Macromol. Symp. ***152,*** *117–126 (2000)*

Synthesis and characterization of poly(ester-urethanes)

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SUMMARY: Segmented poly(ester-urethanes) (PEUs) based on poly(ε-caprolactone) (PCL) as a soft segment and a non-aromatic diisocyanate in the hard segment are synthesized as biodegradable materials. In a first part the environmental degradation of PCL and its copolymers was investigated. In the later stage of the work the morphology and thermal properties of the segmented poly(ester-urethanes) are studied in respect to the soft segment length, content of the hard segment and total molecular weight.

It was established that a strain induced crystallization of amorphous poly(ester-urethane) based on the shortest PCL soft segment (M=2000) occurs when the samples from PEU are stretched at room temperature above a certain elongation ratio.

Introduction

We have recently been involved in a collaborative program1) focussing on the synthesis and evaluation of non-toxic biodegradable polymers which could undergo environmental degradation.

The literature data2-6) and our results7) on the degradation of PEUs based on PCL in the presence of fungi and by composting showed that the length of the PCL segment and also the composition and morphology of PEUs play an important role on the biodegradability of the polymers.

The investigation of the physical properties of the PEUs with respect to their composition would be important in the further considerations about their environmental degradation and proper application as degradable materials.

This work presents our recent results from synthesis and investigation of the environmental degradation, morphology and thermal properties of poly(ester-urethanes) based on poly-ε-caprolactone with different molecular weight as a soft segment and a non-aromatic

CCC 1022-1360/00/$ 17.50+.50/0

diisocyanate 1,1'- methylene-bis(4-isocyanatocyclohexane), extended with butanediol as a hard segment.

Synthesis and characterization of the PEUs

The segmented poly(ester-urethanes) (PEUs) based on poly(ε-caprolactone) with different molecular weight (M=2000, 4000 and 7300) as a soft segment and a non-aromatic diisocyanate, 1,1'-methylene-bis(4-isocyanatocyclohexane) (hydrogenated diphenylmethane diisocyanate) (HMDI), in the hard segment are performed in bulk under an argon blanket at 65°C. The procedure is described in details in our previous paper[8)]. Molecular weight and molecular weight distribution of the polymers are measured by gel permeation chromatography (GPC). The content of the PCL segments in PEU is determined by ^{1}H NMR.

The molecular weight of the polymers is in the range 20 000-60 000. PEUs based on the shortest PCL segment (M = 2000) contain about 77 wt.% PCL component and PEUs based on the longer PCL segments (M = 4000 and 7300) - about 85 wt.% PCL.

Environmental degradation

As shown before, PCL degrades mainly enzymatically and the rate of degradation decreases with increasing molecular weight [9)].

Biodegradability of PEUs was studied in the presence of fungi (Standard method EN 807 for wood preservatives) and by controlled composting test (ASTM method D-5338.92). Degradation by fungi proceeds mainly enzymatically. NMR analysis of the retrieved samples shows that the PCL-segments in PEUs degrade first. This result indicates that the ester bond is more susceptible to biodegradation than the urethane bond.

The results from the controlled composting test are presented in Table 1. GPC and ^{1}H NMR analyses show that the molecular weight of the polymers decreases with exposition time. The rate of degradation depends on the molecular weight of the PCL-segments in PEUs, being much higher for PCL-2000 than for PCL-4000. As it is considered further in this paper, PEUs with PCL-2000 as soft segments are amorphous materials and this facilitates the water uptake and enzymes approach to the material.

Table 1. GPC and NMR analysis of PEUs after composting

No	Sample	PCL-segments, M_w	Time, days	GPC M_n	GPC M_w	M_w/M_n	PCL, wt % (NMR)
1.	P2-33	2000	blank	32700	76500	2.34	77.4
			5	24100	40000	1.66	75.4
			12	11100	22100	1.99	71.9
2.	P4-53	4000	blank	52800	114000	2.16	85.3
			5	48700	75500	1.55	85.5

Thermal properties and strain induced crystallization

All types of PEUs containing PCL with molecular weight 2000, 4000, and 7300 as a soft segment are semi crystalline materials as was shown before[8,10)].

Differential scanning calorimetry (DSC) data, obtained at first heating run, indicate that all PCL soft segments with different length form a crystalline structure during precipitation from a solution. A less perfect crystallization of PCL soft segment compared to the initial PCL prepolymers is observed. This is more clearly expressed in PEUs based on PCL with the lowest length (M=2000). The chemical linkage (connectivity) between the hard and soft segments restricts the phase separation and crystallization of the PCL soft segments.

A more significant difference in the morphology and thermal properties of different types PEUs is observed for the samples which are cast from 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, or after quenching from molten state, or even after slow cooling from a melt. When the PCL soft segment has a higher molecular weight (M=4000 or 7300) crystallization occurs rapidly during evaporation of the solvent or at cooling from melt and even at quenching.

Figure 1, curve 1 presents a wide angle X-ray diffraction (WAXD) diffractogram at room temperature for the nonoriented, casted from a solution PEU (P2-60) foil. This polymer is based on PCL-2000 with total molecular weight M=60 000. Only a broad amorphous halo with maximum at $2\theta = 20°$ is observed which indicates a non-crystalline structure of this sample.

The results from DSC analysis are in a good agreement with the WAXD results and confirm the amorphous (noncrystalline) structure of the PEU (P2-60) samples even after very long period of storage time at room temperature (more than 3 months). The characteristic DSC curves at heating of nonoriented PEU (P2-60) foils are shown in figure 2. After casting from a solution these samples are stored at room temperature for different periods of time - from 27 days to 600 days (Fig. 2, curves 1-4).

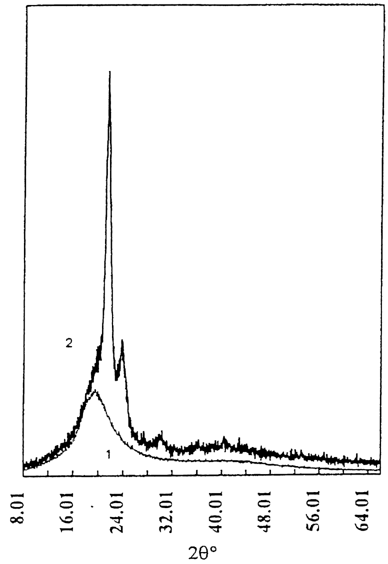

Fig. 1: WAXD of PEU (P2-60) foil casted from CH_2Cl_2- solution, stored 27 days at room temperature: nonoriented foil (curve 1); uniaxial stretched foil, temperature of orientation 20°C, stretching strain 583% (curve 2)

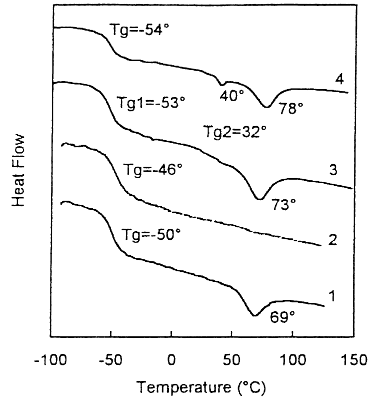

Fig. 2: DSC curves of nonoriented PEU (P2-60) foils casted from CH_2Cl_2- solution, stored 27 days (curve 1, 2), 210 days (curve 3) and 600days (curve 4) at room temperature. First DSC heating run (curve 1, 3, 4); second DSC heating run (curve 2)

One can see that after short storage time only one glass transition temperature (T_g) at -50°C is observed in the DSC curve (Fig. 2, curve 1). Two glass transition temperatures at - 53°C and 32°C are observed after much longer storage time (210 days) (Fig. 2, curve 3). A melting peak at 40C° of a crystalline PCL phase is only observed in the DSC curve after 600 days storage time at room temperature. It can be supposed that a phase separation occurs in the casted PEU foils at room temperature. The lower glass transition temperature (T_{gl} = -53°C) can be attributed to the T_g of the soft segment matrix which is rich of PCL constituent. T_g of the pure PCL (M_n=2000) is determined by DSC at -60°C [2)]. The higher T_{g2} = 32°C is reasonable to be attributed to the glass transition of the domains which are rich in hard segment. Using the value of the chemical groups increments[11)] we have calculated T_g for the pure hard segment about 51°C. As it was mentioned above, shortly after casting the PEU foils show only one glass transition temperature, ranged between T_{g1} and T_{g2} which can be associated with the glass transition of the soft PCL phase when the phase separation is not completed (Fig. 2, curve 1).

The endotherms at 69°C - 78°C which are observed in the DSC curves can be associated to the well known mixing transition temperature (T_{mix}) in the polyurethanes. Generally, two phases, PCL matrix and hard segment domains, exist below this temperature in the PEU. A "homogeneous" mixing of the soft and hard segments occurs at heating above this temperature. The second DSC heating run of this sample performed immediately after cooling from 150°C to -100°C shows only one T_g at -46°C and no mixing endotherm is observed (Fig. 2, curve 2). The increasing of the T_g of PEU at second DSC scan is due to the decreasing of the segmental mobility of the PCL soft segments at a "homogeneous" mixing with the hard segments.

The temperature of the 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 the storage at room temperature after casting from a solution or after melting and cooling to room temperature.

It is known that the tendency of an amorphous polymer to crystallize is greatly enhanced by deformation[12)].This phenomenon is recognized as strain induced crystallization. Since the chains are distorted from their most probable configuration, a decrease in configurational entropy ensues. The lower entropy favours the transformation to the crystalline state. The first crystallites formed by the deformation act as physical crosslinks. When the deformation increases the remaining amorphous chains are subjected to much greater orientation upon elongation.

The characteristic stress-strain curve at 20°C of PEU foil is represented in Figure 3. One can see that at low stretching ratio (below 200%) the slope of the tensile curve resembles the slope of the tensile curve of an amorphous network with a low crosslink density (Fig. 3, region I). At stretching ratio higher than 300% an increasing of the slope of the tensile curve is observed (Fig. 3, region II).

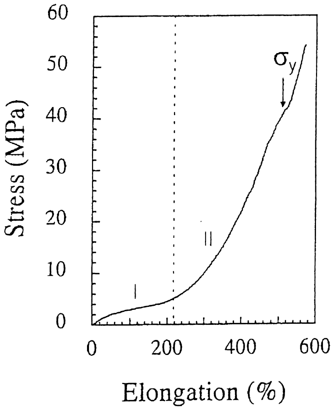

Fig. 3: Stress-strain curves of PEU foils casted from solution in CH_2Cl_2 (after 27 days storage at room temperature). Temperature of orientation 22°C. Maximum stretching strain 567%

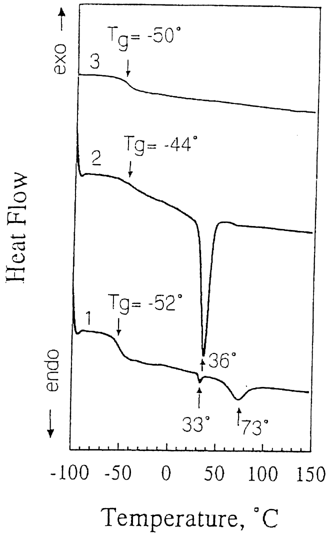

Fig. 4: DSC curves of uniaxial stretched foils of PEU-2. (stored 210 days at room temperature after casting from solution). Temperature of orientation 22°C. Tensile-stressed for 30 min. Stretching ratio under stress (and residual deformation), %: 1 - 100 (3); 2, 3 - 500 (87). First heating (curves 1, 2), second heating (curve 3), 10°C/min

The oriented samples are transparent until 450 - 500% elongation. At higher stretching ratio they become opaque under stress. A plastic yield point (σ_y) is observed in a tensile curve just before the ultimate (breaking) strain. When the tensile stress is removed the shrinking of the oriented foils leads to different residual strain, depending on the stretching ratio and initial grade of the phase separation (storage time after casting) of the PEU foils.

The structure and thermal properties of the oriented foils of PEU are characterized by means of WAXD and DSC. The results obtained show that a strain - induced crystallization is observed in the oriented samples of PEU when the stretching ratio under stress is about 100% and more.

Figure1 (curve 2) presents the WAXD diffractogram of an oriented foil of PEU (orientation temperature 20°C, stretching strain under stress 583%, and residual strain (without stress) 133%). Strong crystal patterns are registered at $2\theta = 21.45°$ and $23.81°$. The position of the crystal reflection in the diffractogram of oriented PEU agrees well with that reported in the literature for polycaprolactone13). This result suggests that the crystalline phase which develops in the PEU foils during the elongation is associated with crystallization of the PCL soft segments.

Figures 4 presents and compare the characteristic DSC curves of the oriented PEU samples with different stretching ratio. The DSC curves of oriented foils of PEU as obtained in a first DSC heating scan indicate strong melting endotherm about 32° - 36°C depending on the stretching ratio. This endotherm can be attributed to the melting of the PCL crystalline phase obtained by strain-induced crystallization.

On the DSC curve at second heating only glass trasition temperature is indicated at -50°C and no melting peak is observed (Fig. 4, curve 3). Consequently, PEU does not crystallize during the DSC cooling run; no temperature induced crystallization is observed at cooling with 10°C/min and even at lower cooling rate (1°C/min).

From Fig. 4 it is clear also that the glass transition temperature,T_g, and the soft-hard segments mixing endotherm,ΔH_{mix}, of the oriented PEU samples in the range 71 -73°C depend also on the stretching ratio (compare curves 1 - 2 in Fig. 4). The results from the DSC analysis of oriented PEU foils indicate that the glass transition temperature, T_g, melting temperature, T_m, associated melting enthalpy, ΔH_m, and the temperature of the soft - hard segments mixing transition, T_{mix}, increase with increasing the stretching ratio. At the same time the enthalpy ΔH_{mix} which is associated with mixing endotherm transition and the change of the heat capacity at glass transition temperature, Δc_p, decrease.

It is interesting to point out that the decrease of the endotherm of the enthalpy which is associated with the soft-hard segments mixing transition is more pronounced at higher stretching strain. For example such transition is missing in the DSC curves of oriented PEU samples at extremely high stretching ratio (500-600%) (Fig. 5, curve 1, 2).

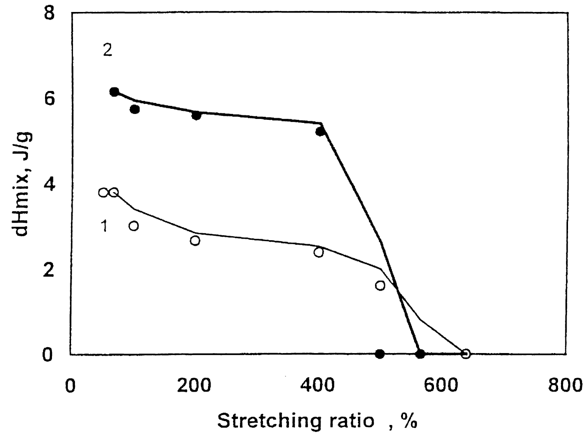

Fig.5: Dependence of the enthalpy of endotherm of the mixing transition (ΔH_{mix}) of oriented PEU foils on the stretching strain. Storage at room temperature after casting from solution 10 days (1) and 210 days (2). Temperature of orientation 22°C. Tensile stressed 30 min

The results in Fig. 5 show also that at identical stretching ratio the values of the ΔH_{mix} for samples which are less phase separated (shortly after casting -10 days) are lower (curve 1) than those for the samples which are allowed to phase separate longer (210 days) (curve 2). A limited number of PEU samples were oriented at different temperature ranged in a very narrow interval (19° - 25°C) to the same stretched strain (500%). They are tensile stressed for 30 min at the orientation temperature. A maximum of the enthalpy of melting (respectivelly crystallinity) and melting temperature of the oriented PEU is indicated at about 21°C.

The results from DSC experiments indicate that the strain induced crystallization of the soft PCL matrix in an amorphous PEU elastomer is attended with an orientation of the non-crystalline phase. It is reasonable to expect that the oriented PEU foils with such phase structure (crystalline PCL matrix and oriented amorphous phase which contains hard segment domains) have to show shape memory effect. The results from a heating experiment at 37°C (slightly above melting temperature of the crystalline PCL phase) of oriented PEU samples indicate that the oriented samples recover their original shape. This effect allows a broad range of applications of such polymer materials. The results from the more detailed study of the shape recovery effect of the oriented foils of PEU will be presented in the next paper.

Conclusions

PEUs degrade mainly enzymatically in the presence of fungi and during the composting test. Their biodegrability is affected by the composition, molecular weight and morphology of the polymers.

It is established that the PEU based on a low molecular weight PCL (M = 2000) is an amorphous elastic material at room temperature after casting from a solution. The hard domains become the fixed points in a physically crosslinked polymer system and it leads to restriction of the crystallization of the PCL soft segments.

It is shown that the strain induced crystallization occurs when the amorphous physical network of this type of PEU is stretched above certain elongation ratio (about 100%) at 19-25°C. The results from WAXD show that the crystalline phase formed can be associated with the crystallization of the PCL soft segments.

The corresponding enthalpy of melting reached at extremely high stretching ratio is about 42 J/g PCL. At comparison with the enthalpy of melting of the starting PCL homopolymer (M_w=2000) it can be estimated that only 30 wt % from PCL soft segments in the PEU crystallize at this stretching conditions.

The DSC analysis shows that at extremely high stretched ratio the hard-soft segments mixing transition in the remaining amorphous phase occurs. The oriented PEUs show a shape memory effect.

Acknowledgement

This work was supported by the Flemish Institute for Science and Technology (IWT), the Fund for Scientific Research-Flandern (FWO) and the Belgian Government (PAI-III programme no 40).

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