

Abstract

In this paper, the effect of LDPEs on the thermal behaviour of polypropylene/low-density polyethylene (PP/LDPE) fibres is presented. The DSC 7 apparatus (Perkin Elmer) for measuring the thermal properties of the PP/LDPE blend fibres was used. The PP/LDPE blend is characterised by individual melting and crystallisation temperatures of components with deviation of the basic thermal quantities compared with PPs and LDPEs. The decrease in the total melting enthalpy of the blend indicates a partial compatibility of PPs and LDPEs at a temperature above the melting point of the components at low concentrations of LDPEs. The dispersed phase has lower crystallinity in this case. LDPEs with low MFIs exhibit higher crystallinity in PP/LDPE blend fibres and contributes to the high total crystallinity of blend fibres.

Key words: polypropylene, polyethylene, fibre blends, thermal behaviour, crystallisation temperature, melting temperature, melting enthalpy.

Introduction

Synthetic fibres based on fibre-forming polymer blends belong to a special fibre group. A variability of properties in fibres and their functionality can be reached by using two or more components in the fibre-forming blend. Fibres from polypropylene/polyethylene (PP/LDPE) blends are mainly used for home and technical textiles. The lower melting point of branched polyethylene (LDPE) and its higher adhesion to many polymers are convenient mainly in thermobonding textile technology [1]. In other kinds of application of polymer blends in textiles, very good results were achieved by exhaust-dyeing of polypropylene/polyamide 6 (PP/PA 6) and polypropylene/polyethylene terephthalate (PP/PET) blend fibres [2].

Most fibre-forming polymer blends are thermodynamically incompatible, and

form heterogeneous systems with a certain miscibility level, blend stability, and various sizes and shapes of the dispersed phase [3]. Processing polymer blends in spinning depends substantially on the compatibility and the rheological properties of polymer components, which strongly influence the morphological structure of fibres defined by the degree of dispersion of components, the size and the shape of the dispersed phase [4].

The supermolecular structure of semicrystalline polypropylene/polyethylene (PP/PE) blends is influenced by blend composition, crystallinity, crystalline morphology and the degree of dispersion of components [5-8]. Quantities such as nucleation density, radial growth rate of spherulites, overall rate of crystallisation and the equilibrium melting temperature are dependent on composition, crystallisation conditions and the molecular mass of the components [9]. In recent years, the results presented have been divergent. Wenig & Mayer [10] concluded that the 'growth' of PP spherulites is not influenced by the presence of PE domains, and spherulitic growth rates do not vary with the blend's composition. This was seen as an indication that PE is not able effectively to penetrate into the PP phase. The unstated implication is that this is further evidence for the immiscibility of PP and PE.

Martuscelli et al. revealed three different types of crystallisation behaviour of PP/PE blend at three ranges of crystallisation temperatures [5]. Below 125°C, simultaneous crystallisation of PPs and HDPEs

was observed. From 125°C to 127°C, two crystallisation peaks were observed with PPs crystallising first. Above 127°C, HDPEs do not crystallise, and the crystallisation of PP was observed only from a melt mixture of PP/PE. Wenig & Meyer [10] and Bartczak et al. [11] have determined that the presence of PEs did not influence the PP spherulite growth rate. In opposite, Kudláček et al. [12] found that this growth rate was influenced by the presence of PEs. Rybníkář [13] has taken this disagreement as the starting point for his own investigation of the crystallisation and morphology of the PP/PE blends. On the basis of his experimental results it was also concluded that PEs had no effect on the rate or character of PP crystallisation.

In other papers, it has been reported that the spherulite growth rate of PP decreased with a decrease in MFI of LLDPEs, while the MFI of LLDPEs had a negligible effect on the nuclei density. This means that the diffusion process controlled the crystallisation rate overall, while the nucleation density was similar for blends with various MFIs. This further confirmed that PPs and LLDPEs were miscible at elevated temperatures, since the more viscous LLDPEs (lower MFI) reduced the crystallisation rate of the PPs [14].

Morphological studies of PP/LDPE blends revealed that the shape, size and orientation of LDPE occlusions remain undisturbed during the crystallisation of PP spherulites. On the other hand, LDPE occlusions introduce large changes in the internal structure of PP spherulites [15].

In this paper, the investigation of thermal behaviour of the PP/LDPE blend fibres at the melting and crystallisation processes are presented. Commercial PPs and LDPEs were used for the preparation of blend fibres. For evaluation of the basic thermal parameters of the PP/LDPE blend fibres, the DSC method was used.

Experimental

Material used

- Polypropylene TI 902 (PP), Slovnaft, a.s. Bratislava, MFI = 27g/10 min
- Low-density polyethylene LDPE SA 20 (MFI \approx 20g/10 min), LDPE SA 200 (MFI \approx 200g/10 min), Slovnaft, a.s. Bratislava

Preparation of PP/LDPE blend fibres

The PP/LDPE fibre blends were prepared within the concentration range of 0 – 100%. Chips of polypropylene and polyethylene were mechanically mixed. The mixture was melted and spun by the classical procedure using a laboratory spinning plant with a single screw extruder $F = 16$ mm at a temperature of 200–250°C and a spinning speed of 150 m.min⁻¹.

Fibres were drawn at a ratio of $\lambda = 2.5$ at 80°C. The linear density of fibres was within the range of $T_{dt} = 260$ –420 dtex x 33F.

Methods used

The thermal characteristics of blend fibres were evaluated with the use of a DSC 7 apparatus (Perkin Elmer) using the procedure given below. A sample of the original fibres was heated at a rate of 10°C/min⁻¹ from 50°C to 220°C. Thus, a melting endotherm of the original sample with melting temperature T_m and melting enthalpy ΔH_m was obtained. Then, the sample was cooled with a rate of 50°C.min⁻¹ and the crystallisation exotherm with the crystallisation temperature T_c and crystallisation enthalpy ΔH_c was obtained. Subsequently, the sample was exposed to second heating with a rate of 10°C.min⁻¹, and the endotherm with the melting point T_{m2} and enthalpy ΔH_{m2} was determined. A nitrogen atmosphere was used during the measurements.

The actual melting enthalpy DH_{100} is related to the enthalpy of the individual

polymer (fibre) and to their weight fraction w in the blend

$$\Delta H_{100} = \Delta H_{exp(w)}/w \quad (1)$$

where w is the weight fraction of low density polyethylene (polypropylene). The total melting/crystallisation enthalpies DH_{tot} of blend fibres were calculated as the sum of melting/crystallisation enthalpies of the PP and LDPE components.

Results and discussion

The basic thermal parameters – the melting (T_m) and crystallisation (T_c) temperatures of PP/LDPE blend fibres – are presented in Tables 1 – 3.

The endotherms obtained at the first heating (scanning 10°C.min⁻¹) of anisotropic

PP/LDPE blend fibres contain two single-peaks, which correspond with the melting and crystallisation behaviour of the individual PPs and LDPEs (Table 1). The endotherms obtained at the second heating correspond to isotropic PP/LDPE blends, and have a similar shape to those obtained during the first heating (Table 3).

The melting temperatures of PP/LDPE fibres reveal the individual behaviours of the polymer components in the blend fibres. The experimental melting temperatures of the component in blend fibres are comparable with the melting temperatures of homopolymers. The moderate decrease in melting temperature for LDPE fibres is proportional to the increase in the MFI of the LDPEs (Tables 1, 3).

Table 1. Melting (T_m) temperature of components in anisotropic PP/LDPE blends at the 1st heating (heating rate = 10 °C.min⁻¹).

| C_{LDPE} , % | LDPE SA 20 | | LDPE SA 200 | |
|----------------|------------------|----------------|------------------|----------------|
| | T_{mLDPE} , °C | T_{mPP} , °C | T_{mLDPE} , °C | T_{mPP} , °C |
| 0 | - | 159,4 | - | 159,4 |
| 20 | 102,7 | 160,8 | 99,2 | 159,8 |
| 40 | 103,7 | 161,6 | 99,4 | 160,3 |
| 60 | 101,9 | 163,6 | 99,9 | 160,4 |
| 80 | 102,9 | 161,9 | 99,2 | 158,6 |
| 100 | 103,9 | - | 97,0 | - |

Table 2. Crystallization (T_c) temperature of components in isotropic PP/LDPE blends at the cooling (cooling rate = 50 °C.min⁻¹).

| C_{LDPE} , % | LDPE SA 20 | | LDPE SA 200 | |
|----------------|------------------|----------------|------------------|----------------|
| | T_{cLDPE} , °C | T_{cPP} , °C | T_{cLDPE} , °C | T_{cPP} , °C |
| 0 | - | 105,3 | - | 105,3 |
| 20 | 91,1 | 105,3 | 89,3 | 106,2 |
| 40 | 88,4 | 105,3 | 87,1 | 103,7 |
| 60 | 84,6 | 106,1 | 83,8 | 104,5 |
| 80 | 85,7 | 105,3 | 83,9 | 103,6 |
| 100 | 84,3 | - | 82,0 | - |

Table 3. Melting (T_m) temperature of components in isotropic PP/LDPE blends at the 2nd heating (heating rate = 10 °C.min⁻¹).

| C_{LDPE} , % | LDPE SA 20 | | LDPE SA 200 | |
|----------------|------------------|----------------|------------------|----------------|
| | T_{mLDPE} , °C | T_{mPP} , °C | T_{mLDPE} , °C | T_{mPP} , °C |
| 0 | - | 156,5 161,7 | - | 156,5 161,7 |
| 20 | 101,9 | 154,4 162,1 | 100,0 | 155,1 161,7 |
| 40 | 101,9 | 154,6 162,3 | 99,6 | 153,9 161,9 |
| 60 | 99,3 | 157,2 164,8 | 98,6 | 153,7 161,9 |
| 80 | 101,2 | 162,3 | 98,1 | 153,3 161,3 |
| 100 | 100,9 | - | 94,7 | - |

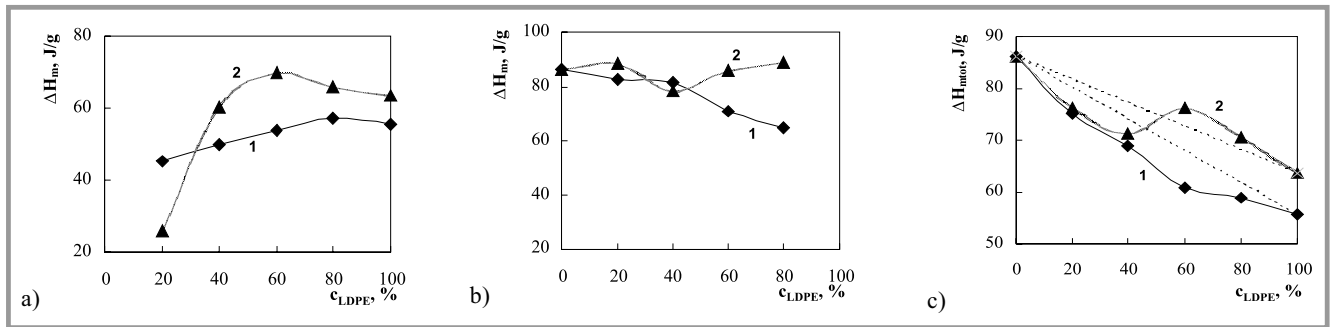


Figure 1. Melting enthalpy (ΔH_{100}) of LDPE (a), PP (b) and PP/LDPE (c) versus of the content LDPE in anisotropic blends at 1st heating 1 – LDPE SA 200; 2 – LDPE SA 20.

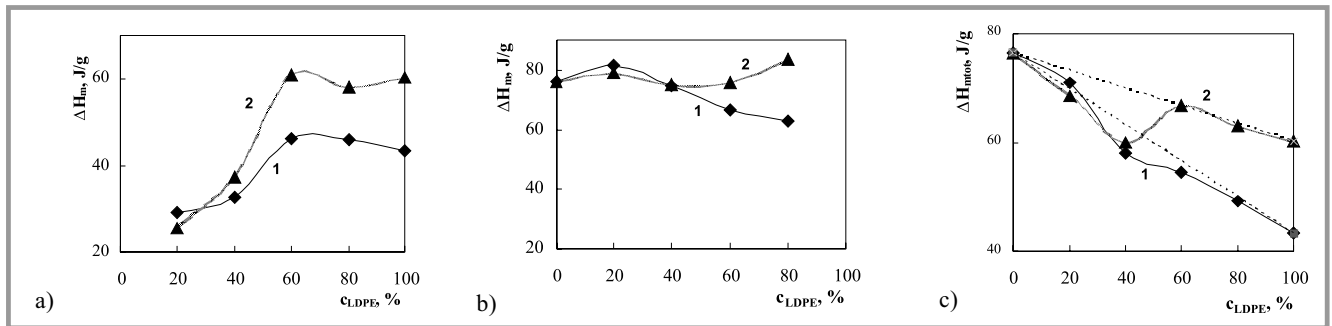


Figure 2. Melting enthalpy (ΔH_{100}) of LDPE (a), PP (b) and PP/LDPE (c) versus of the content LDPE in isotropic blends at 2nd heating 1 – LDPE SA 200; 2 – LDPE SA 20.

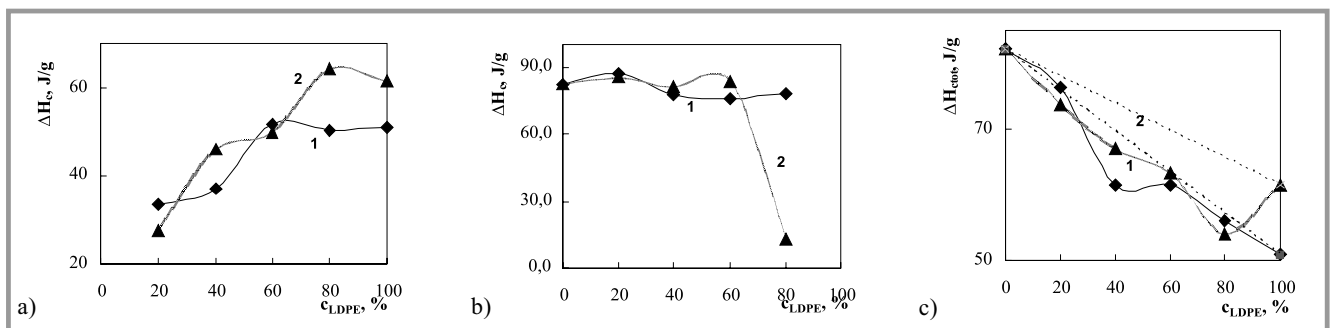


Figure 3. Crystallization enthalpy (ΔH_{100}) of LDPE (a), PP (b) and PP/LDPE (c) versus of the content LDPE in isotropic blends at cooling 1 – LDPE SA 200; 2 – LDPE SA 20.

The higher rate of crystallisation allows the creation of different PP modifications with variable stability (Table 3). The multippeak of PP is related to the crystallines' α, β -modification ($T_m = 154-158^\circ\text{C}$) and α -modification ($T_m = 164-165^\circ\text{C}$) [15].

The crystallisation temperatures of the components in the isotropic PP/LDPE blend decrease unambiguously in proportion with the LDPE content, the changes in morphology of PP/LDPE blend, and in the supermolecular structure of the LDPE phase; for example, the lower crystal sizes of the LDPEs in blends are caused by the higher amount of crystallisation centres. These centres can be created at the interphase of PP/LDPE by PPs (the crystallisa-

tion of the PPs proceeds at higher temperature).

The changes in melting and crystallisation enthalpies of PP/LDPE blends confirm the thermal demonstration of the components during crystallisation, as well as the PP and LDPE interaction in creating the supermolecular structure of the PP/LDPE blends (Figures 1-3).

The melting enthalpies of LDPEs in the anisotropic (1st heating) and isotropic (2nd heating) PP/LDPE blends are proportional to the concentration of LDPEs (Figures 1a, 2a). The crystallisation ability of the LDPE in the blends depends on the LDPE content. If the LDPE forms a dispersed phase (minority phase), its ac-

tual melting enthalpy is comparable with the calculated (additive) value. In the opposite case, if the LDPE represents the matrix (majority phase), its actual melting enthalpy is higher than that calculated. The crystallisation ability of LDPE in the PP/LDPE blend generally increases with the decrease in MFI (Figures 1a, 2a).

The melting enthalpy of the PP component in the anisotropic (1st heating) and isotropic (2nd heating) PP/LDPE blends slightly changes with the concentration of LDPEs (Figures 1b, 2b). This means that its crystallinity is approximately constant irrespective of the content of PPs in the PP/LDPE blend. Only a small difference in the melting enthalpy of PP at its low concentration in the blend was found for

the different MFIs of the LDPE component. This difference may result from the high degree of dispersion of the PP phase in the LDPEs, which could prevent the perfect and total crystallisation of the PP component.

The same results have shown that the LDPE component influence the total crystallinity of the PP/LDPE blends more than the PP component (Figures 1c, 2c). The total blend melting enthalpy is unambiguously lower compared to the additive value at the lower concentration of the LDPE dispersed phase (up to 40% wt.). The dependence of the total enthalpy of PP/LDPE blends versus the LDPE content with the higher molecular weight (MFI = 20g/10 min) is S-shaped and, with a lower molecular weight (MFI = 200 g/10 min), exhibits a negative deviation from the additive values (Figures 1c, 2c).

Summary

The mutual interactions of semicrystalline polymers, polypropylene, and the low-density polyethylene with different MFIs (20 and 200 g/10 min) in blend fi-

bres were studied by the DSC method. The following statements can be made:

- PPs and LDPEs manifest the individual phase transition in the blend fibres with individual peaks on the thermograms.
- The decrease in the total melting enthalpy of the blend indicates a partial compatibility of PPs and LDPEs at a temperature above the melting point of the components at low concentrations of both LDPEs. The dispersed phase has lower crystallinity in this case.
- LDPEs with low MFIs exhibit higher crystallinity in PP/LDPE blend fibres, and contribute to the high total crystallinity of blend fibres. □

Acknowledgments

The support of the Slovak Grant Agency APVT (grant 20-010102) and National Grant Agency of Slovakia VEGA (Grant 1/2475/04) is appreciated.

References

1. Vogel R., *Chem. Fiber Int.*, 46, 1996, pp. 421-423
2. Ondrejmiška K., *Vlákna a textil (Fibres and Textile)*, 1, 1994, pp. 11-16

3. Schäfer K., *Chem. Fiber Int.*, 45, 1995, pp. 116-123
4. Marcincin A., *J. of Thermal Analysis*, 46, 1996, pp. 581-595
5. Martuscelli E., Pracella M., Avella M., Greco R., Ragosta G., *Makromol. Chem.*, 181, 1980, p. 957
6. Lovinger A. J., Williams M. L., *J. Appl. Polym. Sci.*, 25, 1980, p. 1703
7. Teh J. W., *J. Appl. Polym. Sci.*, 28, 1983, p. 605
8. Gupta A. K., Gupta V. B., Peters R. H., Harland W. G., Berry J. P., *J. Appl. Polym. Sci.*, 27, 1982, p. 4669
9. Martuscelli E., *Polym. Eng. & Sci.*, 24, 1984, pp. 563-586
10. Wenig W., Meyer K., *Colloid & Polymer Sci.*, 258, 1980, p. 1009
11. Bartzak Z., Galeski A., Pracella M., *Polymer*, 27, 1986, p. 537
12. Kudláček L., Kaplanová M., Knapé F., *Faserforsch. Textiltech.*, 29, 1978, p. 286
13. Rybníkář F., *J. Macromol. Sci.-Phys.*, B27, 1988, p. 125
14. Li J., Shanks R.A., Ling Y., *Polymer*, 42, 2001, pp. 1941-1951
15. Galeski A., Pracella M., Martuscelli E., *J. Polym. Sci., Polym. Phys. Ed.*, 22, 1984, p. 739
16. Ujhelyiová A., Marcincin A., Kišš M., Marcincinová T., *J. of Thermal Analysis*, 46, 1996, pp. 619-626
17. Varga J., Karger-Kocsis J., *Polym. Bulletin*, 30, 1993, p. 105
18. Fillon B., at al., *J. Polym. Sci., Part B, Polym., Phys.*, 31, 1993, p. 1407
19. Ujhelyiová A., Marcincin A., *Vlákna a textil (Fibres and Textiles)*, 6, 1999, pp. 2-6
20. Marcincin A. *Progr. Polym. Sci.*, 27(5), 2002, pp. 853-913

□ Received 08.12.2004 Received 10.02.2005



Centre of Advanced Technologies

PRO HUMANO TEX

Centre of Advanced Technologies for Textiles Friendly for Human

Integrating actions concerning research, design, manufacturing, and promotion of Polish textiles friendly for human are the most important parts of the mission which the Centre have to carry out. These actions should rise the innovation and competitiveness of small and medium-sized enterprises in Poland.

The following assortments belongs to textiles friendly for human:

- barrier textiles protecting against harmful factors, such as gaseous, liquid, and solid chemical media; biological organisms, such as bacteria, viruses, fungi, and mites; and physical factors, such as electromagnetic and electric fields, UV-radiation, thermal streams, and fumes;
- textiles with thermo- and hygrocontrol features;
- biodegradable textiles.

For manufacturing textiles friendly for human, not only textile technique processes will be used, but also advanced electronic, informatics, chemical, and nano-technologies.

Assortments, which belong to the following fields will be manufactured: general-use clothing for disabled, protective clothing and other individual protective means, furnishing & automotive textiles, and technical textiles.

At present, the Centre associates 2 universities (University of Łódź, Technical University of Łódź) 10 R&D centres (Central Institute of Labour Protection, Warsaw; Institute of Teratechnology, Radom, R&D Centre for Textile Machines POLMATEX-CENARO, Łódź; Textile Research Institute, Łódź; Institute of Chemical Fibres, Łódź; Institute of Dyes and Organical Products, Zgierz; Institute of Textile Material Engineering, Łódź; Institute of Textile Architecture, Łódź; Institute of Knitting Technique and Technologies TRICOTEXTIL, Łódź), and many enterprises (e.g. FILTER-SERVICE, Zgierz; POLONTEX Co, Poraj; TEOFILÓW Co, Łódź; WOLA, Zduńska Wola; MIRANDA, Turek; ALGA-BIS, Łódź; ASTILTEX CONSULTING, Łódź).

The co-ordinator of the Centre of Advanced Technologies PRO HUMANO TEX is the Faculty of Textile Engineering and Marketing, Technical University of Łódź.

The proxy of the co-ordinator is Professor Izabella Krucińska Ph.D., D.Sc.

For more information please contact: Monika Malinowska-Olszowy, tel.: 508297171, e-mail: monika10@mail.p.lodz.pl