CHAPTER III
EXPERIMENTAL

3.1 Materials and Instrument

3.1.1 Chemicals:

- Carbazole monomer (Merck, AR grade)
- Ammonium persulfate (Sigma-Aldrich, AR grade)
- Glutaraldrhyde solution 50% in water (Fluka, AR grade)
- Sodium alginate (Sigma-Aldrich, AR grade)
- Ferric chloride (Sigma-Aldrich, AR grade)
- Dichloromethane (RCI Labscan, AR grade)
- Hydrochloric acid 37 % (RCI Labscan, AR grade)
- Ammonium hydroxide solution 27% (Merck, AR grade)
- Perhydrochloric acid (RCI Labscan, AR grade)
- Calcium chloride (Fluka, AR grade)
- Citric acid (Merck, AR grade)
- Cetyl trimethylammonium bromide (Fluka, AR grade)
- Tween 20 (Sigma-Aldrich, AR grade)
- Sodium dodecyl sulfate (RCI Labscan, AR grade)
- Deionized (DI) water

3.1.2 Instrument:

- Fourier Transform Infrared Spectrometer (Nicolet, Nexus 670)
- X-ray Diffraction Spectromete (Rigaku, Smartlab)
- Thermogravimetric Analyzer (DuPont, TGA 2950)
- Scanning Electron Microscope (Hitachi, S4800)
- Melt Rheometer (Rheometric Scientific, ARES)
- Two point probe couple with an electrometer
- DC power supply (Instek, GFG8216A)

3.2 Experimental

3.2.1 Polymerization of Polycarbazole

The synthesis procedure of polycarbazole followed Gupta *et al.* (2010) using carbazole monomer, ammonium persulfate, hydrochloric acid, and

dichloromethane. The reaction was carried out at room temperature. The 1.2 M of ammonium persulfate was dissolved in 50 ml of 0.5 M hydrochloric acid solution as an aqueous phase. Then 60 mM of carbazole monomer was dissolved in 50 ml of dichloromethane at various monomer: surfactant mole ratios equal to 1:0, 1:0.0034, 1:0068, 1:0.0136, and 1:0.0274 called a non-aqueous phase. The surfactants used were Tween 20, Cetyl trimethylammonium bromide, and Sodium dodecyl sulfate. Then, the aqueous and non-aqueous solutions were mixed for 24 h to induce the polycarbazole monomers to be at the interface between the two phases. After filtering, the green precipitate was collected and dried in hot air oven. Dedoping polycarbazole was performed by stirring the obtained polycarbazole in a solution of 1:10 mole ratio of ammonium hydroxide/polycarbazole. Then polycarbazole was redoped again with concentrated perhydrochlolic acid. The mole ratio of perhydrochlolic acid to carbazole ($N_{HClO4}:N_{PCB}$) was adjusted to be 5:1, 10:1, 50:1, 100:1, and 200:1.

3.2.2 Preparation of Sodium Alginate Hydrogel

A sodium alginate solution in distilled water (1.0 %v/v) was prepared at room temperature under continuous stirring for 40 min. (Kulkarni et al., 1999). The crosslinking of sodium alginate was prepared by ionic and covalent crosslinking methods. In the case of ionic crosslinking method, it was prepared by adding the appropriate volume of $CaCl_2$ solution to the sodium alginate solution at room temperature under continuous stirring for 30 min with $CaCl_2$ concentrations varying from 0.0050, 0.0100, 0.0150, 2.0, and 0.0200 %v/v. In the case covalent method, it was prepared by adding the appropriate volume of citric acid solution to the sodium alginate solution at 80 °C under continuous stirring for 30 min with citric acid concentration varying at 0.25, 0.50, 0.75, and 1.0 %v/v. Both of sodium alginate mixture solutions were poured into plastic petri dishes (10 cm of diameter). The alginate hydrogels were obtained after allowing water evaporation at room temperature for a period of 2 days and kept at 4°C for controlling water content in the alginate hydrogels.

3.2.3 Preparation of Polycarbazole/Sodium Alginate Hydrogel Blends

The synthesized polycarbazole was dispersed into 70 ml sodium alginate solution filled with a crosslinking agent. The concentration of polycarbazole was varied at 0.01, 0.05, 0.1, 0.3, and 0.5 %v/v. The solution was poured into a plastic Petri dish for casting at room temperature for 2 days to get the hydrogel blends.

3.3 Characterizations and Testing

A Fourier Transform Infrared Spectrometer, FT-IR (Nicolet, Nexus 670) was used to characterize the functional groups of the synthesized polycarbazole and the sodium alginate film. This technique was used to identify the absorption mode with 32 scans and a resolution of $\pm$ 4 cm^{-1}, covered a wavelength range of 4000-400 cm^{-1}, used deuterated triglycine sulfate as a detector. Optical grade KBr was used as a background material. The sample was ground with KBr and pressed to form pallets.

An X-ray diffractometer, XRD (Rigaku) was used to investigate the amount of crystallinity in the samples in a based hydrogel form. The diffractometer was operated in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffracted beam with a 5°/min scan rate.

A thermal gravimetric analyzer (DuPont, TGA 2950) was used to amount of moisture content and the decomposition temperatures of sodium alginate hydrogels. The thermal behavior was investigated by weighting example of 5-10 mg, placing it in a platinum pan, and then heating it under nitrogen flow with a heating rate of 10°C/min from 30-800°C.

A Scanning Electron Microscope, SEM (Hitachi, S4800) was used to examine the morphological structure of the synthesized polycarbazole and also was used to determine dispersion of polycarbazole in sodium alginate hydrogels. The samples were attached on to a brass-stub. Prior to observation, samples were gold sputtered.

The crosslinking density of hydrogel was analyzed by the swelling method of Gudeman and Peppas (1995). A sample of the hydrogel (1 cm^2 square) was cut and weighed in air and heptane (a non-solvent). The sample was placed in a stainless steel mesh basket which was suspended in heptane to obtain the accurate weight measurements in heptane. The sample was then placed in a buffer solution for 5 days to reach equilibrium, and then was weighed in air and heptane again. Finally, the sample was dried at 25 °C in a vacuum for 5 days. Once again, it was weighed in air and heptane. M_c, the average weight between crosslinks, was calculated from

$$\frac{1}{\overline{M_c}} = \frac{1}{\overline{M_n}} - \frac{\frac{\overline{v}}{\overline{V_1}}\left[\ln(1-v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2\right]}{v_{2,r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right]} \qquad (3.1)$$

where $\overline{M_n}$ is the number-average molecular weight of the polymer before cross-linking, $\overline{v}$ is the specific volume of alginate ($\overline{v}$ =0.60 cm^3/g of alginate), $\overline{V_1}$ is the molar volume of water (18.1 cm3/mol), $v_{2,r}$ is the volume fraction of the polymer in a relaxed state, $v_{2,s}$ is the volume fraction of the polymer in solvent state, χ_1 is the Flory polymer-solvent interaction parameter of alginate (χ_1 for alginate is 0.473).

The electrical conductivity of the synthesized polycarbazole was determined by pressing samples into disk pellets using a hydraulic press (diameter of 10 mm and 0.2 mm thick). Electrical conductivity was measured using a custom-built two-point probe meter connected with a voltage supplier, in which voltage was varied and the resultant current was measured. The regime where the resultant current is linearly proportional to the applied voltage is called the linear Ohmic regime. The voltage and the current in the Ohmic regime were converted to the electrical conductivity via Equation 3.2:

$$\sigma = 1/\rho = 1/(R_s \times t) = I/(R_s \times V \times t) \qquad (3.2)$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity (Ω.cm), R_s is the sheet resistance (Ω/sq), t is the thickness of the sample pellet (cm), V is the applied voltage (V), I is the measured current (A), and K is the geometric correction factor of the two-point probe meter, where $K = 4.29 \times 10^{-4}$. All sample thicknesses were measured by a thickness gauge (Peacock, PDN-20).

The electromechanical properties of the sodium alginate hydrogels were investigated in terms of electric field strength. A melt rheometer (Rheometric Scientific, ARES) was fitted with a copper parallel plate fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG8216A). A digital multimeter was used to monitor the voltage input. In these experiments, the oscillatory shear mode was applied and the dynamic moduli (G' and G") were measured as functions of frequency and electric field strength. Strain sweep tests was first carried out to determine the suitable strains to measure G' and G" in the linear viscoelastic regime. The frequency sweep tests was carried out to measure G' and G" of each sample as functions of frequency. The frequency was varied from 0.1 to 100 rad/s. Prior to each measurement, the sodium alginate hydrogel samples were pre-sheared at a low frequency under an electric field for 15 min to ensure the formation of equilibrium polarization before the G' and G" measurements. Experiments were carried out at the temperature of 30°C and repeated at least two or three times. The temporal response experiments were also carried out at 800 V/mm. For the electromechanical properties of polycarbazole/sodium alginate hydrogel composites, it was carried out with the same procedure as the pristine sodium alginate hydrogels.

The dielectrophoresis forces of the sodium alginate hydrogel and its composites were determined by measuring the deflection distances of the specimens in the vertical cantilever fixture under electric field. The specimens were vertically immersed in the silicone oil (viscosity=100 cSt) between parallel copper electrode plates (68 mm of length, 40 mm of width, and 2 mm of thickness). The gap between the pair of the electrodes was 30 mm. A DC voltage was applied with a DC power supply (Goldsun, GPS 3003B) connected to a high voltage power supply (Gamma High Voltage, UC5-30P and UC5-30N). A video camera was used to record the movement during experiment. Pictures were captured from the video and the

deflection distances in x (d) and y axes (l) at the end of the specimen and determined by using the Scion Image software (version 4.0.3). The electric field strength was varied between 0 and 550 V/mm at the room temperature of 303 ± 1 K. Both the voltage and the current were monitored. The resisting elastic force of the specimens were calculated under electric field using the non-linear deflection theory of a cantilever, which was obtained from the standard curve between $(F_e l_0^2)/(EI)$ and d/l_0 (l_0 = initial length of specimens); F_e is the elastic force, d is the deflection distance in the horizontal axis, l is the deflection distance in the vertical axis, E is the Young's modulus which is equal to $2G'(1+v)$, where G' is the shear storage modulus taken to be G' (ω = 1 rad/s) at various electric field strength and I is the moment of inertia $1/12t^3w$, where t is the thickness of the sample and w is the width of the sample. The electrophoresis force was calculated from the static horizontal force balance consisting of the elastic force, the corrective gravity force ($mg\tan\theta$), and the buoyancy force ($vg\tan\theta$) as shown in Equation (5.3):

$$F_d = F_e + mg(\tan\theta) - \rho Vg(\tan\theta) \tag{3.3}$$

where g is 9.8 m/s^2, m is the mass of the specimen, and θ is the deflection angle, ρ is the density of the fluid (silicon oil = 0.97g/cm^3), V is the volume of the displaced of fluid.