Cong Meng and Jin-ping Qu*

Mechanical and thermal properties of polybutylene terephthalate/ethylene-vinyl acetate blends using vane extruder

Abstract: The poly(butylene terephthalate) (PBT)/ethylene-vinyl acetate copolymer (EVA) blends with different contents of EVA were prepared by an vane extruder. From the observation of morphologies, impact strength and dynamic mechanical analysis (DMA), the EVA particles were well dispersed in the PBT matrix and improved the impact strength of PBT. Differential scanning calorimetry measurements demonstrate that there is little diversification in the crystal structure and type. Thermogravimetric analysis reveals that as the weight fraction of EVA increases, the thermal stability of composite is enhanced. The rheological analyses indicate that the PBT/EVA blends follow a non-Newtonian behavior and viscosities of the blends are drastically lower than that of pure PBT at higher frequencies. The storage modulus (G′) and loss modulus (G″) of the blends monotonously increase as the frequency rises. This work provides a novel method to develop blends with excellent performance.

Keywords: compatibility; elongation flow; rheology; shear flow; toughen.

1 Introduction

Poly(butylene terephthalate) (PBT) is a special semi-crystalline thermoplastic engineering plastic with numerous superior properties such as solvent resistance, high rigidity and short cycle times in injection molding (1, 2). PBT was widely applied in automotive

*Corresponding author: Jin-ping Qu, National Engineering Research Center of Novel Equipment for Polymer Processing, The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China University of Technology, Guangzhou 510640, China, Tel.: +86 (020) 87112803, Fax: +86 (020) 87112503, e-mail: jpqu@scut.edu.cn
Cong Meng: National Engineering Research Center of Novel Equipment for Polymer Processing, The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China University of Technology, Guangzhou 510640, China

interiors, household appliances and precision components among others. However, PBT is one of the typical notch-sensitive materials with unnotched impact and poor notched impact strengths (3, 4). Apparently, application of PBT in engineering fields is greatly limited by its brittleness.

In order to improve the brittleness of PBT, tremendous efforts have been devoted, including plasticization (5) and copolymerization (6, 7). Another efficient and widely used way to improve brittleness is through blending with other polymers (8, 9), which yields blends with excellent comprehensive properties for specific applications. Examples of these polymers include ethylene-propylene-diene (10), thermoplastic polyurethane (11), acrylonitrile-butadiene-styrene (12) and high-impact polystyrene (13). During these investigations, researchers had a closer look at the effect of compatibilization on the thermal properties, mechanical properties, microstructure, rheological properties and morphology of the uncompatibilized and compatibilized blends.

Ethylene-vinyl acetate copolymer (EVA) is considered as one of the most used polymers in the manufacture of blends. It is prepared by combining ethylene (E) and vinyl acetate (VA) through a copolymerization reaction. In recent decades, considerable work has been devoted for blending PBT with E copolymers such as E-acrylate copolymer and E-octene copolymer. The EVA possesses fractional compatibility with PBT due to the presence of polar ester groups, which is an appropriate choice for blending to yield improved fracture toughness and impact resistance.

Many investigations have been put forward to obtain the PBT/EVA blends with different loading contents of EVA or influences of multifunctional modification. However, there is little consideration about the preparation of blends under elongation flow. In the present study, the PBT/EVA blends have been prepared by a vane extruder, which was invented by Jinping Qu, has a shot thermo-mechanical history for processing polymer materials and has good dispersion for dispersed phase in polymer blends or blends. Then the microstructures, impact and thermal properties of blends processing through elongation flow are investigated.

2 Experimental

2.1 Raw materials

PBT pallets (PBT Valox VX3101N, density 1.31 g/cm^3, melting point approximately 225°C, Vicat softening temperature approximately 170°C, glass transition temperature approximately 43°C) were supplied by SABIC Innovative Plastic Co., Ltd. (China). Poly(ethylene-co-vinyl acetate) (EVA 33-45 PV, with VA contents of 30 wt%, limited density 0.96 g/cm^3, melt flow index about 40 g/10 min, melting point approximately 62°C, Vicat softening temperature less than 40°C) was kindly supplied by GUAGNZHOU HONSEA Chemical Co., Ltd.

2.2 Polymer blend preparation

The PBT (6 h, 120°C) pellets and EVA (6 h, 50°C) particles were separately dried in a vacuum oven to prevent possible moisture degradation before processing. The mixtures of PBT resins with EVA resin were then performed in the high-speed mixer. The vane extruder was used to prepare the blends, and the temperature profile was varied as follows: 235, 240, 220 and 140°C (from hopper to die). Afterward, the extruder was immediately cooled down to room temperature in the water bath and subsequently pelletized and dried in the air oven for 8 h at 100°C. Finally, the drily pellets were compressed to form various samples for further tests such as impact, flexural and tensile specimens. The compression is carried out using a molding machine (Wuxi No.1 Rubber and Plastics Mechanical Co. Ltd., China, QBL-350) with a pressure set at 15 MPa and a temperature of 240°C. The pure PBT was subjected to the same mixing treatment compared with the blends.

The vane extruder is a novel polymer processing device based on elongation flow and comprises by 17 vane plasticizing and conveying units (VPCU) (14–17). The stator (R = 23 mm), vanes, baffles and rotor (R = 20 mm) of VPCU form a closed chamber; when the rotor is rotating, the volume of the closed chamber would change periodically, attributing to the eccentric distance between stator and rotor. A converging channel can be generated in the circumferential direction, thus providing higher stress and dynamic elongated deformation field. The process and specific processing principle have been reported detail.

DMA tests of the pure PBT and PBT/EVA blends were performed with an Ntezsch DMA242c (Germany) under the following conditions: temperatures varying from –100°C to 100°C, a nitrogen atmosphere, a heating rate of 3°C/min and a fixed frequency of 1 Hz. The dimensions of the specimen are (10 mm × 4 mm × 1 mm).

The differential scanning calorimetry (DSC) measurements were performed in a nitrogen atmosphere (Netzsch DSC204, Germany) using specimens of 4–6 mg. All the specimens were heated from room temperature to 240°C for 3 min, cooled down to 30°C and then heated to 240°C at a heating rate of 10°C/min.

The thermal stability of the specimens was investigated using a thermogravimetric analyzer (Netzsch TG2009, Germany). Specimens of 8–12 mg were heated from room temperature to 600°C in a nitrogen atmosphere at the heating rate of 10°C/min.

Dynamic oscillatory shear measurements were carried out on a controlled strain and stress rheometer (Anton Paar MCR302, Germany). The samples were placed in parallel plate geometry with 25 mm diameter and 1 mm gap between the two plates, then the frequency was swept from 0.01 to 100 rad/s. The test temperature and oscillation amplitude experiments were set at 240°C and 5%, respectively.

The fracture surface of the polymers is studied using scanning electron microscopy (SEM) (HITACHI S-3700N, Japan). The samples with a thickness of 4 mm were submerged in the liquid nitrogen for about 20 min then fractured to reveal the internal structure. Before the SEM experiments, all samples were sputtered with gold to enhance their conductivities.

The notched impact test was conducted using pendulum impact tester (INSTRON POE2000). The results were determined using the average of five repeats.

3 Results and discussion

3.1 Morphology observation

The fracture surface morphologies of PBT/EVA blends prepared through the vane extruder are shown in Figure 1. It is obvious that the PBT/EVA blends show a typical "sea-island" structure, where EVA acts as "island" embedded within the PBT matrix and the particle sizes are larger with the addition of EVA. Additionally, the EVA particles are dispersed homogeneously in the matrix when the content is less than or equal to 15 wt%. When the EVA content was 15 wt%, the EVA particles aggregated into gigantic particles. This may be due to the strong interaction among EVA molecular. However, the number of gigantic particles was not too much. It shows that the volume elongation flow
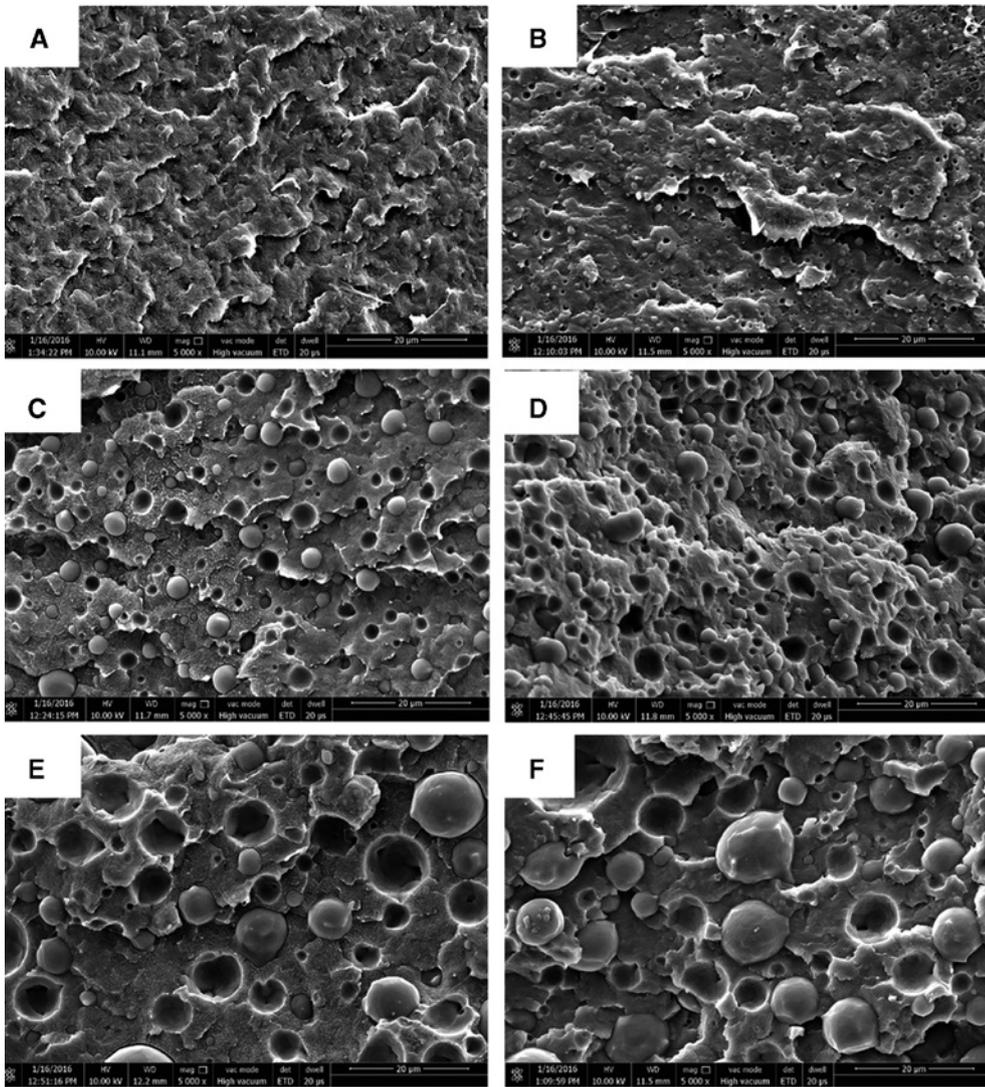
Figure 1: The morphologies of pure PBT and PBT/EVA blends by the vane extruder.
(A) Pure PBT, (B) PBT/EVA 5 wt%, (C) PBT/EVA 10 wt%, (D) PBT/EVA 15 wt%, (E) PBT/EVA 20 wt%, (F) PBT/EVA 25 wt%.

generated in vane extruder had excellently effect on the dispersion of EVA.

3.2 Impact strength

The impact strength of polymers is usually influenced by the interfacial adhesion and phase morphology among components. The notched impact strength of pure PBT and PBT/EVA blends is presented in Figure 2. It is obvious that the impact strength of blends significantly enhances with the addition of EVA. Compared with pure PBT, the composite with 20 wt% EVA was increased by approximately 300% and get the optimum position. Then the property declined when the content reached 25 wt%. This may due to the EVA dispersing uniformly in matrix, which
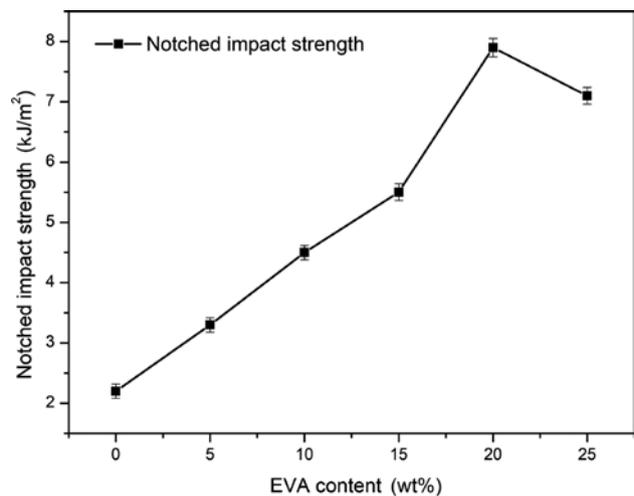

Figure 2: The notched impact strength of pure PBT and PBT/EVA blends prepared by the vane extruder.

enhances the impact strength of blends and then the gigantic particles emerged the defect when the samples were impacted.

3.3 DMA analysis

The dynamic mechanical analysis (DMA) were utilized to obtain the loss factor (tanδ) and storage modulus (E′). These parameters provide a better understanding of the interphase mix and phase structure through analysis of the information related to the glass transition temperatures (13, 18, 19). Figure 3A shows the curves representing the loss factor (tanδ) of pure PBT, PBT/EVA 5 wt% and PBT/EVA 10 wt%. It can be seen that both the curves of pure PBT, PBT/EVA 5 wt% and PBT/EVA 10 wt% have a clear peak at 60–90°C perhaps attributable to the glass transition. Usually, the peak temperature is on behalf of the glass transition (T_g), which the polymer chains begin to move in the amorphous regions. However, Figure 3A depicts that T_g is located at 72, 70.6 and 68.6°C for pure PBT, PBT/EVA 5 wt% and PBT/EVA 10 wt%, respectively. The latter could simply result from the addition of EVA that lowers the glass transition temperature, in accordance with the analysis of the improvement of the notched impact strength above.

The storage modulus (E′) of both the pure PBT, PBT/EVA 5 wt% and PBT/EVA 10 wt% as a function of temperature based on elongation flow is shown in Figure 3B. It is obvious that the storage modulus (E′) of blends decreases as the temperature rises. A distinctive drop could be noticed in the region of temperature ranging from 40°C to 75°C. In the range of explored temperatures, the storage modulus (E′) of pure PBT always looks higher than that of PBT/EVA blends.

3.4 DSC analysis

The DSC measurements are shown in Figure 4. Also, the results of crystallinity (X_c), crystallization temperature (T_c), crystallization onset temperature (T_o) and melting temperature (T_m) of pure PBT and PBT/EVA blends are gathered. The X_c of pure PBT and PBT/EVA blends is calculated using, respectively, Eqs. 1 and 2 (20). The melting enthalpy (ΔH_m^0) of pure PBT is taken as 145.5 J/g, and the weight fraction of PBT in the blending is W_f (21).

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \qquad [1]$$

$$X_c = \frac{\Delta H_m}{\Delta H_m^0}(1-W_f) \times 100\% \qquad [2]$$

The T_c of all studied samples can easily be determined from Figure 4A, and the results show that the temperature is pretty retained around 193°C. This could indicate that the crystallization behavior of the samples is independent of EVA. Compared with pure PBT, the X_c for the blends has a little decrease. Moreover, the blends that vary with increased contents of EVA seem to follow an irregular trend and not consistent with each other. The latter suggests that EVA has no active role in the heterogeneous nucleation of the PBT matrix. These findings are consistent with those recorded by Huang et al. (11). The second heating curves of pure PBT and PBT/EVA blends are shown in Figure 4B. Two main melting endothermic peaks could be observed for all the samples. The latter could result from the formation of rough and/or thinner crystals during the crystallization process. In addition, the melting peak is located in the higher temperature
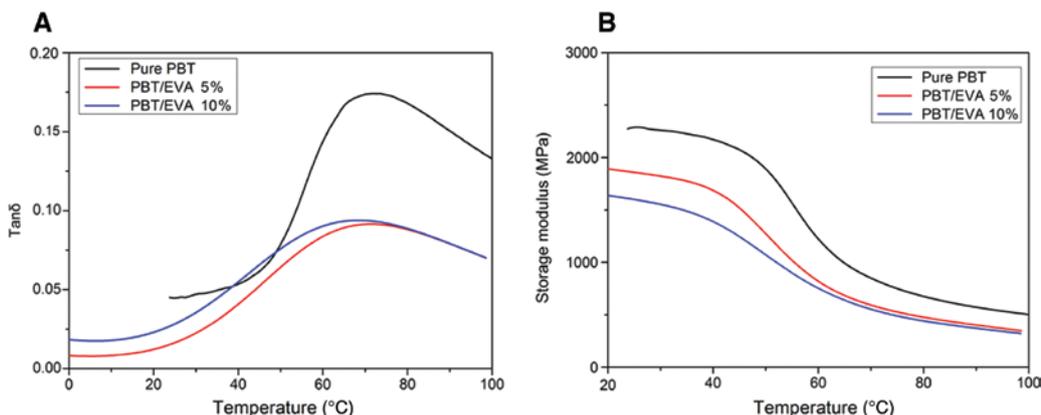

Figure 3: The DMA parameters of PBT and PBT/EVA blends as a function of temperature.
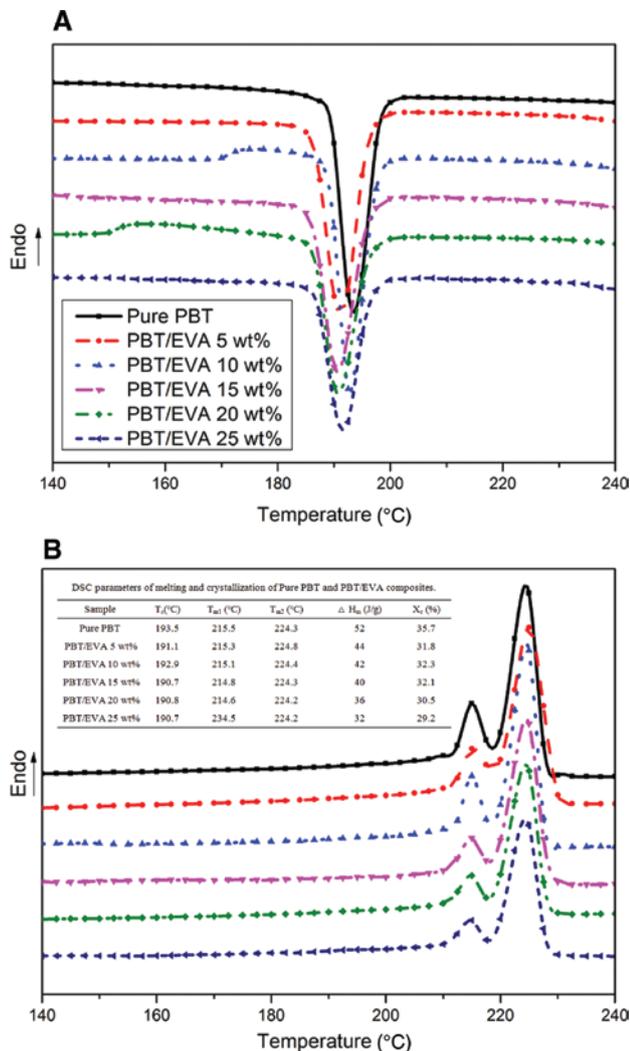(A) Loss factor (tan δ), (B) storage modulus (E′).

Figure 4: The DSC curves of PBT and PBT/EVA blends.
(A) Melt-crystallization, (B) second-heating.

Figure 5: The thermal stability parameters of PBT and PBT/EVA blends. (A) TGA, (B) DTG.

range, consistent with the melting temperature of the original crystallized components (22). The melting temperature is situated around 224°C, and all the samples were maintained at a relatively stable temperature. This implies that the melting process of PBT is not affected by the blending with EVA.

3.5 TGA analysis

The TGA and DTG curves of pure PBT and PBT/EVA blends based on elongation flow are shown in Figure 5. The thermal stability parameters of the samples, including the ending decomposition temperature (T_e), the maximum decomposition temperature (T_{max}), the temperature at 5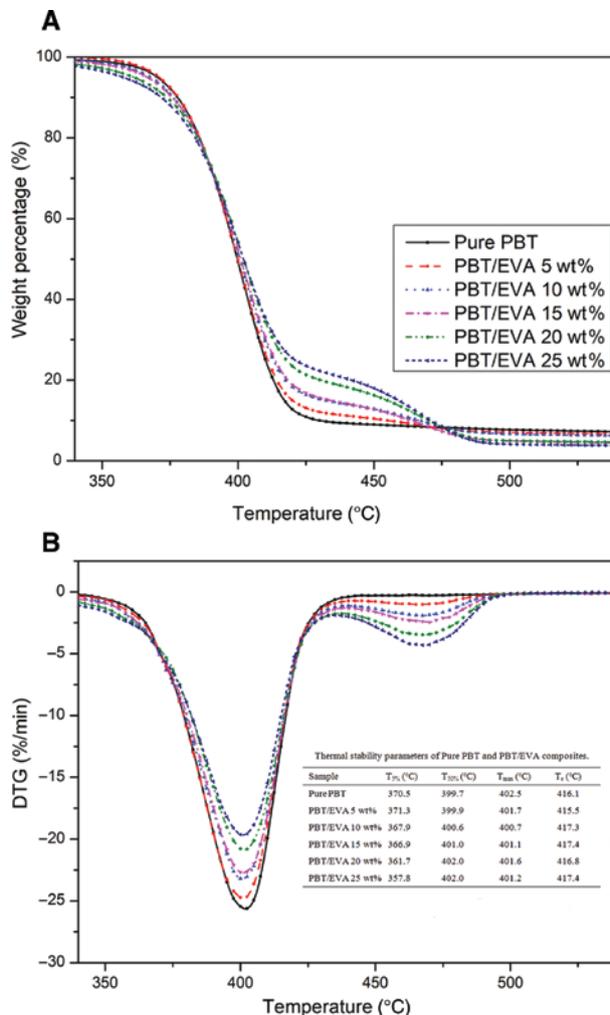0 wt% weight loss ($T_{50\%}$) and the temperature at 5 wt% weight loss ($T_{5\%}$), are listed. Compared with pure PBT, the blends have less char formation at 560°C, where residues of the blends look less and less present as the EVA content increases. The reason for that may have to do with the type of the residues left in the system at 560°C, which could be inorganic based. By increasing the weight fraction of EVA, the weight loss temperatures, $T_{5\%}$ and T_{max}, become reduced. By contrast, the weight loss temperatures, $T_{50\%}$ and T_e, seem to increase except for 5 wt% EVA. In addition, a two-step decomposition process could be observed in Figure 5B. The first recorded at around 370–420°C correspond to the decomposition of pure PBT, and the second step at around 430–440°C relies on the decomposition of EVA. This could indicate a poor compatibility between PBT and EVA. As a result, both materials kept their own decomposition temperatures during the break down process, in accordance with the TGA results.
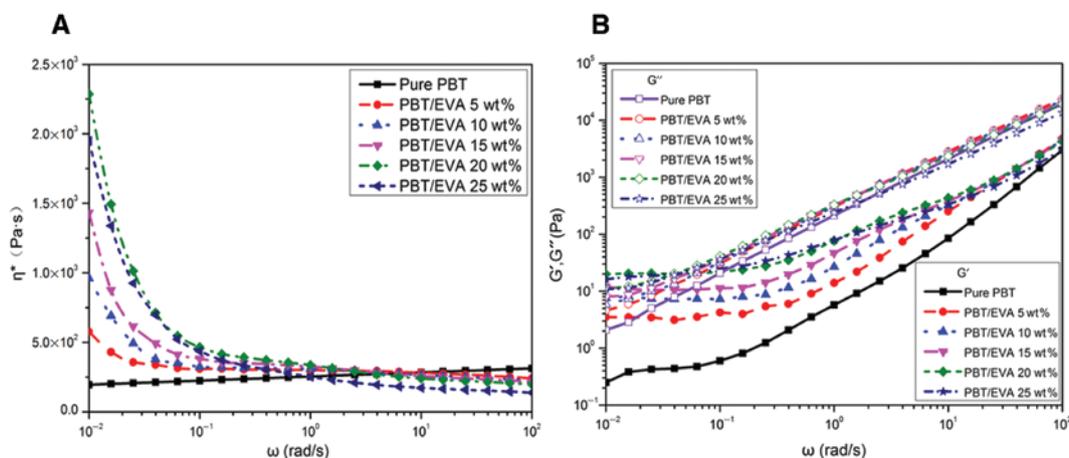
Figure 6: The dynamic rheology of pure PBT and PBT/EVA blends as a function of the frequency at 240°C.
(A) Complex viscosities ($\eta*$), (B) storage modulus (G') and loss modulus (G'').

These findings are also consistent with the ones reported by Chen et al. (23).

3.6 Melt rheology analysis

The complex viscosities ($\eta*$) of pure PBT and PBT/EVA blends based on elongation flow are shown in Figure 6A. It can be seen that pure PBT exhibits a typical Newtonian behavior in the range of explored frequencies, whereas PBT/EVA blends display non-Newtonian behavior with viscosity values far lower than that of pure PBT recorded at high frequencies. It is well known that when the two copolymers are put in an incompatible system, the resulting viscosity would be lower than that of both components taken separately in the range of explored frequencies. The latter constitute the reason of why obtained viscosity value was lower than expected based on simple addition rule. It is obvious that PBT and EVA have poor compatibility and interfacial adhesion that induces a slip between the two phases, leading to lower viscosity values. Similar results were found for PBT/EVA blends investigated by Ma et al. (24).

Figure 6B shows that G' and G'' of pure PBT and PBT/EVA blends are consistent with the theory and increase as the frequency rises. However, it is obvious that G' is less than G'' for all the samples due to their melting during the process to act as viscous liquids at 240°C. This indicates that the samples may reflect viscous behavior during the process of testing. Also, G' and G'' of PBT/EVA blends look significantly improved if compared with pure PBT and reduce as the content of EVA increases, except for PBT/EVA 25wt% at higher frequencies. The latter may be related to the compatibility between both polymers.

4 Conclusions

The PBT/EVA blends with different contents of EVA were prepared by an extruder based on elongation flow. The dispersion of EVA and the physical properties of PBT/EVA blends were examined in detail. From the observation of morphologies, impact property and DMA analysis, the EVA particles were well dispersed in the PBT matrix via elongation flow and improved the impact strength of PBT. DSC measurements demonstrate that there is little diversification in the crystal structure and type. TGA and DTG analyses reveal that as the weight fraction of EVA increases, the thermal stability of composite is enhanced, and two decomposition steps in the DTG curves are identified, which link to the poor compatibility between PBT and EVA. The rheological analyses indicate that the PBT/EVA blends follow a non-Newtonian behavior, and viscosities of the blends are drastically lower than that of pure PBT at higher frequencies. The storage modulus (G') and the loss modulus (G'') of the blends monotonously increase as the frequency rises. This work provides a novel method to develop blends with excellent performance and widens the applications to engineering materials.

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