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Eggshell Nanoparticles and Their Effect on Moisture Barrier Properties of Gellan Gum Films by Morphological Analysis

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Introduction

Currently, there is a great demand in the development of new biodegradable materials due to the modification of environmental laws, which imply environmental awareness and important economic consequences due to the increased use of petroleum-derived materials worldwide. [1]. Bio-based materials are developed from renewable and low-cost or freely available resources, such as agricultural products and food waste, as they are environmentally friendly and therefore offer great energy savings and are free from greenhouse gas emissions [2].

Similarly, polymers of biological origin offer advantages on its use. One such is gellan gum (GG), which is an extracellular polysaccharide produced by the fermentation of *Sphingomonas elodea*, which is widely used as a film-forming matrix due to its ability to provide formation stability and biodegradability [3]. Also, one of the most important methods to modify the functional properties of polymeric films is the addition of various nanomaterials, which depends on shape, size, surface characteristics and degree of dispersion of the materials. It has been reported that nanoparticles used as reinforcing agents improve some properties of polymeric films, which has aroused great interest, especially when the implementation of renewable resources has been chosen for the development of ecological and bio-based reinforcements. An example of this is the use of eggshell waste, due to its chemical composition, low cost and abundance [4]. Therefore, the aim of this work is to evaluate the effects of the addition of eggshell nanoparticles (ENP) to GG films at different loadings (1-3 wt%) on their microstructure and the correlation with their moisture barrier properties.

Experimental procedures

Chicken eggshells were obtained from household waste, cleaned to remove impurities and membrane, and ground into small sizes. To obtain ENP, the powder was ground in a high impact ball mill (Pulverisette 7, Fritsch, Germany) by 2 h at 500 rpm [5]. For film preparation, a stock solution of gellan gum (2 % w/v) was prepared at 90°C and glycerol was added at 5 % (v/v), mixed by magnetic stirring, poured into Petri dishes (100 x 20 mm) and dried (8 h). To evaluate the effect of ENP on GG films, at different concentrations of ENP (1, 2 and 3 % w/v).

To measure the particle size, the ENP were observed by scanning electron microscopy (SEM) (JSM-7800 F, Jeol, MA, USA). And to observe the films a SU3500 (Hitachi Co., Ltd., Matsuda, Japan) was used, and cross-section cuts were made with a knife. All samples were fixed on carbon-doped aluminum holders. Image acquisition was performed using an accelerating voltage of 10 kV. The water vapor permeability (WVP) of the films was evaluated according to standard test method E96 [6]. The contact angle (CA) of a water droplet on the surface of each film was obtained using a CA meter fabricated by our working group and using a Young-Laplace-based method for the measurement that have been implemented as a Java plug-in for ImageJ software.

Results and discussion

Figure 1 shows an image obtained by SEM of eggshell nanoparticles (ENP), and it is observed that ENP tend by nature to agglomerate due to their hygroscopicity, despite this it was possible to measure some particles to confirm its nano-size (around 37 nm) by zooming into a more dispersed specific area (see Figure 1a´), with a round shape but with some shears probably due to milling [4].

Also, Figure 2 shows SEM images of a cross sections of the films, and the contact angle measurement for each film is included in the upper right-hand side. Figure 2a corresponds to the GG film and shows the internal structure of the film with the presence of a continuous zone distinguished by rod-shaped lines, showed the highest WVP value of 3.19±6.75 ($x10^{-10}$ g m/m^2sPa) and 20.09° of CA because the GG itself forms a fragile film with channels or micropores, which facilitate the diffusion of water vapor [7]. Figure 2b belongs to film GG1, a higher structural irregularity is observed, its WVP was 2.22±1.76 ($x10^{-10}$g m/m^2sPa) and 37.25° of CA, since there was no homogeneous dispersion of the ENP in the matrix and this could cause the formation of microholes and allowed the passage of water molecules in some regions. Figures 2c and 2d show films GG2 and GG3, respectively. In both films, a relatively smooth and continuous structure is observed. The WVP were 2.00±2.34 and 1.95±1.47 (g m/m^2sPa) $x10^{-10}$ and CA of 43.94° and 45.91º, respectively. They were homogeneously dispersed and incorporated into the matrix and prevented water molecules adsorption from rapidly passing through the matrix of the films.

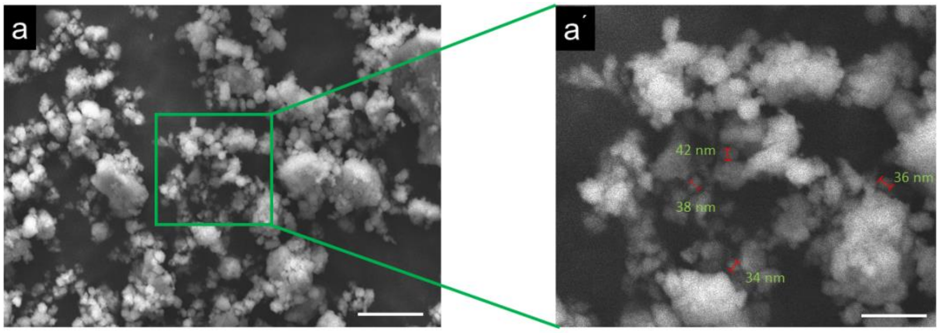

Figure 1. (a) SEM micrograph of eggshell nanoparticles; scale bar 5 µm. (a´) scale bar 100 nm.

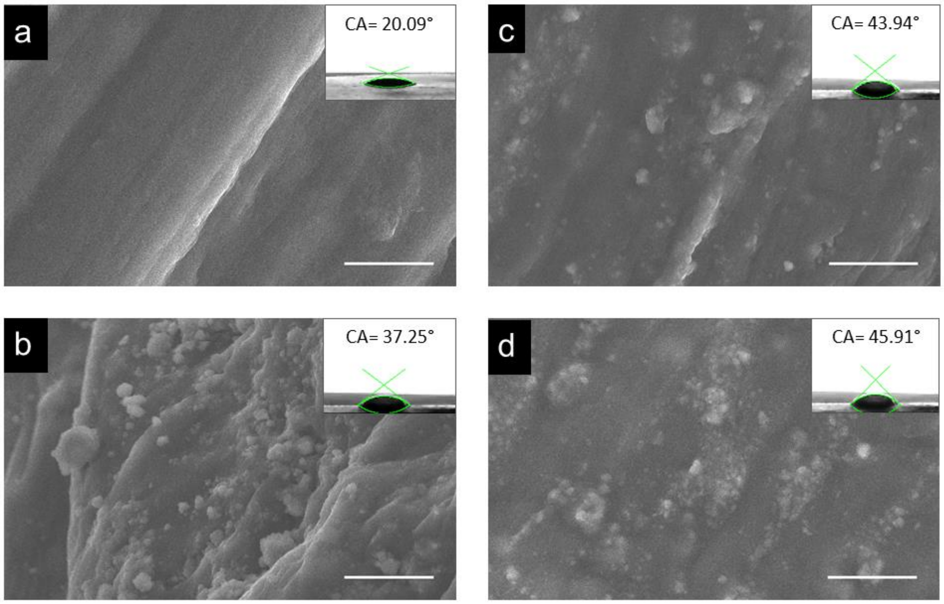

Figure 2. SEM micrographs of the cross section of the films and contact angle measurement of (a) GG, (b) GG1, (c) GG2 and (d) GG3. Scale bar 5 µm.

Conclusions

From the SEM technique, it was possible to observe the morphology and confirm the size at nanometer level of the ENP. Likewise, it was possible to examine the transversal microstructure of the films and facilitate the explanation of the effect caused using different concentrations of ENP added to the films, in which a significant improvement was found in their moisture barrier properties, evaluated by water vapor permeability and contact angle. Therefore, by showing favorable results, they are considered biomaterials with potential application mainly for food packaging.

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