

Wettability and Morphological Characterization of a Polymeric Bacterial Cellulose / corn Starch Membrane

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The uses of polymer blends have stimulated research to promote a better performance of existing raw materials. The implementation of blends in the production of polymeric membranes has shown great results in regenerative medicine and consequently it has improved the application of biomaterials in this area. This study aimed to evaluate the morphology and wettability of a bacterial cellulose/corn starch polymeric membrane. In relation to biomaterials, wettability is an important property to be evaluated because it is possible to observe if the degradation is accelerated even when in contact with biological fluids. The membrane was morphologically evaluated by SEM. Results showed that there was interaction between the polymers. Additionally, by the technique of contact angle it was also possible to observe the ability to absorb water, being highly satisfactory, showing a complete wetting with a contact angle of 10.7° in the initial assessment and 6.6° in the evaluation after 5 seconds.

Keywords: *blends, membrane, corn starch, bacterial cellulose, biomaterial*

1. Introduction

Biomaterials are notably designed to be used in medical devices, in direct contact with biological tissues. They can be defined as part of a system that deals with, improving or replace any tissue, organ or body function¹⁻³.

The choice of a material to be used as biomaterial depends on a series of requirements, among these, biocompatibility and biodegradability can be highlighted. Biocompatibility is related to the behavior of biomaterials, referring to the ability of a material to perform with an appropriate host response in a specific situation. Biodegradability, on the other hand, is a property in which the material is degraded or solubilized being gradually replaced by the tissue that is aimed to be regenerated⁴. Several natural polymers, such as starch, chitin, chitosan and cellulose, are recognized by human body due to their chemical structure hence these polymers are used in biomedical field⁵.

Currently, natural polymers are often used in the production of blends, among these corn starch and cellulose are both the most abundant polysaccharides in nature that can be obtained from renewable sources⁶⁻⁹. A blend can be developed in order to improve mechanical and thermal properties, or for reducing the final cost of polymers^{3,8-13}. Studies show

that the use of the plasticizers in the blend has the objective to obtain a better interaction between all components^{7,8,14}. Natural polymers exhibit the advantages of biodegradability, biocompatibility, non toxicity and high reactivity⁵⁻⁷. The starch belongs to the class of polysaccharides and naturally occurs on stems, roots or in seeds of plants such as corn, wheat, rice, barley and potatoes^{5,15-17}. Starch is the most important polysaccharide polymer used to develop biodegradable films¹⁸ and it consists of two types of polymers of glucose: the amylose that represents about 20-30% of the starch and amylopectin which represents approximately 70-80% of the starch^{6,15-17,19}. The crystallinity is originated from amylopectin while amylose units form an amorphous region, arranged irregularly within ordered amylopectin region⁵.

The bacterial cellulose (BC) is produced by the biosynthesis of the bacteria *Acetobacter Xylinum*, which is gram negative, rod-shaped and aerobic²⁰⁻²³. Chemically, BC is a linear polysaccharide whose structural unit is cellobiose. This biosynthesized polymer has the chemical structure similar to the vegetable cellulose (C₆H₁₀O₅)_n, but presents a high crystallinity (60-90%) and also a higher purity, similar to inert natural components such as lignin and hemicellulose^{7,21,22,24-27}.

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In biomaterials, membranes can be classified as an osteogenic material. This type of material is characterized by the physical environment which promotes and allows the selection and the proliferation of a group of cells. In addition, prevents the action of competing factors other than those specific of regeneration^{28,29}. Fu et al.²⁷ explains in his study that bacterial cellulose accelerates the repair of burned skin. Bacterial cellulose creates a favorable environment for cure because of its chemical structure²⁷.

The present work has the objective to evaluate the morphology and the wettability of a polymeric bacterial cellulose/corn starch membrane by two techniques: scanning electron microscopy and contact angle. The contact angle between the implant and the biological environment is highly influenced by the wettability of the surface, the greater the wettability, greater is the interaction among the means³⁰.

2. Material and Methods

2.1. Material

The Corn starch (Amidex 3001) used in this study was manufactured and obtained from Corn Products (Brasil LTDA). The bacterial cellulose membrane was produced by UNESP. The Glycerin P.A was manufactured by Química Moderna and Sodium hydroxide P.A by Cromoline Química Fina.

2.2. Methods

Bacterial cellulose membrane (BC) was previously treated by immersing it in a solution of sodium hydroxide (NaOH) 10% (w/v) at 90 °C for 30 minutes. This treated BC was added in a mixture containing corn starch, glycerin P.A. and water. This blend remained in constant agitation and heating for 25 minutes at 70 °C. Table 1 presents the raw materials used in the blend and their respective concentrations.

The blend was poured into falcon tubes, where the BC membrane remained submerged for seven days. After this period, it was removed from the solution, washed and dried at room temperature, in a desiccator. In this step occurs the residual solvent evaporation, as the casting technique. Within seven days the BC membrane was ready to be evaluated.

The morphological analysis of SEM was held at JEOL, model KAL equipment-6510LV, available in the laboratory of advanced studies of materials the University Feevale. The sample were metallized with gold layer overlay, as standard procedure and was applied a voltage between 5 and 10 kV.

Contact angle analysis was performed in the laboratory of advanced studies of materials in the University Feevale using the appliance brand Dataphysics model tension meter and OCA-15EC. The sample of presented 1 dimension, 5 cm² and were subjected to 1 drop of deionized water

Table 1. Formulation of polymeric membrane.

Materials	%wt
Corn starch	35.64
Glycerin	35.64
Deionized Water	17.82
bacterial cellulose membrane	0.05

(3 µl). The evaluations were conducted at 0, 5, 10, 15, 20, 25 and 30 seconds.

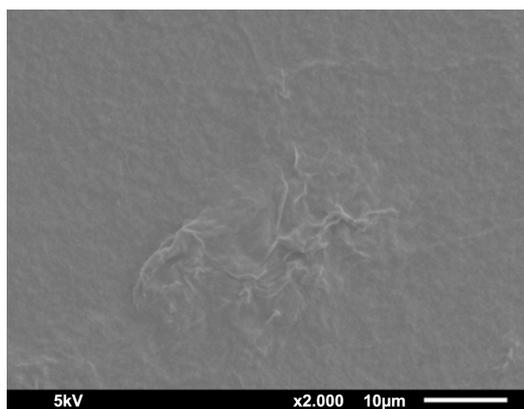
3. Results and Discussion

Results obtained in relation to the SEM and contact angle for BC and BC/starch blend will be discussed in Figure 1.

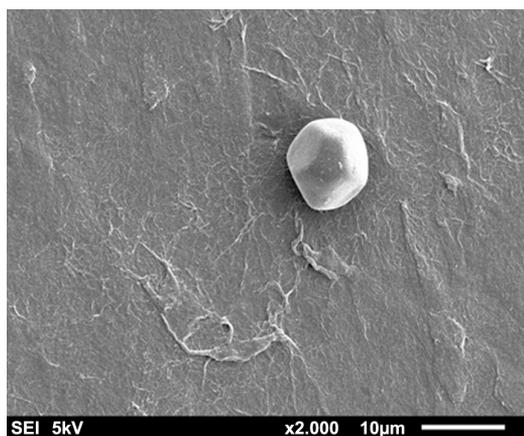
Figure 1a shows a homogeneous surface differently of Figure 1b, where the presence of the bacterial cellulose fibers is evident. These fibers are noticeable due to the treatment of the surface with 10% NaOH (w/v) which is responsible to the changes in bacterial cellulose structure, showing its fibers more apparent in their morphology. According to the literature the homogeneity of a film is a good indicator of the integrity of its structure²⁴.

In the sample it was possible to identify a grain of corn starch that wasn't satisfactorily dispersed in the polymer matrix. It has not been possible to identify the presence of pores in none of the samples.

Contact angle results were presented in the Table 2 and in Figures 2 and 3. It was possible to observe that the contact angles were less than 90 °C and, thus it is possible to affirm that both, BC and BC/starch blend, presented wettability in relation to surface until the first five seconds of analysis.



(a)



(b)

Figure 1. Micrograph of (a) standard BC and (b) blend of BC/starch membrane. 2000 ×.

However, it was possible to evidence that the wettability in the sample was total after five seconds of analysis, when it was no longer possible to verify the contact angle by the equipment. In this case, the drop of water added in the sample was completely absorbed by the same, occurring in this way, the thermodynamic equilibrium at the interface of materials. This balance is probably due to the interactions

Table 2. Time and contact angle for pure BC membrane and blend of BC/starch membrane.

CB		blend of BC/starch membrane	
Time (s)	Angle (°)	Time (s)	Angle (°)
0	32.55	0	10.7
5	30.45	5	6.6
30	26.70		

between the solid and liquid particles, according to the bibliography³⁰.

The contact angle values found for the BC, in zero and 30 seconds of analysis, were of 32.55° and 26.70°, respectively. It was evident that the membrane produced using the method presented in this paper showed the best results in terms of wettability when compared to the standard BC. It was possible to identify the presence of adhered to the surface of the drop default BC with 30 seconds, compared to the time of 5 seconds to blend membrane analysis of BC/starch, being finalized the review by lack of contact angle.

It is assumed that these values are considered quite satisfactory, when compared to literature, where the BC membranes produced in the laboratory performed the result of 31.1° contact angle test³¹. Thus, it is possible to affirm that the other components of the formulations covered in this work left BC membrane more hydrophilic.

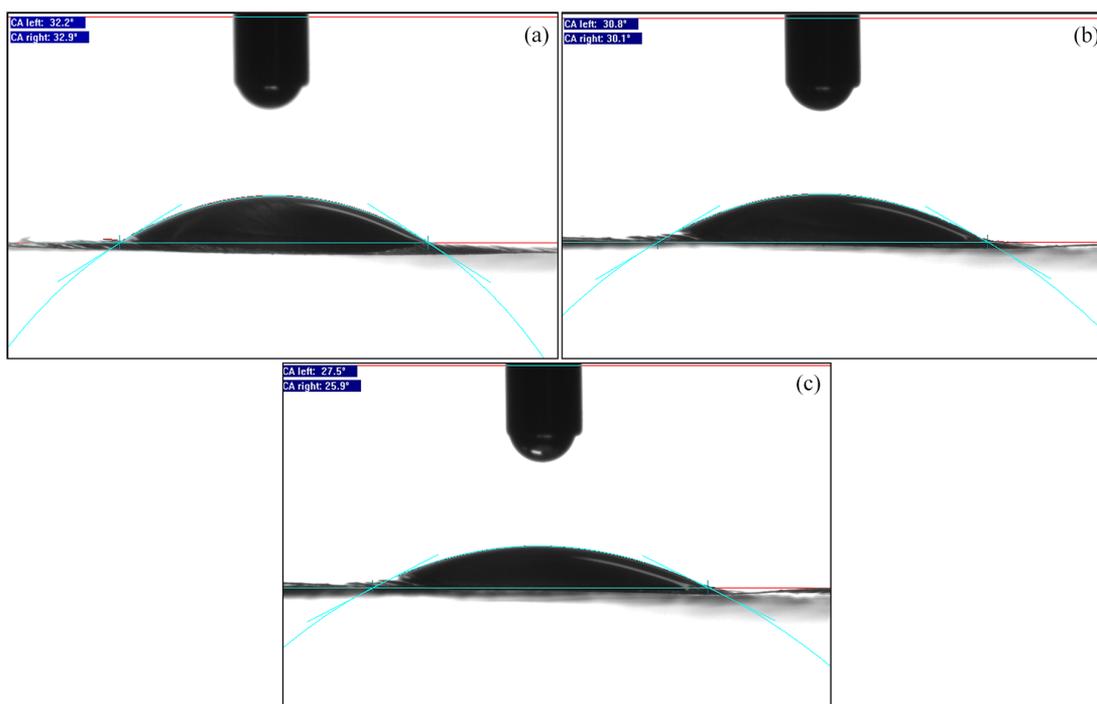


Figure 2. Analysis of contact angle for BC: (a) zero time; (b) 5 seconds; (c) 30 seconds.

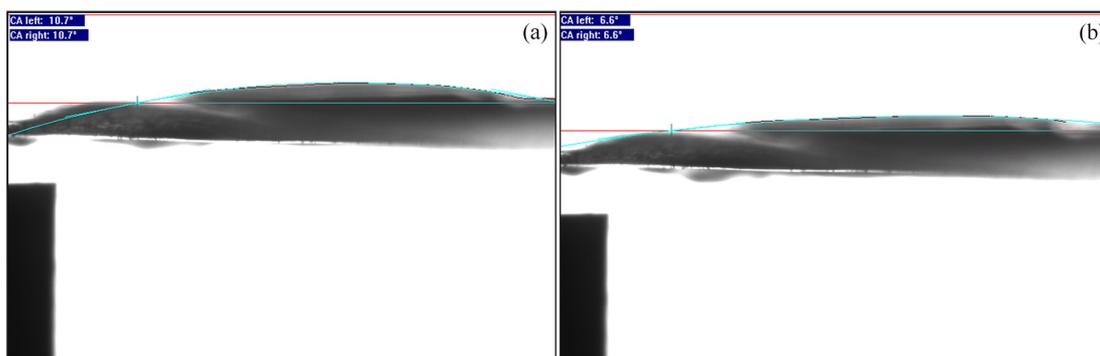


Figure 3. Analysis of contact angle for sample: (a) zero time and (b) 5 seconds.

4. Conclusions

SEM analysis showed that there was compatibility between BC and the other raw materials used in the production of the BC/starch blend, because when compared to standard BC, the sample showed an increase in thickness of cellulose fiber. Similarly, the contact angle analysis presented satisfactory results, because it showed that the addition of starch and glycerol in bacterial cellulose membrane boasted a positive result as regards the wettability.

References

- O'Brien FJ. Biomaterials & scaffolds for tissue engineering. *Materials Today*. 2011; 14(3):88-95. [http://dx.doi.org/10.1016/S1369-7021\(11\)70058-X](http://dx.doi.org/10.1016/S1369-7021(11)70058-X).
- Soares GA. *Biomateriais: fórum de biotecnologia de biomateriais*. Rio de Janeiro: Universidade Federal do Rio de Janeiro; 2005. Available from: <http://www.redetec.org.br/wp-content/uploads/2015/02/tr10_biomateriais.pdf>. Access in: 20 Nov. 2012.
- Vasques CT. *Preparação e caracterização de filmes poliméricos a base de amido de milho e polipirrol para aplicação como biomaterial*. [Thesis]. Florianópolis: Universidade Federal de Santa Catarina; 2007.
- Oliveira LSAF, Oliveira CS, Machado APL and Rosa FP. Biomateriais com aplicação na regeneração óssea: método de análise e perspectivas futuras. *Revista de Ciências Médicas e Biológicas*. 2010; 9(1):37-44. Available from: <<http://www.portalseer.ufba.br/index.php/cmbio/article/view/4730/3503>>. Access in: 20 Nov. 2012.
- Zia F, Zia KM, Zuber M, Kamal S and Aslam N. Starch based polyurethanes: a critical review updating recent literature. *Carbohydrate Polymers*. 2015; 134:784-798. <http://dx.doi.org/10.1016/j.carbpol.2015.08.034>. PMID:26428186.
- Kim HY, Park SS and Lim ST. Preparation, characterization and utilization of starch nanoparticles. *Colloids and Surfaces B, Biointerfaces*. 2015; 126:607-620. <http://dx.doi.org/10.1016/j.colsurfb.2014.11.011>. PMID:25435170.
- Martins IMG, Magina SP, Oliveira L, Freire CSR, Silvestre AJD, Pascoal CP No, et al. New biocomposites based on thermoplastic starch and bacterial cellulose. *Composites Science and Technology*. 2009; 69(13):2163-2168. <http://dx.doi.org/10.1016/j.compscitech.2009.05.012>.
- Woehl MA, Canestraro CD, Mikowski A, Sierakowski MR, Ramos LP and Wypych F. Bionanocomposites of thermoplastic starch reinforced with bacterial cellulose nanofibres: effect of enzymatic treatment on mechanical properties. *Carbohydrate Polymers*. 2010; 80(3):866-873. <http://dx.doi.org/10.1016/j.carbpol.2009.12.045>.
- Mauricio MR, da Costa PG, Haraguchi SK, Guilherme MR, Muniz EC and Rubira AF. Synthesis of a microhydrogel composite from cellulose nanowhiskers and starch for drug delivery. *Carbohydrate Polymers*. 2015; 115:715-722. <http://dx.doi.org/10.1016/j.carbpol.2014.07.063>. PMID:25439953.
- Casarin SA. *Blendas de PHBV e PLC para uso em dispositivo de osteossíntese*. [Thesis]. São Carlos: Universidade Federal de São Carlos; 2010.
- Rawajfeh AE, Salahhaa and Rahel IA. Miscibility, crystallinity and morphology of polymer blends of polyamide-6/ poly(β -hydroxybutyrate). *Jordan Journal of Chemistry*. 2006; 1(2):155-170.
- Schlemmer D. *Preparação, caracterização e degradação de blendas de poliestireno e amido termoplástico usando glicerol e óleo de buriti (Mauritia Flexuosa) com plastificantes*. [Dissertation]. Brasília: Universidade de Brasília; 2007.
- Yu L, Dean K and Li L. Polymer blends and composites from renewable resources. *Science Direct: Progress in Polymer Science*. 2006; 31:576-602. <http://dx.doi.org/10.1016/j.progpolymsci.2006.03.002>.
- Arrieta MP, Fortunati E, Dominici F, López J and Kenny JM. Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends. *Carbohydrate Polymers*. 2015; 121:265-275. <http://dx.doi.org/10.1016/j.carbpol.2014.12.056>. PMID:25659698.
- Gil MH and Ferreira P. Polissacarídeos como biomateriais. *Química*. 2006; 100:72-74.
- Mali S, Grossmann MVE and Yamashita F. Filmes de amido: produção, propriedades e potencial utilização. *Semina: Ciências Agrárias*. 2010; 31(1):137-156. <http://dx.doi.org/10.5433/1679-0359.2010v31n1p137>.
- Vroman I and Tighzert L. Biodegradable polymers. *Materials (Basel)*. 2009; 2(2):307-344. <http://dx.doi.org/10.3390/ma2020307>.
- Priya B, Gupta VK, Pathania D and Singha AS. Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre. *Carbohydrate Polymers*. 2014; 109:171-179. <http://dx.doi.org/10.1016/j.carbpol.2014.03.044>. PMID:24815414.
- Panaiteanu DM, Frone AN, Ghiurea M and Chiulan I. Influence of storage conditions on starch/PVA films containing cellulose nanofibers. *Industrial Crops and Products*. 2015; 70:170-177. <http://dx.doi.org/10.1016/j.indcrop.2015.03.028>.
- Barud HS, Ribeiro SJL, Carone CLP, Ligabue R, Einloft S, Queiroz PVS, et al. Optically transparent membrane based on bacterial cellulose/polycaprolactone. *Polímeros: Ciência e Tecnologia*. 2013; 23(1):135-138. <http://dx.doi.org/10.1590/S0104-14282013005000018>.
- Recouvreur DOS. *Desenvolvimento de novos biomateriais baseados em celulose bacteriana para aplicações biomédicas e de engenharia de tecidos*. [Thesis]. Florianópolis: Universidade Federal de Santa Catarina; 2008.
- Zhijiang C, Chengwei H and Guang Y. Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)/bacterial cellulose composite porous scaffold: preparation, characterization and biocompatibility evaluation. *Carbohydrate Polymers*. 2012; 87(2):1073-1080. <http://dx.doi.org/10.1016/j.carbpol.2011.08.037>.
- Ummartyotin S and Manuspiya H. A critical review on cellulose: from fundamental to an approach on sensor technology. *Renewable & Sustainable Energy Reviews*. 2015; 41:402-412. <http://dx.doi.org/10.1016/j.rser.2014.08.050>.
- Almeida DM, Woiciechowski AL, Wosiacki G, Prestes RA and Pinheiro LA. Propriedades físicas, químicas e de barreira em filmes formados por blenda de celulose bacteriana e fécula de

- batata. *Polímeros: Ciência e Tecnologia*. 2013; 23(4):538-546. <http://dx.doi.org/10.4322/polimeros.2013.038>.
25. Belgacem MN and Gandinia A. *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier B.V.; 2008. Available from: <http://www.if.ufrj.br/biolig/art_citados/Monomers,%20Polymers%20and%20Composites%20from%20Renewable%20Resources.pdf>. Access in: 25 June 2013.
 26. Berti FV. *Desenvolvimento de estruturas vasculares endotelizadas em scaffolds de celulose bacteriana*. [Thesis]. Florianópolis: Universidade Federal de Santa Catarina; 2012.
 27. Fu L, Zhang J and Yang G. Present status and applications of bacterial cellulose-based materials for skin tissue repair. *Carbohydrate Polymers*. 2013; 92(2):1432-1442. <http://dx.doi.org/10.1016/j.carbpol.2012.10.071>. PMID:23399174.
 28. Caminha MW. *Caracterização físico-química de onze biomateriais de enxertos ósseos utilizados na implantodontia*. [Dissertation]. Duque de Caxias: Universidade do Grande Rio “Prof. José de Souza Herdy”; 2012.
 29. Carvalho PSP, Rosa AL, Bassi APF and Pereira LAVD. Biomateriais aplicados a implantodontia. *Revista Implantnews*. 2010; 7(3):56-65. Available from: <<http://www.inpn.com.br/ImplantNews/Artigo/Index/352>>. Access in: 25 June 2013.
 30. Coutinho MP. *Influência da morfologia da superfície na molhabilidade do titânio comercialmente puro*. [Dissertation]. Rio de Janeiro: Instituto Militar de Engenharia; 2007.
 31. Pértile RAN. *Estudo in vitro da interação da linhagem de fibroblastos L929 com membranas de celulose bacteriana para aplicações em engenharia de tecidos*. [Dissertation]. Florianópolis: Universidade Federal de Santa Catarina; 2007.