Cellulose nanocrystal based transparent electroactive polyurethane for active lens application

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ABSTRACT

Cellulose nanocrystal (CNC) is known to be a good source for structural material due to its impressively high mechanical properties and it is also an excellent dielectric filler due to its electrical polarity originated from its crystal structure. This paper reports a soft electro-active polymer made by blending CNC with poly(urethane), which is named as CPPU. CPPU is an electro-active dielectric elastomer, applicable for smart and active lens. In CPPU, CNC plays the role of filler that improves dielectric constant. For homogeneous distribution of CNC in poly(urethane) matrix, hydrogen boned CNC-poly[di(ethylene glycol) adipate] (PDEGA) was prepared by simple blending as diol of urethane bond. Hexamethylene diisocyanate was used for isocyanate salt as cross-linker. The prepared CPPU exhibits high transparency above 90% and excellent dielectric constant. As a result, the CPPU dielectric elastomer shows large deformation under low electric field. Transparency and large deformation behaviors of CPPU are attractive for smart and active lens applications.

1. INTRODUCTION

Electroactive polymers (EAPs) are smart materials suitable for biomimetic actuators, soft robots and physical sensors due to fast response to electrical stimuli, lightweight and high energy density [1]. Among EAPs, dielectric elastomers (DEs) attract much interest, since they have an impressively high electroactive strain, mechanical robustness, inexpensive cost and highly affordable energy density, although it has a critical disadvantage of high operation voltage over 100 MV/m [2]. Thus, most researchers have mainly tried to reduce the operation voltage without performance degradation. In that point, two different approaches have been investigated for DE [3]. One attempt is decreasing mechanical stiffness and the other one is increasing dielectric constant. The increasing dielectric constant is also conducted via two different strategies: chemical modification of elastomer and elastomer composite [4]. Chemical modification of dielectric elastomer is by means of synthesis with new molecular structures or chemical modification of existing elastomers [5]. Thus, it requires complicated chemical processes to improve dielectric constant. Elastomer composite is a conventional strategy to enhance dielectric constant by simply blending high dielectric fillers or conductive fillers in dielectric elastomers to enhance dielectric constant [6].

Cellulose is one of the abundant biopolymers in the world. In micro structural view point, cellulose can be divide into crystal region and an amorphous region. The crystal region, so-called cellulose nanocrystal (CNC), has impressive advantages such as nanoscale dimension, high mechanical strength, biocompatibility and sustainability [7]. CNC has been studied for many applications including structural nanocomposites, optical films and biomaterial composites [8]. One interesting property of CNC is its electrical polarity [9]. Due to the polarity, CNC is a good candidate for dielectric filler to improve dielectric property of EAPs by blending it with polymeric materials without significant sacrificing optical properties of polymers.

Polyurethane (PU) is an elastomer, produced by conjugation of polyol and isocyanate salt. Because of low elastic property and reliably high dielectric constant (7 at 100 Hz), PU is a promising material for high-performance DE [10]. However, the dielectric constant of PU still needs to be improved to achieve high-performance DE. In this paper, a high performance and transparent DE is studied by blending PU with CNC which is operable at low electric field. For high transparency and homogeneous distribution of CNC, CNC-poly[di(ethylene glycol) adipate] (PDEGA) nanocomposite is prepared for diol of PU. For urethane reaction, hexamethylene diisocyanate (HMDI) was used for isocyanate salt as cross-linker. Structural, optical, mechanical, dielectric and electromechanical properties of CPPU were analyzed.

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2. EXPERIMENT

2.1 Materials

Cotton pulp with 98% purity as a source for of CNC was obtained from Buckeye Technologies Inc. Isopropyl alcohol (IPA) for blending agent of CNC and PDEGA was obtained from Daejeong Chemicals. PDEGA as a base material of diol for PU and HMDI as isocyanate salts for PU were obtained from Sigma-Aldrich, USA. Other chemicals such as sulfuric acid (H_2SO_4), dibutyltin dilaurate (DBDL) and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich, USA.

2.2 Fabrication of CNC-PDEGA based polyurethane (CPPU)

PU can be produced by conjugating diols and isocyanate salts. To fabricate CPPU, CNC-PDEGA nanocomposite was prepared, which plays the role of diol. CNCs were prepared by acid hydrolysis reaction using 60 wt% of H_2SO_4. Before acid hydrolysis, cotton pulp was immersed into 4.5% (w/v) NaOH aqueous solution in order to remove non-cellulosic materials and disassemble cellulose microfibers. The acid hydrolysis was carried out at 50 ^oC. The solution turned to light brown, which indicated that CNCs are formed in the solution. After the end of reaction, the residue suspension was diluted using DI-water and centrifuged at room temperature. This process was repeated several times until the suspension was neutralized.

CNC-PDEGA nanocomposite was prepared by simple solvent mixing process using IPA. Initially, CNC suspension was mixed into IPA with 1:10 ratio and sonicated with ultrasonic cleaner for few seconds. PDEGA as same amount of CNC suspension was added to the mixture and again sonicated until getting homogeneous solution. The solution was kept at 60 ^oC for 48 hours to remove solvents.

CPPU was fabricated by urethane reaction between CNC-PDEGA and HMDI. For the reaction, CNC-PDEGA with several concentrations of CNC and PDEGA were dissolved in chloroform. DBDL also mixed into the solution for catalysis. HMDI was added into the solution and mixed few seconds. The ratio of CNC-PDEGA/PDEGA/DBDL/HMDI is 2/25/2/2.5. After mixing all chemicals, the solution was kept at 60 ^oC in oven for reaction. Reacted solution was kept at room condition for 30 minutes to prevent bubble generation by the evaporation. The solution was poured on a PDMS sheet and kept at 60 ^oC to evaporate chloroform for 24 hours.

2.3 Characterizations

Interactions in CNC-PDEGA and CPPU were studied by Fourier transform infrared spectroscopy (FTIR, Vertex 80V, Bruker USA). UV-visible spectroscopy (HP 8452A, Hewlett-Packard USA) was carried out for transmittance of CNC-PDEGA and CPPU. A tensile test was used to investigate the mechanical properties of CPPU. Specimens for the tensile test were cut into 10 mm width and 20 mm length with 5 mm margin on both sides for grip. The tensile test was carried out with 10um/s pulling speed. The dielectric constant of CPPU was calculated from capacitance which was measured using an LCR meter (Agilent 4284a) and a dielectric measurement fixture (Agilent 16451b). To investigate electromechanical behavior, 1.5×1.5 cm^2 CPPU was placed on ITO glass as a bottom electrode to apply electric field. Ag nanowire (AgNW) was sprayed on the sample to form top electrode. An electrical signal was supplied by function generator (Agilent 33220A) and amplified 2000 times via voltage amplifier (Trek 20/20). A laser displacement sensor (Keyence LK-G15) and controller (Keyence LK -G3000) were used to measure the deformation of the sample.

3. RESULTS AND DISCUSSION

3.1 Chemical structure and interaction in CNC-PDEGA and CPPU

Interaction in the CNC-PDEGA was analyzed by FTIR. Figure 1 (a) shows the FTIR spectra of PDEGA and CNC-PDEGA. Characteristic peaks at 1060 and 1174 cm^{-1} correspond to the stretching vibration of C-O (ether). 1750 and 3512 cm^{-1} peaks attribute to the C=O and O-H stretching vibrations. 2920 cm^{-1} and 1135 cm^{-1} peaks correspond to C-H stretching vibration and C-O asymmetric bridge stretching vibration, respectively. The O-H peak of the stretching vibration appears at 3425 cm^{-1}, which is shifted to lower wavelength due to the intermolecular hydrogen bond between CNC and PDEGA. In CPPU curve, 3608 cm^{-1} and 3379 cm-^{1} peaks are shown. The peaks correspond to O-H and hydrogen bonded N-H stretching in urethane bonding, respectively.

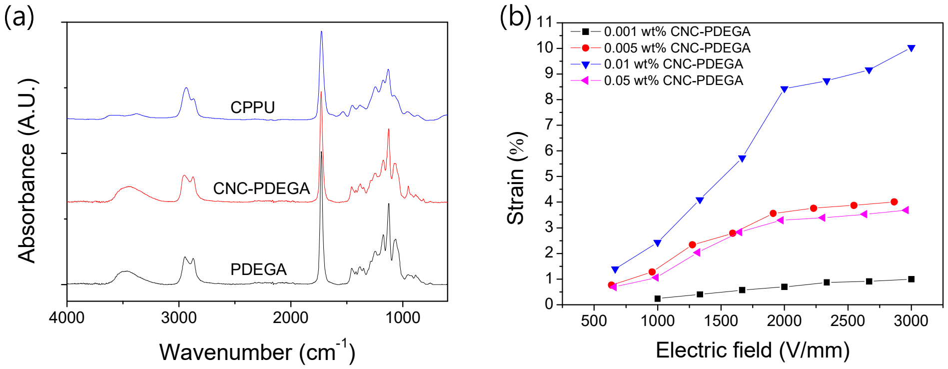

Figure 1. (a) FTIR result spectra of PDEGA, CNC-PDEGA and CPPU and (b) electromechanical strain depending on different electric field and concentration of CNC.

Table 1. Mechanical and dielectric properties of CPPU.

CNC wt% of CNC-PDEGA	Elastic Modulus (kPa)	Yield strength (kPa)	Elastic elongation (%)	Dielectric constant @ 100Hz	Tan δ @ 100Hz
0.001	40.97	6.56	15.96±1.42	131.55	10.41
0.005	48.26	7.27	15.03±1.83	540.35	9.16
0.01	52.34	7.84	13.13±0.32	1646.96	8.41
0.05	61.30	8.74±1.62	12.48±1.18	1239.29	12.46

3.2 Mechanical, dielectric and electromechanical properties

Mechanical and dielectric properties of CPPU with various concentrations of CNC are shown in Table 1. As the CNC concentration increases, elastic modulus and yield strength of CPPU increase from 41 to 61 kPa and 7 to 9 kPa, respectively. Elongation at yielding decreased from 16% to 12%. Previous study on ceramic filler/elastomer nanocomposite also showed a similar trend in mechanical properties [11]. Because of high strength and stiffness, CNC inclusion enhances the mechanical properties of CPPU. The dielectric constant and tan δ and of CPPU are shown in Table 1 with different CNC concentration. The dielectric constant decreases with the increase in frequency due to interfacial polarization of CNC in CPPU. The dielectric constant changes in two regions depending on the CNC concentration. In the first region from 0.001 to 0.01 wt% CNC in CNC-PDEGA, the dielectric constant increases as increasing the CNC concentration. It might be associated with the increasing surface polarization between CNC and PU as increasing the CNC concentration. Moreover, CNCs have high polarity so as to increase dielectric constant of CPPU. In the second region from 0.01 to 0.05 wt%, dielectric constant decreases as the CNC concentration increasing. It might be due to the enhanced hydrogen bonds between CNC and PU, which restrain the movement of dipoles in hard segments of PU and CNC. Transparency of the CPPU samples is important for active lens. Transmittance of CPPU is shown to be 90% in visible range over 400 nm wavelength.

Electromechanical behavior was investigated using the electromechanical test system. Figure 1 (b) shows the strain outputs of the CPPU samples along with the input electric field. As the CNC concentration increases, the strain increases to 0.01 wt% of CNC concentration, thereafter, strain decreases. This result is associated with the combination of elastic modulus and dielectric property. A maximum strain of 10% is shown for the 0.01 wt% CNC case with low electric field, 3 kV/mm.

4. CONCLUSIONS

In this paper, CNC-PDEGA based polyurethane (CPPU) was prepared and analyzed to study its possibility for active lens application. To prepare CPPU, HMDI was used for cross-linker as an isocyanate salt. The CPPU samples were prepared with different concentrations of CNC in CNC-PDEGA and their chemical, optical and physical characteristics were investigated. FTIR results showed the intermolecular hydrogen bond between CNC and PDEGA and hydrogen bond formation between CNC and CPPU. UV-visible spectra showed a good transparency of CPPU, which is important for active lens application. Mechanical properties of CPPU increased as increasing the CNC concentration due to high strength and stiffness of CNC. Dielectric constant of CPPU increased as increasing the CNC concentration up to 0.01 wt %. Thereafter, dielectric constant decreased. This result indicates that CNC plays a role for high dielectric filler in CPPU. High concentration of CNC rather reduced the dielectric constant due to trade-off between dielectric constant enhancement and hydrogen bonds increasing in CPPU. The maximum electromechanical strain of 10 % was obtained from the 0.01 wt% CNC case under 3 kV/mm electric field. This electromechanical performance along with its transparency of CPPU is promising for active lens application.

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