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Thermal characterization and electrical properties of Fe-modified cellulose long fibers and micro crystalline cellulose

Smith Sundar · Mohini Sain · Kristiina Oksman

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Abstract Thermal properties of polylactic acid (PLA) filled with Fe-modified cellulose long fibers (CLF) and microcrystalline cellulose (MCC) were studied using thermo gravimetric analysis (TG), differential scanning calorimetry, and dynamic mechanical analysis (DMA). The Fe-modified CLFs and MCCs were compared with unmodified samples to study the effect of modification with Fe on electrical conductivity. Results from TG showed that the degradation temperature was higher for all composites when compared to the pure PLA and that the PLA composites filled with unmodified celluloses resulted in the best thermal stability. No comparable difference was found in glass transition temperature (T_g) and melting temperature (T_m) between pure PLA and Fe-modified and unmodified CLF- and MCC-based PLA biocomposites. DMA results showed that the storage modulus in glassy state was increased for the biocomposites when compared to pure PLA. The results obtained from a femtostat showed that electrical conductivity of Fe-modified CLF and MCC samples were higher than that of unmodified samples, thus indicating that the prepared biocomposites have potential uses where conductive biopolymers are needed. These modified fibers can also be tailored for fiber orientation in a matrix when subjected to a magnetic field.

S. Sundar (✉) · M. Sain · K. Oksman
Centre for Biocomposites and Biomaterials Processing,
University of Toronto, 33 Willcocks St, Toronto,
ON M5S 3B3, Canada
e-mail: smith.sundar@utoronto.ca

K. Oksman
Division of Manufacturing and Design of Wood and
Bionanocomposites, Luleå University of Technology,
971 87 Luleå, Sweden

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Introduction

Polymer composites have been found to have indispensible applications in various fields such as automotive parts, aerospace, construction, and others [1, 2]. The recent shift toward environmentally friendly materials has paved the way to the development of biodegradable polymers and reinforcers in composites for tailored applications. Among biopolymers, polylactic acid (PLA) has been widely considered as a potential substitute for fossil fuel-based plastics. Mechanical properties of PLA are comparable to polystyrene for stiffness and strength [3]. PLA can be a synthesized form of lactic acid, which is derived from renewable agricultural raw materials such as corn, maize, wheat, etc. which have undergone fermentation. Bio-based reinforcers in composites range from wood pellets and wood fiber, to micro and nano cellulose fibers [4]. Owing to its abundance and remarkable reinforcing capacity, cellulose has been widely accepted as a reinforcer for polymer composites. The reinforcing capacity of cellulose depends on various factors, such as fiber dispersion and orientation. Studies show that orienting cellulose fiber in a matrix can be achieved by applying shear force. Cellulose whisker can orient in a plane perpendicular to shear direction for low shear rates and along the shear direction for higher rates [5]. However, the optimization of fiber motion under flow condition is complicated and extremely difficult to achieve [1]. It is also reported that mechanical properties were improved when composites with oriented fiber were tested along the fiber axis, even at fiber content as low as 10% [1]. Another path to orient cellulose fiber is to subject the reinforcing cellulose fiber to a strong magnetic field (usually up to 20 Tesla (T)), in a matrix suspension. However, such an orientation of cellulose can be achieved only if the fibers are at the nano scale [6]. It is predicted that micron-scale cellulose fibers can be oriented through the modification of cellulose using magnetic entities such as Fe and thus is speculated to improve the mechanical properties of the composites. The high energy required to orient cellulose fibers under a magnetic field can be considerably reduced by modifying the available hydroxyl sites of cellulose to form complexes with Fe. Modified cellulose–metal complexes have been used in medicine in the past and also have the potential to be used in magneto-graphic printing, manufacturing of security paper, and other advanced composites [7, 8].

Studies have shown that the thermal properties of polymers will change with the addition of fillers [10]. However, there is only very limited information on thermal properties and the effect of iron modified, cellulose-based PLA composites. The ultimate objective of this research is to orient micro-scale Fe-modified cellulose fibers in a polymer matrix. This article evaluates the thermal properties of unmodified and iron-modified microcrystalline cellulose (MCC)- and cellulose long fibers (CLF)-based PLA composites prior to fiber orientation. Thermal analysis techniques such as thermo gravimetric analysis (TG), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) were used to characterize the thermal properties of the Fe-modified cellulose-PLA composite. The electrical conductivity of the modified fibers was compared with unmodified fibers using a femtostat. The results are discussed.

Experimental

Materials

Microcrystalline cellulose Avicel, PH-101, was purchased from Fluka, Biochemika, Switzerland and CLF were purchased from Sigma–Aldrich, Canada. Both materials were used as obtained, without any further processing. Two different types of cellulose, CLF and MCC, were used due to their higher aspect ratio and elevated crystallinity, respectively. PLA was used as a matrix for the composites. PLA was obtained from NatureWorks^{TM}, Cargill Dow LLC. This biopolymer has a density of 1.24 g/cm^3, a melting temperature of 160–170 °C, and a glass transition temperature between 55 and 60 °C.

Modification of cellulose

Both celluloses (MCC and CLF) were soaked in NaOH for intra-crystalline swelling and then oxidized using hydrogen peroxide 30%v/v. The oxidized hydroxyl group of cellulose was reacted with a mixture of 16.6 g of Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) (98% purity) and NaOH (1 M). The ratio of $FeSO_4$ to NaOH was 7:12 to liberate Fe^{2+} ions. The liberated Fe^{2+} ions formed metal complexes with cellulose [18]. Hydroxyl groups of cellulose at 2, 3 and 6 positions are involved in the formation of cellulose-Fe bonds. The bonds formed are based on in situ coordination between the Fe^{2+} and cellulose [9, 19].

Compounding

Fe-modified and unmodified MCC and CLF were loaded on to PLA. The loading of fiber to the matrix was 10% of the total weight of the mixture. The mixture was compounded using a brabender mixer at 180 °C for 15 min at 60 rpm.

Profiling

The prepared compound was profiled at 190 °C and 50 rpm into rectangular blocks of 35.0 × 12.04 × 2.02 mm^3 for DMA using a DSM Micro 15, USA extruder.

Electrical conductivity

The conductivity of Fe-modified MCC and CLFs was compared to unmodified samples using a Gamry FAS2 Femtostat. Fe-modified and unmodified cellulose samples were pressed into disks of 5.5 mm diameter and 0.2 mm thickness. A potential difference ranging from 0.5 to 1.5 V was applied to the sample. The variation in current (I) on constant voltage was recorded by monitoring potential differences between the reference electrode and the counter electrode attached to the sample. Conductivity of the sample was calculated by taking the inverse of resistivity.

$$R = \partial \times L/A$$

where R is resistance, ∂ is resistivity, L is the length between electrodes and A is the surface area of the sample.

Thermogravimetric analysis

Thermal properties of PLA–Fe–CLF and PLA–Fe–MCC composites were compared to unmodified composites (PLA–CLF and PLA–MCC) and to pure PLA using a TGA Q 500 series thermogravimetric analyzer (TA Instruments, USA). The temperature ramping rate was 10 °C/min up to 700 °C in a nitrogen environment.

Differential scanning calorimetry

The glass transition temperature (T_g) and the melting temperature (T_m) for the Fe-modified and unmodified biocomposites as well as for the pure PLA were characterized using a Q1000 DSC (TA Instruments, USA). The sample weight was ≈5–7 mg and the materials were first equilibrated at 35 °C and then ramped to 250 °C using a heating rate of 10 °C/min.

Dynamic mechanical analysis

The composites and PLA profiles obtained from extrusion were subjected to a dynamic mechanical analysis using a TA Q800 (TA Instruments, USA). The storage modulus (E') and tan delta (δ) as DMA was run in dual cantilever mode. The sample dimensions were 35.0 mm in length, 12.04 mm in width, and 2.2 mm in thickness. The samples were heated from 35 to 150 °C with a heating rate of 3.0 °C/min; the strain amplitude was 30 μ at a frequency of 1 Hz.

Results and discussion

The presence of Fe–cellulose complexes upon modification of CLF and MCC were established by the results from XPS. In Fig. 1, the XPS spectra (low-resolution mode) of unmodified cellulose, modified cellulose, and pure $FeSO_4$ are shown. The results show the presence of Fe in modified cellulose samples. The XPS spectrum of modified cellulose samples does not show any peaks for sulfur, which is present in the spectra for $FeSO_4$. This suggests the absence of residual $FeSO_4$ present in modified cellulose and also that the Fe present is chemically bound to cellulose [9].

In Fig. 2, the FTIR spectra of modified CLF and MCC were compared to unmodified cellulose. The peaks around 1510–1520 cm^{-1} are expected from the asymmetrical vibration of diketones and/or bi-dentate ligands based on the formation of Fe–cellulose coordinate complexes. The peaks observed in the region of 3700–4000 cm^{-1} are suggested to result from the cleavage of primary and secondary hydroxyl groups of cellulose when they are involved in coordination complex formation with Fe. The peaks observed around 495–500 cm^{-1} essentially arise from metal oxygen bonds [9]. Results from FTIR spectra were helpful in establishing the association of Fe to cellulose through coordinate complex formation.

Thermograms from TG–DTG for CLF-based PLA composites are presented in Fig. 3. The peak degradation temperatures for the tested materials are also presented in Table 1. According to the results (Fig. 3a), among CLF-based composites, the addition of CLFs showed positive

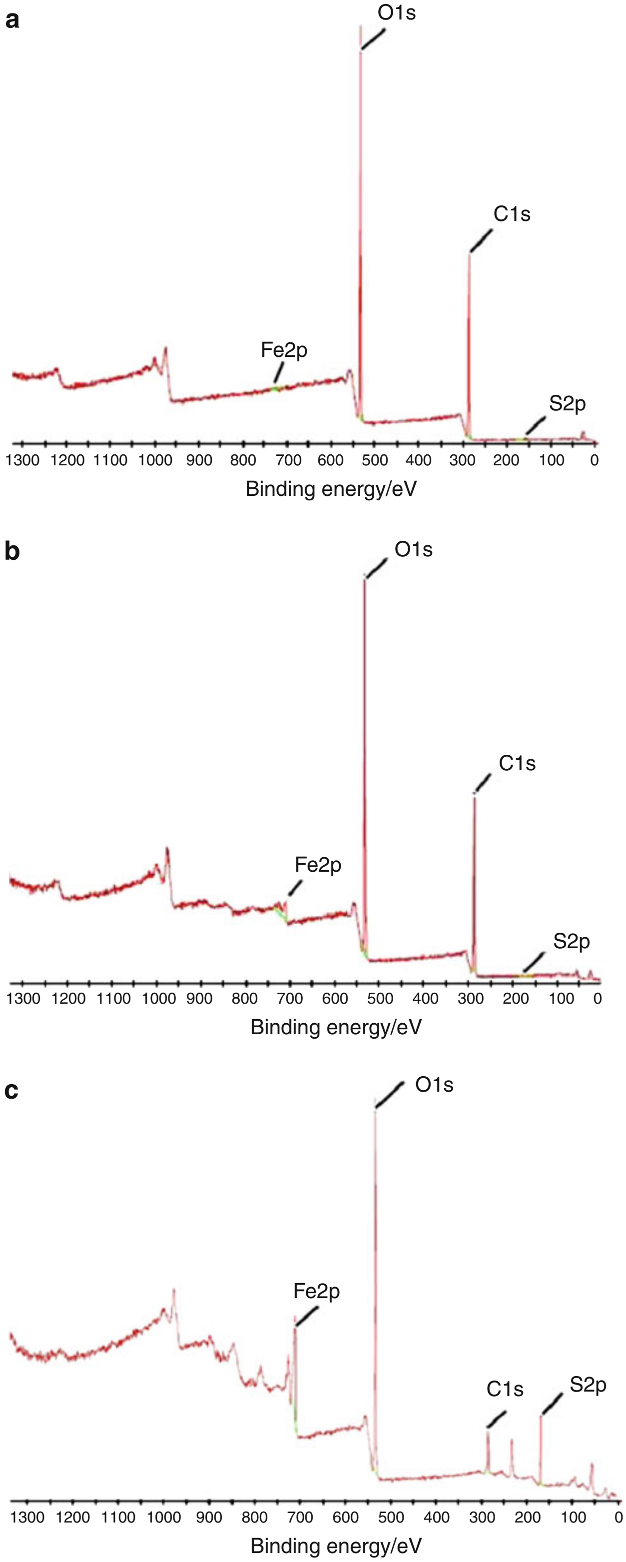
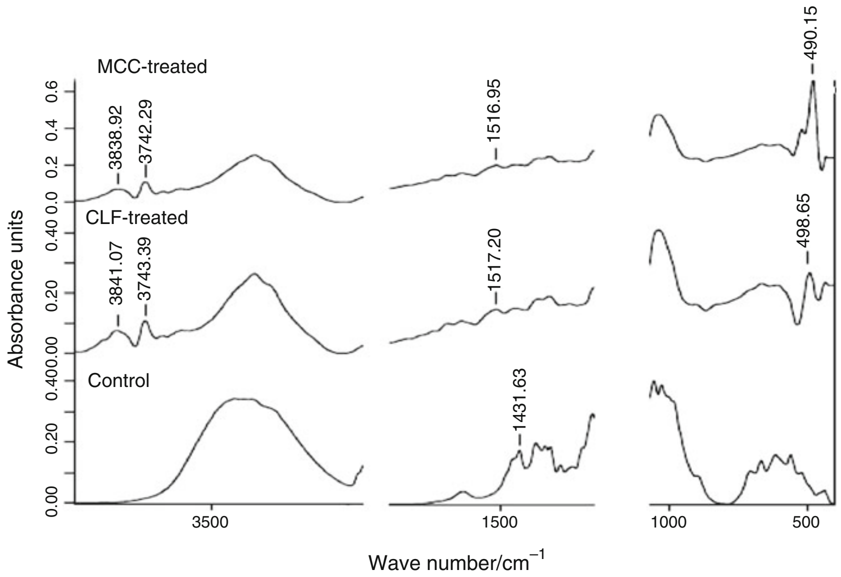


Fig. 1 Low resolution XPS spectra for **a** unmodified cellulose, **b** Fe-modified cellulose and **c** pure $FeSO_4 \cdot 7H_2O$

Fig. 2 FTIR Spectrum for Fe-modified MCC, CLF, and control cellulose



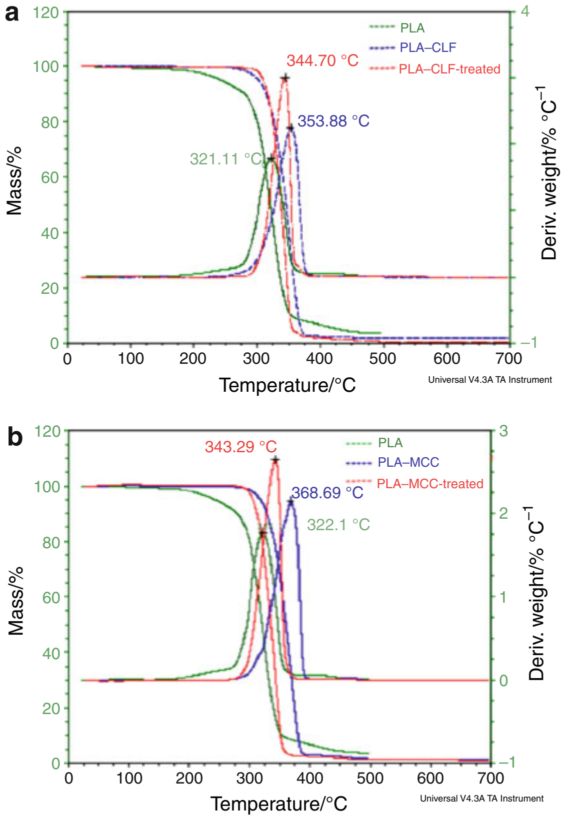


Fig. 3 TG analysis for **a** CLF-based PLA composites and **b** MCC-based PLA composites

Table 1 Degradation, glass transition, melt temperature, and tan δ peak temperature of PLA and the prepared composite materials

Materials	Degaradation T/°C	T_g/°C	T_m/°C	Tan (δ) peak T/°C
PLA	322.1	64.5	150.5	70.6
PLA–CLF	354.6	64.7	150.5	71.6
PLA–Fe–CLF	344.7	66.0	148.7	71.9
PLA–MCC	368.6	64.9	148.4	71.1
PLA–Fe–MCC	343.3	64.5	148.4	71.4

impacts on degradation temperatures. The peak degradation temperatures were highest for composites with CLF at 354.6 °C, the Fe-modified composite showed 10 °C lower degradation at 344.7 °C, and the PLA have the lowest at 322.1 °C. The reason for the higher thermal stability in the PLA–CLF biocomposite might be that the CLFs were not treated with NaOH as had been done for the Fe-modified composites and thus resulted in less structural damage and chain cleavage [10]. However, in the case of PLA–Fe–CLF biocomposites, the cellulose fibers when treated with NaOH for bulking and further treatment with $FeSO_4$ could have resulted in loss of crystalline regions and/or cleavage of the molecular chains resulting in lower degradation temperature than that of PLA–CLF composite. Figure 3b shows similar trend when MCC is used, the degradation temperature was highest for the PLA–MCC composite 368.6 °C and this temperature was decreased to 343.3 °C for PLA–Fe–MCC further to 322.1 °C for pure PLA. The higher degradation temperature of PLA–MCC compared to PLA–CLF could have aroused due to the higher crystallinity of MCC to that of CLF.

Figure 4a, b shows the comparison between Fe-modified and unmodified CLF and MCC in a PLA matrix. The difference between peak degradation temperature for unmodified MCC and CLF was $\approx$15 °C; however, there was not much difference in peak degradation temperature for Fe-modified samples. The higher degradation peak for unmodified MCC when compared to CLF might have arisen from the presence of higher crystalline regions.

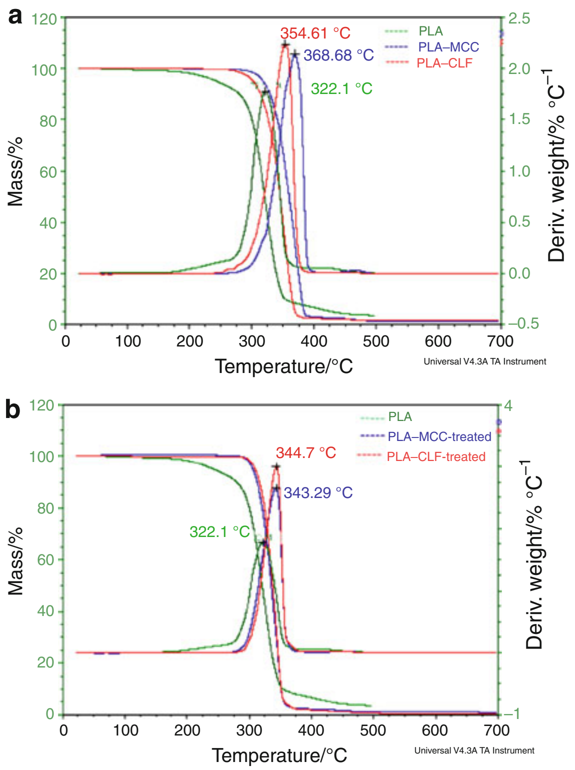


Fig. 4 TG analysis for **a** Comparison between untreated CLF and MCC-based PLA composites and **b** Comparison between Fe-treated CLF and MCC-based PLA composites

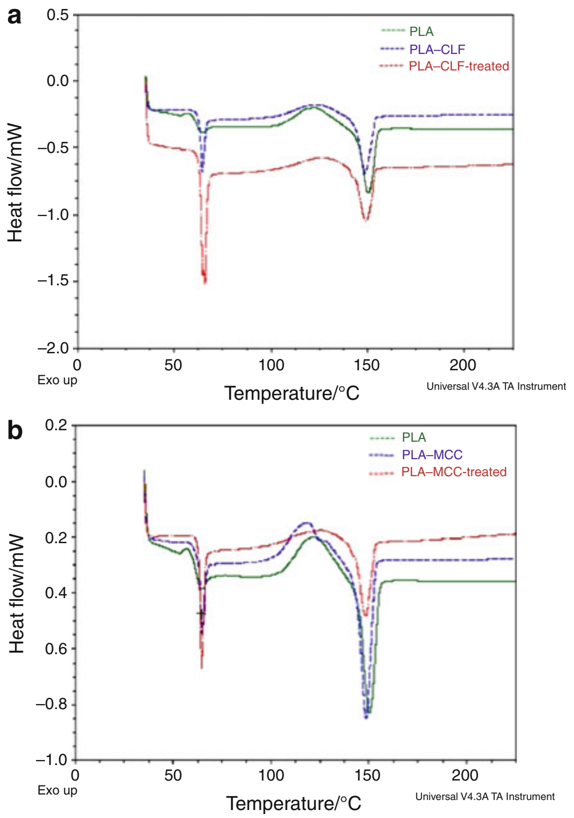


Fig. 5 DSC for **a** CLF-based PLA composite and **b** MCC-based PLA composite

Differential scanning calorimetry was helpful in comparing glass transition temperatures (T_g) and melting temperatures (T_m) of the pure PLA and produced composite materials. Figure 5a shows the results for the endothermic curves for PLA, PLA–CLF, and for PLA–Fe–CLF. The endothermic T_g peaks observed were not considerably different among the different materials. The T_g peaks were between 63 and 67 °C for all the samples. The T_g peak intensity for PLA–FeCLF, and PLA–CLF was higher when compared to neat PLA. The reason for the higher peak intensity for PLA–Fe–CLF is speculated to depend on the heat required to raise the temperature of Fe present in the composite upon modification. The melting temperatures for all composites were comparable; however, T_m for PLA–CLF and pure PLA was $\approx$2 °C higher than the other samples. Both MCC- and CLF-based samples had a wider crystalline temperature (T_c) ranging from 110 to 130 °C. However, the T_c peaks were comparatively sharper for neat PLA and the PLA–MCC composite, which is also believed to be due to the higher crystallinity of MCC.

The dynamic mechanical properties of the CLF- and MCC-based PLA composites were studied to provide information on molecular interaction between the fiber surface and polymer and also the viscoelastic behaviors of PLA. Storage modulus (E') and tan δ curves were recorded in relation to temperature. In Fig. 6, the results show that both Fe-modified and unmodified composites have considerably higher storage modulus in the glassy state than that of neat PLA. The MCC and CLFs acted as reinforcement for the PLA by improving the storage modulus and thus the mechanical properties [11–14]. Figure 7 represents the tan δ-curves for the produced composites and PLA. The results show that the tan δ peaks from pure PLA were in a slightly lower temperature range when compared to PLA with both Fe-modified and unmodified celluloses but this difference is not significant [15–17]. These results indicate that there is no molecular interaction between the PLA and used celluloses.

Electrical conductivity of modified and unmodified cellulose was compared using a femtostat. The cellulose samples were pressed into a disk of uniform diameter and the electrodes were connected to the farthest ends of the sample. The current (I) was measured for different constant voltages (V). The conductivity of cellulose was found from the equation $\sigma = L/RA$, where σ is conductivity, L is the length between electrodes, R is resistivity, and A is the surface area of the sample. The results shown in Fig. 8 explain that for set voltages, modified CLF and MCC have better conductivity than that of the unmodified samples. At 1 V, modified CLF had a conductivity of $1.8 \times e^{-08}$ S m^{-1} while unmodified had a conductivity of $6 \times e^{-08}$ S m^{-1}.

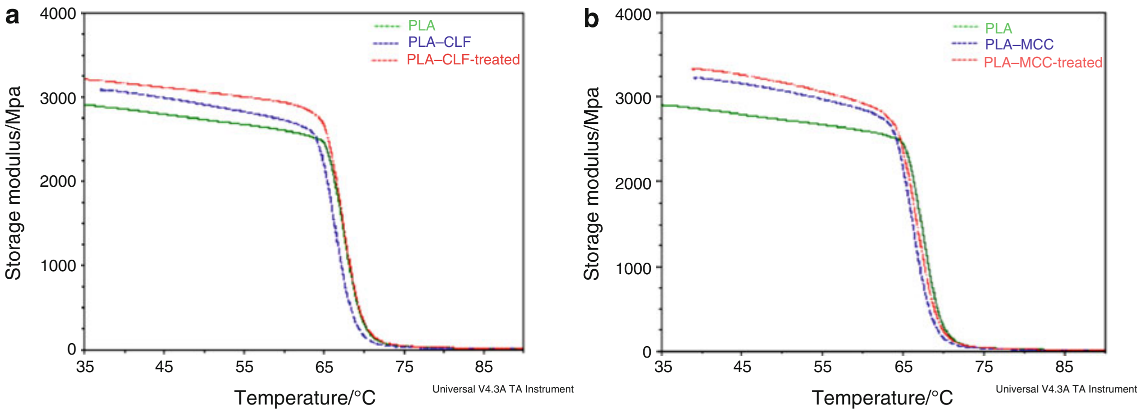


Fig. 6 Storage modulus from DMA analysis. **a** CLF-based PLA composite. **b** MCC-based PLA composite

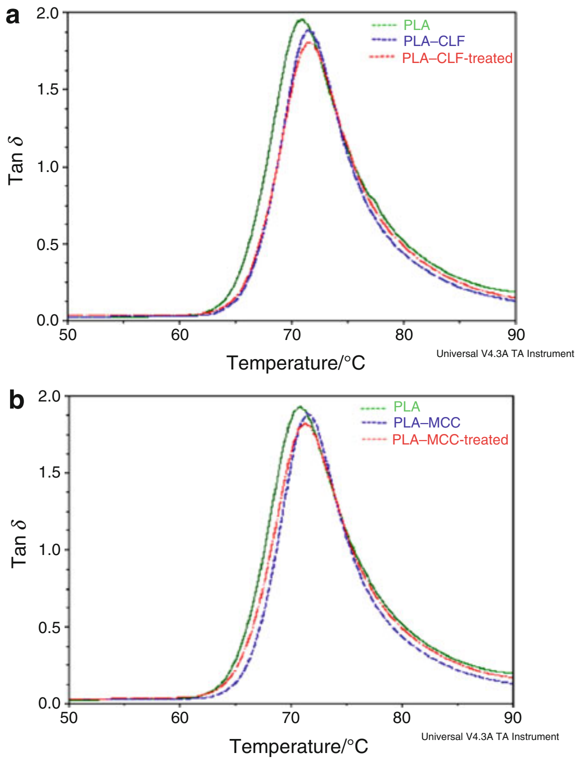


Fig. 7 DMA analysis tan δ peak temperatures for **a** CLF-based PLA composites and **b** MCC-based PLA composites

For MCC, the conductivity was $2.2 \times e^{-08}$ S m^{-1} for modified and $4.5 \times e^{-08}$ S m^{-1} for unmodified samples at 1 V. The higher electrical conductivity of CLF may be explained by a greater number of reactive sites compared to MCC to attach Fe^{2+} to the surface.

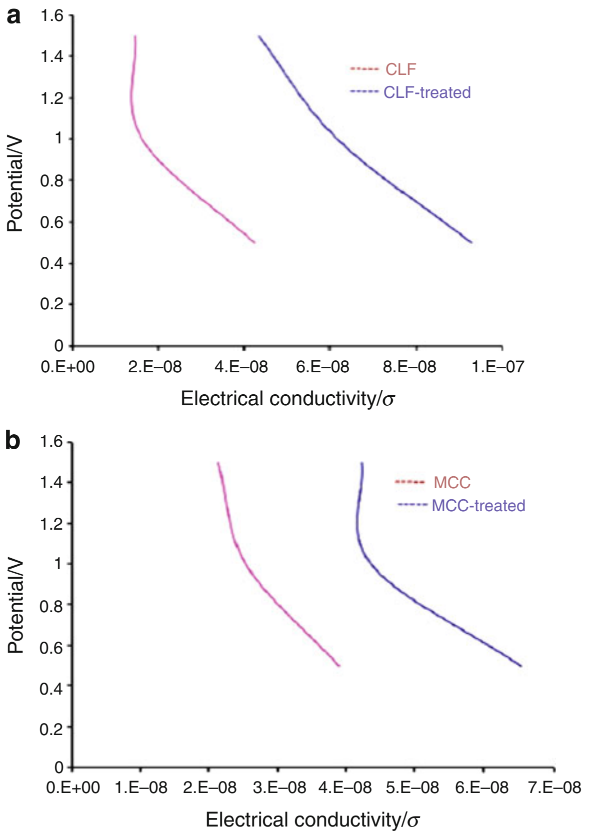


Fig. 8 Electrical conductivity of Fe-modified and unmodified cellulose **a** CLF and **b** MCC

Conclusions

The focus of this study was to study the thermal properties of PLA-based biocomposites with an addition of unmodified and Fe-modified MCC and CLF. Electrical conductivity of Fe-modified and unmodified cellulose that were used in making PLA-based biocomposites were also studied.

The results showed that the addition of small amounts (10 wt%) of MCC and CLF had a positive impact on the degradation temperature of PLA and that the unmodified celluloses demonstrated better thermal stability than the

Fe-modified celluloses. This is expected due to the higher crystallinity attributes of unmodified MCC and CLFs.

The addition of MCC and CLF did not demonstrate as high of an impact on the composites glass transition temperature (T_g) or melt temperature (T_m) and were comparable between PLA filled with Fe-modified and unmodified cellulose. Furthermore, the addition of Fe-modified and unmodified CLF and MCC increased the storage modulus in the glassy state but had no significant effect from the softening temperature of the PLA. The addition of the MCC and CLF did not change the tan δ peak position, thus indicating that no molecular interaction occurred between the PLA matrix and the two different celluloses (MCC and CLF) used.

The electrical conductivity was higher for both Fe-modified celluloses (MCC and CLF) when compared to unmodified cellulose. These Fe-modified celluloses have the potential to be used in conductive biopolymer composites and in the production of fiber oriented polymer composites.

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