Preparation and Heavy Metal Removal from Chitosan Composite

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Recently the removal of trace element using biodegradable polymers is important. This paper involves preparation and evaluation of chitosan/ polyethylene glycol blend served as a heavy metal removal system. The author prepared various blending system with different composition ratios and different crosslinking density. Experimental results indicated that swelling degree and thermal property of the blend film were correlated with blend ratio and crosslink density. The blend film was then investigated its metal-binding performance. Copper sorption capacity was one of major potential applications in a field of wastewater treatment.

Key words: blend, chitosan, metal, polyethylene glycol

Despite a number of researches of metal-chelating by chitosan (CS) or other polymers as [1-5], no study could be found on any development of the metal-chelating capacity by the chitosan/polymer blend system. The blending strategy is an important approach for biodegradable polymers, not only in order to improve their inferior properties of the structural components, but also to achieve the efficient absorbent characteristics in order to treat wastewater and to recover the trace elements [6-10]. Therefore, the author has prepared and studied the blending property of glycol/chitosan (CS/PEG) film. The potential application of blended CS/PEG film is applied for metal-chelating. Also, the biodegradabilities of CS and PEG are usually allowed. The differential scanning calorimeter (DSC) will be utilized to evaluate the miscibility of the blend. If blended polymers are immiscible, different phases would be easily detected. Finally, the removal of heavy metal ion throughout the blend products will be investigated its potential served as a new copper (II) ion absorbing agent.

Experimental part

Methodology

Polymer Blend

Chitosan powder (CS with molecular weight = 480,000 Da and degree of deacetylation = 75-85%) and polyethylene glycol (PEG with molecular weight = 6,000) powder including ethylene glycol diglycidyl ether (EGDGE served as a crosslinker) with different blend ratio were dissolved in acetic acid solution using magnetic stirrer for 72 hrs. The blend solution was subsequently degassed to remove air bubbles, and then spread onto a Teflon dish. Afterwards, the gel was dehydrated. It was noted that the acid film was neutralized by base solution. The CS to PEG blend ratios were 1:4, 1:2, 1:1, 2:1, and 4:1 by weight. Ethylene glycol diglycidyl ether (EGDGE) was used to each sample in different quantity (0.5mL, 1.5mL, and 3.0mL). Form of polymer blend used in this experiment was film.

Swelling Degree

Dried film was soaked in deionized water until reaching equilibrium state. The obtained wet film was wiped in order to separate the excess water on the surface of the film, and weighed. The level of swelling was expressed in accordance with the weight of swollen sample per weight of dried sample.

Thermal Property

Thermal property of 10 mg dried film was measured by using a Perkin-Elmer Pyris DSC–7. Scanning range was from -100 °C to 200 °C.

Metal Absorption

Metal stock solution served as synthetic wastewater was prepared by dissolving an amount of the known metal salts ($CuCl_{\ddot{y}}$) in deionized water. The pH of the test solution was controlled to 4 - 5 using hydrochloric acid. The obtained solution was then adsorbed with the blend film until reaching equilibrium absorption, and the mixture became sediment. The clear liquid was separated by filtration. Amount of Cu (II) ions remaining in this solution was verified by titration with the standard sodium thiosulphate solution [11-14]. The amount of metal absorption was, therefore, calculated by subtracting the amount of copper from the initial amount and reported as (mg) per gm basis of the blend film.

Results and discussions

Film Characterization

Blend solution was homogeneous and transparent, changing from colorless to slightly yellowish as chitosan (CS) content increased (fig. 1). The obtained blend film was brittle, and translucent. It became soften when it was immersed in water. These results indicated that intermolecular hydrogen bonds, in case of a low polyethylene glycol (PEG) composition, were possibly formed between hydroxyl groups, or amino groups of CS molecule and ether groups of PEG molecule, whist intramolecular hydrogen bonds were formed in CS chain at a high PEG composition. It was also reliable for the cross-linking formation through a reaction of amino–, hydroxyl–groups of CS and carboxyl groups of cross-linking agent – Ethylene glycol diglycidyl ether (EGDGE) in the presence of PEG.

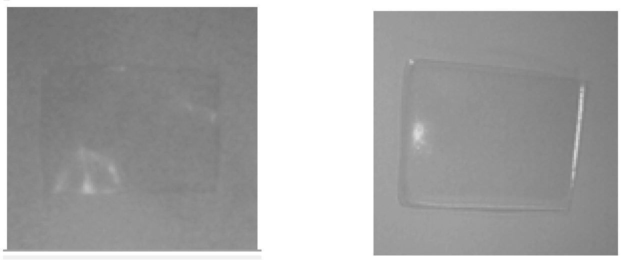

Fig. 1. CS to PEG blend ratios were 1:4 (left) and 4:1(right)

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Swelling behaviour

Swelling degree tended to increase when EGDGE was decreased (fig. 2). This was because decreasing crosslink density increased spacing or phase domain size of polymer network. High crosslink density led the chain segmental immobility to produce its bigger free space. On the other hand, the swelling degree was correlated with the proportion of CS in the blend film. This was because amorphous phase from CS disturbed the crystallinity of the blend to loose crystalline structure in the overall structure. This irregular structure made the polymer chains to pack loosely. This structure also facilitated the efficient water diffusion into the polymer networks. In the contrary, when increasing crystallinity of the blend by PEG content, water molecules were weaken in penetrating into more compact structure.

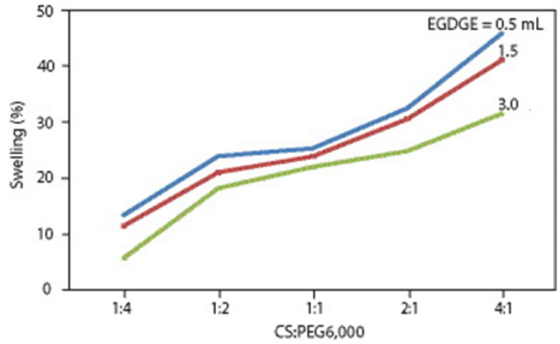

Fig.2. Swelling degree of the blend films

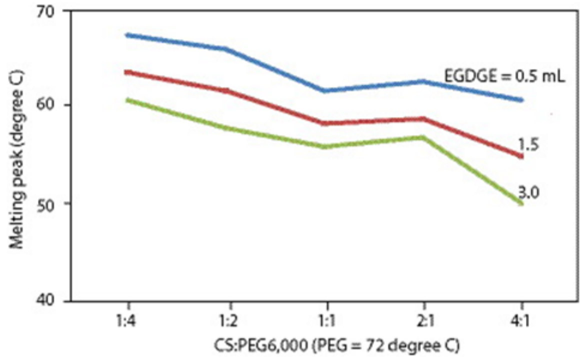

Fig. 3.Melting peak of the blend

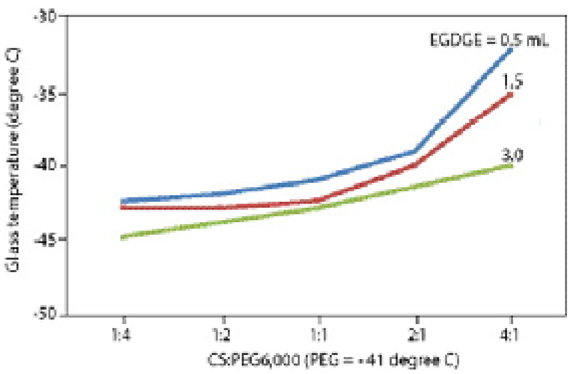

Fig. 4. Glass transition temperature of the blend

Thermal Characterization

Melting temperature (T_m) of the blend film was shifted towards the low temperature when the CS content was increased (fig. 3). The CS hindered the crystallinity of the blend, both in a reduction of the size of crystalline and broadening the distribution of the crystalline. On the other hand, cross-linking agent involved the exchange between a van der Waals bond for a shorter covalent bond and more compact bonds, resulting in a further decrease in Tm.

Conversely, glass temperature (T_g) of the blend film appeared to increase with increasing amorphous CS phase via the presence of its molecular flexibility and weak interchain force (fig. 4). The T_g was decelerated by cross-linking agent because not all the carboxylic groups of cross-linker were involved in a crosslinkage, but the remaining ones might have more strong hydrogen bonds.

Absorption Capacity

In table 1, the CS content in the blend film was obviously shown to have a strong ability to absorb metal ion.

Average value of absorption capacity in mg copper per gm of the blend film. CS, PEG, and EGDGE was chitosan, polyethylene glycol, and ethylene glycol diglycidyl ether, respectively.

Table 1

AVERAGE VALUE OF ABSORPTION CAPACITY IN MG COPPER PER GM OF THE BLEND FILM. CS, PEG, AND EGDGE WAS CHITOSAN, POLYETHYLENE GLYCOL, AND ETHYLENE GLYCOL DIGLYCIDYL ETHER, RESPECTIVELY

MATERIALS	0.5 ML EGDGE	1.0 ML EGDGE	1.5 ML EGDGE
CS:PEG = 1:4	60	40	38
CS:PEG = 1:2	70	50	40
CS:PEG = 1:1	75	55	53
CS:PEG = 2:1	78	62	60
CS:PEG = 4:1	80	75	70

The presence of mainly NH groups of CS molecule was involved in metal-chelating process via dominant mechanisms as follows:

$$-NH_3^+ = -NH_2 + H^+ \quad (1)$$

$$-NH_2 + Cu^{2+} + 2OH^- = [CuNH_2(OH)_2] \quad (2)$$

Amount of cross-linking agent was inversely correlated with adsorption ability of the blend film. The low content of cross-linker easily unattacked on the characteristic groups ($-NH_2$) of CS backbone, and, at the same time, unreacted with ether group of PEG molecule. The blend film with the smallest content of cross-linker also showed the best swelling performance of water as previously described in the swelling degree. Therefore, metal ion was easily combined with the polymer matrix. Since more water was able to be absorbed in the blend and water might stimulate the diffusion of copper ion, the copper absorption rate was enhanced. For further adsorption study the theoretical models such as isotherm model and kinetic model will be present in the next paper.

From all results purposed it is clear that the structure of the blend film can be considered as a potential alternative of a new composite adsorbent for copper ion waste streams.

Conclusions

Modification of polyethylene glycol/chitosan (CS/PEG) blend film by cross-linking agent was prepared and studied its properties. The blend film with lowering of crosslinked epoxide system attempted to impart a high swelling degree. The polymer swelling suppressed the native crystallinity of the blend, increasing the accessibility of water molecules to the sorption sites when increasing CS constituent. In thermal analysis, CS and cross-linker were found to have a significance to crystallinity of the blend. Moreover, the polymer blend was suitable for chelating of copper ion, which was chosen to demonstrate the utility of such blend on the metal complex. The results revealed that copper absorption capacity of the blend film was correlated with CS content, but inversely correlated with amount of cross-linking agent. We believed that the concept of modifying the metal-chelating capacity of this blend film would suggest a wide range of applications in metal ion sorptions.

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