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Study on Reactive Blend Systems of PA1010/ABS/PP

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Abstract. The impacts of multi-monomers melt grafting blends of maleic anhydride(MAH) and Styrene (St) on the crystallization behavior, morphology and mechanical properties of PA1010/ABS/PP blends were studied through the methods of SEM,themal analysis, mechanical properties analysis. The results showed that the graft copolymer generated in situ by the anhydride groups of g-PP and the amino end of PA1010 reduced the interfacial tension of blends efficiently, and the interaction of the styrene groups of the graft copolymer and ABS is helpful to improve the compatibility of three components during the melt blending process. The size of dispersed phase in blends is reduced obviously and the mechanical properties have a great improvement when the percentage of g-PP in the PA1010/ABS/PP blends increases to 10%. The tensile strength of the compatibilized PA1010/ABS/PP blends is improved by 11.7%,and the impact strength and elongation at break are increased 4 times and 4.9 times, respectively.

Introduction

PA1010/ABS/PP is an incompatible system. Some researchers found that a small amount of St was helpful to reduce the degradation of PP in the research of melt grafting PP[1-3]. Multi-monomer melt grafting is prepared using two or more monomers(including grafted monomers and assistance monomers) to implement the melt grafting method. This method can improve grafting rate while maintaining the properties of the grafting base[4-6]. The utilization of grafted products in the blend response has a good result to the compatibilization of blends system[7-8]. In this article, g-PP prepared with PP S1003 melt-grafted by MAH and St is used as compatibilizer of PA1010/ABS/PP, then form PA1010/ABS/PP blends. Melt mobility, the crystallization behavior, morphology and mechanical properties can be studied.

Experimental

Materials PA1010(PA1010was purchased from Shanghai Celluloid Factory in China); ABS(No:H-08, products of rubber synthetic factory of Lan zhou Petrochemical Company); PP(No:S1003,MFR 3.0 g/10 min, Made by Beijing Yanshan Petrochemical Company); MAH(Beijing Yili Fine Chemicals Co., Ltd); St, Tianjin Chemical Reagent Factory; DCP, Fushun Chemical Plant; g-PP made by self.

Sample preparation PP, MAH, St and DCP were mixed in set proportion,The melt grafting reaction conducted by Single screw extruder(Screw diameter Φ=30 mm,L/D=25)at 180°C. Reaction products were purified for analytical testing. PA1010, ABS, PP and g-PP were dried prior to use, and then mixed them in set proportion, conduct the melt extrusion with the SHC-35 Twin-screw extrusion machine(Screw temperature210~230°C) granulate, then the samples for mechanical properties tests were prepared by ZG-630 injection machine.

Characterization To the g-PP graft, after reflux of Xylene, use excessive acetone to precipitate it, then filter, dry it to get the purified grafting products. The purified graft can be analysted by Nicolet 560 Infrared spectrometer after the film formation at 220 ℃ and high pressure.

According to the ASTM1238 standard, we can use XRZ-400-1 Melt Flow Rate Tester(Jilin University Teaching Instrument Factory) to test the melt flow rate(MFR)at 230°C, 2.16kg test load.

The crystallization behavior and melting behavior of sample with DSC-60 Differential scanning calorimetry were tested. The temperature of sample increases to 250°C at a speed of 50°C/min, then keep it for 5 minutes, then decrease to room temperature at a speed of 10°C/min, record the cooling curve; after increase the temperature to 250°C again at a speed of 10°C/min, then record the heating curve.

Observe the brittle samples frozen with liquid nitrogen by SEM .After etched the section by Methylene chloride and xylene, observe it With a JSM-7401F type high resolution emission field scanning electron microscopy(SEM).

Use GOTECH-2000 tensile testing machine to test the tensile and bending properties follow the ASTM D638 and ASTM D790 standards, tensile and bending speed were 50 mm/min and 10 mm/min respectively. Izod Notched impact strength can be tested by XJUD-5.5 Impact testing machine(Chengde Golden Construction detection equipment Co.Ltd) follow the ASTM D256 standard .The sample for test is placed for 24h under room temperature, then take at least 5 in each group to calculate the average.

Results and Discussion

Characterization of grafting ratio and determination of percentage of multi-monomer The fixed mass ratio of MAH was 3% of PP, and the DCP mass ratio was 0.03% of PP. The mass ratio of MAH: St was 1:0.5, 1:1 and 1:2, respectively (Marked as 1#, 2#, 3#PP-g-(MAHco-St, respectively). Figure 1 is the infrared spectra of a purified grafted product .In the figure 1, 1782 cm^{-1} is the carbonyl absorption peak of the anhydride ring, 702 cm^{-1} is the characteristic absorption peak of the benzene ring. 2723 cm^{-1} is the characteristic absorption peak of the methyl, we do not find any changes of the methyl during the reaction, therefore, we put it as the internal standard peak of quantitative analysis .we can carry on the area integral of the carbonyl absorption peak of the anhydride ring at 1782 cm^{-1} and the characteristic absorption peak of the methyl at 2723 cm^{-1},the ratio of peak area is the ratio of absorbance of the two groups(Ra), reflects the relative size of the amount of MAH grafted on PP, that's the relative graft ratio of MAH, and denoted Ra, MAH. We continue to carry on the area integral of the characteristic absorption peak of the benzene ring at702 cm^{-1} and the characteristic absorption peak of the methyl at 2723 cm^{-1}, the ratio of peak area is the ratio of absorbance of the two groups(Ra), reflects the relative size of the amount of St grafted on PP, that' s the relative graft ratio of St ,and denoted Ra, St .As can be seen from figure 1, in the spectra of PP-g-(MAH-co-St), the carbonyl absorption peak at 1782 cm-1 appeared and we can confirm that MAH is grafted to the PP.The Ra, MAH of different ratio of graft is showed in table 1, we can see that the relative graft ratio of MAH increased with the ratio of St, the increase of St in the proportion has obvious promotion on MAH graft .But when the mass ratio of MAH:St is 1:1, the relative graft rate of St is higher, meanwhile, the relative graft rate of MAH has small changes when the mass ratio of MAH:St changes from 1:1 to 1:2 . So we choose 2# graft as the compatibilizer of PA1010/ABS/PP blends.

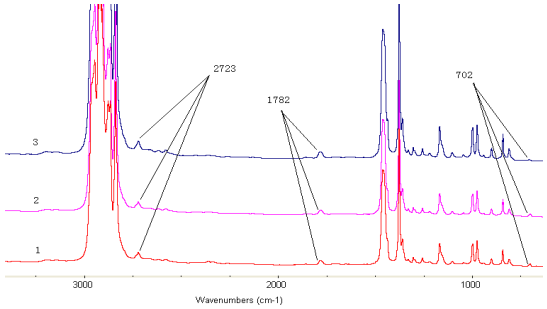

Fig.1 FT-IR spectra of PP-g-(MAH-co-St)
1-(MAH:St=1:0.5), 2-(MAH:St=1:1), 3-(MAH:St=1:2)

Table 1 The Ra,MAH and the Ra,St of different mass ratio of MAH:St

MAH:St	Ra,MAH	Ra, St
1(1:0.5)	1.522	0.120
2(1:1)	2.554	0.131
3(1:2)	2.611	0.055

Phase morphology of blends In Figure 2, (a) and (b) are the SEM photos of PA1010/ABS/PP/ PP-g-(MAH-co-St)(60/20/20/0)and PA1010/ABS/PP/ PP-g-(MAH-co-St)(60/20/20/10)crisp cross-sections which were etched by dichloromethane.We can see that the dispersed ABS,PP showed oval ball, ABS is the etched section, and PP is the raised section. The dispersed phase of PA1010/ABS/PP simple blends is large and distributed unevenly, and shows very poor dispersion, so the dispersed phase system is obvious .The size of dispersed phase decreased obviously when added PP-g-(MAH-co-St) into PA1010/ABS/PP blends(Figure 2(b)). Phase morphology of the blends improved significantly, the size of dispersed phase reduced obviously, particle size was distributed evenly. So we can see that PP-g-(MAH-co-St) reduced the interfacial tension between PA1010 matrix and ABS, PP dispersed phase, and caused the dispersed phase particle to refine and disperse because of thermal shear stress during the melting process, we can get the blends with small dispersed phase size distribution and good dispersion. The phase morphology of PA1010/ABS/PP blends is improved when add in PP-g-(MAH-co-St) ,and also the cross-section is rather rough, therefore we can get that PP-g-(MAH-co-St) can reduce the interfacial tension between PA1010 matrix and ABS, PP dispersed phase significantly and get the the blends with small dispersed phase size distribution and good dispersion at last.

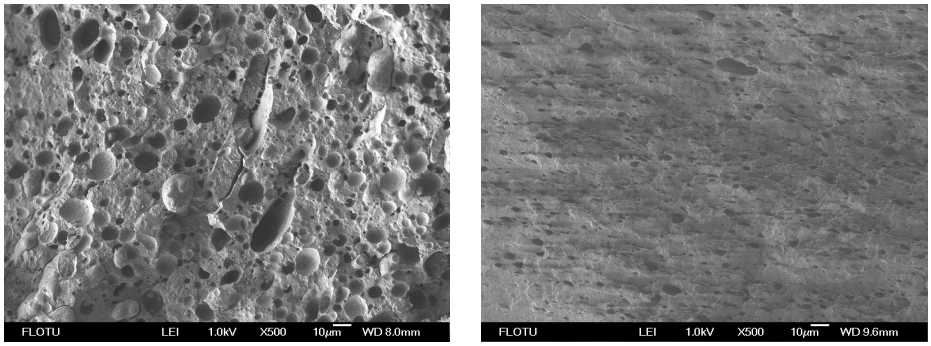

Fig.2 Fracture SEM micrographs of the PA1010/ABS/PP/PP-g-(MAH-co-St) blends (a)(60/20/20/0); (b) (60/20/20/10)

The mechanical properties of blends From table 2 we can see, PA1010/ABS/PP simple blends have poor mechanical properties, poor morphology and weak interfacial adhesion of the simple blends make the dispersed phase to be the defects which lead to the stress concentration of matrix .Blends will be destroyed prematurely by the force .The mechanical properties are improved obviously when add PP-g-(MAH-co-St) into PA1010/ABS/PP blends. PP-g-(MAH-co-St) plays a role in the compatibilization. For the improvement of the morphology, form a more perfect interface layer, improve the interfacial tension, is helpful to the absorption of impact energy, transmission and dispersion during the Plastic deformation of system, also improve the impact properties. Meanwhile, reduce matrix defects that may exist, is helpful to the transmission and dispersion of stress, Improve the capacities of the material to resist external forces .Add Reactive compatibilizer PP-g-(MAH-co-St)into PA1010/ABS/PP

Table2 Contrast of mechanical properties for PA1010/ABS/PP blends

Blends	MFRg/10min	Impact strength(J/m)	Tensile trength (MPa)	Elongation-at-break(%)	Flexural strength MPa)
PA1010/ABS/PP/PP-g-(MAH-co-St)(60/20/20/0)	14.5	8.9	40.2	5.6	62.3
PA1010/ABS/PP/PP-g-(MAH-co-St)(60/20/20/10)	3.2	35.5	44.9	33.1	58.7

blends, not only improves the toughness but also increases the tensile strength, and the mechanical properties of blends also keep balance, there is practical significance to make low cost,

high-performance blends alloy. Meanwhile, the MAH in the multi-monomer melt graft can reduce the interfacial tension, and the St can not only improve the grafting rate of MAH on PP, but also reduce the interfacial tension of PA1010 and ABS,PP and ABS. The MFR of blends is reduced obviously when add PP-g-(MAH-co-St) into PA1010/ABS/PP, that's because MAH can form copolymer with the end amino group of PA6 on the surface, and St can both improve the grafting rate and increase the compatibility with the ABS.

The crystallization behavior of blends In the table 3, the crystallization temperature(Tc) of PA1010 in the blends has a great improvement compared with pure PA1010, therefore the ABS,PP and PP-g-(MAH-co-St) added into PA1010 all play a similar role of nucleating agent, and accelerate the crystallization of the PA1010,and the crystallization temperature increases too. The melt temperature of PA1010 in the PA1010/ABS/PP blends that without compatibilizer has no changes while the melt temperature that added in compatibilizer reduces by 2.1 °C , therefore we can get that compatibilizer can make PA1010 crystal in the blends imperfect and increase the defects .

Table3 The crystallization index of PA1010 phase in the blends

Composition	Tc/℃(PP)	Tc/℃ (PA1010)	Tm/℃(PP)	Tm/℃ (PA1010)
PA1010	-	167.3	-	204.9
PP	123.0	-	169.3	-
PA1010/ABS/PP/PP-g-(MAH-co-St)(60/20/20/0)	120.3	188.1	166.2	204.9
PA1010/ABS/PP/PP-g-(MAH-co-St)(60/20/20/10)	120.8	189.5	166.6	202.8

Conclusions

The study of the phase morphology shows that PP-g-(MAH-co-St) has a stronger effect on the compatibilization of PA1010/ABS/PP blends .The bond of interface is significantly enhanced, the dispersed phase ABS and PP size and particle size distribution also decrease significantly .MAH in the PP-g-(MAH-co-St) graft can form copolymer with the end amino group of PA6 on the surface, and St can both improve the grafting rate and increase the compatibility with ABS .

The data of mechanical properties show that the tensile strength of compatibilized PA1010/ABS/PP blends has a minor increase by 11.7%, and the impact strength and elongation at break are increased 4.0 times and 4.9times respectively. The results show that this method can obtain ternary blends alloy materials that with higher toughness and rigidity. Optimization of the injection molding parameters by orthogonal test needs to consider the interaction of injection molding parameters, if the process parameters are not appropriate, it will cause many defects to the products, so the optimization process needs to consider various factors .

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