

THERMAL PROPERTIES AND MORPHOLOGY OF POLY(ESTER-URETHANES) PREPARED FROM POLYCAPROLACTONE-DIOL

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Abstract

The soft segment crystallinity and morphology of poly(ester-urethanes) (PEUs) based on poly(ϵ -caprolactone) (PCL) as a soft segment and an aliphatic diisocyanate in the hard segment were studied. It was found that the restriction of the crystallization of the PCL soft segment depends on the hard segment concentration, the length of the soft segment, and the total molecular mass of the PEUs. The PEU based on a low molecular mass PCL ($M=2000$) is an amorphous elastic material during a long time after casting from solution or after melt crystallization. A soft-hard segment endothermal mixing transition (T_{mix}) of about 70–80°C is observed in the DSC curves of this PEU sample.

Keywords: glass transition, mixing transition, poly(ester-urethanes), strain-induced crystallization

Introduction

Segmented polyurethanes are composed of alternating soft (low glass transition) segments and more rigid, polar urethane (hard) segments. In potentially biodegradable polyurethanes, the soft segments are usually polyesters [1–9] and the hard segments are formed by the extension of a diisocyanate-terminated prepolymer with a low molecular mass diol.

Our data on the degradation of poly(ester-urethanes) (PEUs) based on poly(ϵ -caprolactone) (PCL) in the presence of fungi and by composting showed that the length of the PCL segment and also the composition and morphology of the PEUs play an important role in the biodegradability of the polymers [10].

Investigation of the physical properties and morphology of the PEUs with respect to their composition would be important for further considerations as concerns their environmental degradation and appropriate application as degradable materials.

It is to be expected that different procedures of sample preparation (precipitation, casting from solution and moulding) will lead to various structures and properties of the PEUs.

We recently presented results relating to the synthesis and physical properties of PEUs based on PCL of different molecular masses ($M=2000$, 4000 and 7300) as a

soft segment and a non-aromatic diisocyanate, 1,1'-methylene-bis(4-isocyanatocyclohexane) (HMDI) extended with butanediol as a hard segment [11].

In the present work, the thermal properties and morphology of PEU based on the shortest PCL soft segment (PCL-2000) are further investigated and discussed in more details.

Experimental

The synthesis of segmented PEUs based on PCL of different molecular masses ($M=2000$, 4000 and 7300) as a soft segment and 1,1'-methylene-bis(4-isocyanatocyclohexane) (HMDI) in the hard segment was performed in bulk under argon at 65°C. The procedure was described in detail previously [11]. The content of the PCL segments in the PEUs was determined by NMR (Bruker 360 MHz).

The molecular masses and molecular mass distributions of the polymers were measured by GPC, using a mixed gel column (Polymer Laboratories), with polystyrene standards, and chloroform as eluent.

A thin film of PEU was cast from a methylene chloride solution (2 mass%) on a glass plate at 20°C. The cast polymer film was dried at room temperature. The thickness of the final dried PEU foils was about 70 μm .

Samples measuring 4×30 mm were cut out from the PEU film. They were uniaxially stretched at 20°C (below the melting point of the PCL crystalline phase) by a Tensile Testing Machine H10KM (Hounsfield, UK) with a test speed of 100 mm min⁻¹ just before the breaking strain.

The melting behaviour of the non-oriented and oriented PEU foils was studied by using a differential scanning calorimeter DSC2920 (TA Instruments, USA) in the normal mode for melting and crystallization transitions at a heating rate of 10°C min⁻¹ and a cooling rate of 1°C min⁻¹, and in modulate mode (oscillation amplitude 1°C, oscillation period 60 s and an average heating rate of 2°C min⁻¹) for glass transitions.

The glass transition temperature (T_g) was taken at the midpoint ($1/2\Delta c_p$) of the stepwise increase in the heat capacity. The heat capacity was calibrated by running a standard sapphire (Al₂O₃) sample. The cell constant was calibrated by using a standard indium sample.

A Philips model PW-1820 X-ray diffractometer employing Ni-filtered CuK α was used to obtain wide-angle X-ray diffraction (WAXD) patterns of the non-oriented and oriented PEU foils at room temperature. The scan rate was 0.01° 2 θ s⁻¹.

Results and discussion

All types of PEUs containing PCL as soft segment, with molecular masses of 2000, 4000 and 7300, are semicrystalline materials, as demonstrated in a recent publication [11].

Table 1 lists the thermal properties (melting and crystallization temperatures and associated enthalpies of melting and crystallization) of PEU based on PCL 2000 and of chosen PEUs based on PCL 4000 and PCL 7300, as obtained in the first and sec-

Table I Thermal properties of the poly(ester-urethanes) and the starting poly(ϵ -caprolactones)

Sample		DSC					MDSC				
Code	PCL-unit	M	M_n	PCL mass%	1st heating ($10^\circ\text{C min}^{-1}$)			2nd heating ($10^\circ\text{C min}^{-1}$)			
					$T_m/^\circ\text{C}$	$\Delta H_m^{\text{th}}/\text{J g}^{-1}$	$\alpha_c^{\text{th}}/\%$	$T_c/^\circ\text{C}$	$\Delta H_c^{\text{th}}/\text{J g}^{-1}$	$T_m/^\circ\text{C}$	$\Delta H_m^{\text{th}}/\text{J g}^{-1}$
										$T_g/^\circ\text{C}$	$\Delta C_p/\text{J g}^{-1}\text{ }^\circ\text{C}^{-1}$
P2-33	2000	32700	77.4	39	19	14	-	-	-	-50	0.39
P2-54	2000	53900	76.8	42	14	10	-	-	-	-50	0.36
P2-60	2000	59500	75.6	42	14	10	-	-	-	-49	0.36
P4-53	4000	52800	85.3	53	67	47	20	46	5	-57	0.15
P7-61	7300	61400	85.8	55	67	47	17	38	45	-58	0.24
PCL		2000	100	53	85	60	30	72	74	-69	0.17
PCL		4000	100	60	109	77	39	82	88	-65	0.09
PCL		7300	100	60	108	76	41	77	81	-65	0.08

a) - with respect to mass% of PCL inPEU

ond DSC heating scans and cooling scan. Table 1 also reports the melting and glass transition parameters of PCL with $M_n=2000$, 4000 or 7300, used as soft blocks in the various PEUs.

The DSC data obtained during the first heating scan indicate that all the PCL soft segments of different lengths result in a crystalline structure during precipitation from solution. Generally, less perfect crystallization of PCL soft segments than of the initial PCL prepolymer is observed. This is more clearly expressed in PEUs based on the PCL of the lowest length ($M=2000$). The chemical bond between the hard and soft segments restricts both phase separation and crystallization of the PCL soft segments.

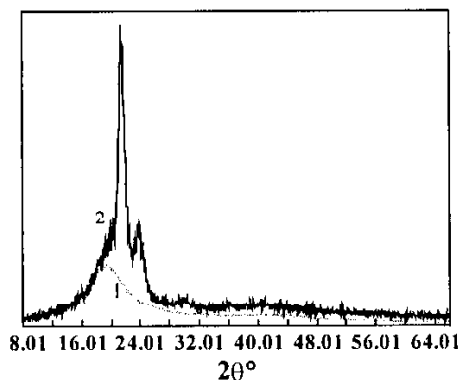


Fig. 1 WAXD of PEU (P2-60) foil cast from solution in CH_2Cl_2 , stored for 27 days at room temperature: non-oriented foil (curve 1); uniaxial stretched foil, temperature of orientation 20°C , stretching strain 583% (curve 2)

More significant differences in morphology and thermal properties of different PEUs are observed for samples cast from a solution or cooled after the first melting. The PEUs based on the shortest PCL soft segment ($M=2000$) are completely amorphous immediately after solvent evaporation, after quenching from the molten state, or even after slow cooling from the melt. Only a glass transition of about -50°C is indicated in the DSC and MDSC curves (Table 1). For these PEUs, Δc_p ranges between 0.36 and $0.39 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, values that correspond to the specific heat increment of the amorphous polymers. When the PCL soft segment has a higher molecular mass ($M=4000$ or 7300), crystallization occurs rapidly during evaporation of the solvent or on cooling from the melt or even on quenching.

Figure 1, curve 1 depicts the WAXD diffractogram at room temperature of the non-oriented PEU (P2-60) foil cast from solution. Only a broad amorphous halo with maximum at $2\theta=20^\circ$ is observed, which confirms the non-crystalline structure of this sample. Curve 2 presents the WAXD of a uniaxial stretched foil of the same PEU and will be further discussed.

The DSC results are in good agreement with the WAXD data and confirm the amorphous (non-crystalline) structure of the PEU (P2-60) samples even after a very long period of annealing at room temperature.

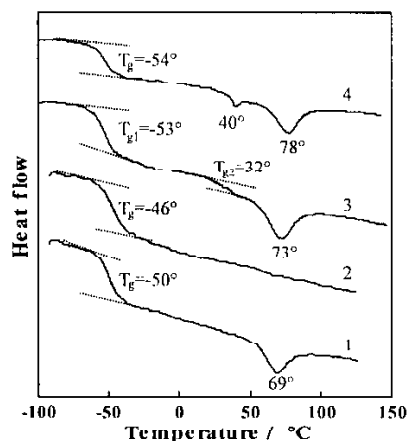


Fig. 2 DSC curves of non-oriented PEU foils cast from CH_2Cl_2 solution, annealed for 27 days (curves 1 and 2), 210 days (curve 3) or 600 days (curve 4) at room temperature. The first DSC heating scans (curves 1, 3 and 4) and second DSC heating scan (curve 2)

The characteristic DSC heating curves of non-oriented PEU (P2-60) foils are shown in Fig. 2. After solution casting, these samples were stored at room temperature for periods of from 27 days to 600 days (Fig. 2, curves 1–4).

It can be seen, that after a short storage time only a glass transition temperature (T_g) at -50°C is visible in the DSC curve (Fig. 2, curve 1). Two glass transition temperatures, at -53 and 32°C , are to be observed after a much longer storage time (210 days) (Fig. 2, curve 3); the melting peak of the crystalline PCL phase at 40°C is observed in the DSC curve only after storage for 600 days at room temperature. It can be supposed that a phase separation occurs in the solution cast PEU foils at room temperature. The lower glass transition temperature ($T_{g1} = -53^\circ\text{C}$) can be attributed to the T_g of the soft segment matrix rich in PCL constituent. T_g for the pure PCL ($M_n = 2000$), determined by DSC, is situated at -60°C [11]. The higher $T_{g2} = 32^\circ\text{C}$ can reasonably be attributed to the glass transition of the PEU domains rich in hard segment. By using the chemical groups increment method [12], we have evaluated a T_g for the pure hard segment of about 51°C . As mentioned above, shortly after solution casting the PEU foils display only one glass transition temperature, ranged between T_{g1} and T_{g2} , and which is associated with the glass transitions of the soft PCL phase when the phase separation is not completed (Fig. 2, curve 1).

The endotherms at 69 and 78°C , indicated in the DSC curves may be associated with the well-known mixing transition temperature (T_{mix}) in polyurethanes [13]. Two phases, PCL matrix and hard segment domains, generally exist below this temperature in the PEU. A 'homogeneous' mixing of the soft and hard segments occurs on heating above this temperature. The second DSC heating run of this sample, performed immediately after cooling from 150 to -100°C , reveals only one T_g at -46°C , and no mixing endotherm is observed (Fig. 2, curve 2). The increase in the T_g of

PEU observed in the second DSC scan is due to the decrease in the segmental mobility of the PCL soft segments after a 'homogeneous' mixing with the hard segments. Analogous thermal behaviour is observed for other PEUs based on PCL-2000 (P2-33 and P2-54).

Table 2 Thermal transitions in non-oriented PEU (P2-60) foils as a function of the storage time (τ_s) at room temperature after casting from solution

τ_s /day	DSC heating run	T_g /°C	T_{mix} /°C	ΔH_{mix} /J g ⁻¹
1	1st	-49	59	0.8
30	1st	-51	67	2.74
210	1st	$T_{g1} = -53$ $T_{g2} = 32$	72	6.74
	2nd	-49	-	-
600	1st	-54	78	6.93

Table 2 reports the glass transition temperature (T_g), the temperature of the mixing transition (T_{mix}), and the corresponding enthalpy (ΔH_{mix}) obtained during the first and second DSC heating runs on PEU samples as a function of the storage time at room temperature after casting from solution. The DSC results show that the T_g of the PEU with low phase separation (shortly after casting from solution) is slightly higher in comparison with the lower glass transition temperature, T_{g1} , of the PEU samples allowed to phase separate for a longer time at room temperature (more than 30 days). This is also due to the contribution of the hard segment, which decreases the chain flexibility of the PCL matrix and consequently increases T_g in more homogeneous (less phase separates) PEU samples.

The temperature of mixing transition, T_{mix} , and the corresponding enthalpy, ΔH_{mix} , increase with the storage time. This indicates that the phase separation in PEU films occurs slowly during storage at room temperature after casting from solution or after melting and cooling to room temperature.

It is interesting to note that strain-induced crystallization is observed in the uniaxially elongated samples of PEU (P2-60) when the stretching ratio is more than 100%. The results from WAXD (Fig. 1, curve 2) and DSC analysis (results not presented) indicate that the crystalline phase obtained is associated with a crystallization of the PCL soft segments. The strain-induced crystallization is favoured with increase of the stretching ratio of PEU samples. These results will be discussed in more detail in a forthcoming paper.

Conclusions

It has been established that the PEU based on a low molecular mass PCL ($M=2000$) and with an aliphatic diisocyanate in the hard segment is an amorphous elastic material at room temperature after casting from solution. The hard domains

become the fixed points in a physically cross-linked polymer system and this leads to restriction of the crystallization of the PCL soft segments. The glass transition temperature of the amorphous PEU based on PCL-2000 is about -50°C and the endothermal mixing transition of soft-hard segments is about $70\text{--}80^{\circ}\text{C}$.

It is shown that strain-induced crystallization occurs when the amorphous physical network of this type of PEU is stretched above a certain elongation ratio (about 100%) at $22\text{--}25^{\circ}\text{C}$. The WAXD results show that the fixing crystalline phase can be associated with stress-induced crystallization of the PCL soft segments.

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