used as a catalyst,[10] and triethylaluminum (1 mol/L in hexane) was used as a cocatalyst. The butadiene content in PPB was measured by ^{1}H-NMR (1,2-butadiene = 0.67% mol/mol, 1,4-butadiene = 6.08% mol/mol). MA (Tianjin Fuchen Chemical Plant, Tianjin, China; analytical reagent grade), benzoyl peroxide (Beijing Xingjin Chemical Plant, Beijing, China, chemical grade), 1,2-dimethylbenzene (Beijing Changhai Chemical Plant, Beijing, China, chemical grade), and Antioxidant 1010 (Beijing Stable Chemical Co., Ltd., Beijing, China, industrial grade) were used as purchased.

PP (Z30S) and SBS (1310) used in the composite were purchased from Maoming Petrochemical Corp. (Maoming, China) and Yanshan Petrochemical Corp. (Beijing, China), respectively. OMMT (NB901) was provided by Huate Chemical Co., Ltd. (Hangzhou, China), and was used as received.

Preparation of MPPB

The grafting reactions were carried out in 1,2-dimethylbenzene solution initiated by benzoyl peroxide at a reaction temperature of 100°C. The grafted copolymer was left in a Soxhlet extractor with acetone for 24 h to remove the unreacted maleic hydride and then dried in a vacuum oven at 90°C. All of the reactions were carried out under the same conditions and the same amount of MA.

Preparation of the PP/OMMT/SBS composites

PP/OMMT/SBS composites with and without MPPB were first blended in a twin-screw extruder (Haake rheometer, Karlsruhe, Germany). The screw temperature distribution was varied from 160 to 170 to 180 to 190 to 200 to 205°C. A series of composites containing different proportions of MPPB were prepared. The compositions are shown in Table I.

Measurements and analytical characterization

FTIR spectroscopy

FTIR spectra of the samples were recorded with a Nicolet (Hayward, CA) 560 FTIR spectrometer in the range 2000–400 cm^{-1} with an average of 32 scans at a resolution of 4 cm^{-1}. The sample was prepared with the KBr pellet technique.

^{1}H-NMR

Samples for ^{1}H-NMR were prepared in a D^2–dichlorobenzene solution (20 wt %) and were measured by a Bruker (Fallanden, Switzerland) Avance-400 NMR spectrometer at 120°C.

High-temperature gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution of the samples were measured by high-temperature GPC (PL GPC-220, Waters, Milford, MA) at 135°C with 1,2-dimethylbenzene as a solvent. Polystyrene was used as the standard ($K = 1.38 \times 10^{-4}$, $\alpha = 0.70$).

Determination of the grafting percentage of MA in MPPB

The grafting percentage of MA in MPPB was measured by acid–base titration, as described by Shi et al.[3] A known weight of functionalized polymer was dissolved by refluxing in 1,2-dimethylbenzene, and a few drops of water were added to hydrolyze all of the anhydride groups into carboxylic acid. Excess alcoholic KOH (0.1N KOH in ethanol) was added to the hot solution. After boiling for 1 h, acidified isopropyl alcohol (0.1N HCl in isopropyl alcohol) was used to titrate the previous solution with 1% thymol blue in dimethylformamide as an indicator. The grafted percentage was established with the following equation:

$$G_r = \frac{M \times C \times (V_0 - V)}{2 \times 1000 \times m} \times 100\% \qquad (1)$$

where G_r is the graft percentage of MA, M is the molecular weight of MA (98.06 g/mol), C is the concentration (mol/L) of acidified isopropyl alcohol, V_0 is the volume (mL) of acidified isopropyl alcohol used to titrate the blank sample, V is the volume (mL) of acidified isopropyl alcohol used to titrate the sample, and m is the weight (g) of the sample.

Mechanical properties

The extrudates were pelletized and then molded into dumbbell-shaped tensile bars (GB1040 1992, 150
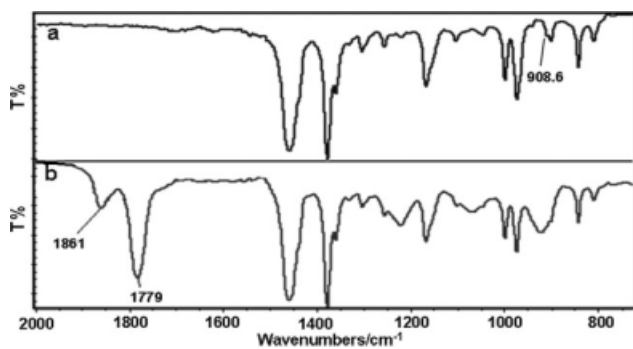
Figure 1 FTIR spectra of (a) PPB and (b) MPPB from 2000 to 600 cm^{-1} (14 wt % MA).

$\times$ 10 $\times$ 4 mm^3) and rectangular bars (ISO179 1999, 80 $\times$10 $\times$ 2 mm^2). The measurements of the mechanical properties were carried at 25°C and a humidity of 65%. The tensile properties were measured according to ASTM D 638 2003 with an Instron (Buckinghamshire, UK) 5500 Series mechanical tester. The impact strength measurement was carried out by a CEAST (Pianezza, Italy) Resil impactor.

XRD measurement

XRD measurements were carried out with a Rigaku (Tokyo, Japan) Geiger Flex D/max_RB X-ray diffractometer with Cu K radiation at a scanning at rate of 2°/min.

POM analysis

POM analysis was performed in a hot-stage polarizing microscope (Mettler-Toledo FP-900/Leica DMLP, Wetzlar, Germany). The samples were prepared by recrystallization at 110°C for 1 h after melting at 200°C for 15 min.

TEM measurement

The dispersity of OMMT in the matrix was evaluated by TEM (Tecnai G2 20, Hillsboro, OR). The samples were prepared by a frozen section procedure.

SEM measurement

The surface morphology of the impact fractured samples was measured by SEM (Leica S440).

RESULTS AND DISCUSSION

FTIR measurements

Figure 1 shows the FTIR spectra of PPB and MPPB. It was clear that, after grafting, two new intensive absorption peaks were observed at 1779 and 1861 cm^{-1}, which corresponded to the C=O vibrational

stretch of the carbonyl group in MA.[4,11] As presented by Zhao et al.,[12] the sample was extracted, and the unreacted maleic hydride was removed; the new absorption peaks indicated that the MA was grafted onto the PPB molecular chain.

^{1}H-NMR analysis

To investigate the location of the grafting reaction, the PPBs before and after grafting were both characterized by ^{1}H-NMR, as shown in Figure 2. In the spectrum of PPB, a medium-strength feature around 5.50 ppm and a very weak feature at about 5.00 ppm were observed, which were assigned to the hydrogens in the double bond of 1,4-addition-butadiene (—CH=CH—) and 1,2-addition-butadiene (=CH$_2$) units.[13] The intensity of the peaks was found to be significantly different, which indicated that the 1,4 addition of butadiene was crucial to the copolymerization. The contents of 1,4-butadiene and 1,2-butadiene were calculated to be 6.08 and 0.67% (mol/mol), respectively, around 9 : 1 in ratio. In the spectrum of MPPB, the peak at 5.50 ppm totally disappeared, which indicated that all of the double bonds in the 1,4-butadiene units were consumed in the grafting reaction. However, the peak at 5.0 ppm was found to show no significant change after the grafting reaction, which implied that the double bond in the 1,2-addition unit of butadiene was not involved in the grafting reaction. This was attributed to the low content of 1,2-addition butadiene, which was only 10% of all of the double bonds. It was also interesting to notice that the intensity of the peak at 2.12 ppm, which corresponded to the saturated hydrogen of butadiene (—CH$_2$—), obviously decreased. From these changes, we concluded that the MA molecules reacted with the double bond in the butadiene unit of PPB, especially the 1,4-butadiene addition unit, and thereby prevented the β scission of the main copolymer chain. The proposed reaction mechanisms for the PP and PPB reactions with MA are shown in Scheme 1, as has been previously reported by Zhao et al.[12]
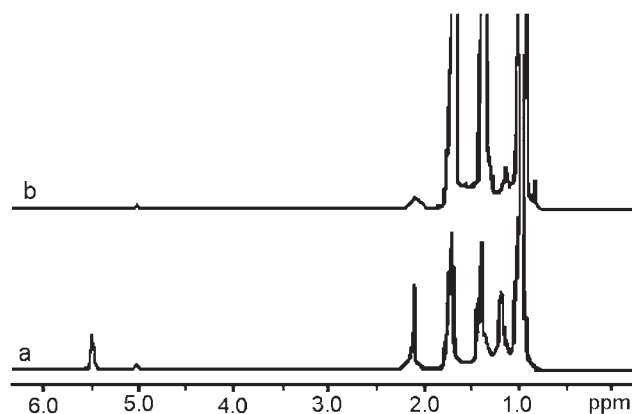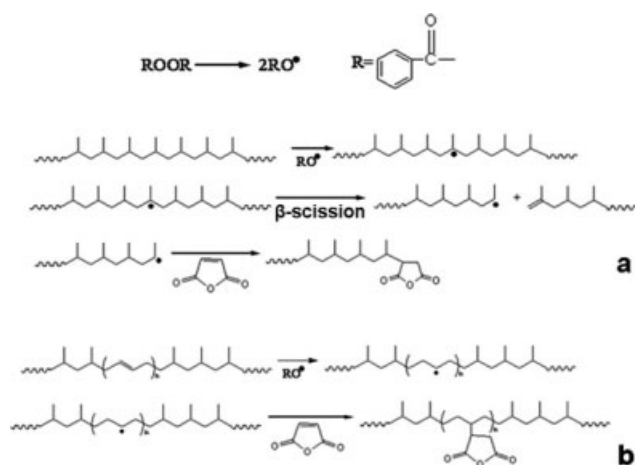

Figure 2 ^{1}H-NMR spectra of (a) PPB and (b) MPPB.

Scheme 1 Proposed reaction mechanisms for the grafting of MA onto (a) PP and (b) PPB.

Because of the inert nature of PP, hydrogen from the PP tertiary carbon must be abstracted to form PP macroradicals. However, these macroradicals are not stable and easily undergo β scission. Therefore, the molecular weight of PP is normally decreased after grafting. When the PPB is used in the free-radical reaction, the macroradicals are obtained by the opening of the double bond in the 1,4-butadiene units, which prevents the β scission of the main copolymer chain. Thus, the molecular weight should remain the same after grafting.

GPC measurements

The molecular weight distributions of the PP and PPB before and after grafting with MA were investigated with GPC, as shown in Figure 3. It was clear that, after the grafting reaction, PP underwent a dramatic degradation. The number molecular weight of PP before and after the grafting reaction shifted from $10^{4.6}$ (39,800 g/mol) to $10^{4.2}$ (15,800 g/mol), a
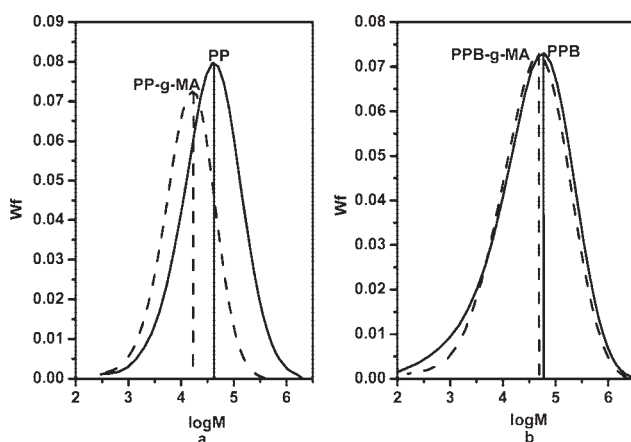

Figure 3 Molecular weight distributions of (a) PP and (b) PPB before and after grafting with MA. Wf, weight fraction.
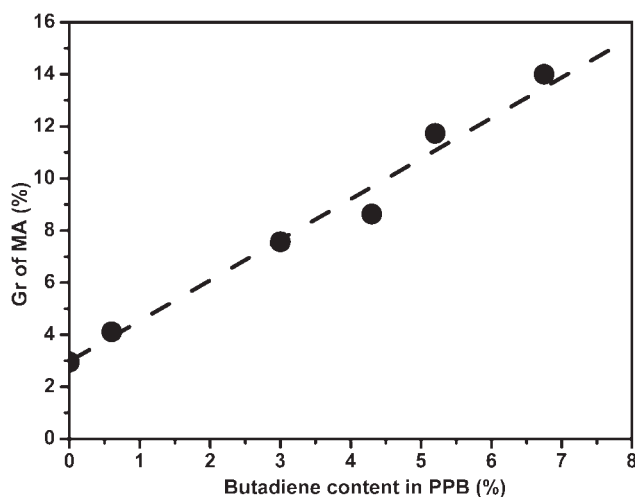

Figure 4 Grafting percentage of MA as a function of the butadiene content in PPB.

decrease of 60%. However, no such significant difference was observed between the molecular weight distributions of PPB before and after grafting. The number molecular weight shifted from $10^{4.8}$ to $10^{4.7}$, that is, 20%. Thus, in comparison to the PP grafting reaction, minimal chain scission was observed; this supported the proposed reaction mechanism of Scheme 1.

Effect of the butadiene effect on the grafting fraction

To investigate the effect of the butadiene content on the grafting fraction of MA, a series of PPB samples with different butadiene contents was used to prepare MPPB. The grafting fraction of MA was measured by chemical titration and plotted as a function of the butadiene content, as shown in Figure 4. As the content of butadiene was increased, the grafting fraction of MA increased linearly. When the PPB contained 5.2% butadiene, the grafting fraction was found to be about 12%, four times of that of homopolypropylene (∼ 3%).

Mechanical properties of the composites

The impact and tensile strengths of the composites with different contents of MPPB were measured and plotted as a function of MPPB content in the composite, and the results are shown in Figure 5. As the content of MPPB was increased, the impact strength of the composite was improved linearly. When the composite contained 10-phr MPPB, the impact strength was increased by 20%. The reason for this might have been that the MPPB increased the compatibility of the components of the composite. Additionally, the formation of the β-phase crystallization of PP in the composite, which is discussed later, is
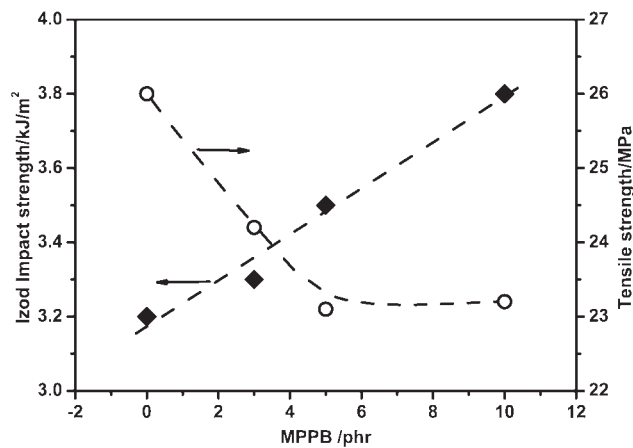
Figure 5 Impact strength and tensile strength of the composites (the dashed lines are guides for eyes).

Figure 6 XRD patterns of the PP/SBS/OMMT composites with different contents of MPPB: (a) 0, (b) 3, (c) 5, and (d) 10 phr.

also known to enhance the impact properties of the material.[14] However, the tensile strength was found to have dropped by 10% when the composite contained 5-phr MPPB, whereupon no further decrease was observed as the concentration of MPPB was increased. The drop in the tensile strength was interpreted in terms of the onset of the β-phase crystallization of PP[15] and the inferior compatibility of the composite at a low concentration of compatibilizer. When the MPPB concentration reached a critical concentration (5 phr), the compatibility of the composite was improved, and the tensile strength became constant.

XRD measurements

Figure 6 demonstrates the XRD patterns of the composite with different contents of MPPB. In the absence of MPPB, only the α-phase crystal phase of PP was formed.[16] However, after the addition of MA-modified PPB, a new peak at $2\theta = 16.0°$ and a slight
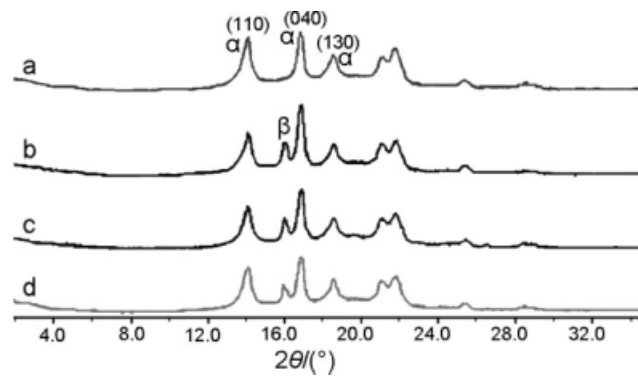
increase of the peak at $2\theta = 21.1°$ relative to the peak at about $21.8°$ were observed; these were attributed to the β-phase crystallization of PP.[17] The introduction of MPPB thus caused the formation of hexagonal β-phase crystals, which are known to have a greater mechanical absorption capacity than their α-crystalline counterparts. Therefore, the presence of the β-phase crystals in the composite contributed to the increase of the impact strength.[17,18] No significant difference in the XRD pattern was observed between the composites containing different proportions of MPPB, however.

POM measurements

The crystal morphology of the composite in the absence and presence of MPPB was investigated by POM, as shown in Figure 7. In both cases, the film was polycrystalline. In the absence of MPPB, large spheroidal microcrystallites were observed. In the case of the composite containing MPPB, the density of the crystallite nuclei was significantly increased,
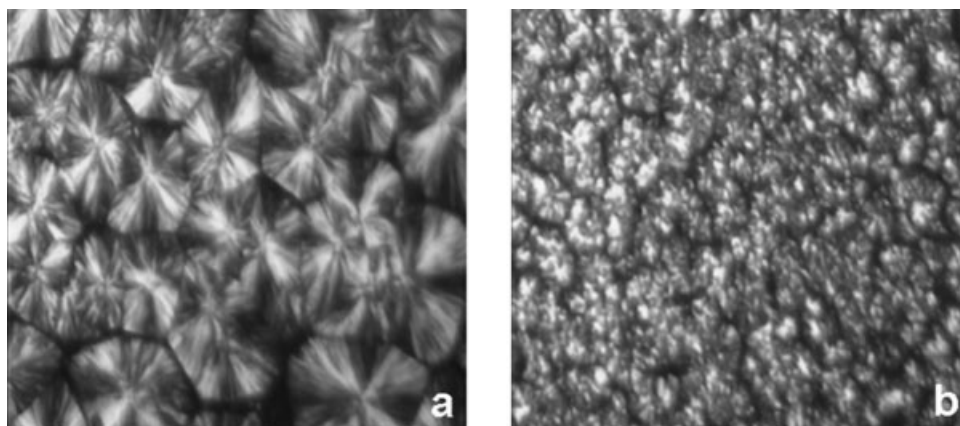

Figure 7 POM images of the PP/SBS/OMMT composites with or without MPPB: (a) PP/SBS/OMMT ($\times$200) and (b) PP/SBS/OMMT/MPPB ($\times$200).
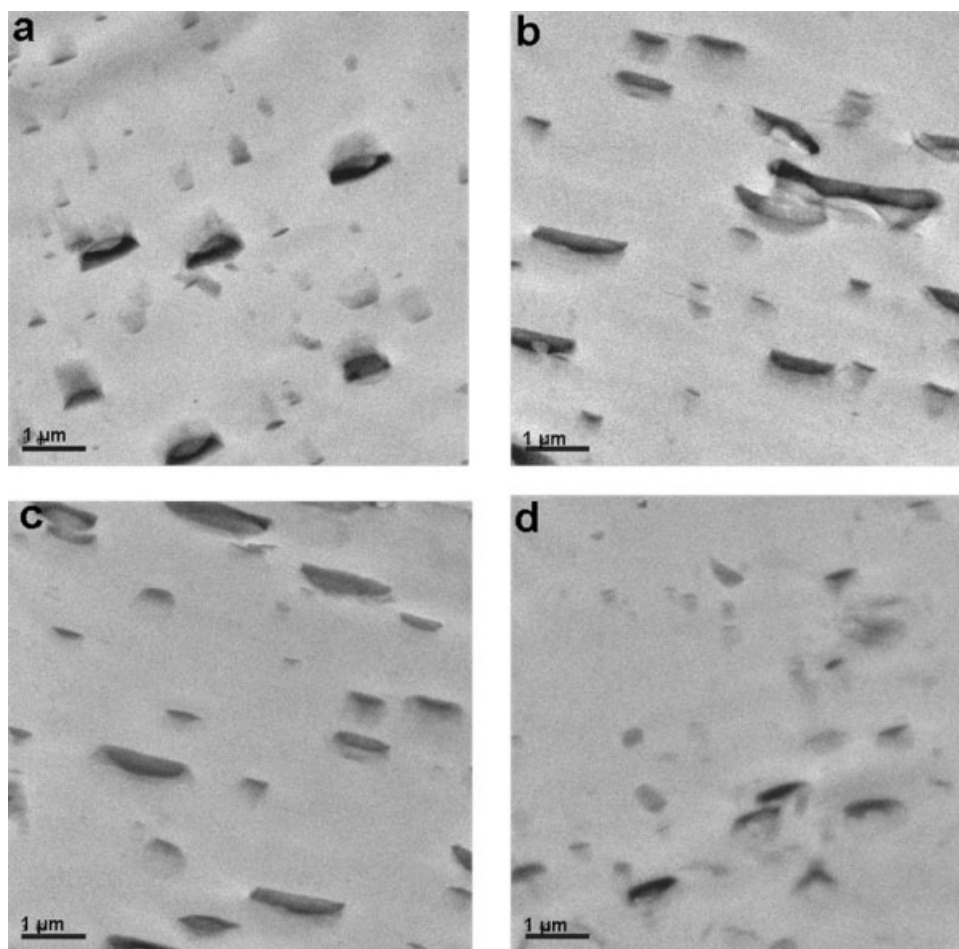
Figure 8 TEM images of the PP/SBS/OMMT composites with different contents of MPPB: (a) 0, (b) 3, (c) 5, and (d) 10 phr.

whereupon the spherulites impinged each other, and the spherulite growth stopped at an early stage, which resulted in smaller-sized, less well-defined domains. This may have been due to the nucleation of β-phase domains by the MPPB dispersed in the PP, as demonstrated by XRD.

TEM measurements

The effect of MPPB on the dispersion of OMMT in the composite was investigated by TEM. The images of the composites with different contents of MPPB are shown in Figure 8. The dark particles in the images corresponded to the OMMT particles. As the OMMT has a stratiform structure, the color of the particles in the images indicates the thickness of the OMMT layers. In the absence of MPPB, most OMMT particles were around 1 μm in size and exhibited a darker color and clear boundary with the matrix. For 3-phr MPPB, the image was similar than that at 0 phr, which indicated no significant change in the morphology. With increasing MPPB concentration, however, it was clear that the color of

the particles became lighter as the OMMT exfoliated. In the composite containing 10-phr MPPB, most of the OMMT particles were well dispersed in the matrix, and the boundary between the OMMT and matrix became indistinct.

SEM images

The impact-fractured surfaces of the samples were characterized by SEM, as shown in Figure 9. It was clear that the fracture surfaces of the composites with different contents of MPPB were significantly different. In the absence of MPPB, the surface was one of a brittle fracture, and a relatively flat surface was observed. A few SBS rubber particles were found in the surface, but the sizes varied significantly from several micrometers to several hundreds of nanometers. In the presence of MPPB, the fracture surface became rugged. The number of the rubber particles exposed at the surface increased, but the sizes decreased and became more uniform. In the composite that contained 10-phr MPPB, nearly all of the SBS particles had a size on the order of about
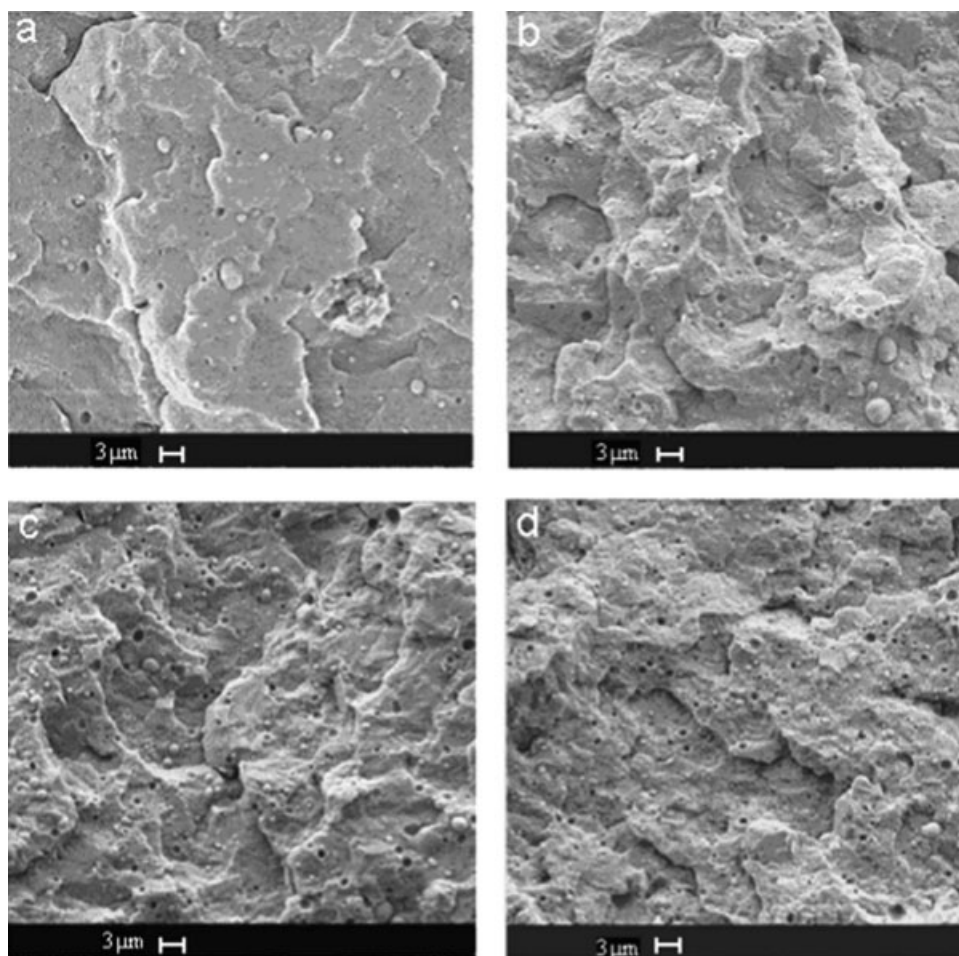
Figure 9 SEM images of the PP/SBS/OMMT composites with different contents of MPPB: (a) 0, (b) 3, (c) 5, and (d) 10 phr.

0.1–0.2 μm; this indicated an improved compatibility of the components in the composite.

Overall, the impact strength of the material was significantly improved by the addition of MPPB to the composite. XRD indicated that this was the result of an increased β-phase content, which is known to improve the impact strength. The large spherulite crystals were replaced by smaller crystallites, presumably seeded by the MPPB content. TEM indicated a better exfoliation of the OMMT, and SEM demonstrated a more uniform distribution of the rubber SBS particles in the presence of MPPB. Such a distribution of rubber particles in plastic matrices is known to improve impact strength. However, as shown in Figure 5, the tensile strength of the material was reduced from about 26 MPa for the PPB/SBS/OMMT composite to about 23.5 MPa upon the addition of 5-phr MPPB, which was understandable because of the dispersion of SBS rubber particles in the plastic matrix and the formation of the β-phase crystallization of PP.[15]

CONCLUSIONS

PPB was used to prepare a MA-functionalized polymer. The use of PPB significantly improved the grafting fraction and prevented degradation. The application of this grafted copolymer in the PP/SBS/OMMT composites improved the compatibility of the components, and the impact strength of the material was improved by 20% with the addition of 10-phr MPPB.

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