Reinforcement on the Mechanical-, Thermal-, and Water-Resistance Properties of the Wood Flour/Chitosan/Poly(vinyl chloride) Composites by Physical and Chemical Modification

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ABSTRACT: In this study, we aimed to physically and chemically modify wood flour (WF)/chitosan (CS) mixtures to reinforce the mechanical-, thermal-, and water-resistance properties of WF/CS/poly(vinyl chloride) (PVC) composites with a three-step modification process. This was a vacuum-pressure treatment of sodium montmorillonite, inner intercalation replacement of organically modified montmorillonite, and surface grafting of glycidyl methacrylate (GMA). The untreated and modified mixtures were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy–energy-dispersive spectroscopy, thermogravimetric analysis, and contact angle measurement. Meanwhile, the mechanical strengths and water absorption of WF/CS/PVC were estimated. The results indicate that the samples had a better performance after they were modified by montmorillonite (MMT) + GMA than when they were modified by only MMT. MMT and GMA showed a very synergistic enhancement to the mechanical-, thermal-, and water-resistance properties of the WF/CS/PVC composites. Specifically, the maximum flexural and tensile strengths were increased by 10.59 and 12.28%, respectively. The maximum water absorption rate was decreased by 61.99%, and the maximum degradation temperature was delayed to the higher value from 314.3 and 374.9°C in the untreated sample to 388.8 and 412.8°C. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40757.

INTRODUCTION

Wood plastic composites (WPCs) are produced from thermoplastic resins [e.g., polyethylene, polypropylene, poly(vinyl chloride) (PVC)] and agricultural and forestry biomass fiber.[1–3] As a type of novel material for replacing solid wood and conventional wood-based composites, such as plywood, middle-density fiberboard, and particle board, the range of application of WPCs has been rapidly expanding from initial decking and nonstructural components to buildings, construction, automotive, indoor, and outdoor products over the last 2 decades.[4,5] However, it is the weak interfacial compatibility between polymer resins and wood fibers that has been widely acknowledged as the troublesome problems to WPCs; this has resulted in insurance and warranty claims for failed products. As WPCs gradually transit from emerging materials to widely accepted mature materials, researchers have become eager to have the

study of the interfacial compatibility for WPCs keep the same pace with its development.

PVC-based WPCs are not exactly the same as polyolefin-based (polypropylene and polyethylene) WPCs; the existence of carbon–chloride bonds in PVC not only breaks the regularity but also endows a strong polarity to whole molecular chains.[6] This leads to a special interface situation. It has been proven that there is a superior interfacial bonding for PVC-based WPCs by the addition of some chemical or natural modifiers, especially those containing amino groups in their molecular chains according to the Lewis acid–base theory. These modifiers include γ-aminopropyltriethoxy silane, ethanolamine, L-arginine, lignin amine, chitin, and chitosan (CS).[7–10] Recently, the efficient utilization of natural modifiers has been paid more attention by many researchers because of higher requirements of government officers and the public for environmentally friendly

materials. Compared to other chemical modifiers with amino groups, natural CS is extracted from marine organisms. It has a tremendous potential for developing potential with the advantages of enormous quantities, nontoxicity, low costs, and antibacterial abilities.[11–13] In our previous studies, CS/wood flour (WF)/PVC composites caused a positive improvement and the promotion of interfacial bonding and antibacterial ability of the surface when the WF and CS mixture was controlled at the optimum ratio, but it was a little weak in water resistance and whole thermal stability.[14,15] Until now, there have been no available published reports for solving the two crucial problems.

Montmorillonite (MMT), which is well known to exist in huge quantities and has excellent physical, mechanical, water-resistance properties, and thermal stability, is widely used as a reinforcement substance in both solid wood materials and polymer products. Lv et al.[16] and Ren et al.[6] prepared MMT/solid wood composites and MMT/PVC composites by the methods of solvent and melt intercalation, respectively. They found that some properties of both solid wood and PVC resin products were obviously promoted because of the fact that some exfoliated clay and silicate layers were inserted into the amorphous region of the wood cell wall and engendered dipole–dipole interactions with PVC molecular chains.[6,16] Moreover, organically modified montmorillonite (OMMT) treated by alkyl quaternary ammonium was reported to be a better choice than MMT for enhancing the properties of composites.[17,18]

Glycidyl methacrylate (GMA) with two active epoxy and acyclic groups favorably reacts with wood and CS by surface grafting to form crosslinking.[19] Similarly to MMT, GMA can also successfully improve the dimensional stability, thermal stability, and mechanical strength of solid wood and CS membranes.[20,21]

In this study, to effectively improve the thermal stability and water resistance and to further elevate the mechanical strengths of CS/WF/PVC composites, we first designed the experiment from inside and outside the compound system by combining physical and chemical modification methods. The CS/WF mixture with best proportion was modified by a three-step process; this was a vacuum-pressure treatment of sodium montmorillonite (Na-MMT), inner intercalation replacement of OMMT, and surface grafting of GMA. The untreated and modified WF/CS mixtures were characterized and analyzed with Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM)–energy-dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), and contact angle (CA) measurement. The effects of modification on mechanical properties and water absorption ability of the WF/CS/PVC composites were investigated as well.

EXPERIMENTAL

Materials
PVC (DG-800) from Tianjin Dagu Chemical, Ltd., Co. (China) was used as the polymer matrix. It had a number-average degree of polymerization of 800 and a density of 1.35–1.45 g/cm^3. WF (*Cunninghamia lanceolata*) with a particle size of 120–150 μm was provided by Guangzhou Minshan New Material, Ltd., Co. (China). CS, with a degree of deacetylation, average

molecular mass, and mesh number of 95%, 860,000, and 50–65 μm, respectively, was purchased from Golden-Shell Biochemical, Ltd., Co. (China). Na-MMT, with a cation-exchange capability of 100 mmol/100 g, was obtained from Zhejiang Fenghong Clay Chemical Co., Ltd. (Huzhou, China). Octadearyl dimethyl ammonium chloride (ODAC), GMA, and ammonium ceric nitrate (CAN) were bought from Shanghai Saen Chemical Technology Co., Ltd. To complete the formulation, the other additives, including acrylamide, calcium zinc stabilizer, diethylhexyl phthalate, glycerin monostearate, and paraffin wax, were obtained from local chemical companies.

Physical and Chemical Modification of WF/CS Mixture
First, both WF and CS were dried at 100°C for 48 h in an oven to ensure a moisture content of lower than 1%. On the basis of our previous results, WF and CS were mixed fully at an optimum mass ratio of 4:3. Subsequently, the WF/CS mixture was immersed into the Na-MMT suspensions of deionized water at a concentration of 1 wt % by vacuum-pressure treatment; the pressures were −0.06 MPa for 1 h and 0.8 MPa for 2 h. Then, the treated mixture continued to undergo intercalated exchange to form OMMT by the addition of ODAC of 3 mmol in an 80°C water bath for 3 h with a continuous mechanical stirring. After that, the mixture was washed, filtered with deionized water, and dried in a vacuum-drying oven until its weight was constant. Third, the WF/CS mixture was modified by chemical surface grafting. The surface grafting process was carried out under nitrogen protection in a three-necked flask equipped with a rotary impeller. The WF/CS mixture (2 g) and deionized water were stirred at 40°C for 15 min to drive the air of the porous matrix away. Then, the reaction temperature was increased to 65°C with the addition of CAN (3 g) for 30 min; subsequently, 10 mL of GMA was added and stirred for 3 h. Finally, the grafted mixture was subjected to Soxhlet extraction with acetone for 6 h to remove any remaining homopolymer and then dried in a vacuum-drying oven at 60°C.

Preparation of the Composites
The method for preparing the CS/WF/PVC composites was the same as that described in our previous work.[14,15] The blending was extruded as an extrudate-like a shape of rod by a counter-rotating twin-screw extruder (SHJ-20, Nanjing, China) in the temperature range 150–180°C with a rotation speed of the twin screw of 10 rpm and a rotation speed of the single screw of 6 rpm. Then, the extrudates were transferred to a conical twin-screw extruder (LSE-35, Guangzhou, China) to produce thin sheet samples. The processing temperature during extrusion was set in the range 125–185°C from the hopper to the die zone. The rotation speed of the twin screw was 30 rpm, and that of the single screw was 12 rpm.

FTIR Spectroscopy
FTIR analysis of the untreated and modified WF/CS mixture was carried out in a Tensor 27 (Bruker, Germany) at room temperature. Data was collected in the wave-number range 4000–400 cm^{-1} at a resolution of 2 cm^{-1} for 64 total scans.

XRD
The degree of MMT intercalation was characterized by an XRD instrument (D8-ADVANCE, Bruker, Germany). The patterns of

XRD were recorded with Cu Kα radiation ($\lambda = 0.1540$ nm) at an operating voltage of 40 kV and with a current of 40 mA. The scanning rate was 0.01°/s in the range of 2θ from 2 to 40°.

SEM–EDS

Micromorphology changes were examined with an SEM instrument (Hitachi S-3400, Japan) with an acceleration voltage of 10 kV, and EDS analysis system (INCA 300, OXFORD, Britain) was used to study the elemental composition, transition, and distribution before and after modification. Its acceleration voltage was 20 kV.

TGA

A TGA system (TGA 209-F1, Netzsch, Germany) was used to analyze the thermal stability of the WF/CS mixture before and after modification during continuous heating. About 8-mg samples were heated from 30 to 800°C at a heating rate of 10°C/min under a nitrogen gas atmosphere.

CA Instrument

The CA measurement was carried out with the sessile drop method on a OCA-40 Micro instrument (DATAPHYSICS, Germany). The angle was measured directly from the image of a droplet of distilled water placed on the surface of a flat solid.[22] The WF/CS mixture needed to be pressed as a flat sheet before the test.

Mechanical Properties of the Composites

The flexural and tensile properties of the composites with untreated and modified WF/CS were tested with a mechanical instrument (CMT5504, Shenzhen, China) corresponding to ASTM D 790-2004 and ASTM D 638-2004. The former involved a three-point bending test with a crosshead speed and span length of 2 mm/min and 88 mm, respectively. The latter was conducted at a tensile speed of 2 mm/min. Both tests were performed in triplicate to obtain an average value, and statistical analysis was done with Duncan's multiple-range tests by SPSS software at 95% confidence levels.

Water Absorption Behavior of the Composites

The examination of the water absorption behavior was done in accordance with a modified method originally described in ASTM D 570-95. Five replicate specimens with dimensions of 20 × 20 × 5 mm^2 were completely immersed in water at 23 ± 2°C for 48 days. The weight changes were measured every 2 days. The rate of water absorption was calculated on the basis of eq. (1):[23,24]

$$\frac{M_t}{M_\infty} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \tag{1}$$

where M_t is the moisture content at certain time, M_∞ is the maximum moisture content measured at the end of the test, D is the diffusion coefficient, and h is the sample thickness corresponding to M_∞. Hence, D could be calculated by the slope of the moisture absorption versus the square root of time.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of the pure MMT and modified WF/CS mixture by MMT and MMT + GMA are shown in Figure 1. The main characteristic peaks of pure MMT are generally at wave
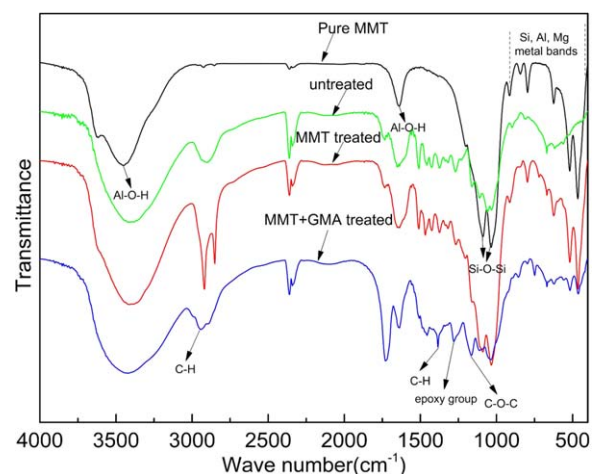

Figure 1. FTIR spectra of the pure MMT and the untreated and treated samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

numbers of 3618, 1637, 1089–1035, and 914–400 cm^{-1}, and these are ascribable to Al—O—H stretching vibrations, Al—O—H bending vibrations, Si—O—Si stretching vibrations, and the oxide bands of metals (Si, Al, and Mg), respectively.[25] The samples modified by MMT displayed new absorption bands at wave numbers of 1089 and 914–400 cm^{-1} and a weak shoulder peak near 3628 cm^{-1} that was overlapped by the —OH stretching vibrations. This was evidence that MMT adhered well to the mixture. On the other hand, compared to the spectra of samples modified by MMT and MMT + GMA, we also noticed that the characteristic absorption bands of 1734 cm^{-1} (carbonyl group), 1265 cm^{-1} (epoxy group), 3001 cm^{-1} (C—H stretching), 1384 cm^{-1} (C—H bending), and 1165 cm^{-1} (C—O—C stretching) appeared simultaneously because the samples were successfully grafted by GMA.[21]

XRD Analysis

The XRD curves of the unmodified and modified WF/CS mixture are presented in Figure 2(a). We observed that there was a strong diffraction peak at 3.417° (2θ) with an interlayer distance of 2.584 nm according to the Bragg law, which could be attributed to the effective intercalation or exfoliation of WF/CS and OMMT treated by the vacuum-pressure of Na-MMT the intercalation replacement of ODAC. The zoomed XRD scans in Figure 2(b) shows that the characteristic peaks for CS and cellulose in WF were at 10.322 and 19.985° and 22.513 and 36.213°, respectively. Some of these peaks engendered some deviation because of the influence on the cellulose crystal diffraction by intercalation and inevitable error during the use of small amounts of mixture samples.

SEM–EDS Analysis

The micromorphological changes in the WF/CS mixture before and after modification were clearly observed from SEM images. As shown in Figure 3, the surface of the unmodified samples was almost smooth [Figure 3(a)], and mesoscopic voids in WF such as bordered pits, simple pits, and interspace among the wood cell wall were also seen. When the mixture was treated by vacuum-pressure and intercalation replacement, a great many
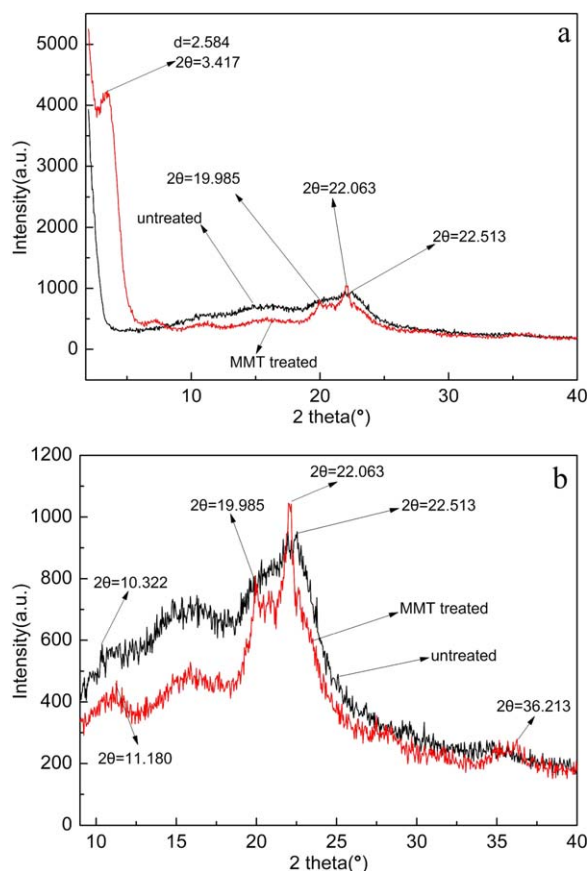
Figure 2. XRD patterns for the samples before and after the intercalation of MMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. SEM images of the different samples: (a1) untreated samples (500×), (a2) untreated samples (1000×), (b1) samples modified by MMT (500×), (b2) samples modified by MMT (1000×), (c1) samples modified by MMT + GMA (500×), and (c2) samples modified by MMT + GMA (1000×).

OMMTs covered the surface of the samples and partially blocked some pores [Figure 3(b)]. The EDS system that was equipped on SEM was employed to further evaluate the element types and relative content in the specific sections of modified samples. Also, with the data in Table I, we concluded that the elements Si (5.11%) and Al (1.48%) accumulated largely on the surface of samples with a small number of Mg (0.31%), Ca (0.27%), and Fe (0.27%) and without Na; this also indirectly verified the successful replacement process from Na-MMT to OMMT. As for the samples modified by MMT + GMA and shown in Figure 3(c), the absorption amount of OMMT on the sample surface was decreased as the continuous phase structure showed up; moreover, there was marked descending tendency for the relative contents of metal elements (Si, Al, Mg, Ca, and Fe). This could be explained as the contribution of GMA grafting. In addition, the presence of cerium (Ce) was attributed to the residue of the initiator (CAN).

TGA

A description and explanation of the thermal degradation processes of the untreated and treated WF/CS mixture are presented in the plots of the thermogravimetry (TG) and differential thermogravimetry (DTG). As shown in the TG plot (Figure 4), the profiles with different samples varied. The degradation process of the samples was generally divided into three stages corresponding to the temperature ranges 30–150, 150–440, and
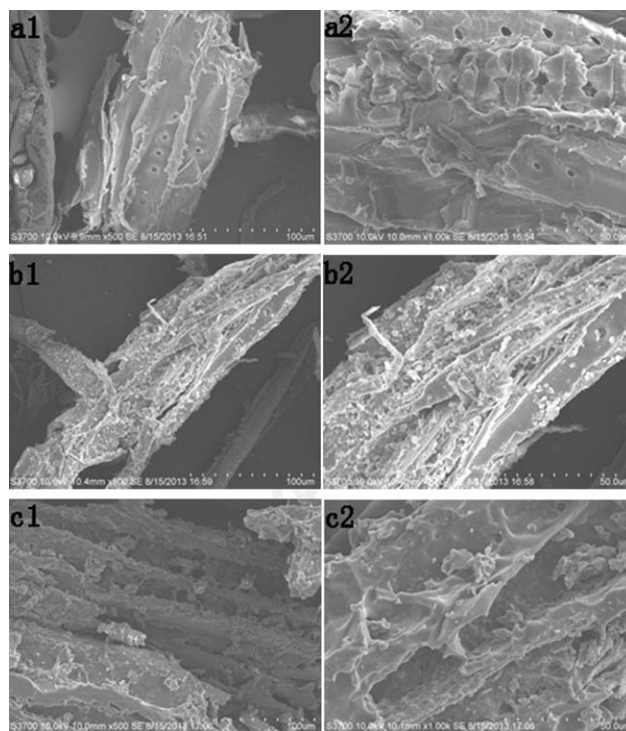
440°C and greater; this represented the volatilization for water and low-molecular compounds; the maximum degradation for CS, hemicellulose, and cellulose in WF; and the continuous weight loss for lignin in WF, respectively.

The unmodified sample showed a higher sensitivity to mass losses (9.55%) than the modified ones (4.66% for MMT only and 1.79% for MMT + GMA) in the first stage. The reason was that both natural WF and CS were hydrophilic substances with strong water absorption in storage before use. In the second stage, the temperature corresponding to maximum mass loss rate was delayed to a higher value, from 314.3 and 374.9°C in the untreated sample to 316.2 and 379.9°C in the samples modified by MMT only; this demonstrated that the thermal stability of the modified samples was ameliorated effectively because the OMMT was absorbed, wrapped on the surface of the mixture, and partly intercalated into the microscale voids of WF. Moreover, in comparison with the samples modified by MMT and MMT + GMA in Figures 4 and 5, we found that the latter seemed to be preferable to the former in thermal stability with the higher maximum degradation temperature values (388.8 and 412.8°C).

In addition, the degradation curves of the samples modified by MMT + GMA also illustrated two peaks of maximum degradation at 175.7 and 224.7°C; these could be explained that a small amounts of low-molecular polymer were polymerized through the self-initiation of carbon–carbon double bonds and epoxy groups in GMA.

Table I. Relative Contents of the Elements for the Modified Samples by Only MMT and MMT + GMA from EDS

Element	Atom number	Modified by MMT		Modified by MMT + GMA	
		Weight percentage	Atom percentage	Weight percentage	Atom percentage
O	8	65.27	61.69	62.32	57.09
C	6	27.29	34.36	34.14	41.66
Si	14	5.11	2.75	1.51	0.79
Al	13	1.48	0.83	0.42	0.23
Mg	12	0.31	0.19	0.08	0.05
Ca	20	0.27	0.10	0.04	0.01
Fe	26	0.27	0.07	0.07	0.02
Ce	58	None	None	1.42	0.15

CA Analysis

The sessile drop method was used for the CA tests between the compressed flat surface of the mixture and distilled water. As shown in Figure 6, the images of distilled water drops clearly exhibited the various results in wettability for the different treatment methods. Meanwhile, compared to the specific data of CA for different groups (112.6, 129.1, and 132.4° for the untreated, MMT-modified, and MMT + GMA modified samples, respectively), the results directly prove that modifications with MMT and MMT + GMA had a positive effect on the promotion of the hydrophobic properties of the sample surface, and the latter obviously performed better than the former. All of these results provide consistent support for the previous and the following analysis.

Mechanical Properties Analysis

After modification, the WF/CS/PVC composites displayed significant increases in their flexural and tensile strengths from 73.28 to 81.04 MPa and 42.68 to 47.92 MPa, respectively, in comparison with those of the untreated specimen (Figure 7). The maximum value was achieved for the samples treated by MMT + GMA. The flexural and tensile strength increased by approximately 10.59 and 12.28%, respectively. Furthermore, the samples grafted by GMA and intercalated by MMT obtained

higher flexural and tensile strengths than the one treated by MMT only; this suggested that the two modification methods engendered a good synergistic enhancement effect and improved the interfacial bonding among the three phases (CS, WF, and PVC) in the composites. Overall, the analysis of the mechanical properties correlated well with the SEM–EDS, CA, and FTIR analyses.

Water Absorption Behavioral Analysis

The results of the water absorption of the WF/CS/PVC composites before and after modification are illustrated in Figure 8. Typical curves of Fickian diffusion behavior were illustrated as well; this indicated that the water absorption rates of the samples increased rapidly in a linear fashion at the initial exposure and continuously increased with the prolongation of the immersion time. Eventually, it slowed down and reached a plateau (pseudo-equilibrium).[26,27] The composite samples also showed a high M_∞ ($M_\infty \approx 11\%$), possibly because of the existence of hydrophilic WF and CS with a large number of hydroxyls. However, as shown in Figure 8 and the data in Table II, the significant changes occurred most clearly when the WF and CS mixture was modified by MMT only and MMT + GMA. The latter appeared to be more effective, with the water resistance corresponding to the significantly lower M_∞ (4.15%) and D
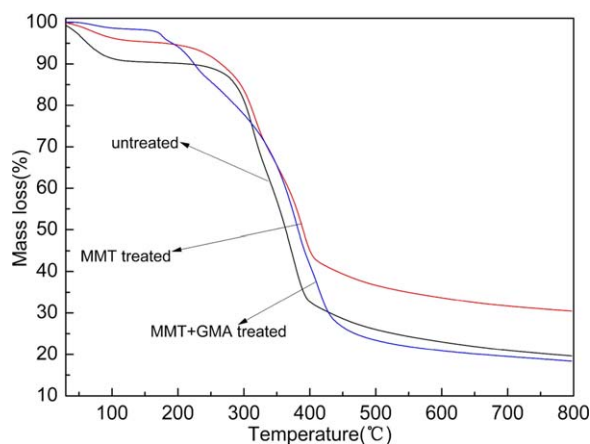

Figure 4. TG curves of the untreated, MMT-only, and MMT + GMA modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
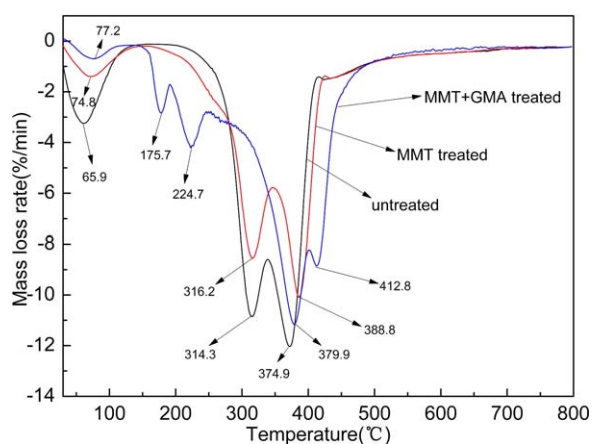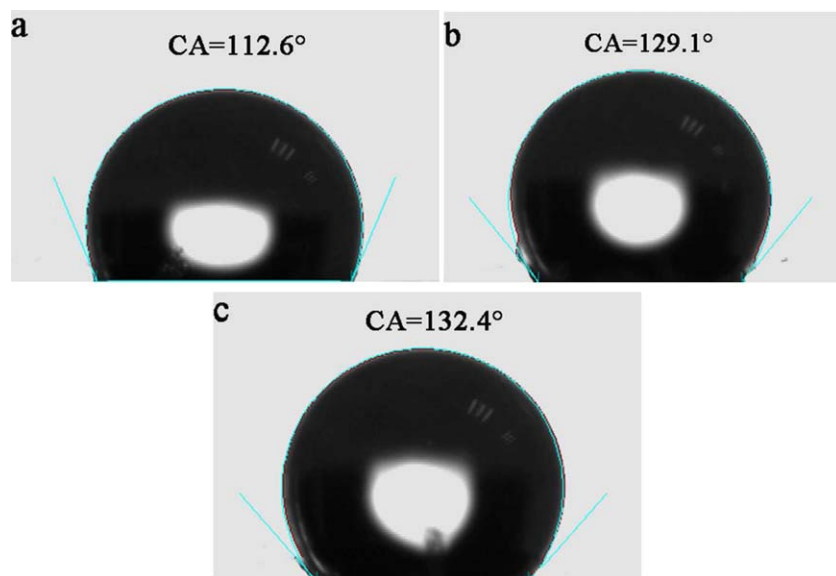

Figure 5. DTG curves of the untreated, MMT-only, and MMT + GMA modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Surface CA variation of different samples: (a) untreated, (b) modified by MMT, and (c) modified by MMT + GMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(0.626) compared to those in the former (4.66% and 0.703, respectively). There was also a remarkable decrease in the slope of the water absorption. Moreover, the pseudo-equilibrium stage was shifted to an earlier time from 40 to 34 days. This was because the hydrophilic mixtures that were enwrapped and intercalated by MMT were partly impeded to absorb water, and the grafting reaction with GMA greatly reduced the amount of hydroxyls on the surfaces of the samples; this led to a superior water-resistance ability.

CONCLUSIONS

In conclusion, sole MMT modification was proven to greatly enhance the thermal stability and water resistance in a WF/CS mixture; it further improved the interfacial compatibility and mechanical strength of its composites (WF/CS/PVC). This was due to the fact that the CA of the mixture change and the MMT was absorbed, wrapped on the surface of mixture, and
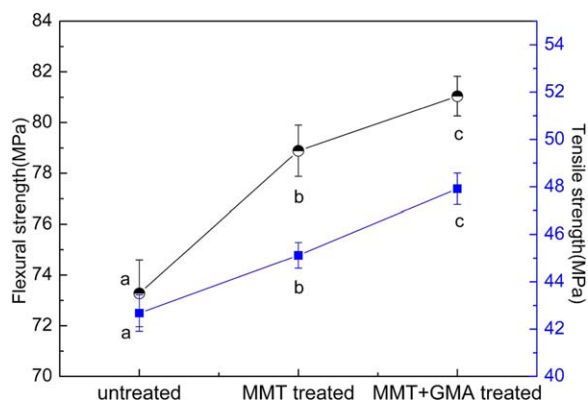

Figure 7. Mechanical strengths of the WF/CS/PVC composites produced by untreated, MMT-only, and MMT + GMA modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
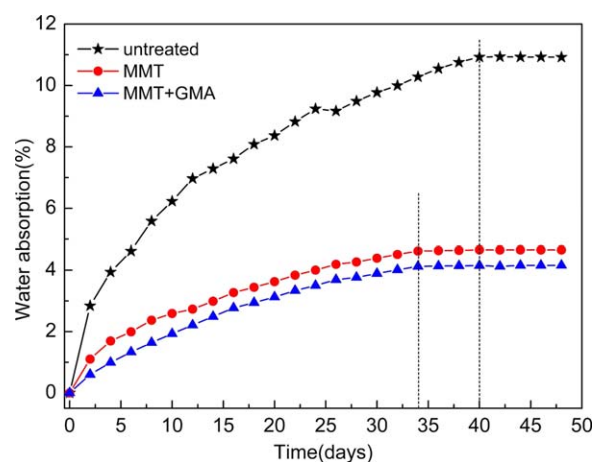

Figure 8. Water absorption rate of the WF/CS/PVC composites produced by the untreated, MMT-only, and MMT + GMA modified samples. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

partly intercalated into the microscale voids of WF. What is more, the MMT intercalation layer and GMA grafting treatment had a better synergistic enhancement effect on the three properties mentioned previously. Specifically, the maximum water absorption rate of the WF/CS/PVC composites decreased by

Table II. Maximum Water Absorption and D Values of the WF/CS/PVC Composites Produced by the Untreated, MMT-Only, and MMT + GMA Modified Samples

Group	M_∞ (%)	D (mm^2/d)
Untreated	10.92	0.762
MMT	4.66	0.703
MMT + GMA	4.15	0.626

61.99%. The maximum flexural and tensile strengths of the WF/CS/PVC composites were increased by 10.59 and 12.28%, respectively. The maximum degradation temperature of the WF and CS mixture was delayed to the higher value from 314.3 and 374.9°C of the untreated sample to 388.8 and 412.8°C.

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