



Material Properties

Effect of a polyetheramine additive on the melt-flowability of poly(butylene terephthalate)

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ABSTRACT

A polyetheramine (PEA) was added to poly(butylene terephthalate) (PBT) to improve its melt-flowability. Fourier transform infrared (FTIR) and solution proton nuclear magnetic resonance spectroscopy (¹H-NMR) were employed to check the change in chemical structure after compounding, while differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), capillary rheometer and a universal testing machine were used to investigate the thermal properties, crystal structure, rheological behavior and mechanical properties of PBT/PEA blends. The results revealed that a loading of 1.0wt% PEA in PBT drastically improved its melt-flowability without the loss of thermal properties and tensile strength. As comparisons, blends of PBT with polyols such as pentaerythritol and di(trimethylolpropane) were also prepared and the properties were evaluated. It was found that the melt-flowability improvement from these polyols was much lower than that from PEA.

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1. Introduction

Poly(butylene terephthalate) (PBT) has been developed for more than 70 years. As an important engineering plastic, it has been widely used in various applications such as automobile and electric/electronic parts due to its excellent mechanical properties, heat resistance, chemical resistance and electrical properties. The general grades of PBT have a relatively low molecular weight and the melt index (MI) is usually higher than 20 g/10min. Recently, high viscosity grades with a MI of about 10 g/10min have been commercialized by many companies to meet the requirement for higher strength PBT. However, it often becomes difficult to use these high viscosity grades to produce small parts with thin walls or precision parts because of its poor melt flowability. This problem becomes more serious in the case where these PBT resins are mixed with an inorganic filler such as glass fiber to improve the physical properties.

So far, very intensive efforts have been devoted to solve the problem of poor processability for high viscosity PBT. One method is to blend the high viscosity resin with viscosity reducer. Mixing high molecular weight PBT with the low molecular weight one [1] or cyclic oligomers [2] can reduce the viscosity to some extent with some loss of strength. Similarly, novolak resin [3] and liquid-crystal polymer [4] are incorporated as modifiers into PBT compositions to enhance the flowability, where high loading of the modifier, such as 20wt%, is necessary and thus limits its application. Also, polyvalent hydroxyl group-containing compound as well as phosphorus compound is added into PBT to produce a high flowability composition for molding [5].

Over recent decades, it has become well-known that dendrimer and hyperbranched polymer have much lower viscosity than their linear counterparts, with the continuous research in this field [6–10]. Naturally, this concept was employed for developing high flowability polyesters. Multi-functional compound components are added in the polymerization and included in the main chain of PBT [11–15]. As a result, the flowability of PBT is greatly improved while the melting point and strength is decreased. As an alternative option, hyperbranched polymer (usually hyperbranched polyester) is used as rheology modifier for PBT [16,17].

More recently, SABIC disclosed a novel process for high flowability PBT where octadecyl amine was melt-mixed with PBT in a

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twin screw extruder to give an amine-terminated PBT [18]. The incorporation of amine in the chain end vastly improves the melt-flowability of PBT. At the same time, a higher melt-crystallization temperature as well as higher crystallization enthalpy is observed with the amine modification, indicated enhanced crystallization. However, the molecular weight of PBT decreases in the process, which may result in an obvious decline of the mechanical properties.

In this work, a polyetheramine (trimethylolpropane tris[poly(propylene glycol), amine terminated] ether, abbreviated as PEA) was included in PBT to enhance its melt-flowability. The chemical structure change was firstly checked by Fourier transform infrared (FTIR) and solution proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$). Then, the thermal properties, crystal structure and rheology behavior of PBT/PEA blends with PEA content of 0.5–5wt% were investigated with differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and capillary rheometer, respectively. As comparisons, polyols such as pentaerythritol (PER) and di(trimethylolpropane) (DTMP) were also blended with PBT to evaluate the flowability-enhancement.

2. Experimental

2.1. Materials and blend preparation

The polyetheramine of trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (PEA) with a number-average molecular weight of 440 was purchased from Sigma-Aldrich while pentaerythritol (PER) and di(trimethylol propane) (DTMP) from TCI. Poly(butylene terephthalate) (PBT, DuPont 6129 NC010) was bought from Chuangxin Plastics Co. (China). All the reagents and resin were used as received.

After drying at 80 °C under vacuum overnight, PBT was melt-mixed with PEA, PER and DTMP at 250 °C for 3 mins in a twin-screw micro-compounder (Shanghai Dehong Rubber Machinery Co., China). The blends are coded as PEA xwt%, PER xwt% and DTMP xwt%, respectively, where x is the weight percentage of the additive in the blend. Dumbbell test pieces with a thickness of 4 mm, length of 147 mm and a neck width of 10 mm for tensile measurements were moulded in a Haitian SA900/260 injection molding machine (Haitian Plastics Machinery Ltd. China) with an injection temperature of 250 °C and mold temperature of room temperature. Before the measurements, all the samples were stored in an aluminium foil bag to protect them from moisture. The inherent viscosity of PBT was measured using a 5 mg/ml solution in 50/50 v/v mixture of tetrachloromethane and phenol at 25.0 ± 0.1 °C with an Ubbelohde viscometer.

2.2. Experimental techniques

Fourier transform infrared–attenuated total reflectance (FTIR-ATR) spectra were recorded in a Nicolet 8700 spectrometer in the range $4000\text{--}600\text{ cm}^{-1}$ for PBT and the blends. Data were collected over 64 scans with a resolution of 2 cm^{-1} .

Solution proton nuclear magnetic resonance spectra ($^1\text{H-NMR}$) were recorded on a Bruker Avance 400 spectrometer in trifluoroacetic acid-d at room temperature. The chemical shift was referred to trifluoroacetic acid-d (11.5 ppm).

Differential scanning calorimetry (DSC) runs were performed on a Polyma DSC214 (NETZSCH) under ultrapure nitrogen purge with 5.5–6.0 mg samples encapsulated in aluminum DSC pans. Before the DSC measurements, calibration was carried out with indium. The sample was firstly melted at 250 °C for 5 mins to remove the thermal history, then cooled to 30 °C at 20 °C/min, held at 30 °C for 5 mins 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.

Wide angle X-ray diffraction (WAXD) was performed on a SAXSess mc2 wide-angle X-ray scattering instrument (Anton Paar, Austria) at room temperature. Nickel-filtered Cu K α radiation ($\lambda = 0.154\text{ nm}$) was used. WAXD patterns were recorded in the 2θ range of $5\text{--}60^\circ$ at a scan speed of $1.0^\circ/\text{min}$. Each step increased 2θ by 0.004° and X-ray was collected for 20 s at each step.

The rheological behavior was characterized with melt index and shear viscosity. The melt index was measured with a melt indexer (SRZ-400E, Changchun Intelligent Instrument & Equipment Co. Ltd, China) at 250 °C under a load of 2.16 kg. Each sample was tested 5 times and the average value was taken as the result. The shear viscosity was determined using a Dynisco LCR7000 capillary rheometer (Dynisco Corporate) at 250 °C under shear rate of $400\text{--}5000\text{ s}^{-1}$.

The tensile strength was measured using the dumbbell pieces (length: 147 mm; thickness: 4 mm; neck width: 10 mm) with an Instron 5966 universal tester (Instron) at 23 °C with an initial gauge length of 50 mm under a crosshead speed of 50 mm/min. At least 6 specimens were averaged to collect the tensile properties for each sample.

3. Results and discussion

3.1. FTIR and $^1\text{H-NMR}$ spectra

FTIR and $^1\text{H-NMR}$ spectra were collected to check the specific interaction and reaction between PBT and the additives. The FTIR-ATR spectra in the carbonyl vibration region ($1800\text{--}1650\text{ cm}^{-1}$) are plotted in Fig. 1 for PBT blank, PEA 1.0wt%, PEA 20.0wt%, PER 1.0wt% and PER 20.0wt%. It is clear that the carbonyl absorption band of PBT blank, PER 1.0wt% and PER 20.0wt% overlap each other well. As a result, it should be safe to say that there were no obvious specific interaction and chemical reaction in PBT/PER blend. As to PBT/PEA blend, a shift of -2.5 cm^{-1} was observed for the carbonyl group of PEA 20.0wt%, which may be due to the specific interaction between the carbonyl group of PBT and amine group of PEA, and/or the formation of amide group originated from the reaction of PBT and PEA during the compounding PBT with 20.0wt% PEA.

Fig. 2 shows the $^1\text{H-NMR}$ spectra of PBT blank, PEA 1.0wt%, PEA 20.0wt% and PEA. α , β and γ regions correspond to CH group, $-\text{OCH}_2-$ and $-\text{CH}_2-$ group, respectively. Obviously, the spectrum of PEA 1.0wt% is almost the same as that of the blank, which suggests no NMR-detectable change in the chemical structure of PBT component occurred during the compounding of PBT with 1.0wt% PEA. As for PEA 20.0wt%, the case is quite different, where four new peaks labeled as 1, 2, 3 and 4 appeared at 8.13, 7.85, 4.46 and 1.95 ppm. Peak 1 (8.13 ppm) can be assigned to the CH group of benzene ring directly linked to the amide group, which was derived from the amidation reaction between PBT and PEA. Peak 2 (7.85 ppm) can be attributed to CH group in the carboxyphenyl end group while peaks 3 (4.46 ppm) and 4 (1.95 ppm) to $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ group in the hydroxybutyl end group, respectively. These signals of the end groups indicate the high level degradation of PBT component during the preparation of PEA 20.0wt%.

As the amidation and degradation occurred in PEA 20.0wt% blend, it is reasonable to conclude that these also took place in PEA 1.0wt% blend. As to the FTIR and $^1\text{H-NMR}$ spectra of PEA 1.0wt% are almost the same as those of PBT blank, which can only mean that the degree of amidation and degradation was low due to the low PEA content and could not be detected by FTIR and $^1\text{H-NMR}$.

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