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Bacterial Cellulose Applied to the Production of an Electrical Insulating Biomaterial

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Biotechnology is the science that in the future will revolutionize the production of biomaterials for the markets, one of its most promising products is bacterial cellulose (BC). The BC has a high degree of purity, because it is not associated with other components such as lignin and hemicellulose of vegetable cellulose and, due to its nanofibrillar network in 3D, it is able to absorb water and has high tensile strength. Other characteristics, such as biocompatibility and biodegradability, result in the renewable character and in a wide range of technological applications, such as the manufacture of transparent / translucent nanocomposites and, in particular, biomedical applications, such as the production of dressings for the recovery of burned skin, where membranes release of drugs through the skin, polymeric materials for bone repair repair and cartilage, as well as several other technological areas and as reinforcement material in transparent / translucent nanocomposites. The BC membrane has been studied aiming at the usability in the production of garments, accessories and high value-added textile products and in the active packaging sector to avoid or identify contamination of food. In the biomaterials sector, numerous BC blends and composites have been synthesized to overcome their limitations and increase their applications. BC blends have antimicrobial, healing, conductive, magnetic and optical properties. The morphological and electrical characterization of BCs was the objective of this work. The BC production was carried out using agroindustrial residue. The biomaterial was morphologically characterized by MEV before and after impregnation with PHB. The incorporation of PHB into BC served to maximize the properties and physico-chemical and insulating biomaterial. Conductivity values compatible with semiconductors were identified for BC. The bio-nanoblend of BC + PHB also showed low conductivity value, similar to pure PHB. All the samples showed IxV behavior that suggests that the samples are ohmic

1. Introduction

Bacterial cellulose is now recognized as one of the most prosperous biomaterials in the industry. Obtained through bacteria, a material is made from renewable natural sources and free of impurities. The biomaterials produced with BC demonstrate great potential in the protection of the human body, as reported in several studies (Arjmandi et al., 2017; Costa et al., 2018). The characterization of composites of BC in the form of film (or membrane) with the addition of insulating compounds suggests the possibility of the electrical isolation, safely, of anybody enveloped by it. The development of electrical insulation is closely associated with the development of electrical appliances. Naturally, products such as asphalt, rubber, mica, cotton yarn or fabric were generally used. Oil impregnated mineral paper was used in transformers, capacitors, and underground

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cables, for example. The first synthetic insulating materials, namely phenolic and alkyd resins, were used in the insulation were the varnishes (Marris, 1956). The bacterial cellulose can be modified and processed into an intelligent material. For, intelligent materials are more often defined as materials capable of significantly altering their properties in response to external stimuli, such as pressure, temperature, and changes in humidity in the environment (Michalak, Krucinska, 2016). The batteries used in almost all mobile devices are being developed to present a malleability with high specific power capacity. Surface coating, flexible and extensible fabrics with polymer nanoemulsion paints are possibilities for obtaining conductive polymers (Wei, Cotton, Ryhänen, 2012). Conductive polymers are also known as conjugated polymers, and the conductivity of such polymers falls in the range of semiconductors, and some of them can be made as conducting as metals when doped by photochemical, chemical or electrochemical methods (MacDiarmid, 2001).

Considering that the insulating means may exist in the solid, liquid or gaseous states, the dielectric withstandability of an insulating medium is characterized by its dielectric strength, which refers to the maximum electric field supported by the insulating medium before it becomes conductive. When an insulating medium is subjected to this critical electric field value, the so-called insulation fault occurs. This failure can be seen as a full fault, in which a disruptive discharge occurs that can cause a short circuit in energized parts, practically reducing them to zero voltage, or a partial failure of the insulation in which the disruptive discharges occur and the voltage between the conductors and the grounded parts is not reduced to zero Examples of partial failures are: corona effect (verified by an intensification of the electric field in gaseous media), the phenomenon of arborescence (that affects the interior of solid dielectrics), the electric trailing (coming from impurities present superficially to the dielectric), partial discharges, among others (Kuffel, 2000; ABNT, 2017).

Basically, an insulation can be classified as external or internal. An example of external insulation is the air itself outside the equipment or system. External insulation is usually subjected to inclement weather conditions, such as ultraviolet (UV) rays, rainfall, thermal variations, humidity, etc. The insulation of the internal type is thus denominated because of its confinement in the interior of equipment, reducing atmospheric interferences. This type of insulation can be solid, liquid or gaseous (Hileman, 1999; Shea, 2001). Among the gaseous type isolates, air is considered a good insulator and is also classified as a self-regenerative medium, so that after disruption, its electrical characteristics are not altered. In some applications, the air is replaced by sulfur hexafluoride (SF6), whose main characteristic is to have high electro-affinity. In SF6, a free electron is rapidly attracted to molecules of the gas preventing it from acquiring sufficient energy to cause disruption in the material. Solid insulation is employed in situations in which a higher insulation capacity is desired in conjunction with the need for mechanical cable support, such as overhead power networks. Porcelain, glass, plastic, gypsum and polymers are examples of materials used in this type of insulation (Hileman, 1999).

In addition, solid insulation presents a non-self-retaining insulation, thus, in the formation of a disruptive discharge in these materials its composition is altered due to the high temperature or due to the transformation of constituent elements of the material, which can lead to carbonization. As an example of liquid insulation can be mentioned the use of oil inside transformers which, besides the insulating function, acts as circulating coolant. This work has as main objective to characterize electrically the bio-nanoblenda of BC. The BC production was carried out using agroindustrial residue

2. Materials and Methods

2.1 Microorganism

For BC production, a strain of *Gluconacetobacter hansenii* UCP1619, obtained from the culture collection of Nucleus of Resource in Environmental Sciences, Catholic University of Pernambuco, Brazil, was used. The strain was maintained in the HS medium described by Hestrin and Schramm (1954) and modified by Hungund and Gupta (2010).

2.2 Inoculum and cultivation conditions

The inoculum culture was prepared by transferring the *G. hansenii* cell suspension stored at -80 °C to the HS medium, followed by static cultivation at 30 °C for two days. The statically grown culture was then shaken vigorously to release attached cells from the cellulose pellicle. The resulting cell suspension (3 mL) was inoculated in a semi-capped glass vessel (250 mL) containing 100 mL of the modified HS medium, as described below, and then statically incubated at 30 °C for 10 days in duplicate experiments (Wu et al. 2014).

After cultivation, BC pellicles were removed from the culture medium, washed in tap water and purified in 0.1 M NaOH for 2 h to remove the retained cells. Subsequently, the hydrated films were weighed. After oven drying at 60 ° C for 6 hours, they were weighed again.

2.3 Preparation of BC and PHB blends by dissolution

The blender was prepared by weighing 10 g of the PHB polymer and placing it in a reagent flask. Acetic acid was added to the flask, which was subjected to heating until no more material was in suspension. The vessel containing the obtained solution was placed in a water bath. Purified and dried CB membranes, previously weighed, were immersed in the solution. The BC/PHB blend was prepared with 30% PHB. After standing, the blender was washed with deionized water and dried in an oven at 50°C until there was no further variation of its mass. The final product visually presented an intimate bond in the mixture of the two components. All dried samples were kept in desiccator.

2.4 Scanning Electron Microscopy (SEM)

Blend samples (CB / PHB) as well as samples of pure CB membranes and pre-dried pure PHB were metallized (SANYU ELECTRON). The Scanning Electron Microscopy (SEM) of the sample surfaces was performed using an instrument JEOL, JSM-5600 operating at 27 KV.

2.5 Electrical characterization of samples

The electrical resistance was measure through the standard two probe method using a Keithley 6430 electrometer - USA. This instrument has several advantages as low noise, high resolution, fast measurements and broad resistance measurement range.

3. Results and discussion

The elimination of water, the incorporation and impregnation of PHB polymer was aimed at reducing porosity, maintaining degradability, durability, mechanical properties and incorporating the characteristics of electrical insulators.

3.1 Characterization of blends of BC / PHB by SEM

Figure 2A shows the surface image of the BC film, in which a network of pulp microfibers arranged randomly can be observed. BC exhibited a cross-linked structure consisting of ultrafine nanofibrils. In the surface image of the pure PHB (Figure 2B) a rough and granular structure with microparticles is observed. On the other hand, the CB / PHB blends image (Figure 2C) shows cellulose microfibers filled by PHB. The presence of PHB microparticles associated to the cellulose microfiber network is also highlighted. It is observed, therefore, that PHB can be seen not only on the surface of cellulose fibrils, but also interconnected between them, indicating that PHB was incorporated between the BC fibrils. Ruka et al. (2013) and Barud et al. (2011) obtained similar results in relation to the surface structure of cellulose blends and PHB analyzed in SEM.
The electrical properties of our samples was investigated using the standard two probe method at fixed temperature (room temperature). This method is the most commonly used method for the measurement of resistivity of very high resistivity samples in sheets/films shapes (Girotto and Santos, 2002; Hileman, 1999). In two-probe resistance measurement technique, current is measured as a function of voltage and the resistance will include a contribution from the probes and the probe contact resistance. Current is sent through one probe and exits through the second probe. The resistance between two probes can be calculated using the following relation:

$$R_{total} = R_s + R_c + R_{sp} = \frac{voltage}{current}.$$

In this relation, R_c is the parasitic contact resistance between the material surface and the probe that touch the surface, R_{sp} is the spreading resistance caused by current flowing into the sample surface and Rs is the real sample resistance.
The resistivity of the sample could be measured up to 1014 ohm.cm. We can measure electrical resistance and knowing all sample dimensions, appraise electrical conductivity. The electrical conductivity calculated in BC samples is $7.5*10^{-4}$ S/m. For PHB and BC+PHB blends, electrical conductivity is $2.2*10^{-8}$ S/m and $2.1*10^{-7}$, respectively. Knowing that typical insulating, semiconductor and conductor samples has electrical conductivity between 10^{-18} to 10^{-7} S/m, 10^{-6} to 10^{3} S/m and 10^{2} to 10^{8} S/m (Kao et. al., 1981, Sze, 1981, Whitaker, 2005), respectively, these electrical conductivity values suggest a semiconductor behavior on BC samples and an insulator behavior on PHB and BC+PHB samples. By using IxV curves to investigate the electrical transport properties we see that all samples suggest an Ohmic dependence (Figure 2) in the voltage range used. The cause for this can be explained as follows: the majority of polymers are good electrical insulator (Moliton, 2005). However, no materials can be completely free of mobile charge carries (free charges) (Glowacki et. al.).

A large amount of insulators is actually a bad Ohmic conductor (at room temperature and sufficiently low voltage). In fact, typical insulators can be described to be band insulators, which means that they have a lower filled band, an empty higher band and a gap between them (Runyan, 1975 and Schroder, 1990). If you are at non-zero temperature situation, as we are in the laboratory, particle-hole pairs can be created which carry the current (occurring a redistribution of charges). Free charges can be created by sample impurities. The band gap is usually larger (approximately 1 eV) than the energy given by the room temperature (approximately 25 meV) and then the number of particle-hole pairs is small. If the particle-hole pair number is low, there are few current carries and the conductivity is low. Thus, as the temperature is sufficiently high and the voltage sufficiently low, compared to the bandgap, an insulator will be an Ohmic conductor. The linear relation between voltage and current (Ohmic behavior) is usually valid only for limited voltage drop. At higher electric fields, super Ohmic behavior can be observed related to formation of space charges caused by electrons trapped usually close to the electrode.

Figure 1: Scanning Electron Microscopy of the films, (A) BC, (B) PHB film and (C) blenda CB + PHB.

The above interpretation is not entirely conclusive. We are submitting the sample to higher voltage values to see if the behavior remains the same as it is being observed until then, i.e. for voltage values that will go up to 100 V. Electric conduction in thin dielectric films is a generally complicated mechanism resulting from the appearance of one or a combination of various processes, such as the Poole-Frenkel, Schottky, hopping conduction, space charge limited conduction and quantum mechanical tunneling. One of the ways to define which effects are determinant in the electric conduction process is to submit the sample to high values of electrical tension. We are investigating the conductivity time dependence too. In this case, we would like to see if the measured current decrease with time increasing. Thus, new results will be publish in future works.

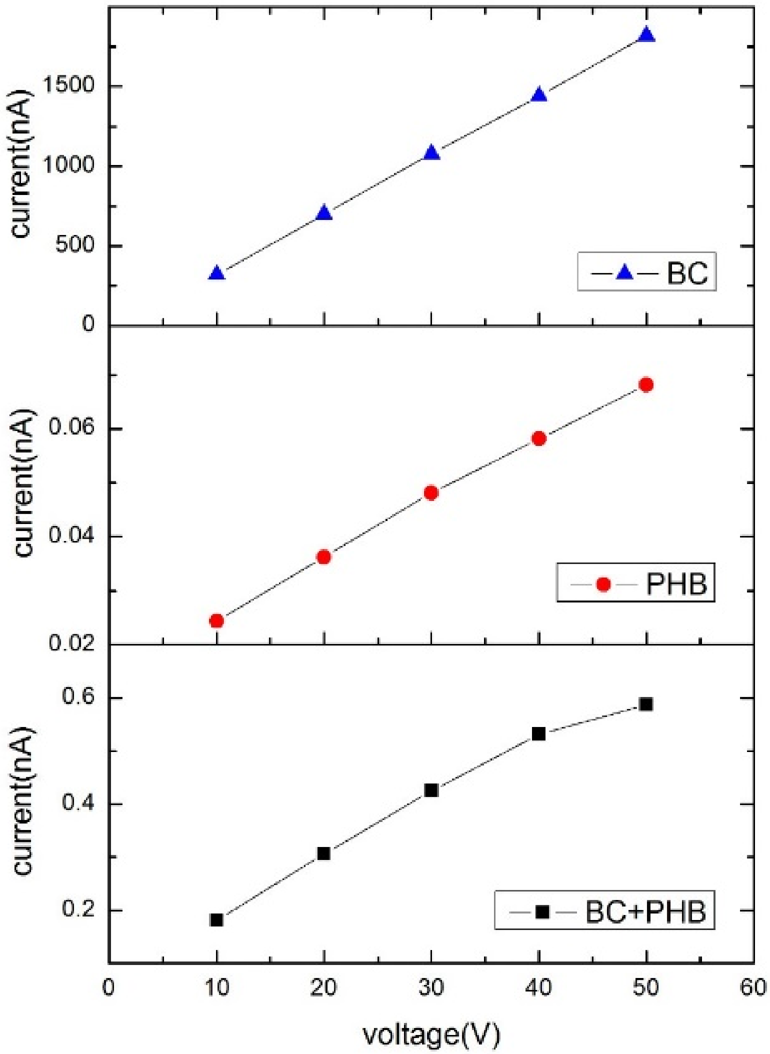

Figure 2: Graphics confirming the Ohmic dependence of the films, (A) CB, (B) PHB and (C) BC + PHB blend

4. Conclusions

Insulating materials are used to protect people from the dangerous effects of electricity that flows through conductors. Sometimes the voltage drop between two points can be high and dangerous. Electric current can flow through materials that are generally not considered to be excellent conductors if the voltage drop is high enough. As our bodies are conductors, we can conduct electricity and we may have bad experiences with electrical shocks. Therefore, we need to shield our bodies from the conductors that carry electricity. The insulating BC is the result of a sustainable design that has been used to develop a bio-nanoblend with characteristic of electrical insulation that can be used in electrical insulation and / or as raw material for the development of electrical and / or electronic components. In addition to the reduction of the cost of production, the production of the electrical insulating biomaterial is connected with the reduction of environmental impacts, both by the use of agroindustrial residues and in the production of a biodegradable polymeric blend.

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