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Elaboration and properties of plasticised chitosan-based exfoliated nano-biocomposites

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ABSTRACT

A series of plasticised chitosan-based materials and nanocomposites were successfully prepared by thermomechanical kneading. During the processing, the montmorillonite (MMT) platelets were fully delaminated. The nanoclay type and content and the preparation method were seen to have an impact on the crystallinity, morphology, glass transition temperature, and mechanical properties of the samples. When higher content (5%) of MMT–Na⁺ or either content (2.5% or 5%) of chitosan-organomodified MMT (OMMT–Ch) was used, increases in crystallinity and glass transition temperature were observed. Compared to the neat chitosan, the plasticised chitosan-based nano-biocomposites showed drastically improved mechanical properties, which can be ascribed to the excellent dispersion and exfoliation of nanoclay and the strong affinity between the nanoclay and the chitosan matrix. The best mechanical properties obtained were Young's modulus of 164.3 MPa, tensile strength of 13.9 MPa, elongation at break of 62.1%, and energy at break of 0.671 MPa. While the degree of biodegradation was obviously increased by the presence of glycerol, a further increase might be observed especially by the addition of unmodified nanoclay. This could surprisingly contribute to full (100%) biodegradation after 160 days despite the well-known antimicrobial property of chitosan. The results in this study demonstrate the great potential of plasticised chitosan-based nano-biocomposites in applications such as e.g., biodegradable packaging materials.

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1. Introduction

In the last years, polymers from renewable resources have attracted great attention due to their large availability, renewability, biocompatibility, and biodegradability [41]. Among this group of polymers, chitosan, a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy- β -D-glucan, is a deacetylated derivative of chitin, which is the second most abundant polysaccharide found in nature after cellulose [30]. Chitosan has been found to be nontoxic, biodegradable, biofunctional, and biocompatible in addition to having antimicrobial characteristics, and thus has a great potential in packaging applications [13]. These films have been reported to be

able to form a barrier against moisture [8], oxygen, and CO₂ [17]. The film properties depend on several parameters such as chitosan molecular weight and the degree of deacetylation, organic acid used, and the possible presence of plasticiser.

Recently, along with the exponential momentum of the development in polymer nanocomposites [2,4,7,27,32], much attention has been focused on the use of nano-sized fillers (at least one dimension in the nanometer range, i.e. 1–100 nm) in improving the performance of and adding new functionalities to polysaccharide-based materials. Chitosan-based nano-biocomposites have recently been reported with montmorillonite (MMT) [11,12,37], carbon nanotubes [23,36], metal oxide nanoparticles [1,19,21,25], cellulose nanofibres [5], nano-hydroxyapatite [33,34] etc. as the reinforcements. These nanocomposites displayed improved properties such as mechanical properties, thermal stability, moisture resistance and new properties such as electrical conductivity, and were aimed at various applications such as packaging, biosensors, tissue engineering (e.g., scaffolds) etc.

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It is worth noting that, for preparing chitosan-based materials or nanocomposites, only solution casting or similar methods involving chemical reactions have been used in all the past studies. Solution casting is known to have the disadvantage in low efficiency and difficulty in scaling-up towards industrial applications. In addition, a great amount of environmentally unfriendly chemical solvents are used and released to the environment in this method. The reason for not using a melt processing method like extrusion or kneading in the past studies is that chitosan, like many other polysaccharides such as starch, has very low thermal stability and degrades prior to melting (infusibility). Therefore, even if the melt processing method is more convenient and highly preferred for industrial production, its adaptation for polysaccharide-based materials remains very difficult. While the processing issues of starch has been emphasised to some extent [3,9,24,26,39], there has been very limited focus on the melt processing of chitosan-based materials/nanocomposites.

In the current study, we aim to develop a new method by melt processing to fabricate plasticised chitosan-based nano-biocomposites. Our recent study [14] has demonstrated the successful use of an innovative melt processing method (internal mixer) as an alternative route to solution casting, for preparing plasticised chitosan-based materials. This current work followed the same processing protocol but focused on the development of chitosan-based nano-biocomposites. Montmorillonite (MMT), which possesses some strong advantages such as wide availability, low cost, versatility, eco-friendliness, and low toxicity and has been frequently used in other polymer nanocomposite systems [2,4,7,27,32], will be used as the nanofiller. The effects of nanoclay content, organomodification, preparation method on the structure, properties, and biodegradation of the plasticised chitosan-based nano-biocomposites were examined.

2. Materials and methods

2.1. Materials

Two types of chitosan were used in the experimental work and their characteristics are shown in Table 1. ChitoClear™ was provided as a white powder with particle diameter lower than 1 mm (100% through mesh 18). The original moisture content of ChitoClear was 8.7 wt.% (wet basis). KiOnutrime-Cs® was provided as a powder in sandy brown colour and in even finer particle size. The original moisture content of KiOnutrime-Cs was 8.3% (wet basis). Considering the difference in molecular chain length, ChitoClear was used as the matrix of the chitosan-based nano-biocomposites, while KiOnutrime-Cs was used as the organomodifier for the nanoclay. The Dellite® LVF sodium montmorillonite (MMT–Na⁺) was supplied by Laviosa Chimica Mineraria S.p.A. (Italy) and has a cationic exchange capacity (CEC) of 1050 µequiv/g. Glycerol (99.5% purity, from Novance, France), acetic acid (Fluka, Sigma–Aldrich), and sodium hydroxide (Carlo Erba Réactifs – SdS, France), and sodium bromide (Sigma–Aldrich) were used as received. Deionised water was used for the sample preparation.

Table 1

Two chitosans used in the experimental work (the data are provided by the suppliers).

Commercial name	KiOnutrime-Cs®	ChitoClear™
Supplier	KitoZyme	Primex
Source	<i>Aspergillus niger</i> (mushroom)	<i>Pandalus borealis</i> (shrimp)
Molecular mass	1.5×10^7 Da	$2.5 \times 10^8 - 3.0 \times 10^8$ Da
Deacetylation degree	78%–80%	96%

2.2. Sample preparation

2.2.1. Organomodification of montmorillonite

Chitosan solution was prepared by adding 4.754 g (dry basis) of the KiOnutrime-Cs Chitosan to 500 mL of 1% (v/v) acetic acid (AcOH). The solution was stirred at room temperature overnight. The pH of the solution was then adjusted to 4.9 with NaOH solution. In parallel, a stock of well-dispersed clay suspension was prepared by adding 20 g of MMT–Na⁺ into 500 mL of water and treating with sonication at 60 °C for 4 h. Then, the chitosan solution and the MMT–Na⁺ suspension were mixed together and the mixture was stirred at 60 °C for 24 h. The mixture was centrifuged at 3000 rpm for 15 min, and then the supernatants were discarded. The precipitate was washed with distilled water and centrifuged again at the same condition, which was repeated twice to make it free from acetate. Hence, the final paste of chitosan-organomodified MMT (OMMT–Ch) was obtained with moisture content of 94.6%. Part of the paste was oven-dried (50 °C, overnight) into powder for use later. Here, the mass ratio of chitosan and clay was thus determined to achieve a monolayer of chitosan absorbed into the nanoclay interlayer spacing through a cationic procedure with respect to the CEC of the nanoclay [10].

2.2.2. Preparation of chitosan-based nanocomposites

The preparation procedure for the chitosan-based nanocomposites used here was similar to that in our previous work [14], with modifications especially regarding the addition of nanoclay. Seven samples with different formulation and/or preparation method were prepared, with the details and the sample codes listed in Table 2. As a typical procedure, glycerol was first introduced into the chitosan powder and manually mixed, followed by the addition of nanoclay (in the form of either paste or dried powder) with further manual mixing. Then, acetic acid aqueous solution (3%, v/v) was added dropwise to the chitosan–glycerol–nanoclay mixture with continuous manual mixing to obtain a paste with a final chitosan concentration of 25 wt.%. In some formulations where no glycerol or clay was used, the above procedure was accordingly adjusted. Also the amounts of the added 3% acetic acid solution listed in Table 2 were adjusted by taking into account the moisture content with the OMMT–Ch paste. However, this would hardly vary the effect of acetic acid solution because the pH value just changes from 2.53 to 2.68 even when the concentration of acetic acid varies from 3.0% to 1.5% (v/v).

The mixtures with different formulations obtained above were then thermo-mechanically kneaded in a Haake Rheocord 9000 internal batch mixer with twin roller rotors at 80 °C for 15 min, with a rotor speed of 100 rpm. Finally, the resulting materials were compression moulded at 110 °C temperature and 160 bar pressure

Table 2

Formulations of the chitosan-based materials/nanocomposites.^a

Sample code	Chitosan ^b	Glycerol	3% AcOH solution ^c	MMT	OMMT–Ch ^d
G0	100	0	300	–	–
G10	90	10	270	–	–
G25	75	25	225	–	–
G25M2.5	75	25	225	2.5	–
G25M5.0	75	25	225	5.0	–
G25O2.5p	75	25	225 (167.7)	–	2.5 (paste)
G25O5.0p	75	25	225 (110.4)	–	5.0 (paste)
G25O2.5d	75	25	225	–	2.5 (dried)
G25O5.0d	75	25	225	–	5.0 (dried)

^a The numbers stand for the portions in weight.

^b Listed are the values of dry chitosan.

^c The numbers in brackets indicate the actual additions after subtracting the water content in the OMMT–Ch paste.

^d Listed are the values of the corresponding inorganic part (MMT) of OMMT–Ch.

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