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Synthesis of Maleic Anhydride grafted polypropylene-butadiene copolymer and its application in PP/OMMT/SBS composite as compatibilizer

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ABSTRACT

Maleic Anhydride (MA) grafted propylene-butadiene copolymer (PPB) was prepared. FTIR and ¹H-NMR results indicated that the MA molecules reacted with the double bond in the butadiene unit of the PPB and the grafting percentage increased with the butadiene content in the initial copolymer. GPC results showed the introduction of butadiene in the copolymer prevented the degradation of the PPB. The MA-g-PPB (MPPB) was applied in PP/SBS/OMMT composite as compatibilizer. In the presence of 10phr MPPB, the impact strength of the composite was improved by ~20%. XRD patterns indicated the formation of β -phase crystallization of polypropylene in the presence of MPPB and a significant decrease of the spherulite size was observed. TEM images showed that the OMMT was better dispersed in the matrix upon the inclusion of MPPB. Better distribution of the rubber-phase and rugged fracture surface were

observed in SEM images as the MPPB proportion was increased.

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

1. 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 low cost. However, critical disadvantages for wider application of this material are its low impact strength and non-polar and inert nature which result in difficulties in blending, coating and inking¹. Functionalization of PP with polar molecules is the most attractive method to improve the properties of this material². 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 polarity⁵, compatibility and interaction of polypropylene with other materials^{6,7}. The grafting reaction normally is carried out by a radical mechanism¹: Peroxide initiator provides radicals, some of which abstract hydrogen from the PP tertiary carbon to form PP macroradicals. However, due to the inert nature of the PP structure and difficulty of control of the free radical reaction, the grafting reaction is normally accompanied by several undesirable side reactions, such as β -scission, chain transfer, and coupling, resulting in the degradation of the material³. The grafting percentage of MA-g-PP is normally around 5% (w/w)^{8,9}.

In this work, a copolymer of propylene and butadiene (PPB) was employed to enhance the reactivity of polypropylene and control the reaction position of the grafting. FTIR and ¹H-NMR were employed for the characterization of PPB before and after the MA grafting. The MA-g-PPB (MPPB) was then applied in the composite of

polypropylene / styrene-butadiene-styrene triblock copolymer / organophilic montmorillonite (PP/SBS/OMMT) as 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 of PP in the composite with/without MPPB. The dispersibility of OMMT in the composites was characterized by Transmission Electron Microscope (TEM). Scanning Electron Microscopy (SEM) was employed to investigate the compatibility of the PP plastic phase and SBS rubber particles.

2. Experimental

2.1 Materials

Both the butadiene-propylene copolymer (PPB) and homo-polypropylene (PP) used for grafting were synthesized in a 1L stainless steel polymerization reactor, in Hexane solution. MgCl₂-supported Ziegler-Natta (Z-N) was used as catalyst¹⁰, and triethylaluminium (1mol/L in hexane) as co-catalyst. The butadiene content in PPB was measured by ¹H-NMR (1, 2-Bd% = 0.67% mol/mol, 1, 4-Bd% = 6.08% mol/mol). Maleic anhydride (Tianjin Fuchen Chemical plant, Analytical Reagent grade), benzoyl peroxide (Beijing Xingjin Chemical plant, Chemical grade) and 1, 2-dimethylbenzene (Beijing Changhai Chemical Plant, chemical grade), Antioxidant 1010 (Beijing Stable Chemical Co., Ltd, industrial grade) were used as purchased.

Polypropylene (Z30S) and SBS (1310) used in the composite were purchased from Maoming Petrochemical Corporation, and Yanshan Petrochemical Corporation, respectively. OMMT (NB901) was provided by Huate Chemical Co., Ltd, and used as

received.

2.2 Preparation of maleic anhydride grafted PPB (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 24h, to remove the unreacted maleic hydride and then dried in a vacuum oven at 90°C. All the reactions were carried out under the same conditions and same amount of MA.

2.3 Preparation of PP/OMMT/SBS composite

PP/OMMT/SBS composites with and without MPPB were first blended in a twin-screw extruder (HAAKE Rheometer). The Screw temperature distribution varied from 160°C, 170°C, 180°C, 190°C, 200°C, to 205°C. A series of composites containing different proportions of MPPB were prepared. The compositions are shown in Table 1.

2.4 Measurements and Analytical characterization

2.4.1 FTIR spectroscopy

FTIR spectra of the samples were recorded with a Nicolet 560 FTIR spectrometer in the range of 2000cm⁻¹-400cm⁻¹ with an averaging of 32 scans at a resolution of 4 cm⁻¹. The sample was prepared using the KBr pellet technique.

2.4.2 ¹H-Nuclear magnetic resonance (¹H-NMR)

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

2.4.3 High Temperature Gel Permeation Chromatography (HTGPC)

The molecular weight and molecular weight distribution of the samples were measured by High Temperature Gel Permeation Chromatography (HTGPC) (PL GPC - 220, Waters) at 135°C using 1, 2-dimethylbenzene as solvent. Polystyrene was employed as the standard ($K = 1.38 \times 10^{-4}$, $\alpha = 0.70$).

2.4.4 Determination of 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 anhydride groups into carboxylic acid. Excess alcoholic KOH (0.1N KOH in ethanol), was added to the hot solution. After boiling for 1h, acidified isopropanol (0.1N HCl in isopropanol) was used to titrate the above solution using 1% thymol blue in dimethylformamide as an indicator. The grafted percentage can be established using

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

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 isopropanol, V_0 is the volume (mL) of acidified isopropanol used to titrate the blank sample, V is the volume (mL) of acidified isopropanol used to titrate the sample, m is the weight (g) of the sample.

2.4.5 Mechanical properties

The extrudates in 2.4 were pelletized and then molded into dumbbell-shaped tensile

bars (GB1040----1992, 150 mm × 10 mm × 4 mm) and rectangular bars (ISO179----1999, 80mm×10mm× 2mm). The measurements of the mechanical properties were carried at 25°C, humidity 65%. The tensile property was measured according to ASTM D638--2003, using an Instron 5500 Series Mechanical Tester. Impact strength measurement was carried out by a CEAST Resil impactor.

2.4.6 X-ray Diffraction (XRD) measurement

XRD measurements were carried out with a Rigaku Geiger Flex D/max_RB X-ray diffractometer, CuK radiation, scanning at rate 2°/min.

2.4.7 Polarized Optical Microscopy (POM) analysis

POM analysis was performed in a Hot Stage Polarizing Microscope (Mettler-Toledo FP-900/Leica DMLP). The samples were prepared by recrystallization at 110°C for 1h after melting at 200°C for 15min.

2.4.8 Transmission Electron Microscope (TEM) measurement

The dispersity of OMMT in the matrix was evaluated by TEM (Tecnai™ G2 20). Samples were prepared by frozen section procedure.

2.4.9 Scanning Electron Microscope (SEM) measurement

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

3. Results and discussion

3.1 FTIR measurements

Figure 1 shows the FTIR spectra of PPB and MPPB. It was clearly seen that after grafting, two new intensive absorption peaks were observed at 1779cm^{-1} and 1861cm^{-1} , corresponding to the C=O vibrational stretch of the carbonyl group in maleic anhydride^{4,11}. As presented by Zhao *et al*¹², the sample has been extracted and the unreacted maleic hydride removed, the new absorption peaks indicate that the maleic anhydride has been grafted onto the PPB molecular chain.

3.2 ¹H-NMR analysis

In order to investigate the location of the grafting reaction, the PPB before and after grafting were both characterized by ¹H-NMR, shown in Figure 2. In the spectrum of PPB, a medium strength feature around 5.50ppm as well as a very weak feature at ~5.00ppm can be observed, which were assigned to the hydrogen in the double bond of 1, 4-addition-butadiene (-CH=CH-) and 1,2-addition-butadiene (=CH₂) units¹³. The intensity of the peaks was found to be significantly different, indicating that 1, 4-addition of butadiene was crucial in 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 5.50ppm has totally disappeared, indicating that all the double bonds in the 1, 4-butadiene units have been consumed in the grafting reaction. However the peak at 5.0ppm was found to show no significant change after the grafting reaction, implying that the double bond in the 1, 2-addition unit of butadiene was not involved in the grafting reaction. The reason could be attributed to the low content of 1, 2-addition butadiene, which was only 10% of all

the double bonds. It is also interesting to notice that the intensity of peak at 2.12ppm, corresponding to the saturated hydrogen of butadiene (-CH₂-), has obviously decreased. From these changes, it can be concluded that the MA molecules reacted with the double bond in the butadiene unit of the PPB, especially the 1, 4-butadiene addition unit, thereby preventing the β-scission of the main copolymer chain. The proposed reaction mechanisms for PP and PPB reaction with MA are shown in Scheme 1, as has been previously reported by Zhao *et al* ¹².

Due to the inert nature of polypropylene, 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 copolymer of propylene and butadiene is used in the free radical reaction, the macroradicals are obtained by opening the double bond in the 1, 4-butadiene units, avoiding the β-scission of the main copolymer chain. Thus the molecular weight should remain the same after grafting.

3.3 GPC measurements

The molecular weight distribution of the PP (a) and PPB (b) before and after grafting with MA was investigated by GPC, as shown in Figure 3. It can be clearly seen that after the grafting reaction, PP underwent a dramatic degradation. The number molecular weight of PP before and after grafting reaction shifted from 10^{4.6} (39,800 g/mol) to 10^{4.2} (15,800 g/mol), a decrease of 60%. However no such significant difference was observed between the molecular weight distribution of PPB before and after grafting. The number molecular weight shifted from 10^{4.8} to 10^{4.7} i.e. by 20%. Thus, in comparison to the PP grafting reaction, minimal chain scission is observed,

supporting the proposed reaction mechanism of Scheme 1.

3.4 Effect of butadiene effect on the grafting fraction

In order to investigate the effect of butadiene content on the grafting fraction of MA, a series of PPB samples with different butadiene content was used to prepare MPPB. The grafting fraction of MA was measured by chemical titration and plotted as a function of the butadiene content, shown in Figure 4. It was seen that as the content of butadiene was increased, the grafting fraction of MA increased linearly. When the PPB contains 5.2% butadiene, the grafting fraction was found to be ~ 12%, 4 times of that of homo-polypropylene (~ 3%).

3.5 Mechanical properties of the composites

The impact and tensile strength of the composites with different content 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 10phr MPPB, the impact strength was increased by 20%. The reason for this might be due to the MPPB increasing the compatibility of the components of the composite. Additionally the formation of β -phase crystallization of PP in the composite which will be shown below was also known to enhance the impact property of the material¹⁴. However the tensile strength was found to have dropped by 10% when the composite contained 5phr MPPB whereupon no further decrease was observed as the concentration of MPPB was increased. The drop of the tensile strength is interpreted in

terms of the onset of β -phase crystallization of PP¹⁵ and the inferior compatibility of the composite at low concentration of compatibilizer. When the MPPB concentration reaches a critical concentration (5phr), the compatibility of the composite was improved and the tensile strength becomes constant.

3.6 XRD measurements

Figure 6 demonstrates the XRD patterns of the composite with different content of MPPB. It was seen that in the absence of MPPB only the α -phase crystal phase of polypropylene was formed¹⁶. However, after the addition of maleic anhydride modified PPB, a new peak at $2\theta = 16.0^\circ$ and a slight increase of the peak at $2\theta = 21.1^\circ$ relative to the peak at $\sim 21.8^\circ$ are observed, attribute to the β -phase crystallization of polypropylene¹⁷. The introduction of MPPB thus causes the formation of hexagonal β -phase crystals, which are known to have greater mechanical absorption capacity than their α -crystalline counterparts. Therefore, the presence of the β -phase crystalline in the composite contributes 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.

3.7 POM measurements

The crystal morphology of the composite in the absence and presence of MPPB was investigated by Polarized Optical Microscopy, shown in Figure 7. In both cases, the film is polycrystalline. In the absence of MPPB, large spheroidal microcrystallites were observed. In the case of the composite containing MPPB, the density of crystallite

nuclei was significantly increased, whereupon the spherulites impinge each other and the spherulite growth stops at an early stage, resulting in smaller sized less well defined domains. This may be due to the nucleation of β -phase domains by the MPPB dispersed in the PP, as demonstrated by XRD.

3.8 TEM measurements

The effect of the MPPB on the dispersion of OMMT in the composite was investigated by TEM. The images of the composites with different content of the MPPB were shown in Figure 8. The dark particles in the images correspond 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 are around 1 μ m in size and exhibit a darker color and clear boundary with the matrix. For 3phr MPPB, the image is similar to that at 0phr, indicating no significant change in morphology. With increasing MPPB concentration however, it can clearly be seen that the color of the particles becomes lighter as the OMMT exfoliates. In the composite containing 10phr MPPB, most of the OMMT particles were well dispersed in the matrix and the boundary between the OMMT and matrix becomes indistinct.

3.9 SEM images

The impact fractured surfaces of the samples were characterized by SEM, shown in Figure 9. It can clearly be seen that the fracture surfaces of the composites with different content of MPPB are significantly different. In the absence of MPPB, the surface is one

of a brittle fracture and a relatively flat surface is observed. A few SBS rubber particles were found in the surface, but the sizes vary significantly from several micrometres 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 which contains 10phr MPPB, nearly all the SBS particles had size of order $\sim 0.1\text{-}0.2\mu\text{m}$, indicating improved compatibility of the components in the composite.

Overall, the impact strength of the material has been significantly improved by the addition of MPPB to the composite. XRD indicates that this is the result of an increased β -phase content, which is known to improve the impact strength. The large spherulite crystals are replaced by smaller crystallite, presumably seeded by the MPPB content. TEM indicates a better exfoliation of the OMMT and SEM demonstrates 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 observed in Figure 5, the tensile strength of the material has been reduced from ~ 26 MPa for the PPB/SBS/OMMT composite to ~ 23.5 MPa upon addition of 5phr MPPB, which is understandable because the dispersion of SBS rubber particles in the plastic matrix and the formation of β -phase crystallization of PP¹⁵.

4. Conclusions

A copolymer of polypropylene and butadiene (PPB) was used for preparing a maleic anhydride functionalized polymer. The use of PPB significantly improved the grafting fraction and prevented degradation. The application of this grafted copolymer in 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 10phr MPPB.

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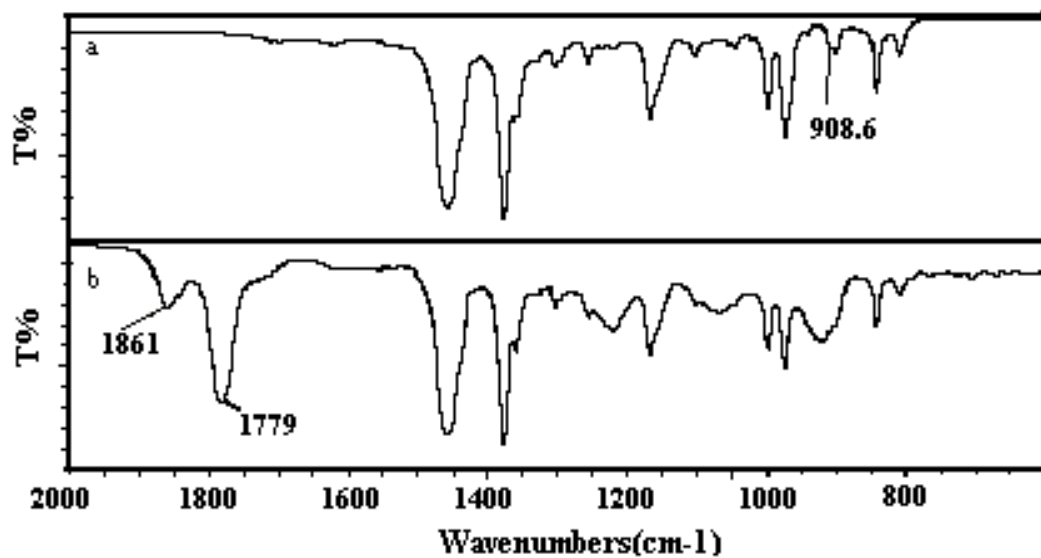


Figure 1 FT-IR spectra of PPB (a) and MPPB (b) from 2000 cm⁻¹ to 600 cm⁻¹ (MA = 14 wt%)

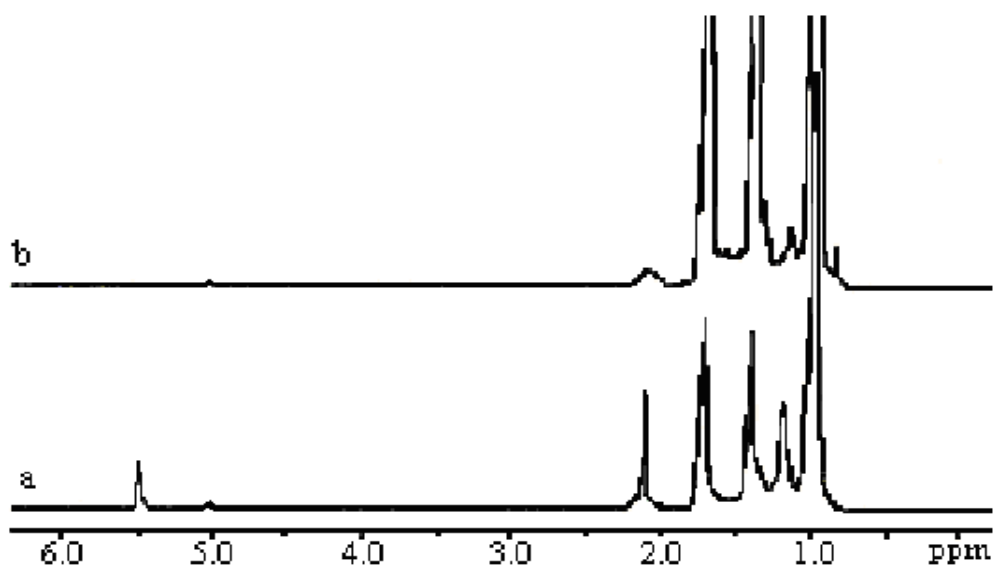


Figure 2 ¹H-NMR spectra of PPB (a) and MPPB (b)

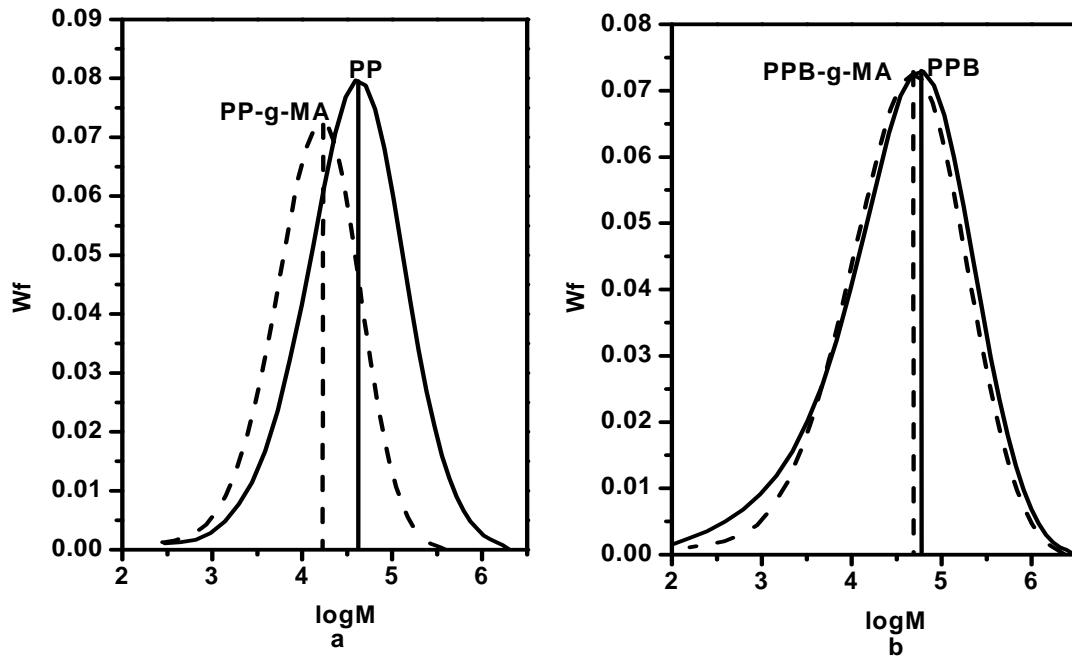


Figure 3 Molecular weight distributions of the PP (a) and PPB (b) before and after grafting with MA

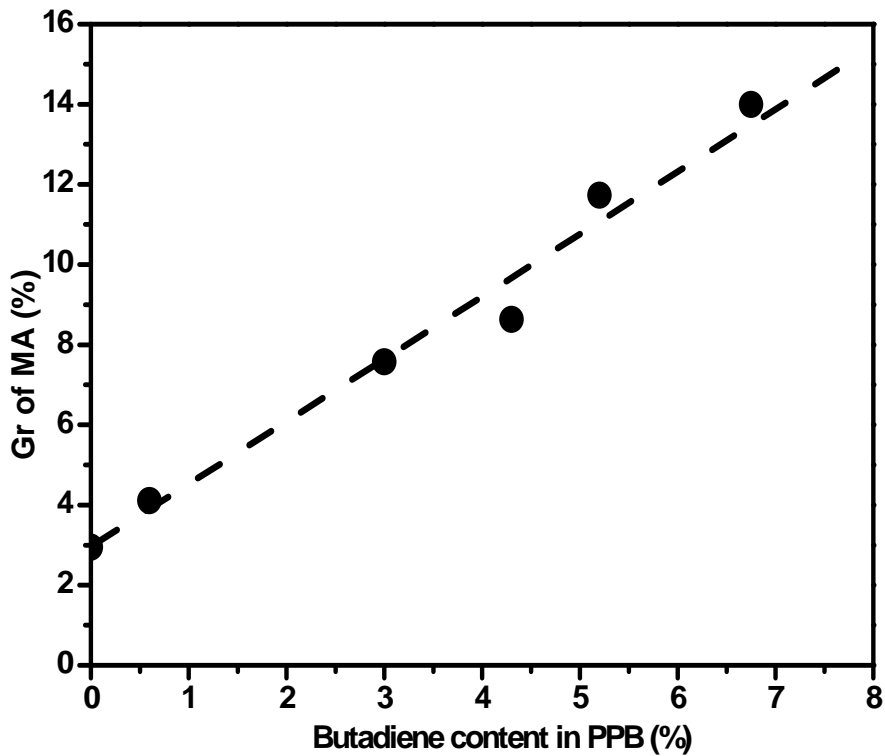


Figure 4 Grafting percentage of MA as a function of butadiene content in PPB

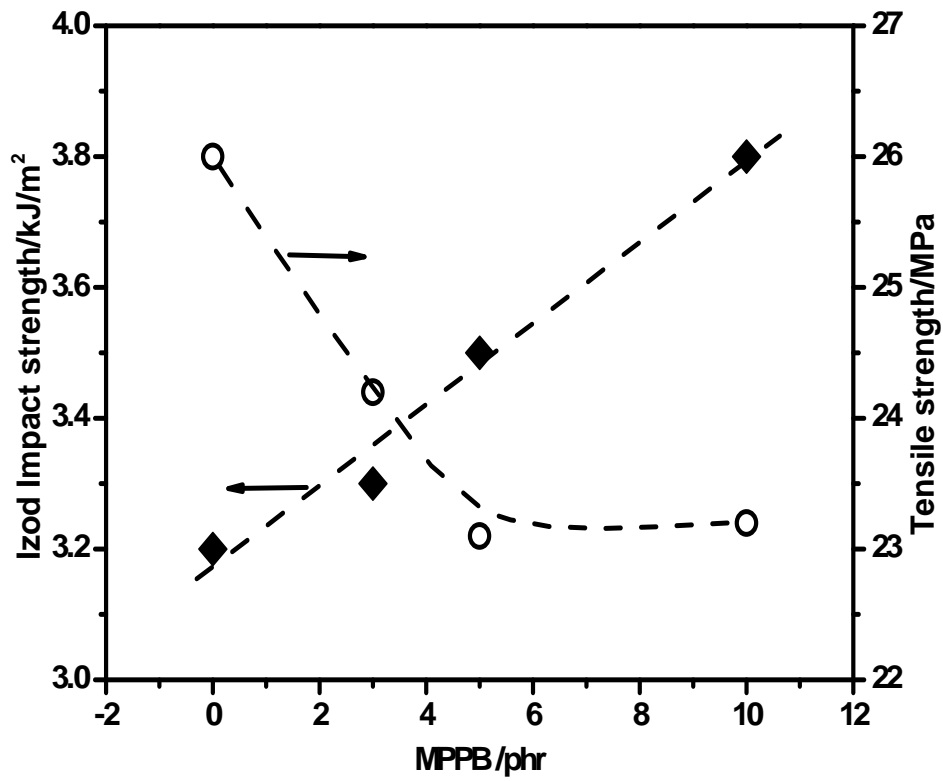


Figure 5 Impact strength and tensile strength of the composite
(The dashed lines are guided by eyes)

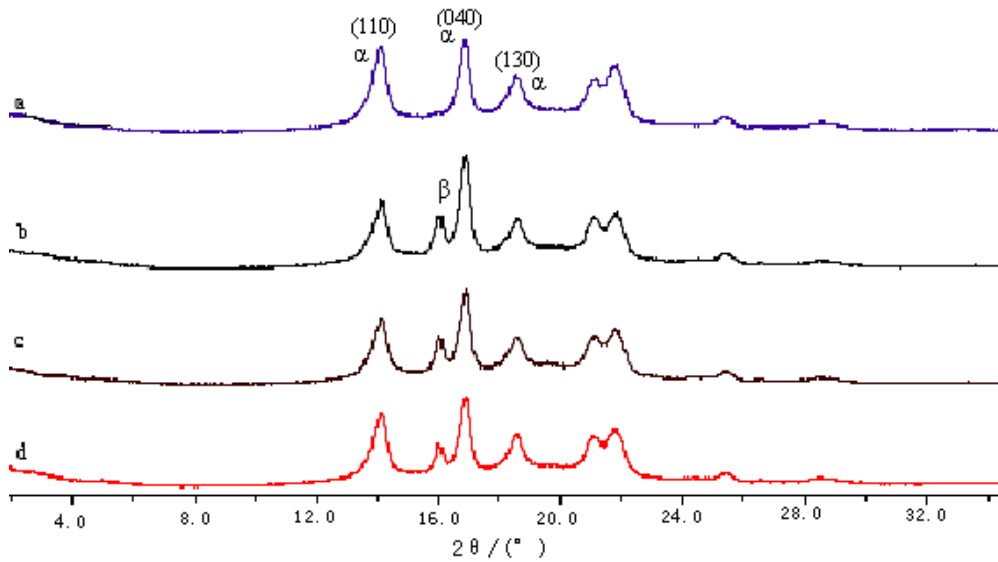
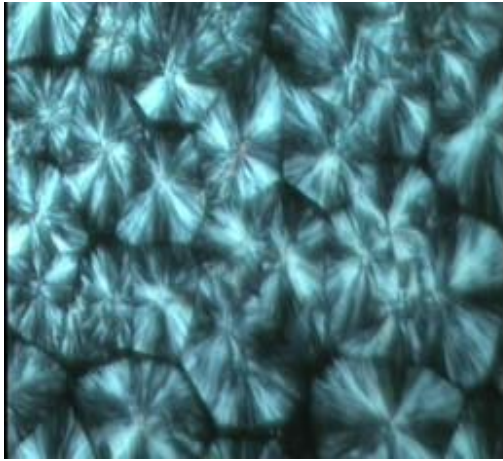
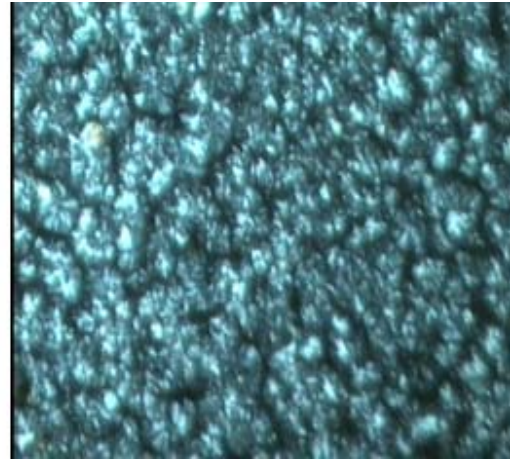


Figure 6 XRD patterns of PP/SBS/OMMT composite with different content of MPPB, (a) 0 phr, (b) 3phr, (c) 5phr, (d) 10phr



PP/SBS/OMMT($\times 200$)



PP/SBS/OMMT/MPPB ($\times 200$)

Figure 7 POM images of PP/SBS/OMMT composite with/without MPPB

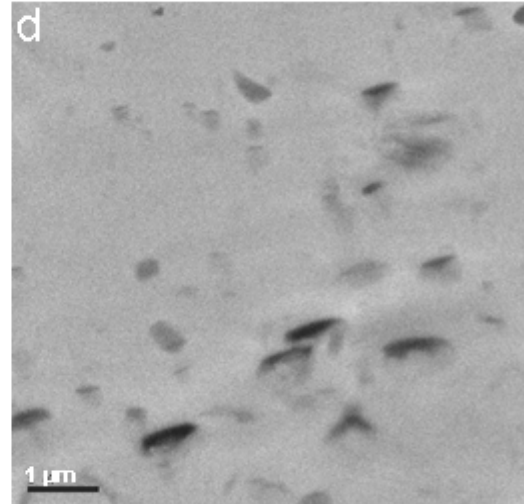
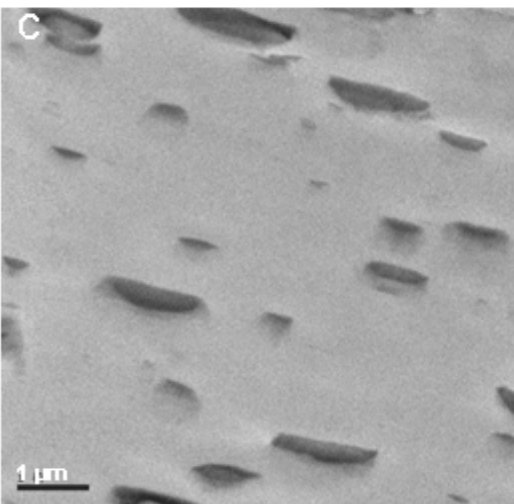
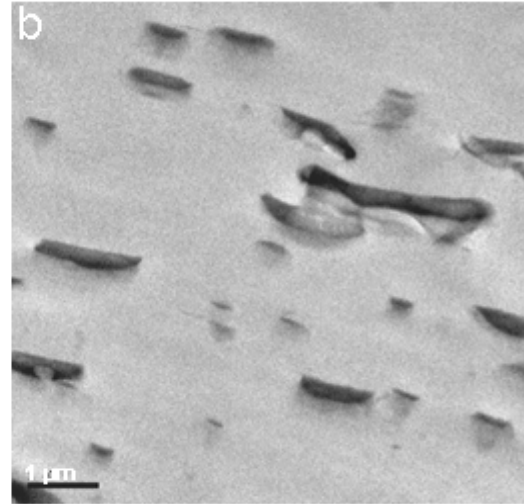
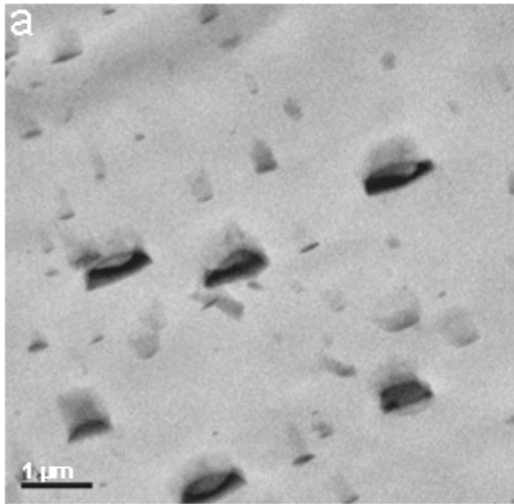


Figure 8 TEM images of PP/SBS/OMMT composite with different content of MPPB, (a) 0 phr, (b) 3phr, (c) 5phr, (d) 10phr

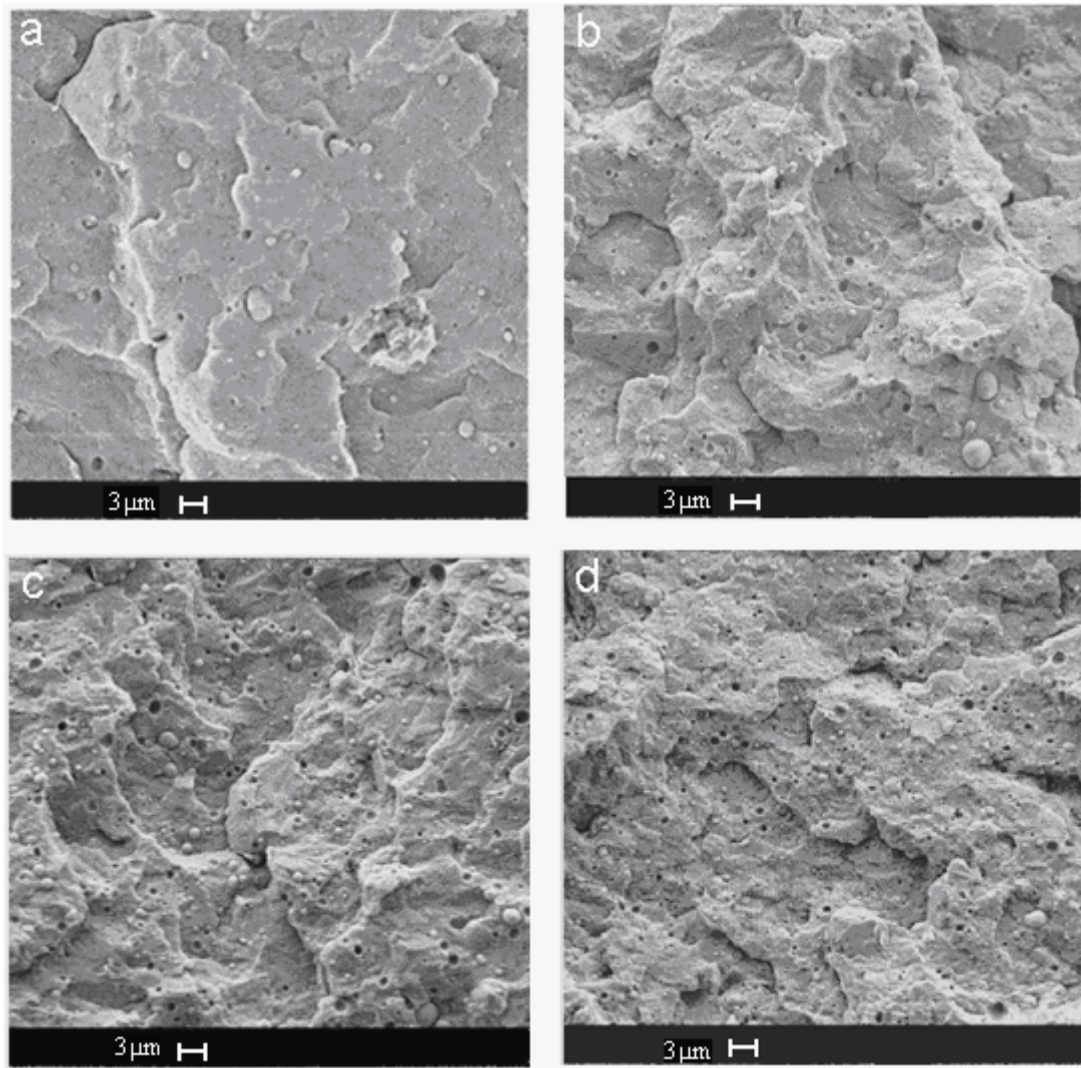
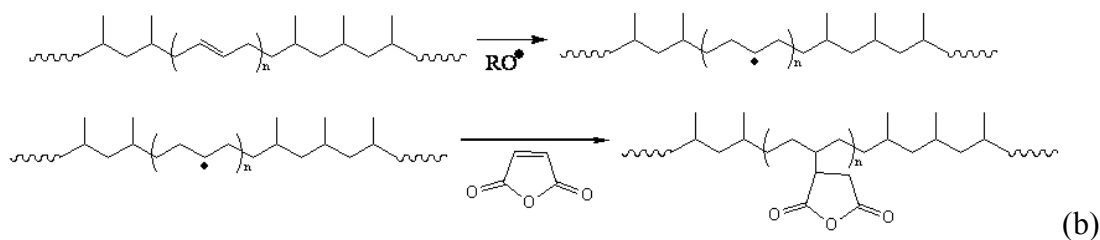
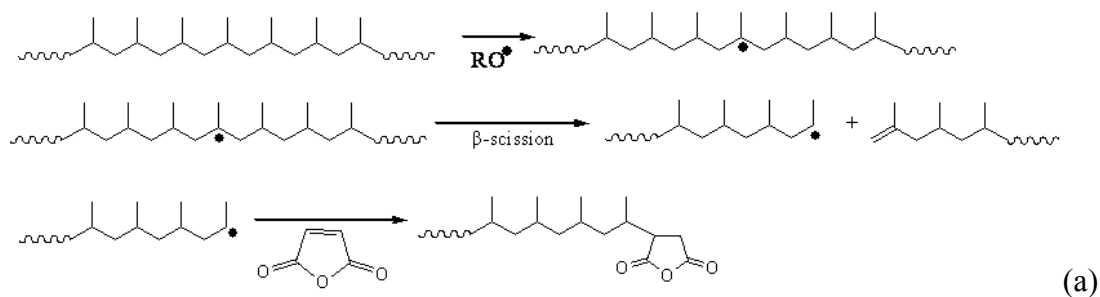
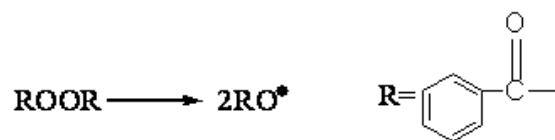


Figure 9 SEM images of PP/SBS/OMMT composite with different content of PPB-g-MA, (a) 0 phr, (b) 3phr, (c) 5phr, (d) 10phr



Scheme 1 Proposed reaction mechanisms for grafting maleic anhydride onto polypropylene (a) and polypropylene-butadiene copolymer (b)

Table 1 Composition of the PP/SBS/OMMT/MPPB composite

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 of the components, the unit is parts per hundred parts of PP, phr.