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ORIGINAL PAPER

Acrylamide–formaldehyde–urea copolymer as a novel compatibilizer for high density polyethylene/plant fiber composite

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Abstract In the present work, a terpolymer of acrylamide–formaldehyde–urea (AMFU) which could interact with both plant fiber and high density polyethylene (HDPE) was synthesized, and which as novel compatibilizer for HDPE/plant fiber was also investigated. The result of SEM demonstrated that interfacial adhesion was observed in the presence of AMFU compatibilizer but void at the interface of HDPE/plant fiber without compatibilizer. Evident improvements on both static and dynamic mechanical property of WPC in the presence of AMFU compatibilizer were observed. Water uptake indicated that WPC with AMFU compatibilizer shown a lower water uptake. This research gives a new way in the design of new compatibilizer for WPC in the future.

Keywords Acrylamide–formaldehyde–urea · Compatibilizer · Copolymer · Wood plastic composites

Introduction

Wood–plastic composites (WPCs) are normally made from a mixture of wood and non-wood fiber or wood flour, plastics, and small amounts of process and property modifiers by extrusion and injection molding under high pressure and temperature, which have many properties advantages over wood-based panels, such as lower thickness swell, lower water absorbance, and more durability against biodeterioration. It nowadays become one of the fastest growing composite materials in the wood composites industry with an average annual growth rate of approximately 18% in Northern America and 14% in Europe [1–3]. Polypropylene (PP), polyethylene

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(PE), and polyvinyl chloride (PVC) are the commonly used thermoplastics for WPCs, which are non-polar substance that are not compatible with polar plant fiber. As a consequence, the adhesion at the plant fiber–matrix interface is typically weak, which results poor properties.

At present, compatibilizers [4–8], especially silane coupling agent and maleic anhydride-modified PE or PP, is a very important modifier in improving the final WPCs properties. However, this compatibilizer is high cost in wood industry, which cannot be accepted in the market. The main mechanism for compatibilizer in improving the adhesion between plastics and wood is covalent bonding, polymer chain entanglement, and strong secondary interactions as in the case of hydrogen bonding. Theoretically, an effectively compatibilizer should be a block copolymer, which contains one section able to form strong adhesion with fiber and have the other block able to form strong bonding with polymer matrix or chain entanglement. Recently, a type of copolymer based on polyaminoamide-epichlorohydrin (PAE, a paper wet strength agent) resin combined with stearic anhydride as new compatibilizers for WPCs have been reported [9, 10], which had shown to improve the strength of the resulting composite. Although many efforts have been performed, the compatibility is still an unsolved issue that limits the further development of WPCs.

Due to urea–formaldehyde adhesive is widely used in the adhesion of wood composite, which could be selected as one domain of copolymer to form interaction with plant fiber. Acrylamide is similar to the molecular structure of urea besides of C=C bond. It could also react with urea–formaldehyde adhesive, in which the leftover of C=C bond can also react with PE chain through radical polymerization. Thus, this copolymer will be a novel and effective compatibilizer for adhesion between plant fiber and polymer matrix.

In this article, the copolymer of acrylamide–formaldehyde–urea (AMFU) which could interact with both plant fiber and plastic sections was synthesized, and as a novel compatibilizer for high density polyethylene (HDPE)/plant fiber was investigated.

Experimental

Materials

The main materials used in this study were HDPE (5000S), a commercial grade resin supplied by Sinopec Yangzi Petrochemical Co., Ltd (China) with the melt flow index of 0.97 g/10 min at 230 °C, exerting a force of 21.6 N. Plant fiber was used as the discontinuous phase with 20 wt% in the composites, which were obtained by grinding rice straw in the laboratory. Formaldehyde (37% solution) was supplied from Shanghai Zhongshi General Chemical Company (China) and urea (98%) was obtained from commercial sources. Acrylamide, ammonium chloride, and dibenzoyl peroxide (BPO) were a product of Sinopharm Chemical Reagent Co., Ltd (China).

Synthesis of compatibilizer and plant fiber treatment

Formaldehyde and urea were mixed in the reactor with a mechanical agitator. The pH of this solution was adjusted to pH 8.0–9.0 by adding sodium hydroxide (30% aqueous solution). The temperature was raised slowly from room temperature to 90 °C in about 30 min, and maintained at this temperature for 30 min. Formic acid (20% aqueous solution) was slowly added to adjust the pH of the solution to pH 4.6–5.2. The resin was cooked until a target viscosity was attained. The resin was cooled down to 60 °C and acrylamide was added to the resulting resin for other 30 min. Finally, the system was cooled to room temperature and the pH was adjusted to neutral (7.0–8.0). The compatibilizers were prepared at a formaldehyde/urea molar ratio of 2 in the presence of acrylamide with acrylamide/urea molar ratio of 0, 0.2, 0.4, and 0.6, respectively. The fiber was spread using 5 wt% compatibilizer and dried at 60 °C for 3 h. Ammonium chloride (1 wt%) was added to the compatibilizer as a hardener.

Preparation of HDPE/plant fiber composites

Polymer, plant fibers treated without and with AMFU compatibilizer were initially weighed with weight ratio of 80:20 and 0.5% BPO initiator. The compounded materials were blended in a HTY-30 parallel counter-rotating twin screw extruder from Nanjing Rubber and Plastics Machinery Plant Co., Ltd (China) with a temperature of about 120 °C to prepare the granules. Then, the granules were injection molded to produce standard GB/T1040-92 tensile specimens and others. Injection molding was performed using a Chen De Plastics Machinery Co., Ltd (China) injection molder (CJ80M3V). Barrel and nozzle temperatures were set to 150 °C.

Instruments

The fractured surface of the specimens from the tensile test was examined by an FEI Quanta200 Scanning electron microscope (SEM). All specimens were coated with gold and then analyzed using the SEM operated at 20 keV. The tensile test was done at room temperature according to GB/T1040-92 on a Shenzhen SANS versatile materials test machine using the Type-I dumbbell-shape specimens. The crosshead speed of the apparatus was adjusted at 50 mm/min. Five specimens were tested and the average value was reported. Dynamic mechanical analysis (DMA) of HDPE/plant fiber composites was carried out on a DMA242C Dynamic Mechanical Analyzer (NETZSCH, Germany). The measurements were carried out with a three-point bending mode to determine the storage modulus under a nitrogen atmosphere at a frequency of 1 Hz and the corresponding relaxation behaviors were recorded as a function of temperature. The temperature range used in the present study varied from 30 to 100 °C. Specimens with and without compatibilizers which had dimensions of 60 × 12 × 6 mm were pre-weighed and then soaked in water at room temperature. The specimens were taken out of water, wiped with tissue paper, weighed once every 24 h for the first 5 days, and then weighed at a longer time

interval until day 25. The water uptake percentage was determined from the weight gain divided by the dry weight of the specimens using Eq. 1.

$$\text{Water absorption } (\%) = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100. \quad (1)$$

Results and discussion

The SEM images of the fractured surfaces of the HDPE/plant fiber composites are shown in Fig. 1. For the HDPE/plant fiber specimen without a compatibilizer, gaps between the plant fibers and HDPE matrix could be clearly observed. The surfaces of the plant fibers were fairly clean, this implied poor interfacial adhesion between plant fiber and HDPE. For the HDPE/plant fiber composites with AFFU as a

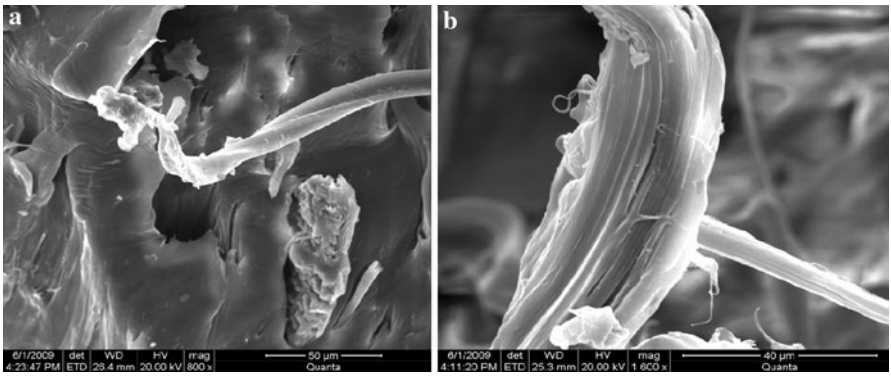

Fig. 1 SEM images of fractured surfaces of the HDPE/plant fiber composites before and after treatment of compatibilizer

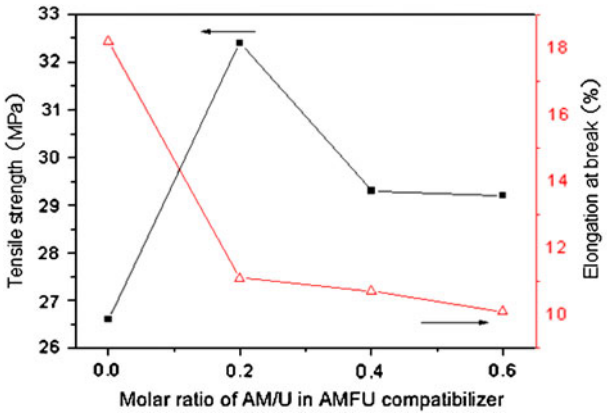

Fig. 2 Tensile properties of HDPE/plant fiber composites with different content of acrylamide in AMFU compatibilizer

compatibilizer, fibers were tightly surrounded with the HDPE. No obvious gap could be seen between two phases. It was difficult to differentiate the fibers from the HDPE, which indicated that when AMFU is used as a compatibilizer, the interfacial adhesion is improved.

Figure 2 showed the tensile strength and elongation at break of the composites. In general, it can be clearly observed that introducing the AMFU compatibilizer increased the tensile strength, but decreased the values of the elongation at break. It is interesting to note that the tensile strength increased with addition of molar ratio of acrylamide/urea in AMFU, increased to a maximum value around a compatibilizer content of acrylamide with molar ratio of AM/U = 0.2 in AMFU. After that, the tensile strength tended to decrease and stabilize, probably caused by the fact that the self-polymerized of compatibilizer. The optimum content of acrylamide (AM/U = 0.2), giving the maximum tensile strength in the composites, indicates high

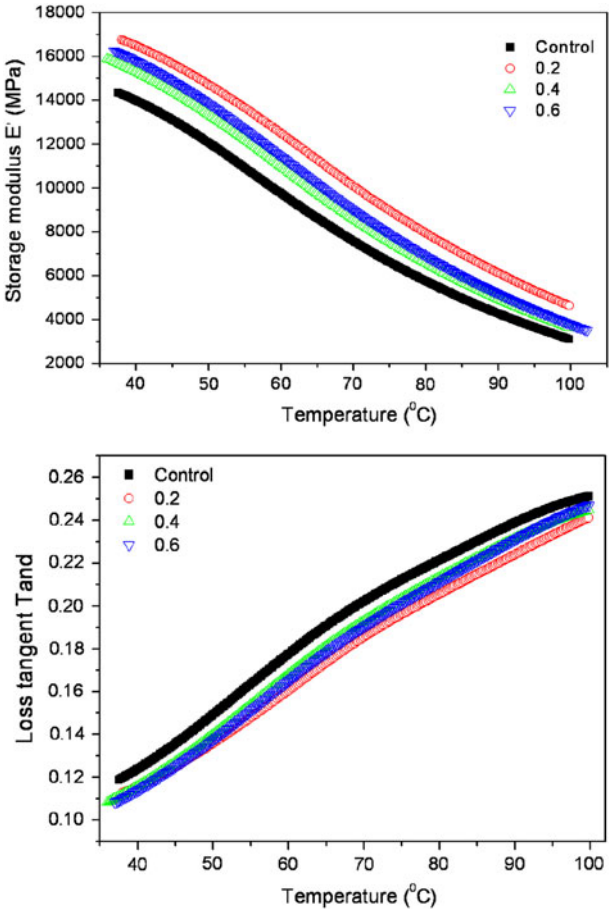

Fig. 3 DMA of HDPE/plant fiber composites with different content of acrylamide in AMFU compatibilizer

interfacial interactions between the HDPE matrix and plant fiber. This explanation can also be substantiated by SEM micrographs in Fig. 1. The decrease in elongation at break was expected since the composites with AMFU compatibilizer now were stiffer and had higher strength.

Figure 3 shows the storage modulus and loss tangent (tan α) versus temperature for HDPE/plant fiber in the absence and presence of AMFU compatibilizer. It showed that greater elastic (storage modulus) properties and lower loss tangent were obtained when composites with AMFU compatibilizers. The increased dynamic properties may be attributed to the adhesion of AMFU compatibilizer in the HDPE/fiber composite, which occur due to the reduced mobility of HDPE chains that are reacted with C=C in AMFU compatibilizer.

The results of the water soaking test are shown in Fig. 4. HDPE/plant fiber composites without a compatibilizer absorbed more water than the composites with AMFU as a compatibilizer for equal soaking times. AMFU with high content of acrylamide lowered the water-uptake rate significantly of the resulting HDPE/fiber composites.

Mechanism

The basic function of a compatibilizer is to form linkages between filler and the plastic matrix. The C=C in acrylamide reacted with PE matrix through radical polymerization, and hydroxymethyl group can form ether bonds with plant fibers. AMFU was thus able to improve the interfacial adhesion between HDPE matrix and plant fiber, thereby increasing the strength of the HDPE/fiber composites. The results in Figs. 2 and 3 indeed indicated that AMFU enhanced the static and

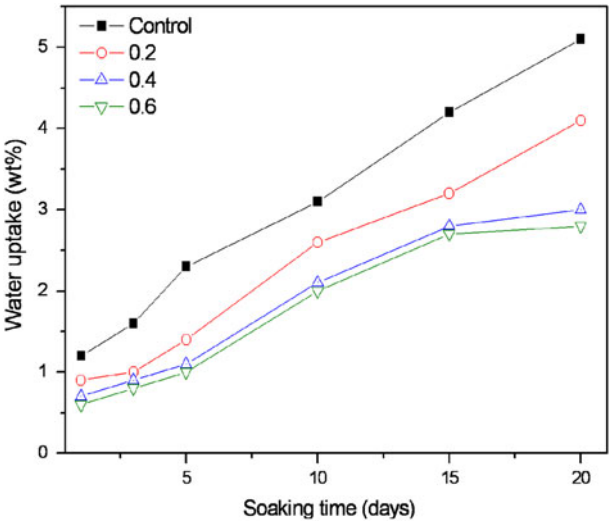

Fig. 4 Effect of acrylamide in compatibilizers on the water-uptake rate of the HDPE/plant fiber composites

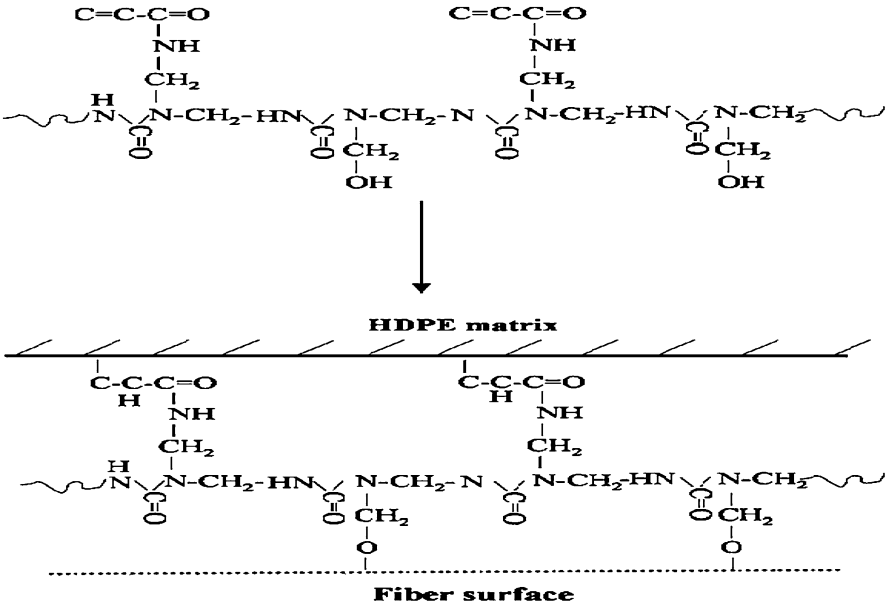

Fig. 5 Sketch map of AMFU and its adhesion of HDPE matrix with plant fiber

dynamic mechanical property. The mechanism of AMFU was described in Fig. 5. The adhesion between wood and HDPE matrix had a significant impact on the water resistance of the HDPE/plant fiber composites. Hydroxymethyl group in UF resin reacted with the hydroxyl groups of the plant fiber, thus blocking the water sorption sites. This factor might account for the lower water-uptake rates of the composites with AMFU compatibilizer.

Conclusions

In this investigation, AMFU copolymers were successfully synthesized through reactions between acrylamide and UF resin. SEM pictures of the fractured composites surfaces revealed that AMFU improved the interfacial adhesion between HDPE matrix and plant fiber. AMFU were effective compatibilizers in terms of increasing the mechanical strength and water resistance of the HDPE/plant fiber composites, and the acrylamide/urea molar ratio of 0.2 in AMFU compatibilizer is the optimum content.

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