INFLUENCE OF THE COMPRESSION MOLDING TEMPERATURE ON THERMOMECHANICAL PROPERTIES OF THE BASALT-REINFORCED POLY(LACTIC ACID) (PLA) COMPOSITES

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The aim of this study was to verify the influence of the compression molding temperature on thermomechanical properties of the basalt-reinforced poly(lactic acid) (PLA) composites. The thermomechanical properties of the composites were determined in the course of dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), static tensile test and tensile impact strength test. The incorporation of basalt fiber into poly(lactic acid) matrix led to obtaining environmentally friendly composite materials with good mechanical properties. The composite production process carried out at different temperature set-ups (170°C, 180°C, 190°C and 200°C) led to the development of composite materials characterized with favorable mechanical properties and specific structure. The simultaneously realized thermal, thermo-mechanical and mechanical analyses allowed to describe the limitation processes resulting from the application of different compression molding temperatures. The best thermomechanical properties were recorded for the composites pressed at the highest temperature (200°C).

Keywords: *poly(lactic acid), basalt fiber, thermomechanical properties, compression molding*

1. Introduction

An ongoing industrial growth related to a more frequent use of composite contruction materials calls for the development of new environmentally friendly engineering materials and manufacturing methods. Biodegradable polymers, such as: poly(hydroxybutyric acid) (PHB), poly(lactic acid) (PLA), cellulose, starch and lignin are often used in order to obtain eco products. Because of its simultaneous biodegradation and production from renewable sources, PLA, often defined as "double green", is the most popular biopolymer among all the above mentioned materials. The main application fields of this polymer include packaging production, prostheses, as well as the automotive industry and electronics [1-7]. Due to its low glass transition temperature, low thermal stability and low resistance to mechanical degradation during polylactide formation in molten state, PLA requires modification by introducion into matrix organic, inorganic and fillers, especially fibrous type [8]. Therefore, various methods of obtaining poly(lactic acid) reinforced composites from particles of different shapes and sizes are the main focus of scientific and industrial research. In recent years, many investigations have addressed natural fiber application as a reinforcement of poly(lactic acid) composite.

Baghaei et al. described mechanical properties and water absorption characteristics of biocomposites made from woven PLA/hemp/Lyocell prepregs with 30 wt% of the fiber. PLA composites reinforced by both hemp and Lyocell showed an improvement in mechanical properties, compared to hemp/PLA composites. The best mechanical properties were recorded for the composite made from satin Lyocell/PLA fabric [9]. The application of recycled injection molded polylactide composites to the composites reinforced with regenerated cellulose fibers (Lyocell) of variable fineness and fiber content of 30 wt% was presented in the study [10]. The threefold reprocessed composites with similar fibre length distribution showed a significantly higher tensile strength compared to the virgin sample. The influence of fibre loading, fineness, and two processing methods on the mechanical properties of lyocell/PLA composites was investigated by Graupner et al. The authors proved that the compression molded composites have a significantly higher tensile and impact strength than the injection molded composites [11]. Variable mechanical properties of the composites were assigned to the fibre aspect ratio and distribution of voids [11,12].

Although basalt fibers are not biodegradable, they are still classified natural as

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they are derived from volcanic rocks and are biologically inert [13]. Basalt fiber is cost-effective and offers exceptional properties over glass fibers. Composites reinforced with this fiber type are characterized by high specific mechano-physico-chemical properties, biodegradability, and non-abrasive qualities [14,15]. Moreover, the production process of basalt fiber is less energy intensive and easier than that of any competing fiber [13].

Chen et al. first introduced basalt fiber as an innovative reinforcement into a poly(L-lactic acid) (PLLA) matrix in order to fabricate composite materials for hard tissue repair [16]. The authors confirmed that basalt fibers uniformly dispersed in the PLLA matrix, significantly improving the mechanical properties and hydrophilicity of the PLLA matrix and retarding the polymer degradation rate. Liu et al. proved that basalt fiber introduced into PLA with a twin screw extruder had a significant reinforcing and toughening effect in comparison with glass fiber [17]. Tábi et al. described PLA composites reinforced with silane treated and untreated chopped basalt fibers, using extrusion, and injection molding [18]. Silane treated chopped basalt fibers resulted much more effective in reinforcing PLA than natural fibers. In another work Tábi et al. presented composites obtained from continuous basalt roving coated with PLA using continuous extrusion coating technology and a special die [19]. After this process the roving was cut and injection molded. The mechanical properties of the long fibre reinforced composites were improved in comparison to chopped fibre reinforced composites produced using a conventional dry mixing, extrusion and injection molding method. The results of the study carried out by Kurniawan et al. proved that out of all fiber surface treatments only the silane treated and atmospheric plasma polymerized composites showed better mechanical properties [20]. To sum up, in the times of global changes severely affecting natural environment, manufacturing and investigating into new material solutions have become one of the most important tasks for scientists. Therefore, in comparison to the state of the art, the novelty in this paper is the use of compression molding processes to obtain poly (lactic acid) composites with high usable temperature and stable thermomechanical properties. In consequence extending the applicability of PLA as a polymer matrix in construction materials is still highly desirable.

It should be underlined that compression molding, despite being a highly energy consuming production technology, is still a favorable technology used in the production of thermoplastic composite materials containing fibrous-fillers in a form of fabrics. Therefore, the possibility of process optimalization, including reduction of processing temperature, is highly desirable. The aim of this study was to verify the influence of the compression molding temperature on thermomechanical properties of the basalt-reinforced polylactide (PLA) composites and to determine the lowest critical processing temperature which allows to produce thermoplastic polymer-based laminates characterized with defined and good mechanical properties.

2. Experimental

2.1. Materials

As a thermoplastic polymeric matrix commercial poly(lactic acid) (PLA) 4043D from Nature Works (USA) was used. PLA was characterized with specific gravity of 1.24 g/cm^3, melt density of 1.08 g/cm^3 and 6 g/10 min (230°C, 2.16 kg) melt flow index (MFI). Basalt fiber woven fabric (BF) type BAS 220.1270.P with 210 g/m^2 with plain weave type used as a filler was delivered by BASALTEX (Belgium).

2.1.1. Composite manufacturing process

The composites were manufactured in a steel mold by compression molding process. First, the polylactide film was pressed at the temperature of 190°C using lab press type-7 PLHS for 3 min in vacuum. Five sheets of 170mm x 170mm were cut from basalt woven fabrics and covered by PLA film layer by layer. The temperature of the compression molding was 170°C, 180°C, 190°C and 200°C for 4 min in vacuum. The fiber content in composites was approximately 75 wt%. The samples were described as 170BF; 180BF; 190BF; 200BF respectively to the molding temperature. Sample preparation scheme is presented in Figure 1.

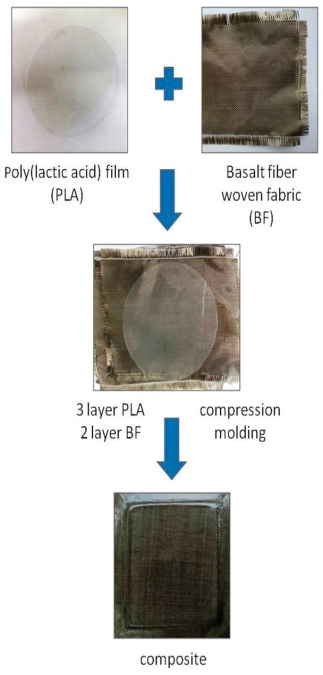

Fig. 1 – Sample preparation scheme.

2.2.Methods

2.2.1.Scanning Electron Microscopy (SEM)

The structure of composites was evaluated by Scanning Electron Microscopy (SEM). The fracture surfaces of the samples were investigated with magnifications of 1000x and digitally captured using a scanning electron microscope - Zeiss Evo 40. The electron accelerating voltage of 12 kV was applied. Prior to the tests, all the specimens were sputtered with a layer of gold.

2.2.2.Determination of weight percentage of basalt in the composites

The basalt fibre content in the composites was determined by resin burn-off. A weighed amount of sample was taken and heated to 800°C to constant weight. The wt% basalt (x) was calculated according to the formula:

$$x = w_2/w_1 * 100$$

where:
w_1 - the weight before heating and w_2- the weight after heating

2.2.3.Dynamic mechanical thermal analysis (DMTA)

The dynamic-mechanical properties of the composites with 10x1,5x50 mm dimensions were measured using DMTA methods (Anton Paar MCR 301, Austria) in a torsion mode, operating at frequency f = 1 Hz in the temperature range between 25°C and 200°C, and at heating rate 2°C min. The position of tanδ at its maximum was taken as the glass transition temperature (Tg).

2.2.4.Differential scanning calorimetry (DSC)

DSC measurements were performed using a Netzsch DSC 204 F1 Phoenix® apparatus with aluminum crucibles and approximately 5 mg samples under nitrogen flow. All the samples were heated up to 210 ºC and held in a molten state for 5 min, followed by cooling down to 20°C. Heating and cooling rates were equal to 10°C/min. This procedure allowed to get more insight into thermal properties of the modified PLA-based composites.

2.2.5.Tensile mechanical properties

Tensile mechanical properties of the composites were investigated with INSTRON 4481 universal testing in accordance with ISO 527-4. All tests were performed at ambient temperature (23°C) with testing speed 5 mm/min with a load cell of 50kN. Each test was performed for 15 specimens.

2.2.6.Tensile impact strength

The tensile impact strength of the unnotched samples with 10x4x80 mm dimension were determined in accordance with ISO 8256, using hammer type PSD50/15 for 15 samples in each series.

2.2.7.Thermogravimetry (TGA)

The thermal properties of the composites were tested by thermogravimetric analyses (TGA) with temperature range between 30°C and 900°C at a heating rate of 10°C/min under nitrogen atmospheres, using a Netzsch TG 209 F1

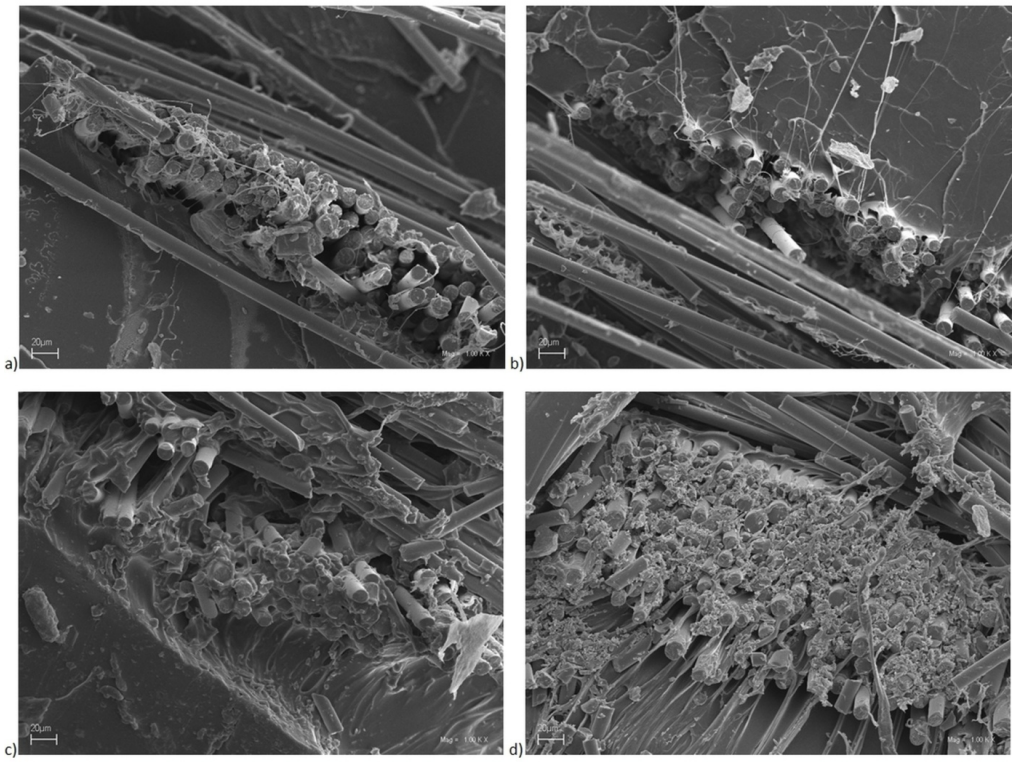

Fig.2 - SEM microphotographs of composite a) 170BF b) 180BF c) 190BF d) 200BF.

apparatus. Approximately 5 mg samples were placed in ceramic pans. The initial decomposition temperature $T_{5\%}$ was determined as a temperature at which the weight loss was 5%. The residual mass (W%) was defined at 900°C.

3.Results

3.1.Scanning Electron Microscopy (SEM)

Figure 2 shows the morphology of the composites. The dark gray color stands for poly(lactic-acid) matrix and light gray for fiber. In samples 190BF and 200BF all basalt fiber was covered with polymer matrix. Moreover, no fiber pull-out effect was observed for these samples. This may prove the good adhesion between fibers and PLA matrix. On the other hand, characteristic hollows in polymer matrix were observed in sample 170BF. This may have been caused by too low temperature during compression molding process and as a result, insufficient saturation of the fiber by PLA matrix.

3.2.The weight percentage of basalt fibre in the composites

The burn-off experiment allowed to determine the exact amount of inorganic fibers in thermoplastic laminates. The weight percentage of basalt in the composites was comparable and it was approximately 75 wt%. The introduction of a considerable amount of fibrous filler to the polymer matrix led to obtaining composites with good mechanical properties.

3.3.Dynamic mechanical thermal analysis (DMTA)

DMTA analysis was carried out to define the influence of compression molding temperatures on the viscoelastic properties of the composites described by storage modulus (G′) and loss factor (tanδ) presented as a function of temperature (Fig.3). The storage modulus (G') represents the elastic portion of viscoelastic behavior connected with solid-state behavior of the sample. Additionally, the values of the composite storage modulus measured at various temperature values and glass transition temperature (Tg) are collected in Table 1. The G′ and Tg values of composites increased simultaneously with the increase of molding temperatures (from 1010 MPa to 1490 MPa and from 65°C to 81°C). The increase of these values is essential from their further application point of view, due to a potential extension of the temperature range of the used composites made of polylactide. This phenomenon may be attributed to the reinforcing effect achieved as a result of the basalt fiber`s presence in polymer matrix. Moreover, the higher temperature of polymer matrix during processing (resulting in lower viscosity of PLA melt) allowed to obtain a better saturation of basalt fabrics and thus led to a

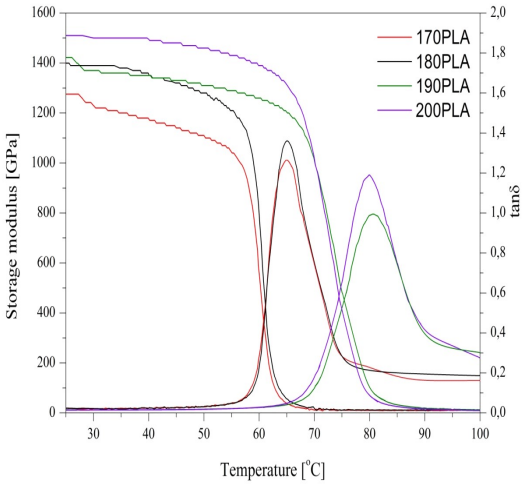

Fig. 3 - DMTA curves of PLA-based composites.

Table 1

The values of composites storage modulus and glass transitions obtained during DMTA analysis

Name	G'[MPa] at 25°C	G'[MPa] at 25°C	Tg [°C]	Tan δ peak
170PLA	1220	1110	65	1.3
180PLA	1400	1280	71	1.4
190PLA	1420	1310	81	1.0
200PLA	1510	1460	80	1.1

better coherence of composite material. Low glass transition temperature of pure poly(lactic acid) (i.e. 50 to 60°C), limits the scope of the PLA-based product use. Therefore, an improved performance of the PLA materials is a key factor in manufacturing environmentally friendly materials. The analysis of the loss factor as a function of temperature allowed to describe not only the changes in molecular structure of the polymer, but also interactions between polymer blends and composite components [21]. It was observed that when a higher processing temperature was applied, the values of the PLA-based composite transition temperature increased significantly. The compression molding temperature increase led to the increase of glass transition temperature measured as a peak of tanδ vs. T curve. According to literature, lowered adhesion between composite material components and filler saturation by polymeric matrix may result in a significant decrease of Tg [21,22]. In considered case, samples produced at lower processing temperatures (170°C and 180°C) reveal lower glass transition temperatures in comparison to those observed for samples prepared at 190°C and 200°C. Therefore, it may be stated that the saturation of basalt fabrics by PLA matrix was insufficient in case of samples produced with the processing temperature below 190°C. It should be

Table 2

Thermal properties of PLA and PLA-based composites obtained during DSC analysis

Material	-	170°C		180°C		190°C		200°C	
	Polymer - pellet	Polymer	Composite	Polymer	Composite	Polymer	Composite	Polymer	Composite
ΔHm	31.9	7.4	10.5	1,5	3.7	6.67	5.74	9.67	10.63
Xc	30.1	7	39.6	1.4	14	6.3	21,7	9.1	40,1
Tm_1	154.2	148.8	151.5	147.4	151.3	149.6	151.8	148.8	151.9
$\Delta Hm_{100\%}$=106 J/g [23]									

also mentioned that the loss factor peak measured at glass transition temperature gives extensive information on material damping properties - the lower tanδ value, the lower ability to dissipate mechanical energy and vibration absorption. This fact corresponds with the DMTA results obtained for grouped samples produced at a lower temperature characterized with insufficient adhesion (170PLA and 180PLA) and correctly saturated (190PLA and 200PLA). The discrepancies in tanδ values measured at peak for 170PLA and 180PLA samples resulted from the insufficient basalt fabric saturation by biodegradable polyester due to high viscosity of polymeric melt during processing. Thanks to a better penetration of polymeric matrix, the 180PLA sample revealed a better composite material coherence which in consequence increased its stiffness. In case of composite series characterized with a proper basalt fabric saturation by PLA (PLA190, PLA200), the difference was a result of macromolecular effects occurring during cooling of the PLA-based composite. Poly(lactic acid) is a thermoplastic polymer with a low crystallization ability. The increasing forming temperature (200PLA) resulted in a longer cooling of the polymeric composite which in turn led to a lowered amount of the brittle amorphous phase, improved impact resistance and allowed for mechanical vibration attenuation, in comparison to samples produced at a lower temperature (190°C).

3.4.Thermal properties

Thermal properties, such as: melting enthalpy (ΔHm), melting temperature measured at first heating (Tm_1), and crystallinity level (Xc) of pure PLA and PLA-based composites, are collected in Table 2. The crystallinity level of composite materials was calculated on the basis of the real filler amount determined in the burn-off experiment, i.e. 75 %. The presented DSC data include: test results for pure PLA in pellet form delivered by the supplier, pure PLA polymeric films prepared under specified temperature conditions, and composite samples produced at various processing temperatures with fixed filler amount (75 wt%). Poly(lactic acid) is a thermoplastic polyester material with a relatively low crystallization ability. Usually, during processing in industrial conditions, ready-to-use products made from unmodified PLA are characterized with amorphous structure which results in high transparency and brittleness. The DSC tests were prepared for both pure PLA and PLA-composites and were carried out on samples formed under identical processing conditions in order to evaluate the influence of basalt fiber presence on crystallization behavior of the composites. It was found that composite materials were characterized by higher melting enthalpy and crystallinity in comparison to pure PLA samples. The highest crystallinity level was observed for PLA pellet used for the film production what might have resulted from a application of free cooling air during pelletization process. The high crystallinity observed for samples produced at processing temperature of 170°C was a consequence of the incomplete polymeric matrix melting during compression molding. Crystalline domains created during cold crystallization of the polymer were not fully melted because of the relatively low processing temperature. This phenomenon can be confirmed by the low glass transition temperature observed during DMTA investigations. Samples prepared in further experiments realized at higher compression molding temperature values (180°C and 190°C) revealed significantly lower crystallinity levels however, the lowest value was observed for PLA and composite sample prepared at 180°C. At this temperature, thermal history of the polymer was fully erased. According to the DMTA data it may be stated that polymer was fully molten however, its high viscosity did not allow for proper saturation of the basalt fabrics which resulted in both low adhesion and low nucleation ability of the filler. The increasing processing temperature caused a significant rise of the crystallinity level of PLA and PLA matrix inside the composites. However, in case of composite materials, the following regularity was observed: the higher the processing temperature, the bigger the difference between Xc of pure PLA. The increasing processing temperature resulted in a longer cooling time and allowed for poly(lactic acid) macromolecule arrangement during solidification. Moreover, the DSC results confirmed that basalt fibers reveal a strong nucleation ability of the PLA matrix.

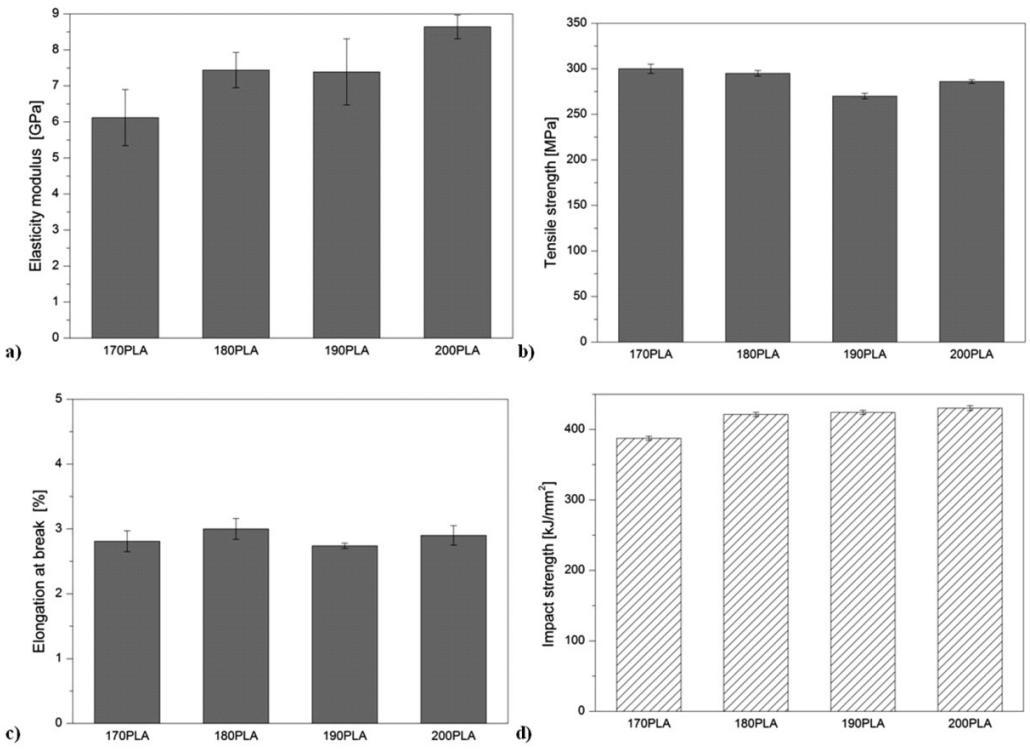

Fig 4 - Mechanical properties of composites.

3.5.Mechanical properties

The values of composite mechanical properties i.e.: elasticity modulus, tensile strength, elongation at break and impact strength are presented in Figure 4. It is worth noticing that the composite mechanical properties increase together with the increase of the compression molding temperature. The composites formed at 200°C showed the best mechanical properties, i.e. the highest stiffness and the best impact strength. In reference to the previously discussed DMTA and DSC results, this fact is understandable. The highest stiffness of the composites produced at 200°C resulted from the best saturation of basalt fabric by PLA matrix caused by low melt viscosity of polymer. Tensile strength slightly decreased with the increase of the processing temperature. This may be attributed to higher amount of crystalline phase in composite material. According to literature, a higher amount of crystalline phase in highly filled poly(lactic acid) composites may be characterized with a slightly lower tensile strength [24]. For all composites with a proper distribution of the polymeric matrix (PLA180-PLA200), a higher impact strength was observed in comparison to PLA170 composite. This may be attributed to the good impregnation of basalt fiber with poly(lactic acid) thermoplastic matrix plasticized at a higher temperature. The highest impact resistance of the composite produced at the highest processing temperature (200PLA) is a simultaneous effect of the increased amount of PLA crystalline domains and better adhesion between polymer and inorganic fibers.

3.6.Thermogravimetry (TGA)

The values concerning degradation process, such as: 5 % weight loss temperature, and the residual mass are collected in Table 3. There was no effect of compression molding temperature on thermal stability of the composite. These observations confirmed that the compression molding parameters of the composites were appropriate and no degradation of the polylactide matrix was recorded.

Table 3

TGA data of the composites investigated under nitrogen atmospheres

Sample	5% Mass loss [C]	Residual mass [%]
170PLA	325.3	30.7
180PLA	327.3	33.1
190PLA	340.8	32.4
200PLA	325.1	31.5

4.Conclusion

The incorporation of basalt fiber into poly(lactic acid) matrix led to obtaining environmentally friendly composite materials with good mechanical properties. The compression molding process temperature significantly affected the mechanical properties of the composites. It is worth noting that the best thermomechanical

properties were recorded for the composites pressed at the highest temperature (200°C). This was a simultaneous effect of processing properties modification (i.e.,decreased viscosity melt during compression process resulting in a better saturation of basalt fabrics) and high crystallinity of polymeric matrix. To conclude, compression molding process is a fast and highly efficient method which allows to prepare reinforced materials of this kind. A good understanding of proper temperature set-ups facilitates production of composite materials characterized with favorable mechanical properties, specific structure and adhesion. Moreover, the study also confirms that basalt fiber can be applied as an effective reinforcement of biodegradable polymeric materials which may result in structure and mechanical properties' modification.

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