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Development of cellulose-reinforced Poly(Lactic Acid) (PLA) for engineering applications

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Abstract. The renewable resource based polymers and composites, especially the Poly(Lactic Acid) (PLA) and natural, plant fiber reinforced composites are one of the most important research fields of biocomposites. Due to the mechanical properties of PLA, it stands out of the other biodegradable polymers, but in order to be able to use PLA in engineering application, reinforcing of PLA is needed. PLA can be reinforced with natural plant fibers, however their high moisture content can degrade PLA through hydrolysis during processing of PLA and the fibers into biocomposites. In this paper the effect of pre-process drying was analyzed on the mechanical properties of 30 weight% flax, cotton, and jute fabric reinforced PLA biocomposites. The results of pre-process drying tests showed that the optimum drying temperature was 100°C for the PLA and 120°C for the plant fabrics. It was demonstrated that the drying temperature of PLA and the fabrics has significant effect on the mechanical properties of the biocomposites.

Introduction

Poly(Lactic Acid) is a renewable natural resource based biodegradable thermoplastic polymer, which belongs to the family of aliphatic polyesters [1]. PLA is one of the main representatives of the biodegradable polymers due to its good mechanical and optical properties. It has low density (1,26 g/cm^3), while its tensile strength is about 65 MPa and tensile modulus is about 3 GPa. According to its mechanical properties, it is comparable to the conventional synthetic polymers such as poly(styrene) (PS) and poly(ethylene terephthalate) (PET). PLA has two stereoisomers, namely PLLA and PDLA which affect both the thermal and mechanical properties. PLLA is a semi-crystalline polymer, while PDLA is amorphous. In a commercial PLA the L:D ratio is usually around 9:1 [2-5]. PLA is considered the most promising biopolymer, thus it is a good choice for producing biocomposites by using natural, plant fibers. With cellulose based natural plant fibers the biodegradability and the environment-friendly features of PLA can be kept. Unfortunately both PLA and natural plant fibers have hygroscopic characteristic, so it is critical to dry the raw materials before the production, because the presence of both remaining water and high processing temperature cause PLA to degrade through hydrolysis [6]. Since there is no universally accepted drying parameters used for the drying of PLA and its reinforcements [7-10], thus in our research, the effect of pre-process drying of PLA and plant fabrics as reinforcements was analyzed on the mechanical properties of natural plant fabric reinforced PLA biocomposites.

Experimental

NatureWorks PLA type 4032D biopolymer was chosen as matrix material with a density of 1.24 g/cm^3, and a melting temperature of 155-170°C. The jute, flax and cotton woven fabrics were supplied by Dél-Alföldi Műszaki Konfekció Ltd (Hungary). The main properties of the fabrics are shown in Table 1.

Type	weave type	surface weight [g/m^2]
jute	plain weaved	400
flax126	plain weaved	126
flax200	plain weaved	200
cotton P695	plain weaved	120
cotton 9/10	plain weaved	375
cotton 350h/P	plain weaved	480

Table 1. Main properties of woven fabrics

Before composite production drying tests were performed to determine the optimal drying conditions for the PLA and the natural fabrics. Three different temperatures were used namely 80, 100 and 120°C. After each drying test, the fabrics were immediately taken into a condition chamber at 28°C and 50% RH to determine moisture uptake characteristics. After the pre-process drying, 30 weight% fiber content biocomposites were made with film-stacking technology by laying plant fabrics and thin PLA films on each other and compression molding this multilayer structure. The effect of processing temperature was also investigated as both PLA, and moreover the plant fabrics are highly susceptible to thermal degradation. According to the melting temperature of PLA 4032D 190, 210, and 230°C processing temperatures were analyzed. Finally, the effect of pre-process drying was analyzed on the mechanical properties of the biocomposites by using tensile, flexural and impact (Charpy) tests.

Results and discussion

The presence of water and high temperature causes hydrolysis in PLA during the biocomposite preparation thus, the drying characteristics were determined (Fig. 1).

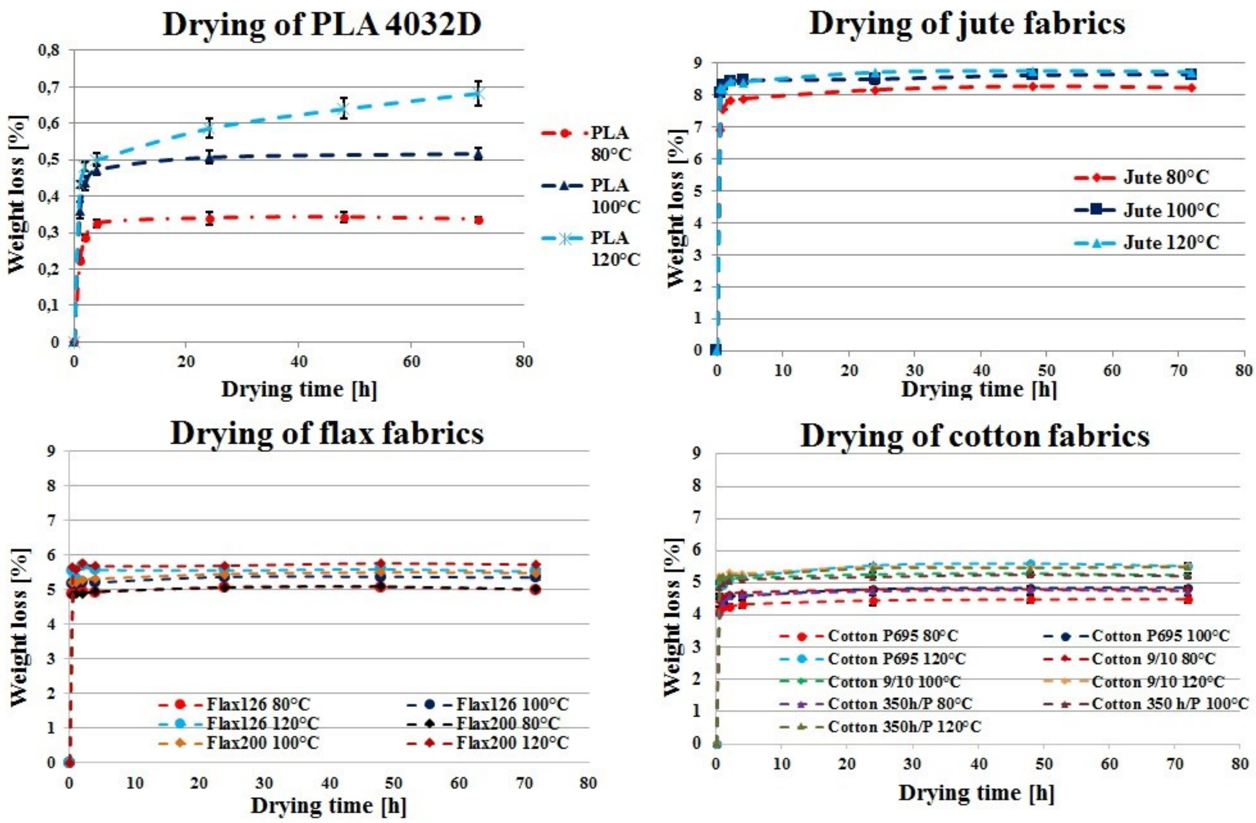

Fig. 1. The drying characteristics of the materials

From the investigated temperatures the optimal drying conditions for PLA was 100°C for about 6 hours. The 120°C drying temperature is not acceptable because most probably hydrolysis occurred due to the high drying temperature and the remaining moisture in the pellets as indicated by the continuously increasing weight loss. For the natural fabrics the optimum drying temperature was 120°C for around 24 hours. The maximum weight losses were 8-9% for jute and 5-6% for both cotton and flax fabrics. Moisture uptake test were also carried out at 28°C and 50% relative humidity to determine the available time to put the layers of PLA films and plant fibers on each other as the preparation for biocomposite production with film-stacking method (Fig. 2).

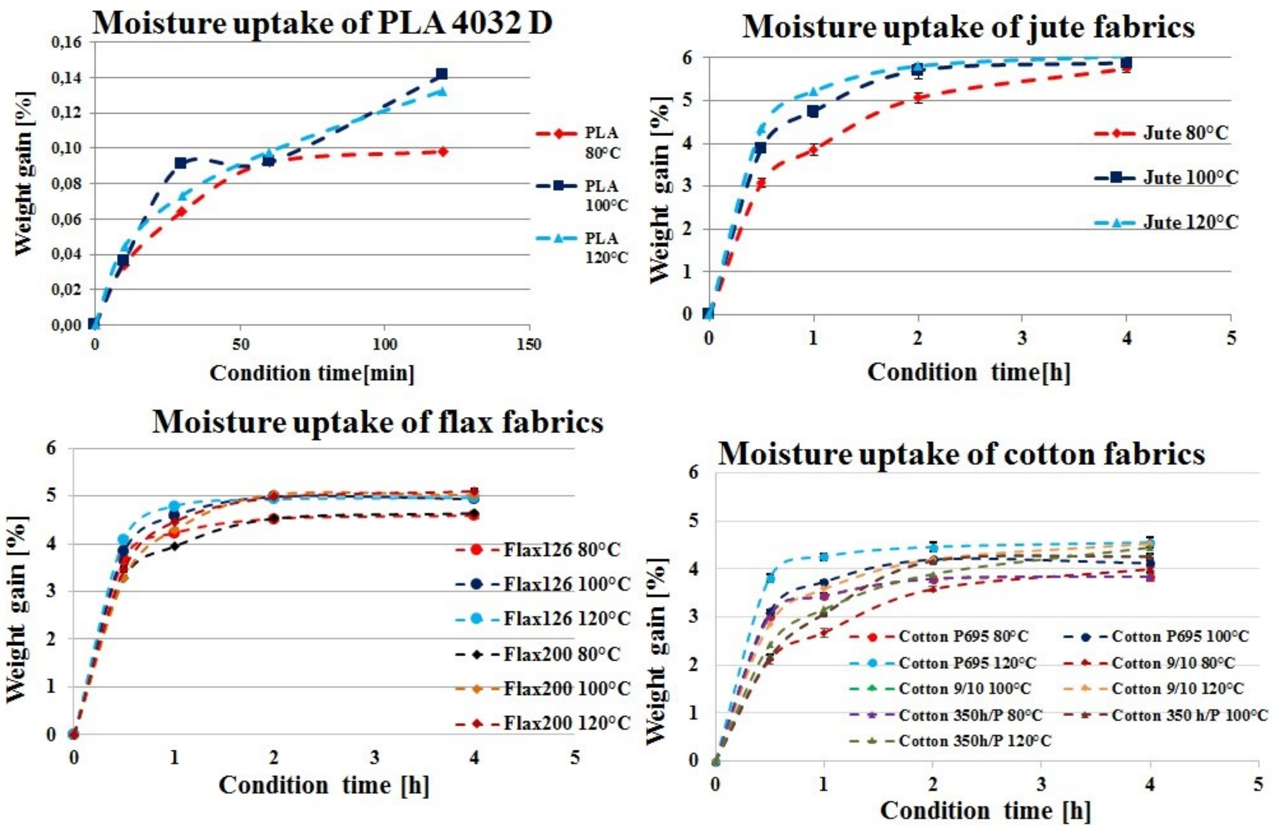

Fig. 2. Moisture uptake of the materials

Based on the literature data, the moisture content of PLA should be kept below 250 ppm to avoid any kind of degradation. This means that only 10 minutes are available after the drying for biocomposite preparation. Some biocomposites were prepared to determine the optimal processing temperature (Fig. 3, Fig. 4). It can be seen that at higher processing temperatures, the components of the natural fabrics such as lignin and hemicellulose start to decompose and this resulted in a decrease of mechanical properties.

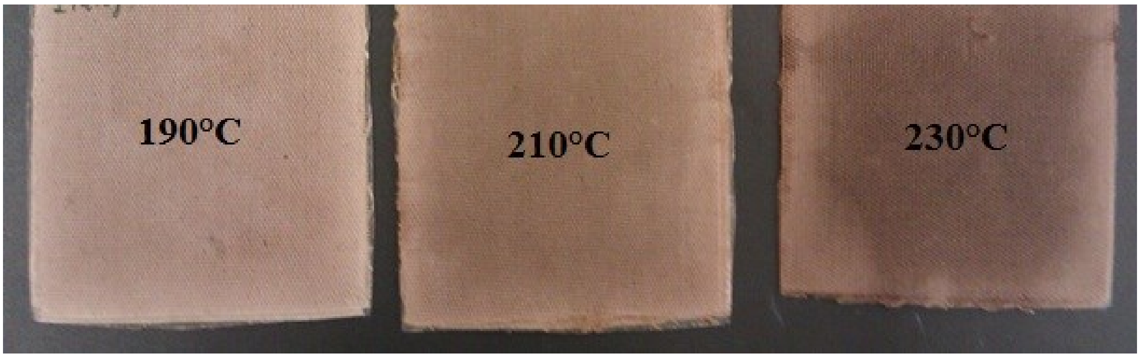

Fig. 3. Composites produced at 190, 210 and 230°C

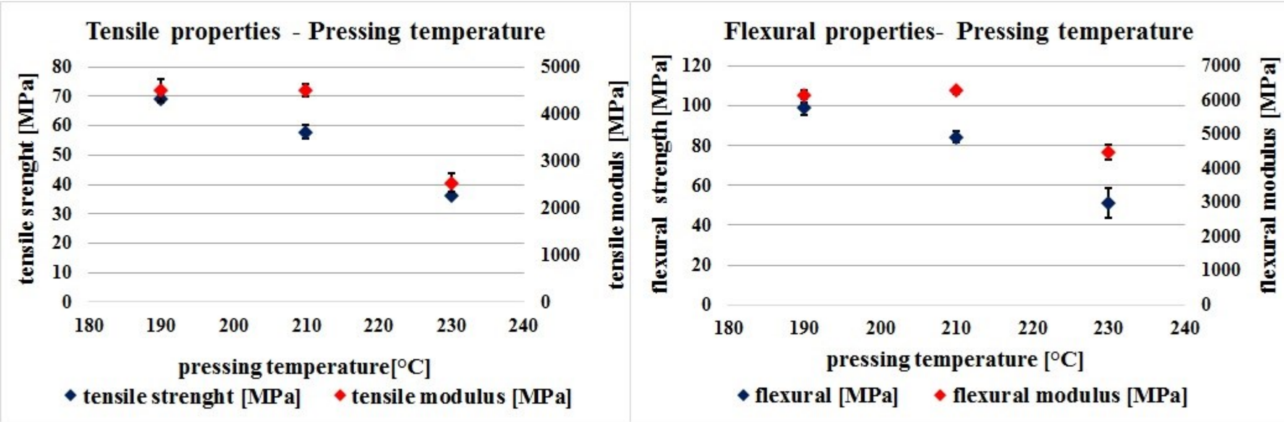

Fig. 4. The effect of processing temperature on the mechanical properties

Accordingly 190°C processing temperature was chosen for further biocomposite production. The biocomposites for the final investigation were prepared with various pre-process drying temperatures to determine its effect on the mechanical properties (Fig. 5-Fig. 7).

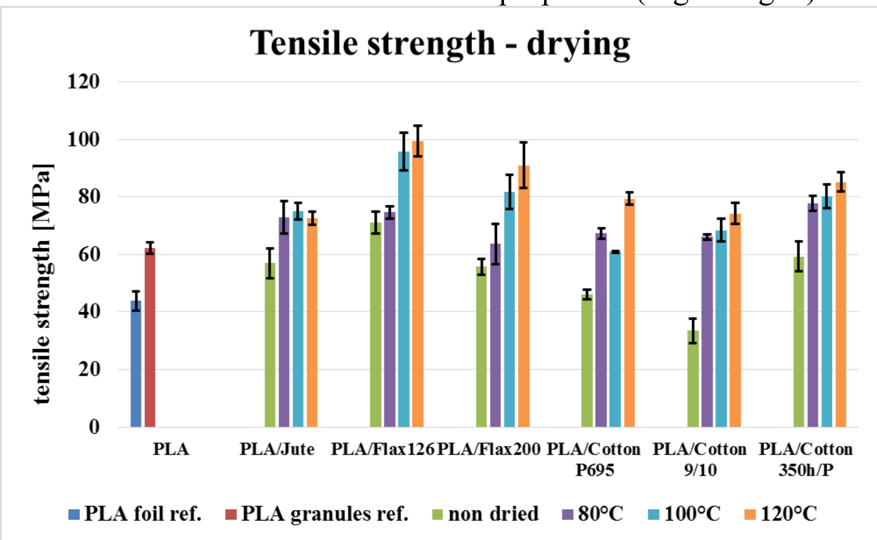

Fig. 5. Tensile strength of the biocomposites

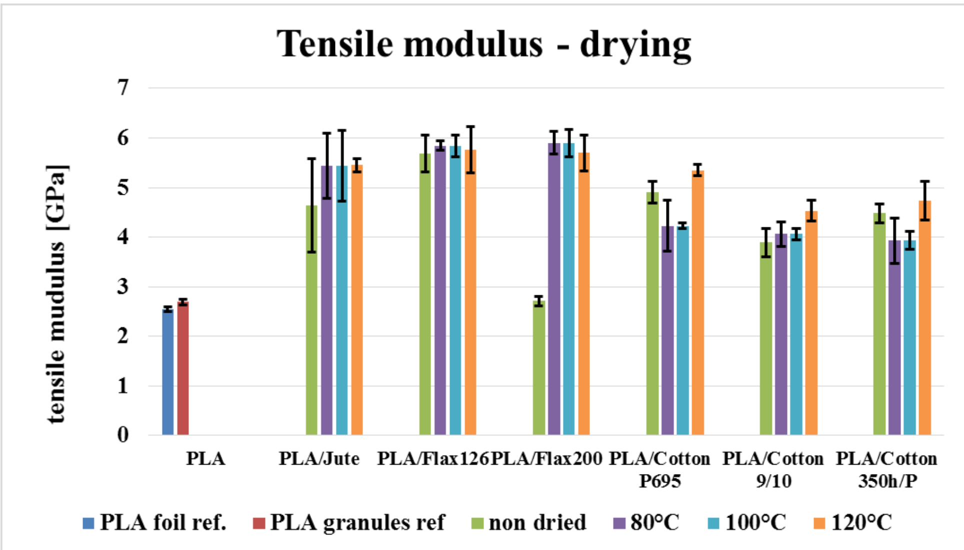

Fig. 6. Tensile modulus of the biocomposites

As it can be seen the pre-process drying was found to have very significant effect on the mechanical properties of the biocomposites. 20-40 MPa improvements can be seen in the tensile strength of the biocomposites only by increasing the drying temperature from 80 to 120°C. Accordingly, the tensile strength of the Flax200 reinforced PLA biocomposite increased from 63.6 MPa to 91 MPa only by increasing the pre-processing drying temperature from 80 to 120°C. The highest tensile strength was found in case of Flax126 fabrics reinforced PLA biocomposite, where the fabric was dried at 120°C. Accordingly, compared to the reference PLA the tensile strength has increased from 62 MPa to 99 MPa and the tensile modulus has increased from 2.69 GPa to 5.67 GPa. In case of the flexural properties (data not shown) jute reinforced biocomposites proved to have the highest strength and modulus. Its flexural strength was 110 MPa and the flexural modulus was 8.03 GPa, while the reference flexural strength of PLA was 58 MPa and the flexural modulus was 3.41 GPa respectively. The impact tests show (Fig. 7) that the pre-process drying had also an effect on the impact strength, however, this effect was not as significant as in the case of tensile and flexural strengths. Nevertheless, the relatively small impact strength of neat PLA of around 15 kJ/m^2 was enormously increased with Cotton 350h/P fabric reinforcement to 60 kJ/m^2.

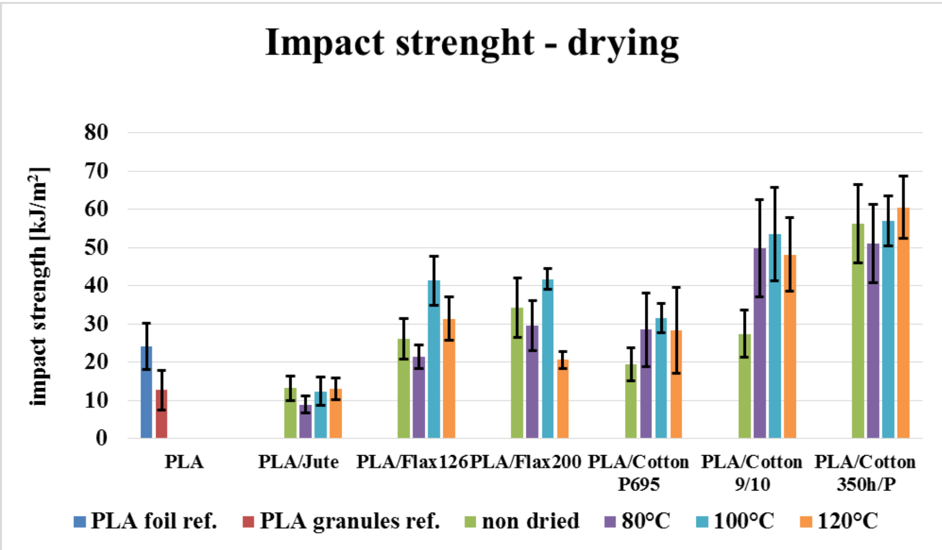

Fig. 7. Impact strength of the biocomposites

Summary

In our work the effect of pre-process drying was analyzed on the mechanical properties of fully renewable resource based biodegradable polymer biocomposites based on Poly(Lactic Acid) (PLA) and flax, jute and cotton fabrics. The reinforcements were dried at various temperatures (80, 100, 120°C), and the mechanical properties of the 30 weight% plant fabric reinforced biocomposites prepared by using film-stacking method was determined. For the natural plant fabrics the optimum drying temperature was found to be 120°C for around 24 hours, while for PLA it was found to be 100°C for around 6 hours. During moisture uptake tests it was demonstrated that only around 10 minutes are available after the drying of the components for biocomposite preparation to be able to avoid any hydrolitical degradation in PLA during processing due to the quick moisture uptake of the fabrics after drying. The investigation of the mechanical properties of the biocomposites revealed that pre-process drying temperature of PLA and the fabrics has significant effect, since 20-40 MPa improvements were found in the tensile strength of the biocomposites only by increasing the pre-process drying temperature from 80 to 120°C. Accordingly, the tensile strength of the Flax200 reinforced PLA biocomposite increased from 63.6 MPa to 91 MPa only by increasing the pre-processing drying temperature from 80 to 120°C. The tensile strength and modulus of the neat PLA increased from 62 MPa and 2.69 GPa to 99 MPa and 5.67 GPa respectively, by using flax fabric as reinforcement. Also, flexural strength and modulus of the neat PLA increased from 58

MPa and 3.41 GPa to 110 MPa and 8.03 GPa respectively, by using jute fabric as reinforcement. Finally, impact tests showed that the pre-process drying had also an effect on the impact strength, however, not as significant as in the case of tensile and flexural strengths. Nevertheless, the relatively small impact strength of neat PLA of around 15 kJ/m^2 was enormously increased with Cotton fabric reinforcement to 60 kJ/m^2.

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