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Influence of fiber modifications on PLA/fiber composites. Behavior to accelerated weathering

Iuliana Spiridon [a], Raluca Nicoleta Darie [a], Heli Kangas [b], *

[a] *"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania*
[b] *VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 VTT, Finland*

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ABSTRACT

Cellulose fibers obtained by organosolv process were used in preparing PLA/fiber composites. In an attempt to improve the adhesion between the fibers and the polymer matrix, the cellulose fibers were treated chemically using stearoyl chloride as well as enzymatically by laccase. The addition of the cellulose fibers to the PLA matrix had a positive effect on some of the mechanical properties of the composites, while some properties were compromised. In addition, the thermal properties were improved, while the rheological properties were decreased. Generally, the fiber modifications did not have the desired effect of improving the mechanical properties further, while for the thermal properties, there was a significant difference when chemically modified fibers were used. Accelerated weathering generally led to the deterioration of the composites properties. However, some properties were better preserved with the inclusion of modified fibers into the PLA matrix, especially with the enzymatically modified fibers.

1. Introduction

The growing environmental awareness (in terms of e.g. environmental pollution and greenhouse gas emissions) and depletion of fossil resources have resulted in an increase of natural resource-based materials in most areas of life and industry. Thus, bio-based composite materials have become a hot topic for academic and industrial research from the view-point of reducing impact on the natural environment.

By comparison with commodity polymers such as polyolefins and Polyethylene terephthalate (PET), polylactic acid (PLA) provides good strength and processability. It is a thermoplastic polyester produced from natural resources like corn, rice and sugar beets [1].

Natural fibers have certain properties which make them good candidates to replace currently used glass or aramid fibers, such as high specific strength and modulus, recyclability and low density. In addition, they are abundant and renewable [2] and can be generally considered as biodegradable and non-toxic.

One of the challenges in using natural fibers as component in composite materials is their moderate adhesion with polymeric matrices. This problem, as well as the low resistance to moisture of composites comprising of natural fibers can be improved by treating these fibers with different chemicals, physicals or enzymatic agents [3,4].

It is well known that surface treatments of lignocellulosic fibers create a lot of structural modifications which influence the interfacial bonding mechanism between the fiber and the matrix. Stearoyl chloride is the most commonly used chemical to decrease the hydrophilic nature of the treated plant fibers, thus improving their compatibility with the plastic matrix [5]. On the other hand, some changes in the morphology of lignocellulosic fibers can be obtained by enzymatic treatments. Lignin polymers are degraded and a reduction in flexural rigidity and tenacity has been observed [6].

Although there is significant work already presented in the literature regarding the preparation of PLA composites containing cellulose from different sources such as wood, cotton, and sisal, no data addressing the changes induced in these types of composites under influence of accelerated weathering has been reported to date [7–10].

It is well known that UV exposure of lignocellulosic fibers affects lignin primarily, resulting in scission of macromolecular chains.

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* Corresponding author.
E-mail addresses: iulianaspiridon@yahoo.com (I. Spiridon), heli.kangas@vtt.fi (H. Kangas).

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Changes also occur in the carbohydrates, especially in hemicelluloses [11,12]. Fiber swelling due to moisture absorption is the main cause of loss in mechanical properties of composite materials after weathering. Also, some cracks in the polymer matrix could occur due to swelling of the lignocellulosic fibers, thus resulting in loss of mechanical properties [13]. The UV treatment mainly affects properties of surface region with minimal influence on bulk properties. UV energy of 400 nm or shorter can break down the covalent bonds of C—C and C—O in PLA [14].

In the present work, cellulose fibers separated by organosolv process were used in the preparation of PLA composites. In order to obtain better adhesion between the composite matrix and the natural fibers, the cellulose fibers were modified either chemically by stearoyl chloride or enzymatically by laccase treatment. The composites were tested for their mechanical properties, hardness, dynamic rheology, thermal properties and hydrophobicity by contact angle measurements. The behavior of PLA/fiber composites during accelerated weathering was also studied. The results were compared to composites prepared using commercially available kraft pulp fibers.

2. Material and methods

2.1. PLA

PLA 2002D from NatureWorks LLC, UK, having a density of 1.24 g/cm^3 and melt flow index (MFI) of 5—7 g/10 min (at 210 °C/2.16 kg) was used as the matrix in composites preparation. It was obtained from renewable annual resources, with a D-lactide content of 4% (96% of L-lactide).

2.2. Cellulose fibers

The cellulose fibers were obtained by Lignofibre (LGF) organosolv process patented by VTT [15]. The birch chips (*Betula pendula and pubescens*) used in the cooking trials were of industrial grade with some aspen impurities, originating from Southern Sweden and obtained from Swedish pulp mill. Alkali extraction of the chips was performed prior to cooking, by treating 1 kg of chips in a batch digester with 2.5 M NaOH at liquid to wood ratio of 5 and temperature of 95 °C for 1 h. The hydrolysates were removed from the chips in a FREX press, the chips were washed twice with water and pressed to solids content of around 52%. The cooking trials were performed in an air bath digester fitted with 6 autoclaves (V = 1 L). The chip batch size in the autoclaves was 100 g and the liquor to wood ratio 5. 100% acetic acid was used as the solvent and phosphinic acid was added 3.5% from wood. As wet chips were used, the actual charge of acetic acid was around 80%. After cooking, the cooking liquor was separated and the pulp was washed once with 70% acetic acid and twice with water. The obtained fibers (LFO) were used in the composites manufacturing as such as well as after chemical and enzymatic modifications, performed to improve the adhesion between the composite components.

In addition to the Lignofibre cellulose fibers (LFO), commercial, unbleached birch kraft cellulose fibers (KF) were used as a reference material in preparation of PLA/fiber composites.

2.2.1. Chemical modification

The surface chemical modification of LFO cellulose fibers was performed in a round-bottomed reaction flask under reflux and under constant mechanical stirring in pyridine medium. A mixture of 8 g cellulose (0.05 mol), 54 mL stearoyl chloride (0.15 mol) and 12 mL pyridine (0.15 mol) were stirred at 80 °C for 2 h. The reaction product was filtered and successively washed with diluted hydrochloric acid, water, sodium bicarbonate solution, water and ethyl alcohol. The product, cellulose stearate (LFOm) was dried at room temperature.

2.2.2. Enzymatic modification

The organosolv cellulose fibers (LFO) were functionalised with Dodecyl 3,4,5-hydroxybenzoate (DOGA) in order to increase the fiber hydrophobicity and compatibility in the composite manufacturing [16]. LFO fibers were suspended in deionised water for 30 min and disintegrated in water (60 g pulp in 1000 mL) for 30 000 revolutions. Powder form enzyme (AB Enzymes LCC10 laccase) was suspended to 10% suspension in 50 mM Na-succinate pH 4.5. The activity of the laccase suspension was quantified based on the oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid (ABTS). The DOGA dispersion was prepared just before addition to fibers using the following amounts of components (calculated for 60 g fiber sample): 2.436 g DOGA (=0.12 mmol/g of pulp), 60 mL acetone, 60 mL water, 0.24 g Polysalz (S), 240 mL water, to which 0.12 g lecithin was added. Suspension was heated gradually to 60 °C with magnetic stirring (a bluish dispersion was formed) and acetone was vaporized away from the dispersion. Laccase treatment of fibers with 500 nkat of enzyme/g of pulp was carried out at pH 4.5, 40 °C, with constant mixing. After 30 min of laccase treatment, a hot, just prepared DOGA dispersion was added to the fiber suspension in 10 portions every 2 min (total addition time 20 min). The fibers were left to react under mixing for 70 min after the last addition, after which the enzymatically modified fibers (LFOenz) were filtrated twice and washed with water.

2.3. Composites processing

PLA-cellulose fiber composites were prepared using different cellulose fibers by adding 30 wt% cellulose fibers to the PLA matrix. Prior to blend preparation, PLA and the cellulose fibers were dried in a vacuum oven for 6 h at 80 °C. Components compounding was performed at 175 °C for 10 min, at a rotor speed of 60 rpm, using a fully automated laboratory Brabender station. Specimens for the mechanical characterization were prepared by compression molding using a Carver press (175 °C with a pre-pressing step of 3 min at 50 atm and a pressing step of 2 min at 150 atm). The compositions of the prepared composites are shown in Table 1.

2.4. Composite characterization

The composite materials were characterized for their mechanical properties, hardness, thermal properties, dynamic rheology and surface chemical properties.

2.4.1. Mechanical properties

All mechanical tests took place at 50% relative humidity and 23 °C. Prior to the measurements, the specimens were conditioned under the same circumstances (50 ± 5% relative humidity) for 24 h. The tensile strength and the Young's modulus were determined according to standard ISO 527 [17]. An Instron 1 kN test machine operated at a crosshead speed of 10 mm/min was used for testing the specimens. At least ten samples were tested for each composition, and the results are presented as an average for the tested samples.

The Charpy impact strength of the composites was tested according to standard EN ISO 179 [18]. A CEAST testing machine with a pendulum of 15J energy was used to measure the un-notched specimens (80 mm × 10 mm x 4 mm). Ten specimens were tested for each material.