Highly Rapid Preparation of a Bio-modified Nanoclay with Chitosan

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ABSTRACT

Nanoclays are widely used in preparation of polymer clay nanocomposites. They are mostly prepared through cation exchange reaction between clay and cationic intercalants. Alkyl ammonium salts and alkyl amines are usually used as intercalants for the nanoclay preparation. Due to the toxicity of the intercalants, the current commercial nanoclays are not suitable for bio-applications. In the present report, a biological macromolecule (chitosan) was selected for the clay modification. The obtained bio-modified nanoclay can be used to prepare polymer-clay nanocomposites for various applications in biomedicine. In addition, this report comprises the first successful attempts to use a new approach for rapid preparation of chitosan-intercalated bentonite under green conditions. The conventional time-consuming manner (6-48 h) was replaced with a novel approach to quicken the reaction very considerably. XRD Studies exhibit that the clay galleries were increased from 12.34 to 16.45Å using a combination of ultrasound (30 min)-microwave (3 min)-irradiation.

INTRODUCTION

Clays are intercalated with intercalants to increase interlayer distance of the clay. Modified clays can be extensively used to prepare polymer-clay nanocomposites. Monomers and polymers can enter the interlayer distance of modified clay in the process of polymer nanocomposite preparation [1]. Low molecular weight intercalants are mostly used for clay modification. Alkyl ammonium salts (e.g. hexadecyltrimethyl ammonium bromide [2-3]) and alkyl amines (e.g. octadecylamine [4]) are the most common family of
intercalants. These materials are mostly toxic which are not proper for bio-applications [3]. For instance, toxicity effect of hexadecyltrimethyl ammonium was investigated on cells growth, and it was concluded that higher amount of modified clay with this intercalant had an adverse effect on fibroblast skin cell growth [5].

Intercalants should possess opposite charge with clay surface to take place cation-intercalant ion-exchange reaction between clay layers. For instance, clays such as bentonite and montmorillonite which have negative charge at their surface should be intercalated with cationic materials such as alkyl ammoniums [2-3].

Inversely, clays with positive charge at their surface such as hydrotalcite have to modify with anionic intercalants such as 2-acrylamido-2-methyl propane sulphonic acid [6].

In this paper, bentonite with negative surface charges was chosen to be modified. Therefore, chitosan, a cationic biopolymer, was used as a macromolecular intercalant.

Chitosan is extensively used in bio-related applications due to its biocompatibility and biodegradability [7-8]. Therefore, chitosan-modified clay can be used in preparation of polymer-clay nanocomposites for bio-applications. Conventionally, modified clays with alkyl ammoniums are not suitable for bio-applications due to their toxicity [5].

Amine groups of chitosan in acidic solution convert to a cationic form -NH$_3^+$ which is necessary for the cation exchange reaction between clay and intercalant [9]. Therefore, chitosan is a good candidate as an intercalant for bentonite modification. The present paper deals with a novel technique for intercalation of bentonite with chitosan by using devices such as microwave and ultrasound to prepare bio-modified clay in a very short time. On the basis of our knowledge, this work has not been reported to be performed by microwave and microwave-ultrasound combination for preparation of bio-modified nanoclay.

**EXPERIMENTAL**

Bentonite (OCMA, particle size 40 μm, from Sefid Sang Aligoodarz Company, Iran) and chitosan (molecular weight 280000 g/mol, degree of deacetylation 83 from Fluka) were used as received. One gram of bentonite was dispersed in 50 mL distilled water and 2 g chitosan was separately dissolved in 312 mL of 1% v/v acetic acid aqueous solution. Both mixtures were then poured in an Erlenmeyer flask. Different treatments were conducted according to Table 1. A domestic microwave oven (Panasonic, model dimension 4, 2002w) and an ultrasound bath (Eyela, Korea) were used for the treatments.

After the heat treatment, the mixture was centrifuged, and washed with 1% acetic acid solution and water. The product was dried in an air-circulating oven at 60°C for 6 h. It was ground and kept in glass capped bottle. Each synthesis was conducted in tripli-
cate to determine the standard deviation of intercalation (SD 0.031).

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of unmodified bentonite and clay biopolymer modified bentonite with two different intercalation induction approaches. The interlayer distance between clay layers for unmodified bentonite (Table 1, sample A1) was recorded to be 12.34Å (2θ 7.15) (Figure 1a). It was increased to 14.12Å ((2θ 6.26), Table 1, sample A2) for the clay modified through microwave irradiation, the one-step method (Figure 1b and Figure 2). Figure 1c shows XRD pattern of the sample A3 (Table 1) prepared

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Intercalation conditions</th>
<th>2θ°</th>
<th>Interlayer distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Pristine clay</td>
<td>7.15</td>
<td>12.34</td>
</tr>
<tr>
<td>A2</td>
<td>Microwave irradiation, 3 min</td>
<td>6.26</td>
<td>14.12</td>
</tr>
<tr>
<td>A3</td>
<td>Stirring at room temperature, 4 h + Microwave irradiation, 3 min</td>
<td>5.63</td>
<td>15.72</td>
</tr>
<tr>
<td>A4</td>
<td>Conventional heating at 60°C, 48 h</td>
<td>5.59</td>
<td>15.78</td>
</tr>
<tr>
<td>A5</td>
<td>Ultrasound, 30 min</td>
<td>5.82</td>
<td>15.17</td>
</tr>
<tr>
<td>A6</td>
<td>Ultrasound, 30 min + Microwave irradiation, 3 min</td>
<td>5.36</td>
<td>16.45</td>
</tr>
</tbody>
</table>

Table 1. Intercalation conditions and interlayer distance for the unmodified and bi modified clay samples.

Figure 2. Schematic structure of unmodified clay (bentonite) and chitosan-intercalated bentonite prepared via microwave irradiation; the methods one-step (down) and two-step (up).
from the similar reaction mixture stirring firstly for 4 h at room temperature followed by microwave irradiation for 3 min (the two-step method, Figure 2). In the combination method, the interlayer distance was increased to 15.72˚A (2θ 5.63). This further enhancement of clay gallery shows that stirring at room temperature before microwave treatment has considerable influence on intercalation improvement. Figure 1b confirms that microwave treatment itself can lead to intercalation of chitosan into clay.

Sample A4 was prepared with conventional heating for clay modification. Modified clays after this time-consuming procedure showed interlayer distance 15.78˚A which is nearly equal 15.72˚A of sample A3 which is intercalated by combination of microwave (3 min) and stirring at room temperature (4 h). Ultrasound device was employed for intercalation in samples A5 and A6. The results (Table 1, Figure 3) showed that successful improved intercalation can be achieved by this way. The highest interlayer distance (16.45˚A) was obtained in sample A6 when ultrasound and microwave irradiation were alternatively used for the intercalation process. In addition of achieving the highest interlayer distance, the total reaction time of the intercalation process is highly reduced to 33 min.

Clay surface has a lot of negative charges which are counterbalance with cations such as Na⁺ and Ca²⁺ in interlayer space between the layers. Cation exchange reaction can take place in intercalation process between Na⁺ and chitosan in slightly acidic media. It should be pointed out that the cation exchange reaction between chitosan and clay is thermodynamically favourable. The Gibbs free energy for adsorption of chitosan on clay surface is shown in eqn (1) [9].

\[ \Delta G = -RT \ln K \]  

where R is the gas constant, T is the intercalation temperature, and K is a parameter which depends on the polymer-clay interaction sites [9]. For instance, \( \Delta G \) at 323 K is -55.6 kJ/mol which indicates thermodynamic tendency for adsorption of chitosan on clay surface [9]. This high negative Gibbs energy indicates that chitosan in spite of its high thermodynamic volume in comparison with usual low molecular weight cationic intercalants can diffuse between interlayer distance of clay.

Intercalation reaction is carried out more easily with raising temperature. Diffusion coefficient of intercalant in intercalation media is enhanced with increasing temperature. Therefore, higher molecular movement of chitosan chains increased the probability of entering chitosan between clay layers to carry out a successful intercalation reaction. The required heat can supply via conventional heating (e.g. using hot plate) for long hours (48 h). In this paper, novel approaches were examined to replace conventional heating with the new ones. It was found that other
sources of heat such as microwave irradiation can be used to supply the required heat of the intercalation reaction as well as diminishing the reaction time to a few minutes. Microwave and ultrasound irradiations increase the molecular movements of the intercalant via different mechanisms (samples A5 and A6, Figure 3). However, both of the methods can promote the intercalant diffusion between clay layers. When microwave and ultrasound were used alternatively, it had a significant influence on increasing the clay interlayer distance up to 16.45 Å (Table 1).

**CONCLUSION**

Accelerated preparation of chitosan-modified nanoclays was reported in this article for the first time. While the conventional heating consumes 6-48 h, our proposed methods (e.g. ultrasound followed by microwave irradiation) take only 33 min to achieve similar intercalation levels. This bio-modified nanoclay as well as its possible polymer nanocomposites can be used in variety of applications especially biomedicine.

**REFERENCES**