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Effects of Compatibilizers on Composites of Acorn Shell Powder and Low Density Polyethylene

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Binary bio-composites of acorn shell (AS) and low density polyethylene (LDPE) were prepared via a twin-screw extruding method. The mechanical properties of the composites decreased with increasing AS content, and all composites maintained similar tensile strength as expected based on the Nicolais-Narkis model, indicating weak adhesion between AS and LDPE. The effects of three compatibilizers, ethylene-acrylic acid (EAA), ethylene-vinyl acetate (EVA), and maleic anhydride grafted polyethylene (PE-g-MAH) on the composites were also studied. The results showed that the three compatibilizers improved the mechanical properties of composites at different levels, and the PE-g-MAH compatibilizing system showed the best mechanical strength, which was increased by about 80% from that of the control. Micro-morphologic investigation revealed a rough fractured surface, indicating that the addition of compatibilizers improved the interfacial bonding properties of the matrix materials LDPE matrix. Dynamic mechanical thermal analysis (DMA) further confirmed that the addition of compatibilizers significantly improved the compatibility of blending components and changed the properties of LDPE matrix materials.

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INTRODUCTION

In recent decades, wood plastic composites (WPCs) have received much attention because of their high output, reasonable price, enhanced mechanical properties, high corrosion resistance, dimensional stability, machinability, and recoverability (Afrifah *et al.* 2010; Fabiyi *et al.* 2010, 2011; Soury *et al.* 2009; Wei *et al.* 2013; Wechsler and Hiziroglu 2007). WPCs are usually produced by mixing plant fibers and thermosets (epoxy and phenolic resins) or thermoplastics such as high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) (Bengtsson *et al.* 2005; Faruk and Matuana 2008; Petchwattana and Covavisaruch 2013; Safinas *et al.* 2013). WPCs are widely used in the automotive, marine, construction, and furniture industries, among others. Normally, additives such as compatibilizers, coupling agents, stabilizers, reinforced agents, colorants, and lubricants are added to a compositing system to improve the properties (Bengtsson and Oksman 2006; Lee and Wang 2006; Nachtigall *et al.* 2007). Among these additives, compatibilizers have received much attention because of

their compatibilizing characteristics, which bestow WPCs with improved mechanical properties (Fabiyi *et al.* 2008; Hosseinaei *et al.* 2012; Huang *et al.* 2013). For PE- and PP-based WPCs, polymers such as PP-g-MAH and PE-g-MAH (MAH is maleic anhydride), ethylene-acrylic acid (EAA), and ethylene-vinyl acetate (EVA) containing several carbonyl groups can be applied to improve their compatibility and comprehensive properties (Kazemi Najafi 2013 ; Li *et al.* 2003; Wu and Wu 2006). For WPCs, how to choose appropriate compatibilizers is a key issue.

There are several lignocellulosic fibrous materials that have been used in the production of plastic composites either as filler or reinforcement. Acorn shell could be also be used. Acorn, an important wildlife forestry source, is the seed for regeneration of oak trees. There are about 900 known oak tree species worldwide, and the annual yield of acorns is over 30 million tons. However, the content of amylopectin of acorn kernels is relatively high, such that they cannot be digested easily. Also, acorn kernels are rich in low-toxic tannin acid, which is difficult to be removed. So large amounts of acorn resources are abandoned annually.

Acorn shell (AS) is rich in cellulose and lignin, and compared with non-food vegetable fibers, AS has advantages such as strong mechanical intensity, resistance to rotting, high chemical stability, and strong hydrophobicity (Koenig and Haydock 1999). In this study, AS/LDPE composites were prepared via twin-screw extrusion followed by injection molding, and their properties were measured. The effects of several compatibilizers on their microstructural, mechanical, and thermal properties were also studied. The objective of this study was to investigate the feasibility of preparing AS-based WPCs.

EXPERIMENTAL

Materials

Acorns were obtained from Purple Mountain (Nanjing, China). Acorn shell powder particles (100 to 200 mesh) were prepared in our laboratory, and the acid-insoluble lignin, holocellulose, pentosan, tannin, and ash contents of acorn shell were determined to be 34.22, 56.69, 21.09, 9.18, and 2.56%, respectively. LDPE (2420H) was purchased from Yangzi Petrochemical Co., Ltd. Ethylene acrylic acid (EAA) and ethylene vinyl acetate (EVA) resins were purchased from Dow Chemical Co., Ltd. Polyethylene grafting maleic anhydride (PE-g-MAH) was prepared by our laboratory (the grafting percentage was 0.9%).

Composite Preparation

First, AS powder (100 to 200 mesh), LDPE, and other compatibilizers were mixed in the required proportions, and then the mixture was introduced into a SHENMA SHR-5A high-speed mixer (China) at 1,500 r/min for 10 s to obtain a homogeneous dispersion.

Second, the blends were extruded on a CTE20 (China) twin screw extruder, and then the prepared samples were granulated into granules on a XH-B02 strand granulator (China). The extruder had five heating zones situated around the head and at the die. The preparation conditions were as follows: the temperatures of the five heating zones were 140, 155, 165, 160, and 150 ^{o}C; the sheering speed was 300 rpm; the adding rate of raw

materials was 15 g/min; and the vacuum pressure was -0.04 MPa. The composites are denoted as follows: AS30/LDPE70 means 30 wt % of AS and 70 wt % of LDPE.

Mechanical Properties Tests

The samples were transformed into special forms by injection with a MiniJet II injection molding machine (HAAKE, Germany) for different mechanical tests. The tensile test samples were in the form of a dog bone according to ASTM D638 type V standard. The tensile test region of specimens was 3.18 ± 0.125 mm thick, 3.18 ± 0.125 mm wide, and 7.62 ± 0.300 mm long.

Flexural and impact testing samples had an oblong form; the width was 10 ± 0.40 mm, the thickness was 3.94 ± 0.25 mm, and the length was 80.00 ± 0.50 mm. A 45° V-type groove was cut on the flexural testing sample, and the impact strength of the sample was measured with a XJJY-5 simple support beam bridge impact testing machine. The tensile and flexural properties were tested by a CMT4303 SANS universal testing machine. Five sample pieces were prepared for each group and tested at 10 mm/min and 25 °C.

Scanning Electron Microscopy (SEM)

Micrographs of the impact resistance fracture surface of testing samples were observed by magnifying 100 times with an S-3400N scanning electron microscope (Hitachi, Japan) under conventional secondary electron imaging conditions at an accelerating voltage of 20 kV.

Dynamic Mechanical Thermal Analysis (DMA)

The storage modulus (E') and loss factor (tan δ) were measured by a Q800 dynamic mechanical thermal analyzer (TA, America), at a heating speed of 3 °C/min and a temperature range from -50 to 110 °C; all samples were measured in tensile mode.

RESULTS AND DISCUSSION

Mechanical Properties

Unmodified composites

The mechanical properties of composites with different weight ratios are shown in Table 1. The tensile strength, breaking elongation, flexural strength, and impact strength each exhibited a general downward trend with increasing AS content. The tensile and flexural strengths were decided by the continuity of the matrix (Lee *et al.* 2006). AS powders were scattered into the matrix LDPE; the addition of AS powder could reduce the continuity of LDPE, leading to the reduction of mechanical properties in the composites.

The flexural modulus increased from 450 MPa (20% AS) to 850 MPa (60% AS), indicating that the composites became increasingly more rigid. Due to the high flexibility of LDPE, when the samples were measured by an impact testing machine, a higher AS content bestowed the composites with poorer continuity and lower impact energy was absorbed, resulting in the changing trend of impact strength.

For the composites' mechanical properties, the influencing factors are more complicated. In addition to the matrix's chemical structure and the interface adhesion, the

components freed from the acorn powder are also important. These factors jointly affect the copolymers' mechanical properties.

Table 1. Effects of Different Compatibilizers on the Mechanical Properties of AS/LDPE Composites

Formulations	Tensile Strength (MPa)	Breaking Elongation (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (kJ/m^2)
LDPE100	19.41	227.73	—	—	—
LDPE80/AS20	15.16	81.25	17.12	452.45	10.23
LDPE60/AS40	13.21	64.85	15.97	651.05	7.67
LDPE50/AS50	8.56	37.98	15.03	740.31	5.14
LDPE40/AS60	7.42	35.46	14.52	856.31	2.91
PE-g-MAH2.5/LDPE47.5/AS50	12.71	37.55	27.01	890.68	5.31
PE-g-MAH5.0/LDPE45.0/AS50	15.2	39.37	27.63	957.39	5.86
PE-g-MAH7.5/LDPE42.5/AS50	16.55	39.23	27.57	928.10	5.73
PE-g-MAH10/LDPE40/AS50	17.01	43.42	27.62	906.65	6.11
PE-g-MAH15/LDPE35/AS50	18.06	47.22	26.92	859.63	6.29
EAA2.5/LDPE47.5/AS50	10.05	38.94	17.21	789.56	5.42
EAA5.0/LDPE45.0/AS50	11.39	41.23	19.92	886.80	5.72
EAA7.5/LDPE42.5/AS50	12.14	42.51	18.94	890.14	6.31
EVA2.5/LDPE47.5/AS50	8.94	38.12	15.94	815.45	5.94
EVA5.0/LDPE45.0/AS50	9.29	43.24	16.91	860.33	7.49
EVA7.5/LDPE42.5/AS50	9.43	42.31	16.31	884.21	6.32

The interfacial adhesion strength between AS and LDPE is weak. If the penetration between AS and LDPE is ignored, the tensile strength of AS/LDPE composites can be calculated with the Nicolais–Narkis (NN) model as follows (Finkenstadt *et al.* 2007),

$$\sigma = \sigma_0 \left[1 - 1.21 V_f^{2/3} \right]$$

(1)

where σ is the estimated AS/LDPE composites' tensile strength (MPa), σ_0 is the tensile strength of pure LDPE (MPa), and V_f is the volume fraction of acorn shell in the composite.

Table 2. Theoretical Values and Measured Values of Tensile Strength of AS/LDPE Composites

Formulations	Measured values / MPa	Density /g·cm^{-3}	V_f	Theoretical values / MPa
LDPE100	19.41	0.91	0	—
LDPE80/AS20	15.16	0.97	0.1473	12.85
LDPE60/AS40	13.21	1.03	0.3209	8.40
LDPE50/AS50	8.56	1.07	0.4121	6.40
LDPE40/AS60	7.42	1.10	0.5165	4.29

The results for tensile strength estimated based on the NN model are shown in Table 2. Obviously, the theoretical values corresponded closely to the measured values, indicating that the interfacial adhesion between AS and LDPE was weak. Therefore, it

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was easy to separate the matrix LDPE from acorn shell particles during tensile testing, and in this case, the composites' tensile strength was decided by the continuity of LDPE.

Compatibilizing modified systems

To ensure excellent machinability, high value, and applicable mechanical properties in composites, an LDPE50/AS50 compositing system was chosen for research on compatibilizing modification. Certain proportions of LDPE were replaced by three compatibilizers: EAA, EVA, and PE-g-MAH. The variations of the comprehensive mechanical properties of the modified composites with different replacement ratios are also presented in Table 1.
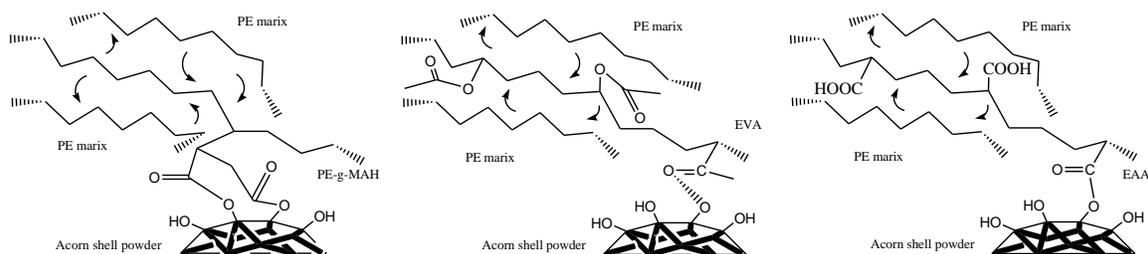
Fig. 1. Compatibilizing modification mechanism of PE-g-MAH, EAA, and EVA

The tensile, flexural, and impact strengths were all improved greatly by adding a little EAA, EVA, or PE-g-MAH (Table 1). Generally, for the three modified systems, the optimum addition was 5 wt% in each case, and too much or too little addition could not significantly improve the comprehensive mechanical properties of the composites. Compared with the unmodified system, the tensile and flexural strengths of modified system with 5 wt% of PE-g-MAH increased by 77.6% and 83.8%, respectively. However, the tensile and flexural strengths both increased by about 33% in the EAA-modified system, and both by less than 15% in the EVA-modified system. Therefore, PE-g-MAH was judged to be the optimal compatibilizer for AS/LDPE composites. The anhydride, carbonyl, and carbonyl groups on the three compatibilizers could link with the hydroxyl groups on the AS powder surface *via* esterification or Van der Waals forces, and their non-polar or weak polar molecular chain is compatible with LDPE, thereby significantly improving the interfacial compatibility of the two phases and the mechanical properties of the composite materials.

A possible modifying mechanism is shown in Fig. 1. Compared with EVA and EAA modifying systems, the anhydride groups on PE-g-MAH display stronger reactivity with the hydroxyl groups on the AS powder surface and show stronger interface adhesion between AS powder and the matrix material. The EAA modifying system shows better mechanical properties than the EVA system; to some extent, this is due to the formation of ester groups between EAA and AS, leading to stronger interface adhesion than are present with Van der Waals forces in the EVA modifying system.

Table 1 also displays the composites' breaking elongation and impact properties. The addition of AS powder reduced the continuity of LDPE, so breaking elongation remained at a low level, within 35 to 50% for all composites. Additionally, all modified composites displayed excellent impact strengths, above 5 kJ/m^2. With the addition of one of the three compatibilizers, the flexural modulus, breaking elongation, and impact

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strength all increased irregularly. In addition, many samples were not broken after testing, indicating that the addition of a compatibilizer endows the copolymers with increased flexibility. For the PE-g-MAH-modified system, the introduction of the polar group in MAH improved the composites' rigidity and compatibility simultaneously, and changed the intrinsic properties of LDPE. Several factors jointly affected the composites' mechanical properties, and some of their properties changed irregularly.

Morphology

Figure 2 shows SEM images of an impact fracture surface of the composites in different compatilizing systems under 100 x magnification. Obviously, LDPE forms a polymer matrix, whereas AS powder is dispersed into the matrix LDPE. Therefore, it is reasonable that the composites' mechanical properties are determined by LDPE and the interface adhesion between the two phases. For the unmodified composite, the images display a relatively glossy and smooth fracture surface, which reveals certain brittle fracture features. The fracture surface is full of pits and exposed acorn powder, indicating that the interface adhesion between AS and LDPE is weak. Although all the fracture surfaces of the modified composites have an uneven appearance, LDPE displays a mesh structure, indicating that plastic deformation took place in the composite.

（a）AS50/LDPE50×100SE

（b）AS50/PE-g-MAH5/LDPE45×100SE

（c）AS50/EAA5/LDPE45×100SE

（d）AS50/EVA5/LDPE45×100SE
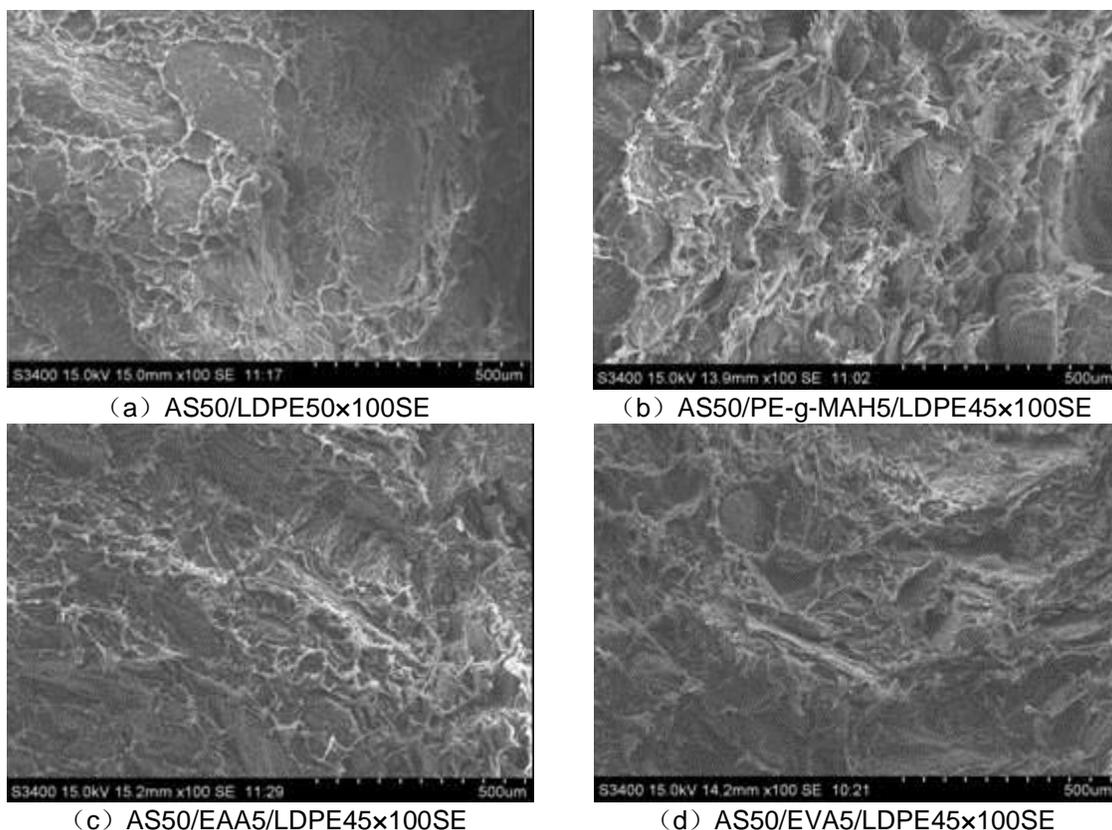
Fig. 2. SEM microphotographs of anti-impact fracture surfaces of AS/LDPE composites with different mixed proportions

Compared with the EAA and EVA modifying systems, the fracture surface of the PE-g-MAH-modified composite was rougher, and more mesh structures could be seen on the fracture surface. All these features indicate that the PE-g-MAH-modified composite

may possess the best mechanical properties, which is in accordance with the results of the mechanical property tests. In addition, during the preparation of composites at high temperature and high shearing, with the help of compatibilizers, there exists strong hydrogen bonding between carbonyl groups of the matrix material and hydroxy groups on the surface of acorn shell powder; the molecular diffusion degree may be greatly increased, leading to increased interface thickness and interface adhesion, which produced an excellent tensile property similar to traditional plastics.

Dynamic Mechanical Properties of Copolymers

The dynamic mechanical behaviors of the different modified AS/LDPE composites were studied. The dynamic mechanical curves are summarized in Fig. 3. Figure 3a depicts the curves of the storage modulus (E'). All curves display a similar trend: E' decreases sharply in a broad range from -50 to 110 ^{o}C. Below -50 ^{o}C, the matrix materials are in a glassy state and the molecular segmental motions of the matrix are frozen, so E' remains at a high level, above 2500 MPa. With increasing temperature, the frozen segmental structure begins to relax gradually, and above 80 ^{o}C, E' values are all close to a constant at a very low level, below 500 MPa, indicating higher molecular chain motions in the composite. Compared with unmodified composites, all modified composites have larger E', with similar values at the same addition. In the PE-g-MAH-modified system, E' increases greatly with increasing PE-g-MAH content below 10 wt%, while E' does not change obviously above 10 wt%. High-content polar groups and excellent interface adhesion bestow the composites with larger E', similar to the changing trend of mechanical properties.
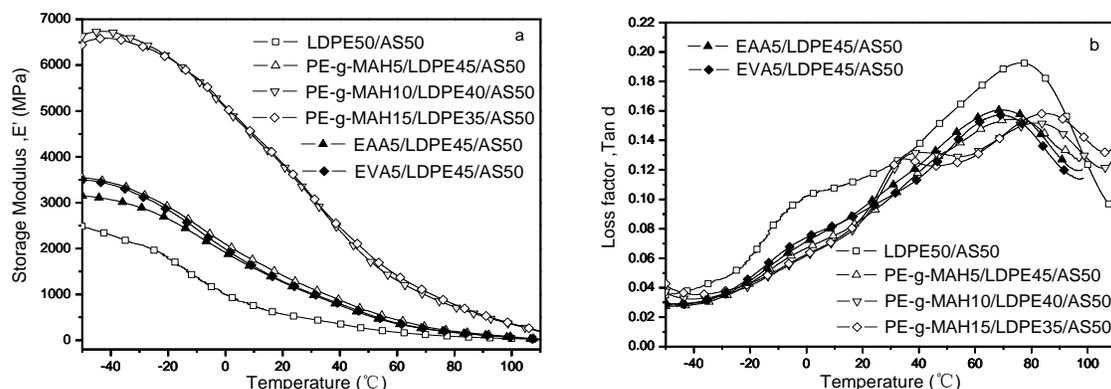
Fig. 3. DMA curves of AS/LDPE composites with different mixed proportions

Figure 3b depicts the composites' loss factor (tan δ) curves. Almost all tan δ curves display at least one peak in the range of 70 to 90 ^{o}C, and many composites display another peak in the range of -10 to 40 ^{o}C. Neither peak corresponds to the glass-transition temperature (T_g), and generally, the T_g of LDPE ranges from -105 to -90 ^{o}C. The high-temperature peak in the tan δ curve is assigned to the α-relaxation transition of the matrix, while the low-temperature peak corresponds to the β-relaxation transition, and α-relaxation and β-relaxation transition correspond to crystalline and amorphous region of LDPE, respectively (Safinas *et al.* 2013). In the three modified systems with the same addition of 5 wt%, the tan δ curves display a similar changing trend. The low-temperature peak almost disappears, and the intensity of the high-temperature peak decreases. The reason for this may be that the compatibilizer limits the movement of the matrix's

molecular chains, leading to a low internal friction in the amorphous and crystalline region of LDPE.

For the PE-g-MAH-modified system, when the composites contain above 10 wt% of PE-g-MAH, another relaxation peak at about 30 $^\circ$C appears, and the α-relaxation transition shifts to high temperature with increasing PE-g-MAH content. The appearance of relaxation peak at about 30 $^\circ$C is probably because excessive addition of PE-g-MAH changes the intrinsic characteristics of the matrix. In addition, the added compatibilizers and many free components freed from the acorn shell powder also form an adsorbed film on the surface of the AS powder. More energy is needed to relax the molecular chains of LDPE that attach to the film on the AS surface, causing α-relaxation transition to a higher temperature (Safinas *et al.* 2013).

CONCLUSIONS

1. The compatibilizers EAA, EVA, and PE-g-MAH all improve the mechanical properties of the composites. Compared with the EAA- and EVA-modified systems, the PE-g-MAH-modified system shows the highest mechanical strength.

2. SEM analysis displays rough impact fractured surfaces for compatibilizing systems, which reveals that the addition of compatibilizers improves the interfacial bonding properties of the matrix materials. DMA further confirms that the addition of compatibilizers significantly improves the compatibility of blending components and changes the properties of LDPE matrix materials.

3. This study presents a novel way of utilizing acorn shell and can be used as a reference for all shell resources. It also has significant implications for the design of fully shell-based novel materials with desirable properties.

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