

PHYSICAL-MECHANICAL PROPERTIES OF BIOCOMPOSITES REINFORCED WITH COIR (NANO)FIBERS

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Abstract

The paper deals with the physical-mechanical characteristics of polymer composites on the basis of natural coir fibers and biopolymer PLA (Polylactic acid) matrices. There are evaluated physical and mechanical properties of composites in dependence on natural fibers length and their amount in biopolymer matrix. There is also described influence of fibers on the course of melt and cold (secondary) polymer composite crystallization by means of differential scanning calorimetry. There is observed that coir fibers work like natural nucleating agents and thus subsequently improve the material properties of PLA.

Keywords:

Biopolymer composites, Polylactic acid, Natural fibers, Coir fibers

1. INTRODUCTION

Application of polymer and biopolymer composites with natural material represents important material alternation which is focused not only into consumer but also into automotive industry [1]. The purpose is mainly to use environmentally friendly materials with required utility properties. One of such biopolymers which is used in practice is polylactic acid (PLA). To improve its mechanical characteristics and retain biodegradability there is possible to strengthen it not only with synthetic but also with natural fibers. In this paper is PLA matrix filled with coir fibers of different sizes in terms of millimeters and nanometers. There are evaluated physical and mechanical composite characteristics in dependence on length and amount of fibers and also their influence on the PLA crystallization whose course influences final material properties.

Polylactic acid is a linear aliphatic thermoplastic polyester, produced from renewable resources. PLA can be commonly synthesized by ring-opening polymerization of lactide or by direct polycondensation of lactic acid. Used lactic acid monomers are obtained from the fermentation of sugar feed stocks. Based on the stereoregularity (L and D) of lactic acid L, D and D-L type lactides can be used in PLA production. An equimolar mixture of D and L isomer results in D-L lactide (so called meso - lactide). It is well established that the properties of polylactides vary to a large extent depending on the ratio and the distribution of the two isomers [2]. Generally, commercial PLA grades are copolymers of poly(L-lactic acid)- semicrystalline PLLA and poly(D,L-lactic acid) - amorphous PDLLA, which are produced from L-lactides and D,L-lactides, respectively. For a commercial PLA a blend of a higher amount of L-lactide and a lower amount of D-lactide is used [3, 4]. The ratio of L- to D, L-enantiomers is known to affect the properties of PLA, such as the melting temperature, degree of crystallinity and even the degradation characteristics [3]. Semi-crystalline nature of PLA has been observed during cooling of melt. The crystallization behavior of polylactides depends on the thermal history (i.e. annealing) [5, 6] molecular mass [5], amount and type of additives [5, 7, 8] and stereo sequence distribution [2, 5]. When semi-crystalline PLA is processed, its crystallinity changes depended on the cooling rate [6]. Typically during injection moulding, due to the high cooling rates, totally amorphous PLA products could be produced. PLA can be recrystallized after processing into a product, the products shrink and significant warpage occurs during recrystallization due to the increasing crystallinity [5].

2. EXPERIMENTAL

2.1 Preparation of (nano)composites

We prepared the composites by adding the coir fibers into hydrophilic polylactic acid matrix NatureWorks[®] biopolymer 3251D within ratio 10, 20 and 30 (wt. %) into the extrusion line with twin screw, temperature profile of 180 °C up to 200 °C and cold granulation on the end of the line. For the composite material preparation it was necessary to remove fine organic impurities and greases from fibers and to modify their length by milling at the shear mill ($n = 3000 \text{ min}^{-1}$) with trapezoidal holes of 0.75 mm (the length of milled fibers was within 0.5 mm up to 2 mm). The same method was used for preparing nanocomposites. Ratio of coir nanoparticles were 2, 4 and 6 (wt. %). Size of nanoparticles: $790 \text{ nm} \pm 15 \%$. We prepared nanoparticles by planetary mill (Pulverisette 7 premium line). Then milled fibers were dried. From these granules of biopolymer composites was for the subsequent evaluation physical-mechanical properties injected on injection moulding machine the test specimen according to international standards.

2.1 Physical-mechanical properties of (nano)composites

For evaluation physical-mechanical properties of (nano)composites there was carried out determination of their density (influencing weight of composite part), impact strength, tensile and flexural properties. Testing samples were conditioned and tested in the standard environment 23/50 acc. to ISO 291. Density of composites was determinate acc. to ISO 1183-1. Tensile properties were determinate acc. to ISO 527: tensile strength (σ_m) and tensile strain at break (ϵ_b) by test speed $50 \text{ mm} \cdot \text{min}^{-1}$ and tensile modulus (E_t) by test speed $1 \text{ mm} \cdot \text{min}^{-1}$. Flexural properties: flexural strength (σ_{fM}) and flexural modulus (E_f) (test speed $2 \text{ mm} \cdot \text{min}^{-1}$) were determinate acc. to ISO 178. Impact strength (a_{cu}) was measured by means of Charpy method acc. to ISO 179-1/1eA. Average values of physical-mechanical properties are given in table 1. By adding coir fibers into PLA matrix there was strong increase in tensile and flexural modulus values (Fig. 1). The other mechanical characteristics (strength, elongation and impact strength) decrease already with a small amount of nanoparticles coir fibers in the PLA composite. In comparison of the fiber length influence is evident that the maximal tensile and flexural modulus increase is achieved at nanocomposites. By adding only 2 wt. % nCF into PLA matrix there was tensile modulus increase by 16 % and flexural modulus even till 35 %. By adding standard coir fibers with the length of 2 mm into PLA matrix there was tensile modulus increase by the same value (16 %) up to fibers volume 30 wt. %. In the case of PLA composites is tensile and flexural modulus course of change similar (in percentages) contrary to the PLA nanocomposites.

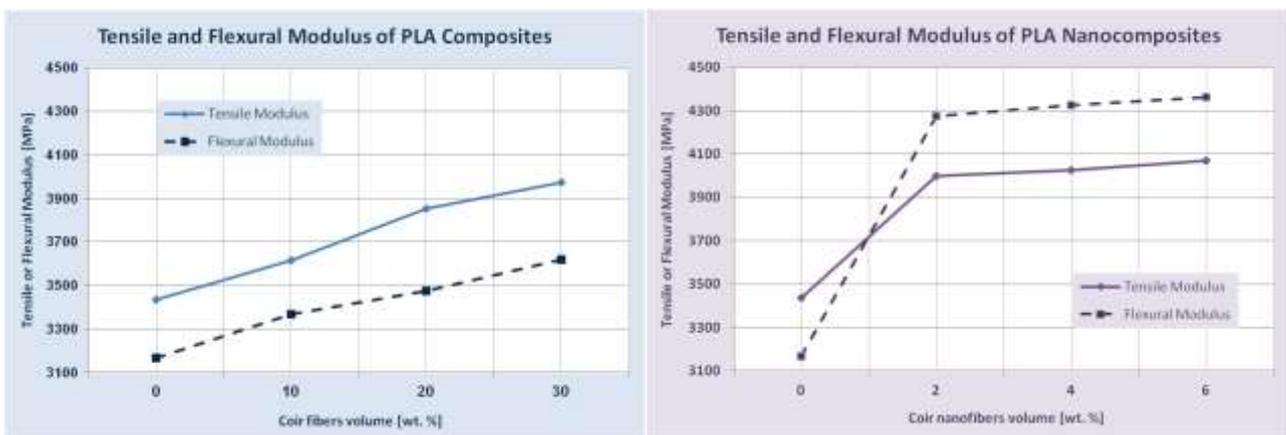


Fig.1 Tensile and flexural modulus of PLA composites and nanocomposites

Table 1 Physical-mechanical properties of PLA (nano)composites

Material	ρ [kg·m ⁻³]	σ_m [MPa]	E_t [MPa]	ε_b [%]	σ_{fM} [MPa]	E_f [MPa]	a_{cU} [kJ·m ⁻²]	
PLA polymer	1247 ± 2	66 ± 2	3435 ± 78	3.5 ± 0.8	92 ± 2	3168 ± 115	18.8 ± 2.3	
composites	10 wt. % CF	1249 ± 2	62 ± 2	3614 ± 65	2.0 ± 0.7	88 ± 1	3366 ± 20	10.6 ± 1.7
	20 wt. % CF	1254 ± 2	58 ± 1	3852 ± 127	1.6 ± 0.1	87 ± 1	3474 ± 49	9.0 ± 0.8
	30 wt. % CF	1262 ± 2	56 ± 2	3974 ± 126	1.6 ± 0.1	86 ± 1	3618 ± 40	8.6 ± 0.9
	2 wt. % nCF	1247 ± 2	63 ± 4	4000 ± 51	1.7 ± 0.3	91 ± 2	4275 ± 26	9.6 ± 2.1
	4 wt. % nCF	1248 ± 2	58 ± 3	4024 ± 66	1.5 ± 0.2	90 ± 2	4326 ± 25	8.9 ± 2.2
	6 wt. % nCF	1249 ± 2	56 ± 1	4068 ± 93	1.5 ± 0.1	89 ± 2	4362 ± 43	8.8 ± 3.7

Note: CF = coir fibers, nCF = nanoparticles of coir fibers

2.1 Physical properties and crystallization of PLA composites

Study of crystallization was carried out with a DSC 6 Perkin Elmer which was calibrated against an indium standard. An empty aluminium pan was the reference. For injection moulding thermal history evaluation in relation to the amount of natural fibers, the samples amount was (10 ± 0,2) mg and analysis run at 10 °C·min⁻¹ heating/cooling ramp in one heating-cooling cycle in a nitrogen atmosphere (flow rate 50 ml·min⁻¹). From the DSC thermograms (Fig. 2) we studied effect of coir fibers on PLA crystallization and physical-thermal properties such as exothermic cold crystallization temperature (T_{cc}), endothermic melting temperature (T_m), melt crystallization temperature (T_c), cold crystallization enthalpy (ΔH_{cc}), melting enthalpy (ΔH_m), melt crystallization enthalpy (ΔH_c) and degree of crystallinity (χ_c). The degree of crystallinity of PLA injection moulding (nano)composites samples was calculated based on the values of cold crystallization enthalpy, melting enthalpy and melting enthalpy of a 100 % crystalline PLA: 93 J·g⁻¹ [1].

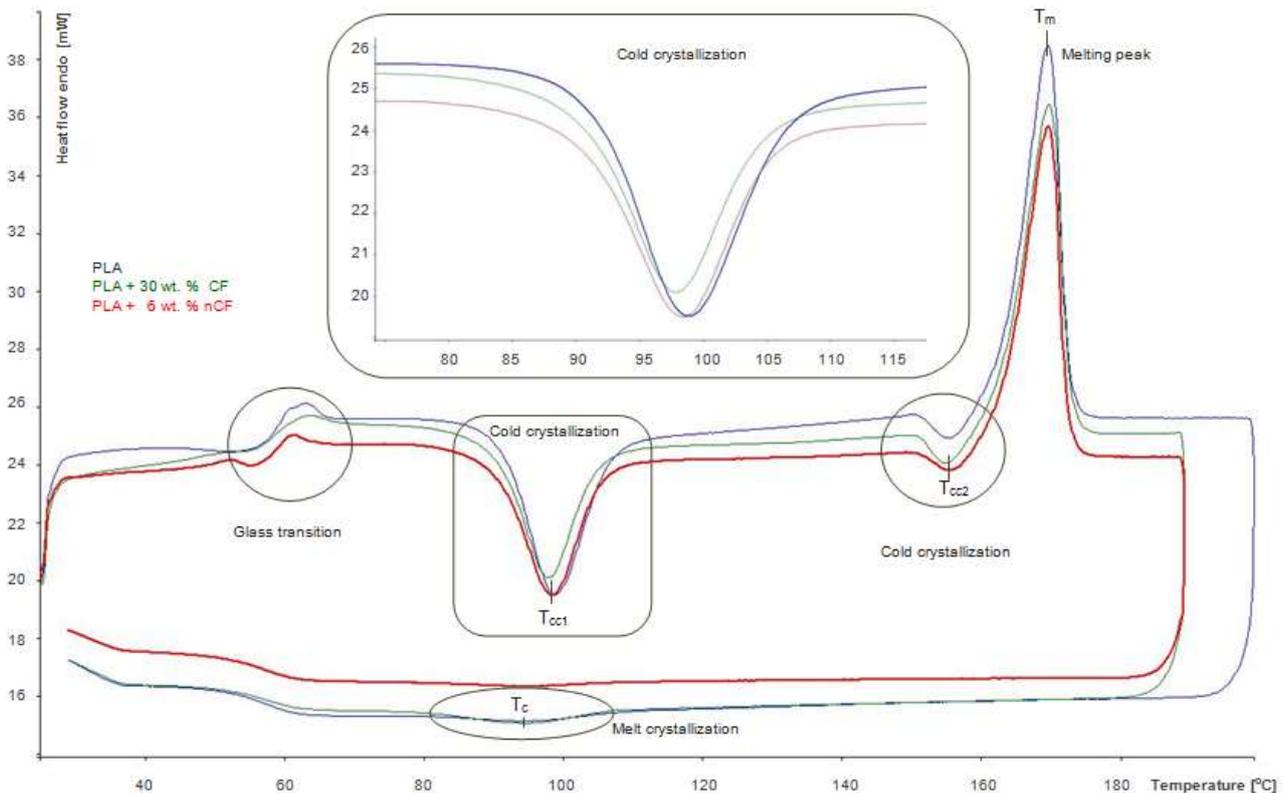

Fig. 2 DSC thermogram for PLA and PLA reinforced with coir fibers or nanofibers

Table 2 Physical-thermal properties of PLA (nano)composites

Material	T _{cc1} [°C]	ΔH _{cc1} [J·g ⁻¹]	T _{cc2} [°C]	ΔH _{cc2} [J·g ⁻¹]	T _m [°C]	ΔH _m [J·g ⁻¹]	T _c [°C]	ΔH _c [J·g ⁻¹]	χ _c [%]	
PLA polymer	98.9	-36.2	155.4	-3.4	169.6	47.7	none	none	8.7	
composites	10 wt. % CF	100.1	-31.0	155.9	-2.3	170.1	41.3	none	none	8.6
	20 wt. % CF	99.2	-29.4	155.7	-2.3	170.1	41.1	94.3	-1.5	10.1
	30 wt. % CF	97.9	-27.3	154.7	-2.6	169.8	40.6	94.8	-3.6	11.5
	2 wt. % nCF	100.9	-30.6	156.0	-1.5	169.9	42.2	none	none	10.9
	4 wt. % nCF	101.4	-31.9	155.9	-1.4	169.8	43.6	none	none	11.1
	6 wt. % nCF	98.2	-28.7	158.3	-1.5	169.6	41.5	95.5	-1.2	12.2

Coir (nano)fibers which were added to PLA matrix increased crystallization abilities of the injected parts (mainly nanofibers). At the pure PLA polymer (during cooling rate 10 °C·min⁻¹) was not observed sharply defined phase transformation associated to melt crystallization of polymer, in contrast to PLA composites reinforced by coir fibers. During heating of the injected part from PLA (heating ramp 10 °C·min⁻¹) there was observed the glass transition temperature T_g ~ 59 °C and cold crystallization within the temperature interval 80 °C to 120 °C (T_{cc1}) and further within the temperature interval 150 °C to 159 °C (T_{cc2}). Such cold crystallization of material is a reason for rapid cooling of the melt in the mould cavity during the injection process. It influencing negative not only the structure change and material properties but also in shape and dimensional injected part instabilities (under temperature over 80 °C). It was proved that adding the coir fibers/nanoparticles to the PLA matrix increases the melt crystallization and decreases the cold crystallization enthalpy which also moved to the lower temperatures (Fig. 2). At comparison crystallization processes of PLA composites with coir fibers and banana fibers (which was published by authors under link [9]) it is possible to state that coir fibers do not achieve the crystallization effect of banana fibers. Such reality can be caused by different surface structure of fibers. By adding 30 wt. % of coir fibers and by adding 6 wt. % of coir nanoparticles there is decrease of real injected parts cold crystallization (ΔH_{cc1}) almost by 25 % or 21 %, respectively.

Miyata and Masuko studied the non-isothermal crystallization of Poly(lactid acid) (PLLA) at various cooling rates ranging from 0.5 to 20 °C·min⁻¹. The amount of crystallinity developed in Poly(lactid acid) depended closely on cooling rate. Samples cooled at rates higher than 10 °C·min⁻¹ could not crystallize and remained amorphous [10]. Experimentally measured values (Table 2) proved that total crystallization of polymer is possible to positively influence by natural coir fibers or more precisely nanoparticles of coir fibers. However their effect do not achieve effect of standard nucleation agents at all which are added into polymer for these reasons. Authors have already investigated the cooling rate influence on PLA composites with coir fibers at link [9] and it is evident that the lower cooling rate of composites, the higher degree of crystallinity and the lower cold crystallization.

3. CONCLUSION

Application of natural fibers represents the very important material replacement. With regard to the environmental point of view, natural fibers can replace synthetic fibers in the composite materials branch. The similar reality concerns the polymers from the renewable resources (bioplastics) which have become a very attractive material during last years. There is mainly reinforced effect [11 - 13] by adding natural fibers to the synthetic or biodegradable polymer matrix but their another benefits, in comparison to the other fibrous materials, rest in their low weight, low abrasion, combustibility, biodegradability, non-toxicity, and mainly their low price which does not depend on the oil price [14 - 15].

There was decrease of composites strength, elongation and impact strength by adding coir fibers into PLA matrix, but on the other hand there was strong increase of tensile and flexural modulus. The highest rigidity

reveal PLA composites filled by nanoparticles of coir fibers (with minimal change of material density). Tensile modulus at PLA composites with 6 wt. % of coir fibers nanoparticles corresponds to the tensile modulus of standard PLA composites with coir fibers volume 30 wt. % (fibers length is within the range 0.5 up to 2 mm).

Coir fibers in the biopolymer matrix can also influence routine and kinetics of the crystallization. There were proved that adding coir fibers to the PLA matrix increase the degree of crystallization but mainly also lowers the cold crystallization which slips to the lower temperatures or more precisely it lowers its temperature interval. The cold crystallization occurs at material as a result of its intense cooling and it is a reason for shape and dimensional injected part instabilities.

We observed that coir fibers work like natural nucleating agents. Owing to this behaviour is possible not only to improve material properties by using natural fibers like reinforcement, but also to improve the composite properties with usage of natural fibers like nucleating agents. We observed different nucleation activity of the natural fibers (however this is not subject of this paper). It can be dedicated to the different surface structure of the fibers. Thus implementation of different natural fibers could lead to different nucleation activity according to the fiber surface structure.

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REFERENCES

- [1] DULEBA, B. et al. Preparation and Characterization of Polypropylene/MMT Nanocomposites. *Advanced Materials Research*, 2014, vol. 893, p. 132-135.
- [2] MOHANTY, A.K. et al. *Natural Fibers, Biopolymers and Biocomposites*. CRC Press, 2005.
- [3] MARTIN, O., AVÉROUS, L. POLY(lactic acid): Plasticization and Properties of Biodegradable Multiphase Systems. *Polymer*, 2001, vol. 42, pp. 6209-6219
- [4] TÁBI, T. et al. Crystalline Structure of Annealed Polylactic acid and its Relation to Processing. *eXPRESS Polymer Letters*, 2010, vol. 4, no. 10, pp. 659-668.
- [5] AHMED, J. et al. Thermal Properties of Polylactides, Effect of Molecular Mass and Nature of Lactide Isomer. *Journal of Thermal Analysis and Calorimetry*, 2009, vol. 95, pp. 957-964
- [6] DI LORENZO, M.L., SILVESTRE, C. Non-Isothermal Crystallization of Polymers. *Progress in Polymer Science*, 1999, vol. 24, pp. 917-950.
- [7] KE, T., SUN, X. Melting Behavior and Crystallization Kinetics of Starch and Poly(lactic acid) Composites. *Journal of Applied Polymer Science*, 2003, vol. 89, pp. 1203-1210.
- [8] LI, H., HUNEAULT, M.A. Effect of Nucleation and Plasticization on the Crystallization of Poly(lactic acid). *Polymer*, 2007, vol. 48, pp. 6855-6866.
- [9] BĚHÁLEK, L. et al. Study of Crystallization of Polylactid Acid Composites and Nanocomposites with natural fibres by DSC method. In *Nanocon 2013: 16-18.10.2014*. Brno, Česká republika [CD-ROM]. Brno: TANGER, 2013. ISBN 978-80-87294-47-5.
- [10] MIYATA, T., MASUKO, T. Crystallization behaviour of poly(L-lactide). *Polymer*, 1998, vol. 39, pp. 5515-5521.
- [11] OKSMAN, K. et al. Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites Science and Technology*, 2003, vol. 63 pp. 1317-1324
- [12] YU, T. et al. Preparation and properties of short natural fibre reinforced poly(lactic acid) composites. *Transactions of Nonferrous Metals Society of China*, 2009, vol. 19, pp. 651-655.
- [13] SINGHA, A.S., THAKUR, V.K. Mechanical properties of natural fibre reinforced polymer composites. *Bulletin Material Science*, 2008, vol. 31, pp. 791-799.
- [14] KOZŁOWSKI, R. *Handbook of natural fibres. Processing and applications (Vol. 2)*. Woodhead Publishing, 2012.
- [15] MUKHOPADHYAY, S. et al. Banana Fibers - Variability and Fracture Behaviour. *Journal of Engineered Fibers and Fabrics*, 2008, vol. 3, pp. 39-45.