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Improved dispersion of cellulose microcrystals in polylactic acid (PLA) based composites applying surface acetylation

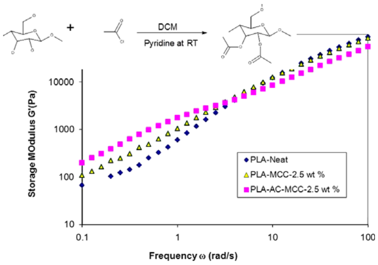
Tapasi Mukherjee [a,*], Marco Sani [b], Nhol Kao [a], Rahul K Gupta [a], Nurul Quazi [a], Sati Bhattacharya [a]

[a] Rheology and Materials Processing Centre, School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne, VIC-3001, Australia
[b] Bio21 Molecular Science and Biotechnology Institute, The University of Melbourne, Parkville, Melbourne, VIC-3010, Australia

HIGHLIGHTS

- Microcrystalline cellulose (MCC) was partially surface acetylated.
- Surface acetylated MCC was used as reinforcement in poly (lactic acid) composites.
- Rheological percolation was evaluated to quantify dispersion.
- Surface acetylation improved dispersion reaching its optimal value at 2.5 wt%.

GRAPHICAL ABSTRACT



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ABSTRACT

Design of sustainable bioplastics can be achieved by preparing composites from renewable materials like microcrystalline cellulose (MCC) fibre and biopolymer such as polylactic acid (PLA). The key driving factor that affects their performance is the quality of dispersion of MCC in the PLA matrix. In this study, surface modification, one way to facilitate improved dispersion, is carried out by acetyl chloride. PLA composites were prepared with the acetylated MCC applying solvent casting technique. Confirmation of acetylated group is accompanied by FTIR and NMR study. Change in crystalline property and thermal behaviour is observed by XRD study. Improvement in storage modulus (G') is reflected in shear rheological tests, reaching an optimal value at 2.5 wt%. This improvement is primarily attributed to a more homogeneous dispersion of MCC in the matrix. Rheological percolation threshold is calculated to quantify the level of dispersion. This study is aimed to quantify the level of dispersion of acetylated MCC, as compared to pure MCC by shear rheology.

1. Introduction

Microcrystalline cellulose (MCC) fibre, as the name suggests, is commercially available and has gained significant interest in the last decade (Lin et al., 2011; Frone et al., 2011). Some of the unique features of MCC include its morphology, low density and mechanical strength (Huda et al., 2006). Polylactic acid (PLA) based cellulose composites have been much explored in the recent years as the key material to develop the next generation of light weight and high performance materials for a variety of defense, infrastructure and energy applications (Jonoobi et al., 2010; Peterson et al., 2007; Pei et al., 2010). The necessity to improve the dispersion of cellulose microcrystals (MCC) in biopolymer matrix like polylactic acid (PLA) has become increasingly important to enhance the mechanical properties of such composites and thereby the commercial viability of such products for biomedical

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* Corresponding author. Tel.: +61 3 9925 2410.
E-mail addresses: tapashi.mukherjee@rmit.edu.au (T. Mukherjee), msani@unimelb.edu.au (M. Sani), nhol.kao@rmit.edu.au (N. Kao), rahul.gupta@rmit.edu.au (R. Gupta), nurul.quazi@rmit.edu.au (N. Quazi), sati.bhattacharya@rmit.edu.au (S. Bhattacharya).

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as well as flexible packaging applications (Braun and Dogan, 2009).

Dispersion is the key challenge to prepare such composites (Braun and Dogan, 2009). The presence of hydroxyl groups on the surface of cellulose restricts its homogeneous dispersion in PLA, by initiating agglomeration or entanglement (Dubief et al., 1999). A possible strategy to overcome this challenge is surface modification, where the hydroxyl group is partially replaced by another functional group. In general, surface functionality of cellulose microcrystals as carried out from the literature review study, can be broadly categorized into three groups; (I) native surface chemistry of the particle as a result of their extraction like acid hydrolysis by sulfuric acid (Frone et al., 2011) (II) physical adsorption of surfactants or polyelectrolytes (Oksman et al., 2006) and (III) covalent modification such as esterification/etherification Braun and Dogan (2009), silylation (Pei et al., 2010) and polymer grafting (Pracella et al., 2010).

In this work the hydroxyl groups, as present on the surface of cellulose was partially substituted by acetyl groups by using acetyl chloride at room temperature. The primary motivation behind this study was to improve the dispersion of MCC in PLA matrix by surface acetylation. Emphasis was laid to characterize the behaviour of dispersion at different level of loadings, ranging from 1 to 5 wt%. Beyond 5 wt% loading, filler–filler interactions were observed. Composites were prepared with this surface acetylated MCC, using PLA as base matrix by solution casting technique and dichloromethane as the solvent (Mukherjee et al., 2012). Acetylation is confirmed by FTIR and NMR study. The behaviour of dispersion is characterized by XRD, DSC, and shear rheological tests. A rheological percolation threshold is calculated to quantify the level of dispersion and the optimal loading for a uniform dispersion.

2. Experimental section

2.1. Material

A polylactic acid biopolymer (Nature Work PLA Polymer 4032D) with a density of 1.24 g cm^{-3} and a melting point of 160 °C was chosen as matrix. A 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, pyridine, dichloromethane was purchased from Sigma Aldrich (Mukherjee et al., 2012).

2.2. Sample preparation

2.2.1. Acetylation of MCC

Acetylation was performed with constant stirring in a 100 ml round bottom flask. A suspension of 2 g of MCC and 20 ml of dichloromethane (DCM) was dispersed by constant stirring for half an hour. A volume of 5 ml acetyl chloride was added to the flask with 1 ml of pyridine in an inert nitrogen atmosphere. The reaction was kept at room temperature for 48 h. 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 excess of acetyl chloride and pyridine. Finally acetylated cellulose microcrystals coded as AC-MCC were oven dried in vacuum at 70 °C for 24 h (Mukherjee et al., 2012).

2.2.2. Preparation of composites.

The desired amount of MCC/AC-MCC was added along with 20 g of PLA into DCM solvent (200–400 ml approx) with mechanical stirring to produce a mixture. It formed a viscous solution over a period of 5 h. The mixture was then conditioned overnight to eliminate bubbles and was then cast into a petridish. DCM was allowed to evaporate off at ambient temperature (ca. 25 °C) for approx. 24 h. Finally, the solidified films, with a thickness of about 0.2 mm, were vacuum dried overnight, and then kept in a desiccator containing silica gel. The resultant composite sheets were coded as PLA-MCC/AC-MCC-1.5, PLA-MCC/AC-MCC-2.5, PLA-MCC/AC-MCC-3.5 and PLA-MCC/AC-MCC-5, the Arabic numerically representing the MCC/AC-MCC content in the PLA based matrix (Mukherjee et al., 2012).

2.3. Characterization

2.3.1. FTIR

FTIR-KBr spectroscopic studies were carried out in drift mode on the samples with a PerkinElmer FTIR spectrophotometer (TA 8000). A total of 32 scans per sample were taken, starting from 4000 to 450 cm^{-1}, with a resolution of 4 cm^{-1}. The spectrum was analysed with Perkin Elmer Spectrum Software (Mukherjee et al., 2012). The samples for FT-IR analysis were prepared by grinding the dry blended powders with KBr, often in the ratio of 1:100(Sample: KBr), using a pestle and a mortar. For the drift spectra, a Perkin-Elmer diffuse reflectance (DR) sampling cell was used.

2.3.2. ^{13}C solid state NMR

The CP/MAS ^{13}C-NMR spectra were recorded on a VNMRS 600 MHz NMR spectrometer equipped with 4 mm CPMAS triple resonance probe. The ^{13}C frequency was 150.8 MHz and the chemical shift resonances were referenced to the adamantane chemical shifts obtained with a similar pulse sequence. Acquisition was performed with a CP pulse sequence using a 5.25 ms proton $\pi/2$ excitation pulse, a spectral width of 50 kHz, an acquisition time of 25 ms using a SPINAL-64 decoupling scheme of 70 kHz strength and a 5 s delay between transients. The Hartmann–Hann match was optimized on the -1 sideband at a MAS speed of 8 kHz with a contact time of 500 ms and a linearly ramped-CP field of 30 ± 0.8 kHz. Typically, 12,000–16,000 transients were accumulated at 25°C. A line broadening of 50 Hz and zero filling to 65k points were used to process the spectra

2.3.3. Morphological tests

Morphology of MCC and the fractured surface of the MCC based PLA composites at different loading of weight percentage, were examined using an FEI Quanta 200 environmental scanning electron microscope (ESEM), at an acceleration voltage of 30 kV and pressure of 0.50 Torr. MCC powder was sprayed on 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 on to a sample holder with the fractured surface facing upwards. The sample holder was then placed in the ESEM sample chamber. Various sample surfaces were scanned to obtain a visual impression of fibre fracture, distribution and the appearance of the fibre/polymer interface (Mukherjee et al., 2012).

2.3.4. Crystallinity study by X-ray diffraction (XRD)

XRD patterns were obtained using a Bruker D4 Endeavor X-ray diffractometer in the angular range of 6–90° (2θ) at a voltage of 40 kV and current of 100 mA. Peak intensities were every 0.02° at sweep rates of 1.0° 2θ/min, to see the change in crystallinity after acetylation if any.

2.3.5. Differential scanning calorimetry (DSC)

Thermal analysis was performed on a DSC-2920 Modulated DSC (TA Instruments) calibrated with indium with a nitrogen atmosphere, with a flow rate of 35 ml/min. An empty aluminium pan served as a reference. Composite sample weights of approximately