Physicochemical surface properties of bacterial cellulose/polymethacrylate nanocomposites: an approach by inverse gas chromatography

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ABSTRACT

Nanocomposites of poly(glycidyl methacrylate) and bacterial cellulose (BC), or poly(poly(ethylene glycol) methacrylate) and BC were produced via the in-situ polymerization of methacrylic monomers, inside the BC 3D network. The nanocomposites surface properties were evaluated by inverse gas chromatography (IGC). The dispersive component of surface energy ($\gamma_d$) varied between 35.64 - 83.05 mJ m$^{-2}$ at 25°C. The surface of the different nanocomposites has a predominant basic character ($K_a/K_d = 4.20-4.31$). Higher specific interactions with polar probes were found for the nanocomposite bearing pendant epoxide groups, that apart from the low surface area ($S_{BET} = 0.83$ m$^2$ g$^{-1}$) and monolayer capacity ($n_m = 2.18$ μmol g$^{-1}$), exhibits a high value of $\gamma_d$ (88.19 mJ m$^{-2}$ at 20°C). These results confirm the potential of IGC to differentiate between nanocomposites with different surface functional groups and to predict their potential interactions with living tissues, body fluids and other materials.

1. Introduction

The design of functional, nanostructured and high-performance composite materials based on bacterial cellulose (BC), i.e. an extracellular form of nanocellulose produced by non-pathogenic bacteria that presents remarkable properties, is of utmost importance for myriad applications particularly in the biomedical and pharmaceutical fields (Silvestre, Freire, & Neto, 2014; Ullah, Santos et al., 2016; Ullah, Wahid et al., 2016). One of the methodologies that is gaining a lot of attention to prepare BC-based nanocomposites, due to its simplicity, is the so-called in-situ polymerization of functional monomers within the BC porous network that originates materials with interesting properties for application as, for instance, stimuli-responsive nanocomposites for drug delivery (Saidi et al., 2017; Vilela, Gadim, Silvestre, Freire, & Figueiredo, 2016, 2017), but also with other monomer types (Mashkour, Rahimnejad, & Mashkour, 2016; Gadim et al., 2014). The incorporation of these polymers within the BC porous structure generates nanostructured materials with different mechanical, thermal, viscoelastic, optical and surface properties. The latter properties are particularly relevant in the context of composite materials whose surface will interact with, for example, living tissues, body fluids or water contaminants, where adsorption and/or adhesion processes dictate their suitability for specific applications (Mohammadi-Jam & Waters, 2014).

Inverse gas chromatography (IGC) is one of the most used techniques to examine the physicochemical surface properties of non-volatile solid materials in the form of films, fibres and powders with both amorphous and crystalline nature, and different morphologies (Lapčík et al., 2016; Mohammadi-Jam & Waters, 2014). The simultaneous measurement of physical and chemical properties by IGC allows to...
envisage the surface behaviour of a given sample in contact with other materials, as well as to determine how the fabrication method can influence the surface properties (Mohammedi-Jam & Waters, 2014). As an illustrative example, Beaumont et al. demonstrated that the drying method (freeze-drying and supercritical drying) applied to cellulose II gel (TENCEL®) influenced the surface properties of the obtained cellulose particles, with the supercritical drying yielding aerogels of higher surface area (Beaumont et al., 2017).

The IGC tool has already made its debut in the evaluation of the surface properties of BC, its derivatives and composite materials (Alonso, Faria, Mohammadkazemi, et al., 2018; Alonso, Faria, Ferreira, & Cordeiro, 2018; Castro et al., 2015; Mohammadkazemi, Aguiar, & Cordeiro, 2017). These studies enabled the assessment of the surface physicochemical changes endowed by chemical (e.g. in-situ glyoxalization of BC (Castro et al., 2015)) or physical (e.g. oxidative polymerization of aniline inside the porous network and surface of BC (Alonso, Faria, Mohammadkazemi, et al., 2018; Alonso, Faria, Ferreira, et al., 2018)) modification in terms of surface energy, polarity and acid-base behaviour because of the interactions with polar and non-polar probes.

In this context and following our interest on natural-based materials and the assessment of their surface properties, the purpose of the present work is to gain a thorough understanding of the surface properties of BC-based nanocomposites with different surface groups by using IGC analysis. Nanocomposite materials were prepared via the in-situ free radical polymerization of methacrylic monomers, containing either epoxide or hydroxyl pendant groups, namely poly(glycidyl methacrylate) (PGMA) or poly(poly(ethylene glycol) methacrylate) (PPEGMA), respectively, inside the BC porous structure, to evaluate the influence of different surface groups on specific interactions, namely surface energy, surface area, monolayer capacity and acid-base properties.

2. Materials and methods

2.1. Chemicals and materials

Bacterial cellulose (BC) was biosynthesized in the form of wet membranes using the Gluconacetobacter sacchari bacterial strain (Trovatti, Serafin, Freire, Silvestre, & Neto, 2011). Briefly, the BC membranes were produced by growing the G. sacchari microorganisms in static conditions at 30°C during 48 h in HS (Hestrin-Schramm) liquid medium (20 g L−1 glucose, 5 g L−1 peptone, 5 g L−1 yeast extract, 2.7 g L−1 Na2HPO4 and 1.15 g L−1 citric acid, pH 5). After incubation, the BC membranes were separated from the media, treated with 0.5 M NaOH (90°C during 30 min) to eliminate the attached cells, washed with distilled water and dried at 40°C.

The in-situ free radical polymerization of GMA inside the BC network was adapted from the procedure described elsewhere (Figueiredo et al., 2015). First, wet BC membranes were weighed and about 60% of their water content was drained. Then, two distinct aqueous reaction mixtures were prepared: one containing GMA in a ratio of 1:2 (wBC/wGMA) and 0.5% APS (w/w relative to monomer), and another containing the same amounts of monomer and radical initiator, and 20% MBA (w/w relative to monomer). The drained membranes and reaction mixtures were both purged with N2 for 30 min. Each reaction mixture was added to the BC membranes and left for 1 h at room temperature for complete incorporation inside the BC network. The polymerization reaction took place in an oil bath for 6 h at 60°C. The obtained nanocomposites (Table 1) were washed with distilled water and dried at 40°C.

The infrared spectra were obtained by Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) using a Perkin Elmer Spectrum Two coupled with a Diamond ATR accessory
2 areas and the scan rate was set to 1.3 Hz. Average surface coverage of, at least in duplicate, producing a reproducibility error of ratio were the variables introduced for the agglomerative hierarchy described in the relevant literature (Alonso, Faria, Ferreira, et al., 2018; Cordeiro, Gouveia, Moraes, & Amico, 2011; Lapčík et al., 2016; Mohammadi-Jam & Waters, 2014).

The theoretical analysis and calculation of the surface energy component, acid-base character and isotherm measurements is thoroughly described in the relevant literature (Alonso, Faria, Ferreira, et al., 2018; Cordeiro, Gouveia, Moraes, & Amico, 2011; Lapčík et al., 2016; Mohammadi-Jam & Waters, 2014).

2.9. Multivariate statistical analysis

Cluster analysis was performed by MINITAB 17 Statistical Software. The hierarchically agglomerative clustering was used to evaluate and achieve the similarity between IGC, AFM and EDS data through the linkage distance (Square Euclidean distance), using the Ward linkage. The dispersive component of surface free energy (\(\gamma_d\)), adsorption potential (\(\gamma_{\text{ads}}\)) of n-octane, acid-base character (\(K_a/K_b\)) ratio, specific component of surface free energy (\(\Delta G_f^\beta\)), surface area (\(S_{\text{sm}}\)), roughness (\(R_s\)) and C/O ratio were the variables introduced for the agglomerative method.

3. Results and discussion

In the present study, three BC-based nanocomposite materials were prepared via the in-situ free radical polymerization of a methacrylic monomer, namely GMA and PEGMA (respectively bearing an epoxide and hydroxyl pendant group), inside the BC three-dimensional network. The reaction schemes of GMA polymerization in the presence and absence of cross-linker, as well as the polymerization of PEGMA are summarized in Fig. 1. GMA was selected because it is a versatile and low-cost commercial monomer used to obtain a hydrophobic homopolymer but also sophisticated (co)polymers that can be further functionalized through nucleophilic epoxide ring opening reactions (Muzammil, Khan, & Stuparu, 2017), which contributes to widen their range of application. On the other hand, PEGMA was chosen due to its amphiphilic nature resulting from the water-soluble side chain and the hydrophobic methacrylate group that originates (co)polymers with interesting properties (Bozkurt & Karadelesi, 2007; Guzmán, Nava, Vazquez-Arenas, & Cardoso, 2017). Only PEGMA was synthesized in the presence or absence of cross-linker to assess the influence of using a cross-linked and non-cross-linked matrix on the surface properties of the corresponding nanocomposites.

The whitish and opaque PGMA/BC nanocomposites are composed of 61 wt.% (PGMA/BC) and 67 wt.% (PGMA-MBA/BC) of PGMA, while the yellowish and translucent PPEGMA/BC nanocomposite contains 87 wt.% of PPEGMA (Table 1). The EDS data (Table 2) showed that the C/O ratio increased around 36% and 34% for PGMA/BC (C/O = 4.50) and PGMA-MBA/BC (C/O = 4.41), respectively, but decreased about 12% for PPEGMA/BC (C/O = 2.90), when compared with the C/O ratio of the native BC (C/O = 3.30). These results bear out the incorporation of PGMA, cross-linked PGMA and PPEGMA into the BC three-dimensional network.
3.1. Morphology and topography of the BC-based nanocomposites

The BC-based nanocomposites were characterized by SEM and AFM to acquire information about their morphology and topography, which is also important for the evaluation of their potentialities for specific applications. Fig. 3 shows the SEM micrographs of the surface of pure BC and PGMA/BC, PGMA-MBA/BC and PPEGMA/BC nanocomposites. The three-dimensional nanofibrillar network characteristic of the BC surface morphology is not clearly visible on the surface of the three nanocomposites because the nanofibrils are imbedded in the respective polymer matrix (i.e. PGMA, cross-linked PMGA and PPEGMA). This is further validated by the AFM 2D topography images displayed in Fig. 4, which show the defined fibir network of BC and the change in surface texture with the incorporation of PGMA, cross-linked PGMA and PPEGMA polymers. Furthermore, the nanocomposites exhibit different surface roughness ($R_a$, arithmetic average roughness) depending on the polymer matrix, as depicted in Table 2. The pure BC presents a surface roughness of $37.7 \pm 1.3$ nm, which is higher than the value ($R_a = 25.2 \pm 3.6$ nm, root mean-square roughness) recently reported for an oven-dried BC sample (Alonso, Faria, Mohammadkazemi, et al., 2018), but much lower than the value (321 nm) obtained by for a freeze-dried BC sample (Jia et al., 2017). The incorporation of 61 wt.% of PGMA and 87 wt.% of PPEGMA inside the BC porous structure promoted a decrease of about 8.5 and 29% of the surface roughness to $34.5 \pm 16.6$ nm and $26.8 \pm 0.1$ nm, respectively, when compared to pure BC. In contrast, the nanocomposite composed of cross-linked PGMA (67 wt.%) presents a higher $R_a$ value ($51.4 \pm 2.1$ nm) than BC and PGMA/BC nanocomposite. This last result demonstrates that use of a non-cross-linked or cross-linked polymer clearly influences the properties of the ensuing nanocomposite because of the level of chain entanglement. These differences in surface roughness suggest that the surface properties of the nanocomposites will be different, as discussed in the paragraphs below.

3.2. Surface properties of the BC-based nanocomposites by IGC

The surface properties of the three BC-based nanocomposites were evaluated using IGC. Several physicochemical properties, namely surface area ($S_{BET}$), monolayer capacity ($n_m$), dispersive component of surface energy ($\gamma_d$), Lewis acidic ($K_a$) and basic ($K_b$) constants, were determined to understand the energetic interactions at the surface of native BC and BC-based nanocomposites (Table 3). The heterogeneity profile (Fig. 5) and the specific free energy of adsorption ($\Delta G^\theta$) (Fig. 6) were also investigated.

According to Table 3, pure BC shows a BET specific surface area of $3.94\text{ m}^2\text{ g}^{-1}$ and a monolayer capacity of $10.38\text{ \mu mol g}^{-1}$, which are
Fig. 3. SEM micrographs of the surface of pure BC, and PGMA/BC, PGMA-MBA/BC and PPEGMA/BC nanocomposites.

Fig. 4. AFM 2D images (5 × 5 μm²) of pure BC, and PGMA/BC, PGMA-MBA/BC and PPEGMA/BC nanocomposites.
higher than the values obtained for BC films at 20°C, \( \text{SBET} = 1.94 \) m\(^2\) g\(^{-1}\) and \( \chi_s \) = 0.005 mmol g\(^{-1}\) (Castro et al., 2015), but lower than the \( \text{SBET} \) value (4.59 m\(^2\) g\(^{-1}\) at 25°C) recently reported for an oven-dried BC (Alonso, Faria, Ferreira, et al., 2018). Furthermore, the nanocomposite containing the cross-linked version of PGMA polymer (i.e. PGMA-MBA/BC) presents values of \( \text{SBET} \) and \( \chi_s \) lower than those of BC, whereas the inclusion of a polymer bearing hydroxyl pendant groups inside the BC network originated a nanocomposite (i.e. PPEGMA/BC) with \( \text{SBET} \) and \( \chi_s \) values that are three times higher than the ones obtained for pure BC.

The \( \text{SBET} \) increase can be due to the particle size decrease or rugosities increase in the material surface. As the obtained \( R_q \) values were not correlated with \( \text{SBET} \), the molecular changes, above referred, were not detected by AFM analysis. As IGC uses small molecules (\( n \)-octane) as probes, which can be inserted in the structural heterogeneities (nanorugosities) at the material, it’s possible to detect changes at a molecular level. Thus, the \( \text{SBET} \) increase was correlated to the pendant chain/groups inside the BC network (nanorugosities increase), and the \( \text{SBET} \) decrease was correlated to the cross-linked polymer which decreases the pendent chain/groups (nanorugosities decrease).

These BET isotherm measurements can be correlated with the heterogeneity of the surface; thus, Fig. 5 shows the heterogeneity profiles of BC and the three nanocomposites at 25°C using \( n \)-octane and dichloromethane as non-polar and polar probes, respectively. For the \( n \)-octane probe (Fig. 5a), PPEGMA/BC presents the lowest adsorption potential (A\(_{\text{max}}\) = 7.38 kJ mol\(^{-1}\)), followed by BC (A\(_{\text{max}}\) = 9.15 kJ mol\(^{-1}\)) and PGMA-MBA/BC (A\(_{\text{max}}\) = 12.6 kJ mol\(^{-1}\)) and PGMA-MBA/BC (A\(_{\text{max}}\) = 12.6 and 14.8 kJ mol\(^{-1}\)). While PPEGMA/BC nanocomposite exhibits a surface with high number of active sites but less energetic, PGMA-MBA/BC has a surface with more energetic dispersive active sites. The less pronounced energetic heterogeneity of PPEGMA/BC can explain the higher \( \text{SBET} \) value of this nanocomposite (12.59 m\(^2\) g\(^{-1}\), Table 3).

In the case of the dichloromethane (acid) probe (Fig. 5b), there is a different tendency with BC exhibiting the lowest adsorption potential, followed by PPEGMA/BC, PGMA-MBA/BC and PGMA/BC. The differences in the energetic profiles is a clear indication of the variances in polarity among nanocomposites.

The dispersive component of surface energy (\( \chi_s \)), which is caused by non-polar long-range interactions (London forces), decreased with temperature rise from 20 to 30°C for both pure BC and the three nanocomposites. These negative values of the temperature dependence of the surface energy (Table 3) are associated with the exothermic nature of the adsorption process and to the chain freedom. Thus, the lowest of \( \Delta \chi_s^d / \Delta T \) obtained to the nanocomposites indicate the polymethacrylate incorporation into the BC.

\( \chi_s \) values obtained for BC ranged from 47.22 ± 0.28 mJ m\(^{-2}\) at 30°C to 58.34 ± 0.28 mJ m\(^{-2}\) at 20°C. Although these values are

Table 3
IGC surface physicochemical properties of BC, and PGMA/BC, PGMA-MBA/BC and PPEGMA/BC nanocomposites.

|          | BC        | PGMA/BC   | PGMA-MBA/BC | PPEGMA/BC |
|----------|-----------|-----------|-------------|-----------|
| \( \text{SBET} / \text{m}^2 \text{g}^{-1} \) | 3.94      | 6.20      | 0.83        | 12.59     |
| \( n_m \) / mmol g\(^{-1}\) | 10.38     | 16.35     | 2.18        | 33.17     |
| \( \chi_s \) / mJ m\(^{-2}\) | 58.34 ± 0.28 | 59.05 ± 0.08 | 88.19 ± 0.08 | 35.46 ± 0.11 |
| \( \Delta \chi_s^d / \Delta T / \text{mJ} \text{m}^2 \text{K}^{-1} \) | -1.11     | -0.99     | -0.71       | -0.07     |
| \( K_a \) | 0.10      | 0.10      | 0.13        | 0.08      |
| \( K_b \) | 0.23      | 0.42      | 0.56        | 0.34      |
| \( K_{ab} \) | 2.27      | 4.20      | 4.31        | 4.25      |

\( \text{SBET} \): surface area; \( n_m \): monolayer capacity; \( \chi_s \): dispersive surface energy; \( K_a \): acidic constant; \( K_b \): basic constant.

\( n \)-octane: \( \chi_s^d \); THF – tetrahydrofuran, DCM – dichloromethane, EtOAc – ethyl acetate and ACN – acetonitrile, at 25°C.
the basic character is quite different among the materials. In fact, the ratio between the basic and acidic surface constants increased from 2.27 for BC to 4.20 for PGMA/BC, 4.25 for PPEGM/BC/BC and 4.31 for PGMA-MBA/BC (Table 3). The augment of the basicity ratio of about 85 – 90% validates the enhancement of the Lewis basic character of the nanocomposites surface when compared to BC, which is a direct result of the inclusion of basic groups. Therefore, PGMA-MBA/BC is the nanocomposite possessing the higher concentrations of electron-donating surface functional groups. These results correlate well with the specific free energy of adsorption data discussed above (Fig. 6).

3.3. Cluster analysis

Overall the three nanocomposite materials exhibit distinct structural, morphological and surface properties as discussed above. Nevertheless, and to confirm possible similarities among them, a hierarchically agglomerative clustering analysis was carried out by gradually merging single variables into extensive groups according to their features similarities. The dispersive component of surface free energy (\(\gamma_s^d\)), adsorption potential (\(A_{\text{max}}\)) of \(n\)-octane, acid-base character (\(K_a/K_b\)) ratio, specific component of surface free energy (\(\Delta G_s^G\)), surface area (\(S_{\text{BET}}\)), surface roughness (\(R_s\)) and C/O ratio were the selected variables for the agglomerative method. Fig. 7 depicts the dendrogram of the above-mentioned variables, where it is possible to observe three clusters. The first cluster presented a similarity of about 95% between both samples (BC and PGMA/BC), whereas the second cluster (PGEMA/BC) showed a similarity of ca. 79% with respect to the first cluster. In turn, the third and last cluster (PGMA-MBA/BC) exhibited a low similarity (close to 17%) with the remaining nanocomposites.

The hierarchical clustering suggests that the incorporation of 61 wt. % of a polymer bearing epoxide pendant groups (i.e. PGIEM) inside the BC porous network originates a nanocomposite (PGMA/BC) with quite similar properties to BC, whereas the inclusion of 87 wt. % of a polymer containing hydroxyl pendant groups (i.e. PPEGM) yields a nanocomposite (PGEMA/BC) with a lower level of similarity towards pure BC and PGMA/BC. Conversely, the nanocomposite composed of cross-linked PGMA and BC (i.e. PGMA-MBA/BC) exhibits significant dissimilarities with the other two nanocomposites as well as with pure BC. In fact, the incorporation of 67 wt.% of cross-linked PGIEM into the BC which reported \(K_a/K_b\) ratios of 0.55 (Castro et al., 2015), 0.75 (Alonso, Faria, Ferreira, et al., 2018) and 1.83 (Mohammadkazemi et al., 2017), but lower than the results reported by Pommet et al., with a \(K_a\) of 0.11, \(K_b\) of 0.41 and \(K_a/K_b\) of 3.73 (Pommet et al., 2008). This is probably also a result of small differences in surface morphology and cellulose structural groups orientation, that affect the interaction between the BC surfaces and the probes. Although the \(K_b\) constant of the three nanocomposites did not suffer a substantial change when compared with BC, the basic character is quite different among the materials. In fact, the ratio between the basic and acidic surface constants increased from 2.27 for BC to 4.20 for PGMA/BC, 4.25 for PPEGM/BC/BC and 4.31 for PGMA-MBA/BC (Table 3). The augment of the basicity ratio of about 85 – 90% validates the enhancement of the Lewis basic character of the nanocomposites surface when compared to BC, which is a direct result of the inclusion of basic groups. Therefore, PGMA-MBA/BC is the nanocomposite possessing the higher concentrations of electron-donating surface functional groups. These results correlate well with the specific free energy of adsorption data discussed above (Fig. 6).

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three-dimensional network originated the most divergent results in terms of: \( \gamma_f \), \( A_{\text{max}} \), \( \Delta G^0 \) and \( R_m \) as clearly discussed in the above paragraphs.

In this perspective, IGC proved once again to be an excellent tool for surface characterization of BC and its nanocomposites. The evaluation of the surface behaviour of the three nanocomposites in contact with polar and non-polar materials can contribute to foresee the potential applications of these materials. For example, while the PGMA-MBA/BC nanocomposite can be used as a functional hydrophobic material with an amphoteric (but predominantly basic) surface character for applications where the surface area is not a decisive factor, the PPEGMA/BC nanocomposite can be applied as a functional hydrophilic material for applications requiring high surface area and basic surface properties.

4. Conclusions

Nanocomposites consisting of either poly(glycidyl methacrylate), cross-linked poly(glycidyl methacrylate) or poly(poly(ethylene glycol) methacrylate) supported on the BC three-dimensional porous structure were successfully prepared and characterized regarding their physicochemical surface properties by IGC. The dispersive component of surface energy (\( \gamma_d \)) varied between 35.64 - 83.05 mJ m\(^{-2}\) at 25°C. Overall, the surfaces of the nanocomposites were rendered with a predominant basic character (\( K_a/K_w \) of 4.20–4.31). The nanocomposite composed of a cross-linked polymer bearing epoxide pendant groups exhibits the higher specific interactions with polar probes, and despite the reduced face energy (\( \gamma_f \)), the nanocomposite possesses better porosity and consequently assess their suitability for specific applications.

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References

Alonso, E., Faria, M., Ferreira, A., & Cordeiro, N. (2018). Influence of the matrix and polymerization methods on the synthesis of BC/PANI nanocomposites: An IGC study. Carbohydrate Polymers, 183, 254–262.

Amin, M. C. I. M., Ahmad, N., Hashim, N., & Ahmad, I. (2012). Synthesis and characterization of thermo- and pH-responsive bacterial cellulose/acyrylic acid hydrogels for drug delivery. Carbohydrate Polymers, 88(2), 465–473.

Beaumont, M., Kondor, P., Plappert, S., Mitterer, C., Opitzek, M., Pothast, A., et al. (2017). Surface properties and porosity of highly porous, nanostructured cellulose II particles. Carbohydrate Polymers, 24(1), 435–440.

Bozkurt, A., & Karadedeli, B. (2007). Copolymers of 4(5)-vinylimidazole and ethyleneglycol methylmethacrylate: Synthesis and proton conductivity properties. Reactive & Functional Polymers, 67, 348–354.

Buyanov, A. L., Gofman, I. V., Revel'kaya, L. G., Khripunov, A. K., & Tkachenko, A. A. (2010). Antisporic awelling and mechanical behavior of composite bacterial cellulose-loc-polycarlyamide or acrylamide-sodium acrylate) hydrogels. Journal of the Mechanical Behavior of Biomaterials, 3(1), 102–111.

Castro, C., Cordeiro, N., Faria, M., Zuluaga, R., Putaux, J.-L., Filipponet, L., et al. (2015). In-situ glyoxalization during biosynthesis of bacterial cellulose. Carbohydrate Polymers, 126, 32–39.