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Preliminary results of bark and straw acetylation

Mátyás Báder[1*], Róbert Németh[1], Boglárka Bekecs[1], Dániel Márton[1]

[1] University of Sopron, Institute of Wood Technology and Technical Sciences, Bajcsy-Zs. Str. 4, Sopron, Hungary, 9400

E-mail: bader.matyas@uni-sopron.hu; nemeth.robert@uni-sopron.hu; bogibekecs@gmail.com; marton.dan@gmail.com

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ABSTRACT

In this study, robinia bark (outer bark, phloem and cambium of *Robinia pseudoacacia* L.) and wheat straw (*Triticum* sp.) were treated with acetic anhydride. Vapour phase acetylation resulted in a slight decrease in equilibrium moisture content. The soaking of samples in acetic anhydride for one day had multiple effects. Air-dry and absolute dry samples were used. The post-treatment after acetylation was also carried out in two ways, heated at 103 °C and 120 °C. For the bark of robinia, the decrease in equilibrium moisture content was between 30-42%. The best results were obtained for the sample dried at 103 °C, acetylated and then re-dried. For wheat straw, a higher efficiency was achieved, with an equilibrium moisture reduction of between 40-55%. The straw conditioned under normal climate (20 °C / 65%), then acetylated and finally heated at 120 °C showed the best results. The colour change of samples treated with acetic anhydride was also significant.

INTRODUCTION

In today's modern world, there is an increasing emphasis on the use of natural materials in all aspects of life. In our research, we sought to determine how the treatment with acetic anhydride (acetylation) affects the interaction of straw and bark with water. In many cases, the materials investigated in this study are waste materials, which are only used in higher quantities in agriculture. However, straw and bark have a high capacity to absorb and release moisture from their environment, and by reducing this significantly, we can obtain natural and health-friendly materials that can be used in a wide range of applications. The acetylation process may be able to address the problem of moisture absorption and, in one step, improve fungal and pest resistance. It is very important that the final product will not contain hazardous substances after treatment and that the disposal of waste after use will not hazardous to the environment. Finally, it is worth considering the costs involved in the process.

Nowadays, mainly acetic anhydride is used for the acetylation of wood at the industrial level. It is a colourless, pungent-smelling liquid that hydrolyses and decomposes into acetic acid when exposed to water. During the acetylation process, acetic anhydride reacts with wood, resulting in the replacement of hydroxyl groups with acetyl groups and the formation of acetic acid as a by-product (Bollmus et al. 2015). This means that the hydrophilic hydroxyl groups are converted into hydrophobic ester groups. Cell walls swell as a result of the treatment, while cell lumina remain empty. Dimensional stability is increased, equilibrium moisture content (*EMC*) and water absorption capacity are reduced, and weight is increased (Sun et al. 2019). Fungal and insect resistance is greatly increased. The properties of acetylated natural materials highly depend on the species, the pretreatment of the material, the reaction medium, the conditions of the reaction process and the post-treatment. The acetylation is not only carried out on the surface but also over the whole cross-section and length, resulting in a product with a relatively homogeneous structure and homogeneous properties. The effect of acetylation is permanent, irreversible, with no chance of leaching. Since a natural substance is used in the treatment (adding of acetyl groups which are present in the lignocellulose materials anyway), the resulting product is non-toxic, non-hazardous to humans and the environment, and fully recyclable.

After acetylation, the expected reduction of *EMC* for wood is 30-40%, which is what we aim to achieve with the treated materials in this study. We are investigating the *EMC* reduction of bark and straw as a result of the reaction, as we hypothesize the reduction of their vapour absorption capacity. Since bark and straw do not have a dense structure like wood (higher porosity), it may be sufficient to treat the test materials in acetic anhydride vapour to reach sufficient modification. If the aforementioned procedure were efficient enough, the modification could be carried out more easily and quickly. This would result in greater cost efficiency. To test how much more effective the liquid-phase acetic anhydride treatment is, this was also carried out. In order to simplify the treatment, it was done at room temperature and different pre- and post-treatments were used.

EXPERIMENTAL METHODS

The acetylation processes were carried out in an airtight desiccator at room temperature. In the course of the experiment, robinia bark (outer bark, phloem and cambium of *Robinia pseudoacacia* L.) and wheat straw (*Triticum* sp.) were treated with acetic anhydride (Lach-Ner, Neratovice, Czech Republic; 99.66% G.R).

In the first experimental phase, the highly volatile acetic anhydride vapour at room temperature was used to react with robinia bark and wheat straw, which are structurally much looser than wood. The samples prepared for the treatments and the control ones were first conditioned in a normal climate (20 °C and 65% relative humidity) to check what their *EMC* is in their untreated state. The treatment samples were placed in an airtight desiccator with an internal circulating fan for seven days (7×24 hours), in which a petri dish filled with acetic anhydride was also placed. This provided the air saturated with acetic anhydride vapour. The acetylated samples were then kept at normal climate conditions, let the extra chemical in the samples that could not react with the samples evaporated. After a few days, all the samples were dried at 103 °C to obtain their absolute dry mass. They were then placed into the climate chamber at normal climate and the change in mass was monitored regularly to determine the rate and extent of moisture uptake.

In the second phase of the experiment, the following 7 different type of samples were created:

- C: Sample stored only in a climate chamber at 20 °C / 65% (not acetylated)
- D: Dried sample only (not acetylated)
- H: Heated sample at 120 °C (not acetylated)
- CAD: Air-dry sample acetylated, then dried at 103 °C
- CAH: Air-dry sample acetylated, then heated at 120 °C
- DAD: Sample dried at 103 °C, acetylated in absolute dry state, then dried again at 103 °C
- DAH: Sample dried at 103 °C, acetylated in absolute dry state, then heated at 120 °C.

The samples for acetylation were wrapped in plastic nets to avoid loss of specimens which would result in false weight measurements. The wrapped samples were placed in large beakers and weighed to ensure complete coverage with the chemical. The beakers were then filled with acetic anhydride (in liquid form) and placed in an airtight desiccator for 1 day to prevent the chemical from evaporating after saturation of the air in the desiccator. After acetylation, the excess chemical was drained off the samples and, after weighing, each sample was dried at 103 or 120 °C for 1 day according to the prescribed treatment schedule. We chose the temperature of 120 °C because it is a safe 20 °C below the boiling point of acetic anhydride. Finally, the samples were conditioned in a normal climate with regular weight checks until its *EMC* was reached.

RESULTS AND DISCUSSION

In the moisture uptake test of the samples treated in acetic anhydride vapour, moisture uptake started very rapidly at the beginning, similarly to other lignocellulose materials, i.e. wood. Not only the moisture uptake, but the time to reach *EMC* was particularly fast for straw (Fig. 1). This could be due to the small size of its parts and loose structure. The water vapour absorption capacity of the treated samples after treatment was found to have decreased, but not to the extent intended. Based on the final *EMC* values, a moisture content

(*MC*) reduction of 15.13% was observed for bark and 9.98% for straw, which were respectively 1.11% (*MC%*) and 1.25% (*MC%*) in terms of net moisture content. The first results were therefore not satisfactory.

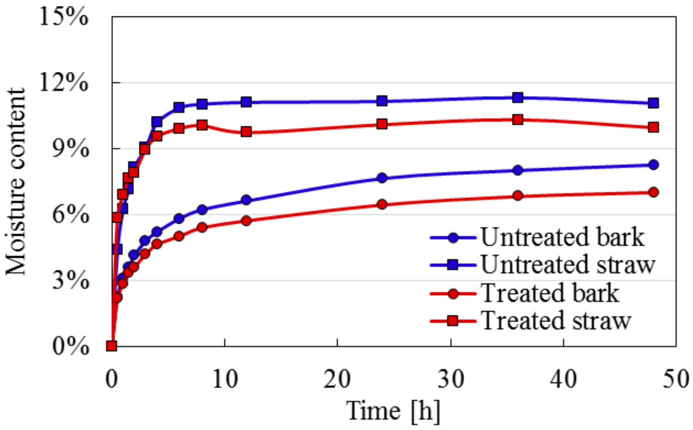

Figure 1: Results of the first experimental phase: the rate and quantity of water uptake

For samples treated in liquid acetic anhydride, spectacular colour changes were observed (Fig. 2). The darkening of the samples is definitely a manifestation of the modification of the material, and consequently significant changes have occurred. The outer bark and cambium of the robinia became not just darker, but much more uniform for samples treated over 100 °C.

What was suspected from the colour change was confirmed by the water vapour absorption test. Treated samples showed a significant decrease in the vapour absorption capacity. Their decrease of *EMCs* were within the expected interval of 30-40%, or in some cases even better. The moisture absorption graphs until *EMC* was reached are shown in Fig. 3.

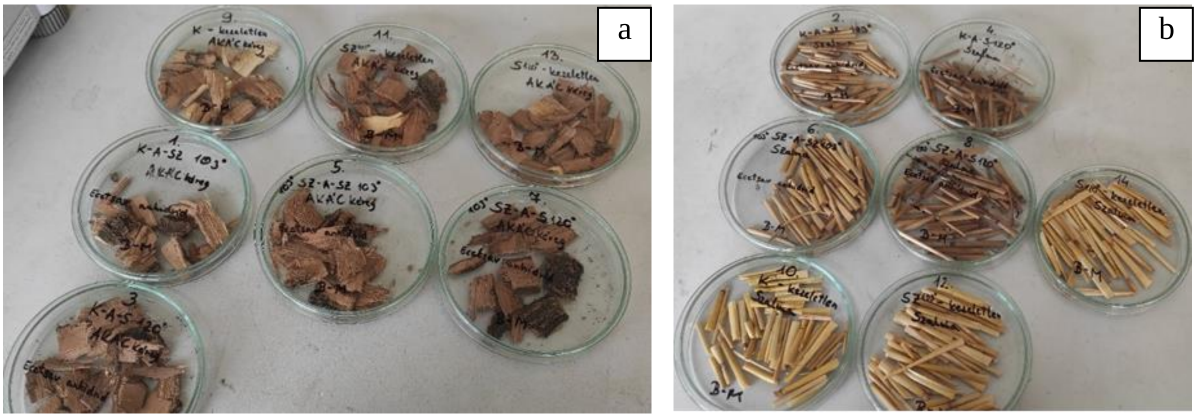

Figure 2: Colour change as a result of acetylation for bark (a) and straw (b)

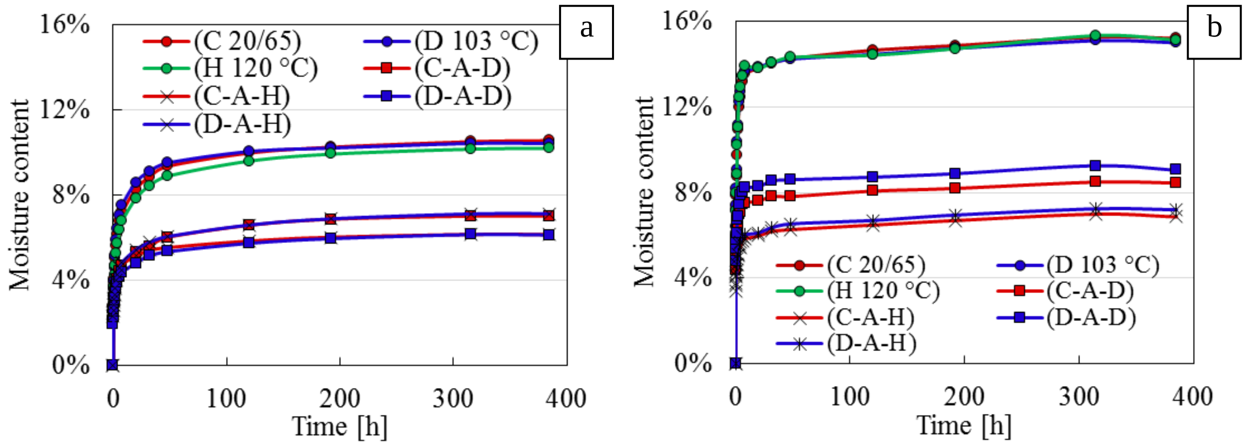

Figure 3: Rate and quantity of water uptake in experimental phase two for bark (a) and straw (b). Abbreviations: A – Acetylated; H – Heated at 120 °C; C – conditioned in climate chamber at 20 °C / 65%; D – Dried at 103 °C

As the graph lines in Fig. 3 are almost overlapping, there was no significant difference in *EMC* between unacetylated samples (conditioned, dried at 103 °C and heated at 120 °C), so it is sufficient to compare the results of acetylation with the untreated-conditioned samples. For robinia bark, the best result (41.93% *EMC* reduction) was obtained for the sample that was acetylated in an absolute dry condition and then dried again at 103 °C (D-A-D). The weakest result was 32.45% for the sample that was acetylated in an absolute dry condition and then heat at 120 °C (D-A-H). The C-A-D sample showed a reduction in *EMC* of 33.54% and the C-A-H sample 41.72% (Fig. 3). Consequently, the results of treatments D-A-D and C-A-H is similar. Another question is which treatment method can be used more economically. It seems that C-A-H treatment combination requires less energy for heating and less live work.

For wheat straw, the largest decrease was for the sample that was acetylated in air-dry condition and then heated (C-A-H; 54.82%). The weakest result was for the sample that was treated in absolute dry condition and then dried again (D-A-D 40.46%). Straw samples treated at 120 °C after acetylation gave better results than sample D-A-D. Presumably due to the much looser structure (thinner cell walls in small cross-section), the chemical was better able to access the hydrophilic groups in the straw, resulting in a greater reduction in *EMC* (Fig. 3). For both raw materials, the most appropriate treatment is to climatize them before acetylation with acetic anhydride and then heat at 120 °C temperature. This is a less costly solution with good results for both raw materials.

CONCLUSIONS

The bark of robinia and wheat straw were treated with acetic anhydride to significantly reduce their equilibrium moisture content. The acetylation was carried out at room temperature. The samples were first modified in acetic anhydride vapour, which resulted in a modest reduction of only 10-15% in equilibrium moisture contents. A one-day soaking in liquid acetic anhydride gave significantly better results. Bark samples dried at 103 °C, acetylated and then dried again gave the largest decrease in equilibrium moisture content (41.93%). Bark climatized at normal conditions (20 °C / 65% relative humidity), acetylated and then heated at 120 °C gave similarly excellent result (41.72% decrease). The weakest decrease also exceeded 30%. For straw, the greatest reduction in equilibrium moisture content (54.82%) was obtained with conditioning, acetylation and then heating at 120 °C, but the other treatments also gave very good results. After acetylation treatments, the colour change of the samples was striking. The heat exposure resulted in minimal darkening of the untreated samples and significant darkening of the treated samples, depending on the treatment prior to acetylation. The robinia bark behaved similarly, and in addition, the colour of the outer bark and cambium became much more uniform in both dried and heated samples.

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