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A Novel Approach to the Preparation of Nano-Blends of PPO/PS/PA6

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Summary

A novel approach of in situ polymerization and in situ compatibilization was adopted to prepare the nano-blend of poly (2,6-dimethyl-1,4-phenylene oxide) (PPO), polystyrene (PS) and polyamide 6 (PA6). Anionic ring-opening polymerization of ε-caprolactam was carried out in the presence of PPO and PS. And PS, the chain of which bore methylmethacrylate (MMA) groups, acted as macroactivator to initiate PA6 chain growth from the PS chain and formed a graft copolymer of PS and PA6 and pure PA6 simultaneously. Thus the nano-structured PA6 dispersed phase in the PPO matrix could be achieved.

Introduction

The phase morphology control of incompatible blend systems has been considered as an important subject to investigate the development of new polymer alloys because it dominates their ultimate mechanical properties. For most incompatible polymer blends, high interfacial tension and weak adhesion at the interfaces between the dispersed phases and the matrix, leads to the formation of a very coarse morphology due to macrophase separation. As a result, inferior mechanical properties arise. A general route to improve the compatibility of blends is by adding or generating an interfacial emulsifier, which is often a block or graft copolymer, namely, the compatibilizer [1]. It can be made either separately and then added to a polymer blend or generated in situ during the blending process. The first method, called physical compatibilization, has the advantage of better controlling the molecular architecture of the compatibilizer. However, it is not always easy for the copolymer to reach and locate at the interfaces where it is most needed. The second method is often called reactive compatibilization. Since the compatibilizer is formed in situ directly at the interfaces during blending, the problem of getting it to the interfaces no longer exists, however, the amount of copolymer formed is limited primarily by the total interfacial volume, which is very small compared to the bulk. It has been shown that for most polymer blends processed under typical melt mixing conditions, the particle size of the dispersed phase is rarely below 100 nm, whatever the compatibilization method employed [2]. A novel reactive blending technique was recently reported by Hu et al., in which, instead of traditional blending technique, an in situ polymerization and in situ compatibilization was performed simultaneously for the blend system of polypropylene (PP) and polyamide 6 (PA6). As a result, the particle size of the PA6 dispersed phase reached nano-scale, and was termed a "nanoblend" [3-5]. The toughness of such nano-structured material was improved remarkably.

Blends of PA6 and PPO are of interest as a high-performance alloy. However, PPO is an amorphous polymer and PA6 is a crystalline polymer, which are thermodynamically immiscible. We have prepared PPO/PA6 nanoblends using the approach of in situ polymerization and in situ compatibilization, in which phenyl ester modified PPO acted as macroactivator [6]. Because PPO and PS are the paradigm of a miscible polymer pair over the entire composition range, at least at atmospheric pressure [7-8], in this paper, we used methyl ester modified PS as macroactivator to prepare PPO/PS/PA6 compatiblilzed blend, and also obtained such a nanoblend of PA6 particles dispersed in PPO matrix.

Experimental

Materials

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) with an intrinsic viscosity of 0.58 (measured at 30ºC in chloroform) was obtained from the Toyobo Co., Japan. The catalyst (NaH) used was a 50% dispersion in mineral oil. The microactivator was ε-caprolactam blocked 2,4-diisocyanatocuene (BDI). The macroactivator (PS-MMA), copolymers of styrene (90 wt%) and methyl methacrylate (10 wt%), was prepared via benzoyl peroxide initiated bulk polymerization. FTIR (KBr): 1729 (C=O), 1205 (C-O), 1124 (O-C), 1500 and 1450 (aromatic C=C), 698 and 752 (characteristic of single substituted benzene), 3000 ~3100 cm^{-1} (characteristic of polystyrene).

Preparation of PPO/PS/PA6 Blends

To a three-necked flask equipped with a mechanical stirrer, a condenser, and a N_2 inlet were charged PPO, PS-MMA and ε-caprolactam (ε-CL). After homogeneous solution was formed at 200 ºC, NaH (50% in mineral oil) and BDI were added in sequence to it under N_2, and the reaction was maintained at 200 ºC for about half a hour, then quenched in iced water quickly.

Characterization

The phase morphology of selected blends was examined with a JEOL JSM-5610LV scanning electron microscope (SEM). The cryogenically fractured surfaces of the samples were sputter coated with gold to prevent charging in the electron beam. Additionally, for blend possessing a nano-meter morphology, transmission electron microscopy (TEM) (Hitachi H-800) was performed. Samples were ultramicrotomed at room temperature and, subsequently, vapor stained using osmium tetroxide (OsO_4).

The melting and crystallization behaviors of the materials were examined using differential scanning calorimeter (Perkin-Elmer DSC-7). Samples were heated quickly from 40 to 280 ºC, and maintained at 280 ºC for 5 min, then cooled down to 40 ºC at 10 ºC / min (crystallization), then heated again to 280 ºC at 10 ºC /min (melting). The corresponding thermal curves were recorded and normalized to the unit weight of the sample. The normalized crystallinity Xc was calculated from the equation

$$X_c = (\Delta H_f / \Delta H^0_f) \times 100\%$$

Where ΔH_f is the experimental enthalpy of melting and ΔH^0_f is the enthalpy of fusion of the perfectly crystalline PA6, 230 J/g (55 cal/g) [9].

Results and Discussion

In Situ Polymerization and in Situ Compatibilization of PPO/PS/PA6

Figure 1 briefly presents the process of the in situ polymerization and in situ compatibilization conducted for PPO/PS-MMA/ε-CL blend system, where the microactivator (BDI) and macroactivator (PS-MMA) coexisted. Some of the ε-CL formed PA6 homopolymer in situ by anionic ring-opening polymerization, while some of ε-CL formed a graft copolymer of PS and PA6 in situ, which could act as a compatiblizer and efficiently control the phase morphology of the blends.

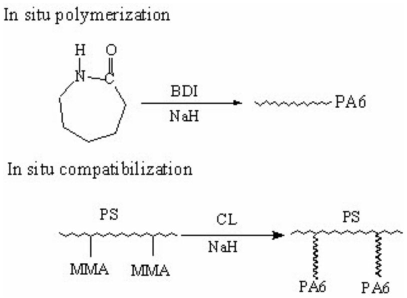


Figure 1. Schematic description of the in situ polymerization and in situ compatibilization

Table 1. Selected characteristics of the reactive blends obtained with PS and PS-MMA componnents

	PPO/PS/ε-CL/NaH/BDI (14/14/72/0.35/2.6 wt%)	PPO/PS-MMA/ε-CL/NaH/BDI (14/14/72/0.35/2.6 wt%)
Conversion of ε-CL	90.6	89.1
PPO/PS/PA6	15/15/70	15/15/70
PA6 extract	69.1	54.5
PS-g-PA6	0	30.5
PS/PA6 in PS-g-PA6	0	49.2/50.8

The materials obtained from the polymerization of the PPO/PS/ε-CL/NaH/BDI (10/10/80/0.4/3 wt%) and PPO/PS-MMA/CL/NaH/BDI (10/10/80/0.4/3 wt%) systems were subjected to several analyses. The conversions of ε-CL were determined by measuring the weight loss of given amounts of polymerized materials before and after solvent extraction in boiling water. They were about 90 wt % for both polymerizing systems, indicating 30 wt% PPO/PS and 70 wt% PA6. The first blend consisted of three polymers (PPO, PS and PA6), whereas the second one consisted of PPO, grafted copolymer (PS-g-PA6) and homopolymer (PA6). In other words, the first blend was of type A/B/C and the second one was A/B-C/C type. The amount of the PA6 homopolymer formed in the second blend was determined by solvent extraction in formic acid at room temperature and was found to be 54.5 wt %. This implies that the PA6 in the form of the PS-g-PA6 graft copolymer was 15.5 wt %. Since the blend contained 15 wt % PPO, 15 wt % PS and 70 wt % PA6, the weight percentage of the PS-g-PA6 in the blend would be 30.5 wt %, of which the PS and PA6 segments were 49.2 wt % and 50.8 wt %, respectively. The above-mentioned characteristics of the two blends are tabulated in Table 1.

The grafted copolymer was obtained by successive solvent extraction in formic acid and then in chloroform. The residue insoluble in both solvents weighted 28.2 wt % (basically in agreement with the above-mentioned analyses.) was considered as the graft copolymer of PS and PA6. This is evidenced by the FTIR spectra shown in Figure 2, where the absorption peaks at 3400~3300 (NH stretching and H_2O), 3084, 1641 (amide Ⅰ band), and 1548 (amide Ⅱ band) cm^{-1}, the characteristic absorption for PA6, and the absorption peaks at 1455 (aromatic C=C), 699 and 750 (aromatic =C-H) cm^{-1}, the characteristic absorption for PS, are observed.

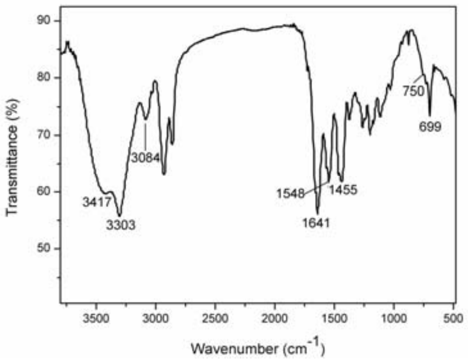


Figure 2. FTIR spectra of the pure PS-g-PA6 copolymer

Morphologies of the Blends

Figure 3(a) shows the morphology of the PPO/PS/PA6 blend obtained from the polymerization of the PPO/PS/ε-CL/NaH/BDI. The PPO/PS components exist as a continuous phase, because the morphology of the blend sample etched PA6 particles from the PPO/PS matrix (not show here), and is similar to the findings reported by Meijie and coworkers [10]. The morphology of Figure 3(a) is very gross, and the average particle size of the PA6 dispersed phase is more than 10 µm, indicating a macrophase separation existed. By contrast, the morphology of the PPO/PS/PA6 blend resulting from the polymerization of the PPO/PS-MMA/ε-CL/NaH/BDI is much finer as shown in Figure 3(b). The PA6 particles distribute uniformly and the average particle size is within nanometer scale (Figure 3(c)). The TEM micrograph (Figure 3(d)) shows the better observation of PA6 nano-sized particles. The dark areas are PPO/PS because PPO/PS were preferentially stained with OsO_4. The average PA6 particle size is as small as 100 nm and part of the PS-g-PA6 graft copolymer should be preferentially located at the interfaces as revealed clearly by light-gray layer surrounding each PA6 particle (Figure 3(e)). However, such system of in situ polymerization and in situ compatibilization is very complicated in that the copolymer formed in situ is not actually uniform, and the PS-g-PA6 graft copolymer with a low PA6 content may coexist with PPO forming the matrix phase. The mechanism of the morphology development can be briefly explained. At the initial stage, the anionic polymerization of ε-CL and the graft copolymerization of ε-CL on PS-MMA coexist

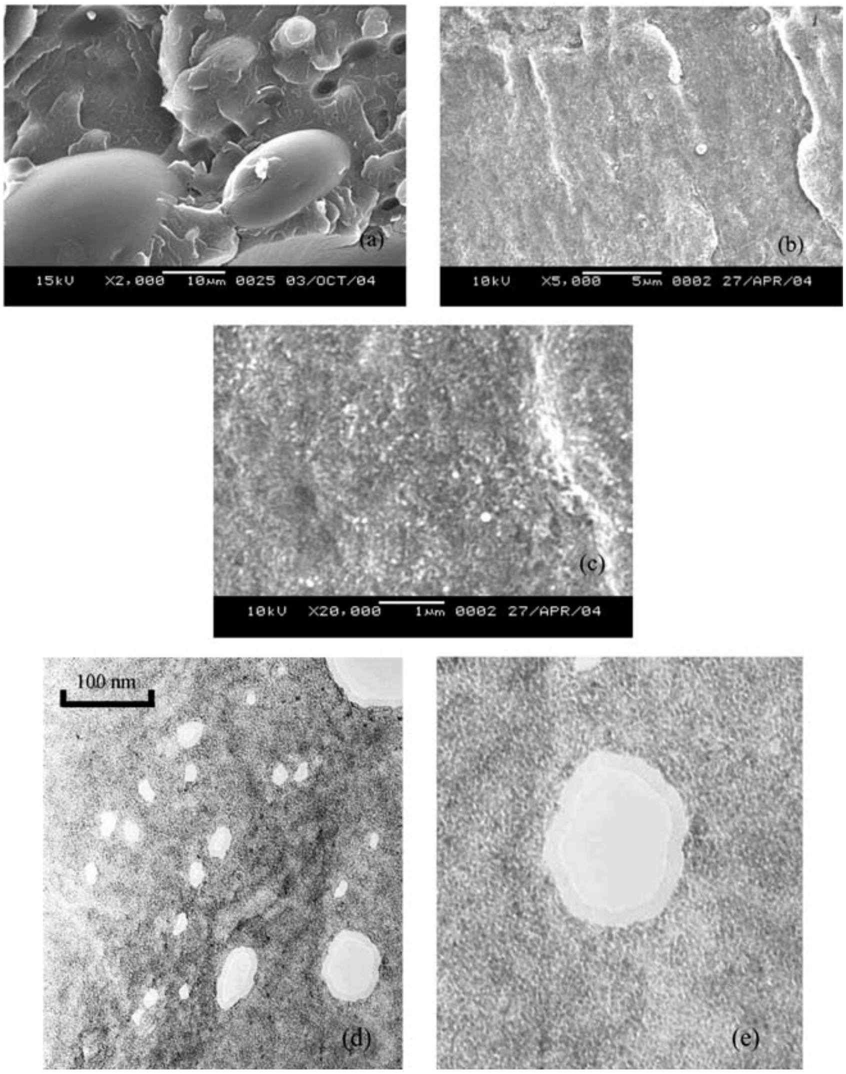


Figure 3. Morphologies of the polymerized PPO/PS/ε-CL/NaH/BDI (14/14/72/0.35/2.6) (a); PPO/PS-MMA/ε-CL/ NaH/BDI (14/14/72/0.35/2.6), 5000 enlarged (b) and 20000 enlarged (c); TEM observation of PPO/PS-MMA/ε-CL/NaH/BDI (14/14/72/0.35/2.6) (d) and magnified one PA6 particle (e)

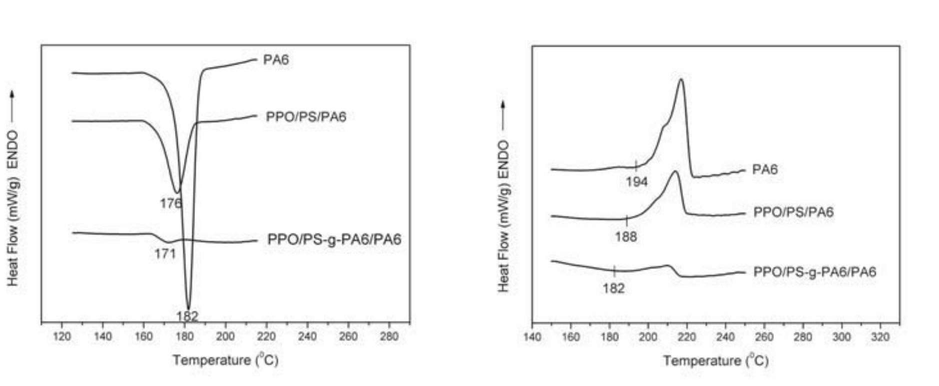
in the homogeneous mixtures. As the conversion of ε-CL reaches a certain point, the polymerization-induced phase separation may take place. At that time, if enough graft copolymers of PS-g-PA6 has been generated in situ, it may act as a compatibilizer to lower the interfacial tension and stabilize the dispersed phases from coalescence. Hence finer PA6 dispersed phases are formed in the PPO and PS matrix. Theoretically speaking, if the rate of forming of the graft copolymerization is higher than that of the homopolymerization and phase separation, the copolymer can stabilize the phase separation at the initial stage, and the morphology with nano-dispersed phases can be achieved.

Melting and Crystallization Behaviors

Table 2. Crystallinity of PA6 in PA6 and PPO/PS/PA6 blends

	PA6	PPO/PS/PA6 (15/15/70 wt%)	PPO/PS-g-PA6/PA6 (15/30.5/54.5 wt%)
ΔH_f (J/g PA6)[a]	38.1	27.0	6.4
X_c (%)	16.6	11.7	3.0

[a] values nomorlized by PA6 component



(a) (b)

Figure 4. DSC cooling (a) and heating (b) scans of PA6 and PPO/PS/PA6 blends

Figure 4 compares the DSC thermograms of the pure PA6, uncompatibilized PPO/PS/PA6 blend and compatibilized PPO/PS/PA6 blend obtained from ε-CL/NaH/BDI (100/0.49/3.6), PPO/PS/ε-CL/NaH/BDI (14/14/72/0.35/2.6) and PPO/PS-MMA/ε-CL/NaH/BDI (14/14/72/0.35/2.6), respectively. Upon heating (See Figure 4(b)), the onset point of PA6 melting is shifted to lower temperature and the melting curve becomes broader in the blend. It is considered that the PS-g-PA6 graft copolymer formed in situ interferes to some extent with the crystallization of PA6. As a result, PA6 forms imperfect crystallites, which resulted in the depression of its melting point. Table 2 shows that PA6 crystallinity in the compatibilized blend decreases dramatically compared to that of pure PA6 and uncompatibilized PPO/PS/PA6 blend, which confirms that the PS-g-PA6 graft copolymer restricted the crystallization of PA6. Upon cooling (See Figure 4(a)), the peak temperature of melt crystallization of PA6 shifts to a lower temperature and the crystallization peak becomes broader and small in the compatibilized blend. It may arise because the nucleation within the nanoscale-confined microdomains is principally homogeneous. Macroscopic impurities, which act as heterogeneous nuclei, cannot remain within the nanoscopic microdomains, which is then a contributing factor to the decrease of the crystallization temperature.

Conclusions

A novel approach of in situ polymerization and in situ compatibilization was adopted to obtain stabilized PPO/PS/PA6 nano-blends. It consists of polymerizing a monomer of PA6 in the matrix of PPO and PS. The PS chain bears ester groups, which act as growing centers to initiate PA6 chain growth. As such, formation of homopolymer of

PA6 and graft copolymer of PS and PA6 takes place simultaneously in the matrix of the PPO, leading to compatibilized PPO/PS/PA6 blends, with a nano-dispersed PA6 particles in it.

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