

Optical Properties of Nanocellulose Dispersions in Water, Dimethylformamide and Poly(Methyl Methacrylate)

**by James F. Snyder, Joshua Steele, Hong Dong, Joshua A. Orlicki,
Richard S. Reiner, and Alan W. Rudie**

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James F. Snyder, Joshua Steele, Hong Dong, and Joshua A. Orlicki
Weapons and Materials Research Directorate, ARL

Richard S. Reiner and Alan W. Rudie
USDA Forest Service

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14. ABSTRACT The effects of cellulose nanocrystal filler concentration on the optical properties of transmittance, haze, and clarity were studied for solutions and composites. Cellulose nanocrystal (CNC) solutions were studied in both water and dimethylformamide (DMF). Cellulose composites employing poly(methyl methacrylate) (PMMA) as the matrix were tested with and without surfactants to aid dispersion. Increasing concentrations of cellulose in solution and in solid films caused light transmittance to decrease and light scattering, as measured by clarity and haze, to increase. The same optical trends were observed in solution samples as the path length (sample thickness) increased. The CNCs in DMF exhibited similar transmittance as those in water, but noticeably reduced light scattering.					
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1. Introduction

Lighter, stronger, and more durable transparent composites are of interest for a broad array of Army platforms. A common approach is to use optically transparent fiber or particulate additives for reinforcement. However, there are often tradeoffs among target mechanical properties, optical properties, and logistical constraints such as cost or availability. If the interfaces are not properly designed, even an additive with good isolated properties may compromise the strength and optical clarity of the composite.

Nanocelluloses are emerging materials that have the potential to provide cost-effective, sustainable reinforcement for transparent composites (Yano, 2005). Cellulose is a carbohydrate building block obtained from many prevalent resources to include wood, hemp, ramie, cotton, and bacteria (Moon et al., 2011). Through different processes it can be separated into nano-scale forms to harness mechanical properties such as a modulus of 100–160 gigapascals (GPa) (Eichhorn et al., 2010; Habibi et al., 2010; Samir et al., 2005). Nanocellulose crystals—as reinforcement in polymers—have shown, theoretically and experimentally, to give increases in strength-to-weight ratio (Samir et al., 2005). Also, thin sheets of 100 weight-percent (wt%) nanocellulose fibrils each measuring about 15 nanometers (nm) in diameter, and thin composites consisting of the fibrils and polycarbonate, exhibited high light transmittance based on data from an ultraviolet spectrometer (Nogi et al., 2009). Although nanocellulose appears to be a good candidate for use as reinforcement in high-modulus/high-strength transparent matrices, there is a lack of technical data exploring performance or processing parameters in applications beyond thin films. In particular, the effects of nanocellulose fibers in higher concentrations, processed in different solvents, and prepared at larger thicknesses remain unresolved, especially in relation to optical properties. Further characterizing the effect of nanocellulose in composites should lead to a better understanding of their utility as reinforcement.

We present here a study of how nanocellulose, specifically cellulose nanocrystals (CNCs), impact optical properties in different media with an ultimate interest in developing transparent composites. The impact of CNCs on the transparency at different thicknesses and concentrations are important and will help to determine a threshold range that can be evaluated for other properties. Composite optical qualities may also provide information regarding the distribution and dispersion of cellulosic particles, which are influenced by processing techniques and particle-matrix surface interactions. Optical data for CNCs in solution can provide insight as to the strength of agglomeration interactions amongst nanocellulose particles and determine the importance of refractive index matching, while minimizing the influence of voids or defects in

the matrix or at the interfaces. The use of polymer matrices extends the investigation to include solid-state surface interactions. Testing across a range of particle concentrations provides additional insight.

2. Experimentation

2.1 Sample Preparation

The interactions and effects of CNCs at different concentrations were investigated through distribution in each of water, dimethylformamide (DMF), and poly(methyl methacrylate) (PMMA). Liquid suspensions were analyzed using a unique cuvette that could accommodate the optical measuring device. The PMMA nanocomposites were cast as thin films.

2.1.1 Dispersion in Liquids

The CNCs were provided by the U.S. Department of Agriculture (USDA) Forest Products Laboratory in an aqueous dispersion (Reiner and Rudie, 2013). Softwood pulp was first treated with sulfuric acid. The acid solution was diluted and neutralized, and the residual solids consisting of the cellulose crystals were allowed to settle. The sugar and salt solution was then decanted and the rest of the suspension was pumped through a filtration system, removing the remaining glucose and sodium sulfate. The remaining solution was centrifuged to remove any remaining larger particles and the CNCs were collected to give an aqueous CNC solution of 6.3 wt%, which was verified when received (Dong et al., 2012).

Simple solvent exchange by means of a rotary evaporator was used to disperse CNCs in DMF. A 150-mL aliquot of the aqueous dispersion of CNCs was added to a 500-mL round-bottom-flask. Then, 150 mL of DMF was added in 50-mL aliquots. After each addition, the mixture was vigorously agitated to properly homogenize the DMF into the CNCs and water dispersion. The flask was then put onto a rotary evaporator. The rotovap had a hot bath set at 75 °C, speed fixed at 80 revolutions per minute, cooling coil running with ice water, and was placed under vacuum until about 150 mL of the liquid (predominantly water) was collected in the trap. The process of adding 150 mL of DMF and removing 150 mL of liquid via the rotovap was repeated several times. The final concentration of nanocellulose was determined to be 6.3 wt%.

CNC concentrations were calculated from the residual mass after drying. An aluminum weighing pan with a measured quantity of CNC dispersion was placed in the oven at 100 °C. After the solvent evaporated, the pan mass was determined every two hours until constant mass was achieved. The residual mass was used to determine the concentration wt% using equation 1:

$$wt\% = \frac{CD-D}{CDS-D} * 100 , \quad (1)$$

where

CD = mass of the CNC and dish, in grams (g);

CDS = mass of the CNC, dish, and solvent, in g;

D = mass of the dish, in g; and

wt% = final weight percentage.

To change the CNC concentration, solvent was either added or slowly evaporated off through gentle heating in an oven. To obtain concentrations less than that of the base solution, more solvent was added based on equation 2:

$$SOL_{add} = \frac{wt\%_{old} * M_{TOT}}{wt\%_{new}} - M_{TOT} , \quad (2)$$

where

wt%_{old} = weight percentage of current solution;

M_{TOT} = total mass of the current solution, in g;

wt%_{new} = new weight percentage target; and

SOL_{add} = the solvent addition needed to get new weight percentage, in g.

Each addition or removal of solvent was followed by high-energy agitation using mechanical stirring and the concentration of cellulose was subsequently measured.

2.1.2 Dispersion in Polymer

Thin-film specimens were prepared by mixing appropriate amounts of the CNCs and PMMA in DMF. The solutions were cast in an oven on a glass substrate. In addition to neat-CNC, freeze dried CNC treated with the surfactants Tween 40 and Tergitol NP-9 were also dispersed in polymer to observe any effects of cellulose surface treatments on solid film optical properties. These CNC particles were treated and freeze dried at the USDA laboratories, then dispersed in DMF in concentrations similar to that of neat-CNC.

To ensure homogenous mixing, the target dispersion of CNC in DMF was combined with a separate PMMA in DMF solution generated using 20 g of PMMA (Molecular weight= 350,000) and 200 mL of DMF. This combination was stirred and heated until the PMMA was completely dissolved in order to create a 100 mg/mL solution concentration.

With the wt% of each solution known, targeted dried film concentrations (total solids basis) were selected and the appropriate ratio of CNC and PMMA solution were mixed together. After mathematically identifying the necessary amounts of each solution to create a desired CNC concentration, the solutions were added together and mixed thoroughly. The mixture of CNC, PMMA, and DMF was poured in a crystallization dish, which had been treated with a

hydrophobic coating on the sides of the dish to reduce adhesion and facilitate removal of the sample.

The dish was placed in an oven set at 60 °C with a low-velocity nitrogen purge for several days until the film was fully dried. Digital calipers were used to measure film thickness.

2.2 Optical Testing

2.2.1 Transmittance, Haze, and Clarity

Visible light is transmitted, absorbed, and/or scattered depending on the properties of the propagation medium. The Haze Gard Plus (BYK Instruments) takes readings based on these three variations of light propagation and calculates three related, but unique, optical measurements: transmittance, haze, and clarity, as depicted in figure 1.

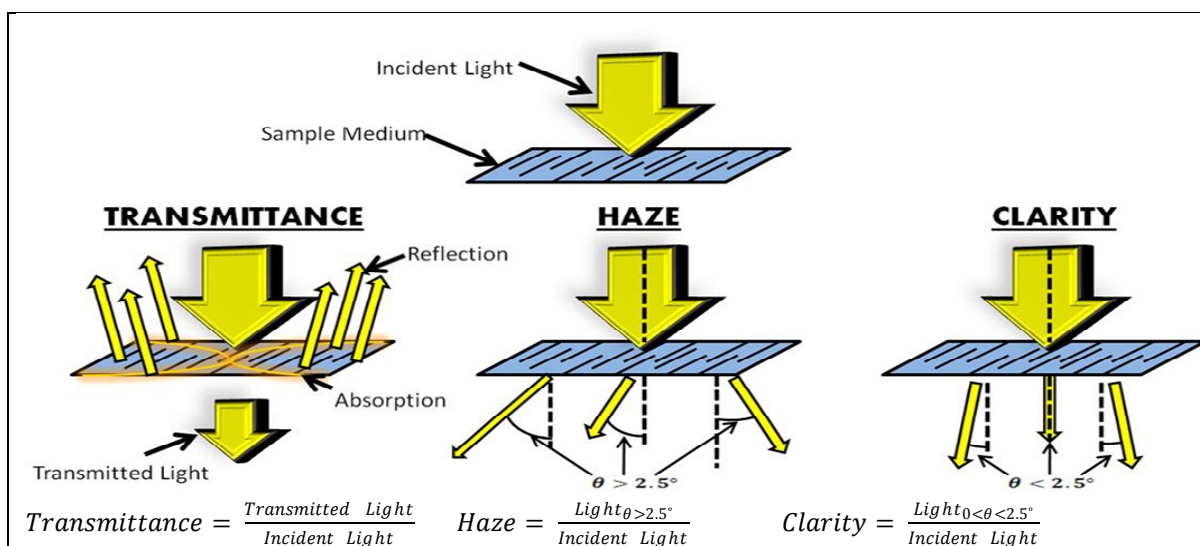


Figure 1. Illustration of measurements made by Haze Gard Plus.

Transmittance is defined as the percentage of light passing through the medium without deflection. The transmitted light is diminished by both backwards scattering and absorption. Backwards scattering occurs when the scatter cross section of the particles are so large that the light is reflected. Absorption typically occurs with light waves of the same energy as an electron orbital transition of the material through which the light is propagating.

Haze and clarity measurements are determined from scattered transmitted light. Haze is the quantity of transmitted light scattered above the angle of 2.5°. Clarity is the quantity of transmitted light scattered below the angle of 2.5°. The Haze Gard Plus is normalized to PMMA, which is a highly transparent polymer. Therefore, when analyzed, a sample of PMMA will have the transmittance, haze, and clarity of 100%, 0%, and 100%, respectively.

Scattering of light by small particles is dependent on the size, composition and refractive index matching of the particulate. Suspended particulates—or voids—increase the likelihood of

scattering in the matrix material. Particles that are smaller than approximately 10% of the incident light wavelength typically cause Rayleigh scattering. Rayleigh scattering increases in proportion to particle size and smaller light wavelengths. For larger particles, the size and refractive index make up the scatter cross section, which determines the angle at which light is scattered. Scatter angle and scatter cross section are positively correlated and when the cross section (e.g., particle size, refractive index) is increased, so is the angle. An increase in the concentration of particles results in a greater number of incident waves being affected.

2.2.2 Testing Procedure

The solution specimens were analyzed using cuvettes, which were fabricated with glass slides and cyanoacrylate adhesive (figure 2).

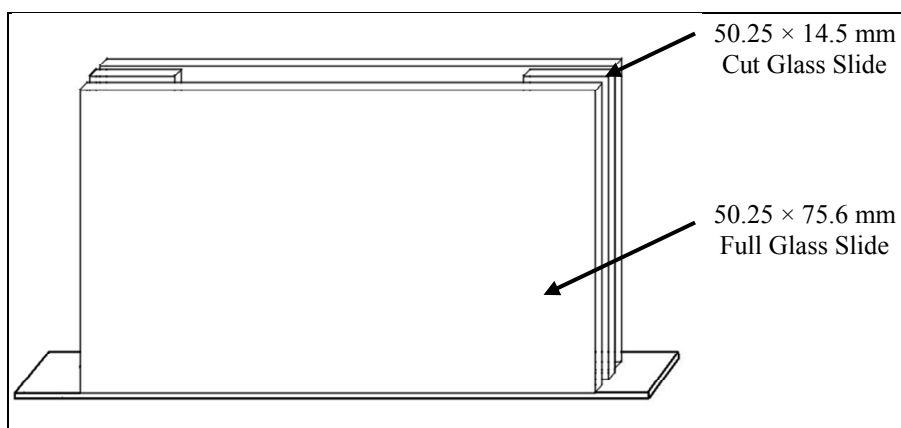


Figure 2. Representative sketch of custom solution cuvette.

The sandwich structure thickness was designated by the number of spacer slides used between the full outer-face slides. The spacer slides and the bottom slide were cut from a larger glass slide using a standard glass cutter. First, the faces of the cuvette and the spacers were glued together with the cyanoacrylate adhesive. Then, the bottom face was laid flush with the rest of the cuvette and sealed with more of the adhesive. The cuvette was then cleaned with household glass cleaner until all surface dirt was removed. The surfaces of the thin-filmed specimens were also wiped with a dry towel to remove any large particles that might block light transmittance.

The Haze Gard Plus required a measurement to be taken at a haze and clarity port before it could determine the light transmitted and scattered through a sample. Before using the equipment, the nanocellulose solutions were poured into the cuvette carefully—so as not to contaminate the outside of the glass. In addition, the thickness at the measurement location was measured for each thin-film sample. The specimen of either type was then pressed tightly against the haze and the clarity port, ensuring that the portal was completely covered by the sample and there were no obstructions between the emitter and the sensor. Once a measurement was taken at both ports, the data was recorded, the procedure was repeated three times, and the average for each property was reported.

3. Results and Discussion

3.1 Solution Specimens

Transmittance, haze, and clarity data for solution samples in cuvettes with a path length of 1.8, 2.7, and 4.5 mm are shown in figure 3 and table 1. The trends shown illustrate the optical properties taken with cellulose concentrations in water of 0.0, 2.0, 4.0, 6.3, 12.5, 21.6, 31.3, and 40.0 wt%, respectively.

The optical results for CNC in water indicate a substantial and approximately linear decrease in transmittance as cellulose concentration increases. Clarity also decreased with increasing concentration—although, in a nonlinear manner and with a significant decrease at 6.32 wt% CNC. The rapid change in clarity could be attributed to the formation of a biphasic suspension of cellulose as the solvent is removed. The CNC rods have been reported to form an ordered structure with a grating effect as the solution concentration reaches roughly 5 wt% (Dong et al., 1996; Dong et al., 1997). Haze demonstrated a similar nonlinear trend and rapid degradation at 6.32 wt% CNC. Noting the data in table 1, haze also demonstrated some increase as the concentration of nanocellulose increased from 4 to 6.32 wt%, while clarity remained effectively static. This was unforeseen because noticeable changes in haze would be expected to be in step with changes to clarity—as they both correlate to particle size and concentration in these systems. These results were observed for both of the smaller cuvette thicknesses. Holding the nanocellulose concentration constant, there were clear decreases in transmittance and clarity properties and increases of haze as thickness was increased. These trends are most likely due to the increased probability of incident light interacting with nanocellulose along a larger path length.

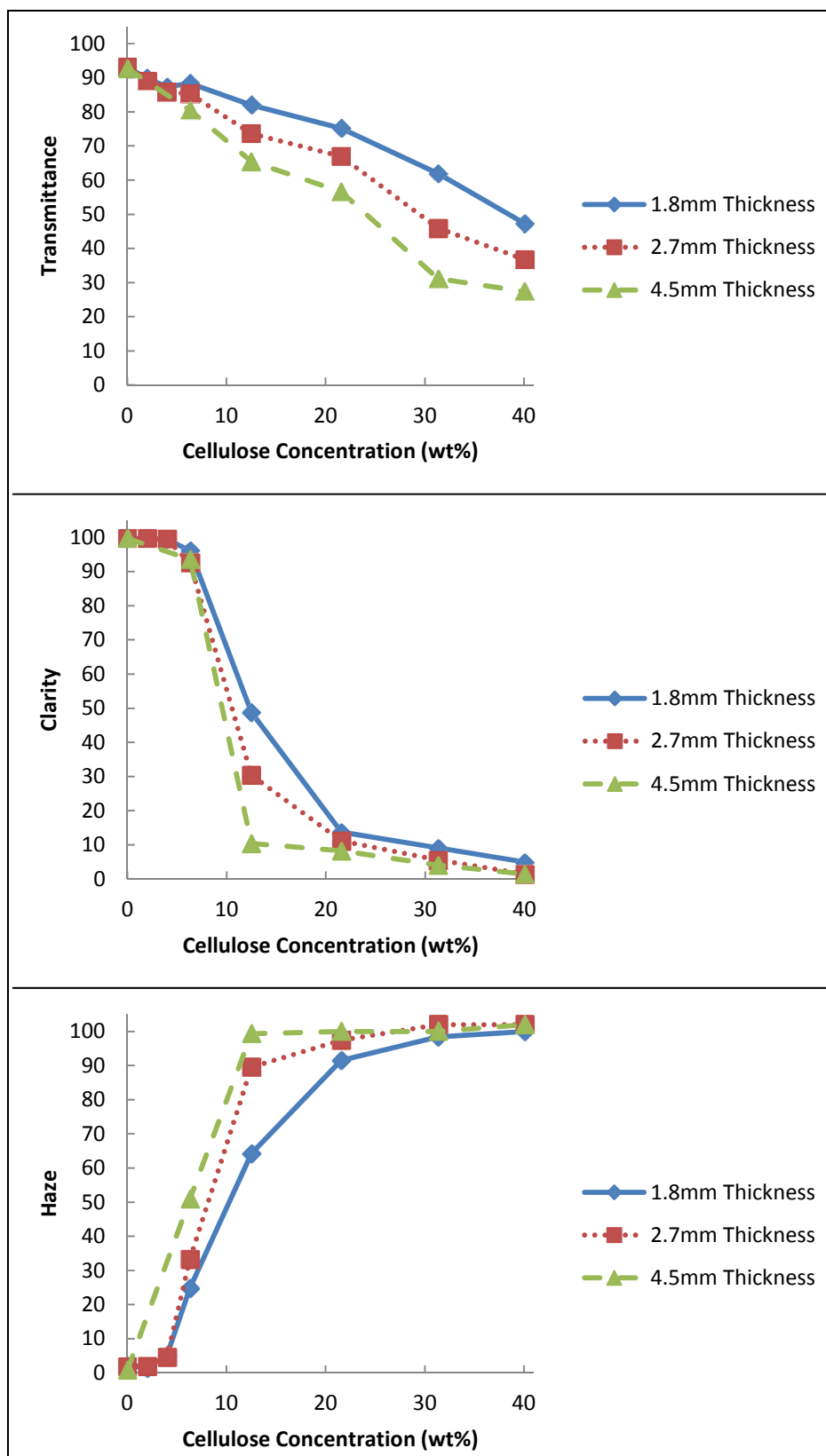


Figure 3. Transmittance, clarity, and haze measurement trends for nanocellulose in water.

Table 1. Recorded optical data for nanocellulose in water.

<i>Thickness 1.8mm</i>			
wt%	Transmittance	Haze	Clarity
0	92.9	2.13	99.7
2	89.9	1.43	99.7
4	87.3	5.15	99.5
6.32	88.4	24.8	96.1
12.5	82	64.2	48.8
21.57	75.2	91.54	13.7
31.34	61.9	98.4	9.03
40.06	47.3	100	4.93
<i>Thickness 2.7mm</i>			
wt%	Transmittance	Haze	Clarity
0	93.2	1.91	99.6
2	89	1.99	99.6
4	85.8	4.7	99.4
6.32	85.3	33.3	92.4
12.5	73.6	89.5	30.4
21.57	67	97.4	11.1
31.34	45.9	102	5.5
40.06	36.8	102	1.43
<i>Thickness 4.5mm</i>			
wt%	Transmittance	Haze	Clarity
0	92.8	0.77	99.7
6.32	80.5	50.9	93.6
12.5	65.5	99.3	10.4
21.57	56.6	100	8.2
31.34	31.1	100	3.97
40.06	27.4	102	1.43

In figure 4 and table 2, the optical properties of cellulose in DMF solutions are shown. Measurements were taken with cellulose concentrations of 10.17, 14.97, 25.16, and 31.75 wt%, respectively. Trends for the transmittance, haze, and clarity are displayed for cuvette thicknesses of 1.8, 2.7, and 4.5 mm, respectively (figure 3).

The data resembles the trends observed for the series of samples containing cellulose in water. As the concentration of cellulose increased, transmittance decreased, haze increased, and clarity decreased. It is also evident that the optical properties were exacerbated when the thickness or measurement path was increased at constant nanocellulose concentrations. Both of these occurrences may be the result of agglomerations of the CNCs and the increased probability of light to be scattered. The data in DMF was taken over a narrower range of cellulose concentrations than that in water and is largely focused on the region of transition from high-transparency to high-scattering. This transition region appears to occur at a higher cellulose concentration in DMF than water, and to be more linear in slope.

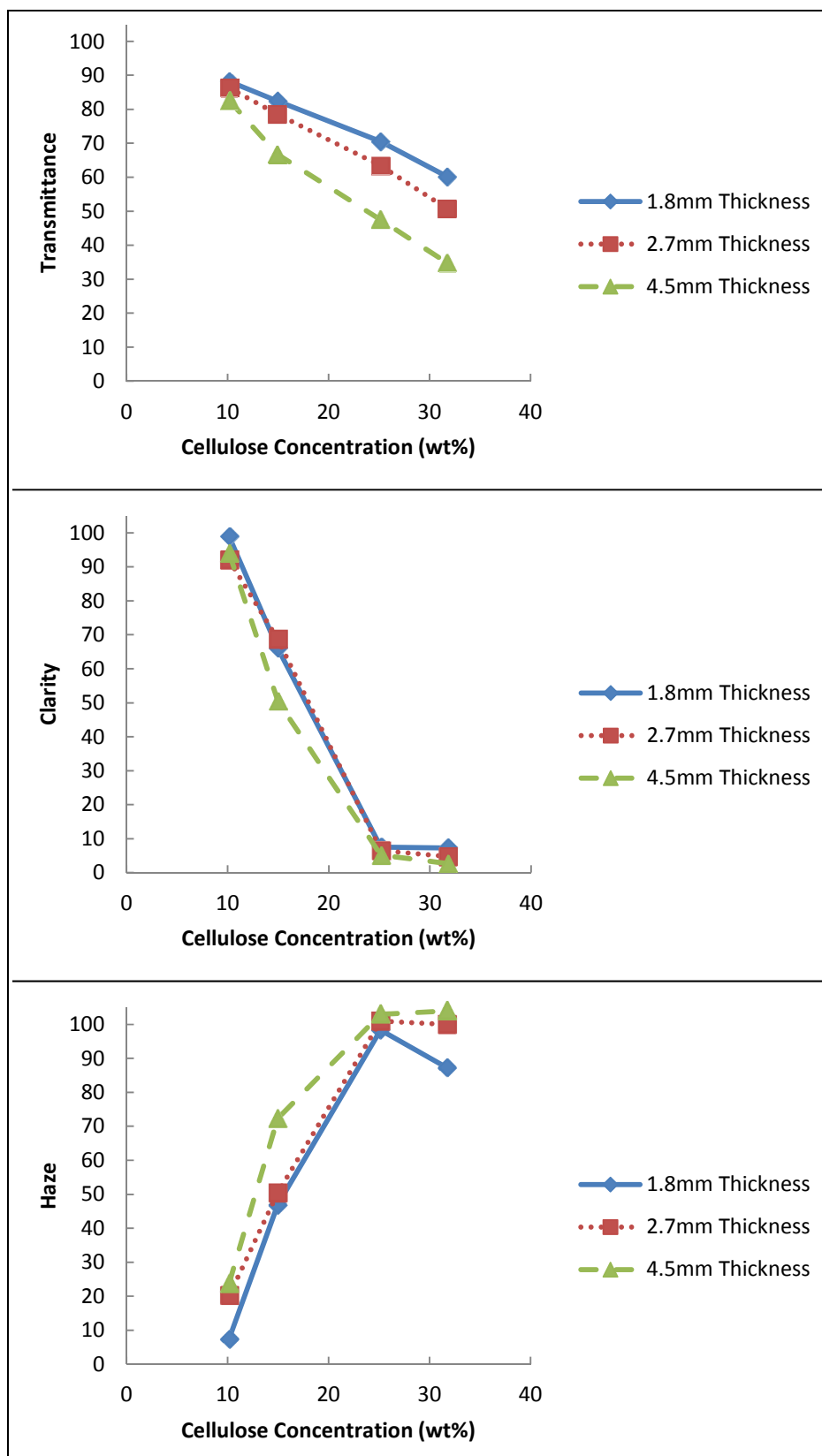


Figure 4. Transmittance, clarity, and haze measurement trends for cellulose in DMF.

Table 2. Recorded optical data for nanocellulose in DMF.

<i>Thickness 1.8mm</i>			
wt%	Transmittance	Haze	Clarity
10.17	88.2	7.55	98.8
14.97	82.4	46.9	66
25.16	70.5	98.3	7.46
31.75	60.2	87.2	7.24
<i>Thickness 2.7mm</i>			
wt%	Transmittance	Haze	Clarity
10.17	86.3	20.2	91.9
14.97	78.5	50.4	68.6
25.16	63.4	101	6.53
31.75	50.7	100	4.73
<i>Thickness 4.5mm</i>			
wt%	Transmittance	Haze	Clarity
10.17	82.6	23.9	94
14.97	66.7	72.3	50.5
25.16	47.5	103	5.2
31.75	34.8	104	2.7

Comparisons of optical properties of cellulose in water and DMF led to an interesting observation. At similar concentrations, the cellulose in DMF had approximately 50% better haze and clarity properties than the cellulose in water—while there was little difference in transmittance. The enhanced properties may be attributed to better dispersion and suppression of the ordered—anisotropic—suspension phase in DMF, which was noted in previous unpublished solubility studies done as proof-of-concept tests. Agglomerations of CNCs increase particle size which increases the scatter cross section, and in turn has a proportional relationship with the haze optical characteristic. The reduced scattering that is apparent in DMF suggest that DMF may maintain better dispersions of CNC at intermediate concentrations, which could reduce frequency of cellulose agglomerations.

Differences in refractive index (RI) can also influence scattering, particularly for larger particles or agglomerations. The RI mismatch affects optical properties at differences in RI as low as 0.001 (O'Brien et al., 2008). CNC, DMF, and water have refractive indices of 1.54, 1.43, and 1.33, respectively. Substantial mismatch occurs for CNCs in both liquids—though less so for DMF—which may contribute to the reduced haze and improved clarity measured for dispersions in that solvent. Unfortunately, due to the severity of the RI mismatches, further testing is required to verify this hypothesis.

3.2 Thin-Film Specimens

The transmittance, haze, and clarity data for polymer films are reported in figure 5. The concentrations of cellulose in polymer were easily controlled as both materials were dispersed in a common solvent, and procedures for increasing or decreasing CNC concentration are not expected to have influenced agglomeration as they may have in liquid samples. However, the thickness was more difficult to control than in liquid samples due to the nature of the film casting procedure. Figure 5 illustrates optical properties plotted against the varying thicknesses between 0.5 mm and 1.0 mm. As shown in the results, the use of surfactants with CNC does not appear to have had significant or consistent effect on the film optical properties.

Focusing first on the effects of concentration on optical properties, the data in figure 5 displays an average drop of 10% transmittance for each increase in 25 wt% of cellulose. Films with 75 wt% CNC demonstrated a 30% decrease in transmittance for all samples below 1 mm. Haze and clarity data showed less defined trends, but clearly exhibited how with higher concentrations of cellulose, haze increased and clarity decreased. These types of results were also seen in the solution samples in section 3.1. Otherwise, few obvious trends correlating optical properties with the film thickness were noted, and for the most part increasing film thickness did not dramatically impact performance over the thickness range studied.

When data between solid and solution are compared, there are some interesting developments that cannot be fully reconciled with the expected behavior. In the solution-based data, haze maximized at 100% and clarity minimized at 0% at 30–40 wt% CNC. In the solid films, at 50 wt% CNC there was a relatively high clarity of 70%–90% and a relatively low haze of 25%–60%. Even at 75 wt% CNC, while both qualities were significantly worse, neither clarity nor haze had been completely degraded. Since the same thicknesses were not obtainable in the solid thin films as the solution cuvettes, further research must be performed to draw more substantial conclusions.

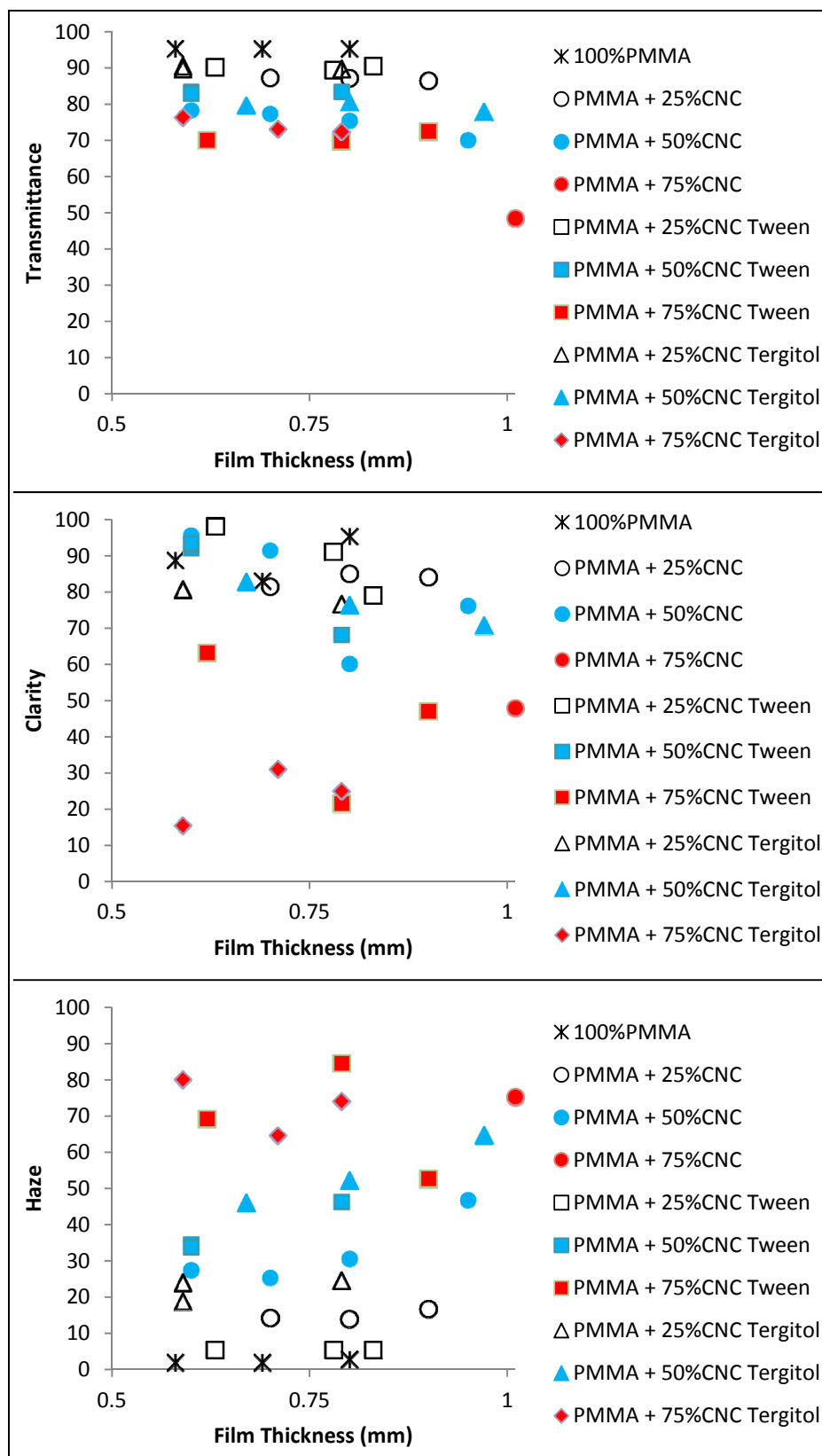


Figure 5. Transmittance, clarity, and haze measurements for cellulose and PMMA thin-films.

4. Conclusions

The optical properties of transmittance, haze, and clarity were measured using the Haze Gard Plus; data on CNCs in solution and thin-film composites was recorded and analyzed. Cellulose prepared in aqueous and DMF dispersions exhibited high haze and low transmittance and clarity, as cellulose concentration and sample thickness were increased. In comparison, DMF provided slightly better optical properties. The thin-film data of cellulose and PMMA exhibited the same trend of optical property changes with respect to higher cellulose concentrations. It should be noted that this was only in respect to cellulose concentration because the effects of thin-film thickness were not conclusive. In comparison to solution cuvette data, the solid films showed smaller optical property decreases at larger cellulose concentration levels. With the prediction that thicker solid samples will show better optical properties as well, manufacturing and testing thicker samples will be among future goals—along with utilizing better mixing and composite generation techniques.

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List of Symbols, Abbreviations, and Acronyms

CNC	cellulose nanocrystal
DMF	dimethylformamide
GPa	gigapascals
nm	nanometers
PMMA	poly(methyl methacrylate)
RI	refractive index
USDA	U.S. Department of Agriculture
wt%	weight-percent

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