

# Natural Paper-layered Composites with Air Barrier Properties Achieved by Coating with Bacterial Cellulose

Marta Kaźmierczak,<sup>a,\*</sup> Tomasz P. Olejnik,<sup>a</sup> and Magdalena Kmiotek<sup>b</sup>

In some respects the safest food packaging material is paper that is completely free of chemical additives, made only from primary cellulosic fibers. There is no information in the literature on giving paper barrier properties using nanocellulose without any additives, especially bacterial cellulose, by applying a coating to a fibrous semi-product. In order to prepare paper-layered composites, paper sheets made of beaten or non-beaten softwood or hardwood cellulose pulp, or their 50/50 (wt./wt.) mix, were used in the experiment. After the application of bacterial cellulose onto the sheets, the paper became completely impermeable to air, which means that fine microbial fibers had filled the voids (pores) between plant cellulose fibers. The results of the experiment could be regarded as a perfect, biodegradable packaging material.

*Keywords:* Packaging material; Paper-layered composites; Multilayer structure; Cellulose

*Contact information:* a: Institute of Food Technology and Analysis, Lodz University of Technology, Stefanowskiego 4/10, 90-924 Lodz, Poland; b: Institute of Papermaking and Printing, Faculty of Management and Production Engineering, Lodz University of Technology, Wolczanska 223, 90-924 Lodz, Poland;

\* Corresponding author: marta.kazmierczak@dokt.p.lodz.pl

## INTRODUCTION

Paper is one of many packaging materials used to store, protect, sell, and distribute food products (Obiora *et al.* 2019). The main advantages of paper are its high mechanical strength, biodegradability, and printability. The most notable drawbacks of paper packaging include poor barrier properties, opacity, porosity, and a lack of thermoforming properties (Raheem *et al.* 2012; Obiora *et al.* 2019). Some of these disadvantages can be eliminated by coating paper with waxes or polymer films; however, despite their advantages, most of such additives are not biodegradable (Raheem 2012).

Apart from primary or secondary plant fibers, many chemical additives (sizing agents, wet and dry strength agents, coating materials, fillers, dyes, and pigments) and process agents (retention agents, biocides, or skimmers) are used in paper production (Sato *et al.* 2005). Their role is to enhance the paper production process and to improve the existing qualities of, or give new functional properties to, manufactured papers used for various applications, including those intended for packaging materials that are in contact with food (Sato *et al.* 2005; Johansson *et al.* 2012). Such papers must meet strict requirements regarding the presence of various types of chemical additives (EU Framework Regulation, EC, 1935/2004).

In view of contamination of the food by the wrapping itself, the safest packaging material is paper that is completely free of chemical additives, made only from primary cellulosic fibers. Packaging paper can be manufactured using kraft pulp (flour, sugar, dried vegetables, and fruits packaging) or kraft mass (small bags, sweets packaging, parchment paper for packaging snacks, bars and oil products, pelour for packaging cakes, pastries and

fast foods, and non-fat baking papers). Another type of paper packaging are paper laminates obtained by coating paper pulp with polymers or aluminum foil for packaging dried products, such as powdered soups, herbs, and spices. The disadvantage of such packaging is the presence of a non-biodegradable coating after use. Polyethylene-coated paper packaging is widely known for its heat sealability and air/moisture barrier properties (Zhang *et al.* 2001; Sato *et al.* 2005). However, the modification applied to such paper hurts its biodegradability and recyclability (Zhang *et al.* 2001; Bajer *et al.* 2017).

The most common additive used in paper production is starch. It can be used as a sizing agent, flocculating agent, and a retention aid. It increases the dry strength of paper. After its transformation into derivatives, such modified starch, alone or in combination with polyvinyl alcohol, can be used as a coating layer, improving the strength properties of paper and giving it water barrier properties (Bajer *et al.* 2017).

The coating layer can be formed from sodium caseinate and glycerol, which ensures excellent water vapor barrier properties and improves the strength properties of paper (Choe and Min 2005; Khwaldia 2010). It is possible to give paper oil-barrier properties without deteriorating its optical and strength properties, thanks to the so-called edible coating containing a whey protein isolate (Johansson *et al.* 2012). Isolated soy protein can also be used to give papers and cardboard resistance to being penetrated by oils, and to improve their color (Gällstedt *et al.* 2005; Basiak *et al.* 2012).

In this paper, the barrier properties against air obtainment were studied via the method of coating the paper with bacterial cellulose layer. Such a solution has already been studied, but not with the use of bacterial cellulose grown on rubber waste.

## **EXPERIMENTAL**

### **Coating**

Bacterial cellulose (BC) obtained from *Lactobacillus plantarum* culture processes was used in all the experiments. All the cultures were grown on rubber waste. In order to prepare paper-layered composites, small paper sheets made of beaten or unbeaten, softwood or hardwood cellulose pulp, or their 50/50 (wt./wt.) mix were used. Beating of pulps was done in a 'Jokro' laboratory mill, in accordance with the PN-EN 25264-3 standard (1999).

Dried and pre-ground bacterial cellulose was fiberized in water and hand-applied to pre-layered base papers, formed in accordance with the PN-EN ISO 5269 (2001) standard using the Rapid-Köthen apparatus. Before the test, the samples were conditioned in accordance with the PN-EN 20187 (2000) standard.

### **Grammage/Paper Weight**

Grammage was determined using a quadrant scale (Lorentzen-Wettré, Stockholm, Sweden), according to the ISO 536 (2012) standard.

### **Bulk density**

Bulk density was calculated on the basis of paper weight and web thickness measured using the 1011 digital thickness gauge (PTA, Mauern, Germany) according to the ISO 534 (2011) standard.

## Air Permeability

Measurement was carried out using a 4101 densometer (Troy, New York, USA), in accordance with the ISO 5636-5 (2003) standard. The time required for the cylinder to move one space down was measured, which corresponds to the passage of 100 cm<sup>3</sup> of air.

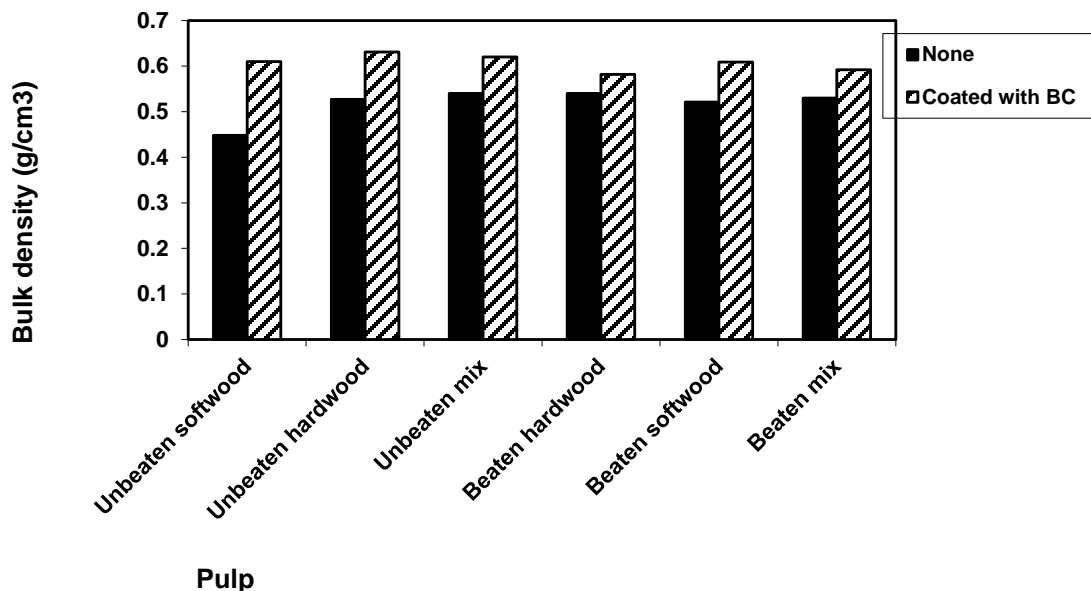
## Scanning Electron Microscopy (SEM)

Micrographs were taken with a 20 kV scanning electron microscope (JEOL 5410LV, Tokyo, Japan) under magnitude x400 and x100. Samples were photographed from the top layer and side surface.

## RESULTS AND DISCUSSION

The coating of paper sheets with bacterial cellulose resulted in an increase in the bulk density. The highest change was observed for paper sheet prepared from unbeaten and beaten softwood, and also for unbeaten hardwood.

The lowest bulk density of non-coated paper sheets was observed in the case of softwood unbeaten pulp. The bulk density, being a measure of the degree of inter-fiber bonding, is one of the most important structural properties of paper and has a great influence on other properties. With higher density, fiber bonding in the sheet is improved (Brännvall and Annergren 2009). The lowest bulk density for unbeaten softwood pulp indicates poor fiber bonding (Fig.1).



**Fig. 1.** Bulk density of uncoated paper sheets and sheets coated with bacterial cellulose

After beating, the inter-fiber bonding increases due to the greater flexibility of wet beaten fibers and increased probability of getting contact with other fibers. Additionally, the number of fiber fragments is higher due to fibrillization effect. This affects the bonded area and more densely packed fibers in the beaten sheets (Brännvall and Annergren 2009), as well as filling the spaces between the fibers during the formation, resulting in increased paper sheet density (Xia and Gong 2011). The bulk densities of the studied beaten pulps

were relatively similar, indicating dense fiber distribution and bonding area.

In the unbeaten mix, the change in the bulk density is not as high, due to the pores being filled by the long fibers of softwood pulp intermixing with the short fibers of hardwood pulp. These result in the formation of more dense and tight structures created by interpenetrating pine and birch fibers. Unground pulps have greater porosity compared to ground pulps, whose fibers become more and more flexible as a result of mechanical modification and whose contact surface increases.

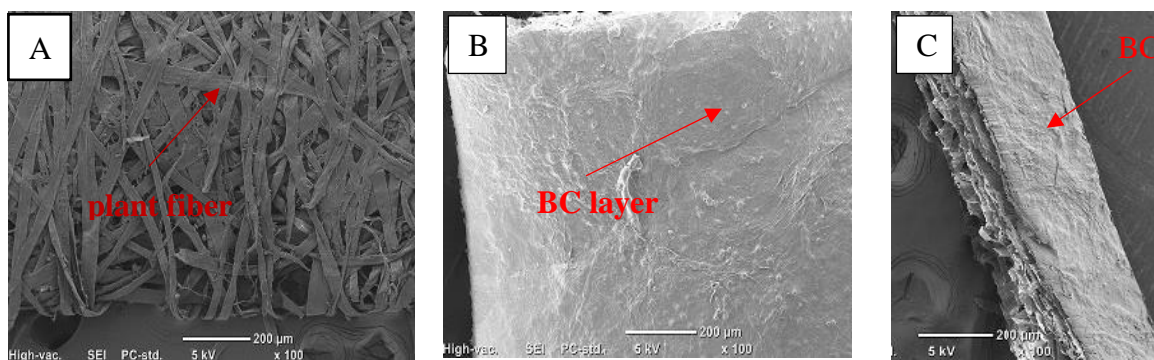
The largest increase in bulk density after coating with bacterial cellulose was observed for unbeaten softwood and hardwood pulps, characterized by the structure of higher porosity, being an effect of the loose structure and low bonding area between fibers. The tiny BC fibers easily penetrate the spaces between fibers, filling the gaps (pores) and leading to the highest increase in bulk density in case of the unbeaten pulps (Fig. 1).

After the application of bacterial cellulose onto sheets of paper made from beaten or unbeaten, softwood or hardwood cellulose pulp, or their 50/50 (wt./wt.) mix, the paper became completely impermeable to air, which means that fine microbial fibers filled the pores between plant cellulose fibers, making it impossible to pass air through the sheets (Table 1). BC fibers act as sizing agent, which entirely penetrated the structure of the paper sheets, forming an inter-bonded and completely filled natural composite of plant-bacterial cellulose fibers.

**Table 1.** Air Permeability (s/100 cm<sup>3</sup>) of Uncoated Sheets and Sheets Coated with Bacterial Cellulose

Medium	Uncoated	Coated
Unground softwood	3.29±0.33	∞
Unground hardwood	4.79±0.27	∞
Unground mixture	4.41±0.38	∞
Ground softwood	6.79±0.46	∞
Ground hardwood	9.52±0.18	∞
Ground mixture	6.69±0.36	∞

The effect of bacterial cellulose coating on the sheets of paper was visualized with the use of scanning electron microscopy, Fig. 2.



**Fig. 2.** SEM micrographs of paper sheet uncoated (A) and coated (B, C) with bacterial cellulose seen from the top (B) and side (C) surface

In Fig. 2a, the top layer of an uncoated paper can be seen with individual plant fibers making up the paper felt. After covering with bacterial cellulose, a homogenic

surface was created without visible holes or pores (Fig. 2b). The plant fibers of the paper were fully hidden and could not be seen through the BC layer. From the Fig. 2c, which shows the side surface of the BC coated paper, restrained penetration of BC was revealed. The coating agent did not penetrate the paper, which meant that layers remained distinct from each other to the point of contact. Only the top layer and spaces between fibers were consolidated with the BC.

There is no information in the literature on giving paper barrier properties using bacterial cellulose without any additives, especially bacterial cellulose, by applying a coating to a fibrous semi-product.

## CONCLUSIONS

1. The effect of paper sheet coating with bacterial cellulose, obtained from *Lactobacillus plantarum* culture processes grown on rubber waste, on the bulk density and air permeability was studied.
2. Paper sheets used in the experiments were formed from birch, pine, or mixed (50/50 wt %) pine and birch pulps before and after mechanical beating, enabling the best milling effects (Danielewicz *et al.* 2018).
3. Coating of beaten or non-beaten paper sheets with the bacterial cellulose results in the loss of permeability of the treated paper due to the filling the pores in the paper sheets with the bacterial cellulose layer, which easily fits to the empty spaces between birch or pine fibers.
4. Paper not permeable to air and coated with a harmless layer of bacterial cellulose has a high potential to be applied in packaging for food.

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