Effect of Maleic Anhydride/Vinyltrimethoxysilane-*co*-Grafting Polypropylene on the Properties of Wood-Flour/Polypropylene Composites by Electron-Beam Preirradiation

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Received 27 March 2010; accepted 16 October 2010
DOI 10.1002/app.33626
Published online 18 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The electron-beam preirradiation and reactive extrusion technologies were used to prepare maleic anhydride (MAH)/vinyltrimethoxysilane (VTMS)-*co*-grafting polypropylene (PP) as a high-performance compatibilizer for wood-flour/PP composites. The grafting content, chemical structure, and crystallization behavior of the compatibilizers were characterized through Fourier transform infrared spectroscopy, differential scanning calorimetry, and an extraction method. The effects of the compatibilizers on the mechanical properties, water absorption, morphological structure, and torque rheological behavior of the composites were investigated comparatively. The experimental results demonstrate that MAH/VTMS-*g*-PP markedly enhanced the mechanical properties of the composites. Compared with MAH-*g*-PP and VTMS-*g*-PP, MAH/VTMS-*g*-PP clearly showed synergistic effects on the increasing mechanical properties, water absorption, and compatibility of the composites. Scanning electron microscopy further confirmed that the adhesion and dispersion of wood flours in the composites were effectively improved by MAH/VTMS-*g*-PP. These results were also proven by the best water resistance of the wood-flour/PP composites with MAH/VTMS-*g*-PP. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 402–409, 2011

Key words: compatibility; composites; polyolefins; morphology

INTRODUCTION

Wood–plastic composites, as environmentally friendly materials, have been widely used in the building and automotive industries, transportation, and other fields because of their excellent performances,[1,2] including good weatherability, low maintenance, and lack of cracking, warping or splintering. Recyclable wood–plastic composites mainly consist of plant flour (fiber), a thermoplastic polymer, and compatibilizers. The plant flour (fiber) is a kind of polar organic filler that contains abundant alcoholic and phenolic hydroxyl groups. Most thermoplastic polymers are nonpolar, for example, polypropylene (PP) and polyethylene (PE). To gain the good mechanical properties of the wood–plastic composites, therefore, a key problem is to solve the interfacial compatibility between the hydrophilic plant fours and the hydrophobic polymers. Recently, many researchers have been paying attention to it.[3–7]

There are large numbers of published works on the interfacial compatibility of wood–plastic composites. Various surface modification techniques have been used to enhance the interaction between wood flour and nonpolar polymers; these include the surface modification of wood flour[8–10] and the addition of interfacial compatibilizers.[11–13] Many studies have indicated that compatibilizers can effectively enhance the mechanical properties of wood–plastic composites.[14,15] One of the most important types of compatibilizers is a polymer grafted with maleic anhydride (MAH) or acrylic ester, such as MAH-*g*-PP,[16–18] MAH-*g*-PE,[19,20] or MAH-*g*-high-density PE/styrene–ethylene–butylene–styrene block copolymer blends.[21] We also reported the preparation of MAH/silicone-*g*-PE by the free-radical method.[22] The electron beam preirradiation technique is an important method for modifying the interface of the composites and for preparing grafting polymers.[23–27]

In this study, we prepared a novel compatibilizer, MAH, and vinyltrimethoxysilane (VTMS)-*co*-PP using

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Contract grant sponsor: Heilongjiang Science Fund for Distinguished Young Scholars; contract grant number: JC 04-06.

Journal of Applied Polymer Science, Vol. 121, 402–409 (2011)

an electron-beam preirradiation technique and a reactive extrusion method. The synergistic effects of the compatibilizer on the mechanical properties and morphological structures of the wood-flour/PP composites were investigated.

EXPERIMENTAL

Materials

PP (melting flow rate = 3.5 g/10 min) was supplied by Harbin HuaAo Co. (Harbin, China). We obtained poplar wood flour (60–100 mesh) by milling in a pulverizer and drying the product at 105°C in an oven. PP wax (mp = 145–150°C), as a lubricant, was offered by Chengdu TongLi Auxiliary Co., Ltd. (Chengdu, China). VTMS was offered by QUFU WanDa Chemical Co., Ltd. (Qufu, China). MAH was purchased from Beijing Yili Chemical Co. (Beijing, China).

Preparation of the compatibilizers

The compatibilizers, including MAH-*g*-PP, VTMS-*g*-PP, and MAH/VTMS-*g*-PP, were prepared from a twin-screw extruder manufactured from Nanjing Jie Ya Extrusion Equipment Co., Ltd (Nanjing, China) by a reactive extrusion method. First, PP powder was preirradiated by an electron beam at different doses (5, 15, and 30 kGy) under an electron accelerator (DD-1.2, Shanghai XianFeng Motor Co. (Shanghai, China)). Second, preirradiated PP powder was mixed with MAH, VTMS, or a mixture of MAH and VTMS with a mass ratio of 1 : 1. The total additions of these monomers were set at 0, 1, 2, 3, 4, and 5 wt %, on the basis of PP powder. Finally, the mixtures were extruded to obtain new compatibilizers for the wood-flour/PP composites.

Compatibilizer purification and grafting content

The crude compatibilizer (3 g; weighed as W) was dissolved in 150 mL of xylene at 130°C for 4 h, and then, about 400 mL of acetone was added to the hot xylene solution of the compatibilizers to remove nonreacted MAH or VTMS. The precipitated compatibilizer was filtered, washed with acetone three times, and then dried in a vacuum oven at 80°C for 24 h. The purified compatibilizer was obtained and weighed (W_2). According to the addition percentage of the monomer and W, the net PP weight (W_1) was obtained. On the basis of the weight method, the grafting content was calculated with the following equation:

$$\text{Grafting content} = (W_2 - W_1)/W_1 \times 100\%$$

Fourier transform infrared (FTIR) analysis

FTIR spectra of PP and the purified compatibilizers were recorded with a Nicolet Avatar 360 FTIR spectrometer (USA) from 4000 to 400 cm^{-1}. Sample films for FTIR were prepared by hot compression at 170°C. FTIR spectra were used to study the chemical functional groups of the compatibilizers.

Differential scanning calorimetry (DSC) tests

The DSC tests of the compatibilizers were carried out on a PerkinElmer Diamond DSC (PerkinElmer Instruments (USA)) under an N_2 atmosphere with temperatures from 30 to 210°C at a heating rate of 30°C/min. We held the samples at 210°C for 5 min to eliminate the thermal history; this was followed by cooling from 210 to 30°C at a cooling rate of 10°C/min. On the basis of the DSC curves, the crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) were obtained.

Preparation of the wood-flour/PP composites

The wood-flour/PP composites were prepared by means of twin-screw extrusion and hot compression (TE-35 twin-screw extruder offered from Nanjing KeYa Extrusion Equipment Co., Ltd (Nanjing, China)) and a curing machine manufactured from Harbin Plastic Co. (Harbin, China)). The temperatures of the six processing zones in the extruder were set to 100, 165, 170, 180, 180, and 180°C, respectively, and the temperature and time for hot compression were 150°C and 2 min, respectively. The components of the composites consisted of 28.5 wt % PP, 60 wt % wood flour, 10 wt % compatibilizer, 1.0 wt % PE wax, and 0.5 wt % antioxidant 1010.

Mechanical property tests

The determination of the tensile and flexural strength of all of the samples was performed on a RGD-20A mechanical instrument produced by Shenzhen Regeer Instrument Cooperation (Shenzhen, China), and the unnotched Izod impact strength was obtained with an XJC-25D impact test machine produced by Chengde Precision Testing Machine Co., Ltd. (Chengde, China) according to GB1042-1992, GB 9341-2000, and GB 1843-1996, respectively. The testing temperature and relative humidity were 20°C and 50%, respectively. The dimensions of the samples were selected on the basis of GB1042-1992, GB 9341-2000, and GB 1843-1996, and the thickness of the samples was 4 mm.

Water absorption tests

According to GB/T1034-1998, the water absorption of the wood-flour/PP composites was determined with the following procedure. The samples were dried at 50°C for 24 h in an oven and weighed (W_1). The dried samples were immersed in 25 or 80°C water for 24 h and were then taken out. We wiped

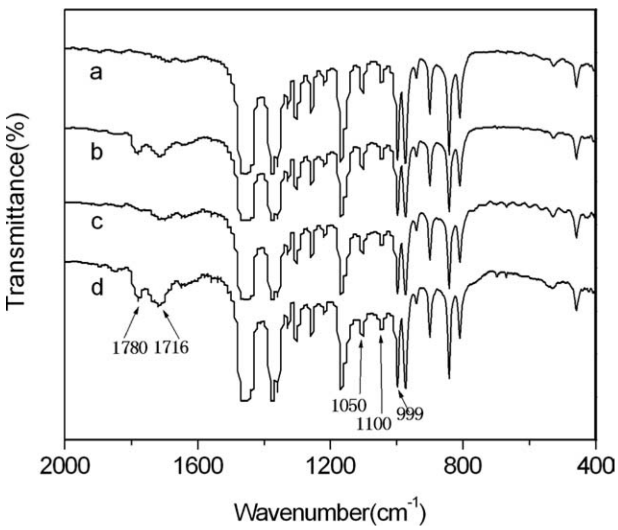


Figure 1 FTIR spectra of (a) PP, (b) MAH-*g*-PP, (c) VTMS-*g*-PP, and (d) MAH/VTMS-*g*-PP.

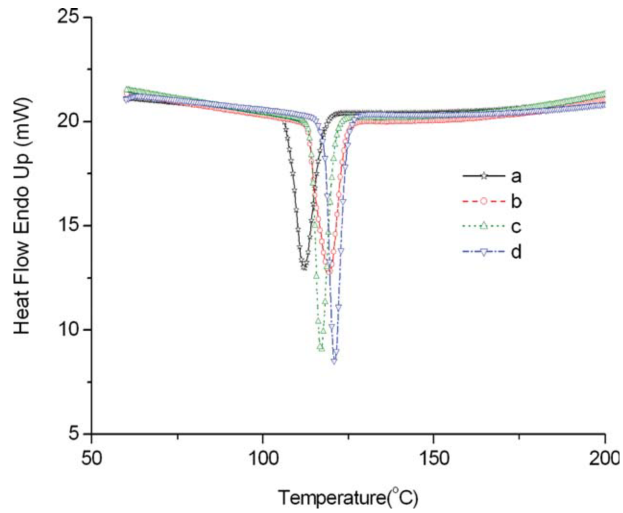


Figure 2 DSC of PP and the compatibilizers: (a) PP, (b) MAH-*g*-PP, (c) VTMS-*g*-PP, and (d) MAH/VTMS-*g*-PP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

off the water on the surface of the samples and weighed them (W_2). The water absorption content was calculated with the following equation:

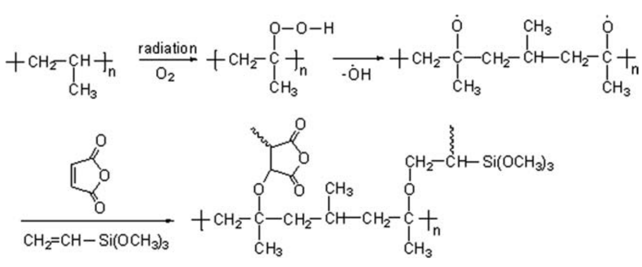
$$\text{Water absorption content} = (W_2 - W_1)/W_1 \times 100\%.$$

Torque rheological behavior tests

The torque rheological behavior was determined on a RM-200A torque rheometer offered from Harpro Electric Co. (Harbin, China). The mixtures of the components were added to a chamber preheated to 180°C, and the speed of the rotor was set at 60 rpm. The content of every sample was kept at 55 g. The equilibrium torques and curves of the torque versus time were recorded by a computer.

Scanning electron microscopy (SEM)

The fractured surfaces of the composites obtained under liquid nitrogen were coated with gold to prevent electrical charging. The morphological structures of samples were observed by a Japanese Rely S570 SEM instrument (Japan) at an acceleration voltage of 20 kV.



Scheme 1 Synthetic reactions of MAH/VTMS-*g*-PP.

RESULTS AND DISCUSSION

FTIR characterization of the compatibilizers

Figure 1 shows the FTIR spectra of the preirradiated PP (spectrum a), MAH-*g*-PP (spectrum b), VTMS-*g*-PP (spectrum c), and MAH/VTMS-*g*-PP (spectrum d). Scheme 1 gives the chemical reaction process of the compatibilizer. From the FTIR analysis, we observed that the adsorption bands at 1716 and 1780 cm^{-1} in spectra b and d were the asymmetric and symmetric carbonyl vibrations of MAH, respectively. This showed that MAH was successfully grafted onto the PP macromolecular chain. The two absorbing peaks (1100 and 1050 cm^{-1}) were assigned as Si—O bond and C—O bond, which overlapped. As shown in Figure 1(c,d), the relative strength of two absorbing peaks at 1100 and 1050 cm^{-1} with the absorbing peak at 999 cm^{-1} increased compared to those in Figure 1(a). This result indicates that VTMS was grafted onto the PP macromolecular chain.

Figure 2 and Table I show the DSC curves and data of the compatibilizers. Compared with values of the preirradiated PP, the T_c values of the compatibilizers increased and ΔH_c decreased. This was because the size and content of the grafting large groups (MAH or VTMS) hindered the rotation and arrangement of PP molecules; this resulted in an

TABLE I
T_c and ΔH_c Values of the New Compatibilizers

	Compatibilizer			
	PP	MAH-*g*-PP	VTMS-*g*-PP	MAH/VTMS-*g*-PP
T_c (°C)	112.1	119.3	117.1	121.0
ΔH_c (J/g)	79.1	76.6	76.0	73.5

TABLE II
Effect of the New Compatibilizers and Irradiation Doses on the Mechanical Properties of the Wood-Flour/PP Composites

	Compatibilizer								
	MAH-*g*-PP			VTMS-*g*-PP			MAH/VTMS-*g*-PP		
Irradiation dose (kGy)	5	15	30	5	15	30	5	15	30
Izod impact strength (kJ/m^2)	6.4	7.9	8.3	5.5	6.6	7.3	8.0	9.7	11.4
Tensile strength (MPa)	26	29	29	22	24	25	31	35	36
Flexural strength (MPa)	44	47	49	32	37	39	48	51	55

increase in T_c and a decrease in the crystallization degree. As shown in Table I, the T_c values of the preirradiated PP, VTMS-*g*-PP, MAH-*g*-PP, and MAH/VTMS-*g*-PP was 112.1, 117.1, 119.3, and 121.0°C, respectively, and their ΔH_c values were 79.1, 76.0, 76.6, and 73.5 J/g, respectively. These results were in agreement with those of the grafting content and size of monomers, which are discussed in the following section.

Effect of the irradiation dose and grafting content on the mechanical properties

Table II gives the effect of the irradiation dose on the mechanical properties of the composites at a fixed loading (4 wt %) of MAH, VTMS, or the mixture of MAH and VTMS. With increasing irradiation dose, the compatibilizers clearly increased the tensile strength, flexural strength, and Izod impact strength of the composites. This fact indicated that a high irradiation dose increased the reactive points on the PP main chains, which were in favor of grafting reactions of monomers. Therefore, we adopted 30 kGy as a fixed irradiation dose to prepare MAH-*g*-PP, VTMS-*g*-PP, and MAH/VTMS-*g*-PP.

Figure 3 shows the effect of the monomer content on the grafting content. Under an irradiation dose of 30 kGy, with increasing monomer addition, the grafting content increased; however, a further increase resulted in a decrease in the grafting content of MAH and VTMS and an increase in the grafting content of the mixture (MAH and VTMS). That is, it was beneficial to obtain a higher grafting content in the system with the mixture of MAH and VTMS.

Figures 4–6 show the tensile strength, flexural strength, and Izod impact strength, respectively, of the composites influenced by the compatibilizers obtained at different grafting contents. It was clear that the mechanical properties increased with increasing grafting content of MAH, VTMS, or the mixture of MAH and VTMS. Remarkably, the compatibilizer obtained from the cografting of both MAH and VTMS on PP (MAH/VTMS-*g*-PP) presented obviously synergistic effects on the tensile strength and Izod impact strength compared with MAH-*g*-PP and VTMS-*g*-PP. These results were attributed to the effective modification of the interfacial interaction between the wood flour and PP by MAH/VTMS-*g*-PP. The morphological structures of

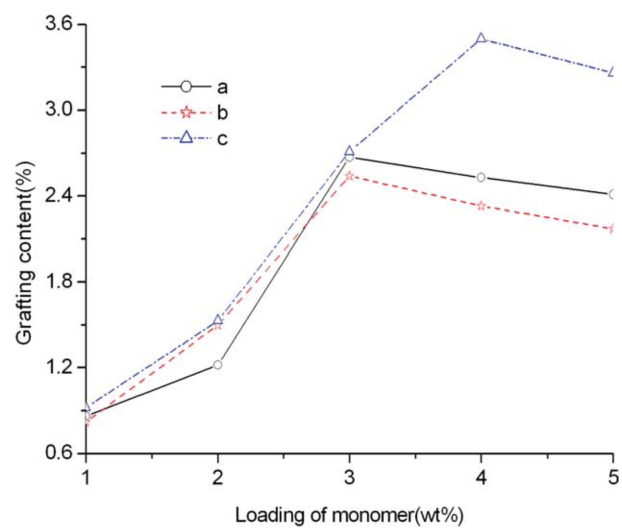


Figure 3 Effect of the monomer content on the grafting content: (a) MAH, (b) VTMS, and (c) MAH/VTMS (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

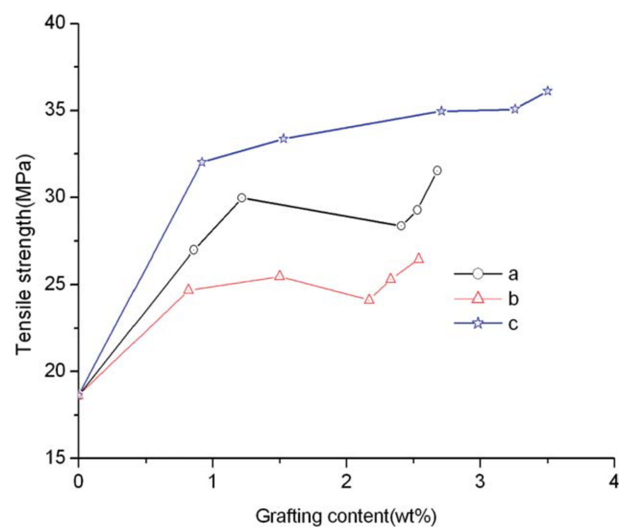


Figure 4 Effect of the grafting content on the tensile strength: (a) MAH, (b) VTMS, and (c) MAH/VTMS (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

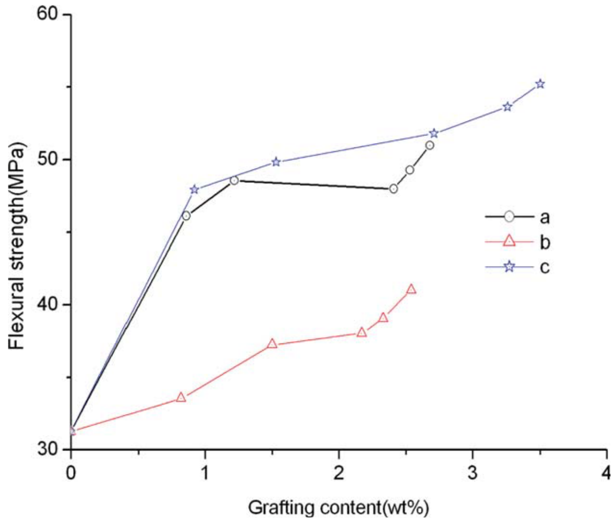


Figure 5 Effect of the grafting content on the flexural strength: (a) MAH, (b) VTMS, and (c) MAH/VTMS (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

the fracture surface of the composites are illustrated in the following section.

Effect of the water absorption on the mechanical properties of the composites

Table III gives the water absorption values of the composites at 20 and 80°C. On the basis of the data of the water absorption content, all of the compatibilizers could decrease the water absorption of the composites, and the water absorption content became larger at high temperatures. With regard to the three compatibilizers, they presented little effect on the water absorption; however, the MAH/VTMS-*g*-PP still showed a low water absorption content. This result was also attributed to the interfacial modification effect of the compatibilizers. Table IV shows the effect of water treatment on the mechanical properties of the wood-flour/PP composites. The mechanical properties decreased to a certain extent with increasing water absorption content.

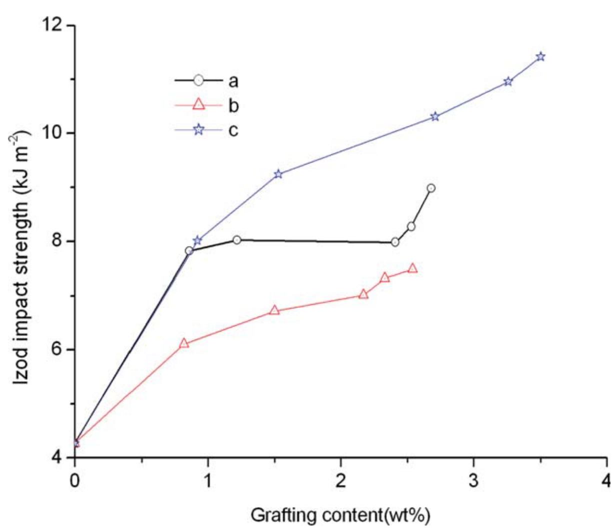


Figure 6 Effect of the grafting content on the Izod impact strength: (a) MAH, (b) VTMS, and (c) MAH/VTMS (1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

TABLE III
Water Absorption Content of the Wood-Flour/PP Composites at 20 and 80°C for 24 h

Composite	Water absorption content (wt %) 20°C	80°C
No compatibilizer	2.4	5.2
MAH-*g*-PP	1.9	3.6
VTMS-*g*-PP	2.0	3.9
MAH/VTMS-*g*-PP	1.8	3.4

Morphological analysis

The SEM patterns of the fractured surfaces of the composites given in Figure 7 provide further information about the interfacial compatibility between the wood flour and PP. In the absence of compatibilizers [Fig. 7(a)], many holes at the interface and the agglomerated wood flours were observed. This result indicates that the interfacial adhesion between the wood flour and PP and the dispersion of wood flour were poor; therefore, it was easy to pull out the wood fibers, and this resulted in the production of many holes and interfacial separation. As shown in Figure 7(b–d), the interfacial compatibility between the wood flour and PP was markedly improved, cavities were obviously reduced, and especially in the presence of MAH/VTMS-*g*-PP, the wood flour was well dispersed in the composites. Good compatibility could effectively transfer the load from the PP matrix to the wood flour. This fact was proven through a clear increase in the mechanical properties of the composites.

Effect of the compatibilizers on the torque rheological behavior

Figure 8 gives the torque–time curves of the composites at 180°C in the torque rheometer. As shown in Figure 8, the torque–time curves of the composite process exhibited four characteristic zones. First, the initial sharp peak was due to the material loading; second, the initial decrease in the torque was due to the material melting. Third, the second peak of torque was attributed to the modification and crosslinking reactions between the compatibilizers and wood flour. Fourth, the torque slightly decreased with increasing time because of the degradation of segmental polymer

TABLE IV
Effects of the Water Treatment on the Mechanical Properties of the Wood-Flour/PP Composites

Mechanical properties	Water treatment	Composites with different compatibilizers			
		None	MAH-*g*-PP	VTMS-*g*-PP	MAH/VTMS-*g*-PP
Tensile strength	Original	18.6	29.3	25.3	36.1
(MPa)	20°C	17.0	28.0	24.4	35.1
	80°C	15.3	25.7	22.6	33.4
Flexural strength	Original	31.3	49.3	39.1	55.1
(MPa)	20°C	29.2	45.4	37.3	52.3
	80°C	26.4	41.4	34.4	49.6
Izod impact strength	Original	4.2	8.7	7.3	11.4
(kJ/m^2)	20°C	3.4	7.5	6.9	10.3
	80°C	2.4	6.2	5.4	8.6

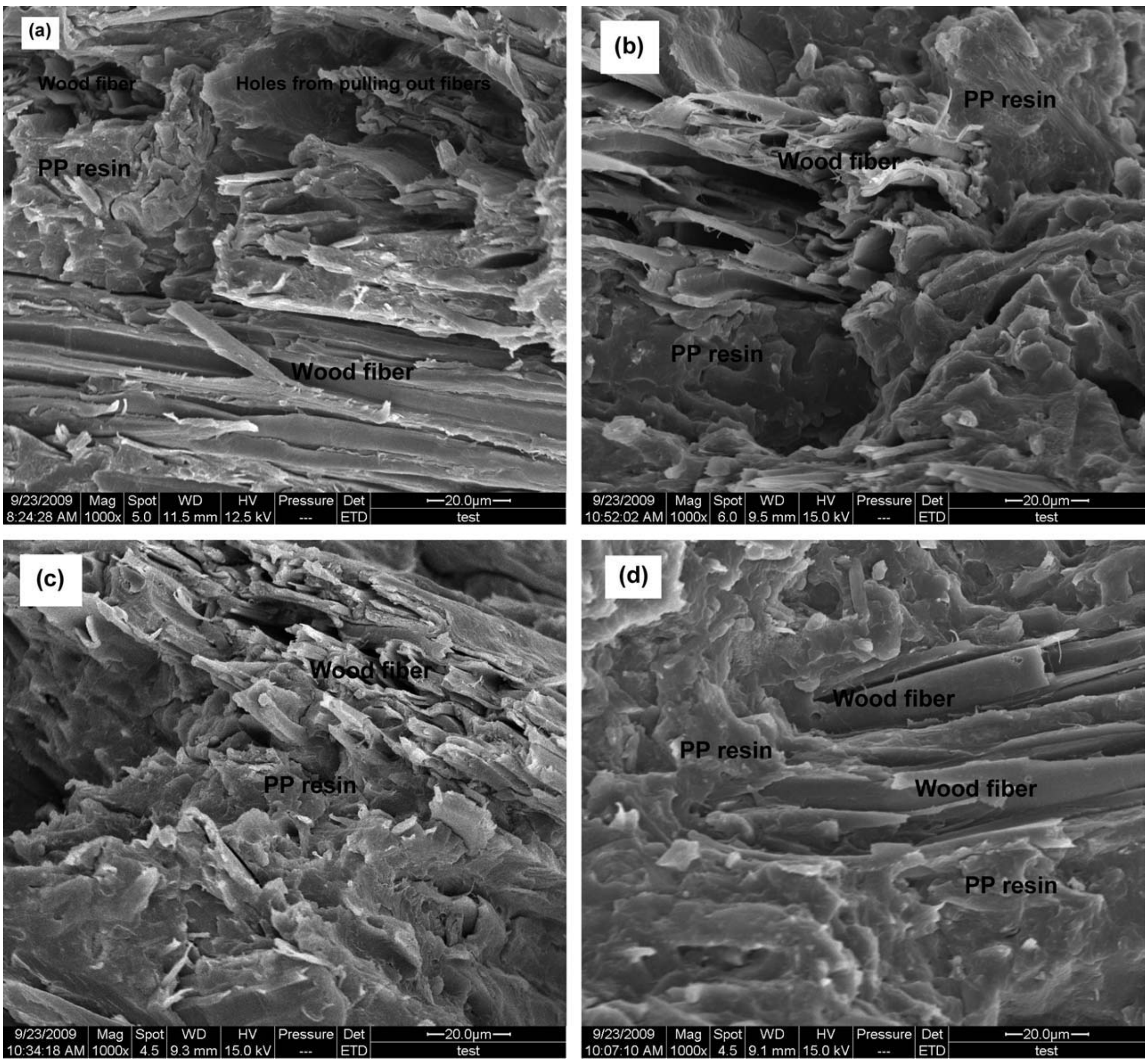


Figure 7 SEM micrograph of the room-temperature fractured surface of the composites: (a) wood-flour/PP composite without compatibilizer, (b) wood-flour/PP composite with MAH-*g*-PP, (c) wood-flour/PP composite with VTMS-*g*-PP, and (d) wood-flour/PP composite with MAH/VTMS-*g*-PP.

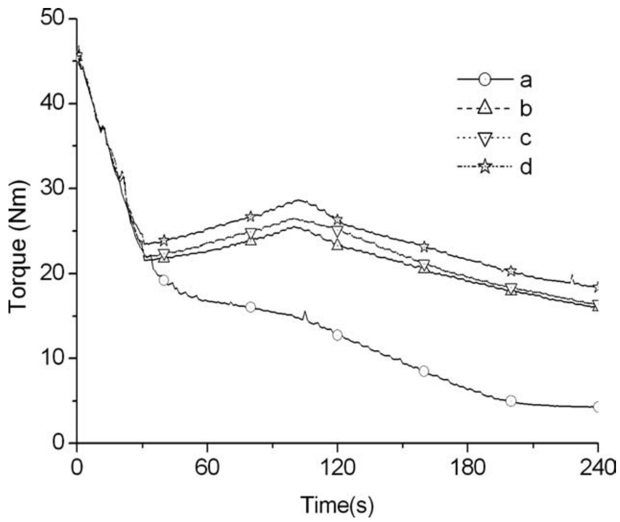
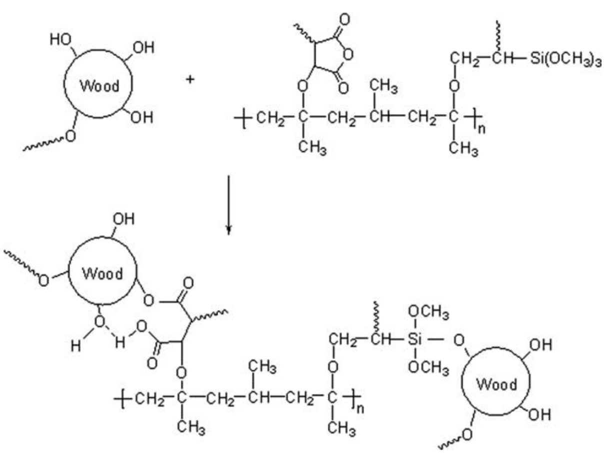


Figure 8 Effect of the compatibilizers on the torque–time curves: (a) without compatibilizer, (b) MAH-*g*-PP, (c) VTMS-*g*-PP, and (d) MAH/VTMS-*g*-PP.

chains. In the presence of MAH/VTMS-*g*-PP, the maximum torque value was shown. This result could be explained by the fact that different reactions with MAH and VTMS groups on MAH/VTMS-*g*-PP with wood flour took place; this resulted in an acceleration in cross-linking. These are discussed later.

Analysis of the synergistic effect

According to results obtained from the mechanical properties, equilibrium torques, and SEM, MAH/VTMS-*g*-PP showed clearly synergistic effects on the mechanical properties and interfacial compatibility of the wood-flour/PP composites. This was mainly attributed to the different chemical modification mechanisms of MAH and VTMS on the surface of the wood flour. Scheme 2 gives the chemical reaction process between the wood flour and reactive groups. In the preparation process of the composite, the MAH groups reacted with hydroxyl groups on the surface of the wood flour to form ester bonds, which could effectively improve the compatibility between wood flour and PP, whereas the VTMS groups reacted with the hydroxyl groups on the surface of the wood flour to form Si—O—C ether bonds. A lot of hydrogen bonds also existed in the interface of the wood flour and the compatibilizer. In addition, the long aliphatic chains on MAH/VTMS-*g*-PP showed good compatibility and entanglement with the PP molecules. Therefore, the addition of MAH/VTMS-*g*-PP led to a clear increase in the mechanical properties of the composites.



Scheme 2 Chemical bonding of MAH/VTMS-*g*-PP to the wood flour.

CONCLUSIONS

A new compatibilizer used for wood-flour/PP composites, MAH/VTMS-*g*-PP, was prepared by electron-beam preirradiation and reactive extrusion. A higher irradiation dose (30 kGy) and the 4 wt % addition of monomers were favorable for achieving a high-performance compatibilizer. Compared with MAH-*g*-PP and VTMS-*g*-PP, MAH/VTMS-*g*-PP showed synergistic effects in improving the mechanical properties and compatibility of the composites and enhanced the water resistance of the composites because of the different kinds of chemical reactions of the MAH and VTMS groups with the hydroxyl groups on the surface of the wood flour. This fact proved that MAH/VTMS-*g*-PP was a very effective compatibilizer for wood–plastic composites.

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