DEVELOPMENT OF BASALT FIBRE AND MONTMORILLONITE NANOPARTICLE CO-REINFORCED POLY(LACTIC-ACID) MATRIX HYBRID COMPOSITES

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Abstract

Sustainable development is still in the focus of researchers. One of the most important problems to be solved is the fate of waste. In the case of polymer technology, one solution could be the application of compostable polymers, like poly(lactic-acid) (PLA). These materials are often comingled with other components, which widens their applicability. In this case, after composting, residual materials can remain, which damage the environment. One solution for this problem is to apply additives and reinforcing materials from natural resources. On the other hand, nowadays several types of nano and micro reinforcing materials are used in polymer composite applications. Besides the generally applied micro-sized reinforcements, nanosized materials may have a good complementary effect on the properties of the composites. In this study, we investigated the effects of basalt fibre as a natural resource-based micro fibre and untreated natural montmorillonite as a natural nanoparticle on the mechanical and morphological properties of PLA.

Keywords: Poly(lactic-acid), hybrid composite, basalt fibre, montmorillonite

1. INTRODUCTION

Due to the low level of crude petroleum reserves in the world and to the already high environmental pollution, environmentally friendly, sustainable materials and processing technologies are becoming increasingly popular, so more and more researchers are involved in the development of bio-composites by using materials made from renewable resources such as biopolymers, natural nano- and micrometer reinforcements. As the amount of plastic products that reach the end of their lifecycle is increasing, different international organizations have taken legal steps to start putting petroleum-based plastics out of the daily routine and more and more countries are beginning to encourage companies to use a polymer made from renewable resources, since polymers / reinforcements that can be found in nature or can be produced from natural materials also have excellent properties. The most widely-researched and used biopolymer nowadays is polylactic acid (PLA), which is a thermoplastic aliphatic polyester produced by the polycondensation of L-lactic acid monomers synthesized from glucose, found in starch or sugar cane, or by lactide ring-opening polymerization. Although it is a semi-crystalline polymer, if processed by conventional melt-state processing technologies, it results in an almost completely transparent, amorphous product. Its mechanical properties are similar to some thermoplastic mass-polymers (e.g. PET, PS): its tensile strength is 60-65 MPa and its Young's modulus is 3 GPa. In addition, it has small tolerance to deformation (elongation at break is only 2-5%), so it is a rigid material that can be made more flexible with plasticizers. Its slow crystallisation is also a disadvantage; a high crystallisation rate can be achieved only by slow cooling from melt state (<1 °C / min) or with nucleating agents. This is important because with a higher crystallisation rate, the material's heat deflection temperature can be twice as high as the amorphous PLA's at 50-60 °C. Post-processing shrinkage is low, therefore the shape of the product does not change in the case of low packing pressure by injection moulding [1-4].

The mechanical and thermal properties of PLA can be greatly influenced with various reinforcements and additives. Such a reinforcing fibre is basalt fibre produced from basaltic rock by rapid cooling. Nowadays it is gaining more and more attention due to its good mechanical properties, such as high elongation at break,

strength and Young's modulus. In addition, it has good thermal and chemical resistance, it is a good thermal, sound and an excellent electrical insulator and is weather-resistant. Its thermal stability provides good processability in a wide temperature range (-200 to 600-800 °C) without significant degradation. Due to the above-mentioned properties and its low price, it is a good reinforcing material that can be added to biodegradable aliphatic polyesters (e.g. PLA) to provide a green composite material with good properties [5,6].

As it was mentioned above, one way to increase the crystallisation rate of PLA is adding nucleating agents. It is therefore necessary to add some minerals, which also function as a nucleating agent. Although the beneficial effects of minerals on the polymer have been known for many years, studies with layered silicates such as nanoscale reinforcements have only started recently. Among nanoparticles, montmorillonite (MMT) is one that is based on natural resources. Based on the results of previous research, it can be seen that only 1-5 wt% MMT can significantly improve the mechanical properties of the polymer matrix. This phenomenon can be explained with two concurrent effects of the MMT. One is its direct reinforcing effect. The second is that the MMT acts as a nucleating agent, therefore the crystalline properties of the polymer are changed, which results in favourable mechanical properties [7-9].

The aim of the present study is to develop a biocomposite material - with a polylactic acid matrix - that can be produced entirely from natural-based materials. For this purpose, basalt fibre and montmorillonite were chosen as reinforcing materials. MMT was untreated so that it would be more environmentally friendly. Our aim is also to improve the properties of polylactic acid and to investigate how the shear force of microfibres dispersed the montmorillonite during the production of the composite materials.

2.   MATERIALS AND METHODS

IngeoTM 8052D type polylactic acid (PLA) from NatureWorks LLC was used as matrix material. KV02 type basalt fibre (BF) supplied by Kamenny Vek GmbH was used as micro-sized reinforcement and Cloisite 116 type montmorillonite (MMT) from BYK-Chemie GmbH was used as nano-sized reinforcement. A Collin Teach-Line ZK25T twin-screw extruder was used for continuous melt mixing. First pure PLA was extruded as reference material, then PLA reinforced with basalt fibre (PLA+BF, 70-30 wt.%). Then we made hybrid composites by adding 1, 2 and 3 wt.% montmorillonite (PLA+BF+1MMT, PLA+BF+2MMT, PLA+BF+3MMT) to the PLA+BF. Screw speed was set to be 10 1 / min in the case of PLA and 25 1 / min in the case of the other compounds and the extrusion temperature was 170 °C. The dried PLA granulates (80 °C; 4 h) were mechanically mixed with the reinforcing materials, then extruded and granulated (particle size: 4 mm). Dumbbell type specimens (with a cross section of 4 mm x 10 mm) were injection moulded on a Demag IntElect 50 / 330-100 injection moulding machine.

Before the mechanical tests, the specimens were analyzed with a differential scanning calorimeter (DSC). The measurements were made in a N_2 atmosphere (50 ml / min). The heating rate was 5 °C / min. The heat of fusion (ΔH_f) of 100% crystalline PLA is 93.1 J / g [10].Tensile tests were performed on a Zwick Z005 universal testing machine according to EN ISO 527. Test speed was 5 mm / min in the case of PLA and 2 mm / min in the case of the composite materials. The tensile moduli were determined in the strain range of 0.1…0.5 %; the gauge length was 110 mm. For the determination of plastic deformation at different loads, a special cyclic tensile test was also performed on this machine, according to a previous publication [11] (**Figure 1 a**). The relaxation time was set to be 30 s and the load was increased by 100 N in each cycle. The machine was used in force-controlled mode, the up and the down load speed was set to 100 N / s. After the tensile tests, the surface of the broken specimens was analysed by scanning electron microscopy (SEM) with a JEOL JSM-6380 LA device. SEM samples were coated with a thin Au layer to provide proper conductivity and to eliminate overcharging.

3. RESULTS AND DISCUSSION

3.1. Tensile characteristics

The tensile strengths, tensile moduli and elongation at break values of the materials are tabulated in **Table 1**. The addition of basalt fibre increased the strength properties of PLA, but the addition of montmorillonite decreased it. The addition of montmorillonite did not change the tensile moduli significantly for hybrid composites containing 1 and 2 wt.% MMT but decreased for the composite containing 3 wt.% MMT. Elongation at break decreased slightly when montmorillonite was incorporated.

Table 1 Tensile properties of PLA hybrid composites

Materials	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]
PLA	60.0 ± 0.6	3002 ± 13	4.4 ± 0.5
PLA+BF	103.8 ± 1.6	7199 ± 143	2.4 ± 0.1
PLA+BF+1MMT	96.7 ± 1.2	7046 ± 55	2.3 ± 0.1
PLA+BF+2MMT	96.9 ± 0.6	7135 ± 62	2.2 ± 0.1
PLA+BF+3MMT	91.1 ± 0.7	6844 ± 92	2.1 ± 0.1

Figure 1 b shows plastic deformation as a function of cycles after a relaxation time of 30 s (ε_{30s}). It can be concluded that the presence of basalt fibre caused a notable decrement in plastic deformation. Moreover, when 1 wt.% MMT was present, further decrement was observed between 10 and 20 cycles (i.e. ~ 25-50 MPa). It means that this material behaves more elastically in the range used.

a)   b)
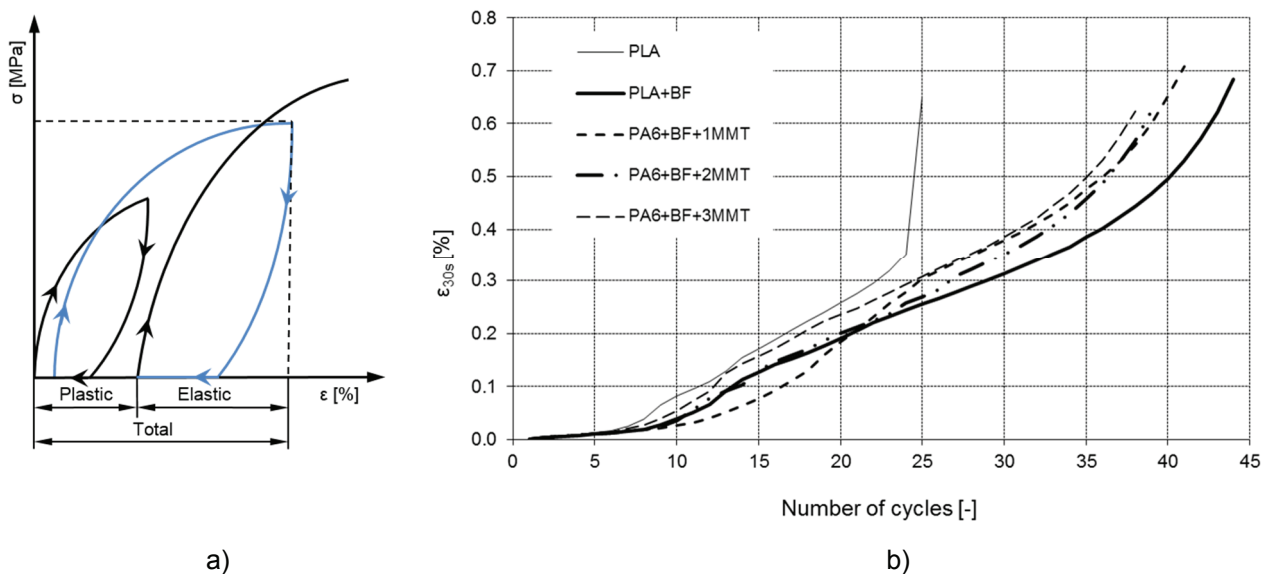
Figure 1 Determination of plastic deformation at increasing load levels. a) Strain-stress curves for cyclic loading; b) plastic deformation as a function of cycles after 30 s relaxation time (ε_{30s})

3.2. Scanning electron microscopy

Figure 2 shows the fracture surfaces of the tensile tested materials scanned with an electron microscope at a magnification of 2500x. In the case of the neat matrix (**Figure 2 a**), the fracture surface is relatively flat, which reflects the relatively rigid behaviour that was observed in the case of the tensile tests. For the basalt fibre reinforced PLA (**Figure 2 b**), it is clearly visible that the fibre has great adhesion with the PLA matrix, which causes improvements in mechanical properties. This is also true for the hybrid composites (**Figure 2 c, d, e).**

For the composite containing 1 wt.% nanoparticles, the aggregation of nanoparticles inside the polymer is not significant as there was no aggregate found on the fracture surface. This means that the dispersion of the nanoparticles is at a good level and explains the significant decrement in plastic deformation. In the case of composites containing 2 and 3 wt.% MMT (**Figures 2 c** and **d**), aggregates are present, which caused a significant decrement in mechanical properties.

a)

b)

c)

d)

e)
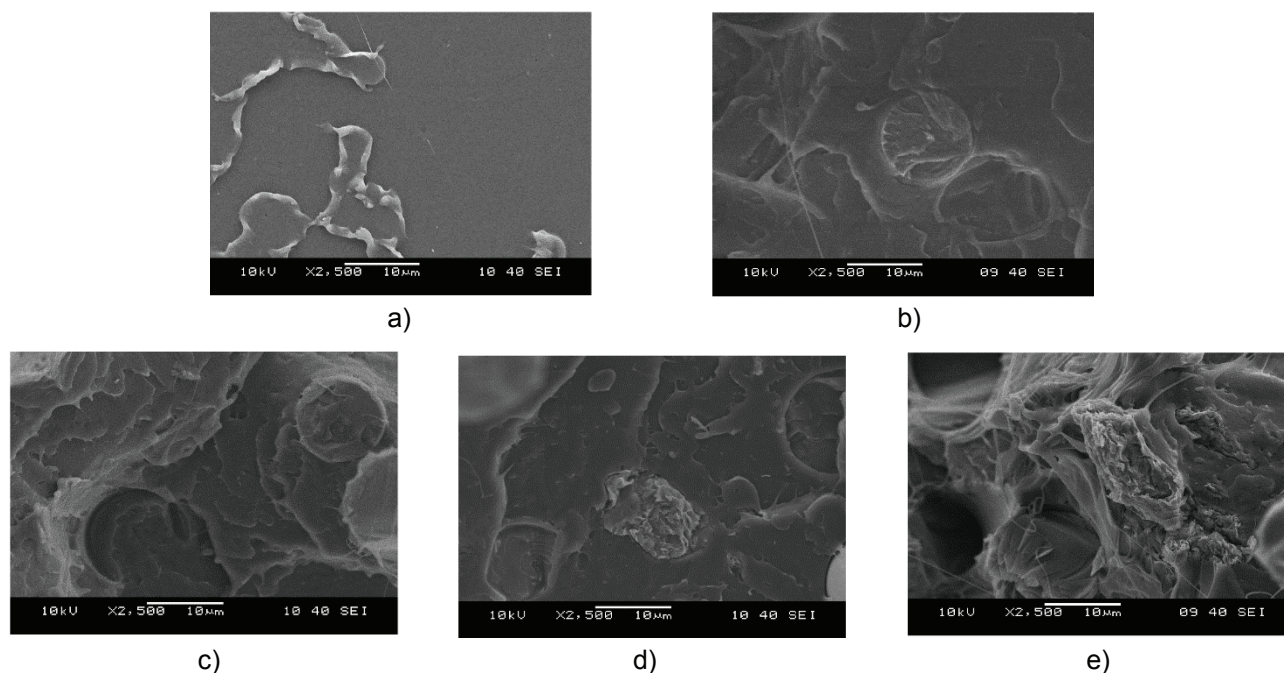
Figure 2 a SEM picture of a) pure poly(lactic-acid); b) basalt fibre reinforced poly(lactic-acid); basalt fibre reinforced materials containing c) 1 wt.% d) 2 wt.% e) 3 wt.% montmorillonite

3.3. DSC analysis

We were curious about the effects of the reinforcements on the morphology of the compounds, so the samples were analysed with a differential scanning calorimeter. **Table 2** tabulates the main results for each sample. The glass transition temperature (T_g), cold crystallisation temperature (T_{cc}), crystalline melting temperature (T_{m1} for α' and T_{m2} for α crystalline form) and crystalline rate after cold crystallisation (X) were analysed and compared in the case of each material. Crystallinity can be determined based on the following equation (1):

$$X = \frac{\Delta H_m}{\Delta H_f \cdot (1-m)} \cdot 100 \ [\%]$$

(1)

where ΔH_m is the measured heat of fusion, ΔH_f is the heat fusion of 100% crystalline PLA and m is the mass ratio of the additives.

Table 2 DSC results of the injection moulded samples

Material	T_g [°C]	T_{cc} [°C]	T_{m1} [°C]	T_{m2} [°C]	X [%]
PLA	59.0	109.9	148.4	154.7	32.0
PLA+BF	59.2	108.8	147.3	154.3	32.2
PLA+BF+1MMT	59.1	109.0	147.6	154.9	34.4
PLA+BF+2MMT	58.6	107.2	147.0	154.8	35.7
PLA+BF+3MMT	58.5	108.7	147.2	154.9	38.9

The presence of the basalt fibre did not change the glass transition temperature but it slightly decreased when the amount of MMT was increased. For the cold crystallisation temperature, the presence of the fillers resulted in lower peak temperatures. It can be explained with the increased thermal conductivity caused by the presence of the inorganic fillers. The first crystalline melting temperature (α') decreased by 1 °C when reinforcing materials were present but the second temperature (α) did not change. It means that the presence of the fillers helped the $\alpha' \rightarrow \alpha$ transition process. Crystallinity did not change when BF was added but increased when nanoparticles were added. Overall, MMT helps the formation of a more stable α crystalline type. This effect is well visible on the measured curves (**Figure 3).** As filler content increases, the first peak becomes less dominant but the second peak becomes more dominant.
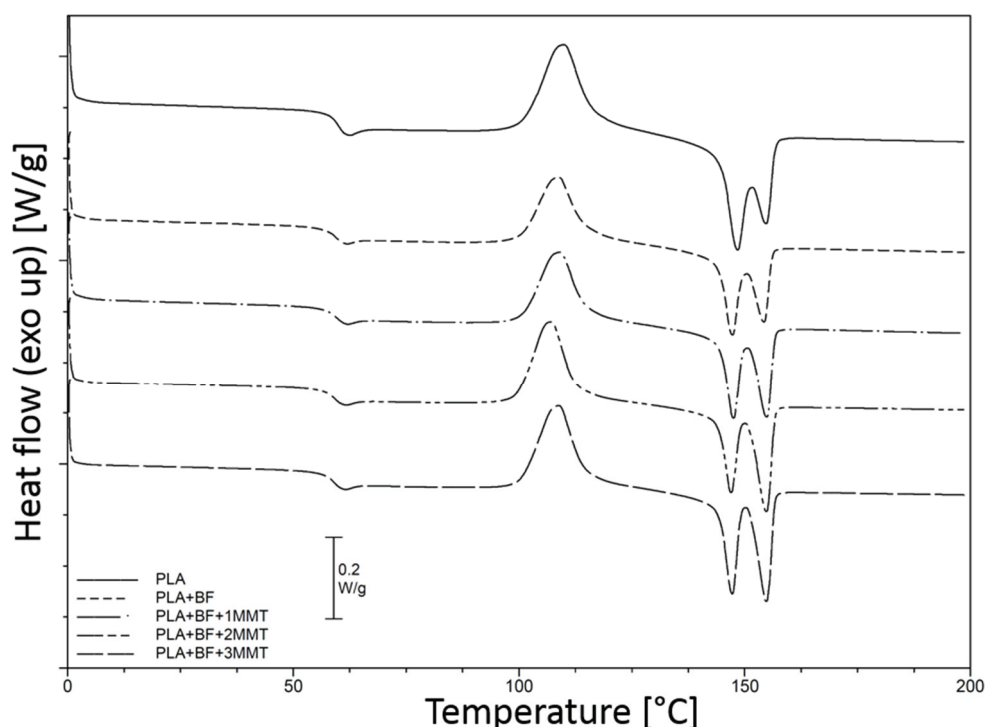
Figure 3 DSC curves of the samples

4.   CONCLUSION

In this research, PLA composites containing basalt fibre and montmorillonite were successfully prepared. The presence of the basalt fibres increased strength significantly. These improved properties slightly worsened when MMT nanoparticles were incorporated into the basalt fibre reinforced composites. The positive effects of the nanoparticles were reflected in reduced plastic deformation at the presence of 1 wt.% MMT. This phenomenon was not observed for higher MMT contents. The proper dispersion of the nanoparticles at 1 wt.% MMT content was confirmed by SEM. At higher MMT loading, aggregates were found on the fracture surfaces, which lead to impaired mechanical properties. The investigation of the morphological changes caused by the reinforcing materials revealed that the presence of basalt fibre and MMT helped the formation of the more stable α crystalline type.

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