ACCEPTED FOR PUBLICATION IN COMPOSITES PART A: APPLIED SCIENCE AND MANUFACTURING
PUBLISHED IN MAY 10, 2014
DOI: 10.1016/J.COMPOSITESA.2014.05.001

TITLE:

INVESTIGATION OF INJECTION MOULDED POLY(LACTIC ACID) REINFORCED WITH LONG BASALT FIBRES

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1. Abstract

In this paper long basalt fibre reinforced Poly(Lactic Acid) (PLA) composites were prepared and analysed. Continuous basalt roving was coated with PLA by using continuous extrusion coating technology and a special die. The continuous basalt roving coated with PLA was cut into 10 mm long pellets, which were injection moulded. The properties of the long fibre reinforced composites were compared to chopped (short) basalt fibre reinforced PLA composites produced by using the conventional dry mixing, extrusion and injection moulding method. The mechanical properties of the long basalt fibre reinforced PLA was found to be superior to short basalt fibre reinforced PLA. Fibre length analysis revealed that the remaining average fibre length highly increased, while electron microscopy demonstrated that there is very strong adhesion between the phases. Finally it was found that the long basalt fibres also have nucleating ability, however, not as efficient as short basalt fibres.

2. Keywords

Mechanical properties (B), injection moulding (E), extrusion (E), Long basalt fibre composite (nominated new keyword)

3. Introduction

In the last decades renewable resource based and inherently biodegradable polymers got into the focus of interest and research, because it is believed that due to their exceptional properties, these polymers will replace some of the petrol based ones used nowadays [1, 2]. These exceptional properties are that they can be fully synthesized from renewable resources and they can also be degraded biologically in compost conditions into water, carbon-dioxide and humus, which latter can be used for nutrition of the next generation of plants for renewable resource and thus biodegradable polymer production. According to these features the life cycle of biodegradable polymers can be fit into the life cycle of nature, so they can ensure sustainability in polymer recycling.

By the fermentation of starch and sugar received both from renewable resources, lactic acid can be produced, which can be further processed by using ring opening polymerisation of the dimer of lactic acid called lactide into the promising biodegradable polymer currently, Poly(Lactic Acid) (PLA) [3]. PLA has good mechanical properties, high strength and stiffness; however, it is considered as a brittle polymer with a strain at break around 3-5% and a notched and unnotched Charpy impact strength of around 3 and 23 kJ/m^2 respectively. Moreover, the very slow crystallisation of PLA [4-8] prevents it to be used in high temperature applications due its low glass transition temperature (T_g) around 50-55°C. Since PLA is a thermoplastic polymer, it can be processed by using conventional plastic processing equipments like injection moulding, extrusion, thermoforming, blow, sheet, or compression moulding [9] into products like cutleries, cups, flower pots, food containers, films, toothbrush handles or biomedical implants [10]. Although the high strength and stiffness of PLA suggest it to be used in engineering applications, nowadays most PLA products on the market are only related to packaging industry.

One of the possibilities of making PLA more suitable for engineering applications is to reinforce it with typically natural plant fibres [11-19] to keep its renewable resource based and biodegradable feature. There are numerous publications in this field, however in most cases only slight reinforcing effect was demonstrated in injection moulded, plant fibre reinforced biocomposites compared to glass or carbon fibre reinforced composites. This can be attributed to the lower mechanical properties of plant fibres, their curved shape caused not exact orientation, the high variation in their mechanical properties, and to their susceptibility to thermal degradation [20]. According to these features in most cases significant reinforcing effect was only found in biocomposites when gentle processing method and long fibre reinforcement was used like film-stacking method with natural fibre fabric [16, 17]. Although injection moulding reduces the length of the fibres and may also degrade them, this technology should be used in order to produce precise, complex, 3D shaped products in high amounts with low cycle time and to make PLA and PLA based composite product manufacturing economical.

Besides the plant fibres, another promising fibre to reinforce PLA is the basalt fibre [21-25]. Although basalt is not a cellulose based plant fibre and thus it is not renewable resource based, but it is a mineral fibre, considered also as natural, because it can be found in nature as the solidification of molten lava, which is virtually present everywhere on the Globe. Moreover, basalt was proved to be chemically and biologically inert so it can be used even in medical implants [26], which also strengthens its natural feature as well as the fact that by its mineralization, it increases the mineral content of the soil, which degradation process takes however much longer time compared to PLA, but it is relatively fast compared to other rocks. Typically two kinds of melt processing technologies are present to produce basalt fibres from basalt rocks: by using the Junkers technology continuous basalt fibres, while by using the spinneret technology short basalt fibres are made [21].

According to some recent publications, basalt was already proved to be a good and novel alternative to reinforce PLA, however, there are only a few publications in this field [26-29].

It was proved by Liu et al. [27] that basalt fibres with the adequate sizing can significantly increase tensile, bending and impact strength of PLA. By using 20wt% of basalt fibres and 20wt% of ethylene-acrylate-glycidyl methacrylate copolymer (EAGMA) it was possible to further increase the impact strength of PLA from 19 kJ/m^2 to 34 kJ/m^2 (unnotched impact strength). Finally it was stated that there is strong connection between the phases, due to the absence of gaps at the fibre-matrix interface, however the surface of the fibres were still poorly wetted by the matrix. Kurniawan et al. [28] treated the surface of the basalt fibres by using atmospheric pressure glow discharge plasma polymerization and analysed the adhesion between the basalt fibres and PLA in hot pressed composites. It was demonstrated that by increasing the plasma polymerisation time above 3 minutes it was possible to increase the tensile strength of the composites above the own strength of PLA. The plasma polymerised fibres were well wetted by the PLA on the electron microscopic micrographs, however the tensile strength of he composite was lower compared to results from Liu et al. [27]. Xi et al. [26] successfully produced PLA based scaffolds reinforced with basalt fibres for hard tissue repair. It was proved that the basalt fibres highly reduce the degradation rate of the scaffold, thus it most likely also decreases inflammatory responses caused by acidification during absorption of the PLA. It was also demonstrated that the basalt fibres have no significant influence on osteoblast viability and growth which confirms that PLA scaffolds reinforced with basalt fibres can be potentially used in hard tissue repair. Finally, in our previous publication [29] related to injection moulded PLA reinforced with short basalt fibres it was demonstrated that it is possible to develop strong adhesion between the PLA and the basalt fibres by using silane sizing. The strong adhesion was proved by electron microscopy by observing excellent wetting of the fibres.

According to the result of the literature, basalt is an excellent reinforcing fibre to produce high strength PLA based composites even in injection moulding conditions, where the length of the fibres are highly reduced. At the same time, as the authors are aware, there are no attempts in the literature to produce not only short but long basalt fibre reinforced injection moulded composites, thus in our work, long (10 mm) basalt fibre reinforced PLA pellets were produced by using extrusion coating technology. The long fibre reinforced pellets were processed by using conventional injection moulding and the properties of the specimens were analysed compared to short basalt fibre reinforced PLA composites.

4. Materials, processing and experimental

Injection moulding grade PLA type Ingeo 3251D from Natureworks Co. was used, which was dried at 120°C for 6 hours prior to processing to remove as much residual moisture as possible to avoid hydrolitical degradation [30]. Continuous basalt roving containing a number of 1000 filaments as well as chopped basalt fibres with fibre length of 10 mm was purchased from Kameny Vek. The average diameter of the fibres was 13 μm and both types had silane treatment (under trade name of KV-12). The continuous basalt roving was coated with PLA in continuous extrusion coating method by pulling the basalt roving through a special coating die similar to the one used in cable extrusion. The details of the special coating die used in our research are described in the publication of Kmetty et al [31]. The extruder used was a LabTech Scientific twin screw extruder (screw diameter = 26 mm, L/D = 40) with a temperature profile of

175-180-185-190-250°C (from the hopper to the die) and a screw rotational speed of 10 rpm. The weight% of the basalt fibres was set by controlling the speed of the roving pulled through the coating die. The coated continuous roving was cut into 10 mm long pellets and annealed prior to injection moulding at 120°C for 2 hours to avoid processing problems (pellet sticking to the screw) caused by cold-crystallisation reported in our previous research [6]. Finally, the long basalt fibre reinforced PLA pellets were injection moulded with an Arburg Allrounder 370S 700-290 injection moulding machine equipped with a diameter 30 mm, L/D = 25 screw. These composites are referred in the paper as long basalt fibre composites. For reference the results from our previous publication [29] were used, where chopped fibre reinforced PLA with a nominal basalt fibre content of 5, 10 ,15, 20, 30, 40 wt% was prepared by using chopped (10 mm) basalt fibres and the conventional dry mixing, extrusion, pelletising and injection moulding method. These composites are referred in the paper as short fibre reinforced composites. Injection rate of 50 cm^3/s, holding pressure of 600 bars, holding time of 20 sec, residual cooling time of 40 sec, melt and mould temperature of 190°C and 20°C was used respectively for both short and for long basalt fibre composites. ISO standard dumbbell, three-point bending (Charpy) specimens with a cross-section of 4x10 mm were injection moulded.

Tensile, three-point bending and Charpy tests were performed by using a Zwick Z020 universal testing machine and a Ceast Resil Impactor impact testing machine respectively. The tests were performed at room temperature and at a relative humidity of 60%, by using a cross-head speed of 5 mm/min for the tensile and bending tests, and a 15 J impact energy hammer for the Charpy impact tests. Notched (2 mm deep notch) and unnotched specimens were also tested; 15 J and 6.21 J impact energy was used for the unnotched and notched specimens respectively.

Differential Scanning Calorimetry (DSC) was performed by using a TA Q2000 type calorimeter by using 3-6 mg of the samples. Heat/cool/heat scans were registered from 0 to 180°C with a heating and cooling rate of 5°C/min and nitrogen gas flow was used. Crystallinity was calculated according to the theoretical enthalpy of fusion of 100% crystalline PLA (93.0 J/g) [7] by using the following formula, where the basalt fibre content was also taken into consideration:

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

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

Dynamic Mechanical Analysis (DMA) was performed on a TA Q800 tester by using the injection moulded three-point bending specimens in dual cantilever mode. Amplitude of 20 μm and a frequency of 1 Hz were used from 0 to 160°C at a heating rate of 2°C/min.

Heat Deflection Temperature (HDT) was measured by using a Ceast HV3 6911.000 HDT analyser. Injection moulded specimens in edgewise mode, with a cross-section of 4x10 mm and support distance of 100 mm were used. The applied pressure was 0.45 MPa and the heating rate was 2°C/min. The HDT value is obtained when the deflection reached 0.33 mm.

Scanning electron microscopy (SEM) was performed by a Jeol JSM 6380LA type electron microscope. The fracture surfaces of the tensile specimens were used for the observations. Au/Pd alloy was sputtered onto the surface prior to observation to avoid electrostatic charging.

Finally, fibre length distribution was measured for the short and for the long basalt fibre composites after injection moulding. The fibre length distribution was measured by calcinating the samples taken from or from the middle of the injection moulded specimens and by determining the length of the fibres by using optical microscopy (type Olympus BX 51M). 200 fibre lengths were determined for each sample to characterise distribution.

5. Results and discussion

5.1. Determining fibre content

During coating of continuous basalt roving with PLA, it was only possible to obtain a uniform coating when the speed of the roving pulled through the coating die was between 120 to 200 mm/sec. Below 120 mm/sec and above 200 mm/sec unsteady melt flow occurred resulting in unevenly or uncoated stages in basalt roving. On the cut surface of the properly coated basalt roving cut into 10 mm long pellets (Fig. 1.) it was proved by using SEM, that the PLA matrix has not wetted the basalt roving and the individual fibres entirely, but it only coated the roving (Fig. 2.) as it was presumed.

During extrusion coating, due to the relatively low pressure the PLA matrix has not infiltrated the basalt roving, nevertheless, in this stage of processing, the entirely wetting of the basalt fibres is not necessary. At the same time, if the individual fibres are not dispersed and wetted during injection moulding, this could cause an increase in the standard deviation of the mechanical properties of the injection moulded samples.

After cutting the continuous basalt roving coated with PLA into 10 mm long pellets, the fibre content of the pellets was determined in the function of the roving pulling speed (Fig. 3.).

It was found that the basalt fibre content of the coated roving increased linearly from an average value of 14.8wt% to 25.8wt% with increasing roving pulling speed from 120 to 200 mm/sec. In the rest of this paper, the long basalt fibre materials made by using various roving pulling speeds are referred after their basalt fibre content and not after the pulling speed.

5.2. Analysis of reinforcing fibres

After injection moulding the long basalt fibre reinforced PLA pellets into test specimens, the adhesion between the phases and the separation of the basalt roving into individual fibres was analysed on the fracture surface of the already tested specimens by using Scanning Electron Microscope (SEM). Only the fracture surface of 20wt% short and 20.4wt% long fibre reinforced PLA composites were selected for publication (Fig. 4.), since all other fracture surfaces showed very similar topography (data not shown).

It can be seen, that the separation of the individual fibres of the basalt roving in the pellets took place during injection moulding. Moreover, excellent wetting of the basalt fibres was also found for both short and long basalt fibres, which suggests strong adhesion between the phases. Despite the significant fibre brakeage that generally occurs during injection moulding, the initial 10 mm length of the long basalt fibres remained noticeably higher compared to the length of short basalt fibres. To be able to quantitatively characterise the remaining length of the fibres in the injection moulded composites, fibre distribution analysis was performed (Fig. 5.).

It is observable that the remaining average fibre length in the composites was significantly higher for the long basalt fibre reinforcement compared to short fibre reinforcement. In the case of 20.4wt% of long and 20wt% of short basalt fibre reinforcement the remaining average fibre length was found to be 658 μm and 159 μm, which means an aspect ratio of 50 and 12 respectively according to the 13 μm diameter basalt fibres. For both short and long basalt fibre reinforcement, the remaining fibre length decrease with increasing fibre content, which can be related to increased fibre-fibre friction caused by the increased number of fibres.

5.3. Mechanical properties

After injection moulding the long basalt fibre reinforced PLA pellets into test specimens, the tensile, bending and impact (Charpy) mechanical properties were determined and compared to the properties of short basalt fibre reinforced PLA composites (Fig. 6.-8.). Although in the long basalt fibre reinforced pellets, the basalt roving was only coated with PLA, and the individual fibres in the roving were not completely wetted, even so their separation and wetting took place during injection moulding. This is represented by previous SEM observations and also by the similarly low standard deviation of the mechanical properties of the long fibre reinforced composite samples compared to short basalt fibre reinforced composites, which is expectable according to the accuracy and reproducibility of the injection moulding technology.

For the tensile and flexural strength of the basalt fibre reinforced PLA composites, it can be seen that it was possible to obtain better properties with increasing fibre length (Fig. 6.). At 20wt% fibre content by increasing fibre length from 159 μm to 658 μm and thus the aspect ratio from 12 to 50, the tensile and flexural strength increased from 98 MPa and 144 MPa to 124 MPa and 182 MPa respectively. It can also be observed that 20wt% long basalt fibre composites have more or less the same tensile and flexural strength as 30wt% short basalt fibre composites, thus according to the increased fibre length 10wt% less fibre reinforcement was enough to reach the same strength as short fibre reinforced composites. The highest tensile and flexural strength values were reached with the composites containing the highest amount of long basalt fibre reinforcement (25.8wt%), namely 127 MPa and 197 MPa respectively.

As for the modulus values, both tensile and flexural modulus for long and short basalt fibre reinforced PLA composites were found to be practically the same (Fig. 7.) with an average gradient of 142 and 218 MPa/wt% basalt for tensile and flexural modulus respectively with an initial tensile and flexural modulus of PLA of 2970 and 3300 MPa respectively. Thus, for 20wt% short and 20.4wt% long basalt fibre content, tensile modulus was found to be 6000 and 5900 MPa while flexural modulus was found to be 7300 and 7700 MPa respectively. Generally, the modulus of a reinforced polymer composite with the same matrix material is dependent on the amount and on the modulus of the reinforcement used. Since the same type and the same amount of fibre was used, and the only difference was found in the length of the reinforcement, this resulted in the insignificant differences between the modulus values of the long and short basalt fibre reinforced composites.

In order to be able to use PLA as engineering material not only high strength and stiffness must be developed, but also the impact strength of PLA has to be increased, since it is considered as a brittle material. Theoretically long fibre reinforcement mostly affects the impact properties of the composites. Accordingly, it is found that by using only 15wt% long basalt fibres the unnotched and notched impact strength of PLA enormously increased with increasing fibre length from 23.0 to 69.7 kJ/m^2 (203% increase) and from 2.7 to 18.7 kJ/m^2 (593% increase) respectively (Fig. 8.).

This is also a very significant improvement compared to short basalt fibre reinforcement, where the unnotched and notched impact strength of the composite for the same 15wt% reinforcement was only 29.3 kJ/m^2 and 5.9 kJ/m^2 respectively. By further increasing the long basalt fibre content from 14.8wt% to 25.8wt% neither the unnotched nor the notched impact strength has increased further significantly, which can be explained since the length of the longest fibres responsible for the increased impact strength are reduced most probably by fibre-fibre friction due to the higher amount of fibres as demonstrated previously. Nevertheless, the significantly increased impact strength compared to short fibre composites confirms the increased remaining fibre length of the long basalt fibre reinforcement. These results are in accordance with the literature of long fibre reinforced thermoplastics, for example Thomason [32, 33] analysed the properties of long glass fibre reinforced and injection moulded polypropylene, and found that the impact strength is significantly improved, while the modulus remained almost constant with increasing fibre length. Moreover, our results are also in accordance with the composite theory, which indicates that both short and long fibre reinforced injection moulded composites contain short fibres, where the "too short" fibres (below the critical fibre length according to the Kelly-Tyson equation) act like a filler, thus they are only responsible for increasing stiffness, while short fibres (above critical fibre length) are responsible for increasing stiffness and strength, and finally, the long fibres are responsible for increasing both stiffness, strength and impact properties. According to this theory, by increasing average fibre length, it almost has no effect on stiffness, moderate effect on strength (depending on the amount of fibres with a length below and above critical fibre length) and major effect on impact properties, as it was also found in our results.

5.4. Thermal analyses

To be able to use PLA in engineering applications, not only its low impact strength, but also its low heat deflection temperature (HDT) of around 45-55°C has to be increased. The very low HDT value of PLA is caused by its low T_g and low crystalline ratio, which latter is in turn caused by its very slow crystallisation, especially in low cycle time melt processing technologies with typically rapid cooling, like injection moulding. During injection moulding of PLA according to the cooling rate of even 500-1000°C/min, the products remain mostly amorphous and thus transparent. Highly effective nucleating agents like talc are necessary to obtain high crystallinity, which could retard the significant distortion of the PLA products above T_g, resulting in a HDT of around 120°C. During analysis of the DSC cooling curves, it was found that long basalt fibres also have nucleating effect as it was already proved for the short basalt fibres [29]. At the same time, the nucleation was found to decrease with increasing fibre length, which is demonstrated by the much smaller and broader exothermic peak on the cooling scan of the long basalt reinforced PLA composite compared to short basalt reinforcement (Fig. 9.).

This effect can be explained by the heterogeneous nucleating effect, where the formation of nuclei is induced by the number of impurities in the polymer material including fillers, or reinforcements. In most cases additives with high specific area like the flake shaped talc are proved to have better nucleating efficiency, thus even though the amount of the basalt fibres were the same, the higher number of short basalt fibres resulted in higher nucleating efficiency compared to long basalt fibres. According to the remaining average fibre length of the 20wt% short and 20.4wt% long basalt fibre reinforcement of 159 µm and 658 µm respectively, the number of basalt fibres is three times more, which act as increased number of impurities in the polymer matrix inducing the formation of nuclei and could explain the higher heterogeneous nucleating efficiency of the short basalt fibres, but nevertheless, this hypothesis still needs to be proved.

Consequently, by quantitatively analysing DSC data, it was found that the final crystallinity of the injection moulded samples (high cooling rate) and the samples cooled at 5°C/min decreased by increasing fibre length (Fig. 10.).

Although in case of 20wt% short basalt fibres and low cooling rate of 5°C/min, the nucleation effect was so significant, that the samples reached the possible maximum crystallinity of 42.9%, but for the long basalt fibre composites final crystallinity was only 18.8%. In comparison, for the injection moulded samples, the crystallinity values were found to be naturally lower due to high cooling rates, namely 18.7% and 5.1% for the short and long basalt fibre composites respectively. From the results it is evident that basalt fibre reinforced PLA products with high HDT cannot be made simply by relying on the nucleating properties of the basalt fibres, at the same time the significant stiffness increasing effect of the basalt fibres may assist to achieve this goal.

The basalt fibres not only found to have nucleating effect, but it could also retard the high modulus loss above T_g. When heating a PLA product above T_g, first it will suffer major distortion due to decreased modulus, but afterwards, due to cold-crystallisation, the modulus of PLA will increase, and the distorted shape will be stiff again. According to the developed crystalline ratio during cold-crystallisation, the deformed product will have a much higher HDT (around 120°C if the annealing is complete) compared to original one with low crystalline ratio. Unfortunately, this phenomenon cannot be used to anneal products after processing to be able to withstand high heat due to the enormous deformation occurring below the temperature of cold-crystallisation. At the same time, if the product contains proper amount and adequately stiff fibre reinforcement which could as much as possible retard this deformation and the major drop in modulus above T_g until the cold-crystallisation of the product is finished, then high HDT can be ensured. Unfortunately, this significant drop in modulus above T_g can still be observed on the storage modulus of short and long basalt fibre reinforced PLA as well as the favourable increase in modulus caused by cold-crystallisation (Fig. 11.).

The most important index-number that characterises the deformation retarding capability of the basalt fibres is the lowest storage modulus between T_g and cold-crystallisation around 60-80°C. It can be observed that again it is advantageous to use long fibre reinforcement, since by increasing basalt fibre content, the lowest storage modulus increased more significantly in case of long basalt fibre reinforced composites compared to short basalt fibre reinforced ones. For 20wt% basalt fibre reinforced composites, by increasing fibre length, the lowest storage modulus vales increased from 45 to 121 MPa, while for the highest amount of reinforcement, namely for 40wt% of short and 25.8wt% of long basalt fibre reinforcement, the lowest storage modulus values were found to be 166 and 199 MPa respectively.

HDT analyses were also performed to quantitatively characterise the maximum possible service temperature of the composites. Despite it was found previously that the long basalt fibres increased the lowest storage modulus determining HDT more significantly than short basalt fibres, this increase in stiffness caused by long basalt fibres and the increased crystallinity caused by their nucleating ability was still not enough to adequately retard deformation above T_g till the beginning of cold-crystallisation, and thus it was still not enough to develop a PLA based composite with a HDT value of much higher than 60°C. Nevertheless, probably by adding further nucleating agents, due to the increased stiffness and crystallinity caused by the basalt fibres, and the nucleating agents respectively, their cross-effect may ensure a much higher HDT, even for example as high as the HDT value of crystalline (annealed) PLA of more than 120°C.

6. Conclusions

In our research long basalt fibre reinforced Poly(Lactic Acid) (PLA) composites were prepared by using extrusion coating and injection moulding technology. The long basalt fibre composites were produced by first using a continuous basalt roving pulled through an extrusion coating die in continuous technology, then by cutting the basalt roving coated with PLA into 10 mm long pellets, and finally by injection moulding the pellets. By controlling the speed of the basalt roving, it was possible to set the fibre ratio between 14.8 to 25.8 wt%. The properties of the long basalt fibre reinforced PLA were compared to chopped (short) basalt fibre reinforced PLA composites with 5-10-15-20-30-40 wt% basalt fibre content prepared by using chopped (10 mm) fibres and conventional dry mixing, extrusion, pelletising and injection moulding method.

By using scanning electron microscopy (SEM) on the fracture surfaces, excellent wetting of the basalt fibres was found, which suggests strong adhesion between the phases. Moreover, despite to the enormous fibre brakeage that generally occurs during injection moulding, the significantly higher average fibre length of the long fibre reinforced PLA composites compared to short fibre reinforced ones was even observable in the fracture surface of injection moulded tensile specimens. This statement was confirmed by fibre length measurements performed on the injection moulded samples demonstrating that remaining average fibre length increased from 159 μm to 658 μm and thus the aspect ratio from 12 to 50 (13 μm fibre diameter) according to 20wt% of short and 20.4wt% of long basalt fibre reinforced composites respectively.

The investigated mechanical properties of the long basalt fibre reinforced PLA composites were superior compared to the short basalt fibre reinforced composites. By increasing fibre length, in the case of 20wt% reinforcement, the tensile strength increased from 98 MPa to 124 MPa, flexural strength increased from 144 MPa to 182 MPa, while unnoched and notched impact strength increased enormously from 29.9

kJ/m^2 to 70.1 kJ/m^2 and from 5.8 kJ/m^2 to 18.3 kJ/m^2 respectively. The 20wt% long basalt fibre reinforced composites had more or less the same tensile and flexural strength, than 30wt% short basalt fibre reinforced composites, thus 10wt% less basalt fibre content was enough to obtain same mechanical properties in case of long basalt fibre reinforcement.

The long basalt fibres were also proved to have nucleating ability, however, it was found that the nucleating ability of the basalt fibres decrease by increasing fibre length. In case of same reinforcing ratio the decreased heterogeneous nucleating efficiency of the long basalt fibres compared to short basalt fibre can be related to the higher average remaining fibre length and thus to the smaller number of basalt fibres, which could act as impurities in the polymer matrix inducing the formation of nuclei. Moreover, the basalt fibres not only proved to have nucleating ability, but it could also retard the well-known significant storage modulus loss above glass transition temperature (T_g). Naturally, the storage modulus loss could be more significantly moderated by increasing fibre length. Despite the significant stiffness increasing effect of long basalt fibres and their nucleating ability, it only increased the heat deflection temperature (HDT) from 55 to 61°C. Most probably by adding further nucleating agents not only to increase stiffness, but also to increase crystallinity more significantly, their cross-effect may ensure a much higher HDT, even for example as high as the HDT value of the crystalline (annealed) PLA of more than 120°C.

Finally it was demonstrated that it is possible to produce long basalt fibre reinforced PLA composite products in series with excellent mechanical properties not only by using high cycle time technologies like compression moulding, but by using highly productive continuous extrusion coating technology followed by injection moulding.

7. 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.

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9. Figure Captions

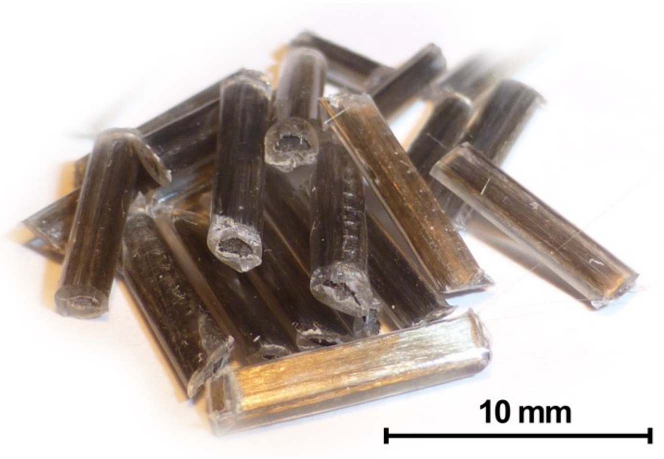

Fig. 1. 10 mm long pellets of basalt roving coated with PLA

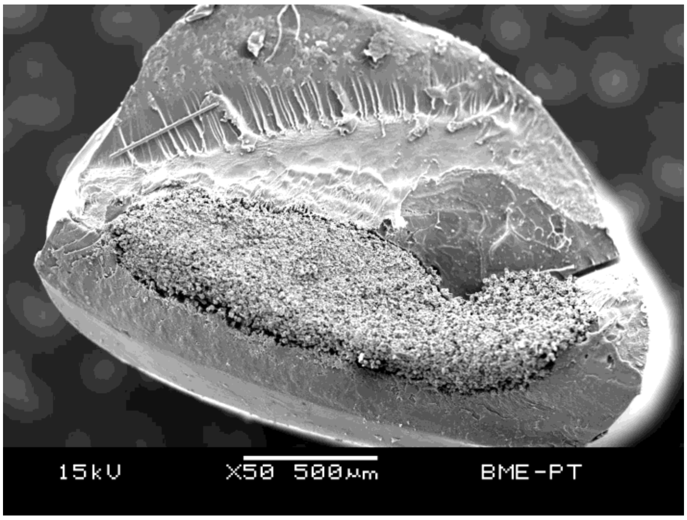

Fig. 2. The cross section of the basalt roving coated with PLA

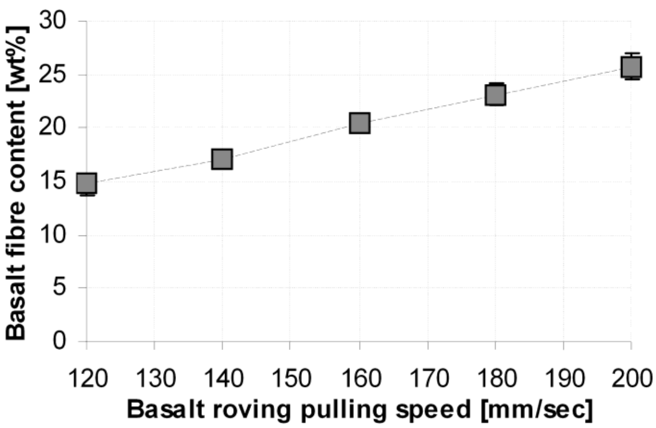

Fig. 3. Basalt fibre content of the coated basalt roving produced by using various pulling speeds

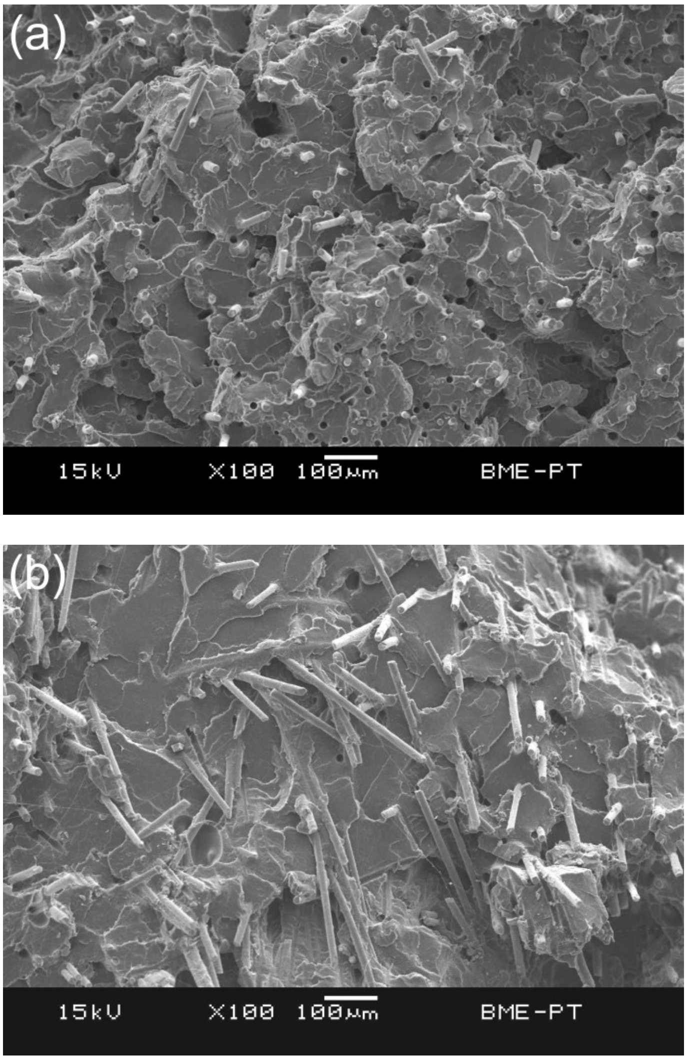

Fig. 4. Fracture surface of 20 wt% short (a) and 20.4 wt% long (b)

basalt fibre reinforced PLA composite

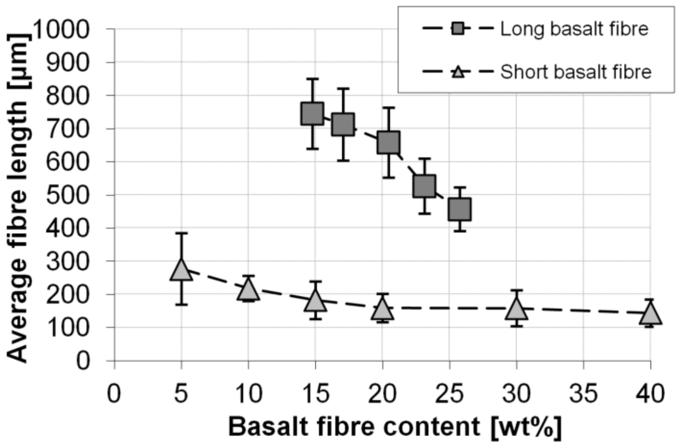

Fig. 5. Average fibre length of the short and long basalt fibre reinforced injection moulded composites

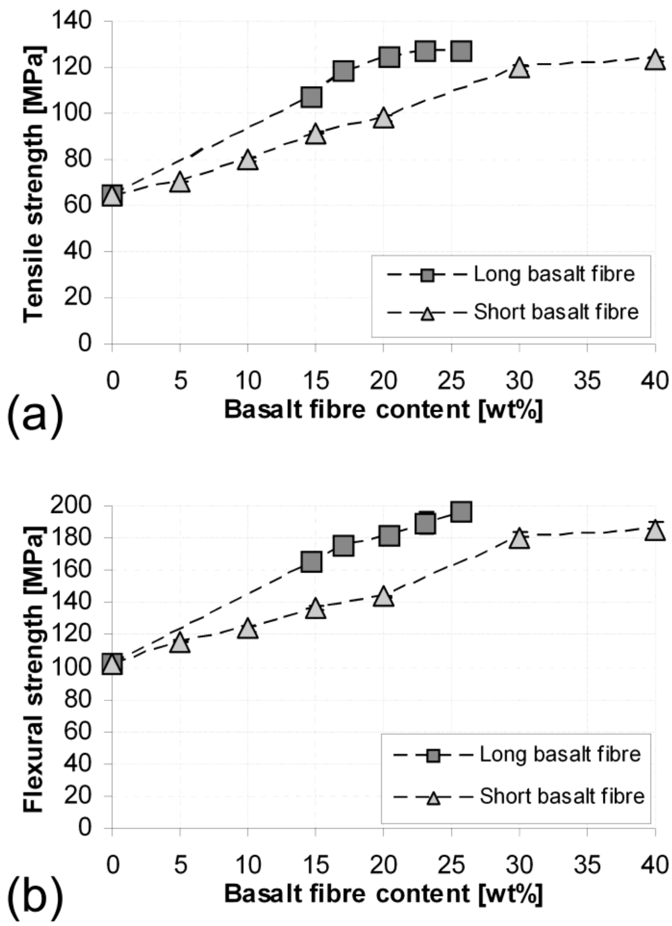

Fig. 6. Tensile (a) and flexural (b) strength of the long and short basalt fibre reinforced PLA composites

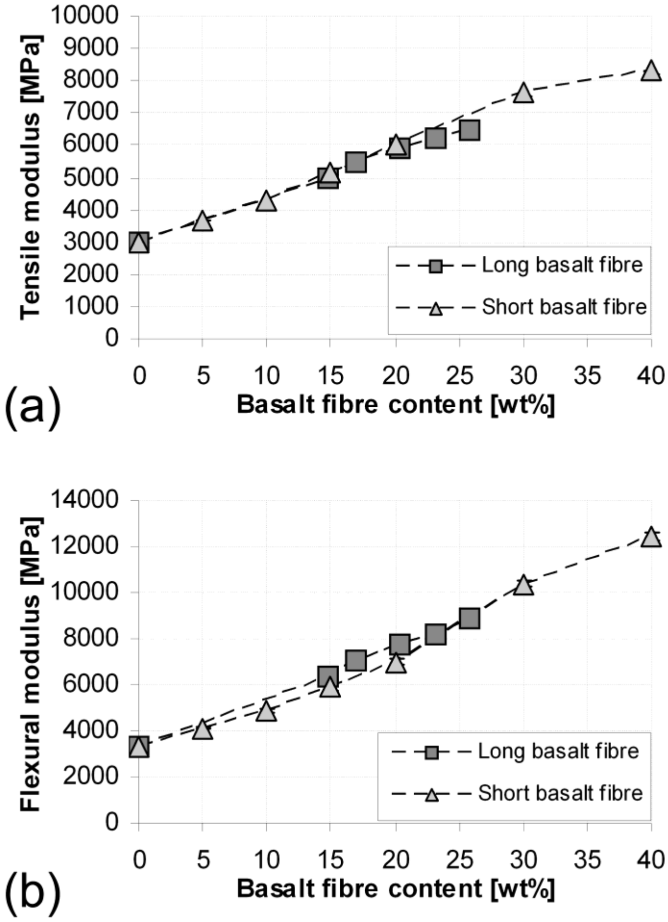

Fig. 7. Tensile (a) and flexural (b) modulus of the long and short basalt fibre reinforced PLA composites

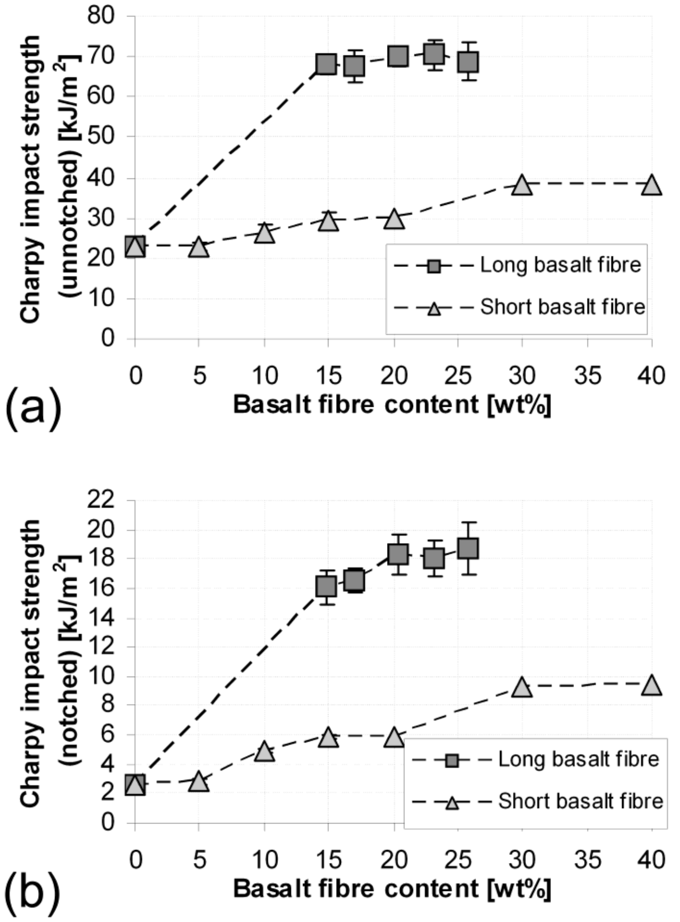

Fig. 8. Unnotched (a) and notched (b) charpy impact strength of the long and short basalt fibre reinforced PLA composites

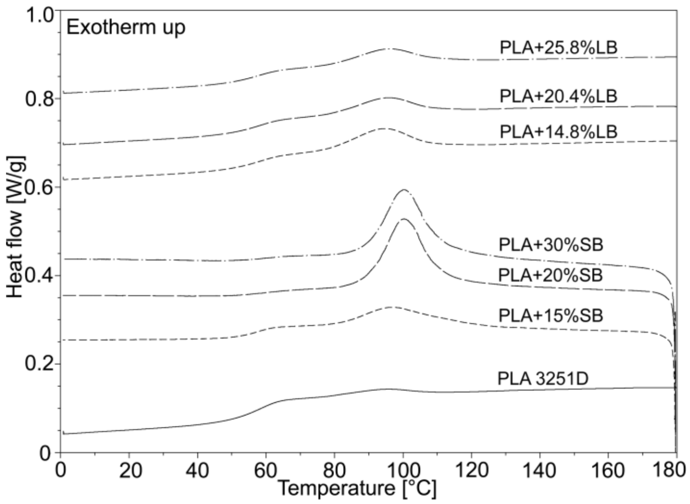

Fig. 9. Cooling curves of long (LB – Long Basalt) and short (SB – Short Basalt) fibre reinforced PLA composites,

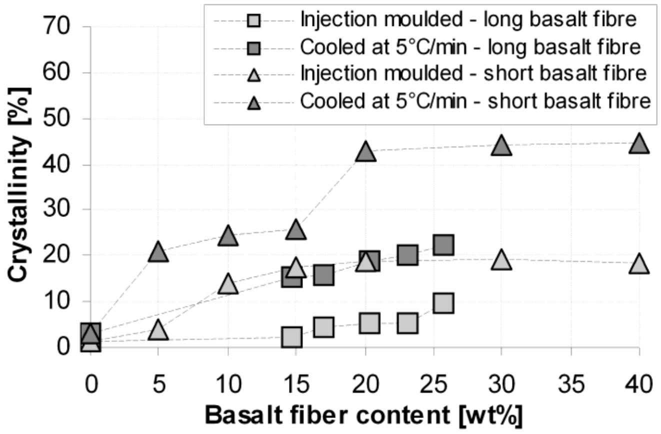

Fig. 10. Crystallinity of the long and short basalt fibre composites

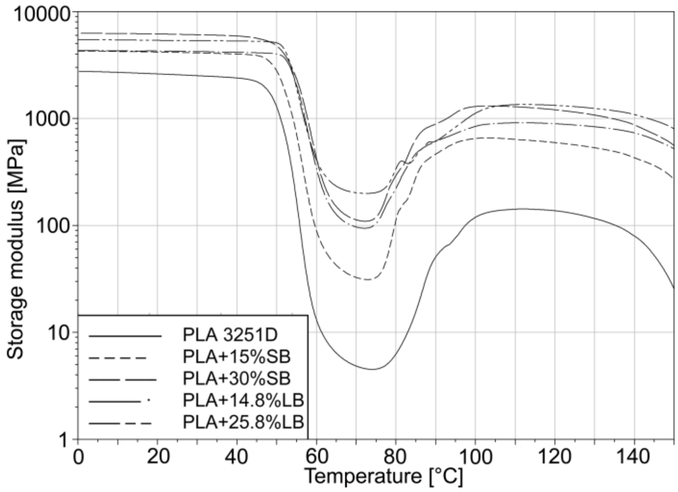

Fig. 11. Storage modulus of PLA and short (SB – Short Basalt) and long basalt (LB – Long Basalt) fibre reinforced PLA