

***In-situ* Polymerization of Polyaniline on Cellulose Nanofibers: Effects on Electrical Conductivity and Tensile Properties**

Jon Langkammer
University of Minnesota

Abstract: Samples of aqueous cellulose nanofibers were combined with an acidic aniline solution and an oxidizer to achieve *in-situ* polymerization of aniline. To obtain a higher degree of flexibility, a plasticizer was added in some instances. Samples with varying mass ratios of nanofibers and PANI were prepared. Tensile tests and four-probe electrical conductivity measurements were performed. Results showed that samples with the most nanofibers were strong and quite rigid, while samples with more polyaniline (PANI) displayed a higher degree of conductivity, but were very brittle. The samples with a mix of nanofibers, polyaniline and plasticizer displayed a combination of conductivity and some flexibility, but future studies are needed to optimize the formulations.

Introduction

Cellulose nanofibers have recently attracted much attention as a substrate for energy and electronic devices. This mechanically strong nanomaterial is deposited with intrinsically conductive polymers to impart electrical conductivity. However, will the mechanical advantage of cellulose nanofibers be compromised through addition of such polymers? This project was aimed at determining the effect of depositing polyaniline, a conductive polymer, on the mechanical properties and overall conductivity of the resulting composite films.

Experiments

Aniline was mixed with 1M hydrochloric acid (HCl) with ratios listed in Table 1. The aniline/HCl solution was added to an aqueous suspension of nanocellulose (prepared through friction grinding of bleached kraft pulp) and the mixture was sonicated. Ammonium persulfate (APS) was used as an oxidizer, and it was first mixed with 1M HCl (Table 1).

Table 1: Formulations of components

HCl/Aniline (mL/g)	HCl/APS (mL/g)	APS/Aniline (g/g)
5.43	2.19	2.48

After the aniline/cellulose mixture had been sufficiently mixed, the APS solution was slowly added while stirring. This initiated an exothermic polymerization process, which was allowed to continue (under continuous stirring) for four hours. Following polymerization, the pH of the solution was neutralized by multiple cycles of washing with distilled water and dewatering using a centrifuge (4,194 g for 15 minutes). The neutralized polyaniline/cellulose mixture was doped with 50 mL of 2.5M HCl for 3 hours. The resulting mixture was again pH neutralized before being formed into a sheet specimen using either a vacuum Buchner Funnel system or casting. If the plasticizer (sorbitol) was used, it was added following pH neutralization after the doping process, and the solution was subsequently casted. Casting was done by pouring the solution into a 7 cm diameter aluminum boat and left to dry in the oven. Differing mass percentages of PANI and cellulose were obtained by increasing or decreasing the respective components, while maintaining the ratios listed in Table 1 and fixing the total weight.

Results and discussion

Characterization

FTIR spectroscopy was used to verify the presence of PANI. Figure 1 shows the FTIR spectra of the cellulose nanofiber sheet (control sample) and a PANI-nanofiber sheet.

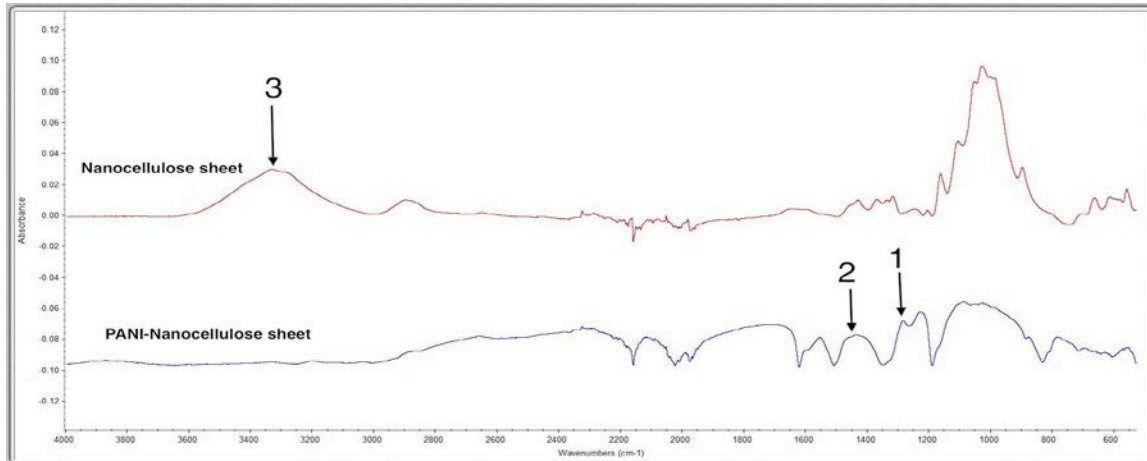


Figure 1: FTIR spectra of control and conductive sheet

The peak labeled “1” occurs at 1288 cm⁻¹, representing stretching vibration of the C-N⁺ group found in conductive PANI’s oxidation or protonation states [1]. Peak 2 occurs at 1441 cm⁻¹, which represents the vibration stretching of the p-substituted skeletal C=C double bond, found in the benzoid ring of PANI [1]. Figure 2 depicts chemical structure of polyaniline for reference.

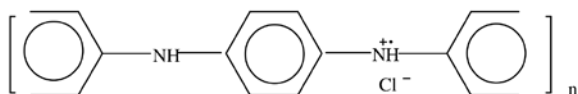


Figure 2: PANI structure[2]

Referring back to Figure 1, peak 3 indicates O-H stretching. The peak is pronounced in the case of nanocellulose sheet and not in the PANI/nanocellulose. A reasonable explanation for this observation is that in the case of conductive sheet, a large amount of PANI was deposited, making the OH groups almost invisible because nanofibers are fully covered by the polymer. Another suggested reason, but not proven, is that those OH groups contributed to bond covalently with PANI [3].

Sheet resistance

The sheet resistance of the specimens was measured using the four-probe method. Measurements were taken from multiple samples and some variability was observed (indicated by standard deviations). The first sample shown in Table 2 is the control, i.e., nanocellulose sheets without PANI, which exhibited non-measurable conductivity. With increasing PANI deposition (without doping), the resistance decreased correspondingly (samples 2 and 3), i.e., conductivity increased. At the same amount of PANI content (42%), doping further improved the overall conductivity of the sheet (samples 3 vs. 4).

Table 2: Sheet resistance values

PANI content in Film	Doping amount (mL)	HCl molarity (M)	Average resistance (Ω/sq)
0%	0	none	Not measurable
30%	0	none	295 (69)*
42%	0	none	53 (13.6)
42%	50	2.5	11 (0.77)

*Standard deviation in parenthesis

Effect of moisture content

The conductivity values presented in Table 2 were measured from dry nanocellulose/PANI sheets. Since water is electrically conductive, and is present everywhere in the environment, it would be useful to examine how stable the conductivity is when exposed to moisture. To observe moisture effects, the samples were promptly weighed and then measured for conductivity once removed from the oven. The samples were then kept in the lab ambient condition for a day, after which weight and conductivity readings were taken again. Following the measurements, the samples were conditioned at 50% relative humidity (RH) at 20 °C and then at 65% RH (also 20 °C) to periodically monitor weight and conductivity. The weight readings were converted to moisture content (MC) based on the oven-dry weight of the sheet. Results are plotted in Figure 3, which shows the resistance vs moisture content of two different regions of a sheet. The sheet examined consisted of 52% nanocellulose and 48% PANI and was doped with HCl (1M in this case). A substantial gain in conductivity (~75% drop in resistance) was observed as MC was increased from zero (37 Ω /sq) to 17% (9 Ω /sq).

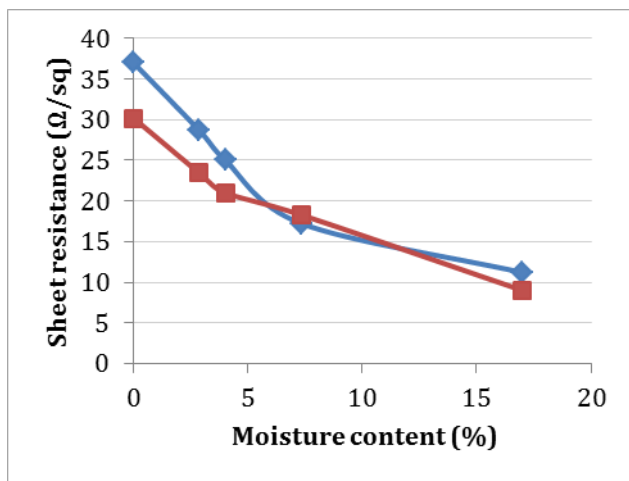


Figure 3: Moisture dependence of sheet resistance

Tensile test results

Tensile testing was carried out to determine whether PANI and/or plasticizer were affecting the mechanical properties of the nanofiber sheet. It should be noted that sheets consisting of only PANI and nanofibers were not able to be tensile tested due to the brittle nature of PANI. The sheets were first conditioned for at least 24 hours in the 50% relative humidity room. The sheets were then cut into dog bone shapes using a die before tensile tested. Figure 4 shows the stress-strain curves of the sheet specimens.

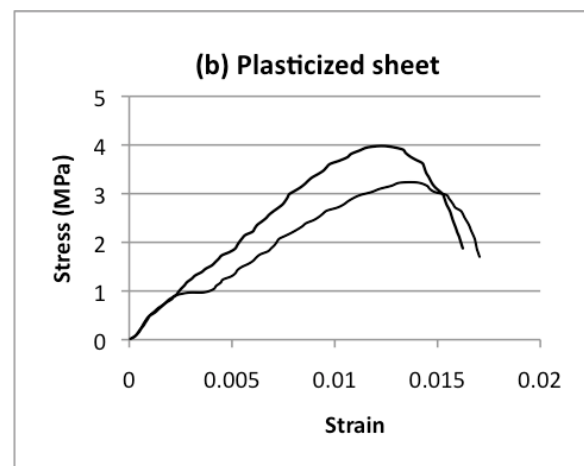
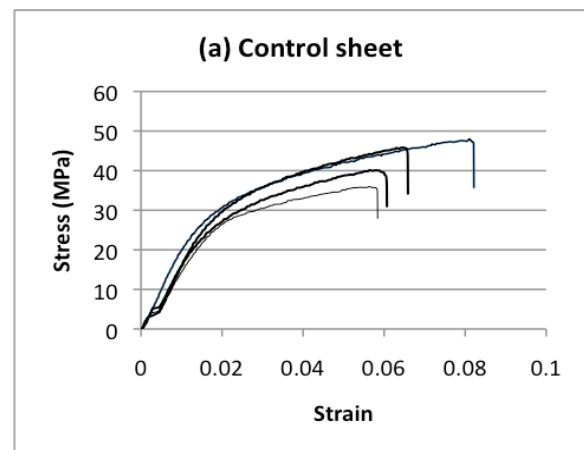


Figure 4: Stress-strain curves of nanocellulose sheet (a) and nanocellulose/PANI/sorbitol sheet (b).

Table 3 summarizes results from the tensile testing. A large difference in mechanical properties was observed from the introduction of PANI and sorbitol. The cellulose/PANI/sorbitol sheets were weaker, more brittle, and less compliant compared to nanocellulose sheets. It implies that electrical conductivity was imparted to cellulose at the expense of mechanical properties of the composite sheets.

Table 3: Tensile test results

Sheet	Tensile strength (MPa)	Modulus of elasticity (MPa)	Strain at break
Control	40.75 (6)*	1793 (41.5)	0.063 (0.022)
Cellulose/ PANI/ sorbitol sheet	3.61	276.6	0.0165

* Standard deviation in parenthesis; no values indicated for plasticized sheets as there were only two replicates.

Note: The control sheet consisted of pure nanocellulose and had a moisture content of 3.11% upon testing. The nanocellulose/PANI sheet consisted of 30% cellulose nanofibers, 25% PANI, and 45% sorbitol. It was tested at approximately 5% MC.

Conclusion

Addition of PANI has a favorable effect on the conductivity of cellulose and can result in resistances ranging from many hundreds of ohms/sq to very few. Conductivity is not only dependant on the amount of PANI used, but also on if doping is done and on the moisture content of the finished sheet.

Deposition of PANI on cellulose results in a large loss of mechanical properties especially ductility (meaning it becomes more brittle). If a flexible and conductive sheet is to be made, it will be necessary to either employ a plasticizer or invest more time in perfecting a ratio or process so as to find a balance between flexibility and conductivity.

References

- [1] U.M. Casado, R.M. Quintanilla, M.I. Aranguren, N.E. Marcovich, Synthetic Metals, 162 (2012) 1657
- [2] Y. Atassi, M. Tally, M. Ismail, Higher Institute for Applied Sciences and Technology, Syria, 2008
- [3] CD-Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength, Institute of Paper, Pulb and Fiber Technology. Web:<https://www.ipz.tugraz.at/index.php/wbPage/wbShow/cd?lang=en>

Acknowledgements

The author would like to acknowledge the University of Minnesota Undergraduate Research Opportunity Program (UROP) and the USDA McIntire Stennis Fund (Project No. MIN-12-067) for financial support. The guidance and help from UROP faculty mentor Prof. William Tze and research group members Dr. Han-Seung Yang and Islam Hafez are also appreciated.