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HYDROPHOBATION OF NATURAL FIBRES FOR APPLICATION IN WPC MATERIALS

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Abstract

The objective of the present study was to improve the method of hydrophobation of natural fibers for its application in WPC. For outdoor applications such as in decking's and ventilated facades improved durability against weathering is desired. This problem is associated with the water adsorption of the natural cellulosic fibres. Commercial paper sizing agents AKD was used for the optimization of surface hydrophobation of natural fibres (wood flour; Rettenmaier BK 40/90). Parameters studied included: Application method, AKD brand, concentration, pH, elimination of extractives, catalyst and influence of temperature and pressure). As results, an important improvement against wetting was seen using contact-angle measurements on water drops. Anyhow the dynamic water vapor adsorption did not change notably by the AKD-treatment. Finally, treated fibres was prepared as compound to confirm potential reduced water adsorption of the resulting WPC material. The influence of the processing conditions was studied by hot pressing, injection molding and extrusion of the modified natural fibers and PP. Mechanical performance of the WPCs was determined in terms of bending and tensile test. It was concluded that the AKD treatment had a positive effect in the mechanical and water absorption properties of the composites. The processing conditions influenced in the water uptake of the composites being the best procedure injection molding and pressing. This work was performed within the EU-project HIFIVENT (GA: 605891) FP7-SME-2013.

Keywords:

Hydrophobation, WPC, Composites, NFPC, Fiber modification

1 INTRODUCTION

The production of wood plastic composites WPC or NFPC natural fiber composites is growing in the last decade due to be an alternative the fossil derivatives and the possibility to use waste of residues of natural fibers as reinforced material. However, there are some challenges that are pending to solve in order to improve the market applicability of the new products. The weatherabilty of WPC, especially for outdoor applications is a weak point for using these kind of products for facades, roofing etc. The mechanical properties and the fire performance are others issues that need further research in the following years. Some efforts have been done in this line by applying techniques for the modification of natural fibers based on the reaction of hydroxyl groups of the lignocellulosic material to decrease the water absorption of the fibers and to maximize the compatibility of the fibers with the matrix. Natural fibres are mainly composed of cellulose, hemicellulose and lignin which contain several hydroxyl groups able to react with water. So, they are highly hydrophilic.

The presence of a large number of hydroxyl groups in the chemical structure of cellulose and their ability to interact with water is the reason for the high hygroscopicity of natural fibres. From the point of view of Materials Science, cellulose hydrophilic character is the major responsible for most of its limitations, especially for its limited use in polymeric formulations. Accordingly, intensive research has been done in the last decades to change or at least minimize such characteristic.

Hydrophobation is achieved by substituting hydroxyl groups by poorly hydrophilic chemical groups, such as long saturated hydrocarbon chains. Relevant chemical hydrophobation attempts include silylation [Petzold 2003], [Gañan 2005], esterification [Seppanen 2004], [Dankovich 2007], chemical grafting [Li 2008], [Cunha 2006], and others [Bourbonnais 2011], [Belgacem 2005]. Recent methods based on vapor deposition reactions [Cunha 2010], [Shen 2005] have also shown very promising results at lab scale.

2 MATERIALS

AKD:

Aquapel T215 (provided by ASHLAND, 15% active material (18%solids))

Natural Fibre:

Wood Flour: BK 40/90 provided by Rettenmaier

Plastic:

PP 160, extrusion grade, provided by BEOLOGIC.
Additives:

Polyethylenimine, PEI (BASF)

$NaHCO_3$ (Aldrich)

All the materials were used as received. Natural fibers were dried at 80ºC overnight before the modifications.

3 METHODS

3.1 Contact angle system

The contact angle of a drop of water in the surface of the natural fibers was performed in a Goniometer (Dataphysics OCA 15Plus). Contact angles over 90 degrees are considered as hydrophobic.

3.2 Water absorption (EN 317/ ISO 62)

Samples for water absorption test were prepared (Processing PP (50%) / fibres (BK40-90) (50%)) using a Twin-screw extruder and Injection Moulding. The Swelling and water absorption were measured according to EN 317 "Particleboards and fibreboards. Determination of swelling in thickness after immersion in water"

3.3 Mechanical properties

A study of the influence of the AKD treatment in the water uptake of the composites was carried out. Hence, 500 g of wood flour were treated with AKD following the procedure described below. This treated wood flour (T-WF) was formulated with PP in 50% composite. Samples for mechanical and water uptake test were produced using an injection machine Battenfeld Plus 35 (18mm, 21L/D).

Tensile strength and elasticity modulus:" Plastics. Determination of tensile properties. Part 2: Test conditions for moulding and extrusion plastics" EN-ISO 527-2:93

Flexural tests according to EN ISO 178 "Plastics: determination of flexural properties"

Impact tests according to EN ISO 179-1 "Plastics: determination of Charpy impact properties-Part 1: non instrumented impact tests"

4 RESULTS

4.1 Optimization of the AKD treatment

Different variables were studied for the optimization of the AKD treatment method: pH, pre and post treatment of the fibers, use of catalysts, method of application, concentration of AKD, etc.

The method was optimized for wood flour and then applied to the rest of natural fibres.

It was observed that the optimum concentration was 5 % of AKD (Fig1.)

Different kind of methods of application were studied (soaking, autoclave and spraying). Autoclave process did not work properly. The water of the solution became brown quickly probably due to the release of extractives that inhibit the reaction of AKD with the surface of the fibers. Soaking process showed the best results at all AKD percentages.

The purification of the fibers (adjusting the pH to 8 and to 3 followed by water rinsing to remove extractives and impurities) improve the effectiveness of the treatment but not as much as desired. These results indicates that it is not worth making the pre-treatment in terms of cost and time.

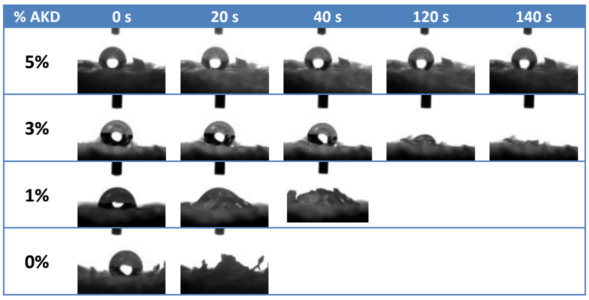

Fig. 1: Goniometer images for the wood flour treated with different concentrations of AKD.

Use of catalyst: Both PEI and $NaHCO_3$ improve the hydrophobation reducing the total amount of AKD necessary to reach similar contact angles. In the case of $NaHCO_3$, concentrations above 0.1% increase the pH more than 8 reducing the effect of the AKD as observed previously.

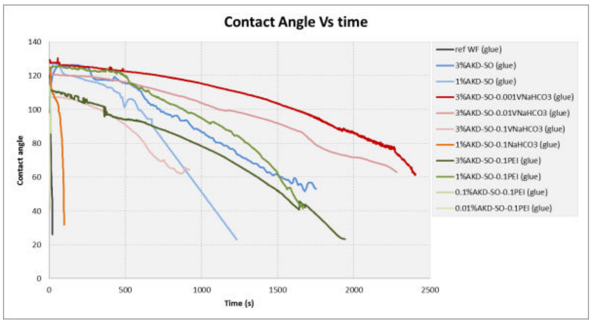

Figure 2. Influence of catalysts on the contact angle.

Conclusions :

According to the results, the following conditions were selected:

-Dilution of wood fibers in water (15 mL/g) and stirring at 60ºC.

-Adjustment of the pH to 7 by addition of NaHCO3.

-Addition of AKD (3% of emulsion) and PEI (0,1% respect AKD)

-Maintain the temperature and the stirring for 30 minutes.

-Filtration of the solution and drying of the recovered fibers in an oven at 105ºC during 30 minutes.

4.2 Mechanical properties of composites

Mechanical tests: Impact Test (EN ISO 179)

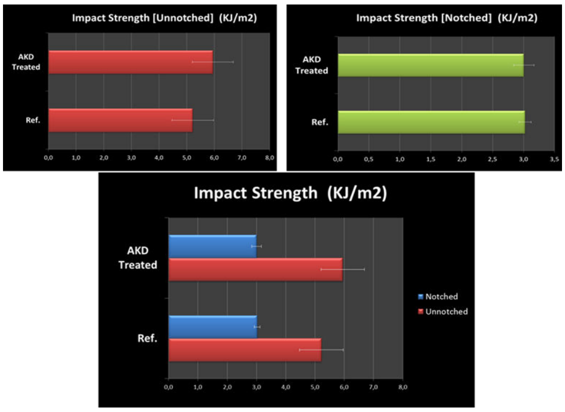

Figure 3. Impact test results of the AKD-treated and not treated samples.

The samples treated with AKD showed a higher value for unnotched. This effect is attributed to the coupling effect of the AKD that introduce an apolar chains in the surface of the fibers that allow to increase the compatibility of the fibers with the matrix improving the mechanical properties of the composite. The notched results are very similar.

Three point Bending Test (EN ISO 178)

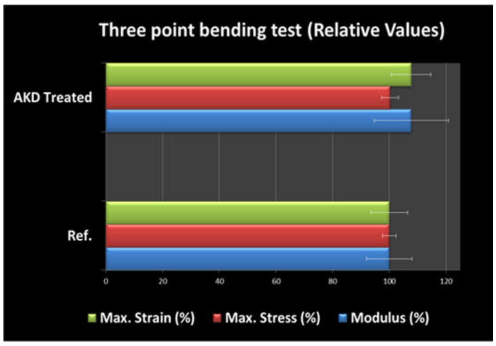

Figure 4. Bending test results of the AKD-treated and no treated samples.

Regarding bending test, AKD-treated fibers increased the maximum strain and the modulus maintaining the maximum stress. The results (after 130 days) are included in the next graph:

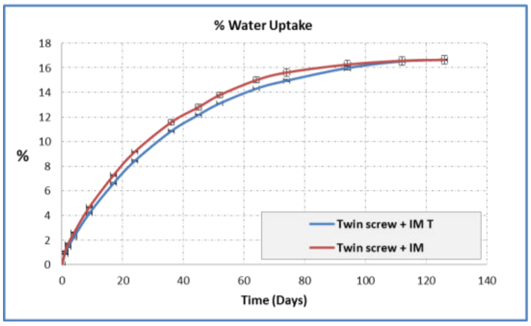

Figure 40. Water uptake curves for AKD- treated and untreated samples.

The differences between the AKD-treated and untreated composites are not as good as expected based on the previously observed contact angle results. Probably, an excessive shear in the twin-screw destroys the AKD effect by cutting the fibers and releasing hydroxyl groups free for water uptake.

At this point, was decided to study the influence of the shearing in the water uptake of the composites. To do this, were prepared different composites by different processing conditions from low to high shear:

- Direct melt blending on press (low shear)
- Single-screw - Injection Moulding – Pressing (high shear)

5 RESULTS:

In the two cases, the treated fibers improved the performance of the composites by 3-4 %. The absolute value of the water uptake was inferior in the case of injection moulding. This effect can be better observed if we compare the two procedures:

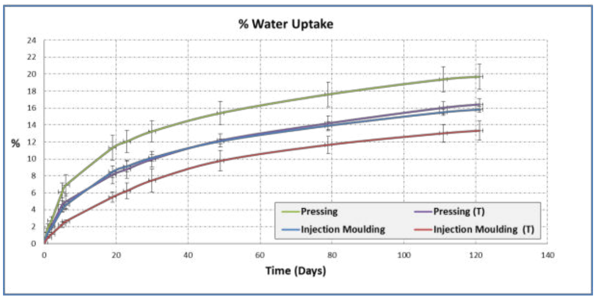

Figure 6. Comparison between the processing methods in the water uptake test.

The best results were obtained with the injection moulding samples treated with AKD. In the following graph the summary of the results after 120 days are included:

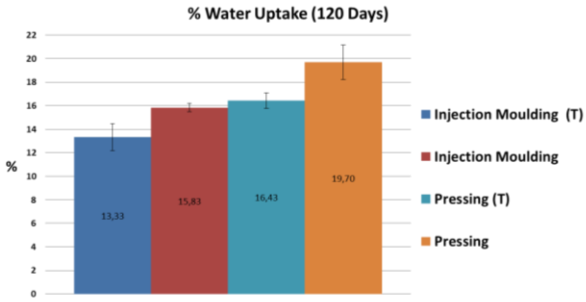

Figure 7. Percentage of water uptake after 120 days.

Analysing the results, the negative effect of the pressure was higher than of the shearing. The best result (13,33% water adsorption) was obtained with treated fibres combined with injection moulding.

6 SUMMARY

A method for the treatment of natural fibers with AKD for the application in NFPC has been developed. Different variables has been studied and the best method has been applied for the preparation of treated wood flour and composites. A very goood result in terms of contact angle has been observed for the AKD treated fibres. However, this effect is not observed for the water uptake of the samples, this is probably due to that a a superficial treatment does not avoid the water uptake of the inner hydroxylic groups of the fibers.

A NFPC composite based on PP and treated fibers were prepared and the influence of the process methods were studied at different processing conditions. We could conclude that two effects are playing a role in the process:

<u>Shear effect</u>: An excessive shear destroy the hydrophobation effect of the AKD treatment.

<u>Pressure effect</u>: In injection moulding, the pressure effect increase the protection of the fibers by encapsulation with the matrix (PP) decreasing the water uptake.

7 ACKNOWLEDGMENTS

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