Rheological Behavior of Polyester Blend and Mechanical Properties of the Polypropylene–Polyester Blend Fibers

Anton Marcinčin,[1] Eva Körmendy,[1] Marcela Hricová,[1] Andrej Rusnák,[1] Arun Pal Aneja[2*]

[1]*Department of Fibres and Textile Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, 812 37 Bratislava, Slovakia*
[2]*College of Technology and Computer Science, East Carolina University, Greenville, North Carolina 27858-4353*

ABSTRACT: The article deals with method of preparation, rheological properties, phase structure, and morphology of binary blend of poly(ethylene terephthalate) (PET)/poly(butylene terephthalate) (PBT) and ternary blends of polypropylene (PP)/(PET/PBT). The ternary blend of PET/PBT (PES) containing 30 wt % of PP is used as a final polymer additive (FPA) for blending with PP and subsequent spinning. In addition commercial montane (polyester) wax Licowax E (LiE) was used as a compatibilizer for spinning process enhancement. The PP/PES blend fibers containing 8 wt % of polyester as dispersed phase were prepared in a two-step procedure: preparation of FPA using laboratory twin-screw extruder and spinning of the PP/PES blend fibers after blending PP and FPA, using a laboratory spinning equipment. DSC analysis was used for investigation of the phase structure of the PES components and selected blends. Finally, the mechanical properties of the blend fibers were analyzed. It has been found that viscosity of the PET/PBT blends is strongly influenced by the presence of the major component. In addition, the major component suppresses crystallinity of the minor component phase up to a concentration of 30 wt %. PBT as major component in dispersed PES phase increases viscosity of the PET/PBT blend melts and increases the tensile strength of the PP/PES blend fibers. The impact of the compatibilizer on the uniformity of phase dispersion of PP/PES blend fibers was demonstrated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4222–4227, 2006

Key words: polypropylene; poly(ethylene terephthalate); poly(butylene terephthalate); blend fibers; phase structure

INTRODUCTION

The large number of published papers reveals that research in polymer blends has been studied in both academic and industry.[1–3] The properties of the polymer blends depend on properties of the individual components. They are also significantly impacted by phase structure for immiscible polymers. Compatibility of polymers during blending, interaction at the interphase, rheological properties of the components, and blending process parameters play a critical role in the development of the phase structure. This determines the ultimate properties of the polymer blends for application in fibers and films. These phenomena have been investigated in papers concerning the polymer blends based on fiber-forming semicrystalline polymers such as polypropylene (PP) and polyesters (PES) with suitable compatibilizer.[4–6] This is because PP and PES belong to a group of polymers, which provide a two-phase system instead of a homogeneous mixture. Fibers obtained from blends of PP and poly(ethylene terephthalate) (PET) with PP as major component provide enhanced property of dyeability, elasticity, and sorption characteristic.[7,8]

The phase structure offer interesting features for the fiber-forming polymer blends. First, the combination of polyester such as PET/poly(butylene terephthalate) (PBT) and PET/poly(trimethylene terephthalate) (PTT) result in miscible blends.[9] Second, three-component polymer blends, which are characterized as *in situ*-reinforced, obtained by the melt blending of two miscible polyesters (PET/PBT) are immiscible with polymer such as PP.[10] The chemical composition of the homopolymer influences the blend morphology. While the PET/PBT blends forms homogenous phase in the melt, there is a separation of components in PP/PES blends. Morphology and polymer structure in three-component blends can be influenced after thermal treatment of drawn fibers above the melting point of component PBT but below the melting point of PET. The components with the lowest melting temperature are disoriented under these conditions, while the remaining components retain their microfibrillar shape. This results in a composite like structure.[11,12]

TABLE I
Rheological Parameters of PET, PBT, and Their Blends
at 275°C (Ostwald de Weale Equation)

Polymer blend	Composition (%)	n	Viscosity, η (Pa s)	
			$\dot{\gamma} = 100$ s^{-1}	$\dot{\gamma} = 500$ s^{-1}
PP	100	0.53	229	108
PET	100	0.93	80.9	72.3
PET/PBT	85/15	0.95	75.3	71.0
PET/PBT	70/30	0.93	82.8	74.5
PET/PBT	50/50	0.96	94.8	89.1
PET/PBT	30/70	0.97	96.8	91.6
PET/PBT	15/85	0.96	93.3	87.9
PBT	100	0.97	89.7	84.8

n, power law index; $\dot{\gamma}$, shear rate; k, coefficient.

Size and shape analysis of the PET particles dispersed in the matrix of PP fibers indicate that deformation of these particles into microfibers have a relative narrow distribution of thickness of 0.2 μm and length of 10–50 μm.[7] It is possibly this part of the microfibers forms, which form a branched structure with essentially higher length of the particles than individual microfibers.

In the desired molecular weight of PET for fiber-forming properties, the length of the PET microfibers in PP/PES spun fibers is inversely proportional to the melt viscosity of the dispersed PET component. Conversely, the thickness of the microfibers is proportional to the viscosity of PET. Less deformed PET particles during spinning of PP/PES fibers are subsequently deformed during the drawing process.[7]

Some of our previous results have shown a synergistic impact of the presence of PBT, in the blend with PET during processing of PP/PES blend in and subsequent spinning. The lower melting temperature of PBT, formation of copolymer with PET in the blend melt, crystallinity suppression and higher deformability of the PET/PBT (PES) blend[13] may possibly contribute to the lowering of processing temperature,

improving the rheological and mechanical properties of the blend of PP/PES fibers.

In this article, the impact of the presence of PBT in the ternary PP/(PET/PBT) blend fibers is presented. We discuss the rheological properties of the PP, PET and PBT, their binary and ternary blends, and mechanical properties of the blend fibers over a wide range of the blend composition. In addition, the impact of commercial oligomeric polyester based on montane wax "Licowax E" (as compatibilizer) on the rheological behavior and mechanical properties of the PP/PES is discussed. The interactions of PET and PBT components in the blend are estimated using DSC analysis. The compatibility of polymer components (PP, PET, and PBT) during blending and spinning was investigated by analyzing the coefficient of variation of mechanical properties such as tenacity and elongation of the PP/PES blend fibers.
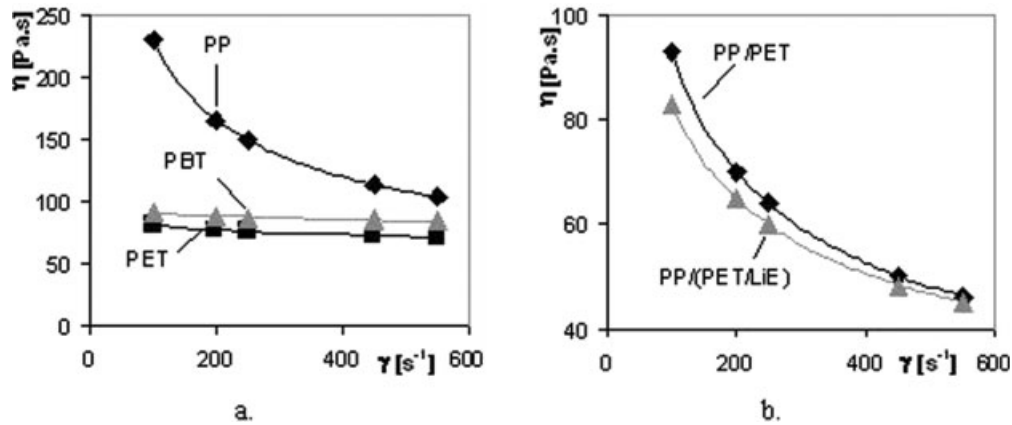
EXPERIMENTAL

Polymers and additives

The following polymers and additives were used in our study:
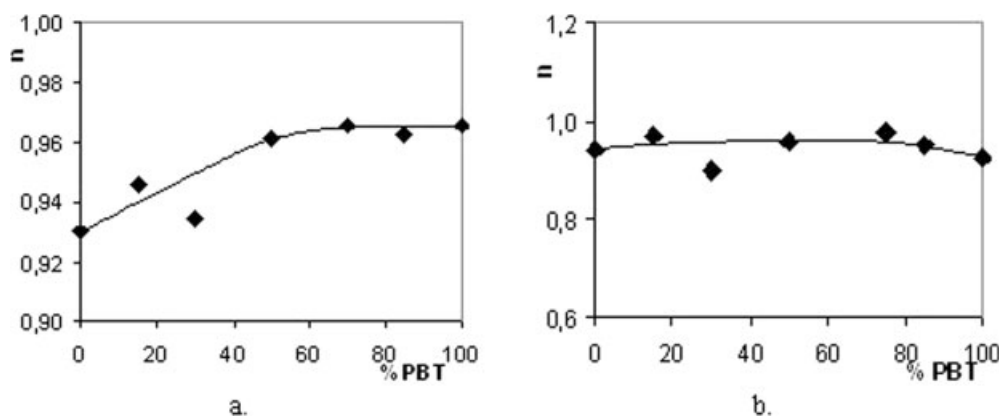
Figure 1 Dependence of power law index n of PET/PBT blends on content of PBT. (a) Without LiE, (b) with LiE.

Figure 2 Impact of shear rate on viscosity. (a) Pure components PP, PET, and PBT; (b) PP/PET blends (30/70) wt %; concentration of LiE = 1.5 wt %.

Polypropylene TF 331 (PP), MFI = 18.0 g/10 min (Slovnaft a.s., Bratislava, Slovakia)
Poly(ethylene terephthalate), (PET), IV = 0.55 L g^{-1} (phenol-tetrachlor etan 1 : 3) (SH, Senica, Slovakia)
Poly(butylene terephthalate) Celanex 2000 (PBT), MFI = 19.8 g/10 min (Ticona GmbH, Kesterbach, Germany)
Montane wax Licowax E (LiE), (Clariant AG, Basel, Switzerland)

Preparation of the polymer blends, final polymer additive, and blend fibers

PP/PET/PBT blend fibers were prepared in two steps:

A. The first step consisted in blending of polymer components. Powdered (grinded) polymers (and compatibiliser), were mixed in laboratory mixer at room temperature. The mixture was used for preparation of the blend chips, e.g., PET/PBT and final polymer additive (FPA). This was done by melt blending, using the laboratory twin-screw extruder with F = 28 mm, with zone temperatures 75°C (feedstock), 235°C,

275°C (4 zones) and 280°C (head). Temperature of the melt was 275°C. The (PET/PBT) composition in FPA was in complete concentration range of 0–100%. PP content in FPA was constant at 30 wt %. The PET/PBT blends for rheological measurements were prepared at the same conditions.

B. In the second step the blend consisting of PP/PES was melt spun into fibers from the mixture of the PP and FPA chips with total concentration 8 wt % of the PES phase using spinning equipment with extruder of ϕ = 30 mm. The parameters of spinning were: spinneret 48 holes, temperature 275°C, spinning speed 400 m min^{-1}. Multifilaments were drawn using the laboratory drawing equipment. The draw ratio was λ = 3 : 1 at a temperature of 110°C.

Analytical methods

Rheological measurements

Rheological properties of pure polymer components and polymer blends was obtained using capillary
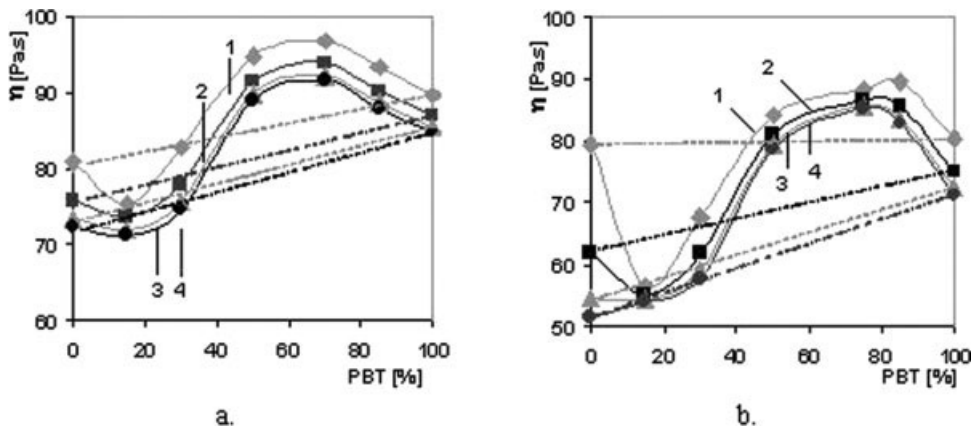
Figure 3 Impact of PBT concentration on viscosity (a) PET/PBT blends and (b) PET/PBT/LiE. (1) $\dot{\gamma} = 100$ s^{-1}; (2) $\dot{\gamma} = 250$ s^{-1}; (3) $\dot{\gamma} = 400$ s^{-1}; (4) $\dot{\gamma} = 500$ s^{-1}.

TABLE II
Rheological Parameters of PP/PES Blends at 275°C (Ostwald de Weale Equation)

Polymer blend	Composition (%)	n	Viscosity, η (Pa s)	
			$\dot{\gamma} = 100 \ \text{s}^{-1}$	$\dot{\gamma} = 100 \ \text{s}^{-1}$
PP/(PET/PBT)	30/70/0	0.58	93.3	47.5
PP/(PET/PBT)	30/60/10	0.75	85.1	56.9
PP/(PET/PBT) + LiE	30/70/0	0.64	83.2	46.6
PP/(PET/PBT) + LiE	30/60/10	0.78	81.3	57.0

n, power law index; $\dot{\gamma}$, shear rate; k, coefficient.

extrusiometer Göttfert N 6967 with extruder $\phi = 20$ mm at 275°C. The measurement conditions were similar to those during spinning. Newton and Oswald de Waele laws were used for determination of basic rheological parameters: apparent viscosity $\eta = \tau/\dot{\gamma}$ and power law index n ($\tau = k \ \dot{\gamma}^n$), which characterize the Newtonian behavior of the polymer melt, where τ is the shear stress; $\dot{\gamma}$, shear rate; η, apparent viscosity; n, power law index; k, coefficient.

DSC measurement

DSC 7 (Perkin–Elmer) was used for the evaluation of thermal properties of the PP/PES blends and for estimation of the supermolecular structure and component interaction at the interphase. The heating and cooling rate was 10°C/min, in the temperature range of 50–280°C.

Mechanical properties of the blend fibers

An Instron (Type 1112) was used for measurements of the mechanical properties of fibers. Coefficient of variation of fiber tensile strength CV_T was evaluated from 30 measurements.

RESULTS AND DISCUSSION

The dynamic viscosity η and power law index n of PET/PBT blends in a wide range of component composition at 275°C reveal similar rheological behavior as the pure component PET and PBT. The viscosity of PET is reduced by about 10% when compared to PBT and both show very small deviation from the Newtonian characteristic (Table I, Figs. 1 and 2). In general, low deviation from the Newtonian flow is desirable for fiber-forming polyesters. PET/PBT melt blends exhibits nearly Newtonian behavior ($n \cong 1$) with no dependency of viscosity on shear rate (Figs. 1 and 2).

Lower viscosity of PES components and their blends in comparison with PP [Fig. 2(a)] enables formation of a blend of PP/PES into fibers with high deformed particles of dispersed (PES) phase in PP matrix. Desired rheological properties and favorable impact of the compatibilizer in the PET/PBT blend provide for the creation of the polyfibrilar structure of the PP/PES fibers similar to that of blends obtained from PP/PET fibers.[7]

Considering the similarity of the rheological characteristics of the PET and PBT and the assumption of the miscibility of these polyesters above their melting temperature, there is high probability of synergistic behavior of PET/PBT blend. The dependence of viscosity on the PET/PBT composition results in an S shape curve along the additive line [Fig. 3(a) and (b)]. Additive viscosity was obtained as proportional contribution of components viscosity (assumption of the similar density of PET and PBT melt at constant temperature). A slight decrease in the experimental viscosity at a low concentration of PBT in PET/PBT blend (about 15 wt %) results from reduction in the original compact PET structure. This reduction is supported by the presence of more flexible PBT chains and by the decrease in the number of aromatic rings in a unit volume of the blend. The heterogeneity of the polymer blend on molecular and supermolecular level can also contribute to the decrease of the blend viscosity (Fig. 3). Conversely, when PBT is present as a major component in the blend, the experimental blend viscosity distinctly increases above the additive line. The maximum in the positive deviation in viscosity occurs at about 70 wt % of PBT (Fig. 3). The higher viscosity of the PES blends demonstrates stronger interactions between polymer chains and functional groups related to PBT. This phenomena results from a relative higher number of the polar
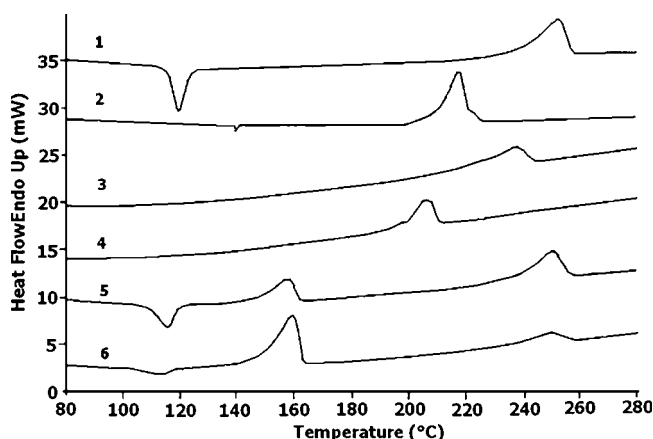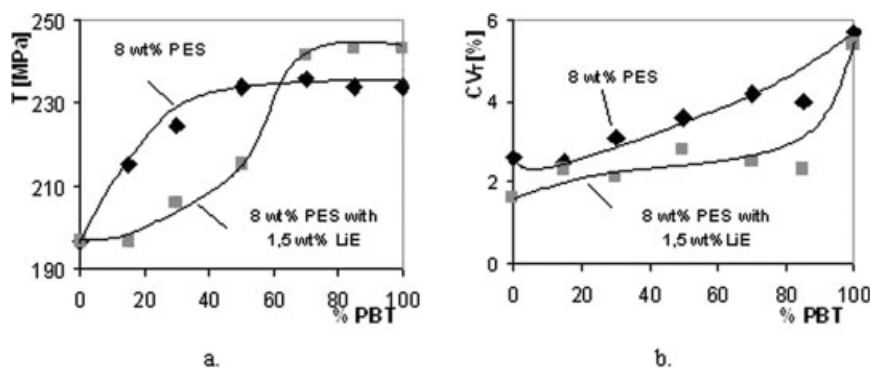

Figure 4 DSC analysis of the PET/PBT and PP/PET blends. (1) PET; (2) PBT; (3) PET/PBT (70/30); (4) PET/PBT (30/70); (5) PP/PET (30/70); (6) PP/PET (70/30).

Figure 5 Impact of PBT concentration in PES (PET/PBT) additive on (a) tensile strength and (b) coefficient of variation of tensile strength for PP/PES blend fibers.

ester groups and aromatic rings in the blend, as well as higher stiffness of PET blocks in the PET/PBT co-polymer.

Commercial compatibilizer of montane wax (Licowax E, LiE) present at very low concentration (1.5 wt %) decreases the experimental PES viscosity. This is similar to the viscosity behavior of individual components. The impact of LiE on PBT viscosity is less significant than that for PET [Fig. 3(b)]. Results indicate that decrease of the polymer viscosity is probably due to the chemical interactions of ester functional groups of both PES and compatibilizer (re-esterification). Plasticizing effect at low content of the compatibilizer (1.5 wt % of polyester wax LiE) without chemical interaction is less likely. The S shape dependence of the viscosity on blend composition is even more pronounced by the presence of compatibilizer LiE [Fig. 3(b)]. Both the negative deviation of experimental viscosity at low concentration of PBT in the blend and positive deviation at high concentration of the PBT phase are increased in the presence of the compatibilizer. The experimental and additive viscosity lines are identical at about 30 wt % of the PBT in the PET/PBT blend. This concentration possibly corresponds with phase inversion of the PET and PBT components.

FPA obtained from PP/PET blend with concentration of 30 wt % of PP exhibits higher deviation from Newtonian flow (close to PP) and higher viscosity at low shear rate in comparison with PET (Table II, Fig. 2). Small concentration of PBT contributes to a decrease of the FPA viscosity and also to superior flow characteristics. The presence of compatibilizer contributes to enhanced flow properties of FPA with reduced non-Newtonian behavior of the blend. In addition it simultaneously decreases the viscosity mainly at higher shear rate (Table II). From this point of view the ternary blend PP/PES 30 : 70 (PES = PET + PBT) as FPA was used for blending with PP and spinning.

The phase structure of the PP/PES blend fibers can be significantly impacted by the supermolecular

structure of the PET/PBT polymer additive. The miscibility of the polyester components above the melting temperature, dissimilar crystallization kinetics on cooling of the blend, and chemical interactions between PET and PBT lead to changes in supermolecular structure of the dispersed phase.

DSC analysis of PET/PBT (30/70) and (70/30) blends indicate only one melting point corresponding to the major component present (Fig. 4). Melting temperatures are slightly reduced. Results on miscible PET and PBT in amorphous phase below melting temperature show suppression of crystallization of minor components and possible chemical interaction in the blend. From this point of the view the higher deformability of the PES dispersed phase in the PP matrix can be expected. Immiscible polymer blend of PP/PET is characterized by melting temperatures of the individual components (Fig. 4).

It is expected that the probability of occurrence of weak bonds in the blend fibers is proportional to non-uniformity of the phase structure due to size, shape, and distribution of the dispersed phase in the local microvolume of matrix. Assuming uniform material properties of polymers and processing conditions during blending and spinning, the mechanical properties of the blend fibers and their nonuniformity
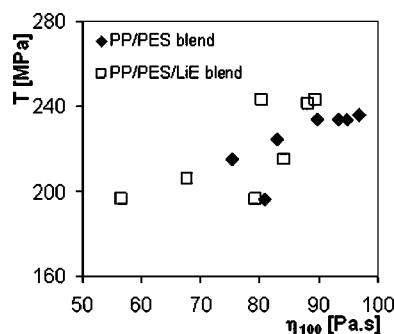
Figure 6 Impact of apparent viscosity of PES dispersed phase at shear rate 100 s^{-1} and 275°C on tensile strength of the PP/PES blend fibers.

TABLE III
Elongation (E) of Blend PP/PES (92/8) Fibers

PP/PES blend fibers	Composition of PES phase in the fibers (%)	E (%)	
		8 wt % of PES	8 wt % of PES, 1.5 wt % of LiE
PP/PET	100	26.0 ± 1.22	29.2 ± 1.66
PP/(PET/PBT)	85/15	26.5 ± 2.01	28.2 ± 1.86
PP/(PET/PBT)	70/30	27.2 ± 1.90	27.5 ± 1.84
PP/(PET/PBT)	50/50	27.6 ± 2.35	26.4 ± 1.43
PP/(PET/PBT)	30/70	25.4 ± 2.08	27.3 ± 1.53
PP/(PET/PBT)	15/85	25.5 ± 1.94	27.4 ± 1.21
PP/PBT	100	25.8 ± 2.45	26.4 ± 1.24

Elongation of PP fibers $E = 27.5\%$.

indicates compatibility and distribution of the particles of dispersed phase in the matrix.

The impact of PET/PBT composition on tensile strength at break of the PP/PES blend fibers (8 wt % PES) is shown in Figure 5(a). Results indicate the contribution of higher compatibility of the PET/PBT blend with PP in comparison with individual PES components. Superior tensile strength of the fibers with higher content of PBT is probable due to slightly higher molecular weight of PBT, higher adhesion bonds at interphase, and stiffening of PBT in presence of PET component. Furthermore, the positive impact of compatibilizer (Licowax E) on tensile strength of the blend PP/PES fibers with PBT as major component in dispersed polyester phase has been observed (Fig. 5).

In spite of the positive impact of PBT in PET dispersed phase on the rheological properties of the PP/PES melt blend and mechanical properties of fibers, the internal nonuniformity of PP/PES fibers decreases with increasing PBT concentration [Fig. 5(b)]. The coefficient of variation of tensile strength, CV_T, increases linearly with PBT concentration. This property is reduced in the complete range of PES composition for PP/PES blend fibers in presence of compatibilizer [Fig. 5(b)].

The S shape dependence of tensile strength on composition of PES dispersed phase corresponds to similar dependence of viscosity versus polyester composition discussed earlier. The shape suggests the reinforcement of the structure of the dispersed PES phase at higher concentration of PBT in PES (Fig. 6).

Elongation of the blend PP/PES fibers is not changed by the composition of the PES dispersed phase or by the compatibilizer. However, compatibilizer significantly contributes to improvement of the internal (structural) unevenness of the PP/PES blend fibers (Table III).

CONCLUSIONS

The present work investigates the influence of PET/PBT blend composition on rheological properties, phase structure, and mechanical properties of PP/PES blend fibers. From the experimental results we conclude:

PBT as a minor component in PET/PBT blend alters the compact structure of the PET with resultant decrease in viscosity. Conversely, the presence of the minor component of PET leads to reinforcement of the PBT with enhanced viscosity in relation to the additive line.

The flow characteristics of PET/PBT blend are close to Newtonian behavior. Individual components on the other hand exhibit higher deviation from Newtonian behavior relative to the blend.

Oligomeric polyester montane wax LiE used as a compatibilizer decreases the viscosity of PET, PBT, and their blends. Fibers obtained from blends with compatibilizer exhibit distinctly higher evenness of phase structure.

Tensile strength of fibers obtained from PP/PES blends are superior relative to PP/PET fibers.

References

1. Yavari, A.; Asadinezhad, A.; Khonakdar, H. A.; Böhme, F. Polymer 2005, 46, 5082.
2. Aravind, I.; Albert, P.; Ranganathaiah, C.; Kurian, J. V.; Thomas, S. Polymer 2004, 45, 4925.
3. Papadopoulon, C. D.; Kalfoglon, N. K. Polymer 2000, 41, 2543.
4. Bettini, S. H. P.; Angelli, J. A. M. J Appl Polym Sci 2002, 85, 2076.
5. La Mantia, F. P.; Scalfaro, R.; Colletti, C.; Dimitrova, T.; Magnanini, P.; Paci, M.; Filippi, S. Macromol Symp 2001, 176, 265.
6. Champagne, M. F.; Huneault, M. A.; Roux, C.; Peyrel, W. Polym Eng Sci 1999, 39, 976.
7. Körmendy, E.; Marcinčin, A.; Hricová, M.; Kovačič, V. Fibres Text East Europe 2005, 13, 20.
8. Marcinčin, A.; Brejka, O.; Jačanin, O.; Golob, V.; Marcinčinová, T. Fibres Text East Europe 2000, 4, 66.
9. Avramova, N. Polymer 1995, 36, 801.
10. Evstatiev, M.; Schultz, J. M.; Petrovich, S.; Georgiev, G.; Fakirov, S.; Friedrich, K. J Appl Polym Sci 1998, 67, 723.
11. Fakirov, S.; Evstatiev, M. Adv Mater 1994, 6, 395.
12. Evstatiev, M.; Fakirov, S.; Friedrich, K. Appl Comp Mater 1995, 2, 93.
13. Yu, Y.; Choi, K.-J. Polym Eng Sci 2004, 37, 91.