Influence of water absorption on chosen strength properties of single-polymer polyester composites

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DOI: dx.doi.org/10.14314/polimery.2018.4.2

Abstract: Investigations of the selected properties of single-polymer polyester composites (SPC) in dry condition and immersed in water are presented. Materials were tested for possible applications in shipbuilding. Water absorption till saturation limit was examined, at temperatures of 3, 23 and 100 °C, through the determination of water diffusion coefficient. Some material properties were determined through impact resistance tests of materials varying in fiber content [0 (A), 5 (B), 10 (C), 15 (D), 20 wt % (E)]. The highest impact resistance (6 J/cm^2) was found for the composite with more than 15 % of reinforcement in dry condition.

Keywords: polyesters, single-polymer composites, impact resistance, water absorption.

Wpływ absorpcji wody na wybrane właściwości wytrzymałościowe jednoskładnikowych kompozytów poliestrowych

Streszczenie: Zbadano wybrane właściwości mechaniczne jednoskładnikowych kompozytów poliestrowych o zawartości masowej włókien 0 % (A), 5 % (B), 10 % (C), 15 % (D), 20 % (E), w stanie suchym i po zanurzeniu w wodzie, w celu określenia możliwych zastosowań takich materiałów w przemyśle stoczniowym. Współczynnik dyfuzji wody wytworzonych kompozytów oznaczano na podstawie jej absorpcji do stanu nasycenia, w temperaturze 3, 23 i 100 °C. Przeprowadzono testy udarności Charpy'ego próbek kompozytów o różnym udziale włókien. Stwierdzono, że najlepszą udarność (6 J/cm^2) wykazują kompozyty w stanie suchym z zawartością włókien powyżej 15 % mas.

Słowa kluczowe: poliestry, jednoskładnikowe kompozyty polimerowe, udarność, absorpcja wody.

Composites have been used since the civilization began to develop, however, mass production of polymer matrix composites started in the second half of the 20th century. Dynamic increase in the production of such materials was primarily spurred by the development of production technology and polymer processing as well as huge increase in the demand for this type of material in many areas of life [1–9].

Recent years have brought a wider scope of applications of polymer matrix composites. They are used as construction material in automotive industry (*e.g.*, car body and equipment components) as well as in railway industry (interior, wagon roofs, cargo tanks), aviation (fuselages, fuel tanks, nose and stabilizer ends) or shipbuilding (boat hulls, superstructures). Widespread use of these materials is associated with the trend of reducing the weight of vehicles in order to improve their performance and reducing production costs, while maintaining good mechanical properties, high corrosion resistance, simplicity of forming, absorption of mechanical vibrations, dielectric and low heat conductivity properties [5, 7, 8, 10, 11].

Maritime market uses yearly about 90 thousand tons of composite materials produced in Poland, and 95 % of total demand are fiber reinforced composites for boats built, of this 45 thousand tons per year is used for the production of small boats, less than 25 m in length, and small leisure boats, including canoes [8, 9, 12]. An interesting alternative is composites reinforced with metallic amorphous materials, which exhibit excellent mechanical properties and in special cases magnetic as well [13, 14].

The increasing use of composite materials with polymer matrix, as well as environmental policy in the European Union, caused that the problem of waste management cannot be longer ignored, and countries, governments, and companies must challenge with effective waste management.

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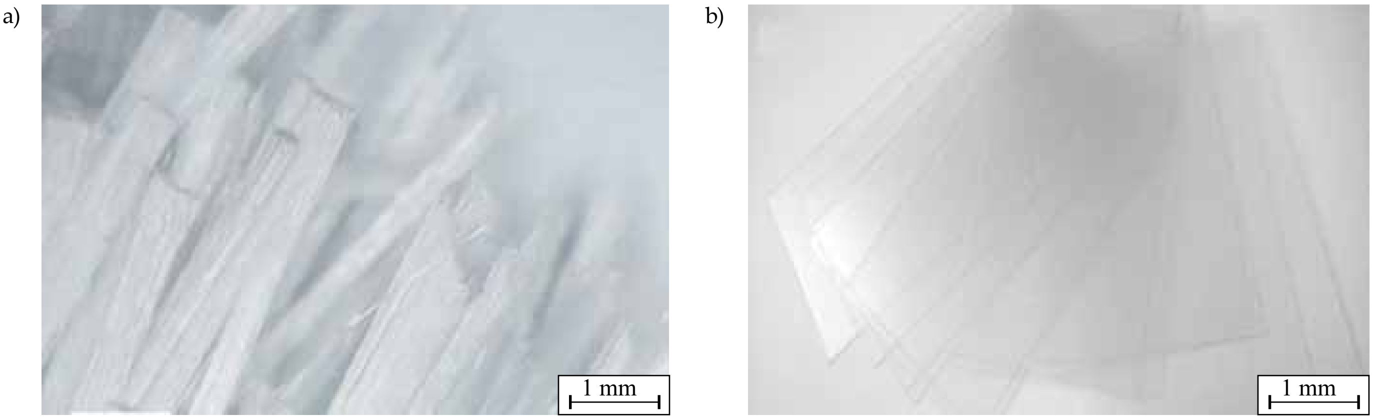

Fig. 1. Components of single-polymer composite material: a) PET – reinforcement, b) PET-G – matrix

Currently waste composites go to landfills or are burned in municipal waste incineration plants. During the last years the costs of waste storage and incineration have been growing. Therefore, demand for easy-to-recycle composite materials significantly increased [1–3, 5, 8, 9, 12]. In order to fulfill EU environmental policy requirement, single-polymer composites (SPC), in which both the matrix and the reinforcement are made of the same or similar polymer material, gained interest of manufacturers. In this type of composite, components may differ from each other in molecular weight, density or degree of branching. In contrary to traditional heterogeneous composite materials, the advantage of SPC is its uniformity in terms of chemical properties, where matrix and reinforcement differ mainly in mechanical and heat properties. Thus, there is no need to separate these components during recycling, which greatly simplifies the process and reduces the associated environmental impact [1–12].

The industrial use of composite materials with polymer matrix requires the studies of effect of such factors as morphology, structure, interaction between phases and chemical structure of components on their performance, *e.g.*, water absorption. In this paper authors aim to compare the capacity of single-polymer polyester composites with varied reinforcement contents to absorb water and how this effects on chosen mechanical properties. It is a response to market demand for reinforced materials having desired mechanical characteristics, combined with their great advantage, *i.e.*, environmentally friendly full recycling after use.

EXPERIMENTAL PART

Materials

Single-polymer polyester composites consist of reinforcement phase [poly(ethylene terephthalate), PET] – stretched polyester fiber with enhanced strength and low shrinkage, purchased from Polish company TORLEN (Fig. 1a), and matrix material: colorless polyester film [poly(ethylene terephthalate) glycol-modified, PET-G] 0.5 mm thick, from VIVAK (Fig. 1b).

The properties of the raw materials used are shown in Table 1.

Samples preparation

Examined materials have been produced by film-stacking on the test bench. This method involves placing the reinforcing component between two films (the matrix, PET-G) made of the same polymer as the reinforcement (PET) but having a lower melting point. Then hot pressing enabling plasticizing the film without melting the reinforcing phase was applied. Applied pressure must be sufficiently high for the molten polymer matrix in order to completely infiltrate empty spaces between the polyester fibers. Further, in order to avoid deterioration the properties of fiber reinforcement, very fast heating and cooling were used. Process of this composite manufacturing may be divided into the several stages (Fig. 2): preparation of reinforcement and matrix phases, drying, pressing (two stages), cooling, removal of the product from the mold, and finishing.

In order to carry out the experiments five types of composite plates size 150 × 100 × 1 mm and different weight percentage of reinforcement: 0 % (A), 5 % (B), 10 % (C), 15 % (D) and 20 % (E) were used. Experimental part of the research consists of determination of water absorption and impact resistance by Charpy method carrying out due to assess the optimum reinforcement of the composite phase fraction for possible applications in shipbuilding.

Table 1. Short specification of the materials [15, 16]

Phase	Material	Density g/cm^3	Tensile strength	Melting temperature °C	Water absorption after 24 h, wt %
Reinforcement	PET	1.37	60 cN/tex	262	–
Matrix	PET-G	1.27	53 MPa	192–222	0.22

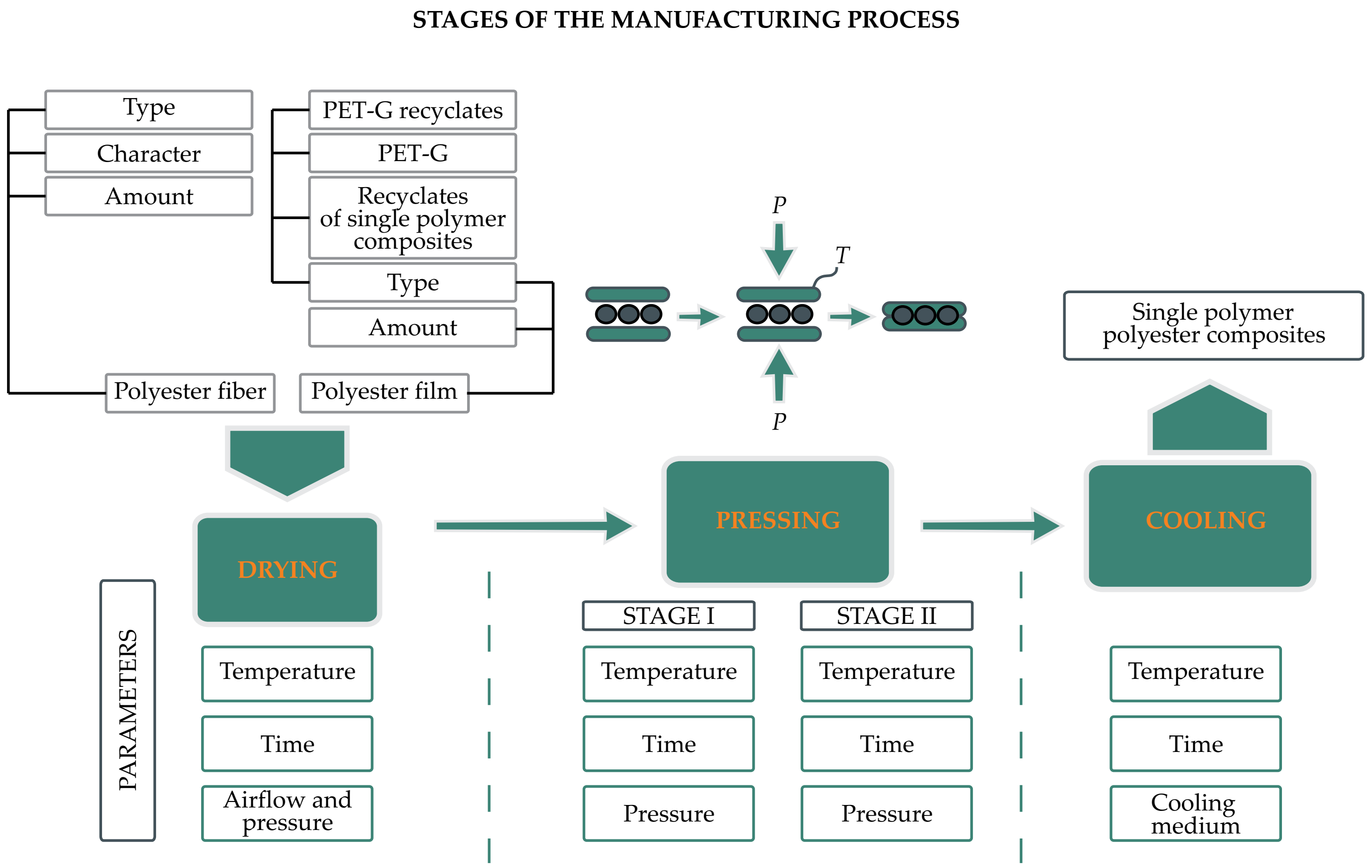

Fig. 2. The stages of single-polymer polyester composite manufacturing

Methods of testing

Determination of water absorption

The determination of water absorption was carried out using the weight method. This method was chosen because of its widespread application, recognized as recommended method for comparative studies of different materials. The method is covered by the PN-EN ISO 62:2008 standard.

Before the measurement, the sample was dried at 60 °C for 24 hours, then cooled down in a desiccator and weighed to the nearest 0.1 mg. The measurements were performed in distilled water, for square samples having a side of 100 ± 1 mm at temperatures: 3, 23 and 100 °C. The samples were weighed every 30 min. Water absorption was calculated using the Formula (1):

$$c = \frac{m_2 - m_1}{m_1} \cdot 100\ \% \qquad (1)$$

where: c – absorption of water [wt %], m_1 – sample weight after drying [g], m_2 – saturated sample weight [g].

If we assume that temperature and humidity are constant, the diffusion coefficient (D) in a plate with infinitely large opposite surfaces, where diffusion runs across the thickness of the composite, is expressed by Formula (2):

$$D = \pi \cdot \left[\frac{h}{4 \cdot M_m}\right]^2 \cdot \left[\frac{M_1 - M_2}{t_1^{1/2} - t_2^{1/2}}\right]^2 \qquad (2)$$

where: D – diffusion coefficient [mm²/s], M_m – water content corresponding to saturation [%], M_1 – percentage of water absorbed in time t_1 [t_1 in s], M_2 – percentage of water absorbed in time t_2 [t_2 in s], h – sample thickness [mm].

Impact resistance determined by the Charpy test method

Impact resistance test has been chosen as a measure of degradation of tested composites. Impact resistance was determined by the Charpy test method in accordance with PN-EN ISO 179-1:2010 standard. The samples tested for impact resistance were bar shape type, without a notch, cooled with liquid nitrogen.

The results for impact tests were calculated from Formula (3):

$$a_{cU} = \frac{E_c}{h \cdot b} \qquad (3)$$

where: a_{cU} – impact resistance [J/cm²], E_c – corrected energy absorbed during sample fracture [J], h – thickness of profile for tests [cm], b – width of profile for tests [cm].

RESULTS AND DISCUSSION

Water absorption was calculated using the Formula (1) and the results are shown in Fig. 3.

Figures 4–6 depict water absorption by composites with different fraction of reinforcements. The water dif-

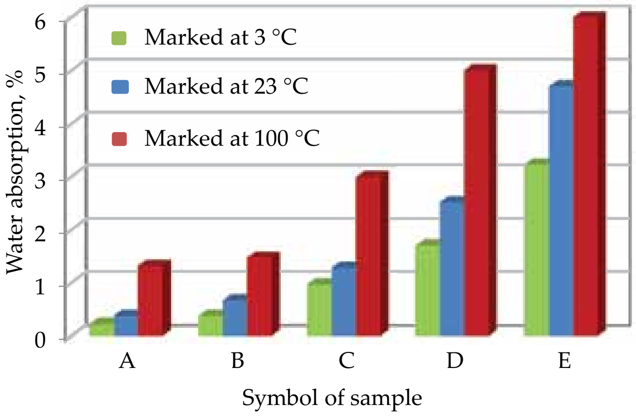

Fig. 3. Water absorption by single-polymer polyester composite reinforced with oriented fiber

fusion coefficient was determined based on these charts and 2nd Fick's law (Fig. 7). The largest increment of the water absorption was observed for specimen E, with 20 % of reinforcement, in 100 °C, due to the delamination process, caused by boiling water, and this is related to the phenomenon of reducing the viscosity of water as the temperature increases.

Poly(ethylene terephthalate) glycol-modified is a polymer material characterized by low water absorption. According to manufacturer's information water absorption by PET-G immersed in cold water may amount to approximately 0.2 % [15]. Therefore, the maximum values of water absorption in carried out tests obtained for pure matrix material equal 0.22, 0.38 and 1.32 % seem to be justified. We can also see (Fig. 3) that PET fibers introduced into the matrix increased the water absorption of the composite. The higher weight content of reinforcement, the higher water absorption is. Water diffusion through the interfacial boundary is facilitated due to boundary incoherence. The diffusion runs along and across the boundary due to its porosity. The phenomenon is also confirmed by results of water diffusion coefficient for the tested materials (Fig. 7). The water diffusion coefficients, tested at higher temperature for pure epoxy resin and [17] epoxy laminate reinforced with Kevlar fiber [18] are, respectively, $3 \cdot 10^{-7}$ and $20 \cdot 10^{-7}$ mm^2/s. Therefore, the values obtained in this study, Fig. 7, indicate a moderate rate of water diffusion, lower in composites with low reinforcement content and lower temperature of the sample. In case of materials intended for components working constantly immersed in water these data are of less importance than for composites used in the aviation industry or for structures subjected to cyclic absorption/desorption of water. Additionally, it has been observed that temperature has negative effect on esthetical and utility properties of the tested materials. At a temperature of 100 °C the transparency decreased as

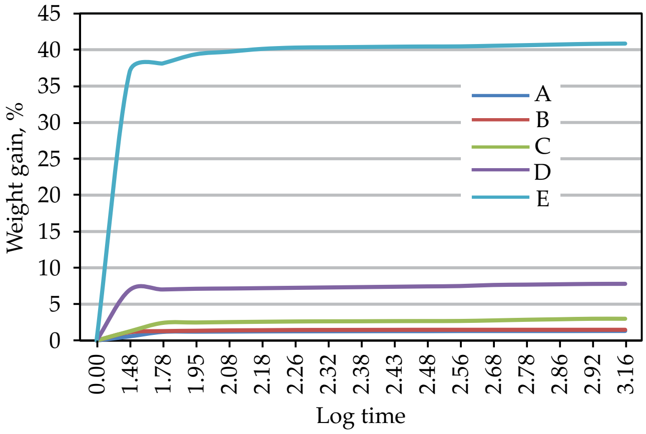

Fig. 4. Water absorption curves for composites tested at 100 °C

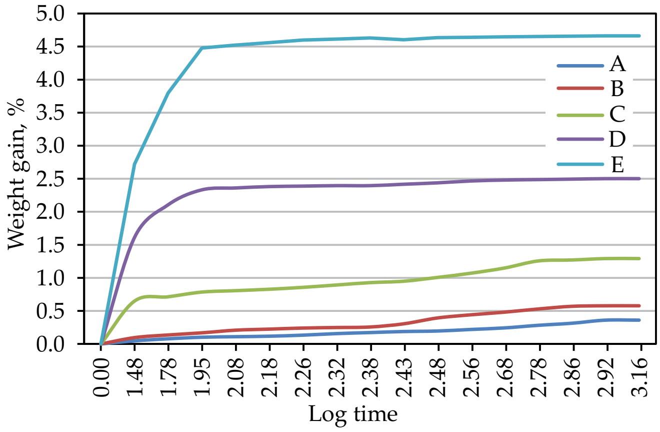

Fig. 5. Water absorption curves for composites tested at 23 °C

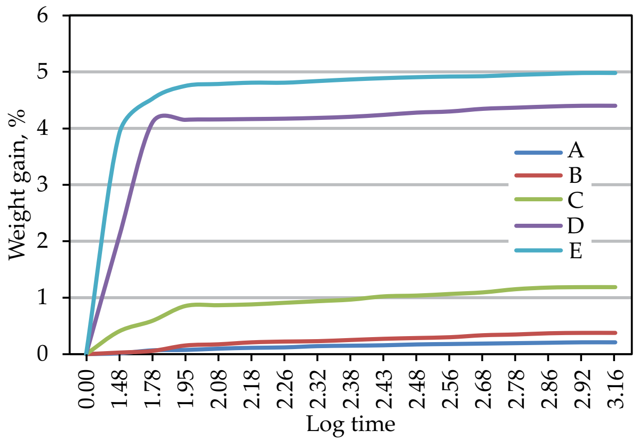

Fig. 6. Water absorption curves for composites tested at 3 °C

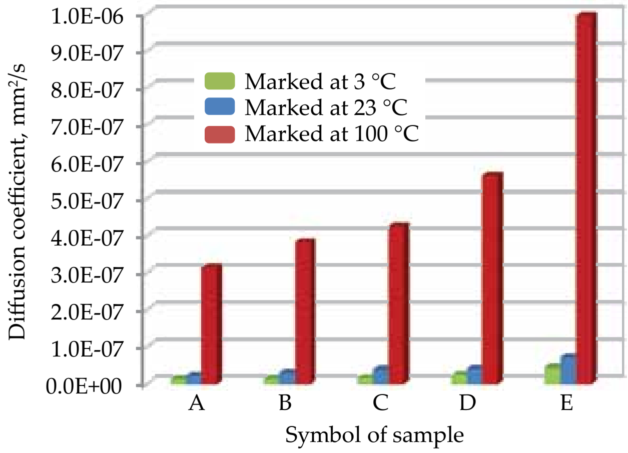

Fig. 7. Diffusion coefficient of water for composites with different content of the reinforcement phase

Fig. 8. Examples of delamination of composite materials (with 15 wt % content of reinforcement) resulting from the action of boiling water

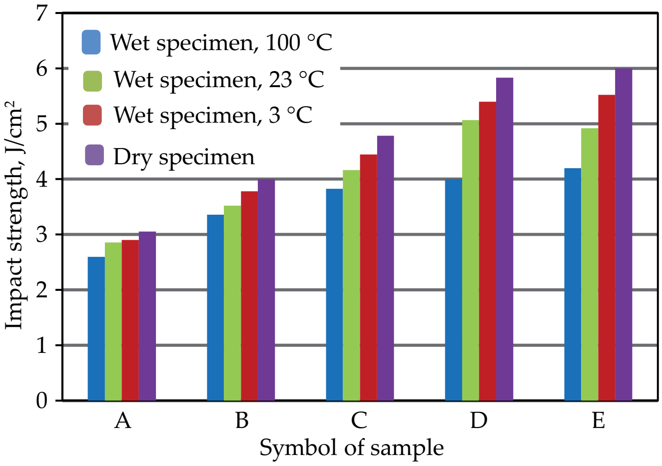

Fig. 9. Results of the Charpy impact test

the material surface grew dull. Furthermore for composites with the 15 and 20 wt % of reinforcement (specimens D and E), the material was observed to deteriorate due to delamination (Figs. 4 and 8) caused by boiling water. This is probably due to water absorption by fibers, which undergo swelling and change their dimensions, and due to the difference in water absorption by the matrix and the reinforcement, leading to stresses at the fiber-matrix boundary. Visible defects in the material saturated with water significantly accelerate destruction processes under impact loads.

The results of the Charpy impact test are shown in Fig. 9. As can be observed on the chart, the toughness changes depending on the fraction of the reinforcement phase and water absorption conditions. Comparison of obtained results shows (Fig. 9) that as a result of destruction caused by hot water the material lost its impact resistance even by about 30 % in comparison to its value for the dry composite with 20 wt % of reinforcing fibers.

However, the addition of reinforcement phase for dry samples causes even increase of impact resistance up to 200 % in comparison to matrix material without the reinforcement. Mechanism of material destruction as the result of impact test in case of material without reinforcement takes place through stretching (Fig. 10a) while composite materials were delaminated (Fig. 10b).

CONCLUSIONS

Materials with smaller weight content of reinforcement have lower water absorbing capacity and impact resistance compared to unsaturated material. Distilled water was used in tests to minimize the influence of other components (occurring in natural reservoirs) on the behavior of tested composite materials. In further researches, the authors will take into account natural environment of floating structures, *i.e.*, fresh and sea water, and ambient temperature, and their influence on the structure and pro-

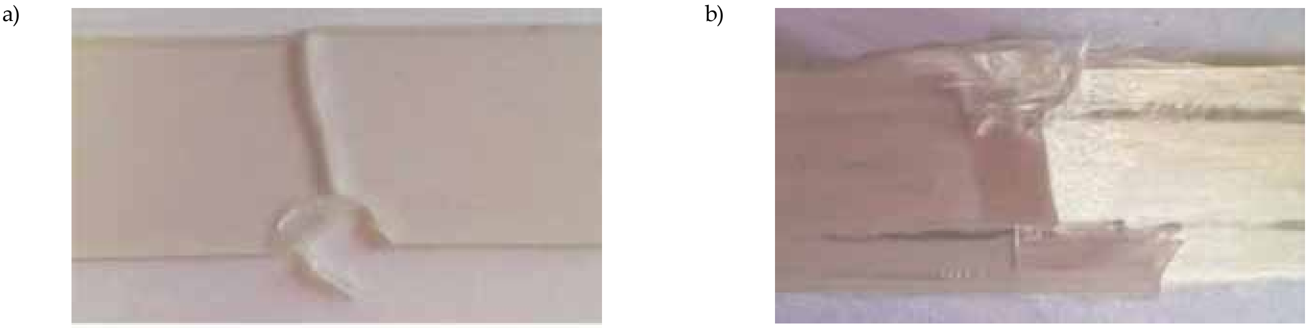

Fig. 10. Images of a sample after impact resistance determination: a) PET-G, b) specimen E (composite PET-G with 20 wt % of PET)

perties of the manufactured material, and fuzzy approach in the statistical analysis of obtained experimental results will be applied [19]. Taking into consideration the results of this study, we can state that the examined composites, particularly those with 15 % or more weight fraction of reinforcement phase, do not have satisfactory properties in saturated condition and further research will be done after the modification of manufacturing parameters, guaranteeing better saturation of fibers by the matrix or by inclusion of additional, pro-adhesive treatment.

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Received 22 VI 2017.

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