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# Changes of breaking length of cotton paper with the addition of nanofibers in a PLA/P3HB composite

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Abstract: In this study it was attempted to enhance strength properties of paper. The aim was to produce paper modified with nanofibers, which would exhibit enhanced strength properties. Tests were conducted on cotton-comber pulp and the composite of PLA (poly(lactic acid)) and P3HB (poly(3-hydroxybutyrate)) nanofibers. Control sheets were formed from cotton-comber pulp, while experimental sheets were produced with a 2% and 5.5% addition of ground nanofibers. Tests of selected strength properties showed their considerable changes.

*Keywords*: cotton pulp, paper, nanofibers, polylactic acid, poly-3-hydroxybutyrate

## INTRODUCTION

Research initiated at the Institute of Chemical Wood Technology on modification of paper using PLA/P3HB nanofibers brought exceptionally good results. Cotton paper with a 5.5% addition of ground nanofibers showed improved strength properties. Breaking length increased by 17%, folding endurance increased by 14% and air permeability increased by as much as 35% (Modzelewska et al. 2015). Such good results recorded at the preliminary stage provided an incentive to continue these studies.

Cotton-comber pulp is used to produce paper products, of which superior strength properties are required. Such products include e.g. securities. They are produced at the addition of various fillers and chemical additives. Nanofibers exhibit high tensile strength and resilience. Their introduction of paper products may considerably improve strength properties (Przybysz 1997).

Additives introduced to paper pulp have a varied effect on properties of the final product. They may alter its strength, optical properties or eliminate disturbances in the technological process (Wandelt 1996).

The added nanofibers to paper pulp prior to the formation of paper should behave like a secondary fine fraction, which fills free spaces between cellulose fibers. This affects overall strength of paper products by binding fibers together.

The aim of this study is to produce paper modified with nanofibers, which would exhibit enhanced strength properties. Tests were conducted on hardwood pulp and a composite of PLA (polylactide) and P3HB (poly(3-hydroxybutyrate)) nanofibers. Control sheets were formed from cotton-comber pulp, while experimental sheets were produced with an addition of ground nanofibers. Tests for breaking length verified the presented hypothesis.

## MATERIALS AND METHODS

### Materials

*PLA/P3HB nanofibers*

The experimental material comprised nonwoven fabric produced under laboratory conditions from PLA/P3HB nanofibers, paper sheets produced from cotton pulp and sheets produced from a combination of cotton pulp and ground PLA/P3HB nanofibers.

PLA (poly(lactic) acid) is a biodegradable polymer obtained from corn meal. It is used as implants in dentistry, absorbable suture material or disposable dishes degradable within 80 days.

P3HB (poly(3-hydroxybutyrate)) is a biodegradable polymer, which is produced and accumulated by bacteria *Ralstonia eutropha.* It is used to produce shampoo bottles or cosmetics containers. It is degraded by soil bacteria, particularly under anaerobic conditions.

*Cotton-comber pulp*

Long-fiber pulp made of cotton, flax and hemp is the top quality semi-finished fibrous product used in manufacturing of paper products. Cotton-comber pulp is usually obtained from cloth. It is typically of high chemical purity, strength and its price is relatively high, so it is mostly used in the production of paper goods for special purposes, e.g. securities (Przybysz 1997, Wandelt 1996).

The properties of the cotton-comber pulp used in this study (data provided by the manufacturer of the pulp): cotton-comber pulp, bleached, refined, dried; brightness 85% (ISO 2470), drying-content 90%, length of fibres 2-4 mm (visually), degree of beating 19÷24 SR value (Schopper-Riegler value) (ISO 5267/1).

**Methods**

*Production of PLA/P3HB nanofibers by wet electrospinning*

To produce nanofibers appropriate technological parameters were established for the specific polymer solution used. The basic parameter is the adequate concentration of the solution, for which the process of nanofiber electrospinning is most efficient. It needs to be remembered that the spinning solution has to be composed of an appropriate solvent, which is relatively readily evaporated during nanofiber formation (Bendkowska 2008, Qin et al. 2001, Kozłowski and Ogurkowski 2008, Park and Harris 2001, Tyrolczyk et al. 2012). The appropriate concentration of the spinning solution was determined using an Anton Paar MCR 101 rotation rheometer, equipped with an electrorheological cell, facilitating accurate identification of changes occurring in the spinning solution in the electric field generated during nanofiber electroformation.

In the production of nanofibers from natural polymer parameters for the spinning solution were adopted as in Table 1.

Table 1. Parameters of PLA and PHB solution

| **PLA : PHB polymer ratio** | **70 : 30** |
|---|---|
| Concentration of the spinning solution | 7 % |
| Solvent | Chloroform |
| Temperature of the spinning solution | 20 °C |
| Temperature of the chamber | 20 °C |
| Inside diameter of the capillary | 0.8 mm |
| Voltage | 10.0 – 25.0 kV |
| Distance between electrodes | 150 mm |

Thus produced nanofibers exhibited the best strength properties. The composition was selected based on the final report of the project POIG. 0103.01-00-004/08. Functional nano- and microtextiles – NANOMITEX.

*Production of paper sheets under laboratory conditions*

After an appropriate milling time was established, at which pulp obtained slowness of 28-30°SR, paper sheets were formed. Sheets were manufactured in the Rapid-Köthen device in accordance with the European standard PN-EN ISO 5269-2:2007. Sheets from cotton pulp were manufactured with no additives (as the control) and with an addition of 2% of nanofibers.

*Measurements of breaking length*

Samples prepared following the respective standards were tested for the following parameters:

- weight GSM acc. to PN-ISO 536:2012
- breaking length acc. to PN-EN ISO 1924-2:2010.

RESEARCH RESULTS

The experimental material comprised paper sheets manufactured from cotton pulp and sheets produced by combining cotton pulp with ground PLA/P3HB nanofibers. Those sheets were subjected to selected tests and the recorded results were averaged and presented in Table 2.

Table 2. Average results of selected properties of pure and composite materials tested

| **Properties** | **testing material** | | | | | |
|---|---|---|---|---|---|---|
| | **Paper: cotton** | | **Paper: cotton + 2% PLA/P3HB nanofibers** | | **Paper: cotton + 5,5% PLA/P3HB nanofibers** | |
| | Average results | Standard deviation | Average results | Standard deviation | Average results | Standard deviation |
| **Breaking length [km]** | 3.51 | 0.14 | 2.31 | 0.18 | 4.11 | 0.21 |

Assuming that strength of reference samples, i.e. sheets produced from cotton pulp with no additives, constitutes 100%, strength of paper with an addition of PLA/P3HB nanofibers was calculated in percent and presented in graph 1 (fig. 1).

Conducted tests clearly showed that the introduction of ground nanofibers to cotton pulp did not bring expected results. Strength parameters of nanofibers were not transferred to the paper material produced under laboratory conditions, thus providing no improvement of strength properties.

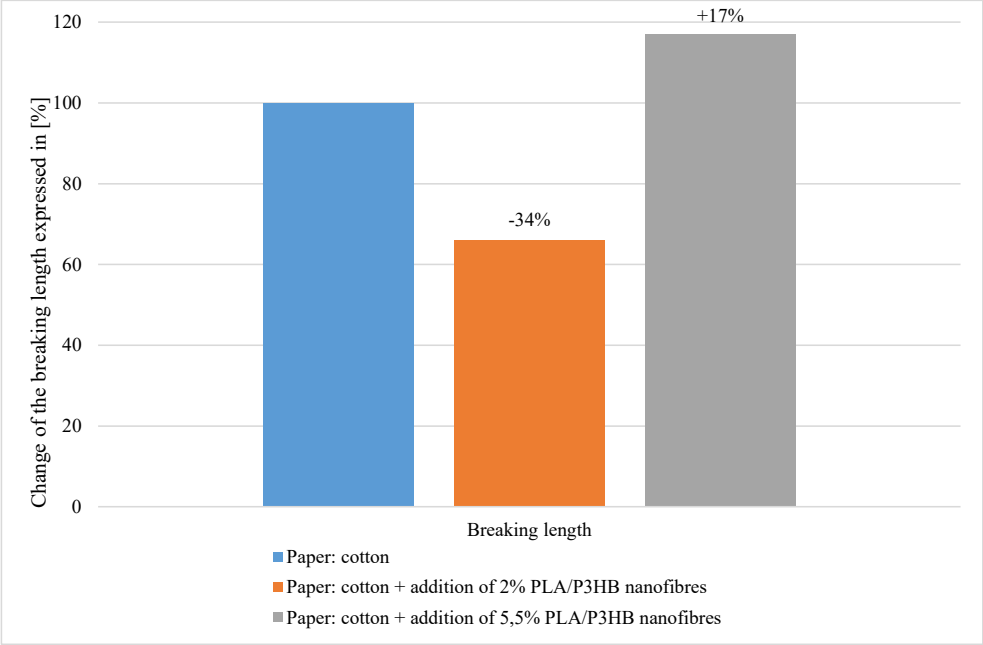

Figure 1. Summary of average results for breaking length

Analysis of results showed that this modification had a significant effect on properties of the produced paper product. It was observed that paper with a 2% addition of ground nanofibers exhibited inferior properties in this test, while their addition at 5.5% resulted in their marked increase.

## CONCLUSIONS

Tests showed that a 5.5% addition of nanofibers resulted in an improvement of breaking length of cotton-comber paper, while their 2% addition caused a considerable deterioration of this property. Attempts at a reduction of the nanofiber addition resulted from economic reasons; however, they did not bring satisfactory effects.

An increase in breaking length in the sample with a 5.5% addition of nanofibers may be explained by filling of free spaces in the paper structure and increased interactions between cellulose fibers. In the case of their 2% concentration nanofibers could have behaved as fillers thus weakening these interactions, at the same time causing a reduction of strength properties.

Results of these preliminary studies provide an incentive for further studies on this subject. It is important to focus on other concentrations and cellulose pulps. At other variants such a configuration may prove advantageous.

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**Streszczenie:** W niniejszych badaniach podjęto próbę zwiększenia właściwości wytrzymałościowych wytworu papierniczego. Ich celem było uzyskanie papieru zmodyfikowanego nanowłóknami, który charakteryzowałby się podwyższonymi właściwościami wytrzymałościowymi. W badaniach wykorzystano masę bawełnianą oraz kompozyt nanowłókien PLA (poli(kwas mlekowy)) oraz P3HB (poli(3-hydroksymaślan)). Uformowano arkusiki kontrolne z masy bawełnianej oraz arkusiki z 2% i 5,5% dodatkiem zmielonych nanowłókien. Badania wybranych właściwości wytrzymałościowych wykazały znaczną ich zmianę.