Tailored Optical and Mechanical Properties of Nanocellulose Composites: From Green Natural Fibers to Strong Hybrid Reinforcements

Y S Lin and P Y Kuo

Department of Forestry and Natural Resources, National Ilan University, No.1, Sec. 1, Shennong Rd., Yilan City, Yilan County 260, Taiwan (R.O.C.)

Email: pykuo@niu.edu.tw

Abstract. Nanocellulose is an emerging green material possessing many advantages, including biodegradability, light weight, superior strength, high transparency, and low coefficient of thermal expansion. This novel nanostructure was selected as core material in the Japanese Revitalization Strategy. Nanocellulose is a family referring to many nanostructured cellulosics with various size and aspect ratios, such as nanocellulose crystals (NCCs) and nanocellulose fibers (NCFs). NCCs are short, brittle, and highly transparent, while NCFs are long, flexible, and superior ductile. Both are promising reinforcements, but the hybrid effect of NCCs and NCFs are rarely found in previous research. The purpose of this study is to tailor optical and mechanical properties of nanocellulose composites using various ratios of NCCs/NCFs, and then further observe any synergism between NCCs/NCFs. The experimental method was divided into four phases, including acid hydrolysis to prepare NCCs, tailoring the formula of composites (NCCs/NCFs/Epoxy), removing water by solvents, and then finally curing the composites by amine crosslinker. The results show the newly prepared composites have less density than glass, ten times more in tensile strength, and competitive transmittance in optical properties. Our future work will apply this newly developed composite in flexible electronic substrates, such as smart windows and solar panels.

1. Introduction
The goal of electronic devices is always looking for materials small, lightweight, and strong for the next generation applications. To achieve this goal, many new materials are synthesized and tested and most of them are made by polymers. Polymers are lighter than the common substrate material-glass, and easy to produce through roll-to-roll process, but one of the major challenges of polymer is its thermal expansion which is ten times or hundred times higher than glass. Thus, many attentions from academia and industry turn to nanocellulose which exhibits competitive low coefficient of thermal expansion values (2.7-17.65 ppm K\textsuperscript{-1})\textsuperscript{[1,3]} compared to glass.

Nanocellulose is a bio-based material matching the above features for the next generation applications and is biodegradable, flexible, foldable, and disposable. Many flexible electronic devices apply nanocellulose as substrate, such as foldable organic-light-emitting diodes and organic solar cell\textsuperscript{[4, 5]}. However, nanocellulose is not just one simple material. Actually, nanocellulose is a family of nanostructured cellulose,
including nanocellulose fibers (NCFs), nanocellulose crystals (NCCs), bacterial nanocellulose fibers (BNCFs), TEMPO-oxidized nanocellulose (TEMPO-NCs), etc. These nanocellulose exhibit different thermal, mechanical, and optical properties and then lead to specific features of its derived-composites. It is necessary to match the features of nanocellulose and its further applications.

NCFs and NCCs are two most promising and commercial nanocellulose due to its low cost and simplicity of preparation process, but two of them also have many differences. NCFs are long, flexible, excellent on reinforcement, but they can increase haze and viscosity dramatically. NCCs are short, rigid, easy to assemble into layer-structure, but they are brittle and relatively limited on reinforcements. Previous studies use NCFs or NCCs to prepare these lightweight electronic devices. However, none of them discuss the hybrid effect of NCFs and NCCs on their mechanical and optical properties. Although much work of NCFs or NCCs composites on electronic devices have been done, very rare of them analyzed the substrate properties in detail. There is a necessity to understand the fundamental properties of the hybrid effect and we believe that combing two of them might tune the properties to match the needs of changing dynamics in the industry.

Therefore, this research aims to combine NCFs and NCCs in different ratios, and then impregnate them into epoxy resins to form the composites. Tensile strength of the composites is tested via universal testing instrument. Transmittance and haze of that are measured by haze meter. The morphology of nanocellulose and composites are analyzed using scanning electron microscope. A commercial annealed glass is prepared for a comparative purpose.

2. Materials and Methods

2.1 Materials

Cellulose nanofibers were purchased from University of Maine and its solid content is around 3.0%. The defect rate of cellulose nanofibers is less than 10%. The average width of cellulose nanofiber is 50 nm. Sulfuric acid was purchased from Honeywell Fluka™ and the concentration is between 95-97%. Filter membrane made by hydrophilic polyethersulfone (PES) was purchased from Pall Corporation and the size of membrane is 90mm in diameter, 132 µm in thickness, and 0.1 µm in pore size. Dialysis tubing was purchased from Spectrum Spectra/Por 1 with molecular weight between 6000 to 8000 Da and is made by regenerated cellulose. Acetone was purchased from Ko-Hua local chemical company in Yilan, Taiwan. Epoxy resin and curing agent were offered by First Cosmetics Manufacture local chemical company in Taipei, Taiwan. Liquid nitrogen was from Shung Gas Co., Ltd.

2.2 Methods

The preparation process can be divided into four phases including phase 1 - NCFs preparation, phase 2 - NCCs preparation, phase 3 - Composites preparation, and phase 4 - Characterizations (Fig.1 Left).

2.2.1 Phase 1 – NCFs preparation

NCFs were supplied by University of Maine, but the morphology of raw NCFs shows heterogeneous fiber diameter ranging from a few nm to dozens of nm. Thus, fiber selection through precipitation test was conducted after received NCFs. NCFs were separated into five layers and only the top layer solution of NCFs was used for the NCF film and the bottom layer was used for NCCs preparation.

2.2.2 Phase 2 – NCCs preparation

Acid hydrolysis is the most common way to prepare NCCs. NCFs of 1g based on dried weight was added into 64% of sulfuric acid solution and then stirred for 10 minutes at 45°C. Ice water/acetone mixture was
then added to stop the hydrolysis reaction. Then NCCs was isolated from the solution using centrifuge and was added into dialysis tubing for removing the excess acid.

2.2.3 Phase 3 – Composite preparation
Both NCFs and NCCs were mixed and filtered through PES membrane and use acetone to replace water using solvent exchange technique. Then the membrane was immersed into epoxy resins for 30 minutes and then it was moved to the vacuum oven to remove bubbles and then cured at room temperature. The components formula is listed below:

| Codes    | NCCs % | NCFs % |
|----------|--------|--------|
| R (Neat Epoxy) | 0      | 0      |
| C1F0    | 100    | 0      |
| C3F7    | 30     | 70     |
| C1F1    | 50     | 50     |
| C7F3    | 70     | 30     |
| C0F1    | 0      | 100    |

2.2.4 Phase 4 – Characterizations
2.2.4.1 Density measurement
The weight of neat epoxy and nanocellulose/epoxy composites were measured by scale and the volume was measured by the water displacement method.

2.2.4.2 Haze measurement
The transmittance, haze, LAB color space are measured by NDH 7000II.

2.2.4.3 Mechanical properties
The tensile strength was tested by universal tester HJM-2015 and the specimens were cut into ASTM D638 type V shape and the test speed were adjusted to make sure the samples reach stress rupture strength within 90 seconds.

2.2.4.4 Morphology
The morphology of nanocellulose and its composites were observed by scanning electron microscope (SEM). The mode of SEM is HITACHI TM-1000 and the accelerated voltage is 15kV and the magnifications are between 50-10,000.

2.2.4.5 Statistical analysis
Five specimens were prepared for each formulation and statistically analyzed by ANOVA and post-hoc test.
3. Results and Discussion

3.1 Density
The density of annealed glass is around 2.5 g/cm³ which is higher than most of that of polymers. The neat cured epoxy resins have the density of 1.5 g/cm³ which is slightly lower than NCFs/epoxy composites (1.74 g/cm³).

3.2 Mechanical Strength
The tensile strength of annealed glass is 70 kgf/cm² which is ten times lower than the neat epoxy resin 750 ± 166 kgf/cm² (Figure 2a). Compared to neat epoxy resins, the average tensile strength of NCFs/epoxy composites is 803 ± 132 kgf/cm², and it is significantly higher than annealed glass.

3.3 Transmittance and Haze
The optical properties of neat epoxy and NCFs/epoxy composite is quite similar. The transmittance of neat epoxy resin is around 90.5 ± 0.032 %, while the transmittance of NCFs/epoxy composites is 89.4 ± 0.119 % (Figure 2, right). Thus, the addition of NCFs into epoxy resins does not reduce the transmittance. Moreover, the haze of NCFs/epoxy composites (18.4 ± 0.005) is twice more than that of neat epoxy resins (9.1 ± 0.005). Finally, the color space of NCFs/epoxy composites does not show any significant difference.

3.4 Morphology
The morphology of NCFs films and its composites were observed through scanning electron microscope (SEM). As shown in figure 3, the cross section of neat epoxy resins is quite smooth, and the cross section of
NCFs/epoxy composites is a sandwich structure containing a middle layer of NCFs and two exterior layers of epoxy resins.

Figure 3 (a) The cross-section of neat epoxy resins and (b) that of NCFs/epoxy composites

4. Conclusions and future work
The mechanical properties, optical properties, and morphology of NCFs composites were observed. Nanocellulose composites exhibits lower density than that of annealed glass and the mechanical strength is ten times more than that of annealed glass. The transmittance of NCFs composites shows competitive transmittance compared to neat epoxy resins and two-fold increase in haze. Nanocellulose composite is a promising bio-based material to replace annealed glass due to its excellent mechanical strength and competitive optical properties.

Acknowledgments
This study was carried out with support from National Ilan University and Higher Education Deep Plowing Program.

References
1. Phanthong, P.; Reubroycharoen, P.; Hao, X.; Xu, G.; Abudula, A., and Guan, G. Nanocellulose: Extraction and Application. *Carbon Resources Conversion*. 2018, 1(1), 32-43.
2. Lee, P.S. Development and Applications of Transparent Conductive Nanocellulose Paper Au - Li, Shaohui. *Science and Technology of Advanced Materials*. 2017, 18(1), 620-633.
3. Sun, X.; Wu, Q.; Zhang, X.; Ren, S.; Lei, T.; Li, W.; Xu, G., and Zhang, Q. Nanocellulose Films with Combined Cellulose Nanofibers and Nanocrystals: Tailored Thermal, Optical and Mechanical Properties. *Cellulose*. 2018, 25(2), 1103-1115.
4. Zhu, H.; Xiao, Z.; Liu, D.; Li, Y.; Weadock, N.J.; Fang, Z.; Huang, J., and Hu, L. Biodegradable Transparent Substrates for Flexible Organic-Light-Emitting Diodes. *Energy & Environmental Science*. 2013, 6(7), 2105-2111.
5. Fang, Z.; Zhu, H.; Yuan, Y.; Ha, D.; Zhu, S.; Preston, C.; Chen, Q.; Li, Y.; Han, X.; Lee, S.; Chen, G.; Li, T.; Munday, J.; Huang, J., and Hu, L. Novel Nanostructured Paper with Ultrahigh Transparency and Ultrahigh Haze for Solar Cells. *Nano Letters*. 2014, 14(2), 765-773.