



Bacterial cellulose–poly(vinyl alcohol) nanocomposites prepared by an in-situ process

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ABSTRACT

Bio-nanocomposites were prepared by an in-situ growth process through the direct addition of poly(vinyl alcohol) (PVA) into the *Acetobacter xylinum* inoculated medium and compared with composites made by impregnation of bacterial cellulose (BC) gels with a PVA solution. Mechanical property tests showed that the presence of PVA in the BC acts as a plasticizer, interrupting hydrogen bonding between cellulose fibrils within the BC network. This resulted in a reduction in Young's modulus and an increase in toughness compared to pure BC sheet, especially for in-situ grown samples. Interestingly, the small amount of added PVA turns the BC sheet into optical transparent nanocomposite films with excellent mechanical properties.

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1. Introduction

Research into cellulose synthesised by micro-organisms has received a great deal of attention in recent decades [1]. Some bacteria such as *Acetobacter xylinum* are able to synthesise nanofibrils of bacterial cellulose (BC) through the polymerisation of glucose molecules converted into β -1,4-glucan chains in the interior of BC [2]. In static culture conditions, these bacteria produce a thick gel or pellicle which has unique properties such as high purity, high crystallinity, remarkable mechanical properties and an ability to form homogenous membrane sheets [2,3,4]. As this nanosize mat possesses excellent biocompatibility and an ultrafine reticulated structure, BC has found a multitude of applications in the paper, textile, and food industries, and as a biomaterial in cosmetics and medicine [5].

Various efforts have been made to maximise the benefits of nanocomposites based on BC, either by combining the synthesized pellicles with other materials or by modifying the cellulose biosynthesis [1]. Nanocrystals of BC, which are obtained by hydrolysing the amorphous part of BC, have been applied as a reinforcing agent in cellulose butyrate acetate [6], and starch [7]. By disintegrating the BC gel in the wet state, in order to easily blend it with other cellulose fibres, paper prepared from apple and radish pulp showed a

significant improvement in mechanical properties [4]. High volume fraction composites were prepared by Yano et al. by impregnating BC sheets with thermoset resins [8]. These materials showed a high stiffness in combination with optical transparency, but were quite brittle. For applications where ductility and toughness are required, ductile polymer matrices are more of interest. A membrane for the pervaporative separation of ethanol/water has been prepared by impregnating BC with 1.5% chitosan solution in 1% aqueous acetic acid [9]. More recently, an all-cellulose nanocomposites entirely made from BC was successfully prepared by immersing a BC sheet in solvent (lithium chloride/N,N-dimethylacetamide [10].

Alternatively, various substances have been directly incorporated into the cultural medium, via an *in-situ* growth process. For use in the healing of wounds, ulcers and burns, chitosan was added to the culture medium [11]. Carboxymethylated-bacterial cellulose, as copper and lead ion removal membrane, has been obtained by adding the water-soluble carboxymethylated cellulose directly into the culture medium [12]. BC was also grown in the presence of potato and corn starch [13], and poly(vinyl alcohol) (PVA). PVA, in particular, has attracted a lot of interests, because of its water solubility, good mechanical properties and biocompatibility [14]. It was found that the presence of PVA can influence the in-situ growth of BC through the formation of spherulites [15]. Seifert et al. found that the addition of cellulose derivatives and PVA into the culture medium gave biocomposites with better water retention and ion absorption [16].

In this study, two different preparation methods for BC/PVA nanocomposites are compared; (i) in-situ growth of BC in the

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presence of PVA (In-situ BC) and (ii) impregnation of bacterial cellulose gels with a PVA solution (Impreg BC). The two composites obtained are characterised for what concerns their morphological and mechanical properties.

2. Experimental

2.1. Materials and methods

Bacterial cellulose was prepared according to a method described previously [2,4]. A concentration of 5% v/v PVA ($M_w = 84,000$ – $124,000$ g/mol; 98–99% hydrolysed) (Aldrich, USA) solution in distilled water was prepared by stirring for 30 min at 80 °C. A sample of 100 g purified BC gel was impregnated with 100 ml of the PVA solution overnight and then pressed (115 °C for 5 min at 70 MPa) into a sheet. This sample is hereafter called Impreg BC. The same concentration of (sterilised) PVA solution (100 ml) was alternatively added directly into the medium (medium B in [4]) of the growing BC. This sample is referred to as In-situ BC. The In-situ BC was washed in fresh water and then left overnight on a porous wire sieve to remove the water. As a control, sheets of pure bacterial cellulose (simply referred to as BC) gel and PVA were also prepared.

It should be noted that, although the initial PVA concentration for the preparation of In-Situ BC and Impreg BC is similar, the final amount of PVA present in the two composites is different, because of the different purification steps. The estimated PVA matrix content in Impreg BC composites is 3.7%, while the PVA content in the In-situ BC composites is 1.4% before purification.

2.2. Characterization

The morphology of BC/PVA composites was observed using a JEOL JSM-6300F Field Emission Scanning Electron Microscope (SEM). All specimens were coated with gold before SEM observation.

Tensile tests were performed on a tensile testing machine (Instron 5564) at a cross-head speed of 5 mm/min using a 1 kN static load cell. The tensile test specimens were rectangular strips (40 mm × 5 mm), cut from 0.3 mm thick sheets, and were tested at ambient conditions, after been dried overnight at 80 °C in vacuum. All measurements were performed for at least five samples in each case and the average value was recorded.

Structural characterisation was carried out using a Siemens D5000 X-ray diffractometer (40 kV, 40 mA) with Cu K α radiation ($\lambda = 0.154$ nm) was used. The aperture slits were set at 0.1° and the scanning step was 0.02° with a scan time of 2.5 s per step.

3. Results and discussion

Since any chemicals added to the medium can affect the BC growth [16–20], the morphology of the in-situ grown BC was studied. Fig. 1 shows the morphology of BC and BC/PVA bio-nanocomposites prepared by the different methods.

The morphology of BC nanofibres (Fig. 1a) is characterized by a network of interconnected fibrils that contain entanglements and aggregations [4]. The preparation of BC by an in-situ process with a solution of PVA 5%v/v directly added to the culture medium did not significantly affect the morphology of the bacterial cellulose. Apart from the fact that the diameter of the BC fibrils can be seen to change slightly, no significant changes occur in the arrangement of the fibrils. Impregnation of PVA 5%v/v into a BC gel has however some effect on the ribbon morphology of BC. Aggregations form more easily and thicken in certain parts, resulting in an increase in the diameter of the BC fibre bundles. The same can be seen also for Impreg BC, where the fibres bundles are even more slightly thicker than those of In-situ BC. From the SEM images of Fig. 1(b) and (c) it can also be seen that the

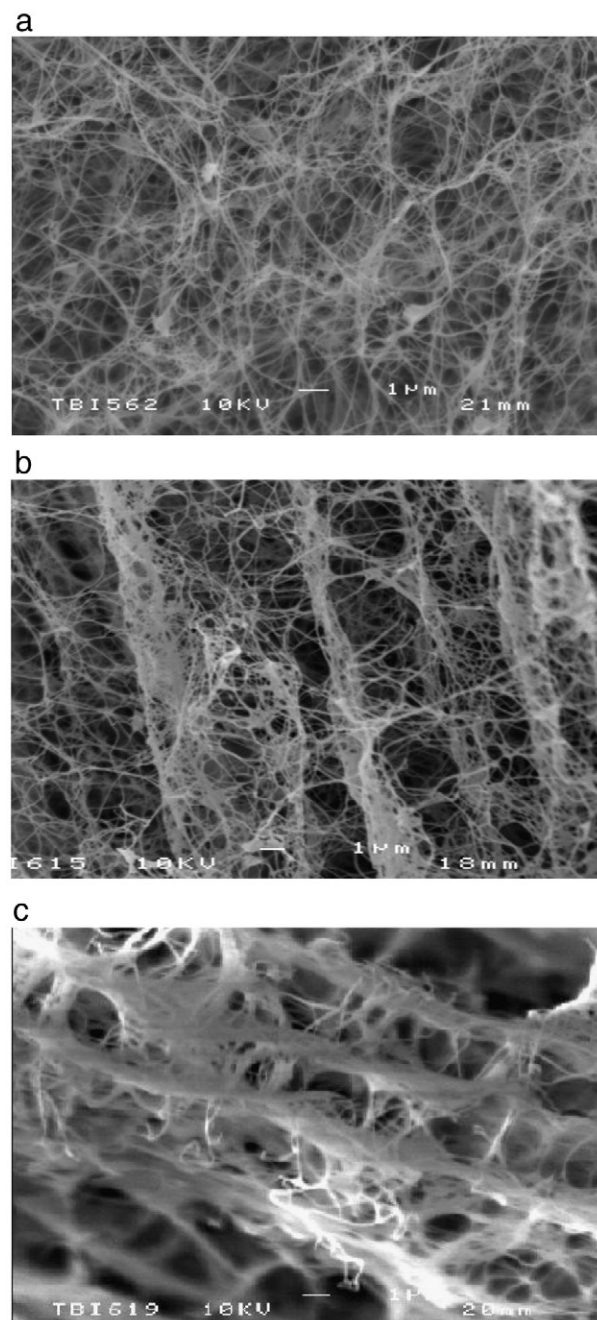


Fig. 1. SEM micrographs of: (a) BC (Magnification 5000), (b) In-situ BC (Magnification 8000) and (c) Impreg BC composites (Magnification 5000), showing the presence of PVA on the BC ribbons and the more homogeneous network for In-situ BC.

amount of PVA in Impreg BC is higher than in In-situ BC and less homogeneously distributed.

The different morphologies found are expected to significantly influence the mechanical performances. In general, the presence of an external phase between cellulose fibres tends to weaken the strong attractive hydrogen bonding between them [3,10], affecting the mechanical properties of the cellulose films. In the case of composites made by the impregnation method the presence of PVA reduces both the tensile strength and stiffness of the films by a factor of two, with the Young's modulus decreasing from 18.8 GPa (BC) to 9.1 GPa (Fig. 2).

The in-situ grown BC/PVA composite, instead, provides a better combination of the characteristics of BC and PVA, notably high strength and ductility. At first the composite responds elastically,

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