Reinforcing Function of Surface Acetylated Cellulose on Polylactic Acid (PLA) Based Biopolymer

T. Mukherjee, N. Kao, Rahul K.Gupta, N. Quazi and S.N Bhattacharya

School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne Victoria 3000, Australia.

Poor dispersion of microcrystalline cellulose (MCC) in polylactic acid (PLA) based matrix results in cracks or failure of such composites due to the tendency of MCC to agglomerate, owing to the presence of hydroxyl groups on their surface. In this study, surface modification of MCC, a possible alternative to arrest agglomeration, is accompanied by esterification reaction. This resulted in improved dispersion, strong interfacial adhesion and, thereby, improved storage modulus.

1.   Introduction

Cellulose fibers in microcrystalline form (MCC) have been much explored as a reinforcing material in biopolymer based matrix material such as polylactic acid or polylactide (PLA) [1-4]. Like any other composites, the challenge lies in dispersing MCC uniformly in the PLA matrix. Due to the presence of hydroxyl groups on their surface, MCC has the tendency to stick together or agglomerate resulting in crack formation and failure of the composite. To overcome this issue, scientists have tried to use variations of the dispersion methods that they have used for traditional particles and pigments such as nanoclay reinforcement [5]. A possible way to achieve good dispersion during processing is to "switch off" MCC self-interactions by binding with a hydrogen-bond-forming solvent. Several "solubilising schemes" have been explored to improve the MCC dispersion mechanism, including the use of surfactants [6], acetylation [7], silylation [3], grafting [8], etc.

In this paper, surface acetylation of cellulose has been attempted by acetyl chloride via esterification reaction. Composites were prepared with this surface acetylated MCC, using PLA as the base matrix. Their behaviour is characterized by FTIR, morphological and shear rheological tests.

2.   Sample preparation

Material: PLA biopolymer (Naturework PLA Polymer 4032D) with a density of 1.24 g cm^{-3} and a melting temperature of 160 °C was chosen as the matrix. Microcrystalline cellulose (MCC) with a mean particle size of 20 μm, supplied in powder form by Sigma Aldrich, was used as a raw material. Acetic anhydride, acetyl chloride, pyridine, and dichloromethane were purchased from Sigma Aldrich.

Acetylation: Acetylation was performed with constant stirring in a round bottom flask equipped with a condenser. Reaction with acetyl chloride is carried out at room temperature in an inert nitrogen atmosphere. A suspension of 2 g of MCC and 20 ml of dichloromethane was dispersed by constant stirring for half an hour. 5 ml of acetyl chloride was added to the flask with 1 ml of pyridine. The reaction was kept at room temperature for 48 hours. After the reaction, the product was isolated by precipitation in 20-50 ml ethanol and then filtered. The final product was then washed 3-5 times with ethanol/acetone to eliminate all non-bonded chemicals (i.e. unreacted compounds and reaction by-products). Finally acetylated cellulose microcrystals coded as AC-MCC were oven dried in vacuum at 70 °C for 24 hours.

Preparation of composites: Composites were prepared by the solvent casting technique, using dichloromethane (DCM) as the medium. The desired amount of AC-MCC was added along with 2.0 g of PLA into DCM to produce a mixture. The mixture was then conditioned overnight to eliminate bubbles and then cast into a Petri dish. The DCM was allowed to evaporate at ambient temperature (25 °C) for 24 h. Finally the solidified films, with a thickness of around 1 mm, were vacuum dried overnight, and then kept in a desiccator containing silica gel. Composites with pure cellulose are coded as PLA-MCC, while composites with acetylated cellulose are coded as PLA-AC-MCC.

3.   Characterization

3.1   Fourier transform infrared (FT-IR) spectroscopy

FTIR spectra of the powdered MCC and AC-MCC were recorded using a Perkin Elmer FTIR spectrophotometer (TA 8000). The powders were measured using a KBr-drift method, in the range of 4000-450 cm^{-1}. The spectrum was analysed with Perkin Elmer Spectrum software

3.2   Morphology tests by environmental scanning electron microscopy (SEM)

Morphology of MCC and the fractured surface of the MCC based PLA composites at different loading by weight percentage, were examined using an FEI Quanta 200 environmental scanning electron microscope (ESEM), at an acceleration voltage of 30 kV and pressure of 0.5 torr. MCC powder was sprayed in a carbon tape to study its morphology. The fractured surface was prepared by immersing the specimen in liquid nitrogen and manually fracturing the specimen. Samples were then mounted onto a sample holder with fracture surface facing upwards and the sample holder was placed in the ESEM sample chamber. Various sample surfaces were scanned to obtain a visual impression of fiber fracture, distribution and the appearance of the fiber/polymer interface.

3.3   Shear rheology

Dynamic frequency sweep tests were conducted using an ARES Rheometer (TA Instrument) based on constant strain rate. The tests were conducted using a 25 mm parallel plate at a temperature of 180 °C. All measurements were performed using a force transducer with a range of 0.2 to 200 g-cm torque. Prior to any tests, the zero gaps between the parallel plates were calibrated at the required temperature to take care of the thermal expansion. Dynamic Strain Sweeps were conducted to check the linear viscoelastic region (LVR) of these composites. All tests were conducted only in the LVR. Dynamic frequency sweep tests were conducted between the frequency of 0.1 and 100 rad/s at 180 °C. Tests for each sample composition were repeated five times with the data reported being the mean.

4.   Results

4.1   Acetylation of MCC (FT-IR Analysis)

The reaction scheme of acetylation with acetyl chloride, along with FTIR results, is represented in Fig.1 on the next page. The spectral curve shows the appearance of a new peak in the carbonyl area around 1752 cm^{-1}, as associated with the formation of the ester group. Intensity of the peaks located around 3350 cm^{-1} was assigned to –OH stretching which decreased after acetylation.

4.2   Morphology of the composites

Fig. 2(a) shows the neat fractured surface of PLA, while Fig. 2(b) represents the morphology of MCC. From Fig. 2(b) the aspect ratio can be calculated in the range of 4.45 - 7.5. Fig. 2(c) shows PLA-MCC composite at 2.5 wt % loading. Cellulose nucleation with
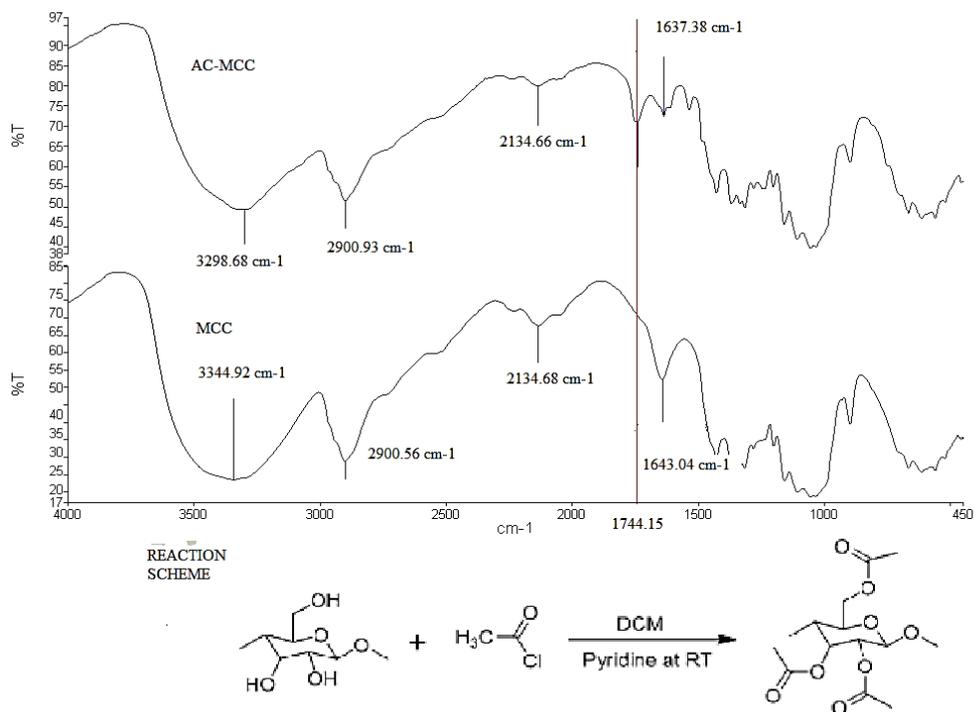
Fig.1 FTIR Study of the AC-MCC as compared to pure MCC

agglomeration starts at this state and Fig. 2(d) compares with PLA-AC-MCC at the same loading. Agglomeration is more evident at a higher loading of MCC (5 wt %) as shown in Fig. 2(e), which is arrested to an extent in PLA-AC-MCC as shown in Fig. 2(f).
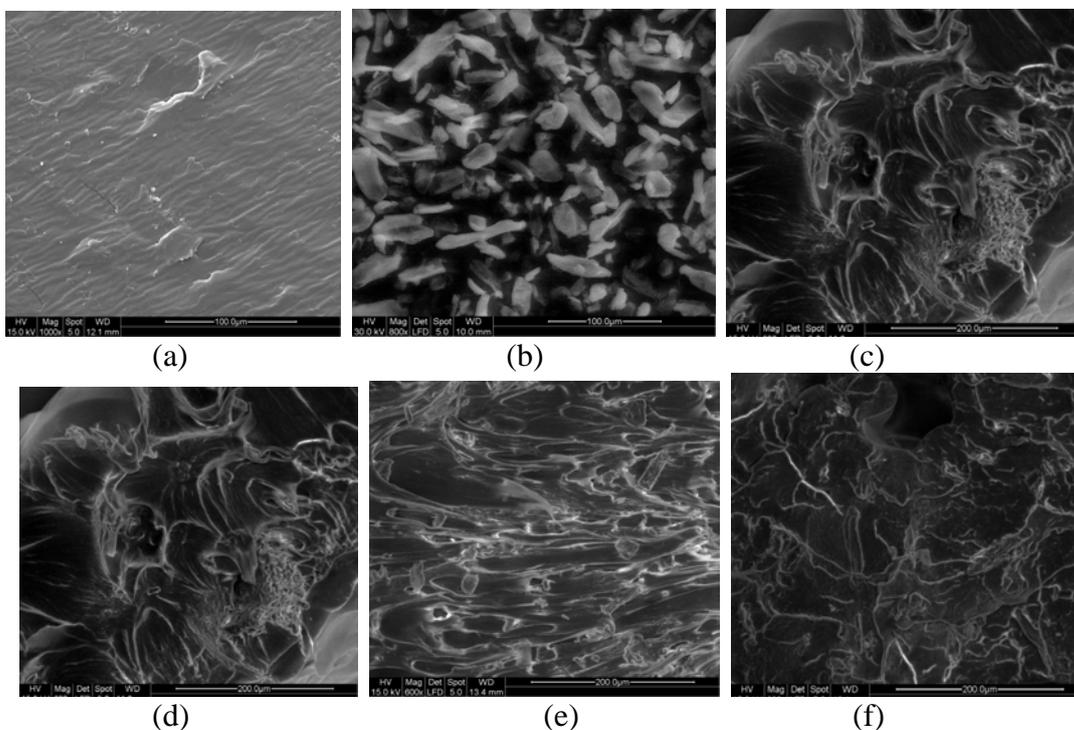.

Fig. 2. (a) Neat PLA surface (b) morphology of MCC (c) PLA-MCC (2.5 wt %)
(d) PLA-AC-MCC (2.5 wt %) (e) PLA-MCC (5 wt %) (f) PLA-AC-MCC (5 wt %)

4.3. Shear rheology

Fig. 3 compares the storage modulus of the acetylated MCC reinforced PLA based composites with that of pure MCC based PLA composites at various loading (2.5-20 wt %) at 180 °C. At higher loading (15-20 wt %), there is evidently a substantial improvement in G' for PLA-AC-MCC composites, as compared to the PLA-MCC composites. For a 15 wt. % loading of AC-MCC, G' is increased by a frequency-dependent factor ranging from 2.5 to 10. At 20 wt %, it increased by the very significant factor of 100 over the full frequency range.
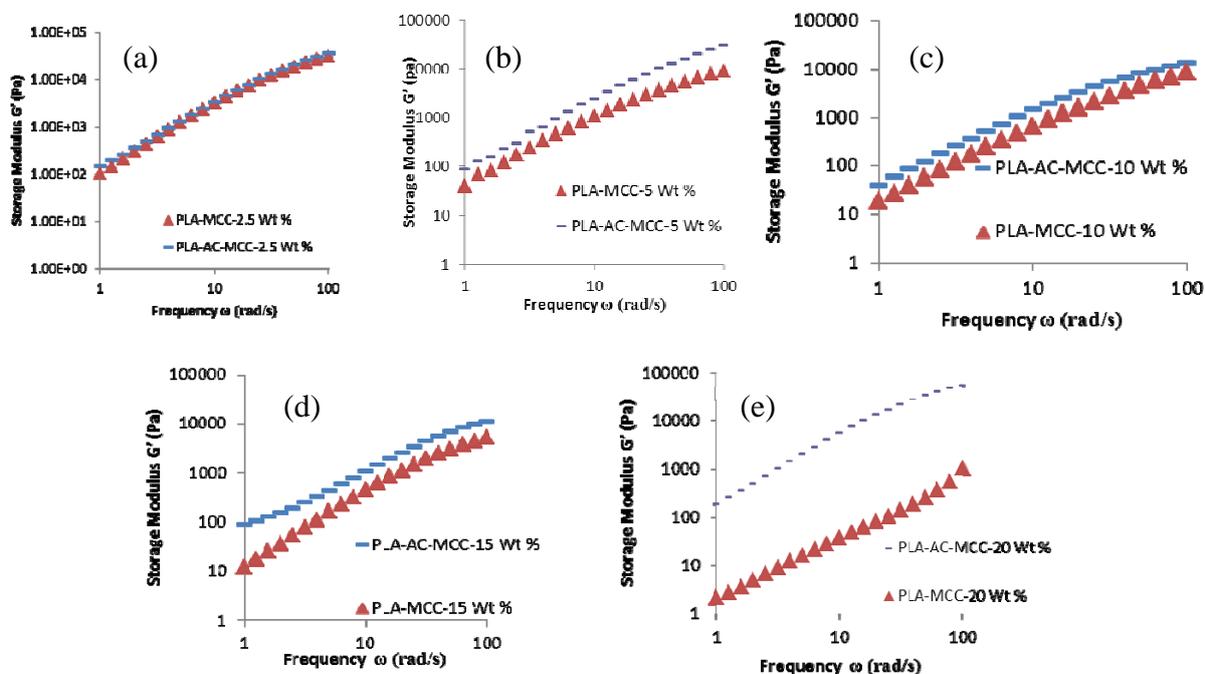

Fig. 3 Comparision of storage modulus (G') of PLA-AC-MCC composites at 180 °C with acetylation at (a) 2.5 wt % (b) 5 wt % (c) 10 wt % (d) 15 wt % (e) 20 wt %

5.   Conclusion

Successful acetylation of microcrystalline cellulose was accompanied by acetyl chloride at room temperature. When composites were prepared by this surface acetylation, improvement in dispersion was observed in the morphological studies. This improved the storage modulus of the resulting composites, which is more significant at a higher loading. The superior reinforcing function of MCC will expand the practical application of PLA-based materials as replacements for traditional petrochemical plastics.

Reference
[1]   Oksman K, Mathew A P, Bondeson D and Kvien I 2006 *Compos. Sci. Technol.* **66** 2766
[2]   Siqueira G, Bras J and Dufresne A 2010 *Polymers* **2** 728
[3]   Pei A, Zhou Qi and Berglund L A 2010 *Compos. Sci. Technol.* **70** 815
[4]   Pilla S, Kim S G, Auer G K, Gong S and Park C 2009 *Polym. Eng. Sci.* **49** 1653
[5]   Eichorn S, Dufresne A *et al.* 2010 *J. Mater. Sci.* **45** 1
[6]   Oksman K, Mathew A P *et al.* 2006 *Compos. Sci. Technol.* **66** 2776
[7]   Braun B and Dorgan J R 2009 *Biomacromolecules* **10** 3334
[8]   Pracella M, Haque M M and Alvarez V 2010 *Polymers* **2** 554