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DYNAMIC MECHANICAL THERMAL ANALYSIS 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

The temperature dependence investigated by means of DMTA of dynamic storage modulus E', dynamic loss modulus E'' and loss tangent tgδ of blends obtained from polyamide 6 and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (Biopol D600G) indicated, that the dynamic mechanical properties of the blends containing up to 40% Biopol D600G are governed by the properties of polyamide 6. First at the 50% Biopol D600G content in the blend the transitions of the Biopol phase become visible and dominant. The shifts of the loss modulus maxima of the blends might indicate some interactions between the blend components in the amorphous phase.

Keywords: polyamide 6/biopol blends, DMTA, polyamide 6/biopol blends

Introduction

Dynamic mechanical thermal analysis (DMTA) is a powerful tool for investigating polymer blends allowing evaluation of miscibility relations. The loss tangent (tgδ) temperature dependency indicates changes in the molecular mobility from localized skeleton motions in the subglass region to segmental motions at the glass transition and is known to be sensitive to the heterogeneity of a size larger than ca 15 nm [1]. The α maximum of the loss tangent curve, if accompanied by a maximum at the loss modulus E'' curve, testifies the glass transition and is often identified with the glass temperature. Miscibility of polymers, occurring in the amorphous phase, is determined by a single glass temperature (T_g), which increased monotonically as a function of composition. Immiscible blends are characterized by separate glass transition temperatures of individual polymers. Blends with some degree of miscibility show separate glass temperatures, but shifted towards each other.

Biodegradable bacterial poly(β-hydroxybutyrate-co-β-hydroxyvalerate), P(HB-co-HV), produced by Zeneka under the trade name ‘Biopol’ were subjected to thorough structure investigations by bulk and surface analysis techniques [2, 3]. Blending of PHB and P(HB-co-HV) with other thermoplastics were undertaken in order to improve the physical properties, and to reduce the cost of the biodegradable material [4–8]. Polymer blends containing poly(3-hydroxyalkanoate)s were reviewed by Vergoogt *et al.* [9]. Most of the blends are immiscible, miscibility in the melt was found

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for blends with poly(ethylene oxide) [5]. The present paper reports results concerning the phase properties of blends containing (P(HB-co-HV) and polyamide 6.

Qualitative prediction of trends in polymer–polymer miscibility is often performed by estimating the solubility parameters δ. Closer match of the two non-hydrogen bonded solubility parameters and greater relative strength of any specific intermolecular interaction present between the blend components leads to greater probability of miscibility [10]. The non-hydrogen bonded solubility parameters (in $(\mathrm{J\ cm^{-3}})^{1/2}$) of polymers used at this work and calculated by the group contribution method using the group molar attraction and molar volume constants determined by Coleman [10] are as follows: 21.43 for polyamide 6, 23.74 for poly(hydroxybutyrate), 21.39 for poly(hydroxyvalerate), 23.36 for P(HB-co-HV) with 16 wt% of hydroxyvalerate content calculated by addition of miscibility parameters of monomers HB and HV, under consideration of their mass fractions in the copolymer. Critical values of the solubility parameter difference depends on the specific interaction involved and vary from 0.2 for dispersive forces only to 6.0 for very strong interactions. Between polyamide 6 and P(HB-co-HV) dipole–dipole interactions and hydrogen bonding are possible to occur. For this reason the calculated solubility difference of 2.93 probably not exceeds its critical value and miscibility of these polymers is not excluded.

Experimental

Materials

Biopol D600G, poly(β-hydroxybutyrate-co-β-hydroxyvalerate) with 12% HV content 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).

Blend preparation

Prior to 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. Pure components were processed analogously to the blends.

Dynamic mechanical thermal analysis

Measurements were conducted using a Polymer Laboratories DMTA Mark III apparatus at the frequency of 10 Hz in a double cantilever geometry in the temperature range from –90 to 210°C at a heating rate of 4°C $\mathrm{min^{-1}}$.

Results and discussion

Figure 1 shows temperature dependence of storage modulus (*E′*), loss modulus (*E″*) and loss tangent (tgδ) for the blend components. The glass transition regions of both polymers are close and partly overlap. Loss tangent maximum occurs for polyamide 6 at 52.1, and for Biopol D600G at 34.5°C. Polyamide 6 shows a β relaxation with tgδ maximum at –44.9°C. The maxima of loss moduli *E″* precede the tgδ maxima and occur for polyamide 6 at 42.0 and for Biopol D600G at 30.9°C. Greater differences in the dynamic mechanical properties of polyamide 6 and Biopol D600G are seen from the *E′* and *E″* curves in the temperature region above the glass transition. The storage modulus *E′* of polyamide 6 after passing the glass transition drops in one order of magnitude and shows a broad plateau, ending in a sharp drop of the curve *E′* (*T*) (intersect of tangencies at 201°C). The storage modulus *E′* of Biopol D600G shows after the glass transition continuous decrease, sharp above 140°C (intersect of tangencies at 137°C), without any plateau. The presented points of intersect of tangencies specify softening of the crystalline phase of both polymers. Temperature dependencies of storage modulus *E′* for Biopol D600G, polyamide 6 and their blends are shown in the Fig. 2. The *E′* values of blends containing from 10 to 40% Biopol D600G are close to *E′*(*T*) dependence of polyamide 6. In case of the blend containing 50% Biopol D600G the storage modulus *E′* decreases at first, similarly to pure Biopol, but above the softening point of Biopol D600G (140°C) short plateau is visible until the softening of the polyamide 6 phase at ca 200°C.

Temperature dependencies of the loss modulus *E″* of the blends and polyamide 6, shown in Fig. 3, exhibit single maxima in four cases in the range from 37 to 41°C, therefore below the *E″*(*T*) maximum for polyamide 6 (42°C). Only for the blend containing 20% Biopol D600G the *E″*(*T*) maximum was found at 43.3°C, above the *E″*(*T*) maximum for polyamide 6. As the *E″*(*T*) maximum for Biopol

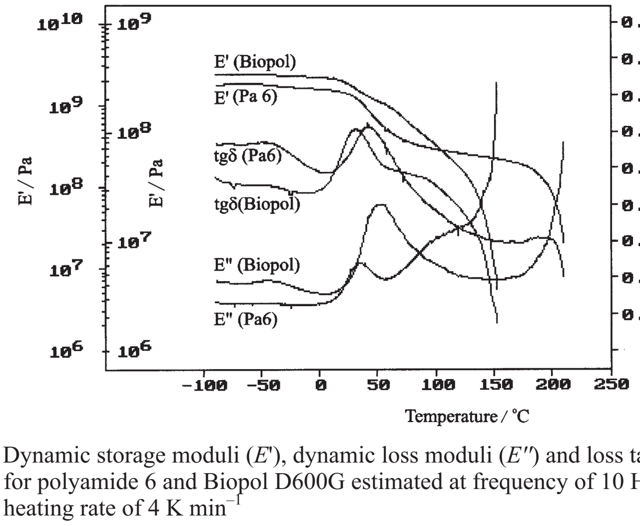

Fig. 1 Dynamic storage moduli (*E′*), dynamic loss moduli (*E″*) and loss tangents (tgδ) for polyamide 6 and Biopol D600G estimated at frequency of 10 Hz and the heating rate of 4 K min^{-1}

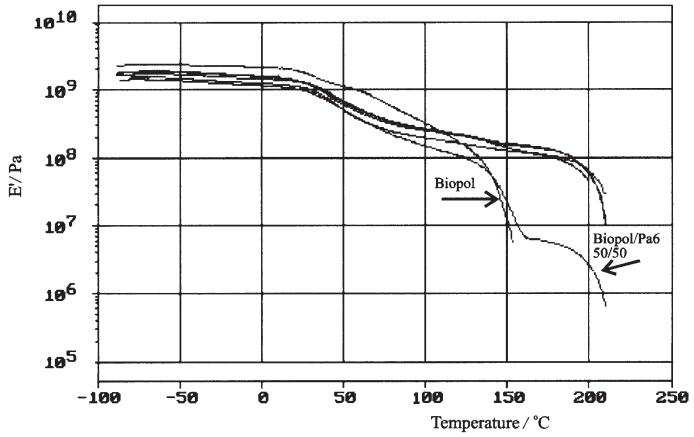

Fig. 2 Dynamic storage moduli (E') for polyamide 6 and its blends containing 10, 20, 30, 40 and 50% of Biopol D600G estimated at frequency of 10 Hz and the heating rate of 4 K min^{-1}

D600G was found at 30.9°C, shifting of the $E''(T)$ maxima of the blends could result from interactions and partial miscibility in the amorphous phase. Temperature dependencies of the loss tangent tgδ for polyamide 6 and its blends with Biopol D600G, presented in Fig. 4, show maxima for polyamide 6 and blends containing 10, 20, 30, 40 and 50% Biopol D600G respectively at the following temperatures: 52.1, 48.7, 54.6, 52.1, 49.9 and 55.0°C. The glass transition region of the blend containing 50% Biopol D600G is especially broad and the tgδ values increase rapidly above the softening point of Biopol D600G. The magnitude of the tgδ values at peak increases with the higher Biopol D600G content in the blends, but the damping remains relatively low, indicating maintenance of elastic properties of the blends.

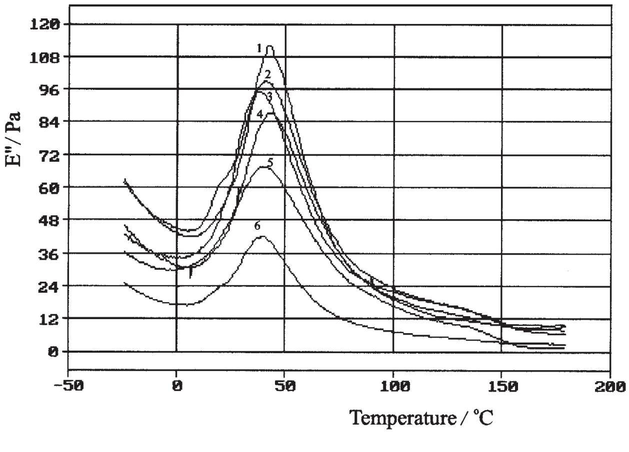

Fig. 3 Dynamic loss moduli (E'') for polyamide 6 and its blends estimated at frequency of 10 Hz and the heating rate of 4 K min^{-1}. (1 – Pa6, 2 – 30% Biopol, 3 – 40% Biopol, 4 – 20% Biopol, 5 – 50% Biopol, 6 – 10% Biopol)

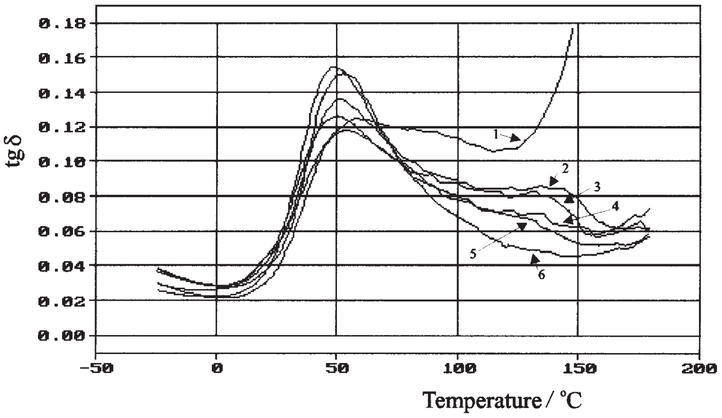

Fig. 4 Loss tangent (tgδ) values for polyamide 6 and its blends estimated at frequency of 10 Hz and the heating rate of 4 K min^{-1} (1 – 50% Biopol, 2 – 40% Biopol, 3 – 30% Biopol, 4 – 20% Biopol, 5 – 10% Biopol, 6 – PA6)

Conclusions

The dynamic mechanical storage moduli E' of blends obtained by melt mixing of polyamide 6 and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (Biopol D600G) are almost unaffected by the blend composition up to 40 wt% of Biopol D600G content, indicating continuous polyamide 6 matrix in which Biopol domains are fixed. The influence of the Biopol component was observed first at 50 wt% content, for which two-step drops of the E' value was observed, at temperatures corresponding to the softening points of crystalline phases of the components. The E' plateau between the softening points may be explained by the existence of continuous phases of the components.

The possibility of interactions between the blend components in the amorphous phase is confirmed by the shifts of the loss modulus maxima of the blends.

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