Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 45–52

PHASE TRANSITIONS OF POLYAMIDE 6/ POLYURETHANE BLENDS COMPATIBILIZED BY COPOLYURETHANEAMIDES

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Abstract

Blends obtained from polyamide 6 and a thermoplastic polyurethane compatibilized by diblock copolyurethaneamides were investigated by means of DMTA and DSC. The blends were prepared by compounding in a Brabender mixer. The compatibilizer affected the glass transition temperature of the amorphous phase of the blends. The non-isothermal crystallization temperature of the polyamide phase was lowered in the presence of the polyurethane and the copolyurethaneamide.

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

Introduction

Compatibilization is necessary at many blends of interest to achieve a desirable property balance. In the polyolefin/polyamide blends the reactive compatibilization is preferred by in-situ formation of copolymer between maleic-anhydride grafted polyolefine by reaction of the grafted functional group with the terminal amine group in polyamide [1, 2]. The modification of polyamide 6 is also possible by application of thermoplastic elastomers or rubbers [2–4]. The polyamide 6/acrylonitrile–butadiene–styrene blends obtained with an imidized acrylic polymer as a compatibilizer revealed super-tough properties over a wide range of the component proportions [5, 6].

The classical compatibilizer is a diblock copolymer with blocks identical or miscible with the blend components. Block copolymers locate at the interface between two phases improving interfacial adhesion and contribute to mechanical reinforcement of the interface [7]. Decreasing of interfacial tension block copolymers increase the degree of dispersion and stabilize the phases *vs*. coalescence [8].

Previous research on the miscibility of polyamide 6/thermoplastic polyurethane blends revealed that multiphase systems are obtained, where the elastomeric polyurethane phase is finely dispersed in the polyamide matrix. The presumed low level of mutual interaction in the amorphous phase did not influence the temperature position of the loss tangent at the α transition, but caused some changes in the β transition of the blends [9].

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The aim of this work was to investigate the influence of block copolyurethane-amides, used as compatibilizers, on the miscibility enhancement in polyamide 6/thermoplastic polyurethane blends.

Solubility parameters of the blend components

The well known concept of Hildebrand's solubility parameter δ [10] has been often used for prediction of the probability of mixing of polymers. Since the heat of mixing of two substances A and B is dependent on $(\delta_A-\delta_B)^2$, the less the solubility parameter difference, the greater the probability of mixing [10].

Solubility parameter is defined as the square root of the cohesive energy density:

$$\delta=\left(\frac{\Delta E}{V}\right)^{1/2} \tag{1}$$

where ΔE represents the energy of vaporization at zero pressure and V is the molar volume.

The solubility parameter may be treated as a vector composed of dispersive δ_d, polar δ_π and hydrogen bonding δ_h components:

$$\delta^2=\delta_d^2+\delta_\pi^2+\delta_h^2 \tag{2}$$

The calculation of the solubility parameters is possible from the chemical structure of the polymer or any compound, if group molar attraction constants F, attributed to either Small [11], Hoy [12], van Krevelen [13] or Coleman [14], are known:

$$\delta=\frac{\sum F_i}{V} \tag{3}$$

where F_i – molar attraction constant of the i-th group, V – molar volume.

Askadskii [15] introduced a modified approach, which allows to calculate solubility parameters of a very broad range of polymers and organic liquids, because it applies atomic constants, estimated for various atoms under consideration of their surroundings, i.e. what particular atoms are chemically bonded to them. The method of Askadskii is a semi-empirical approach, based on the principle of additivity of characteristics of atoms building the repeating unit of a polymer and of characteristics of energy of intermolecular interactions:

$$\delta^2=\frac{\sum_i k_i\Delta E_i}{N_A\sum_i \Delta V_i}=\frac{\sum_i k_i\Delta E_i^*}{N_A\sum_i \Delta V_i} \tag{4}$$

where ΔE_i – molar cohesion energy; ΔE_i^* – effective molar cohesion energy; k – coefficient of molecular packing, k is the ratio of the van der Waals volume, which the atoms occupy in the solid matrix to the molar volume of the repeating unit; ΔV_i – van der Waals volume of the i-th atom; N_A – the Avogadro's number; ΔE_i^* – values were calculated from experimentally determined solubility parameters values for different atoms and types of intermolecular interactions [16].

In this work three types of polymers were used:

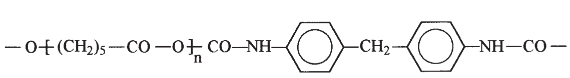
1. poly(ε-caprolactam)–polyamide 6,
2. thermoplastic polyurethane and
3. copolyurethaneamides.

In the structure of these polymers three types of repeating units were incorporated, which are presented below and described in Table 1:

$$-(CH_2)_5-NH-CO-$$

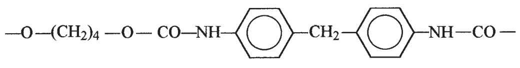
PCM

ε-caprolactam repeating unit



CL–MDI

blocks built of ε-caprolactone diol and 4,4'-diisocyanate diphenylomethane



BT–MDI

blocks built of 1,4-butanediol and 4,4'-diisocyanate diphenylomethane

The block copolymers, like thermoplastic polyurethanes and the copolyrethaneamides are usually phase separated and it is reasonable to calculate and compare the solubility parameter of the different phases built of blocks of one kind. The results of performed calculations are presented in Table 1.

Table 1 Calculated solubility parameters using Coleman [14] and Askadskii [15] approaches

Repeating unit code	Polymers containing the repeating unit	Solubility parameter/(J cm^{-3})$^{1/2}$	
		Coleman	Askadskii
PCM	polyamid 6 and polyamid blocks in the copolyurethaneamides	21.4	23.4
PCL–MDI	soft segments in the thermoplastic polyurethane and polyurethane blocks in the copolyurethaneamides	19.9	19.5
BT–MDI	hard segments in the thermoplastic polyurethane	24.4	23.6

As seen from the solubility parameter difference, miscibility of polyamide 6 could occur more likely with hard segments of the thermoplastic polyamide (BT–MI), than with the soft segments (PCL–MDI), but it should be rather restricted while the polyurethane hard segments and polyamide 6 crystallize on cooling. The soft segments PCL–MDI of the polyurethane seem to be hardly miscible with polyamide 6. Due to existing dipole–dipole and hydrogen bonding interactions between polyamide 6 and the thermoplastic polyurethane, some degree of compatibility is present, which was expected to be enhanced by the incorporation of polyurethaneamides into the blend compositions, since the polyurethaneamides contain blocks of the same chemical structure, as the blend components.

Experimental

Materials

Poly(ε-caprolactam)–polyamide 6 (trade name 'Stilamid S-25' from Zakłady Włókien Chemicznych 'STILON' in Gorzów Wielkopolski) was preliminary dried in vacuum at 100°C for 4 h. Thermoplastic polyurethane was synthesized by the prepolymer method, from poly(ε-caprolactone)diol, (M_n=2000 g mol^{-1}), 4,4'-diisocyanate diphenylomethane and 1,4-butanediol as the chain extender, using a prepolymer with 8.21% NCO content and [NCO]/[OH] mole ratio of 1.05. The block copolyurethaneamides, designated as UA40 UA70, UA80 and UA90 of the mass content of poly(ε–caprolactam) appropriately 40, 70, 80 and 90% were synthesized using adapted procedure by Allen *et al*. [17]. At first urethane prepolymer with the free NCO content of 3.60 mass% was obtained from poly(ε-caprolactone)diol and 4,4'-diisocyanate diphenylomethane. Separately NaH dispersion was added to ε-caprolactame in the proportion of 0.46 g per 1 mole of ε-caprolactam and intensively stirred at 80°C for 30 min. Thus obtained poly(ε-caprolactam)anions were reacted with the urethane prepolymer at 160°C. The reaction was completed by annealing at 160°C for 4.5 h. The mass content of poly(ε-caprolactam) blocks in the block copolyurethaneamides corresponds to the used ε-caprolactam to urethane prepolymer proportions.

The blends were prepared by compounding in a Brabender Plasticorder mixer at 240°C for 4 min at 100 rpm. The removed melt was pressed into plates, from which test specimens were cut out.

Dynamic mechanical thermal analysis

The measurement were performed using a Polymer Laboratories DMTA PL Mk III apparatus in a double cantilever geometry in the bending mode from –100 to 220°C at a heating rate of 4 K min^{-1} and at frequencies of 1, 10, 30, 50 and 100 Hz.

Differential scanning calorimetry

Examination of the crystallization of the blends and their components was performed using a Perkin Elmer DSC7/Unix calorimeter. The samples were closed in sealed aluminum pans, annealed at 240°C for 2 min and run from 240 to 30°C at the cooling rate of 10 K min^{-1} under nitrogen as the purge gas.

Table 2 DMTA results (at 10 Hz) for investigated blends, at 5 mass% compatibilizer content, ordered by increasing temperature positions of the loss tangent peak

Blend composition			Loss tangent peaks				Loss modulus peaks	
TPU/ mass %	PA6/ mass%	Compatibilizer designation	Peak β		Peak α		Peak β	Peak α
			°C	value	°C	value	°C	°C
25	70	UA90	–	–	48.8	0.3282	–61.0	36.3
5	90	UA90	–60.9	0.0452	49.8	0.1973	–65.3	32.5
20	75	UA90	–	–	52.7	0.4227	–60.2	37.8
5	90	UA70	–63.3	0.0498	54.7	0.2096	–77.2	32.5
10	85	UA80	–59.6	0.0429	54.8	0.2156	–59.6	37.7
20	75	UA80	–59.9	0.0416	55.3	0.2537	–58.9	39.1
10	85	UA70	–62.0	0.0445	55.5	0.3332	–70.0	37.0
5	90	UA80	–58.9	0.0483	56.1	0.1966	–60.1	40.3
10	85	UA40	–59.5	0.0381	56.5	0.2154	–62.9	39.2
5	90	UA40	–57.8	0.0424	56.7	0.1888	–61.0	39.5
15	80	UA70	–58.5	0.0430	56.9	0.2430	–60.0	39.8
15	80	UA80	–60.2	0.0456	56.9	0.2045	–66.5	39.9
20	75	UA70	–57.0	0.0406	56.9	0.2667	–65.0	41.5
25	70	UA40	–	–	57.3	0.3284	–39.1	36.8
20	75	UA40	–60.3	0.0389	58.5	0.2415	–66.4	39.7
25	70	UA80	–54.8	0.0379	58.7	0.2361	–58.3	42.0
25	70	UA70	–	–	58.8	0.3620	–52.0	42.3
15	80	UA90	–	–	60.3	0.2110	–	40.5
0	100		–58.7	0.0407	62.4	0.1631	–62.1	43.6

Results and discussion

In the case of binary blends obtained from polyamide 6 and the same thermoplastic polyurethane (TPU) as used in this work, the position of the loss tangent (tgδ) maximum did not change with the increase of TPU content in the blends [18].

Table 3 DSC crystallization parameters for investigated blends, at 5 mass% compatibilizer content, ordered by decreasing temperature position of the crystallization peak

Blend composition			Characteristics of the crystallization peak				
Compatibilizer designation	PA6/ mass%	PU/ mass%	Beginn. of peak/°C	End of peak/°C	Max./ °C	Enthalpy/ $J\ g^{-1}$	Onset/ °C
	100	0	209.0	182.5	194.7	–62.8	198.0
UA70	90	5	201.0	168.5	194.2	–65.1	197.5
UA80	90	5	208.0	164.0	193.5	–68.1	196.8
UA40	85	10	201.5	179.0	193.5	–56.7	197.6
UA90	90	5	201.0	179.0	193.1	–59.7	196.6
UA40	75	20	203.0	166.0	193.1	–52.6	197.2
UA80	75	20	208.0	154.5	192.3	–61.7	198.2
UA90	70	25	199.5	164.5	191.8	–57.0	195.8
UA90	85	10	199.9	170.8	190.4	–56.9	194.4
UA90	80	15	198.1	165.6	190.1	–55.1	193.5
UA70	85	10	201.5	164.0	190.0	–65.6	194.2
UA80	70	25	198.6	161.3	190.0	–50.8	194.7
UA80	80	15	199.5	151.5	189.7	–62.7	194.2
UA70	70	25	197.7	165.2	188.8	–37.8	193.0
UA40	80	15	197.3	166.5	187.8	–55.6	191.8
UA70	80	15	194.2	176.0	186.8	–53.6	191.7
UA70	75	20	198.6	170.0	183.6	–48.1	188.9
UA40	70	25	197.7	155.7	183.5	–40.3	187.8

For the ternary blends, composed of polyamide 6, the TPU and 5 mass% of a copolyurethaneamide a clear shift of the maximum of the α peak of the loss tangent curve occurred. The appropriate results for the frequency of 10 Hz are presented in the Table 2. The greatest peak temperature shift was observed for the blend containing 25 mass% TPU, 70 mass% PA6 and 5 mass% of the UA90 copolyurethaneamide with the temperature position of the peak at 48.8°C. The next value (49.8°C) was found for the blend containing copolyurethaneamide UA90 as well, but only 5 mass% of the TPU and 90 mass% PA6. The blend containing 20 mass% TPU, 75 mass% PA6 and the copolyurethaneamide UA90 shows tgδ maximum at 52.7°C. Occurring of appropriate maxima at the loss modulus E'' temperature dependencies allows attribution of observed α peaks to the glass transition. The values of the tgδ estmated at α transition maxima indicate that the damping increases generally with the increase of the TPU content in the blends.

The results of the crystallization runs are summarized in the Table 3. Almost in all cases shift to the lower temperatures of the onset of the crystallization and of the crystallization peak was observed. The delaying of the crystallization of the polyamide phase was greater at higher TPU contents in the blends. It was not found that the changes in copolyurethaneamide composition produced regular changes in the crystallization of the blends.

At the DMTA investigations loss tangent peak for the glass transition of the separated TPU phase was not visible. Therefore in the investigated blends the polyurethane is dispersed in the polyamide amorphous phase. The copolyurethaneamides were able to act as compatibilizers in the examined systems. The influence of the compatibilizer was evident but not exactly composition dependent, indicating possible differences in the dispersion grade of the TPU in the polyamide matrix.

Conclusions

Binary polyamide 6/thermoplastic polyurethane blends did not show loss tangent shift to the lower temperatures in dependency of the polyurethane content. Addition of 5 mass% of block copolyurethaneamide improved the miscibility but an equivocal, systematic dependence of the loss tangent shift on the blend's composition was not found. The damping at the glass transition increased with the increase of the TPU content in the blends.

The polyurethane phase both in the binary blends and in the compatibilized blends is dispersed in the amorphous polyamide matrix below the detection level of DMTA, also the magnitude of dispersed particles is below 15 nm [12].

At application as compatibilizers of block copolyurethaneamides with the content of polyamide blocks in the range from 40 to 90 mass% blends were obtained, which showed considerable shifts of the loss tangent peak position in relation to pure polyamide 6. Essentially loss tangent shifts were found for compatibilized blends already at 5 mass% of the TPU, with only slight increase of its value at the glass transition. This proportion might be the favorable for modification of polyamide 6 with thermoplastic polyurethanes and block copolyurethaneamides.

Higher TPU content caused greater delaying of the crystallization of the polyamide phase. The calculated solubility parameter differences (Table 1) allow the assumption of partial miscibility in the molten state. Therefore this result may be explained by the diluting effect of the polyurethane, influencing the primary nucleation process.

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