Shape Memory Properties of Poly(ε-Caprolactone) Based Thermoplastic Polyurethane Secondary Blends

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Thermoplastic polyurethanes with introduced poly(ε-caprolactone) (PCL/TPU) show shape-memory properties. Such materials are widely used for orthopaedic splints production but create large amount of waste. Generally, this waste disposed of to landfill; therefore, utilization problem arise. The goal of this investigation was to study possibilities of different PCL/TPU production waste recycling and secondary application. For investigation secondary blends of three types of PCL/TPU were prepared by mastication and mechanical properties and shape memory behaviour have been studied. The mechanical testing results suggest that after recycling PCL/TPU and their blends properties remain unaltered. All investigated thermoplastics are compatible and form simple blends without synergetic or anti-synergetic effects. Only some interaction between PCL/TPU-1 : PCL/TPU-2 blend components was observed. After recycling, individual PCL/TPU and their blends show significant shape memory behaviour under drawing at high temperature – their recovery rate was about 80 % – 90 % for a tensile deformation of 50 %. Thus, secondary PCL/TPU blends show mechanical properties and shape memory behaviour closely comparable to the virgin materials. Therefore, they can be repeatedly used for orthopaedic splints production.

Keywords: thermoplastic polyurethane, poly(ε-caprolactone), waste, mechanical properties, shape memory effect.

1. INTRODUCTION

Shape-memory materials, especially shape-memory alloys, have found wide technical applications, such as sensors, transducers, actuators, and medical implants [1–3]. Used as medical devices, Ni-Ti and other alloys exhibit outstanding advantages, such as small size and high strength, but at the same time, they have obvious disadvantages, such as high manufacturing cost, limited recoverable deformation, complicated surgery process, and appreciable toxicity [1–4]. Therefore, new types of shape-memory materials have been explored. They are shape-memory polymers [2, 5–8], ceramics, and hydrogels [3]. Most of shape-memory polymers (SMP) are thermo-responsive; that is, their temporary deformation can be eliminated or their permanent shape can be recovered at a critical temperature (referred to as the transition temperature or switching temperature). Generally speaking, these polymers often have cross-linked structures (either chemical cross-linking [9] or physical cross-linking [10]), which determine their permanent shapes. Their shape memory is usually based either on glass transition or on melting [2, 6, 11]. Because different polymers exhibit different glass transition temperatures and melting temperatures, they can display shape-memory effects in various temperatures, fulfilling different requirements of practical applications. Compared to metallic alloys, shape memory polymers show much a better versatility of chemical structure, lower manufacturing cost, easier pretreatment procedure, larger recoverable deformation, and lower recovery temperature [12–17]. They have found wide industrial applications such as heat-shrinkable materials [18] and they are expected to get more intelligence and to be used in self healing or other high-tech applications [2, 19, 20].

Among these polymers, shape memory polyurethane draws the most attention due to the easy control of the critical recovery temperature for use in different purposes [15–17]. Generally, shape memory polyurethanes shape memory effect is because of the so-called micro-phase-separated heterogeneous structure which composed of the hard segment phase (aromatic diisocyanates and small size diols or diamines) and soft segment phase (aliphatic polyether or polyester diols). The hard segment phase has a higher thermal transition temperature (T_{trans}), while the soft segment has a lower phase transition temperature. Usually, the soft segment phase transition temperature acts as the switching temperature [11]. Fig. 1 illustrates the molecular mechanism of shape memory process of SMP material.
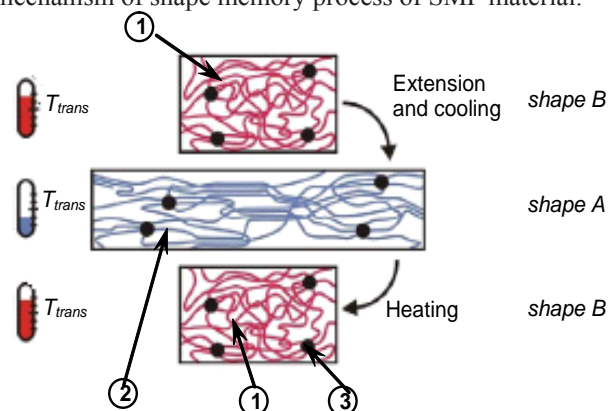

Fig. 1. Molecular mechanism of thermally induced shape memory effect: 1 – switching segment, relaxed; 2 – switching segment, elongated and fixed; 3 – netpoint [2, 6]

Most of SMP are non-biodegradable. For medical implantations, the shape memory polymers are expected to be both biodegradable and highly shape-recoverable and to have a recovery temperature near the human body temperature that the handling of the medical devices would

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be easy. The temporary deformation may be realized near room temperature, and the original shape may be recovered automatically when the device is used.

Poly(ε-caprolactone) (PCL) is biocompatible and biodegradable aliphatic polyester that is bioresorbable and non-toxic for living organisms. Because of its unique combination of biocompatibility, permeability, and biodegradability, PCL has been widely applied in medicine as artificial skin, artificial bone, and containers for sustained drug release [21, 22]. PCL has a low melting point of about 60 °C. This material degrades by enzymatic reactions or by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and, as a result, has received a great deal of attention as an implantable biomaterial with good ultimate mechanical properties [23]. If PCL is introduced into segmented polyurethane as a soft segment, the shape-memory property would be expected. Properties of such polyurethanes are described in [24 – 29].

Low temperature thermoplastic polyurethanes with poly(ε-caprolactone) based soft segments (PCL/TPU) are used in medical procedures including radiotherapy patient immobilization, orthopedic splinting or casting, plastic and reconstructive surgery splinting, and orthotic or prosthetic socket cone production or reproduction [30 – 32]. However, the medical application of PCL/TPU for orthopedics splints creates large amount of waste that generally is disposed of to landfill [33]. Although the majority of biodegradable plastics are more easily degraded in composting and soil disposal environments than conventional plastics, but due to the complex nature of polymer breakdown, it is impossible to identify all the compounds present in a mix of degradation products, some of which are toxic (i. e., isocyanates) [34]. Besides, biodegradable plastics make a contribution to landfill gas production that will increase greenhouse gas emissions [34]. Therefore, it is desirable to reprocess biodegradable polymers and find application areas of recycled materials.

In this paper the possibilities of recycling and secondary use of thermoplastic polyurethanes with poly(ε-caprolactone) based soft segments applied for orthopedic splints are investigated. The blends from different types of PCL/TPU waste are prepared and their mechanical properties and shape memory behaviour have been examined.

2. EXPERIMENTAL

2.1. Materials

For the analysis three types of poly(ε-caprolactone) based thermoplastic polyurethanes (PCL/TPU) such as *Beachcast*, *Turbotreat*, *Turbocast*, produced by T-Tape BV (Holland), have been used. The characteristics of these polyurethanes are presented in Table 1.

The investigated low temperature polyurethanes were blended together and blends – PCL/TPU-1 : PCL/TPU-2, PCL/TPU-1 : PCL/TPU-3, PCL/TPU-2 : PCL/TPU-3 – were prepared. Initially polyurethanes were mixed at different proportions and masticated. Prepared blends then were softened in high frequency (w = 2.45 MHz) chamber for 120 s. After that blends were pressed at 2 MPa pressure for 120 s and plates of 2 mm thickness were produced.

Table 1. Main properties of investigated PCL/TPU materials

Sample	Grade	T_g, °C	Shape memory, %	Surface coating
PCL/TPU-1	Beachcast	60–65	100	Not coated
PCL/TPU-2	Turbotreat	70–75	90	Double PU* coated
PCL/TPU-3	Turbocast	60–65	100	Single PU coated

NOTE: *PU – polyurethane.

Typically, for tensile testing dumbbell-shaped specimens of effective dimension of (10×50) mm^2 were cut from 2 mm thick PCL/TPU plates. The specimens with effective dimension of 5×20 mm^2 were applied for bending test.

2.2. Testing

Mechanical properties. Mechanical properties at tension were measured using an universal testing machine FP 10/1 (Germany) according to the requirements of LST ISO EN 8256 standard. The sample gauge length between clamps was 50 mm and the stretching speed was 50 mm/min.

Three point bending test was used at supports radius of r = 2 mm and bending punch radius of R = 4 mm. The distance between supports was 27 mm.

The tensile and bending tests results were average of six measurements.

Cyclic tensile investigations. The shape memory effect was quantified by cyclic, thermo-mechanical investigations. The measurements were performed by means of a tensile testing machine H10KT (Tinius Olsen, Great Britain) equipped with a temperature controllable chamber. The cyclic tensile testing path is shown in Fig. 2, a.

First, specimen 120 s was heated to 70 °C and then stretched to 50 % strain at speed of 20 mm/min (1); second, the specimen was cooled to ambient temperature while 50 % strain was kept for 15 min to fix temporary elongation (2); third, the lower clamp returned to the original position (3); fourth, the specimen was heated again to 70 °C to recover (4) and the second cycle started (5).

The above cycle was repeated three times and the stress-strain curves were recorded for analysis. The schematic representation of typical stress-strain behaviours is shown in Fig. 2, b. ε_m is the maximum strain in the cyclic tensile tests, ε_u is the strain under unloading at low temperature, and $\varepsilon_p(N)$ is the residual strain after recovering in the N th cycle.

The important quantities to be determined for describing the shape memory properties of the material at the strain ε_m are the strain recovery ratio R_r and the strain fixity ratio R_f. Both were determined according to the Eq. (1) – (3) from thermo-mechanical cyclic measurements [2, 20, 26].

The strain recovery ratio R_r quantifies the ability of the material to memorize its permanent shape and is a measure of how far a strain that was applied in the course of the programming $\varepsilon_m - \varepsilon_p(N-1)$ is recovered in the following shape memory transition:
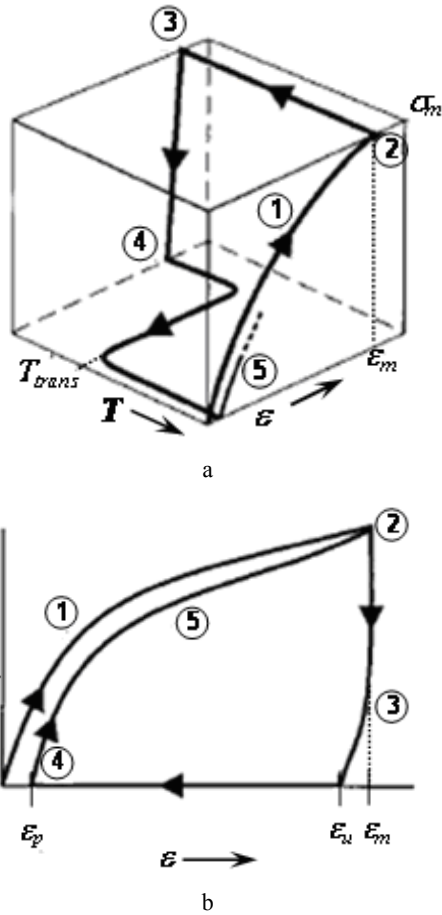
a

b

Fig. 2. Cyclic tensile testing path (a) and schematic stress-strain curves (b) under drawing at high temperature and thermal recovery

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \quad . \tag{1}$$

The total strain recovery ratio $R_{r, tot}$ is defined as the strain recovery after N passed cycles based on the original shape of the sample:

$$R_{r, tot}(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m} \quad . \tag{2}$$

The strain fixity ratio R_f describes the ability of the material to fix the mechanical deformation which has been applied during the process. R_f is given by the ratio of the strain in the stress-free state after the retraction on the tensile stress in the Nth cycle $\varepsilon_u(N)$ and the maximum strain ε_m:

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \quad . \tag{3}$$

3. RESULTS AND DISCUSSIONS

3.1. Mechanical properties of blends

Stress-strain properties of the investigated thermoplastic polyurethanes at room temperature are shown in Table 2. It can be seen that all PCL/TPU show similar yielding properties during drawing. PCL/TPU-2 and PCL/TPU-3 also has close tensile strength values (about 27 MPa – 30 MPa), while PCL/TPU-1 shows lower

strength value (about 22 MPa). However, the strain at break of PCL/TPU-1 is about 4-time higher than that of other thermoplastics. It is related to the difference in chemical composition of different PCL/TPU, but surface coatings also influence the tensile properties.

Table 2. Tensile properties of thermoplastic polyurethanes

Sample	Yield point, MPa	Tensile stress, MPa	Strain at break, %
PCL/TPU-1	17.6	22.1	2700
PCL/TPU-2	16.0	29.6	685
PCL/TPU-3	17.8	27.2	724

The dependences of mechanical properties on the blends composition are shown in Fig. 3. As can be seen, the blending does not worsen thermoplastic polyurethanes properties. According to the curves presented in Fig. 3, a, it is evident that all blends show intermediate tensile strength values compared to that of virgin PCL/TPU materials.

The strain at break values determined for blends are also similar with the respect to their composition (Fig. 3, b). However, PCL/TPU-1 blends show intensive strain decrease in 2.5 – 3.0 times, when low content (20 wt%) of PCL/TPU-2 or PCL/TPU-3 is added. Further increase of second component almost does not influence on the blend deformation properties.

The bending strength of PCL/TPU-3 blends also show intermediate values between these of virgin materials. Meanwhile, the resistance to bending changes, when PCL/TPU-1 and PCL/TPU-2 is blended (Fig. 3, c). In this case synergetic behaviour is observed since blend show from 1.3 times up to 2 times higher bending strength values compared to that of pure PCL/TPU-1 or PCL/TPU-2.

Thus, the mechanical testing results suggest that investigated PCL/TPU materials are compatible and form simple blends without synergetic or anti-synergetic effects. Only some interaction between components in the case of PCL/TPU-1/PCL/TPU-2 blend is observed.

3.2. Thermo-mechanical cyclic tensile investigations

The investigated PCL/TPU materials show shape memory behaviour. As can be seen from Fig. 4, PCL/TPU strip was changed into the ring shape at 70 °C temperature and then cooled rapidly to room temperature, and it returned to the original shape, when put in 70 °C water.

It is well-known that there is always a microphase separation in segmented polyurethanes, i.e. a hard phase and soft phase appear [2, 10, 11]. In the case of PCL polyurethane, the soft phase consists of PCL segments and the hard phase is composed of diisocyanate and ethylene glycol. Compared to common polyurethanes, PCL/TPU soft phase is highly crystalline at room temperature. It is this specialty that leads to its shape memory property. When PCL/TPU specimen is heated up to 70 °C temperature, which is above of the soft segment phase melting transition temperature (T_{trans}), the soft segments are in a random state. When it is stretched, the soft segments are extended. If the temperature is lowered below T_{trans}, the soft segments crystallize.

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As a result, the internal stress is stored in the material and associated deformation is fixed temporally. If it is heated above T_{trans}, the soft segments become flexible and they resume to the folded configuration because of the internal stress stored between hard segments. As a result, the specimen recovers to its original shape.

The investigations suggest that all PCL/TPU blends display shape memory effect, also [35]. Transition from the temporary shape to the permanent shape occurred within 80 s – 92 s. Thus, PCL/TPU blends preserve shape memory properties after physical recycling.

recovery ratio and stress at 50 % strain are tabulated in Table 3.

Fig. 4. PCL/TPU real shape memory circle: a – original strip shape; b – ring shape at 20 °C; c – recovered shape at 70 °C (specimen dimension 10 mm × 50 mm)
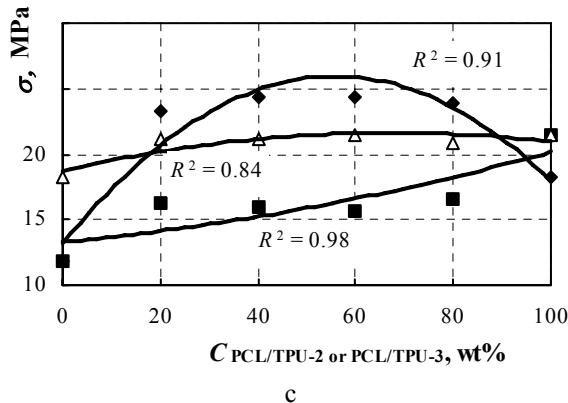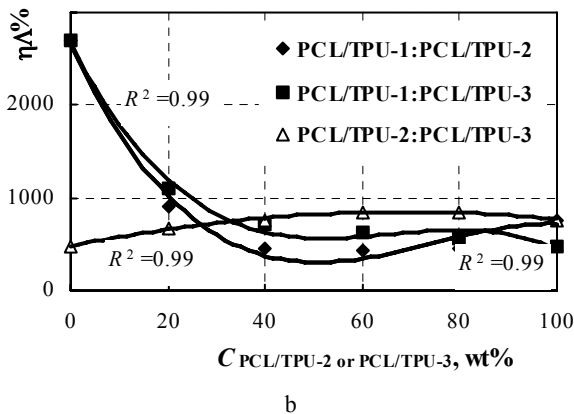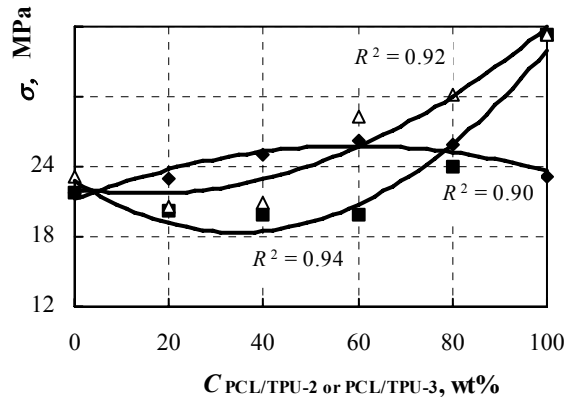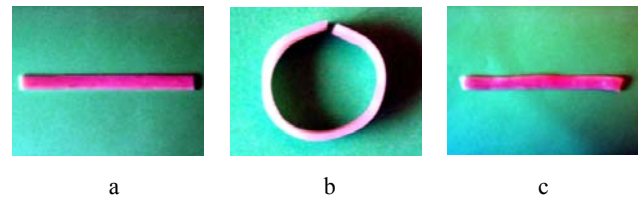

a

b

c

Fig. 3. Dependence of the mechanical properties on blend composition: a – tensile strength, b – elongation at break, c – bending strength

The stress-strain behaviour of shape memory PCL/TPU-1 and PCL/TPU-2 thermoplastics and their blend PCL/TPU-1 : PCL/TPU-2 = 60 : 40 wt% by drawing at high temperature and thermal recovery cyclic tensile testing are shown in Fig. 4. The data of the fixity ratio,
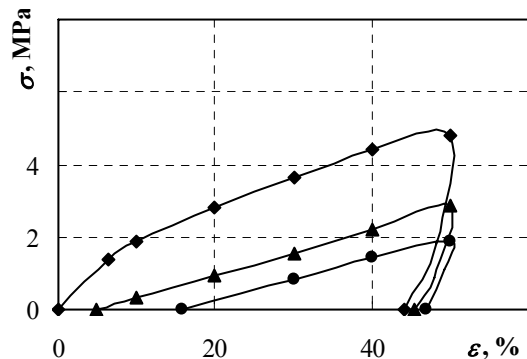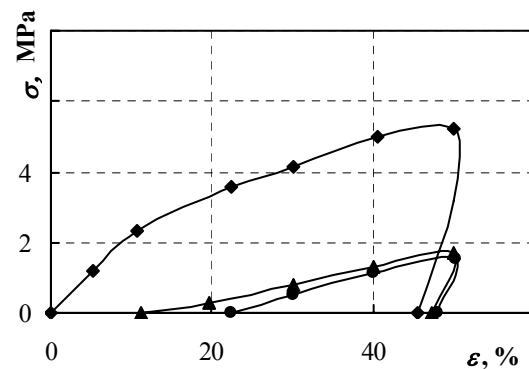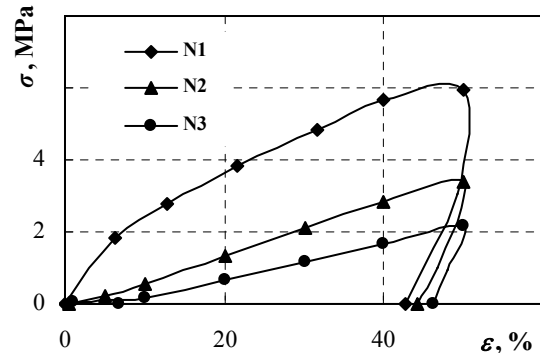
Fig. 5. Cyclic tensile curve of PCL/TPU-1 (a), PCL/TPU-2 (b) and their blend PCL/TPU-1:PCL/TPU-2 = 60:40 wt% (c)

As it can be expected, the best shape memory properties show lowest glass transition temperature thermoplastic PCL/TPU-1. It has a fixity ratio of more

Table 3. Cyclic tensile properties of the shape memory polyurethanes with poly(ε-caprolactone) under drawing at high temperature and thermal recovery

Cycle No.	$\varepsilon_p(N)$, %	$\varepsilon_u(N)$, %	σ at $\varepsilon = 50$ %, MPa	$R_f(N)$, %	$R_r(N)$, %	$R_{r,tot}(N)$, %
PCL/TPU-1						
1	0.0	42.6	6.0	85.2	–	100
2	0.4	44.2	3.4	88.4	99.2	99.2
3	0.8	46.3	2.2	92.6	99.2	98.5
PCL/TPU-2						
1	0.0	45.6	5.2	91.2	–	100
2	11.5	46.6	1.7	93.2	77.0	77.0
3	22.3	48.0	1.6	96.0	71.9	55.4
PCL/TPU-1 : PCL/TPU-2 = 60 : 40 wt%						
1	0.0	44.2	4.8	88.4	–	100
2	5.0	45.5	2.9	91.0	90.0	90.0
3	15.8	46.9	1.9	93.8	76.0	68.4

than 85 % and high recovery ratio up to 99 %. For PCL/TPU-2 polyurethane is characteristic higher fixity ratio, but markedly lower recovery ratio – only 77 %.

The shape memory behaviour of the blend PCL/TPU-1 : PCL/TPU-2 = 60 : 40 wt% is more close to PCL/TPU-1. Its fixity ratio reaches more than 88 % and recovery ratio 90 %. However, further thermal cycle markedly increases residual strain ε_p and the blend recovery behaviour became similar to that of PCL/TPU-2 component.

After first cycle all investigated materials show lower cyclic tensile properties. The differences between first thermal cycle and the remaining cycles is partially because of reorganization of molecules involving their orientation, crystallization, or weak point broken during elongation. After one cycle, the stress-strain behaviour of materials becomes very similar.

As can be seen from Fig. 5 and Table 3, values of stress at 50 % strain are significantly dependent on the cyclic thermal investigations. In the case of PCL/TPU-1 and its blend with PCL/TPU-2 stress decrease in 1.7 – 1.8 after second thermal cycle, and in 2.5 – 2.7 – after third cycle. However, for PCL/TPU-2 decreasing rate of stress at 50 % strain is significantly higher – it reaches more than 300 % and do not depend on thermal cycle number.

Thus, the reprocessing of shape memory PCL/TPU does not worsen shape memory behaviour. Therefore, waste of individual PCL/TPU materials or their blends of various compositions can be used for orthopedic splints production repeatedly.

4. CONCLUSIONS

Secondary blends from different shape memory poly(ε-caprolactone) based thermoplastic polyurethanes with glass transition temperature from 60 °C – 65 °C up to 70 °C – 75 °C were prepared by mastication. The changes in mechanical properties and shape memory behaviour of blends from polyurethanes waste were studied.

All polyurethanes are compatible and form simple blends without synergetic or anti-synergetic effects. Only some interaction between PCL/TPU-1 : PCL/TPU-2 blend components was observed.

After recycling virgin PCL/TPU and their blends display a significant shape memory effect. The recovery ratio was about 80 % – 90 % under drawing at temperature above their transition temperature.

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