CHAPTER V
CHITOSAN-PEG-CLAY AEROGEL NANOCOMPOSITE

Abstract

Chitosan aerogel nanocomposite in water based system is proposed. The reaction is successful in water at room temperature by using the water soluble chitosan-HOBt aqueous solution and water soluble conjugating agent (WSC). SEM result indicates the porous structured of chitosan aerogel nanocomposite. The water absorption at room temperature of chitosan aerogel nanocomposite increases when the amount of crosslink decreases.

Keywords: Chitosan; Aerogel nanocomposite; Na^+-montmorillonite clay

1. Introduction

Aerogels are unique materials with many specific properties such as extremely high porosity (> 98%), large surface area (~ 10^6 m²/kg), very low density (~3 kg/m²) and low thermal conductivity (~ 0.05 W/mK).[1] The structure, comprised of nano-sized pores and linked by each of primary particles can be tailored via the sol-gel process under supercritical drying.

It should be noted that, aerogels have been received much attention in fields such as catalysis,[2] thermal insulation,[3] adsorption[4] and drug delivery system[5] etc. Even if a large majority of the aerogel studies are dealing with inorganics especially silica-based aerogel,[6] some class of organic aerogels is also reported.

Natural materials and biopolymers such as alginic acid, pectic acid, cellulose, and chitin-chitosan, etc. are attractive for aerogel precursors due to their availability and environmentally benign nature. One of the most abundant organic compounds is chitin-chitosan which is a component of the shells of crustaceans and cell walls of fungi. Chitosan is derivatized from chitin via alkaline deacetylation. Chitosan can be dissolved in acid and this make it be more attractive material than chitin. In the past, the development of chitosan material is for example, solution crosslinking and casting to produce films[7] or membranes[8] and gels,[9] dropping solution in poor solvent to prepare beads,[10] or using as powder forms for waste water treatment.[11] An alternative way to develop chitosan is to functionalize it with specific molecules via chemical reaction to obtain derivatives such as O-carboxymethylchitosan,[12] N- carboxymethylchitosan,[13] N-phthaloyl chitosan,[14] N-carboxybenzyl chitosan,[15] N-succinyl-N'-octyl chitosan,[16] and N-alkyl-N-trimethyl chitosan.[17] It should be noted that in either development, chitosan solubility becomes the most problem. Dissolving chitosan in acid, especially acetic acid, is a practical way but completed removing the solvent in material preparation is not the easy task.

Chen et al. (2005) reported the preparation of chitosan aerogel by using the blending system of chitosan-acetic acid solution and PNIPAAm gel/PP nonwoven composites. The chitosan matrices were crosslinked by glutaraldehyde. The results indicated that not only chitosan gels displayed antibacterial ability but also the porous chitosan sponge that obtained from freeze-drying exhibited good

biocompatibility to fibroblast.[18] However, we have to aware of the toxicity of the contaminated acidic solvents and dialdehyde crosslinker. Previously, we reported about the conjugating reaction of chitosan in water-based system.[19] This may lead to the aerogel formation if we pay attention on the (i) formation of gel via the conjugating reaction and (ii) the porous structure formed after drying process.

2. Experimental

2.1 Materials

Chitosan (%DD = 95) was supplied from Seafresh Chitosan (Lab) Company Limited, Thailand. 1-Hydroxybenzotriazole monohydrate (HOBt·H$_2$O) and water-soluble carbodiimide hydrochloride (WSC·HCl) were purchased from Wako Pure Chemical Industries Co. Ltd., Japan. Na$^+$-montmorillonite clay was supplied from Southern Clay Product, Inc., Texas. Poly(ethylene glycol) (PEG, M_n 1450 Da) were purchased from Sigma-Aldrich, Inc., USA. Succinic anhydride was provided from Fluka Chemika, Switzerland. All chemicals were used without further purification.

2.2 Instruments

Qualitative and quantitative Fourier transform infrared spectra were obtained from a Thermo Nicolet Nexus 670 with 32 scans at a resolution of 2 cm^{-1} in a frequency range of 4000-400 cm^{-1} using a deuterated triglycinesulfate detector (DTGS). TG-DTA thermogravimetric analyses were carried out using a Perkin Elmer Pyris Diamond with N$_2$ flow rate of 20 mL/min and a heating rate of 10 °C/min starting from 30 to 900 °C. The morphology was investigated by using a JEOL JSM-5200 scanning electron microscopy (SEM) at 15 kV.
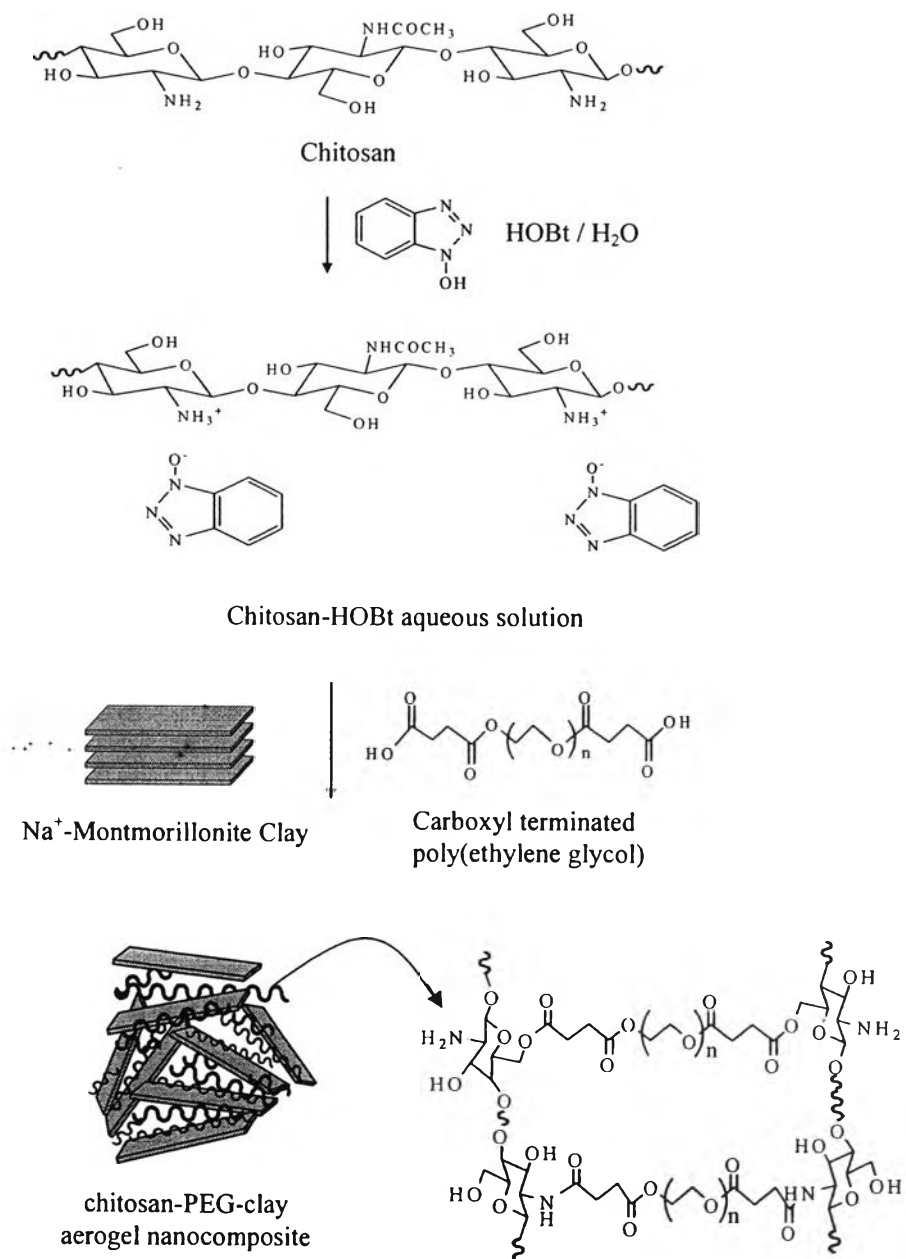
2.3 Preparation of chitosan-PEG-clay aerogel nanocomposite, 3

Chitosan (0.5 g, 3.06 mmol) was vigorously stirred with HOBt·H$_2$O (0.47 g, 3.06 mmol) to that of chitosan in deionized water 40 mL at ambient temperature until the clear solution was obtained, 1. Na$^+$-montmorillonite clay for 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 g was suspended in 10 mL deionized water. PEG (M$_n$ 1450, 20.00 g, 13.8 mmol) was reacted with succinic anhydride (2.76 g, 2.76 mmol)

at 65°C for 24 hours. The crude product was purified by reprecipitating in diethyl ether, washing for several times and drying in vacuum to obtain carboxyl terminated poly(ethylene glycol) (COOH-PEG-COOH), **2**.

To the solution of **1** (40 mL), **2** (1.70 g, 1.53 mmol), WSC (0.59 g, 3.06 mmol), and Na^+-montmorillonite clay suspension were added and stirred at room temperature for 24 hours. Carboxyl terminated poly(ethylene glycol) (COOH-PEG-COOH), **2**, was varied in 0.34, 0.68, 1.02, 1.36 and 1.70 g. The product was lyophilized to obtain **3**.

FTIR (KBr, cm^{-1}): 2874 (CH stretching), 1732 (C=O ester), 1650 (amide I), and 1565 cm^{-1}(amide II).

Scheme 1. Synthesis of chitosan-PEG-clay aerogel nanocomposite.

3. Results and Discussion

Preparation of chitosan-PEG-clay aerogel nanocomposite, 3
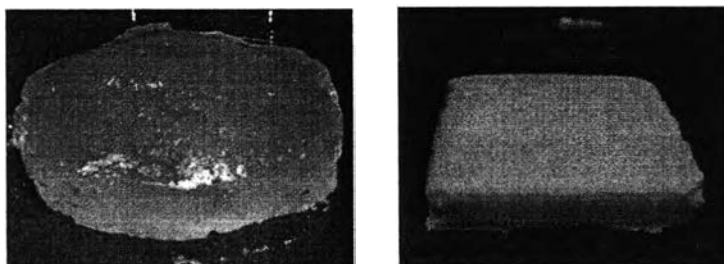

Figure 1. Appearances of; (a) chitosan gel nanocomposite, and (b) chitosan aerogel nanocomposite.

The forming nanocomposite gel consists of three parts which are (i) polymer solution, (ii) clay, and (iii) crosslinker. The aerogel nanocomposite can be obtained from freeze-drying. In this study, dicarboxylated poly(ethylene glycol) was used as crosslinker to obtain chitosan gel and combined with Na^+-montmorillonite. All reactions were carried out in water at room temperature to give **3**. Chitosan-PEG-clay gel nanocomposite was lyophilized to obtain chitosan-PEG-clay aerogel nanocomposite (Figure 2) before analyzing by FTIR. There are major peaks of saccharide unit, i.e. v_{CO} of C-O-C ~ 1090 cm^{-1}, pyranose ring ~ 890 cm^{-1}, and $v_{OH} \sim 3390$ cm^{-1}. Carboxyl terminated poly(ethylene glycol) shows the peaks v_{OH} of carboxylic ~ 3400 cm^{-1}, v_{CO} of C-C(=O)-O ~ 1100 cm^{-1}, v_{CO} of ester ~ 1730 cm^{-1}, and v_{CH} stretching of 2875 cm^{-1}. Na^+-montmorillonite clay gives vibrational band of silicate as follows; v_{OH} at 3635 cm^{-1}, and v_{SiO} of Si-O-Si ~ 1045 cm^{-1}. The product obtained shows the important peaks at 2874, 1732, 1650, and 1565 cm^{-1} corresponding to CH stretching, C=O ester, amide I, and amide II respectively.
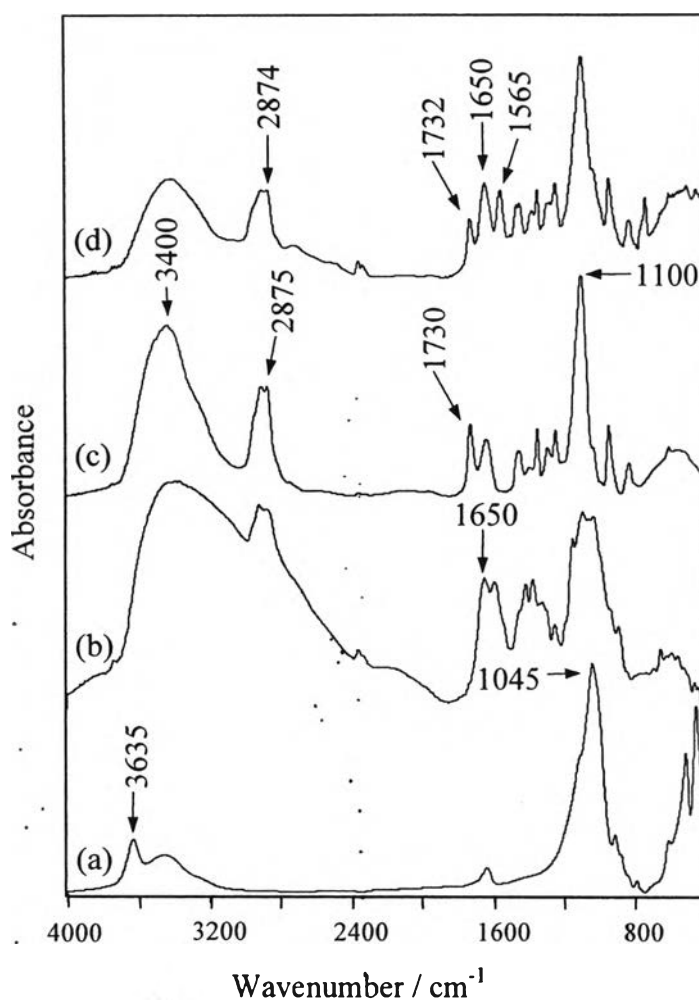
Figure 2. FTIR spectra of; (a) Na$^+$-montmorillonite clay, (b) chitosan, (c) **2**, and (d) **3**.

Figure 3 demonstrates the degradation temperature of chitosan aerogel after combining with Na$^+$-montmorillonite clay in various weight of clay. It is known that chitosan shows the degradation temperature between 200°C to 400°C under air atmosphere whereas Na$^+$-montmorillonite clay gives a long range of degradation from 50°C to 700°C due to its moisture contents and some inorganic salts and the degradation temperature of carboxyl terminated poly(ethylene glycol) is between 300°C to 450°C. The chitosan aerogel nanocomposites show the degradation step from 200°C to 400°C referring to the weight loss of chitosan, carboxyl terminated poly(ethylene glycol), and Na$^+$-montmorillonite clay.
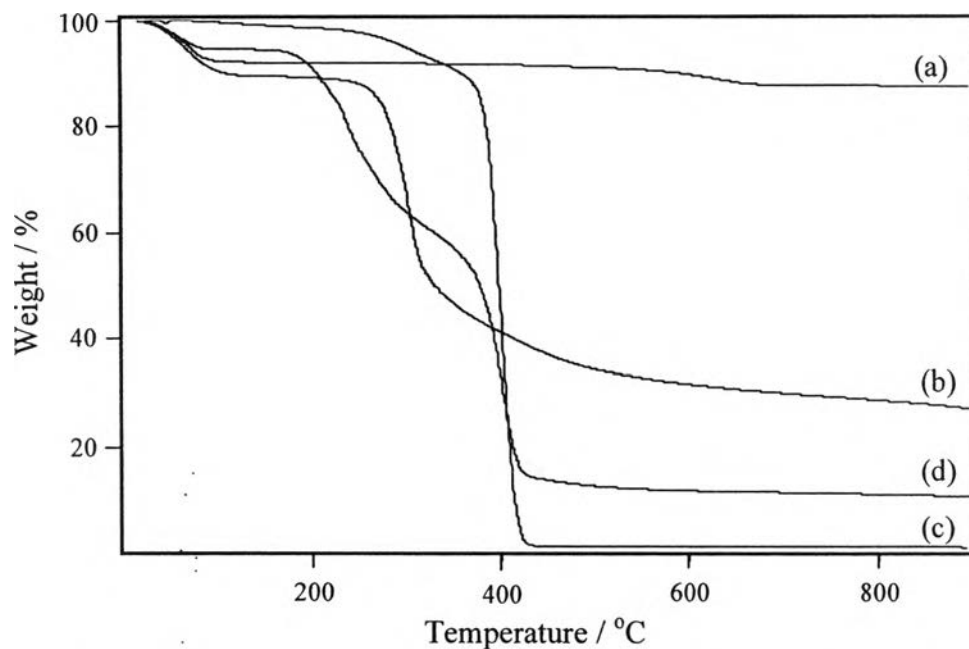
Figure 3. TGA thermograms of; (a) clay, (b) chitosan, (c) **2**, and (d) **3**.

Figure 4 shows the results of Na-montmorillonite clay in chitosan under the weight ratios of Na-montmorillonite clay to chitosan from 2% - 14% Na-montmorillonite clay. When the weight ratio of Na-montmorillonite clay was increased, the degradation temperature of aerogel nanocomposites decreases. This might be due to Na^+-montmorillonite clay obstructs the chitosan chain packing resulting in the weaken intermolecular hydrogen bonds.
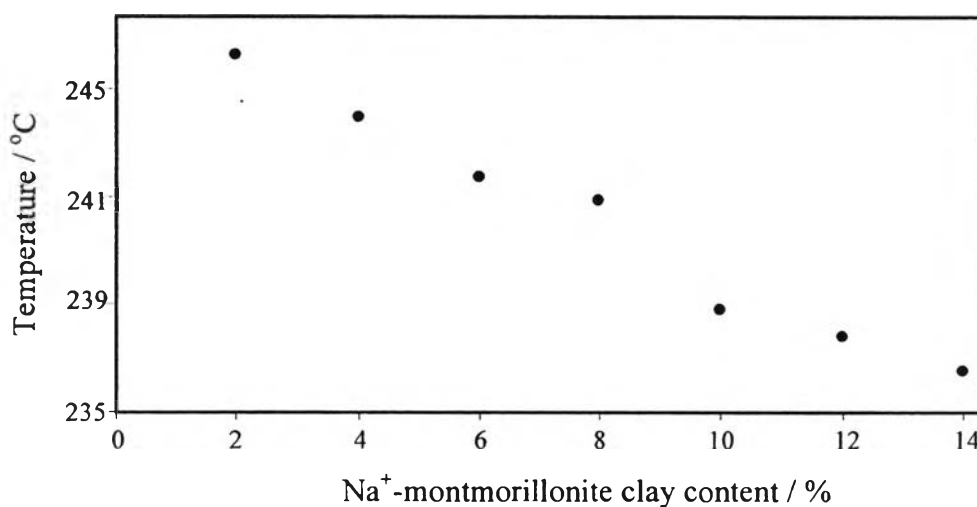

Figure 4. Degradation temperature of aerogel, **3**, with various Na^+-montmorillonite clay content.
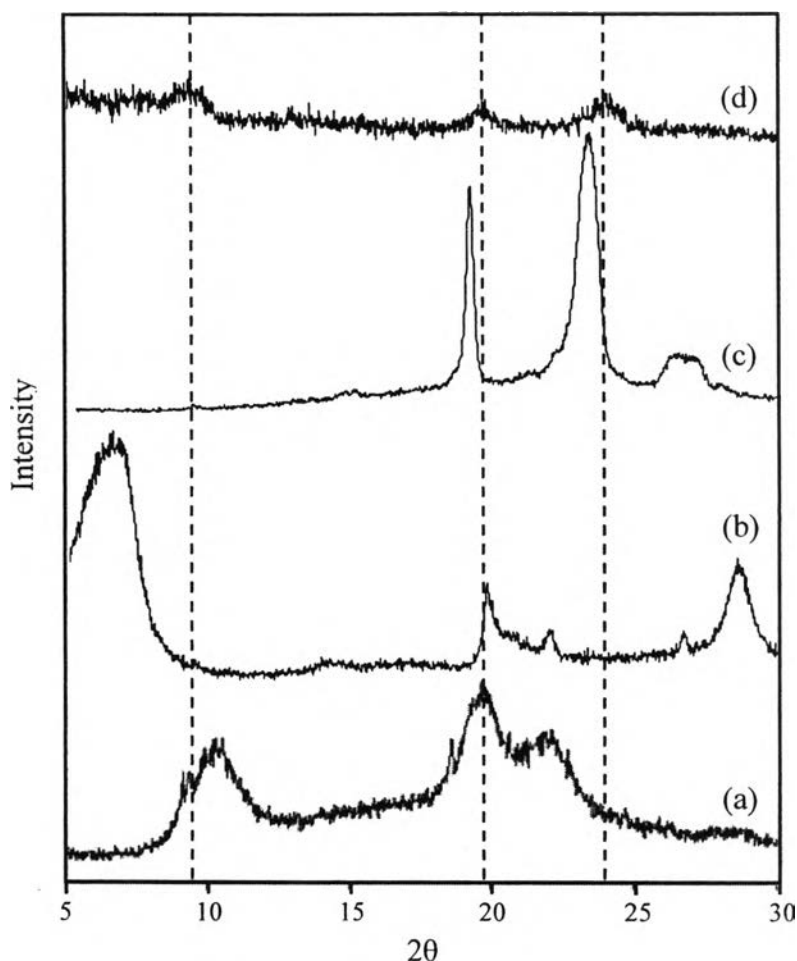
Figure 5. XRD patterns of; (a) chitosan, (b) Na⁺-montmorillonite, (c) carboxyl terminated PEG, and (d) chitosan aerogel nanocomposite.

Figure 5 (d) shows the XRD pattern of chitosan aerogel nanocomposite comparing with that of the pure Na⁺-montmorillonite (Figure 5 (b)). When the exfoliating of chitosan-PEG into clay layer occurred, the packing structure of clay layer will change.

The water absorption weight gains in aerogel nanocomposites at room temperature was calculated using eq 1. The carboxyl terminated poly(ethylene glycol) is highly efficient in cross-linking as observed from the water absorbency. The water absorption was as high as 2800% when the content of carboxyl terminated PEG was at 10%. The gradual decrease of water absorption is observed as the content of carboxyl terminated PEG increased. Although the gel strength needs to be

quantitatively analyzed, we founded that the gel swelled and was easily to be torn apart.

$$\text{Water absorption (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

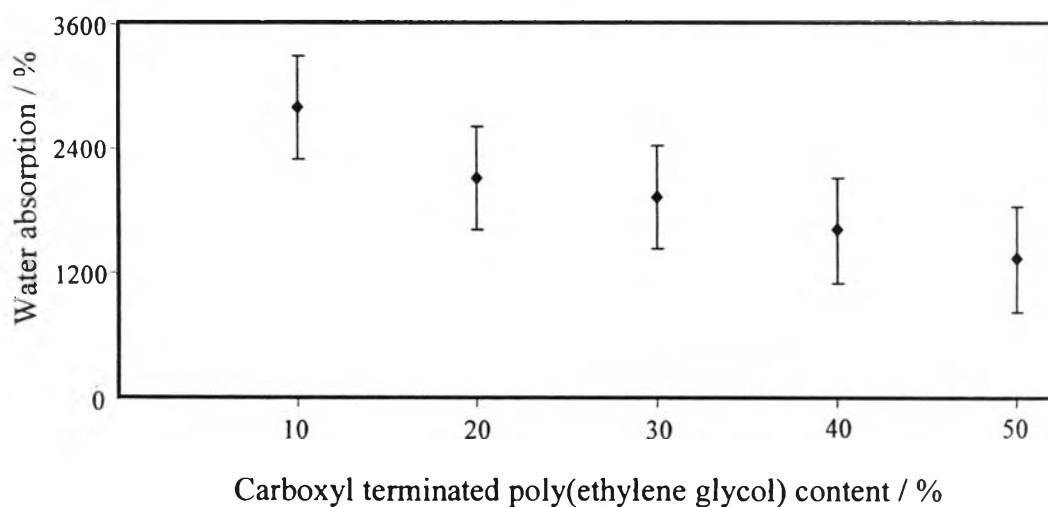Carboxyl terminated poly(ethylene glycol) content / %

Figure 6. Water absorption with various amount of carboxyl terminated poly(ethylene glycol) at room temperature.

Figure 7 shows the dense surface of chitosan aerogel nanocomposite. In general, aerogel BET surface areas range from 200-1000 m^2/g.[20] In the case of **3** the porous network is identified and the surface areas are 231.07 m^2/g.

(a)   (b)

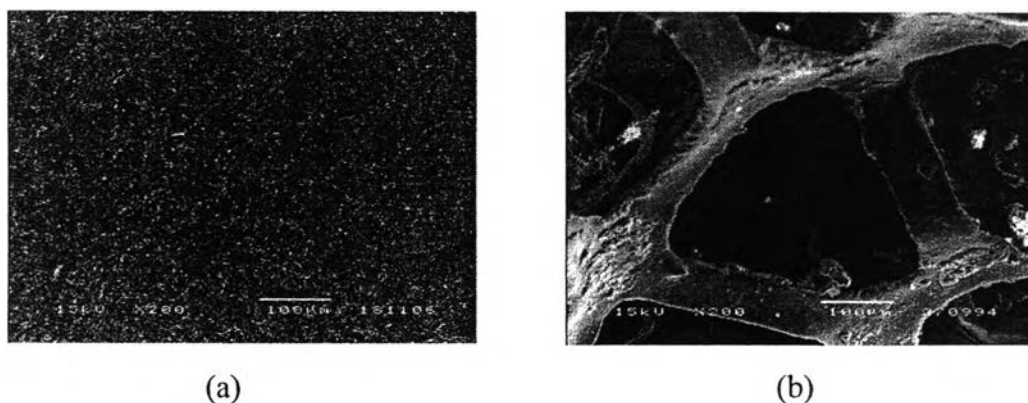**Figure 7.** SEM micrographs of; (a) chitosan-clay hydrogel (× 200), and (b) chitosan aerogel nanocomposite (× 200).

4. Conclusions

The present work demonstrated an effective conjugation of chitosan in simple conditions, i.e. in water at room temperature, using the water soluble chitosan-HOBt aqueous solution, and WSC conjugating agent. Chitosan aerogel nanocomposite were successful based on FTIR, TGA, SEM results. The morphology of chitosan aerogel nanocomposite showed porous structure and the water absorption at room temperature of chitosan aerogel nanocomposite increased when the amount of crosslinker decreased.

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