BASALT FIBER REINFORCED POLY(LACTIC ACID) COMPOSITES FOR ENGINEERING APPLICATIONS

T. Czigány[1,2*], J. G. Kovács[2], T. Tábi[1,2]
[1] MTA–BME Research Group for Composite Science and Technology, Muegyetem rkp. 3., H-1111 Budapest, Hungary
[2] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3., H-1111 Budapest, Hungary
* Corresponding author (czigany@eik.bme.hu)

Keywords: *Biodegradable polymer, Poly(lactic acid), Basalt fibers, Injection molding*

1 Introduction

Nowadays, due to the increasing environmental consciousness bio-based and biodegradable polymers (biopolymers in short) are located in the focus of interest. By replacing conventional, petrol based polymers with biopolymers the urging waste management problems could be moderated or even solved, moreover, the petrol-dependency of plastic industry could be decreased, and in the future a new, biomass-based (mainly starch and cellulose based) plastic industry could be launched. However, nowadays, the biopolymer production in the World is only around 0.5% of the overall plastic production, but it is believed to increase significantly in the upcoming decades.

One of the most promising biopolymer is Poly(Lactic Acid) (PLA) [1-4], which can be produced by the fermentation of starch and sugar into lactic acid and the polycondensation of the lactic acid itself. Due to the fact that starch can be found all over the World in high amounts in agricultural plants like corn (maize), wheat, rice, potato, tapioca, it can be seen easily that PLA could be the first widely used pioneer of the biomass-based plastic industry. PLA is a thermoplastic material, thus it can be processed by using conventional thermoplastic processing equipments like injection molding, extrusion, thermoforming, compression or blow molding. It also has good mechanical properties, tensile strength of 60 MPa, tensile modulus of 3 GPa, however, it is considered as a brittle material with a Charpy notched and unnotched impact strength of 2.7 and 23.0 kJ/m^2 respectively, and also its low heat deflection temperature (HDT) of 50-60°C according to its low glass transition temperature (T_g) only allows it to be used in indoor applications. At the same time, its biodegradation only takes place in industrial compost (above 60°C) after an initial hydrolysis, thus the PLA products can be used for years at room-temperature, which makes PLA even an intelligent polymer. Nowadays, PLA products are already commercialized and more and more PLA products are on the market, however, these products are mainly related to the packaging industry.

Although PLA is mainly used for packaging, as a renewable resource based polymer with good mechanical properties, it may be interesting for durable engineering applications [5] especially when taking into consideration that below its T_g biodegradation will not begin. A lot of effort has been done to reinforce PLA with typically natural plant fibers to keep its “bio” feature [6-12] or with nanoparticles to reach other beneficial properties like modified gas barrier [13] or photooxidation [14] properties. Some good results have been achieved by using natural plant fiber reinforcement like increased strength and stiffness, however, the best results were in most cases achieved by using very long cycle time technologies like film-stacking or solvent-casting [5, 11]. If a fiber reinforced PLA part is to be used in engineering application, than injection molding is the technology to be used because it is a very productive, highly automated technology capable of producing very complex, 3D shaped parts in one step without the need of further machining. Typically only a slight increase was found in the mechanical parameters of injection molded PLA parts reinforced with natural plant fibers due to the temperature and shear sensitive property of the cellulose-based natural plant fibers.

A possible alternative for the natural plant fibers is the mineral basalt fibers. Basalt is also considered as natural, because it is generated by the solidification of molten lava, and it is also bioinert, which increases its "natural" property. By melting the basalt rocks, either continuous (spinneret technology) [15] or short (Junkers technology) basalt fibers can be produced. The basalt fibers have a constitution similar to glass fibers and their surface can be modified easily in order to be used as reinforcement in composite products [16-19].

Deák et al. [16] proved the usability of short basalt fibers and found that the impact strength of the injection molded composite parts with 3-glycidoxypropyltrimethoxysilane coupling agent was highly improved. Liu et al. [17] demonstrated that the impact strength of the PLA can be significantly improved from 19 kJ/m^2 (unnotched Charpy) to 34 kJ/m^2 by using 20wt% basalt fibers and 20wt% ethylene-acrylate-glycidyl-methacrylate (EAGMA) copolymer. Kurniawan et al. [18] found that better fiber-matrix adhesion can be developed by using atmospheric pressure glow discharge plasma polymerization treatment on the basalt fibers. It was also found that by increasing plasma polymerization time, the tensile strength of the composites increased. Finally, Chen et al. [19] proved that it is possible to produce basalt fiber reinforced PLA based scaffold for medical applications. It was found that basalt fibers retard inflammatory responses due to retarding degradation of PLA, and it was also found that basalt fibers were not influencing osteoblast viability, thus the developed composite can be potentially used in hard tissue repair.

According to these results, basalt fibers seem to be a potential alternative to plant fibers and it can be used effectively to reinforce PLA. In our previous research [20] it was demonstrated according to PLA based composite preparation that the drying conditions of the reinforcement or the filler and the PLA could significantly influence the adhesion between the phases highly affecting mechanical properties. In the publication dealing with basalt fiber reinforced PLA [17-19], the drying condition was either not shown or the drying temperature was found too low according to our former results.

According to all these results, in our research, optimized drying conditions were used to analyze its effect on the properties of basalt fiber reinforced PLA in order to be able to produce bio-based, durable material for engineering applications.

2 Materials and methods

Semi-crystalline injection molding grade PLA type AI1001 was purchased from eSUN, Shenzen, China, with a D-Lactide content of 4%. It was dried at 120°C for 6 hours prior to processing. This somewhat high drying temperature was already demonstrated to be useful in minimizing residual moisture and maximizing the possible adhesion between the PLA and the reinforcement or filler [20]. Chopped basalt fibers from Kameny Vek (Dubna, Russia) were obtained with silane treatment. The average diameter of the fibers was 13 μm, while the initial fiber length was 10 mm. Although basalt fibers are not susceptible to moisture, the basalt fibers could still contain chemically not bonded residual moisture on the surface, thus it was also dried along with PLA at 120°C for 6 hours. The materials were dry mixed and compounded by using a twin-screw extruder type LabTech Scientific twin screw extruder with a screw diameter of 26 mm, an L/D ratio of 40 and a screw rotational speed of 30 rpm. 5-10-15-20-30-40 wt% basalt fiber reinforced PLA composite extrudates were produced, which were pelletised and annealed at 120°C for 1 hour prior to injection molding. ISO standard tensile, three-point bending and Charpy specimens with a cross section of 4x10 mm and 80x80 mm flat specimens with a thickness of 2 mm were injection molded for the measurements by using an Arburg Allrounder 370S 700–290 injection molding machine with a screw diameter of 30 mm and an L/D ratio of 25. The main injection molding parameters can be seen in Table 1.

Injection molding parameter	Value
Injection volume (according to flat, tensile or flexural specimens)	50 cm^3 (flat) 44 cm^3 (tensile) 42 cm^3 (flexural)
Switch-over point	12 cm^3
Injection rate	50 cm^3/s
Holding pressure	600 bar
Holding time	20 sec
Residual cooling time	30 sec
Screw rotational speed	15 m/min
Backpressure	30 bar

Temperature profile along the barrel (from nozzle to hopper)	190-185-180-175-165°C
Temperature of the mold	20°C

Table 1. Main injection molding parameters

The tensile (σ_t – tensile strength, E_t – tensile elasticity modulus, ε_t – strain at maximum force) and flexural properties (σ_f – flexural strength, E_f – flexural elasticity modulus) were analyzed by using a Zwick Z020 universal testing machine using a cross-head speed of 5 mm/min. Charpy impact strength (α_{cu} – unnotched Charpy impact strength, α_{cn} – notched Charpy impact strength) was measured by using a Ceast Resil Impactor impact testing machine equipped with a 15 J hammer. 2 mm deep notched and unnotched specimens were also tested by using 6.21 J and 15 J of impact energy respectively. All the mechanical tests were performed at room temperature and at a relative humidity of 60%.

Differential Scanning Calorimetry (DSC) was performed by using a TA Q2000 type calorimeter to determine the potential nucleating ability of the basalt fibers. Heating/cooling/heating scan was used at a heating and cooling rate of 5°C/min under nitrogen atmosphere. Crystallinity was calculated by using the following equation:

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1-\alpha)} \cdot 100 \qquad (1)$$

X [%] is the crystallinity, ΔH_m [J/g] is the enthalpy of fusion, ΔH_{cc} [J/g] is the enthalpy of cold-crystallization, ΔH_f [J/g] is the enthalpy of fusion for the 100% crystalline PLA of 93 J/g [21], and α [-] is the mass fraction of the basalt fibers.

Dynamic Mechanical Analysis (DMA) was performed on a TA Q800 analyzer. The flexural specimens with a cross section of 4x10 mm with a support distance of 35 mm were used for the tests in dual cantilever mode. 0-160°C temperature range was investigated with a heating rate of 2°C. Amplitude of 20 μm and a frequency of 1 Hz was used.

The deflection of the flat specimens was investigated by placing them into an oven, in a single cantilever and measuring the deflection of the other side of the specimens by using digital caliper at 25, 40, 50, 60, 80, 100, and 120°C.

Heat Deflection Temperature (HDT) was also measured by using a Ceast 6505/000 analyzer. The tensile specimens with a cross section of 4x10 mm and a support distance of 110 mm were used with a specific load of 0.45 MPa and a heating rate of 2°C/min. The HDT value was obtained when the deflection of the specimens reached 0.33 mm.

Finally Scanning Electron Microscopy (SEM) was also performed on the fracture surface of the specimens by using a Jeol JSM 6380LA type electron microscope. Prior to investigation Au/Pd alloy was sputtered on the surface of the specimens to avoid electrostatic charging.

3 Results and discussion

It was found that by using basalt fibers the reinforcing effect was much more significant compared to plant fiber reinforcement PLA composites (Table 2.).

Material/Mechanical property	Tensile			Flexural		Charpy	
	σ_t [MPa]	E_t [GPa]	ε_t [%]	σ_f [MPa]	E_f [GPa]	α_{cu} [kJ/m^2]	α_{cn} [kJ/m^2]
PLA	64.5	2.97	2.93	101.5	3.30	23.0	2.7
PLA/5% basalt fiber	70.4	3.70	2.82	115.7	4.11	22.8	2.8
PLA/10% basalt fiber	80.2	4.27	2.81	123.7	4.86	26.5	4.9
PLA/15% basalt fiber	91.6	5.15	2.75	136.7	5.93	29.3	5.9
PLA/20% basalt fiber	98.0	6.00	2.69	143.5	7.00	29.9	6.5
PLA/30% basalt fiber	119.7	7.62	2.28	180.0	10.37	38.3	9.3
PLA/40% basalt fiber	123.5	8.31	2.30	185.6	12.46	38.4	9.5

Table 2. Mechanical parameters of the basalt fiber reinforced PLA composites

As it can be seen in Table 2, tensile strength and tensile modulus as well as flexural strength and flexural modulus linearly increased with increasing basalt fiber content. By using 30wt% basalt fibers, an impressive tensile strength and tensile modulus of 119.7 MPa and 7.62 GPa and a flexural strength and flexural modulus of 180.0 MPa and 10.37 GPa was reached respectively. One of the main drawbacks of PLA, its low impact strength was also highly increased from 23.0 to 38.4 kJ/m^2 and from 2.7 to 9.5 kJ/m^2 according to unnotched and notched impact strength respectively. It can also be observed that by using 40wt% basalt fibers, the mechanical properties are almost the same as for the 30wt% basalt fiber reinforced composite, which means that in the case of 40wt% basalt fiber reinforcement, the fibers were highly sheared and most-likely major fiber breakage occurred during processing thus the 40wt% basalt fibers could not further improve the mechanical properties compared to the 30wt% basalt fiber reinforcement.

According to the results, probably very good adhesion developed between the PLA and the basalt fibers, which was also proved by using SEM images (Fig.1.-3.).

Fig.1. Cross-section of 20wt% basalt fiber reinforced PLA composite

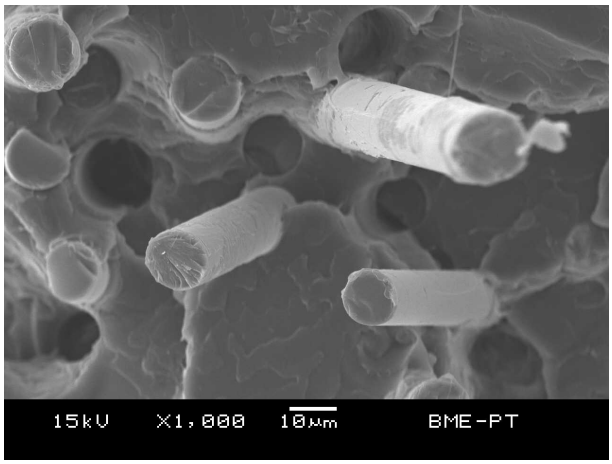

Fig.2. Cross-section of 30wt% basalt fiber reinforced PLA composite

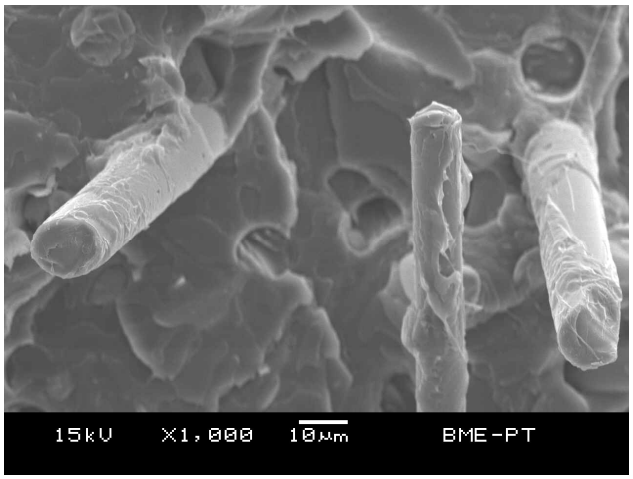

Fig.3. Cross-section of 40wt% basalt fiber reinforced PLA composite

As it was assumed, strong adhesion developed between the phases which is represented by the absence of any gap between the well embedded fibers and the matrix as well as strong adhesion is also represented by the well wetted basalt fibers.

After investigating mechanical properties, the thermal properties were also examined by DSC to analyze the effect of basalt fibers on the crystallinity of PLA (Fig.4.).

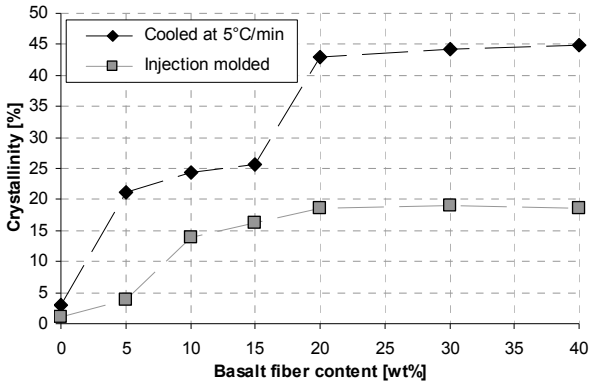

Fig.4. Crystallinity of the basalt fiber reinforced PLA composites

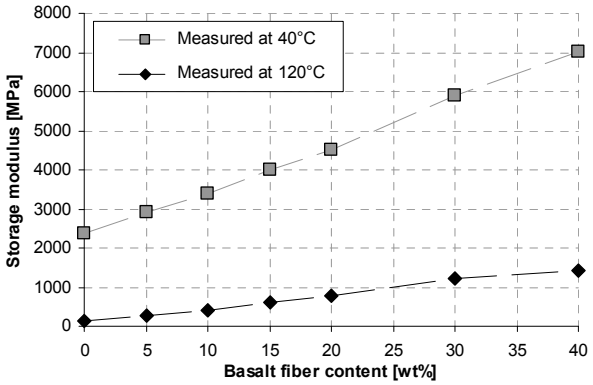

Fig.5. Storage modulus of the basalt fiber reinforced PLA composites measured at 40 and 120°C

It can be stated that the basalt fibers not only have excellent reinforcing effect on PLA, but it was also found that they have nucleating effect, which caused significantly higher crystallinity compared to neat PLA even though high cooling rate processing technology (injection molding) was used. For the injection molded specimens, the highest crystallinity reached was around 20%, which is more or less the half of the maximum possible achievable crystallinity of PLA. At the same time, when low cooling rate was used during DSC measurement (5°C/min), above 20wt% basalt fibers, the samples reached the possible maximum crystallinity of PLA which is indicated by the absence of cold-crystallization in the second heating scan. Again, it was demonstrated that basalt fibers have nucleating ability, which is an important aspect, because if it is possible to develop significant crystallinity during continuous injection molding production, then PLA products with high heat deflection temperature can be made.

DMA measurements were also performed in order to find out the usability of the developed composites and to analyze the effect of the developed crystallinity on the temperature dependence of storage modulus (Fig.5.).

As it can be seen, naturally basalt fibers increased the storage modulus of PLA and this increase is linear as a function of basalt fiber content in the investigated 0-40wt% basalt fiber region. By using 40wt% of basalt fiber reinforcement, the storage modulus increased by 194% and by 940% according to the storage modulus measured at 40°C and 120°C respectively. Typically, amorphous PLA loses most its storage modulus above T_g and enters into rubbery state. Although above T_g PLA will cold crystallize and its storage modulus will increase, but with increasing heat, first the major loss of storage modulus and the deformation of a PLA product will occur, thus a PLA product without significant crystalline ratio or without reinforcement cannot be used for structural applications. Even by using fiber reinforcement, in most cases the fibers cannot retard, but can only reduce the modulus loss above T_g.

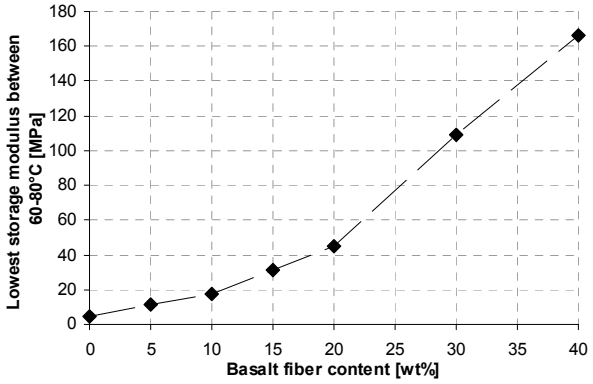

Fig.6. Lowest storage modulus of the basalt fiber reinforced PLA composites between 60 and 80°C

If the major modulus loss could be avoided by using the mentioned options, then PLA products with high HDT can be produced. This usability is represented by the lowest modulus of the PLA above T_g (Fig.6.). The pure PLA specimen loses nearly all its storage modulus and becomes practically useless above T_g. This lowest storage modulus value is significantly increased by incorporating basalt fibers into PLA, at the same time for the 40wt% basalt fiber reinforced PLA, the lowest modulus of 166 MPa measured at 71°C was still not enough to avoid deformation of the specimen.

For semi-crystalline PLA this lowest storage modulus at the same temperature is 250 MPa, which is important, because this material is considered as "heat stable PLA" with a HDT value of more than 120°C.

In order to examine the temperature caused deflection and deformation of the composites directly, the flat specimens were placed into a heated oven, in a single cantilever and the deflection was measured on the other side of the specimens (Table 3.). Note that in this measurement, the maximum possible deflection of the specimens was 38 mm.

Material	Deflection [mm] measured at…						
	25°C	40°C	50°C	60°C	80°C	100°C	120°C
PLA	0	0	0.2	9.9	38.0	38.0	38.0
PLA/15% basalt fiber	0	0	0	3.8	15.5	16.3	16.9
PLA/20% basalt fiber	0	0	0	1.2	8.3	8.6	9.0
PLA/30% basalt fiber	0	0	0	1.1	4.7	4.8	5.2
PLA/40% basalt fiber	0	0	0	0.8	4.6	4.6	5.1

Table 3. Deflection of the basalt fiber reinforced PLA composites

As it was discussed, and as it can be seen, pure PLA specimens highly deform above T_g as indicated by the rapidly increasing deflection above 50°C. This deflection was highly retarded by the usage of basalt fibers, which can be explained by the storage modulus increasing effect of the fibers and also by the increased crystallinity caused by the nucleating effect of the basalt fibers. Although the deflection of the specimens was highly retarded, the standard HDT analysis only showed a slight increase (Fig.7.).

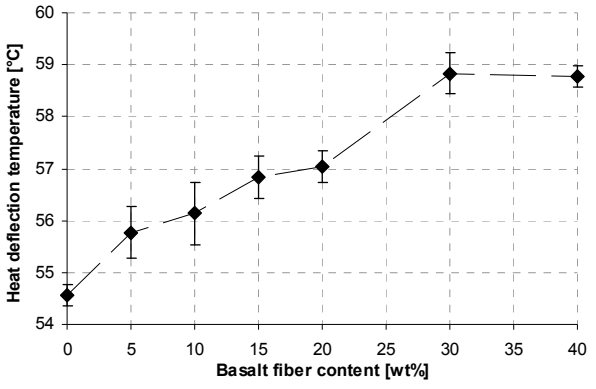

Fig.7. Heat deflection temperature of the basalt fiber reinforced PLA composites

Despite the previous results according to significantly decreasing the deflection of the specimens, the HDT value of the basalt fiber reinforced PLA composites increased only by some degree of Celsius, which can be explained by the very small permitted deflection (0.33 mm) according to a standard HDT test.

Nevertheless, the significant increase in storage modulus and the nucleating effect of basalt fibers suggest that by adding further nucleating agents, like the highly effective talc [22], the HDT value of the composites could reach 120°C.

4 Conclusions

In our work, the reinforcement of the most promising biodegradable polymer, the poly(lactic acid) (PLA) with mineral basalt fibers was investigated to analyze the usability of the prepared composite material for durable, engineering applications. According to our previous results, optimized drying conditions were used to analyze its effect on the properties of basalt fiber reinforced PLA composites. 5, 10, 15, 20, 30 and 40wt% basalt fiber content PLA composites were prepared by using extrusion and injection molding. It was found that basalt fibers highly increased all of the measured mechanical properties (tensile, flexural,

impact) and this increase was linear with increasing basalt fiber content in the case of tensile strength, tensile modulus and flexural strength, flexural modulus. By using 30wt% basalt fibers, a tensile strength and tensile modulus of 119.7 MPa and 7.62 GPa and a flexural strength and flexural modulus of 180.0 MPa and 10.37 GPa was reached respectively and moreover, one of the main drawbacks of PLA, the low impact strength was also enormously increased from 23.0 to 38.4 kJ/m^2 and from 2.7 to 9.5 kJ/m^2 according to unnotched and notched impact strength respectively. The scanning electron microscope observations revealed that there was very strong adhesion between the two phases which was indicated by the well embedded and well wetted basalt fibers. The basalt fibers were not only found to have significant reinforcing effect on PLA, but they also had nucleating effect. At the same time, the desired semi-crystalline PLA, which represents high HDT value of 120°C could only be achieved by using low cooling rate of 5°C/min. When using high cooling rate technologies like injection molding, more or less the half of the possible maximum crystallinity of PLA was found to be developed. The basalt fibers not only had nucleating effect but they also increased storage modulus. By using 40wt% basalt fibers, the storage modulus increased by 194% and by 940% according to the storage modulus measured at 40°C and 120°C respectively. It was also demonstrated that the basalt fibers could highly retard the deflection and deformation of the specimens above T_g, when PLA enters into rubbery state. At the same time, despite the significantly decreasing deflection with increasing basalt fiber content, the standardized HDT value of the specimens only increased by 5°C by using 40wt% basalt fibers, which can be explained by the very small permitted deflection (0.33 mm) according to a standard HDT test. Nevertheless, the major increase in storage modulus and the nucleating effect of basalt fibers indicate that by using further nucleating agents, like the highly effective talc, PLA based composites with high HDT value can be produced. Finally, in our work it was proved that is it possible to produce renewable (PLA) and natural (basalt) resource based composites with high mechanical properties not only by using very high cycle time processing technologies like film stacking or solvent casting to avoid fiber breakage but it is possible to use highly productive, low cycle time injection molding technology to produce accurate parts with complex geometries for high demand engineering applications.

Acknowledgments

The authors thank Arburg Hungária Kft. for the Arburg Allrounder 370S 700-290 injection molding machine and Lenzkes GmbH for the clamping tool system.
This work is connected to the scientific program of the 'Development of quality-oriented and harmonized R+D+I strategy and functional model at BME' project. This project is supported by the New Széchenyi Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002). This project is supported by the grant TÁMOP-4.2.2.B-10/1-2010-0009. This work was supported by the Hungarian Scientific Research Fund (OTKA K105257). This paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. Tibor Czigány would also acknowledge to Charles Simonyi scholarship.

References

[1] X. Ren "Biodegradable plastics: A solution of a challenge?". *Journal of Cleaner Production*, Vol. 11, pp 27-40, 2003.
[2] O. Martin, L. Averous "Poly(lactic acid): plasticization and properties of biodegradable multiphase systems". *Polymer*, Vol. 42, pp 6209-6219, 2001.
[3] L. Yu, K. Dean, L. Li "Polymer blends and composites from renewable resources". *Progress in Polymer Science*, Vol. 31, pp 576-602, 2006.
[4] L. T. Lim, R. Auras, M. Rubino "Processing technologies for poly(lactic acid)". *Progress in Polymer Science*, Vol. 33, pp 820-852, 2008.
[5] E. Bodros, I. Pillin, N. Montrelay, C. Baley "Could biopolymers reinforced with randomly scattered flax fibre be used in structural applications?". *Composites Science and Technology*, Vol. 67, pp 462-470, 2007.
[6] A. Iwatake, M. Nogi, H. Yano "Cellulose nanofiber-reinforced polylactic acid". *Composites Science and Technology*, Vol. 68, pp 2103-2106, 2008.
[7] L. Suryanegara, A. N. Nakagaito, H. Yano "The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites". *Composites Science and Technology*, Vol. 69, pp 1187-1192, 2009.
[8] J. Ganster, H.-P. Fink, M. Pinnow "High-tenacity man-made cellulose fibre reinforced thermoplastics – Injection moulding compounds with polypropylene

and alternative matrices". *Composites Part A*, Vol. 37, pp 1796-1804, 2006.

[9] K. Oksman, M. Skrifvars, J.-F. Selin "Natural fibres as reinforced in polylactic acid (PLA) composites". *Composites Science and Technology*, Vol. 63, pp 1317-1324, 2003.

[10] D. Plackett, T. L. Andersen W. B. Pedersen, L. Nielsen "Biodegradable composites based on L-polylactide and jute fibres". *Composites Science and Technology*, Vol. 63, pp 1287-1296, 2003.

[11] D. Plackett, T. L. Andersen, W. B. Pedersen, L. Nielsen "Biodegradable composites based on l-polylactide and jute fibres". *Composites Science and Technology*, Vol. 63, pp 1287-1296, 2003.

[12] B. Bax, J. Müssig "Impact and tensile properties of PLA/Cordenka and PLA/flax composites". *Composites Science and Technology*, Vol. 68, pp 1601-1607, 2008.

[13] K. Fukushima, A. Fina, F. Geobaldo, A. Venturello, G. Camino "Properties of poly(lactic acid) nanocomposites based on montmorillonite, sepiolite, and zirconium phosphonate". *Express Polymer Letters*, Vol. 6, pp 914-926, 2012.

[14] S. Bocchini, A. Frache "Comparative study of filler influence on polylactide photooxidation". *Express Polymer Letters*, Vol. 7, pp 431-442, 2013.

[15] V. V. Gur'ev, E. I. Neproshin, G. E. Mostovoi "The effect of basalt fiber production technology on mechanical properties of fiber". *Glass and Ceramics*, Vol. 58, pp 62-65, 2001.

[16] T. Deák, T. Czigány, P. Tamás, Cs. Németh "Enhancement of interfacial properties of basalt fiber reinforced nylon 6 matrix composites with silane coupling agents". *Express Polymer Letters*, Vol. 4, pp 590-598, 2010.

[17] T. Liu, F. Yu, X. Yu, X. Zhao, A. Lu, J. Wang "Basalt fiber reinforced and elastomer toughened polylactide composites: Mechanical properties, rheology, crystallization and morphology". *Journal of Applied Polymer Scienc*e, Vol. 125, pp 1292-1301, 2012.

[18] D. Kurniawan, B. S. Kim, H. Y. Lee, J. Y. Lim "Atmospheric pressure glow discharge plasma polymerization for surface treatment on sized basalt fiber/polylactic acid composites". *Composites Part B: Engineering*, Vol. 43, pp 1010-1014, 2012.

[19] X. Chen, Y. Li, N. Gu "A novel basalt fiber reinforced polylactic acid composite for hard tissue repair". *Biomedical Materials*, Vol. 5, pp 1-8, 2010.

[20] T. Tábi, J. G. Kovács "Examination of starch pre-process drying and water absorption on injection moulded poly(lactic acid)/starch blends". *Polymer Engineering and Science*, Vol. 51, pp 843-850, 2011.

[21] A. Riga, J. Zhang, J. Collis "Characterization of drawn and undrawn poly-L-lactide films by differential scanning calorimetry". *Journal of Thermal Analysis and Calorimetry*, Vol. 75, pp 257-268, 2004.

[22] D. Battegazzore, S. Bocchini, A. Frache "Crystallization kinetics of poly(lactic acid)-talc composites". *Express Polymer Letters*, Vol. 5, pp 849-858, 2011.