

Effects of Polyetheramine on the Properties of Polyamide 6

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Abstract

To modify the properties of polyamide 6 (PA6), trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (PEA) was added to PA6 matrix by melt-mixing. By FTIR, ¹H-NMR, DSC, melt index, relative viscosity and mechanical properties measurements, it was found that PA6/PEA blends have excellent melt-flowability, good thermal stability, high strength and good color. The melt flowability of PA6 can be significantly improved by a low loading of PEA without the loss of mechanical strengths.

Keywords

Polyamide (PA6); Trimethylolpropane tris[poly(propylene glycol); Amine terminated] (PEA); Melt flowability; Viscosity reducer

Introduction

Polyamide 6 (PA6) has been developed more than 70 years and has become one of the most important engineering plastic due to its high strength, excellent corrosion resistance, suitable wear resistance and favorable self-lubricating property. However, the application of PA6 grades with high molecular weight was limited due to the high melt viscosity. It often becomes difficult to use these grades to produce small parts with thin wall or precision parts because of its poor melt flowability. This problem becomes more serious in case where these grades are mixed with inorganic filler.

So far, many efforts have been devoted to solve the poor process ability or high viscosity PA6. One method is to blend the high viscosity resin with no volac resin, ionomer, hyper branched polymers or liquid-crystal polymers to enhance the flowability, but it may need high loading of modifier (such as 10%) and thus limits its application. Another effective method is to directly synthesis star-branched PA6 with high flowability [1-12].

In this work, a low molecular weight polyetheramine additive, trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (PEA, $M_n=440$) was included into PA6 to modify its properties. PEA was chosen due to its unique structure as well as commercial availability. It is a kind of amine terminated polyether with three

-NH₂ groups. On the one hand, these -NH₂ groups of PEA are possible to form hydrogen bonds with C=O groups in PA6 chains, break some of the hydrogen bonds between PA6 segments and thus improve the melt flowability. On the other hand, the side -CH₃ group near -NH₂ group in PEA lowers its chemical reactivity and should greatly restrain the reaction between PEA and PA6. The PA6 blends with low loading of PEA were prepared by melt mixing and their structures and properties were investigated by FTIR, ¹H NMR, DSC, WAXD, melt indexer and Ubbelohde viscometer.

Experimental

Materials

PA6 used in this study was a product (Grade: M2800) of Guangdong Xinhui Meida Nylon Co. Ltd (China). Trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (PEA, $M_n=440$), sulfuric acid-d₂ and chloroform-d were purchased from Sigma-Aldrich Co. LLC. They were used as received.

Preparation of the blend samples

After dried at 110°C under vacuum overweight, PA6 was melt-mixed with PEA under nitrogen purge at 250°C for 5mins in a twin-screw micro compounder (Shanghai Dehong Rubber Machinery Co. China). The blend is coded as PEA xwt%, where x is weight percentages of PEA in the blend. Pure PA6 after the melt processing was coded as blank.

FTIR-ATR

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra were recorded in a Nicolet 8700 spectroscope in the range of 4000-600cm⁻¹ for the films of PA6 blank and the blends. The films were prepared by hot-press at 250°C for 2 min under a pressure of 10MPa. Data were collected over 64 scans with a resolution of 0.5 cm⁻¹.

¹H-NMR spectra

¹H-NMR spectra were obtained on a Bruker Advance 600 spectrometer using sulfuric acid-d₂ as solvent for the blends and chloroform-d for PEA at room temperature. The chemical shift was referred to sulfuric acid-d₂ (10.981 ppm) or chloroform-d (7.260 ppm).

WAXD

Wide angle X-Ray diffraction (WAXD) was performed on a SAXSmc2 wide-angle X-ray scattering instrument (Anton Paar, Austria) at room temperature. Nickel-filtered Cu K α radiation ($\lambda=0.154$ nm) was used. WAXD patterns were recorded in the 2 θ range of 5-60° at a scan speed of 1.0°/min. Each step increased 2 θ by 0.004° and pattern was collected for 20s at each step.

Relative viscosity

The relative viscosity (η_r) of the PA6 and PA6/PEA blends were measured at 0.01g/ml (concentration of PA6 component) of solution in 96% sulfuric acid at 25.00 \pm 0.01°C in water bath of JWC-32C1 (Shanghai S.R.D Scientific Instrument Co., LTD) employing an Ubbelohde viscometer.

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Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) runs were performed on Polyma DSC214 (NETZSCH) under ultrapure nitrogen purge with 5.5-6.0 mg samples encapsulated in aluminum DSC pans. Before the DSC measurement, the calibration was carried out with indium. The sample was firstly melt at 250°C for 5mins to remove the thermal history, then cooled to 30°C at 20°C/min, maintaining the temperature at 30°C for 5mins and finally heated to 250°C at a scanning rate of 20°C/min. The area and maximum of the crystallization exothermic peak during the cooling run were taken as the crystallization enthalpy and temperature (ΔH_c and T_c), respectively. Similarly, those of the melting endothermic peak in the heating run were recorded as the melting enthalpy and temperature (ΔH_m and T_m), respectively. Figure 1 showed that the thermal program.

Mechanical properties

The tensile strength was measured using the dumbbell pieces (length: 147 mm; width: 10 mm; thickness: 4 mm) from injection molding with an Instron 5996 universal tester (Instron) at 23°C with an initial gap of 50 mm under a crosshead speed of 50 mm/min. At least 6 specimens were used and the average value was taken as the result for each sample.

The Rheological behavior

The rheological behavior was characterized with melt index, which was measured with an SRZ-400E melt indexer (Changchun Intelligent Instrument & Equipment Co. Ltd, China) at 250°C under a load of 2.16 kg. Each sample was tested for at least 3 times and the average value was taken as the result.

Results and discussion

FTIR

FTIR spectroscopy is a particularly suitable technique for investigating the structure change and the specific intermolecular interaction. The spectra of PA6/PEA blends were collected to check the interaction between the PA6 and PEA blends and summarized in Figure 2. The C-H stretching bands between 3100-2800 cm^{-1} , C=O stretching centered at about 1638 cm^{-1} and -NH- absorption band centered at about 3300 cm^{-1} were observed for all the samples. No obvious difference was observed between the blank and the blends, which may suggest that there is no significant chemical reaction between PA6 and PEA.

The expanding FTIR absorption peaks of -N-H and -C=O were plotted in Figure 3a and 3b, respectively. Comparing with PA6 blank, the -N-H and -C=O absorption peaks of the blends shifted to higher wave number. Even these shifts were only about 2 cm^{-1} , it should suggest that the hydrogen bonds between -N-H and -C=O became weaker with the introduction of PEA into PA6 and thus the interaction between PA6 chains became smaller. These results should be due to the interactions between PEA and PA6. The -NH₂ group of PEA may form hydrogen bonds with the -NH group and -C=O group of PA6.

¹H-NMR

The ¹H-NMR spectra of PA6 blank, PA6/PEA blends and PEA were depicted in Figure 4. Clearly, no any new signal can be observed

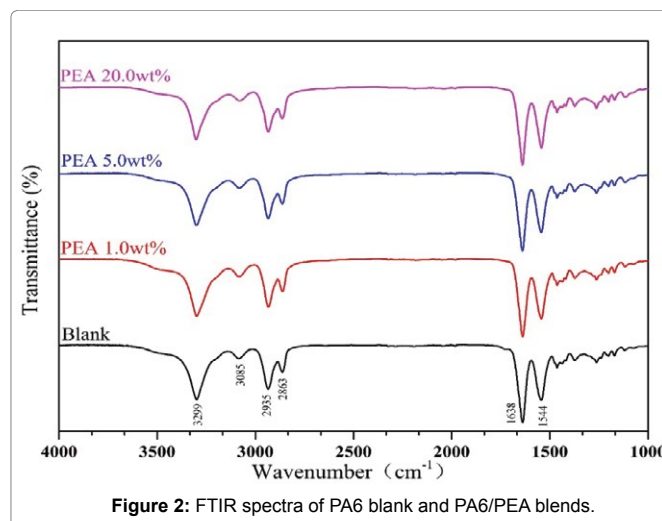
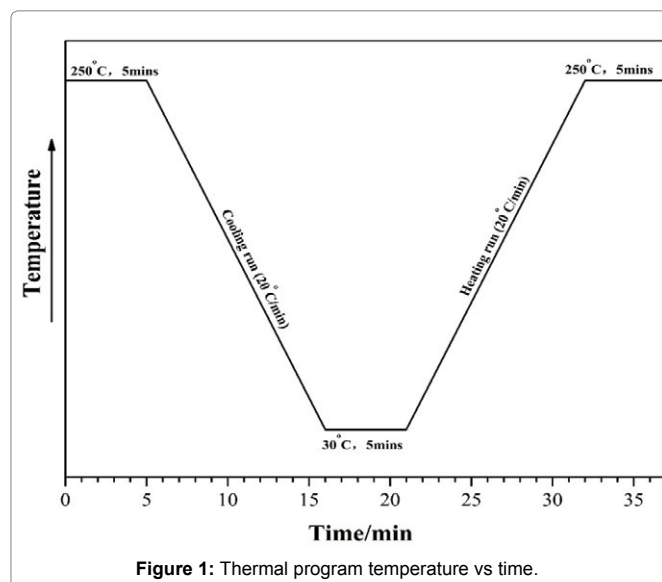
for the blends and the spectra of the blends were only the overlap of those of PA6 blank and PEA. This result should indicate that there was no obvious chemical reaction between PA6 and PEA during the melt-mixing.

WAXD

WAXD was used to check the effect of PEA on the crystal structure of PA6. As shown in Figure 5, it is clear that WAXD patterns of the blends were almost the same as PA6 blank. For all the samples, the diffraction peaks were observed at scattering angle 2θ of 19.0° and 23.5°, corresponding to γ (2,0,0) and γ (0,0,2/2,2,0) planes of the PA6 blank, respectively. Furthermore, no additional new diffraction peak was detected for the blends [15-19]. These results indicated that the inclusion of PEA into PA6 matrix did not influence the crystal structure of PA6 and PA6 in the blend crystallized in the stable γ form under the studied conditions [15,20].

Relative viscosity (η_r)

The relative viscosity (η_r) of PA6/PEA blends was measured to check if there was decrease in the molecular weight during the melt-



mixing and the results were listed in Table 1. The relative viscosity (η_r) of the blend was about 2.9 and almost the same as PA6 blank, which confirmed that there is no obvious change in molecular weight of PA6. This result was in agreement with the results of FTIR and $^1\text{H-NMR}$.

The thermal properties

The thermal properties of PA6/PEA blends with PEA contents of 0.5-20wt% were evaluated with DSC. The DSC curves were plotted in Figure 6 and the results were summarized in Table 2. The crystallization enthalpy ΔH_c , the melting enthalpy ΔH_m and the melt-crystallization temperature T_c of PA6 component in the blend were some higher than those of PA6 blank (Figure 6 and Table 2), which suggested that PEA enhanced the crystallization of PA6 component under the studied conditions. The enhanced crystallization may be due to that PEA improved the chain mobility of PA6. On the other hand, the melting temperature T_m of PA6 component in the entire blend is about 221°C, which hardly changed with PEA content and almost the same as that of

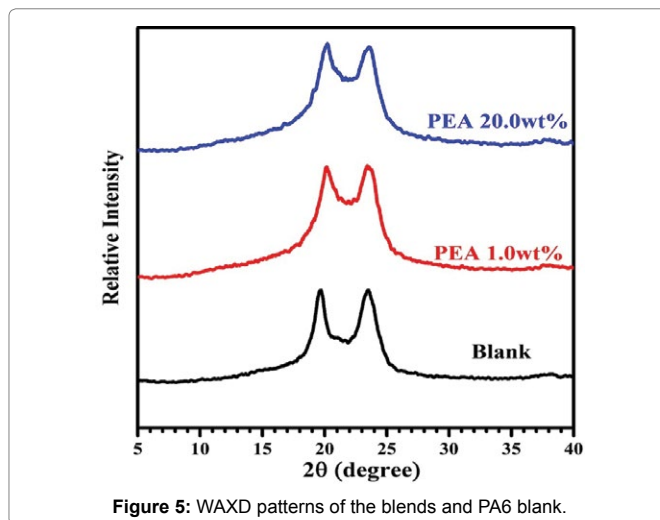


Figure 5: WAXD patterns of the blends and PA6 blank.

Table 1: The relative viscosity (η_r) of PA6 blank and PA6/ PEA blends.

η_r	Average	Variance
Blank	2.85	0.06
PEA 1.0wt%	2.79	0.01
PEA 5.0wt%	2.85	0.06
PEA 20.0wt%	2.89	0.02

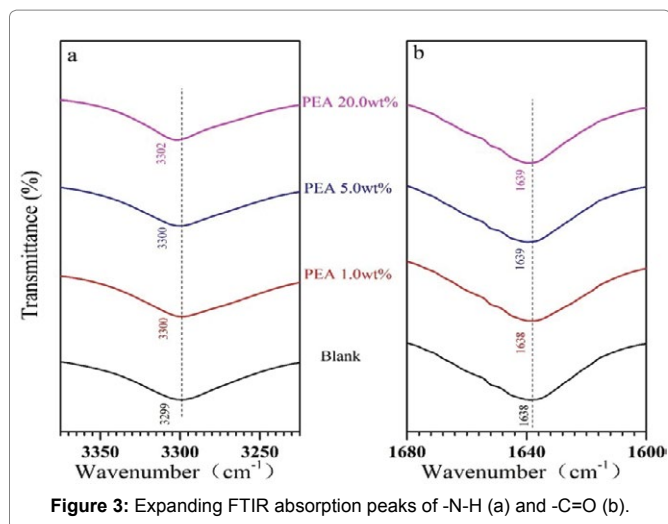


Figure 3: Expanding FTIR absorption peaks of -N-H (a) and -C=O (b).

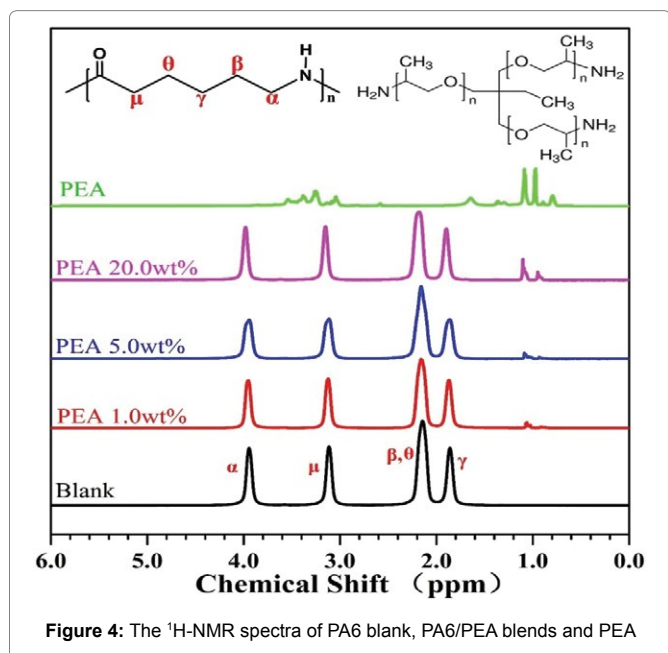


Figure 4: The $^1\text{H-NMR}$ spectra of PA6 blank, PA6/PEA blends and PEA

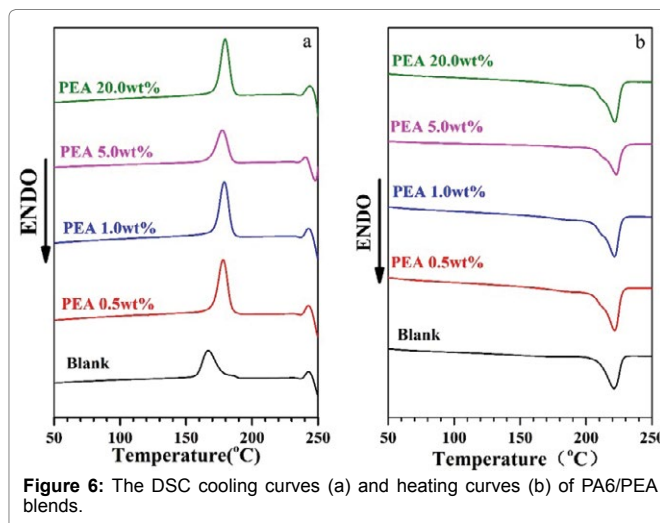


Figure 6: The DSC cooling curves (a) and heating curves (b) of PA6/PEA blends.

PA6 blank (Figure 6 and Table 2). These results should also indicate that there are no obvious chemical reactions between PA6 and PEA.

Mechanical properties

It is well known that the addition of low molecular organic additives usually depresses the mechanical strength. As to PEA, one may wonder the case is similar. Thus, the tensile properties of PEA1.0wt% blend was measured and listed in Table 3 to check whether the loading of PEA affected the strength of PA6. From Table 3, it was clear that the two samples had almost the same tensile properties, which indicated that an addition of PEA 1.0wt% almost didn't affect the strength of PA6 under the investigated conditions. This result should be due to the following two facts: one was the low loading of PEA and another was the enhancement effect of PEA on PA6 crystallization as mentioned previously.

Table 2: The thermal properties of PA6/PEA blends.

Sample	T_c (°C) ^a	ΔH_c (J/g) ^a	T_m (°C) ^b	ΔH_m (J/g) ^b
Blank	167	40	221	43
PEA 0.5wt%	178	66	222	72
PEA 1.0wt%	179	66	221	68
PEA 5.0wt%	178	55	223	58
PEA 20.0wt%	180	48	220	51

^a Determined by the cooling curves; ^b Determined by the heating curves.

Table 3: The mechanical properties of PA6 blank and PEA 1.0wt%.

Properties	Test standard	Blank	PEA 1.0wt%
Thermal deformation temp. (°C) ^a	ASTM D648	62.5	62.5
Tensile strength (MPa) ^b	ASTM D638	64.6 ± 1.2	62.8 ± 0.8
Tensile modulus (GPa) ^b	ASTM D638	1.82 ± 0.04	1.82 ± 0.04
Bending strength (MPa) ^c	ASTM D790	90.1 ± 0.7	88.5 ± 2.2
Flexural modulus (GPa) ^c	ASTM D790	1.99 ± 0.08	2.07 ± 0.09
Notched impact strength (J/m) ^d	ASTM D256	87 ± 2	77 ± 1
Mold shrinkage (%) MD ^e	ASTM D955	2.2	2.2
Mold shrinkage (%) TD ^e	ASTM D955	2.0	2.0
Shore hardness	ASTM D2240	72	72

^a Measured under a heating rate of 2°C/min and load of 1.8MPa; ^b Measured at 23°C with a rate of 50mm/min; ^c Measured at 23°C with a rate of 1.3mm/min; ^d Measured at 23°C; ^e Measured at 23°C after aging for 24h.

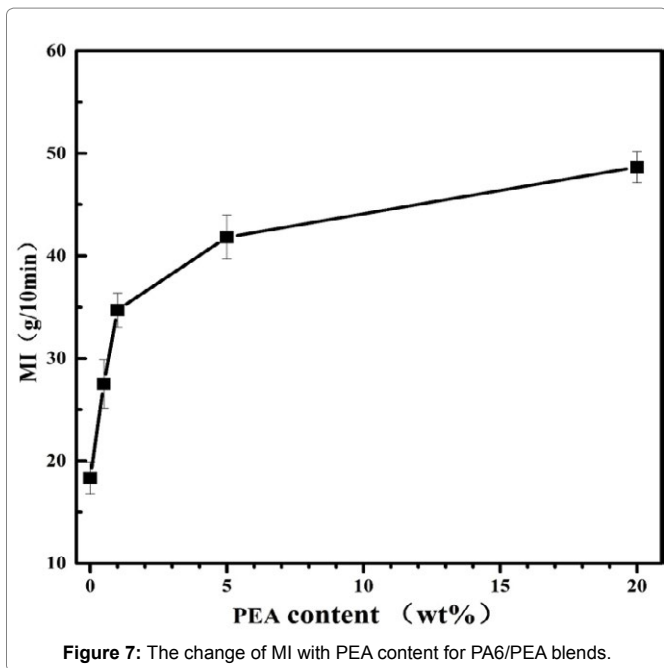


Figure 7: The change of MI with PEA content for PA6/PEA blends.

The rheology behavior

The effect of PEA on the rheology properties of PA6 was evaluated by melt indexer. The melt index (MI) of the blank was 18g/10min at 250°C under a load of 2.16kg. With the incorporation of PEA 0.5wt%, 1.0wt%, 5.0wt% and 20.0wt%, the MI increased to 28g/10min, 35g/10min, 42g/10min and 49g/10min (Figure 7), respectively. Obviously, the increase of MI was very fast at the beginning and then became slow with the increase of PEA content. The reason of this behavior is not clear in the present stage. One possible reason may be the aggregation of PEA in PA6 matrix for high loading of PEA. Anyway, the MI data unambiguously demonstrated that PEA significantly improved the melt flowability of PA6. As PEA form

hydrogen bonds with the C=O groups in PA6 chains as suggested by FTIR results, some of the hydrogen bonds between PA6 chains should have been broken and the interaction between PA6 chains has been weakened with the introduction of PEA. As a result, the melt flowability of PA6 increased and MI increased with PEA content under the studied conditions.

Conclusions

Trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (PEA) was incorporated into PA6 matrix by melt-mixing to modify its properties. FTIR, ¹H-NMR and relative viscosity measuring results suggested that there is no obvious chemical reaction or degradation during the blending. However, DSC results revealed that PEA enhanced the crystallization while didn't affect the melting point and crystal structure of PA6 component in the blends with PEA content lower than 20.0wt%. Furthermore, the incorporation of PEA can significantly improve the melt flowability of PA6 without the loss of mechanical properties as demonstrated by MI and Mechanical properties measurements. All the results suggested PEA was a very effective viscosity reducer for PA6.

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