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Phase Morphology of Polypropylene-Polyethylene Terephthalate Blend Fibres

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Abstract

The article deals with the phase morphology of polypropylene-polyethylene terephthalate (PP/PET) blend fibres. The development of the morphology of the blend PP/PET fibres in the spinning and drawing processes, in dependence on molecular weight and the rheological properties of PET in the dispersed phase has been investigated. In experimental work both the length and diameter of PET deformed particles in PP matrix have been evaluated. In general, it was found that the length of the PET microfibrils in PP fibres after spinning and drawing is indirectly proportional to the molecular weight of the PET. However, in the drawing process the increment of the microfibril length of the dispersal phase is higher for PET with a higher molecular weight in comparison to the length after spinning. This means that the length of PET particles in the PP matrix is strongly influenced by spinning conditions for a lower molecular weight of PET and by the drawing conditions for a higher molecular weight of PET.

Key words: polypropylene-polyethylene terephthalate, blend fibres, phase morphology, spinning, drawing, microfibrils, molecular weight, rheological properties.

Introduction

The compatibility of polymer components, the positive interactions of polymer chains at interface in a heterogeneous blend, and suitable rheological conditions during spinning play a decisive role in the development of the phase morphology of polymer blend and blend fibres [1-3].

The two levels of rheology of the immiscible polymer blend are considered in the shear or elongation flow. Macrorheology describes the rheological behaviour of the blend melt (viscosity and elasticity), and microrheology deals with the deformation of particles (drops) of the dispersed phase in the matrix in the competitive processes of drop break-up and coalescence during mixing and spinning. The size and shape of the deformed dispersed phase determine the final-phase morphology of the polymer blend [4,5].

In general, the deformation of the particles - the droplets of disperse phase in matrix - in the steady uniform shear flow can be expressed using two dimensionless parameters [6-8]:

■ capillary number $Ca = \eta_m \dot{\gamma} r / \sigma$

■ the ratio $K = \eta_d / \eta_m$

where:

- $\dot{\gamma}$ - the shear rate,
- r - the radius of undeformed drop,
- σ - the interfacial tension,
- η_d - the viscosity of the dispersed phase,
- η_m - the viscosity of the matrix.

The deformation (ε) of the droplet of the dispersed phase is characterised by the

length (l) and diameter (d) of the drop deformed into a spheroid.

$$\varepsilon = (l-d)/(l+d) \quad (1)$$

For a small deformation according to Taylor's theory, one can write:

$$\varepsilon_T = 5/(4K) \quad \text{for } K > 1 \text{ and } Ca < 1 \quad (2)$$

$$\varepsilon_T = Ca (19K+16)/(16K+16) \quad \text{for } K < 1 \text{ and } Ca < 1 \quad (3)$$

Cox extended Taylor's theory and derived the expression for droplet deformation in an extensional flow:

$$\varepsilon(t) = 3/2 Ca [(19K+16)/(16K+16)] [1 - e^{-19K/20Ca \int \dot{\gamma}_E t}] \quad (4)$$

where:

$Ca = \eta_m \dot{\gamma}_E r / \sigma$, $\dot{\gamma}_E$ - the elongation gradient of the flow, ε is often calculated for $t=0$.

Competition between the drop break-up and coalescence results in the critical deformation ε_c . In the case of shear flow, the deformation ε_c passes through a minimum of $\varepsilon_c \approx 0.5$ at a K-ratio lying within the range of values $K=0.1-1.0$, whereas for elongation flow $\varepsilon_c \approx 0.2$ at higher $K=1-5$.

The macrorheological behaviour of the blend of the Newton law for the shear and extensional flow and the Ostwald-de Waele power law are most often used to describe the behaviour of the polymer melt. The deviation of the experimental blend viscosity from the additive value is very often used for estimating the 'technological compatibility' of polymer components [2,9].

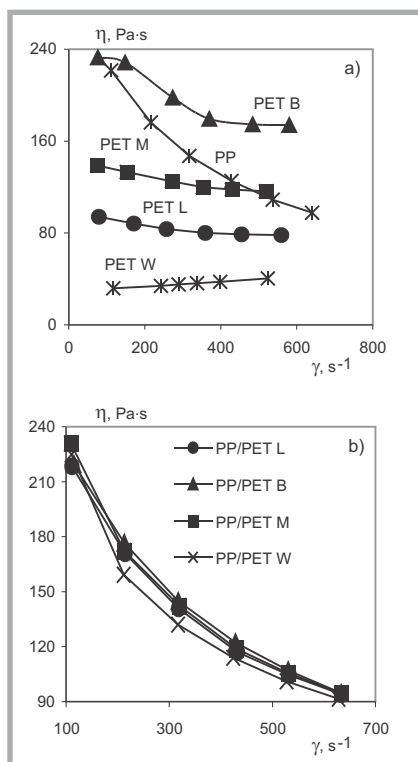


Figure 1. Dependencies of melt viscosity of polymers (a) and PP/PET blends (b) vs. shear rate.

Several papers have been devoted to the development of the phase morphology and properties of PP/PET fibres using reactive or non-reactive additives such as PP grafted by maleic anhydride, or by oxazoline and using suitable block copolymers [3,10]. Experimental results indicate more suitable mixing and spinning conditions, a higher uniformity in blend phase morphology and a higher evenness of fibre properties at a lower viscosity of the PES dispersed phase that has been achieved by compatibilisers [11]. PP/PET blend fibres which already have a relatively low concentration of the PET dispersed phase (8-10%) provide exhaust dyeability by disperse dyes and improved elasticity [3,12,13].

This paper deals with the development of phase morphology during the preparation of PP/PET blend fibres in dependence on molecular weight (melt viscosity) of the PET dispersed phase in the PP matrix. Some mechanical-physical properties of PP/PET blend fibres related to their morphology are also discussed.

Experimental

Materials used

- Polypropylene CF 331 (PP CF 331), MFI=12 g/10 min, Slovnaft a.s., SK.

- Polyethylene terephthalate (PET), Slovenský hodváb, Senica a.s., SK:

- PET B (bottle), IV=0.85 lg⁻¹, MW≅28500 g mol⁻¹
- PET M (multifilament), IV=0.65 lg⁻¹, MW≅19300 g mol⁻¹
- PET L (low mol.), IV=0.55 lg⁻¹, MW≅15100 g mol⁻¹
- PET W (hydrolysed PET L), IV=0.45 lg⁻¹, MW≅11260 g mol⁻¹

Intrinsic viscosity [η] were evaluated in phenol-tetrachlorethan 1:1 solution at 298 K using an Ubbelohde viscosimeter.

The molecular weights of the PET were calculated using the Koepf-Werner equation: $[\eta]=7.55 \times 10^{-4} M^{0.685}$.

Preparation of PP/PET blend fibres

PP/PET blend fibres were prepared in two steps:

- Mixing the polymer components in powder state and preparing the PP/PET blend chips by melt blending, using the laboratory twin-screw extruder with $\phi=28$ mm at 275°C. The content of PET in PP was a constant 8% by weight.
- In the second step, the PP/PET fibre blend was prepared by melt-spinning the PP/PET blend using the model laboratory spinning equipment with the extruder $\phi=30$ mm. The parameters of the spinning process were as follows: temperature 275°C, spinning speed 400 m min⁻¹. The fineness of the undrawn fibres was $T_{dt}=960$ dtex. Multifilaments were drawn using the laboratory drawing equipment. The drawing ratio was 1:3, the temperature 110°C. The fineness of drawn multifilaments was $T_{dt}=320$ dtex x f 48.

Methods used

Rheological measurements

The rheological properties of components and polymer blends were measured using a Göttfert N 6967 capillary extrusion viscosimeter with extruder $\phi=20$ mm at 270°C. The conditions of measurement were close to those in the spinning equipment, namely dynamic conditions in the extruder before

Table 1. Rheological characteristic of PP and PET at 270°C.

Polymer	η , Pa·s $\dot{\gamma}=100$ s ⁻¹	log K	n
PP CF 331	218	3.3	0.53
PET B	238	2.6	0.86
PET M	136	2.3	0.91
PET L	92	2.2	0.90
PET W	35	1.2	1.13

re extrusion of the blend melt. We used the Newton and Oswald-de Waele laws for determining the basic rheological parameters of apparent viscosity and power law index n, which characterises the Newtonian behaviour of the polymer melt:

$$\eta = \tau / \dot{\gamma} \quad (5)$$

$$\tau = K \dot{\gamma}^n \quad (6)$$

where:

- τ - the shear stress,
- $\dot{\gamma}$ - the shear rate,
- η - the apparent viscosity,
- n - the power law index,
- K - the coefficient.

Morphology of PP/PET fibres

The length and diameter of the deformed fibrils in the PET dispersed phase were measured after etching PP matrix in xylene at 140°C, and after separating the PET microfibrils. Both the light microscopy observation and scanning electron microscopy (SEM) techniques were used. The distribution curves of diameter and length of the PET particles in PP were evaluated, and average values were determined. The deformation of the PET particles in the PP matrix was calculated.

Results and Discussion

Figure 1 and Tables 1, 2 reveal the rheological behaviour of PP and PET components as well as of the PP/PET blend. The apparent melt viscosity of PET is on average proportional to the molecular weight of the polymers. Close values of viscosity are observed for PP and PET M. Both polymers are applied for PP and PET

Table 2. Rheological characteristic of PP/PET blend (8% PET) at 275°C.

Polymer blend	η , Pa·s $\dot{\gamma}=100$ s ⁻¹	log K	n	$(\eta_{exp}-\eta_{td}) / (\eta_{PP} - \eta_{PET})$	
				$\dot{\gamma}=100$ s ⁻¹	$\dot{\gamma}=500$ s ⁻¹
PP+PET B	218	3.4	0.51	0.13	0.13
PP+PET M	220	3.4	0.50	0.14	-0.19
PP+PET L	215	3.4	0.51	0.05	-0.01
PP+PET W	218	3.4	0.49	0.08	-0.06

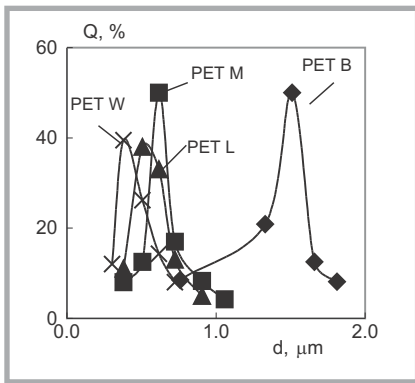


Figure 2. Distribution of diameter (d) of PET deformed particles in PP/PET undrawn fibres.

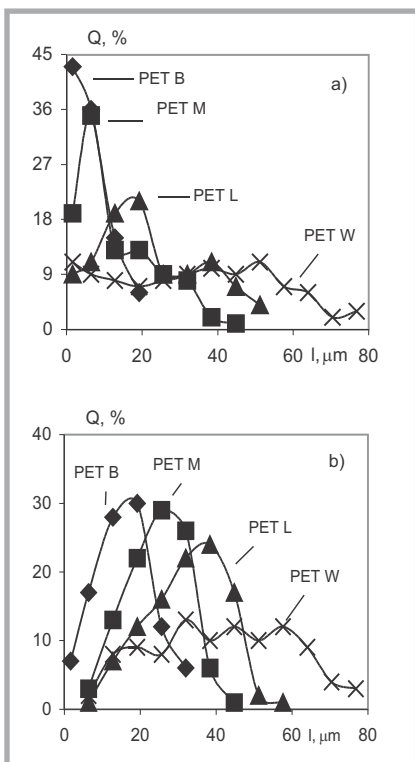


Figure 3. Distribution of length (l) of PET deformed particles in PP/PET undrawn (a) and drawn (b) fibres.

multifilament as well. Further results show an expected difference in the Newtonian behaviour of the polymers. The PET polymers exhibit relatively small deviation from the Newtonian flow (n values are close to 1). In contrast, the power law index of PP is relatively low (0.53).

The basic rheological parameters of the PP/PET blends at low PET content (8%) are strongly determined by the rheological behaviour of the PP matrix. A significant change in viscosity of the PP/PET blends on shear rate, which is similar to that for unmodified PP without regard to the difference in PET viscosity,

is observed along the whole scale of the PET's molecular weight (Figure 1b). The dependencies on Figure 1b also indicate a slight decrease in blend viscosity for blends containing the PET with lower molecular weight. A marginally positive deviation of blend viscosity from those of additives (Table 2) reveals the reinforcing effect of the PET particles in PP at lower shear rate.

The rheological properties of the PET dispersed phase related to the PP matrix significantly influence the morphology of PP/PET blend and blend fibres. The distribution of the PET particle sizes (both length and diameter in chips), and of undrawn and drawn fibres reveal the development of the morphology while spinning the PP/PET blend. The changes in average volume, particle length and diameter result from the deformation of the PET particles in the PP matrix, and from their break and coalescence while melting in the extruder and during deformation in both the spinning and drawing processes. The break and coalescence of PET particles are supported by their amorphous state in the PP matrix. Further, the average volume, shape and size of particles are determined by the prevailing process. Figures 2, 3 and 4a indicate unambiguously that the deformation of PET particles in the PP matrix decreases proportionally with the increase in viscosity (molecular weight) of the polyester component. The distribution curves are the narrowest for PET, with the lowest viscosity in the case of fibril length. Analysis of the size distribution allows us to calculate the average lengths and diameters of the PET particles in chips, after spinning and also after drawing PP/PET fibres (Tables 3 and 4). The average microvolume of PET

particles significantly decreases in blend chips proportionally to the molecular weight of the PET. The PET with the highest viscosity (PET B) provides little-deformed drops in the PP matrix after melting and mixing in the twin-screw extruder. After spinning, the length of microfibrils for the PET with the lowest melt viscosity is ten times higher in comparison with that of the high molecular PET B type. This means that melting and spinning these chips leads to an increase in the microvolume of PET particles, probably due to the coalescence mechanism and to creating the higher deformed droplet in shear and extensional flow in the spinning line. The microvolume of dispersed particles in the PP/PET undrawn fibres does not exhibit any clear dependence on PET viscosity. Finally, drawing PP/PET fibres again leads to a change in the microvolume and in the shape of the PET microfibrils. A higher increment of the length of particles after drawing was observed for the higher molecular weight of PET (Figure 4). The relatively small change in the shape of PET microfibrils between the undrawn and drawn fibres is exhibited by the PET with the lowest viscosity (PET W). There are two important pieces of information in Tables 3, 4 and Figure 4 regarding the development of the phase morphology of the PP/PET blend fibres. First, the elongation stress and deformation in the spinning line significantly contribute to the deformation of the PET dispersed phase in the PP matrix at the lower viscosity of PET melt. Second, the coalescence of PET dispersed particles occurs in the melting and spinning of the PP/PET blend, and break-up phenomena are significant in drawing blend PP/PET fibres with low PET viscosity (Tables 3 and 4).

Table 3. Average size of PET particles in PP/PET blend and in blend undrawn fibres (l - length, d - diameter, v - volume of particles, deformation $\epsilon = (l-d)/(l+d)$).

Composition: 8% PET in PP	Blend chips				Undrawn fibres			
	$l_1, \mu\text{m}$	$d_1, \mu\text{m}$	$v_1, \mu\text{m}^3$	ϵ_1	$l_2, \mu\text{m}$	$d_2, \mu\text{m}$	$v_2, \mu\text{m}^3$	ϵ_2
PP+PET B	1.9	1.7	4.3	0.05	3.3	1.5	5.8	0.37
PP+PET M	1.7	1.2	1.9	0.17	6.5	0.7	2.5	0.81
PP+PET L	1.1	0.8	0.6	0.16	19	0.5	3.7	0.95
PP+PET W	1.8	0.5	0.4	0.56	32	0.4	4.0	0.98

Table 4. Average size of PET particles in PP/PET blend drawn fibres.

Composition: 8% PET in PP	Drawn fibres			
	$l_3, \mu\text{m}$	$d_3, \mu\text{m}$	$v_3, \mu\text{m}^3$	ϵ_3
PP+PET B	16	0.70	6.1	0.92
PP+PET M	28	0.40	3.5	0.97
PP+PET L	38	0.25	1.8	0.98
PP+PET W	45	0.15	0.7	0.99

The influence of molecular weight and the morphology of the PET dispersed phase on the basic mechanical physical properties of PP/PET fibres reveal that the tenacity of blend fibres decreases proportionally to the decrease in molecular weight of the PET component (Table 5). The elongation at break of annealed blend fibres is about 15% higher than for unmodified PP fibres (Table 6). The mechanical properties of PP/PET blend fibres are close to the properties of PP fibres for PET B in the PP matrix. The lower molecular weight of the PET component and the finer morphology of blend fibres lead to a faster decrease in tenacity and a faster increase in elongation at break of PP/PET blend fibres.

Conclusion

In the experimental work, the phase structure of PP/PET blend fibres in de-

pendence on the molecular weight of the PET dispersed phase was investigated. It was found that:

- the deformation of PET particles in PP matrix in spinning is indirectly proportional to the viscosity of the dispersed phase;
- the polyfibrillar structure of PET particles in the PP matrix is created in spinning line at a significantly lower viscosity of PET in comparison with PP matrix viscosity;
- high molecular PET with a higher viscosity than PP matrix provides a distinct polyfibrillar morphology in PP/PET blend fibres in the drawing process;
- tenacity of PP/PET blend fibres decreases proportionally to the decrease in the molecular weight of the PET dispersed phase.

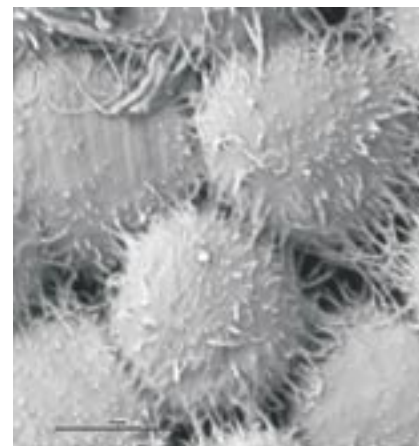


Figure 5. SEM of cross-section of PP/PET L blend fibres after etching PP matrix in xylene.

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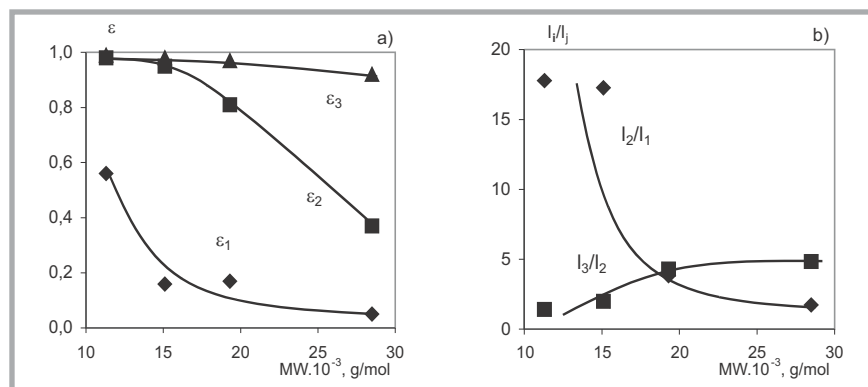


Figure 4. Dependence of deformation of PET dispersed particles in PP/PET blend fibres (a) and increment of particle length after spinning l_2/l_1 and after drawing l_3/l_2 (b) on molecular weight of PET.

Table 5. Tenacity and variation coefficient of tenacity of drawn non-annealed and annealed PP/PET fibres containing 8% PET in PP.

Fibre	Fineness, dtex	Non-annealed fibres		Annealed fibres	
		T, cN/dtex	CV _T , %	T, cN/dtex	CV _T , %
PP	335 f 45	2.7	4.6	2.7	3.6
PP+PET B	334 f 45	2.6	4.7	2.5	3.7
PP+PET M	353 f 45	2.5	4.5	2.3	2.6
PP+PET L	355 f 45	2.4	4.9	2.1	3.1
PP+PET W	370 f 45	2.3	4.4	2.0	3.0

Table 6. Elongation and variation coefficients of elongation of drawn non-annealed and annealed PP/PET fibres containing 8% PET in PP.

Fibre	Fineness, dtex	Non-annealed fibres		Annealed fibres	
		E, %	CV _E , %	E, %	CV _E , %
PP	335 f 45	104	7.1	24.5	5.9
PP+PET B	334 f 45	120	5.2	25.5	3.8
PP+PET M	353 f 45	122	5.7	28.8	3.9
PP+PET L	355 f 45	120	5.0	29.5	3.4
PP+PET W	370 f 45	123	6.1	29.7	3.7

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