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Polylactic acid biocomposite filaments with improved mechanical properties

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Fully biodegradable polylactic acid/microcrystalline cellulose composites, with surface-modified reinforcing cellulose, are suitable for 3D printing applications.

Polylactic acid (PLA) is currently being studied as a potential material to replace petroleum-based plastic products.[1] This biodegradable alternative is especially attractive because it can be recycled and thus contribute to sustainability. PLA, however, does come with some drawbacks. For example, it exhibits low thermal stability and relatively poor mechanical performance. To improve these properties, some researchers have incorporated reinforcements (e.g., carbon nanotubes, hydroxyapatite, or layered silicates) into the PLA matrix.[2] More recently, however, the focus has shifted toward using biodegradable reinforcements to produce a fully biocompatible nanocomposite material (a 'green' composite).

Cellulose is a typical choice of biodegradable reinforcement for PLA composites because it is a tough, fibrous, water-insoluble material.[2, 3] It is extremely difficult, however, to achieve uniform dispersion of cellulose within the PLA matrix. This is because PLA is hydrophobic, whereas cellulose is hydrophilic. Aggregations of cellulose therefore tend to occur and make uniform dispersion difficult.[2] It is thus challenging to realize the full theoretical benefits of cellulose addition. In recent studies, chemical and physical modifications have been investigated in an attempt to adjust the compatibility between the cellulose and PLA,[4] but there is still a shortage of information on this topic.

In this work,[5] we have therefore investigated a novel route for tailored, fully degradable biocomposite filament production, for use in 3D printing applications. We used a two-step process to prepare our biocomposite filaments. First, we conducted PLA/microcrystalline cellulose (MCC) film casting. This was followed by an extrusion process, in which we used different quantities of PLA and MCC (1, 3, or 5wt% cellulose), depending on the desired final composition. In an effort to improve the dispersion of the MCC within the PLA, we also investigated surface modification of the MCC with titanate.

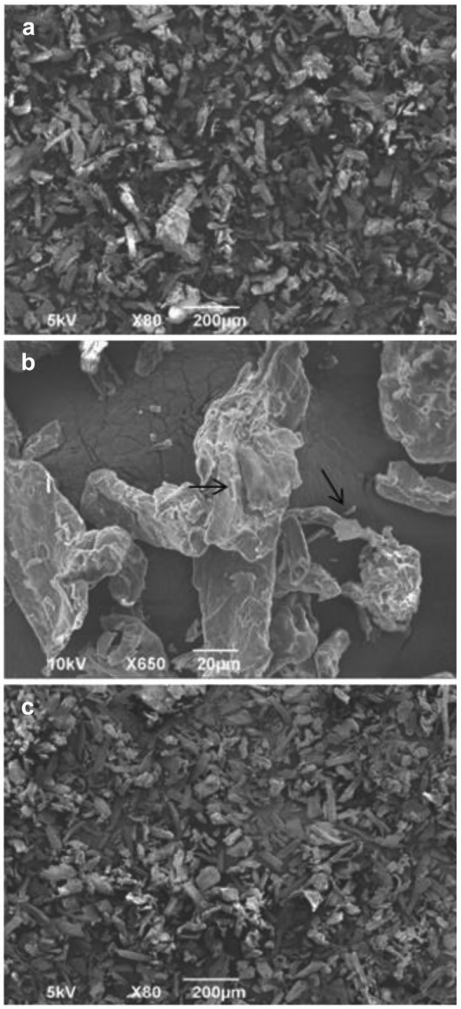

Figure 1. *Scanning electron microscope images showing the morphology of (a) and (b) unmodified cellulose, and (c) titanate-modified cellulose. Arrows in (b) point to nanofibrils, many of which agglomerate to create the microcrystalline cellulose particles.*

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We conducted a series of measurements to examine the influence of the cellulose content and modification on the morphological, mechanical, and thermal properties of the biocomposites. These tests included scanning electron microscopy (SEM), x-ray photoelectron spectroscopy, dynamic mechanical thermal analysis, differential scanning calorimetry (DSC), as well as a water absorption test. In the final part of our work, we used a fused deposition modeling (FDM) technique to successfully conduct 3D printing of our extruded cellulose-reinforced PLA filaments.

It is possible to observe the influence of the titanate on the cellulose morphology in the SEM images (see Figure 1). These images show that the treated cellulose is much smoother than the equivalent untreated cellulose. In addition, our DSC analyses (see Figure 2) indicate that for the PLA/unmodified-cellulose composites, the glass transition range is broader than for neat PLA and that it broadens with MCC content. This trend suggests that the addition of cellulose causes an increase in the

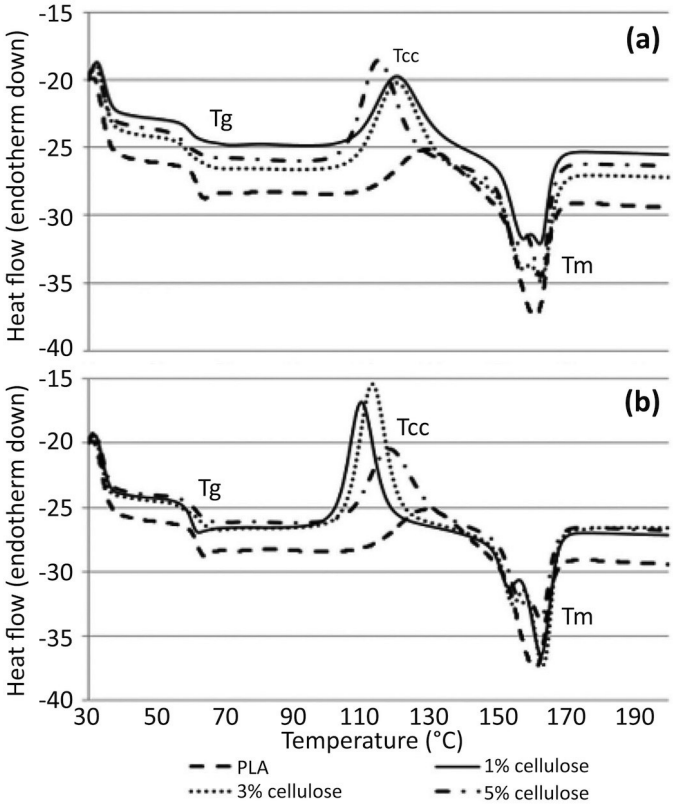

Figure 2. *Differential scanning calorimetry thermographs of (a) neat polylactic acid (PLA) and PLA/unmodified-cellulose composites and (b) neat PLA and PLA/modified-cellulose composites. The glass transition (Tg), cold crystallization (Tcc), and melting (Tm) temperature peaks are labeled in each case.*

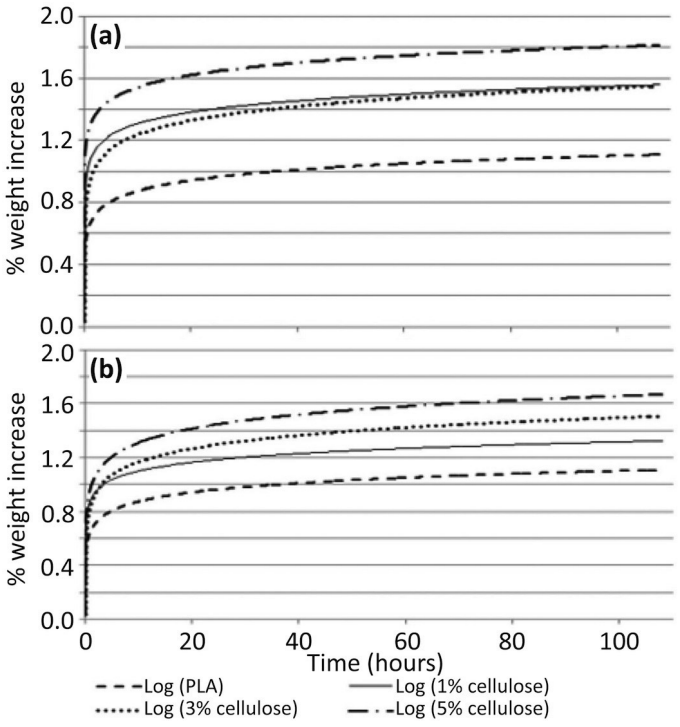

Figure 3. *Water absorption curves for (a) neat PLA and PLA/unmodified-cellulose composites and (b) neat PLA and PLA/modified-cellulose composites.*

crystallinity, which therefore leads to an improvement in the mechanical performance. Furthermore, we find that the cold crystallization peak of the unmodified-cellulose composites is sharper and shifted to lower temperatures than for neat PLA. This indicates that the crystallization occurs faster in the composites, with cellulose acting as a nucleating agent for PLA crystallization. We also note that the cold crystallization peaks of the composite filaments with surface-modified MCC (for the 1 and 3wt% samples) is sharper and shifted to lower temperatures than for neat PLA and for the unmodified-MCC equivalents. This illustrates that the modified cellulose also acts as a nucleating agent for PLA. We find the 3wt% modified-cellulose composite exhibited the optimum results.

We have also evaluated the effect of the MCC reinforcement content on the hygroscopicity of the composites (see Figure 3). In these water absorption curves, we observe the same pattern for both the neat PLA and for the PLA/MCC composites. That is, initially the water absorption increased considerably, but the absorption rate reached a plateau after 24 hours. With the addition of 5wt% unmodified and modified cellulose, the water uptake increased to 1.8 and 1.65%, respectively

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(after 4.5 days), compared with 1.18% for the neat PLA filaments. With this finding, we confirm the hydrophilic nature of cellulose. We also observe a lower water absorption for the composites that contain modified cellulose compared with unmodified cellulose, which indicates that the addition of the titanate coupling agent caused a reduction in the hydrophilicity of the cellulose.

In summary, we have demonstrated that employing a solvent casting method, followed by extrusion, is a promising method for the production of PLA/MCC biocomposite filaments for FDM applications. We found that the addition of MCC increases the crystallinity of the PLA and thus its mechanical properties. Furthermore, surface modification of the MCC (with titanate) gives rise to an improvement in the mechanical properties of the biocomposites and to a reduction in water absorption, compared with unmodified-cellulose biocomposites and neat PLA. Overall, we find that these materials provide an opportunity to create fully degradable biocomposite prototypes via 3D printing, for possible lightweight applications in the biomedical, automotive, and construction sectors. In future work, we hope to conduct further studies to improve the dispersion of cellulose in the PLA matrix, e.g., the investigation of other cellulose surface-modification treatments.

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