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DYNAMIC MECHANICAL THERMAL ANALYSIS OF POLYAMIDE 6/THERMOPLASTIC POLYURETHANE BLENDS

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Abstract

Blends obtained from polyamide 6 and polyester or polyether polyurethanes were investigated by means of DMTA. The blends were prepared by compounding in a twin-screw Brabender – Plasticorder. Changes in composition did not influence the glass temperature of the amorphous fraction of the polyamide, but also no distinct transition for separated polyurethane soft segment was visible. Therefore the blends seem to be multiphase systems, where the elastomeric polyurethane phase is dispersed in a continuous polyamide phase. From changes in the β relaxation region of the polyamide better miscibility of polyester polyurethanes comparing to polyether polyurethanes was explained by hydrogen bonding in the common amorphous phase.

Keywords: DMTA, DSC, polyamide 6, thermoplastic polyurethane blends

Introduction

Dynamic mechanical thermal analysis (DMTA) based on applying small oscillating mechanical strain and on resolving of the resulting stress into in-phase with the strain (real or storage) and out-of-phase (imaginary or loss) components detects essentially changes in the state of molecular motions during a temperature scan. The ratio of the loss component to the storage component is known as the loss tangent (tan δ), where δ is the phase shift of the stress sinusoid in relation to the strain sinusoid. Analogous to stress, also the dynamic Young's modulus (E) could be resolved into storage component (E') and loss component (E''). Temperature dependence of the dynamic loss modulus and of the loss tangent indicates in case of multiphase systems structural inhomogenities and morphology.

For polymers rapid decrease in modulus occurs as the temperature is increased through the glass-transition region. Linear, amorphous and not crosslinked polymers show short rubbery plateau region followed by continuous decrease of modulus. Crosslinking causes stabilisation of the modulus at about three decades below the value of the glassy state. For segmented polyurethanes

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two distinct transitions correspond to the glass transition of the soft segments and to the softening of the hard segments, due to dissociation of hydrogen bonds. These transitions are further influenced by sample composition, degree of phase separation, intersegment solubility, segmental length and sample preparation. The increase in storage modulus observed after primary sharp drop by above the glass-transition is connected with crystallisation of soft segments, followed by melting, accompanied by decrease in modulus at 10°C for polyether polyurethanes or at 50°C for polyester polyurethanes [1]. The level of the rubbery plateau and thermostability of polyurethanes, resulting from the hydrogen bond concentration, depend from the hard segment content in the sample. At a low hydrogen bond concentration the formed crosslinks are not able to mechanical response. Incorporating of biuret groups raises the softening temperature of the hard segments, broads the glass-transition region and causes slight increase in modulus in region between the glass temperature of the soft segments and the softening temperature of the hard segments, as for polymers, crosslinked by valence bonds. Crosslinking by allophanate bonds leads to intermediate effects [2]. For segmented polyurethanes the loss tangent peak is broader at the higher temperature side than for amorphous ones. It becomes especially distinct when the hard segment phase changes its morphology from discontinuous to continuous domains [3]. Phase mixing between hard and soft segment domains is indicated by broadening of the loss peak and in lowering of its slope. Higher glass temperatures of the soft segments as in the source polyols make evident some phase mixing between soft and hard segments [4].

Polyether polyurethanes show a loss tangent peak below the glass transition (β relaxation) at −120°C, corresponding to the relaxation of the backbone methylene groups. Polyester polyurethanes show at −60°C addition small peak, which is independent from the hard segment content. This peak is attributed to motions of NH or C=O groups, which are hydrogen bonded to water molecules [4].

DMTA spectrum of polyamide 6 shows three loss tangent peaks. The highest peak at about 49°C indicates the glass transition. The position of this peak depends on dryness of the sample. The β relaxation at −52°C corresponds to the relaxation of hydrogen bonded amide groups. Position of this relaxation depends on the amount of water absorbed by the sample. The γ relaxation at −115°C is attributed to motions of the methylene backbone groups [5].

Changes in the position and size of the loss tangent peaks characterise the state of the phase structures and the extent of mutual interactions in polymer mixtures. Segmented polyurethanes are two phase polymers. Their hard segment phase may possible interact with the amide groups of polyamides by reason of similarity of the chemical structure of urethane and amide groups, both able to form hydrogen bonding. Presence of methylene sequences in the polyurethane soft segments and in polyamides suggests some miscibility between both structures. DSC investigations on the glass temperatures of polyamide 6/ thermoplastic polyurethane blends showed, that at blends with a polyurethane, consisting only of soft segments, lowering of the glass temperature was proportional to the polyurethane content in the blend, whereas at blends with a polyurethane consisting of soft and hard segments, by increasing the polyurethane concentration in the blends, the glass temperature of the blends after initially decrease until 10% polyurethane content gradually increased and neared the glass temperature of the pure polyamide [6]. For polyamide 6/polyurethane blends, obtained as interpenetrated networks or by mixing in the melt, for lower polyurethane contents (below 44 wt%) a single peak on the loss tangent curve was observed, which was independent from the blend composition. For higher polyurethane contents an α peak was observed, corresponding to the glass temperature of the soft segments of polyurethane [5]. Mutual miscibility of polyurethane and polyamide segments could be enhanced, when both structures are linked together as a block copolymer [7, 8].

Experimental

Materials

Two types of thermoplastic polyurethanes were used. The polyether polyurethane (PU-01) was obtained by the prepolymer method from polyoxytetrametylenediol (PTMG from the Quarker Oats Co.), 4,4'-diisocyanate diphenylmethane (Suprasec - ICI) and 1,4-butanediol (1,4-BD from B.A.S.F). The polyester polyurethane was obtained in the same way with poly(ethylene, butylene)adipate (Poles 55/20 from Zakłady Chemiczne Organika-Zachem) as the polydiol component. The hard segment content of the polyurethanes was calculated as 40 wt%. Polyamide 6 was a commercial product (Stilamid S-25 from Zakłady Włókien Chemicznych 'Stilon').

Blend preparation

The blends were prepared by compounding in a twin-screw Brabender – Plasticorder mixer at 230°C. The blends were then pelletized and injection moulded into plates of dimensions 100 mm×50 mm×2 mm, from which test specimens were cut.

Dynamic mechanical thermal analysis

The measurements were conducted using a Polymer Laboratories DMTA Mark III at frequencies of 1, 10 and 50 Hz in a single cantilever geometry at constant strain of 62.5 mm (×4). Data were collected from –90°C to 140°C at a heating rate of 4 deg·min^{-1}.

Discussion

In this work results obtained by the frequency 10 Hz are presented. The temperature dependence of the loss tangent for the polyether polyurethane PU-01 and the polyester polyurethane PU-02 is shown in Fig. 1. The same dependence for the polyamide 6 is shown in Fig. 2. The peak of α relaxation of the polyether soft segments was found at –43°C (PU-01) and of the polyester soft segments at –4°C (PU-02). The storage modulus for both polyurethanes drops by three decades at passing through the glass temperature region. The softening of the hard segment phase begins at about 130°C and proceeds quicker for the polyether polyurethane as less hydrogen bonded. For polyamide 6 the peak of

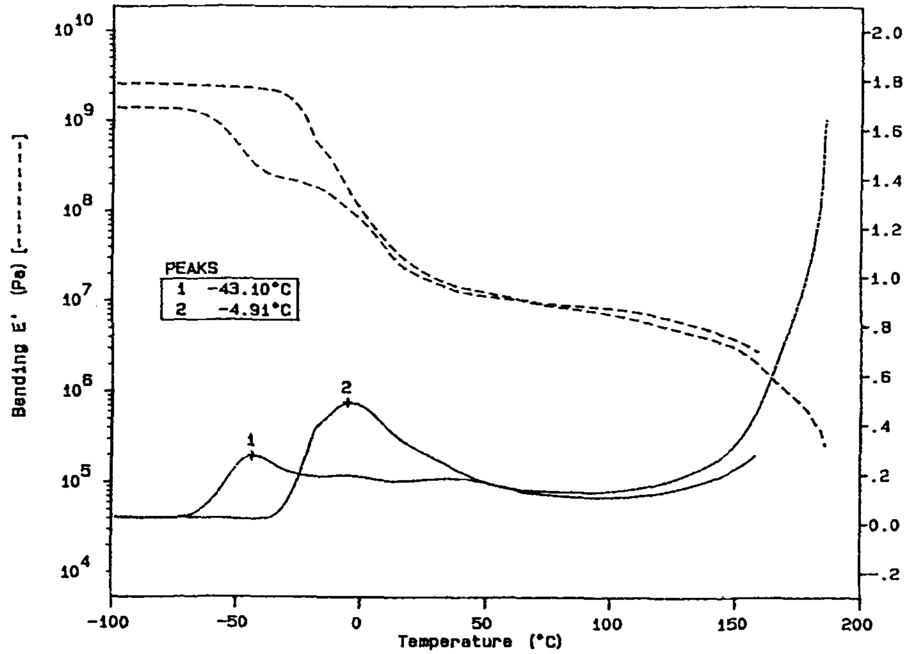

Fig. 1 Variation of the storage modulus (*E*') and of the loss tangent (tan δ) with temperature for the polyether polyurethane (PU-01) and the polyester polyurethane (PU-02)

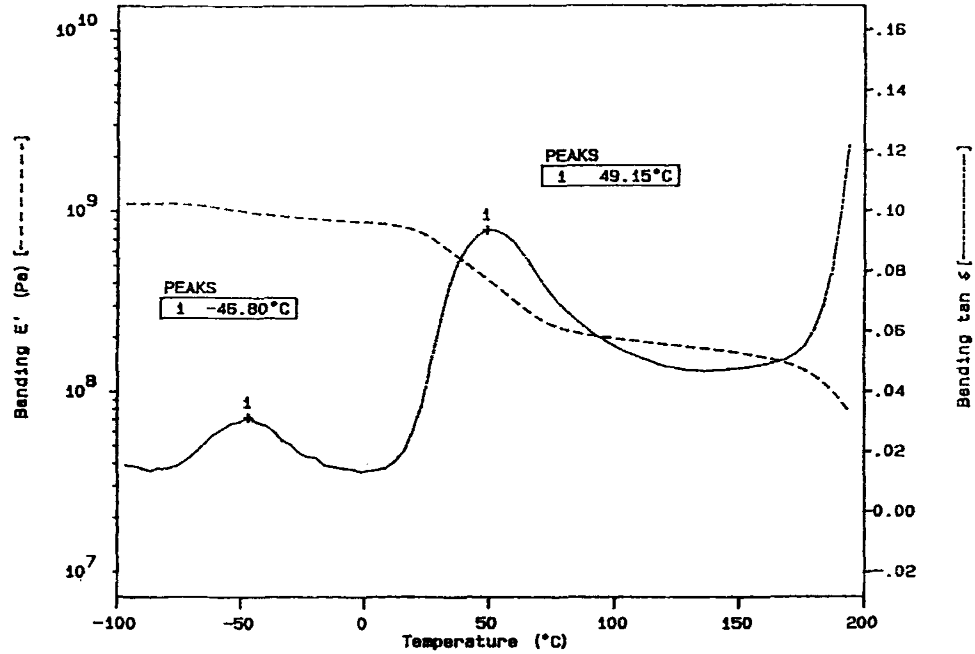

Fig. 2 Variation of the storage modulus (*E*') and of the loss tangent (tan δ) with temperature for polyamide 6

α relaxation was found at 49°C and at –47°C of the β relaxation, attributed to amide groups involved in week hydrogen bonds.

Figure 3 shows series of tan δ profiles for polyester polyurethane PU-02, polyamide 6 and for their blends. The profiles obtained for the blends and polyamide 6 almost overlap, when shown together with the tan δ profile with a high loss peak for the polyurethane PU-02. However also at a higher resolution, as shown in Fig. 5, tan δ profiles for the blends polyamide 6/PU-02 show no peaks, which could be strictly attributed to separated phase of the polyester soft segments. The peak for the α relaxation of the blends occurred closely to the peak of polyamide 6, at 49–52°C, and their position was not dependent from the composition of the blends.

Tan δ profiles for polyether polyurethane PU-01, polyamide 6 and their blends shows Fig. 4. Unlikely as for the blends of polyester polyurethane PU-02 and polyamide 6 (Fig. 3) the tan δ values for the blends containing 17.5 wt% and 20 wt% were in the whole temperature region higher, then for the pure polyamide and then for compositions containing less polyurethane. Figures 5 and 6 indicate next differences between blends obtained with polyurethanes containing polyester or polyether soft segments, observed in the range of

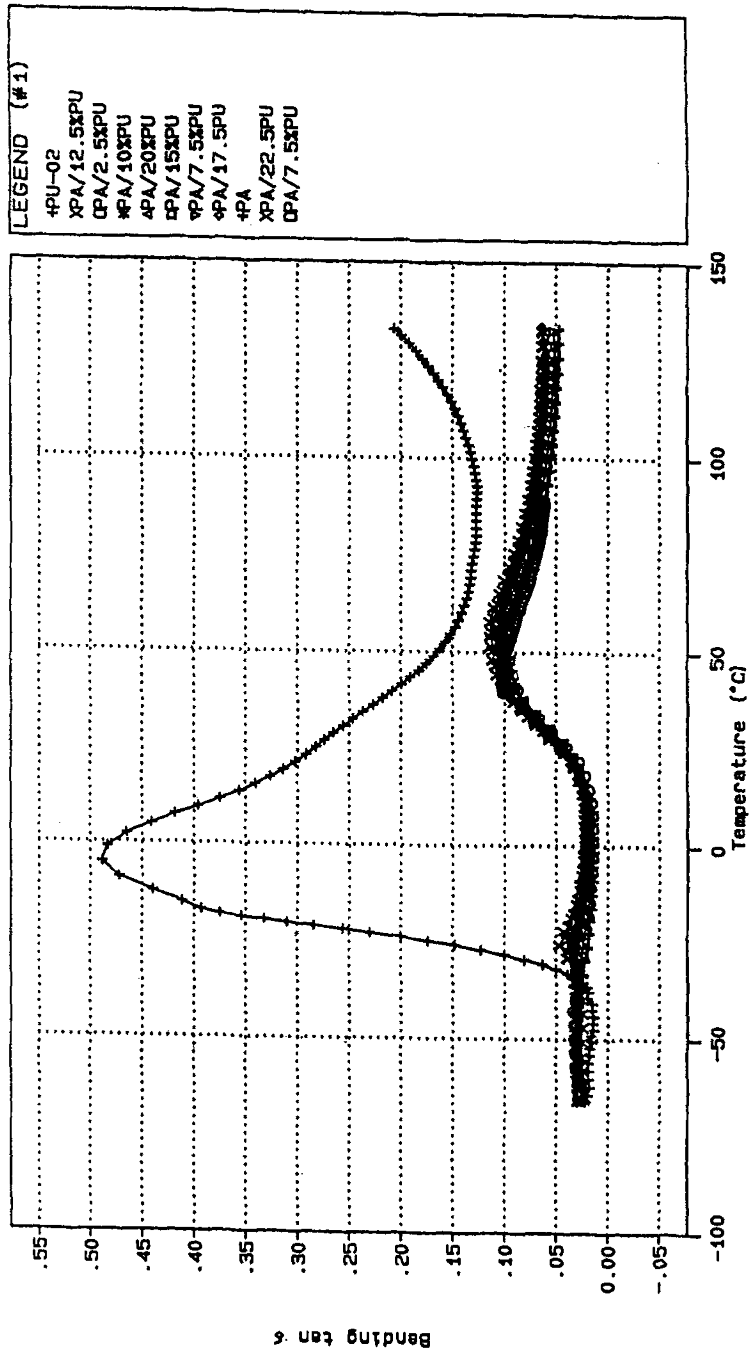

Fig. 3 Loss tangent plots for the polyester polyurethane (PU-02), polyamide 6 (PA) and for their blends

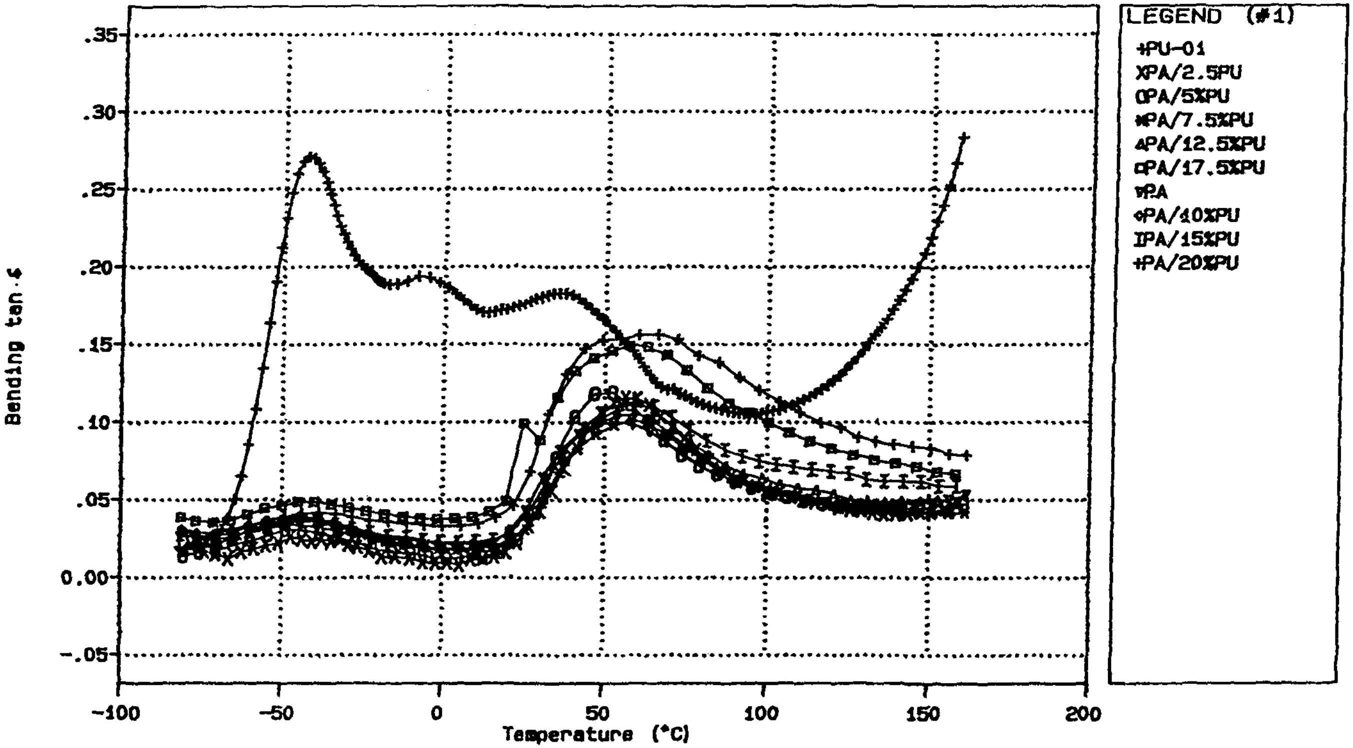

Fig. 4 Loss tangent plots for the polyesther polyurethane (PU-01), polyamide 6 (PA) and for their blends

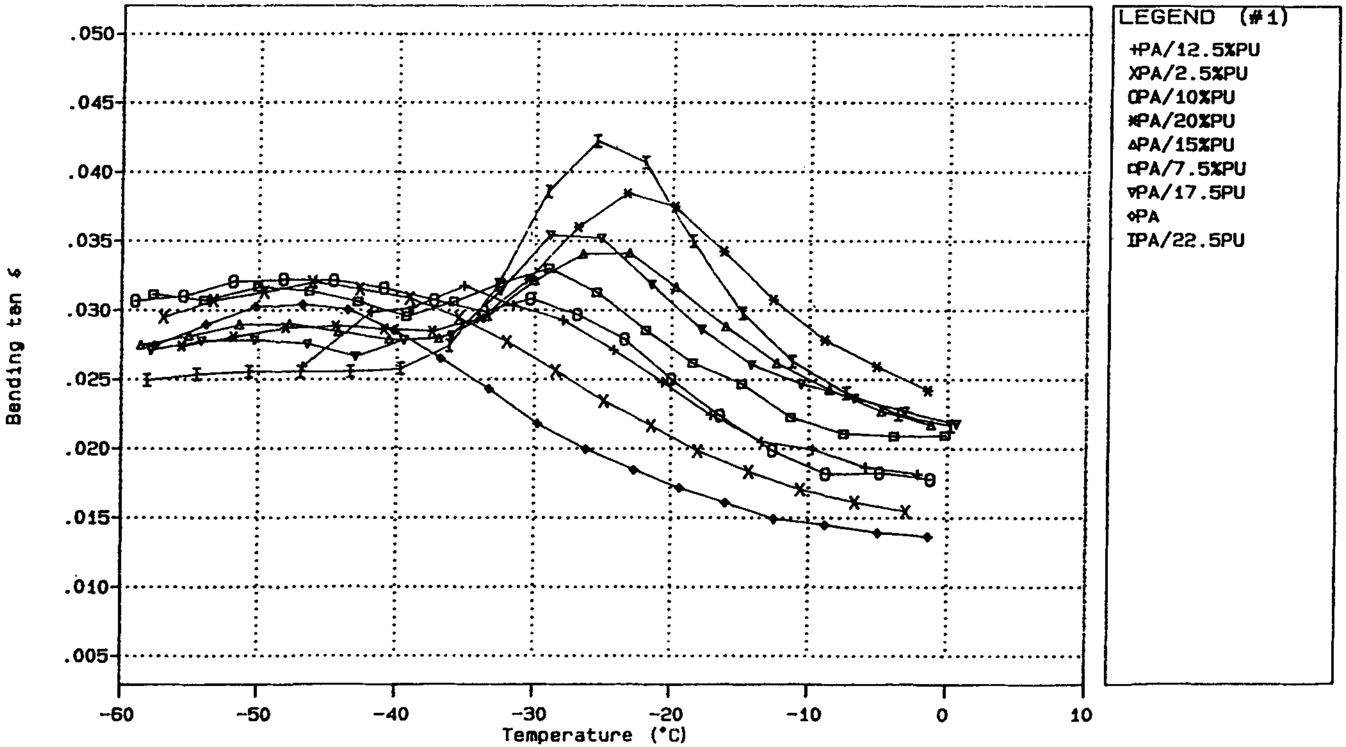

Fig. 5 Variation of the loss tangent (tan δ) with temperature for polyamide 6 and its blends with the polyester polyurethane (PU-02) in the β transition region of polyamide

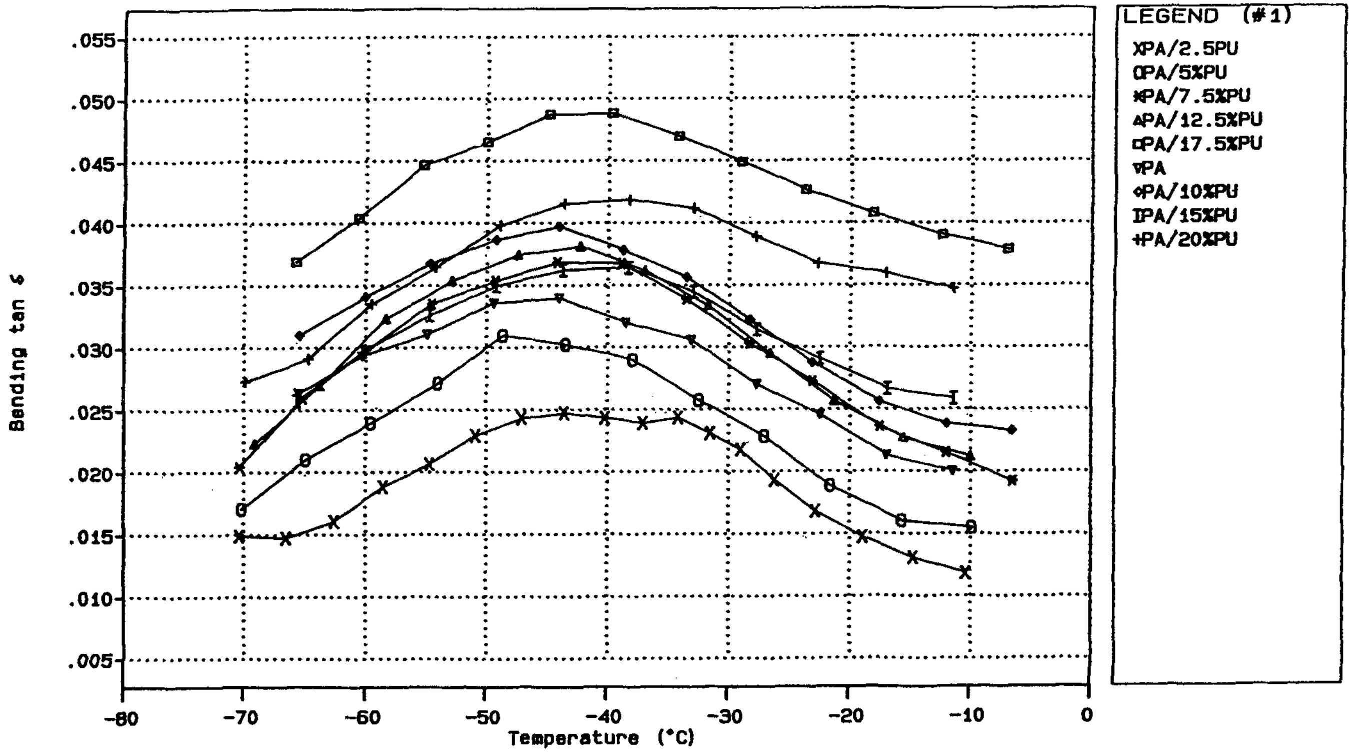

Fig. 6 Variation of the loss tangent (tan δ) with temperature for polyamide 6 and its blends with the polyether polyurethane (PU-01) in the β transition region of polyamide

the β relaxation of polyamide 6. Blends containing 22.5 wt%, 20 wt%, 17.5 wt% and 15 wt% polyester polyurethane PU-02 show distinct loss tangent peaks in the temperature region from –30°C to –20°C. Broader loss tangent peaks for blends containing 12.5 wt%, 10 wt% and 7.5 wt% occur between –4°C and –20°C. The tan δ values of the β relaxation of polyamide 6 are slightly lower then the values for the blends. For blends obtained with polyether polyurethane PU-01 the shape and temperature position of the tan δ peaks in the polyamide β relaxation region are not dependent from the composition of the blends. The tan δ profiles for polyamide 6 and blends containing 2.5 wt% and 5 wt% are very close. The next group of higher tan δ profiles corresponds to blends containing 7.5 wt%, 10 wt%, 12.5 wt% and 15 wt% polyether polyurethane. The highest tan δ profiles correspond to blends containing 17.5 wt% and 20 wt% polyether polyurethane. It indicates increasing incompatibility of this type of blends.

Conclusions

The changes in the loss tangent profiles of the polyester polyurethane/polyamide 6 blends in the region of the polyamide β relaxation indicate composition dependent hydrogen bonding between amide groups of the polyamide and ester groups from the polyester soft segments. This effect is not visible in case of polyurethane containing less compatible polyether soft segments. Thus, the interaction between polyamide 6 and thermoplastic polyurethanes in the blends depends basically on the chemical structure and on concentration of the polyurethane soft segments. The glass temperature of the blends was not dependent from the composition, but also no distinct transition for separated polyurethane soft segment was visible. Therefore the blends seem to be multiphase systems, where the elastomeric polyurethane phase is dispersed in a continuous polyamide phase.

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Zusammenfassung — Mittels DMTA wurden Gemische aus Polyamid 6 und Polyester oder Polyetherpolyurethanen untersucht. Die Gemische wurden durch Mischen in einem Brabender-Plasticorder Doppelschneckengerät gefertigt. Der Glasumwandlungspunkt der amorphen Fraktion des Polyamides wird durch Veränderungen der Zusammensetzung nicht beeinflußt, es war aber auch keine klare Umwandlung für einzelne Polyurethan-Softsegmente erkennbar. Die Gemische scheinen somit Multiphasensysteme zu sein, bei denen die elastomerische Polyurethanphase in einer kontinuierlichen Polyamidphase dispergiert ist. Aufgrund von Veränderungen im ß-Relaxationsbereich des Polyamides wird eine bessere Mischbarkeit von Polyesterpolyurethanen als von Polyetherpolyurethanen durch Wasserstoffbrückenbindungen in der normalen amorphen Phase erklärt.