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Novel strategy for ternary polymer blend compatibilization

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Abstract

A novel strategy for compatibilization of ternary polymer blends was described. PP (polyolefins)/PA6 (engineering plastics)/PS (styrene polymers) was selected as a model ternary blend system, and the compatibilization effect was investigated by means of SEM, rheometer, dynamic mechanical thermal analysis and mechanical testing. The results indicated that, as a ternary polymer blend compatibilizer, styrene and maleic anhydride dual monomers melt grafted polypropylene [PP-*g*-(MAH-*co*-St)] showed more effective compatibilization in the PP/PA6/PS ternary blend system than PP-*g*-MAH, PP-*g*-St and their mixture. The good compatibilizing effect of PP-*g*-(MAH-*co*-St) can be explained by two mechanisms. One is the in situ formation of [PP-*g*-(MAH-*co*-St)]-*g*-PA6 copolymer at the PP/PA6 interface, and the other is that it also contains styrene blocks, resulting in chemical affinity with PS and PP homopolymers.

Keywords: Polymer blend; Compatibilization; Polypropylene

1. Introduction

In the past decades, there is considerable interest in binary compatibilized polymer blends (not including the compatibilizers). In contrast, ternary or multi-component polymer blends have received relatively less attention because of the difficulty in compatibilization, especially in the preparation of an effective compatibilizer for ternary or multi-component polymer blends. Although increasing the number of polymer components does lead to complications, there are several important reasons for studying the multi-component polymer blends. Except the purpose being to develop new high-performance materials arising from synergistic interactions, moreover, there has been significant interest in the recycling of plastic materials because of environmental as well as economic concerns in recent years.

It is well known that polyolefins (PP, PE, etc.), styrene polymers (PS, ABS, etc.) and engineering plastics (PA, PC, etc.) occupy the largest share of the plastic market and are the most recycled polymeric materials. Usually, these plastics are used or recycled in mixed state. It is hard to define or separate these plastics, respectively, from recycled materials. Combining different plastics, with the help of compatibilizer, is a convenient way to upgrade the properties of recycled materials.

In general, the compatibilization of binary polymer blends is carried out using two main routes [1–13]. One is the addition of a pre-made block or graft copolymer which has chemical affinity with two immiscible homopolymers, and the other is the addition of a precursor that can induce in situ coupling reaction of functionalized polymers to form a block or graft copolymer at the polymer–polymer interface. For polyolefins, styrene polymers and engineering plastics ternary polymer blends, a ternary system compatibilizer is necessary in the blending. Some researchers tried the compatibilization of this ternary polymer blend by using complex compatibilizers [14–16]. For example, Debolt and Robertson [14,15] have investigated the compatibilization effects of the mixture of an ionomer resin (for nylon 66) and a styrene-*block*-ethylene-*co*-butylene-*block*-styrene copolymer (SEBS, for polystyrene) on nylon 66/polystyrene/polypropylene ternary polymer blends.

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How to design a multi-functionalized compatibilizer for polyolefins, styrene polymers and engineering plastics ternary blends? It would be satisfying if we can make the polyolefin-based compatibilizers that have the above two functions at the same time: one is the in situ formation of block or graft copolymer at the interface by chemical reactions with reactive groups of engineering polymers, and the other is intermolecular attraction or chemical affinity with styrene polymers. As known, styrene and maleic anhydride dual monomers (or glycidyl methacrylate, acrylic acid, etc.) melt grafted polypropylene (or polyethylene, etc.) have been successfully prepared [17–24]. At the presence of styrene (St), the graft degree of functional monomer is increased and the degradation of PP is depressed. In the grafting process, the functional monomer, St and their copolymer can react with the PP macroradicals producing long chain branches [20,21]. Therefore, the resulting grafted PP molecule will have both reactive group and PS segment [25,26]. In this paper, the multi-monomer grafted PP is utilized to compatibilize the PP (polyolefins)/PA6 (engineering plastics)/PS (styrene polymers) model blend system, and a novel strategy for the compatibilization of ternary polymer blends is presented.

2. Experimental

2.1. Materials

Both isotactic polypropylenes (PP, 2401) having a melt flow rate (MFR) of 3.0 g/10 min and polystyrene (PS, 666D) having MFR of 8.0 g/10 min were obtained from Yanshan Petrochemical Co. Polyamide 6 (PA6, 1013B) was of commercial grade from Ube Co. Maleic anhydride (MAH) and styrene monomer (St) were products of Beijing Chemical Co. (analytical grade) and used as received. The peroxide, dicumyl peroxide (DCP) from Beijing Xizhong Chemical Co. was adopted as initiator and used without further purification. The compatibilizers, PP-*g*-MAH (MAH graft content is 0.085 wt.%), PP-*g*-St (St graft content is 0.92 wt.%), and PP-*g*-(MAH-*co*-St) (MAH and St graft content are 0.68 and 0.75 wt.%, respectively), were carried out in our laboratory according to the method given in the literature [21].

2.2. Blend preparation

Ternary polymer blends of PP/PA6/PS were prepared by melt blending using a co-rotation twin-screw extruder with a screw diameter of 35 mm and *L*/*D* ratio of 48. The screw rate was set at 120 rpm. The barrel of the extruder has seven temperature-control zones and their temperatures were set at 190–200–210–220–230–230–220 °C (from hopper to die). Before blending, the compositions were dried in a vacuum oven at 80 °C for 10 h and used immediately. The weight ratio of (PP + compatibilizers)/PA/PS is fixed at 50/25/25. Based on formulation of the blends with PP-*g*-(MAH-*co*-St) as compatibilizer ((PP + compatibilizer)/PA/PS = (45 + 5)/25/25), each of blends has almost same functional group content in mole ratio. The palletized blends were dried and injection moulded into standard ASTM specimens using a ZT-630 injection moulding machine for mechanical tests.

2.3. Analysis and characterization

The morphology of the blends was investigated with a S-450 (Hitachi) scanning electron microscopy (SEM). Fracture surfaces taken from impact fracture sections were examined. Each of the samples was coated with 20-nm thick gold using a sputtering coater. The accelerating voltage was set to 20 kV. Shear viscosity as a function of shear rate was determined at 230 °C using a Rh2000 capillary rheometer. Dynamic mechanical thermal analysis (DMTA) of the blends was performed using a TA 2980 model. The experiments were carried out at a frequency of 1 Hz, and at a heating rate of 5 °C/min. The storage modulus (E') and loss modulus (E'') were measured for each sample in the temperature range of −70 to 150 °C. The mechanical property measurements of the samples were carried out according to ASTM standards at room temperature. Tensile and flexural tests were carried out using a GOTECH-2000 universal testing machine. The test speeds were set at 50 and 10 mm/min, respectively. The average of at least five measurements for each blend was reported. The Izod notched impact strength of the materials was measured with an XJUD-5.5 impact-testing machine. For each kind of blends, seven specimens were tested and the average value was given.

3. Results and discussion

The morphological characteristics of the blends with different compatibilizers are presented in Fig. 1A–E. As shown in Fig. 1A, the SEM micrograph of the PP/PA6/PS blend without compatibilizer shows a poor dispersion for PS or PA6 disperse phases and a "ball-and-socket" topography due to the poor interfacial adhesion between PP matrix and disperse phase. The crack in the blend propagates along the interface, and clear surfaces are visible. However, with the addition of compatibilizers, the morphological characteristics of the polymer blends are greatly altered. The particle size of PA6 or PS domains is much smaller and uniform in compatibilized blends than uncompatibilized blends. The phase interfacial adhesion also significantly increased. The domain size strongly depends upon the compatibilizers used. For the blends with PP-*g*-(MAH-*co*-St) as compatibilizers (Fig. 1E), the morphology displays a very fine dispersion of minor phase and strong interfacial adhesion with PP matrix. The good compatibilizing effect of PP-*g*-(MAH-*co*-St) can be explained by two mechanisms. First, the MAH groups in compatibilizer react with amine groups in PA6 to form copolymer, leading to good adhesion at interface between PP and PA6. In addition, hydrogen bonding may also exist between MAH and amine groups, further increasing compatibility [27]. Second, since the compatibilizer also contains styrene blocks, resulting in good compatibility with PS. Consequently, the remarkable compatibilizing effect of PP-*g*-(MAH-*co*-St) induced a drastic decrease in interfacial

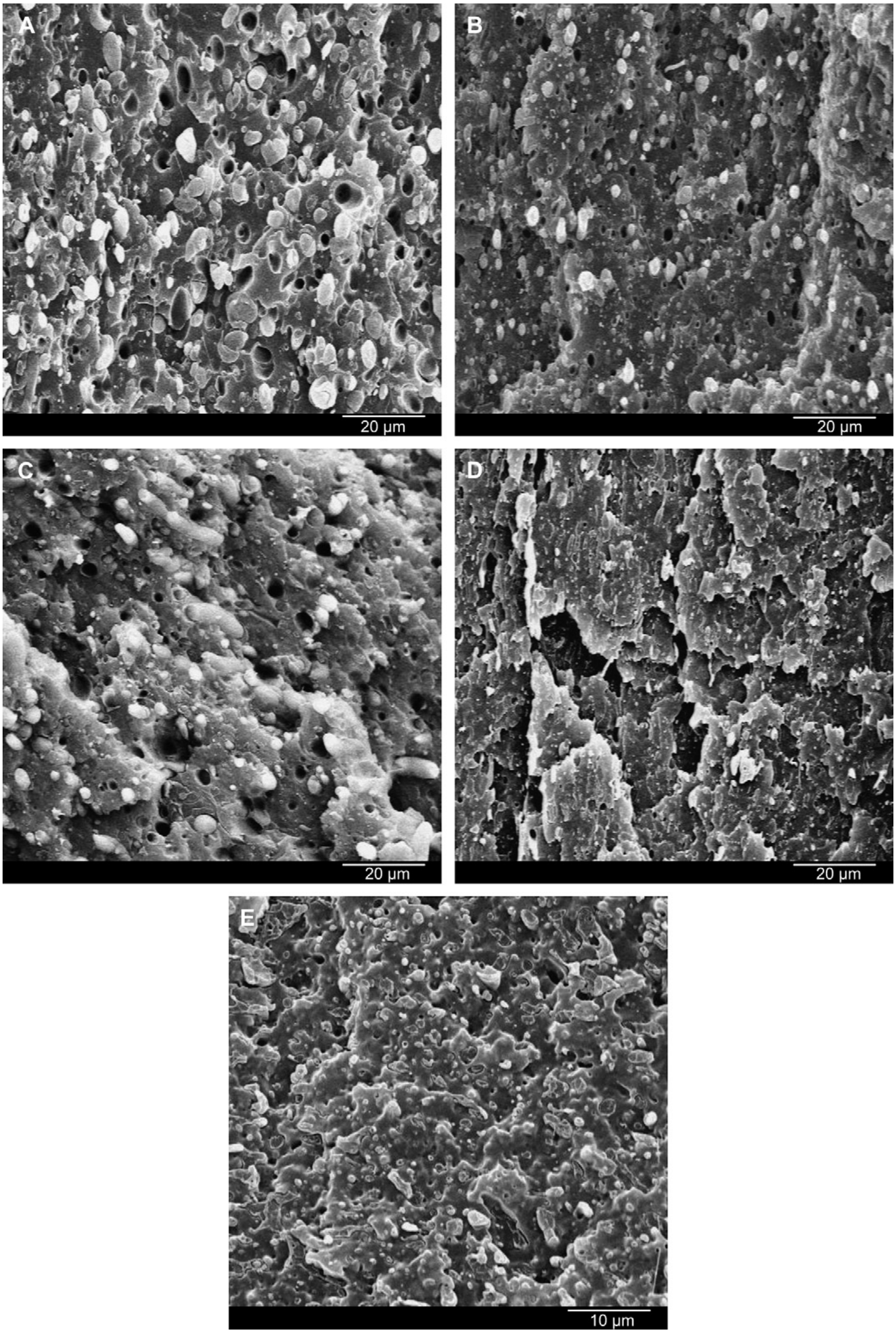

Fig. 1. SEM micrographs of impact fracture surfaces of the blends: (A) PP/PA6/PS; (B) PP + PP-*g*-MAH/PA6/PS; (C) PP + PP-*g*-St/PA6/PS; (D) PP + PP-*g*-MAH + PP-*g*-St/PA6/PS; (E) PP + PP-*g*-(MAH-*co*-St)/PA6/PS.

tension and suppression of coalescence between the originally immiscible polymer phases.

The shear viscosities of PP/PA6/PS ternary blends with different compatibilizers are measured in the capillary rheometer at 230 °C and are showed in Fig. 2. As expected, comparing with the others blends, the [PP + PP-*g*-(MAH-*co*-St)]/PA6/PS blend shows the highest shear viscosity. Because rheology behavior of polymer blends is generally a reflection of the

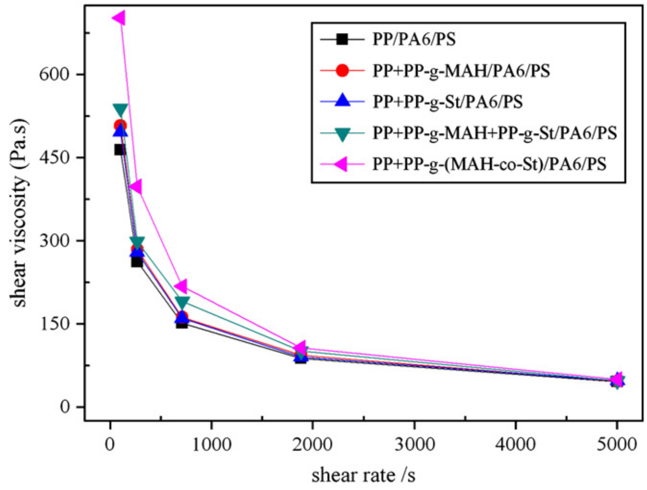

Fig. 2. Plot of shear viscosity vs. shear rate for PP/PA6/PS blends with different compatibilizers.

change in molecular weight and the interaction among the components [28], the increase in shear viscosity should be mainly due to the two mechanisms of the compatibilization as described above. The reactions between the MAH groups in the compatibilizer and amine groups in PA6 increase the molecular weight and the degree of branching, and both increase the shear viscosity of the blends. Meanwhile, the intermolecular attraction between PS segments in PP-*g*-(MAH-*co*-St) with the PS phase also increases the blends' shear viscosity. This result is also a clear evidence of the compatibilizing effect of PP-*g*-(MAH-*co*-St).

For the dynamic mechanical thermal properties, Fig. 3 gives storage modulus (E') as a function of temperature of the blends with each of compatibilizers and with the uncompatibilized blends. Over the temperature range, E' of the blends with PP-*g*-(MAH-*co*-St) as compatibilizer is larger than the other blends. This could be attributed to the stronger interfacial interaction between matrix phase and dispersed phase (as shown in Fig. 1E), which is responsible for more efficient stress transfer across interface. Table 1 gives the mechanical properties of uncompatibilized and compatibilized blends. As shown in Table 1, the tensile and flexural strengths are improved as a result of addition of compatibilizers. It is easily considered that the remarkable compatibilizing effect of PP-*g*-(MAH-*co*-St) increased the properties and further retained a balance between tensile and impact strengths.

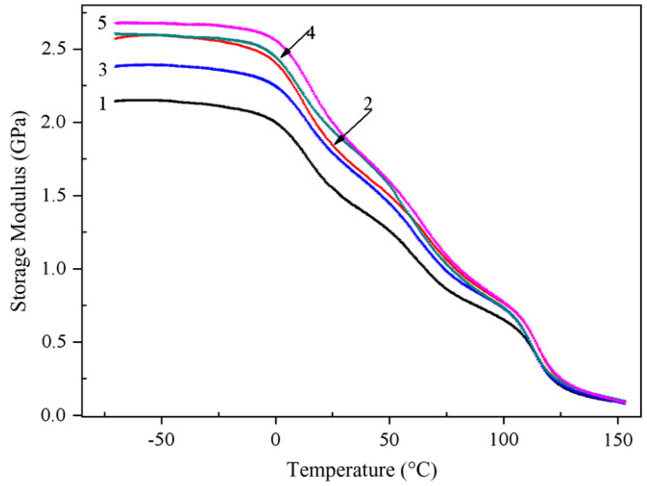

Fig. 3. Storage modulus (E') as a function of temperature for the PP/PA6/PS blends with different compatibilizers: (1) PP/PA6/PS; (2) PP + PP-*g*-MAH/PA6/PS; (3) PP + PP-*g*-St/PA6/PS; (4) PP + PP-*g*-MAH + PP-*g*-St/PA6/PS; (5) PP + PP-*g*-(MAH-*co*-St)/PA6/PS.

Table 1
Mechanical properties of the PP/PA6/PS blends with different compatibilizers

	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)
PP/PA6/PS	41.81	65.53	2.79
PP + PP-*g*-MAH/PA6/PS	46.40	69.53	2.04
PP + PP-*g*-St/PA6/PS	45.87	67.29	2.56
PP + PP-*g*-MAH + PP-*g*-St/PA6/PS	47.09	72.32	2.10
PP + PP-*g*-(MAH-*co*-St)/PA6/PS	49.28	76.98	2.60

4. Conclusion

A novel and effective strategy for compatibilization of polyolefins (PP, PE, etc.), styrene polymers (PS, ABS, etc.) and engineering plastics (PA, PC etc.), three kinds of polymer blends have been demonstrated. Compared with PP-*g*-MAH, PP-*g*-St and their mixture, the PP-*g*-(MAH-*co*-St) is a more effective ternary polymer blend compatibilizer in the PP/PA6/PS blends, which is due to the in situ formation of PP-*g*-PA6 copolymer at the PP/PA6 interface and the increased chemical affinity with PP/PS homopolymers. Accordingly, the PP/PA/PS blends with the PP-*g*-(MAH-*co*-St) as compatibilizer exhibit better synergy, as reflected by the improved mechanical properties, finer dispersion and more strengthened interfacial adhesion. Moreover, this strategy can be easily extended to the compatibilization of PP/PA/SBS, PE/PA/PS, PP/PC/PS ternary blend systems, etc. In conclusion, this work provides a strategy not only for the high-performance, but also for recycling and reuse of polyolefins, styrene polymers and engineering plastics, three kinds of polymers.

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