Influence of Hemp Fibers Pre-processing on Low Density Polyethylene Matrix Composites Properties

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Abstract. In present research with short hemp fibres reinforced LLDPE matrix composites with fibres content in a range from 30 to 50 wt% subjected to four different pre-processing technologies were produced and such their properties as tensile strength and elongation at break, tensile modulus, melt flow index, micro hardness and water absorption dynamics were investigated. Capillary viscosimetry was used for fluidity evaluation and melt flow index (MFI) evaluated for all variants. MFI of fibres of two pre-processing variants were high enough to increase hemp fibres content from 30 to 50 wt% with moderate increase of water sorption capability.

1. Introduction
The plant fiber reinforced plastics (PFRPs) manufacturing technique is interrelated with such key composite parameters as volumetric composition, reinforcement type and form, and matrix type. The selection of fibers type, fibers extraction process and fibers surface modification technique, fibers volume fraction and interfacial properties, reinforcement packing arrangement and orientation are matters of greatest importance. The interactive effect of all these parameters can influence the variation in mechanical properties of PFRPs produced through different manufacturing processes. [1]. Hemp as a yearly renewable lignocellulose fibers source with a low ecological footprint evaluated by 26 criteria [2] and with a high yields in temperate climate zone [3] are an attractive source of reinforcement for PFRPs.

However, hemp fibers properties can differ greatly depending on variety, agricultural complex applied, weather of growing season, type, grade, harvest quality, preprocessing methods, yield, etc. [4]. Only natural fibers of high technical quality guarantee sufficient reproducibility of the mechanical characteristics of bio composites [5]. Investigation of non-controllable (weather) and controllable factors (variety, agricultural complex, stem and fibers processing parameters) influences on fibers and composite properties will allow to discuss and to evaluate anticipated unavoidable variation intervals of composite properties [6] in the same way as in textile industry.

The latest development, due to the environmental and ecological factors, biobased polymers from renewable resources have found increasing attention as potential alternatives to currently dominating petroleum based polymers [7]. Study shows that current producers of bio-based polymers had estimated production capacity nearly 12 million tons by 2020. With an expected total polymers production of about 400 million tons in 2020, the bio-based share should increase from 1.5% in 2011 to 3% in 2020, meaning that bio-based production capacity will grow faster than overall production [8].
Biobased linear low density polyethylene (LLDPE) from renewable raw materials behaves the same as PE based on petroleum. Projections for year 2016 evidence that biodegradable bioplastics share will reach only 13.4% from anticipated bioplastics production volume 5 779 000 t/per year, rest 86.6% will refer to biobased / non-biodegradable bioplastics [11] due to the fact that they can easily be recycled and can thus be included in the current waste separation process, and processed into new bioPE products using conventional technologies without requiring extra investments [12].

2. Experimental methods

Research focused on improving the mechanical properties of LLDPE composites reinforced with hemp fibres. As show previous studies, due to their polar and hydrophilic nature, natural fibres are incompatible with the hydrophobic polymers. This incompatibility could lead to the weak interfacial adhesion as well as to the non-uniform dispersion of fibres within the composite. To overcome incompatibility several strategies have been tested to enhance the adhesion between the lignocellulosic fillers and the polymer matrix. These strategies generally involve fibres modifications by physical or chemical methods [13, 14, 15 and 16]. Chemical modification of natural fibres involves various chemical treatments in order to reduce the content of hydroxyl groups or introduce cross-linking between the filler fibres and the polymeric matrix. Water boiling, sodium hydroxide treatment, esterification with acetic anhydride and grafting with maleic anhydride (MAH) were used (Table 1).

| Without pre-processing WP | Pre-treatment | MAH coupling, 5%MAH |
|---------------------------|--------------|---------------------|
| Water boiling WB          | Alcali, 2%Alc| Acetilation, 11% Acetil |
| Decortification, scutching| 2 hours, 100°C| 1 hour, 20°C        |
|                           | 4 hours, 20°C |                     |
| Washing with destilled water, drying |             |                     |
| Cutting, grinding, sifting, fibers length < 1mm |             |                     |
| Camera drying, 12 hours 105oC |             |                     |
| Two step roller mixing-compounding (LabTechScientific) |         |                     |
| temperature 155°C and 120°C, 10 minutes |             |                     |

Fibres of hemp variety Bialobrzeskie grown in the East part of Latvia and linear density 3.62 tex were used in this study to reinforce linear low density polyethylene (LLDPE) grade LL 6201 matrix. Fibers of three variants marked as WB, Alc and Acetil (Table 1) were subjected to the pretreatments discussed above. Composites were prepared by components mixing on two rolls mills, then cooled, granulated and pressed in 1 mm thick sheets from which were cut off specimens for tensile tests following standard ASTM D 638 M-93.

Tensile tests were conducted on a universal material testing equipment UTS-100 (standard ASTM D 638 M – 93). Fluidity was estimated by melt flow index method MFI (T=1900 C, P=2.16 kg) according to the standard ASTM D 1238-90b. Microhardness (MH) was examined by Vickers M41 at load 200g. Water exposure experiments (standard ASTM D 570-98) were done at room temperature (+23°C).

3. Results and Discussion

Properties of produced composites vary in vide ranges: mean tensile strength in a range from 7.7 to 22.5 MPa, tensile modulus in a range from 647 to 11 604 MPa, microhardness in a range from 55.4 to 93.4 (Fig. 1, 2).

Tensile strength 22 MPa and modulus 1.31 GPa of the first samples group with MAH coupling (Fig.1) are quite close to the corresponding properties of Hemp/PP 30 wt %: 30 MPa, 1.56 GPa [1].
Samples of II group without pretreatment (WP) and with alcali pretreatment (Alc) shows light difference in position and could not proposed that alcali pretreatment applied in experiment improve substantially hemp/LLDPE composites mechanical properties.

III group with poor mechanical properties evidence that water boiling and acetilation with technologies used in experiment influence fibers structure.

![Figure 1. Tensile properties of Hemp/LLDPE 30 wt% composites](image1)

![Figure 2. Tensile properties of Hemp/LLDPE composites as function of fibers content](image2)

As seen from Fig.2 (right) tensile modulus grow fast with fibers content increase from 30 to 50 wt% for MAH coupling, at the same time tensile strength increase is moderate. Acetilation of fibers doesn’t change substantially tensile strength of composite compare to LLDPE (Fig.1) and drop below this level with the increase of fibers content fro 40 to50 wt%. Tensile modulus of acetilated fibers composite increases from 2 times to 17.5 times compare to LLDPE modulus if fibers content increase from 30 to 40 wt% (Figure 2, right).

![Figure 3. Composites elongation at break. Hemp/LLDPE 30 wt% (left) and 30-50 wt% (right)](image3)

Elongation at break of variants with 30 wt% fibers vary in range 1.25 % except variant with MAH having the highest elongation value 11.53 % (Figure 3, left). In result of hemp fibers acetilation pretreatment elongation at break of LLDPE matrix composite drops down fast with fibers content increase reaching minimum 3.43 % for Hemp/LLDPE 50 wt%. Elongation of composites grafted with MAH are almost 2% higher for all three variants (Figure 3, right).

Microhardness quantize the resistance of a material to the plastic deformation. The highest values of microhardness show composite without fibers pretreatment, microhardness gradually decrease starting with NaOH pretreated (Alc) to the acetilated fibers (Acetil) composite (Figure 4, left). Microhardness increase 1.35 times when fibers content with acetilation pretreatment increase from 30 to 40 wt% and after decrease to the level of the composite microhardness with the fibers content 30 wt%.
Microhardness increases dramatically when fibers content of MAH grafted PE increase from 40 to 50 wt%.

![Figure 4. Microhardness, MPa. Hemp/LLDPE 30 wt% (left) and 30-50 wt% (right)](image)

Acetic anhydride pretreatment of hemp fibers ensure good fluidity for all three Acetil variants. Melt flow index decreases 9.3 times when content of fibers increases from 30 to 50 wt% (Figure 5.) Melt flow index of compositions with 30 wt% fibers content decreases from 1.7 g/10 min (water boiled fibers) to 0.4 g/10 min (alcali treated fibres) with medium for this range 0.8 g/10 min (MAH 30).

![Figure 5. Melt Flow Index, g/10min](image)

Water sorption of variants with fibers content 30 wt% vary from 7.1 to 8.3% (Figure 6, left.). Water sorption capability grows fast following acetilated and MAH grafted fibers content increase from 30 to 50 wt% (Fig. 6, right).

![Figure 6. Water sorption % after 240 h. Hemp/LLDPE 30 wt% (left) and 30-50 wt% (right)](image)
Composite density increase following increase of fiber content from 30 to 50 wt% (Fig. 7, left).

4. Conclusions
Hemp/LLDPE composites with different properties are produced:

- with density in a range from 0.93 to 1.23 G/cm³; increase with fibers content increase;
- tensile strength vary in a range from 7.7 to 22.5 MPa;
- elongation at break vary in a range from 3.4 to 11.5 %; decrease with fibers content increase;
- tensile modulus vary in a range from 647 to 11 604 MPa; increase substantially with fibers content increase;
- microhardness vary in a range from 55.4 to 93.4; decrease substantially if fibers are subjected to preprocessing;
- water sorption after 240 h vary in a range 7.1 to 13.2 % and increase substantially with fibers content increase.

In result of acetilation and water boiling tensile strength decrease and increase in result of coupling with 5 wt% MAH. Elongation at break increases after hemp fibers alcali treatment and coupling with 5 wt% MAH. Tensile modulus substantially increase after coupling with 5 wt% MAH and decrease if hemp fibers are subjected to the water boiling and acelilation. Microhardness drops down and water sorption increase for all applied fiber pretreatments.

Grafting with a such coupling agent as maleic anhydride allows produced hemp/LLDPE 30 wt% composites with mechanical properties close to the corresponding properties of Hemp/PP and Flax/PP 30 wt% composites. Although water boiling improve fluidity, other composite properties do not convince that water boiling pretreatment could improve hemp fibers compatibility with LLDPE matrix as well the same corresponds to the alcali 2wt% pretreatment. 11wt% acetilation pretreatment offer good fluidity and low elongation at break, but substantially lessen composite tensile strength and microhardness.

Short hemp fibres reinforced LLDPE matrix composites with fibres content in a range from 30 wt% to 50 wt% could be used in technical applications where elastomeric materials that resist crack growth under strain are needed.

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