Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 117–121

DSC STUDIES ON MELTING AND CRYSTALLIZATION OF POLYAMIDE 6/BIOPOL BLENDS

J. T. Haponiuk and A. Tercjak

Technical University of Gdańsk, Chemical Faculty, Polymer Technology Department
80-952 Gdańsk, Poland

Abstract

Blends obtained from Biopol D600G and polyamide 6 reveal in DSC investigations multiphase structure with a distinct crystalline polyamide 6 phase. Due to rapid crystallization of the polyamide 6 the crystallization of the Biopol D600G is retarded. The grade of crystallization of Biopol D600G is lower in the blends than in the pure state, as calculated from the melting enthalpies. Crystallization of polyamide 6 in the blends is faster and results in increasing of the grade of crystallization of polyamide 6 phase comparing to the unblended component.

Keywords: biopol/polyamide 6 blends, DSC

Introduction

Poly(β-hydroxybutyrate-co-β-hydroxyvalerate), P(HB-co-HV), obtained by bacterial biosynthesis and known as 'Biopol' is a completely biodegradable polymer, which mechanical properties are close to the properties of polyolefines [1–4]. At increase of hydroxyvalerate units in the copolymer decreases its crystallinity from about 80% for pure polyhydroxybutyrate (PHB) to about 60 for 12% hydroxyvalerate (HV) content in the P(HB-co-HV).

Natural homopolymer PHB is miscible with poly(ethylene oxide), poly(vinylidene fluoride), poly(vinyl chloride) [5, 6], poly(chloropropylene oxide), poly(ethylene glycol) and poly(methyl methacrylate) [7, 8] and immiscible with poly(butyl adipate), ethylene-propylene elastomer, poly(ethyl,vinyl acetate), poly(methyl methacrylate) [7] and ethyl cellulose [8].

Copolymer P(HB-co-HV) with 16% HV content is partly miscible with poly(styrene-co-acrylonitrile), poly(acrylonitrile-co-butadiene-co-styrene), completely miscible with poly(vinyl chloride) and immiscible with polystyrene, poly(ε-caprolactone), poly(tetramethylene glycol) and poly(*L*-lactide) [6, 7].

The aim of this work was investigation of phase transitions of the crystalline phases present in the blends of P(HB-co-HV) and polyamide 6 in relation to the phase transitions of the pure components.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Materials

Poly(β-hydroxybutyrate-co-β-hydroxyvalerate) with 12% HV content (Biopol D600G) was submitted by Zeneca Bio Products Billingham. Poly(ε-caprolactam) – polyamide 6 came from Zakłady Włókien Chemicznych Stilon S.A. in Gorzów Wielkopolski (trade name: (Stilamid S-27). Before blending both components were dried in vacuum at 60°C for 3 h. Blends of the 50/50, 60/40, 70/30, 80/20, 90/10 ratios by mass of polyamide 6 to Biopol D600G were obtained by double processing in a single screw laboratory extruder of Brabender Plastograph GNF 106/2 at 225–230°C. The pure components were processed analogously to the blends.

Differential Scanning Calorimetry

The phase transitions of obtained samples (8–12 mg) were investigated by means of a Perkin Elmer DSC7/Unix differential scanning calorimeter in the temperature range from –50 to 230°C under nitrogen as the purge gas. The heating rate was 20 K min^{-1} and the cooling rate was 10 K min^{-1}.

Results and discussion

The parameters of the melting endotherms of the (Biopol D600G)/polyamide 6 blends, obtained at the 1st and 2nd heating runs and the parameters of the crystallization exotherms are presented in the Table 1. The DSC curves of the blends and pure components recorded during 1st heating run are presented in the Fig. 1 and the corresponding crystallization curves are presented in the Fig. 2.

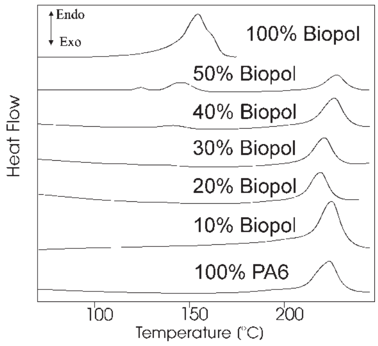

Fig. 1 DSC melting curves of Biopol D600G/polyamide 6 blends

The melting and crystallization peaks occur in the temperature ranges close to the temperature positions of the pure components. For this reason the phase transition were assigned to the separated crystalline phases of the components and the transitions enthalpies were recalculated in the Table 1 in relation to the blend's mass com-

Table 1 DSC parameters of melting and crystallization of Biopol D600G/polyamide 6 blends

Biopol fraction in blend/mass%	Parameters of melting								Parameters of crystallization			
	Biopol D600G phase				Polyamide 6 phase				Biopol D600G phase		Polyamide 6 phase	
	M.p. peak/°C		Transition ΔH/J g^{-1}		*M.p.* peak/°C		Transition ΔH/J g^{-1}		Peak$_{\max}$/°C	Transition $-\Delta H$/J g^{-1}	Peak$_{\max}$/°C	Transition $-\Delta H$/J g^{-1}
	1	2	1	2	1	2	1	2				
Biopol	144.7 154.9	149.5	52.0	54.5	–	–	–	–	80.7	38.2	–	–
50	159.5 147.0	145.5 122.0	38.2	37.2	231.4	227.5	51.6	52.8	–	–	193.0	67.4
40	154.3 138.0	141.8 122.0	18.8	12.3	229.1	226.2	68.8	68.2	–	–	191.0	83.7
30	150.7 134.2	–	26.0	–	225.8	221.1	54.0	54.1	–	–	187.8	70.9
20	140.0 152.0	–	36.5	–	223.4	218.9	54.4	54.9	–	–	186.9	67.0
10	146.8	–	26.0	–	228.2	224.8	62.4	66.0	–	–	189.2	66.2
PA 6	–	–	–	–	222.9	223.6	63.2	51.5	–	–	184.0	63.3

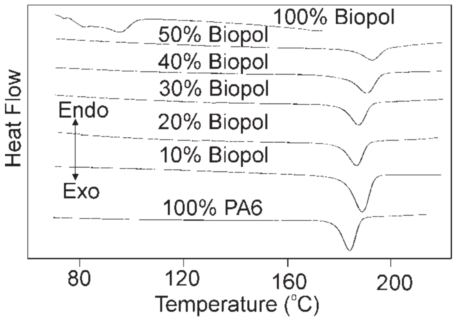

Fig. 2 DSC crystallization curves of Biopol D600G/polyamide 6 blends

positions. The melting temperature of the crystalline P(HB-co-HV) is characterized in the Table 1 by two extreme temperatures of the double peak. The melting temperatures of the P(HB-co-HV) crystalline phase in the blends are generally a bit lower than the melting temperature of the pure Biopol D600G. In the 1st heating run melting peak of the crystalline P(HB-co-HV) was observed for all investigated blends. In the 2nd heating run, measured after quenching at 200 K min^{-1} to 30°C and 5 min crystallization time at this temperature, melting endotherms appeared only for blends containing 40 and 50 mass% of Biopol D600G.

The first and second heating runs for the blend containing 30% of Biopol D600G are shown in the Fig. 3. Melting temperatures of the crystalline PA6 phase in the blends, are in the range for the 1st heating run from 223.4 to 231.4°C (222.9°C for pure PA6) and for the 2nd heating from 218.9 to 227.5°C (223.6°C for pure PA6). Melting enthalpies of the copolyester crystalline phase in the blends are lower than melting enthalpies of the crystalline phase of pure copolyester P(HB-co-HV).

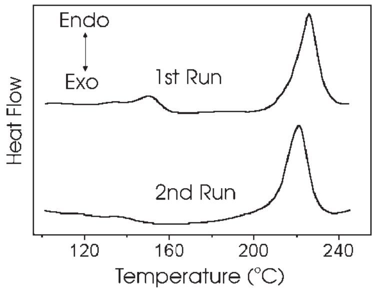

Fig. 3 The first and second heating runs for the sample containing 30% of Biopol D600G

Maxima of the crystallization peak of the PA6 phase in the blends appear at higher temperatures as for pure polyamide. The shift to higher temperatures is greater for smaller polyamide content in the blends. Crystallization enthalpies of polyamide phase in the blends are higher than the crystallization enthalpy of pure polyamide 6. At crystallization runs, performed at the cooling rate 10 K min^{-1}, Biopol D600G was not able to crystallize.

Conclusions

Poly(β-hydroxybutyrate-co-β-hydroxyvalerate) with 12% HV content (Biopol D600G) blended in the melt with polyamide 6 forms a binary system, consisting of the two pure polymers, showing separate melting regions. The melting enthalpy estimated at the 1st heating run proves that even for a long term crystallization at ambient temperature the development of crystalline copolyester phase has been increasingly inhibited as the amount of polyamide 6 in the blends was raised. On the contrary, the non-isothermal crystallization of the polyamide 6 phase has been facilitated by the presence of the copolyester. Thermal properties of the investigated immiscible, partially crystalline blends reveal therefore noticeable reciprocal influence of the components.

References

1 A. K. Błędzki and E. Fabrycy, Polimery, 8 (1992) 343.
2 J. M. Liddell, 'The Chemical Industry – Friend to the Environment?', The Royal Society of Chemistry, Cambridge 1992, p. 10.
3 Zeneca Bio Products, 'Biopol – Properties and Processing', Billingham, 1993.
4 G. J. H. de Koenig, 'Prospects of bacterial poly[(R)-3-hydroxyalkanoates', Technische Universitet Eindhoven, Eindhoven 1993, p. 1.
5 B. Pearce, J. Jesudason, W. Orts, R. H. Marchessault and S. Bloembergen, Polymer, 33 (1992) 4647.
6 F. Gassner and A. J. Owen, Polymer, 33 (1992) 2508.
7 H. Verhoogt, B. A. Ramsay and B. D. Faris, Polymer, 35 (1994) 5155.
8 M. Scandola, Can. J. Microbiol., 41 (1995) 310.