



Polysaccharide based hydrogels reinforced with halloysite nanotubes via polyelectrolyte complexation

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ABSTRACT

Inspired by the charge density variation, low cost and environmentally friendly clay minerals such as halloysite nanotubes (HNTs), herein we prepared nanocomposite (NC) hydrogels reinforced with HNTs via polyelectrolyte complexation (PEC) of xanthan gum and chitosan using glucuronic acid δ -galactone as acidifying agent in the aqueous media. The charge density of HNT and PEC of biopolymers can be influenced by the microstructure, physical interactions, swelling, and mechanical properties of the NC hydrogels. *In vitro* cell cultures of NC hydrogels on osteoblasts (MC3T3-E1) cell line showed improvement in cell proliferation than PEC hydrogels and may possibly be applied in biomedical fields such as tissue engineering.

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1. Introduction

Natural polysaccharide-based hydrogels has an important role in biomedical applications because of their tunable swelling behavior, and biocompatibility [1]. Since hydrogels is prepared from hydrophilic polysaccharide matrices that are crosslinked by physical, chemical and ionic crosslinkers have been utilized for the synthesis of a variety of polysaccharide hydrogels [1]. However, the mechanical strength of the aforementioned hydrogels is quite limited. In recent years, nanofillers have been explored as the basic framework for the preparation of mechanically improved nanocomposite (NC) hydrogels [2]. Among various kinds of nanofillers, Halloysite nanotubes (HNTs) as nanoclay minerals have been considered as an important nanofillers for making NC hydrogels for a variety of biomedical applications [3–6]. HNT is a two-layered aluminosilicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), with a predominantly hollow tubular structure [7]. The outer surface of the SiO_2 has negative surface charge with a small contribution from the positive Al_2O_3 inner layer. The tubular morphology and high aspect ratio with two layers of alumina silicate structure of HNTs making them as excellent reinforcements in polymer nanocomposites for a variety of biomedical applications [3–6].

PECs of chitosan (CS) and xanthan gum (XG) have already been studied and applied for various potential applications such as drug

delivery devices and tissue engineering [8,9]. In order to avoid the use of solvents, recently glucuronic acid δ -galactone (GDL) used as acidifying agent for the preparation of PECs based on CS and XG by insitu, to avoid the fast complexation [10,11]. However, PECs have low mechanical properties and in order to improve the mechanical performance of PEC hydrogels, here we prepared HNT reinforced NC hydrogels composed from CS and XG via PEC in the aqueous environment. Thus, the objective of this research work is to analyze the effects of HNT morphology and PEC of CS and XG on the structural interactions, swelling behavior, crystalline nature, microstructure, and mechanical properties of NC hydrogels for their possible use in the biomedical applications.

2. Materials and methods

2.1. Materials

Chitosan-medium molecular weight with an 84% degree of deacetylation (CS), xanthan gum (XG), D-(+)-glucuronic acid δ -lactone (GDL), halloysite nanotubes (HNTs) were purchased from Sigma-Aldrich (St Louis, MO, USA) chemicals Co. All chemicals were used as received without further purification. Throughout study double-distilled water (DDW) was used to prepare the solutions.

2.2. Preparation of NC hydrogels

Pristine XG and CS-based PEC hydrogels were fabricated as reported elsewhere [10,11]. In this study, NC hydrogels reinforced

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with HNTs were fabricated by a simple eco-friendly method in aqueous media. Briefly, different amounts of HNTs (0, 2.5, 5, 7.5, and 10 wt%) were added into 25 mL of DDW and sonicated for 30 min. Then, 0.75 g of XG was dissolved in the HNT dispersion under magnetic stirring for overnight. Further, 0.75 g of CS polymer was dispersed in XG-HNT solution and sonicated for 30 min followed by stirring for 1 day. After complete dispersions of CS in XG-HNT solution, 0.5 g of GDL was added. The obtained NC hydrogels were lyophilized for one week at -80°C . The detailed procedure for characterization, are given in the Supporting information.

3. Results and discussion

The preparation of NC hydrogels reinforced HNTs is schematically illustrated in Fig. 1A. First, XG was dissolved in HNT aqueous dispersion. During the dispersion process, the negative charge of anionic carboxylic groups from XG could interact with the inner positive surface of HNT through complexation. Then the CS polymer was dispersed in HNT-XG solution followed by the addition of the GDL. In this case, the NH_2 groups of CS polymer converted into NH_3^+ ions [10,11] and interacted with anionic XG as well as the outer surface of the negatively charged HNTs through the complexation and led to the formation of NC hydrogels.

As shown by the FTIR spectra in Fig. 1B HNT exhibits characteristics bands at 3695 cm^{-1} and 3621 cm^{-1} owing to the inner hydroxyl and inner surface hydroxyl groups, respectively [12]. Other characteristics bands obtained at 1115 cm^{-1} (apical Si—O), 1031 cm^{-1} (Si—O—Si bonds), 753 cm^{-1} and 690 cm^{-1} (perpendicular Si—O). As can be seen in FTIR spectra of XG characteristics absorption peaks at 3428 cm^{-1} , 2924 cm^{-1} , 1730 cm^{-1} and 1057 cm^{-1} are assigned to O—H, C—H stretching vibrations and —C=O

of pyruvate groups and ester groups respectively. In addition, a single broad peak at 1610 cm^{-1} was also observed due to the formation of complexation between NH_3^+ of CS and —COO^- of XG. In NC hydrogels, characteristics peaks belong to XG-CS were shifted to lower stretching frequency suggesting strong hydrogen bonding as well as ionic bond interactions between XG-CS complex with HNTs. In this case, the inner hydroxyl groups of HNTs were completely disappeared owing to the reaction of H^+ (produced from GDL) with Al—OH and loss of hydrated water molecules [12]. As shown by the XRD pattern in Fig. 1C, HNT exhibits a characteristic peak at 12° is due to basal plane (0 0 1) reflection of HNT layer space [5]. However, the incorporation of HNTs into XG-CS complex system up to 5 wt% did not show the basal plane, while high HNT content showed a very weak XRD pattern. These results clearly indicated that the reinforcement of HNTs into hydrogels mainly attributed to good intercalation of interfacial adhesion and surface cage interactions of HNTs with XG-CS complex system due to their electrostatic interaction [13].

In general, HNT clay minerals are not stable and fast sedimentation in the aqueous solutions is observed [5]. In this study, the electrostatic interaction can play an important role for homogeneous dispersion and stability of HNTs within PEC hydrogels. Thus, the dispersion state of HNTs with hydrogels and their microstructure has confirmed by morphological analysis, as shown in Fig. 2. The PEC hydrogels showed the compact and smooth structure with good porous structure, which indicates good complexation between XG and CS. Further, the incorporation of HNTs (from 2.5 wt% to 10 wt%) into hydrogels showed porous structure with irregular pore shape and size at low magnification, whereas at higher magnification rougher surface and noticeable HNT agglomeration was observed for NC hydrogels when incorporated with 10 wt%.

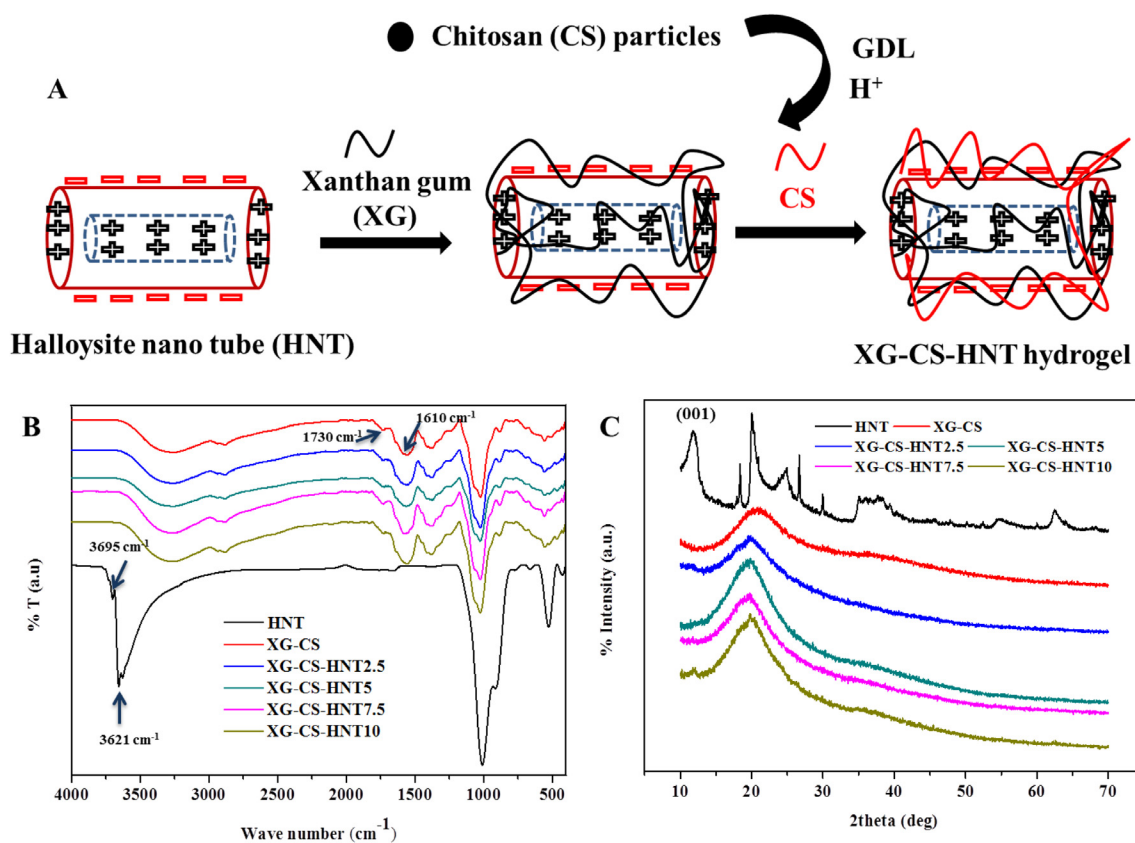


Fig. 1. (A) Schematic representation of formation of NC hydrogels reinforced with HNTs, (B) FTIR spectra and (C) XRD patterns of NC hydrogels reinforced with HNTs.

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