RAMAN ANALYSIS AND MAPPING OF CELLULOSE NANOCRYSTAL–POLYPROPYLENE COMPOSITE

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ABSTRACT

In this study, Raman spectroscopy was used to investigate the spatial distribution of cellulose nanocrystals (CNCs) in extruded polypropylene (PP) filaments. Raman maps, based on cellulose and PP bands, obtained at 1 micron spatial resolution showed that the CNCs were aggregated to various degrees in the PP matrix. Of the three composites analyzed, two showed clear existence of phase separated regions – Raman images with PP strong and cellulose absent or *vice versa*. For the third composite, the situation was slightly improved but a clear transition interface between the PP-abundant and CNC-abundant regions was observed indicating that the CNC remained poorly dispersed. Nevertheless, tensile and modulus tests of the composites indicated up to 10% improvement compared to PP alone.

BACKGROUND

There is growing interest in making composites that are based on renewable materials [1]. CNCs are such a material that is mechanically strong and is conveniently produced from naturally abundant cellulose fibers. The strategy is to enhance the properties of synthetic polymers while using the CNCs as the load bearing component in the composite. This will give rise to composites with improved strength. Obtaining information on CNC-polymer material's composition and structure is essential for correlating structure to properties. Research focused on fundamentals is needed to find out the mechanistic basis and to answer questions involving the detailed chemistry of CNCs, polymer, and their functional groups. Such findings will allow new experimental strategies for optimizing composite processing and production. In the present investigation, PP containing 2 wt % CNC was investigated.

Although a number of techniques were used in the CNC-PP composite characterization work, present study focuses on the use of Raman spectroscopy. Confocal Raman microscopy was chosen for detailed analysis at the microscopic level because it provides spatially resolved and chemically specific information at one micron spatial resolution. The technique has recently been used to investigate the distribution of cellulose and lignin in the cell walls of woody tissues [2, 3].

EXPERIMENTAL

Four samples analyzed by Raman microscopy included a PP control and three cellulose/PP composites as listed in Table 1. The methods used in their preparation are as follows.

TABLE 1: SAMPLES ANALYZED BY RAMAN MAPPING

Sample ID	Description*
A2	PP, control
E6	Acetylated CNC:PP = 2:98
35a	PP:MAPP:nanoF-MCC = 96:2:2
D5	PP:MAPP:CNC = 96:2:2

*PP = Polypropylene; CNC = cellulose nano crystal; MAPP = maleated polypropylene; nanoF-MCC = nano-crystalline fraction of microcrystalline cellulose

CNCs were prepared by sulfuric acid hydrolysis of wood pulp [4] using 64% sulfuric acid (acid:cellulose = 8:1). PP (Certene PHM-20) and maleic anhydride grafted polypropylene (MAPP) (Eastman Chemical; Epolene G-3015) were obtained commercially. Microcrystalline cellulose (MCC) labeled as Avicel 591f was obtained from FMC Biopolymer. This MCC contained carboxymethylcellulose as a dispersant.

CTAB (cetyl trimethyl ammonium bromide) form of CNCs was prepared by neutralizing an aliquot of CNCs with solid sodium bicarbonate. A stoichiometric amount of CTAB was dissolved in a small amount of warm water (1/10 of CNC aliquot). (The CNC preparation typically produces CNCs containing about 1wt % sulfur; the amount of CTAB was calculated as a 1:1 molar stoichiometry.) The CTAB solution was added quickly to the stirred CNC aliquot. This suspension was centrifuged and the clear liquid decanted. The CNC was washed by suspending in water and centrifuging three times. A solvent exchange was done on the CNCs by suspending in a solvent three times and centrifuging. The series of exchange solvents was 95% ethanol, acetone, diethyl ether and xylenes.

*CTAB-CNC/PP composite (**D5**)* - In a round-bottom flask, 43 g of 4.65 wt % CTAB-CNCs in xylenes was added to 150 mL of xylenes, 2 g of MAPP, and 30 mL of pyridine. These were refluxed under nitrogen with stirring for 16 hours. PP (96 g) was dissolved in 800 mL of xylenes at boiling. The CNC/MAPP reaction mixture was added to the dissolved polypropylene and mixed for 10 minutes. The composite was allowed to cool, transferred onto aluminum foil and the xylenes allowed to evaporate. The composite was then placed in a vacuum oven at 125°C overnight.

*Acetylated CNC/PP composite (**E6**)* - Acetylated CNCs were prepared according to similar reaction procedures described above where acetic anhydride was substituted for the MAPP. The preparation of the polypropylene composite followed the same protocol as above.

*Fractionated MCC/PP composite (**35a**)* – Nano-crystalline cellulose particles were obtained by fractionating commercial MCC. MCC was repeatedly centrifuged, decanted, and diluted until the nanocrystalline fraction was obtained. This fraction was then compounded with PP and MAPP in a high-shear thermokinetic mixer at 5000 rpm and granulated.

*PP (**A2**)* -100 g PP was dissolved in 900 mL of boiling toluene. The solution was allowed to cool and the PP transferred onto aluminum foil and toluene allowed to evaporate. The PP was then placed in a vacuum oven at 125°C overnight.

Extrusion - The powder resulting from the solvent casting of samples A2, E6, and D5 and the compounded sample (35a) were milled to ~20 mesh in a Wiley Mill. The materials were then extruded into filaments using a Laboratory Mixing Extruder (Dynisco, Franklin, MA) with a 3 mm die orifice. The temperature of the rotor and die was set to 185 °C and 175 °C, respectively. The rotor and uptake speeds were adjusted to give a 1 mm nominal fiber diameter.

Raman analysis and mapping – The FT-Raman spectra were obtained using a Bruker RFS-100 spectrometer (Bruker Optics Inc., Billerica, MA) equipped with a 1-W 1064-nm Nd:YAG diode-pumped laser. For Raman mapping, sample cross sections of extruded fibers were analyzed using a 633 nm based Raman microprobe spectrometer, LabRam HR 800 (Horiba Jobin Yvon, Edison, NJ, USA). This spectrometer is equipped with a confocal microscope (Olympus BX40), a piezoelectric x, y stage, and a CCD detector. Spectra of samples A2, E6, 35a and D6 from various sample regions were obtained by using the serial (raster) mapping technique. Each sample was placed on an automated piezoelectric x, y mapping stage, and Raman spectra were obtained at different points on the surface by moving it equivalently under the microscopic objective. For mapping in the x, y plane at chosen spatial resolutions, the specimen was moved in the two spatial dimensions (x and y) and a spectrum was recorded at each (x, y) position. An Olympus 100X MPlan metallurgical objective, NA 0.90, was used for the Raman studies. Component specific Raman image of a sample were constructed by plotting the area intensity of the selected band as a function of position. Further details were similar to those provided in reference [2].

Tensile and modulus tests – These tests of fiber samples were performed at 23 °C and 50 % relative humidity using an MTS Insight testing system. Tests were done using a 1 inch gauge length at a nominal strain rate of 1 min^{-1}. At least ten specimens were tested for each sample.

RESULTS AND DISCUSSION

Raman spectroscopy is an excellent method for analyzing the CNC-PP composites. FT-Raman spectra of PP, 50/50 MCC/MAPP, and acetylated CNC (Fig. 1) were obtained to assess signal quality and to determine the specific band positions of PP and cellulose. Based on the spectra of acetylated cellulose and PP (Fig. 1c and Fig. 1a, respectively) the bands of cellulose and PP were easily discerned in the spectrum of 50/50 MCC/MAPP composite (Fig. 1b). In the spectra in Fig. 1 two of the cellulose bands are identified at 1098 and 1120 cm^{-1} while numerous peaks due to PP are annotated as PP.

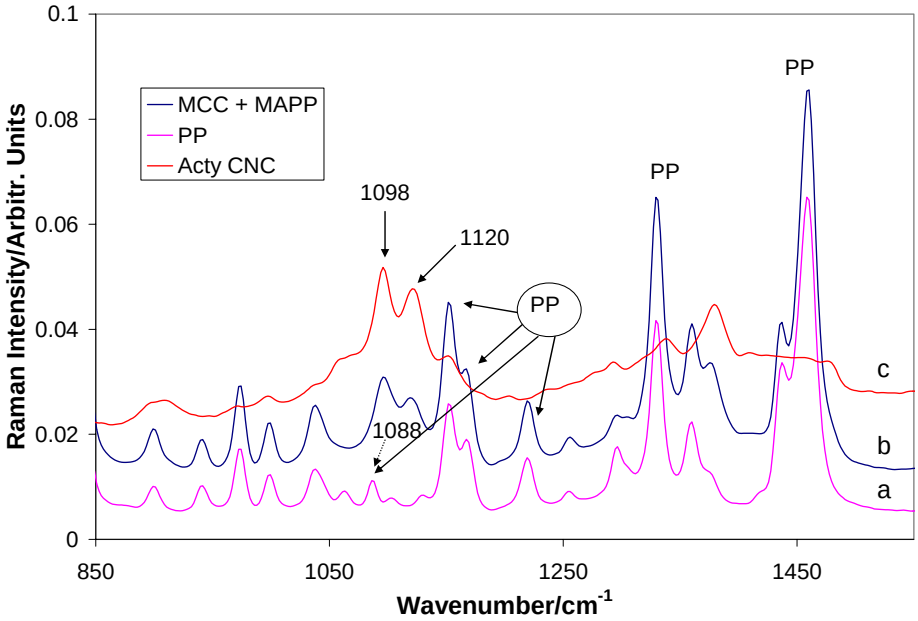

Figure 1: FT Raman spectra of PP (a), 50/50 MCC/MAPP (b), and acetylated CNC (c) in the region 850 – 1550 cm^{-1}. Compared to PP cellulose signals are weaker although contributions at 1098 and 1120 cm^{-1} due to the latter could be easily detected in the MCC/MAPP composite spectrum.

Raman microscopy was used to study the four samples (identified in Table 1) including the PP control.

PP Distribution in A2

To generate maps for PP, the intensity in the region 1413 – 1500 cm^{-1} (peak position 1460 cm^{-1}) was used. Such a map is shown in Fig. 2(a) for the sample A2. The image intensity of PP in the cross section surface was non-uniform and is due to one or more of the following factors – physical state (crystalline vs. amorphous), crystallite orientation, and concentration variation.

For a composite, when the Raman images based on the PP and cellulose bands were compared it became clear that they were almost complimentary to each other. (PP images of any composite are not shown in this paper but in Fig. 2 in regions where cellulose intensity is close to zero PP intensity was high.). Or in other words, in locations where PP was strong cellulose was

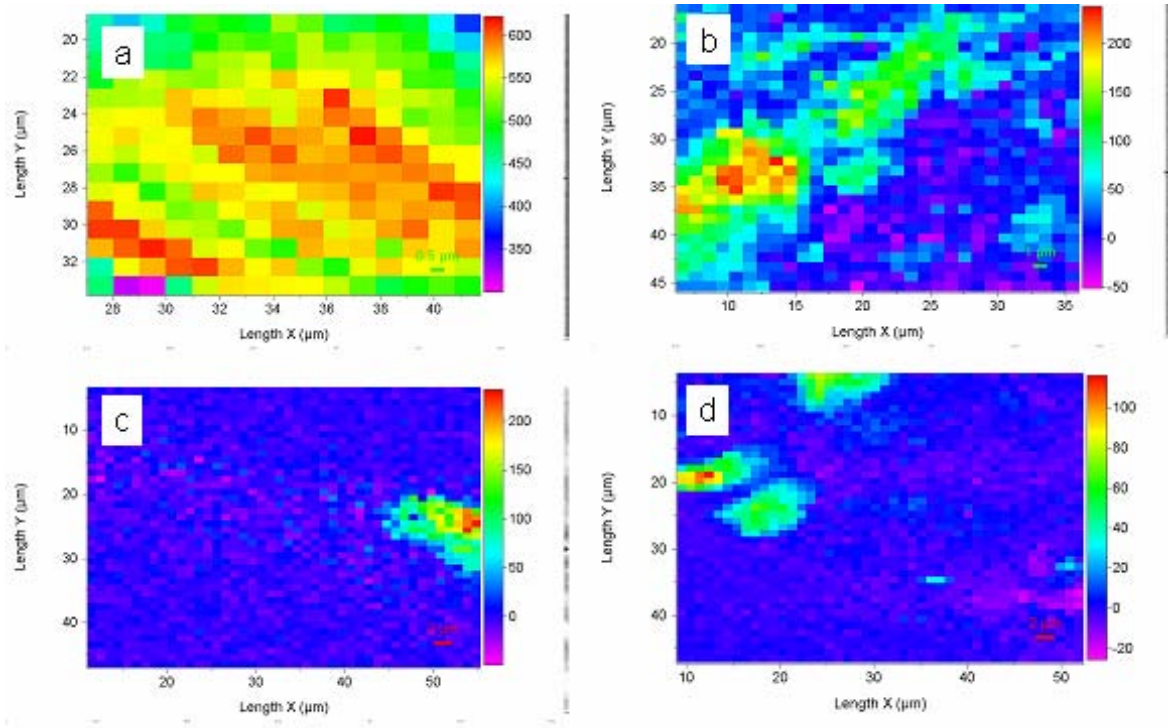

Figure 2: Raman images (false color) of spatial distributions of composite components - (a) PP in sample A2, (b) CNCs in sample E6, (c) CNCs in sample 35a, (d) CNCs in sample D5. Note different scale bar values in different images (a = 0.5µ, b = 1µ, c = 2µ, d = 2µ). Intensity scale for each Raman map appears on the right of the image. In the electronic version of the document (see paper's PDF file), component concentrations are indicated as follows - red, green, and blue regions indicate high, medium, and very low, respectively. Some locations show negative values and arise from the manner in which intensities were calculated for the images.

CNC Distribution in E6, 35a, and D5

Cellulose bands at 1098 and 1120 cm^{-1} (region 1079 – 1140 cm^{-1}) were used to visualize the spatial distribution of CNCs in the samples of the three composites [Fig. 2(b) – Fig. 2(d); samples E6, 35 a, and D5, respectively]. These images are typical for the various regions that were investigated in each sample.

weak/absent and *vice versa*. Therefore, a phase separated structure clearly existed in the sample regions. The CNC-rich regions were present as big- and small-aggregates (E6 or 35a and D5, respectively) and the PP abundant regions were present as continuous phases. A summary of the Raman mapping study and tensile tests is provided in Table 2.

TABLE 2: SUMMARY OF RAMAN MAPPING STUDY AND TENSILE AND MODULUS DATA

Fiber ID → Parameter ↓	A2	E6	35a	D5
Number of scans	15	11	20	15
Number of scans that showed cellulose	NA	8	3	12
% of scans with cellulose	NA	72	15	80
Avg. area of scans, μm^2	22 X 23	21 X 29	32 X 39	36 X 38
Cellulose dispersion; average domain size, μm^2	NA	aggregated; 78	aggregated; 120	better dispersed; 16
Dispersion index, DI	NA	0.013	0.008	0.063
Tensile stress, MPa	34.0 ± 1.8*	—	35.4 ± 2.4	37.5 ± 2.2
Modulus, MPa	990.0 ± 78.2*	—	814.1 ± 106.4	1156.6 ± 133.9

*Standard deviation

Table 2 lists various parameters (column 1) used in the context of the Raman mapping study. For instance, the number of scans indicates how many different regions of a sample were analyzed and the average domain size is the average dimension of cellulose (the dispersed phase) in the blend. Comparing the % of scans that showed cellulose for the three composite samples (Table 2, row 4), for 35a value of 15% was obtained which was more than four times lower compared to the E6 and D5. This is likely resulted due to the presence of larger size aggregates on CNCs in this sample (Table 2, row 6). Lastly, Dispersion index is analogous to the compatibility number in polymer composites, because the latter indicates mixing at the molecular level. In the case of nanocrystals, dimensions are considerably larger than polymeric, but many heterogeneous systems can be considered as compatible though they show a large degree of phase separation and two distinct glass transitions. Thus the compatibility or homogeneity of a polymer blend is related to both the experimental probe size and the domain size of the phase [5]. A Dispersion number is here defined as

DI = Experimental probe size/Domain size

When DI = ∞ the blend is compatible, when DI = 1, the blend is semicompatible, and when DI = 0 the blend is incompatible. Taking probe size as one micron for the Raman microprobe, the values for compatibility number were calculated and are reported in Table 2. Clearly, none of the composite blends came close to being even semicompatible although for D5 blend the compatibility number was significantly higher compared to E6 and 35a. This was further supported by the fact that a clear transition interface between the PP-abundant and CNC-abundant regions was observed and was a reflection of the immiscibility of the two phases.

Tensile and modulus tests

Tensile and modulus tests of fiber samples with CNCs indicated up to 10 % improvement compared to PP alone. This is significant progress but further improvements in the mechanical properties are expected to result from an improved CNC-PP interface. A superior interface would be better able to transfer stresses from PP to the CNCs.

CONCLUSIONS

Three different PP composites containing CNCs were prepared and characterized using Raman mapping and tensile test methods. Compared to PP, only limited gains in the mechanical properties of the extruded composite fibers could be obtained. A Raman mapping investigation performed at the microscopic level revealed that the PP and CNC phases remained largely immiscible and better compatibility was obtained only for the D5 composite.

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