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THERMAL, SURFACE AND MECHANICAL PROPERTIES OF PCL/PLA COMPOSITES WITH COCONUT FIBRES AS AN ALTERNATIVE MATERIAL TO PHOTOPOLYMER PRINTING PLATES

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Abstract: In this paper, methods of thermal, mechanical and surface analyses of biodegradable PCL/PLA composites with the addition of different concentrations of coconut fibres were performed. The aim was to assess the potential of these composite materials for the relief-printing plates as an alternative to classical photopolymer materials. Differential scanning calorimetry, surface free energy calculations and hardness measurements were performed on the samples. Results have shown that most thermal transitions that are characteristic for PLA and PCL do not take place in the area of temperatures applicable in the printing process. Most thermal transitions were not affected by the addition of coconut fibres. Coconut fibres in the composite structure contributed to the increased hardness of the material. Moreover, the hardness range of the prepared PCL/PLA composites was within the range of some classic photopolymer printing plates. By adding coconut fibres in higher concentrations, surface free energy of the materials decreased, which enables a wider application of the material for the production of printing plates. From the obtained results it can be concluded that there is a potential for the use of PCL/PLA biodegradable composite materials in the manufacture of various relief-printing plates for different printing techniques (letterpress, embossing, label printing).

Keywords: biodegradable material; coconut fibres; PCL; PLA; relief printing

1 INTRODUCTION

The application of biodegradable materials in the past years has increased in various industries, from the medical, automotive and agricultural applications to graphic technology, which uses a large proportion of biodegradable materials, primarily in the development of packaging and 3D printing. In the production of printing plates, biodegradable materials were used in the beginning of the development of relief, specifically flexographic printing, when the printing plates were made of rubber. In the middle of 20th century, synthetic polymers have been introduced to graphic technology and quickly replaced natural materials. Until today, most printing plates for various types of relief printing are produced using synthetic photopolymer materials. Printing plates made of photopolymer materials differ in composition, hardness and thickness depending on the printing substrate, the image to be printed and used printed ink. There are three main types of printing inks: solvent-based, water-based and UV-curable, so it is important to choose the printing plate material that will be compatible with the printing ink.

Biodegradable materials are subject to conversion process to water, biomass, carbon dioxide or methane, affected by micro-organisms. They can be of natural or synthetic origin. The process of biodegradation of materials consists of two phases. The first stage is the reduction of the polymer chain by breaking carbon bonds in the conditions of heat, humidity and the presence of microorganisms. The second phase of biodegradation begins when low-molecular carbon chains become energy sources for microorganisms.

Polycaprolactone (PCL) (Fig. 1) is a biodegradable polymer of synthetic origin. It was synthesized in the early 1930s. It is a hydrophobic and a semi-crystalline polymer. Its crystallinity is reduced by the increase in molecular mass. It has a low melting point, at 60 °C, and the glass transition temperature of −60 °C. In order to increase the resistance to cracking it can be mixed with other polymers, such as cellulose propionate, cellulose acetate, butyrate and polylactic acid.

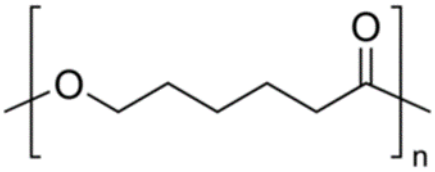

Figure 1 Structural formula of PCL [1]

Because of its properties, it has great potential for use in medical purposes where it is most explored in the field of artificial tissue creation. PCL is biodegradable in nature by bacteria and fungi, but is not degradable within a human or animal organism because of the lack of certain enzymes. Pure PCL requires two to four years to completely disintegrate, depending on the molecular weight of the polymer [2].

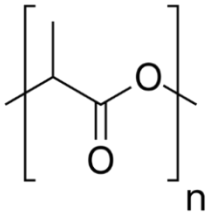

Figure 2 Structural formula of PLA [4]

Polylactic acid (PLA) (Fig. 2) is one of the most widely used biodegradable aliphatic polymers today. It was discovered in the 19th century. It is classified as

thermoplastic polyester. It can be obtained from lactic acid by the fermentation of agricultural crops such as maize. The melting temperature of PLA is 170 °C, while the glass transition temperature is about 60 °C. It is thermally unstable, and above the melting temperature, its thermal degradation begins [3].

PLA is soluble in chlorinated solvents, benzene, tetrahydrofuran and dioxane [5]. The time of biodegradation of polylactic acid in commercial composting plants is from 3 to 6 months [6]. Share of PLA is growing in the production of environmentally friendly packaging materials. It is also used in medicine to make bolts that are embedded in the joints, knees, arms, and rods for ligaments [7]. In 2012, about 180 thousand tons of PLA were produced, and by 2020 this figure would reach up to one million tons in one year [8].

The aim of this paper is to assess the applicability of the environmentally friendly printing plate made of PCL/PLA composites an alternative to conventional photopolymer materials.

Specifically, the new approach to the printing plate production primarily intended for embossing will be achieved through the adjustment of the composition of mixture of biodegradable polylactic acid (PLA) and polycaprolactone (PCL) to meet the necessary qualitative properties. In addition, natural coconut fibres will be added to the produced material in order to improve the mechanical properties of the polymer composite needed for the usage as a printing plate material.

2 EXPERIMENTAL RESEARCH

2.1 Preparation of samples

For this research, 16 PCL/PLA composite samples were prepared (Tab. 1). They were mixed in the Brabender kneader. Weight of all the samples was 40 grams because that is the volume which kneader can take in. The kneader consists of two connected chambers in which the rollers rotate in the opposite direction with narrow interspace along the wall. Walls and rollers are heated by heater.

The samples were placed in the kneader at a temperature of 190 °C because at that temperature the complete melting of PLA will occur. The kneader speed was 60 rpm. The samples were mixed for 5 minutes after which they were taken away and cut into pieces (Fig. 3). Afterward, the tiles were made of cut samples in press at a temperature of 190 °C and a pressure of 16 MPa. The dimensions of tiles were 10 × 10 cm. The pressing procedure lasted for 7 minutes - 2 minutes of preheating and 5 minutes of pressing. Obtained tiles were ready for further tests after cooling. From the tiles, the samples of weight of about 10 milligrams were cut for the differential scanning calorimetry (DSC). For measuring the contact angle and hardness, 1 × 10 cm samples were cut.

Figure 3 Cut samples for press

Table 1 List of the samples

Sample number	Sample name
1	PCL-0
2	PCL + 0.5 % of fibres
3	PCL + 1.5 % of fibres
4	PCL + 3 % of fibres
5	PCL/PLA 90 %/10 %
6	PCL/PLA 90 %/10 % + 0.5 % of fibres
7	PCL/PLA 90 %/10 % + 1.5 % of fibres
8	PCL/PLA 90 %/10 % + 3 % of fibres
9	PCL/PLA 80 %/20 %
10	PCL/PLA 80 %/20 % + 0.5 % of fibres
11	PCL/PLA 80 %/20 % + 1.5 % of fibres
12	PCL/PLA 80 %/20 % + 3 % of fibres
13	PCL/PLA 70 %/30 %
14	PCL/PLA 70 %/30 % + 0.5 % of fibres
15	PCL/PLA 70 %/30 % + 1.5 % of fibres
16	PCL/PLA 70 %/30 % + 3 % of fibres

2.2 Methods of measurement and analysis

Methods of measurement and analysis used in this paper were differential scanning calorimetry (DSC), material hardness measurement, and determination of surface free energy. List and characteristics of the devices used in this paper are shown in Tab. 2.

Differential scanning calorimetry (DSC) is one of the thermal analysis methods. It is used for measuring thermal flow difference between the sample and the reference material during the exposure of the sample to a controlled temperature and atmosphere.

Table 2 List of used devices

Name of the device	Technical characteristics of the device
DSC Mettler Toledo 823e	Temperature data: temperature range with internal refrigerator from −90 to 450 °C, temperature accuracy from ±0.2K, heating speed from 0.01 to 300 K/min; cooling speed from 0.01 to 50 K/min; calorimetric data: sensor type – ceramic, number of thermocouples – 56, resolution – 0.04 μW, measuring speed – max. 50 values per second.
Goniometer Dataphysics OCA 30	Contact angle: 0 ÷ 180°; ± 0.1° Surface tension: $10^{-2} \div 2\times10^{3}$ mN/m resolution: ± 0.01 mN/m USB-CCIR camera: 768 × 576 pixels FOV: 1.32 × 0,99 ÷ 8.50 × 6.38 mm Integrated thermometer: −60 ÷ 700 °C
Durometer Zwick Roell	Shore A and Shore D scale

The material used as the reference sample is aluminium oxide (Al_2O_3). DSC analysis has ability to monitor the transformations in the solid state, phase changes and to determine the thermodynamic parameters during the controlled heating and cooling of the sample. The parameters that can be determined by DSC analysis are glass transition temperature, crystallization temperature, melting temperature, polymer crystallinity percentage, specific heat capacity, transformation enthalpy and many others [9].

The device used in this paper was Mettler Toledo 823e. The samples of the weight of about 10 mg were put in an aluminium bowl, hermetically sealed by a press and then placed in a device where glass transition temperature, melting temperature, crystallization temperature and possible changes caused by coconut fibre were determined. The tests were conducted in a stream of nitrogen at the flow rate of 50 cm^3/min with refrigerator cooling with heating/cooling rate of 10 °C/min. Measurements were performed in two heating cycles and one cooling cycle in a temperature range of −90 to 200 °C. First heating cycle was performed to erase the thermal history of the sample preparation [10, 11].

Hardness of the material is defined as the ease with which the material can be cut, punctured or subject to abrasion. The process is carried out by placing few layers of polymer (minimal height is 4 mm) at top of one another and placing them beneath the needle. The hardness value is being read on the digital screen on the Shore A scale [12]. The device used in this measurement was durometer Zwick Roell. Eight measurements were performed for each of 16 samples and average value of the Shore A hardness has been calculated.

To determine the surface free energy of biodegradable printing plates, it was first necessary to determine the contact angles for the three reference liquids: water, diiodomethane and glycerol. Contact angle measurements were performed by means of goniometer Dataphysics OCA 30.

The contact angle was measured using Sessile drop method. Eight drops of every liquid were applied at the different places on the sample. The drop volume was 1 μm. Average value of the contact angle was calculated for each of the three liquids and then surface free energy of biodegradable printing plates was calculated by OWRK method which is suitable for this type of the material [13, 14].

3 RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry

The results of DSC measurements for all samples are presented in Tab. 3. They were obtained from the DSC diagrams. As an example, Fig. 4 presents the DSC diagram of the 16th sample (PCL/PLA 70 %/30 % + 3 % of fibres). DSC diagram of 16th sample shows three thermograms. Red thermogram represents the first heating cycle, green thermogram represents the second heating cycle and blue thermogram represents the cooling cycle. The first and the second heating cycles have 4 transitions.

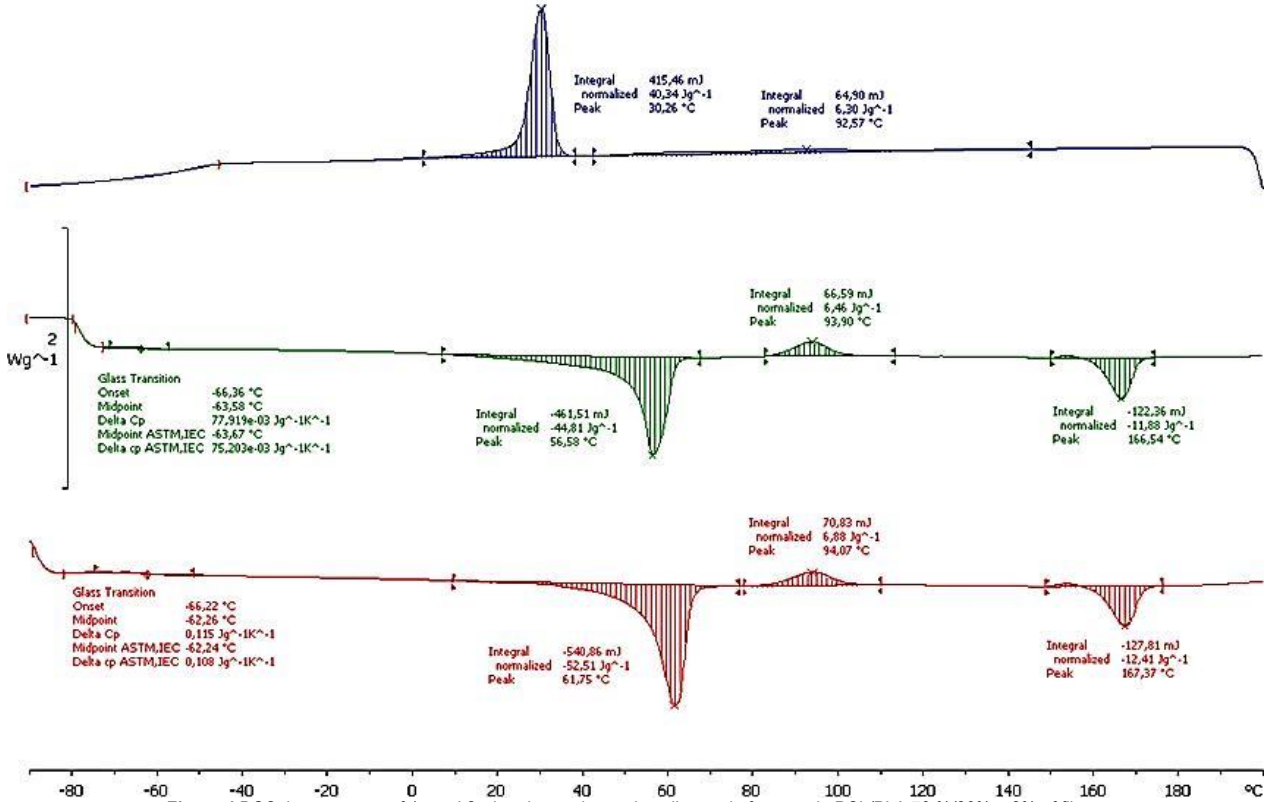

Figure 4 DSC thermograms of 1st and 2nd heating cycles and cooling cycle for sample PCL/PLA 70 %/30% + 3% of fibres

Table 3 DSC data for PCL/PLA mixtures, 2nd heating cycle

Share of PCL/PLA / Share of fibres		PCL			PLA				
		T_g / °C	T_m / °C	ΔH_m / J g^{-1}	T_g / °C	T_{cc} / °C	ΔH_{cc} / J g^{-1}	T_m / °C	ΔH_m / J g^{-1}
PCL	0 %	−63.21	57.06	−74.43	/	/	/	/	/
	0.5 %	−62.66	56.92	−71.42	/	/	/	/	/
	1.5 %	−63.70	57.90	−69.87	/	/	/	/	/
	3 %	−63.41	56.94	−70.46	/	/	/	/	/
PCL/PLA 90/10	0 %	−62.72	58.03	−67.66	*	96.84	2.10	167.79	−3.72
	0.5 %	−62.96	57.07	−63.88	*	91.71	1.86	166.68	−3.61
	1.5 %	−63.70	56.77	−57.64	*	90.43	1.26	166.41	−4.08
	3 %	−62.20	56.80	−55.29	*	90.13	2.29	166.28	−3.75
PCL/PLA 80/20	0 %	−57.33	57.62	−52.82	*	98.28	4.80	168.26	−7.38
	0.5 %	−63.20	57.10	−53.13	*	94.42	3.81	167.22	−7.87
	1.5 %	−61.10	57.38	−52.49	*	94.36	4.21	167.65	−8.49
	3 %	−62.62	56.93	−53.10	*	91.91	4.57	166.72	−7.84
PCL/PLA 70/30	0 %	−63.95	56.61	−43.83	*	99.43	8.29	167.75	−11.97
	0.5 %	−62.84	56.76	−47.88	*	99.75	6.04	167.39	−11.56
	1.5 %	−63.50	56.81	−43.55	*	95.47	7.41	167.12	−11.48
	3 %	−63.67	56.58	−44.81	*	93.30	6.46	166.54	−11.88

It can be seen in Fig. 4 that first transition is at −63.37 °C and it represents the glass transition temperature. Next transition is in the interval from 0 to 70 °C and it represents PCL melting. Endothermic peak of melting is at 56.58 °C. Third transition is cold crystallization of PLA in the interval from 80 to 110 °C. Exothermic peak of cold crystallization is at 93.90 °C. The last transition is PLA melting. It begins at 150 °C and ends at 180 °C. Endothermic peak of PLA melting is at 166.54 °C. Thermogram of cooling cycle shows two transitions. The first is PCL crystallization in the interval from 0 to 40 °C with exothermic peak at 30.26 °C and the second one is PLA crystallization which begins at 50 °C and ends at 130 °C with exothermic peak at 92.57 °C.

Tab. 3 shows results of the second heating cycle from DSC analysis for all the samples. In the table one can find values of PCL glass transition temperature (T_g), PCL melting temperature (T_m), PCL melting enthalpy (ΔH_m), PLA cold crystallization temperature (T_{cc}), PLA cold crystallization enthalpy (ΔH_{cc}), PLA melting temperature (T_m), and PLA melting enthalpy (ΔH_m). PLA glass transition temperature (T_g) is marked with asterisks, which means it could not be determined because it overlaps with PCL melting interval.

Table 4 DSC data for PCL/PLA mixtures, cooling cycle

Share of PCL/PLA / Share of fibres		PCL		PLA	
		T_c / °C	ΔH_c / J g^{-1}	T_c / °C	ΔH_c / J g^{-1}
PCL	0 %	27.25	66.49	/	/
	0.5 %	27.76	62.93	/	/
	1.5 %	30.25	60.52	/	/
	3 %	28.78	60.47	/	/
PCL/PLA 90/10	0 %	32.05	59.63	59.20	0.07653
	0.5 %	31.41	54.69	/	/
	1.5 %	31.78	52.97	/	/
	3 %	31.97	48.70	60.46	0.36
PCL/PLA 80/20	0 %	31.79	50.68	61.45	1.34
	0.5 %	30.94	45.34	95.42	3.07
	1.5 %	30.90	48.19	94.36	6.92
	3 %	30.77	44.14	92.74	3.18
PCL/PLA 70/30	0 %	30.62	42.10	60.78	4.06
	0.5 %	30.77	41.44	91.42	5.79
	1.5 %	30.48	37.43	59.14	3.86
	3 %	30.26	40.34	92.57	6.30

Tab. 4 shows results of cooling cycle from DSC analysis for all samples. In the table one can find values of PCL crystallization temperature (T_c), PCL crystallization enthalpy (ΔH_c), PLA crystallization temperature (T_c), and PLA crystallization enthalpy (ΔH_c). It is possible to conclude that the addition of coconut fibres causes changes in some of the thermal properties of the prepared composites. Specifically, the fibre addition does not significantly affect the glass temperature, nor does the melting temperature, as expected.

This result suggests that the addition of coconut fibres to the polymeric mixture does not significantly affect the mobility of the polymer in the polymer network. Visible changes are present in the cold crystallization temperature and enthalpy of crystallization for all measured samples and in the melting enthalpy for the PCL/PLA 90 %/10 % sample. The values are shifted to lower points after addition of higher fibre concentration, which is common for composite materials.

3.2 Measurement of hardness

Shore A method of hardness measurement showed the highest hardness of sample PCL/PLA 70 %/30 % + 0.5 % of fibres, 92.7 (Fig. 5). Lowest hardness was measured on sample PCL/PLA 90 %/10 % + 3 % of fibres - 86.98. However, a decrease in hardness of the sample PCL/PLA 90 %/10 % + 3 % of fibres can be attributed to measuring method due to high concentration of fibres in tough polymer material. Due to the surface structure which is created by fibres in higher concentration in material, measurement of hardness can be difficult and give imprecise result.

Except for the sample that deviates from the trend, it is possible to conclude that coconut fibres in polymer structure contribute to the increased hardness of the material. The highest general hardness of the material, regardless of the amount of added fibres, is present for the sample with the highest share of PLA. Also, the hardness range of tested polymer materials is within the range of some classical photopolymer printing plates. Therefore, it is possible to conclude that by a combination of ratios of PCL and PLA

and the amount of added fibres it is possible to adjust the hardness of material to the needs of the printing plate.

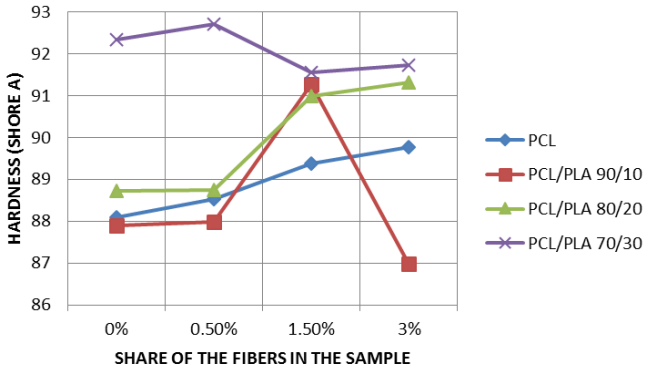

Figure 5 Material hardness (Shore A)

3.3 Calculation of surface free energy

The highest surface free energy was calculated for the sample PCL/PLA 80 %/20 % + 1.5 % of fibres and its value is 41.92 mN/m. The lowest surface free energy was calculated for the sample PCL + 3 % of fibres and its value is 33.1 mN/m (Fig. 6).

It is possible to conclude that the addition of coconut fibres in higher concentrations causes the decrease in free surface energy. The possible cause of that is shortening of the chains in the polymer network, and the properties of the fibres. This change of the surface properties of tested material is actually positive in the terms of applicability for the production of the relief printing plate.

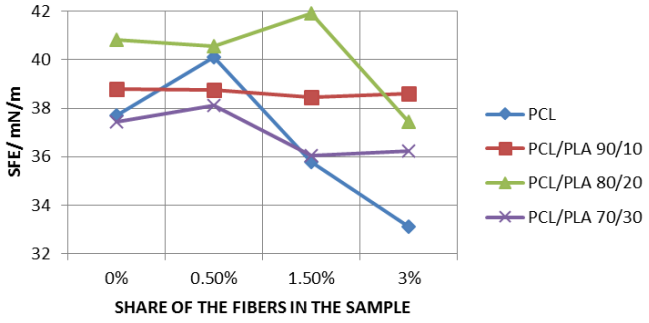

Figure 6 Surface free energy of samples

Namely, the surface free energy range of photopolymer printing plates for some relief printing techniques is in the range of measured surface free energy of PCL/PLA mixtures with fibres. Needed surface free energy of the photopolymer printing plate depends on the type of printing ink which will be used (solvent-based, water-based or UV-curable ink). Consequently, the results show that by choosing the right ratio of used biodegradable polymers in mixture and amount of coconut fibres it is possible to obtain the desired surface free energy of material and ensure its application in form of relief printing plate.

4 CONCLUSION

In this paper, thermal, mechanical and surface analyses of biodegradable PCL/PLA composites with the addition of different coconut fibres weight shares were carried out. The aim was to use different methods of measurement and analysis to determine potential applicability of used materials for production of the relief printing plate as an alternative to conventional photopolymer materials. From the research results of this paper, the following can be concluded:

- Most thermal changes characteristic for PLA and PCL do not take place in the applicable temperature range for relief printing. Exceptions are: PCL melting temperature at 60 °C which is not affected by the addition of fibres – this prevents the application of the obtained material for the foil stamping; second is PCL crystallization temperature during the cooling cycle at 30 °C. The influence of crystal transition on surface properties of the polymer mixtures should be examined in the following research;
- Coconut fibres in the composite structure contribute to the increased material hardness. The hardness range of the tested polymers is within the range of some classical photopolymer printing plates, so it can be concluded that the combination of PCL and PLA ratios and specific amount of added fibres enable adjustment of the material hardness;
- Addition of coconut fibres in higher concentrations causes the decrease in free surface energy which is positive change in terms of application for the production of relief printing plate. Surface free energy range of photopolymer printing plates is within the range of the measured surface free energy of PCL/PLA mixtures with fibres. Furthermore, calculated surface free energy is in the range applicable for the relief printing application;
- Materials produced and tested in this research have the potential for the application for various types of relief printing plates (letterset, embossing, printing plates for label printing).

Note: This investigation was presented at the International Conference MATRIB 2017 (29. 6. - 2. 7. 2017, Vela Luka, Croatia).

5 REFERENCES

[1] http://www.sigmaaldrich.com/catalog/product/aldrich/440744?lang=en&region=US (Accessed on 2 June 2017)

[2] Woodruff, M. A.; Hutmacher, D. W. The return of a forgotten polymer - Polycaprolactone in the 21st century. // Progress in Polymer Science, 35-10, pp. 1217-1256 (2011).

[3] Ebnesajjad, S. Handbook of Biopolymers and Biodegradable Plastics, 1st edition, Elsevier, 2012.

[4] https://en.wikipedia.org/wiki/Polylactic_acid (Accessed on 29 May 2017)

[5] Garlotta, D. A Literature Review of Poly(Lactic Acid). // Journal of Polymers and the Environment, 9, 2(2001), pp. 63-84.
[6] https://www.biogreenchoice.com/category_s/1866.htm (Accessed on 29 May 2017)
[7] Hamad, K.; Kaseem, M.; Yang, H. W.; Deri, F.; Ko, Y. G. Properties and medical applications of polylactic acid. // eXPRESS Polymer Letters, 9, 5(2015), pp. 435-455.
[8] http://www.bakeryandsnacks.com/Processing-Packaging/PLA-bioplastics-production-could-hit-1m-tonnes-by-2020-nova-Institut (Accessed on 30 May 2017)
[9] Kodre, K. V.; Attarde, S. R.; Yendhe, P. R.; Patil, R. Y.; Barge V. U. Differential Scanning Calorimetry: A Review. // Journal of Pharmaceutical Analysis, 3, 3(2014), pp. 11-22.
[10] http://hr.mt.com/dam/LabDiv/Campaigns/gp/gtap/thermal_analysis_of_polymers _en.pdf (Accessed on 2 Jun 2017)
[11] Day, M.; Nawaby, A. V.; Liao, X. J. A DSC study of the crystallization behaviour of polylactic acid and its nanocomposites. // Journal of Thermal Analysis and Calorimetry, 86, 3(2006), pp. 623-629.
[12] https://www.fkit.unizg.hr/_download/repository/Struktura_i_svojstva_materijala-nastavni_materijal.pdf (Accessed on 2 Jun 2017)
[13] Żenkiewicz, M. Methods for the calculation of surface free energy of solids. // Journal of Achievements in Materials and Manufacturing Engineering, 24, 1(2007), pp. 137-145.
[14] Tomašegović, T. Functional model of photopolymer printing plate production process. Doctoral thesis, 2016.

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