



CHAPTER III EXPERIMENTAL

3.1 Materials

Chitosan (95% DD, M_v of 5.6×10^5) was supplied by Seafresh Chitosan (Lab) Company Limited, Thailand. Poly (ethylene glycol) (PEG) (M_n 1450 Dalton) was purchased from Sigma-Aldrich, Inc., USA. 1-Hydroxybenzotriazole monohydrate (HOBt·H₂O) and 1-ethyl-3-(3-dimethylaminopropyl-carbodiimide) hydrochloride (EDC·HCl) were purchased from Wako Pure Chemical Industries Co. Ltd., Japan. Succinic anhydride was provided from Fluka Chemika, Switzerland. Pristine sodium montmorillonite (clay) with cation exchange capacity of 120 mequiv/100g (trade name: Cloisite Na⁺) was purchased from Southern Clay Product Inc. Montmorillonite clay surface modified with 15-35% octadecylamine (ODA) and 0.5-5 wt. % aminopropyltriethoxysilane (trade name: Nanoclay, Nanomer[®] I.31PS) was purchased from Sigma Aldrich Chemie GmbH, Germany.

3.2 Instruments and Equipment.

3.2.1 Structural Analysis

Fourier transform infrared (FTIR) spectra were obtained from an attenuated total reflection (ATR) accessory equipped on a Perkin Elmer Spectrum 1. The analysis was carried out with 32 scans at a resolution of 4 cm^{-1} over frequency range of $4000\text{-}400 \text{ cm}^{-1}$.

3.2.2 Surface Analysis

The BET surface areas of aerogels were determined by using an Autosorp-1 gas sorption system (Quantachrome Corporation). The calcined samples were preheated in nitrogen for 3-4 h at $100 \text{ }^\circ\text{C}$. Adsorption characteristics were measured under liquid nitrogen atmosphere.

3.2.3 Thermal Analysis

Thermogravimetric analyses were carried out using a Perkin Elmer Pyris Diamond with N₂ flow rate of 20 mL/min and a heating rate of $10 \text{ }^\circ\text{C/min}$ starting from 30 to 600°C .

3.2.4 Morphological Studies

The effectiveness of clay exfoliation was studied by using wide angle X-ray diffraction (WAXD) by a RIGAKU RINT 2000 with $\text{CuK}\alpha$ as an X-ray source ($\lambda=0.154178$ nm). The scanning range was $2-15^\circ$ with scanning rate of $2^\circ/\text{min}$.

3.3 Methodology

3.3.1 Preparation of chitosan hydrogel.

Chitosan-HOBt aqueous solution was prepared as reported previously [8]. Chitosan (0.1g, 0.61 mmol) was mixed with HOBt·H₂O (0.094g, 0.61 mmol) in 10 mL of deionized water at ambient temperature until the clear solution was obtained. PEG (M_n 1450, 20.00 g, 13.8 mmol) was reacted with succinic anhydride (2.762 g, 27.6 mmol) in the presence of pyridine 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). To the solution of chitosan-HOBt aqueous (10 mL), carboxy-terminated poly (ethylene glycol) 10% WSCl (0.235 g, 1.22 mmol, 10 mL) were added. The reaction was carried out at ambient temperature for 15 minutes to obtain chitosan hydrogel. The crude gel was dialyzed and lyophilized to obtain chitosan aerogel CD-1. In similar, chitosan aerogel CD-3, CD-5 and CD-7 were prepared by adding carboxy-terminated poly(ethylene glycol) 30%, 50% and 70% respectively.

3.3.2 Chitosan/clay nanocomposite hydrogel and aerogel.

Clay (closite Na^+ or nanoclay) for 1-5 wt % and COOH-PEG-COOH (1.70 g, 1.53 mmol) was added into chitosan-HOBt 10 mL solution and stirred at room temperature for 24 h. WSC was added into clay suspension solution to obtain chitosan/clay nanocomposite hydrogel. The product was lyophilized to obtain chitosan/clay aerogel. The content ratios of chitosan and clay were varied to be 1:0.01, 1:0.02, 1:0.03, 1:0.03, 1:0.04 and 1:0.05 to obtain aerogels CU-1, CU-2, CU-3, CU-4 and CU-5. Similarly, in the cases of unmodified clay, the aerogels obtained are CM-1, CM-2, CM-3, CM-4 and CM-5 for the ratios of chitosan: modified clay for 1:0.01, 1:0.02, 1:0.03, 1:0.04, and 1:0.05, respectively.