INFLUENCE OF FIBRES MODIFICATION ON BIOCOMPOSITE PROPERTIES

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ABSTRACT

Natural fibres focus an increasing interest as reinforcement for polymer composites. The interfacial adhesion plays an important role in a stress transfer through the heterogeneous materials and the resulting mechanical properties. Thermoplastic composites presented in this paper were composed of poly(lactic acid) and flax fibres. The fibres prior incorporation by melt compounding into the polymer matrix were submitted to a chemical or physical treatment.

Melt rheology, mechanical properties, surface energy, HDT and flammability were evaluated for the PLA composites reinforced with the neat and modified fibres. It has been shown that for the specific requirements a selected way of treatment should be selected.

1. INTRODUCTION

Materials derived from natural resources have focused a substantial interest within recent decade because of a high demand for petrochemical products and permanently increasing oil prices. Poly(lactic acid) (PLA) is currently the most popular polymer derived from the renewable resources. PLA is a thermoplastic, aliphatic polyester, which is useful in the packaging, electrical and automotive industry, e.g. the applications at which the biodegradable materials started competing with cheaper synthetic plastics. In order to reduce its price and improve the tensile properties a polymer matrix can be modified by addition of different fillers. Polymer composites made of biodegradable polymers and natural fibres (flax, hemp, kenaf etc.) or wood flour, admixed in different amounts (biocomposites) display the combined features of all components or quite new properties resulting from mutual interactions between the constituents [1-4]. Natural fibres are advantageous over the glass fibres as far as their density is concerned. Using natural fibres of 1.5 g/cm^3 density one can produce light weight materials, compared to glass fibres, density of 2.5 g/cm^3 [5,6]. One of the major problems related to polymer composites reinforced with natural fibres is a lack of adhesion between the fibres and polymer matrix. A possible improvement of the adhesion may be obtained by modification either the fibre surface or the matrix polymer.

The objective of this study was to evaluate the influence of a flax fibre modification on the properties of polylactide composites filled with natural fibres.

2. EXPERIMENTS

2.1 Materials

Poly(lactic acid) NW2002D (NatureWorks) was used as a matrix polymer (PLA), whereas the flax fibres of 4 mm length were used as a filler (F). Both the neat and modified fibres were used. Modification was performed by the physical or chemical manner at the DWI in Aachen, VTT in Finland and UAR in Austria. The methods of modification were following:

Physical treatment:
- boiling – heating in a presence of caustic soda and detergents
- plasma – treatment by atmospheric plasma

Chemical treatment:
- bleaching – treating with hydrogen peroxide

In Figure 1 the native and bleached flax fibres have been presented. With the bleached fibres one can manufacture products of a white color.

Figure 1: Flax fibres untreated (left) and bleached (right)

Polymer composites were prepared by melt mixing of PLA with flax fibres at 30 wt.% loadings using an internal mixer of the HAAKE Rheocord 9000 system at 160ºC for 10 min at 60 rpm. PLA and flax fibres were dried prior to mixing in order to avoid a hydrolytic degradation of poly(lactic acid). After mixing the material was grinded, then injection molded into the dumbbell samples.

2.2 Test methods

Poly(lactic acid) and PLA based composites were subjected to the uniaxial tension tests using the tensile machine Lloyd LR 10K.

Melt rheology was characterized with the oscillatory rheometer Haake RT20P at 160ºC. The measurements of the wetting angle and the surface energy calculations were performed with SEE System, Advex Instruments. The liquids used for a drop geometry analysis were water, ethylene glycol and diiodomethane.

Heat deflection temperature (HDT) was evaluated with the CEAST HDT3Vicat apparatus equipped with the oil bath.

Flammability was estimated by UL94 standard in a vertical and horizontal mode using the Atlas HVUK Flame Chamber.

3. EXPERIMENTAL RESULTS

3.1 Tensile properties

Tensile properties of PLA and PLA/flax composites have been presented in Figures 2 and 3. The properties depend on the method of flax fibres modification. The highest tensile strength was observed for PLA filled with the boiled fibres. This composite exhibited an improvement for 35% in comparison to the matrix polymer (Fig. 2). Addition of flax fibres caused also in a remarkable increase in the Young modulus. The value of the tensile modulus for PLA composite filled with the bleached flax fibres

reached 4800 MPa, which is for 100% higher than that measured for poly(lactic acid) (Fig. 3). Insignificant differences between the tensile modulus measured for PLA composites reinforced with the modified and un-modified fibres suggest a similar adhesion level at the matrix-fibre interface.
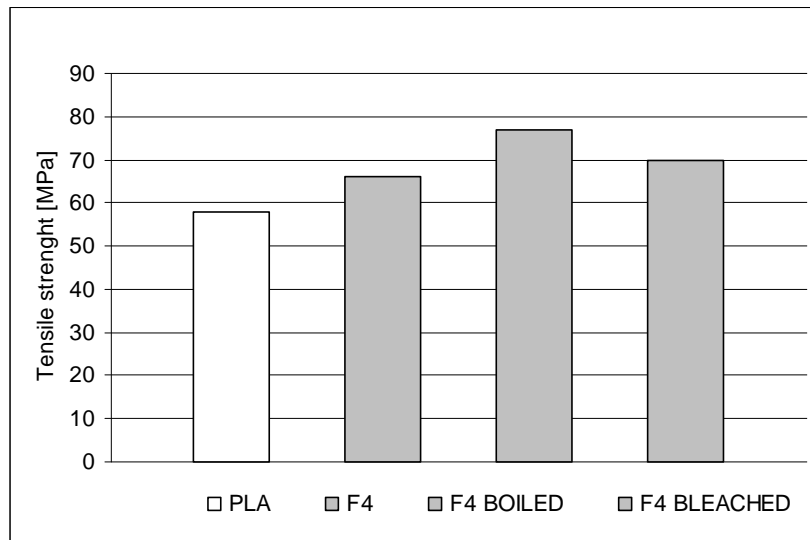

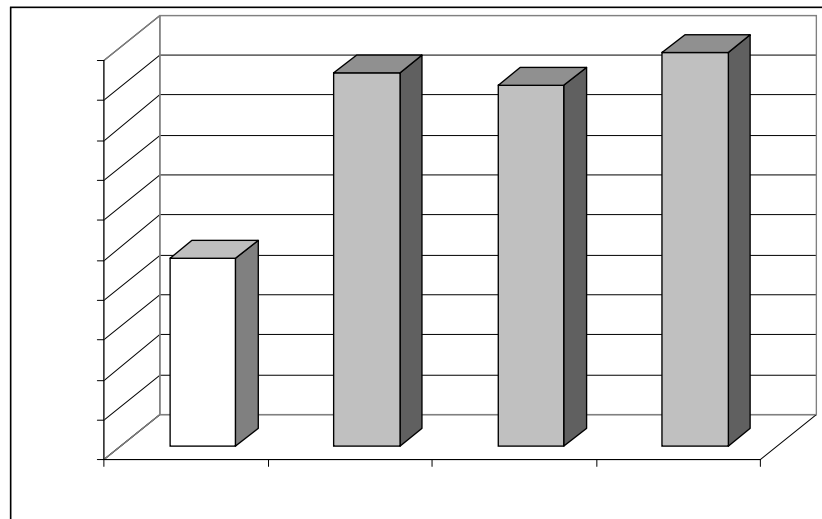Figure 2: Tensile strength of PLA and PLA composites with flax fibres

Figure 3: Young modulus of PLA and PLA composites reinforced with flax fibres

3.2 Melt rheology

Addition of the flax fibres to poly(lactic acid) brought about a considerable increase in the melt viscosity (Fig. 4). The differences between particular materials have been clearly visible at the low deformation rates. The composite filled with modified fibres exhibited much higher melt viscosity than that with a neat flax fibres. Assuming that the high melt viscosity demonstrates a high interaction between the filler and PLA one conclude a high efficiency of bleaching for the fibre surface modification. The differences between the melt viscosity at 1 rad/s of individual materials have been presented in Figure 5. However, at higher deformation rates the melt viscosity is

comparable for all PLA composites, which suggest that the extrusion conditions for all these materials should be similar. The expectations follow from a strong pseudoplasticity of the molten PLA composites filled with modified fibres.
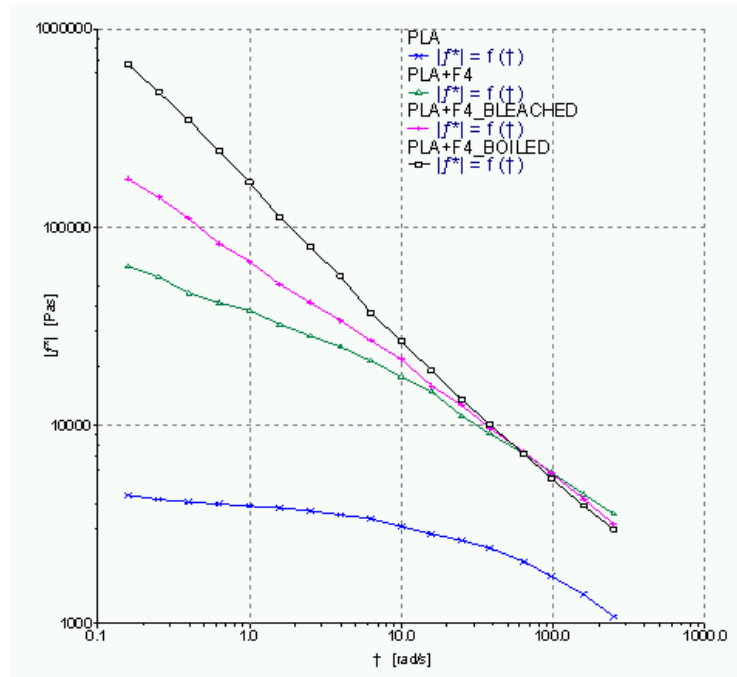

Figure 4: Melt viscosity of poly(lactic acid) and PLA composites with flax fibres
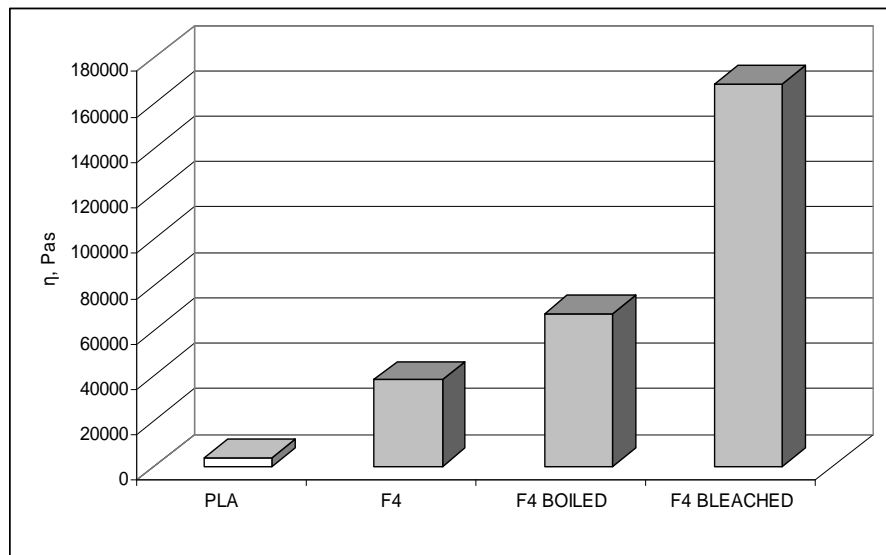

Figure 5: Melt viscosity of PLA and PLA/flax composites at 1 rad/s

3.3 Surface energy

The surface energy of poly(lactid acid) and PLA composites filled with flax fibres has been presented in Figure 6. Polar (P) and apolar (A) parts have been extracted in order to evaluate the influence of flax fibres on PLA.

Poly(lactic acid) is predominantly hydrophobic, with some polar energy component which correspond to the chemical structure of this polymer. Addition of 30% of flax

fibres caused an increase in the surface energy, which resulted from an enhancement of the polar part. Flax fibres, similarly to other natural fibres, are build up of cellulose, which contains the glucose units with many hydroxyl (thus hydrophilic) groups. However, for the plasma modified fibres, a polar part became markedly lower. Instead, the apolar share increased to an extent, which made a total surface energy comparable to that of PLA/flax composites (45 mJ/m^2). These examples evidence that a polarity of the fibre surface depends markedly on the modification, thus explaining a different strength of the interactions with PLA matrix.
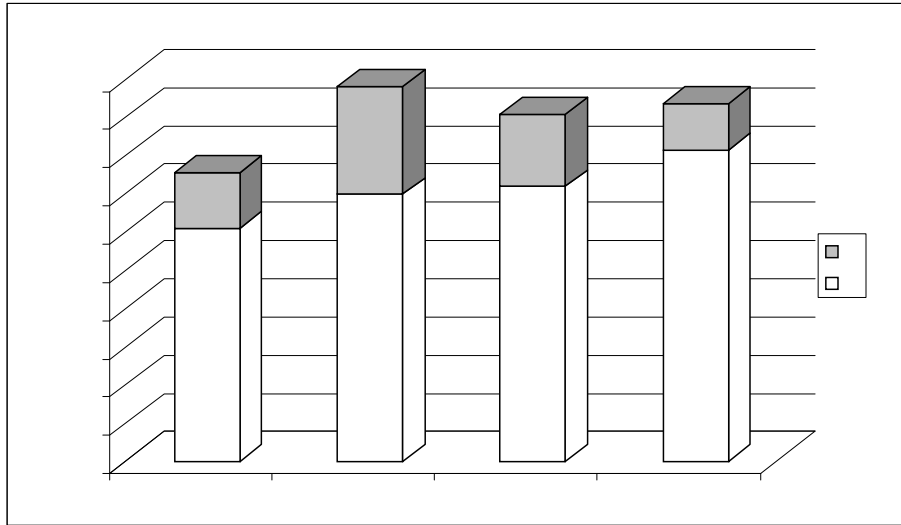

Figure 6: Surface energy of PLA and PLA composites with flax fibres

3.4 Heat deflection temperature

Addition of the flax fibres caused an increase in the heat deflection temperature (HDT) for 3.5°C. Modification of fibres brought about an additional increase of HDT for ca. 1°C (Figure 7). An increased adhesion of the flax fibres to PLA matrix, which resulted from the surface modification has caused a slightly higher bending resistance of the composites as a function of temperature.
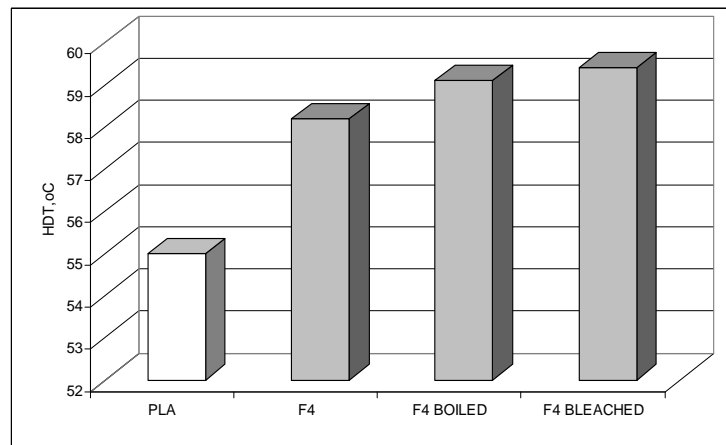

Figure 7: Heat deflection temperature for PLA and flax filled biocomposites

3.5. Flammability

Flammability was evaluated in the vertical and horizontal mode according to UL94 criteria. Time to self-extinguishing of a fire initiated with a flame at the sample or time to spreading along a sample for a specific distance has been measured and presented in Figures 8-10.

For the vertical measurements the quickest fire spreading over 50 mm distance was observed for poly(lactic acid) (20 min.). Addition of flax fibres caused extension of that time up to 60 min. (Figure 8). Modification of the fibre surface brought about a further improvement in the fire resistance. Biocomposites reinforced with the boiled fibres exhibited a prolonged fire spreading time for another 10 min. The highest effect was observed for PLA filled with the bleached fibres (95 min.) and plasma treated fibres (90 min.). Such results suggest the fire retarding effect of flax fibres and a reduced free volume in the composites PLA/bleached flax and PLA/plasma treated flax, caused by an enhanced interfacial adhesion.
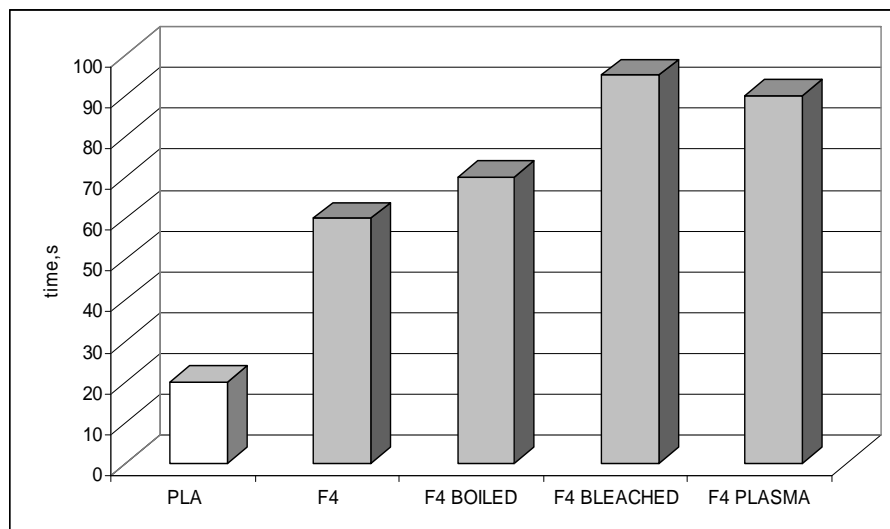

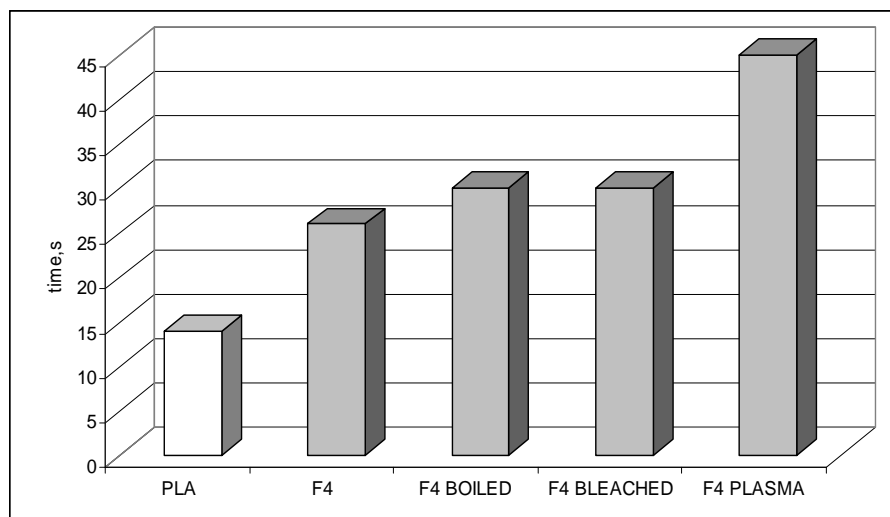Figure 8: Vertical flammability of PLA and PLA biocomposites

Figure 9: Horizontal flammability time (0-25 mm)

Fire speed along the sample in a horizontal mode was also the highest for PLA. The distance of 25 mm was done within 14 min, whereas for the PLA/flax composite it took 26 min. (Fig. 9). Bleaching and boiling brought about a similar effect, extending the fire spreading time up to 30 min. The composite filled with the plasma modified flax fibres shifted the fire spreading time up to 45 min.
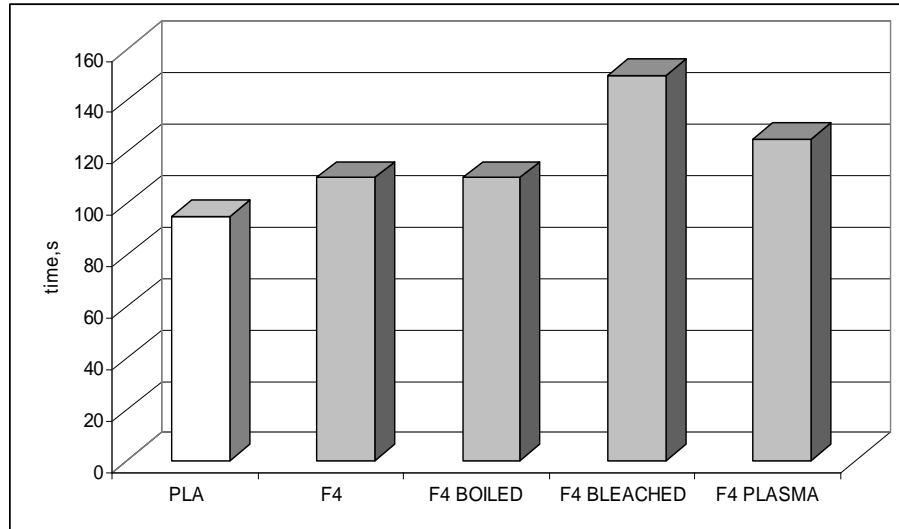

Figure 10: Flammability time (25-150 mm) for PLA and PLA biocomposites

Differences between the materials were lower when the fire spreaded for a higher distance (Figure 10). Again, the shortest time required for travelling of fire from 25 mm up to 150 mm length, was measured for PLA (95 min). However, the flammability of composites reinforced with the flax fibres and boiled fibres was only slightly lower (110 min.). Bleached fibres caused extension in the fire spreading time up to 150 min., which was markedly higher than the flammability time for PLA filled with the plasma treated flax fibres (125 min.).

4. CONCLUSIONS
Reinforcement of PLA with flax fibers brought about a substantial enhancement of stiffness and a moderate increase in the tensile strength. A method of the fiber surface modification influences the mechanical properties at different extent – bleaching is more pronounced at low deformations, whereas a result of boiling is slightly more efficient at a total stress transfer.

Markedly increased adhesion between PLA matrix and the flax fibers caused by bleaching was clearly manifested in a molten state at low deformation rates. Higher stresses at increased shear rate destructed the interfacial links. Modification of the fibre surface influences not only the bulk properties of biocomposites, but also their surface energy, which is of importance for printing.

Addition of flax fibres to PLA brought about a slight increase in the heat deflection temperature. Modification of the fibre surface is advantageous for HDT increase.

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