

THERMAL PROPERTIES OF POLYAMIDE 6/ POLYURETHANE BLENDS

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Abstract

Equilibrium melting temperatures and crystallization parameters of polyamide 6/polyurethane blends were investigated. Thermal properties of the crystalline phase of blends obtained from polyamide 6 and polyurethane containing 40 wt% of hard segments, are only limited influenced by the overall blend composition. Because from separate measurements single glass transitions for all samples were estimated, so in the investigated case the blending process may occur mainly between amorphous fraction of polyamide 6 and the polyurethane or, what is more probable, the polyurethane phase is dispersed in the continuous polyamide matrix, although some interactions exist.

Keywords: blends, DSC, polyamide 6, polyurethane

Introduction

Blending of polymers offers a means of tailoring product characteristics to specific applications. At blends of polyamide 6 improvement of such properties as impact, dyeability, vapour permeation, antistatic is anticipated. Various polymers used as blend components with polyamide 6 include also polyurethanes [1-3]. The miscibility is usually estimated from the glass transition of the amorphous phase. This work is focused on changes in the crystalline phase caused by blending of polyamide 6 with a thermoplastic polyurethane.

Experimental

Materials

Stilamid S-25, polyamide 6, was obtained from Zakłady Włókien Chemicznych 'Stilon', Poland. The polyurethane of hardness of 84°ShA (TPU-84) was synthesised from poly(butylene, ethylene)adipate (Poles 55/20, Zakłady Chemiczne 'Zachem'), 4,4'-diisocyanate diphenylmethane (Suprasec, ICI) and 1,4-butanediol (B.A.S.F.).

The hard segment content was calculated as 40 wt%.

Blend preparation

The blends of polyamide 6 and the polyurethane TPU-84 were prepared by compounding in a twin-screw Brabender mixer. The blends were then pelletized and injection moulded into plates of dimensions 100 mm×50 mm×2 mm, from which test specimens were cut.

DSC

A Perkin-Elmer DSC 7 scanning calorimeter was used. The samples were sealed in aluminium pans and all scans were run under a nitrogen purge gas. To ensure complete melting before every crystallization the samples were held at 240°C for 3 min and then cooled at the rate 200 deg·min⁻¹ to the crystallization temperature. All samples were crystallized for 30 min.

Results and discussion

Equilibrium melting temperature

To determine the equilibrium melting temperature T_m , the samples were crystallized from the melt at 6 different temperatures (from 145 to 170°C) and then heated at the rate 20 deg·min⁻¹ to determine the melting peak temperature (T_m). The crystallization temperatures (T_c) were then plotted against T_m .

Table 1 Equilibrium melting temperature of polyamide 6/polyurethane TPU-84 blends

Wt% TPU-84	T_m (onset)/ °C	T_m (peak) °C
0	218.3	231.3
2.5	218.0	230.1
5	218.2	231.2
7.5	217.7	226.8
10	215	223.9
12.5	214.4	223.1
15	214.3	224.9
17.5	214.3	223.1
20	216.1	224.4
22.5	216	224.9

The theory of polymer crystallization predicts that the characteristic melting temperature should increase linearly with crystallization temperature according to the following equation developed by Hoffman and Weeks [4]:

$$T_m = T_m^{\circ}(1-1/\eta) + T_c/\eta$$

where η is a constant depending on the crystal dimensions.

The equilibrium melting temperatures were obtained by extrapolating the plot of T_m , measured at the onset and at the highest value of the melting peaks vs. T_c to the temperature, where T_m is equal to T_c .

Equilibrium melting temperatures of the investigated blends are lower, than for pure polyamide 6, but a clear dependency on the overall blend composition was not observed. Beginning from polyurethane content 7.5 wt% changes occur within $\pm 1.5^{\circ}\text{C}$, what would mean, that the crystalline phase could incorporate only a certain amount of polyurethane.

Non-isothermal crystallization

The crystallization parameters determined from the cooling scans at $20 \text{ deg}\cdot\text{min}^{-1}$ are summarized in Table 2. A shift in the temperature at the onset of crystallization would signify modification in the nucleation process. The changes in the crystallization peak width and the heat of crystallization would relate to the effect of blending on rate of crystals growth and degree of crystallinity, respectively [5].

Table 2 Crystallization parameters of polyamide 6/TPU-84 blends

Wt% of TPU-84	Onset/ $^{\circ}\text{C}$	Peak/ $^{\circ}\text{C}$	$-\Delta H/J\cdot g^{-1}$	$-\Delta H/J\cdot g^{-1}$ PA6	Peak width/ $^{\circ}\text{C}$
0	193.6	181	69.2	69.3	4.28
2.5	192.7	180.1	64.7	66.4	6.69
5	191.7	179.5	59.3	62.4	3.33
7.5	188.5	176.7	53.2	57.5	3.26
10	188.7	176.1	50	55.6	1.12
12.5	188.9	176.2	51.2	58.5	3.11
15	188.6	176.2	48.4	56.9	2.26
17.5	187.8	175.2	49.2	59.6	3.06
20	188.1	175.3	48.4	60.5	4.13
22.5	188.1	175.4	47.7	61.5	3.67

From onset of the crystallization it is seen, that the nucleation is slightly retarded in blends with TPU-84. The temperature at the onset of crystallization for blends containing more than 7.5 wt% of the polyurethane was found to be almost independent of the blend composition. The crystallization peak width,

measured at the half of the peak, had the lowest value for 10 wt% of TPU-84. For this composition the highest tensile strength was also found [6]. The heat of crystallization ($-\Delta H$, per gram of PA6 in the blend) for compositions up to 10 wt% of TPU-84 decreased, then for higher contents of the polyurethane increased, but did not reach the value estimated for pure polyamide.

Conclusions

Thermal properties of the crystalline phase of blends obtained from polyamide 6 and polyurethane containing 40 wt% of hard segments, are only limited influenced by the overall blend composition. Because from separate measurements single glass transitions for all samples were estimated [6], so in the investigated case the blending process may occur mainly between amorphous fraction of polyamide 6 and the polyurethane or, what is more probable, the polyurethane phase is dispersed in the continuous polyamide matrix, although some interactions exist.

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Zusammenfassung — Es wurden die Gleichgewichts-Schmelztemperaturen und Kristallisationsparameter von Polyamid 6/Polyurethangemischen untersucht. Die thermischen Eigenschaften der kristallinen Phase von Gemischen aus Polyamid 6 und Polyurethan mit 40 Gew% Hartanteilen werden nur in begrenztem Maße durch die Gesamtzusammensetzung des Gemisches beeinflusst. Anhand separater Messungen wurden die einzelnen Glasumwandlungen für alle Proben abgeschätzt, weshalb im untersuchten Falle der Mischungsprozess wahrscheinlich hauptsächlich zwischen der amorphen Fraktion von Polyamid 6 und dem Polyurethan erfolgt oder aber, was noch wahrscheinlicher ist, daß die Polyurethanphase in der kontinuierlichen Polyamidmatrix dispergiert wird, wenn auch einige Wechselwirkungen existieren.