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Poly(CL/DLLA-b-CL) multiblock copolymers as biodegradable thermoplastic elastomers

T. Ryynänen[1], *A. Nykänen*[2], *J. V. Seppälä*[1*]

[1]Helsinki University of Technology, Department of Chemical Technology, Laboratory of Polymer Technology, P.O. Box 6100, FI-02015 TKK, Finland
[2]Helsinki University of Technology, Department of Engineering Physics and Mathematics, Laboratory of Optics and Molecular Materials, P. O. Box 2200, FI-02015 TKK, Finland

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Abstract. Lactic acid and ε-caprolactone based polymers and their derivates are widely used in biomedical applications. Different properties are introduced by modifying the composition. In this study, poly(ε-caprolactone/D,L-lactide)-b-poly(ε-caprolactone) multiblock copolymers were synthesized as poly(ester-urethane)s (PEUs) by polymerizing in two steps involving ring-opening polymerization of precursors and by diisocyanate linking of precursors to produce thermoplastic elastomers (TPEs). The precursors and products were characterized by SEC, ^{1}H-NMR and DSC, and dynamic mechanical study (by dynamic mechanical analysis, DMA) as well as morphological characterization (by transmission electron microscopy, TEM) of the product TPEs was carried out. Tensile and creep recovery properties of them were also studied. According to the characterizations, all the polymerizations were successful, and the prepared TPEs showed clear elastic behavior. In the DMA scans, rubbery plateau in the storage modulus curves between T_g and terminal flow region was clearly detectable indicating elasticity. The TEM images demonstrated phase separation of amorphous and crystalline blocks when the degree of crystallinity of the hard blocks was high enough. The elongations of TPEs varied between 800–1800%, while the modulus was 7–66 MPa. Two different types of recovery tests indicated the creep properties of TPEs to be highly dependent on the degree of crystallinity.

Keywords: *biodegradable polymers, lactide, ε-caprolactone, poly(ester-urethane)s (PEUs), thermoplastic elastomers (TPEs)*

1. Introduction

Widening the range of mechanical properties of biodegradable polymers has been increasingly studied for last decades. Ever-growing applications scope of biomaterials runs efforts to design polymers with new more sophisticated characteristics. One of often favorable characteristic for biomedical materials is elasticity. Elasticity is traditionally achieved by cross-linking techniques and the rubbery properties are resulting from the chemical network structure of thermosets [1]. However, in many biomedical applications, thermoplasticity of an elastomer is a highly favourable property enabling processing, remoulding and even injection of the elastomer *in situ*. This kind of thermoplastic elastomers (TPEs) can be prepared by introducing phase-separating blocks in the polymer chain so building up physically cross-linked reversible network [2].

TPEs typically are block copolymers consisting of amorphous soft segments and crystalline hard segments. There are only a few different polymerization methods that have been used to prepare biodegradable block copolymer structured elas-

*Corresponding author, e-mail: jukka.seppala@tkk.fi
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tomers. One of those methods is chain extension where different types of precursors are linked to produce high molecular weight block copolymers with linking agents. Chain extension method in block copolymerization has formerly been utilized in the biopolymer group of our laboratory [3–8], and in some other groups [9–11]. The most widely used linking agents have been diisocyanates which combine hydroxyl terminated precursors to poly(ester-urethane)s. In addition to that, several research groups have prepared block copolymer structures by living ring-opening polymerization, or by something close to that, using pre-prepared macroinitiators (segment A) to initiate the ring-opening polymerization of segment B [12–16]. Newer polymerization techniques, such as atom transfer radical polymerization (ATRP), have been utilized to make the control of the resulting block copolymer architecture more precise [17].

Along with development of different polymerization methods, the variety of monomers and different compositions of block copolymers have been key factors in the design of TPEs. The use of conventional biopolymer monomers such as different lactones has been widely reported in literature [9–17]. Typically semi-crystalline poly(L-lactide) and poly(D-lactide) have been used as the hard blocks [9–18] while amorphous poly(ε-caprolactone) [10–12, 18], poly(1,3-trimethylene carbonate) [13–15] and poly(ethylene oxide) [19] have been often used as soft components in block structured biodegradable TPEs.

This study is natural continuum of the earlier work in the field of poly(ester-urethane)s carried by our biopolymer group in Helsinki University of Technology [1, 3–7]. In this study, poly(ε-caprolactone/D,L-lactide)-b-poly(ε-caprolactone) multiblock copolymers were synthesized to produce biodegradable thermoplastic elastomers. The objective was to enhance the recovery and creep properties of amorphous poly(ε-caprolactone/D,L-lactide) copolymers by linking semicrystalline poly(ε-caprolactone) blocks between linear polymer chains. In other words, the purpose was to achieve physical cross-linking by secondary hydrogen bonds between polymer chains by adding crystalline segments to an amorphous copolymer. Poly(ε-caprolactone) was chosen to act as hard block as it is known capable to crystallize [7, 20]. The CL/DLLA semi-random copolymers in molar compositions of 30/70, 50/50 and 70/30 were chosen to act as soft blocks because they were known to be fully amorphous by the study of Hiljanen-Vainio *et al*. [20]. The aim was to evaluate the effect of different quantities of crystalline phase to the recovery properties of the TPEs. Thus mechanical and recovery properties of these TPEs were rather extensively studied in addition to thermal and dynamic mechanical tests.

2. Experimental

2.1. Materials

The poly(ε-caprolactone/D,L-lactide) and poly(ε-caprolactone) precursors were polymerised from D,L-lactide (DLLA; Purac) and ε-caprolactone (CL; Solvay). DLLA was recrystallized from toluene and CL was dried over molecular sieves. Stannous octoate ($SnOct_2$; Sigma) and 1,4-butanediol (BD; Fluka Chemica) were used as received in the ring-opening polymerization of precursors. In the linking reaction, 1,6-hexamethylenediisocyanate (HMDI) was used, without further treatment, as chain extender.

2.2. Preparation of poly(ε-caprolactone/D,L-lactide) and poly(ε-caprolactone) precursors

The poly(ε-caprolactone/D,L-lactide) and poly(ε-caprolactone) precursors, respectively amorphous and semicrystalline segments of the elastic poly(ester-urethane) multiblock copolymers, are denoted by P(CL/DLLA-BD) and P(CL-BD), and e.g., by P(30/70-1) and P(100-1). The precursors were polymerized in melt from CL and DLLA at 160°C under nitrogen atmosphere for six hours in a batch reactor designed for agitation of viscous materials. The monomers were fed to the reactor with an appropriate amount of 1,4-butanediol as co-initiator (0,5, 1,0 or 5,0 per 100 monomer units) for hydroxyl termination and control of molecular weight of the precursor. Stannous octoate was used as initiator with amount of 0,02 mol%. The reaction procedure is thoroughly discussed in the previous publication of our group by Helminen *et al*. [1].

2.3. Chain extension of precursors into elastic poly(ester-urethanes)

PEUs were polymerized in a 200 ml round-bottomed flask reactor equipped with one-armed stirrer. Precursors were first added to the reactor in the molar ratio of 1:1 and melted at 160°C in argon atmosphere before 30 mol% excess of 1,6-hexamethylene diisocyanate as chain extender was fed to the reactor. In earlier work by our group [3] on the chain extending reactions of isocyanates with hydroxyl groups, the high temperature was introduced as a means to avoid the use of solvents and catalysts typically used in the functionalization of hydroxyl groups with isocyanates. If high temperatures are allowed a more straightforward route to the desired products is achieved without the use of these additional components. The amount of HMDI was calculated from the theoretical molecular weight of the synthesized precursors, and the 30 mol% excess used in linking reactions results from earlier experience in diisocyanate chemistry in our group [3, 4]. The reaction time was 7–12 minutes determined of the growth rate of the viscosity of the reaction mixture.

2.4. Characterisations

Molecular weights (M_n and M_w) and molecular weight distributions (MWD) were determined relative to polystyrene standards by size exclusion chromatography (SEC). The Waters Associates system was equipped with a Waters 717plus autosampler injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10^4, 10^5, 10^3, and 100 Å) connected in series, and a Waters 2414 refractive index detector. All samples were analyzed at room temperature. Chloroform (Riedel-de Haën; stabilized with 1% ethanol) was used as eluent, and was delivered at a flow rate of 1,0 ml/min. The samples were dissolved in chloroform at a concentration of 1,0% (w/v). The injection volume was 200 µl.

For ^{1}H-NMR measurements, the samples were dissolved in chloroform-d_1 (Aldrich; deuteration degree not less than 99,8%) in 5 mm NMR tubes at room temperature. The sample concentration was about 1,0% by weight. NMR spectra were recorded on a Varian Gemini 2000 300 MHz NMR spectrometer working at 300 032 MHz for proton.

Differential scanning calorimetric (DSC) measurements were carried out on a Mettler Toledo Star^e DSC 821^e. The measurements were run from –100 to 180°C at heating and cooling rates of 10°C·min^{-1}. The glass transition temperatures (T_g), melting temperatures (T_m), and melting endotherms (ΔH) of the precursors and linked elastomers were measured during the second heating period.

Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer 7 Series instrument. The specimens were die-cut from 2,0 mm thick hot-pressed polymer plate. The measurements were carried out using the three-point bending geometry (sample size 2,0×5,0×18,0 mm) over a temperature range of –70 to 60°C at a rate of 4°C·min^{-1}. All measurements were carried out at 1 Hz.

Transmission electron microscopy (TEM) was used in morphological studies of the TPEs. Contrast for the morphological characterization was achieved by a sample preparation technique that relies on different rates of diffusion of a RuO_4 stain into the amorphous and semi-crystalline regions [21]. First, the sample surface was cut at temperature of –100°C to make a smooth surface for the stain to penetrate into the sample. The samples were then stained in vapor of 0,5% RuO_4 stabilized aqueous solution (Electron Microscopy Science) for a period of three days. The stained sample was microtomed using a Leica Ultracut UCT ultra-microtome with a diamond knife at temperature of –100°C, and 70 nm thick sections were collected on 300-mesh sized lacey carbon coated copper grids. Bright field TEM was performed with Tecnai 12 transmission electron microscope using 120 kV accelerating voltage.

Tensile properties of the samples were measured with an Instron 4204 tensile testing machine applying the standard ISO 6239-1986 for small test specimens. The specimens were die-cut with a bone shaped die-cut head from the same 2,0 mm thick polymer plate as the specimens for DMA tests. To find out the difference on tensile properties occurred by different preparing methods of the samples, some parallel tests were also run with injection moulded specimens. The moulding temperatures were between 70 to 150°C and the injection moulding pressure was 6 bar. The tensile tester was equipped with 1 kN load cell and was operated at crosshead speed of 20 mm·min^{-1}. The tensile strength, strain and modulus of the polymers were

measured for three to five parallel specimens that had been air-conditioned for 72 h at 23°C and 50% relative humidity.

The first series of recovery tests were run on an Instron 4204 tensile testing machine using the same type of small die-cut bone shaped test specimens as on tensile testing. The crosshead speed was 20 mm·min^{-1} and the samples were strained to 100% elongations. After 10 minutes recovery time the permanent deformations were measured. Tests were carried out in duplicate for air-conditioned specimens. The second series of recovery tests were run by Perkin-Elmer 7 Series DMA instrument for film samples. The dimensions of the film shaped samples were 5×17 mm, and they were cut out from 0,1 mm thick hot-pressed polymer film. The samples were tested in tensile mode. Constant stress of 2 MPa (1 MPa for TPE(70/30-1)-b-(100-5)) was applied for 10 minutes and the %-strain was observed as function of time. After 10 minutes, the stress was dramatically dropped to 9 kPa which was used as zero-stress to enable observing of strain during the 20 minutes recovery time. The permanent deformations [%] were calculated from the ratio of permanent strain after 20 minutes recovery time to maximum strain of the tested film samples.

3. Results and discussion

3.1. Polymerizations

The preparation of poly(ester-urethane)s consisted of two steps, as shown in Figure 1. The precursors, i.e. soft and hard blocks of a poly(ester-urethane) multiblock copolymer, prepared in the first step differed from each other both structurally and in molecular weights. The three types of soft blocks prepared were amorphous poly(ε-caprolactone/D,L-lactide) copolymers with number average molar masses around 13 000 g/mol. They differed from each other in molar ratios of monomers CL/DLLA by values of 30/70, 50/50 and 70/30. Each of these three soft blocks were linked separately with two semi-crystalline poly(ε-caprolactone) precursors of different molecular weight, i.e., with hard blocks of different size. The number average molecular weights of the two hard blocks were 22 900 and 11 500 g/mol. In addition, soft block P(70/30-1) was linked with a small hard block P(100-5) with size of 2400 g/mol. Copolymer precursor P(30/70-1) and PCL precursor P(100-0,5) were linked as such to act as references and enable comparison with TPEs. The compositions of precursors and TPEs are presented in Table 1.

The precursors and the PEU elastomers were characterized with SEC and ^{1}H-NMR both indicating

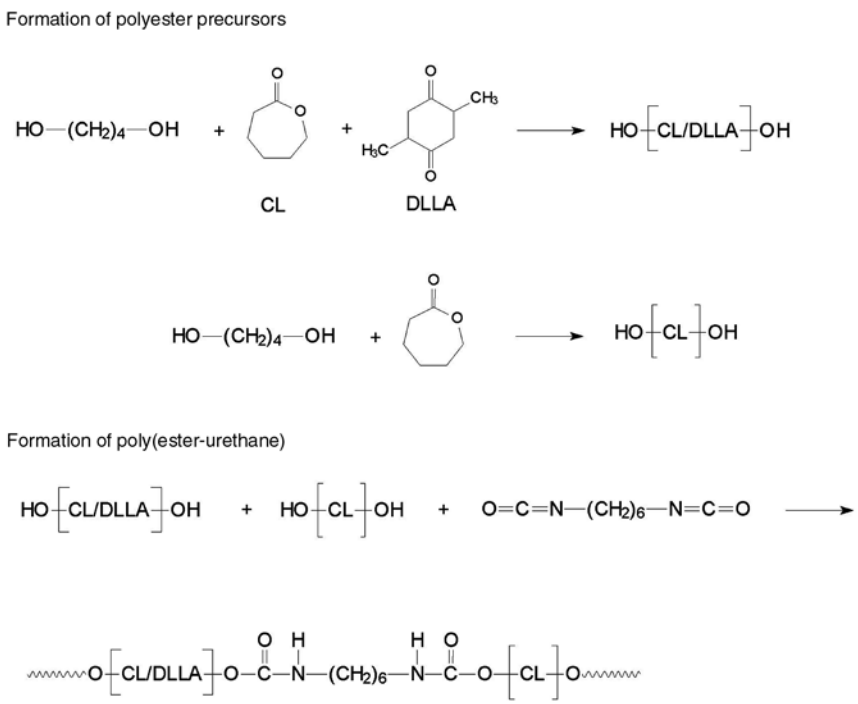

Figure 1. Reaction scheme of poly(ester-urethanes)

Table 1. Overview of the characterizations of precursors and TPEs

Sample	Theoretical		SEC[b]			^{1}H-NMR
P(CL/DLLA-BD)	M_n [g/mol]	LA[a]	M_n [g/mol]	M_w [g/mol]	MWD	LA[a]
P(30/70-1)	13 600	70	21 700	33 400	1.5	71.9
P(50/50-1)	13 000	50	17 200	24 600	1.4	48.8
P(70/30-1)	12 400	30	23 400	37 000	1.6	31.0
P(100-0.5)	22 900	–	39 900	59 300	1.5	–
P(100-1)	11 500	–	25 000	38 500	1.5	–
P(100-5)	2 400	–	4 900	5 800	1.2	–
TPE(30/70-1)-b-(100-0.5)	–	23.3	118 000	304 100	2.6	24.3
TPE(30/70-1)-b-(100-1)	–	35.0	64 700	188 300	2.9	35.6
TPE(50/50-1)-b-(100-0.5)	–	16.7	84 100	276 800	3.3	17.1
TPE(50/50-1)-b-(100-1)	–	25.0	91 000	212 400	2.3	24.8
TPE(70/30-1)-b-(100-0.5)	–	10.0	86 700	200 100	2.3	9.6
TPE(70/30-1)-b-(100-1)	–	15.0	113 300	258 800	2.3	15.5
TPE(70/30-1)-b-(100-5)	–	25.0	97 200	208 300	2.1	25.8
refP(100-0.5)	–	–	156 500	375 200	2.4	–
refP(30/70-1)	–	70	63 900	156 100	2.4	71.1

[a]D,L-lactide units per 100 monomer units
[b]Determined relative to polystyrene standards

that the polymerizations had been successful. The results are presented in Table 1. Similarly to earlier studies of our group, the molecular weights of the precursors determined by SEC were almost twice the theoretical due to the calibration of the SEC with polystyrene standards [1]. The CL/DLLA ratios in copolymers were calculated from the ^{1}H-NMR spectra by comparing the peaks 2,28 ppm for CL and 5,14 ppm for DLLA. The compositions of copolymers were close to theoretical, as seen from the lactide contents shown in the Table 1. After linking reaction the PEUs contained 3–8 precursors as estimated from the number average molecular weights listed in Table 1.

3.2. Thermal and dynamic mechanical properties

Thermal and dynamic mechanical properties of precursors and PEUs were characterized by DSC

Table 2. Thermal and dynamic mechanical properties of precursors and TPEs

Sample	DSC					DMA	
P(CL/DLLA-BD)	T_g [°C]	T_m [°C]	ΔH [J/g]	DCrys [%]	T_g (E'') [°C]	T_g (tanδ) [°C]	H(tanδ)[a]
P(30/70-1)	8	–	–	–			
P(50/50-1)	–13	–	–	–			
P(70/30-1)	–41	–	–	–			
P(100-0.5)	–	57	–72	52			
P(100-1)	–	56	–79	57			
P(100-5)	–	47	–91	65			
TPE(30/70-1)-b-(100-0.5)	–	57	–39	28	13	16	0.31
TPE(30/70-1)-b-(100-1)	–	55	–33	24	11	17	0.57
TPE(50/50-1)-b-(100-0.5)	–8	58	–41	29	–7	–3	0.25
TPE(50/50-1)-b-(100-1)	–12	54	–25	18	–10	–3	0.45
TPE(70/30-1)-b-(100-0.5)	–48	56	–48	34	–55	–33	0.09
TPE(70/30-1)-b-(100-1)	–36	53	–39	28	–44	–23	0.18
TPE(70/30-1)-b-(100-5)	-40	32	-4	3	–38	–26	0.47
refP(100-0,5)	–	60	–66	47	–	–	–
refP(30/70-1)	14	–	–	–	12	21	3.29

[a]Height of the tanδ peak at T_g

and DMA and the results are presented in Table 2. The DSC results were obtained during the second heating scan to erase the thermal history of the sample. In the DSC spectra of copolymer precursors, no signs of melting behavior were detected, supporting the hypothesis of highly transesterified semi-random structure of copolymers leading to amorphous structure. By increasing the DLLA content [mol%] in the precursor from 30 to 70, the T_g detected increased dramatically from –41 to +8°C. For the semi-crystalline PCL precursors T_g could not be detected, but the melting peaks in DSC spectra were clear. The degree of crystallinity of PCL precursors varied between 52–65%. The crystallinity determination was made by comparing of melting enthalpies of precursors with melting enthalpy of 100% crystalline PCL (139,5 J/g) [22]. As assumed, the thermal properties of the precursors were combined in the TPEs. In Figure 2, the DSC spectra of two precursors P(50/50-1) and P(100-1) as well as the spectrum of the resulting poly(ester-urethane) TPE(50/50-1)-b-(100-1) are plotted one upon the other. In the spectrum of TPE both T_g and melting peaks of the precursors are obtained, indicating of successful linking. Both T_g and T_m of all TPEs were between the corresponding values of precursors. The degree of crystallinity values of TPE-PEUs increased from 3 to 34%, apparently depending on the molecular weight of the hard precursor in the TPE multiblock copolymer. The degree of crystallinity of TPEs was calculated in the same way as for PCL homopolymer precursors by comparing the melting enthalpies of the samples with 100% crystalline PCL without

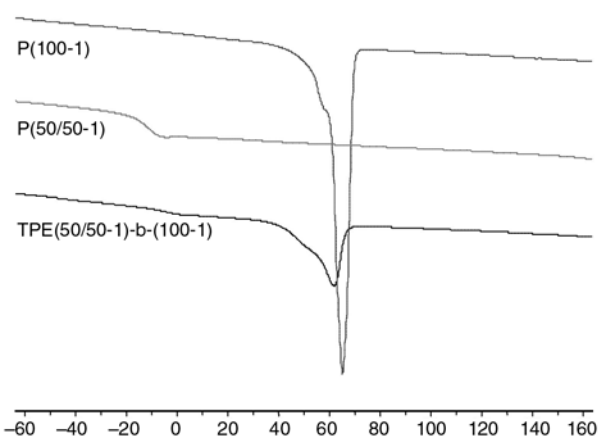

Figure 2. DSC spectra of TPE(50/50-1)-b-(100-1) and the precursors

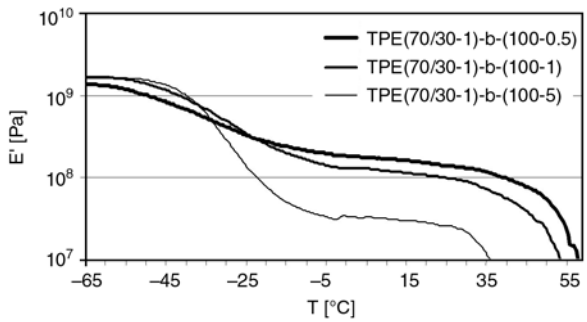

Figure 3. Storage modulus curves of TPEs

normalization to the PCL, the obtained values still being unexpected low (–10…–20%).

DMA was used to study the temperature dependence of the moduli of the PEU elastomers. In a DMA scan, T_g was evaluated with two separate values presented in Table 2. These were the temperature where the peak occurred in tanδ curve and the temperature of the maximum in the loss modulus curve. The height of the tanδ peak at T_g was presented to express the magnitude of the transition. As expected, both T_g values evaluated by DMA were in good correlation with T_g values by DSC. As the degree of crystallinity increased, the height of the tanδ peak at T_g decreased in linear correlation. Similar to cross-linked elastomers [1], the rubbery plateau in the storage modulus curves between T_g and terminal flow region was clearly detectable indicating elastic behavior of TPEs. The storage modulus curves of elastomers TPE(70/30-1)-b-(100-5), TPE(70/30-1)-b-(100-1) and TPE(70/30-1)-b-(100-0.5) are plotted in Figure 3 to emphasize the plateau region. The increasing size of the crystalline PCL block in TPEs lengthened the rubbery plateau towards higher temperatures, as can be seen in the Figure 3.

3.3. Morphology studies

The contrast for morphological characterization was examined by TEM. In Figure 4, the TEM images of elastomers A: TPE(70/30-1)-b-(100-5), B: TPE(70/30-1)-b-(100-1) and C: TPE(70/30-1)-b-(100-0.5) were plotted next to each other with a view to emphasize the role of the size of the hard block, i.e., degree of crystallinity, in the separation of amorphous and crystalline phases. These and similar series of images can be taken from elastomers consisting of same type of amorphous soft block, differing from each other in the size of the

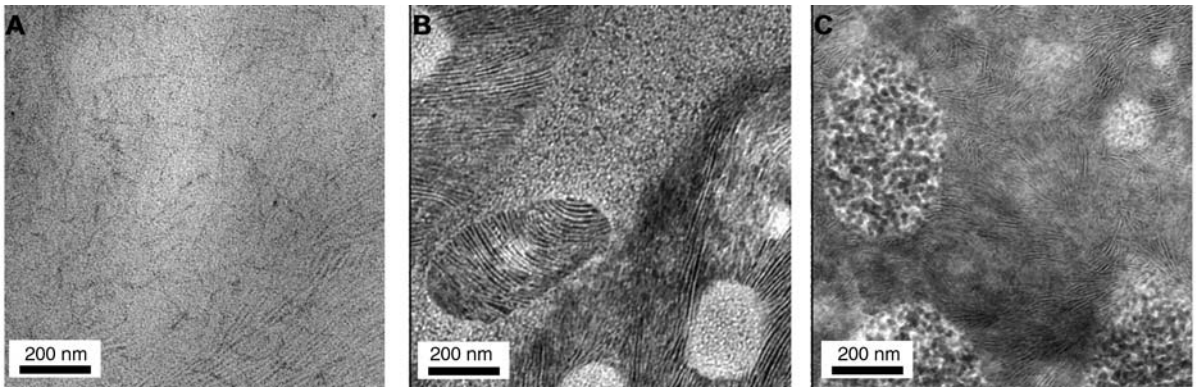

Figure 4. TEM images of elastomers A: TPE(70/30-1)-b-(100-5), B: TPE(70/30-1)-b-(100-1) and C: TPE(70/30-1)-b-(100-0.5)

hard block. The degree of crystallinity increases from left to right by the values: A: 3%, B: 24% and C: 34%. In the TEM images, dark color indicates the amorphous areas while white is the color of crystalline phase. This results from the tendency of amorphous materials to permeate RuO_4 stain more readily than crystalline ones. In all three images, some crystallinity or lamellar areas can be detected, while the images B and C show significantly more lamellas than image A. Also, in images B and C the phase separation of amorphous and crystalline areas was clearly detectable.

3.4. Mechanical properties

The tensile properties of the PEU-TPEs were measured by Instron 4204 tensile testing machine, and tensile strength, strain and modulus are presented in Figure 5. In the multiblock copolymer TPEs, the tensile properties of both precursors were combined, which is easily observed by comparing the

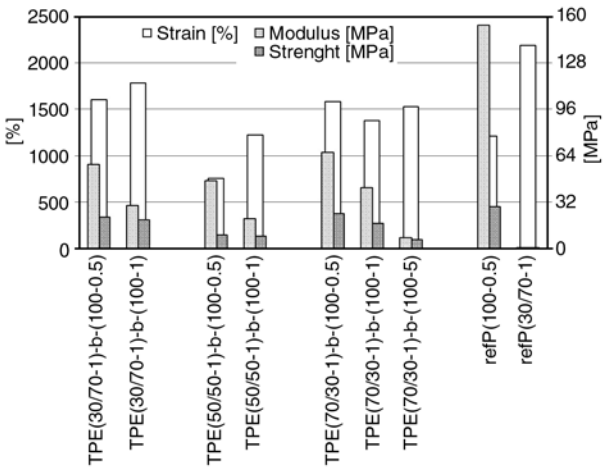

Figure 5. Mechanical properties of elastomers

results with results of the reference PEUs denoted refP(100-0.5) and refP(30/70-1). By increasing the molecular weight of the hard block in a PEU-TPE, i.e., increasing the degree of crystallinity, the modulus and strength increased as well. The copolymer with composition of 50/50 had slightly lowest mechanical properties. The elastomers were so resilient that when the gauge lengths of the dog-bone specimens were drawn out the specimens only did not break but also the ends of the specimens between the grip holders begun to strain. This caused false strain values by increasing the actual maximum strain percent. However, this quasi-elongation was detectable in strain-stress diagrams, and it was possible to be eliminated from the results. Anyway, the maximum strain percent values of the elastomers were very high, >2000%. PCL is known to be highly elastic as proved by the reference PEU refP(100-0.5) with maximum strain of 1200%. However, D,L-lactide still increased elongation so that the PEU-TPEs with the highest lactide contents of the soft copolymer block had the highest maximum strain percent values, i.e., from 1600 to 1800%. The fully amorphous reference polymer refP(30/70-1) without crystalline PCL blocks strained >2000%.

To examine the role of preparation technique of the test specimens to the tensile test results, two TPEs were also tested with extruded specimens. Figure 6 illustrates the difference in results caused most likely by orientation of linear polymer chains during the extrusion. The die-cut samples showed dramatically lower modulus and strength values compared with extruded specimens. This can be explained by the hardening occurred by orientation of polymer chains. Some of the die-cut samples

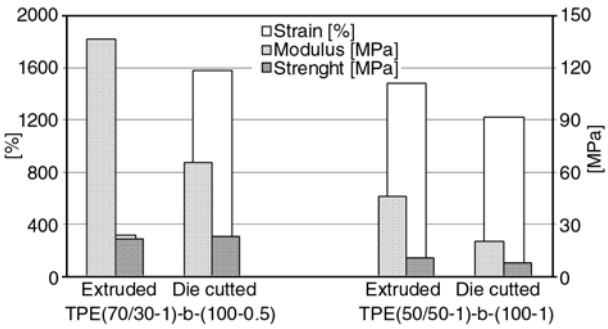

Figure 6. The role of different preparing techniques of the samples in mechanical properties of elastomers

were slightly blistered, and the changes in quality of the specimens might affect results as well.

3.5. Creep recovery properties

The creep recovery properties of the TPEs were measured with two different test procedures both using the tensile mode. The first test series were run by Instron 4204 tensile testing machine with dog-bone specimens, and second series by DMA Perkin-Elmer 7 Series instrument for film samples. In the first test series the specimens were strained to 100% elongation once, relaxed, and after 10 min relaxation time the permanent deformations were measured. The stresses needed for 100% straining varied much depending on the materials. In the second test series constant stress was applied for 10 min before relaxation to point out the effect of orientation of polymer chains. In both tests, the composition of the amorphous block of the copolymer did not have significant effect on recovery properties whereas these properties were mainly dominated by the size of the hard block of them, i.e., the degree of crystallinity. The TPEs having a copolymer with CL/DLLA ratio 50/50 as soft block, recovered slightly worse than other TPEs, as could be expected on basis of tensile testing. The results of the first creep recovery test after 100 percent elongation are presented in Figure 7. The lower the overall degree of crystallinity is the smaller is the permanent deformation of the specimens. These results describe the recovery properties of single, short-term deformation of material when no orientation of polymer chains obviously occurs. When orientation apparently is involved in long-term tests, as in our second test series, the results were different as shown in Figures 8 and 9.

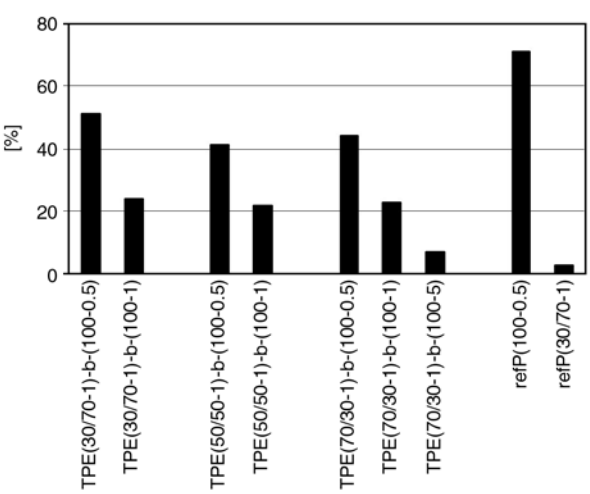

Figure 7. Permanent deformations of elastomers after recovery from 100% strain

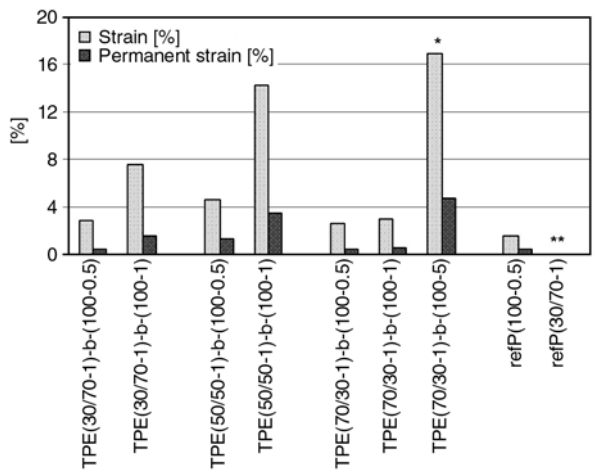

Figure 8. Strain after 10 minutes applied stress (2 N, *1 N) and permanent strain after 20 minutes recovery time of elastomers. (**Not measured, sample too soft)

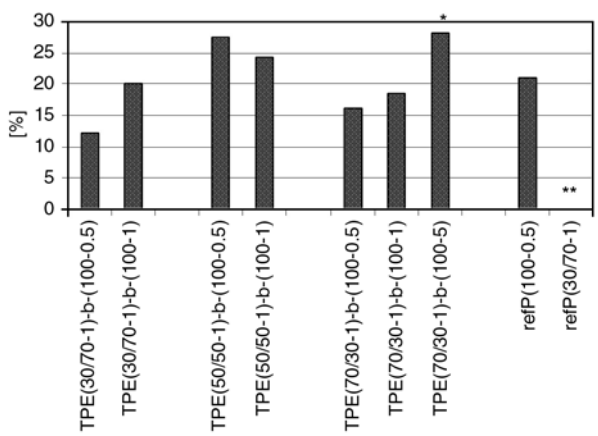

Figure 9. Permanent deformations after 10 minutes applied stress (2 N, *1 N) and 20 minutes recovery time of elastomers. (**Not measured, sample too soft)

Under the same constant stress, TPEs with lower overall degree of crystallinity not only strained more but also the relative permanent deformation was higher than for elastomers with higher degree of crystallinity. This supports the assumption that crystalline phases are required to enhance recovery properties of TPEs.

4. Conclusions

In this study, poly(ester-urethane) thermoplastic elastomers (PEU-TPEs) were prepared by simple two-step melt polymerization technique. On basis of tensile testing the products were elastic showing at the same time feasible strength values. The TEM images of the products revealed morphological feature of elastomers by the fact that phase separation of the crystalline and amorphous phases was clearly observed when the degree of crystallinity increased. As known, phase separation is required for good creep resistance. The recovery properties of the products were promising, and by modification of the polymer composition further still better creep resistance can obviously be achieved. The distinct rubbery plateau in storage modulus curves confirmed, too, the elastic behaviour of the TPEs. However, one important feature to be studied in the future is the conservation of mechanical properties during hydrolytic degradation of PEU-TPEs.

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