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Facile and Effective Method for the Preparation of Sodium Alginate/TiO_2 Bio-Composite Films for Different Applications

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Nanocomposites of sodium alginate (SA) and TiO_2 nanoparticles have gained attention in the last decade for their versatile uses in several applications. Indeed, TiO_2 is particularly appealing for its photocatalytic and antimicrobial activity and inherent safety. In this paper, TiO_2 nanoparticles are successfully embedded, synthesized by a microwave-assisted method, into SA matrix by a simple solvent casting method to form flexible and self-consistent SA/TiO_2 films. FT-IR, XRD, and contact angle measurements confirm the formation of homogeneous and hydrophilic bio-composites films that may be suitable for packaging or life science applications.

1. Introduction

Sodium alginate (SA) is a naturally occurring polysaccharide mainly extracted from brown algae. Thanks to its interesting properties, SA could be used in many applications and has received much attention in the last decade.[1] An interesting feature is its ability to form nanocomposite materials with nanopowders.[2] Among them, nanosized TiO_2 is of great interest for its physical, chemical, and photocatalytic properties and can be engineered to be used in many applications. It also has antimicrobial properties but it is not toxic for humans, thus it can be used in medicine and food packaging.[3,4] For all these reasons, the development of bio-composites of SA and TiO_2 has recently gained increasing attention.[5] In life sciences, SA/TiO_2 composites are studied as photocatalytic antimicrobial agents for food packaging,[6] wound healing,[7] and drug delivery.[8] In our recent paper, TiO_2 nanoparticles were prepared by microwave (MW)-assisted synthesis.[9] The use of MW energy provides a faster, safer, and more effective heating than conventional one, thus reducing times and energy consumption during synthesis and/or sintering processes.[9–11] In this work, a facile and rapid way to prepare SA/TiO_2 composites was studied. TiO_2 nanoparticles obtained by MW-synthesis were embedded in SA matrix and SA/TiO_2 composite films were successfully prepared by solvent casting method. The influence of TiO_2 in the bio-polymeric structure was investigated by XRD, FT-IR, and contact angle measurements.

2. Results and Discussion

Figure 1 shows the photographs of SA and SA/TiO_2 composite films prepared by solvent casting method. All prepared films are self-standing and show a smooth surface. The addition of TiO_2 nanoparticles visibly reduces the transparency of the films and this effect increases with increasing the powder content in the composite. Notably, thanks to the lower particle size of the MW-synthesized nanoparticles compared to the commercial ones (respectively ≈30 and ≈300 nm as measured by DLS), **SA/TiO2-MW-3** and **SA/TiO2-MW-6** samples show a higher transparency than **SA/TiO2-P25-6** produced using commercial powders. This characteristic may be preferable in sectors where transparency is necessary, i.e., food packaging.

In **Figure 2**, FT-IR spectra of the films are shown. In the spectrum of pure SA film (Figure 2a) all typical SA absorption bands are visible.[12] No relevant differences are observed in the nanocomposite films with respect to the pure SA film (Figure 2b–d), suggesting low or no chemical interactions between TiO_2 and SA, as reported also by Bakil et al.[7]

Figure 3 shows XRD spectra of SA and SA/TiO_2 bio-composite films. The broad signals at 13.7° and 22.5° are attributed to amorphous SA structure.[13] In the XRD profiles of SA/TiO_2 composites, TiO_2 signals are also visible, thus confirming the successful incorporation of TiO_2 nanoparticles into SA matrix. Indeed, in

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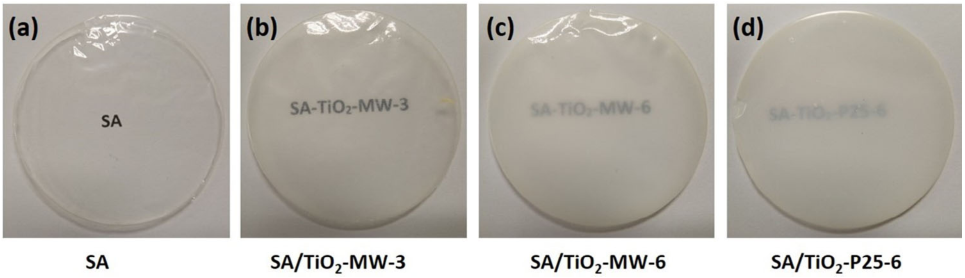

Figure 1. Digital photographs of all prepared SA and SA/TiO_2 composite films.

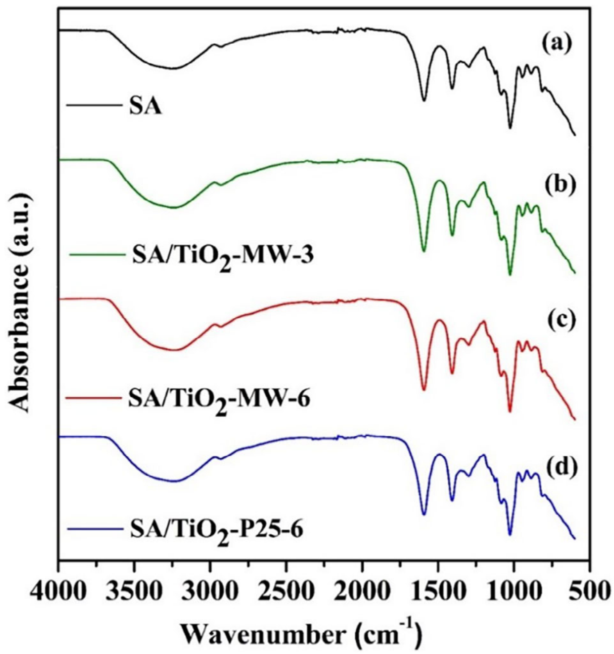

Figure 2. FT-IR spectra of SA and SA/TiO_2 films prepared by solvent casting method.

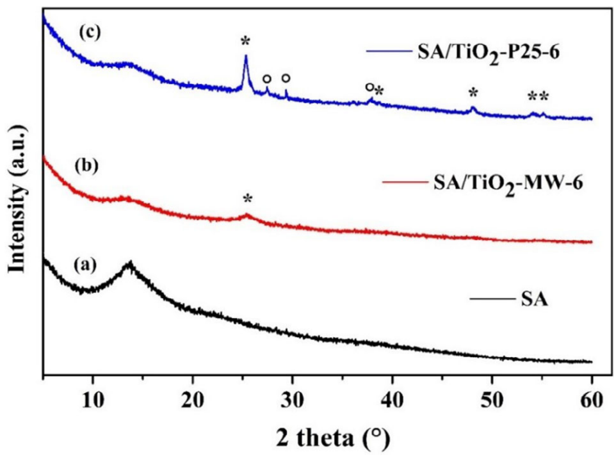

Figure 3. XRD spectra of SA and SA/TiO_2 composite films prepared by solvent casting method. * Anatase (JCPDS 00-021-1272) and ● Rutile (JCPDS 01-073-1782).

the spectrum of **SA/TiO_2-MW-6** (Figure 3b), the broad peaks at 2θ values of 25.2°, 37.8°, and 48° correspond to some reflections of the TiO_2 anatase phase (JCPDS 00-021-1272). Conversely, in the spectrum **SA/TiO_2-P25-6** (Figure 3c), some rutile peaks (JCPDS 01-073-1782) can also be observed. This is not surprising, since the commercially available P25 TiO_2 is known to be a ≈3:1 mixture of anatase and rutile.[14] Moreover, in this spectrum TiO_2 peaks are sharper than those observed in **SA/TiO_2-MW-6**, likely due to the higher crystal size of P25 powders with respect to those prepared by MW-synthesis.

The hydrophilicity of SA and SA/TiO_2 composite films was evaluated by water contact angle measurements (**Figure 4**). The WCA of SA film is ≈71° (Figure 4a) suggesting its hydrophilicity. When TiO_2 nanoparticles are dispersed in SA polymeric matrix (Figure 4b–d), the contact angle of the film increases slightly up to 78° in **SA/TiO_2-MW-6** (Figure 4c). This indicates a lower hydrophilicity of the bio-composites that show an improved water resistance than the bare SA film, as also previously reported.[6]

3. Conclusion

In this paper we report a rapid and facile method to prepare bio-composite SA/TiO_2 films for packaging and life sciences applications. TiO_2 nanoparticles were prepared by MW-synthesis and embedded in SA matrix. Semitransparent, self-standing, and flexible SA/TiO_2 films were obtained by solvent casting method. FT-IR and XRD analyses confirm the successfully embedment of TiO_2 in SA matrix and the homogeneity of the hydrophilic films.

4. Experimental Section

Materials: Sodium alginate (500-650 cP viscosity, Farmalabor s.r.l., Canosa di Puglia, IT) and TiO_2 P25 (Evonik-Degussa, Essen, DE, USA) were used without further purification. Synthetic TiO_2 nanoparticles were prepared by MW-assisted method.[9]

Preparation of SA and SA/TiO_2 Composite Films: SA-based films (**Table 1**) were prepared by solvent casting method. Firstly, 1% w/v of aqueous SA solution was prepared by stirring 24 h at r.t. Then TiO_2 nanopowders were added and the suspension was further stirred 24 h. Lastly, 10 mL of the suspension was placed in a Petri capsule at 30 °C for solvent evaporation. SA films were prepared similarly.

Characterization: XRD analyses were performed by an X'Pert PRO diffractometer (PANAlytical, Malvern, UK) equipped with a fast detector (X'Celerator) using Cu-kα radiation (λ = 1.5405 Å) in the 3–60 2θ range with a step size of 0.017 2θ. FTIR-ATR spectra were recorded in five different points for each sample by a Bruker (Billerica, MA, USA) VERTEX

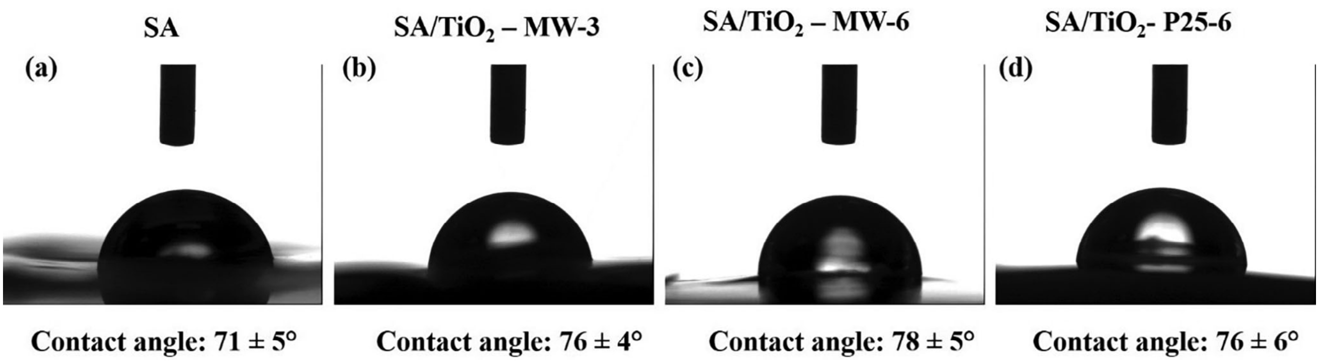

Figure 4. Water contact angle of SA and SA/TiO_2 bio-composite films.

Table 1. SA e SA-TiO_2 films prepared by solvent casting method.

Sample	TiO_2	TiO_2 wt% (based on SA)
SA	–	0%
SA/TiO_2-MW-3	MW-synthetized	3%
SA/TiO_2-MW-6	MW-synthetized	6%
SA/TiO_2-P25-6	Commercial P25	6%

70 FTIR spectrophotometer in the range of 600–4000 cm^{-1} using ATR Golden-Gate (Diamond top-plate) accessory and MCT-Mid band detector. Water contact angle (WCA) was measured using an optical contact angle device (OCA 15 EC, DataPhisycs Instrument GmbH, Germany).

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Conflict of Interest

The authors declare no conflicts of interest.

Keywords

bio-composites, MW-synthesized TiO_2 nanoparticles, sodium alginate

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