BASALT FIBRE REINFORCED POLY(LACTIC ACID) BASED COMPOSITES FOR ENGINEERING APPLICATIONS

T. Tábi[1,2*], N. K. Kovács[2], J. G. Kovács[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*
**tabi@pt.bme.hu*

Keywords: Biodegradable polymer composite, Poly(Lactic Acid), basalt fabric, film-stacking

Abstract
In our research we have investigated the usability of basalt fabrics and roving as a novel reinforcement for the renewable resource and inherently biodegradable polymer Poly(Lactic Acid) (PLA). The composites were prepared by using film-stacking method, thus by laying basalt fabrics and PLA film onto each other and compression moulding this layered structure. PLA film was produced film (sheet) extrusion from pellets. The effect of processing parameters, namely pressure and temperature was analysed on the mechanical properties of the composites. It was found that both parameters are highly effective in significantly increasing the wetting of the basalt fabric, and thus the mechanical properties. Finally, unidirectional composites were also prepared by the same method to be able to determine the maximum achievable strength of the basalt fibre reinforced PLA composites.

1. Introduction

In the recent decades, interest has grown enormously in the field of renewable resource based and inherently biodegradable polymers [1-3]. One of the most promising candidates of these biodegradable polymers is Poly(Lactic Acid) (PLA) [4, 5]. It can be synthetized from starch and sugar, where the former can be found all over the Globe in widely grown agricultural feedstock like corn (maize), wheat, potato, rice, pea. PLA, as a biodegradable polymer, can be composted into non-toxic materials like humus, water and carbon-dioxide, and according to these exceptional properties the complete life cycle of a product made of PLA can be fully fitted into the life cycle of nature. PLA is a thermoplastic polymer so it can be processed by using conventional plastic processing equipments [5] like injection moulding, extrusion, compression moulding, blow moulding, film blowing into for example cutleries, cups, bottles, food containers, trays, toothbrush handles, etc. Furthermore, PLA has good mechanical properties, like around 65 MPa of tensile strength and 3 GPa of tensile modulus, but it is considered as a brittle polymer with a notched and unnotched Charpy impact strength of 3 kJ/m^2 and 23 kJ/m^2 respectively. Although PLA has good mechanical properties, its applications are still mainly related to packaging and no or very few attempts are made to use PLA in engineering applications. In order to be able to use PLA as durable engineering material, fibre reinforcement has to be used and composite structures have to be prepared. To keep the “green” nature of PLA based composites, typically natural and renewable resource (cellulose) based plant fibres are mainly used for biocomposite preparation [6-11]. In recent years, much research has already been done in the field of natural (plant) fibre reinforced PLA composites, but in most cases only moderate reinforcing effect was found due to the to the inferior mechanical properties, high susceptibility to thermal degradation [12] and high standard deviation of the of natural plant fibres compared to glass or carbon fibres. The plant fibre reinforced PLA composites with the highest mechanical properties were in most cases reached by using film-stacking technology [10, 11], however, in these cases, the tensile strength was found still only around 100 MPa.

An alternative to plant fibres could be the usage of basalt fibres as reinforcement [13, 14]. Typically two kinds of melt processing technologies are present to produce basalt fibres from basalt rocks: continuous basalt fibres can be produced by using the Junkers technology, short basalt fibres are made by using the spinneret technology [15]. Although basalt fibres are not plant fibres and not renewable resource based ones, but they can be considered as “natural” due to the fact that basalt can be found in nature as the solidification of molten lava, and thus it can be found virtually everywhere all around the Globe in high amounts. Moreover, basalt is bioinert, and by its decomposition through mineralization, the mineral content of soil increases which strengthens its natural character. All these properties make basalt fibres a promising and novel natural reinforcement for biodegradable polymers. At the present time, the literature of basalt fibre reinforced PLA composites consists of only a few papers [16-19].

Kurniawan et al. [16] analysed the adhesion between the PLA and the basalt fibres surface treated with atmospheric pressure glow discharge plasma polymerization in hot pressed composites. It was possible to increase the tensile strength of the composites above the own strength of PLA, when plasma polymerisation time exceeded 3 minutes. It was demonstrated by electron microscopic micrographs, that the plasma polymerised fibres were well wetted by the PLA. Liu et al. [17] demonstrated that basalt fibres with the adequate sizing can significantly increase the mechanical properties of the basalt fibre reinforced PLA. It was also possible to further increase the impact strength of PLA from 19 kJ/m^2 to 34 kJ/m^2 (unnotched impact strength) by using 20wt% of basalt fibres and 20wt% of ethylene-acrylate-glycidyl methacrylate copolymer (EAGMA). PLA and basalt reinforced PLA can also be used in medical applications as Xi et al. [18] successfully produced PLA based scaffolds reinforced with basalt fibres for hard tissue repair. They proved that basalt fibres highly reduce the degradation rate of the PLA based scaffold, thus due to decreased acidification during absorption of the PLA, basalt fibres could also reduce inflammatory responses. It was also demonstrated that the basalt fibres have no significant influence on osteoblast viability and growth which proves that basalt fibre reinforced PLA scaffolds can be potentially used in hard tissue repair. Finally, in our previous publication [19] related to injection moulded, short (chopped) basalt fibre reinforced PLA composites, it was proved that it is possible to develop strong adhesion between the PLA and the basalt fibres by using silane sizing. Electron microscopy observations supported this statement as excellent wetting of the fibres was found.

According to the result of the literature, basalt is an excellent reinforcing fibre to produce high strength PLA based composites, at the same time, there were no publications found on producing basalt fabric reinforced PLA composites by using film-stacking method. Thus in our research the usability of basalt woven fabric reinforced PLA composites prepared by using film-stacking method was analysed. Moreover, the effect of processing parameters (temperature, pressure) were analysed on the mechanical properties of the composites. Finally, by using the optimum processing unidirectional composites were also prepared by using the same method to be able to analyse the maximum achievable strength of the basalt fibre reinforced PLA composites.

2. Materials and methods

Injection moulding grade PLA type 3052D (D-Lactide content is about 4%) was purchased from NatureWorks (Minnetonka, MN, USA). It was dried at 120°C for 4 hours prior to film extrusion. Basalt fabric type BAS 220.1500.P and basalt roving type KVT 150tex13-I was purchased from Kameny Vek (Dubna, Russia). The properties of both basalt fabric and roving can be seen in Table 1.

Properties of the raw material	
Density (bulk)	2.67 g/cm^3
Moisture content	0.1%
Melt temperature	1350°C
Properties of the fabric	
Area density	220 g/m^2
Type of weaving	plain
Properties of the roving	
Diameter of filament	13 μm
Linear density	150 tex
Tensile strength	65 cN/tex
Elasticity modulus	85 GPa
Sizing	Silane
Amount of sizing	0.4-0.6%

Table 1. Properties of the basalt fabric and roving used

PLA film with a thickness of 40-50 μm was produced by using a Labtech Scientific LCR 300 type sheet extrusion machine equipped with a Labtech Scientific LE25-30/CV single screw extruder and a slit die. A temperature profile of 210-220-220-225-230°C was used (from the hopper to the die) with a screw rotational speed of 20 rpm. After making PLA films, the films and the basalt fabrics were stacked onto each other and this layered structure was compression moulded (Figure 1.) with various processing parameters listed in Table 2. Unidirectional composites were also produced by first winding up the basalt roving onto a flat surface and then stacking the layer of the unidirectional basalt roving and the PLA films onto each other.

Figure 1. Film-stacking process (left) and the final basalt fabric reinforced PLA composite specimens (right)

Number of test composite	Layer structure	Temperature [°C]	Pressure [bar]
1	6 PLA – 5 basalt fabrics	190	100
2	6 PLA – 5 basalt fabrics	220	100
3	6 PLA – 5 basalt fabrics	250	100
4	6 PLA – 5 basalt fabrics	190	300
5	6 PLA – 5 basalt fabrics	220	300
6	6 PLA – 5 basalt fabrics	250	300
7	6 PLA – 5 basalt roving	220	300

Table 2. Processing parameters for basalt fabric or roving (unidirectional) reinforced PLA composite production

Prior to compression moulding melt flow index (MFI) measurements were made on the PLA in order to be able to determine the processing temperature window for the composite production. MFI measurements were performed by using a Ceast 7027.000 type melt flow indexer at various temperatures with a load mass of 2.16 kg. After selecting the processing temperatures based on the MFI results, the stacked layers of basalt fabrics (or roving) and PLA films were compression moulded. Compression time was 5 minutes in all cases, and the composites were cooled to room temperature with pressure on. In all cases, the thickness of the composites was 0.7-0.8 mm, while the fibre ratio was around 75wt% for the fabric reinforced and 60wt% for the roving reinforced unidirectional composites. Dumbbell shape specimens were cut from the composites for mechanical characterisation in warp direction. Tensile tests were performed to characterise the composites by using a Zwick Z020 universal testing machine. The tests were performed at room temperature and at a relative humidity of 40-60% by using a cross-head speed of 5 mm/min. 6 specimens were tested for each composite. Finally, Differential Scanning Calorimetry (DSC) was made on the basalt fabric reinforced PLA composite by using a TA Q2000 type calorimeter by using 3–6 mg of the samples. Heat/cool/heat scans were registered from 0 to 200°C with a heating and cooling rate of 10°C/min and nitrogen gas flow was used.

3. Results and discussion

Prior to compression moulding, the melt flow index (MFI) of PLA 3052D was determined to be able to analyse the processing window (Figure 2.).

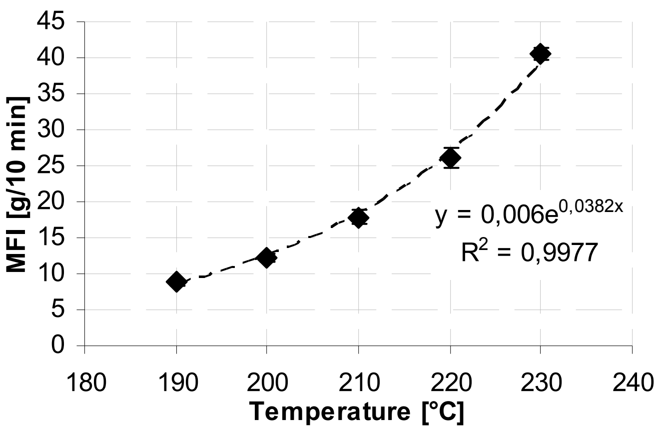

Figure 2. Melt flow index of PLA 3052D

It can be seen that by increasing the temperature, MFI increases exponentially within the analysed temperature range of 190-230°C. It is also evident from the results, that the MFI of

PLA is very sensitive to temperature, thus it highly changes only due to slight variations in temperature. Above 230°C, the MFI was so high that it was not possible to measure, at the same time, processing PLA above 230°C is not recommended by the manufacturer due to high probability of thermal degradation. According to the results, 190, 220, 250°C temperatures and 100, 300 bar pressures were selected as processing parameters. 250°C was selected as high processing temperature, at which PLA has high flowability and thus good wetting capability, however, it may degrade. It is believed, that by increasing processing temperature, two contradictory effects exists. First is that by increasing processing temperature, the melt flow of PLA will be higher, promoting better wetting of the basalt roving, subsequently, the possible highest temperature should be used. Secondly, by increasing processing temperature, the possibility of thermal degradation of PLA and the composite increases, accordingly, the possible lowest temperature (above melt temperature) should be used. These two contradictory effects of processing temperatures suggest the existence of an optimum value. On the results of the tensile tests of basalt fabric reinforced PLA composites, it is visible, that both temperature and pressure had significant effect (Figure 3.)

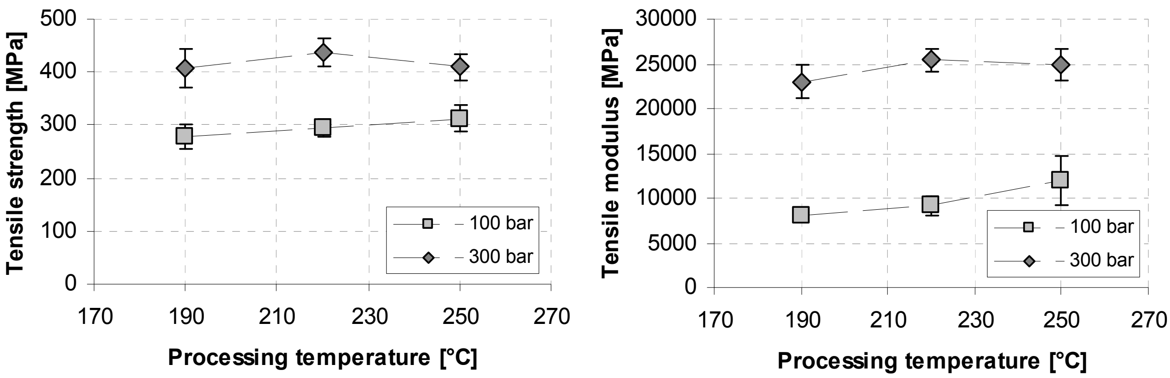

Figure 3. Tensile strength (left) and tensile modulus (right) of the basalt fabric reinforced PLA composites

All of the composites reached impressive mechanical properties with 300-400 MPa of tensile strength and 10-25 GPa of tensile modulus. As it can be seen, both tensile strength and modulus highly increased by increasing temperature and pressure, at the same time processing pressure had more significant effect than temperature; namely, by increasing temperature, tensile strength and modulus increased from 279 MPa and 8010 MPa to 319 MPa and 11910 MPa respectively (at 100 bar), while by increasing pressure, tensile strength and modulus increased from 294 MPa and 9170 MPa to 437 MPa and 25400 MPa respectively (at 220°C). The basalt fabric reinforced PLA composite material with the best and very impressive mechanical properties, namely 437 MPa of tensile strength and 25400 MPa of tensile modulus was produced at 220°C and at 300 bar. It also can be observed that the assumption was right, thus by increasing temperature, there is an optimum value, where the flowability of the PLA is high enough for proper wetting of the basalt fabric, but low enough to avoid major thermal degradation. This optimum temperature was found at 220°C. In this case, proper wetting of the basalt fabric was not only measurable on the mechanical properties, but it was even observable in the colour of the composite specimens produced at various temperatures (Figure 4.). The mechanical properties of the composites produced at 190°C and at 250°C were lower due to poor wetting (190°C) or due to probable thermal degradation (250°C).

Figure 4. Test specimens produced at 220°C (left) and at 190°C (right) by using 300 bar pressure

In this research, it was also analysed whether these two processing parameters have synergistic effect or not. As it is visible on Figure 3., the gradients connecting the measurement results are practically parallel, which suggests that the possible cross-effect of the two processing parameters are negligible. According to the optimal processing parameters (220°C, 300 bar), unidirectional composites were also produced to be able to analyse the possible maximum achievable strength and stiffness of basalt fibre reinforced PLA composites (Figure 5.).

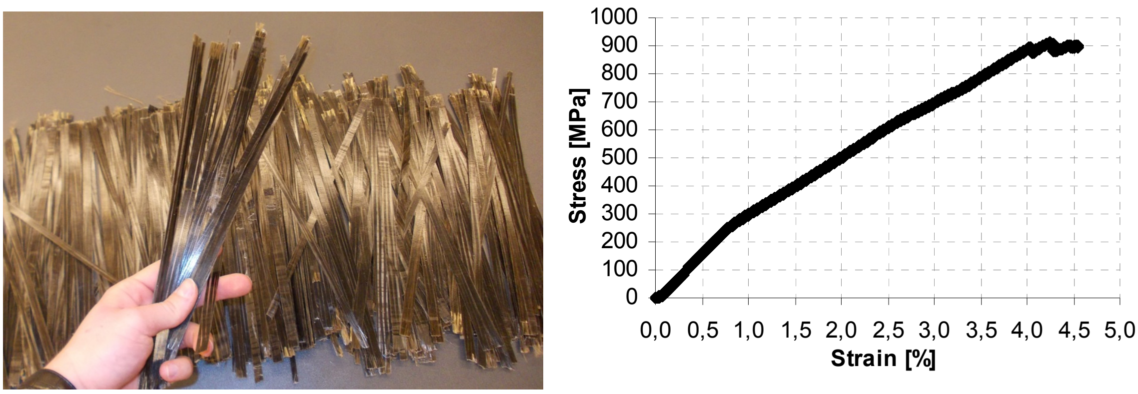

Figure 5. Unidirectional basalt fibre reinforced PLA specimens (left) and its tensile testing curve (right)

It was proved that a very impressive tensile strength of 910 MPa and tensile modulus of 32 GPa can be achieved for unidirectional basalt fibre reinforced PLA composites. Finally, differential scanning calorimetry was performed to analyse the nucleating properties of basalt fibres (Figure 6).

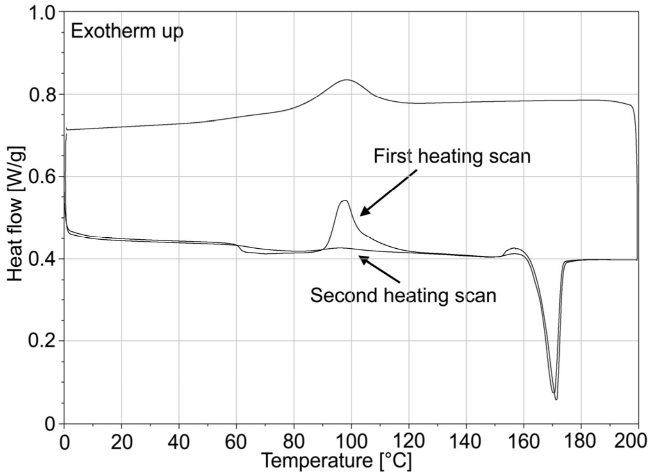

Figure 6. DSC curve of the basalt fabric reinforced PLA

Basalt fibres found to have nucleating properties as an exothermic peak is visible on the cooling scan, moreover, it was found that at the cooling rate of 10°C/min basalt fibres had so significant nucleating properties that the cold crystallisation exothermic peak disappeared in the second heating scan indicating that PLA reached the possible maximum crystallinity during cooling. Crystalline PLA has a strong advantage over amorphous PLA, namely its heat deflection temperature is around 120°C, while the same value for amorphous PLA is around 50°C. At the same time, as first heating scan suggests, the crystallinity of the compression moulded specimen was not complete due to higher cooling rate during processing than 10°C/min. This uncompleted crystallisation is indicated by the existence of cold crystallisation in the first heating scan. Subsequently, the heat deflection temperature of the compression moulded specimens is more likely close to 50-60°C (heat deflection temperature was not measured). Nevertheless, probably by adding nucleating agents, it is possible to achieve high crystallinity during real processing thermal conditions, resulting in increased heat deflection temperature of even more than 120°C.

4. Conclusions

In our work, the usability of basalt fabric and roving reinforced, renewable resource based Poly(Lactic Acid) composites was analysed. Basalt fabric and unidirectional basalt roving reinforced PLA composites were prepared by using film-stacking method with a fibre ratio of 75wt% and 60wt% respectively. The effect of processing parameters, namely pressure and temperature was analysed on the mechanical properties of the composites. It was demonstrated, that both temperature and pressure had significant effect on the mechanical properties of the composites, at the same time pressure had much more significant effect than temperature. It was proved, that the possible cross-effect of the two processing parameters are negligible. According to our presumption, temperature had two contradictory effects, namely by increasing temperature, wetting of the basalt fabric increases, while PLA may degrade thermally at high temperatures. This optimum processing temperature was found at 220°C. All of the composites reached impressive mechanical properties with 300-400 MPa of tensile strength and 10-25 GPa of tensile modulus, while the basalt fibre reinforced PLA composite material produced at 220°C and at 300 bar gave the best and impressive mechanical properties, namely 437 MPa of tensile strength and 25400 MPa of tensile modulus. According to the unidirectional basalt fibre reinforced PLA composites an enormous tensile strength of 910 MPa and tensile modulus of 32 GPa could be achieved. Finally, by using differential scanning calorimetry it was proved that basalt fibres have so significant nucleating ability, that by slow cooling rate (10°C/min), PLA can fully crystallise, however, to be able to crystallise PLA during processing conditions, the addition of nucleating agents is necessary.

5. Acknowledgements

This paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. This publication was supported by the Italian-Hungarian and the Mexican-Hungarian bilateral agreement of the Hungarian Academy of Sciences. This work was supported by the Hungarian Scientific Research Fund (OTKA K105257, PD105995). 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). The authors thank Arburg Hungária Kft. for the Arburg Allrounder 370C 700-290 injection moulding machine, Lenzkes GmbH for the clamping tool system and Piovan Hungary Kft. for their support.

References

[1] X. Ren. Biodegradable plastics: a solution or a challenge?. *Journal of Cleaner Production*, 11(1):27-40, 2003.

[2] M. Flieger, M. Kantorová, A. Prell, T. Rezanka, J. Votruba. Biodegradable plastics from renewable resources. *Folia Microbiologica*, 48(1):27-44, 2003.

[3] R. Chandra, R. Rustgi. Biodegradable polymers. *Progress in Polymer Science*, 23(7):1273-1335, 1998.

[4] Z. Kulinski, E. Piorkowska. Crystallization, structure and properties of plasticized poly(l-lactide). *Polymer*, 46(23):10290-10300, 2005.

[5] L. T. Lim, R. Auras, M. Rubino. Processing technologies for poly(lactic acid). *Progress in Polymer Science*, 33(8):820-852, 2008.

[6] A. Iwatake, M. Nogi, H. Yano. Cellulose nanofiber-reinforced polylactic acid. *Composite Science and Technology*, 68(9):2103-2106, 2008.

[7] M. Kowalczyk, E. Piorkowska, P. Kulpinski, M. Pracella. Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers. *Composites Part A: Applied Science and Manufacturing*, 42(10):1509-1514, 2011.

[8] S. Y. Cho, H. H. Park, Y. S. Yun, H. J. Jin. Cellulose nanowhisker-incorporated poly(lactic acid) composites for high thermal stability. *Fibers and Polymers*, 14(6):1001-1005, 2013.

[9] B. Bax, J. Müssig. Impact and tensile properties of PLA/Cordenka and PLA/flax composites. *Composite Science and Technology*, 68(7-8):1601-1607, 2008.

[10] D. Plackett, T. L. Andersen, W. B. Pedersen, L. Nielsen. Biodegradable composites based on L–polylactide and jute fibres. *Composite Science and Technology*, 63(9):1287-1296, 2003.

[11] E. Bodros, I. Pillin, N. Montrelay, C. Baley. Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications?. *Composite Science and Technology*, 67(3-4):462-470, 2007.

[12] M. M. Kabir, H. Wang, K. T. Lau, F. Cardona. Effects of chemical treatments on hemp fibre structure. *Applied Surface Science*, 276:13-23, 2013.

[13] T. Czigány, T. Deák, P. Tamás. Discontinuous basalt and glass fiber reinforced PP composites from textile prefabricates: effects of interfacial modification on the mechanical performance. *Composite Interfaces*, 15(7-9):697-707, 2008.

[14] B. Wei, H. Cao, S. Song. Environmental resistance and mechanical performance of basalt and glass fibers. *Material Science and Engineering: A*, 527(18-19):4708-4715, 2010,

[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*, 58(1-2):62-65, 2001.

[16] 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*, 43(3):1010-1014, 2012.

[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 Science*, 125(2):1292-1301, 2012.

[18] C. Xi, Y. Li, N. Gu. A novel basalt fiber reinforced polylactic acid composite for hard tissue repair. *Biomedical Materials*, 5(4):1-8, 2010.

[19] T. Tábi, P. Tamás, J. G. Kovács. Chopped basalt fibres: A new perspective in reinforcing poly(lactic acid) to produce injection moulded engineering composites from renewable and natural resources, *Express Polymer Letters*, 7(2):107-119, 2013.