

KAUNAS UNIVERSITY OF TECHNOLOGY

Vitalija Skrockienė

**DEVELOPMENT AND EVALUATION OF
SECONDARY THERMOPLASTIC
POLYURETHANE/POLYCAPROLACTONE
BLEND AND NANOFILLER COMPOSITES**

Summary of Doctoral Dissertation
Technological Sciences, Materials Engineering (08T)

Kaunas, 2015

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

Vitalija Skrockienė

**ANTRINIO TERMOPLASTINIO
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MIŠINIO IR NANOUŽPILDŲ KOMPOZITŲ
KŪRIMAS IR VERTINIMAS**

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INTRODUCTION

Plastics production rate in Europe increased from 10 million tones to ca. 280 million tones in the period from 1950 to 2010, and it is still increasing (by about 9% annually) (The European plastics industry, 2011). In plastics industry, thermoplastics are most widely used. About 80 % of all plastic products are made from thermoplastics, and these are mostly used in the production of packages, textile fibres and different coatings (Dewil, 2006). Therefore, large amounts of plastic production waste are formed that contaminate the environment. That is why the recycling of plastics is of particular importance not only because of the increasing amount of used plastics and environmental issues, but also due to diminishing natural resources.

Polycaprolactone based thermoplastic polyurethane/polycaprolactone blends (TPU-PCL) can be widely used in medicine for orthopaedic splint production. However, while producing such splints, large amount of waste is left, which is generally disposed of at landfills. Although the soft segment polycaprolactone is considered as biodegradable plastic that decomposes faster than other plastics, the decomposition of TPU-PCL may extract insalubrious agents, like isocyanates. Moreover, the TPU-PCL plates used in the orthopaedic splint production are expensive, and TPU-PCL recycling could bring both environmental and economical benefits.

Thermoplastics can be easily reprocessed, yet, with each recycling process, their mechanical properties will deteriorate. Without any additives, thermoplastics can be reprocessed only 2–3 times, as due to heat impact, they begin to degenerate (Central Pollution Control Board, 2012). Due to worsened properties after reprocessing, the industry is not keen on using reprocessed plastics at the production of products that set high quality requirements for production, in order to keep their operational properties intact. The problem is solved in two ways: using the secondary plastics at production of products where the worsened mechanical and physical properties are satisfactory, or by modifying the secondary plastics by various additives, e.g. fillers with inorganic particles, such as clay, calcium carbonate, zinc or magnesium oxide, which improve the properties of reprocessed plastic (Jeppsson, 2005; Al-Salem et al., 2009). It has been already established that polymer composites filled with micro-size inorganic fillers are characterised by higher Young's modulus, hardness, coefficient of linear thermal expansion and temperature of heat deformation, yet, by lower impact and tensile resistance, compared to unfilled polymers. Meanwhile, due to higher surface area, high aspect ratio-to volume ratio, and high stress transfer, the influence of nanofillers on mechanical and thermal properties of thermoplastics is much bigger than in case of using microfillers. The use of

nanofillers increases the modulus and hardness of some polymer materials, as well as their tensile and impact resistance. Also, compared to microfillers, nanofillers ensure many other properties – transparency, surface smoothness, fire resistance. The level of separation of nanofillers in polymer matrix and the interaction between the fillers and the matrix are the most important for the properties of nanocomposites. In order to improve the dispersion and lamination of the fillers, their particles are mostly modified by chemical agents. Meanwhile, plasma, the new method for surface modification, is an environmentally friendly method, although, there are only several literature references on this topic in which the surface of clay particles is modified by plasma.

In this work, for modification of the properties of secondary blends, two inorganic fillers that are mostly used in plastics industry, namely clay and calcium carbonate, were chosen. These fillers tend to increase the viscosity, rigidity, strength and biodegradability properties of the thermoplastics (Leong et al., 2004; Deshmukh et al., 2011).

The aim of the doctoral dissertation is to investigate the possibility of secondary use of thermoplastic polyurethane and polycaprolactone blend and improvement of its properties by using of nanofillers.

The tasks of the research were following:

- to determine the influence of the mechanical reprocessing duration of thermoplastic polyurethane and polycaprolactone blend waste on the structure and properties of secondary blends;
- to investigate the influence of unmodified layered silicate bentonite, organically modified montmorillonite, and calcium carbonate fillers on the structure and properties of secondary thermoplastic polyurethane and polycaprolactone blend;
- to investigate the influence of atmospheric-pressure plasma modification on the layered silicate bentonite fillers;
- to determine the structure and properties of secondary thermoplastic polyurethane and polycaprolactone blend filled with layered silicate bentonite fillers treated by atmospheric-pressure plasma.

Scientific novelty and practical importance. Mechanical recycling of plastics is one of the most simple and environmentally friendliest methods, therefore, in this research, it is suggested to use this method for recycling the thermoplastic polyurethane and polycaprolactone blend waste obtained from the production of orthopaedics splints and in such way decrease the rate of plastic waste.

Recycling of thermoplastic polyurethane and polycaprolactone blend waste do not change its structure. The obtained secondary blends have better rheological properties, although, compared to primary blends, their

deformation capacity and stiffness are lower. It is suggested to use bentonite clay and organically modified montmorillonite fillers for the improvement of mechanical properties of the secondary blends. The layered silicate fillers improve the deformation properties of the composites, and increase the intensity of their hydrolytic degradability.

In order to improve the interaction between the filler and the polymer matrix, it is proposed to treat the layered silicate bentonite surface by atmospheric-pressure argon, air and oxygen plasma. This filler modification method is environmentally-friendly, cheap, yet, currently rarely used and little investigated.

After evaluating the structure and properties of secondary thermoplastic polyurethane and polycaprolactone blend filled with layered silicate bentonite fillers treated by atmospheric-pressure plasma, it is suggested to re-use the thermoplastic polyurethane and polycaprolactone blend waste at the production of orthopaedics splints.

Relevance. Research in the opportunities of secondary use of polymer waste is important both on scientific and practical levels. Use of waste in the production of new materials is characterised both by environmental and financial advantages, as it is substantially cheaper than synthesizing new polymer materials. Moreover, the use of fillers allows obtaining polymer materials with better mechanical properties after recycling compared to primary polymer materials. Filler surface modification by plasma improves the interaction between the fillers and polymer matrix, and therefore, its properties. Using plasma technology, many wet chemistry processes can be eliminated. Therefore, this research is very important from the scientific point of view.

Defensive statements:

- The mechanical properties and hydrolytic degradability of thermoplastic polyurethane and polycaprolactone secondary blend depend on the duration of mechanical reprocessing.
- Organically modified montmorillonite fillers decreases the resistance to hydrolysis, but increases stiffness of the thermoplastic polyurethane and polycaprolactone blend.
- The modification of layered silicate bentonite surface by the atmospheric-pressure oxygen and argon plasma increases the interlayer spacing of its particles and dispersion in the polymer matrix.
- Layered silicate bentonite fillers treated by atmospheric-pressure oxygen and argon plasma improve the deformation and degradability properties of the secondary thermoplastic polyurethane and polycaprolactone blend.

Approval of the research results. The results of the research are presented in 9 scientific publications: 4 – in the issue, which corresponds to the list of Institute of Scientific Information (ISI), 1 – in the issue, which corresponds to the list of database of an Institute of Scientific Information (ISI Proceedings), 2 – in reviewed proceedings of international and Lithuanian scientific conferences and 1 – in periodic publication. The results are presented at 5 international and 6 Lithuanian conferences.

Structure of the thesis. The thesis consists of introduction, 3 chapters, conclusions, list of references (146 entries), list of scientific publications and appendixes. The dissertation material is presented 92 pages, including 64 figures and 20 tables.

CONTENT OF THE DISSERTATION

Introduction determines the relevance of the presented investigations, definition of the research aim and objectives, survey of the scientific novelty and practical value of the dissertation.

Chapter 1 introduces the literature review of publications related to the theme of dissertation. The main part of literature review is related to the thermoplastic polyurethane filled with clay and calcium carbonate (CaCO_3) fillers, its possibilities of recycling. The possibilities of plasma modification of clay particles are discussed, also.

Chapter 2 presents materials characterization, samples preparation and their investigation methods.

Materials. The waste from two types of low temperature polycaprolactone based thermoplastic polyurethane/polycaprolactone blends *Beachcast* (TPU-PCL-1) and *Turbotreat* (TPU-PCL-2) (T-Tape Company, Netherlands) were used for investigations. These materials were generated from orthopaedic device manufacturing process at the cutting stage.

The untreated bentonite clay *Nanofill N116* (N116) from Souther Clay Products (Gonzales, TX) was used for investigation. Three types of organically modified montmorillonite nanoclays Cloisite 10A (C10A), Cloisite 15A (C15A), and Cloisite 30B (C30B) were kindly provided by Souther Clay Products (Gonzales, TX). All types of organoclays were surface-treated by ion exchange reaction between Na^+ existing in the gallery of the nanoclay and quaternary ammonium cations. Three types of calcium carbonate fillers – *Rugener FH32* (Dammann, Germany), *Omyacarb 2TVH* (Vapenna, Czech Republic), and *Ultra-Pflex*[®] (UP) (Minerals Technologies, Germany) – were used for investigation.

Plasma modification of bentonite. N116 was treated in a plasma reactor (PVD-75, Kurt. J. Lesker) with polarized anode. The plasma modification was performed on 10 g of powdered bentonite with ionized air,

argon, or oxygen gas. Herein after, the samples are named: N116-air, N116-arg, and N116-oxy, respectively. The modification was conducted at room temperature, at a pressure of $2 \cdot 10^{-2}$ mbar, with plasma power of 350 W, and modification time of 20 min.

Sampling. The blends was obtained by the mixing TPU-PCL-1:TPU-PCL-2 = 60:40 wt % (aTPU-PCL) on an open laboratory mill PD 320 at friction ratio of 1.25 two-roll mill up to 1400 s. The temperature of the mill was about 55 °C; it was controlled by means of cold water running inside the rolls. The test samples of composites were prepared by compression moulding.

Experimental. Fourier transform infrared (FTIR) spectra were collected in a spectrophotometer (ALPHA Platinum, Bruker). Measurements were carried out using the attenuated total reflectance (ATR) technique. Each spectrum was scanned with a resolution of 2 cm^{-1} in the range from 4000 cm^{-1} to 350 cm^{-1} .

X-ray diffraction (XRD) analysis of materials was performed using a diffractometer DRON-6 equipped with a copper target ($\lambda = 1.54 \text{ \AA}$) and flat diffracted beam pyrolytic graphite monochromator. Diffraction patterns were recorded at 35 kV and 20 mA. Scanning was carried out in the 2θ range of $2^\circ - 60^\circ$ at the step size of $0.02^\circ (2\theta)$ and counting time of 0.5 s/step.

Differential scanning calorimetry (DSC) (DSC Q10 V9, 0 Build 275 (TA Instruments, USA)) was used to determine the melting/crystallization behaviour of the TPU-PCL. Temperature heating/cooling cycles from -50°C to $+250^\circ \text{C}$ were performed at $10^\circ \text{C}/\text{min}$ and $5^\circ \text{C}/\text{min}$, respectively.

Atomic force microscopy (AFM) topographic images were obtained using a NT-206 (Micro-test machines Co) atomic force microscope using contact mode probe in air at ambient conditions ($22 \pm 4^\circ \text{C}$). The topographical images were collected using a V-shaped silicon cantilever (force constant of 0.35 N/m , tip curvature radius $< 10.0 \text{ nm}$, cone angle 20°).

Scanning electron microscopy (SEM) analysis of nanocomposite structure was performed using a microscope Quanta 200 FEG (FEI, Netherlands). All microscopic images were done on the same technical and technological conditions: the electron beam heating voltage – 20.00 kV , beam spot – 5.0 , magnifications – $500\times$, work distance – 6.0 mm , low vacuum – 80 Pa , detector – LFD.

Tensile tests were carried out at ambient temperature using universal testing machine H25KT with load cell of 1 kN (Tinius Olsen, England). A cross-head speed of $100 \text{ mm}/\text{min}$ was used. Measurements were performed at the room temperature with the specimens having gage area of $10 \text{ mm} \times 10 \text{ mm}$ and thickness of $2 \pm 0.1 \text{ mm}$. Six specimens were tested for each set of samples.

The powder contact angles are determined using the capillary penetration method. 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.

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 (Bitra STR - 1). Tests were carried out at temperature range of 100 °C – 240 °C.

For hydrolytic test the samples with dimensions of 10 × 10 × 2 mm were placed in 3 % NaOH solution. After a predetermined time of ageing the hydrolytically degraded samples were removed, washed with distilled water, and completely dried at 25 °C.

Chapter 3 presents the results of experimental investigations.

The influence of the duration of mechanical recycling of TPU-PCL waste on the properties of secondary blends. During recycling process a material undergoes various operations that bring out several modifications in the molecular structure. In Fig. 1 melt flow index of TPU-PCL is reported as a function of the reprocessing time, when temperature of 180 °C and load of $P = 21.16$ N were used.

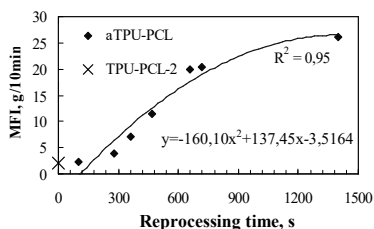


Fig 1. Dependence of TPU-PCL melt flow index upon reprocessing time (test temperature $T = 180$ °C, load $P = 21.168$ N)

As the reprocessing time increases, MFI increases due to the TPU-PCL chain scission, which is known as chemical reaction resulting in the breaking of skeletal bonds of polymer. TPU-PCL-1 has significant higher flow temperature (about 200 °C), therefore only MFI of TPU-PCL-2 is shown. It is clear that the viscosity of recycled materials is higher. The viscosity of aTPU-PCL rapidly and evenly increases, as reprocessing time increases due to the breakage of molecular chains.

The mechanical properties of the investigated materials are listed in Table 1. The decrease of tensile strength and elongation at break is usual consequence of reprocessing of polymers.

During reprocessing polymers undergo various changes in molecular structure that were investigated by X-ray technique (Fig. 2). Three diffraction peaks are noted. The two peaks at $2\theta = 21.5^\circ$ and $2\theta = 22.1^\circ$ with interplanar spacing (d -spacing) of 0.41 nm, and 0.41 nm are related to the lateral distances in the contours (interfaces) of the hard crystallised segments (Nanda, 2006). These diffraction peaks were superimposed on the amorphous halo for the dispersion of aTPU-PCL chains with regular interplanar spacing (Trovati, 2010). Additional low intensity peak of TPU-PCL-1 can be seen at an angle of $2\theta = 9^\circ$ ($d = 0.98$ nm), possibly due to the ordered hard domain (Mishra, 2011). This peak diminishes during mastication of TPU-PCL-1 and TPU-PCL-2 blends.

Table 1. Dependence of TPU-PCL mechanical properties on the reprocessing time

Material	Reprocessing time, s	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
TPU-PCL-1	-	82.4 ± 3.6	23.8 ± 1.9	2824 ± 118
TPU-PCL-2	-	65.6 ± 1.2	20.3 ± 1.6	2727 ± 169
aTPU-PCL	600	23.6 ± 1.6	31.1 ± 1.0	2167 ± 139
	660	25.0 ± 0.6	22.6 ± 0.8	1989 ± 122
	720	25.9 ± 1.9	23.2 ± 0.8	2137 ± 126
	960	31.1 ± 2.3	23.8 ± 1.2	2038 ± 78
	1400	34.8 ± 2.0	23.1 ± 0.5	1877 ± 102

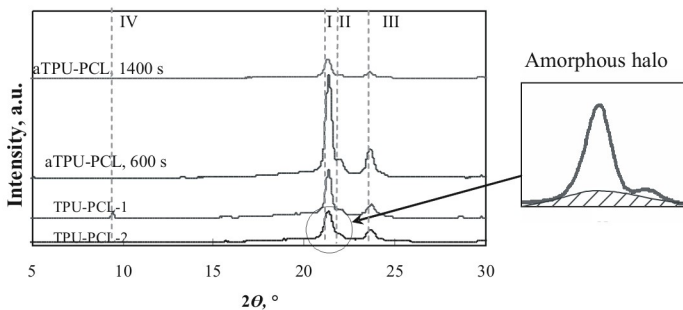


Fig. 2. X-ray diffractograms of TPU-PCL-1, TPU-PCL-2 and aTPU-PCL blend reprocessed for different times

As can be seen from Table 2, crystallinity of TPU-PCL-1 is higher than that of TPU-PCL-2. Meanwhile, crystallinity degree of secondary

aTPU-PCL is higher than those of primary materials only at the initial stage of mastication (up to 600 s). However, further increase of reprocessing time up to 1400 s, decreases the crystallinity of aTPU-PCL in 1.7 times.

Table 2. Changes of the crystallinity of various TPU-PCL upon composition and reprocessing time

Material	Reprocessing time, s	Crystallinity, %
TPU-PCL-1	-	36
TPU-PCL-2	-	32
aTPU-PCL	600	48
aTPU-PCL	1400	29

In order to understand the influence of recycling on the degradability of TPU-PCL, hydrolytic degradation tests in 3 % NaOH solution at different immersion time were performed. It was found that the weight loss of aTPU-PCL is affected by the reprocessing time (Fig. 3). As can be seen the weight loss of aTPU-PCL decreases when the reprocessing time increases. The highest biodegradability intensity of aTPU-PCL was obtained in the beginning of reprocessing (280 s) as may be assumed due to in homogeneity of blend (Fig. 3). It leads of water molecules more easily penetrate within the materials and to cause their rapid destruction.

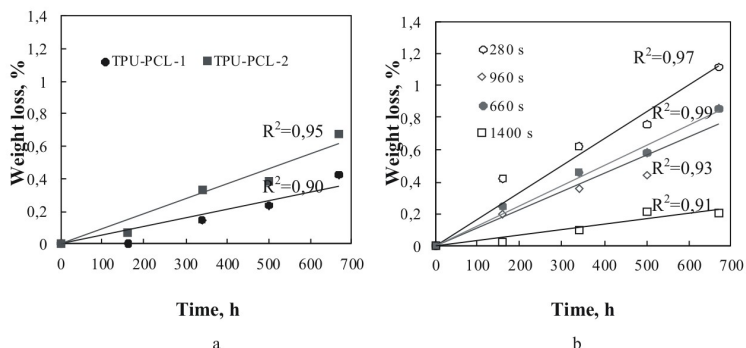


Fig. 3. Dependence of weight loss of TPU-PCL before (a) and after recycling (b) upon the different reprocessing time

FT-IR spectroscopy has been used to detect the change of aTPU-PCL structure due to the physical modification. The spectra of TPU-PCL-1, TPU-PCL-2 and aTPU-PCL at 1400 s of reprocessing time are compared in Fig. 4. The changes in the peaks of N-H and C=O stretching were monitored. In typical polyurethanes, hydrogen bonds are formed between hard segments via -NH groups in urethane linkages and between hard and soft segments via N-H and soft segment ether or carbonyl groups (Yoon, Haan, 2000). The

peak at 3375 cm^{-1} and a small shoulder at 3433 cm^{-1} can be attributed to the stretching vibration of hydrogen bonded and free -NH groups, respectively. The peak intensity of hydrogen bonded -NH stretching decreases due to the thermal degradation of aTPU-PCL during reprocessing (Pattanayak, Jana, 2005). On the other hand, the intensity of free carbonyl stretching vibration peak -C=O at 1721 cm^{-1} increases during reprocessing and indicates that phase mixing between hard and soft segments occurs due to the increase of adhesion between the hard and soft segments and that free urethane groups transformed into the strong hydrogen bonded urethane (Dimitry, 2010). Other characteristic infrared bands in the range $2863 - 2935\text{ cm}^{-1}$ are related to the asymmetric and symmetric C-H stretching vibration of CH_2 , and 1523 cm^{-1} N-H bending of the urethane group. There are no distinct peaks assigned to NCO group at about 2230 cm^{-1} for all samples, suggesting that the isocyanate group failed to reach a detectable level (Lee, 2009).

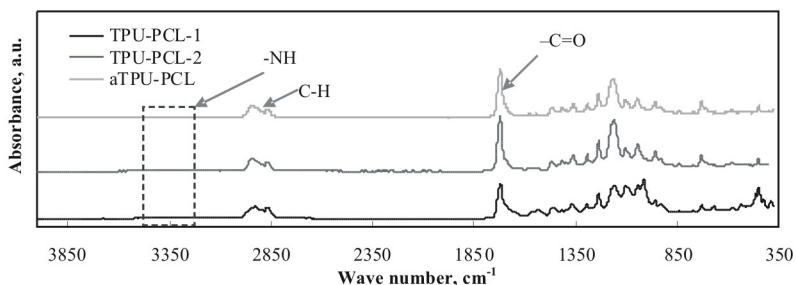


Fig. 4. FT-IR spectra of TPU-PCL-1, TPU-PCL-2, and aTPU-PCL

Fig. 5 represents DSC traces of aTPU-PCL and their nanocomposites after recycling (1400 s). In the tested temperature range ($-50\text{ }^{\circ}\text{C}$ to $+250\text{ }^{\circ}\text{C}$) for thermograms crystallization and melting peaks are characteristic. The structure of TPU-PCL includes hard and soft segments, which are expected to exhibit generally two melting temperatures T_m . Peak areas were obtained automatically by data acquisition system. Presented curves clearly demonstrate endothermic peaks located at $56.03\text{ }^{\circ}\text{C}$ with high enthalpy values of 47.39 J/g and 51.85 J/g , for TPU-PCL-1 and TPU-PCL-2, respectively, which indicate T_m of the soft segment domains. The hard segment T_m peak region is not detected probably due to the inactive movement of the hard segment, which had a small heat capacity change and uniform dispersion of hard segment micro domains within the TPU-PCL matrix (Chen, 1997; Li, 1992).

aTPU-PCL blend shows the increase in melting temperature ($T_m = 57.42\text{ }^{\circ}\text{C}$) and twice higher heat fusion compare with to that of pristine TPU-PCL-1 and TPU-PCL-2 (Table 3, Fig. 5, a). Therefore, according to the

obtained data aTPU-PCL appears to be more crystalline as TPU-PCL-1 or TPU-PCL-2.

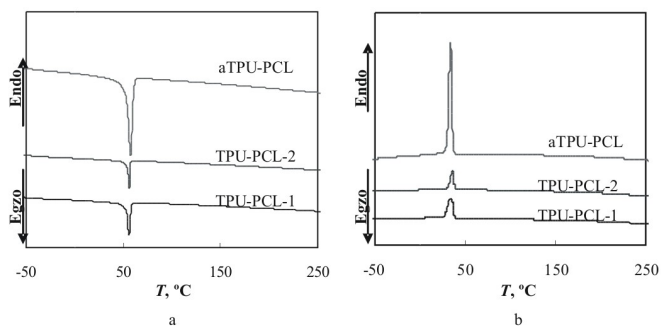


Fig. 5. DSC thermograms of TPU-PCL-1, TPU-PCL-2 and aTPU-PCL: (a) heating, and (b) cooling

Table 3. DSC data for TPU-PCL before and after recycling

Material	T_m , °C	ΔH_m , J/g	T_c , °C
TPU-PCL-1	56.03	47.39	34.56
TPU-PCL-2	56.03	51.85	36.37
aTPU-PCL	57.42	102.0	34.39

The influence of the duration of mechanical recycling and the type and amount of clay filler on the properties of aTPU-PCL blends. The investigation of the nanoclays influence on the mechanical properties of aTPU-PCL during reprocessing shows that N116 increases tensile strength and the elongation at break of aTPU-PCL only marginally ($\sim 7\%$ and $\sim 2\%$), when the reprocessing time changes from 600 s up to 1400 s (Table 4). However, mechanical properties of aTPU-PCL:N116 have the close values as aTPU-PCL after recycling as it is characteristic to the polymer composites with micrometer-sized particles. Mechanical properties of aTPU-PCL nanocomposites with 3 wt % of C30B nanoclays gradually improved during recycling. However, they are slightly lower than obtained in the case of aTPU-PCL. The reduction of the strength may be attributed to the interactions between the nanoclay and polymer chains that restrict chain mobility.

The SEM images of aTPU-PCL:N116 and aTPU-PCL:C30B (97:3 wt %) nanocomposites after tensile test and at different reprocessing time are displayed in Fig. 6. It is obvious that N116 platelets are not well dispersed in aTPU-PCL matrix and small aggregates with dimension of up to $2\ \mu\text{m}$ can be seen throughout and occasional larger particles of several micrometers can be also visible (Fig. 6, a). The voids between the polymer

and nanoclays aggregates show the poor interaction between aTPU-PCL matrix and N116. The low degree of filler-matrix interaction and aggregation of N116 contribute to the decrease of mechanical properties of aTPU-PCL:N116 composites. Therefore, the reprocessing with two-roll mill technique used for formation of exfoliated aTPU-PCL:N116 nanocomposite was not adequate. The dispersion of C30B particles in aTPU-PCL matrix are not uniform across the specimen with formation of small 0.5 μm aggregates at the beginning of reprocessing (Fig. 6, b). However, SEM images show significantly higher interaction between C30B and polymer matrix comparing to that of nanocomposite with N116. At the end of recycling C30B particles are well dispersed and homogenously distributed in aTPU-PCL matrix.

Table 4. Dependence of aTPU-PCL and nanoclay composites (97:3 wt %) mechanical properties on the reprocessing time

Material	Reprocessing time, s	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
aTPU-PCL:N116	660	37.8 \pm 1.3	19.7 \pm 1.7	1872 \pm 156
	720	31.7 \pm 1.8	21.3 \pm 1.1	1975 \pm 192
	960	34.1 \pm 1.3	21.5 \pm 1.2	1911 \pm 53
	1400	34.9 \pm 1.0	21.1 \pm 1.0	1895 \pm 40
aTPU-PCL:C30B	660	29.6 \pm 2.8	17.7 \pm 1.4	1819 \pm 55
	720	27.0 \pm 0.8	20.6 \pm 0.2	1933 \pm 88
	960	27.3 \pm 1.6	19.4 \pm 0.3	1844 \pm 129
	1400	31.3 \pm 1.9	19.9 \pm 0.6	1999 \pm 29

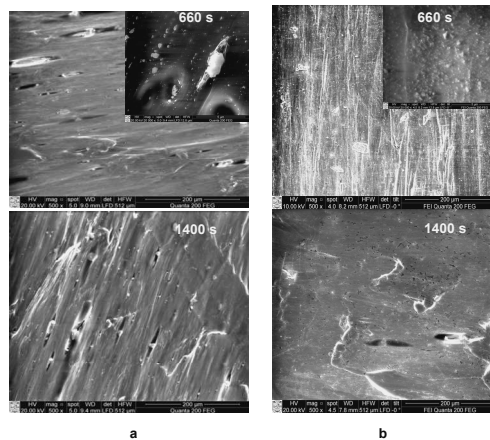


Fig. 6. SEM images of fractured (a) aTPU-PCL:N116 (97:3 wt %) and (b) aTPU-PCL:C30B (97:3 wt %) surfaces at the different reprocessing time after tensile test

Generally, nanoclays improve biodegradation intensity of polymers. C30B have high influence on the hydrolytic degradation of aTPU-PCL. The hydrolytic degradation of aTPU-PCL:C30B increases 5 times when the content of C30B increase from 1 wt% up to 5 wt%. The increase of degradation rate can be attributed to the presence of hydroxyl groups on the edges of C30B, which can catalyze the hydrolysis reactions of the polymeric matrix. On the other hand, N116 has insignificant influence on aTPU-PCL resistance to hydrolysis when nanoclay content increases up to 5 wt% (Fig. 7).

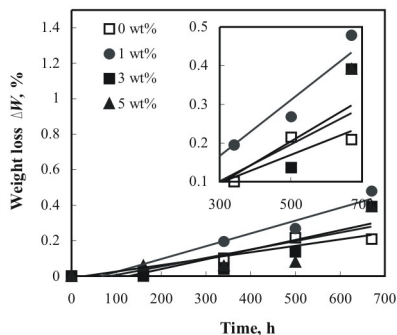


Fig. 7. Dependence of aTPU-PCL:N116 weight loss on the nanoclay content after reprocessing

The analysis of dependence of aTPU-PCL:C30B (97:3 wt %) composites hydrolytic degradation on the different reprocessing time shows that the weight loss increases with increase of the reprocessing time (Fig. 8, a). At the end of reprocessing, the weight loss of nanocomposite is about 10 times higher compared to that of aTPU-PCL. Such behaviour can be explained by decrease of aTPU-PCL:C30B crystallinity and increase of amorphous zones, which are more prone to degradation. The hydrolytic degradation of aTPU-PCL:N116 nanocomposites during recycling shows that the weight loss of aTPU-PCL:N116 is almost the same at the reprocessing, except the first recycling stage (660 s) (Fig. 8, b). Besides, the degradability intensity of aTPU-PCL:N116 is 7 times lower compared with aTPU-PCL:C30B. This can be related to the higher dispersion of C30B particles compared to that of N116.

X-ray diffractograms in 2θ range of $2^\circ - 10^\circ$ show that the spacing between the planes in the atomic lattice d of modified C30B and unmodified N116 particles are $d_{001} = 1.87$ nm ($2\theta = 4.72^\circ$) and $d_{001} = 1.23$ nm ($2\theta = 7.17^\circ$), respectively (Fig. 9). The gallery of C30B is exfoliated and expanded by molecular chain of the organic modifier, because the spacing d of C30B is slightly higher than that of N116. In the case of aTPU-PCL with

3 wt % of N116 it is evident that there is only marginal d -spacing increase with respect to N116 after different reprocessing times (Fig. 9, a). The position of the diffraction peak maximum after 660 s of reprocessing changes marginally ($2\theta = 6.77^\circ$), however, new peak at lower angle ($2\theta = 1.30^\circ$, $d_{001} = 3.14$ nm) appears, showing that part of nanoclay are separated. At 1400 s of reprocessing of aTPU-PCL:N116 diffraction peak becomes broader and slightly shifted toward lower angle position ($2\theta = 6.15^\circ$, $d_{001} = 1.44$ nm), indicating that most of the N116 was not successfully exfoliated in aTPU-PCL matrix and composites with multi-layered structure were obtained.

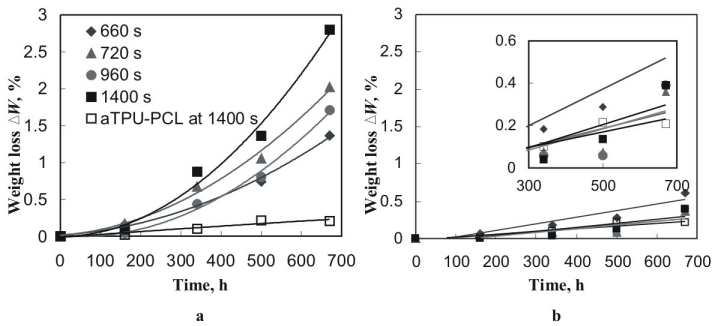


Fig. 8. Dependence of (a) aTPU-PCL:C30B (97:3 wt%) and (b) aTPU-PCL:N116 (97:3 wt%) weight loss on the different reprocessing time

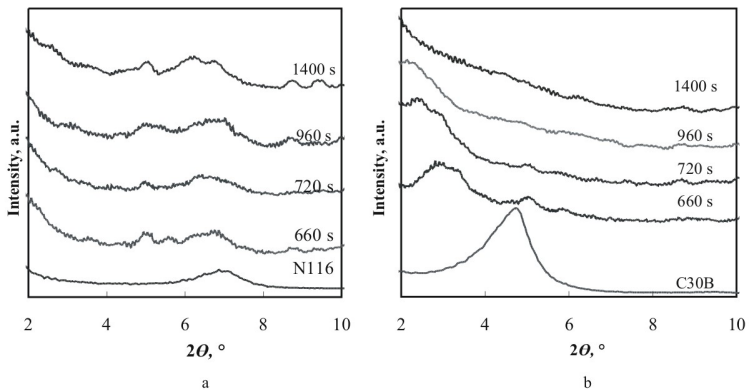


Fig. 9. X-ray diffractograms of nanoclay and aTPU-PCL:nanoclay composites after different reprocessing time: (a) aTPU-PCL:N116 (97:3 wt %), (b) aTPU-PCL:C30B (97:3 wt %)

The intensity of d_{001} diffraction peak of C30B weakens gradually, its position shifts towards lower angles and becomes broader with the increase

of nanocomposite reprocessing time (Fig. 9, b). The d_{001} values decrease from 1.45 nm (660 s) to 1.89°nm (960 s). The main diffraction peak of C30B disappears after 1400 s of reprocessing, indicating that the exfoliated aTPU-PCL:C30B composite was obtained. The interlayer distance remains unchanged when the processing time is prolonged up to 1400 s. It is suggested that the further molecular diffusion of aTPU-PCL does not occur during reprocessing.

The influence of nanoclay on the structure of aTPU-PCL after reprocessing is shown in the Fig. 10. Only the weak bands at 2916 cm^{-1} and 2850 cm^{-1} appear in aTPU-PCL:C30B samples that not exist in aTPU-PCL. Al-O stretching and Si-O bending vibration in the range of 400 – 600 cm^{-1} disappear in aTPU-PCL nanocomposite, indicating polymer chains intercalation into the gallery of clay (Lee, 2009, Zhang, 2003). It was also found that the positions of the peaks from distinctive functional groups were nearly identical in both aTPU-PCL and aTPU-PCL:nanoclay composite. It means that the segmented structure of TPU-PCL was not affected by the presence of clay (Lee, 2009).

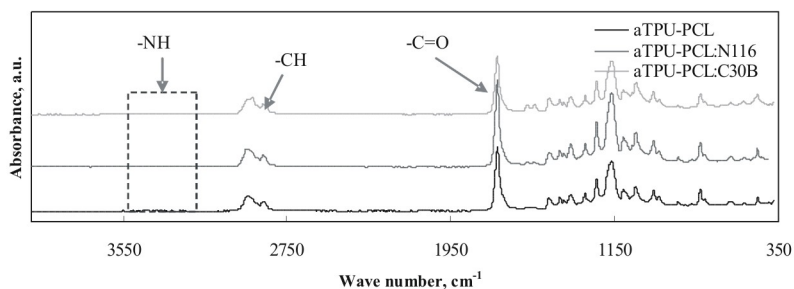


Fig. 10. FT-IR spectra of aTPU-PCL, aTPU-PCL:N116 (97:3 wt %), and aTPU-PCL:C30B (97:3 wt %)

From Table 5, it is clear that T_m of aTPU-PCL changes insignificantly by the addition of nanoclay. In the case of aTPU-PCL:N116 soft segment melting temperature is located at 55.20 °C, while T_m of aTPU-PCL:C30B is observed at the higher temperature (57.26°C). The heat of fusion of aTPU-PCL decreases from 102.0 J/g to 53.88 J/g and 51.05 J/g in the presence of N116 and C30B, respectively. It is clear that the extent of interaction is more in the case of aTPU-PCL:C30B nanocomposite as reveals the lowest heat of fusion. The soft segment chains were restricted by the clay particle galleries and therefore, could not crystallize. DSC cooling curves show the shift of crystallization temperature T_c to 35.64 °C for aTPU-PCL:C30B against broader peak at 34.39 °C for unfilled aTPU-PCL.

Table 5. DSC data for aTPU-PCL:nanoclay (97:3 wt %) after reprocessing

Material	T_m (°C)	ΔH_m (J/g)	T_c (°C)
aTPU-PCL:N116	55.20	53.88	35.64
aTPU-PCL:C30B	57.26	51.05	34.06

The influence of the bentonite modified by plasma on the properties of the aTPU-PCL blends. To determine the shape, size, and morphology of N116 particles SEM analysis was used. Micrographs of unmodified and plasma modified samples are presented in Fig. 11. It is clear that particles of all samples are irregularly shaped and rough edged. It is known that these factors play an important role in the interaction between filler and polymer matrix. As can be seen the particles layers of unmodified N116 are compact with the diameter in the range of 3 – 20 μm (Fig. 11, a). The surface of argon plasma modified bentonite N116-arg particles is almost the same as unmodified ones (Fig. 11, a, b).

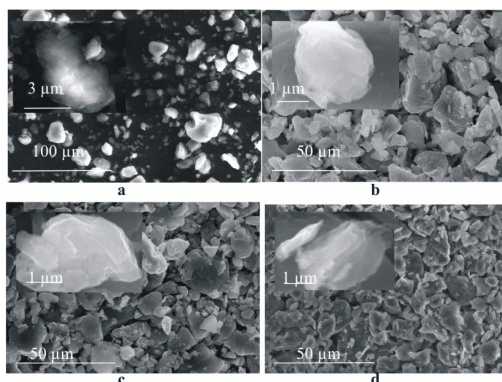


Fig. 11. SEM images of N116 particles before and after plasma modification: (a) N116, (b) N116-oxy, (c) N116-arg, (d) N116-air.

The small-angle X-ray diffractograms (XRD) show that the plasma modification changes the structure of N116 (Fig. 12). d_{001} reflection of N116, placed at 1.23 nm, decreased in intensity and shifted to the higher values of 1.38 nm and 1.29 nm, after the oxygen and argon plasma modification, respectively. This effect is consistent with the greater hydration of gas-treated samples (Valdrè, 2007). The different and higher d values suggest that water is located in the interlayer. The intensity of peak reduction could suggest a greater disorder of the layer stacking and that other structural sites in addition to the interlayer could be affected by gas modification (Valdrè, 2007). On the other hand, the air plasma modified N116 shows contrary XRD results. The basal spacing of N116-air decreases up to 1.17 nm after modification.

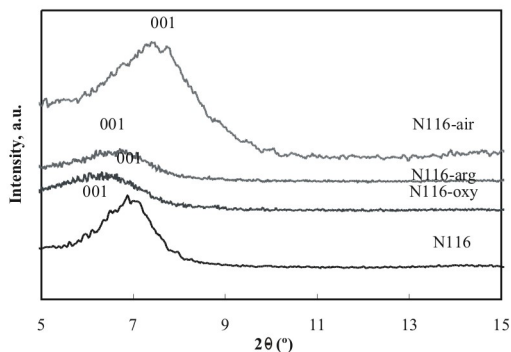


Fig. 12. Small-angle X-ray diffraction patterns of N116 before and after plasma modification

The infrared spectra of bentonite particles before and after plasma modification are presented in Fig. 13. Three major regions of bands can be seen: -OH stretching region, H₂O and CH₂ region, and 1200 – 350 cm⁻¹ region. The spectrum of N116 shows a band at 3615 cm⁻¹ due to the -OH stretching coupled to an aluminum atom (Al-OH). The decreasing peak intensity at this wavenumber after air plasma modification indicates the clay dehydration (Neira-Velázquez, 2011). The infrared spectrum of untreated N116 revealed a weak infrared band at 3385 cm⁻¹ due to the -OH band stretch in Al-OH and Si-OH (Nanda, 2006). A shoulder near 3230 cm⁻¹ was ascribed to an overtone of the bending mode of cation hydration water (Asl, 2013).

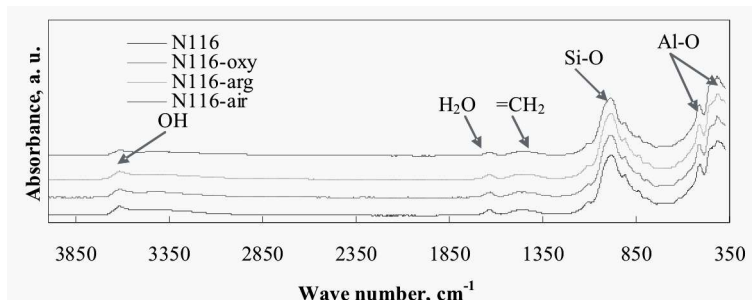


Fig. 13. FT-IR spectra of N116 before and after plasma modification: (a) OH stretching and (b) H₂O and CH bending, and (c) 1200 – 350 cm⁻¹ regions

As can be seen from Table 6 unmodified N116 does not influence on the mechanical properties of aTPU-PCL. Young's modulus of nanocomposites slightly decreases after the addition of plasma treated N116. However, incorporation of 3 wt % of N116-arg causes an increase of the

elongation at break and tensile strength in ~18 % with respect to aTPU-PCL. Meanwhile, the addition of N116-oxy increases the elongation at break in 31 % and tensile strength in 6 %. However, N116-air weakens the mechanical properties of aTPU-PCL. Consequently, the air plasma is not appropriate for the bentonite modification.

Table 6. Mechanical properties of aTPU-PCL and its nanocomposites with modified and unmodified N116

Material	Young's modulus E_Y , MPa	Tensile strength σ , MPa	Elongation at break ϵ , %
aTPU-PCL	34.8 ± 2.0	23.1 ± 0.5	1877 ± 102
aTPU-PCL:N116	34.9 ± 1.0	21.1 ± 1.0	1895 ± 40
aTPU-PCL:N116-oxy	33.2 ± 1.4	24.7 ± 1.2	2460 ± 43
aTPU-PCL:N116-arg	29.4 ± 1.8	27.5 ± 1.6	2224 ± 149
aTPU-PCL:N116-air	29.7 ± 1.5	20.5 ± 1.5	1787 ± 144

SEM technique was used to observe the changes in microstructure of aTPU-PCL:clay nanocomposites. Fig. 14, a reveals that the untreated N116 particles are not well dispersed in aTPU-PCL matrix. The clay particles with dimension of 2 μm or smaller can be seen throughout and larger particles of several μm can be obtained also. SEM images show significantly higher dispersion level of plasma modified N116 particles in aTPU-PCL matrix comparing to that of unmodified ones. As can be seen from Fig. 14 irregular-shaped plasma modified N116 particles have different mean sizes in the range of 1 – 0.3 μm .

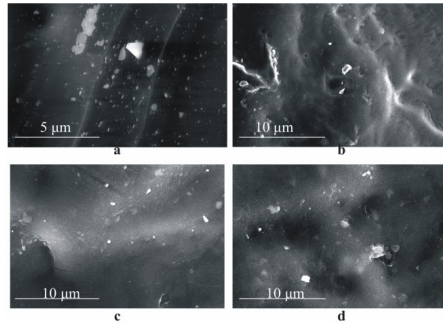


Fig. 14. SEM images of aTPU-PCL:clay nanocomposites before and after plasma modification: a – aTPU-PCL:N116, b – aTPU-PCL:N116-oxy, c – aTPU-PCL:N116-arg, d – aTPU-PCL:PN116-air

X-ray diffraction, an effective method of characterizing intercalation and exfoliation of clays, was used for further investigations of aTPU-PCL:clay nanocomposites. The strong characteristic peak at

$2\theta = 7.17^\circ$ similar to that shown by unmodified N116 and a new peak at lower angle $2\theta = 1.30^\circ$ ($d_{001} = 3.14$ nm) can be found for aTPU-PCL nanocomposites with 3 wt% of N116 indicating the intercalation. On the other hand, the basal diffraction peak of plasma treated N116 completely disappeared, implying that exfoliation of plasma modified N116 filler occurred (Fig. 15).

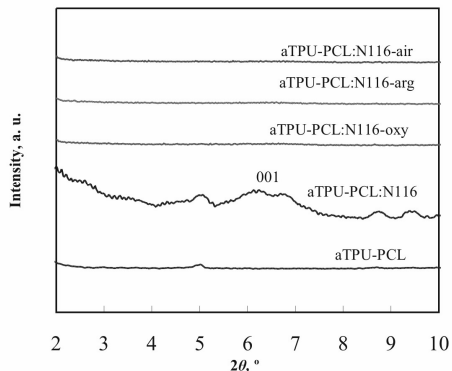


Fig. 15. Small-angle X-ray diffraction patterns of aTPU-PCL and aTPU-PCL:clay (97:3 wt %)

FT-IR spectra of aTPU-PCL and its nanocomposites are shown in Fig. 16. Three major bands regions of aTPU-PCL:clay nanocomposites can be seen in FT-IR spectra: free and hydrogen bonded N-H stretching, CH stretching, and free and hydrogen bonded carbonyl. The weak N-H stretch peak centered on 3333 cm^{-1} indicate the hydrogen-bonded urethane. The smaller peak at 3435 cm^{-1} consistent with stretching vibration of N-H.

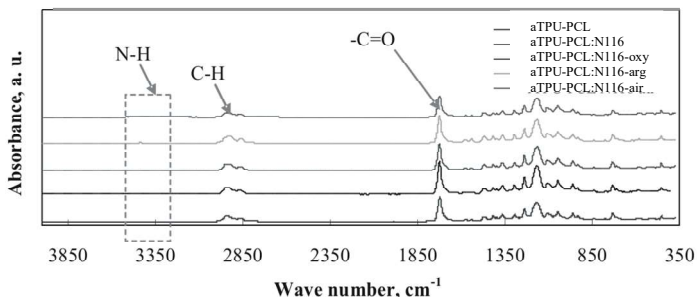


Fig. 16. FT-IR spectra of aTPU-PCL and aTPU-PCL:clay nanocomposites

The extent of hydrogen bonding was marginally affected by the clay particles. This is because clay particles interfere with hydrogen bond formation by urethane -NH groups.

The influence of the type and amount of calcium carbonate filler on the properties of the aTPU-PCL blend. It is known that calcium carbonate (CaCO_3) can exist in three crystallographic modifications, which are calcite, aragonite and vaterite (Jin et al., 2011). The SEM images of CaCO_3 used for the investigations are shown in Fig. 17. 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 $2.5 \mu\text{m}$, while size of aggregates are close to $30 \mu\text{m}$ (Fig. 17, a).

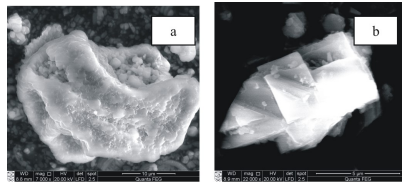


Fig. 17. SEM images of CaCO_3 fillers: (a) FH32, (b) 2TVH

It was found that aTPU-PCL begins to flow at 100°C temperature. The MFI values of aTPU-PCL change from $0.10 \text{ g}/10 \text{ min}$ to $93.20 \text{ g}/10 \text{ min}$ as temperature increases from 100°C to 240°C (Fig. 18). The above temperature of 260°C , thermal degradation of aTPU-PCL begins (Fig. 18). Comparison of the melt flow properties of pristine TPU-PCL and aTPU-PCL shows that the recycling increases MFI due to the chain scission during reprocessing of waste by two-roll mill. Though aTPU-PCL begins to flow at the same temperature as was obtained in the case of TPU-PCL (100°C), its degradation temperature is 20°C lower than that of pristine TPU-PCL.

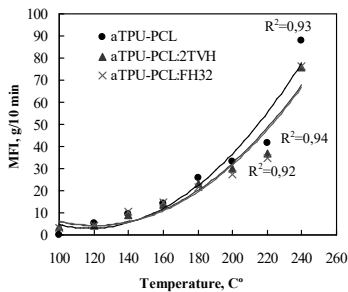


Fig. 18. Melt flow index of TPU-PCL and aTPU-PCL composites (aTPU-PCL: $\text{CaCO}_3 = 94:6 \text{ wt } \%$) versus test temperature (test load $P = 21.168 \text{ N}$)

Investigation of the influence of the CaCO_3 fillers size, type and amount on the mechanical properties of aTPU-PCL blend showed, that the aTPU-PCL:FH32 composites with vaterite shape fillers have higher influence on the mechanical properties of aTPU-PCL (Table 7).

Table 7. Mechanical properties of aTPU-PCL and its composites with CaCO_3

Composite	Filler content, wt %	Tensile strength σ , MPa	Elongation at break ϵ , %	Young's modulus E_Y , MPa
aTPU-PCL	0	23,1 ± 0,5	1877 ± 102	34,8 ± 2,0
aTPU-PCL:FH32	2	23,6 ± 0,6	2131 ± 104	32,8 ± 1,5
	4	22,9 ± 0,8	2111 ± 87	36,8 ± 2,1
	6	22,7 ± 0,5	2119 ± 98	37,2 ± 2,0
aTPU-PCL:2TVH	2	23,7 ± 1,1	2157 ± 86	36,6 ± 0,8
	4	22,5 ± 0,8	2065 ± 75	34,9 ± 2,1
	6	22,4 ± 0,6	2044 ± 97	31,1 ± 1,3

In order to better understand the effect of CaCO_3 fillers on the biodegradation of aTPU-PCL, the hydrolytic degradation tests were performed. The obtained data are presented in Fig. 19, where weight loss ΔW is plotted against the time of immersion. As can be seen, the ΔW increases as degradation time increase. The weight loss of aTPU-PCL only slightly depends on the type of filler used. The degradation of the aTPU-PCL 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) (Jin et al., 2011).

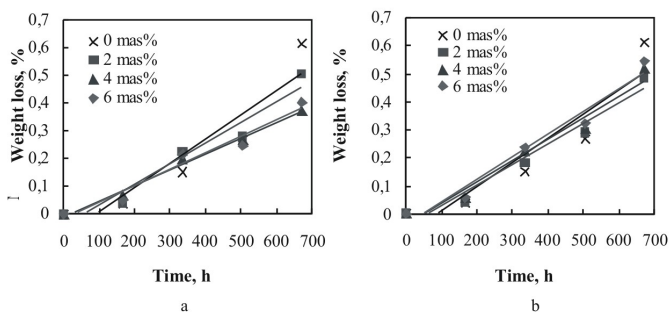


Fig. 19. Weight loss of aTPU-PCL with fillers: (a) 2TVH, (b) FH32

The fillers content practically does not influence ΔW values of aTPU-PCL. Only a slight influence of CaCO_3 content can be observed in the case of aTPU-PCL: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.

CONCLUSIONS

1. The investigations of the influence of mechanical reprocessing duration on the properties of thermoplastic polyurethane and polycaprolactone blend (TPU-PCL) show:
 - The secondary TPU-PCL blend, obtained by mechanical recycling of different orthopedic device manufacturing wastes, shows the mechanical properties close to the primary components due to similarities in component microstructures;
 - the flow properties of secondary TPU-PCL blend increase by ~11 times, is about 125 times higher than that of the primary component, when reprocessing time increases from 100 s to 1400 s;
 - the mechanical properties of the secondary blend improve with increasing the reprocessing time from 100 s to 1400 s. However, the elongation at break and Young's modulus of blend decreases up to 31 % up to 46 %, respectively, while strength remains almost unchanged, comparing to the primary blend components;
 - the mechanical recycling of secondary blends decreases their crystallinity up to 29 %, although blends maintain the crystal structure;
 - the hydrolytic resistance of secondary blends is lower than that of the primary components.
2. The investigation of the effects of organic modification of layered silicate fillers on the properties of secondary TPU-PCL blend at different reprocessing time, shows:
 - the secondary TPU-PCL blend with MMT modified by bis-(2-hydroxyethyl) methyl (hydrogenated tallow alkyl) ammonium cations formed exfoliated nanocomposite, and blend with the same content unmodified bentonite fillers formed intercalated composites at the reprocessing duration of 1400 s;
 - OMMT fillers decrease the crystallinity of secondary TPU-PCL blend in 32 %. Meanwhile the unmodified bentonite fillers decrease the blend crystallinity more significantly (up to 48 %);
 - both unmodified bentonite and OMMT fillers do not change the thermal, rheological properties of secondary TPU-PCL blend, but increase Young's modulus up to 25 %;
 - the layered silicate fillers facilitate hydrolysis reactions of secondary TPU-PCL blend. The degradation of the blend with MMT modified by bis-(2-hydroxyethyl) methyl (hydrogenated tallow alkyl)

ammonium cations proceeds significantly faster. In this case 5 wt% of filler decreases weight loss of secondary blend in 13 times after 670 h of degradation in NaOH solution. The hydrolytic resistance of blend with OMMT is significantly lower than that of the composites with unmodified bentonite.

3. The oxygen, argon and air plasma modified bentonite layers are completely separated and randomly dispersed in the secondary TPU-PCL blend matrix, showing the formation of exfoliated nanocomposite. This is due to the expansion of interlayer spacing and a weakening of interactions between the bentonite layers spacing after oxygen or argon plasma modification. Independently of plasma gases used, the addition of 3 wt % of plasma modified bentonite fillers cause the decrease of secondary TPU-PCL blend crystallinity in 9 %. The mechanical properties of nanocomposites depend on the used plasma gasses. The highest increase in the tensile strength (in 19 %) of secondary blend was observed by the using argon plasma modified bentonite. While the blend filled with oxygen plasma modified bentonite shows the highest elongation at break of 31 %.
4. Investigation of the influence of the calcium carbonate (CaCO_3) fillers size, type and amount on the properties of secondary TPU-PCL blend showed, that the mechanical and rheological properties of blend remain unchanged up to 6 wt % fillers content. However, CaCO_3 fillers tend to slightly increase the hydrolytic degradation rate of secondary blend up to 1.6 times. The modification of filler particles surface by stearic acid has no influence on the rate of degradation of the composite structure.

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REZIUMĖ

Termoplastinio poliuretano (TPU) su minkštaisiais polikaprolaktono (PCL) segmentais ir polikaprolaktono (PCL) mišiniai (TPU-PCL) yra plačiai taikomi medicinoje. Ortopedinėse įmonėse, gaminant ortopedinius įtvarus, lieka daug tarpšabloninių plastiko atliekų, kurios dažniausiai išmetamos į sąvartyną. PCL yra biologiškai skaidus polimeras, kuris suyra dirvožemyje ar komposte greičiau nei kiti plastikai, tačiau skaidydamasis TPU-PCL išskiria gamtai nuodingus junginius. Atlikus užsienio literatūros šaltinių apžvalgą, nerasta duomenų apie TPU ir PCL mišinio perdirbimo galimybes. Tokie tyrimai buvo atliekami Lietuvoje, tačiau išsamesnė perdirbimo parametru įtaka antrinio TPU-PCL mišinio struktūrai ir savybėms nebuvo tirta. Todėl tyrimai apie TPU ir PCL mišinio atliekų perdirbimo galimybes yra svarbūs.

Tyrimų rezultatai parodė, kad antrinis TPU-PCL mišinys yra homogeniškas, mišinio komponentai yra suderinami ir suformuoja vienfazę sistemą. Ilginant perdirbimo trukmę, mažėja antrinio mišinio kristališkumo laipsnis. Dėl oksidacijos reakcijų ir mechaninės makromolekulių destrukcijos antrinis mišinys greičiau lydosi, jo klampa mažėja, tampa lengviau jį perdirbti. Antrinis TPU-PCL mišinys pasižymi artimomis pirminiams komponentams mechaninėmis, deformacinėmis, šilumos savybėmis dėl jų mikrostruktūros panašumo. Antriniui TPU-PCL mišiniui būdingas didesnis skaidumas NaOH tirpale nei išeitinių mišinio komponentų. Tačiau problema yra tai, kad po perdirbimo, plastikas pasižymi prastesnėmis mechaninėmis savybėmis, lyginant su pradiniais komponentais. Šioms savybėms pagerinti turi būti naudojami sluoksninio silikato ir kalcio karbonato užpildai. Dažniausiai naudojamas sluoksninis silikatas yra montmorilonitas.

Kalcio karbonato mikromatmenų užpildai yra naudojami kaip inertiniai užpildai, o nanodydžio – kaip aktyvūs užpildai, gerinantys medžiagų fizikines savybes. Taigi, šiuos užpildus yra tikslinga panaudoti norint pagerinti antrinių polimerinių žaliavų savybes. Organiškai modifikuoto, sluoksninio silikato užpildai turi daug didesnę įtaką antrinių TPU-PCL mišinių savybėms. Plazma modifikuoti sluoksniniai silikatai pasižymi geresniu dispergavimo ir išsisluoksniavimo laipsniu mechaniškai perdirbto antrinio TPU-PCL mišinio matricoje, lyginant su nemodifikuotu užpildu. Gaunami eksfoliuotos struktūros TPU-PCL nanokompozitai, pasižymintys geresnėmis deformacinėmis savybėmis, mažesniu kristališkumu laipsniu. Sluoksninio silikato užpildų modifikavimas plazma yra gamtai nekenksmingas. Po apdorojimo žemos temperatūros oro,

deguonies ir argono plazma, užpildai geriau išsisluoksniuoja TPU-PCL mišinyje ir pagerina polimerinio kompozito savybes.

Darbo tikslas ir uždaviniai

Šio **darbo tikslas** – ištirti termoplastinio poliuretano ir polikaprolaktono mišinio antrinio panaudojimo ir savybių gerinimo užpildais galimybes.

Šiam tikslui pasiekti keliami tokie **uždaviniai**:

- nustatyti termoplastinio poliuretano ir polikaprolaktono mišinio atliekų mechaninio perdirbimo trukmės įtaką antrinių mišinių struktūrai ir savybėms;
- ištirti nemodifikuoto sluoksninio silikato bentonito, organiškai modifikuoto sluoksninio silikato montmorilonito ir kalcio karbonato užpildų įtaką antrinio termoplastinio poliuretano ir polikaprolaktono mišinio struktūrai ir savybėms;
- ištirti atmosferinio slėgio plazmos apdoravimo įtaką sluoksninio silikato bentonito užpildams;
- nustatyti antrinio termoplastinio poliuretano ir polikaprolaktono mišinio, užpildyto atmosferinio slėgio plazma apdorotais sluoksninio silikato bentonito užpildais, struktūrą ir savybes.

Darbo mokslinis naujumas ir praktinė vertė

Plastikų mechaninis perdirbimas, yra vienas paprasčiausių ir gamtai draugiškiausių, todėl šiame darbe siūloma termoplastinio poliuretano ir polikaprolaktono mišinio atliekas, gautas gaminant ortopedinius įtvarus, perdirbti naudojant šį būdą ir taip sumažinti didėjančią plastiko atliekų masę.

Termoplastinio poliuretano ir polikaprolaktono mišinių atliekų perdirbimas beveik nekeičia jo struktūros. Gauti antriniai mišiniai pasižymi geresnėmis reologinėmis savybėmis, tačiau, lyginant su pirminiais mišiniais, jiems būdinga mažesnė deformacinė jėga, standumas. Antrinių mišinių mechaninėms savybėms gerinti siūloma naudoti sluoksninio silikato bentonito ir organiškai modifikuoto montmorilonito užpildus. Sluoksninio silikato užpildai didina nanokompozitų skaidumo intensyvumą.

Siekiant pagerinti sąveiką tarp užpildo ir polimerinės matricos, siūloma sluoksninio silikato bentonito paviršių apdoroti atmosferinio slėgio argono, oro ar deguonies dujų plazma. Šis užpildų modifikavimo būdas yra gamtai nekenksmingas, pigus, tačiau paminėtina tai, kad šiuo metu naudojamas retai ir mažai tirtas.

Įvertinus termoplastinio poliuretano ir polikaprolaktono mišinių perdirbimo trukmės, ir deguonies, oro ar argono dujų plazma apdorotų užpildų įtaką antrinių mišinių mechaninėms savybėms, siūloma šiais

užpildais modifikuotas termoplastinio poliuretano ir polikaprolaktono mišinio atliekas pakartotinai panaudoti ortopedinių įtvarų gamybai.

Darbo aktualumas

Polimerinių atliekų antrinio panaudojimo galimybių tyrimai svarbūs tiek moksliniu, tiek praktiniu požiūriu. Atliekų panaudojimas kuriant naujas medžiagas turi ne tik ekologinę, bet ir finansinę naudą, nes tai kur kas pigiau nei sintetinti naujas polimerines medžiagas. Be to, užpildų taikymas leidžia po perdirbimo gauti polimerines medžiagas su tokiomis pačiomis mechaninėmis savybėmis kaip pradinės polimerinės medžiagos. Užpildų paviršiaus modifikavimas plazma pagerina sąveiką tarp užpildų ir polimerinės matricos, todėl polimero kompozitas pasižymi geresnėmis savybėmis. Tai leidžia išvengti užpildų modifikavimo cheminėmis medžiagomis. Todėl šie tyrimai ypač aktualūs moksliniu požiūriu.

Ginamieji teiginiai

- Antrinio termoplastinio poliuretano ir polikaprolaktono mišinio mechaninės savybės ir atsparumas hidrolizei priklauso nuo mechaninio perdirbimo trukmės.
- Organiškai modifikuoto montmorilonito užpildai mažina antrinio termoplastinio poliuretano ir polikaprolaktono mišinio atsparumą hidrolizei ir didina standumą.
- Sluoksninio silikato bentonito užpildų paviršiaus apdorojimas atmosferinio slėgio deguonies ir argono dujų plazma didina jo dalelių tarplokštuminį atstumą ir tokiu būdu gerina dispergavimo polimerinėje matricoje galimybes.
- Atmosferinio slėgio deguonies ir argono dujų plazma apdoroto sluoksninio silikato bentonito užpildai gerina antrinio termoplastinio poliuretano ir polikaprolaktono mišinio deformacines ir skaidumo savybes.

Darbo aprobacija

Eksperimentiniai tyrimai atlikti Kauno technologijos universiteto Dizaino ir technologijų, Cheminės technologijos fakultetuose bei Lietuvos energetikos institute.

Pagrindiniai darbo rezultatai yra paskelbti 9 publikacijose: iš jų 4 moksliniai straipsniai įrašyti mokslinės informacijos instituto (ISI) pagrindinio sąrašo periodiniuose leidiniuose, 1 straipsnis – ISI duomenų bazėse referuojamame konferencijų pranešimų leidinyje, 3 publikacijos – kituose recenzuojamuose mokslo leidiniuose ir 1 periodiniame straipsnių leidinyje. Rezultatai pristatyti 5 tarptautinėse ir 6 respublikinėse konferencijose.

Darbo sandara ir apimtis

Bendra darbo apimtis – 92 p. Darbą sudaro įvadas, literatūros apžvalga, metodikos ir tyrimo rezultatų skyriai, išvados, literatūros ir publikacijų darbo tema sąrašai. Darbe yra pateikti 64 paveikslai, 20 lentelių, 11 formulių ir 146 šaltinių literatūros sąrašas.

IŠVADOS

1. Ištyrus grįžtamojo perdirbimo trukmės įtaką antrinio termoplastinio poliuretano ir polikaprolaktono mišinio (TPU-PCL) savybėms, nustatyta:
 - skirtingų mechaninių savybių TPU-PCL mišinių atliekos plastikuojančioms šlytims sudaro antrinius mišinius, kurių savybės dėl komponentų mikrostruktūros panašumo, yra artimos pirminių komponentų savybėms visame tirtame perdirbimo trukmės intervale;
 - didėjant perdirbimo trukmei nuo 100 s iki 1400 s, antrinio TPU-PCL mišinio lydalo takumas padidėja ~11 kartų ir yra apie 125 kartus didesnis, lyginant su pradinio komponento takumu;
 - didėjant atliekų perdirbimo trukmei, antrinio TPU-PCL mišinio mechaninės savybės gerėja. Tačiau, lyginant su pirminiais komponentais, trūkimo ištįsa sumažėjo 31 %, Jungo modulis – 46 %, o stipris tempiant – nekinta;
 - antrinių TPU-PCL mišinių mechaninis perdirbimas sumažina jų kristališkumą iki 1,7 karto, tačiau mišiniai išlaiko savo kristalinę struktūrą;
 - antriniai TPU-PCL mišiniai yra ne tokie atsparūs hidrolizei, lyginant su pradiniais mišinio komponentais.
2. Ištyrus sluoksninio silikato užpildų modifikavimo įtaką antrinio TPU-PCL mišinio savybėms, esant skirtingai atliekų perdirbimo trukmei, nustatyta:
 - metil-bis(2-hidroksietil) taukų amoniūmą modifikuotų MMT užpildų dalelės visiškai išsisklaido ir pasiskirsto aTPU-PCL mišinio matricoje, tuo metu nemodifikuoto bentonito užpildų įmaišymo atveju gaunamas tik interkaliuotas kompozitas, esant TPU-PCL mišinio perdirbimo trukmei 1400 s;
 - organiškai modifikuoti montmorilonito (OMMT) užpildai sumažina antrinio TPU-PCL mišinio kristališkumą iki 32 % ir, didėjant maišymo trukmei, tolygiai mažėja. Tuo metu nemodifikuoti bentonito užpildai antrinio mišinio kristališkumą sumažina daugiau – iki 48 %;

- tiek organiškai modifikuoti, tiek ir nemodifikuoti bentonito užpildai nekeičia šiluminių, reologinių antrinio TPU-PCL mišinio savybių, tačiau didina mišinio Jungo modulį (iki 25 %).
 - sluoksninio silikato užpildai spartina antrinių TPU-PCL mišinių hidrolizės reakcijas. Didžiausiu hidrolizės intensyvumu pasižymi mišiniai su metil-bis(2-hidroksietil) taukų amoniu modifikuotu MMT užpildu. Šiuo atveju 5 mas % šių užpildų atliekų mišinio masės netektį padidina 13 kartų, lyginant su antriniais mišiniais be užpildų. Be to, mišinių su OMMT užpildais, hidrolizės reakcijos vyksta daug intensyviau nei nemodifikuoto bentonito panaudojimo atveju.
3. Deguonies, argono ar oro plazma modifikuotas bentonitas visiškai išsisluoksniuoja ir pasiskirsto antrinio TPU-PCL mišinio matricoje, gaunant eksfoliuotą nanokompozitą. Tai lemia argono ir deguonies plazmos modifikavimo metu padidėjęs bentonito dalelių tarplokštuminis atstumas. Nustatyta, kad įmaišius 3 mas % modifikuotų plazma bentonito užpildų, nepriklausomai nuo naudotos dujų plazmos tipo, antrinio TPU-PCL mišinio kristališkumas sumažėja 9 %. Tuo metu nanokompozitų mechaninės savybės priklauso nuo užpildų modifikavimui naudojamo dujų plazmos tipo. Nustatyta, kad tik argono plazma modifikuotas bentonitas padidina antrinio mišinio stiprį (iki 19 %), o deguonies plazma – deformacines savybes (31 %).
 4. Kalcio karbonato (CaCO_3) dalelių dydžio, tipo ir kiekio įtakos antrinio TPU-PCL savybėms tyrimai parodė, kad didėjant CaCO_3 užpildų kiekiui mišinyje iki 6 mas %, kompozito mechaninės ir reologinės savybės nekinta. Tačiau šie užpildai sumažina perdirbtų atliekų atsparumą hidrolizei iki 1,6 karto, o užpildo dalelių paviršiaus apdorojimas stearino rūgštimi, kompozicijos struktūros irimo greičiui įtakos neturi.

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