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Influence of Calcium Carbonate Fillers on the Properties of Recycled Poly(ε-caprolactone) Based Thermoplastic Polyurethane

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In this work the effects of different crystallographic modifications of calcium carbonate ($CaCO_3$) filler on the melt flow, mechanical properties, hydrolytic degradation, and shape memory behaviour of recycled low-temperature poly(ε-caprolactone)-based polyurethane (rTPU) were evaluated. Composites were prepared by two-roll milling varying filler content from 2 wt% to 6 wt%. It was found that at temperature range from 20 °C to 50 °C $CaCO_3$ fillers do not change Young's modulus, they decrease tensile stress and deformation of rTPU, but improve its mechanical properties at elevated temperatures (up to 65 °C). rTPU melt flow index increases due to chain scission during the recycling and filler mixing with mill. Therefore, destruction temperature of rTPU is 20 °C lower than that of TPU. The $CaCO_3$ does not change shape memory properties independently of filler type and transition from secondary shape to the primary shape at 70 °C temperature is completed within 17 s for both filled and unfilled rTPU. The investigation of hydrolytic degradation shows that $CaCO_3$ only slightly increases degradation rate of rTPU.

Keywords: thermoplastic poly(ε-caprolactone) based polyurethane, calcium carbonate fillers, hydrolytic degradation, mechanical properties, melt flow, shape memory.

1. INTRODUCTION

Biodegradable polyurethanes (PU) are an important class of biomaterials due to their excellent physical properties and relatively good biocompatibility. Their mechanical, shape memory properties and biodegradability can be changed by varying the chemistry and molecular weight of their components for different applications [1–3].

PU are generally prepared from the isocyanate and polyol. They form multiblock copolymer consisting of alternating urethane based hard segment and polyether and/or polyester soft segment. The hard segment provides dimensional stability by acting as reinforcing filler and as thermally reversible crosslink. The soft segment provides the elastomeric character to the polymer backbone [4, 5]. Poly(ε-caprolactone) is one the most frequently used building blocks for soft segments of degradable polyurethanes [4, 6]. The mechanical properties and degradability of such PU can be improved by adding a small amount of fillers [7–9].

The properties of the filled polymer systems mostly depend on size and shape of filler particles, their content as well as on the type of interaction with polymer matrix [10, 11]. Particles shape plays a significant role in ability to intercept stress applied to the elastomeric composite. In general, anisometric particles – those having a significant difference in length versus width – are more effective as reinforcements than isometric particles – those similar in length and width. Isometric fillers that are approximately round, cubic or blocky in shape, are considered as low aspect of ratio fillers [12].

Calcium carbonate is commonly used filler in the plastics industry. It can exist in a number of crystallographic modifications: calcite, aragonite and vaterite [13]. Ground natural calcite is usually micron-sized (easier to disperse) with a broad size of distribution and irregular shape and is used as extender filler. On the other hand, nano-sized $CaCO_3$ can be used as active fillers because of its substantial improvement of polymers mechanical properties [14–19].

In order to reduce high surface energy and particle-particle interactions, which lead to agglomeration, $CaCO_3$ is often coated by surface modifiers. The most widely used is the surface treatment with stearic acid or one of its salts. As a result, an ultra thin layer of hydrophobic alkyl chains is chemically bonded to the surface. The coated organic film represents the interface between the filler and the polymer matrix, and hence, influences the wetting and adhesion properties of the two phases involved [19].

In [18, 20] it was found that $CaCO_3$ nanofillers can be used to improve tensile properties of polyurethanes. Micro-sized $CaCO_3$ filler particles improve rheological properties, thermal stability, and reduce the cost of composition of TPU matrix, also [21].

Low-temperature poly(ε-caprolactone) based thermoplastic polyurethane (TPU) is usually used for short-life orthopedic splints [22]. The medical application of TPU creates large amount of waste. The possibility of recycling and secondary use of TPU was investigated in [23]. It was found that secondary TPU blends show mechanical properties and shape memory behaviour closely comparable to that of the pristine materials and can be repeatedly used i. e. for orthopaedic splints production. However, the recycled and roll-milled TPU possess lower

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thermal resistance than that of pristine TPU [24]. It can be explained by chain scission, resulting in the breaking of skeletal bonds of TPU during mastication by the two-roll mill. The goal of this study is to determine the effects of calcium carbonate fillers morphology on the mechanical, melt flow, shape memory properties and hydrolytic degradation of recycled poly(ε-caprolactone) based thermoplastic polyurethane composites.

2. EXPERIMENTAL

2.1. Materials

For the investigation the waste from low temperature poly(ε-caprolactone) based thermoplastic polyurethane (TPU) sheets "Beachcast" and "Turbotreat" (T-Tape Company, Netherlands) obtained after orthopaedic device cutting was used. The main properties of these commercially available TPU are presented in [23]. Two types of calcium carbonate fillers – "Rugener FH32" (Dammann, Germany) and "Omyacarb 2TVH" (Vapenna, Czech Republic) – were used for investigation. The characteristics of $CaCO_3$ fillers are listed in Table 1.

Table 1. Properties of used calcium carbonate type fillers

Commercial name	Code	pH value	Surface treatment	Average particle size, µm
Rugener FH32	FH32	8.0 – 9.5	Stearic acid	2.8
Omyacarb 2TVH	2TVH	9.0	Does not indicated	2.5

2.2. Preparation of specimens

Samples for investigation were obtained by blending of TPU waste with two-roll mill PD 320 ("Metalist", Russia) with friction of 1.25, roll diameter of 160 mm, linear rate of 24 min^{-1} and milling duration for 20 min. The temperature of the mills was 55 °C and it was controlled by means of cold water running inside the rolls. After waste homogenization the $CaCO_3$ fillers were added and compounding was continued additionally 20 min.

TPU/$CaCO_3$ composites were prepared by varying filler content from 2 wt% up to 6 wt%. The main properties of TPU waste blends Beachcast/Turbocast = = 40/60 wt% were: Yóung's modulus $E = 193$ MPa, tensile stress was $\sigma = 25.4$ MPa and deformation was $\varepsilon = 2245$ % [24].

The test samples of recycled TPU (rTPU) were prepared by the compression moulding. The polymer was placed in the mold with the cavity dimensions of $(150 \times 130 \times 2)$ mm, softened at the temperature of $T = 70$ °C for 5 min and then pressed at 4.9 MPa for 2 min. After remove of the pressure the molds were cooled in room temperature. For testing the die-cut specimens were used after 3 days of storage at ambient temperature.

2.3. Testing methods

Contact angle. The powder contact angles are determined using the capillary penetration method (Fig. 1). The contact angle of powder sample was measured with a tensiometer DCAT 21 (DataPhysics Instruments GmbH, Germany). In the experiment, the powder is attached to balance and brought into contact with liquid. The penetration rate of liquid is determined by the slope of weight versus time plots.

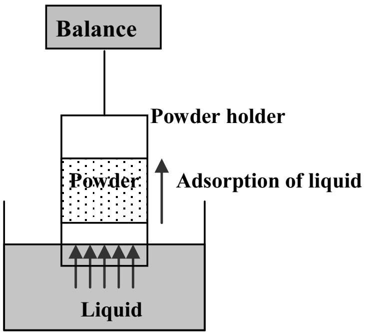


Fig. 1. Scheme of capillary penetration method

Contact angle $\theta°$ is correlated with the penetration rate based on Washburn's theory [25] according to the equation:

$$t = \left[\eta / (C \cdot \rho^2 \cdot \gamma \cos\theta)\right] \cdot m^2 , \tag{1}$$

where t is the time after contact (s), η is viscosity of liquid (g^2/s), C is material constant characteristic of solid (powder) sample, ρ is density of liquid (g/cm^3), m is weight of liquid adsorbed on solid (g).

Mechanical properties. Dumbbell shape specimens for tensile tests were prepared from compressed sheet using appropriate punch. Specimens have gage area of 10 mm × 10 mm and thickness of 2.0 mm ±0.1 mm. Six specimens were tested for each set of samples and the mean values were calculated. Tensile tests were carried out at ambient temperature using universal testing machine "H25KT" with a load cell of 1 kN (Tinius Olsen, Redhill, England). A cross-head speed was 20 mm/min. The tests were carried out in environmental chamber (H10kS) at temperature rising rate 2 °C/min. The measurements were performed at 20 °C, 50 °C, 60 °C, 65 °C temperature.

Shape memory properties. rTPU strips (5 × 50 mm) were changed into the ring shape at 70 °C temperature of water and then cooled rapidly to room temperature, and returned to the original shape when again was put in 70 °C water.

Melt flow index. Melt flow index (MFI) is defined as the weight of polymer, in grams, flowing in 10 minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. MFI was determined by using plastometer (Bita STR-1) with a capillary die diameter of 2.095 mm ±0.005 mm when a fixed pressure is applied to the melt via a piston and a load of total mass of 2.16 kg ($P = 21.168$ N). Tests were carried out at temperature range of 100 °C – 240 °C. MFI was calculated according to equation:

$$MFI = 600 \cdot \frac{m}{t} , \tag{2}$$

where m is weight (g), t is test time (s).

The degradation temperature was estimated as intersection point of two tangents of MFI-temperature curve.

Hydrolytic degradation. Samples with dimensions of $(10 \times 10 \times 2)$ mm were placed in a 3 % NaOH solution. After a predetermined time the hydrolytically degraded samples were removed, washed with distilled water, and completely dried at 25 °C temperature. The degree of degradation was determined from the weight loss ΔW using equation:

$$\Delta W = \frac{W_0 - W_t}{W_0} \cdot 100 , \tag{3}$$

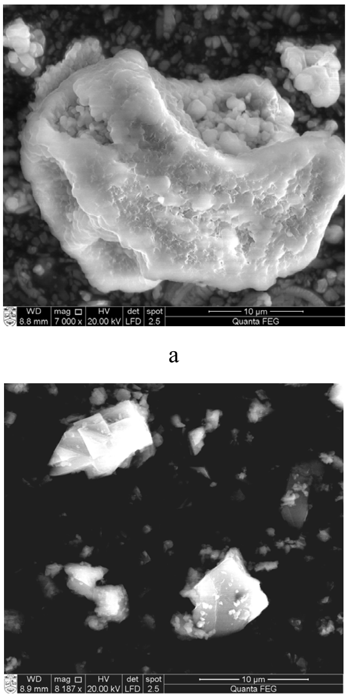
where W_0 is the dry weight of sample before testing (g) and W_t is the dry weight after time t (g).

Scanning electron microscopy (SEM). SEM analysis was performed using a microscope "Quanta 200 FEG" (Netherlands) at 10 keV or 20 keV. It has 1.5 nm resolutions, high output thermal field emission (> 100 nA beam current) microscope with high sensitivity (18 mm) backscatter detector for atomic number contrast.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of calcium carbonate fillers

It is known that calcium carbonate can exist in three crystallographic modifications, which are calcite, aragonite and vaterite [26]. The SEM images of $CaCO_3$ used for the investigations are shown in Fig. 2. It is evident that FH32 and 2TVH fillers have different crystal modifications. The aggregates of FH32 fillers have shape similar to vaterite: micro-sized particles have morphology close to spherical and consistent size with an average diameter close to 2.5 μm, while size of aggregates are close to 30 μm (Fig. 2, a).



a

b

Fig. 2. SEM images of $CaCO_3$ fillers: a – FH32; b – 2TVH

Vaterite modification is less stable, stronger and has a higher solubility than that of aragonite and calcite modifications. The crystals of vaterite have spherical shape, particles are usually colorless with diameter ranging from 0.05 μm to 5 μm [26]. Other calcium carbonate filler 2TVH has shape similar to calcite (Fig. 2, b). The size of 2TVH micro particles is around 2.8 μm. Calcite is the most stable modification of calcium carbonate.

The wettability of calcium carbonate fillers is important parameter for the evaluation of the interaction characteristics between filler and polymer. Fig. 3 shows the changes of water weight adsorbed by $CaCO_3$ powders during 160 s of immersion. The adsorbed liquid weight exhibits a sigmoidal character of time dependence.

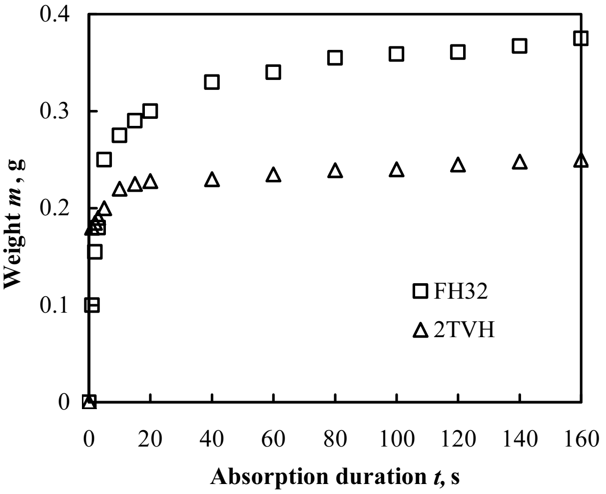


Fig. 3. The wettability properties of FH32 and 2TVH powder with water

The change in weight of adsorbed liquid can be divided into two phases: the initial phase shows a very intensive rate of weight change, which tapers off in late phase. This phase proceeds about 10 s for 2TVH powder and about 20 s – 25 s for FH32 powder. After this period of time the absorption process intensity slows down. It was calculated that the average contact angles for FH32 and 2TVH powders are equal to 0° and 27°, respectively. Thus FH32 filler possess better wettability properties than 2TVH filler.

3.2. Melt flow properties

Melt flow properties and thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss [27]. It was found that TPU begins to flow at 100 °C temperature. The MFI values of TPU change from 0.10 g/10 min to 93.20 g/10 min as temperature increases from 100 °C to 240 °C (Fig. 4). The highest MFI value (MFI = 93.01 g/10 min) is observed at temperature of 260 °C. The above temperature of 260 °C, thermal degradation of TPU begins.

Comparison of the melt flow properties of pristine TPU and rTPU shows that the recycling increases MFI due to the chain scission during reprocessing of waste by two-roll mill. Thought rTPU begins to flow at the same temperature as was obtained in the case of TPU (100 ºC), its degradation temperature is 20 °C lower than that of pristine TPU (dramatic increases in MFI indicate polymer degradation [28]) (Fig. 4). The highest MFI value of rTPU is obtained at 240 °C temperature (MFI = 87.98 g/10 min).

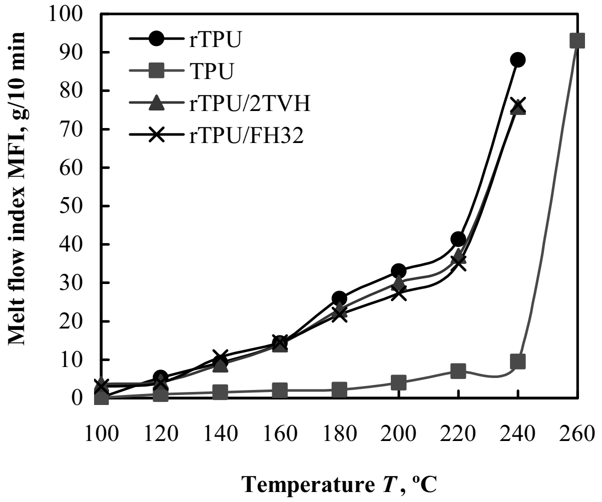


Fig. 4. Melt flow index of TPU and rTPU composites ($rTPU/CaCO_3$ = 94/6 wt %) versus test temperature (test load P = 21.168 N)

It was found that at investigated temperature range MFI does not depend on the type of $CaCO_3$ fillers. The 6 wt % of $CaCO_3$ increase initial MFI values of rTPU composites at 100 °C temperature (about 3.30 g/10 min). However, at the higher temperatures MFI of composites is only slightly less than that for unfilled rTPU.

3.3. Mechanical properties

The effect of $CaCO_3$ fillers on the stress-strain behaviour of rTPU is presented in Fig. 5. It was found that it does not depend on the fillers type. In all curves expression of yield is clearly visible.

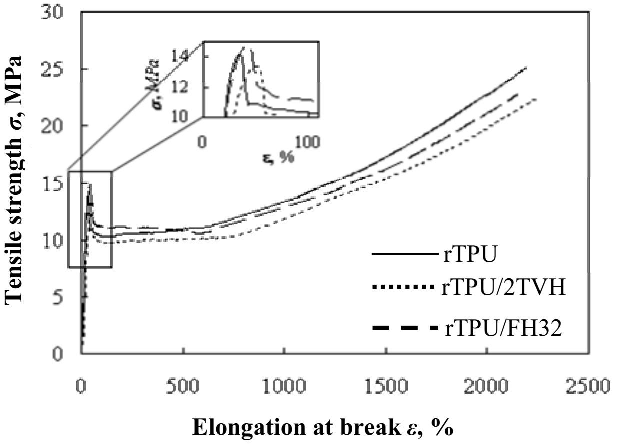
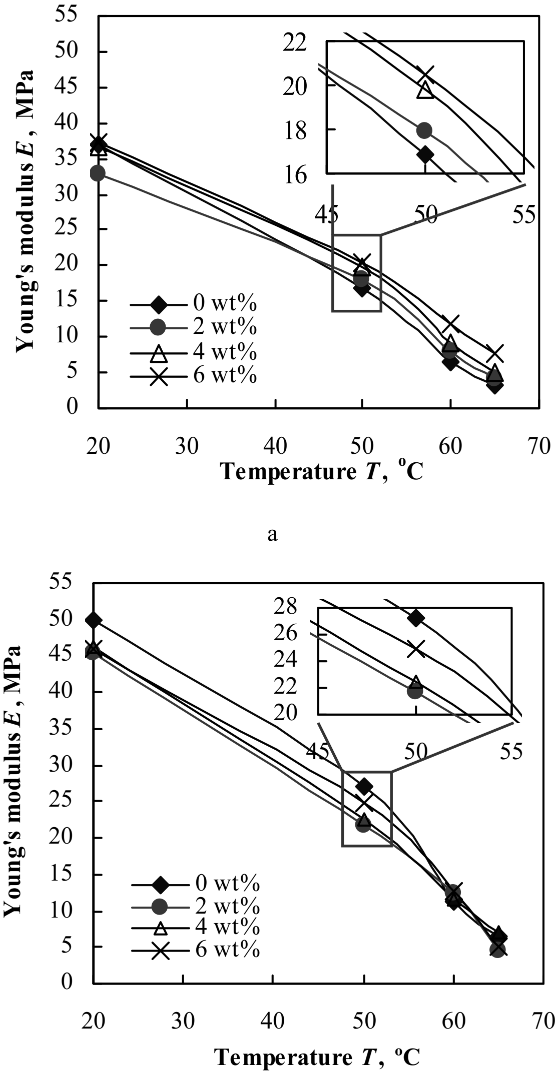


Fig. 5. Influence of $CaCO_3$ fillers type on the stress-strain behaviour of rTPU at ambient temperature ($rTPU/CaCO_3$ = 94/6 wt %)

The influence of $CaCO_3$ type and content on the rTPU mechanical properties under tension at temperatures range from 20 °C to 65 °C is shown in Fig. 6. As it can be seen, bellow soft segment melting temperature (~ 50 °C) of rTPU, the Young‘s modulus of $rTPU/CaCO_3$ composites are lower than that of unfilled rTPU. On the other hand, above the melting temperature of rTPU soft segment, the modulus of rTPU/FH32 composites increases as filler content increases. In the case of rTPU/2TVH composites E is similar to that of rTPU.

In [29] it was stated that modulus values of shape memory PU at ambient temperature are resulted by both decrease of soft segment crystallinity and the presence of filler reinforcement. Above the soft segment melting point temperature crystals of these segments melt and the increase of modulus from filler became dominant.

Other tensile results at temperature range of 20 °C – 65 °C are presented in Table 2. The tensile stress at ambient temperature decreases, as filler content increases up to 6 wt %. On the other hand, above the temperature of 60 °C, the stress of rTPU increases when $CaCO_3$ fillers are added. The maximum increase 37 % and 22 % is observed at different content of fillers: 6 wt % for FH32 and 2 wt % for 2TVH, respectively.



a

b

Fig. 6. Young‘s modulus E dependence upon temperature, filler content, and type of rTPU: (a) 2TVH, (b) FH32

In addition, rTPU composites show an improvement in deformation at temperature 60 °C and higher. The 7 % and 28 % increases were observed, when fillers contents were 2 wt % and 4 wt % for 2TVH and FH32, respectively.

Table 2. Tensile properties of rTPU composites

Filler type and content, wt%		Yield stress σ_y, MPa				Tensile stress σ, MPa				Deformation ε %			
		Temperature T, °C											
		20	50	60	65	20	50	60	65	20	50	60	65
FH32	0	14.4	6.4	1.9	0.7	24.1	17.7	1.9	0.7	2262	2010	342	108
	2	14.0	7.4	2.0	0.8	23.6	19.7	2.0	0.9	2131	2220	401	138
	4	14.8	6.7	2.1	1.0	22.9	18.7	2.1	1.0	2155	2165	513	140
	6	14.5	6.6	2.6	1.4	22.7	19.9	3.0	1.4	2118	2194	479	230
2TVH	0	19.0	10.0	3.2	1.2	23.5	20.9	3.2	1.2	1920	2059	797	231
	2	19.6	7.5	2,9	1.0	23.3	19.3	4.0	2.9	1930	1743	1110	274
	4	19.4	7.9	3.1	1.1	19.4	18.7	3.4	1.1	1049	1832	956	261
	6	19.1	8.5	3.8	1.0	19.1	18.1	3.9	1.0	771	1851	1164	196

However, at the room temperature the increase of $CaCO_3$ content deteriorates tensile stress properties. It may be supposed that influence of fillers depends on the $CaCO_3$ crystallographic modification.

As can be seen from Table 2, the rTPU/FH32 composites with vaterite shape fillers have higher influence on the mechanical properties of rTPU. The same influence of $CaCO_3$ crystallographic modification on the mechanical properties of polymers was observed in [30]. It was shown that tensile stress of polypropylene (PP) composites with vaterite forms fillers (2 wt% – 10 wt%) was higher than that of $CaCO_3$ fillers with other crystallographic modification. On the other hand it was found in [31] that addition of $CaCO_3$ filler (content 5 wt% – 30 wt%) increases the Young's modulus and decreases the yield stress and deformation of isotactic PP independently of filler crystallographic modification.

3.4. Investigation of shape memory properties

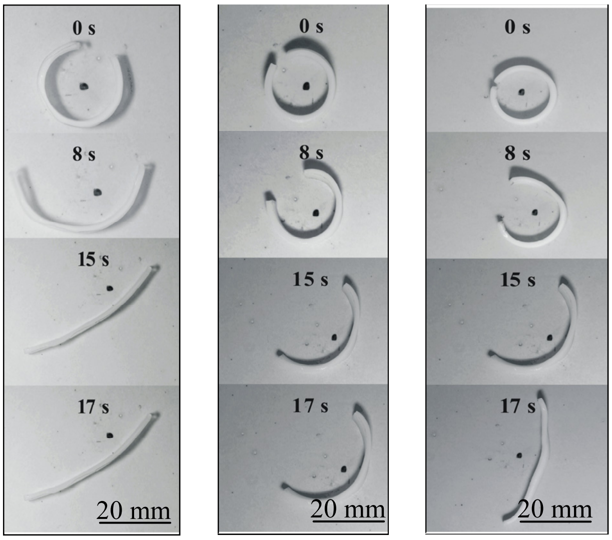
The shape memory effect of TPU is caused by the so-called micro-phase-separated heterogeneous structure which composed of the hard and soft segment phases. The hard segment phase has a higher thermal transition temperature (T_{trans}), than that of the soft segment. Usually, the soft segment phase T_{trans} is used as the switching temperature [32 – 36].

The investigation of the shape memory properties of TPU and rTPU at 70 °C temperature showed that the transition from the temporary shape to the permanent shape of both TPU and rTPU occurred in the same time within 75 s – 90 s [37 – 39]. As can be seen from the Fig. 7, the $CaCO_3$ filled rTPU composites show shape memory behaviour.

The transition of unfilled rTPU and filled rTPU composites from the temporary shape (circle) to the permanent shape (rod) is completed within ~ 17 s in water at a temperature of 70 °C independently on the fillers type and content.

3.5. Hydrolytic degradation

In order to better understand the effect of $CaCO_3$ fillers on the biodegradation of rTPU, the hydrolytic degradation tests were performed. The obtained data are presented in Fig. 8, where weight loss ΔW is plotted against the time of immersion. As can be seen, the ΔW increases as degradation time increase.



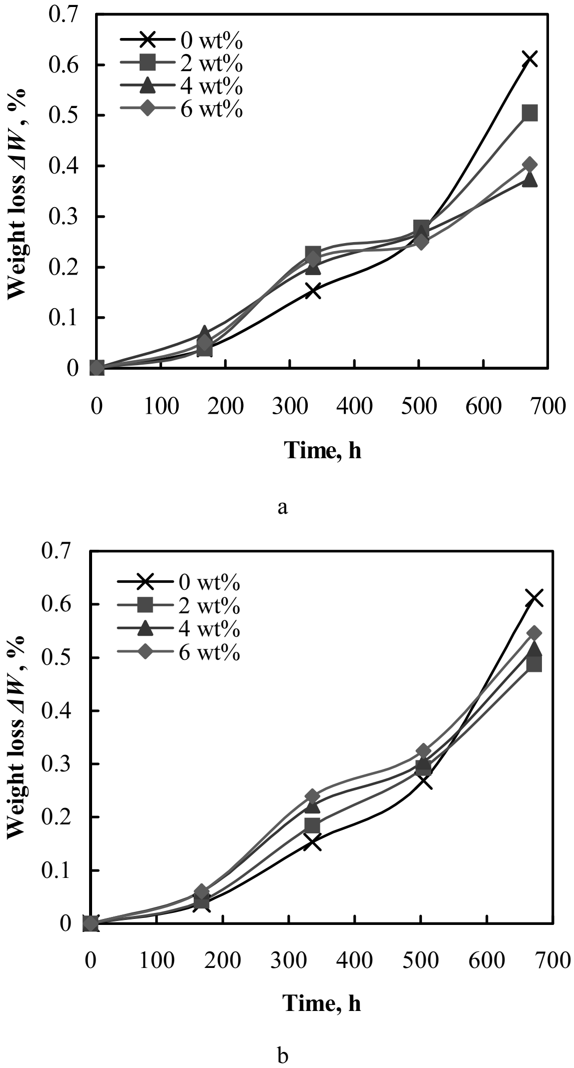
a b c

Fig. 7. Real shape-memory circle at 70 °C of (a) rTPU, (b) rTPU/FH32 and (c) rTPU/2TVH composites with 6 wt% of fillers

The weight loss of rTPU only slightly depends on the type of filler used. The degradation of the rTPU with vaterite shape fillers FH32 proceeds in higher rate than that of in the case of calcite shape filler 2TVH. Such behaviour can be explained by the higher solubility of vaterite (FH32) [26].

The fillers content practically does not influence ΔW values of rTPU. Only a slight influence of $CaCO_3$ content can be observed in the case of rTPU/FH32 composition at 300 h degradation time. In this case as FH32 content increase from 1 wt% to 6 wt%, the weight lost values increase from 0.18 % to 0.23 %. However, as degradation time increases up to 500 h, the weight loss does not depend on the composition.

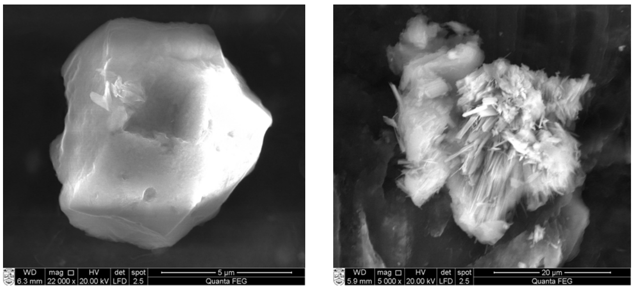
SEM analysis showed that crystallographic modifications of $CaCO_3$ fillers changes during the hydrolytic degradation period. It is known that exposed to water vaterite converts to calcite (at low temperature) or aragonite [26].



a

b

Fig. 8. Weight loss of rTPU with fillers: a – 2TVH; b – FH32



a b

Fig. 9. SEM images of fillers after 3 months of hydrolytic degradation: a – FH32, b – 2TVH

As can be seen from Fig. 9, during 3 month of hydrolytic degradation $CaCO_3$ fillers, incorporated to rTPU, change crystallographic modification: vaterite (FH32) transforms to calcite (Fig. 9, a) and calcite (2TVH) transforms to aragonite (Fig. 9, b). As can be seen, aragonite crystal lattice differs from that of calcite, resulting in a different crystal shape, an orthorhombic system with acicular crystals.

4. CONCLUSIONS

The effects of different crystallographic modification (calcite and vaterite) of $CaCO_3$ fillers on the melt flow, mechanical, shape memory properties, and hydrolytic degradation of recycled low temperature poly(ε-caprolactone) based thermoplastic polyurethane have been investigated.

The influence of $CaCO_3$ type fillers on the mechanical properties of rTPU depends on the fillers crystallographic modifications, content and environmental temperature. The fillers negatively influence tensile properties of rTPU at ambient temperature. On the other hand, $CaCO_3$ fillers act as reinforcing filler at the temperatures above the melting point of soft segment crystals of rTPU (above 50 °C). Furthermore, vaterite form $CaCO_3$ has higher influence on the mechanical properties of rTPU than that of calcite shape fillers.

The $CaCO_3$ fillers slightly decline melt flow, increase hydrolytic degradation rate, and do not affect shape memory properties of rTPU.

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