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## Effect of electron beam radiation processing on mechanical and thermal properties of fully biodegradable crops straw/poly (vinyl alcohol) biocomposites



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#### HIGHLIGHTS

• Crops straw/PVA biocomposites are manufactured through thermal processing.

• EB radiation processing of CS/PVA biocomposites is proposed.

• At doses below 50 kGy, mechanical and thermal properties are improved.

• At doses below 50 kGy, interface compatibility between CS and PVA is improved.

• At doses above 50 kGy, the comprehensive properties are destroyed.

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ABSTRACT

Fully biodegradable biocomposites based on crops straw and poly(vinyl alcohol) was prepared through thermal processing, and the effect of electron beam radiation processing with N,N-methylene double acrylamide as radiation sensitizer on mechanical and thermal properties of the biocomposites were investigated. The results showed that, when the radiation dose were in the range of 0–50 kGy, the mechanical and thermal properties of the biocomposites could be improved significantly through the electron beam radiation processing, and the interface compatibility was also improved because of the formation of stable cross-linked network structure, when the radiation dose were above the optimal value (50 kGy), the comprehensive properties of the biocomposites were gradually destroyed. EB radiation processing could be used as an effective technology to improve the comprehensive performance of the biocomposites, and as a green and efficient processing technology, radiation processing takes place at room temperature, and no contamination and by-product are possible.

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#### 1. Introduction

Crops straw (CS) as an important biomass resource, mainly composed of cellulose, hemicellulose, lignin and other ingredients, with the characteristics of high yield, wide distribution and variety, etc., crops straw has long been a valuable resource for farmers and agricultural development. However, a large number of carelessly discard crops straw, and burning in the open air, cause serious environmental pollution, and which brings great harm to the safety of highway, railway transportation and security of civil aviation flights, also a very big threat to human health and safety, and has become a social problem (Chen and Xie, 2014; Li et al., 2014; Zhang et al., 2014; Tao et al., 2013; Gadde et al., 2009). In order to solve the problems, it is very important to rationally and

efficiently use the crops straw resource.

Wood-plastic composites (WPC) are mainly made of plastic and waste wood, rice husk, crops straw or other vegetable fibers, and the products are extensively used in packaging, gardens, transportation, construction, upholsteries, furniture manufacturing, car interior decoration, etc. (Kim and Pal, 2010; Klyosov, 2007; Koronis et al., 2013; Zini and Scandola, 2011). So, the crops straw and plastic composites are highly promising low carbon, green and recyclable biocomposites (Zahedi et al., 2013; Zhang and Hu, 2014; Mihai and Ton-That, 2014; Babaei et al., 2014). However, it is not easy to produce WPC product with high-performance and lower production cost, because of the poor interfacial compatibility between the strongly polar crops straw and the common non-polar plastic matrixes (PE, PP, PS, PVC, etc.), and the strong self-interaction of the crops straw, which cause poor dispersion and mechanical properties. Generally, the compatibility and mechanical properties of WPC could be improved to a certain extent by surface

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esterification, etherification, graft copolymer or coupling agent pretreatment of the filler. However, these pretreatment processes are complex, not environmentally friendly and the effects are not obvious, so, which are not perfect strategies for preparing highperformance WPC, merely from the perspective of surface modification of filler (Kalia et al., 2009; John and Anandjiwal, 2008; Chen et al., 2014; Zhao et al., 2006; Cui et al., 2008). For these reasons, it could be another effective method to develop WPC with good performance from post-processing.

Radiation processing is controlled application of ionizing radiation, and includes  $\gamma$ -rays, accelerated electrons and X-rays to have desired effect on the product. The major advantages of the radiation processing are, that it takes place at low temperatures (room temperature) and that in many cases no contamination with residues is possible. Radiation creates free radicals in the polymer matrix, which are generated from chemical bonds, these radicals could re-combine and form new chemical bonds, leading to a three-dimensional network, having much improved properties regarding heat stability, chemical and mechanical performance (Makuuchi and Song, 2012). In the present work, without the surface pretreatment of crops straw (CS), fully biodegradable crops straw/poly(vinyl alcohol) biocomposites (CS/PVA) were prepared through thermal processing, and the effect of electron beam radiation processing on mechanical and thermal properties of CS/ PVA was investigated.

#### 2. Experimental

#### 2.1. Materials

PVA 1799 was commercially provided from SINOPEC Sichuan Vinylon Works (Chongqing, China). The PVA raw materials were prior washed with distilled water until a pH of 7 and dried at 80 °C to constant weight as the experimental sample. Wheat straw flour (Average particle size: 75  $\mu$ m) was obtained from Shaanxi Jinhe Agricultural Science & Technology Co., Ltd. (Xi'an, China). Radiation sensitizer, N,N-methylene double acrylamide, AR, Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Glycerol, AR, Chengdu Kelong Chemical Reagent Factory (Chengdu, China). The water used throughout the experiment was distilled water.

#### 2.2. Preparation of CS/PVA through thermal processing

The pre-dried PVA and CS with equal parts were firstly

mechanically mixed in a high-speed mechanical blender, and the mixture with appropriate proportion of glycerol and water as synergistic plasticizer were added to the aforementioned blends at 40 wt%, the amount of radiation sensitizer was 2%. The blends with the plasticizer and radiation sensitizer were subsequently stored in a sealed container, which was placed at room temperature until completely swollen (Chiellini et al., 2003; Finch, 1992; Furuta et al., 2001; Wang et al., 2003; Kojiro et al., 2008; Zhang et al., 1991). Then, the swollen blends were extruded in a single-screw extruder (Φ: 20 mm, L/D: 30, RM-200C-EP-20-25C, Harbin Hapro Electric Technology Co., Ltd., Harbin, China; the temperature distribution along the extrusion direction: 60, 160, 160, and 125 °C; the screw speed: 25 rpm) and cut into pellets. Finally, the CS/PVA pellets obtained earlier were injection molded into standard specimens (tensile bars:  $127 \times 10 \times 4 \text{ mm}^3$ ; flexural bars:  $80 \times 10 \times 4 \text{ mm}^3$ ; impact bars:  $80 \times 10 \times 4 \text{ mm}^3$ ) for post-processing and performance test according to GB/T 29418-2012 standard using an injection molding machine ( $\Phi$ : 30 mm, MA1200-SMS-A, Haitian Plastics Machinery Co., Ltd., Ningbo, China; the temperature distribution along the injection direction: 160, 180, 180, 160 and 110 °C).

#### 2.3. Electron beam radiation processing of CS/PVA

The above molded standard specimens without any pretreatment were directly irradiated at room temperature by using a GJ-2-type high-frequency high voltage electron accelerator (2 MeV, Shanghai Pioneer Electric Plant, China) at radiation dose 25, 50, 100, and 200 kGy, and the irradiation was carried out in multiple steps with 25 kGy per step, respectively; the absorbed dose was measured by using cellulose triacetate dosimetry system according to GB/T 25439-2010. Fig. 1 shows the technological process of preparation and radiation processing of CS/PVA.

#### 2.4. Characterizations

#### 2.4.1. Mechanical properties tests

Before characterizations, all the testing samples were preconditioned under  $(23 \pm 2)$  °C and  $(50 \pm 5)$ % relative humidity for 48 h. The mechanical properties of the biocomposites were examined using CMT 2103 testing systems (Shenzhen SANS Testing Machine Co., Ltd., China). The tensile tests were conducted with a speed of 50 mm/min, and the flexural tests were evaluated at specified deflection with a speed of 2 mm/min. Five measurements were carried out for each sample and mean values were



Fig. 1. Technological process of preparation and radiation processing of CS/PVA.

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