Spatially Resolved Characterization of CNC-Polypropylene Composite by Confocal Raman Microscopy

Abstract. *Raman spectroscopy was used to analyze cellulose nanocrystal (CNC)-polypropylene (PP) composites and to investigate the spatial distribution of CNCs in extruded composite filaments. Three composites were made from two forms of nanocellulose (CNCs from wood pulp and the nanoscale fraction of microcrystalline cellulose), and two of the three composites investigated used maleated PP as a coupling agent. Raman maps based on cellulose and PP bands at 1098 and 1460 cm^{-1} respectively and 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 strong PP and absent cellulose, 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. The spectroscopic approach to investigating spatial distribution of composite components was helpful in evaluating CNC dispersion in the composite at the microscopic level, which helped explain the relatively modest reinforcement of PP by CNCs.*

Keywords. Raman, mapping, cellulose nanocrystal, polypropylene, composite.

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Introduction. Although a number of techniques can be used to characterize CNC-PP composites, our study focuses on analysis by Raman spectroscopy. This technique requires no sample preparation and provides structural information that is sensitive to intra- and inter-molecular interactions. Confocal Raman microscopy was selected for detailed analysis at the microscopic level because it provides chemically specific information at high spatial resolution. Compared to electron microscopy, where there is much higher resolution, but poor contrast between CNCs and PP, Raman microscopy easily discriminates between these. Raman mapping cannot image single CNCs and is expected to generate information on the distribution of CNCs in the CNC-PP composite. Among numerous other applications, the mapping technique has been used to investigate the distribution of cellulose and lignin in the cell walls of woody tissues [1].

Methodology. PP and composite samples were analyzed by both FT-Raman and Raman mapping methods. For Raman mapping, sample cross sections, 30 microns thick, of extruded fibers were analyzed using a 633 nm-based Raman microprobe spectrometer. At the chosen spatial resolution, spectra from various sample regions were obtained using the serial (raster) mapping technique. Raman images for both CNC and PP distributions were generated based on the characteristic bands in the spectral region 800–1650 cm^{-1}. Additional details of the mapping process can be obtained from [2].

Results

PP Distribution in the Control Sample. A map of PP distribution in sample PP-CON (control PP) was generated using the 1413–1500 cm^{-1} region Raman intensity (peak position 1460 cm^{-1}) (Fig. 1a). The 1460 cm^{-1} region bands of PP are due to methyl group deformations. The image intensity of PP in the cross-section surface was found to be non-uniform. This is likely due to variations in the physical state (crystalline vs. amorphous) and/or crystallite orientation. Effects of such factors on PP Raman spectrum have been studied previously. To visualize the contribution of the weak PP bands (1088 and 1104 cm^{-1}) that were present in the cellulose imaging region, a map was generated using these bands. The Raman image suggested that the concentrations in various PP-CON sample regions were close to zero. This implies that the existence of such nearby PP bands poses no problem for studying the distribution of CNCs.

CNC Distribution in the PP Composites. Cellulose bands at 1098 and 1120 cm^{-1} (the region 1079–1140 cm^{-1}) were used to visualize the spatial distribution of CNCs in the samples of the three composites [Figs. 1(b)–1(d)]. These images are typical of the various regions that were investigated in each sample. Spectra from the selected points in the cellulose-rich regions in the images corresponded to the neat spectra of cellulose. Although in

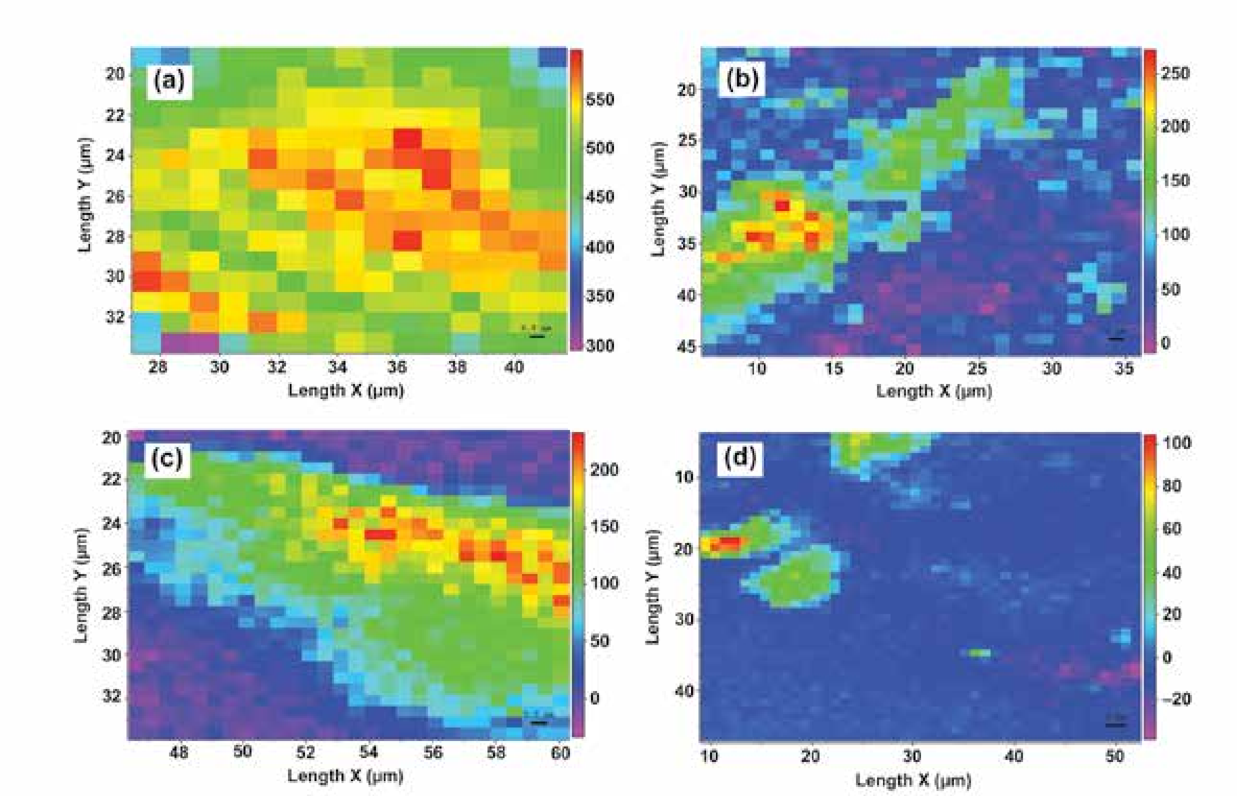

Figure 1. Raman images (false color) of spatial distributions of composite components: (a) PP in sample PP-CON, (b) CNCs in sample AC_CNC-PP, (c) CNCs in sample FRACT_CNC-PP, (d) CNCs in sample MAPP_CNC-PP. Note the different scale bar values in different images (a = 0.5 µm, b = 1 µm, c = 0.5 µm, d = 2 µm).

the cellulose imaging region (1079–1140 cm^{-1}), weak PP features at 1088 and 1104 cm^{-1} exist, their contributions to the images were found to be negligible based on the 1079–1140 cm^{-1} region-based identical Raman imaging for the control sample PP-CON.

For the composites, 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 the composites are not shown in this paper. However, in regions where the cellulose intensity was close to zero in Fig. 1, PP intensity was high. In other words, in locations where PP was strong, cellulose was weak or absent, and vice versa. Therefore, a phase-separated structure clearly existed in the sample regions. The CNC-rich regions were present as large and small aggregates (AC_ CNC-PP or FRACT_CNC-PP and MAPP_ CNC-PP respectively), and the PP-abundant regions were present as continuous phases. A summary of the Raman mapping study and the tensile tests are provided in Table III in reference 2.

Conclusions: The Raman mapping approach to investigating the spatial distribution of composite components was helpful in evaluating CNC dispersion in the composite at the microscopic level, which helped explain the relatively modest reinforcement of PP by the CNCs. This summary is based on our Applied Spectroscopy paper [2]; interested readers should go to the original article for further information.

References

[1] Agarwal, U. P. Raman imaging to investigate ultrastructure and composition of plant cell walls: distribution of lignin and cellulose in black spruce (*Picea mariana*). Planta 224: 1141–1153 (2006).

[2] Agarwal, U. P., Sabo, R., Reiner, R. S., *et al*. Spatially resolved characterization of cellulose nanocrystal-polypropylene composite by confocal Raman microscopy. Appl. Spectrosc. 66: 750–756 (2012).

Production and Applications of Cellulose Nanomaterials

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