Electro-responsive Polythiophene/Carboxymethyl Cellulose Smart Hydrogels

Nanticha Danmatam[1,2]
Email: nanticha_d@cmu.ac.th
Datchanee Pattavarakorn*,[1,3]
Email: datchanee.p@cmu.ac.th
[1]Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, 50200, Chiang Mai, Thailand
[2]Graduate School, Chiang Mai University, 50200, Chiang Mai, Thailand
[3]Materials Science Research Center, Faculty of Science, Chiang Mai University, 50200, Chiang Mai, Thailand

Abstract

In this study, the conductive polythiophene/carboxymethyl cellulose (PTh/CMC) hydrogels were prepared. Polythiophene (PTh) was synthesized via chemical oxidative polymerization method by using ferric chloride ($FeCl_3$) as oxidizer. Monomer to oxidizer ratio and reaction time on electrical conductivity of PTh were investigated. The results showed that highest electrical conductivity (247.4432 ± 0.3569 S/cm) of PTh was found at the monomer to oxidizer ratio equal to 1:1 and reaction time was 24 hr. The effect of CMC concentration was also studied in order to obtain better hydrogel matrix properties. It was found that hydrogel prepared from 20 %wt CMC solution and crosslinked with citric acid had proper swelling ratio and highest tensile strength. PTh/CMC composite hydrogels were then prepared, conductive PTh particles was added in CMC solution and hydrogels were casted and crosslinked in citric acid solution. The electro-responsive properties, bending response, of the PTh/CMC composite hydrogel under DC electric field was finally examined.

Keywords: Carboxymethyl Cellulose, CMC, Polythiophene, Hydrogel, Smart hydrogel, Electroactive material

Introduction

Actuators are materials and devices capable of producing mechanical work as a response to external stimuli, e.g., electric field, magnetic field, heat, light, temperature, pH, and electrochemical stimuli. Among various external stimuli, using electrical excitation is the most attractive stimulation method because of the ease to control, convenience, and practical actuation. Variety of materials used as actuator materials have been reported, nano porous metals, carbon nanotubes, ionic polymer metal composites, and conductive or electroactive polymers. Polymer-based actuators are gaining attention due to the large variety of different physical and chemical inputs providing mechanical variations, broad range of strain, stress and conformation variations, simple processing in a large variety of forms and shapes, as well as the broad application spectra.

Electroactive polymers (EAPs) are type of flexible, elastic polymers or elastomers that change size or shape when stimulated by an electric field. Among EAP materials, conductive polymers are one attractive choice to be used in actuator because of their proper properties that make them fit as a promising material for artificial muscles (Bar-Cohen, 2001, 2008). Conductive polymers (CPs) or intrinsically conducting polymers (ICPs) are recognized as a class of organic materials with unique electrical and optical properties similar to inorganic semiconductors and metals. In recent year, the study on polythiophene conductive polymer gains attention due to its good thermal stability, good chemical stability, good environmental stability, have a semiconducting properties, good electronic and optical activities, and good mechanical properties (Uygun et al., 2009). Also, the polymerization of polythiophene is easy and stable which make it outstanding from other conducting polymers.

Nowadays, the fabrication of soft material actuators has been a subject of continuous interest. Especially, hydrogels prepared from natural or bio-based polymers have received immense considerations over the past decade due to their safe nature, biodegradability and/or biocompatibility, softness, and flexibility to sustain mechanical deformations (Shi et al., 2016). The conductive polymer/biopolymer hydrogels are considered as good candidates for some potential uses, which include bioconductors, biosensors, electro-stimulated drug delivery systems, tissue engineering, as well as soft actuators and soft machines. Carboxymethyl cellulose (CMC) is a derivative of cellulose in the form of carboxymethyl cellulose sodium salt (NaCMC), obtained from the reaction of the hydroxyl groups of the anhydroglucose units (AGUs) of cellulose with chloroacetic acid. It has attracted a great attention because of their low toxicity, renewability, biodegradability, and biocompatibility (Chen et al., 2020).

In this work, a series of polythiophene/carboxymethyl cellulose (PTh/CMC) hydrogels is aimed to fabricate. Conductive polythiophene is polymerized and doped via in-situ oxidative polymerization. CMC hydrogel was fabricated by studied on the effect of CMC concentration in citric acid solution on swelling ratio and mechanical properties. PTh/CMC hydrogels are then prepared and characterized for mechanical properties and the electroactive bending response properties of the PTh/CMC hydrogels are investigated under application of DC field.

Objective

To fabricate polythiophene/carboxymethyl cellulose hydrogels for use as soft actuator and evaluate the electroactive bending response properties of the polythiophene/carboxymethyl cellulose hydrogels.

Scope of research

1. Conductive polythiophene (PTh) synthesis procedure is optimized by varying monomer to oxidizer ratio and reaction time to obtain maximum electrical conductivity.
2. Carboxymethyl cellulose (CMC) hydrogels are prepared. The effects of CMC concentration on swelling ratio and mechanical properties are examined.
3. The polythiophene/carboxymethyl cellulose (PTh/CMC) hydrogels are prepared. The electroactive performances are investigated in the way of electroactive bending response properties under an applied DC electric field.

Research Methodology

1. Polythiophene synthesis and hydrogels preparation

1.1 Synthesis of polythiophene

Polythiophene (PTh) was synthesized and doped via oxidative polymerization by ferric chloride as an oxidizer at room temperature. The synthesis procedure was optimized by varying monomer to oxidizer ratio (1:1, 1:3, 1:6) and reaction time (6 and 24 hr.)

1.2 Fabrication of CMC hydrogels

CMC hydrogels were prepared at room temperature which citric acid was used as crosslink agent. The effects of CMC concentration (10, 20 and 30 %wt) on swelling ratio and mechanical properties were examined.

1.3 Fabrication of PTh/CMC hydrogels

PTh/CMC hydrogels were prepared at room temperature with PTh to CMC ratio of 1:10 and citric acid was used as crosslink agent.

2. Characterization methods

2.1 Electrical conductivity

The electrical conductivity of PTh was measured using the custom-built two-point probe coupled to an electrometer (Keithley, Model 6517A). The specific conductivity, σ (S/cm) of the pressed PTh pellets were obtained by measuring the bulk pellet resistance, R (Ω).

2.2 FT-IR

Transmission infrared spectra of the PTh were determined using a Fourier transform infrared spectrometer (PerkinElmer, Frontier L128-0010) at a resolution of 2 cm^{-1}, measurements were performed in a wavenumber range of 400 to 4000 cm^{-1}.

2.3 Scanning electron microscopy (SEM)

The morphology of PTh were observed with a low vacuum scanning electron microscope (LV-SEM, JEOL Ltd, JSM 5910 LV) with an accelerating voltage of 15 kV.

2.4 Thermogravimetric analysis (TGA)

The thermal properties of the PTh were assessed by TGA using a simultaneous thermal analyzer (Rikagu TG-DTA8120, Rikaru Corporation, Inc.). PTh samples (10 ± 0.2 mg) were placed in an Al_2O_3 pan and tested under a dynamic nitrogen atmosphere with a temperature range of 25 - 800 °C and a heating rate of 10 °C/min.

2.5 Solubility test

The CMC hydrogels were cut into square shape (2 cm in length and 2 cm in width) and immersed in distilled water for 24 hr. After that, the hydrogels were removed from distilled water and excess distilled water on hydrogels surface was wiped with tissue paper. The solubility of the hydrogels was calculated using following equation (Jing, Mi, Napiwocki, Peng, & Turng, 2017).

$$\text{Solubility} = [(W_2 - W_1)/W_1] \times 100\% \qquad (1)$$

Where W_1 and W_2 were hydrogel initial weight and weight after immersing in water, respectively.

2.6 Mechanical properties

Tensile properties of the CMC hydrogels were measured using a Lloyd universal testing machine (model LRX) according to ASTM D882-02 in a pull-with-yield mode. Hydrogel specimens were cut in dumbbell shape (type IV). The gauge length and cross speed were 25 mm and 10 mm/min, respectively.

2.7 Electro-response properties measurement

The electro-response properties of the PTh/CMC hydrogel were investigated in the term of the bending response. The samples were vertically immersed in silicon oil, 100 cSt, with a DC electric field applied between two copper electrodes (30 mm long, 30 mm wide, and 1.0 mm in thickness; the distance between the electrodes is 50 mm). All of experiments were recorded by video camera and the amount of deflection bending angle (θ) was calculated from the following equation,

$$\theta = \arctan (A/B) \tag{2}$$

where A was the measured deflection distance and B is the sample length. Which were detected by Image J program.

Results and Discussion

1. Electrical conductivity of PTh

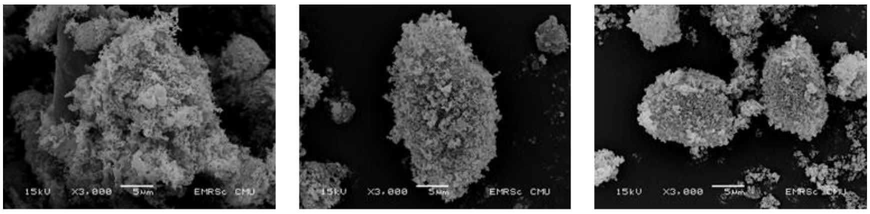
Electrical Conductivity of PTh was shown in Table 1. It was found that PTh 1-1_24 (monomer to oxidizer ratio = 1:1 with 24 hr. reaction time) had highest electrical conductivity (247.4432 ± 0.3569 S/cm).

Table 1: Electrical conductivity of PTh.

Sample	Electrical conductivity (S/cm)
PTh 1-1_6	49.8668 ± 5.0325
PTh 1-1_24	247.4432 ± 0.3569
PTh 1-3_6	6.5536 ± 7.7907
PTh 1-3_24	0.1927 ± 0.1081
PTh 1-6_6	0.0028 ± 0.0012
PTh 1-6_24	0.0015 ± 0.0003

With increase in a molar ratio to 1:6 with reaction time of 24 hr., PTh showed a rapidly decrease in electrical conductivity (0.0015±0.0003 S/cm). It can be seen that electrical conductivity was decreased with increasing monomer to oxidizer ratio and reaction time. This result probably due to the over-oxidation of PTh when reacted with a high amount of oxidizer ($FeCl_3$) resulting in low electrical conductivity (David, Mathad, Padmavathi, & Vanaja, 2014).

2. Morphology of PTh



PTh 1-1_24 PTh 1-3_24 PTh 1-6_24

Figure 1: Surface micrographs of PTh particles.

Figure 1 shows surface micrographs of PTh particles by Scanning Electron Microscopy (SEM). The PTh particles showed an aggregated oval-shaped structure with the particle radius size of 100–150 nm. Moreover, PTh 1-1_24 had highest fibril characteristic which affect to the highest conductivity value.

3. FTIR spectra of PTh

Figure 2 shows FTIR spectra of PTh samples. The spectra showed peaks as follows; the peak at 1446 cm^{-1} corresponding to aromatic C=C stretching, the peak at 1303 cm^{-1} corresponding to C=C symmetric stretching, the peak at 1085 cm^{-1} corresponding to C-H aro-matic in-plane bending vibration, the peak at 725 cm^{-1} corresponding to C-H out of plane stretching, the peak at 745 cm^{-1} corresponding to C-S bending vibration, the peak at 1193 cm^{-1} corresponding to C-H aromatic in-plane bending vibration, the peak at 1397 cm^{-1}corresponding to C=C stretch of quinoid ring. Moreover, two peaks were appeared at 674 cm^{-1} and 641 cm^{-1} corresponding to C-S-C ring stretching and doped Cl^{-} ion (Kamat, Puri, & Puri, 2012; Thanasamy, Jesuraj, Konda kannan, & Avadhanam, 2019). However, peak at 674 cm^{-1} which observed in PTh 1-6_24 was appeared to shift to 641 and 629 cm^{-1} for PTh 1-3_24 and PTh 1-1_24, respectively. This shift may due to the formation of a complex between Cl^- and C=C (from proper ratio of oxidizer and thiophene monomer) which resulted in the higher electrical conductivity of PTh as monomer to oxidizer ratio was varied from 1-6 to 1-3 and 1-1, respectively.

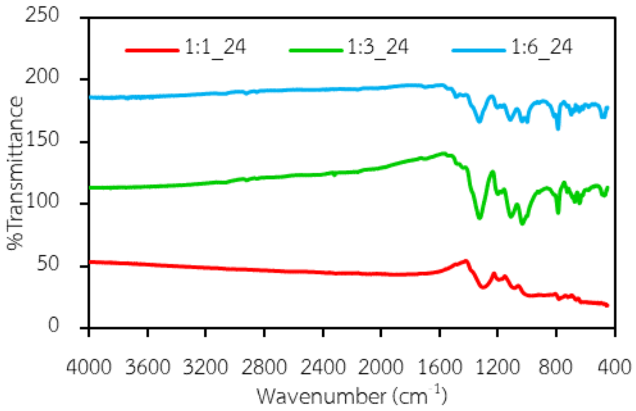


Figure 2: FTIR spectra of PTh.

4. Thermal properties of PTh

Thermal properties of PTh were tested in a nitrogen atmosphere; the TGA and DTG curves of PTh powder are presented in Fig. 3(a) and 3(b), respectively. It can be seen in Fig. 3(a) that thermal decomposition of the PTh occurred in 3 stages. The first stage of weight loss appeared at a temperature range of 50 - 100 °C, it was due to the evaporation of moisture, solvent, and unreacted monomer. The second stage of weight loss was seen at 250 - 300 °C, it was resulted from the loss of dopant component of polythiophene. The third stage of weight loss appeared from 350 - 400 °C, it was attributed to degradation of polythiophene (Acharya, Mishra, & Roy, 2010; Futane, Raut, & Dhande, 2016). From TGA curve, it was found that initial decomposition temperature for a 10% weight loss (T_{onset}), the decomposing temperature for a 50% weight loss (T_{50}) and the temperature for a maximum degradation rate (T_{max}) of PTh 1-6_24 were higher than PTh 1-3_24 and PTh 1-1_24. It can be verified that thermal stability of PTh was increased with the increase of oxidizer ratio. The higher thermal stability might be due to the presence of chloride ion in PTh polymer chain.

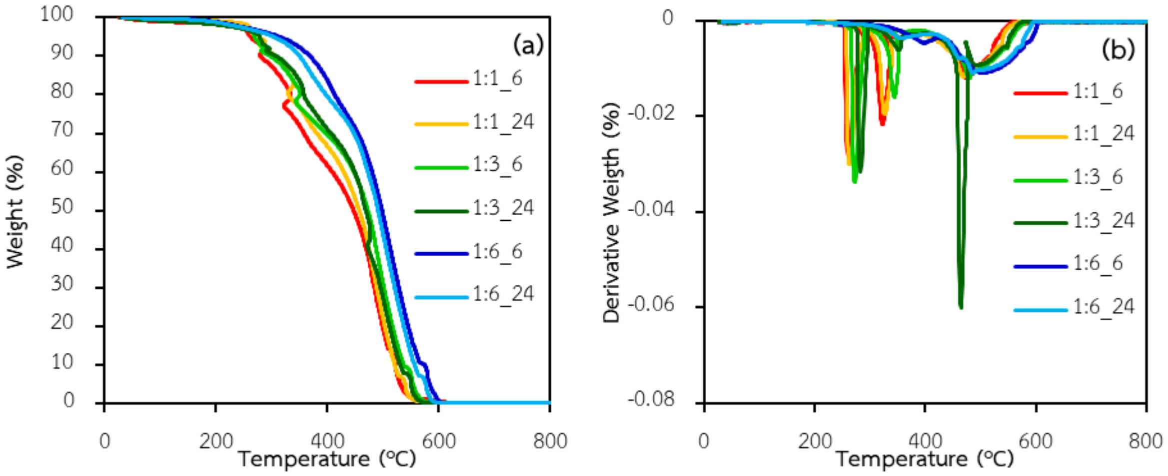


Figure 3: TGA (a) and DTG (b) thermograms of PTh.

5. Solubility of CMC hydrogels

The water solubility was monitored by examining the weight change in distilled water at room temperature which tabulated in Table 2. The results showed that CMC10 had lowest solubility (-2.66 ± 1.38) due to the dissolved of excess citric acid. CMC30 had highest solubility (2.73 ± 1.38), this could be from free CMC molecules, that do not crosslink with citric acid, interact with water molecules. While CMC20 showed not significantly change in solubility (0.31 ± 0.28) this could be referred to the maximum degree of crosslink between CMC and citric acid.

Table 2: Solubility, thickness, and tensile properties of CMC hydrogels.

Sample	Solubility	Thickness (mm)	Tensile strength (KPa)	Elongation at break (%)	Young's modulus (MPa)
CMC10	-2.66 ± 1.38	1.37 ± 0.23	220.90 ± 42.05	83.43 ± 9.90	9004.86 ± 5905.36
CMC20	0.31 ± 0.28	1.73 ± 0.03	1031.55 ± 50.14	130.53 ± 15.48	1599.00 ± 233.57
CMC30	2.73 ± 1.38	2.10 ± 0.03	810.96 ± 70.43	105.20 ± 16.28	1386.57 ± 179.39

6. Mechanical properties of CMC hydrogels

From Table 2, CMC20 hydrogel exhibited highest tensile strength and elongation at break, 1031.55 ± 50.14 KPa and 130.53% ± 15.48, respectively. This probably due to the optimal ratio between CMC and citric acid for crosslink causing in proper mechanical properties. In contrast, the increasing CMC concentration to 30 %wt leading to the decrease of tensile strength and elongation at break.

7. Electro-response properties of PTh/CMC hydrogel

The electroactive performance of PTh/CMC hydrogel, fabricated with PTh 10%wt in 20% CMC solution (PTh 1-1_24, which had highest electrical conductivity and tensile strength), in the term of the bending response test under an applied electric field strengths of 400 V/mm.

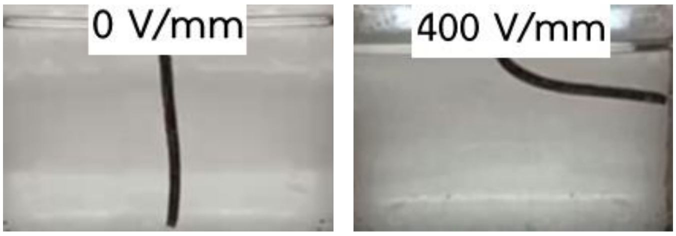


Figure 4: Bending response of PTh/CMC hydrogel under DC electric field of 0 and 400 V/mm.

From Figure 4, the PTh/CMC hydrogel bend toward the cathode electrode with highest bending angle of 76.218 degree after it was activated with 400 V/mm DC field. The bending behavior of hydrogel under the electric field occurred from the polarization of Na^+ and H^+ of CMC matrix and $-S^+-$ of PTh therefore the hydrogel is bended to cathode side, and it thereby the free end bend toward the cathode side.

Conclusion

PTh 1-1_24 synthesized with monomer to oxidizer ratio = 1:1 and 24 hr. reaction time had highest electrical conductivity of 247.4432 ± 0.3569 S/cm. The results show that CMC hydrogel prepared from 20%wt CMC solution exhibited the proper solubility and highest tensile strength. In addition, the PTh/CMC composite hydrogel immediately responded to DC electric field stimulus by bending toward cathode electrode. The highest bending angle of 76.218 degree was observed under the electric field strength of 400 kV/mm.

Acknowledgements

This research work was partially supported by the Center of Excellence in Materials Science and Technology, Faculty of Science, Chiang Mai University and the Graduate School, Chiang Mai University.

References

Acharya, A., Mishra, R., & Roy, G. S. (2010). Characterization of CdSe/Polythiophene nanocomposite by TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA and FTIR. *Armenian Journal of Physics,* 3, 195-202.

Bar-Cohen, Y. (2001). Electroactive Polymers as Artificial Muscles - Reality and Challenges. *19th AIAA Applied Aerodynamics Conference*.

Bar-Cohen, Y. (2008). Electroactive Polymer Actuators and Sensors. *MRS Bulletin,* 33, 173-181.

Chen, W., Bu, Y., Li, D., Liu, C., Chen, G., Wan, X., & Li, N. (2020). High-strength, tough, and self-healing hydrogel based on carboxymethyl cellulose. *Cellulose,* 27(2), 853-865.

David, T., Mathad, J. K., Padmavathi, T., & Vanaja, A. (2014). Part-A: Synthesis of polyaniline and carboxylic acid functionalized SWCNT composites for electromagnetic interference shielding coatings. *Polymer,* 55(22), 5665-5672.

Futane, R. S., Raut, V. M., & Dhande, S. D. (2016). Synthesis and characterisation of polythiophene and Tio2 doped polythiophene thin films by chemical bath deposition. *Rasayan Journal of Chemistry,* 9, 842-848.

Jing, X., Mi, H.-Y., Napiwocki, B. N., Peng, X.-F., & Turng, L.-S. (2017). Mussel-inspired electroactive chitosan/graphene oxide composite hydrogel with rapid self-healing and recovery behavior for tissue engineering. *Carbon,* 125, 557-570.

Kamat, S. V., Puri, V., & Puri, R. K. (2012). Room temperature synthesis and characterization of polythiophene thin films by chemical bath deposition (CBD) method. *Materials Chemistry and Physics,* 132(1), 228-232.

Shi, Z., Gao, X., Ullah, M. W., Li, S., Wang, Q., & Yang, G. (2016). Electroconductive natural polymer-based hydrogels. *Biomaterials,* 111, 40-54.

Thanasamy, D., Jesuraj, D., Konda kannan, S. K., & Avadhanam, V. (2019). A novel route to synthesis polythiophene with great yield and high electrical conductivity without post doping process. *Polymer,* 175, 32-40.

Uygun, A., Turkoglu, O., Sen, S., Ersoy, E., Yavuz, A. G., & Batir, G. G. (2009). The electrical conductivity properties of polythiophene/TiO2 nanocomposites prepared in the presence of surfactants. *Current Applied Physics,* 9(4), 866-871.