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Properties of Recycled Natural Fiber Reinforced Composites Materials

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The paper presents the results of the examinations concerning the properties of recycled polymer composites made of polylactide (PLA) and filled with various fractions from processing of fiber hemp. Filler in the form of hemp hurds and hemp straw was obtained from collaboration with Olimax NT Sp. z o.o. (Poland). Hemp hurds, hemp pulp, and hemp straw was dosed in the amount of 10% mass share of the mixture. Both polymer material and fillers were dried before the process and then the standardized samples were prepared using the injection molding technology. Tensile stress tests, hardness tests, and thermal properties tests were performed in order to determine the properties of molded pieces. After completion of primary tests, the samples were fragmented by means of the industrial low-speed mill. The obtained milling products were processed again using the injection technology, with process parameters the same as during primary processing. The obtained normalized samples were subjected again to the analysis of mechanical and thermal properties. Furthermore, the microscopic observations were performed in order to verify dispersion of the fillers in the polymer matrix.

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1. Introduction

Plastics represent the increasingly big part of the materials processed and used by human and widely used in the higher number of industries. The factors that determine their application include very good functional properties and low manufacturing costs, translating into low prices. Furthermore, the economy of manufacturing of polymer materials is also improved by the fact that the products are obtained using one-step technology without the need for performing additional finishing operations [1–10].

The most of the currently used thermoplastics are not biologically degradable. This results from their structure [5–8].

Using the biodegradable polymers offers advanced opportunities for "programming" the product life, which means that after the life end is reached, microparticles, affected by catalysts, start a dynamic division leading to degradation of polymers and its physical decomposition. Biodegradable polymers can be filled with selected auxiliary substances. These include organic colorants, mineral fillers and organic nucleating substances, fibers, nanofillers, etc. [10–16].

The examinations focused on the analysis of certain mechanical and thermal properties of composites made of polylactide filled in 10% by hemp hurds pulp and hemp straw pulp (Fig. 1).

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Fig. 1. Hemp hurds, hemp hurds pulp, and hemp straw pulp.

2. Description of the study

The aim of this study was to determine certain mechanical and thermal properties of the composite obtained based on PLA, hemp hurds, and hemp straw with different degree of fragmentation. Biodegradable polymer (polylactide) Biopolymer 4043D manufactured by NatureWorks LLC was used in the form of granules with white color.

Filler was provided by hemp hurds and hemp straw with different degree of fragmentation, from crops of the OLIMAX enterprises, initially cleaned and mechanically fragmented to the form presented in Fig. 1. (The dumbbell specimens were obtained.) The examinations were performed on two types of specimens made of non-filled PLA, which represented the reference point and PLA filled in 10% with hemp hurds, hemp hurds pulp, and hemp straw pulp. The second stage of the examinations involved mechanical recycling and re-processing of the moulded pieces made of these materials and comparison of the results. The material prepared in this way was injected using the KM65/160/C4 hydraulic injection molding machine (KraussMaffei). Processing parameters

Fig. 2. Molded piece from polylactide filled in 10% with hemp hurds.

Fig. 3. Molded piece from polylactide filled in 10% with hemp hurds pulp.

Fig. 4. Molded piece from polylactide filled in 10% with hemp straw pulp.

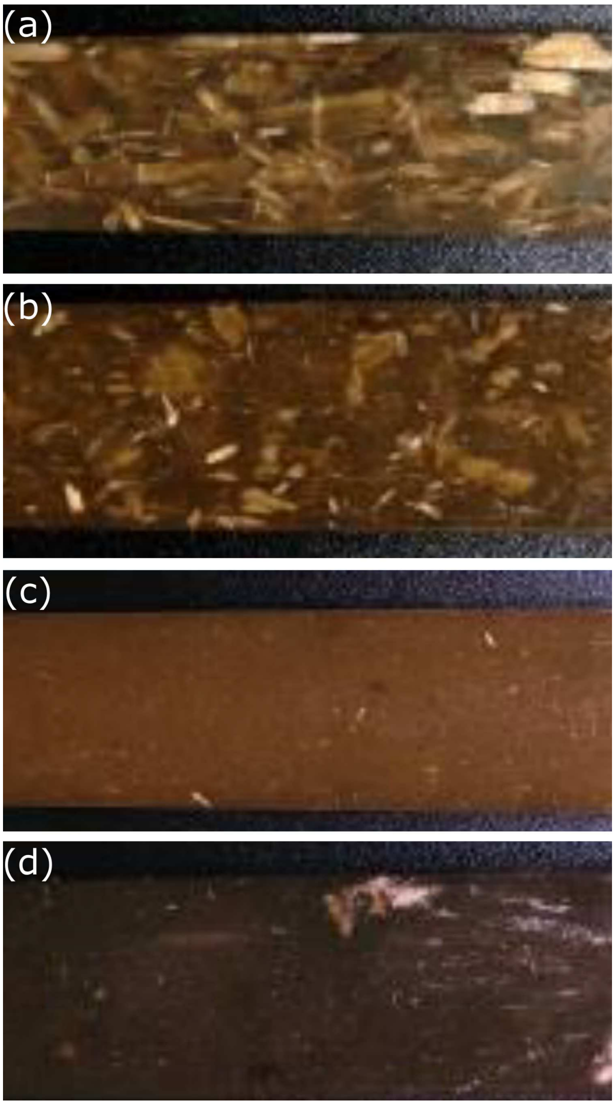

Fig. 5. Comparison of the surface and size of the filler for the materials studied. (a) Primary molded piece (hemp hurds), (b) molded piece after recycling (hemp hurds), (c) molded piece (hemp hurds pulp), (d) molded piece (hemp straw pulp).

for both non-filled and filled PLA were as follows: injection temperature 220 °C, mold temperature 40 °C, injection pressure 90 MPa, clamping pressure 60 MPa, cooling time 20 s, clamping time 10 s. The specimens were obtained using two-cavity mold. The obtained molded pieces are presented in Figs. 2–4 (PLA filled with hemp hurds and hemp hurds pulp and hemp straw pulp — type 1A normalized molded pieces).

Another stage of the study was microscopic observations of the specimens. This analysis consisted in observation of the surface of molded pieces using the optical microscope (the KEYENCE VHX-900F microscope with VHZ00R lens, Fig. 5). Microscopic observations were conducted at ten-times magnification. The primary molded piece contains large size fragments of the hemp hurds which was not fragmented during the homogenization process. Recycling of molded pieces leads to a substantial fragmentation of hemp hurds and its better dispersion in the polymer mass. An even dispersion of the filler in the polymer mass can be observed for the molded pieces filled with hemp hurds pulp, whereas the hemp straw pulp shows the tendencies for forming clusters.

3. Results

3.1. Hardness measurements using the ball indentation method

Hardness evaluated by the ball indentation method was measured on the measurement station composed of ball hardness tester with spherical indenter (diameter 5 mm). The examination was performed based on the standard PN-EN ISO 2039-1:2004.The measurements were performed for the specimens made of non-filled PLA (series I), for the specimens of PLA with addition of hemp hurds (series II), reprocessed specimens filled with 10% of hemp hurds (series III), specimens re-processed specimens filled with 10% of hemp straw pulp (series IV) and hemp straw pulp (series V, also 10%). Figure 6 presents the results of the examinations of hardness measurements using ball indentation method.

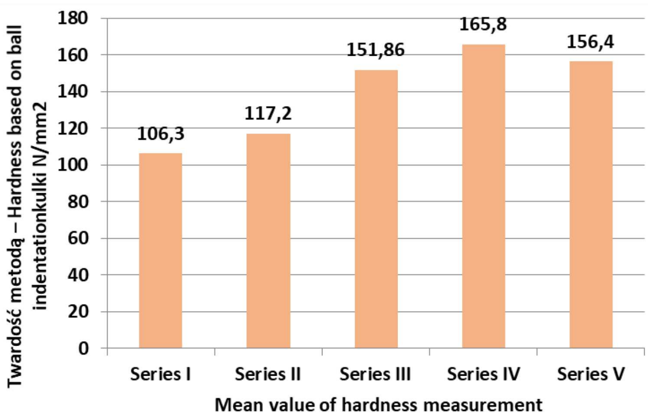

Fig. 6. Results of hardness measurements using ball indentation method.

The results represent the mean value of five measurements for five analysed molded pieces. The reduced load was determined in accordance with the formula:

$$F_r = F_m \frac{\alpha}{(h-h_r)+\alpha} = F_m \frac{0.21}{h-0.25+0.21},$$

where F_m — measuring load of the indenter [N], h_r — reduced depth of imprint (= 0.25 mm), $h = h_1 - h_2$ — the depth of the imprint, in mm, after the correction for the deformation of the frame, h_1 — the depth of the indenter impression under the applied load, h_2 — deformation of the instrument under the measuring load, α — the ratio of the reduced load to the indenter h_r:

$$HB = \frac{1}{5\pi}\frac{F_r}{h_r}$$

where HB — hardness determined by pressing the ball, F_r — reduced measuring load, h_r — reduced depth of imprint.

3.2. Determination of mechanical properties during static tensile strength test

Mechanical properties at static tensile strength test were determined using a universal strength tester (Hegewald&Peschke inspektdesk 20). The examination was performed based on the standard PN-EN ISO 527-1:2012. The specimens were examined similarly to the determination of hardness using the ball indentation method. Figure 7 presents the results of determination of mechanical properties during static tensile strength test. The highest value was found for non-filled PLA specimens. The lowest value was documented for the specimens filled with 10% hemp hurds and subjected to mechanical recycling and reprocessing. Filling the polymer with hemp pulp and subjecting it to recycling through reduction of particles did not lead to a substantial decrease of properties. The results obtained can be connected with mechanical shortening of macroparticle chains during recycling. The size of the filler is also critical.

$$\sigma = \frac{F}{A},$$

where σ is the specified stress value, expressed in MPa, F is the corresponding force, measured in newtons, A is the initial cross-section of the specimen, expressed in square mm.

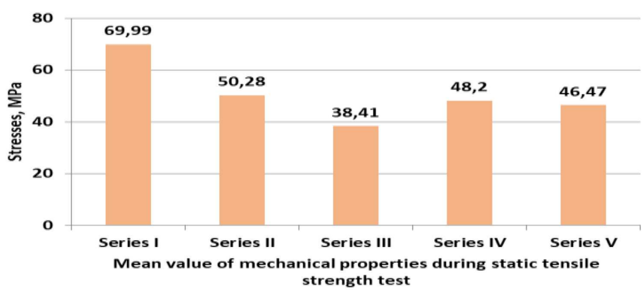

Fig. 7. Mechanical properties for static tensile strength test.

3.3. Analysis of thermal properties using differential scanning calorimeter

In order to determine thermal properties, we used differential scanning calorimeter DSC 214 Polyma (NETZSCH). The examination was performed based on the standard PN-EN ISO 11357-1:2016-11.

The total quantity of heat transferred, Q, corresponds to the time integral to the heat flow rate

$$Q = \int \frac{\mathrm{d}Q}{\mathrm{d}t}\,\mathrm{d}t.$$

Heat flow rate is a quantity of heat transferred per unit time ($\mathrm{d}Q/\mathrm{d}t$), expressed in watts (W) and miliwatts (mW). The results are shown in Fig. 8.

ΔQ is a quantity of heat absorbed (endothermic, ΔQ positive) or released (exothermic, ΔQ negative) within a specified time t, and temperature T, range by a specimen undergoing a chemical or physical change or temperature change.

Specific heat capacity at constant pressure is a quantity of heat necessary to rise the temperature of unit mass of material by 1 K at constant pressure.

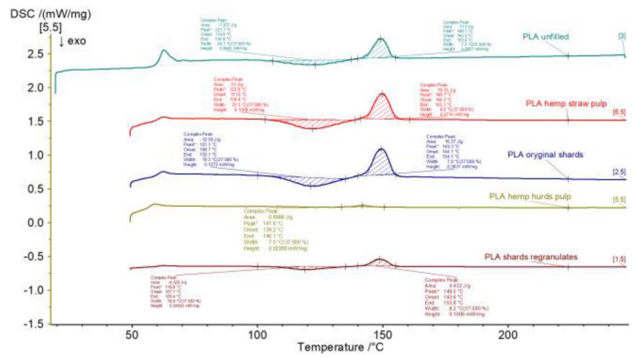

Fig. 8. Thermograms obtained for the materials studied.

The examinations demonstrated that polylactide filled in 10% with hemp hurds, hemp hurds pulp, and hemp straw pulp with reprocessing shows a reduction of selected mechanical and thermal properties. The analysis revealed only an increase in hardness of reprocessed material with respect to non-filled polylactide and polylactide filled with 10% of hemp hurds and not subjected to reprocessing. The factor that impacts on this phenomenon is recycling and reprocessing during which hemp hurds are more fragmented in the mill and dispersed in the polymeric mass during homogenization in the plasticizing system. Determination of the mechanical properties for static tensile strength test demonstrated a substantial decline in the load for hemp hurds subjected to recycling. Hemp hurds pulp and hemp straw transferred lower load, but this decline was not as significant. The highest value was found for the specimens made of non-filled PLA, whereas the lowest values were obtained for the molded pieces made of PLA filled in 10% with hemp hurds and subjected to recycling.

Similar relationships can be observed for the analysis of thermal properties. The molded pieces filled with hemp hurds and subjected to mechanical recycling showed a substantial decline in cold crystallization enthalpy and melting enthalpy, which can suggest the shortening of polymer chains and reduction in intensity of phenomena connected with formation of partially crystalline phase.

4. Summary

The obtained results suggest unequivocally the necessity for continuation of the research and more extensive analysis of properties of these composites with consideration for different amounts of filler and additional research that allows for the determination of the effect of environmental factors on these composites and, consequently, indication of the areas of their future application.

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