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Effect of chitosan and ions on actuation behavior of cellulose–chitosan laminated films as electro-active paper actuators

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Abstract Cellulose-chitosan laminated films were made for Electro-Active Paper (EAPap) actuators and the effect of chitosan and different types of free ions namely, Cl^-, NO_3^- and CF_3COO^- were investigated on the actuation behavior. The fabrication process of the films was explained and the actuation performance was tested in terms of bending displacement of the actuators. It was observed that, chitosan content and type of free ions influence the tip displacement of the actuators. Cl^- was found the best free ion among others, and detail observations are explained. By laminating chitosan layer on the cellulose films, the humidity sensitiveness of cellulose EAPap actuators was reduced.

Keywords Cellulose · Chitosan · Anion · Electro-active paper · Bending actuator

Introduction

Cellulose is the most abundant natural polymer on earth, consisting of glucose-glucose linkages arranged in linear chains (Brown Jr. et al. 1996, Gindl 2006). Cellulose is found in plants as micro fibrils, these form the structurally strong frame work in the cell walls, making it an inexhaustible source of raw material for environmental friendly and biocompatible products. Cellulose is mostly prepared from wood pulps and cottons and sea plants. Cellulose derivatives are used for coatings, laminates, optical films, pharmaceuticals, foods and textile industries (Klemm et al. 2005). Despite of many studies and researches on cellulose, potential of cellulose has not been fully explored. Recently, the discovery of cellulose as a smart material has been reported and can be used for biomimetic sensor/actuator devices and microelectromechanical systems (Kim et al. 2006a). EAPap actuator can produce a large bending displacement with low actuation voltage and low power consumption. This material has merits in terms of lightweight, dry condition, biodegradability, abundance, large displacement output and low actuation voltage. Possible application areas of this material are micro-insect robots, flying objects, flying magic paper, flower-robots, smart-wall-papers, e-papers and MEMS sensors. However, this material is sensitive to humidity, and its performance is degraded with time (Kim et al. 2006b).

As an attempt to improve the performance of EAPap actuator, polypyrrole and polyaniline conductive polymers were coated on cellulose EAPap materials (Kim et al. 2006c). The conductive polymer-coated EAPap actuator exhibited a large displacement output, but it was still sensitive to

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humidity and the degradation was not improved. The performance degradation may be associated with the break of fixed ions connected to hydroxyl groups in cellulose. There are some ions remained in cellulose EAPap from the dissolving process of cellulose fibers (Mark 1989). Fixed ion is an ion that is fixed to the molecular chain of cellulose. Free ion is an ion that is easily movable. In the presence of electric field, these fixed ions can hardly move to positive electrode. On the contrary, free ions are approximately free, so as to move to the negative electrode in the presence of electric field. As the free ions migrated to the negative electrode, and the repelling force between sodium ions let the film bend to the positive electrode direction. Thus, as fixed ion movable in the presence of electric field, free ions migration does not produce any bending displacement (Yan et al. 2003). Thus, it is necessary to hold fixed ions firmly in the presence of electric field. For this sake, we attempted to introduce chitosan in cellulose EAPap material. Chitosan, a homopolymer of glucosamine and N-acetylgluco-samine units linked by 1-4 glucosidic-bonds, is obtained by N-deacetylation of chitin, which is the second most naturally occurring bio-polymer after cellulose (Li et al. 2002). Chitosan is a biocompatible polymer reported to exhibit a great variety of useful biological properties.

Recently, the antibacterial and antifungal activity of chitosan has been followed with the great interest. Mixtures of the natural polysaccharides chitosan and cellulose are of great interest, since the molecular structures of cellulose and chitosan are very similar (Fig. 1, Li et al. 2002), which is expected to give high compatibility between cellulose and chitosan, so

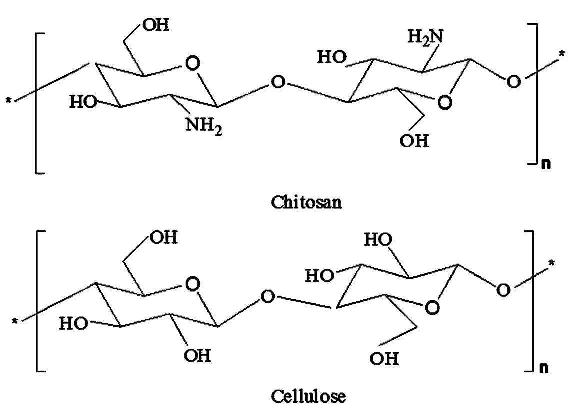

Fig. 1 Structure of cellulose and chitosan

blending deformation of cellulose and chitosan is expected to be useful. They also combine the availability of cellulose with the unique properties of chitosan. Articles made of these composites can be both technical purposes, as sorbents, for examples, and in medicine as film dressings, etc. (Rogovina et al. 1998; Twu et al. 2003). A composite chitosan-cellulose membrane has been prepared by coating chitosan on filter paper (Yang et al. 2002). In the present investigation, effect of chitosan and different types of free ions namely, Cl^-, NO_3^- and CF_3COO^- on actuation behavior of the cellulose–chitosan laminated film are demonstrated. The fabrication process, actuation behavior and test results are discussed here.

Experimental

Chitosan (Medium molecular weight; Mw = 600,000; viscosity 200×10^3 cps; deacetylation degree 86.8 %) provided by Aldrich, USA. Cotton cellulose (MVE, DPw 4580) was purchased from Buckeye Technologies Co., USA. Its alpha cellulose is 99.3%, dry basis weight is 569.5 g/m^2 and the dry density is 0.581 g/cm^3. Cotton is a cellulosic fiber, which took highest place among the family of fibers including natural and synthetic. Owing to the several good properties it has, cotton plays most prominent role in apparel industry. Cotton possesses many useful characteristics such as comfort, it is soft to the hand, has good absorbency, color retention, good strength, (Mondal and Hu 2007; Janhom et al. 2004). Hydrochloric acid (36.5–38%) and N,N-Dimethylacetamide (DMAc, anhydrous, 99.8%) were purchased from Sigma Aldrich, USA. The anhydrous DMAc was carefully dried with molecular sieves (4 A°) one week before use. Extra pure lithium chloride and glycerol (as a plasticizer) were purchased from Junsei Chemicals Co., Japan. Nitric acid (60%, extra pure) and trifluoroacetic acid (99.0%) were purchased from DC Chemicals Co. Ltd and Samchun Pure Chemicals Co. Ltd., South Korea, respectively.

Cellulose and LiCl were heated under reduced pressure at 110°C for 1 h, and the LiCl was dissolved in DMAc. Then the cellulose was mixed with LiCl-DMAc solution according the proportion of cotton cellulose pulp/LiCl/DMAc is equal to 1.25/8.75/90 and heated at 155°C, followed by cooling to 40°C for

2 h. Chitosan solution was prepared by mixing a desired amount of acid (like hydrochloric acid, nitric acid and trifluoroacetic acid), glycerol, chitosan and deionized water and stirred for 1 h, and kept for 24 h at room temperature. The chitosan concentration was 0.666 wt% (the viscosity is about 140.5 mPa·s at 25°C).

Two types of laminated films namely laminated films I and II, were prepared to study the effect of anion and chitosan amount on the actuation behavior. Laminated film I was made to investigate the effect of anions: 40 g cellulose solution was cast on the glass plate in room temperature and allowed for 2 h. Immersing the glass plate into water, the cast solution became a wet film. The wet cellulose film was fixed on its edges and washed with flowing tap water for 8 h, and then immersed in deionized water for 24 h. After drying the film 2 h in air, the mixture of glycerol (0.75 g) and water (5 g) was coated again, and laid in air for 1 day. The chitosan solution (the chitosan mass concentration is 0.666 wt%) made by different acids (hydrochloric acid, nitric acid and trifluoroacetic acid) were then cast on the cellulose film and laid in air for 2 days. Depending on the type acids used, the samples were named as Chi- HNO_3, Chi-HCl and Chi- TFA. Table 1 shows the details of the laminated films I. The mass of acid (HX) and chitosan was calculated by the formula as,

$$m_{HX}/M_{HX} : m_{GA}/M_{GA} = 0.95 : 1$$
$$m_{GA}/M_{GA} : (m_{GA}/M_{GA} + m_{AGA}/M_{AGA}) = 0.868 : 1$$
$$m_{GA} + m_{AGA} = m_{chitosan} \quad (1)$$

m_{HX}, m_{GA}, m_{AGA} and $m_{chitosan}$ are the mass of HX, glucosamine-part, acetyl glucosamine-part and chitosan, respectively. M_{HX}, M_{GA} and M_{AGA} are molar mass of HX, glucosamine structure unit and acetyl glucosamine structure unit, respectively.

Laminated film II was made for studying the effect of chitosan amount. Laminated film II was also prepared as explained earlier. Depending on the amount of chitosan, samples were named as Chi-05, Chi-10 and Chi-20. Table 2 shows the details of the films. The moisture content were measured as follows: A piece of the film about 0.1 g was cut from the whole film, and put it in an oven at 100°C for 2 h, and measure its original weight (W_0). It was put it in the environmental chamber. The temperature was controlled to 25°C and the humidity was controlled to 30, 40, 50, 60, and 70%RH for 2 h, and measure the weight (W_i). The moisture content (%) (W_a) is calculated as,

Table 1 Details of the laminated film I

Element		Sample		
		Chi-HNO_3	Chi-HCl	Chi- TFA
Cellulose concentration (wt%)		1.25	1.25	1.25
Pure cellulose (g)		0.5	0.5	0.5
Glycerol-1 (g)		0.5 × 1.5	0.5 × 1.5	0.5 × 1.5
Chitosan concentration (aqueous, wt%)		0.666	0.666	0.666
Chitosan (g)		0.1	0.1	0.1
HX (pure, g)		HNO_3–0.0313	HCl- 0.0181	TFA- 0.0567
HX : glucosamine unit (mol)		0.95	0.95	0.95
Glycerol-2 (g)		0.1 × 1.5	0.1 × 1.5	0.1 × 1.5
Anion concentration of the film ($\times 10^{-5}$ mmol/mm^{-2})		2.208	2.208	2.208
Moisture content (%)	Humidity (30%)	11.05	11.28	12.77
	Humidity (40%)	15.16	15.82	17.35
	Humidity (50%)	20.60	22.02	25.23
	Humidity (60%)	25.16	27.82	29.25
	Humidity (70%)	38.44	40.53	52.46

Table 2 Details of the laminated film II

Element		Sample		
		Chi-05	Chi-10	Chi-20
Cellulose concentration (wt%)		1.25	1.25	1.25
Pure cellulose (g)		0.5	0.5	0.5
Glycerol-1 (g)		0.5 × 1.5	0.5 × 1.5	0.5 × 1.5
Chitosan concentration (aqueous, wt%)		0.666	0.666	0.666
Chitosan (g)		0.05	0.1	0.15
HCl (pure, g)		0.0091	HCl- 0.0181	0.0272
HX : glucosamine unit (mol)		0.95	0.95	0.95
Glycerol-2 (g)		0.05 × 1.5	0.1 × 1.5	0.15 × 1.5
Anion concentration of the film ($\times 10^{-5}$ mmol/mm^{-2})		1.104	2.208	3.312
Moisture content (%)	Humidity(30%)	11.12	11.28	12.34
	Humidity(40%)	13.16	15.82	16.35
	Humidity(50%)	19.34	22.02	24.23
	Humidity(60%)	23.15	27.82	29.54
	Humidity(70%)	35.44	40.53	48.46

$$W_a = (W_i - W_0) / W_0 \times 100 \quad (2)$$

The moisture content (%) of the films was listed in Tables 1and 2.

Finally, gold electrodes were coated (0.1 μm thickness) on both the sides of the films (both for laminated films I and II) by a physical vapor deposition. Figure 2 shows the configuration of the cellulose-chitosan laminated films. The effect of chitosan and anion on the actuation behavior of cellulose–chitosan laminated films was investigated by measuring the bending displacement at the tip of the laminated films. Details of the displacement measurement system are explained in the previous paper (Kim et al. 2006b). In the displacement test, one side the film is fixed vertically such that the other side is free. When an electric field is applied on electrodes, the film bends and the displacement at the tip of the film is measured using a laser displacement sensor, which is termed as tip displacement. Generally, tip displacement depends on the actuation voltage and frequency. As the voltage increases the displacement increases. However, as the frequency increases, the displacement increases and decreases after a certain frequency value. This frequency that shows the maximum tip displacement is termed as resonance frequency.

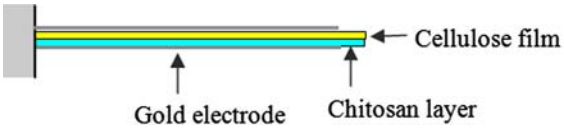

Fig. 2 Configuration of the cellulose-chitosan laminated films

Results and Discussion

Cellulose-chitosan laminated films-I and -II were successfully made. Figure 3 shows the scanning

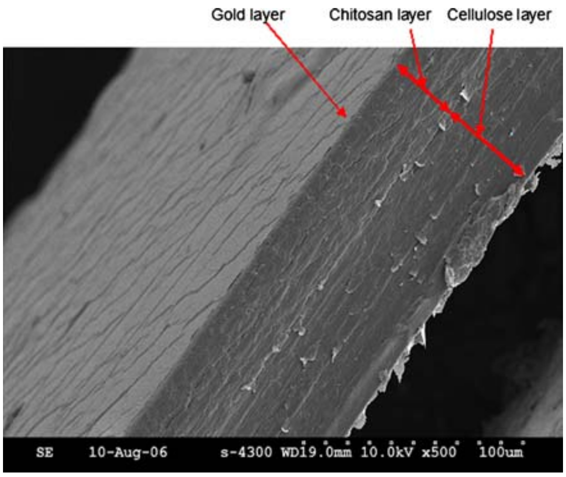

Fig. 3 Scanning electron microscope image at the cross section of the laminated film I

electron microscope (SEM) image at the cross section of the laminated film I. The cellulose film thickness is about 40 µm and the chitosan layer thickness is about 20 µm. Since the gold layer is so thin that its thickness can be hardly seen. To investigate the actuation principle, of cellulose-chitosan laminated EAPap actuator, dc actuation test was performed. On the dc voltage (4.5 V), the tip of the sample moved from the vertical position to the negative electrode (cathode), the moving rate was very slow in the beginning, but it became fast and saturated as the time increased. The actuation principle of cellulose EAPap actuator has been claimed as a combination of piezoelectric effect associated with ordered regions in the cellulose film and ion migration effect associated with water molecules and ions included in disordered regions in the cellulose film (Kim et al. 2006a). In addition to the actuation principle cellulose EAPap actuator, the chitosan layer will give another effect. Figure 4 shows the additional effect of chitosan layer in cellulose-chitosan laminated films as an EAPap actuator. The cations ($-NH_3^+$) connected with chitosan molecular chains are fixed ions that cannot move freely, but the anions (X^-) are free ions that can freely move. Thus, under low dc voltage condition, the fixed ions ($-NH_3^+$) cannot nearly move to negative electrode (cathode), while the free ions (X^-) move to positive electrode (anode). As the anions (X^-) assemble at anode, the repelling force between the anions (X^-) makes the film bend to negative electrode.

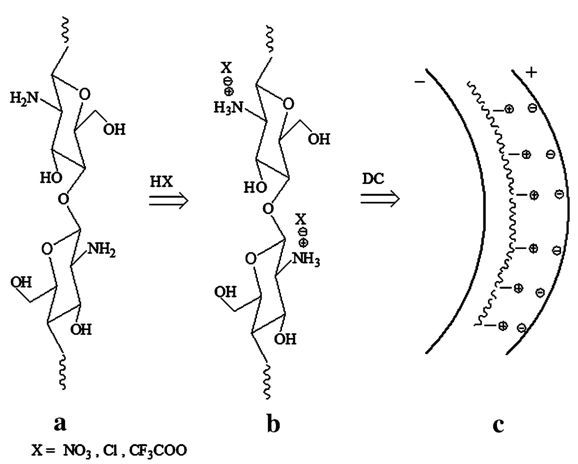

Fig. 4 Actuation principle of the cellulose-chitosan laminated films under dc voltage: **a**. Chitosan chains, **b**. With acetic acid, **c**. When dc field is applied

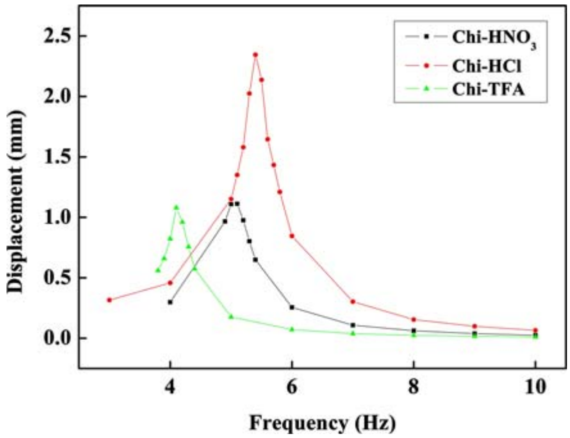

Fig. 5 Actuation behavior of laminated films I (Chi-HNO_3, Chi-HCl, Chi-TFA): 25°C, 60%RH, 2 V

Figure 5 shows the typical actuation behaviors of the laminated film I (Chi-HNO_3, Chi-HCl, Chi-TFA) with the actuating frequency variation. Temperature, humidity and voltage of the testing were 25°C, 60%RH and 2 V, respectively. For Chi-HNO_3, Chi-HCl and Chi-TFA, the displacements increased with the frequency from 3 to 10 Hz. As the frequencies were 5.1, 5.4 and 4.1 Hz, the tip displacements of Chi-HNO_3, Chi-HCl and Chi-TFA cases showed peak values (1.1, 2.3 and 1.0 mm). These frequencies that show the maximum tip displacements are resonance frequencies. The resonance frequency of Chi-HCl is higher than others. As Figure 4 explains, the actuation principle is based on the movement of anions. By comparing displacement outputs of laminated films I, Cl^- is the best anion (free ion) that improves the displacement output of cellulose EAPap actuators among other anions.

Figure 6 shows the typical actuation behaviors of the laminated films II (Chi-05, Chi-10, Chi-15) with the actuating frequency variation. The test condition was same as the previous test. The peak displacements of 1.8, 2.3 and 1.9 mm were observed at 4.1, 5.4 and 6.7 Hz for Chi-05, Chi-10, Chi-15 samples, respectively. Note that as the amount of chitosan increased, the number of Cl^- per unit area increased, resulting in the enhanced repelling force. This improved the displacement output of the samples. However, the thickness also increased with the increase of chitosan content, and since the electric

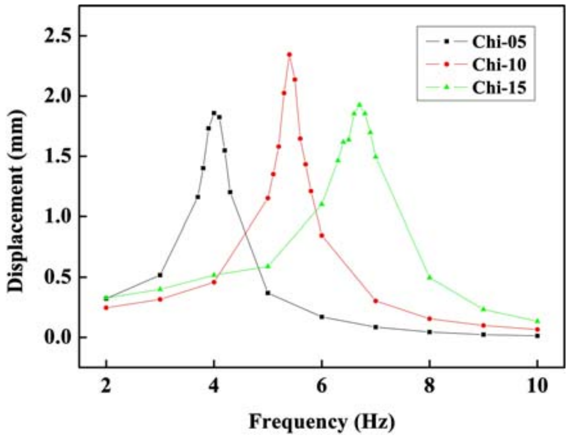

Fig. 6 Effect of chitosan on displacement of laminated film II (Chi-05, Chi-10, Chi-15), 25°C, 60%RH, 2 V

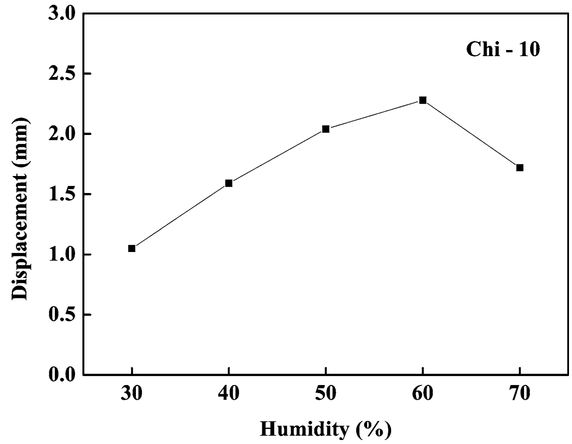

Fig. 8 Effect of humidity on the displacement for Chi-10: 25°C, 2 V

field strength per unit thickness decreased, the free ions (Cl^-) moving rate might be lowered.

Figure 7 shows the actuation behaviors of the Chi-10 with the actuating frequency and voltage variations. The testing condition was same as the previous one. The displacement increased with the voltage, and peak displacements of 1.4, 2.4, and 3.0 mm were seen at the resonance frequency, 5.4 Hz when the actuating voltage was 1, 2 and 3 V, respectively. As the voltage increased, the free ions (Cl^-) moving force increased, thus the tip displacement increased.

Figure 8 shows the actuation behaviors of the Chi-10 with the humidity change. The displacement increased with the humidity increase, but decreased after 60%. As humidity increased, the moisture content of the film increases, and the film becomes soft so as to improve the mobility of anion (Cl^-), which results in the tip displacement improvement. On the contrary, the displacement can be decreased when the humidity level is too high. With high humidity condition, the chitosan molecular chains neutralized with HCl can possess water-solubility. Eventually, the mobility of the chitosan molecular chains that contain ammonium fixed ions ($-NH_3^+$) increases slowly with the moisture content in the presence of electric field. And this mobility increase of the chitosan molecular chains can deteriorate the ion migration effect. Fixed ions in cellulose EAPap should be remained in the presence of electric field to attract free ions.

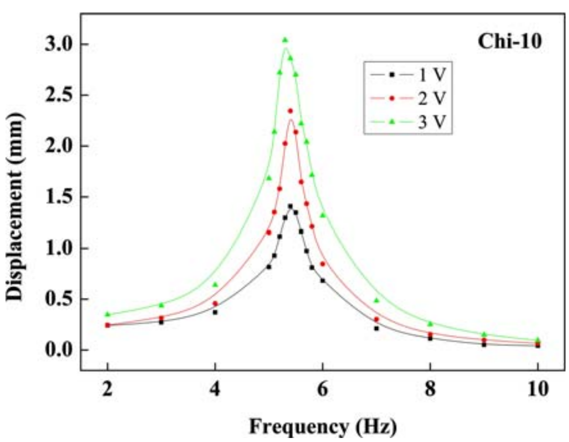

Fig. 7 Effects of frequency and voltage on the displacement for Chi-10: 25°C, 60%RH

Figure 9 shows the displacement change of the Chi-10 with time. Two different humidity levels were tested. The temperature was 25°C and the voltage was 2 V. When the humidity level was 30% RH, the film thickness was 50 ± 3 μm and the resonance frequency was 8.7 Hz. When the humidity level was increased to 60% RH, the film thickness was 60 ± 3 μm and the resonance frequency was 5.2 Hz. The test was made at the resonance frequency. As the humidity level increased, the film became soft, and the resonance frequency decreased. On the 30% RH case, the tip displacement was not large initially, but it was stable with time. However, the large tip displacement for 60% RH case was clearly decreased with time. This may be due to the depletion of the ion concentration in the film as time

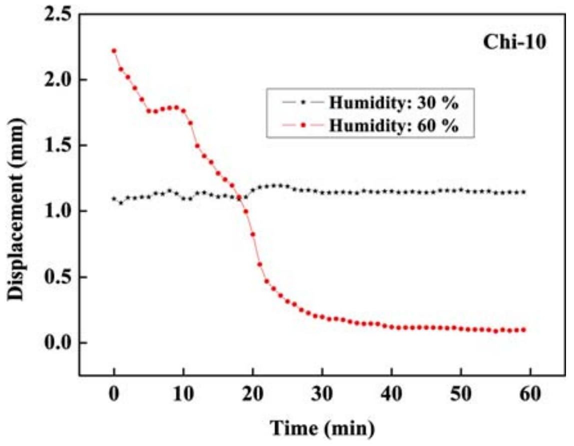

Fig. 9 The displacement change of Chi-10 with time: 25°C, 2 V, 8.7 Hz for 30%RH and 5.2 Hz for 60%RH

increased. Such a durability problem with time still remains as a challenge of cellulose based EAPap.

Conclusions

Effects of anion types and chitosan content on the actuation behaviors of cellulose– chitosan laminated films were investigated in terms of bending displacement of the actuators. The mobility of Cl^- was the best among other free ions, NO_3^-, Cl^- and CF_3COO^-, in cellulose EAPap actuators. The actuation principle of the actuator is based on two parts: a combination of piezoelectric effect and ion migration effect associated with ordered and disordered domains in cellulose, and an ion migration effect in the chitosan layer. Bending displacement of the actuators was increased with the voltage and the maximum displacement was obtained near the resonance frequency of the actuator. The displacement was increased with the chitosan content due to the increase of the number of free ions per unit area, which increases the repelling forces between the anions. But the effect of the film thickness is disadvantageous. The maximum bending displacement of the actuator was found at 60% relative humidity, which is promising to reduce the humidity sensitivity. However, the bending displacement for 60% RH case decreased with time. This kind of durability problem still remains as a challenge of cellulose based EAPap.

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