Preparation and Characterization of Hydrogel Nanocomposites Based on Oxidized Starch and Incompletely Condensed Polyhedral Oligomeric Silsesquioxanes

F. Sadrykia, N. Arsalani*

Abstract

Incompletely condensed polyhedral oligomeric silsesquioxanes (POSS) are nanosized particles (1-3 nanometer) that can be used as reinforcing fillers in hydrogel nanocomposites based on oxidized starch with polymeric cross linkers containing amine groups like chitosan. In this work we have prepared hydrogel nanocomposites based on oxidized starch and incompletely condensed POSS nanomaterials for the first time. POSS nanomaterials synthesized by hydrolysis and condensation method. Different percentages of POSS nanomaterials were composited to different ratios of oxidized starch and chitosan. The mechanical and thermal properties increased for composites containing POSS nanomaterials. The swelling percentage varies in different ratios of oxidized starch/chitosan and maximum of swelling percentage was 970%. In many cases the swelling percentage and solubility decreased for samples containing POSS nanomaterials. Also these hydrogel nanocomposites were characterized with various methods like FT-IR, SEM, XRD, TGA and DSC.

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Keywords: Incompletely Condensed Polyhedral Oligomeric Silsesquioxanes Oxidized starch; Hydrogel nanocomposites; Swelling percentage Solubility.

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1. Introduction

Hydrogels are three-dimensional polymeric networks that can absorb water, but they don’t dissolve in water. Polyhedral oligomeric silsesquioxanes (POSS) are nanosized materials (1-3 nm) with this formula: (RSiO1.5)n. We can make fully condensed silsesquioxanes or incompletely condensed silsesquioxanes with different methodologies. In many cases POSS nanoparticles are used to improve mechanical properties of polymer in polymer nanocomposites. POSS nanoparticles are biocompatible, so they can be used in drug delivery systems. Chitosan is a biocompatible and biodegradable polysaccharide that can be used in drug delivery systems too. Oxidation process of natural polysaccharides like starch, resulted in modified starch.

In general, starch/chitosan films are strong, stable and flexible. They can be used for controlled release delivery systems, Chen et al. (2009), Qiu and Park (2001), Kuang et al. (2011), Sarnino et al. (2009), Zohuriaan et al. (2008), Mahdavinia et al. (2006).

In this study we used POSS nanoparticles to improve thermal and mechanical properties of polymer in polymer nanocomposites. In this work, oxidized starch-chitosan hydrogel nanocomposites containing incompletely condensed POSS nanoparticles were synthesized by blending method and characterized with various methods.

2. Materials and Methods

2.1. Materials

Chitosan (Aldrich, medium molecular weight), oxidized starch (Glucan corporation company), distilled water, sodium hydroxide, phenyl trimethoxysilane (Acros 85%), tetrahydrofuran (Merck).

2.2. Methods

The nanosized heptaphenyltricycloheptasiloxane trisodium silanolate [Na3O12Si7 (C6H5)7] molecules were synthesized by hydrolysis and condensation method, Zheng et al. (2012). In this method we were synthesized incompletely condensed POSS molecules by using phenyltrimetoxysilane [C₆H₅Si(OCH₃)₃] and sodium hydroxide (NaOH) in THF solution.

We prepared oxidized starch/chitosan hydrogel nanocomposites filled with the reinforcing nanosized incompletely condensed POSS molecules, [Na₃O₁₂Si₇(C₆H₅)₇⁻] by using blending method.

In this work, the needed amount of chitosan was dissolved in acid solution: (solution A). The needed amount of oxidized starch and different weight percentages of POSS also dissolved in water: (solution B). Then, solution B was added to solution A and heated at appropriate temperature then the obtained solution added to appropriate crosslinking agent. Finally hydrogel nanocomposite beads were washed with distilled water for three times, and dried by freeze drying method.

3. Results and Discussions

3.1. Characterization of Obtained Hydrogel Nanocomposites

Obtained hydrogel nanocomposites were characterized with various methods like FT-IR, SEM, XRD, TGA and DSC.

SEM images of obtained hydrogel nanocomposites showed that surface of polymer differs by adding POSS nanomaterials and dot mapping images of Si atoms showed fine POSS nanoparticles’ dispersion in polymer matrix. Fig. 1.
Fig. 1. SEM images of (a) 2/1 ratio of oxidized starch/chitosan hydrogel nanocomposites; (b) 2/1 ratio of oxidized starch/chitosan hydrogel nanocomposites containing 7% POSS; (c) dot mapping of 2/1 ratio of oxidized starch/chitosan containing 7% POSS.

DSC results obtained for 2/1 ratio of oxidized starch/chitosan and 2/1 ratio of oxidized starch/chitosan containing 5% POSS nanoparticles, demonstrated higher degradation and glass transition temperature because of crystalline structure of POSS nanoparticles.

TGA results of oxidized starch/chitosan ratio of 2/1 containing 5% POSS nanoparticles, in comparison with TGA results of 2/1 ratio of oxidized starch/chitosan showed some differences.

Table 1 shows that degradation of POSS containing hydrogel nanocomposite occurs at higher temperature in comparison with 2/1 ratio of oxidized starch/chitosan at the same weight loss percentages.

Table 1. Degradation temperature and glass transition temperature of POSS containing hydrogel nanocomposites obtained by DSC and TGA.

<table>
<thead>
<tr>
<th>Temperature of Degradation</th>
<th>T_{10}</th>
<th>T_{40}</th>
<th>T_{60}</th>
<th>glass transition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized starch/chitosan: 2/1</td>
<td>165</td>
<td>335</td>
<td>665</td>
<td>181</td>
</tr>
<tr>
<td>POSS 5%, 2/1 (Oxidized starch/chitosan: 2/1)</td>
<td>245</td>
<td>345</td>
<td>750</td>
<td>202</td>
</tr>
</tbody>
</table>

X ray diffraction patterns of POSS nanoparticles have a sharp peak at 20 value of around 7 and around 20. Also oxidized starch/chitosan ratio of 2/1 makes this peak wide.

Because of small amount of POSS nanoparticles (5%) and decreasing their crystallinity in polymer matrix, sharp peaks of POSS aren’t shown in hydrogel nanocomposites. Fig. 2.

Fig. 2. XRD curve of 2/1 ratio of oxidized starch/chitosan containing 5% POSS.
FT-IR spectra of the neat POSS nanoparticles shows a sharp peak in 1131.74 cm$^{-1}$ that is because of Si — O Si bonds.

2/1 ratio of oxidized starch/chitosan hydrogel nanocomposite’s IR spectra shows peaks in around 1640 (chitosan’s N — H bond) and wide peaks around 1029 (oxidized starch’s peak).

FT-IR spectra of oxidized starch/chitosan containing 5% POSS is similar to spectra of neat 2/1 ratio of oxidized starch/chitosan and don’t show sharp peaks of POSS because Si — O — Si overlaps with oxidized starch’s peaks. Fig. 3.

![FT-IR spectra of 2/1 ratio oxidized starch/chitosan containing 5% POSS.](image)

3.2. Swelling Measurements

For measuring the swelling percentage of freeze dried hydrogel nanocomposite, we weighted a bead of it and then immersed it in distilled water for 1 hour at room temperature then we dried the swollen hydrogel by removing it on a piece of paper and then weighted it again.

Swelling percentage was calculated using this formula:

\[
\text{swelling percentage} = \frac{W_s - W_d}{W_d} \times 100
\]  

\(W_s = \text{weighted of swollen hydrogel}\)

\(W_d = \text{weighted of dried hydrogel}\)

The results showed that the swelling percentage varies in different ratios of oxidized starch/chitosan and maximum of the swelling percentage was 970%. In many cases the swelling percentage and solubility decreased for samples containing higher percentages of POSS nanomaterials (Table 2).

| POSS 5%, 2/1 (Oxidized starch/chitosan: 2/1) | 970 |
| POSS 7%, 2/1 (Oxidized starch/chitosan: 2/1) | 677 |

Table 2. Swelling percentages of hydrogel nanocomposites.
4. Conclusions

In this study we were prepared oxidized starch/ chitosan hydrogel nanocomposites filled with incompletely condensed POSS molecules.

The SEM and dot mapping analysis showed fine dispersion of POSS nanoparticles in polymer matrix. POSS nanomaterials synthesized by hydrolysis and condensation method and used for improving thermal and mechanical properties of hydrogel nanocomposites. TGA and DSC results confirmed improvement of thermal and mechanical properties. Also preparation of hydrogel nanocomposites were confirmed with FT-IR and XRD method.

The results showed that swelling percentage and solubility decreased for samples containing POSS nanomaterials.

Acknowledgment

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References