

Synergistic compatibilization and reinforcement of HDPE/wood flour composites

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ABSTRACT: Multi-monomer grafted copolymers, high-density polyethylene-grafted-maleic anhydride-styrene (HDPE-g-(MAH-St)) and polyethylene wax-grafted- maleic anhydride ((PE wax)-g-MAH), were synthesized and applied to prepare high-performance high-density polyethylene (HDPE)/wood flour (WF) composites. Interfacial synergistic compatibilization was studied via the coordinated blending of high-density polyethylene-grafted-maleic anhydride (MPE-St) and polyethylene wax-grafted- maleic anhydride (MPW) in the high-density polyethylene (HDPE)/wood flour (WF) composites. Scanning electron microscopy (SEM) morphology and three-dimensional WF sketch presented that strong interactive interface between HDPE and WF, formed by MPE-St with high graft degree of maleic anhydride (MAH) together with the permeating effect of MPW with a low molecular weight. Experimental results demonstrated that HDPE/WF composites compatibilized by MPE-St/MPW compounds showed significant improvement in mechanical properties, rheological properties, and water resistance than those compatibilized by MPE, MPE-St or MPW separately and the uncompatibilized composites. The mass ratio of MPE-St/MPW for optimizing the HDPE/WF composites was 5:1. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42958.

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INTRODUCTION

Wood plastics composites (WPC) have been paid great attention by scientists and manufacturers because preparing WPC was an effective method to take advantage of the recycled plastics and the forest and agricultural by-products.^{1–3} Many conventional plastics manufacturing machines including extruder, injector, and intensive mixer can be used to prepare valuable WPC composites. Compared to other inorganic fibers fillers, WPC had prominent properties such as lower cost, lower density, better biodegradability, greater strength, lower abrasiveness to processing machines, and better processability.^{4–6}

However, most of conventional thermoplastics containing polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) were hydrophobic while the natural fillers were hydrophilic.^{7–12} Therefore, solving the incompatibility between hydrophobic thermoplastics and hydrophilic natural fillers was crucial for improving performance of WPC, especially when the fillers content increased above 50 wt %.¹³ Until now several methods have been reported in literatures to improve the interfacial

adhesion between hydrophilic wood fibers and hydrophobic thermoplastics. Among those methods, surface modifications and treatments with alkali, organosilane, acetic anhydride, diazonium salt or compatibilizer on natural fillers were studied widely.^{8,14–18}

The grafted copolymers were easy to directly melt-blending the untreated natural fillers with the polymers and compatibilizer during the preparing procedure of WPC. Therefore using the graft copolymers as compatibilizer for WPC was an attractive and convenient method.^{19,20} Ascribing to the strong interfacial interaction by hydrogen bond and chemical reaction between maleic anhydride (MAH) and the hydroxyls of the natural cellulosic fibers, polyolefin-g-MAH was widely used as compatibilizer for WPC.²¹ However, when the WPC was filled with high mass content of natural fillers, common polyolefin-g-MAH wasn't efficient to afford sufficient interfacial interaction because maleic anhydride was difficult to homopolymerize to high grafting degree.²² Some efforts including multi-monomer grafted copolymers and synergistic compatibilization have been made to improve the compatibility and then maintain better

performance of WPC.^{11,12,20} What's more, in order to increase the grafting degree of MAH, some co-monomers such as styrene (St), methyl methacrylate (MMA), and butyl acrylate (BA) were chose to prepare the multi-monomer grafted copolymers with MAH.^{12,22,23} Reaction with co-monomers can increase the grafting degree and extend the length of the grafted chains.

Although the influence of surface treatment of wood flour with MPE or polypropylene-grafted-maleic anhydride (MPP) on the properties of WPC had been extensively investigated,¹¹ litter information was available in the open literature on the effect of combining MPE with MPW on the mechanical and dynamic rheological properties of the WPC. In this study, we aimed to identify the synergistic compatibilization between MPE-St and MPW in enhancing the properties of the WPC. Emphasis was also placed on the study of the mechanism of synergistic compatibilization presented by Scanning electron microscopy (SEM) morphology and three-dimensional WF sketch.

EXPERIMENTAL

Materials

HDPE (60550AG) from Lanzhou Petrochemical Co., China was used as the matrix. It had a melting flow rate (MFR) of 7.5 g/10 min (at 190°C and a 2.16 kg load). Wood flour (WF) with particle size of 250 μm–600 μm was provided by JRS (Josef Rettenmaier & Soehne).

MPE (HDPE-g-MAH, CMG5804) supplied by Nantong Sunny Polymer New Material Technology Co., was used as the compatibilizer. MPE-St [HDPE-g-(MAH-St)] was synthesized by solid-phase graft MAH and St onto HDPE (60550AG) by using of benzoyl peroxide (BPO) as an initiator at 120°C.²³ MPW (PE wax-g-MAH) was synthesized by solid-phase graft MAH onto PE wax (PEW) initiated by BPO at 100°C.²⁴ The solid-phase graft copolymerization process was performed in a stainless steel reactor. All reactants were mixed in a predetermined proportion and reacted in nitrogen.

Preparation of HDPE/WF Composites

Prior to extrusion, the WF was dried in an oven at 80°C for 24 h and pre-mixed with HDPE and compatibilizer in a high-speed mixer for about 3 min. All composites samples were prepared with 50 wt % WF and the content of the compatibilizer varied from 0 to 10 phr (parts per hundred of HDPE/WF composites in weight). HDPE/WF composites were compounded using a co-rotating twin-screw extruder (diameter 35 mm and L/D = 48). The extrusion temperature ranging from 160°C to 180°C was individually controlled in eight temperature zones along the extruder barrel. The extrudate were cut into pellets using the crusher and the pellets were then injection-molded (CJ80M2, Chengde plastic machinery Co., China) into standard specimens at temperature ranging from 160°C to 180°C.

Measurements

Acid–Base Titration. After dissolution of 1.0 g of graft copolymer (MPE, MPE-St, and MPW) in 100 mL of xylene at 125°C, 0.2 mL of water was added to hydrolyze anhydride functions into carboxylic acid functions. Then the solution was refluxed for 1.0 h to complete the hydrolysis and graft copolymer was completely soluble in xylene at reflux conditions. The carboxylic

acid concentration was determined by titration with 0.05 mol/L alcoholic potassium hydroxide in isopropanol, using a solution of 1% phenolphthalein in isopropanol as the indicator. The content of MAH was then calculated from the titrating agent's volume and its concentration according to the eq. (1).^{25,26}

$$\text{MAH\%} = \frac{(V_1 - V_2) \times 0.05}{2W \times 1000} \times 98 \times 100 \quad (1)$$

where V_1 and V_2 (mL) are the volumes of alcoholic potassium hydroxide in isopropanol used in the blank test and in the test with samples, respectively, and W is the weight (g) of the graft copolymer sample. The molecular weight of MAH is 98 g/mol.

FTIR Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet 6700 FTIR Spectrometer. For purifying purpose, MPE, MPE-St, and MPW were extracted by acetone in Soxhlet extractor for 24 h and then were dissolved in xylene and deposited in acetone for 4 times to remove the non-grafted monomers. At last, the precipitate was washed with acetone and dried at 60°C till constant weight.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was performed on an S-3400N SEM instrument made by Hitachi Co., Japan to study the fracture surface morphology of the impacted specimens after the surface was sputtered with a thin layer of gold.

Mechanical Properties. Tensile and flexural tests were performed on a universal test machine (CMT4024-20KN, Shenzhen Sans Co.,) under room temperature according to GB/T 1040.2-2006:1993 with dumbbell sample dimensions of 150 × 10 × 4 mm and GB/T9341-2000 with sample dimensions of 80 × 10 × 4 mm, respectively. Izod notched impact test was performed according to GB/T1843-1996 with sample dimensions of 80 × 10 × 4 mm.

Dynamic Rheological Properties

The dynamic rheological characterization was performed in a rheometer (RS600, Thermo Hakke, America) with 25 mm parallel plate's fixture and 1 mm gap between plates. Oscillatory dynamic measurements were carried out at a constant temperature of 160°C, a constant strain of 0.1% and within the linear viscoelastic range. The dynamic rheological properties: storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) were recorded as a function of angular frequency in the range of 0.01–100 Hz (dynamic frequency sweep test).

Water Resistant Performance

The water resistance was evaluated by the water absorption (WA) as a function of time. Before testing WA, the samples were dried in an oven under 50°C for 48 h, and then the samples were transferred to a dried ambience for cooling and tested to obtain the original weight (W_0). Then the samples were soaked in water under ambient temperature. After a certain soaking time, the samples were tested to obtain the soaked weight (W_t). WA was calculated by $WA = (W_t - W_0) / W_0 \times 100\%$. The testing lasted for 60 days.

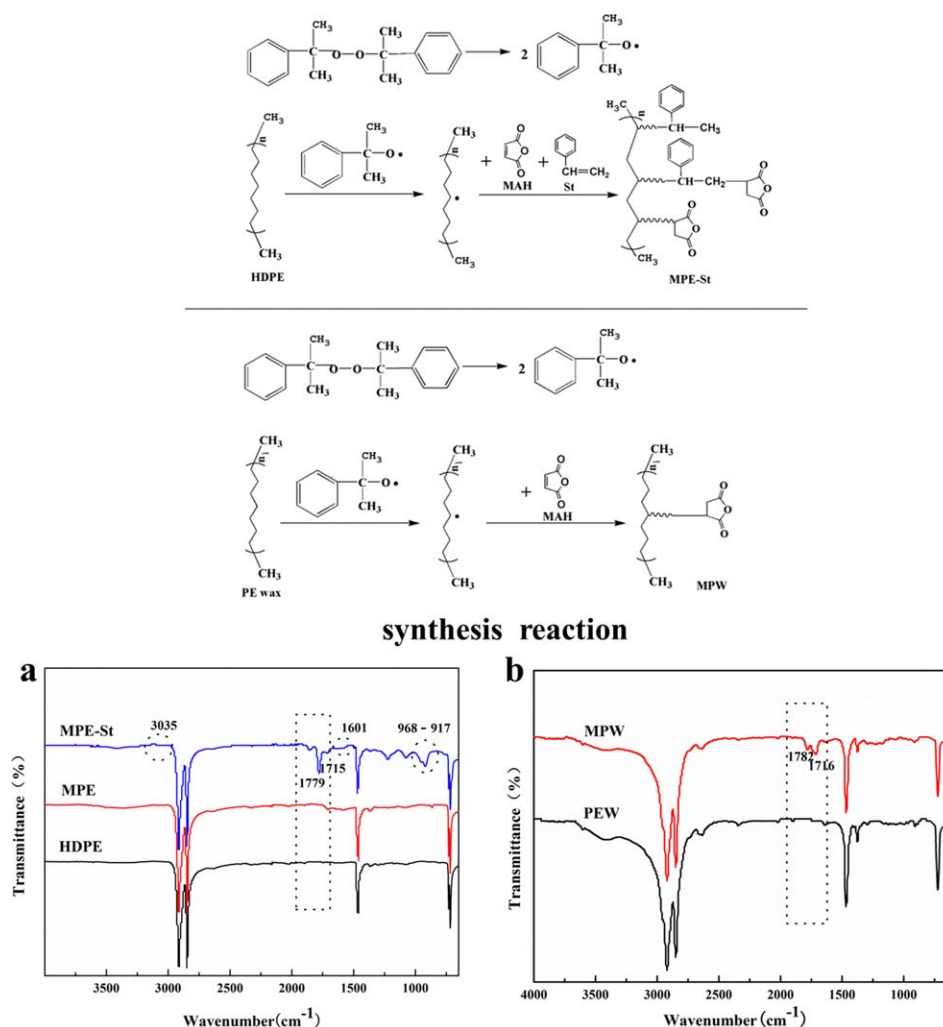


Figure 1. Synthesis reaction and FTIR of (a) HDPE-g-(MAH-St) and (b) (PE wax)-g-MAH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

FTIR Analysis and Acid-Base Titration

The synthesis reaction and Fourier transform infrared (FTIR) of HDPE, MPE, MPE-St, and MPW were presented in Figure 1.^{22,23,27,28} Comparing the FTIR spectra of HDPE, MPE, and MPE-St in Figure 1(a), the same peaks could be seen at the exception of the area 1860–1600 cm^{-1} , 900–1000 cm^{-1} , and 3000–3100 cm^{-1} . We registered the appears of two new absorption bands of average intensity around 1779 cm^{-1} and 1715 cm^{-1} , which corresponded to the vibrations of elongation of the carbonyls groups C=O of MAH. The first peak was assigned to the grafted anhydride, which was due to symmetric (strong) and asymmetric (weak) C=O stretching vibration of succinic anhydride rings grafted on the PE backbone, respectively.¹¹ The second peak was assigned to the grafted maleic acid formed from ring-opening reaction of the succinic anhydride because of moisture.²⁹ Meanwhile new absorption bands around 1601 cm^{-1} were characteristic peak of the stretching vibration of benzene ring skeleton, then 968–917 cm^{-1} and 3035 cm^{-1} were attributed to vibrations of the C–H on benzene ring.²³ Furthermore, comparing the FTIR spectra of PEW and MPW in

Figure 1(b), two new absorption bands of average intensity around 1782 cm^{-1} and 1716 cm^{-1} corresponding to the stretching vibration of the carbonyls groups of MAH were found.

Therefore, the formation of graft copolymers of HDPE and grafting monomers (MAH and St) or PE wax and MAH were confirmed. The results were in agreement with the results reported by Ihemouchen *et al.*,¹¹ Hong *et al.*,¹² Bengtsson *et al.*,²⁹ and Kazemi-Najafi *et al.*³⁰

An acid–base titration was used to measure the grafting degree of MAH of MPE, MPE-St, and MPW. The grafting degree of MAH of MPE, MPE-St, and MPW calculated from the average of three trials, were 0.3%, 2.1%, and 0.9%, respectively. It meant that synthetic graft copolymer compatibilizer, MPE-St, and MPW, had much higher grafting degree of MAH than that of commercial MPE.

Morphology Analysis and Compatibilization Mechanism of HDPE/WF Composites

The SEM morphology of the impact fracture surfaces of the HDPE/WF composites and WF sketch were shown in Figure 2.

Figure 2(a) revealed that many cavities and fiber blemishes were on the surface and cross-section of original WF extending into the inner. In the case of uncompatibilized composite samples, the Figure 2(b) SEM micrograph showed that the addition of wood flour to HDPE matrix resulted in a phase-segregation morphology. Distinct boundaries and gaps between the HDPE matrix and WF were observed clearly on the fractured surfaces, this was mainly due to weak interfacial interactions between the WF fillers and the HDPE matrix.^{31,32} These defects were responsible for failure and could lower the mechanical properties of HDPE/WF composites.

The SEM morphology of HDPE/WF composites compatibilized by MPE-St (5 phr) in Figure 2(c) exhibited that WF particles were all surrounded by HDPE matrix and the interface of matrix/WF became obscure, which meant a fine WF dispersion and strong interfacial interaction between HDPE and WF. Meanwhile numerous fiber breakages implied that the stress acting on HDPE matrix can be effectively transferred across the strongly interacted interface to the reinforcing fibers. As a result, the fracture mode of the composites was fiber breakage. The molecular weight of HDPE was too high to sufficiently permeate into the cavities of WF, few matrix was observed inside the fractured WF fibers. Figure 2(d) showed the morphology of HDPE/WF composites compatibilized by MPW (5 phr). Wood flour was covered to a large extent and even cavities were impregnated owing to interfacial interaction between wood flour and MPW with high grafting degree of MAH and low molecular weight. But, MPW could not entangle with HDPE chains due to its low molecular weight, resulting in a weaker compatibilization than that of MPE-St at the same content. Figure 2(e) was the SEM morphology of HDPE/WF composites compatibilized by MPE-St/MPW (5/1) compounds, WF particles were firmly embedded in the matrix, and most broken cavities were also sufficiently permeated by the matrix. As the sketch shown, MPE-St with higher grafting degree of MAH formed strong interfacial interacted layers, MPW with low molecular weight and high grafting degree of MAH promoted interfacial adhesion by permeating into the cavities of WF. Consequently, interfacial compatibilization between HDPE and WF was synergistically improved by the strong interfacial interacted layers formed by MPE-St together with the permeating effect of MPW. Similar results have been reported by Hong *et al.*,¹² studying the synergistic effect of GPE/GPW compounds.

The suggested interfacial interaction between MPE-St/MPW compounds and WF fibers was shown in Figure 3. The interfacial interaction was enhanced through the chemical reaction and hydrogen bonding between anhydride groups of MAH and hydroxyl groups of WF fibers.³³ As a result, stress on the matrix could be efficiently transferred to the WF fibers via the strong interfacial interacted layers, which were formed by MPE-St/MPW compatibilizer compounds.

Mechanical Properties of HDPE/WF Composites

Figure 4 demonstrated the effect of compatibilizer types and content on the mechanical properties of HDPE/WF composites. We noticed an increase in tensile strength, flexural strength, flexural modulus, and Izod notched impact strength of

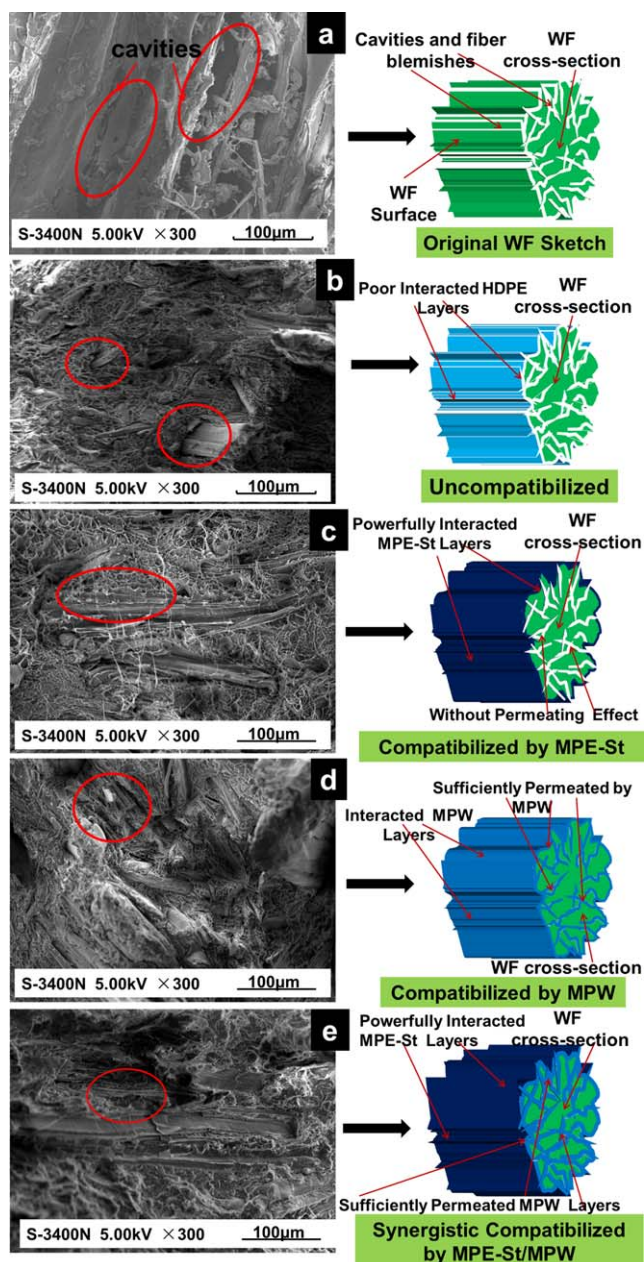


Figure 2. SEM morphology of the impact fracture surfaces: (a) original WF, (b) uncompatibilized, (c) MPE-St/MPW=5/0, (d) MPE-St/MPW = 0/5, and (e) MPE-St/MPW = 5/1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites blended with compatibilizer compared to uncompatibilized composites. These results are predictable and are consistent with many research works.^{11,12,30} Fang *et al.*³⁴ pointed that dispersion of the fibers seems to be a dominating factor for the mechanical properties of HDPE/wood flour composites. Therefore, the incorporation of compatibilizer promoted the dispersion of WF in the HDPE matrix and then improved the interfacial adhesion between WF and the matrix, as analyzed by SEM morphology and FTIR. The treatment resulted in the formation of chemical bonds between the hydrophobic part of compatibilizer and the matrix surface and the hydrophilic part

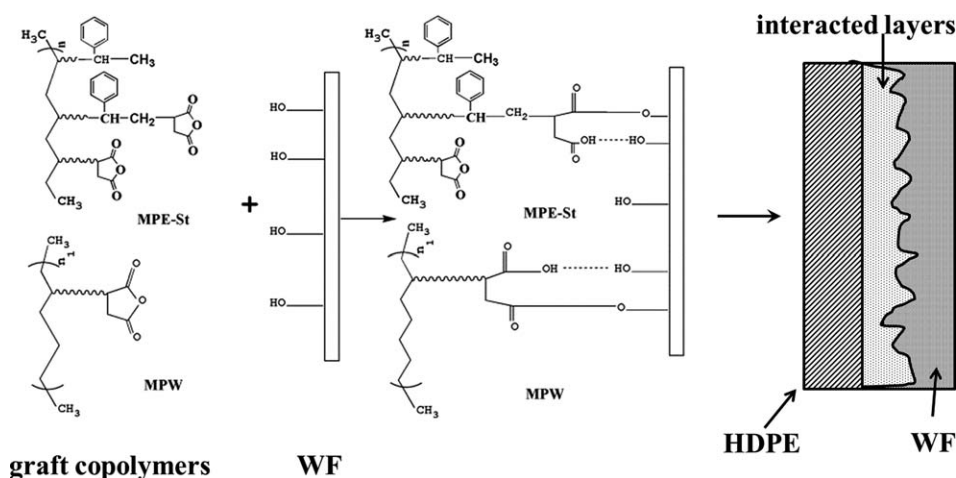


Figure 3. Interfacial compatibilization mechanism of MPE-St/MPW compounds compatibilizer on HDPE/WF composites.

of compatibilizer with the fiber surface.³⁵ That is to say, the graft copolymers, MPE-St, MPW, and MPE, were effective to compatibilize the HDPE/WF composites.

What's more, we found that the optimum contents of MPE-St, MPW, and MPE were 5 phr in separately compatibilized composites. Among these composites compatibilized by the graft

copolymers, the composites compatibilized by synthetic grafted copolymers (MPE-St and MPW) displayed superior tensile strength, flexural strength, flexural modulus, and Izod notched impact strength than those compatibilized by MPE at the same content. This increase was mainly due to better dispersion of the wood flour in the PE matrix. That is to say, the synthetic graft copolymers provided more effective compatibilization than

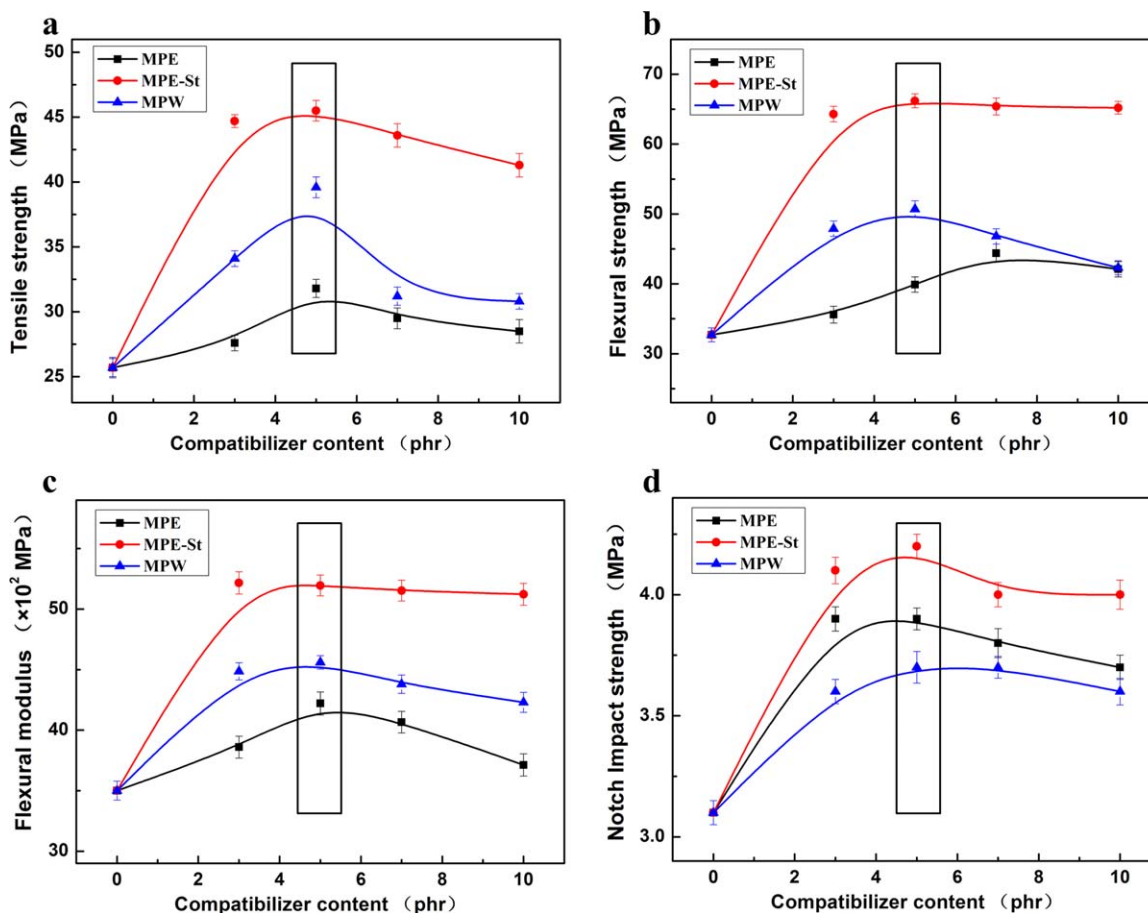


Figure 4. Effect of compatibilizer type and content on (a) tensile strength, (b) flexural strength, (c) flexural modulus, and (d) Izod notched impact strength of HDPE/WF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

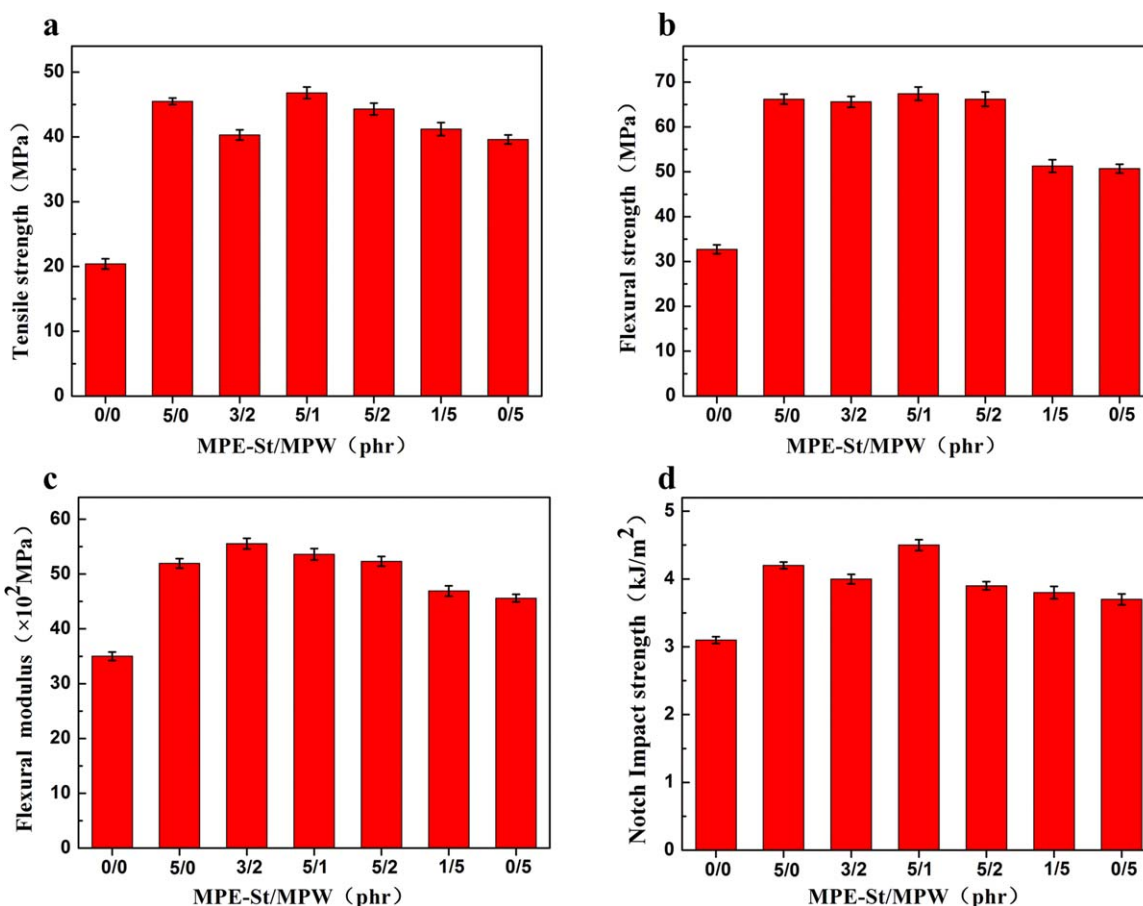


Figure 5. Effect of MPE-St/MPW mass ratio on (a) tensile strength, (b) flexural strength, (c) flexural modulus, and (d) Izod notched impact strength of HDPE/WF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the purchased compatibilizer because of higher grafting degree of MAH. The results were similar to Ihemouchen *et al.*'s research.¹¹

The effect of MPE-St/MPW mass ratio on the mechanical properties of the composites was illustrated in Figure 5. The best tensile strength, flexural strength, and Izod notched impact strength were fulfilled when the mass ratio of MPE-St/MPW was 5:1, except that the flexural modulus was highest when MPE-St/MPW was 3:2. The increased concentration of MPW in compatibilizer compounds might lead to reduction in mechanical properties of HDPE/WF composites due to its low molecular weight. Therefore, the content of MPW in the compatibilizer compounds was of a great importance to achieve optimal compatibilization effect and performance of composites. Bettini *et al.*⁹ had demonstrated that excess low-molecular-weight lubricant would reduce the efficiency of compatibilizer and lead to decrease of performance of the composites. Considering the comprehensive performances, MPE-St/MPW = 5/1 was the suggested optimal mass ratio for HDPE/WF composites.

Dynamic Rheological Properties of the HDPE/WF Composites

The influence of MPE-St/MPW mass ratio on the dynamic rheological properties of the HDPE/WF composites was also

investigated and the results were shown in Figure 6. The oscillatory dynamic measurements can provide information about both elastic and viscous properties, so the characterization of the dispersion and interfacial interaction would be explored in more detail than other flow measurements. The G' , G'' , and η^* all increased when WF was added. This was probably a result of the stiffness of WF and the effect of WF particle-particle contact which was more like to occur in this system containing 50 wt % WF with low apparent density.⁹ Treatments of wood flour with compatibilizer caused a considerable decrease in G' , G'' , and η^* . This reduction may mainly be explained by the improved dispersability of wood flour in HDPE and the chemical interactions between hydroxyl groups of WF and MAH lowering the surface energy of WF particles. Ou *et al.*³⁶ and Xie *et al.*³⁷⁻³⁹ had also reported the similar results.

The G' , G'' , and η^* of the composites compatibilized by MPE-St/MPW compounds were higher than those compatibilized separately by MPE-St and MPW. This was probably a result of stronger interfacial adhesion between the matrix and WF supplied by the MPE-St/MPW compounds. Consequently, stress was more efficiently transferred from the matrix to WF fibers. The composites compatibilized separately by MPE-St displayed the lowest G' , G'' , and η^* excluding virgin HDPE. This phenomenon may be explained by the plasticizing effect of MPE-St

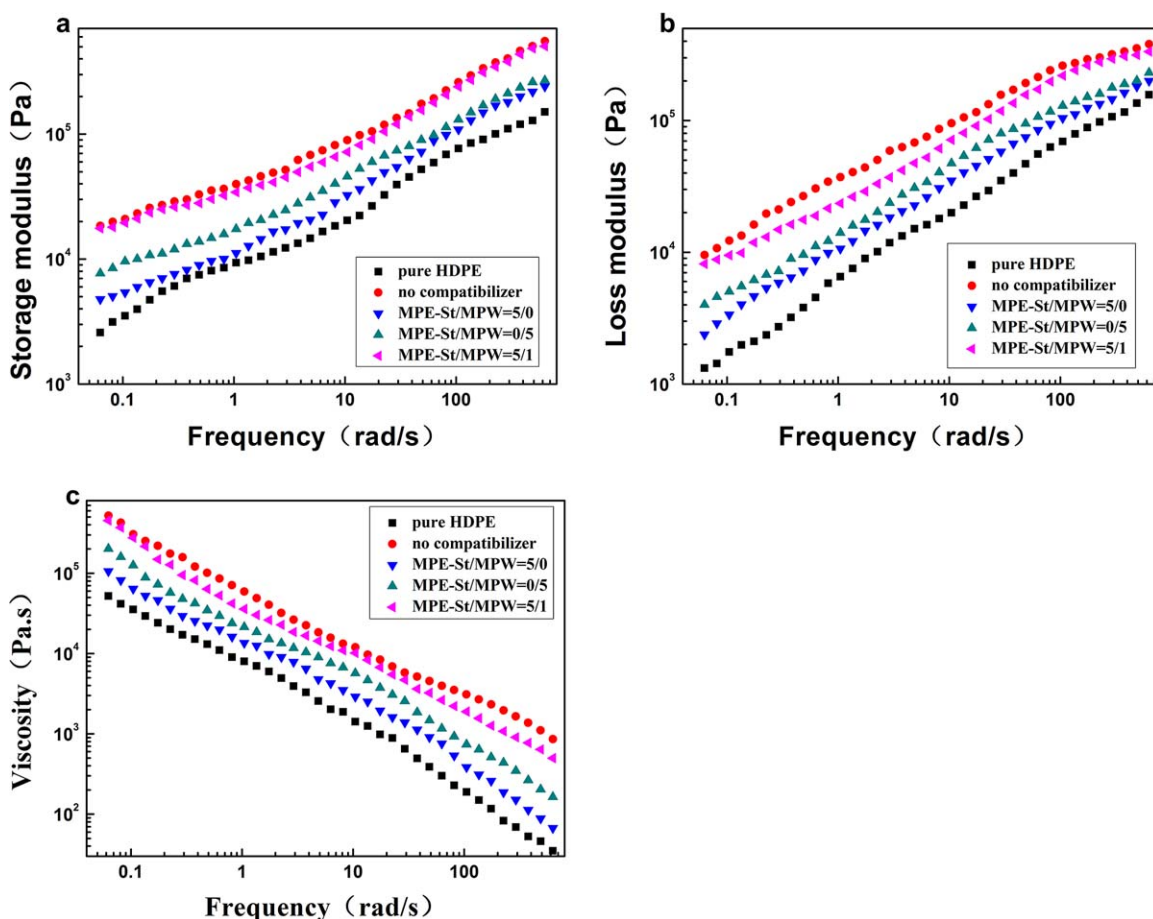


Figure 6. Influence of MPE-St/MPW mass ratio on (a) storage modulus (G'), (b) loss modulus (G''), and (c) complex viscosity (η^*) of the HDPE/WF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with long grafted side chains and the decrease of motion-resistance of polymeric molecules. These results were consistent with the result reported by Hong *et al.*¹²

Water Absorption (WA) of the HDPE/WF Composites

The moisture was predominantly absorbed by wood flour component in the composites, because PE matrix was water resistant. The numerous free hydroxyl groups of three main compositions (hemicellulose, lignin, and cellulose) presented in the wood flour cellulosic cell wall were responsible for forming hydrogen bonding with water molecules.^{34,40,41} The water absorption of the composites was dependent on the availability of free hydroxyl functions on the surface of the fibers. Figure 7 illustrated the effect of MPE-St/MPW mass ratio on the water absorption of the HDPE/WF composites. The rate of water absorption was higher in the initial stage, and then gradually slowed down. Water absorption of the compatibilized composites was much lower than that uncompatibilized composites. What's more, the HDPE/WF composites compatibilized by MPE-St/MPW compatibilizer compounds showed the lowest water absorption. Comparing the WA at sixtieth day, WA of uncompatibilized composites was 12.7% without the trend of stopping absorption, WA of composites compatibilized by MPE-St/MPW compounds (5/1) was only 3.6% and tended to

stop, and WA was 4.2% at 5 phr MPE-St and 6.3% at 5 phr MPW. That is to say, the HDPE/WF composites compatibilized by MPE-St/MPW compounds had the best water resistance properties. The study of Migneault *et al.*⁴² presented that the

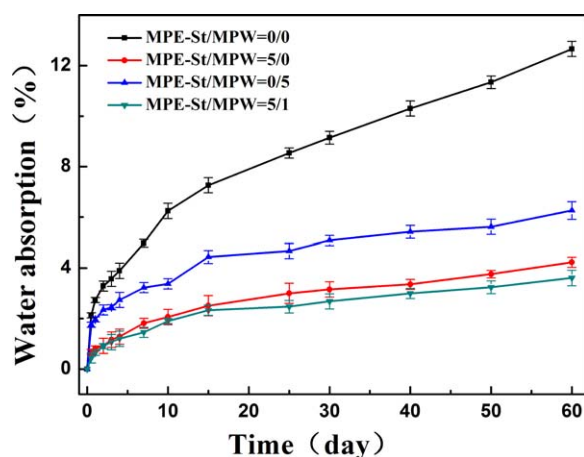


Figure 7. Effect of MPE-St/MPW mass ratio on the water absorption of the HDPE/WF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more exposed fibers, the higher water absorption of composites. Well-proportioned dispersion of WF particles in the HDPE matrix with the effect of strong compatibilization reduced WA, and then the water diffusion rate between the WF particles would be weakened. As discussed in the FTIR results, the amount of free hygroscopic hydroxyl groups were reduced in the WF due to the reaction with anhydride groups on MPE-St and MPW. Moreover, the stronger interfacial interacted layers formed by MPE-St and MPW sufficiently protect WF particles from water. Therefore, the composites compatibilized by MPE-St and MPW compounds had excellent water resistance. Similar results have been reported by Fang *et al.*³⁴

CONCLUSIONS

The studies of well-defined amounts of anhydride compounds by acid–base titration and the FTIR analyses of their reaction products confirm the formation of graft copolymers of HDPE and grafting monomers (MAH and St) or PE wax and MAH. The high performance HDPE/WF composite was successfully prepared by the synergistic compatibilization of MPE-St/MPW compounds at multi-scale interfaces of the composite. MPE-St with high graft degree of MAH afforded the strong interfacial interaction while MPW with a low molecular weight enhanced the interfacial interaction by permeating into the cavities of wood flour. The HDPE/WF composites compatibilized by MPE-St and MPW compounds displayed dramatically higher performance in terms of mechanical properties, rheological properties, and water resistance than these compatibilized separately by MPE, MPE-St, and MPW and the uncompatibilized composites. The suggested mass ratio of MPE-St/MPW to optimize composites was 5:1. The content of MPW in compatibilizer compounds should not be too high due to its low molecular weight, which may lead to reduction in mechanical properties of the composites.

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