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Cross-Linked Waxy Maize Starch-Based "Green" Composites

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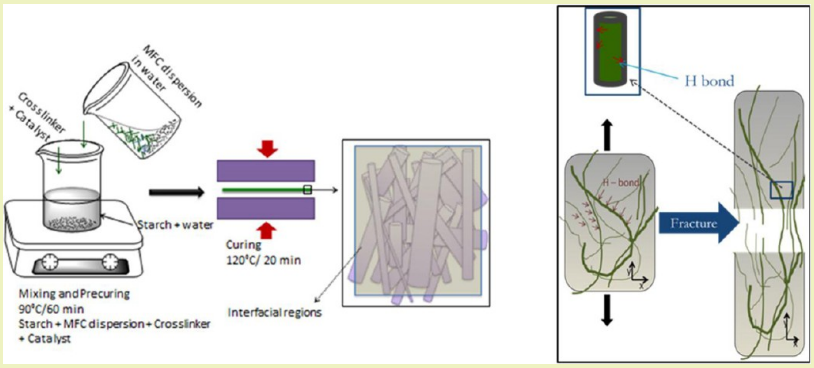
Supporting Information



ABSTRACT: In this research, "green" composites were fabricated by blending waxy maize starch (WMS) with micro/nanofibrillated cellulose (MFC). Further, an environmentally friendly, sustainable, and water-soluble cross-linker, 1,2,3,4-butane tetracarboxylic acid (BTCA), was used to cross-link WMS to fabricate cross-linked starch-based composites. The method described here provides a benign and convenient way to produce cross-linked starch-based composite films ($\approx 300\ \mu m$ in thickness), comparable to commercially available plastic sheets. The process can be easily scaled up for commercial production. Industrially pregelatinized WMS was used to obtain smooth, transparent, and defect-free films. Cross-linking helped in reducing the moisture absorption as well as made the films and composites insoluble in water. MFC (15% MFC)-cross-linked WMS composite films exhibited excellent tensile properties with a Young's modulus of over 2.3 GPa, fracture strain of 3.1%, and fracture stress of 39 MPa, as a result of MFC incorporation. The toughness of these composites was also significantly higher, even without the use of plasticizers such as sorbitol. These materials can be good candidates for replacing petroleum-based resins such as epoxies and their composites.

KEYWORDS: *Waxy maize starch, Cross-linking, Butane tetracarboxylic acid, Green composite, Micro/nanofibrillated cellulose*

INTRODUCTION

Natural polymers such as native starch have been chemically and physically modified to form thermoplastic or cross-linked resins for a variety of applications or to enhance their film forming properties.[1−3] Starch is a polysaccharide composed of two polymers of glucopyranose: a linear amylose molecule with (1−4) glycosidic linkages and a branched amylopectin molecule with (1−6) glycosidic linkages. While amylose is a low molecular weight polymer consisting of 1000−10,000 glucose units and is linear, amylopectin is a larger branched macromolecule with degree of polymerization (DP) sometimes exceeding one million.[4]

Out of many starch varieties (maize, tapioca, potato, rice, etc.) available commercially, waxy maize starch (WMS) was selected for this research. WMS is a genetically modified maize starch containing more than 99% amylopectin, which is known to aid the formation of amorphous, smooth, homogeneous, transparent, and defect-free films.[5−7] Regular native starches involve substantial amounts of time in gelatinization and precuring that result in a semisolid viscous resin difficult to fabricate into homogeneous films (Figures S1 and S2, Supporting Information).[3] Commercially available pregelatinized and instantized food grade WMS used in this project was cross-linked with 1,2,3,4-butane tetracarboxylic acid (BTCA) for use as "green" resin. The advantage of using industrially pregelatinized starch instead of native starch was the complete and easy gelatinization of starch ensuring a maximum reaction, formation of a smooth film, as well as shorter a blending time compared to native starch. Complete gelatinization (and associated loss of crystallinity) of the amylopectin before casting the film was identified earlier by Lopez-Rubio et al.[6] as an important step needed in the formation of high quality amylopectin films.

It is well known that due to the highly hydrophilic nature of the thermoplastic starches resulting from the presence of hydroxyl groups, it is susceptible to changes in the atmospheric humidity that affects the stability and mechanical properties of thermoplastic starch films. Cross-linking of starch with bi- or polyfunctional cross-linkers interconnects the starch molecules by covalent bonding, thus increasing the molecular weight and

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consequently the modulus (stiffness), tensile strength, as well as water resistance.[8] BTCA, used in this research, is relatively inexpensive and nontoxic and is commercially available at a lower cost[9] as compared to the more commonly used cross-linkers.[9−12] Many researchers also claim that BTCA is a more effective cross-linker than any other polycarboxylic acid, including the extensively used polymaleic acid (PMA).[13,14] It is postulated that the high reactivity and effectiveness of BTCA as a cross-linker, among other polycarboxylic acids such as polymaleic acid,[13,14] citric acid,[15] and malonic acid,[3] results from its ability to create highly reactive cyclic anhydrides under thermally increased conditions.[16] BTCA, which has previously been used as an effective cross-linker for cellulose for making wrinkle resistant fabric,[17,18] was shown to successfully cross-link WMS in this study. The reaction conditions between WMS and BTCA were studied and optimized in the present study. Also, sodium hypophosphite ($NaPO_2H_2$, Nahyp) was used as an effective catalyst for the cross-linking reaction. It is believed that Nahyp accelerates the process of esterification by increasing the speed of the formation of the cyclic anhydride intermediate.[13] Both BTCA and Nahyp are water-soluble, which enabled the reaction to be carried out in an environmentally friendly aqueous condition, rather than using organic solvents. To synergize the effect of starch and cellulose, cellulose in the form of micro- and nanofibrillated cellulose (MFC) was used as the reinforcing element. Blending starch and cellulose provided the synergistic effect resulting in much higher tensile properties.

In this paper, the primary focus was to obtain environmentally friendly resin films that had Young's modulus comparable to epoxy resins[19] and composites but with higher toughness and higher water resistance compared to native starch. The starch-based composite films were not only green and sustainable but the fabrication process developed was easy and water-based, which could be easily scaled up. While each film prepared in the study was approximately 18 cm × 30 cm with a thickness of 0.003 cm, the process has the ability to produce larger quantities without compromising the properties. Thus, through this research, a convenient, completely green, nontoxic, and water-based process has been developed for engineering composite films with potential commercial applications such as packaging and coating. The cross-linked starch may also be used in other applications including composites.

■ EXPERIMENTAL PROCEDURE

Materials. Instantenized and water-soluble, pharmaceutical grade waxy maize starch (WMS) powder was obtained from Nutra Bio (Middlesex, NJ). Analytical grade BTCA and Nahyp were purchased from Sigma Aldrich (Saint Louis, MO). MFC in water (KY-100G) was obtained in the form of paste from Dicel Chemical Industries, Japan, containing about 10% MFC and 90% water.

Fabrication of Films. *Fabrication of Cross-Linked WMS-Based Films.* In order to obtain cross-linked WMS resin, starch powder (20 g) was added to 500 mL of water while being stirred using a magnetic stirrer. The powder was easily soluble in water and resulted in a low viscosity, homogeneous, and transparent solution. To ensure maximum possible gelatinization, the mixture was heated at 90 °C for 30 min with continuous stirring. Predetermined BTCA weights (5%, 10%, 15%, and 25% based on starch weight) were added separately to the gelatinized starch followed by addition of Nahyp (50% by weight of BTCA) as catalyst. The mixture was precured by stirring continuously for 60 min at 90 °C with a magnetic stirrer. Both BTCA and Nahyp are completely soluble in water; the heating and stirring ensured homogeneous mixing of these materials making the functional groups easily accessible for further reaction. After cooling, the precured starch was cast to form thin films on Teflon-coated glass plates and dried in an oven for 48 h at 40 °C. The precured solution had low viscosity, flowed easily, and could be conveniently cast into relatively defect-free transparent films. The dried films were peeled off from the Teflon-coated plates (18 cm × 30 cm) and stored in sealed polyethylene bags. The precured films were further heated in a Carver hydraulic hot press (model 3891-4PROA00, Wabash, IN) for complete cross-linking (curing) at 120 °C under a pressure of 0.1 MPa for 20 min. The films were easily washed by soaking in water, followed by ultrasonication for 1 h to get rid of all the excess unreacted chemicals. The films were further washed by soaking overnight for thorough washing and further removal of the remaining chemicals. After which, the films were taken out of the water, dried completely, and characterized. It was important to thoroughly wash off the unreacted BTCA and Nahyp as they are hygroscopic (absorb water) and can act as a plasticizer if they remain trapped in the specimen. Presence of unreacted chemicals can potentially distort the mechanical properties of the films.

Fabrication of Cross-Linked WMS Resin-Based Composite Films. To obtain cross-linked WMS resin-based composite films, a dispersion of MFC in gelatinized starch was prepared by adding predetermined weights of WMS, MFC paste, and sorbitol to 500 mL of water and stirring with a high-speed mechanical stirrer at 90 °C for 1 h. The stirring speed had to be increased from 600 to 1100 rpm at higher loadings of MFC to prevent fibril clustering. This was followed by the addition of 5 g of BTCA and 2.5 g of Nahyp, and the entire mixture was precured at 90 °C for 1 h while stirring at high speed. The mixture was cast on Teflon-coated glass plates to form films. The films were dried as described earlier followed by curing at 120 °C for 20 min leading to the formation of the MFC-cross-linked WMS composite films. The composite films were washed following the same procedure described earlier for the cross-linked films.

Fabrication of MFC-BTCA Films. In order to investigate the interaction of BTCA with MFC, a film was fabricated with MFC and BTCA. To prepare the film, MFC paste (15 g) was dispersed in water using high-speed mechanical stirring. BTCA (25% by weight of MFC) was added. The mixture was precured at 90 °C for 1 h to ensure complete dispersion. The film was cast on Teflon-coated glass plates, cured at 120 °C for 20 min, and washed following the same procedure described above.

Attenuated Total Reflectance−Fourier Transform Infrared (ATR-FTIR) Analysis. ATR-FTIR spectra were collected using a Nicolet Magna 560 FTIR spectrometer with a split pea accessory for ATR. Each scan was an average of 150 scans recorded from 4000 to 550 cm^{-1} wavenumbers obtained at a resolution of 4 cm^{-1}. In order to construct a calibration curve from the ATR-FTIR spectra, the absorption peak at 1725 cm^{-1} resulting from the ester carbonyl ($C{=}O$) stretching vibration was chosen as the analyte peak that monitored the concentration of ester. Because the absorption due to the aliphatic $-C-H$ stretching vibration at 2929 cm^{-1} remains unchanged after the cross-linking reactions, it was chosen as the reference peak for the internal standard. The ratio of absorbance to the analyte peak and reference peak was plotted against concentration of BTCA. This method is similar to the calibration method used by Coma et al.[20] to assess the degree of cross-linking of cellulose with citric acid.

Scanning Electron Microscopy (SEM). WMS starch powder, MFC, BTCA-MFC film, fracture surface of cross-linked WMS resin, and the surface topographies of MFC−WMS (cross-linked) composites fractured in tensile mode were characterized using LEO 1550 field emission SEM. The specimens were placed on standard aluminum specimen mounts (pin type) with double-sided adhesive electrically conductive carbon tape (SPI Supplies, West Chester, PA). The specimens were coated with carbon using a Denton vacuum coater, (model BTT IV, Denton Vacuum, Moorestown, NJ). The coated specimens were then observed on the SEM using an accelerating voltage of 5 kV to observe the surface topography and characterize their fracture behavior.

Determination of Swelling Power. The swelling power of cross-linked starch specimens in DMSO was obtained by using the modification of a method demonstrated by Zhou et al.[21] The cross-linked starch films were conditioned in 21 °C and 65% relative humidity for 2 days prior to soaking in 10 mL DMSO at room temperature for

24 h. The films were accurately weighed (m_d) before immersing in DMSO. The swollen films were filtered out from the solvent, washed with water and ethanol, wiped lightly, and weighed (m_s). The swelling power values for cross-linked WMS in DMSO were calculated as follows

$$\text{Swelling Power} = \frac{m_s - m_d}{m_d} \quad (1)$$

The swelling power of cross-linked WMS in water was also determined using a modification of the method described above for DMSO. The cross-linked starch films were conditioned in 21 °C and 65% relative humidity for 2 days prior to soaking in 50 mL water, and films were accurately weighed (m_d) before immersing in water. The films were soaked for 3 days in water instead of 1 day (to reach equilibrium) keeping all the other experimental conditions exactly the same. The swollen films were wiped lightly using Kimwipes and weighed (m_s). The swelling power of the cross-linked films in water was calculated using the same equation given for DMSO.

Thermogravimetric Analysis (TGA). Native and cross-linked WMS as well as composite specimens were scanned from 25 to 600 °C using a thermogravimetric analyzer (TGA-2050, TA Instruments, Inc., New Castle, DE) at a rate of 10 °C/min in nitrogen atmosphere to characterize their thermal stability and degradation behavior.

Tensile Testing. The WMS resin and composite films were cut into rectangular pieces of dimensions to characterize their tensile properties. To confirm that the tensile properties were isotropic, the rectangular films for tensile testing were cut randomly in different directions from the original film (18 cm × 30 cm). The film thickness (approximately 0.3 mm) varied with the specimen and was measured accurately before the tensile testing. The composite films with higher loading of MFC were thicker. The films were conditioned for 3 days at ASTM standard conditions of 65% relative humidity 21 °C temperature prior to testing. The tensile properties of resin and composite films were characterized using Instron, model 5566 (Instron Co., Canton, MA), according to ASTM D882-02. A gauge length of 30 mm and a strain rate of 0.6 min^{-1} were used for all specimens. At least five specimens were tested to obtain the average values.

RESULTS AND DISCUSSION

Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) Analysis. To confirm the esterification reaction between WMS and BTCA, ATR-FTIR spectra comparing WMS, BTCA, and ester of WMS formed with BTCA were collected. These spectra are presented in Figure 1A. The ATR-FTIR spectrum of BTCA presented in Figure 1A shows a sharp peak at 1689 cm^{-1} assigned to the carboxyl carbonyl stretching. Native WMS does not show any carbonyl peak, while WMS reacted with BTCA shows the ester carbonyl peak at 1725 cm^{-1}. The cross-linking proceeds through esterification via formation of a cyclic anhydride intermediate aided by the catalyst Nahyp, the reaction mechanism being similar to cellulose cross-linking with BTCA shown by Yang.[22] Starch esterified with carboxylic acids typically show ester carbonyl peak at around 1725 cm^{-1}. FTIR of corn starch cross-linked with citric acid showed an ester peak at 1724 cm^{-1},[8] while potato starch esterified with ferulic acid showed an ester peak at 1726 cm^{-1}.[23]

Figure 1B illustrates the extent of esterification of WMS as a function of initial BTCA content using an internal calibration curve. The internal calibration curve (Figure 1B) was constructed by the method shown previously by Ghosh Dastidar and Netravali[3] for cross-linking of native starches with malonic acid. A gradual increase in the A_{1725} (absorbance of the ester carbonyl stretch)/A_{2929} (absorbance of aliphatic stretching) ratio, implied an increase in the extent of esterification reaction with an increase in the initial BTCA concentration. Recent studies by Coma et al.[20] have shown that the A_{1725}/A_{2929} ratio is linearly related to the percentage of cross-linking of cellulose with citric acid, calculated by a chemical titration method. An increase in the internal calibration curve indirectly indicates an increase in the degree of substitution (and cross-linking) with BTCA, similar to research results reported by Ghosh Dastidar and Netravali[3] and Coma et al.[20]

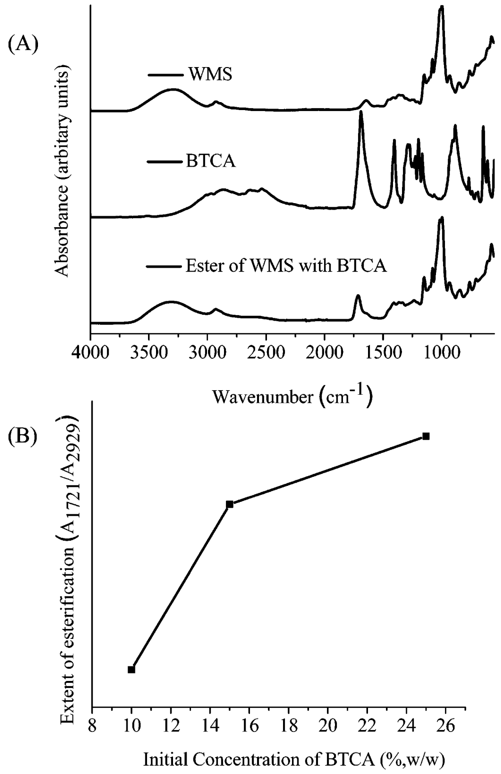

Figure 1. (A) FTIR of WMS, BTCA, and ester of WMS formed with BTCA. (B) Extent of esterification of WMS as a function of initial BTCA content using the internal calibration curve.

The film prepared with just BTCA and MFC did not show any ester carbonyl peak (Figure S3, Supporting Information) after curing indicating that 120 °C is not enough for cross-linking of BTCA with MFC. Some papers have shown that higher temperatures and longer times are needed for reaction of MFC with BTCA.[17,24] Because it was desired to specifically understand the effect of starch cross-linking, the MFC was not cross-linked with BTCA.

Swelling Power of Resin. The swelling power of WMS cross-linked with BTCA in water and DMSO as a function of the initial concentration of BTCA is shown in Figure 2. The swelling power of cross-linked WMS in water and DMSO, as shown in Figure 2, decreased as the initial concentration of BTCA (percentage of cross-linking) increased. The insolubility of WMS (esterified with BTCA) in these solvents also indirectly suggests strengthening polymer network by cross-linking. Cross-linking leads to formation of a rigid network of gel, reducing the absorption of water that does not allow it to swell. Swelling occurs by diffusion of solvent molecules (water or DMSO) within the polymer network. Cross-linking of starch helps in reducing the moisture sensitivity, thus reducing the swelling of starch in water or other solvents such as DMSO, which would be important for industrial application of starch.[2] As mentioned earlier, starch is inherently hydrophilic because of the hydroxyl groups, and the absorbed moisture affects its mechanical properties as a result of plasticization. The stability of starch in

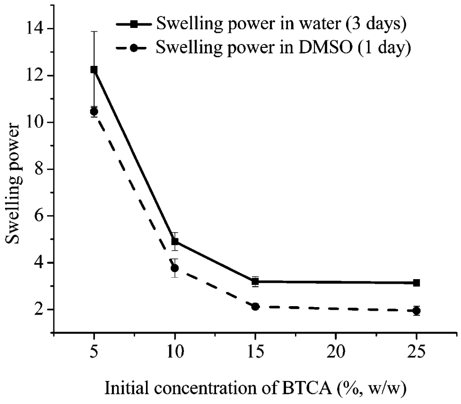

Figure 2. Swelling power of WMS cross-linked with BTCA in water and DMSO as a function of BTCA concentration.

water can be increased by cross-linking, which makes it potentially more useful for commercial applications. Figure 3 shows the stability of the WMS resin and composite in water. It was observed that the MFC–WMS (gelatinized but not cross-linked) composites rapidly disintegrated in water, while the MFC-cross-linked WMS composites only swelled in water but remained stable and retained their original shape even after continuously shaking for several months as shown in Figure 3. It can be concluded that cross-linking increases the stability of the resin (and subsequently in composite) in water due to formation of a network structure. Because of formation of a denser network structure resulting from cross-linking, regions previously accessible to solvents are reduced, and swelling is prevented. Covalent cross-links also prevent dissolution of the films by holding the molecules together and preventing unrestrained solvent absorption. Similar behavior has been noted in the previous literature on other cross-linked starches.[8,21,25]

MFC–WMS Composite Films. *Mechanical Properties.* A strong interfacial adhesion is expected between WMS and MFC as a result of the chemical match between the two,and strong hydrogen bonding resulting from the hydroxyl groups. A good H-bonding interaction is also expected between MFC and BTCA (cross-linker) due to the presence of four carboxylic acid groups, which makes BTCA hydrophilic. In addition, as shown by Huang and Netravali,[26] MFC has a broad size distribution in terms of the fibril diameter and the small diameters of the nanofibrils. Along with its high aspect ratio, MFC provides a significantly large area for the interfacial interaction. This strong interfacial interaction increases the load transfer efficiency from broken to intact fibers in the composites, reduces the critical length required for effective load transfer, and thus increases the mechanical properties.[26,27] The native WMS films and cross-linked WMS films (both without MFC) were too brittle and hence could not be tensile tested. The cross-linked films also revealed numerous defects after curing. A reason for defect formation in this method could be that internal stresses are caused during the curing process. Other influences are the existence of cracks or uneven geometries of the sample. These influences, however, were easily mitigated by incorporation of MFC in the sample manufacturing. The resulting composite films were relatively defect-free and were easily cured without developing cracks and/or wrinkles. MFC (15% MFC)-cross-linked WMS composite films exhibited excellent mechanical properties with high stiffness and toughness (Young's modulus of 2341 MPa, fracture strain of 3.1%, and fracture stress of 39 MPa), even without the use of any plasticizer. The hydrophilicity of the MFC fiber network makes the film sufficiently ductile to be tensile tested without the use of any plasticizer. However, it should be noted that even though MFC is hydrophilic, it is highly crystalline in nature and hence does not allow it to absorb a significant amount of moisture.[26] Because of the similarities of the chemical structure of starch and cellulose, incorporation of MFC is an environmentally friendly and facile way for fabrication of smooth, defect-free, flexible films that are easier to handle and do not need any plasticizers. The strengthening of the network structure and reduction in moisture absorption (as observed from the swelling power data) due to cross-linking of the WMS resin with BTCA also contributed to the higher modulus of the composites. Figure 4 shows typical stress vs strain plots for WMS resin (not cross-linked, no MFC) and MFC (15%)–WMS (cross-linked) composite, both containing 5% sorbitol as plasticizer. Clearly, the MFC-reinforced composite showed a higher toughness than WMS resin, as was expected. Plasticizers such as glycerol and sorbitol (polyols) absorb moisture that increases the free volume within the polymer and reduces their glass transition temperature. This, in turn, results in lower Young's modulus and higher fracture strain values as well as a reduction in brittleness and an increase in toughness.[6] It should be emphasized that incorporation of MFC instead of polyol-based plasticizers increased the fracture strain without compromising the Young's modulus. Thus, MFC is a potential environmentally friendly substitute for glycerol and sorbitol in fabricating cross-linked starch-based films. The fracture stress, fracture strain, and toughness data are presented

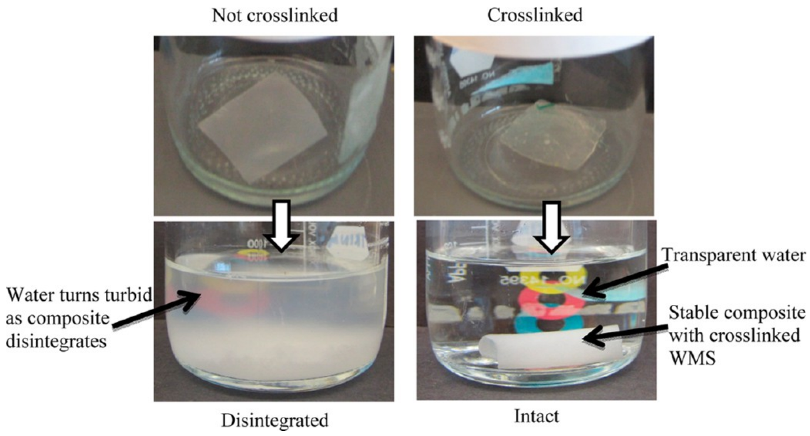

Figure 3. Stability of cross-linked composite in water.

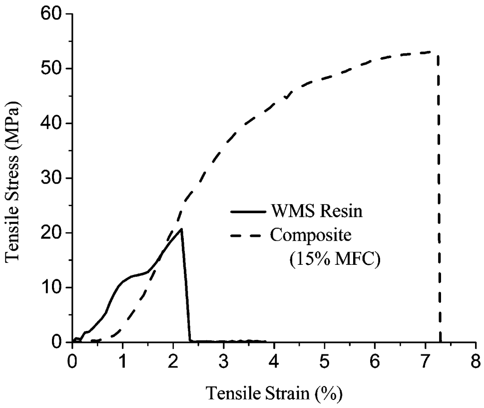

Figure 4. Tensile properties of WMS resin and composite.

in Table 1 and show significant improvement with cross-linking and subsequent incorporation of MFC. Addition of 5% sorbitol to the cross-linked MFC (15%)—WMS composite film, however, decreased the Young's modulus from 2341 to 1686 MPa. The reduction in Young's modulus with plasticizer was expected. As mentioned earlier, it was not possible to conduct tensile tests on cross-linked WMS resin films (without MFC) even after adding 5% sorbitol owing to the brittleness of the films as well as experimental difficulty in fabricating defect-free films. Hence, no data could be collected for pure cross-linked WMS resin films. It should be noted that there was no significant change in mechanical properties when sorbitol content changed from 2.5% to 5%. This may suggest that the sorbitol in excess of 2.5% may be aggregating. It may also be possible that excess sorbitol may get washed off during the washing process.

Table 1. Mechanical Properties of WMS and MFC—WMS (cross-linked) Composites as a Function of sorbitol (%)

MFC (%)	sorbitol (%)	modulus (MPa)	fracture stress (MPa)	fracture strain (%)	toughness (MPa)
0	5	1354 (50)	17.6(65)	3.1(37)	0.4 (90)
15	0	2341 (32)	39 (20)	3.1 (29)	0.7 (47)
15	2.5	1679 (6)	45 (25)	10 (43)	3.3 (74)
15	5	1686 (40)	44 (33)	7.8 (32)	2.3 (44)

Table 2 provides mechanical properties for MFC—WMS (cross-linked) composites as a function of MFC content. It is evident from data presented in Table 2 that Young's modulus increases with an increase in MFC content from 15% to 50% (2.5% sorbitol). As mentioned earlier, this is because the cellulose fibrils are known to possess very high Young's modulus of up to 140 GPa owing to their high degree of molecular orientation and highly crystalline nature.[1,10] In addition, MFC also forms strong hydrogen bonding with the starch resin leading to higher interfacial adhesion, which also contributes to the higher Young's modulus and fracture stress.[27] The tensile properties of the MFC-reinforced composites were also completely isotropic, which can be attributed to the network structure of the MFC fibrils as revealed in the SEM images (discussed later).

Table 2. Mechanical Properties of MFC-Cross-Linked WMS Composites as a Function of MFC Loading

MFC (%)	sorbitol (%)	modulus (MPa)	fracture stress (MPa)	fracture strain (%)	toughness (MPa)
15	2.5	1679 (6)	45 (35)	10 (43)	3.3 (74)
25	2.5	1737 (8)	56.5 (21)	6 (35)	2.3 (58)
35	2.5	2207 (16)	58 (16)	7 (33)	2.9 (51)
50	2.5	2566 (12)	63 (15)	7.6 (38)	3.5 (52)

The properties of MFC-cross-linked starch-based composites were comparable or in some cases higher than petroleum-based polymers such as nylon-6 (Young's modulus: 1800 MPa; fracture stress: 70 MPa).

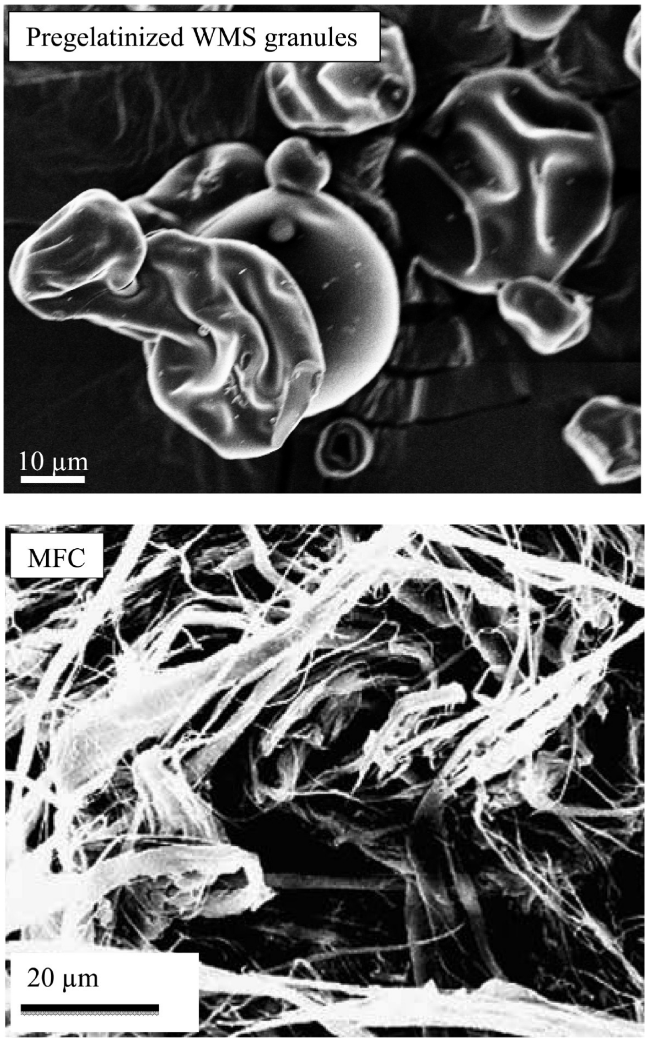

Figure 5. SEM images of (top) pregelatinized WMS granules and (bottom) MFC fibers.[1]

Microscopic Analysis. Figure 5 (top) shows SEM images of pregelatinized WMS granules as is obtained from the vendor. The collapsed granules of industrially pregelatinized and instantized WMS, used in the present study, dissolved easily in water at 90 °C and formed a homogeneous transparent solution. It was possible to uniformly disperse MFC in the solubilized WMS by mechanically stirring at a high shear rate to ensure that no aggregates were formed. Lopez-Rubio et al.[6] have reported that the formation of high quality amylopectin films is dependent on the full gelatinization (and associated loss of crystallinity) of the amylopectin before casting the film. Figure 5 (bottom) shows the SEM image of MFC fibers.[1] From the SEM image, it is clear that the MFC is a mixture of fibrils with broad range of distribution of the diameters, including both microsized and nanosized fibrils.[1]

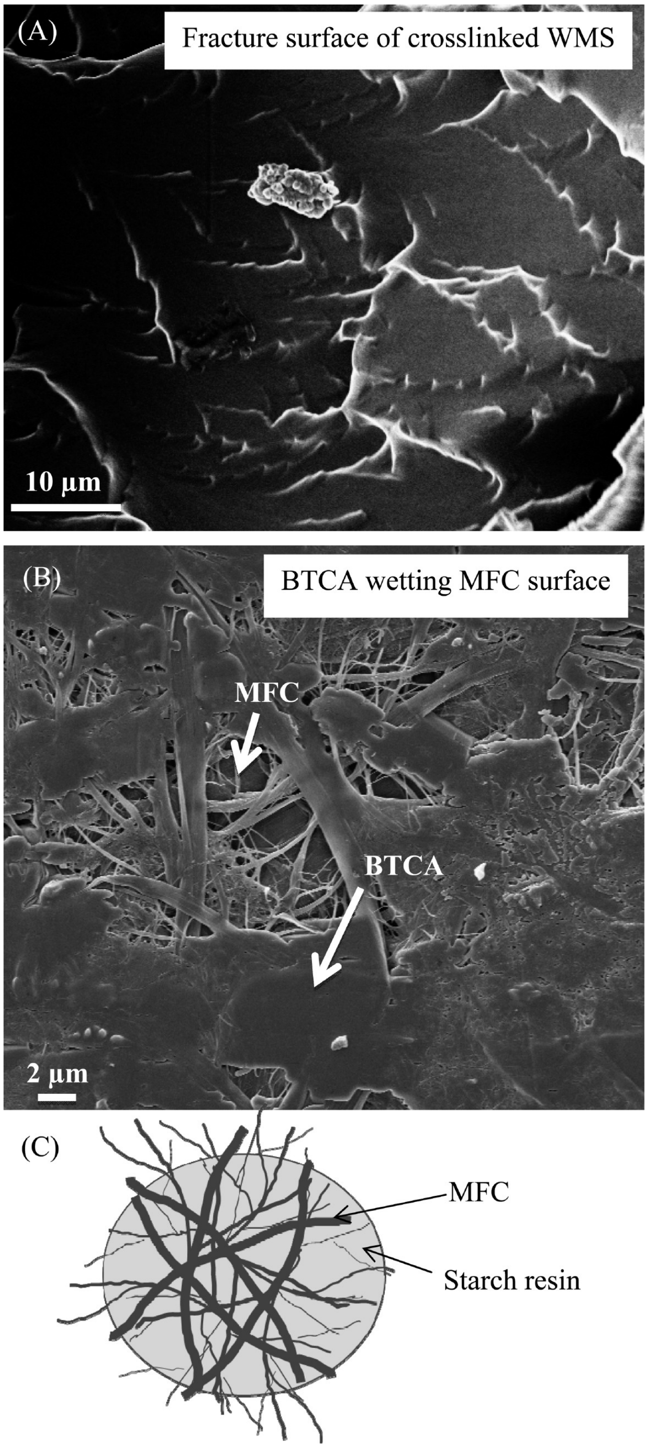

Figure 6. SEM images. (A) Fracture surface of cross-linked WMS. (B) BTCA wetting MFC network. (C) Schematic of MFC−WMS composite showing the network structure of MFC incorporated in the starch-based resin.

Figure 6A shows the SEM image of the fracture surface of cross-linked WMS resin. The SEM image of cross-linked WMS, not reinforced with MFC, shows a glassy fracture surface, as expected for a brittle fracture for resins such as epoxies.[12,28]

Figure 6B shows the SEM image of the film prepared by curing BTCA with MFC. The image clearly shows that BTCA spreads on the surface of the network structure of MFC. This may be attributed to the strong H-bonding interaction between the hydroxyl groups in MFC and the four carboxylic acid groups in BTCA. It is expected that the strong interaction between the reinforcing filler and the cross-linker also contributes to the higher tensile properties of the composites. As explained earlier, no cross-linking reaction was observed between BTCA and MFC at 120 °C. The random network and branched structure of MFC

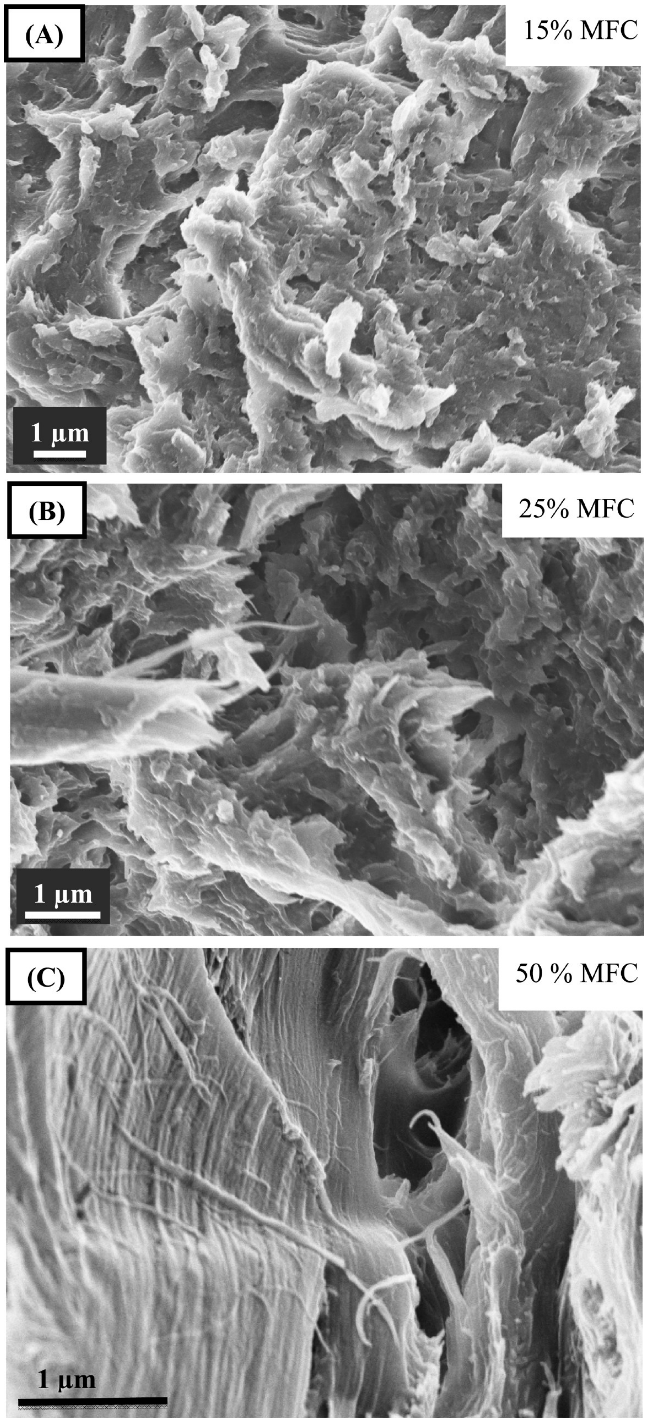

Figure 7. SEM images of MFC−WMS cross-linked composites.

in Figure 6C also accounts for the isotropic properties of the composites

Figure 7 shows the SEM images of typical fracture surfaces of MFC−WMS cross-linked composites failed in tension. The fracture surfaces of MFC−WMS cross-linked composites showed surface roughness due to incorporation of MFC, rather than a smooth fracture surface of the brittle resin. The images show a close association between the fiber and the resin. Owing to similar chemical compositions of starch and cellulose, significant hydrogen bonding is expected between the two. The fiber (MFC)−resin (cross-linked WMS) interaction plays a significant role in improving the mechanical properties of the composites.[28,29] The SEM images showed that the MFC fibrils were embedded into the starch resin to a large extent. The surface topography of composite with 50% MFC is distinctly different from the composites incorporated with 15% and 25% MFC. It is assumed that as the loading of MFC increased to 50%, MFC became one of the dominant phases rather than reinforcing filler with the cross-linked WMS resin occupying the voids within the porous MFC network. It was difficult to draw any definite conclusion about the dispersion of the fibers from the SEM images.

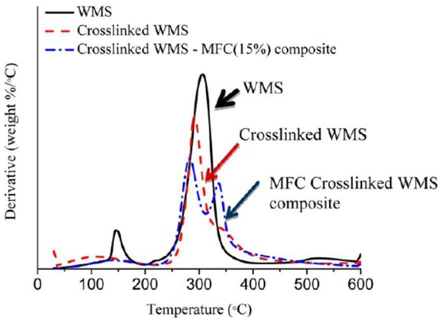

Figure 8. DTGA of WMS. Cross-linked WMS and MFC (15%)-cross-linked WMS composite.

Thermal Properties. The DTGA plots, constructed from the TGA plots (Figure S4, Supporting Information) in Figure 8 show that gelatinized WMS and cross-linked WMS resins as well the composite start to degrade at about the same temperature (≈270 °C). There was around 90% weight loss at 600 °C in the case of gelatinized WMS (not cross-linked) resin compared to 70% weight loss observed for the cross-linked WMS resin. WMS already had a high initial thermal degradation temperature that did not change on cross-linking. The DTGA plot for the MFC (15%)-cross-linked WMS composite showed a two-stage thermal degradation for the composite. This is confirmed by the two sharp peaks observed in the DTGA curve at around 270 and 300 °C. The peak observed around 270 °C for the cross-linked MFC−WMS composite is same as that observed for the WMS resin and represents the onset of resin degradation. The peak (at ≈300 °C) corresponds to the degradation of MFC, which is thermally more stable than cross-linked WMS.[1,26] These results suggest that there was only slight enhancement in thermal degradation properties on incorporation of MFC possibly because the fibrils stay as a separate phase in the composites and also because the difference between their degradation temperature is not so significant as in the case of clay particles.

■ CONCLUSIONS

Cross-linked waxy maize starch-based environmentally friendly composites reinforced with MFC were fabricated using a facile easy method. A nontoxic, water-soluble, carboxylic acid, BTCA, was selected to cross-link WMS. Cross-linking reduced the water absorption and led to a decrease in swelling power of the WMS films in both water and DMSO. The stability of the films in water also increased after cross-linking. Incorporation of MFC proved to be a benign way to improve the flexibility of the film without compromising other tensile properties including Young's modulus. However, in the present research, no conclusion could be drawn on the effect of MFC dispersion and interfacial interaction on the composite properties. Understanding the curing kinetics, reaction, and efficiency and characterization of the interfacial interaction of cross-linked WMS-based composites is an important future research. The "green" cross-linked starch with or without MFC can potentially replace some petroleum-based resins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Comparison between regular starches and industrially pregelatinized starches, gelatinized for 60 min at 90 °C (Figure S 1); rheology of different native starches gelatized for 60 min at 90 °C (Figure S 2); ATR-FTIR of MFC, BTCA, and BTCA MFC films (Figure S 3); TGA of WMS, cross-linked WMS, and MFC (15%)-cross-linked WMS composite (Figure S 4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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