

Cellulose/PDMS hybrid material for actuating lens

Kishor Kumar Sadasivuni, Md Mohiuddin, Xiaoyuan Gao, Asma Akther, Seongcheol Mun, Jaehwan Kim*

Center for EAPap Actuator, Department of Mechanical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, South Korea

ABSTRACT

Miniaturization of optical systems has promoted a revolution in lens technology and this emerging field has much interest for medical practitioners as well as electronic engineers. Tunable liquid lens capable of adjusting its focal length have special curiosity in this regard where in micro-scale actuators are often integrated. Here we demonstrate a lens consisting of a transparent elastomer liquid composite containing organo modified cellulose nanocrystals. The actuator with the working voltage of only up to 0.8kV was capable to produce an area expansion and thereby altering the curvature of the lens (focal length) reversibly in 5 seconds. The effect of filler concentration on optical property and dielectric behavior of the composites were also analyzed.

Key Words: Lens, PDMS, Cellulose Nanocrystal, Electro-optic Effect, Nanocomposite.

1. INTRODUCTION

Cellulose is an organic, fibrous, water-insoluble substance regarded as most abundant natural, organic, renewable polymer and the major component of plant cell walls. Cellulose consists of micro fibrils which are formed by hydrogen bonding between cellulose molecule chains and these micro fibrils have both crystalline and amorphous regions in them. Shorter crystalline parts with high crystalline degree can be made by breaking down those micro fibrils. Acid hydrolysis of cellulose fibers produce crystalline rod-like residues know as cellulose nanocrystals (CNCs) [1]. These environmentally-friendly CNCs possess excellent optical and mechanical properties [2, 3], and can be easily incorporated with polymers to produce reinforced composites [4] through proper chemical modification methods. Availability, low cost, high aspect ratio, low density, renewability, biodegradability and unique structural morphology made CNCs the unique among nanomaterials used in biomedical (drug delivery systems, bactericidal wound dressing, bandage, surgery cloth etc.) and technical (nanofiller, reinforcing agents, filtration, packaging, cosmetics, food additives etc.) applications.

Recent years have witnessed miniaturizing optical systems receiving focus from several interdisciplinary fields of research. Research for developing tunable lenses is ongoing and there are several approaches for tenability by changing the focal length and curvature [5-7]. Focal length of the lenses can be tuned both mechanically and electrically [8, 9] and such reconfigurable lenses can be classified into some general categories like liquid crystal, electro-wetting and liquid-filled. Polydimethyl siloxane (PDMS) is a widely discussed polymer for lens application. Liquid mixture of PDMS-OCNC potentially offers an attractive possibility to create highly tunable optical components.

In this paper, we report a reconfigurable PDMS-Organic modified cellulose nanocrystals (OCNC) composite lens system where focal length and curvature can be controlled by applying voltage. The optical lens made of PDMS-OCNC can provide attractive opportunities in many applications by way of its ability to dynamically tune the lens by changing the optical properties. Here we will discuss about the experiment and material characterization focusing on the materials, preparation and modification of CNCs followed by a brief experimental schematic and also the final outcome of the developed lens.

*Jaehwan@inha.ac.kr; phone +82-32-860-7326; fax +82-32-832-7325; www.eapap.com

2. EXPERIMENT

2.1 Materials

Cotton pulp was procured from Junsei Chemicals, South Korea whereas sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), sodium dodecyl benzene sulphonate (SDBS), tetrahydrofuran (THF) and Polydimethylsiloxane (PDMS) were purchased from Sigma-Aldrich.

2.2 Fabrication of hydrophobic cellulose nanocrystal

Cellulose cotton pulp was treated with NaOH solution at 80 °C followed by strong stirring using magnetic stirrer to remove residual, contaminants and non-cellulosic substances. The stirred solution was then washed and filtered with DI water to achieve pH neutrality. Purified fiber solution was hydrolyzed with aqueous H_2SO_4 and washed again. Finally, the aqueous CNC solution was centrifuged and stored at low temperature (around 4 °C). It is found that diameter of these synthesized rod-like CNCs is in the range from 30 to 70 nm, length 200 to 400 nm and width average 20nm shown in Figure 1.

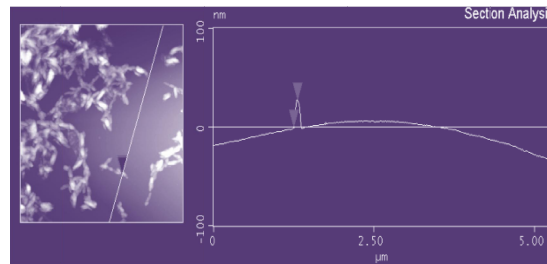


Figure 1. AFM image of CNCs coated on smooth silica surface.

2.3 Surface modification of cellulose nanocrystals

Surfactant SDBS was used to reduce the surface tension of hydrophobic CNCs, to do so, pH of CNC was reduced to 4 using aqueous H_2SO_4 resulting in the fully dissociation of carboxyl groups from the surface of nanocrystals [10]. Prepared CNC suspension was added drop-wise into aqueous ammonium salt solution; simultaneously stirring the mixture overnight at room temperature. Prepared suspension was freeze dried and dispersed in THF using ultrasonic treatment followed by centrifugation to separate excessive SDBS. The schematic of modification is given in Figure 2.

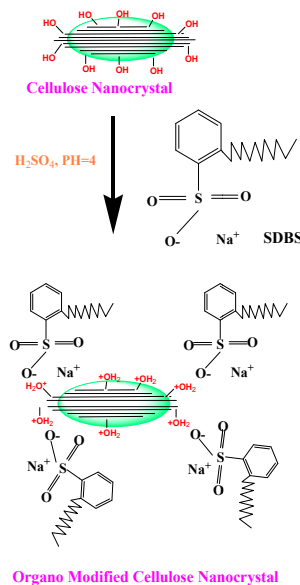


Figure 2. Illustration of Organo modification of CNC.

2.4 PDMS/OCNC nanocomposite preparation

PDMS solution was prepared by mixing base and the viscous PDMS mixture was stirred well to ensure homogeneity. It was then mixed with OCNC (prepared in the last section) to fabricate the PDMS/OCNC0.001% nanocomposite. Solution mixing process was employed for synthesizing PDMS/OCNC nanocomposite as the process exhibits more versatility and ensures better dispersion of OCNC in PDMS polymer.

2.5 Nanocomposites characterization

Diode Array Spectrophotometer (8452A, HP) was used to investigate transparency of PDMS/OCNC nanocomposite within visible wavelength, between 400-700 nm. A semiconductor device analyzer (HP 4283A) was employed to measure the dielectric constant of nanocomposite within low frequency range. Setup for lens actuator with function generator (33220A; Agilent), high voltage amplifier (20/20; Trek), data acquisition system (PULSE, B&K) and LabVIEW software installed in a computer used to stimulate actuator.

3. RESULTS AND DISCUSSION

The transparency of the PDMS/OCNC composite was checked by UV-visible spectrometry. From the transmittance versus wavelength plots, an increase in transmittance at 400-700 nm, which is approximately the lower limit of the visible region, was observed. It is also found that the average transmittance values decreased from 70 to 45 with increasing the weight percent of OCNCs in PDMS at 500 nm shown in Figure 3. This is due to the fact that the increase in density of the filler with increase in concentration makes the light scattering through the film difficult.

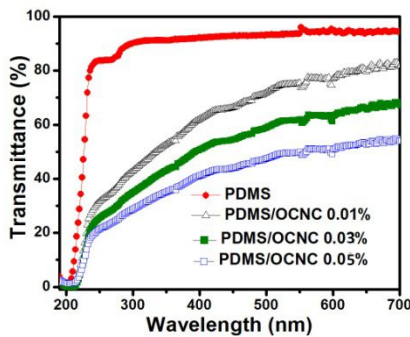


Figure 3. Optical transparency of PDMS and CNC composites with different percentage of composition.

SEM image obtained for both PDMS and its composite PDMS/OCNC0.01% are shown in Figure 4. Neat PDMS surface is very smooth whereas the composite has rough surface containing homogeneously dispersed OCNCs. This indicates good and uniform dispersion of OCNCs nanoparticles in PDMS.

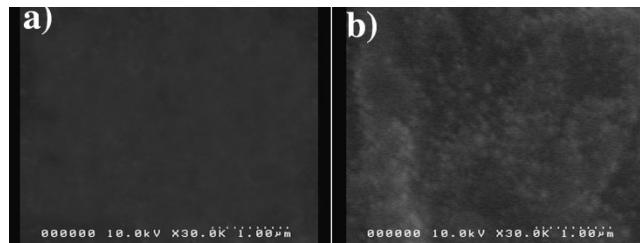


Figure 4. SEM image of a) PDMS and b) PDMS/OCNC0.01%.

In addition, the dielectric responses of the samples were also measured for the PDMS matrix and its composites at 20-500 Hz frequency shown in Figure 5. The dielectric measurement also shows that the incorporation of the OCNC in the PDMS matrix increases the dielectric constant. As the concentration of OCNC increased, movement of free charge carriers occurred due to the interfacial polarization and thus enhanced its dielectric constant [11]. According to Maxwell-

Wagner-Sillars (MWS) process polymer-filler interfacial (like donor-acceptor complexes) interaction is necessary to get changes in the composite dielectric properties [12]. Here CNCs act as good charge carriers and the huge interfacial area of nanocomposite provides numerous sites for the reinforced MWS effect [13-19]. Generally in the MWS effect, charges accumulate at the interface between two dielectrics with different relaxation time when a current flows across. This is possible by the presence of moderate number of oxide functionalities (charge centers) and conjugation (carrier centers) on the OCNC surface which forms a capacitor network and thus causes optimized electrical transmission.

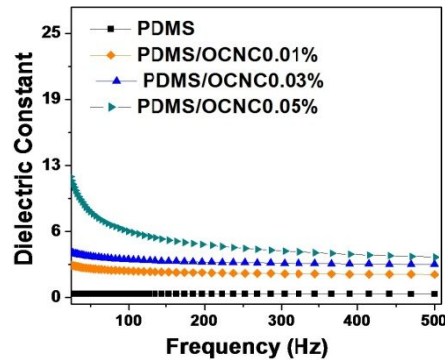


Figure 5. Dielectric constant of PDMS/OCNC composites.

The variation in the focal length of the PDMS/OCNC composite in the presence of electric field was tested. For this a device was composed of elastic liquid in a chamber having electrode, a reservoir of liquid, and a channel to the electrode. Neat PDMS required about 3000V for changing the value of refractive index whereas the composite needed only 800V. This indicates the presence of ionic dipoles within the composite which activate upon electric field. This electro-optic effect has much significance in the lens fabrication. The liquid crystal lens changes its refractive index distribution by the variable applied voltage, and it is simple and shock-resistant since the focal length is electrically tunable without any moving elements [20-23]. Depending on the applied voltage, the lens can change its curvature. Figure 6 illustrates the influence of applied electric field (0.8kV/cm) on the PDMS/OCNC0.001%. The voltage applied to the electrodes of the lens system causes an area expansion and hence changes its curvature, varying the focal length. While conventional focusing systems are reliable and have a good focusing ability, the requirement of electric motor to control the distance between the glass lenses make them difficult to miniaturize for compact lens system [24-30]. However, this PDMS/OCNC composite could be applied to miniature reconfigurable lens arrays.

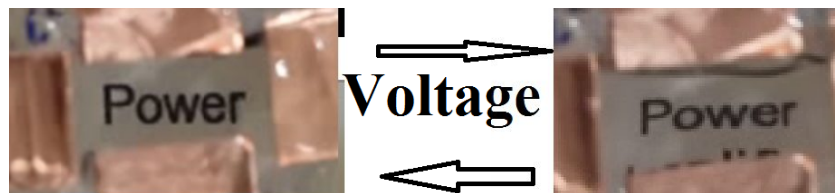


Figure 6. Focal length change of PDMS/OCNC composite by applied voltage.

4. CONCLUSIONS

The electro-optic effect of the PDMS/OCNC composite was examined by varying the focal length up on applied voltage. The surfactant SDBS was used to prepare well dispersed hydrophilic CNCs in hydrophobic PDMS matrix. The mechanism reveals the fabrication of an electro active composite at low voltage due to ionic dipole effect of OCNCs. The optical and electrical properties purely depend on the amount of filler. With increasing the filler content, the optical transparency decreased and dielectric property increased. The balanced optical and actuation performance was obtained by optimised filler concentration. Finally the products out of PDMS/OCNC composite can be used in the fabrication of portable electronic devices and in the reconfigurable lens systems.

ACKNOWLEDGMENT

This work was supported by National Research Foundation (NRF-2013M3C1A3059586) Republic of Korea.

REFERENCES

- [1] Sadasivuni, K. K., Kafy, A., Zhai, L., Ko, H. U., Mun, S. and Kim, J., "Transparent and Flexible Cellulose Nanocrystal/Reduced Graphene Oxide Film for Proximity Sensing," *Small*, doi: 10.1002/sml.201402109, (2014).
- [2] Rusli, R. and Eichhorn, S. J., "Determination of the stiffness of cellulose nanowhiskers and the fiber-matrix interface in a nanocomposite using Raman spectroscopy," *Appl. Phys. Lett.* 93(3), 033111 - 033111-3 (2008).
- [3] Mariano, M., Kissi, N. E. and Dufresne, A., "Cellulose Nanocrystals and Related Nanocomposites: Review of some Properties and Challenges," *J. Polym. Sci. Pol. Phys.* 52(12), 791–806 (2014).
- [4] Cao, X. D., Habibi, Y., Magalhaes, W. L. E., Rojas, O. J. and Lucia, L. A., "Cellulose nanocrystals-based nanocomposites: fruits of a novel biomass research and teaching platform," *Curr. Sci.* 100(8), 1172-1176 (2011).
- [5] Kulishov, M., "Tunable electro-optic microlens array. II. Cylindrical geometry," *Appl. Opt.* 39(20), 3509-3515 (2000).
- [6] Kuiper, S. and Hendriks, B. W. H., "Variable-focus liquid lens for miniature cameras," *Appl. Phys. Lett.* 85, 1128–1130 (2004).
- [7] Moench, W. and Zappe, H., "2004 Fabrication and testing of micro-lens arrays by all-liquid technique," *J. Opt. Pure Appl. Op.* 6(4), 330–7 (2004).
- [8] Ren, H., and Wu, S.-T., "Variable-focus liquid lens," *Opt. Express* 15(10), 5931-5936 (2007).
- [9] Ren, H. and Wu, S. T., "Tunable-focus liquid microlens array using dielectrophoretic effect," *Opt. Express* 16(4), 2646–2652 (2008).
- [10] Yang, J., Han, C. R., Duan, J. F., Ma, M. G., Zhang, X. M., Xu, F. and Sun, R. C., "Synthesis and characterization of mechanically flexible and tough cellulose nanocrystals–polyacrylamide nanocomposite hydrogels," *Cellulose* 20(1), 227–237 (2013).
- [11] Sadasivuni, K. K., Yadav, M., Gao, X., Mun, S. and Kim, J., "Cellulose based soft gel like actuator for reconfigurable lens array," *Proc. SPIE* 9060, 906016 (2014).
- [12] Sadasivuni, K. K., Ponnamma, D., Kumar, B., Strankowskie, M., Cardinaels, R., Moldenaers, P., Thomas, S. and Grohens, Y., "Dielectric properties of modified graphene oxide filled polyurethane nanocomposites and its correlation with rheology," *Compos. Sci. Technol.* 104, 18–25 (2014).
- [13] Kafy, A., Sadasivuni, K. K., Kim, H. C., Akther, A. and J. Kim, J., "Designing flexible energy and memory storage materials using cellulose modified graphene oxide nanocomposites," *Phys. Chem. Chem. Phys.*, doi: 10.1039/C4CP05921B, (2015).
- [14] Ponnamma, D., Guo, Q., Krupa, I., Al-Maadeed, M. A. S. A., Varughese, K. T., Thomas, S. and Sadasivuni, K. K., "Graphene and graphitic derivative filled polymer composites as potential sensors," *Phys. Chem. Chem. Phys.* 17, 3954-3981 (2015).
- [15] Ponnamma, D., Sadasivuni, K. K., Strankowski, M., Guo, Q. and Thomas, S., "Synergistic effect of multi walled carbon nanotubes and reduced graphene oxides in natural rubber for sensing application," *Soft Matter* 9, 10343-10353 (2013).
- [16] Sadasivuni, K. K., Castro, M., Saiter, A., Delbreilh, L., Feller, J. F., Thomas, S. and Grohens, Y., "Development of poly(isobutylene-co-isoprene)/reduced graphene oxide nanocomposites for barrier, dielectric and sensing applications," *Mater. Lett.* 96, 109–112 (2013).
- [17] Sadasivuni, K. K., Ponnamma, D., Thomas, S. and Grohens, Y., "Evolution from graphite to graphene elastomer composites," *Prog. Polym. Sci.* 39(4), 749–780 (2014).
- [18] Sadasivuni, K. K., Ponnamma, D., Kim, J. and Thomas, S., [Graphene-Based Polymer Nanocomposites in Electronics], Springer Publisher, Switzerland, 67 (2015).
- [19] Ponnamma, D., Sadasivuni, K. K., Strankowski, M., Moldenaers, P., Thomas, S. and Grohens, Y., "Interrelated shape memory and Payne effect in polyurethane/graphene oxide nanocomposites," *RSC Adv.* 3, 16068-16079 (2013).
- [20] Nose, T., Masuda, S. and Sato, S., "A liquid crystal microlens with hole-patterned electrodes on both substrates," *Jpn. J. Appl. Phys.* 31(1), 1643-1646 (1992).
- [21] Choi, Y., Park, J.-H., Kim, J.-H. and Lee, S.-D., "Fabrication of a focal length variable microlens array based on a

- nematic liquid crystal,” *Optical Mater.* 21(1-3), 643-646 (2003).
- [22] Ren, H., Fan, Y. H. and Wu, S. T., “Liquid-crystal microlens arrays using patterned polymer networks,” *Opt. Lett.* 29(14), 1608-1610 (2004).
- [23] Berge, B. and Peseux, J., “Variable focal lens controlled by an external voltage: An application of electrowetting,” *Eur. Phys. J. E* 3(2), 159-163 (2000).
- [24] Kwon, S. and Lee, L. P., “Focal length control by microfabricated planar electrodes-based liquid lens (μ PELL),” *Proc. Int. Conf. on Solid State Sensors and Actuators Transducers*, 1342, 1348-1351 (2001).
- [25] Chronis, N., Liu, G. L., Jeong, K.-H. and Lee, L. P., “Tunable liquid-filled microlens array integrated with microfluidic network,” *Opt. Express* 11(19), 2370-2378 (2003).
- [26] Agarwal, M., Gunasekaran, R. A., Coane, P. and Varahramyan, K., “Polymer-based variable focal length microlens system,” *J. Micromech. Microeng.* 14(12), 1665 (2004).
- [27] Mugele, F. and baret, J.-C., “Electrowetting: from basics to applications,” *J. Phys.: Condens. Matter* 17(28), R705-R774 (2005).
- [28] Seyrat, E. and Hayes, R. A., “Amorphous fluoropolymers as insulators for reversible low-voltage electrowetting,” *J. Appl. Phys.* 90(3), 1383-1386 (2001).
- [29] Jones, T. B., Gunji, M., Washizu, M. and Feldman, M. J., “Dielectrophoretic liquid actuation and nanodroplet formation,” *J. Appl. Phys.* 89(2), 1441 (2001).
- [30] Jones, T. B., “Liquid dielectrophoresis on the microscale,” *J. Electrostatics* 51-52, 290-299 (2001).