

Preparation of PP-g-PA6 copolymers through reactive blending

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Block or graft copolymers have gained much interests recently, not only because of their general application as compatibilizers in blends with thermodynamically immiscible polymer pairs [1], but also of many special and important characteristics of themselves, such as the formation of self assembly morphologies, which can be used for drug delivery, nanoreactor and molecular templating, etc. [2, 3]. In general, copolymers can be prepared by ionic polymerization [4], controlled radical polymerization [5] and some other special polymerization methods [6, 7]. However, for some specific polymer pairs, such as polypropylene (PP) and polyamide 6 (PA6), it is still a challenge to prepare premade PP-g-PA6 copolymer. Although, maleic anhydride can react with the end amino group of PA6 and in situ forming PP-g-PA6 graft copolymer at the phase interface when maleic anhydride modified PP (PP-g-MAH) is used as an interfacial compatibilizer in PP and PA6 blends [8, 9], the amount of such copolymer is too small to be extracted out because of the relatively low grafting degree of MAH on PP. Preparing such kind of copolymers is still unpractical so far. Recently, Leibler et al. [10] successfully increased the MAH content by preparing the poly (ethylene-ethylacrylate-MAH) copolymer (PE-1) before blending with PA6. They have extracted the PE-1-g-PA6 copolymer out from the blending system in their work. In this communication, we will report another

novel exploration of preparing PP-g-PA6 copolymers through reactive blending.

Isotactic-PP homopolymer was purchased from Montell (Profax 6331, melt index 10 dg/min at 230 °C, density 902 kg/m³). Dicumyl peroxide (DCP), ϵ -caprolactam, adipic acid, 3-isopropenyl- α,α' -dimethylbenzene isocyanate (TMI), ω -aminocaproic acid and m-cresol were obtained from Aldrich Co. Ltd. Formic acid, xylene and acetone were purchased from Riedel-de Haën. All the chemicals are reagent grade and used as received.

PA6 “end-functionalized” by unsaturated double bonds (PA6-TMI) was synthesized by condensation polymerization under the protection of nitrogen gas. Condensation polymerization of ϵ -caprolactam was initiated by ω -aminocaproic acid at 260 °C. The molecular weight was adjusted by stoichiometrically adding adipic acid into the polymerization system. At the end of polymerization, a certain amount of 3-isopropenyl- α,α' -dimethylbenzene-isocyanate (TMI) was added into the polymeric melt. The isocyanate group in TMI will react with the end carboxyl (COOH) group of PA6 to form amide [11], which will result in the TMI attachment to the PA6 molecular chain ends (PA6-TMI). About 50 ml of m-cresol was added to terminate all the reaction and drop down the system temperature to room temperature. After precipitated in acetone, filtrated and dried in a vacuum oven at 85 °C for 48 h, end functional PA6 powder were stored in a dry box for further blending with PP. The molecular weight of end functionalized PA6 was measured by relative viscosity method. Table 1 lists the PA6 samples with and without TMI end functionalization used in this experiment.

PP/PA6 blend was prepared by reactive blending of PP and the PA6-TMI using DCP as initiator. Melt blending was performed in a Brabender internal mixer at 230 °C for 5 min. The blend weight ratio employed was PP/PA6-

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Table 1 Synthesized PA6 samples

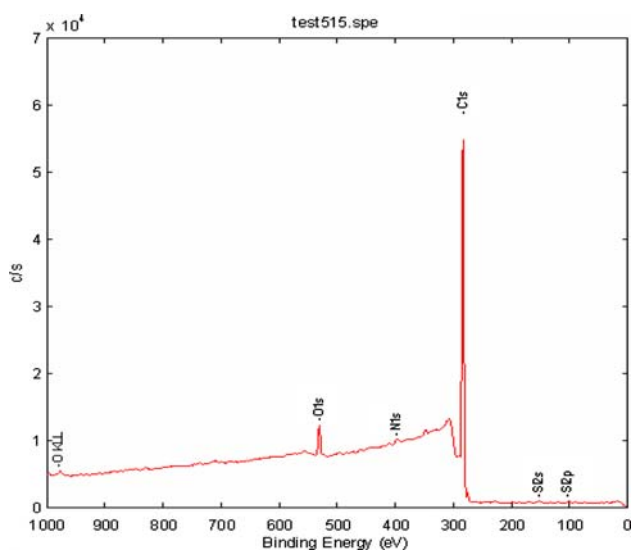
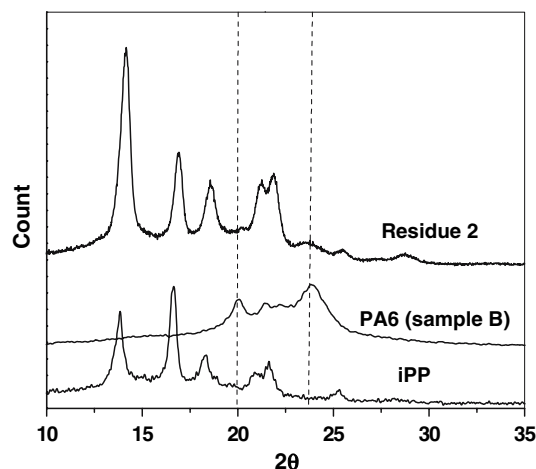
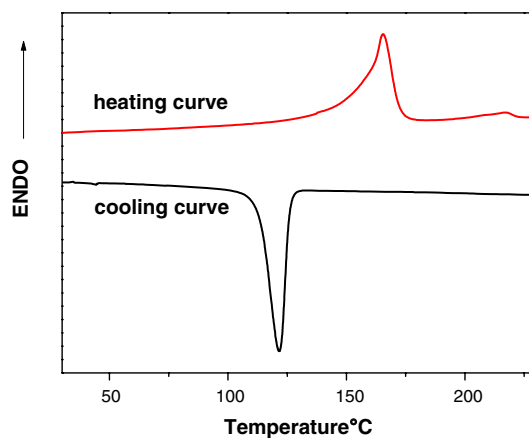
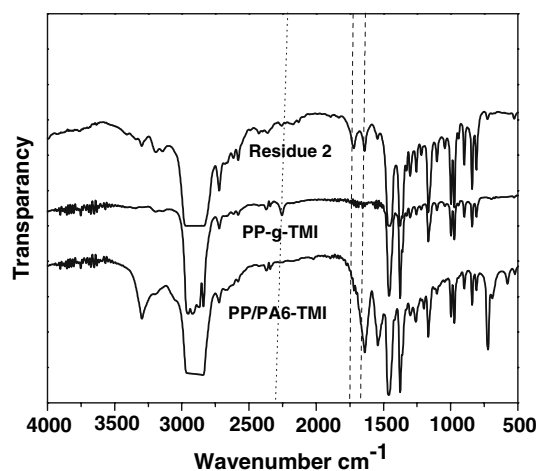
Sample code	Mn (g/mol) ^a	TMI content (mol)
A	~2,000	0
B	~2,000	0.01

^a Calculated from the relative viscosity data with 10% formic acid solution at 23 °C

TMI/DCP = 90/10/0.5. The final product was first extracted by boiling formic acid for 24 h to remove unreacted PA6. The remaining part (which will be referred to as **Residue 1**) was then extracted in a soxhlet extractor for 72 h using xylene as the extraction agent to remove the ungrafted PP from **Residue 1**. This extracting cycle was repeated three times. The final undissolved remaining material was collected and dried at 80°C for 48 h and will be referred to as **Residue 2** in subsequent discussions. After the above extraction cycles, **Residue 2** should consist mainly of PP-g-PA6 graft copolymer.

PP-g-TMI graft copolymer was prepared through directly melt grafting of TMI monomers onto PP backbone. Certain content of PP, TMI and DCP were mixed simultaneously inside the Brabender internal mixer, and the grafting reaction was carried out at 200 °C for 5 min. Ungrafted TMI was removed by extracting the raw PP-g-TMI product with acetone.

Figure 1 shows the XPS analysis result of **Residue 2**. It reveals that there exist N and O elements in the **Residue 2**, which indicates that there are unremovable polyamide molecules in this residue. And the detailed elemental analysis shows that the PA6 content is about 17wt% in **Residue 2**.

**Fig. 1** XPS result of **Residue 2****Fig. 2** XRD results of **Residue 2** and its original components**Fig. 3** DSC heating and cooling curves of **Residue 2** (10 °C/min)**Fig. 4** FTIR figures of PP/PA6-TMI blend, PP-g-TMI and **Residue 2**

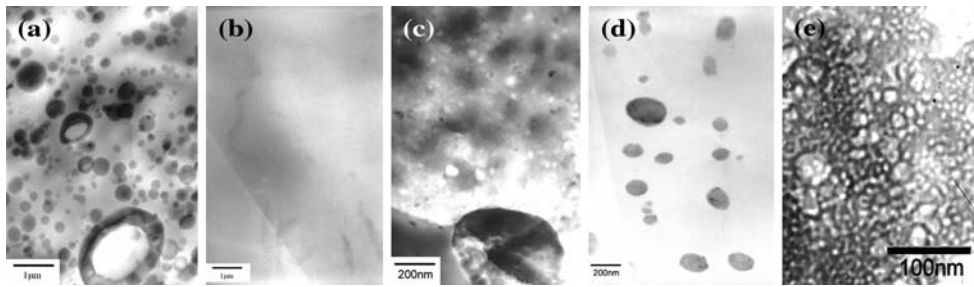


Fig. 5 TEM photographs of different polymer blends and extracted residue: (a) PP/PP-g-MA/A, (b) **Residue 1** of blend a); (c) PP/DCP/B; (d) **Residue 1** of blend c); (e) **Residue 2** of blend c). Note that A and B are the PA6 samples as listed in Table 1

Figure 2 is the XRD results of **Residue 2** and the relevant components. Only very small PA6 diffraction peaks can be found in the **Residue 2** XRD spectrum. This may be resulted from the fractionated crystallization of PA6 in PP-g-PA6 copolymer [12] (See Fig. 3, no PA6 crystallization peak could be found in the DSC curve of **Residue 2**) or the formation of the γ form crystals whose diffraction peak is located at 21.4° and was overlapped by that of PP [13].

The FTIR analysis shown in Fig. 4 indicates that the two characteristic vibration peaks of amide group around $1,600\text{--}1,500\text{ cm}^{-1}$ in **Residue 2** have been slightly shifted to higher wave numbers when compared with the original PP/PA6-TMI blend (i.e., before formic acid and xylene extractions). This is thought to be resulted from the disappearing of inter chains hydrogen bonds in PA6 because of the isolated PA6 grafted chain on PP backbones in **Residue 2** [14]. And the absorption peak of isocyanate group around $2,300\text{ cm}^{-1}$ in PP-g-TMI disappears both in PP/PA6-TMI blends and **Residue 2**, which indicates the reaction between TMI and the end amino group of PA6 during the melt blending process.

It can also be seen from Fig. 4 that the absorption peak for the isocyanate group ($\sim 2,300\text{ cm}^{-1}$) that can be found in PP-g-TMI has disappeared in both of the PP/PA6-TMI blend and **Residue 2**. This indicates the reaction between TMI and the end amino group of PA6 has occurred during the melt blending process.

Figure 5 shows the TEM photographs of PP/PA6 blends processed through different routes. Figures 5a and b are conventional PP/PP-g-MA/PA6 blends before and after extraction by formic acid, respectively. It can be seen that most of the PA6 phase has been removed after formic acid extraction (Fig. 5b), which indicated that little PP-g-PA6 copolymer could be formed by simply using PP-g-MA as compatibilizer. While in Fig. 5d, we can easily find unextractable PA6 particles in **Residue 1**, which should be ascribed as PP-g-PA6 component. Meanwhile, for the melt-blended PP/DCP/B system without subject to extraction treatments (Fig. 5c), it can be seen that the interface between PP and PA6 in PP/PA6-TMI blend (Fig. 5c) is more diffuse than that in conventional PP/PP-g-MA/PA6

blends (Fig. 5a). This should be the contribution of relatively higher PP-g-PA6 content in the PP/PA6-TMI blend. Figure 5e shows the morphology of **Residue 2** (PP-g-PA6 copolymer). This co-continuous morphology is quite similar to those obtained by Leibler et al. in PE-g-PA6 copolymers [10].

In summary, a method of preparing PP-g-PA6 copolymers has been introduced in this study. This was achieved by first end-functionalized PA6 with TMI (PA6-TMI). The PA6-TMI was reacted with PP through reactive blending using DCP as initiator. Using this method, consideration amount of PP-g-PA6 can be obtained. The PP-g-PA6 copolymer was extracted and characterized.

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