Influence of the matrix and polymerization methods on the synthesis of BC/PANi nanocomposites: an IGC study

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Abstract

Inverse gas chromatography (IGC) is a resourceful technique that evaluates the materials surface properties. The current work emphasizes the use of IGC to evaluate the surface physico-chemical changes during different bacterial cellulose (BC) processing methods as well as upon polyaniline (PANi) incorporation. The processing methods caused changes in the BC surface group distribution, where upon freeze-drying and regeneration a more acidic behaviour is obtained, when compared to oven-drying. Through freeze-drying the structural pore preservation increases the BC porosity, whereas through regeneration the porosity decreases compared to BC oven-drying. Regarding the nanocomposites, the overall properties evaluated by IGC were significantly changed. The γ_s^{total} increases up to 150%, indicating a more reactive surface in the nanocomposites. Also is observed a 7-fold increase in the K_b/K_a and a less porous surface. Hence, the current work highlights the use of IGC as a viable technique to evaluate the physico-chemical changes upon different BC modifications.

Introduction

The synthesis of new nanocomposites, where it is explored new behaviours and functionalities, is of great importance. An array of advancements into functionalizing bacterial cellulose (BC) are presented in the literature. These new materials need to be extensively characterized in order make them suitable for the new application as new materials.

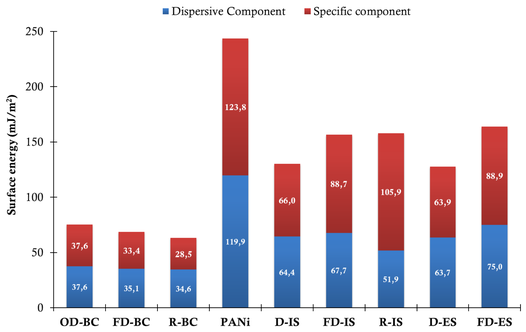
Bacterial cellulose/Polyaniline (BC/PANi) nanocomposite is a special type of BC-reinforced nanocomposite, with the ability to conduct electricity. With the incorporation of PANi into the BC network, it is expected several changes to the starting material due to the changes in the established intermolecular forces. Making use of a set of conventional analysis techniques, Alonso E. et al. (2017) observed that the BC membrane and polymerization method affected the final properties of the new BC-reinforced material..

The current poster represents the logical continuation of our work, evaluating the changes occurred onto BC with the different BC processing methods and PANi incorporation by IGC at a chemical level through the surface energy, energetic profile and acid-basic surface character and at a morphological level through the BET surface area, diffusion analysis and morphology indexes from the non-linear alkanes. This way, the current work aims to use IGC as a viable alternative to other techniques used to surface characterization, regarding the physico-chemical changes occurred onto BC during the BC processing methods as well as through PANi incorporation using different polymerization methods.

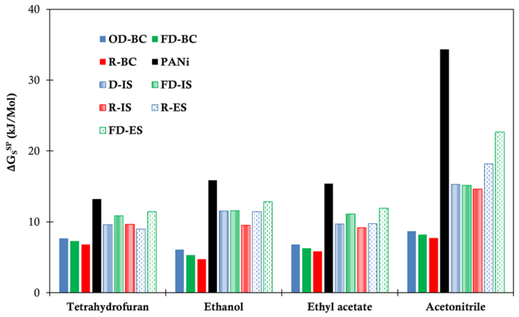
Results and discussion

Surface energy

Regarding the BC/PANi nanocomposites, a substantial increase in the γ_s^d values is observed upon PANi incorporation. This increase is due to the PANi presence which has high γ_s^d value when compared to the different BC matrixes. Similarly, γ_s^{sp} follows the same increase. Throughout the analysis of both dispersive and specific components of the surface energy, it is observed changes in the surface reactivity of the different BC matrixes, as well as the resulting nanocomposites. This way, different γ_s^{total} values were obtained, which through Tukey's post hoc analysis, four groups are observed: *(i)* BC matrixes, *(ii)* drained BC/PANi nanocomposites, *(iii)* regenerated and freeze-dried BC/PANi nanocomposites and *(iv)* PANi powder.



Acid-base character

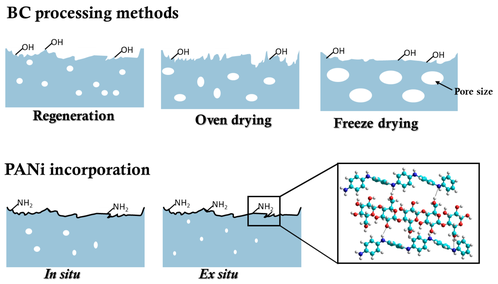


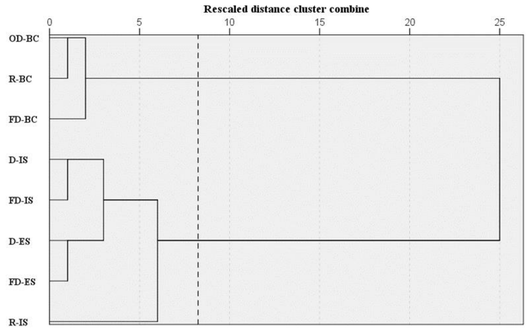
With PANi incorporation into BC, the ΔG_s^{sp} of ethanol increases more significantly when compared to tetrahydrofuran, suggesting a higher increase of the basic character at the surface of BC-reinforced nanocomposites.

From the K_b/K_a ratio, PANi presents the expected basic character (K_b/K_a of 3.46) as a result from the presence of amine groups. With PANi introduction onto the BC matrixes, the BC surface acidic behaviour (K_b/K_a 0.75 and 0.55) is shifted into a basic behaviour (K_b/K_a ranging from 1.88 to 3.77), corroborating the fact that the PANi polymer can be found at the nanocomposite surfaces.

Surface morphology

In terms of morphological analyses, the S_{BET} of the different BC matrixes is drastically reduced (64-85%) with PANi incorporation. This was due to the obstruction of the BC pores, which not only decreased the area available for probes to access but also makes harder for probes to cross the sample. This was corroborated by the morphology indexes assessed using different non-linear alkanes, where for cyclooctane, a decreased surface availability is observed, shifting from an adsorption (BC matrixes) to a steric hindrance (BC/PANi nanocomposites) behaviour.





Cluster analysis

Cluster analysis was performed in order to obtain meaningful visual data through the similarity between the samples, using only the IGC data. The Sneath criterion (dashed line) and the agglomeration schedule were used to determine the number of relevant clusters. It is observed that the samples cluster into two groups: BC matrixes and BC/PANi nanocomposites. The resulting clusters represent meaningful information, indicating that through PANi incorporation the BC surface properties are greatly influenced.

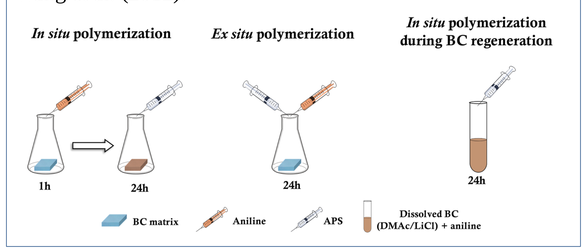
Materials and methods

Preparation of the BC membranes

Oven-dried BC (OD-BC) was obtained by placing a wet BC membrane on the oven at 40 ºC. ***Drained BC*** (D-BC) was obtained through manual pressing, while ***freeze-dried BC*** (FD-BC) was obtained by freezing followed by freeze-drying. For ***regenerated BC*** (R-BC), an oven-dried BC was cut into small pieces and added to a solution of LiCl 8% (w/v) in dimethylacetamide, obtaining a BC concentration of 0.5% (w/v). Then, it was placed in an oil bath at 110 ºC during 1 h followed by sonication during 1 h at room temperature. The mixture stired overnight, obtaining a clear viscous solution.

PANi synthesis conditions

All polymerization reactions occurred under 24 h and under low stirring (<100 rpm). The membranes were washed thoroughly until no aggregates could be observed. Then, the resulting blends were oven dried at 40 ºC. A BC:ANi mass ratio of 0.10, as well as a Ani:HCl:APS molar ratio of 1:1.2:1 was employed, following the optimal conditions reported by Wang et al. (2012).



Conclusions

The current work shows that IGC is a powerful versatile technique, used as an alternative to the recurring usual characterization techniques. Changes with the BC processing methods were more evident in the morphology results, obtaining a more porous BC when freeze-drying, while obtaining a more compact material upon BC regeneration. By oven-drying BC, a rougher surface is observed. PANi incorporation led to significant changes in the BC properties, where the highly energetic and basic properties of PANi were observed in the BC/PANi nanocomposites. Moreover, the BC pores were obstructed due to PANi incorporation, which are supported by the increase in the morphology indexes by the different non-linear alkane probes. The cluster analysis, demonstrated that the IGC not only was able to evidence changes upon PANi incorporation, as it also evidenced the effect of the polymerization method.

Contact Information

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