EXTRACTION OF DISCARDED CORN HUSK FIBERS AND ITS FLAME RETARDED COMPOSITES

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ABSTRACT

Discarded corn husk fibers/ polylactic acid composites containing ammonium polyphosphate and pentaerythritol as flame retardants were prepared by blended hot mastication process. The factors affecting the results were hot processing temperature, time, and pressure, mass fraction of discarded corn cob husk fibers made by flame retardant treatment, etc. Under the optimal technology conditions, the flame retardancy and mechanical properties were determined as follows: limiting oxygen index was 35.2 %; bending strength was 84 MPa; tensile strength was 40 MPa; impact strength was 6.4 KJ/m2. The flame retarded composites made of pre-treated corn husk fibers and polylactic acid with good flame retarded and mechanical properties could be used in building materials, furniture, decorative materials and other fields.

Keywords: Discarded corn husk , flame retardant treatment, polylactic acid, composites, flame retarded properties, mechanical properties

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1. INTRODUCTION

China is a big country of corn production and corn husk resources as a byproduct of corn cob are very rich. Corn husk is now focused on the development of carboxymethyl cellulose, dietary fiber, high-purity crystalline xylose, pigments, braid or burning (1-6). Zhao et al. (7) studied the optimal process conditions and chemical composition of corn husk fiber by treatments of chemical and biological degumming methods. Corn husk fibers were used as reinforced materials to fabricate composites instead of wood with significantly economic and environmental benefits (8). The immature technology of reuse of discarded corn husk has caused the potential resource of corn cob husk to be wasted.

Polylactic acid (abbreviated PLA) is an excellent biodegradable material. Under the action of microorganisms, the discarded PLA will be decomposed into $C0_2$ and H_20 with no pollution to the environment. So, it is a completely eco-cycle type of biodegradable material that can be used as environmentally friendly materials instead of conventional polymer materials (9).

Discarded corn husk fiber and PLA are flammable materials. According to reports, the number of fires each year around the world, was more than 510 million, and nearly 10 million people died because of them. In the face of fire losses and demand for MDF (medium density fiberboard), the products with flame retardant treatment prevent unnecessary losses caused by the fires, with great social and economic significance (10).

Feng et al. (11) studied the flame retardant treatment of polyester, cotton and polypropylene. When the content of flame retardant agent with ammonium polyphosphate and decabromodiphenyl ether was 25 %, the limiting oxygen index was 30.2 %, but the mechanical properties of composite materials were poor. Liang et al. (12) introduced the effect of intumescent systems with flame retardant reagent for polypropylene composite materials. Wei et al. (13) fabricated the flame retardant system with ammonium polyphosphate (APP), pentaerythritol (PER) and 4A zeolite for polypropylene. The results showed that 4A zeolite was a better co-agonist to promote porous carbon layer with catalytic esterification. After, Reti et al. (14) studied the flame retardant treatment of ammonium polyphosphate and pentaerythritol for polylactic acid through horizontal and vertical burning test methods and its limiting oxygen index was more than 40 % , and it achieved good flame-retardant effect. Li et al. (15) studied the flame retardant treatment of IFR and organic soil for PLA and the results showed that it improved flame retardant effect by adding IFR or OMT alone, but generated melt dripping phenomenon. Xu et al. (16) studied the flame retardant effect of zeolite to PVC. And zeolite absorbed HCl with porous structure and reduced HCl gas emission. Yang et al. (17) studied the flame retardant performance of graphite, expandable graphite and expanded graphite/PE composites. The results showed that the graphite had certain flame retardant effect, expandable graphite had good flame retardant effect. But the mechanical properties of expanded graphite/PE composites were poor. Ling et al.(18) introduced aluminum hydroxide (ATH) as a flame retardant to fabricate retarded composites with PLA and bamboo powder.

In this paper, the corn husk fibers were pre-treated with hydrogen peroxide and urea. The pre-treated corn husk fibers were used as reinforced material and PLA particles were used as matrix material. With good mechanical properties and limiting oxygen index of 35.2 % , the flame retarded composites made of pre-treated corn husk fibers and polylactic acid were fabricated by blended hot mastication process. And, it could be used in building materials, furniture, decorative materials and other fields.

2. EXPERİMENT

2.1. Materials

PLA particles with diameter 2-4 mm (provided by Xiangye waste plastic materials management department of Dongguan) and discarded corn husk (provided by Shandong Province) were used.

2.2. Chemicals

Urea (provided by Tianjin quartz factory), sodium hydroxide (provided by Tianjin Kermel Chemical Reagent Co.,Ltd), hydrogen peroxide (provided by Tianjin Kermel Chemical Reagent Co.,Ltd) , hydrochloric acid (provided by Tianjin Kermel Chemical Reagent Co., Ltd., 98 %), ammonium polyphosphate (provided by Qingdao HaiHua flame retardant materials co., Ltd), pentaerythritol (provided by Tianjin Kermel Chemical Reagent Co.,Ltd) and 13X and 4A zeolites powder with diameter 2-4 μm (provided by Henan huanyu molecular sieve co., Ltd) were used.

2.3.Equipment

HH-S26S type digital thermostat water bath (provided by Jintan earth Automation Instrument Factory), SK-160B two-roll mixer (provided by Sinan Rubber Machinery Co.,Ltd, Shanghai), QLB-50D/Q press machine (provided by Zhongkai Rubber Machinery Co., Ltd., Jiangsu), NHY-W prototype machine (provided by testing machine factory, Chengde), RG1-5 tester (provided by Reger instrument Co., Ltd, Shenzhen) and LFY-606B Digital oxygen index detector (Shandong institute of textile instrument) were used.

2.4.Extraction of discarded corn husk fibers

(1).Process

Preparation of corn husk → corn husk fibers were pre-treated with hydrogen peroxide→hot distilled water washing →treatment of sodium hydroxide →cold distilled water washing → drying.

(2).Process parameters

Pre-treatment of urea and hydrogen peroxide: bath ratio 1:15, temperature 30 ℃, urea concentration 6 g/L, hydrogen peroxide concentration 8 g/L, time 40 min;

Treatment of sodium hydroxide: bath ratio 1:15, temperature 100 ℃, sodium hydroxide concentration 2 %, time 30 min.

Drying: temperature 80, time 3 h.

2.5.Process flow of flame retarded composites based on pre-treated corn husk fibers and polylactic acid.

The process parameters: hot processing temperature was 165, hot processing time was 5 min, hot processing pressure was 10 MPa and the length of pre-treated corn husk fiber was 10 mm. The mass fraction of pre-treated corn husk fibers treated with flame retardant and ammonium polyphosphate was 10:1, Species of flame retardants were used ammonium polyphosphate, pentaerythritol and Magnesium hydroxide (They were seen in Table 3).

The process flow of flame retarded composites based on pre-treated corn husk fibers and polylactic acid was shown in Fig.1.

2.6. Testing of flame retarded composites based on pre-treated corn husk fibers and polylactic acid

Tensile, flexural, and impact strength tests were done according to standard GB/T 1447-2005 on a RG1-5. The test of flame retarded property was done according to standard GB/T 8924-2005 on a LFY-606B digital oxygen index detector. The tensile, flexural, and impact strength tests were carried out by universal testing machine(Sifu type TH-8102S) at speed of 10 mm/min. The flame retarded property test was carried out by Oxygen index apparatus (type LFY-606B). Corn husk fibers and their composites were examined using a scanning electron microscopy (SEM, TM-1000, Hitachi, Japan).

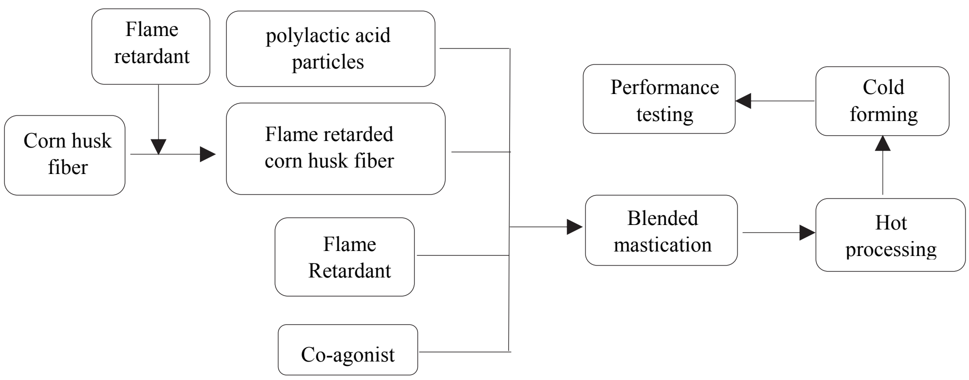

Fig.1. The process flow of flame retarded composites

3. Results and discussion

3.1. Properties of corn husk fiber

The basic physical properties and chemical composition of discarded corn husk fiber pre-treated according to 2.4 were shown in Table 1 and Table 2.

Table 1. Basic physical properties of discarded corn husk fiber

Fiber extraction rate（%）	Residue rate（%）	Fineness (dtex)	Breaking strength (cN/dtex)
34.12	23.48	252-295	1.30-1.67

Table 2. Chemical composition of corn husk fiber

Composition	Cellulose	Hemicellulose	Lignin	Pectin
Content（%）	57.74	34.03	4.46	3.77

From Table 1 and Table 2, the fineness of corn husk fiber was 252-295 dtex. So, the fineness of it was not ideal for bunchy fiber. Then the content of hemicellulose was high and the corn husk fiber was rigid. The electron microscope picture of the degummed corn husk fiber was shown in Fig.2.

From Fig.2, it was seen that there were mostly fiber bundle. And, the corn husk fiber pre-treated with urea and sodium hydroxide was not suitable for use as spinning fiber.

Fig.3 was polarizing microscope picture of the degummed corn husk fiber. From Fig.3, it was seen that the surface of the corn husk fiber was rough for pectin or retention of sodium hydroxide.

Fig.2. Electron microscope picture of the degummed corn husk fiber（50×）

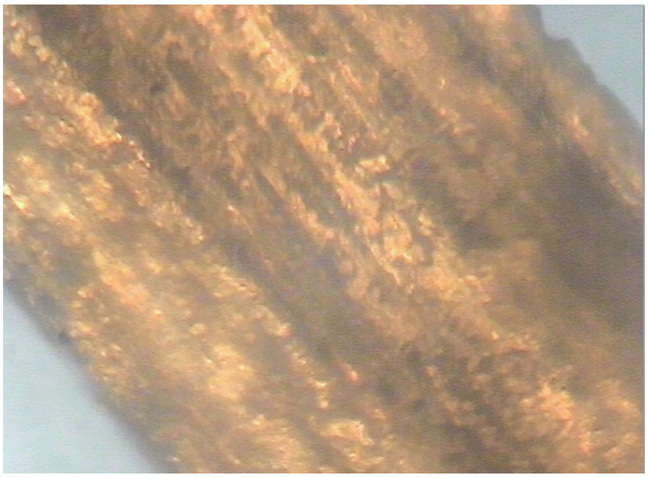

Fig.3. Polarizing microscope picture of the degummed corn husk fiber (400×)

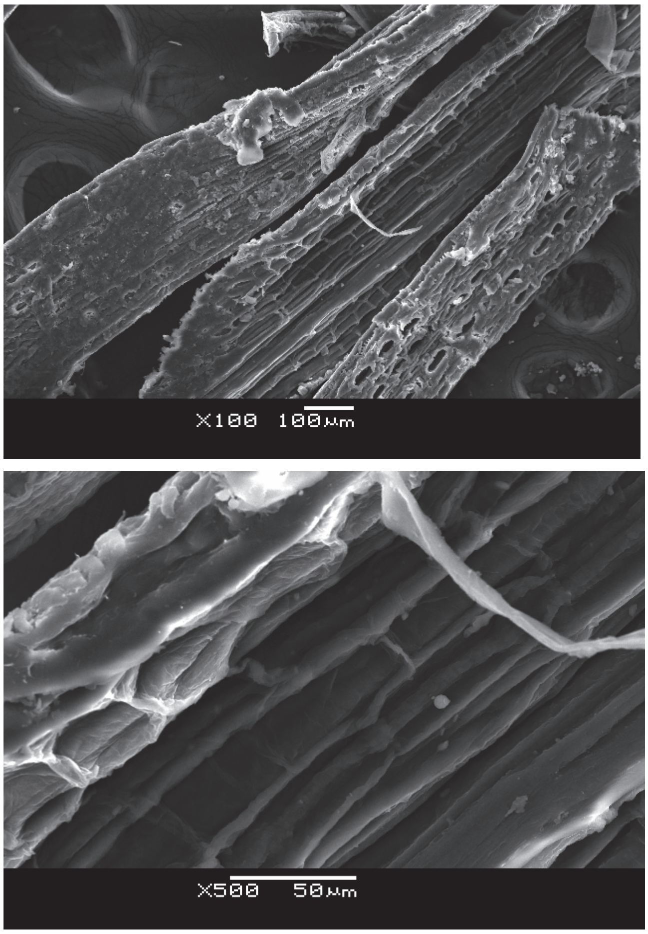

Fig. 4 a-b. Scanning electron micrographs of the degummed corn husk fiber

From Fig.4a, it was clearly seen that the degummed corn husk fibers by the pre-treatment of urea and sodium hydroxide were mostly fiber bundle and the surface of the corn husk fiber was rough for uneven of pectin or retention of sodium hydroxide. From Fig.4b, it was clearly seen that there were vertical stripes and cross section on corn husk fiber and they were similar to hemp fiber(19). Then, there were close connection between single fibers and it was difficult to separate the single fibers.

The degummed corn husk fibers by the pre-treatment of urea and sodium hydroxide were not suitable for use as spinning fibers and they could be used as reinforced materials to composites. The rough surface with vertical stripes and cross section on corn husk fiber could increase the mechanical connection capacity of reinforced material and matrix material. And, it improved the mechanical properties of composites (20) and the composites could be applied to furniture or home decoration instead of wood.

3.2. The optimal technology conditions and properties of flame retarded composites made of pre-treated corn husk fibers and polylactic acid

Selection of orthogonal table L_{16} (5^4), it was shown in Table 3. Flame retardant corn husk fiber/polylactic acid fiberboard's oxygen index was shown in Table 4. The optimal technology conditions of flame retarded composites made of pre-treated corn husk fibers and polylactic acid were obtained by range analysis and variance analysis to measured results.

The flame retarded property of composites was evaluated by limiting oxygen index. The range analysis was shown in Table 5. It was seen that the order of the impact on the limiting oxygen index was mass fraction of flame retardant> mass fraction of co-agonist> mass fraction of pre-treated corn husk fibers made by flame retardant treatment> Species of flame retardants> Species of co-agonist from Table 5.

Table 3. Factor level table for fabrication of flame retarded composites made of pre-treated corn husk fibers and polylactic acid

Level	Mass fraction of pre-treated corn husk fibers made by flame retardant treatment/ %	Species of flame retardants	Mass fraction of flame retardant /%	Species of co-agonist	Mass fraction of co-agonist /%
	A	B	C	D	E
1	30 %	1	5	4A	0
2	35 %	2	10	13X	1
3	40 %	3	15	4A	2
4	45 %	4	20	13X	3

(Note : Species of flame retardants were as follow: 1 mean that mass fraction of ammonium polyphosphate : pentaerythritol was 2 : 1 ; 2 mean that mass fraction of ammonium polyphosphate : pentaerythritol was 3 : 1 ; 3 mean that mass fraction of ammonium polyphosphate: magnesium hydroxide was 1 : 1 ; 4 mean that mass fraction of ammonium polyphosphate: Magnesium hydroxide was 1 : 2.)

Table 4. Flame retardant corn husk fiber/polylactic acid fiberboard's oxygen index

Group number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Oxygen index	25.3	28.1	30.2	31	31.4	27.9	29.4	27.5	31.8	32	29.2	29.5	35.9	34.7	27.4	27.2

Table 5. Range analysis

level	A	B	C	D	E
1	28.650	31.100	27.400	29.963	28.050
2	29.050	30.675	29.100	29.850	29.125
3	30.625	29.050	31.050		30.875
4	31.300	28.800	32.075		31.575
Range	2.650	2.300	4.675	0.113	3.525

Table 6. Variance analysis and significant test

Sources of variance	Sum of deviation squares	Degrees of freedom	Average on sum of deviation squares	F value	Signifcance
A	19.08188	3	6.360625	9.813886	*
B	15.89188	3	5.297292	8.173256	*
C	51.77188	3	17.25729	26.626490	***
D	0.050625	1	0.050625	0.078110	
E	31.11688	3	10.37229	16.003540	**
Error	1.29625	2	0.648125		
Total error	119.2094	15	7.947292		

The variance analysis and significant test were shown in Table 6. From Table 6 , it was seen that mass fraction of flame retardant was the most significant and mass fraction of co-agonist was the second.

3.2.1. Effect of mass fraction of flame retardant on limiting oxygen index

From Table 5 and Table 6, it could be seen that the effect of mass fraction of flame retardant on limiting oxygen index was the most obvious. Mass fraction of flame retardant was changed from 5 % to 20 % in Table 3. So there was an increase of 4.675 % in the average value of limiting oxygen index, from 27.400 % to 31.075 %. During combustion process of the composites, the flame retardant diluted flammable gas and formed intumescent carbon layer with isolation for hot oxygen. With the increase of mass fraction and uniformity of flame retardant in the composites, the limiting oxygen index was greater. When the mass fraction of flame retardant was 20 %, the limiting oxygen index was the highest in the paper.

3.2.2. Effect of mass fraction of co-agonist on limiting oxygen index

With the increase of mass fraction of co-agonist, the limiting oxygen index was also increased. 13X zeolite reduced the release of heat radiation and the intumescent carbon layer was resistant to severe thermal oxygen environment. 13X zeolite formed stably intumescent carbon layer, reduced the melt dripping, saved a lot of aliphatic bonds, reduced the rupture of P-O-C bonds and slowed down the speeds of thermal cracking and diffusion（21）. Then, it prohibited the accumulation of aromatic substances and saved the pyridine nitrogen. Thus, it improved the flame retardancy and mechanical properties of composites. There was an increase of 3.525 % in limiting oxygen index with the comparation of composites added 13X zeolite and composites without 13X zeolite. But, the limiting oxygen index began to decline, due to the mass fraction of co-agonist was too high. The was because 13X zeolite particles began to reunite for its too much and were not very good dispersion. So, a reasonable mass fraction of 13X zeolite could improved the limiting oxygen index. When the mass fraction of co-agonist with 13X zeolite was 3 % , the flame retarded property was the best.

Table 7. Mechanical properties(thickness of 4 mm)

tensile strength（MPa）	bending strength (MPa)	impact strength (KJ/m^2)
40	84	6.4

The comprehensive analysis was done by orthogonal experiment. The flame retarded composites made of pre-treated corn husk fibers and polylactic acid were fabricated by blended hot mastication process. The optimal technology conditions were hot processing temperature 165 ℃, hot processing time 5 min, hot processing pressure 10 MPa, mass fraction of pre-treated corn husk fibers with length of 10 mm made by flame retardant treatment 45 %, mass fraction of flame retardant with ammonium polyphosphate and pentaerythritol (2:1) 10 %, mass fraction of co-agonist with 13X zeolite 3 %. And, the mass fraction of pre-treated corn husk fibers and ammonium polyphosphate was 10:1 with flame retardant treatment of pre-treated corn husk fibers. Under the optimal process conditions, the limiting oxygen index was 35.2% and the mechanical properties were shown in Table 7.

The scanning electron microscopy (SEM) of tensile sample of flame retarded composites made of pre-treated corn husk fibers and polylactic acid was shown in Fig.5.

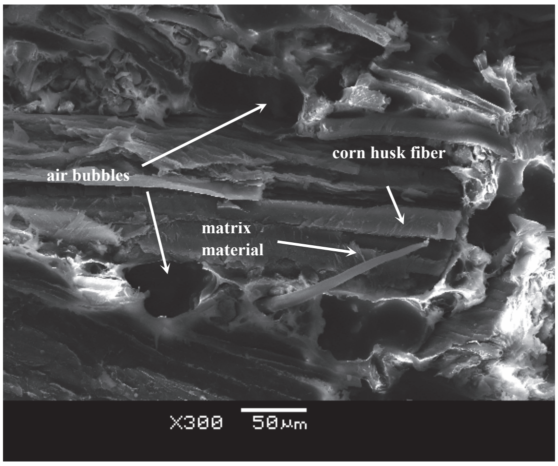

Fig.5. Scanning electron microscopy (SEM) of tensile sample

From Fig.5, it was shown that fiber, flame retardants and co-agonist were distributed homogeneously in the composites. The infiltration of matrix material to corn husk fibers was better and fibers pull phenomenon was obvious in Fig.5, so the mechanical properties were good. But, there were air bubbles in composites for the decomposition and reaction of flame retardants and co-agonist in blended hot mastication process.

4. CONCLUSION

The discarded corn husk fiber was lignin content of 4.46 %, cellulose content of 57.74 %, fineness of 252-295 dtex, breaking strength of 1.30-1.67 cN • $dtex^{-1}$ by the treatment of pre-treated of urea (bath ratio 1:15, temperature 30 ℃, concentration of urea 6 g/L, concentration of hydrogen peroxide 8 g/L, time 40 min) and sodium hydroxide (bath ratio 1:15, concentration of sodium hydroxide 2 %, time 30 min, temperature 100 ℃). The degumming effect of discarded corn husk fiber by the pre-treatment of urea and sodium hydroxide was good. During the degumming, the residual liquid of urea could be used as fertilizer and the utilization of sodium hydroxide was higher. So, the pre-treatment of urea and sodium hydroxide was small to environmental pollution.

The flame retarded composites made of discarded corn husk fibers and polylactic acid were fabricated by blended hot mastication process. The optimal technology conditions were hot processing temperature 165 ℃, hot processing time 5 min, hot processing pressure 10 MPa, mass fraction of pre-treated corn husk fibers made by flame retardant treatment 45 %, mass fraction of flame retardant with ammonium polyphosphate and pentaerythritol (2:1) 10 %, mass fraction of co-agonist with 13X zeolite 3 %. And, the mass fraction of pre-treated corn husk fibers and ammonium polyphosphate was 10:1 with flame retardant treatment of pre-treated corn husk fibers. Under the optimal process conditions, the flame retardancy and mechanical properties were as follows: limiting oxygen index was 35.2 % ; bending strength was 84 MPa; tensile strength was 40 MPa; impact strength was 6.4 KJ/m^2. The flame retarded composites made of discarded corn husk fibers and polylactic acid with good flame retarded and mechanical properties can be used in building materials, furniture, decorative materials and other fields.

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