



Fabrication and characterization of biodegradable composites based on microfibrillated cellulose and polyvinyl alcohol

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ABSTRACT

Microfibrillated cellulose (MFC) based thin membrane-like fully biodegradable composites were produced by blending MFC suspension with polyvinyl alcohol (PVA). Desired MFC content in the composites could be easily obtained by varying the PVA solution concentration. Chemical crosslinking of PVA was carried out using glyoxal to increase the mechanical and thermal properties of the composites as well as to make the PVA partially water-insoluble. Examination of composite surfaces and fracture topographies indicated that the MFC fibrils were well bonded to PVA and uniformly distributed. Infrared spectroscopy showed that acetal linkages could be formed in the MFC–PVA composites by a glyoxal crosslinking reaction. Sol–gel and swelling results indicated that crosslinking reaction made PVA partially insoluble and reduced its swelling ability. The MFC–PVA composites had excellent tensile properties which were further enhanced by crosslinking. Thermogravimetric analysis (TGA) showed higher thermal stability for MFC–PVA composites compared to PVA. The crosslinked MFC–PVA composites showed even higher thermal stability. Differential scanning calorimetry (DSC) indicated that crosslinking increased the glass transition temperature and reduced melting temperature and crystallinity of PVA in MFC–PVA composites. Results also indicated that nano- and micro-fibrils in MFC inhibit the crystallization of PVA. These composites could be good candidates for replacing today's traditional non-biodegradable plastics.

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1. Introduction

Polymers with broad range of properties play a significant role in our everyday life [1]. However, with increased use of polymeric products, there are increased concerns on the impact these polymers have on the environment [2]. Most traditional polymers are produced using fossil feed-stocks and are non-biodegradable. Over 30 million and 15 million tons of plastic waste, in the US and western Europe, respectively, are generated each year [2]. At the end of their life majority of the conventional plastics and composites are disposed of in landfills where they may stay as is for several decades without degrading making that land unusable. About 6–7% of the petroleum produced today is used for making polymers, fibers and other chemicals. It is estimated that we are currently consuming petroleum at an 'unsustainable' rate, 100,000 times faster than the nature can create it [3]. At the current rate of consumption, it is estimated that the current petroleum reserves will last for only 50–60 years [2].

These concerns have forced the development of environmentally friendly, sustainable and biodegradable polymers and composites in recent years [2–4]. Biodegradable polymers are generally defined as those that decompose in natural aerobic (composting) and

anaerobic (landfill) environments [2]. Biodegradation of biodegradable polymers can be achieved by enabling microorganisms in the environment to metabolize the polymer to produce an inert humus-like material that is less harmful to the environment and can get easily blended with the natural soil. They may be composed of either biopolymers, whose components are derived from renewable raw materials, or biodegradable petroleum-based polymers [2–4].

Microfibrillated cellulose (MFC) can be obtained by mechanical treatment, primarily shearing, of pulp cellulose fibers to small diameter fibrils through refining and high-pressure homogenization processes [5–8]. Since the widths of the fibrils in MFC are in submicron range, they are considered as nanofibers [5,6,9–11]. However, being cellulose, MFC is biodegradable. The MFC has high aspect ratio and high tensile properties as a result of high orientation and crystallinity. Their modulus is estimated at 140 GPa and tensile strength between 2 GPa and 6 GPa [12]. Most efforts until now have been focused on fabrication of MFC based composites using non-biodegradable phenolic and other resins [5,9–11]. Such composites, although greener, are not fully biodegradable and still need to be disposed of in landfills at the end of their life.

Polyvinyl alcohol (PVA) is a thermoplastic and biocompatible petroleum based polymer. It is also one of the rare polymers with a carbon–carbon single bond backbone that is fully biodegradable [2]. Because of the hydroxyl (–OH) groups on alternating carbon

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atoms PVA is strongly hydrophilic and soluble in water, which helps to promote its degradation through hydrolysis [2]. Besides, hydroxyl groups in PVA are expected to form hydrogen bonds and acetal linkages with other materials such as cellulose and aldehydes when put together [13,14].

MFC contains very short fibers while PVA has relatively lower stiffness and strength [5–14]. Fabricating biodegradable MFC reinforced PVA composite may be a potential way to address the application limitations of MFC and PVA. Such composites should have excellent mechanical properties because of strong hydrogen bonding between MFC and PVA. MFC–PVA composites have been reported earlier but without any PVA modifications [15].

Crosslinking has been commonly used to improve the mechanical and thermal properties as well as solubility of polymers. When used as resin, crosslinked polymers can also improve composite properties. Crosslinking is the process of chemically joining two or more molecules at different locations along the length by covalent bonds. Crosslinkers are commonly selected on the basis of their chemical reactivities with the functionalities present on the polymers [16]. Glyoxal is the smallest dialdehyde which has the ability to crosslink a wide range of polymer, including cellulose and PVA [17,18]. Glyoxal and glutaraldehyde have been shown to crosslink both cellulose and PVA, separately [9,18,19]. However, glyoxal is also readily biodegradable and less toxic than glutaraldehyde [17–20].

Both PVA and MFC are fully biodegradable and as a result composites made using the two are also expected to be biodegradable [2,5–11]. However, biodegradation investigation experiments involving MFC–PVA composites and glyoxal crosslinked PVA are currently ongoing in our lab and will be reported when the study is complete.

In the present study, two types of thin membrane-like MFC reinforced biodegradable composites: MFC–PVA composites and glyoxal crosslinked MFC–PVA composites have been fabricated and characterized. The MFC content in these composites could be easily controlled as desired. The membrane-like composites had smooth surfaces and their tensile and thermal properties were excellent. The crosslinked composites had significantly better properties.

2. Materials and methods

2.1. Preparation of PVA and crosslinked PVA using glyoxal

PVA powder (M_w 31,000–50,000, 98–99% hydrolyzed, Aldrich, St. Louis, MO) was added to the deionized water at a weight ratio of 1:9 to form PVA solution kept in a water bath at 80 °C and stirred for 30 min. Glyoxal solution (Glyoxal, 25 wt.% solution in water, Aldrich, St. Louis, MO) was added to the PVA solution. The glyoxal:PVA weight ratio was 3:100. The pH of the mixture was adjusted to 3 using phosphoric acid (85 wt.% solution in water, Mallinckrodt Baker, Phillipsburg, NJ). The mixture was stirred at 80 °C for 1 h for precuring. The precured mixture was then cast on Teflon[®] coated glass plates and dried at RT to form flat precured crosslinked PVA film. The precured film was cured in an oven at 100 °C for 1 h and hot pressed at 80 °C under a pressure of 4 MPa for 30 min to form cured crosslinked PVA film. The PVA film was prepared by casting PVA solution without the addition of glyoxal as control, for comparison. Thicknesses of all specimens were about 0.2 mm.

2.2. Preparation of MFC suspension

MFC in water (KY-100G) was obtained from Daicel Chemical Industries, Japan. The MFC was added into deionized water at a

weight ratio of 1:199. The mixture was stirred using mechanical stirrer at 80 °C for 1 h and followed by ultrasonication (Branson Ultrasonics, Model 2510, Mumbai, India) at 65 °C for 1 h to form MFC suspension and to separate the fibrils.

2.3. Fabrication of MFC–PVA composites

The PVA powder was added to the MFC suspension at desired weight ratios. The MFC suspension and PVA powder mixtures were stirred at 80 °C for 1 h and ultrasonicated at 65 °C for 1 h. The mixtures were cast on Teflon[®] glass plate and slowly dried at RT to form MFC–PVA composites (5%, 10%, 15%, 20%, 30%, 40% and 50% MFC contents (by wt) in the composites). The MFC–PVA composites were hot pressed at 80 °C and 4 MPa for 30 min to form the final composites. As mentioned previously the specimen thicknesses were about 0.2 mm.

2.4. Fabrication of crosslinked MFC–PVA composites using glyoxal

The PVA powder was added to the MFC suspension at desired weight ratios. The mixtures of MFC suspension and PVA powder, at desired ratios, were stirred at 65 °C for 1 h and ultrasonicated at 65 °C for 1 h. Glyoxal solution (25 wt.% solution) was then added to the MFC suspension and PVA mixture to obtain the wt ratio of glyoxal to PVA and MFC of 3:100. The pH values of all the mixtures were adjusted to 3 using phosphoric acid. The mixtures were stirred at 80 °C for 1 h for precuring (partial crosslinking). The precured mixtures were then cast on Teflon[®] coated glass plates and dried at RT to form precured crosslinked MFC–PVA composites. The precured composites were cured in an oven at 100 °C for 30 min and hot pressed at 80 °C and 4 MPa for 30 min to form cured, crosslinked MFC–PVA composites. The MFC content in crosslinked MFC–PVA composites was controlled at 10% (by wt) for comparison with corresponding noncrosslinked MFC–PVA composites. The specimen thicknesses again were about 0.2 mm.

2.5. Characterization

2.5.1. SEM analysis

MFC–PVA composites (10% MFC) were sputter coated with gold and their surface and fracture topographies were observed with scanning electron microscope (SEM Leica 440, Leica Microsystems, Cambridge, UK) at an accelerating voltage of 15 kV.

2.5.2. ATR-FTIR spectroscopy

Chemical analysis of MFC–PVA composites (10% MFC) and its glyoxal crosslinked specimens was carried out using an FTIR spectrophotometer (Nicolet Magna-IR 560, Thermo Scientific, Waltham, MA) in attenuated total reflection (ATR) mode using a split pea accessory. Spectra, averaged over 64 scans, were taken in the range of 4000–800 cm^{-1} wavenumber at a resolution of 4 cm^{-1} . All composite specimens were dried prior to conducting the spectroscopy.

2.5.3. Sol–gel and swelling analyses

PVA and glyoxal crosslinked PVA specimens (crosslinked PVA film and the crosslinked MFC–PVA composites, 10% MFC) were fully dried at 105 °C for 12 h prior to conducting the sol–gel test. The specimens were weighed to obtain their initial dry weights and then immersed in distilled water in 150 mL glass bottles. The mixtures in the glass bottles were then placed on a shaker table (MAXQ 4450, Thermo Scientific, Waltham, MA) at 65 °C and 150 rpm until the control (noncrosslinked) PVA was completely dissolved. The solid contents for all crosslinked specimens were then washed three times and filtered using a Whatman[®] filter paper (Number 4, 20–25 μm pore size) to obtain final residues. The water-soluble portion (sol) and particles smaller than the pore size

of the filter paper were removed. The final residues of the crosslinked PVA and the crosslinked MFC–PVA composites, were dried at 105 °C for 12 h to obtain their dry wt (gel). Ratios of the gel wt of the crosslinked PVA to their corresponding initial dry wt were used to determine the PVA gel (crosslinked) percentages. The MFC wt in the crosslinked MFC–PVA composites were regarded as constant before and after the test.

PVA and glyoxal crosslinked PVA specimens (crosslinked PVA film or crosslinked MFC–PVA composite, 10% MFC) were dried at 105 °C for 12 h prior to conducting the swelling test. The specimens were weighed to obtain their initial dry wt and then immersed in distilled water in 150 mL glass bottles at RT for 24 h. The surface water from the swollen specimens was wiped using Kimwipe® paper tissue to remove excess water weighed again to obtain the swollen wt. Ratios of the wt of absorbed water by the specimens to their corresponding initial dry wt were used to determine the swelling powers of the control and crosslinked PVA. The MFC wt in the crosslinked MFC–PVA composites was regarded as constant, before and after the test.

2.5.4. Tensile properties and moisture content

The tensile tests were performed using an Instron universal testing machine (model 5566). The specimens for PVA, MFC–PVA composites (5%, 10%, 15%, 20%, 30%, 40% and 50% MFC), glyoxal crosslinked PVA and glyoxal crosslinked MFC–PVA composites (10% MFC) were cut to 10 mm × 60 mm strips. Tensile properties of all specimens were measured from the tests conducted as per ASTM D-882–02. Specimen gauge length of 30 mm and strain rate of 0.02 were used for all specimens. Specimens were conditioned at 21 °C and 65% RH for 3 days prior to testing.

Percent moisture content (MC%) of all conditioned specimens were measured as per ASTM D 2654-89a. To obtain the MC% values specimens were dried at 105 °C until their wt stabilized. The MC% values were calculated using the dry wt and corresponding conditioned wt.

2.5.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA Model Q500, TA Instrument, New Castle, DE) was used to analyze the thermal properties of all specimens. Specimens were dried in an oven at 45 °C for 12 h prior to conducting the tests. All TGA tests were performed under a nitrogen atmosphere by keeping the flow rate of 60 ml/min, between 25 °C and 800 °C and at a scanning rate of 10 °C/min.

2.5.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC, Model Q2000, TA Instrument, New Castle, DE) was used to analyze the glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_f) and crystallinity of PVA, MFC–PVA composites (10% MFC) and their glyoxal crosslinked specimens. All specimens were dried in an oven at 105 °C for 12 h prior to conducting the test. All DSC analyses were performed under a nitrogen atmosphere by keeping the flow rate of 50 ml/min, between –20 °C and 250 °C and at a scanning rate of 10 °C/min.

3. Results and discussions

3.1. SEM images of MFC–PVA composite surface and fracture topographies

Fig. 1 shows typical SEM images of MFC–PVA composite (non-crosslinked, 10% MFC), surface topography (A) that shows the MFC distribution and fracture surface (B) after tensile testing. From Fig. 1A, it can be clearly seen that the MFC fibrils are randomly organized but uniformly distributed within PVA and some of them

are just at the surface of the composite. Fig. 1B clearly shows the MFC fibrils protruding out from the PVA at the fracture surface. However, the protruding fibril lengths are very short. This indicates that the PVA–MFC bonding is strong. The MFC fibrils also seem to be distributed uniformly within the PVA at the fracture surface. This is expected since both PVA and MFC have hydroxyl groups and can mix and disperse easily and also form hydrogen bonds at multiple locations. In addition, the fibrils also look oriented in the direction of the stress. This is due to the high fracture strain of the noncrosslinked composites which allows orientation during the tensile test.

3.2. ATR-FTIR analysis of crosslinked and noncrosslinked MFC–PVA composites

Fig. 2A shows typical crosslinking of glyoxal with PVA or MFC. In the present case three possible crosslinking reactions can occur; between the PVA molecules, between the MFC fibrils and between PVA and MFC.

Fig. 2B shows the ATR-FTIR spectra for control MFC–PVA composites (a) and glyoxal crosslinked MFC–PVA composites (b). A broad band at 3550–3200 cm^{-1} , wavenumber seen in both spectra, is a result of the hydroxyl (O–H) stretching vibration resulting from the strong intra-molecular and inter-molecular hydrogen bonds [21,22]. The absorption band observed between 3000 cm^{-1} and 2820 cm^{-1} wavenumbers is due to the stretching of aliphatic C–H bond [22]. The absorbance intensity ratio of bands for O–H to C–H showed a decrease from 1.81 for spectrum (a) to 1.28 for spectrum (b). This lower absorption clearly indicates a reduction in the O–H groups due to crosslinking by glyoxal [22]. Absorption at 1750–1700 cm^{-1} (stretching of C=O) for noncrosslinked specimen (spectrum (a)) was weak (intensity ratio of C=O to C–H = 0.35) and indicates the presence of carbonyl (C=O) in the composites from the non-hydrolyzed acetate group remaining in the PVA, confirming the results obtained by Gohil et al. [21] and Mansur et al. [22]. In spectrum (b), however, a sharp absorption (intensity ratio of C=O to C–H = 0.63) observed at 1750–1700 cm^{-1} wavenumber indicates strong presence of C=O in the crosslinked resin of the composites. This shows that in addition to the non-hydrolyzed vinyl acetate groups, some residual unreacted aldehyde groups from glyoxal also exist in the crosslinked MFC–PVA composites, both contributing to the stronger C=O absorption. Glyoxal may exist as half (one group) reacted or fully unreacted. The absorption at 1150–1050 cm^{-1} wavenumber in spectrum (a) is due to C–O stretching vibration from the acetate group [21–23]. The intensity of absorption band for C–O stretching vibration was stronger in spectrum (b) (intensity ratio of C–O to C–H = 3.38) than in spectrum (a) (intensity ratio of C–O to C–H = 2.72), resulting from the formation of the acetal linkages (shown in Fig. 2A) upon reaction of the composites with the glyoxal.

Overall, the ATR-FTIR results indicate that the MFC–PVA composites were crosslinked based on the decreased intensity of bands for O–H stretching vibration combined with the increased intensity of bands for C=O and C–O stretching vibrations. As mentioned earlier, the crosslinking reactions can occur between the MFC fibrils or the PVA resin or between MFC and PVA.

3.3. Sol–gel and swelling analyses

Sol–gel and swelling analyses were performed for noncrosslinked (control) and crosslinked PVA, as well as for the crosslinked MFC–PVA composites to evaluate the crosslinking levels. Table 1 presents the sol–gel and swelling results for crosslinked PVA as well as control PVA. The results show that the PVA gel (crosslinked) percentages of the crosslinked PVA and the resin in the crosslinked MFC–PVA composites were 7.0% and 6.6%, respectively, while the

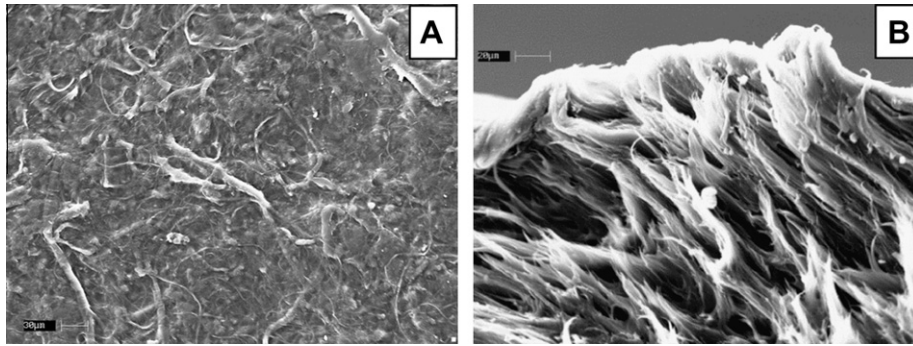


Fig. 1. Typical SEM images. (A) Surface topography of the MFC–PVA composites. (B) Fracture surface of the MFC–PVA composite. Both specimens contain 10% MFC.

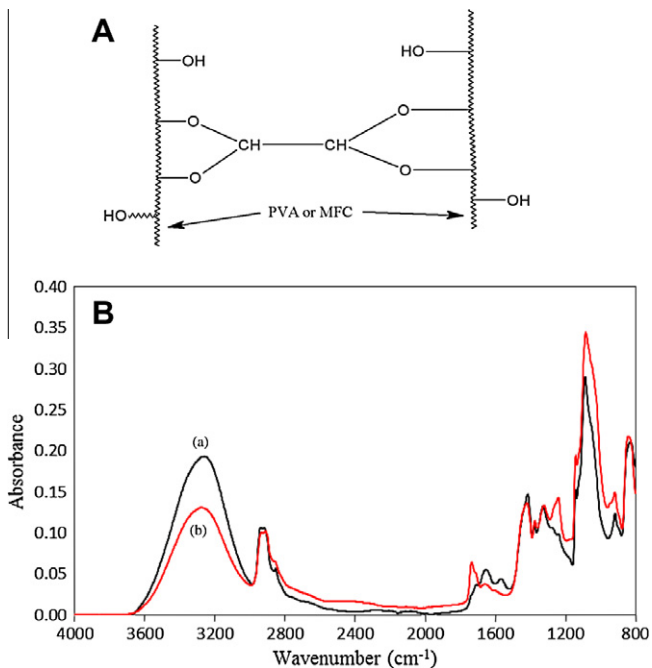


Fig. 2. (A) Schematic of the acetal linkage in glyoxal crosslinked PVA or MFC structure. (B) FTIR spectra of MFC–PVA composites (a: 10% MFC) and glyoxal crosslinked MFC–PVA composites (b: 10% MFC).

Table 1
Sol–gel and swelling power results of PVA and glyoxal crosslinked PVA.

Tests	PVA	Crosslinked PVA	PVA in crosslinked MFC–PVA composites
Gel percentage (%)	0	7.0 (8.3) [*]	6.6 (10.3)
Swelling power (%)	105.6 (5.5)	78.3 (2.7)	75.1 (8.8)

^{*} Values in the parentheses are % coefficient of variation values.

control PVA dissolved completely during the sol–gel test. The low gel percentage suggests that the PVA was only partially crosslinked. The results also show that the swelling powers of crosslinked PVA and the resin in the crosslinked MFC–PVA composites were 78.3% and 75.1% respectively, much lower than control PVA (105.6%), confirming the crosslinking, though only partial.

3.4. Tensile properties and moisture content

Table 2 presents the tensile test and moisture content results for pure (control) PVA and noncrosslinked PVA composites with

Table 2
Tensile properties for MFC–PVA composites with varying MFC content.

Weight percentage of MFC content in MFC–PVA composites	Young's modulus (MPa)	Fracture stress (MPa)	Fracture strain (%)	Moisture content (%)
0 (PVA)	248 (22.9) [*]	34.1 (13.3)	331 (15.4)	9.1 (4.2)
5	687 (10.3)	43.3 (4.6)	34.7 (13.4)	7.7 (5.5)
10	1033 (7.2)	53.5 (5.6)	25.2 (23.7)	7.4 (11.8)
15	1399 (13.6)	65.0 (8.0)	18.3 (12.1)	7.3 (25.1)
20	1707 (8.0)	69.6 (8.3)	15.2 (12.4)	8.0 (1.0)
30	2538 (10.7)	81.6 (7.7)	8.9 (18.8)	8.1 (2.9)
40	3409 (9.4)	89.9 (13.5)	8.0 (26.2)	7.1 (12.6)
50	3898 (21.3)	84.9 (11.9)	5.1 (31.7)	7.7 (20.3)

^{*} Values in the parentheses are % coefficient of variation values.

MFC contents from 5% to 50%. The Young's modulus of the control PVA was 248 MPa. The Young's modulus of the MFC–PVA composites were significantly higher than for PVA and increased with the MFC content, as can be expected. For composites with 5 and 10% MFC content, the Young's moduli were 687 MPa and 1033 MPa, respectively. When the MFC content increased to 50% the Young's modulus increased to 3898 MPa, about 16 times that of control PVA. This is expected since the Young's modulus for MFC is much higher [12]. The fracture stress for the control PVA was 34.1 MPa. The fracture stress values for MFC–PVA composites with 5 and 10%, MFC content were 43.3 MPa and 53.5 MPa, respectively, and increased to 89.9 and 84.9 MPa when the MFC content increased to 40 and 50%, respectively. This is again because the MFC has fracture stress is between 2 GPa and 6 GPa [12]. The fracture stress of MFC–PVA composites with 50% MFC, however, was lower than the composites with 40% MFC. This is due to the lower fracture strain (5.1%) of the composites with 50% MFC content compared to 8% obtained for composites with 40% MFC. Similar trend of increase in Young's modulus and fracture stress with increase in MFC content have been reported earlier by Lu et al. [15]. The fracture strain for control PVA was 331%. The fracture strains for the MFC–PVA composites were much lower than that obtained for PVA and decreased as the MFC content increased. This is due to the lower fracture strain value of MFC. The moisture content for PVA was 9.1%, and the moisture content values for MFC–PVA composites were observed to be within a narrow range of 7.1% to 8.1%. This is because moisture content values of MFC and PVA are very close.

Table 3 presents tensile test and moisture content results for PVA, MFC–PVA composites (10% MFC) and their corresponding glyoxal crosslinked specimens. The Young's moduli of the crosslinked

Table 3

Tensile properties for PVA, MFC–PVA composites and their glyoxal crosslinked specimens.

Specimens	Young's modulus (MPa)	Fracture stress (MPa)	Fracture strain (%)	Moisture content (%)
PVA	248 (22.9)*	34.1 (13.3)	331 (15.4)	9.1 (4.2)
Crosslinked PVA	666 (9.5)	47.7 (7.5)	184(16.3)	5.5 (28.5)
MFC–PVA (10 wt.% MFC content)	1033 (7.2)	53.2 (5.6)	25.2 (23.7)	7.4 (11.8)
Crosslinked MFC–PVA (10 wt.% MFC content)	1404 (9.4)	53.7 (7.1)	29.6 (16.8)	7.3 (1.7)

* Values in the parentheses are % coefficient of variation values.

PVA and crosslinked MFC–PVA composites increased to 666 MPa and 1404 MPa, from 248 MPa for control PVA and 1033 MPa for MFC–PVA composites, respectively. It is obvious that the increase in Young's modulus for the PVA and MFC–PVA composites is due to the crosslinking of the PVA which makes the structure rigid [24]. In the case of the MFC–PVA composites, not only the PVA is crosslinked but the MFC fibrils can also get crosslinked between themselves as well as with PVA. The reduction in moisture content from 9.1% for the PVA to 5.5% after crosslinking and from 7.4% for the MFC–PVA composites to 7.3% for the crosslinked MFC–PVA composites is also responsible, at least partially, for higher Young's modulus. From data in Table 3, it is also clear that after crosslinking, PVA fracture strain is significantly lower. However, MFC–PVA composites fracture strains did not change after crosslinking since this property is controlled by the MFC. While crosslinking increased the PVA fracture stress from 34.1 MPa to 47.7 MPa, MFC–PVA composites showed no significant change. This is because the crosslinked composites showed sharp yielding. And after the yielding, the stress remained the same. As a result, no change in the fracture stress was observed. Similar effect has also been observed in the case of bacterial cellulose reinforced PVA composites [25].

It should be noted that tensile properties of MFC–PVA composites and crosslinked MFC–PVA composites are comparable or higher than many traditional polymers, including polyethylene (Young's modulus: 800 MPa; fracture stress: 15 MPa), polypropylene (Young's modulus: 1900 MPa; fracture stress: 40 MPa), and nylon 6 (Young's modulus: 1800 MPa; fracture stress: 70 MPa) [26]. In addition, fabrication process for the biodegradable MFC–PVA composites is convenient and simple and the cost for raw materials is low. Therefore, both crosslinked and noncrosslinked MFC–PVA composites have the potential to replace traditional non-biodegradable plastic materials in many applications, including racket frame, ski pole, circuit board, automobile inside etc. These degradable composites may be easily protected from water by applying varnish or other water-resistant coatings to increase their durability. Also, their moisture sensitivity is lower after crosslinking, making them more useful.

3.5. Thermogravimetric analysis

Fig. 3A presents typical TGA thermograms of PVA, MFC–PVA composites (10% and 40% MFC) and MFC. Thermogram 3A (a) for control PVA shows two decomposition onset temperatures, (T_{d1}) and (T_{d2}), at 257 °C and 400 °C, respectively. Weight losses for the PVA were 30% at 272 °C, 50% at 281 °C and up to 94% at 800 °C. Two-step-degradation of PVA has been reported earlier by Peng and Kong [26]. A likely explanation for this is that PVA first degrades into smaller molecular weight polymer at around 250 °C by chain scission and degrades further into carbon char at temperatures above 350 °C. Results of this study confirm the earlier findings [27]. Thermograms 3A (b) and 3A (c) for MFC–PVA composites with 10 and 40% MFC, respectively, also show two decomposition temperatures. Their T_{d1} and T_{d2} are very close to those observed for PVA, at 255 °C and 400 °C, respectively. Weight losses observed for the MFC–PVA composites (10% MFC) were 30% at 272 °C, 50% at 288 °C and 92% at 800 °C. Weight losses observed for the MFC–PVA composites (40% MFC) were 30% at 285 °C, 50% at 313 °C (both temperatures higher than those obtained for MFC–PVA composites with 10% MFC) and 92% at 800 °C. Thermogram 3A (d) for MFC showed a single decomposition onset temperature (T_d) at 315 °C. Weight losses observed for pure MFC were 30% at 326 °C, 50% at 340 °C and 85% at 800 °C, indicating higher thermal stability than PVA and close to the values obtained by Quiévy et al. [28]. Thus it is obvious that MFC reinforcement is responsible for the higher thermal stability of the MFC–PVA composites. This conclusion is in agreement with the result in obtained in a previous study by Lu et al. [15].

Fig. 3B presents typical TGA thermograms of PVA, MFC–PVA composites (10% MFC) and their corresponding glyoxal crosslinked specimens. Thermograms 3B (a) and 3B (b) are for PVA and MFC–PVA composites, respectively, and have been described in the last paragraph. Thermogram 3B (c), for crosslinked PVA, also shows a two-step degradation pattern with T_{d1} and T_{d2} observed at 370 °C and 410 °C, respectively. However, the steps are not as distinct compared to the control PVA. The weight losses observed were 30% at 303 °C, 50% at 368 °C and 91% at 800 °C. These temperatures are significantly higher than those obtained for control PVA indicating that the crosslinked PVA has significantly higher thermal stability as is the case for many polymers [29–31]. Similarly thermogram 3B (d) for crosslinked MFC–PVA composites also shows a two-step degradation pattern with T_{d1} and T_{d2} observed at 380 °C and 410 °C, respectively. Weight losses observed were 30% at 305 °C, 50% at 358 °C and 90% at 800 °C. As is expected these values are close to those obtained for the crosslinked PVA, the major constituent. These results clearly indicate that glyoxal crosslinking can increase the thermal stability of PVA and the MFC–PVA composites in addition to enhancing their tensile properties.

3.6. Differential scanning calorimetry

Typical DSC thermograms for PVA and glyoxal crosslinked PVA are presented in Fig. 4A. Thermogram 4A (a) shows T_g and T_m of

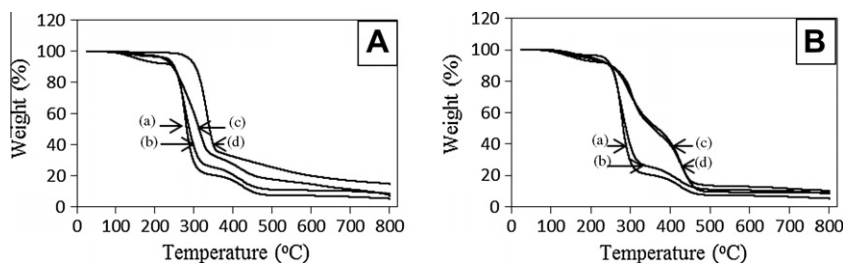


Fig. 3. TGA thermograms. (A) PVA (a), MFC–PVA composites (b: 10% MFC), MFC–PVA composites (c: 40% MFC) and MFC (d). (B) PVA (a), MFC–PVA composites (b: 10% MFC), glyoxal crosslinked PVA (c) and glyoxal crosslinked MFC–PVA composites (d: 10% MFC).

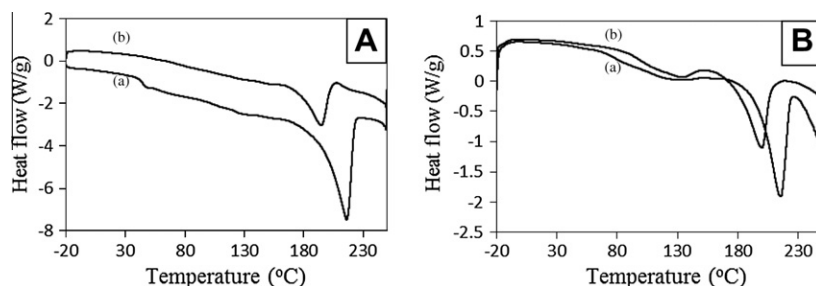


Fig. 4. DSC thermograms. (A) PVA (a) and glyoxal crosslinked PVA (b). (B) MFC–PVA composites (a: 10% MFC) and glyoxal crosslinked MFC–PVA composites (b: 10% MFC).

92.1 °C and 195.4 °C, respectively, for PVA. The ΔH_f of 86.9 J/g, compared to 138.6 J/g for 100% crystalline PVA resulted in a crystallinity of 62.7% for control PVA [32–35]. Thermogram 4A (b) for the crosslinked PVA shows T_g and T_m of 110 °C and 175.4 °C, respectively. The ΔH_f and the crystallinity of the crosslinked PVA were 55.3 J/g and 39.9%, respectively. The lower ΔH_f and higher T_g further confirm that the PVA was partially crosslinked by glyoxal. The higher T_g and lower crystallinity after crosslinking due to restricted segmental motion, have been observed in most polymers [1,32,36,37].

Fig. 4B presents typical DSC thermograms of (a) MFC–PVA composites and (b) glyoxal crosslinked MFC–PVA composites. The T_g and T_m for the MFC–PVA composites were observed at 92.0 °C and 197.5 °C, respectively. These values are close to those obtained for PVA. While the T_g of cellulose is around 230 °C, the MFC is highly crystalline and hence does not show any T_g . Also, no T_m for cellulose can be observed since it degrades prior to melting [38,39]. As a result, the DSC thermogram mainly represents the PVA behavior. The conclusion here is in agreement with the phenomenon observed by Lu et al. [15]. The ΔH_f and the crystallinity of the PVA in MFC–PVA composites were 61.4 J/g and 44.3%, respectively, which were much lower than 86.9 J/g and 62.7%, respectively, obtained for control PVA. It is likely that the nano- and micro-fibrils in the MFC can inhibit the crystallization of PVA, as they are well dispersed. The fibrils can suppress the free movement of polymeric chains restricting their ability to fold and thus lower the crystallinity [40]. Thermogram 4B (b) is for crosslinked MFC–PVA composites but mainly represents crosslinked PVA behavior. The T_g and T_m observed were 110.2 °C and 178.8 °C, respectively, and confirm that glyoxal crosslinking can increase T_g , decrease the T_m of PVA. These changed characteristics are reflected in the crosslinked MFC–PVA composites. The ΔH_f and crystallinity of PVA in crosslinked MFC–PVA composites were 50.5 J/g and 36.4%, respectively. These are lower than the PVA in MFC–PVA composites and slightly lower than those for the crosslinked PVA, showing the combined effect of crosslinking and the ability of the MFC to restrain the molecular motion needed for crystallization.

4. Conclusions

The biodegradable membrane-like MFC–PVA composites with differing MFC contents were produced using simple immersion method. The SEM images of surface and fracture topographies indicated that MFC was uniformly distributed in PVA and the MFC–PVA bonding was strong. Crosslinks can be formed using glyoxal between PVA, MFC and MFC–PVA. Crosslinked PVA was partially water-insoluble with decreased swelling ability. PVA and MFC–PVA composites showed higher mechanical properties and thermal stability after crosslinking. MFC reinforcement also was responsible for higher thermal stability of the composites. At the same time the fracture strain decreased significantly with crosslinking. The

DSC also showed higher T_g and lower T_m and lower crystallinity of the PVA in MFC–PVA composites as a result of glyoxal crosslinking.

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