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Surface modification of microfibrillated cellulose for epoxy composite applications

Jue Lu, Per Askeland, Lawrence T. Drzal*

Composite Materials and Structures Center, Michigan State University, East Lansing, Michigan 48824-1226, United States

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Abstract

Microfibrillated cellulose (MFC) possessing a 'web-like' morphology was successfully modified with three different coupling agents: 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and a titanate coupling agent (Lica 38). The surface modification was confirmed using infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), environmental scanning electron microscopy (ESEM), and contact angle measurements. These modifications changed the surface character of MFC from hydrophilic to hydrophobic. The untreated and treated MFC were successfully incorporated into an epoxy resin system using acetone as the solvent. Better and stronger adhesion between the microfibrils and the epoxy polymer matrix was observed for the treated fibers, which resulted in better mechanical properties of the composite materials.

Keywords: Microfibrillated cellulose; Surface treatment; Epoxy

1. Introduction

Composites are widely used in many applications, such as automotive, construction, packaging, etc. due to their combination of excellent stiffness and strength along with their low density. In recent years, natural fibers have drawn much attention as an alternative to traditional glass fibers in commercial composite materials [1–3]. Natural fibers have many advantages, such as sustainability, renewability, recyclability, wide availability, low density, biodegradability, and last but not least, low cost, which offer greater opportunities to develop a new class of light weight, environmental friendly, structural composites. Although natural fibers, such as sisal or flax, have relatively high stiffness, their high variability in diameter and length reduce their performance in composite applications, which reduces their value in use. Recently the identification of nano-sized cellulose microfibrils increases the choices of fibers and expands their use because of their excellent mechanical properties in composites [4].

There are two types of nano-sized cellulose which have been studied as reinforcements in a polymer matrix. One is cellulose nanowhiskers [4–6], which result from a combination of mechanical processing and acid hydrolysis of cellulose-rich natural resources, such as sea animals and plants. Depending on their origin, these cellulose whiskers have diameters in the range of 2–20 nm, and their lengths can reach several tens of microns depending on their origin. Thus they have a very high aspect ratio which results in a significant load-carrying capability. As they are devoid of chain folding and contain only a small number of defects, their modulus was estimated to be around 130 GPa and strength should be in the order of 7 GPa [7]. Another nano-sized cellulose fiber is called microfibrillated cellulose (MFC), which can be traced back to the early 1980s [8,9]. MFC is obtained through a simple mechanical process which includes refining and high pressure homogenizing. The mechanical shear forces during processing promote fibrillation of the cellulose fibers, producing microfibrils with the diameters in the range of 10–100 nm, but the web like structure still

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* Corresponding author.
E-mail address: drzal@egr.msu.edu (L.T. Drzal).

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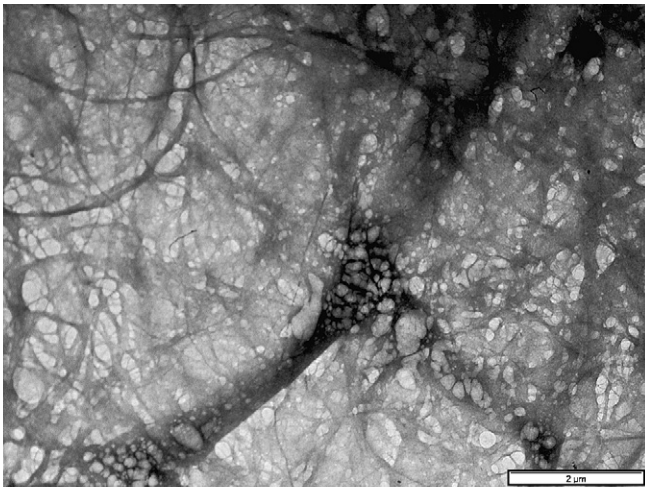

Fig. 1. Transmission electron micrograph of microfibrillated cellulose.

remains, as shown by TEM in Fig. 1. It was found that the phenol–formaldehyde (PF) composites reinforced with MFC exhibit high strength and toughness, which is comparable to the one reinforced with magnesium, but with much lower density [10]. MFC also showed significant reinforcing effect when combined with polyvinyl alcohol [11]. The easy processing and low cost for producing MFC makes it an alternative to cellulose nanowhiskers in reinforcing polymer matrix.

One disadvantage of cellulosic fibers for their application in industry is the strong hydrophilic nature of their surface, which inhibits homogeneous dispersion in most non-polar polymer matrices and causes a weak interface, thus reducing the mechanical properties of the composites. Significant efforts to chemically modify the natural fibers to make them compatible with hydrophobic polymer matrices have been conducted [12,13]. Indeed, good dispersion of fibers in the polymer matrix and good adhesion is an important prerequisite for obtaining good mechanical properties of the resulting composites. In the case of cellulose nanowhiskers and MFC, a stable dispersion can only be achieved in water or very polar organic solvents, such as *N*,*N*-dimethylformamide (DMF) [14]. Thus, the use of nano-sized cellulose whisker as a reinforcing phase so far is mostly limited to polymer matrices which are either water soluble, such as polyvinyl alcohol, or an aqueous suspension of polymer, such as latex. To improve their versatility, cellulose whiskers have been treated either with a surfactant [15] or chemicals, such as alkenyl succinic anhydride [16], isocyanates [16], maleated polypropylene [17], or chlorosilane [18]. Stable suspensions of cellulose whisker in non-polar solvents such as toluene and cyclohexane can be achieved with surface modification, but the mechanical performances of the resulting composites were unchanged [19] or even strongly reduced [16,17], which is possibly due to destruction of the crystal structure of cellulose.

In this research, surface chemical modification of MFC was investigated. The purpose of this surface treatment is to help a better dispersion of cellulose in the non-polar polymer matrix and increases the interfacial bonding. It was demonstrated that 3-aminopropyltriethoxysilane (APS) surface treated MFC has good reinforcing effect on cellulose acetate [20]. In this work, epoxy was chosen as a model polymer matrix, because it is a commonly used thermosetting resin with excellent mechanical properties and resistance to environmental degradation. It is also widely used in coating industry with either waterborne or organic solvent borne system. The objective of this work was to examine the effect of surface treatments of MFC on the dispersion of fibers and the mechanical properties of the resulting epoxy composites.

2. Experimental

2.1. Surface treatment of MFC

MFC was purchased from Daicel Chemical Industries, Ltd., which is a 9.9 wt% solid content in water suspension. MFC was obtained by a homogenizing process on kraft pulp consisting of 50% lodge pole pine, 40% of white spruce and 10% of Douglas fir [10]. As shown in Fig. 1, MFC appears as an interconnected web with tiny fibrils and microfibril bundles which have diameters in the range of 10–100 nm. The micro-sized fibers also exist as shown in Fig. 2. Their specific surface, measured by the BET technique using nitrogen as the adsorbed gas, was found to be 7.54 m^2/g. The actual surface area could be much higher than this value as the sample for BET analysis was freeze dried, which could cause the fibers to aggregate. MFC was diluted with water at a fiber content of 0.5 wt%, sonicated for 5 min and stirred for 24 h. This aqueous suspension was solvent exchanged with ethanol 3 times and then with acetone 3 times. The content of MFC in acetone was adjusted to be 0.6 wt%. Three different coupling agents were employed in the study. They are: 3-aminopropyltriethoxysilane (APS, United Chemical Technologies, Inc.), 3-glycidoxypropyltrimethoxysilane (GPS, United Chemical Technologies, Inc.) and a titanate coupling agent (Lica 38, Kenrich Petrochemicals, Inc.). They are used as received. In

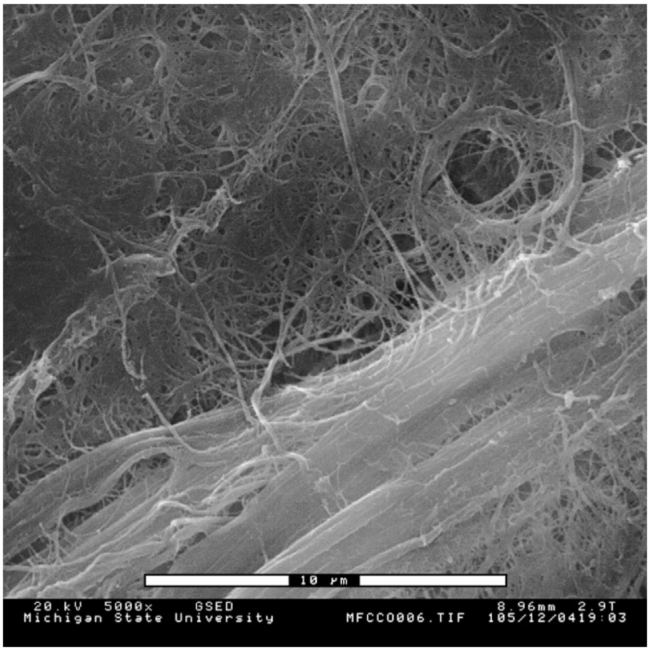

Fig. 2. ESEM micrograph of microfibrillated cellulose (MFC) film.

a typical silane treatment, silane was added into MFC acetone suspension to yield a 0.3 wt% final concentration. The suspension was stirred for 24 h. The silane treated MFC was filtered and then dried at room temperature for 24 h followed by treatment at 120 °C for 2 h in air. For the titanate coupling agent treatment, Lica 38 was dissolved in a small amount of acetone, and the solution was added drop wise into 0.6 wt% MFC acetone suspension while stirring, yielding a 0.15 wt% final concentration. The suspension was stirred for 3 h, filtered and then washed several times with acetone. The film was then dried at room temperature for 24 h.

2.2. Film preparation

The epoxy system used is EPON™ Resin 863 and a curing agent polyether amine (D-230) with a ratio of 100/35.2 (Resolution Performance Products). This resin system was chosen due to its low viscosity (300 cP at 25 °C) and low reactivity at room temperature (gel time is 6 h at 33 °C). The desired amount of epoxy was added into MFC acetone suspension, sonicated for 5 min and stirred for 4–5 h (the weight percent of MFC to epoxy is 5 wt%). The calculated amount of curing agent was then added and the mixture was stirred for another hour. The suspension was degassed in a vacuum oven for 10 min and then poured into a Teflon petri dish with controlled leveling. The composites were cured at 40 °C for 12 h and postcured at 120 °C for 2 h. The evaporation of acetone occurred simultaneously with the curing process of epoxy as experienced in a typical organic solvent borne epoxy coating. The thickness of the films was approximately 500 μm.

2.3. Characterization of surface treatments

Both the untreated and treated MFC were characterized by Fourier transform infrared (FTIR) spectroscopy using a Perkin-Elmer system 2000 with an attenuated total reflectance (ATR) sampling attachment. The contact angle measurements were performed using a Krüss DSA 10 on the films prepared by film casting. An X-ray photoelectron spectroscopy spectrum (XPS, Physical Electronics 5400 ESCA) was used to study the surface of treated and untreated MFC. The treated MFC films were Soxhlet extracted with acetone for 48 h before XPS analysis to remove physically bonded silane.

2.4. Characterization of the composite morphology

An environmental scanning electron microscope (ESEM, Phillips Electroscan 2020) was used to observe the morphology of dried MFC films and the fracture surfaces of epoxy composites. Images were measured using an accelerating voltage of 15 kV and an operating pressure of 3–5 torr of water vapor. All composite samples were fractured in liquid nitrogen and the fractured surfaces were sputter-coated with gold using a Denton sputter coater to improve image quality.

2.5. Thermal and mechanical tests

Samples for dynamic mechanical analysis were prepared to dimensions of approximately 25 × 5 × 0.3 mm. Dynamic mechanical analysis was conducted in a tension mode on a DMA 2980 (TA instruments). Temperature scans were run from 0 °C to 150 °C at a heating rate of 4 °C/min with a frequency of 1 Hz and amplitude of 30 μm. Thermogravimetric analysis (TGA) was performed using a TGA 2950 (TA instruments) from 25 °C to 580 °C at a heating rate of 10.0 °C/min under a nitrogen flow. Approximately 10 mg of epoxy composite film was used.

3. Results and discussion

3.1. Effect of solvent

During the preparation of MFC–epoxy composite films, the evaporation of acetone occurred simultaneously with curing of the epoxy. Incomplete evaporation of acetone may affect the properties of the resulting composites, which could counter the benefits of MFC. Fig. 3 shows the FTIR spectra of

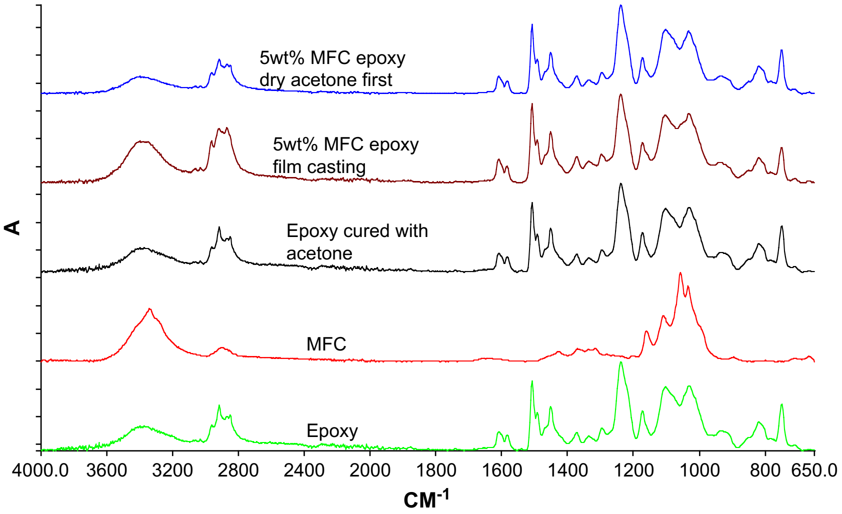

Fig. 3. FTIR spectra of neat epoxy, MFC, and epoxy–MFC composites cured with and without acetone.

the different epoxy matrix samples. It is clear that the spectrum of the epoxy cured with acetone is identical to the one without acetone, indicating that acetone was completely evaporated during the curing process. For the MFC–epoxy composites, two samples using different processing methods were prepared and their spectra were also compared. One sample was prepared by mixing epoxy with the MFC acetone suspension, and acetone was completely removed under vacuum at elevated temperature before adding the curing agent. The other sample was prepared by co-curing epoxy with acetone evaporation. As shown in Fig. 3, the spectra of two samples have approximately the same adsorption bands, which also confirm that no acetone remained in the resulting composites.

Fig. 4 shows the surface of the MFC–epoxy composite film observed by the optical microscopy. Fig. 4(a) shows a non-uniform phase morphology which constitutes many granular domains. This is possibly due to the evaporation of acetone and the faster crosslinking nature of the surface molecules which forms a particulate structure [21]. The roughness of the film would greatly affect the measurement of the sample thickness, and thus the mechanical properties of the films. To avoid this, the top surface was carefully polished revealing excellent dispersion of the MFC in the epoxy film, as shown in Fig. 4(b).

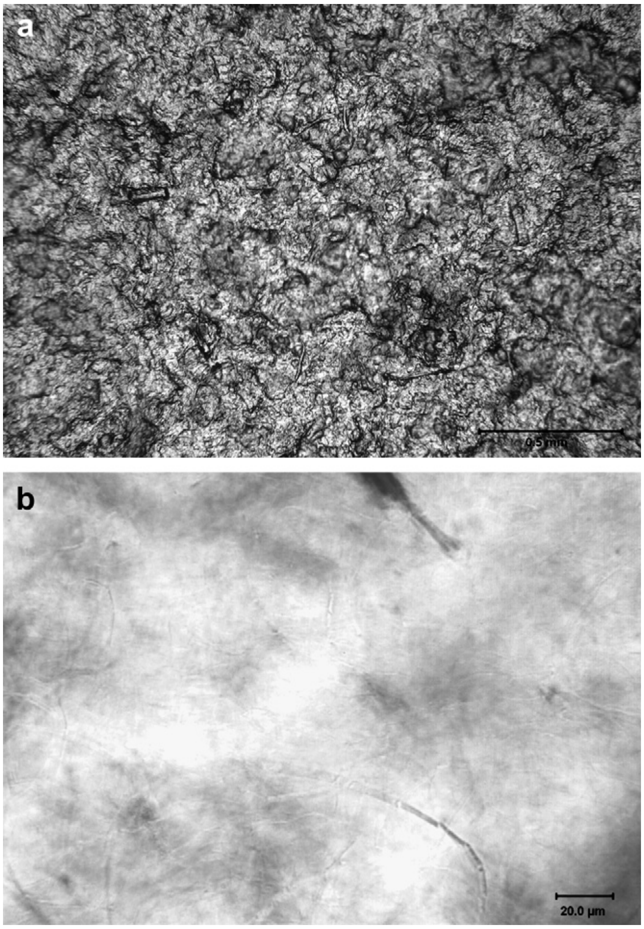

Fig. 4. The optical microscopic images of the surface morphology of MFC–epoxy composite film: (a) before polishing, and (b) after polishing.

3.2. Surface modification with silane and titanate coupling agent

The surface modification of natural fibers with silane has been well studied [12]. The reaction involves the hydrolysis and condensation of triethoxysilanes which forms ≡Si–OH-bearing oligomers. The oligomers can form hydrogen bonds with –OH groups of cellulose at room temperature, and a condensation reaction takes place to give Si–O–C bonds. The special character of MFC offers some challenges on surface modification with silane. As a traditional method, silane adsorption can be carried out in aqueous suspension where MFC was originally dispersed. The problem is that MFC is not able to be re-dispersed in an organic solvent after drying due to the strong aggregation of MFC. Another option is to solvent exchange MFC from water to acetone after silane treatment, and then the condensation of silane onto the MFC surface can proceed via solvent heating without the presence of water. It was found that the solvent exchange process washed away the adsorbed silane which is hydrogen bonded on the MFC surface before condensation. Thus silane treatment was carried out in the MFC acetone suspension after solvent exchange. The hydrolysis of silane utilizes the residual water in acetone after solvent exchange (approximately 1 wt%), and 24 h reaction time was used to make sure the completion of reaction. The condensation reaction of silane on MFC surface was expected during the curing of epoxy resin. The APS and GPS were selected for their potential reaction with the epoxy or curing agent functionalities which could produce covalent bonding with the epoxy matrix.

The FTIR spectra of treated and untreated MFC are presented in Fig. 5. MFC shows some characteristic bands for cellulose: the hydrogen bonded OH stretching at ca. 4000–2995 cm^{-1}, the CH stretching at 2900 cm^{-1}, the OH bending of adsorbed water at 1635 cm^{-1}, the CH_2 bending at 1430 cm^{-1}, the CH bending at 1380 cm^{-1}, the C–O stretching at 1058 and 1035, the CH bending or CH_2 stretching at 900 cm^{-1} which indicates the amorphous structure, and the OH out of plane bending at 687 cm^{-1} [22]. The spectrum of APS treated MFC (designated as AMFC) after drying at room temperature for 1 day shows the bands at 1565 and

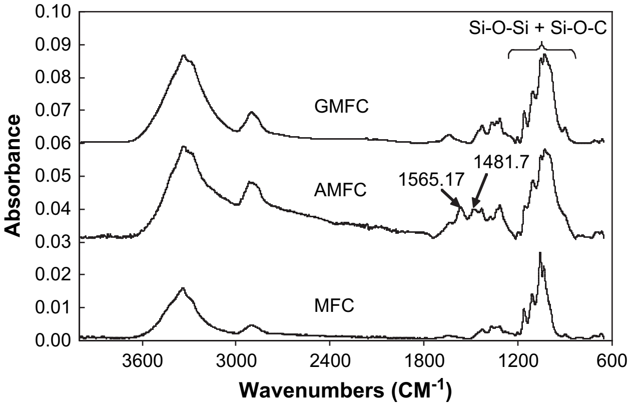

Fig. 5. FTIR spectra of untreated and silane treated MFC.

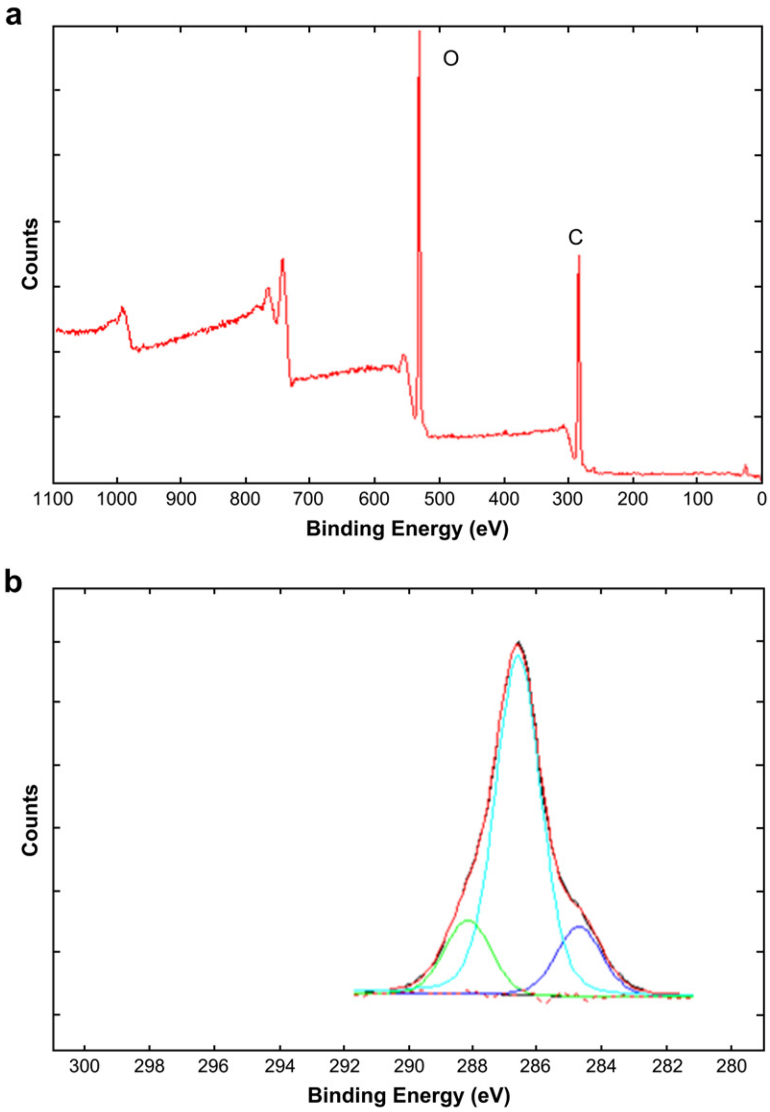

Fig. 6. XPS spectrum of MFC (a) and deconvolution of its C_{1s} peak (b).

1481 cm^{-1} which are typical of the amine groups that are strongly hydrogen bonded to the hydroxyl groups of both silanol and cellulose [23,24]. There is a weak band shown at 998 cm^{-1} assigned to unreacted silanol groups produced in the silane hydrolysis. Although the strong absorption of the two bands in the region of 1000–1200 cm^{-1} region makes it difficult to completely assign the Si–O–Si and Si–O–$C_{cellulose}$, the intensity of the peak at 1035 cm^{-1}, which is an overlap of Si–O–Si band and the C–O stretching of cellulose, is increased after silane treatment, further evidence of silane adsorption. The spectrum of GPS treated MFC (designated as GMFC) also shows a weak band at 998 cm^{-1} and an increased intensity of the peak at 1035 cm^{-1}.

XPS is a powerful tool to investigate chemical changes resulting from the surface modification of MFC. The XPS spectra of untreated and APS treated MFC are presented in Figs. 6 and 7, respectively, and the relative atomic concentration and oxygen-to-carbon ratios are summarized in Table 1. The O/C atomic ratio of MFC measured by XPS is 0.7, which is slightly below the theoretical O/C value of 0.83 based on the formula of cellulose, possibly because there are some other components on the surface such as adventitious carbon. For silane treated MFC, the presence of silicon and nitrogen was detected, which were present in the initial structure of APS, indicating clearly the bonding of silane to MFC. In addition, the O/C ratio decreases from 0.7 to 0.4 and 0.6, respectively, with the silane treatment due to the bonding of APS and GPS. The deconvolution of the peak corresponding to carbon atoms in the XPS spectrum of MFC (Fig. 6(b)) shows the presence of three types of carbon bonds: C–C (C1, 284.6 eV), C–O (C2, 286.1 eV), and O–C–O (C3, 287.6). As shown in Fig. 7(b) and Table 2, the intensity of the C1 peak dramatically increases from 14.2% for MFC up to 52.8% for the APS treated MFC, which is due to the presence of the propyl groups on APS. Additionally, the intensity of the C2 and C3 peaks decreases. In the case of GPS, the intensity of the C1 peak slightly increases with the very slight decrease of the C2 and C3 peaks. It is clear that APS displays a better

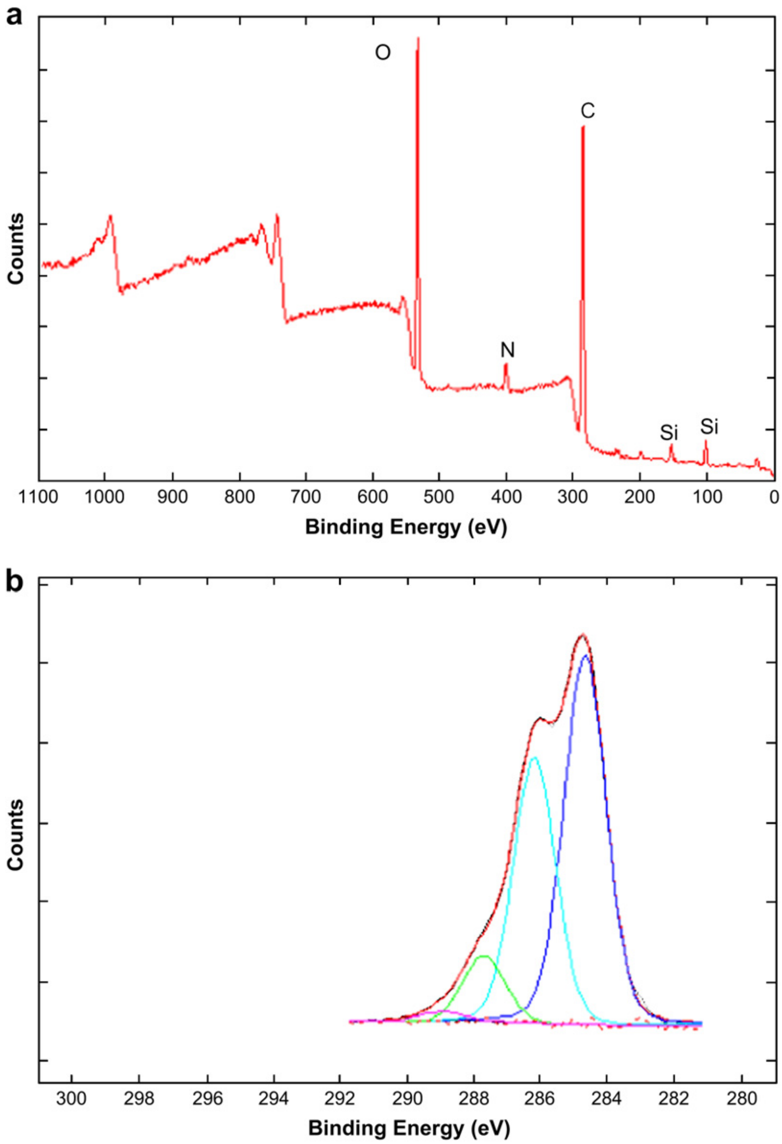

Fig. 7. XPS spectrum of APS treated MFC (a) and deconvolution of its C_{1s} peak (b).

adsorption affinity toward the MFC substrate. This can be attributed to the presence of the NH_2 group in APS, which can form hydrogen bonding with −OH group on cellulose.

The titanate coupling mechanism is quite different from the silanes. It is proposed that the coupling happens by alcoholysis, surface chelation or coordination exchange [25]. When there are hydroxyl groups present on the surface of the substrate, the monoalkoxy and neoalkoxy type titanium derived coupling agents react with the hydroxyl groups to form a monomolecular layer. Fig. 8 shows the reaction mechanism of Lica 38 and cellulose. The FTIR spectra of titanate treated MFC did not have significantly different absorbent bands compared to the untreated one (not shown). The more obvious evidence for the titanate coupling was gained by the XPS analysis and TGA analysis. As shown in Fig. 9, the presence of the titanium (peak at 460 eV) and phosphorous (peak at 140 eV) atoms on the cellulose surface clearly indicates that the titanate coupling agent has reacted onto the cellulose surface. In addition, the deconvolution of the peak corresponding to carbon atoms in the XPS spectrum of MFC (Fig. 9(b)) shows that the intensity of

Table 1
The atomic concentration of MFC and surface treated MFC

	O/C	C_{1s}	O_{1s}	N_{1s}	Si_{2p}	P_{2p}/Ti_{2p}
MFC	0.7	58.2	41.4			
AMFC	0.4	66.2	26.5	3.5	3.5	
GMFC	0.6	61.5	37.2		0.9	
TMFC	0.6	59.6	36.5			2.6/0.7

Table 2
Relative carbon composition of MFC before and after surface treatment

	C1 (C−C)	C2 (C−O)	C3 (O−C−)
MFC	14.2	69.2	16.6
AMFC	52.8	37.1	10.1
GMFC	25.7	58.8	15.5
TMFC	39.2	50.1	10.8

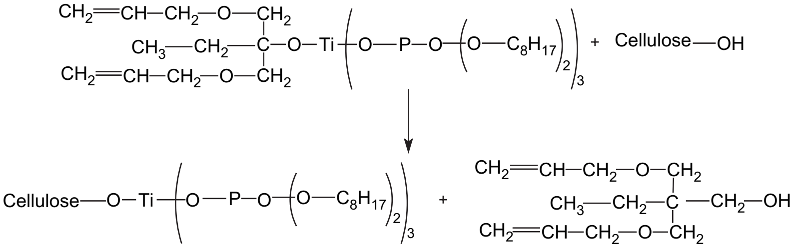

Fig. 8. The reaction mechanism of Lica 38 on the cellulose surface.

the C1 peak (C–C) has greatly increased from 14.2% to 39.2%, which results from the long alkyl chains of the titanate coupling agent; and the intensities of C2 and C3 peaks decrease with the surface treatment, respectively. All of these results confirm the successful bonding of the titanate coupling agent onto MFC.

Fig. 10 shows the comparison of the ESEM images of the untreated and titanate treated sample. The treated fibers appear much smoother than the untreated fibers, indicating that the treatment has altered the surface morphology of the MFC. Fig. 11 shows the TGA curves of the untreated and titanate treated MFC. The thermostability of the treated MFC is less stable compared to the untreated one because the surface modifier decomposes at a lower temperature than cellulose. As shown in Fig. 11, the onset temperature of the decomposition

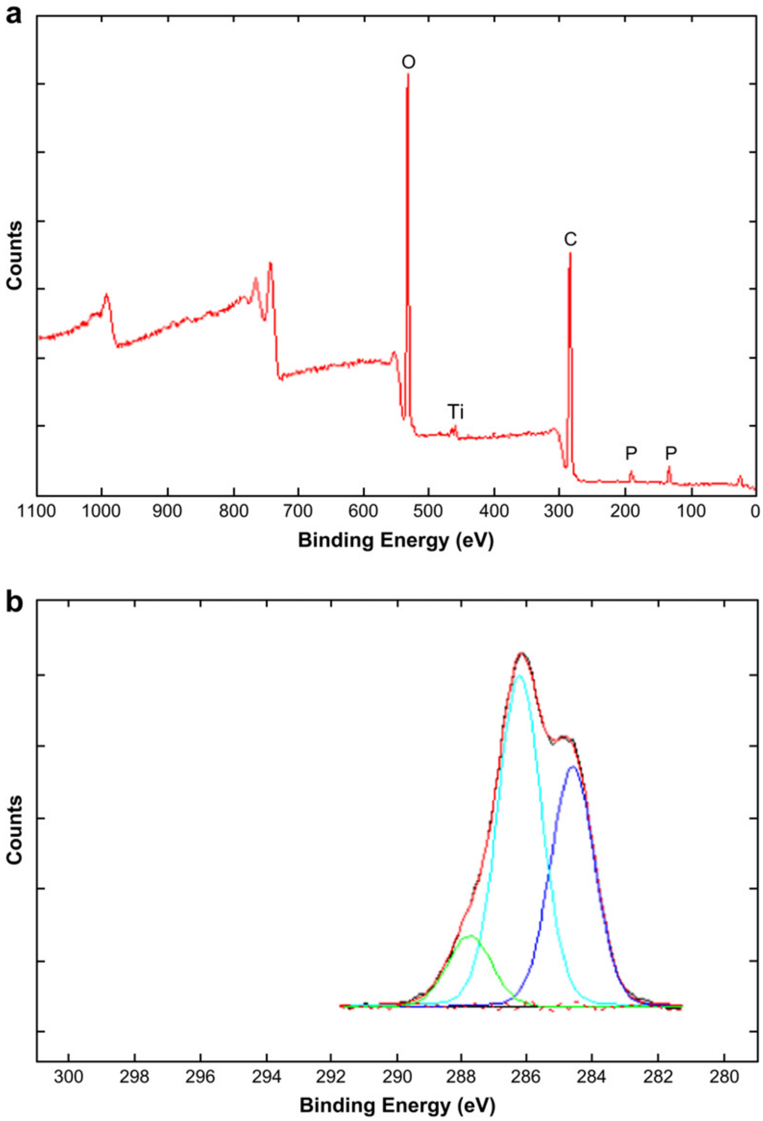

Fig. 9. XPS spectrum of titanate treated MFC (a) and deconvolution of its C_{1s} peak (b).

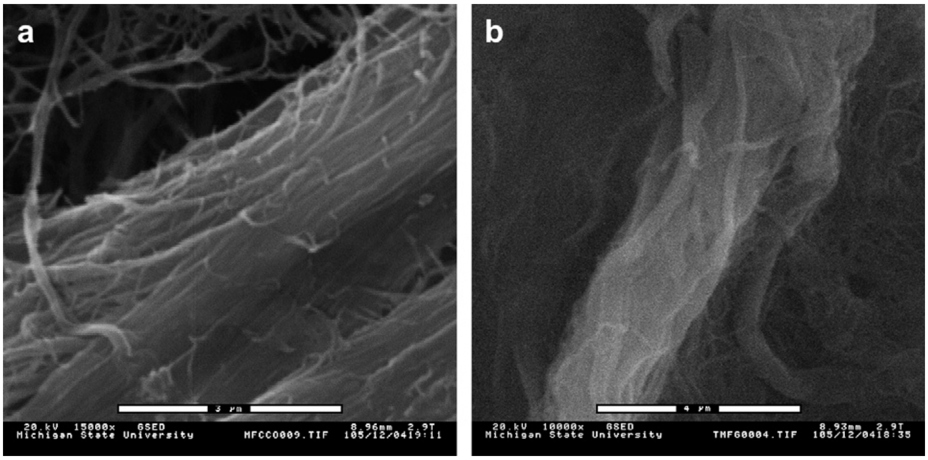

Fig. 10. ESEM image of titanate treated MFC (b) compared to untreated one (a).

for titanate treated MFC is 250 °C compared to 350 °C for untreated MFC. The first derivative of weight loss of the TMFC shows two degradation peaks at 310 °C and 362 °C, which correspond to the decomposition of the surface modifier and cellulose, respectively. Again, the TGA confirms the successful grafting of the titanate coupling agent on MFC.

Fig. 12 shows the water contact angle measurement for a drop of water on the surface of treated MFC. The untreated MFC film is very hydrophilic due to the OH-rich molecular structure, which gives a contact angle of 15°. The silane treatment of MFC increases the value of water contact angle to 90° and 64° for AMFC and GMFC, respectively. Fig. 12 also shows that the titanate treatment completely changes the hydrophilic surface of MFC to the hydrophobic one. The water contact angle increases from 15° to 110°, which is more hydrophobic than the silane treated MFC. This is possible due to much less polarity of the alkyl chain of the titanate modifier.

As we notice that MFC is stable in acetone after solvent exchange, can even be stored for a year at 4 °C, although some degree of aggregation is expected due to its hydrophilic nature. The chemically modified MFC shows the same stability. These untreated and treated MFC were incorporated into epoxy resin system to see their effect on the mechanical properties of composites.

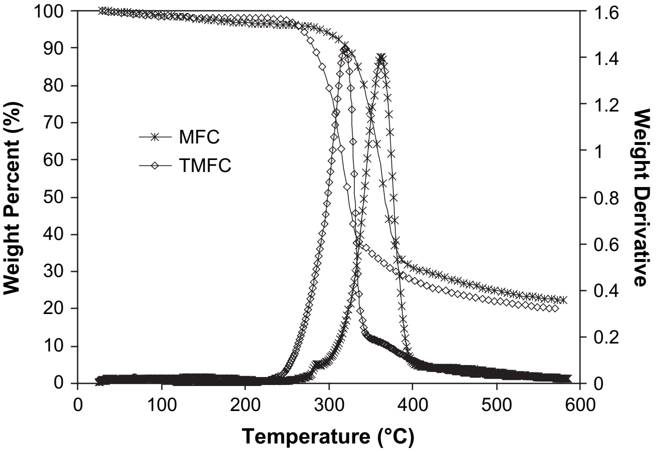

Fig. 11. Thermal stability of untreated and titanate treated MFC.

3.3. Dynamical mechanical analysis

The effect of the incorporation of MFC into epoxy resin as well as the effect of the surface treatment on the thermal mechanical behavior of the composite material was investigated with DMA at the MFC content of 5 wt% based on epoxy (3.7 wt% based on the total amount of epoxy and amine). The evolution of the storage modulus E' as a function of temperature is reported in Fig. 13. For the neat epoxy, a plateau is observed up to 70 °C, followed by a drastic decrease, which corresponds to the main α transition from the glassy to the rubbery state. The incorporation of MFC into the matrix greatly increases the storage glassy modulus. As summarized in Table 3, the E' at 30 °C increases from 2.6 GPa for neat epoxy to 3.1 GPa for 5 wt% MFC–epoxy film, which reaches the same reinforcing effect of 40 wt% microcrystalline cellulose in epoxy reported by other researchers [26]. A more significant increase was observed for the storage modulus above the glass transition temperature. The storage rubbery modulus, taken as the E' value at 130 °C, increases from 9.7 MPa for neat epoxy to 37.3 MPa for 5 wt% MFC–epoxy film, which is a better indicator of the reinforcing effect of MFC. The surface modification has a positive effect on the properties of the composite film. The storage modulus at 30 °C varies from 3.11 GPa to 3.25, 3.15 and 3.45 GPa for APS, GPS and titanate treated MFC, respectively. More significantly, the storage modulus at 130 °C for APS treated MFC–epoxy film is doubled compared to the untreated one, which indicates a better dispersion of APS treated MFC in the epoxy matrix and also a stronger fiber polymer matrix interface due to the high reactivity of the amine functional groups on the APS to the epoxy matrix. The sample treated with GPS does not show such a reinforcing effect which is possibly due to the lower affinity of GPS to cellulose and lower reactivity of epoxy functions on the GPS with the curing agent. The titanate treated MFC gives a better reinforcing effect at the room

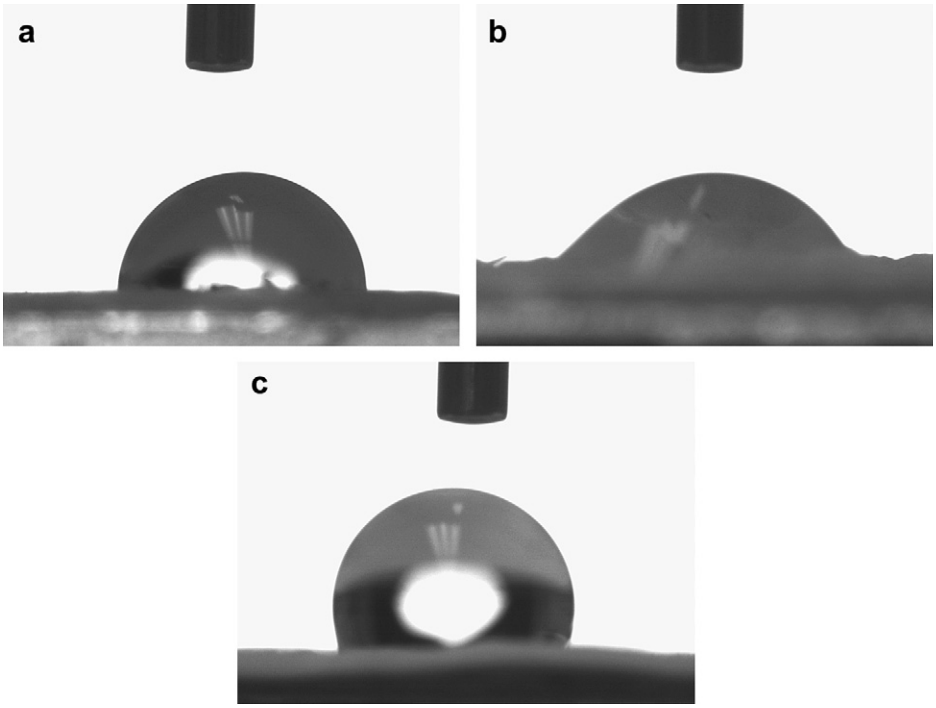

Fig. 12. Shape of water drop on the silane and titanate treated MFC film: (a) AMFC, (b) GMFC, and (c) TMFC.

temperature, but not at the rubbery state, due to an absence of a chemical reaction between the aliphatic chains of the titanate with the epoxy. Fig. 14 shows the evolution of the loss factor, tan δ as the function of temperature. The neat epoxy shows a peak at 85.2 °C, corresponding to its glass transition temperature. The addition of MFC shifts the tan δ peak to a lower temperature and lowers the magnitude of the tan δ peak as a result of reducing the fraction of polymer matrix in the sample [27]. The effect of surface treatment of MFC on the tan δ is consistent with the storage modulus behavior. With the surface treatment of APS, the tan δ peak shifts to a higher temperature compared to the untreated one and the intensity of the tan δ peak decreases, indicating a better dispersion and interfacial adhesion is achieved with the fiber surface treatment. The surface treatment with GPS only shows very slight effect on the tan δ behavior. Conversely, with the surface treatment of

Table 3
A summary of E' and tan δ for neat epoxy and composites reinforced with untreated and treated MFC

	E' at 30 °C (GPa)	E' at 130 °C (MPa)	tan δ (°C)
Epoxy	2.59 ± 0.08	9.67 ± 0.80	85.21
5 wt% MFC	3.12 ± 0.12	37.28 ± 5.27	80.57
5 wt% AMFC	3.25 ± 0.03	65.61 ± 4.07	85.34
5 wt% GMFC	3.15 ± 0.07	38.60 ± 3.24	80.44
5 wt% TMFC	3.45 ± 0.21	32.15 ± 6.36	72.49
MFC film	9.72	8.16	

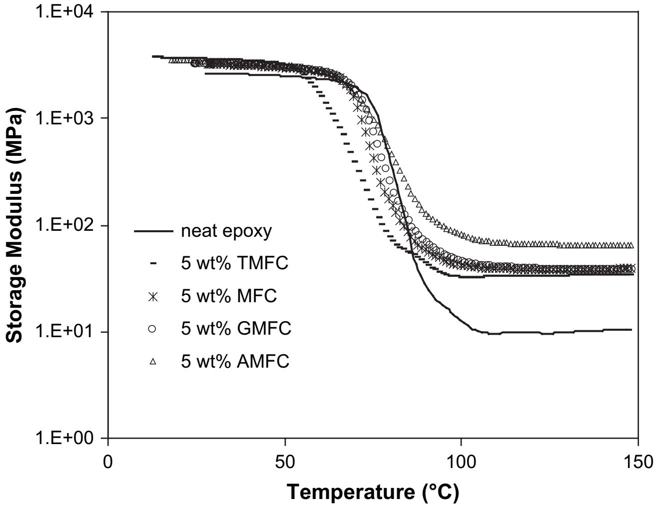

Fig. 13. Storage tensile modulus E' vs temperature at 1 Hz for neat epoxy and untreated and chemical treated MFC reinforced composite films.

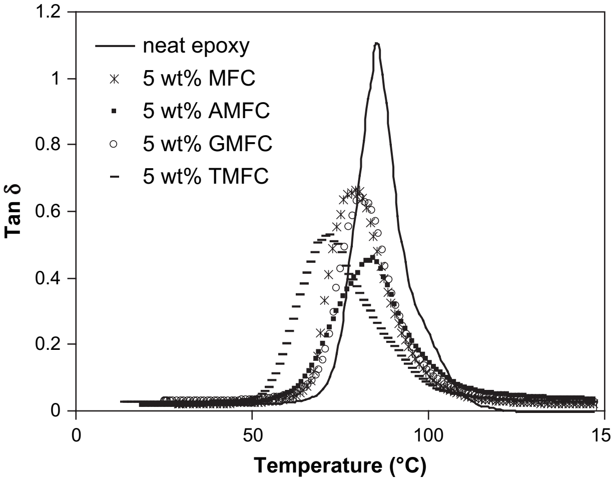

Fig. 14. The tan δ vs temperature at 1 Hz for neat epoxy and untreated and chemical treated MFC reinforced composite films.

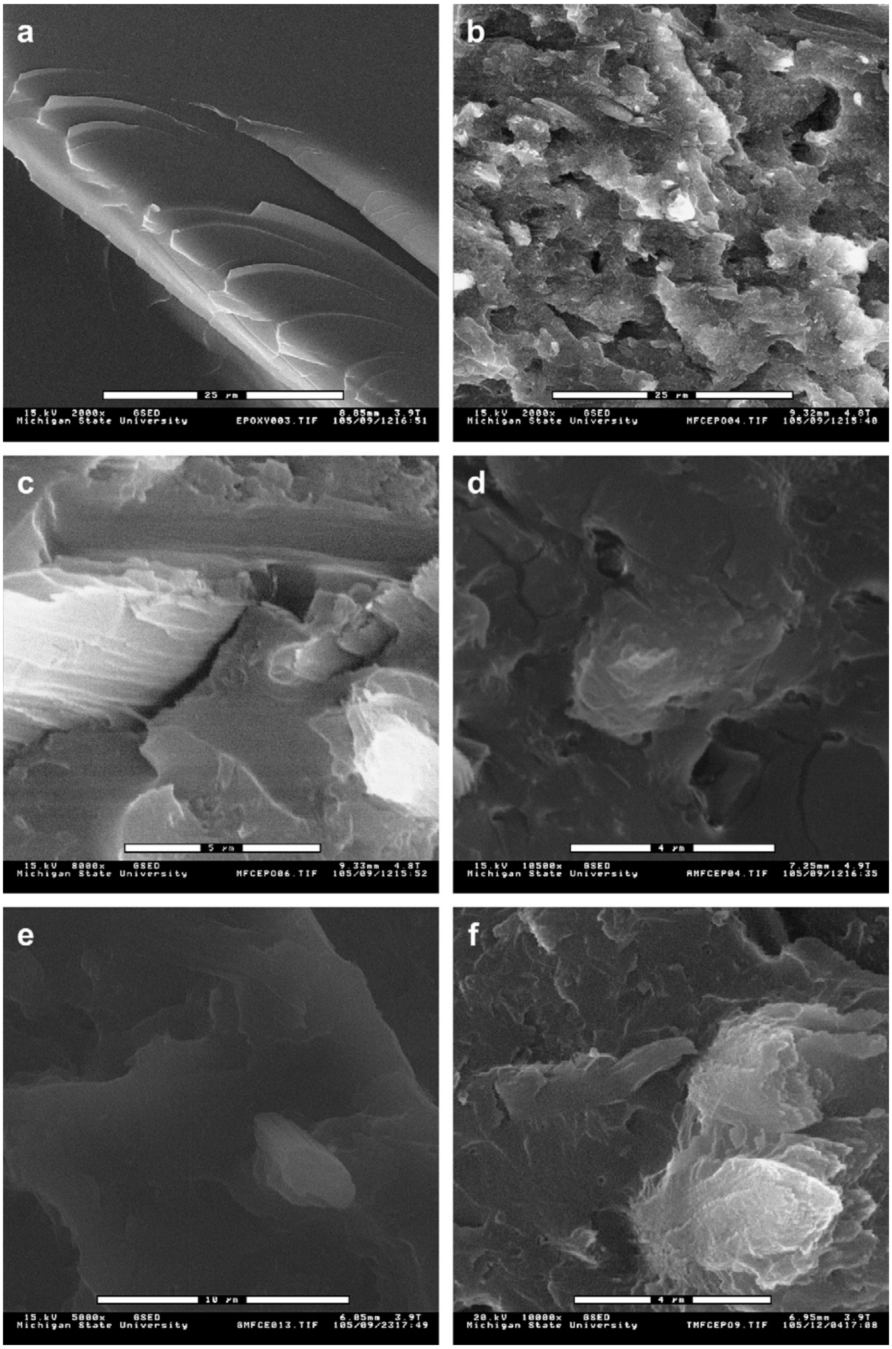

Fig. 15. ESEM micrographs of cryo-fractured surfaces of neat epoxy (a) and epoxy composites reinforced with untreated (b) and (c), and treated MFC (d) AMFC, GMFC (e), and TMFC (f).

titanate coupling agent, although the intensity of the tan δ peak decreases, the tan δ peak shifts to a lower temperature, suggesting an increase of the mobility of epoxy chains at the fiber interface due to the chemically inert and bulky features of the coupling agent.

3.4. Scanning electron microscopy analysis

SEM is used to directly observe the dispersion and interface bonding of MFC in the epoxy polymer matrix as shown in Fig. 15. All the surfaces are freshly cryo-fractured and coated with a thin layer of gold to increase conductivity. As shown in Fig. 15(a), neat epoxy shows a very smooth surface reflecting its brittle nature. The fracture surface of MFC–epoxy film is rougher (Fig. 15(b)). The MFC fibers appear as the white dots on the surface with a relatively good dispersion. The interfacial bonding between the fibers and the polymer matrix was observed only with the micro-sized fiber or fiber bundles due to the resolution limitation of ESEM. Fig. 15(c) shows that the surface of an untreated fiber embedded in the polymer matrix looks very clean, and there is a large gap between the fiber and the polymer matrix, indicating very poor interfacial

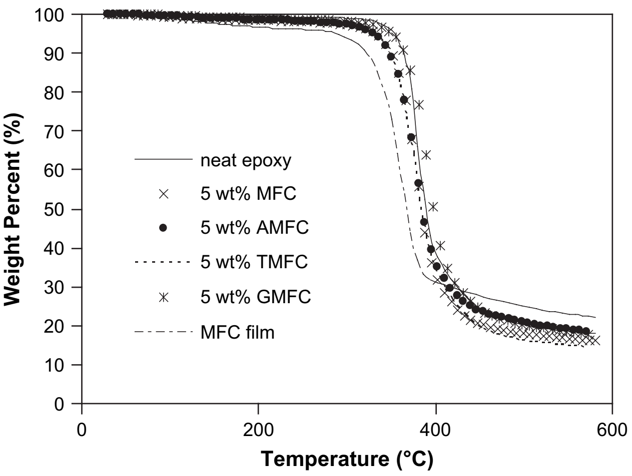

Fig. 16. TGA curves for neat epoxy and untreated and chemical treated MFC reinforced composite films.

bonding. For the APS treated fibers shown in Fig. 15(d), the fiber surface looks like coated with a layer of polymers, because the bonded APS has reacted with the polymer matrix. The surface of GPS treated fiber (Fig. 15(e)) looks relatively clean but still with a somewhat better adhesion. The last micrograph shows that the titanate treatment has a significant improvement on the fiber–matrix interface, reflected by the rough surface and coated polymer layer on the surface. The better adhesion between the fiber and polymer matrix can be reflected by the increase in the tensile strength, but the accurate measurement of tensile strength is much dependent on the quality of samples. In this work, it was difficult to get accurate measurement of tensile properties due to the poor surface quality of the epoxy composite films, thus the strength data are not reported here.

3.5. Thermal stability

The thermogravimetric curves of neat epoxy and the epoxy reinforced with treated and untreated MFC are presented in Fig. 16. Decomposition of neat epoxy occurs between 325 and 450 °C, and the degradation of MFC starts at 280 °C, which is earlier than epoxy. Thus the thermal stability of composite is slightly decreased by the addition of 5 wt% MFC. The surface treatment of MFC does not have any significant effect on the thermal stability of the resulting composite, although the residual weight following decomposition slightly increases.

4. Conclusions

Microfibrillated cellulose was successfully modified with three different coupling agents: 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and a titanate coupling agent (Lica 38). The surface modification was confirmed using FTIR, XPS spectroscopy and ESEM as well as contact angle measurement. This type of modification changed the character of MFC from hydrophilic to hydrophobic, but the crystalline structure of the cellulose microfibrils was not affected. Among them, the titanate coupling agent gave the most hydrophobic surface possibly due to the lower polarity of the alkyl chain of the titanate modifier. The untreated and treated MFC were successfully incorporated into epoxy resin system by using acetone as the solvent. The better dispersion of MFC and stronger adhesion between microfibrils and matrix were confirmed by ESEM, which resulted in better mechanical properties of composite materials. At a 3.7 wt% addition of MFC, the storage modulus at 30 °C increased about 20%, with the aminosilane treated MFC (AMFC) having a modulus increase of greater than 25%. At 130 °C the modulus increase was more substantial with the AMFC, increasing the modulus from ~10 MPa to over 65 MPa. The described surface modification can be applied to MFC as well as to other nanocellulose reinforcements such as cellulose nanowhiskers as well.

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