RAMAN SPECTROSCOPIC STUDIES OF LOAD TRANSFER IN NANO-CELLULOSE-FILLED POLY(LACTIC ACID) COMPOSITES

William T. Y. Tze[1], Jin Yao[1], Melissa Taylor[2], and John Simonsen[2]

[1] Dept. Bioproducts & Biosystems Engineering, University of Minnesota, 2004 Folwell Ave, St. Paul, MN 55108-6130, USA

[2] Dept. Wood Science & Technology, Oregon State University, 120 Richardson Hall, Corvallis, OR 97331-5751, USA

Introduction

Poly(lactic acid), or PLA, is a biodegradable polymer derived from sugars from plant biomass. It is an attractive sustainable alternative to certain petroleum-based polymers, such as polyolefin. One drawback of PLA is its brittleness. Increasing attempts are made to use structural elements of plant cell walls in the form of nano-cellulose to reinforce mechanically disadvantaged bioplastics. In reinforcing polymers in general, external loads are channeled to filler materials, which being stiffer and stronger, would better sustain the load.

The transfer of load within a cellulose-filled composite can be discerned by monitoring the stress increase in fillers when the composite is externally loaded. The local stress of cellulose can be measured directly using Raman spectroscopy by observing the frequency shift of the 1095 cm^{-1} peak of cellulose. This peak was reported to shift 4.5 cm^{-1} for every 1 GPa increase in axial stress [1]. This Raman technique was recently applied to cellulose nanocomposites to study load transfer from PLA to bacterial cellulose nanofibers [2]. The research revealed that nanofibers of higher surface areas (3-day culture) exhibit a higher PLA-to-cellulose load transfer than nanofibers of lower surface areas (6-day culture).

A practical approach of improving load transfer to cellulose filler is to enhance its adhesion to the matrix polymer. This adhesion effect has yet to be shown in cellulose nanocomposites. Thus, the objective of this research is to study, using Raman spectroscopy, load transfer from PLA to nano-cellulose that was chemically modified. This study employed a low loading (0.5 weight %) of nano-cellulose to advance the robustness of the technique. Raman studies of composites with low filler loadings are challenging because the spectra would be dominated by polymer. Hence another objective of this paper is to establish the protocol for spectra processing to isolate cellulose bands for frequency shift analyses.

Materials and Methods

PLA of injection-molding grade (3051D) was acquired

from NatureWork. Microfibrillated cellulose (MFC), prepared from high-pressure delamination of bleached wood pulp fibers, was obtained from the University of Maine Forest Bioproducts Research Initiative. MFC is regarded a nano-cellulose because its fibril thickness is typically 1-50 nm. The MFC was reacted with lactide at 180°C for 1 hour (details will be reported in a separate paper). The modified MFC was blended at 0.5 dry-wt % into a PLA solution before being cast into a film.

The composite film was loaded in tension with increments of 0.5% strain. After each stretch, the film was held in position for spectra collection. Prior to collecting spectra, an elapse time of 5 min was allowed for instantaneous stress relaxation. The spectrum was collected using a confocal Raman microscope (WITec), which uses an Ar-ion laser of 514.5 nm wavelength. Each spectrum was collected in 4 min at a laser power of 35 mW and a 10x objective (0.3 numerical aperture).

Results and Discussions

Spectra of composite films (Fig. 1), due to a high fraction of PLA, were very similar to neat PLA spectra.

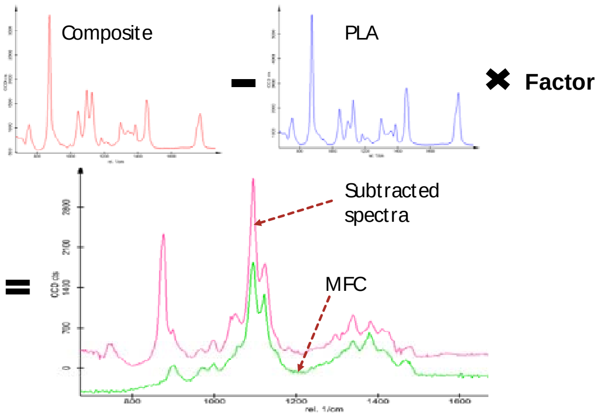

Fig. 1 Spectra subtraction to obtain cellulose bands.

Although it is intuitive to subtract the Raman spectrum of composite using a separately acquired spectrum of neat PLA, several issues exist. First, it is difficult, if not impossible, to acquire spectra of both composite and matrix polymer (PLA) in the same signal intensity. To address this difference, an adjusting factor was used (Fig. 1). For example, if the neat PLA signal is higher in intensity, an appropriate value for the factor would be less than one so that the intensity is reduced prior to subtraction. Second, if certain peaks of polymer (PLA) in the composite spectra shift slightly due to molecular interactions with the fillers, the subtraction would not result in a complete removal of the peak concerned, thereby making it difficult to judge whether or not the subtraction is successful. To address this issue, the method of Banerjee and Li [3] was adopted in which a completely subtracted spectrum (Fig. 2B) would exhibit a first derivative curve that has a minimum absolute area compared to under- or over-subtraction (Fig. 2C and 2D). Thus, the adjusting factor was optimized in this study to attain subtracted spectra whose first derivative curves had minimum absolute areas. Spectra from the subtraction were favorably similar to neat MFC (Fig. 1).

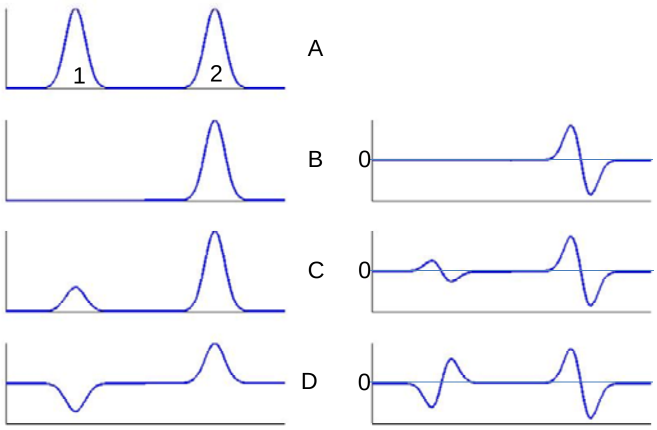

Fig. 2. A multicomponent spectrum (A) and subtracted spectra (B-D) with their respective first derivatives (right). Component 1 is (B) completely, (C) under-, and (D) over-subtracted.

The subtracted spectra were curve-fitted using the XPSPeak shareware to four component peaks (Fig. 3) in the frequency range of 1020-1172 cm^{-1}. The position (in cm^{-1}) of the 1095 cm^{-1} peak could then be determined.

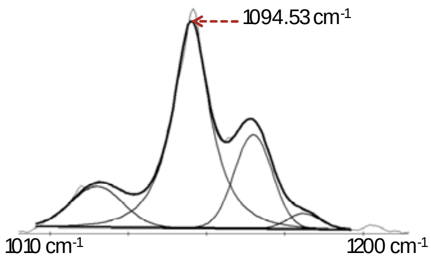

Fig. 3. Curve-fitting of a composite peak of cellulose to determine the position of the 1095 cm^{-1} peak.

The positions of this peak in spectra collected at different locations along the composite X and Y planes were determined to be less than 0.1 cm^{-1} in variability.

When the composites were tensile-loaded, the peak shift, hence local stress of the lactide-modified nano-cellulose increased more abruptly than untreated nano-cellulose (Fig. 4). This result signifies a higher load transfer when filler/matrix compatibility was increased.

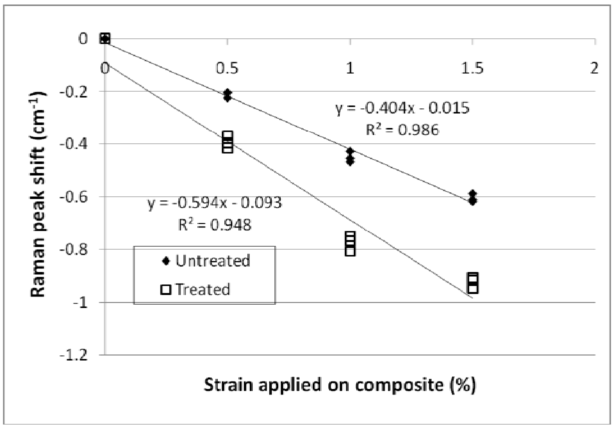

Fig. 4. Raman peak shift for untreated and lactide-treated MFC in stretched PLA composites

Conclusion

A spectra processing protocol was established to isolate cellulose spectra from Raman spectra of microfibrillated cellulose/PLA composites and to determine the position of the 1095 cm^{-1} stress-sensitive peak. This protocol was applied to monitor local stresses in PLA composites of treated and untreated MFC, verifying that a higher load transfer is attained by increasing compatibility with PLA.

Acknowledgement

This research was funded by the National Research Initiative, USDA Cooperative State Research, Education and Extension Service (grant no. 2008-35504-19158).

References

1. Eichhorn, S. J., Sirichaisit, J., and Young, R. J. Deformation mechanisms in cellulose fibres, paper and wood. *J. Mater. Sc.*, **36** (2001) 3129-3135.
2. Quero, F., Nogi, M., Yano, H., Abdulsalami, K., Holmes, S. M., Sakakini, B. H., and Eichhorn, S. J. Optimization of the mechanical performance of bacterial cellulose/poly(L-lactic) acid composites. *Appl. Mater. and Interfaces*, **2** (2010) 321-330.
3. Banerjee, S. and Li, D. Interpreting multicomponent infrared spectra by derivative minimization. *Appl. Spectroscopy*, **45** (1991), 1047-1049.