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Electromechanical properties of multi-walled carbon nanotube/gelatin hydrogel composites: Effects of aspect ratios, electric field, and temperature

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ABSTRACT

The effects of multi-walled carbon nanotube (MWNT) aspect ratio, electric field strength and temperature on the electromechanical properties of MWNT/gelatin hydrogel composites were investigated. The highest aspect ratio of MWNT provides the composites with the highest dynamic moduli under electric field. The MWNT/gelatin hydrogel composites of 0.01, 0.1, 0.5, and 1 vol.% and the pure gelatin hydrogel possess the storage modulus sensitivity values of 0.69, 1.23, 0.94, 0.81 and 0.47, respectively, at 800 V/mm. The results can be interpreted in terms of the enhanced polarizability between the carboxyl groups of gelatin under the presence of MWNT. The effect of temperature on the electromechanical properties of MWNT/gelatin hydrogel composites investigated between 30 °C and 90 °C shows three distinct regimes of temperature-dependent storage modulus behavior. In the deflection testing, the effects of electric field on the deflection distance and the dielectrophoresis force of the MWNT/gelatin hydrogel composites were also investigated. MWNT/gelatin hydrogel composites suspended in the silicone oil between electrodes, respond rapidly with a deflection toward the anode site, indicating the attractive force between anode and the polarized carboxyl group as the gelatin structure possesses negative charges.

1. Introduction

Electroactive polymers (EAPs) have been continuously utilized and developed for several applications such as muscle-like actuator, complaint electrode, robotics and drug release. Hydrogel is a promising material structure for the development of EAPs since it possesses a reversible response subject to external stimuli such as temperature [1,2], pH [3], ionic strength [4,5], and electric fields [6–8]. Gelatin is one type of hydrogels or EAPs; it is a biopolymeric-protein derived from animal collagen by thermal and hydrolyzing processes with either acid or bases. It is stable as a film, a hydrogel, or a composite [9]. Because gelatin possesses non-immunogenicity, biodegradability, biocompatibility, bioactivity and commercial availability at relatively low cost, it has been widely used in the medical fields such as drug delivery, wound dressings, and artificial muscles [10]. Usually, gelatin is produced by denaturing a naturally derived collagen in a solution through either an acidic or base process at high temperature in which the triple-helix structure is split to random coil structure. During the gel forming process at the temperature around 40 °C, the gelatin random chain in a warm aqueous solution undergoes a disorder–order transition into the coil–helix structure when cooled [11]. However, gelatin exhibits poor water resistance and low mechanical properties when compared with synthetic polymers, these limit its possible application as an EAP [12]. Therefore gelatin needs to be reinforced either through chemical crosslinking or using some filler materials. Chemical crosslinking enhances thermal and mechanical properties through covalent bonds between the reactive side groups in gelatin molecules. However, this process presents the residual crosslinking agents that lead to toxic side effects. MWNTs are chosen to enhance the mechanical and electromechanical properties in the gelatin hydrogel because they can provide the biocompatibility and great mechanical properties. In the previous works, Fraczek et al. [13] reported that MWNTs induced rapid tissue regeneration process. Nevertheless, the biocompatibility of MWNTs depended on their size, shape, length, and chemical surface. Chlopek et al. [14] reported that MWNTs possessed good biocompatibility to the cells studied (fibroblasts and osteoblasts). The use of multiwall carbon-nanotube (MWNT) as a reinforcement in gelatin has been studied by Li et al. [15]. They studied gelatin with MWNTs that can be embedded as an additive to enhance the mechanical properties of the gelatin hydrogel. Haider et al. [16] investigated the swelling of MWNT/gelatin hydrogel composites. MWNT could maintain the stability

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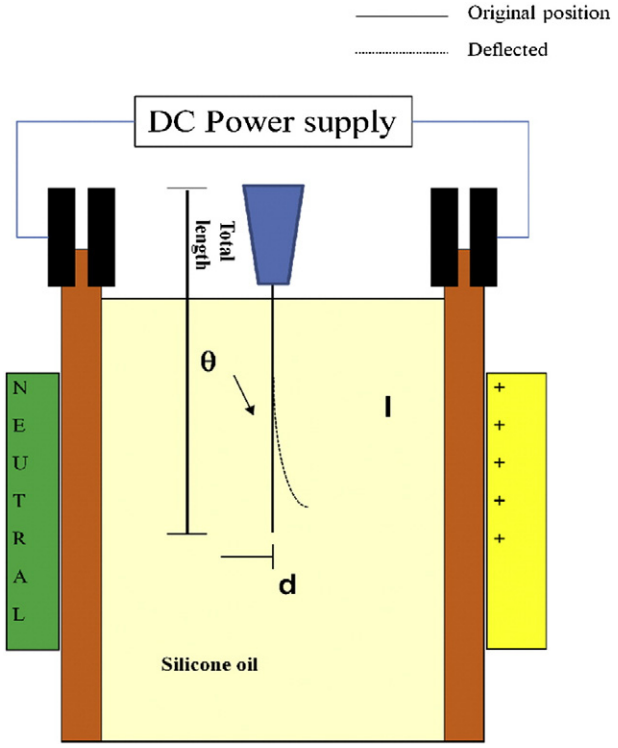

Fig. 1. Schematic diagram of the apparatus used to observe the dielectrophoresis force on the hydrogel samples.

of the composites without crosslinking agent due to the hydrophobic effect of the MWNT. Carbon nanotubes (CNTs) are an attractive form of carbon, consisting of concentric cylinders of graphite layer to graphene cylinders. CNT diameters are smaller than conventional carbon or glass fibers about 1000 times. Usually, nanotube aspect ratios are over 1000. The structural characteristics of CNTs are high aspect ratio, high surface area, and excellent mechanical, electrical and thermal properties. The MWNTs, used to enhance the mechanical properties of other hydrogels, have been previously investigated [17,18]. Chatterjee et al. [17] studied the mechanical strength of chitosan hydrogels with carbon nanotubes (CS/CNT). The 0.01 wt.% CS/CNT provided the greater mechanical strength than the crosslinked CS hydrogel. Tong et al. [18] investigated carbon nanotube/poly(vinyl alcohol) hydrogel to enhance the mechanical properties of the hydrogel and found that the 0.5 wt.% CNT/PVA hydrogel exhibited the improved tensile modulus, tensile strength and strain at break by 78.2%, 94.3% and 12.7%, respectively. Therefore MWNTs are excellent-promising-reinforcing materials for biopolymers that have been developed to several applications such as biosensor [19], and bioelectronic materials [20].

The objective of our investigation is to determine the electromechanical properties of multi-walled carbon nanotube/gelatin hydrogel composites containing an anionic surfactant (i.e., sodium dodecylsulfate) as candidate materials for actuator in robots or micro-devices. The electrical properties, thermal properties, and electrorheological properties were investigated in terms of MWNT concentration and aspect ratio, electric field strength, and temperature.

Table 1
Determination of density, diameter, and conductivity of multi-walled carbon nanotubes (MWNTs).

Samples	Quoted diameter of tube (nm)	Measured diameter of tube (nm)	Aspect ratios	Density (g/cm^3)	Average conductivity (S/cm)
MWNTs	3–10	9.47 ± 1.59	2100	2.103 ± 0.10	3237 ± 240
	10–20	18.38 ± 0.43	1200	2.170 ± 0.13	2161 ± 328
	20–30	27.09 ± 2.39	740	2.140 ± 0.10	1977 ± 195
	30–50	42.63 ± 3.85	470	2.143 ± 0.15	1693 ± 142

2. Experimental

2.1. Materials

Gelatin (Type B, bovine skin) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich (Singapore) and Loba Chemie (India), respectively. Various multi-walled carbon nanotubes (MWNTs, >95 wt.% purity), as purchased from Alphanano Technology Co., Ltd., China, have specified diameters of 3–10, 10–20, 20–30, and 30–50 nm.

2.2. Preparation of MWNT/gelatin hydrogel composites

The final volume fractions of MWNTs were 0.01, 0.1, 0.5, and 1 vol.% in which MWNT volumes were compared with the volume of gelatin. The MWNTs (0.00063; 0.0063; 0.032; 0.063 g) were dispersed in 10 ml aqueous medium filled with SDS (~0.03 g) by a transonicator (Elma, S 70H, D 78224) at 30 °C, 50/60 Hz, 150 W, and 15 min. Then gelatin (~2.94 g) was dissolved in distilled water (20 ml; pH = 6.40) at 40 °C 2 h by magnetic stirring. Finally, two solutions were well-mixed at 40 °C overnight through magnetic stirring to obtain mixtures with various MWNT/gelatin volume fractions of 0.01, 0.1, 0.5, and 1 vol.%. Then the solutions were poured into Petri dishes to obtain the MWNT/gelatin hydrogel composites through solvent casting. The hydrogel composites were allowed to settle in as a sheet at 25 °C. The thickness of hydrogel composites was about 1.64 mm.

2.3. Characterization and testing of MWNT/gelatin hydrogel composites

True density of each multi-walled carbon nanotubes (MWNT) was measured by a gas pycnometer (Thermo Nicolet, Nexus 670) which was operated in He gas atmosphere (20 psi) at 25 °C with a purging gas time of 1 min. The true density of MWNT was measured repeatedly 20 times to obtain the average value and the standard deviation.

The electrical conductivity measurement (Keithley, Model 8009A) of the MWNT film samples was measured at 25 °C, and the fixture consisted of two probes that made contact with the surface of the MWNT film samples. The test fixture was connected to the power source (Keithley, Model 6517A) to supply a constant voltage source and for reading the resultant current. The applied voltage and the resultant current were used to determine electrical conductivity of the MWNT film samples by the following Eq. (1):

$$\sigma = \frac{I}{\rho} = \frac{I}{R_s t} = \frac{I}{KVt} \tag{1}$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity (Ω cm), t is the specimen thickness (cm), R_s is the sheet resistivity (Ω), I is the measured current (A), K is the geometric correction factor, and V is the applied voltage (V).

Scanning electron micrographs were taken with a scanning electron microscope (SEM; S-4800, Hitachi, Tokyo, Japan) to determine the morphology and sizes of the MWNT in a powder form, pristine gelatin, and MWNT/gelatin composites at various MWNT concentrations. The cross-section micrographs of gelatin and MWNT/gelatin composites were obtained by using an acceleration voltage of 10 kV with magnifications of 60 000 times. SEM imaging software (SEMAFORE 5.21) was used to provide tube diameter.

The topology and phase images of specimens were obtained from the atomic force microscopy (AFM, Park System, XE-100) where images were taken in the non-contact mode with the cantilever (NSC-14-CrAu) tapping at a scan rate of 0.25 Hz. The electrostatic force microscope (EFM) was determined at signal amplitude of 5 V, and a scan size of 1.25 × 1.25 μm^2. Each sample was scanned at two height levels above