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Study of apatite layer formation on SBF-treated chitosan composite thin films

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ABSTRACT

Surface modifications of thin films based on chitosan (Ch), pure Ch and either Ch/montmorillonite (MMT) or Ch/nanoclay composites, were characterised by infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Biomineralisation of the Ch-based materials without any prior surface treatment was evaluated by immersing films in simulated body fluid (SBF) at 37 °C for 14 days. Samples were compared before and after soaking. Results obtained from SEM-EDX, AFM, and infrared spectroscopy (ATR-FTIR) were compared, and all prepared films showed growth of a new phase containing calcium. The composition of thin films influenced the amount of new phase formed as well as the degree of crystallinity of the newly formed phase. The largest increase was observed for the Ch composite with modified nanoclay. Moreover, increased growth of the new phase on the surface of films after immersion in SBF solution significantly influenced the thermal properties of the materials.

1. Introduction

Currently, there is a growing tendency toward the use of natural polymers obtained from renewable sources, especially those sourced from food industry waste and the agricultural and pulp and paper industries [1–4]. Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly owing to two major reasons: the first, environmental concerns and the second is the realization that our petroleum resources are finite [4–7]. Chitosan (Ch) is a deacetylated form of chitin that naturally occurs in some fungi however its presence is much less widespread than chitin. The polysaccharide is a copolymer of glucosamine and N-acetylglucosamine connected by a β (1–4) linkage [1,4]. Its ease of preparation, good biocompatibility, bioactivity, biodegradability, and non-toxicity to humans, has led to the widespread use of Ch has in biomedical applications, as well as in the food processing, cosmetics, biotechnology, and pharmaceutical fields [6–13]. The search for new applications calls for further developments in production methods, along with investigations of the structure and degradability of Ch and its composites. Polymer composites play a very important role in the development of polymer applications. In this context, this study focused on the development and evaluation of the physicochemical properties of new composites of Ch biopolymers and inorganic additives. The bioactivity of polymer materials is typically assessed *in vitro* by monitoring the formation of apatite layers on the surface of films after being immersed in a simulated body fluid (SBF) solution [14–16]. Moreover, Ch composites containing hydroxyapatite can be prepared via biomimetic processes using SBF solution [17]. Characterisation of Ch films with inorganic additives with and without SBF treatment have previously been reported in the literature [17–21]. Apatite layers were shown to form on the surface of Ch materials by mineralization. Mineralized composites containing hydroxyapatite and other additives could be a promising approach to supporting hard tissue regeneration [15].

In this paper, the influence of type of nanoclay used in Ch composites on the morphology and thermal properties of prepared films before and after immersing films in SBF solution at 37 °C for 14 days is discussed. To ensure good miscibility between biopolymer and montmorillonite (MMT) in composites, layered silicate has been modified with alkylammonium surfactants, quaternary ammonium salts or organosilicon compounds to produce organoclays [22,23]. Chitosan/nanoclay composite materials offer excellent physicochemical properties

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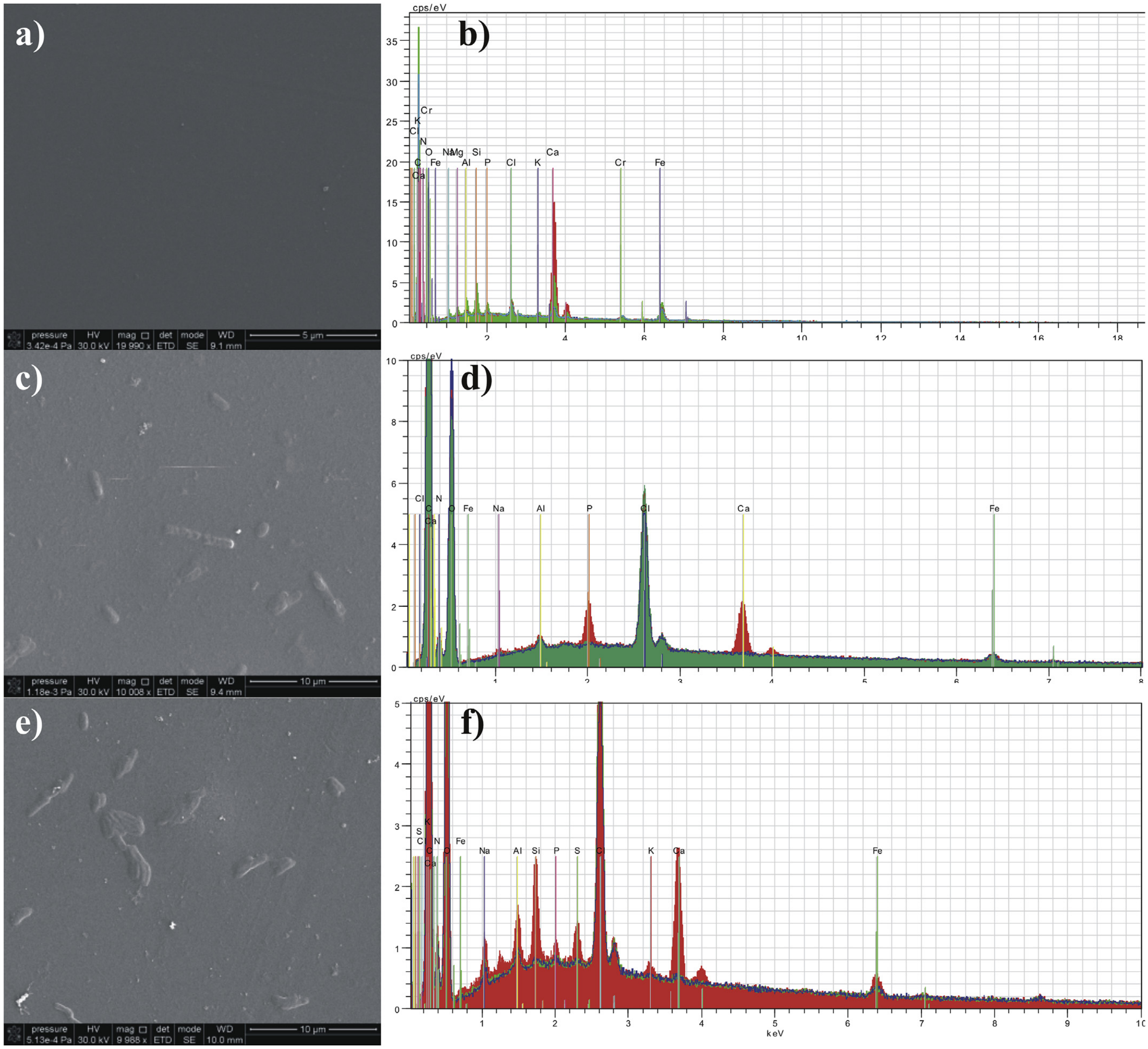

Fig. 1. Morphology and EDX analysis of the surface of Ch film before and after immersion in SBF solution: a-b) before immersion, c-d) after 1 week, e-f) after 2 weeks.

that depend on interfacial interactions [24,25]. Surface modification of MMT by organic compounds, such as octadecylamine and aminopropyltriethoxysilane, enhances biodegradability as well as the mechanical, thermal, and barrier properties that are superior to Ch composites with unmodified MMT (Ch/MMT) [23–25]. To the authors' knowledge, biomineralisation of Ch composites with nanoclay have not previously been investigated. In this study, composites were characterised based on scanning electron microscopy (SEM), tapping-mode atomic force microscopy (AFM), infrared spectroscopy (ATR-FTIR), and thermogravimetric analysis (TGA). These types of thermal analysis, microscopy, and spectroscopy techniques are useful methods for studying the structure, intermolecular interactions, homogeneity, surface roughness, and morphology of polymer composites.

2. Materials and methods

Unless otherwise stated, all materials, chemicals, and reagents used in this work were supplied by Sigma Aldrich (Poznan, Poland). All chemicals were of analytical grade. Chitosan powder with a degree of deacetylation (DD) of 78% and viscosity-average molecular weight of 0.59×10^6 was used. Montmorillonite samples were used without further purification. To modify the MMT surface, two different types of nanoclay were used: (1) surface-modified containing 25 wt% of octadecylamine, (2) surface modified containing 2.5 wt% of aminopropyltriethoxysilane and 25 wt% of octadecylamine. No further modification of the MMT and nanoclay were carried out after surface modification.

To create thin films, 1.0 wt% aqueous solution was prepared by dissolving Ch powder in an acetic acid solution (1 wt%).