Carbohydrate Polymers 80 (2010) 927–933

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Mechanical properties and size stability of wheat straw and recycled LDPE composites coupled by waterborne coupling agents

Xuan Kuang [a,b], Rui Kuang [b], Xiaodong Zheng [b], Zhiling Wang [a,*]

[a] College of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China
[b] College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China

ARTICLE INFO

Article history:
Received 28 November 2009
Received in revised form 3 January 2010
Accepted 7 January 2010
Available online 11 January 2010

Keywords:
Wood thermoplastic composites
Coupling agent
Isocyanate
Waterborne polyacrylate latices

ABSTRACT

In this study, two novel coupling agents (CAs) were used for manufacturing wheat straw (WS)/recycled low density polyethylene (LDPE) composites, one being waterborne polyacrylate latex (PAL), the other being blend prepared from polymethylene polyphenylene isocyanate (PAPI) and the PAL. The effects of the PAL components, the ratio of PAPI/PAL, the loaded content of the CA composed of PAPI and PAL, and the ratio of WS/recycled LDPE on the mechanical properties and thickness swelling stability of the composites were investigated. The PAL could improve composite quality, while the CA composed of PAPI and optimized PAL resulted in a more significant improvement. As the loaded content of the CA with PAPI/PAL of 30/70 was 4.5 wt%, the composite behaved the maximum internal bonding (IB) strength and the IB strength after soaked in boiling water for 2 h (2 h WIB). IB strength were significantly enhanced with WS content ranging from 90 to 40 wt%.

1. Introduction

Faced with serious shortage of wood resources in China, the wood industry is showing increased interest in production of lingo-cellulose based composites from other materials. One of the potential candidates is the composites using agricultural residues and recycled thermoplastics. Wheat straw (WS) is a renewable agricultural by-product. In China, more than 1.2×10^{12} tons of WS is produced annually (Han, Yan, Liu, & Hu, 2002). Although, the chemical composition of WS is similar to wood that is made of cellulose fibers in an amorphous matrix of hemicelluloses and lignin, but its structure is more loose and its strength is lower; it also contains less lignocellulose cells and more ash and extrusion materials with lower molecular weights than wood. Furthermore, the silica and a waxy substance on its exterior surface prohibit WS to be bonded by conventional adhesives such as urea formaldehyde (UF) or phenol formaldehyde (PF) (Mo, Cheng, Wang, & Sun, 2003; Yao, Xu, & Feng, 2003).

Wood–plastic composites (WPCs) enjoyed an outstanding annual growth rate of 9.8% and have gained increased recognition by consumers because of the success in applications of many building materials (Markarian, 2005; Pritchard, 2004), such as decking, docks, railings, fencing, landscaping timbers, construction template, indoor furniture, etc., partially due to the need to replace solid wood and neat plastic. WPCs were typically manufactured through injection molding or extrusion processes, which dispersed wood component as filler at 40–60 wt% into a thermoplastic or thermoset plastic matrix. Wood flour in sizes ranging from 20 to 100 mesh was frequently used for WPCs, such as pine, maple and oak. The fibers of wood or other natural plant were available. The most popular thermoplastic used in Europe was virgin polypropylene (PP), while polyethylene (PE), polystyrene and polyvinyl chloride (PVC) were being used in America, India, Singapore, Malaysia, Japan and China.

Hydrophilic wood or natural plant fibers and hydrophobic thermoplastics are incompatible in thermodynamics, which results in a weak adhesion strength at the two-phases interface. Therefore, the poor ability to transfer stress from the matrix to the reinforcing filler leads to a decrease of mechanical properties and size stability for WPCs under moist conditions. Thus, coupling agents (CAs) should be incorporated to improve the compatibility. A number of studies have demonstrated that maleated anhydride modified polypropylene (MAPP) could enhance the interfacial adhesion strength and mechanical properties of WPCs (Adhikary, Pang, & Staiger, 2008; Karmarkar, Chauhan, Modak, & Chanda, 2007; Keener, Stuart, & Brown, 2004; Kim, Lee, & Choi, 2007; Lee, Yang, Kim, Jeong, & Lim, 2004). Snijder and Bos (2000) reported that the molecular weight of MAPP was more important than maleated anhydride (MA) content in the MAPP for coupling efficiency (Snijder & Bos, 2000). Kuo, Wang, Chen, Hsueh, and Tsai (2009) studied that the tensile strength and modulus of rupture (MOR) of WPCs with a ratio of wood flour/plastic matrix/MAPP/zinc stearate of 47:47:3:3 were larger than those of LDPE and PP themselves. In

* Corresponding author. Tel.: +86 13296597469; fax: +86 0531 82765969.
E-mail address: chm_wangzl@ujn.edu.cn (Z. Wang).

0144-8617/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.01.008

addition, there have also been some other CAs used for WPCs (Bouza, Lasagabaster, Abad, & Barral, 2008; Jun, Wang, Chang, & Kai, 2008; Zou, Xiong, & Tang, 2008). Bengtsson and Oksman (2006) used vinyltrimethoxy silane for coupling wood flour/high density polyethylene (HDPE) composites. The toughness, impacts strength and creep property of the composites were superior to those without silane, but the flexural modulus of coupled samples were much lower than those of non-coupled samples. Karmarkar et al. (2007) introduced a CA, the modified PP (*m*-TMI-g-PP) synthesized by grafting *m*-isopropenyl-α, α-dimethylbenzyl-isocyanate (*m*-TMI) onto isotactic polypropylene. The *m*-TMI-g-PP improved the mechanical properties of composites. In our previous work, we reported a CA, the free isocyanate group-terminated urethane prepolymer synthesized by polyether polyols and excess amount of polymeric diphenylmethane diisocyanate (pMDI). The CA significantly improved the mechanical and physical properties of WS/recycled polyethylene (PE) composites (Wang, Wang, Zhang, Wang, & Ren, 2009).

For the WPCs coupled by MAPP and silane, the moisture content in raw materials plays a very important role in coupling effectiveness. Godavarti, Williams, and Deaner (2001) pointed out that achieving the improved properties of polyolefin and wood fiber composites coupled by MAPP, the wood fiber was a special prepared material with less than 0.5 wt% moisture content based on the wood fiber weight. Bengtsson and Oksman (2006) dried wood flour to moisture content of 0.3 wt% in manufacturing WPCs coupled by silane.

To our knowledge, none of current investigations for WPCs dealed with waterborne CAs. In this work, two novel waterborne CAs were used for manufacturing WS/recycled low density polyethylene (LDPE) composites, one being waterborne polyacrylate latex (PAL), the other being blend prepared from polymethylene polyphenylene isocyanate (PAPI) and the PAL. The synthesis of PAL was carried out through seeded emulsion polymerization pathway. WS/recycled LDPE composites were made based on wood board process, that is, a CA was firstly blended with WS and recycled LDPE to coat on them, then the mixture was directly molded into composite boards under high temperature and pressure. Thus, the moisture in the materials was efficiently released during the process. The effects of the PAL components, the ratio of PAPI/PAL and the loaded content of PAPI and optimized PAL as well as the ratio of WS/recycled LDPE on the mechanical properties and thickness swelling stability of the WPCs were investigated. WS and recycled thermoplastics as raw materials also are of prime important for resolving problems of environmental pollution and lack of wood resources.

2. Materials and method

2.1. Materials

PAPI was purchased from Yantai Wanhua Polyurethane Ltd. Co. (Yantai, China), which contains free isocyanate group of 31.3 wt% with an average functionality of 2.7. Industrial grade polyacrylate monomers, namely butyl acrylate (BA), 2-ethylhexyl-acrylate (2-EHA), acrylonitrile (AN), acrylate acid (AA), vinyl acetate (VA) and β-hydroxyethyl acrylate (HEA) were from Dongfang Chem Ltd. Co. (Beijing, China). Analytical grade potassium persulfate (KPS) initiator, sodium dodecyl sulfate (SDS) and polyoxyethykene nonylpheny ether (OP-10) emulsifiers, hydroquinone retarder and ammonia water (25–28 wt%) were purchased from Sinopharm Chemical Reagent Ltd. Co. (Shanghai, China). All chemicals were used as received. Distilled water was used throughout the work. WS was collected from local farmers. Recycled LDPE was purchased from a recycling store, which was derived mainly from post-consumer plastics wastes.

2.2. Preparation and characteristic of CAs

2.2.1. PALs

PALs were synthesized in a two-stage seeded emulsion polymerization pathway. The recipes of four PALs used for composites were listed in Table 1. For each PAL synthesis, the monomers apart from HEA, OP-10 and SDS emulsifiers and distilled water were firstly blended to produce a pre-emulsion. Under stirring, one fourth of the pre-emulsion was poured into a four-neck glass reactor. When heated to 70 °C, one third of the aqueous solution of initiator KPS was then added into the reactor. The constant temperature was kept until the content became blue, seed emulsion was obtained. Continually, the seed emulsion was heated to 75–80 °C, the remainders of the pre-emulsion and the aqueous solution of the initiator were dripped into the reactor for 3 h, respectively. After this, the HEA was fed into the reactor. The polymerization continued for another 2 h. After cooled to room temperature, the pH of the latex was adjusted to 5.5–6.5 using ammonia water. When hydroquinone retarder was added, the polymerization was stopped. The latices were coded as PAL-1, PAL-2, PAL-3 and PAL-4, respectively.

The viscosity of final latices were measured with a circumvolving viscometer (Model NDJ-1, Chengdu, China). Glass transition temperatures (T_g) were determined by a differential scanning calorimeter (DSC, Model ALC-244, Pyris-6, Perkin-Elmer Co., USA) at 10 °C/S scan rate. Infrared (IR) spectra was analyzed using a Fourier Transform IR Spectrometer (Magna 750, America) at room temperature. To determine the solid content of latex, a small amount of PAL was dried at 105 °C in a vacuum furnace to obtain oven-dry polyacrylate. The percentage of solid content was calculated from the initial emulsion weight (w_0) and the oven-dry weight (w), the determining formula is as follows:

$$\text{Solid content } (\%) = \frac{w}{w_0} \times 100$$

2.2.2. Blends from PAPI and PAL

Due to the high reactivity of free isocyanate groups in PAPI molecule at the room temperature, PAPI is impossible to occur stability in an aqueous latex for a long period. So for the preparation of the CA composed of PAPI and PAL, it should be finished before coated on WS and recycled LDPE within 1 h. PAPI and a PAL was mixed at weight ratio of 70/30, 50/50 and 30/70, respectively. Stirring was essential to obtain a homogeneous product.

Table 1
Recipes for preparation of four PALs.

PAL examples	Monomers						Emulsifiers		Initiator	H_2O (ml)
	2-EHA (g)	BA (g)	VA_C (g)	HEA (g)	AA (g)	AN (g)	SDS (g)	OP-10 (g)	KPS (g)	
PAL-1	80	0	7	0	2	10	0.8	1.5	1.5	190
PAL-2	0	40	47	0	2	10	0.8	1.5	1.5	190
PAL-3	0	80	7	0	2	10	0.8	1.5	1.5	190
PAL-4	80	0	2	5	2	10	0.8	1.5	1.5	190

2.3. Preparation of WS/recycled LDPE composites

2.3.1. Pretreatment of raw material

WS was first cut into pieces of 4–6 cm in length using a wood piece cutter (Model BX-213, Germany), and then ground into slightness particles using a mill (Model PSKM330, Germany). After this, the particles were sieved using a sieve shaker. Particles of more than 0.2 mm in diameter were further dried to 4.0 wt% moisture content based on dried WS weight, and then sealed in plastics bags for further study. Recycled LDPE was ground into about 4 mm × 2 mm fragments using a plastic smashing device, and also stored in plastics bags for subsequent use.

2.3.2. Composite preparation

The dried WS particles and the LDPE fragments were mixed in a high-intensity mixer (Model FM 130DPS, Beijing, China) for 5 min at room temperature. At a high pressure, a CA was sprayed into the mixer for another 5 min. The final mixture was pre-pressed into the formed mat in the wood mould measuring 300 mm × 300 mm. The mat was hot pressed into a 300 mm × 300 mm × 7 mm final board using a hot-presser (Model 80 tons, Shanghai, China). Triplicates were performed for each specific composite. The finished composite boards were conditioned in a laboratory at room temperature of 25 ± 1 °C for at least 8 days, and then cut into samples of various sizes for further testing.

2.3.3. Performance testing of composites

Mechanical and physical properties of prepared composites were evaluated according to standard methods GB/T 4897.7 (Shiying, Ling, & Fengshan, 2003) and GB/T 17657 (Shiying, Zhiqiang, & Yaluan, 1999). The mechanical properties including internal bonding (IB) strength, the IB strength after soaked in boiling water for 2 h (2 h WIB), MOR, and modulus of elasticity (MOE) were tested using a testing machine (SHIMADZU, AG-200A, Japan). The specimen for IB test was effectively bonded with a polyvinyl acetates glue, and then was subjected to a tensile loading at a uniform crosshead speed of 2 mm/min until failure occured. The loading direction was vertical to the surface of specimen board surface. The determining formula is as follows:

$$\mathrm{IB} = \frac{P_{\max}}{l \times b}$$

where $P_{\max}$ is the maximum load as specimen failure, l and b are specimen length and width, respectively. Physical properties, namely densities and the thickness swell stability after immersed water for 24 h (24 h TS) were evaluated. For the test of 24 h TS, a sample was firstly soaked in water at a temperature of 25 ± 1 °C, the board thickness h_1 and h_2 were measured before and after water immersion for 24 h, respectively. The following formula is used.

$$\text{24 h TS } (\%) = \frac{h_1 - h_2}{h_1} \times 100$$

All reported values are the average of nine samples from three replicated composites. Square samples (50 mm × 50 mm) were used for testing IB, 2 h WIB, 24 h TS, and densities, rectangle pieces (150 mm × 50 mm) were used for testing MOR and MOE. All measurements were performed at a ambient temperature of 25 ± 2 °C and 50 ± 5% relative humidity.

2.3.4. Experiment design and data analysis

The effects of four variable factors on composite properties were examined, which were the PAL components, the ratio of PAPI/PAL, the load contents of the CA comprised of PAPI and PAL as well as the ratio of WS/recycled LDPE. The previous investigation showed that the hot pressing time of 1.1 min/mm, the maximum pressure of 4.0 MPa and the hot pressing temperature of 180 °C could met the requirements of finishing boards of different densities (Wang et al., 2009). Thus, these processing parameters were chosen for all the subsequent composite manufacture.

For all the described experiments, data was analyzed using a SAS software (Yingchuang institute, Model 8.0, Guangzhou, China, 1999). Analysis of variance (ANOVA) and least significant difference (LSA) ($P = 0.05$) were performed.

3. Results and discussion

3.1. Influence of monomer components on PAL properties

The properties of four PALs synthesized with various fraction of monomers 2-EHA, BA, VAc and HEA, as well as same fraction of AA and AN monomers were indicated in Table 2. As seen, the constitute and content of monomers in recipes resulted in a sharp difference for the physical nature of resultant copolymers. Obviously, PAL-1 behaved the lowest T_g (−58.3 °C) and viscosity (231.4 mPa s) in the PALs. This is contributed to a higher content 2-EHA used in its polymerization. 2-EHA molecule involved a softer alkyl side chain than other used monomers. Thus, a weaker interaction existed among the copolymer molecules of PAL-1. Contrastively, PAL-2 and PAL-3 showed obvious the reversing characteristic upon increasing the T_g and viscosity due to copolymerized hard monomer VAc content increased. The highest T_g, −8.7 °C for PAL-2 in four PALs originated from the use of a higher content VAc in polymerization.

It is well known that cross-linking agents could reinforce the polymer networks. PAL-4 and PAL-1 employed the same fraction soft monomer 2-EHA, the only difference in monomer components was the EHA content. The T_g of PAL-4 with HEA was −48.5 °C, while the T_g of PAL-1 without HEA decreased to −58.3 °C. Especially, another purpose for using HEA in PAL-4 copolymerization was to introduce more hydroxyl groups upon its copolymer molecules. To quantitatively characterize the structure, PAL-4 was picked out and analyzed by IR spectra, the result was shown in Fig. 1.

The absorption of stretching vibration C=C at 1640 cm^{-1} had not been found. This reflected that there was no residual monomer in the copolymer. As expected, the absorption assigned to O—H stretching vibration occurred at around 3450 cm^{-1}, which was from HEA copolymerizing. Additionally, the characteristic absorption associated with polyacrylates were also found, some from stretching vibrations were assigned as follows: 2995–2953 cm^{-1}, C—H; 1739.4 cm^{-1}, C=O; 1271, 1240 cm^{-1}, C—O; around 1173.3 cm^{-1}, C—O—C.

3.2. Influence of PAL components on the composite properties

Based on exploring experiments, each of above four PALs with different components at a load of 4.0 wt% (based on dried WS weight) was used for manufacturing WS/recycled LDPE composites. The weight ratio of WS/recycled LDPE of 20/80 was chosen. The average values of obtained composite properties were indicated in Table 3. It was seen that the PALs could improves the mechanical properties and thickness swell stability, such as, the IB of composites with PAL-4 increased from 0.0980 to

Table 2
Properties of synthesized four PALs.

PAL samples	Solid content (wt%)	Emulsion viscosity (mPa s)	Store life (months)	T_g (°C)
PAL-1	35.1	231.4	>12	−58.3
PAL-2	35.3	436.3	>12	−8.7
PAL-3	35.6	584.1	>12	−24.6
PAL-4	35.4	869.8	>12	−48.5

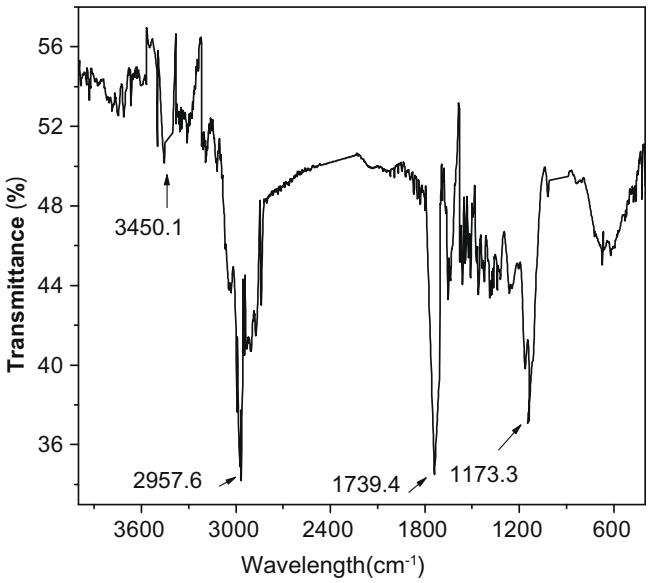

Fig. 1. IR spectrum of PAL-4 copolymers.

0.1789 MPa, the 2 h WIB was up from 0.0211 to 0.0810 MPa , the 24 h TS decreased from 39.31% to 24.69% compared with those no coupled composites. This suggested that PALs could enhance the compatibility and adhesion strength of the interfaces among WS and LDPE, which leaded to a better stress transfer from the matrix to reinforcing constituent.

It was also observed in Table 3 that the composite properties with PAL-4 were obviously superior to those with other PAL. There was no significant difference between the both loaded PAL-1 and PAL-4. It was well understood that the effects of PALs on the composite quality was closely related with their monomer components. As discussed above, the macromolecules of PAL-1 contained much more and softer alkyl groups than other PALs, while the macromolecules of PAL-4 was rich in the hydroxyl groups from copolymerized HEA. Thus, when WS and LDPE were hot pressed, the WS coated weak polar PAL-1 could efficiently combine LDPE penetrated into its cavity due to improved compatibility in interfaces, while the LDPE coated PAL-4 may be bound efficiently with WS by hydrogen bonds because PAL-4 molecules were rich in the hydroxyl groups. These increased adhesion strength of the two-phase interface between WS and LDPE.

3.3. Influence of ratio of PAPI/PAL on composite properties

The use of PAPI as a thermosetting adhesive for wood-based composites has been steadily increasing over the past decade. It has some unique characteristics, such as fast curing rate, formaldehyde emission-free, good weather resistance (Frazier & Ni, 1998; He & Yan, 2005, 2007). To further improve the properties of WS/recycled LDPE composite, PAPI was mixed with above optimized PAL-4 in weight ratio of 70/30, 50/50 and 30/70, respectively. The obtained blend at a load of 4.0 wt% (based on the dried WS weight) was used for coupling WS/recycled LDPE composites. The chosen weight ratio of WS/recycled LDPE of 20/80 was the same as above.

The effects of different ratio of PAPI/PAL-4 on composite properties were plotted in Fig. 2. The results showed that the property improvement of composites was more significant compared with those without and only with PAL-4 ($P < 0.05$). As expected, the composites loaded the CA at the ratio PAPI/PAL-4 of 70/30 behaved the maximum MOE and MOR as well as the least 24 h TS, the IB and 2 h WIB almost were also maximum values. This is because the CA involved the higher fraction PAPI that contained a higher content of high reactive isocyanate groups. In contrast to those only coupled by PAL-4, IB of the composites increased by 112.9%, 2 h WIB by 122.1%, MOR by 121.5%, MOE by 97.8%, while 24 h TS decreased by 47.1%.

It had been revealed that multiple reactions existed during isocyanate bonding wood (Bao et al., 2003; Gironès et al., 2007). However, IR spectroscopy had indicated that the reaction of forming urethane bonds between free isocyanate groups of PAPI and the hydroxy groups in wood should be under an excess of free isocyanate groups and anhydrous condition (Weaver & Owen, 1995). In current work, the moisture content in raw materials was 9 wt% (based on dried WS weight). Even though the moisture could be efficiently released during hot-pressing process, it is difficult that PAPI reacts with the hydroxyl groups in the macromolecules of WS and PAL-4 to form urethane bonds and provide direct covalent linkages between WS particles. The coupling chemistry of the CA in the composites was extraordinary complicated since highly sensitive of isocyanate groups to moisture. Under current condition, polyurea and biuret may be the end products of PAPI reacting with the moisture in raw materials. Thus, the strong hydrogen bonds between the CA and WS particles should be a major linkage for the coupling mechanism. In addition, PAPI has a great propensity to wet and penetrate into WS cavities. The wet ability and its low viscosity allows for its microscopic penetration. This resulted in a increased interaction between the interfaces of CA and WS particles.

Unexpected, Fig. 2 showed that the composite property values did not decrease continually with the decrease of PAPI content in the CA. The composites added CA at the ratio of PAPI/PA4 of 30/70 behaved the maximum IB and 2 h WIB, while MOR, MOE and 24 h TS were similar to those at the ratio of PAPI/PAL-4 of 70/30. This suggested an important coupling action of PAL-4 in the CA. The dilute PAL-4 certainly emulsified PAPI, and increased the wetting area and penetration capability of PAPI into WS cavities. On the other hand, the formation of an intramolecular hydrogen-bonded WS could accelerate the interphase due to PAPI reacting with the moisture in PAL-4 and WS. Moreover, the copolymer chains in PAL-4 could entangle with LDPE chains during hot-

Table 3
Effects of PAL components on WS/recycled LDPE composite properties.

PAL examples	IB (MPa)	2 h WIB (MPa)	MOR (MPa)	MOE (MPa)	24 h TS (%)
–	0.0980 ± 0.0003 C	0.0211 ± 0.0002 BC	9.09 ± 0.07 A	1378.8 ± 13.8 A	39.31 ± 1.49 A
PAL-1	0.1709 ± 0.0010 A	0.0705 ± 0.0005 A	10.04 ± 0.06 A	1102.8 ± 9.5 A	21.69 ± 0.06 B
PAL-2	0.1234 ± 0.0012 B	0.0386 ± 0.0002 B	9.96 ± 0.07 A	1231.5 ± 21.1 A	23.31 ± 0.14 B
PAL-3	0.1661 ± 0.0009 A	0.0426 ± 0.0004 B	11.07 ± 0.13 A	1283.1 ± 17.4 A	25.33 ± 1.02 B
PAL-4	0.1789 ± 0.0006 A	0.0810 ± 0.0003 A	12.14 ± 0.09 A	1399.4 ± 20.5 A	24.69 ± 1.50 B

Data were means ± standard deviation from nine samples of triplicate boards. Different letters within the same column mean significantly different at $P = 0.05$. A, B, C and D order mean effect degree from big to small. Composites: PAL at a load of 4.0 wt%, WS/recycled LDPE being 20/80, the density being 0.93 g/cm^3.

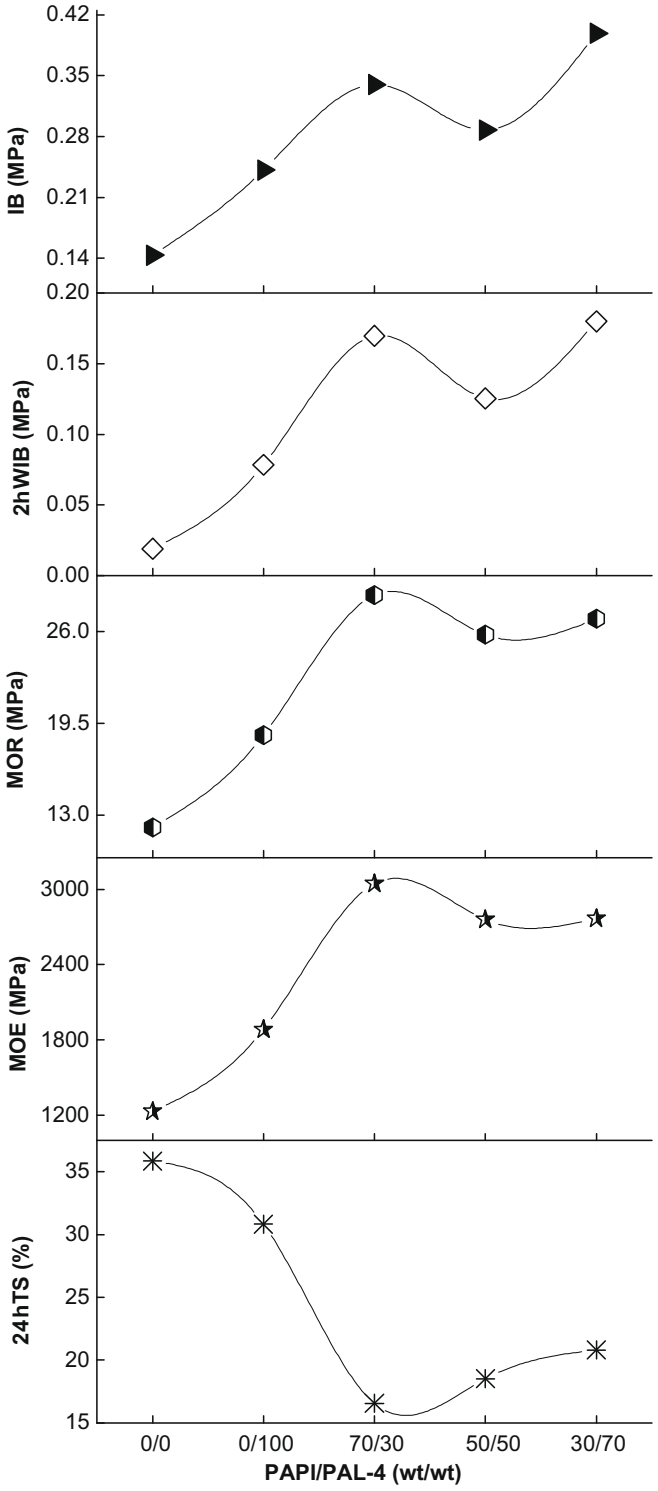

Fig. 2. Effects of PAPI/PAL-4 ratio on composite properties. Composites: a density of 0.93 g cm^{-3}.

pressing process. Thus the improved interfacial adhesion leaded to a increase in mechanical properties and size stability.

IB strength could reflect the interface bond quality in composites, and had been considered to be the most property in wood based panel products (Suzuki & Miyagawa, 2003). In current study, the composites added the CA of PAPI/PAL-4 of 30/70 behaved the maximum IB and 2 h WIB, in addition, PAPI price was over three times that of PAL-4. Therefore, taking the price-performance ratio into account, the ratio of PAPI/PAL-4 of 30/70 for the CA was chosen for following studies.

3.4. Influence of loaded content of CA on composite properties

Fig. 3 showed the relationship between composite properties with and without the CA at the ratio of PAPI/PAL-4 of 30/70. It exhibited that, with the CA content increasing from 1.5 to 4.5 wt%, the IB and 2 h WIB increased significantly ($P < 0.05$), while the improved rates of the MOR, MOE and 24 h TS became relatively slow. Whereas the property values added CA at 6.0 wt% behaved a obvious decrease. The maximum IB, 2 h WB, MOR, MOE, and the lowest 24 h TS values could be observed in the composites with the CA at a load of 4.5 wt%. This indicated that 4.5 wt% load should

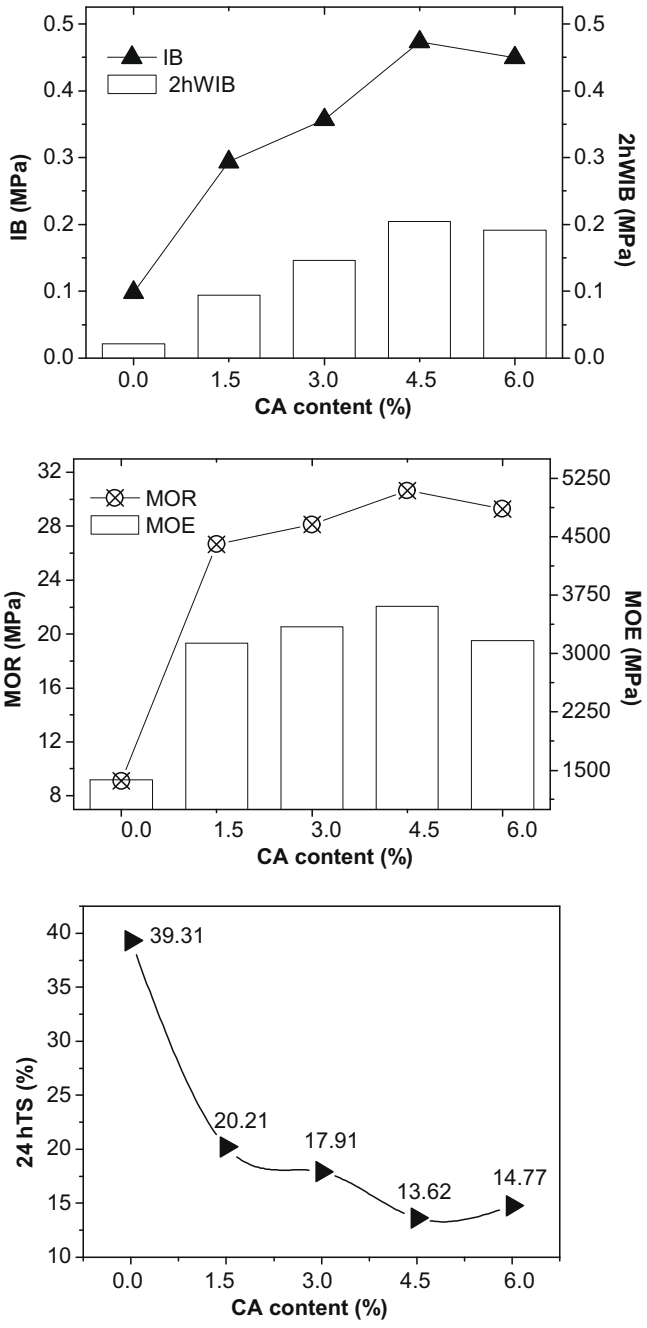

Fig. 3. Effects of loaded content of the CA with ratio of PAPI/PAL-4 of 30/70 on composite properties. Composites: a density of 0.93 g/cm^3.

be the critical value. Beyond this, a weak boundary layer between the interface of WS and LDPE arose from an excess of the CA, resulted in a decrease of composite properties. This was contributed to a weak strength and low modulus for PAL-4 copolymer.

3.5. Influence of ratio of WS/recycled LDPE on properties

Table 4 summarized the effects of different ratio of WS/recycled LDPE on the composite properties. It was observed that, even the CA was used at the optimized load of 4.5 wt%, and PAPI/PA4 at the optimized 30/70, the property difference for composites with WS/recycled LDPE ranging from 90/10 to 40/60 were very evident., the IB, 2 h WIB and 24 h TS were improved significantly ($P < 0.05$), as for MOR and MOE there was no significant difference. The maximum MOR value was found in the composite at the ratio of WS/recycled LDPE of 80/20. When WS levels decrease from 90% to 40 wt%, the IB and 2 h WIB increased by 310.4% from 0.1111 to 0.4656 MPa, and 510.0% from 0.0310 to 0.1891 MPa, respectively, while 24 h TS decreased from 40.43% to 9.36%. Above results showed that all, raw material component, CA types and composition as well as its loaded content should be taken into account to obtain high quality composites. The fact provided the direct evidence of a weak interfacial adhesion under the presence of WS in a relatively excessive level. The interphases under this condition probably took two forms, WS–CA–WS and WS–CA–LDPE. The interface of WS–CA–WS run short of the entanglement of CA chain to LDPE segment, and the CA with LDPE penetrating into WS, which resulted in a poor stress transfer between the interface. In addition, PAPI in the CA only accounted for 30 wt% at 4.5 wt% load (based on dried WS weight), so it could not sufficiently coat onto all WS surface and wet and penetrate into its interior. On the other hand, the silica and a waxy substance on the exterior surface of WS prohibited PAL-4 molecules to bond strongly with WS. This produced the poor interfacial strength between hydrophilic WS and uncovered LDPE. Failure of stress transfer during loading would arise from the location, which leaded to a decrease of mechanical properties and size stability.

3.6. Influence of optimized levels on composites properties

Based on above analysis and discussion, the CA at the ratio of PAPI/PA4 of 30/70 and an addition of 4.5 wt% as well as the ratio of WS/recycled LDPE of 30/70 were chosen as optimized levels. The hot pressing temperature of 180 °C, the maximum pressure of 4.0 MPa and the hot pressing time of 1.1 min/mm were continually used in the composite preparation. The obtained property values were compared with national standard GB/T 4897.7 for heavy-duty load-bearing composites for use in humid condition (Shiying et al., 2003).

Table 5 showed that the optimized levels resulted in a significant improvement in tested mechanical properties and thickness swell stability. The IB, 2 h WIB, MOR, MOE and 24 h TS of the composites were strong enough to meet the requirement for heavy-duty load-bearing composites for used in humid condition. The loaded content of 4.5 wt% CA consisted of only 1.35 wt% PAPI and 3.65 wt% PAL-4. To manufacture high property composites with low cost, the loaded content of CA and composite densities could be determined based on the application requirements.

4. Conclusion

In this study, WS/recycled LDPE composites were manufactured using two novel waterborne coupling agents (CAs), one being waterborne PAL, the other being blend prepared from PAPI and the PAL. Synthesis of PAL was carried out through the seeded emulsion polymerization. The composites were produced by wood board process. PALs could improve the composite mechanical properties and reduce thickness swell stability. The effect of PAL-4 with HEA monomer copolymerizing on composite properties was superior to those without it because the hydroxyl groups in HEA promoted the formation of an intramolecular hydrogen-bonded WS. The composite properties with different ratio of PAPI/PAL-4 were significantly improved than those only coupled by PAL-4. The strong hydrogen bonds between the CA and WS particles should be mainly responsible for the coupling. With the decrease of PAPI content in the CA, the composite property values did not decrease continually. The composites added the CA at PAPI/PA4 of 30/70 behaved the maximum IB and 2 h WIB, while MOR, MOE and 24 h TS were similar to those at the ratio of PAPI/PAL-4 of 70/30. When the CA content increased from 1.5 to 4.5 wt%, the IB and 2 h WIB increased significantly, while the rates of the MOR and MOE increase as well as 24 h TS decrease were relatively slow. However, all the property values at the load of 6.0 wt% the CA behaved an obvious decrease. The composite properties were steadily improved in a whole with increasing LDPE level from 10 to 40 wt% at the optimized addition of 4.5 wt% the CA. PAPI/PA4 of 30/70, the load of 4.5 wt% the CA and WS/recycled LDPE of 30/70 were the optimized levels. All of

Table 4
Effects of different ratio of WS/recycled LDPE on composite properties.

WS/recycled LDPE (wt/wt)	IB (MPa)	2 h WIB (MPa)	MOR (MPa)	MOE (MPa)	24 h TS (%)
90/10	0.1111 ± 0.0008 D	0.0310 ± 0.0001 D	18.68 ± 0.0354 AB	2466.9 ± 14.2 AB	40.43 ± 0.05 A
80/20	0.2540 ± 0.0012 C	0.1115 ± 0.0006 C	22.67 ± 0.0391 A	2802.3 ± 21.0 A	28.79 ± 0.04 B
70/30	0.3475 ± 0.0027 B	0.1550 ± 0.0004 B	22.19 ± 0.0475 A	2511.3 ± 19.8 AB	16.43 ± 0.03 C
60/40	0.4656 ± 0.0030 A	0.1891 ± 0.0010 A	22.88 ± 0.0093 A	2253.1 ± 10.6 B	9.36d ± 0.06 D

Data were means ± standard deviation from nine samples of triplicate boards. Different letters within the same column mean significantly different at $P = 0.05$. A, B, C and D order mean effect degree from big to small. Composites: CA comprised of PAPI/PAL-4 of 30/70.

Table 5
Composite properties under optimized levels.

Items	Density (g cm^{-3})	IB (MPa)	2 h WIB (MPa)	MOR (MPa)	MOE (MPa)	24 h TS (%)
Properties	0.93	0.77	0.30	28.37	3697.19	5.84
GB/T4897.7-2003[a]	–	⩾0.75	⩾0.25	⩾22	⩾3350	⩽9

[a] GB/T4897.7-2003, national standard of People's Republic of China.

mechanical properties and thickness swelling stability of manufactured composites with a density of 0.93 g cm^{-3} were strong enough to meet the national standard for heavy-duty load-bearing composites for use in humid condition.

Acknowledgements

This work was supported by funds of contract Grant numbers 2006JY27 and Y2008D53 from the Science and Technology Support Program and Natural Fund of Office of Science and Technology of Shandong Province in China.

References

Adhikary, K. B., Pang, S., & Staiger, M. P. (2008). Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE). *Composites B: Engineering, 39*(5), 807–815.

Bao, S. C., Daunch, W. A., Sun, Y. H., Rinaldi, P. L., Marcinko, J. J., & Phanopoulos, C. (2003). Solid state two-dimensional NMR studies of polymeric diphenylmethane diisocyanate (PMDI) reaction in wood. *Forest Products Journal, 53*(6), 6371–6380.

Bengtsson, M., & Oksman, K. (2006). Silane crosslinked wood plastic composites: Processing and properties. *Composites Science and Technology, 66*(13), 2177–2186.

Bouza, R., Lasagabaster, A., Abad, M. J., & Barral, L. (2008). Effects of vinyltrimethoxy silane on thermal properties and dynamic mechanical properties of polypropylene–wood flour composites. *Journal of Applied Polymer Science, 109*(2), 1197–1202.

Frazier, C. E., & Ni, J. (1998). On the occurrence of network interpenetration in the wood–isocyanate adhesive interphase. *International Journal of Adhesion & Adhesives, 18*, 81–87.

Gironès, J., Pimenta, M. T. B., Vilaseca, F., Carvalho, A. J. F., Mutjé, P., & Curvelo, A. A. S. (2007). Blocked isocyanates as coupling agents for cellulose-based composites. *Carbohydrate Polymers, 68*(3), 537–543.

Godavarti, S., Williams, R. K., & Deaner, M. J. (2001). Polyolefin wood fiber composite. US Pat. No. 6265037.

Han, L. J., Yan, Q. J., Liu, X. Y., & Hu, J. Y. (2002). Straw resources and their utilization in China. *Transactions of the Chinese Society of Agricultural Engineering, 18*(3), 87–91.

He, G., & Yan, N. (2005). Effect of moisture content on curing kinetics of pMDI resin and wood mixtures. *International Journal of Adhesion & Adhesives, 25*(5), 450–455.

He, G., & Yan, N. (2007). Curing kinetics of polymeric diphenylmethane diisocyanate with different wood species. *International Journal of Adhesion & Adhesives, 27*(3), 244–249.

Jun, Z., Wang, X. M., Chang, J. M., & Kai, Z. (2008). Optimization of processing variables in wood–rubber composite panel manufacturing technology. *Bioresource Technology, 99*(7), 2384–2391.

Karmarkar, A., Chauhan, S. S., Modak, J. M., & Chanda, M. (2007). Mechanical properties of wood–fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group. *Composites Part A: Applied Science and Manufacturing, 38*(2), 227–233.

Keener, T. J., Stuart, R. K., & Brown, T. K. (2004). Meleated coupling agents for natural fiber composites. *Composites Part A: Applied Science and Manufacturing, 35*(3), 357–362.

Kim, H.-S., Lee, B.-H., & Choi, S.-W. (2007). The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. *Composites Part A: Applied Science and Manufacturing, 38*(6), 1473–1482.

Kuo, P.-Y., Wang, S.-Y., Chen, J.-H., Hsueh, H.-C., & Tsai, M.-J. (2009). Effects of material compositions on the mechanical properties of wood–plastic composites manufactured by injection molding. *Materials and Design, 30*(9), 3489–3496.

Lee, S.-Y., Yang, H.-S., Kim, H.-J., Jeong, S., & Lim, B.-S. (2004). Creep behavior and manufacturing parameters of wood flour filled polypropylene composites. *Composite Structures, 65*(3), 459–469.

Markarian, J. (2005). Wood–plastic composites: Current trends in materials and processing. *Plastics Additives & Compounding, 7*(5), 20–26.

Mo, X., Cheng, E., Wang, D., & Sun, X. S. (2003). Physical properties of medium-density wheat straw particleboard using different adhesives. *Industrial Crops and Products, 18*(1), 47–53.

Pritchard, G. (2004). Two technologies merge: Wood plastic composites. *Reinforced Plastic, 48*(6), 24–26.

Shiying, C., Ling, L., & Fengshan, Z. (2003). *National standard of Peoples Republic of China GB/T4897.7, particleboard*. Beijing: Standard Press of China. pp. 1–25.

Shiying, C., Zhiqiang, C., & Yaluan, L. (1999). *National standard of People's Republic of China GB/T17657, test method of evaluating the properties of wood based panels and surface decorated wood based panels*. Beijing: Standard Press of China. pp. 2–41.

Snijder, M. H. B., & Bos, H. L. (2000). Reinforcement of polypropylene by annual plant fibers: Optimisation of the coupling agent efficiency. *Composite Interfaces, 7*(2), 69–75.

Suzuki, S., & Miyagawa, H. (2003). Effect of element type on the internal bond quality of wood-based panels determined by three methods. *Journal of Wood Science, 49*, 513–518.

Wang, Z., Wang, E., Zhang, S., Wang, Z., & Ren, Y. (2009). Effects of cross-linking on mechanical and physical properties of agricultural residues/recycled thermoplastics composites. *Industrial Crops and Products, 29*(1), 133–138.

Weaver, F. W., & Owen, N. L. (1995). Isocyanate–wood adhesive bond. *Applied Spectroscopy, 49*(2), 171–176.

Yao, J., Xu, X. W., & Feng, Y. Y. (2003). FTIR studies on the chemical composition of wheat straw in different layers. *Spectroscopy and Spectral Analysis, 23*, 58–60.

Zou, P., Xiong, H., & Tang, S. (2008). Natural weathering of rape straw flour (RSF)/HDPE and nano-SiO_2/RSF/HDPE composites. *Carbohydrate Polymers, 73*(3), 378–383.