Preparation of HDPE/SEBS-*g*-MAH and Its Effect on Mechanical Properties of HDPE/Wood Flour Composites

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ABSTRACT: In this article, high density polyethylene/styrene-ethylene-butylene-styrene block copolymer blends (HDPE/SEBS) grafted by maleic anhydride (HDPE/SEBS-*g*-MAH), which is an effective compatibilizer for HDPE/wood flour composites was prepared by means of torque rheometer with different contents of maleic anhydride (MAH). The experimental results indicated that MAH indeed grafted on HDPE/SEBS by FTIR analysis and the torque increased with increasing the content of maleic anhydride and dicumyl peroxide (DCP). Styrene may increase the graft reaction rate of MAH and HDPE/SEBS. When HDPE/SEBS MAH was added to HDPE/wood flour composites, tensile strength and flexural strength of composites can reach 25.9 and 34.8 MPa in comparison of 16.5 and 23.8 MPa (without HDPE/SEBS-*g*-MAH),

increasing by 157 and 146%, respectively. Due to incorporation of thermoplastic elastomer in HDPE/SEBS-*g*-MAH, the Notched Izod impact strength reached 5.08 kJ m^{-2}, increasing by 145% in comparison of system without compatibilizer. That HDPE/SEBS-*g*-MAH improved the compatibility was also conformed by dynamic mechanical measurement. Scanning electron micrographs provided evidence for strong adhesion between wood flour and HDPE matrix with addition of HDPE/SEBS-*g*-MAH. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3161–3170, 2007

Key words: polyethylene/wood flour composites; compatibility; mechanical property; dynamic mechanical analysis; morphology

INTRODUCTION

Nowadays, plastics have become an important material in our daily lives because of its applications in many fields. But a lot of waste plastics have been causing the serious environmental problem that it is hard to decompose at ambient temperature. Wood flour is a waste material and has advantages of low density, renewability, biodegradability, and nontoxicity. It can be added in thermoplastics as an inexpensive filler to form new composites called wood plastic composites (WPC). This can make full use of waste plastics and wood flours to solve environmental problem. The two components can compensate for each other, for example, thermoplastics may compensate for the processability of wood flour and wood flour may enhance the strength of thermoplastics. So much attention has been paid to this new material.[1–6] The composites have many advantages, including biodegradability, low density, low cost,

high stiffness, availability of renewable natural resources, and so on. Therefore, wood plastic composites have been widely used for many fields such as floors, fences, furniture, automobiles, etc.[7–10]

However, a key problem in WPC is the weak compatibility between hydrophobic thermoplastic and hydrophilic wood flour, which destroys the mechanical properties to a large content and furthermore limits applications of WPC. So many scholars have done many researches on improving the interfacial compatibility.[11–18] Different types of compatibilizers have been tested in the composites to enhance the mechanical properties. It has been found that polyethylene grafted with maleic anhydride is a very effective compatibilizer for high density polyethylene (HDPE)/wood flour composites. The improved compatibility was due to esterification between polyethylene grafted with maleic anhydride and hydroxyl groups of wood flour.[19]

In this article, high density polyethylene/styrene-ethylene-butylene-styrene block copolymer blends (HDPE/SEBS) grafted by maleic anhydride (HDPE/SEBS-*g*-MAH) was prepared by means of torque rheometer and its effect on compatibility of HDPE/wood flour composites was investigated by mechanical property test, dynamic mechanical measurement, and scanning electron microscopy (SEM). SEBS as a thermoplastic elastomer was incorporated in the

compatibilizer to enhance the impact strength of the composites.

EXPERIMENTAL

Materials

High density polyethylene (HDPE-5000S) used in this work was manufactured by Daqing Petrochemical Company (Daqing, China). Larch wood flour (60–80 meshes) was offered by Xinglong Company (Tonghe Town, China). Styrene-ethylene butylene-styrene block copolymer (SEBS-YH503) was purchased from Baling Petrochemical Company (Yueyang, China). HDPE-g-MAH was purchased from Shanghai Rizhisheng Company (Shanghai, China). Maleic anhydride (MAH), styrene (St), xylene, and acetone were purchased from Beijing Yili Chemical Company (Beijing, China). Dicumy peroxide (DCP) was procured from Guoyao Group Chemical Agent Company (Shanghai, China). Antioxidant 1010 was purchased from Yangzi Petrochemical Company (Nanjing, China).

Preparation of HDPE/SEBS-g-MAH

HDPE and SEBS were mixed with the weight ratio of 7 : 3, and then were extruded in twin screw extruder as the raw material.

The grafting of maleic anhydride onto HDPE/SEBS was carried out in a RM-200A torque rheometer. The chamber was initially heated to 180°C and the rotor was set a speed of 50 rpm, then the mixture of HDPE/SEBS, maleic anhydride, dicumy peroxide, antioxide 1010, and styrene (Table I) was added into the chamber and the graft reaction was continued for 240 s. The torque changed with time was recorded during the reaction.

TABLE I
Experimental Recipe of Preparation of HDPE/SEBS-g-MAH

Sample	MAH (wt %)	DCP (wt ‰)	St/MAH	Antioxidant 1010 (wt ‰)
0	–	–	–	–
1	1	2	0	3
2	2	2	0	3
3	3	2	0	3
4	4	2	0	3
5	2	1	0	3
6	2	3	0	3
7	2	4	0	3
8	4	2	0.5	3
9	4	2	1	3
10	4	2	1.5	3

St/MAH was the weight ratio of styrene and maleic anhydride and the contents of MAH, DCP, St, and antioxidant 1010 were all calculated by the mass of HDPE/SEBS.

Purification of HDPE/SEBS-g-MAH

Crude HDPE/SEBS-g-MAH (3 g) was dissolved in 150 mL xylene at 130°C for 4 h, and then about 400 mL acetone was added into the hot xylene solution of HDPE/SEBS-g-MAH to remove nonreacted MAH. The precipitated HDPE/SEBS-g-MAH was filtered, washed with acetone for three times, and then dried in vacuum oven at 80°C for 24 h.

FTIR spectroscopy analysis of HDPE/SEBS-g-MAH

FTIR spectra of purified HDPE/SEBS-g-MAH were recorded using a Nicolet Avatar 360 spectrometer from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans. The samples purified were prepared by hot compression to form 10–100 μm thickness.

The relative graft degree of MAH, R_a (MAH) was determined by the absorbance ratio of the areas of the bands at (1790 + 1714) and 1380 cm^{-1}. The absorption band at 1380 cm^{-1} due to the bending vibration of methyl in HDPE/SEBS was chosen as an internal standard peak in this study. The absorption bands at 1790 and 1714 cm^{-1} were assigned to carbonyl vibration of maleic anhydride and carboxyl of hydrolyzed maleic anhydride, respectively.

Preparation of HDPE/wood flour composites

Larch wood flour, HDPE, and interfacial compatibilizer were mixed in a high rate mixer for 5 min. The components were extruded from the twin screw extruder, and then pressed on a curing machine at 150°C for 2 min to form sheets and cutted specimen for testing.

Mechanical property tests

Determination of tensile strength, flexural strength, and Notched Izod impact strength of all samples was performed by a Regeer computer controlled mechanical instrument and Notched Izod impact instrument, respectively, according to ASTM standards.

Dynamic mechanical analysis (DMA)

The DMA of the composites was performed with a NETZSCH242 analyzer using a 3-point bending rectangular measuring system at a frequency of 1 Hz. The size of the rectangular samples was 50 × 10 × 3 mm (length × width × thickness). The measurements of samples were carried out over a temperature range of −160 to 130°C at a rate of 3°C/min under nitrogen flow. The storage modulus (E') and loss tangent (tan δ) were recorded as a function of temperature.

Scanning electron microscopy

The fractured surfaces of the composites that were prepared in liquid nitrogen were coated with gold to prevent electrical charging. The prepared samples were observed by a QUANTA 200 scanning electron microscope under vacuum at an acceleration of 20 kV.

RESULTS AND DISCUSSION

Maleation of HDPE/SEBS

Figures 1–3 are the torque–time curves monitoring the torques of graft reaction. In three figures, the torque–time curves of graft reaction exhibited four characteristic zones: first, initial sharp peak due to the material loading; second, initial decrease of torque due to the material melting; third, the second peak of torque attributed to graft reaction and probably to some crosslinking reactions by free radicals leading to segmental crosslinking of polymer chain; fourth, the torque slightly decreased with time increasing, due to degradation of segmental polymer chain. These three figures present the effect of different MAH contents, different DCP contents, and different weight ratios of MAH and DCP on the torque–time curves of graft reaction. The curves show that graft reaction and torque are strongly influenced by the reaction conditions. It is interesting that when styrene was added in the system of graft reaction, the time of torque peak occurred ahead. With the ratio of MAH and DCP increasing, this phenomenon was more obvious. It demonstrated that styrene accelerated the graft reaction of HDPE/SEBS and maleic anhydride. This result can be explained that that maleic anhydride grafted on HDPE/SEBS with-
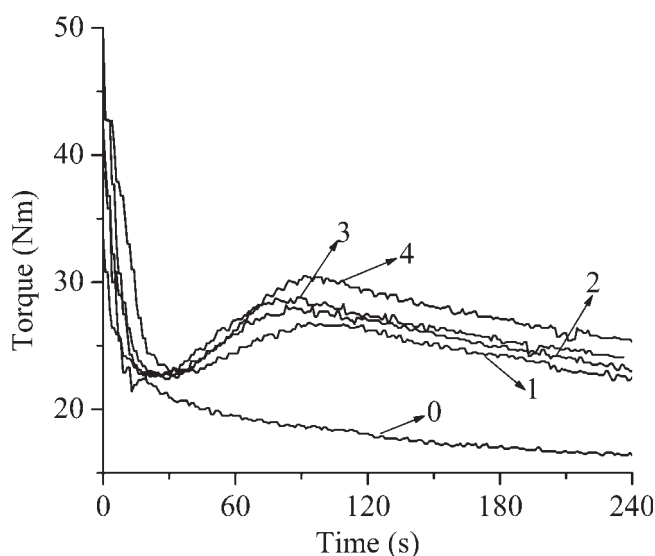
out styrene was difficult due to deficiency of electron density around the double bond as well as the high steric hindrance of maleic anhydride. When styrene was added, styrene and maleic anhydride can interact with each other one-to-one to form a charge transfer complex (CTC), which increased electrical asymmetry of the double bond of maleic anhydride, resulting in enhancing the maleic anhydride's reactivity,[20,21] hence the time of graft reaction occurred earlier.

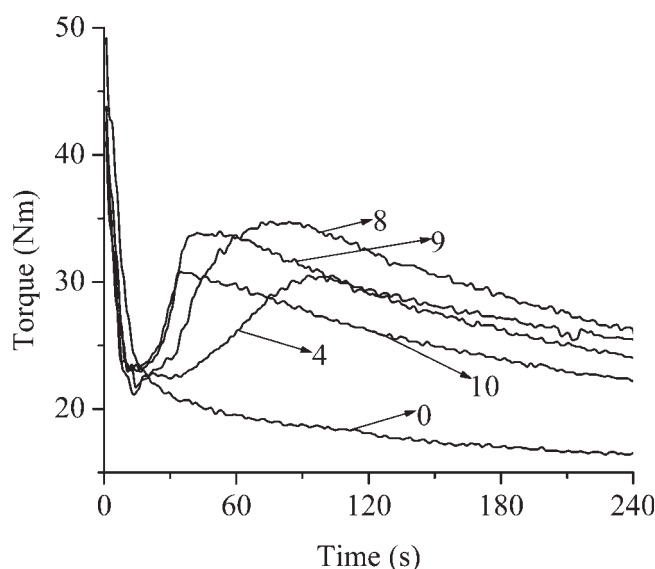FTIR spectrum of Sample 1 is shown in Figure 4. From the FTIR analysis result it can be obtained that

Figure 2 Effect of DCP content on torque–time curves.

Figure 1 Effect of MAH content on torque–time curves.

Figure 3 Effect of ratio of MAH/St on torque–time curves.
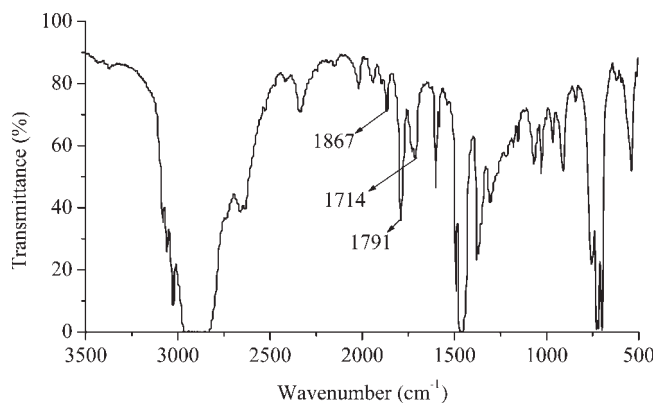
Figure 4 FTIR spectra of Sample 1.

adsorption bands at 1867 and 1791 cm^{-1} were asymmetric and symmetric carbonyl vibration of maleic anhydride, whereas the band at 1714 cm^{-1} was

assigned to carboxyl (hydrolyzed MAH). This demonstrated that maleic anhydride indeed grafted onto HDPE/SEBS.

Mechanical properties

Figures 5–7 show the effect of different MAH contents, different DCP contents, and different weight ratios of MAH and DCP on the R_a (MAH) of HDPE/SEBS-g-MAH and mechanical properties of HDPE/wood flour composites. From Figure 5, the experiments were performed in the MAH content range of 1–4 wt %, based on the mass of HDPE/SEBS. It was found that R_a (MAH) and mechanical properties of the composites show the same trend. That is, as MAH content increased, they reached a maximum at a MAH content of 3 wt %. Thereafter, they decreased. This is can be explained that more
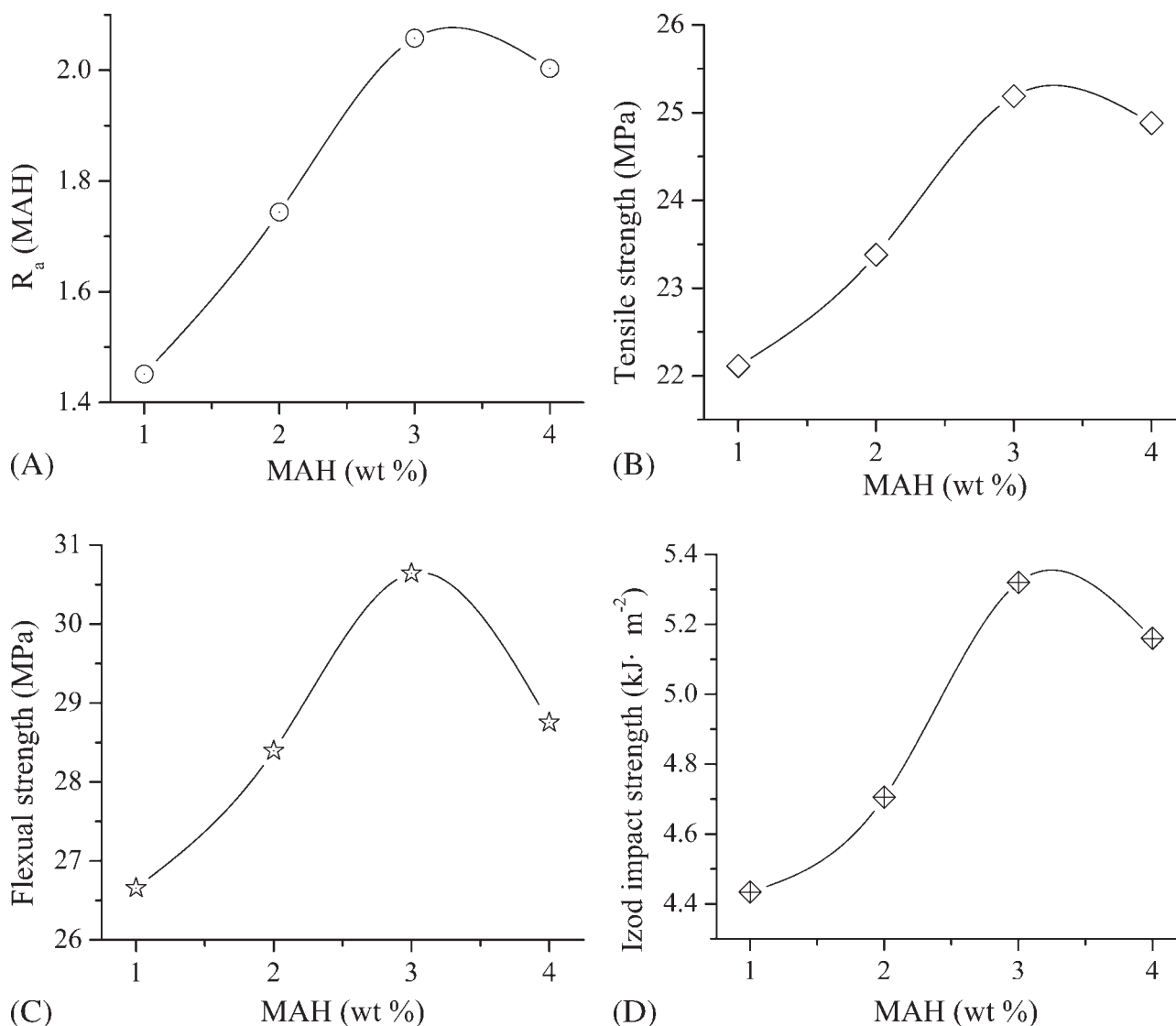

Figure 5 Effect of MAH content on R_a (MAH) and mechanical properties of HDPE/wood flour composites. Composition (weight ratio): HDPE/wood flour/(HDPE/SEBS-g-MAH) = 56/40/4.
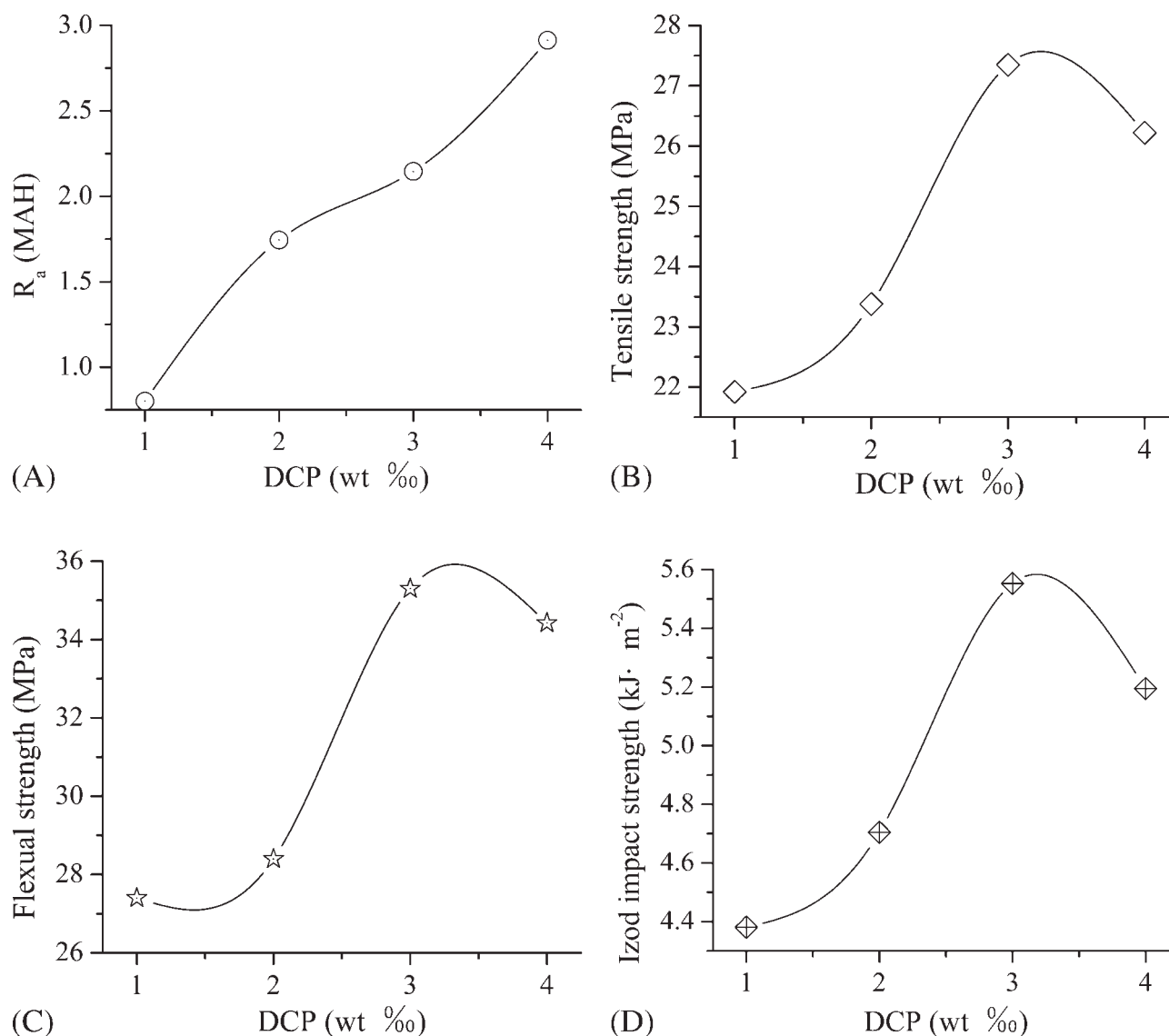
Figure 6 Effect of DCP content on R_a (MAH) and mechanical properties of HDPE/wood flour composites. Composition (weight ratio): HDPE/wood flour/(HDPE/SEBS-g-MAH) = 56/40/4.

MAH grafted on HDPE/SEBS chain with MAH content increasing. It led to increase of tensile strength, flexural strength, and impact strength by more esterification between HDPE/SEBS-g-MAH and wood flour and entanglements between HDPE/SEBS-g-MAH and HDPE. But at higher MAH content, some side reactions, such as crosslinking reaction, decreased R_a (MAH), furthermore, decreased mechanical properties of the composites. This was proved as shown in Figure 1 that higher MAH content resulted in obvious increase of torque.

From Figure 6, R_a (MAH) increased with an increase of DCP content. This was because increase of DCP content produced more free radicals for grafting of MAH on HDPE/SEBS. But mechanical property curves of the composites did not show the same trend as R_a (MAH). It can be explained

that although the graft degree increased, the mechanical properties decreased due to much crosslinking of HDPE/SEBS-g-MAH when DCP content was higher.

From Figure 7, R_a (MAH), mechanical properties increased with an increase of the MAH/St up to 0.5, beyond which it decreased. This is due to the fact that proper styrene content can increase grafting of MAH on HDPE/SEBS, as it was discussed above. The increase of graft degree of MAH led to increase of mechanical properties. But when MAH/St was over 0.5, mechanical properties decreased and they were even lower than the system with compatibilizer without styrene. It can be explained that compatibilizer may contain homopolymer of styrene which resulted in decrease of the mechanical properties of the composites to a large content.
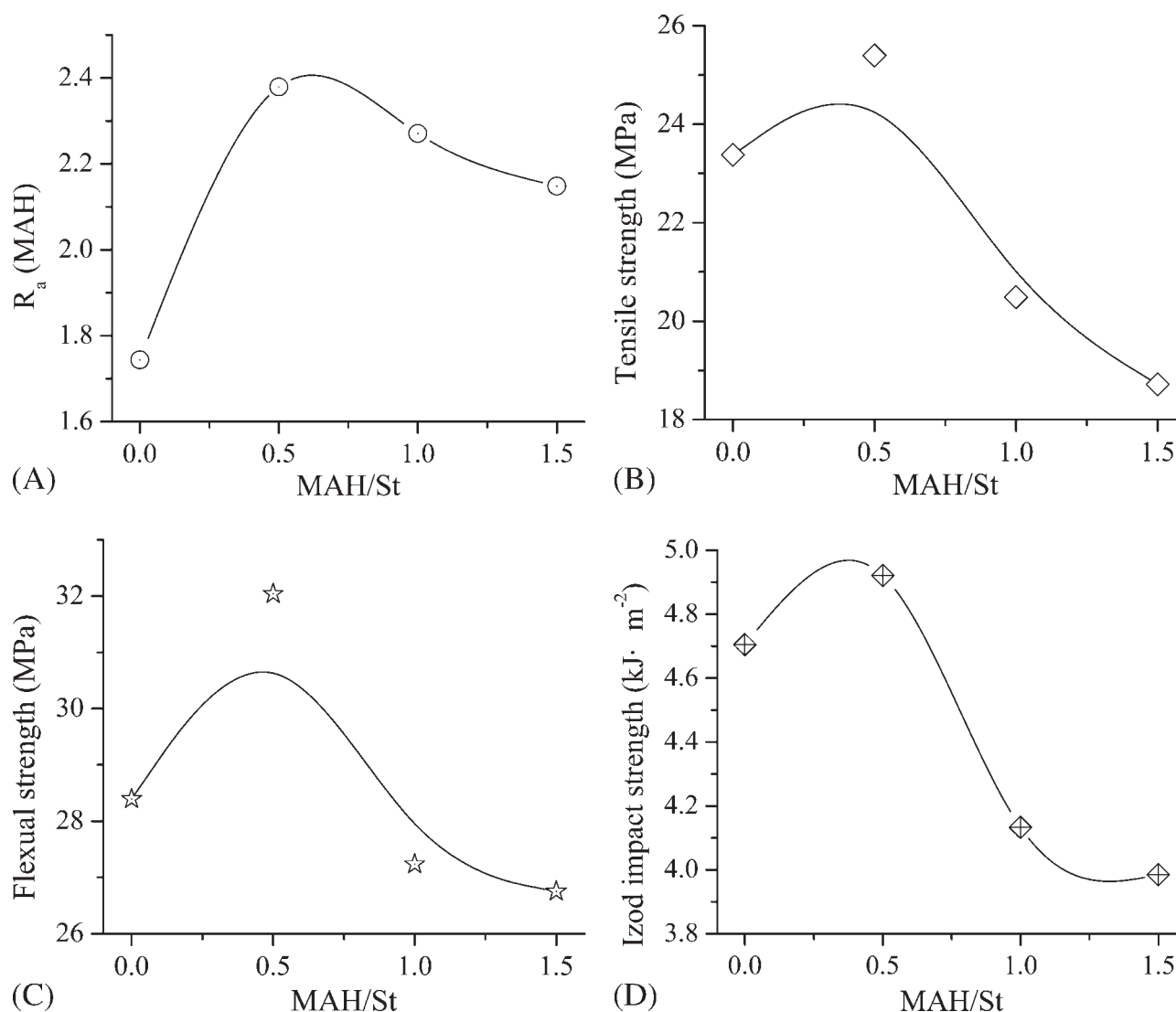
Figure 7 Effect of MAH/St on R_a (MAH) and mechanical properties of HDPE/wood flour composites. Composition (weight ratio): HDPE/wood flour/(HDPE/SEBS-g-MAH) = 56/40/4.

To confirm that HDPE/SEBS-g-MAH can obviously enhance the mechanical properties, the mechanical properties of the composites with different compatibilizers that are HDPE/SEBS-g-MAH, HDPE-g-MAH, and HDPE-g-MAH/SEBS were compared. The results were shown in Table II. From Table II, HDPE/SEBS-g-MAH as compatibilizer obviously increased the mechanical properties of the

TABLE II
Mechanical Properties of the Composites with Different Compatibilizers

Compatibilizer	Tensile strength (MPa)	Flexural strength (MPa)	Notched Izod impact strength (kJ m^{-2})
Control	16.56	23.83	3.50
HDPE/SEBS-g-MAH	27.35	35.30	5.55
HDPE-g-MAH	19.27	27.49	3.97
HDPE-g-MAH/SEBS	18.53	27.08	4.04

HDPE-g-MAH/SEBS was a mixture of HDPE-g-MAH and SEBS with the weight ratio of 7 : 3. Control referred to the composites without compatibilizer. The composition of the HDPE/wood flour composites: HDPE/wood flour = 60/40 for control and HDPE/wood flour/(HDPE/SEBS-g-MAH) = 56/40/4 for others.

composites. When the mixture of SEBS and HDPE-*g*-MAH was used as compatibilizer, the impact strength was increased, but the tensile strength and flexural strength were decreased, in comparison of HDPE-*g*-MAH. This was due to the fact that SEBS was a thermoplastic elastomer. When it was add to the composites, the impact strength can be enhanced, but HDPE-*g*-MAH and SEBS were two uncompatible components, so it led to slightly decrease the tensile and flexural strength. In comparison of HDPE-*g*-MAH and HDPE-*g*-MAH/SEBS, HDPE/SEBS-*g*-MAH was more effective in tensile strength, flexural strength, and Notched Izod impact strength. This can be explained that when maleic anhydride grafted the blend of HDPE and SEBS as the compatibilizer, HDPE/SEBS-*g*-MAH that contained thermoplastic elastomer may form a flexible interphase between wood flour and HDPE matrix and enhance

the toughness of the composites, so it led to increase the Izod impact strength. Esterification between HDPE/SEBS-*g*-MAH and wood flour, and entanglements between HDPE/SEBS-*g*-MAH and HDPE led to increase the mechanical properties.

It is well known that HDPE and wood flour are two immiscible polymers and weak interfacial adhesion between two phases. To improve mechanical properties of the composites, addition of different contents of HDPE/SEBS-*g*-MAH has been studied. Figure 8 gives the tensile strength, flexural strength, and Notched Izod impact strength data of HDPE/wood flour composites with different interfacial compatibilizer (Sample 6) loadings. It was found that different interfacial compatibilizer loadings can obviously enhance mechanical properties of the composites, compared with the system without interfacial compatiblizer, because of the improvement of
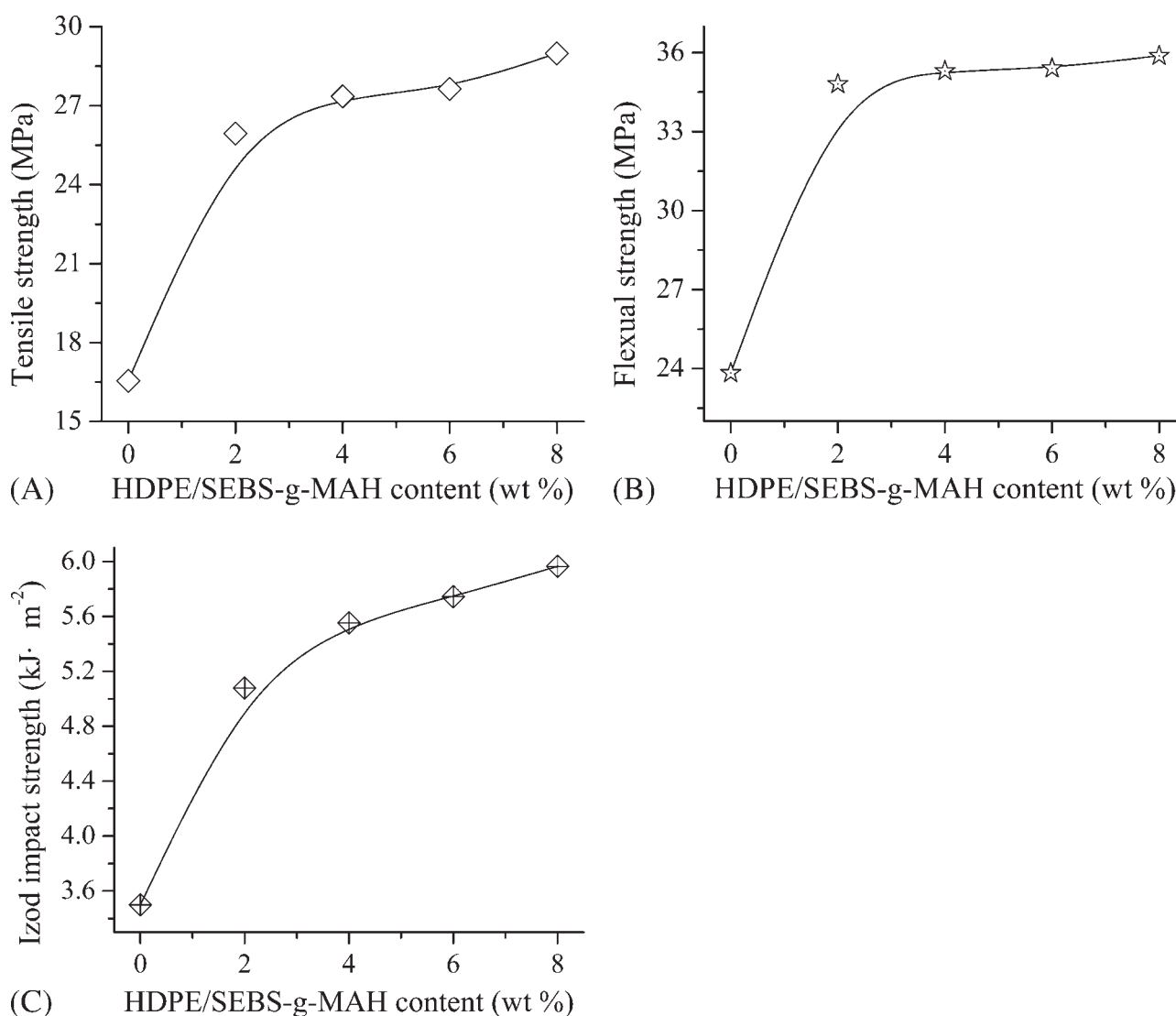

Figure 8 Effect of different HDPE/SEBS-*g*-MAH loadings on the mechanical properties of HDPE/wood flour composites (the content of wood flour was fixed on 40 wt %).

interfacial adhesion between wood flour and HDPE. It can be seen from Figure 8 that the mechanical properties of the composites increased with the increase in compatibilizer loadings. When the addition of HDPE/SEBS-g-MAH was 2 wt %, tensile strength and flexural strength of composites reached 25.9 and 34.8 MPa in comparison of 16.5 and 23.8 MPa (without HDPE/SEBS-g-MAH), increasing by 157% and 146%, respectively. The Notched Izod impact strength reached 5.08 kJ m^{-2}, increasing by 145% in comparison of system without compatibilizer. This result can be explained by their strong interfacial adhesion between wood flour and HDPE. It can combine two components with poor compatibility together and allow the transference of the stress from HDPE matrix to wood flour, so the mechanical strength of the composites system increased.

Dynamic mechanical analysis

Dynamic mechanical measurements can provide information about interaction between molecules in the composites.[22–24] Figure 9 presents the curves of temperature dependence on the dynamic mechanical properties for materials investigated in the study. In Figure 9(A), tan δ was shown as a function of temperature for HDPE, HDPE/wood flour composites, and HDPE/wood flour composites with 4 wt % compatibilizers (Sample 6). There was one major transition which presented γ transition of HDPE at about −130°C. This major transition can give information about the interfacial behavior of composites. It can be seen that the damping peaks of the compo-

sites broadened and the peak amplitude was decreased, compared with HDPE. This was probably due to a retardation of the relative motion of lamella.[25] When the compatibilzer was added to the composites, the peak amplitude was decreased. This is can be explained that strong interaction between wood flour and HDPE led to decrease of the number of molecular segments, because of improved adhesion between wood flour and HDPE. In Figure 9(B), storage modulus (E') was shown as a function of temperature for HDPE, HDPE/wood flour composites, and HDPE/wood flour composites with 4 wt % compatibilizers (Sample 6). It can be seen that the E' of HDPE/wood flour composites was higher than that of HDPE. This means that HDPE with wood flour had enhanced stiffness. Compared with HDPE/wood flour composites, the addition of 4 wt % compatibilizers (Sample 6) resulted in increase of E'. This phenomenon indicated that adhesion between wood flour and HDPE matrix was enhanced, leading to higher stiffness of the composites than that of unmodified system.

Morphology analysis of HDPE/wood flour composites

Observation of the fracture surfaces of the composites by SEM can provide the information of adhesion between wood flour and HDPE matrix. From Figure 10(A), it can also be observed that wood flour embedded in HDPE matrix. The interphase region between the wood flour and HDPE matrix was clean, and gaps in the interphase region was very
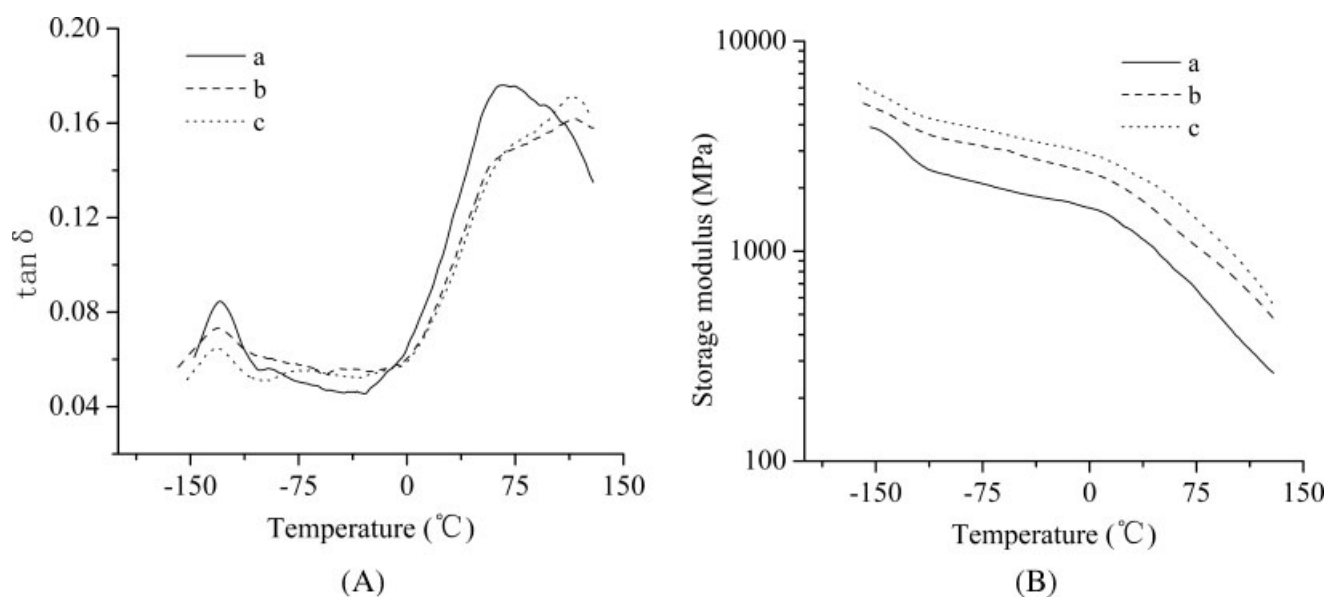

Figure 9 Dynamic mechanical spectra for materials. (a) HDPE. (b) HDPE/wood flour composites (HDPE/wood flour = 60/40). (c) HDPE/wood flour composites with compatibilizer (HDPE/wood flour/(HDPE/SEBS-g-MAH (Sample 6)) = 56/40/4).
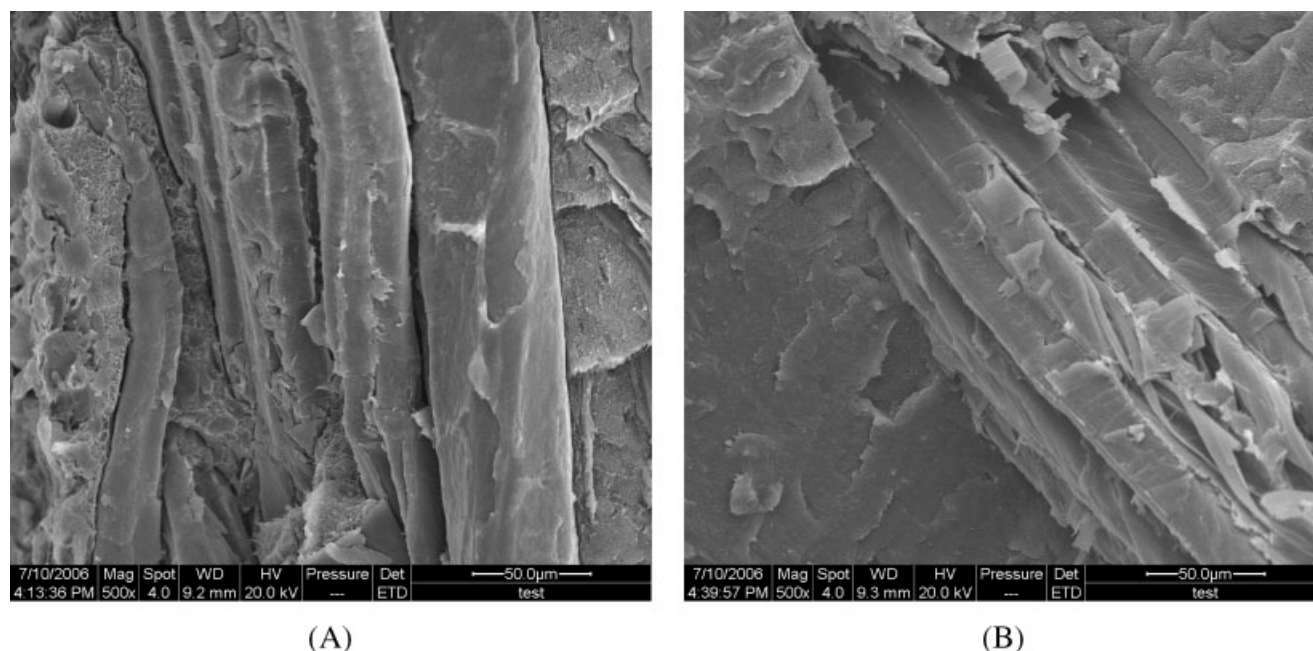
Figure 10 SEM micrographs of fractured surfaces of composites and the scales were all 500×. Composition (weight ratio): (a) HDPE/wood flour = 60/40. (b) HDPE/WOOD flour/(HDPE/SEBS-*g*-MAH (Sample 6)) = 56/40/4.

obvious which indicates poor adhesion between the surfaces. This led to weak mechanical properties. On the other hand, from Figure 10(B) when adding 4 wt % HDPE/SEBS-*g*-MAH to the composites system, wood flour was tightly embedded into the HDPE matrix and no obvious gaps could be seen in the interphase region and some wood flours were torn up. This phenomenon can be explained that HDPE/SEBS-*g*-MAH improved the adhesion between wood flour and HDPE matrix, due to the fact that there are esterification between HDPE/SEBS-*g*-MAH and wood flour, and entanglements between HDPE/SEBS-*g*-MAH and HDPE. In macroscopic aspect, it behaved that the mechanical properties of composites can be obviously increased, which was in agreement with results above.

CONCLUSIONS

HDPE/SEBS-*g*-MAH prepared by means of torque rheometer was found to be an effective compatibilizer for HDPE/wood flour composites. The experimental results showed that MAH indeed grafted on HDPE/SEBS by FTIR analysis and the torque increased with increasing the content of maleic anhydride and dicumyl peroxide. Styrene may increase the graft reaction rate of MAH and HDPE/SEBS. When HDPE/SEBS-*g*-MAH was added to HDPE/wood flour composites, tensile strength and flexural strength of composites can reach 25.9 and 34.8 MPa in comparison of 16.5 and 23.8 MPa (without HDPE/SEBS-*g*-MAH), increasing by 157% and 146%,

respectively. Because of the incorporation of thermoplastic elastomer in HDPE/SEBS-*g*-MAH, the Notched Izod impact strength reached 5.08 kJ m^{-2}, increasing by 145% in comparison of system without compatibilizer. This result demonstrated that HDPE/SEBS-*g*-MAH played an important role in improving the interface adhesion between wood flour and HDPE matrix and the result was also proved by the tests of dynamic mechanical properties and SEM.

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