A novel household fill material fabricated from waste peanut shells and thermoplastic polyurethane with flame retardant and antibacterial functions

Lihua Lv*
Chunyan Wei
Yongzhu Cui
Xiao Wang
Xinyue Wang
School of Textile and Material Engineering, Dalian Polytechnic University,
Dalian, P.R. China
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Large amounts of peanut shells were abandoned each year in China and the abandoned peanut shells were subjected to incineration or landfill, which not only polluted environment, but also wasted resources. So, a household fill material with flame retardant and antibacterial functions was fabricated with abandoned peanut shell and discarded thermoplastic polyurethane by plasticizing, blending and hot pressing. The main factors that affect the flame retardant performance and the regression model of limiting oxygen index were obtained by response surface analysis. The regression model helped to predict materials flame retardant ability and achieve the optimal preparation condition, which as follows: the peanut shell mass fraction 49.5 %, ammonium polyphosphate mass fraction 4.4 %, Thermoplastic polyurethanes (TPU) flame retardants mass fraction 14.2 %, under these conditions, the limiting oxygen index of materials was 32.78 %. While after added 3 wt% Tetraneedle like ZnO whiskers at the same condition, the limiting oxygen index was 32.7 %, and the antimicrobial ratio of Staphylococcus aureus, Escherichia coli and Salmonella reached 96.03, 96.98 and 92.33 % respectively.
Key words*: abandoned peanut shells, thermoplastic polyurethanes, household fill material, flame-retardant, antibacterial functions*

1. Introduction

Recent years, fire accidents caused by household items have been more common, and have caused high mortality rate. Most of household fill materials are plant materials, fiber, sponge or foam plastic, which have high heat release rate, calorific value and flame propagation speed during burning, so they are hard to put out. At the same time lots of smoke and toxic gases are produced and make people suffocated to death. This is not only a serious threat to people's lives, but also pollutes the environment badly. Therefore, the household fill materials with flame retardant function can not only avoid fire accidents, protect the safety of people's lives and property, but also reduce air pollution caused by smoke. In addition, according to the survey shows in 1995, about 17 million people died of bacterial infection all around the world, which account for 32.7% of the total number of deaths. Infection of Escherichia coli (O–57) in Japan and the outbreak of "bird flu", "swine flu" subsequent in China are a warning that variety of harmful bacteria has caused tremendous harm to our health. Therefore, to develop a household fill material with flame-retardant and antibacterial function is very necessary.

As many as 5 million tons of peanut shells were abandoned each year in China [1], and most of the abandoned peanut shells were burned down or buried, which not only wasted resources, but also polluted the environment. Lightsey et al. [2] have studied the preparation process of peanut shell powder/polyolefin composites in 1975. Sanadi [3] studied the applications of peanut shells and other agricultural waste in composites. Mehmet et al. [4] tested the elasticity and breaking strength of fiberboard, which prepared by different proportions of peanut shell powder and wood fibers. Raj [5] prepared walnut shell and peanut shell powder reinforced polyethylene materials, and optimized the process conditions to meet the mechanical properties. Nishikawa et al. [6] prepared composites with peanut shell powder and polylactic acid, and evaluated the water absorption and bending properties. Matuana [7] investigated the properties of composites, which peanut shells as filler, PVC as the matrix, coupling agent is modified polypropylene by aminopropyltriethoxysilane and Maleic anhydride. Mr. Galli [8] invested the characteristics of peanut shell filler.

The research of peanut shell powder/polyolefin composites was developed since 1981 in China [9]. Huang [10] studied peanut shell powder and polypropylene composites, which prepared by twin-screw extruder, and the process parameters were optimized. Zhang [11] prepared peanut shell and sawdust reinforced composites by parallel twin-screw extruder. He [12] investigated the application of polypropylene sheet filled with peanut shells and wood flours on automotive. Institute of Chemistry, Chinese Academy of Sciences developed a PVC wood plastic board [13] with PVC, cavings and peanut shells through rolling or extrusion molding. Su [14] summarized the research of cellulose powder reinforced thermosetting polyester and readily biodegradable polymer. Liu et al. [15] prepared bamboo powder, wood powder, peanut shell powder and rice hull powder reinforced material and studied the affect of coupling agent, consumption of compatibilizer and category of materials on composite mechanical properties, and found that the peanut shell powder reinforced material has a better mechanical properties. In addition, peanut shells have low density, low cost, and good biodegradability, suitable for household fill material.

Thermoplastic polyurethane is widely used in industrial, medical, health, sports and other fields, while every year will produce large amounts of abandoned TPU, how to use it rationally has become many scholars research topic. In this work, a household fill material with flame retardant and antibacterial function was prepared, waste peanut shells as reinforce material, waste thermoplastic polyurethane as matrix material. The research of household fill material, on one hand, makes full use of discarded peanut shells, to expand the application field and recovery methods of the waste peanut shells, save resources effectively, on the other hand, reduces the environment pollution caused by abandoned TPU, in the meantime realized resources recycle and resolve a series of social and ecological problems because of using waste plastic products. More importantly, the household fill materials with flame retardant and antibacterial functions create high value at a low cost by traditional production process and equipment.

2. Experimental

2.1. Materials and Composite preparation

Abandoned peanut shell obtained from Huludao city (Liaoning, China), were crushed to powder by pulverizer (JFSD-100-II Jiading grain and oil process instrument factory, Shanghai), soaked in 5% ammonium polyphosphate solution, (Haihua flame-retardant materials Co., Ltd, Qingdao) and dried by cotton drying machine (XMTD2001 Gexin instrument factory, Shanghai). The peanut shell powder was soaked for 12 h in the solution, containing ethanol as an organic solvent and 1.5wt% silane coupling agent as solute (KH-550 Daoning Chemical Co., Ltd, Nanjing). The bath ratio was 1:15 and dried at 80 °C. Weighting raw materials waste TPU (Xiangye plastic materials management department, Dongguan), TPU flame retardant (Rui Hong Chemical Materials Co., Ltd, Shenzhen), Tetra-needle like ZnO whiskers (Jingyu Technology Co., Ltd, Chengdu) and peanut shell powder according to calculated ratio. Mix raw materials by double roll kneader (SK-160B Sinan Rubber Machinery Co., Ltd., Shanghai). Hot press the mixed materials by vulcanizing machine (QLB-50D/Q Zhongkai Plastic Co. Ltd, Jiangsu) then cooling and demolding.

2.2. Testing index

Limiting oxygen index is calculated according to equation (1) and based on GB/T5454-1997 standard.

$$LOI = (O_2) / [(O_2) + (N_2)] \times 100 \quad (1)$$

LOI - Limiting oxygen index (%),
O_2 - Flow rate of oxygen (L/mi),
N_2 - Flow rate of nitrogen (L/min).

Antibacterial percent is calculated according to equation (2) and based on FZ/T 01021-1992 standard.

$$R\ (\%) = A – B / A \times 100 \quad (2)$$

R - Antibacterial ratio (%),
A - Mean bacteria recycle quantity of the blank sample (cfu/piece),
B - Mean bacterial recycle quantity of the antibacterial plastic sample (cfu/piece).

3. Results and discussion

3.1. Flame retardant analysis

The most common design method of Response Surface Methodology is Box-Behnken[16], which is suitable for optimizing experiments with two to five factors. Compared with single factor or orthogonal, it needs less ex-

Tab.1 Box - Behnken experiment factors and levels

Level	Factors		
	X1 Peanutshell content (%)A	X2 Ammonium polyphosphate content (%) B	X3 Flame retardant content (%) C
-1	45	0	10
0	50	5	15
1	55	10	20

Tab.2 Box - Behnken experimental design and results

No.	Peanut shell Content (%) A	Ammonium polyphosphate content (%) B	Flame retardant agent content (%) C	Limit oxygen index (%)
1	0	1	1	31.88
2	0	0	0	32.92
3	1	-1	0	27.03
4	0	1	-1	30.45
5	1	1	0	29.49
6	-1	0	1	30.14
7	0	-1	-1	28.12
8	0	-1	1	28.76
9	1	0	-1	28.96
10	-1	-1	0	29.03
11	1	0	1	29.32
12	-1	0	-1	29.02
13	-1	1	0	30.06

Tab.3 Variance analysis of limiting oxygen index regression equation

Items	Sum of the squares	Degree of freedom	mean square error	F	Prob > F
model	27.22	9	3.02	10.30	0.0403
X_1	1.49	1	1.49	5.07	0.1098
X_2	9.99	1	9.99	34.03	0.0100
X_3	1.58	1	1.58	5.37	0.1034
X_{12}	11.37	1	11.37	38.72	0.0084
X_{22}	7.30	1	7.30	24.88	0.0155
X_{32}	4.04	1	4.04	13.77	0.0340
X_1X_2	0.51	1	0.51	1.74	0.2786
X_1X_3	0.14	1	0.14	0.49	0.5336
X_2X_3	0.16	1	0.16	0.53	0.5187
Residuals error	0.88	3	0.29		
	28.10	12			
R^2	0.9687				
Adj R^2	0.8746				

periment, short experiment cycle, high precision of the achieved regression equation. It can also optimize the experiment conditions and investigate the effect of each variable and their interactions on the response value. Box - Behnken design is applied in this experiment, materials limiting oxygen index as response value and the quadric mathematical model is established, according the model to optimize parameters and determine the best process parameters [17-18].

Factors are peanut shell mass fraction (A), ammonium polyphosphate mass fraction (B) and flame retardant mass fraction (C). Each factor has three levels and the value in each level is range from 45 to 55%, 0 to 10%, and 10 to 20% respectively. The coding equations (3), (4) and (5) as follows:

$$X_1 = \frac{2(A-55)}{55-45} + 1 \quad (3)$$

$$X_2 = \frac{2(B-10)}{10} + 1 \quad (4)$$

$$X_3 = \frac{2(C-20)}{20-10} + 1 \quad (5)$$

The equation (3, 4 and 5) shows that, A = 45, 50, 55,and the X_1= -1, 0, 1. B = 0, 5, 10, and the X_2= -1, 0, 1. C = 10, 15, 20, and the X_3= -1, 0, 1.

According to the center combination design principle of Box – Behnken, response surface analysis experiments were designed with three factors, three levels and thirteen experimental points. Peanut shell mass fraction, flame retardant mass fraction, ammonium polyphosphate mass fraction as independent variables, limit oxygen index as response value. The experimental factors and levels are shown in Tab.1.

Thirteen experimental points can be divided into two classes. Analytic point, posed by independent variable X_1, X_2, X_3, and have twelve analytic points. Zero point, the central point and could help to estimate the error of each experiment. The limit oxygen index is shown in Tab.2.

By center combination (Box-Benhnken) design experiment, the regression model of the limiting oxygen index is achieved.

$$\begin{aligned} Y = 32.92 &- 0.43X_1 + 0.12X_2 + \\ &+ 0.44X_3 - 0.23X_{12} - 0.97X_{22} - \\ &- 1.33X_{32} + 0.36X_1X_2 - \\ &- 0.19X_1X_3 + 0.20X_2X_3 \end{aligned} \quad (6)$$

Variance analysis result of the regression equation is shown in Tab.3.

From Tab.3 we can learn that the regression model is highly significant ($P < 0.05$). $R^2 = 0.9687$, it means that the model have a good fit to the actual experiment.

The result of variance analysis also shows that the variables in X_1, X_2, X_3 are significant factors, the most significant factor is X_2, that is, the mass fraction of ammonium phosphate. The interaction between peanut shell and ammonium polyphosphate mass fraction has significant effect on the response value. Three factors in square items very significant, therefore the relationship between factors and response value is nonlinear.

In order to corroborate the optimal points of various factors, build first order partial derivatives of X_1, X_2, X_3 to Y, and make it equal to zero. So obtained the following three equations (7):

$$-0.43-4.46X_1+0.36X_2-0.19X_3=0$$

$$1.12+0.36X_1-3.58X_2+0.2X_3=0$$

$$0.44-0.19X_1+0.2X_2-2.66X_3=0 \quad (7)$$

Solving the equation group and achieved $X_1 = -0.108$, $X_2 = 0.121$, $X_3 = 0.164$, then they were substituted into the equation (3), (4), (5) and obtained the peanut shell mass fraction A = 49.46%, ammonium polyphosphate mass fraction B = 4.395%, flame retardant mass fraction C = 14.18%. While it can be learn from the experimental design table of Box-Behnken that the optimum conditions are not included in the thirteen designed experiments, so the verify experiment was developed to confirm the results. Under the condition of peanut shell mass fraction 49.5%, ammonium polyphosphate mass fraction 4.4%, TPU flame retardant mass fraction 14.2%. Under this condition, the limiting oxygen index is 32.78%. In order to verify the reliability of the results, plug the results that under the optimal process into the regression equation and achieved the response value of limit oxygen index is 32.81%, which consistent with the theoretical predictions basically. The usage of proposed model can also predict the flame retardant properties of materials.

3.2 Antibacterial properties analysis

3.2.1. Single factor analysis of experimental results

1, 3, 5% of the antimicrobial agent was added in household fill material to investigate the effect of antimicrobial agent content on the flame retardant performance, and the tested result is shown in Fig.1.

The Fig. 1 shows that the influence of Tetra-needle like ZnO whiskers antimicrobial agent on the materials flame retardant performance is negligible. Because the Tetra-needle like ZnO whiskers antibacterial agent has a unique three-dimensional structure, the angle of each needle corner is 109.29°, which is similar to tetrahedron and good chemical stability. So it can be dispersed in the materials. Zn^{2+} in Tetra-needle like ZnO whiskers antibacterial agent can not only penetrate the membrane of bacteria into the cells, the cells lose their ability to divide and death, but also make the microbial transmission and respiratory system damage.

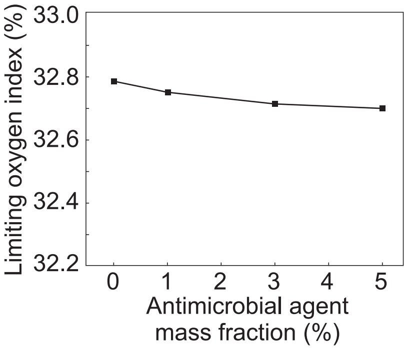

Fig.1 Antimicrobial agent mass fraction on the properties of flame retardant materials

3.2.2. Analysis results of orthogonal experimental

Antimicrobial agent mass fraction, hot-pressing temperature, hot-pressing pressure, hot pressing time as factor, using L_9 (3^4) orthogonal table design experiment, results of orthogonal experimental is shown in Tab.4. Range analysis results of Tab.4 are shown in Tab.5.

From Tab.6 we can learn that S. aureus and E. coli mass fraction is the primary factor that impact antibacte-

Tab.4 Orthogonal experimental results of peanut shells / TPU flame retardant and antibacterial composite

No.	Antimicrobial agent content (%) A	Hot-pressing temperature (°C) B	Hot-pressing pressure (MPa) C	Hot-pressing time (min) D	*Staphylococcus aureus* inhibition rate (%)	*E. coli* inhibition ratio (%)	*Salmonella* inhibition rate (%)
1	1	160	10	5	74.32	73.32	70.17
2	1	170	14	10	75.96	75.48	73.52
3	1	180	12	15	73.52	74.77	71.89
4	3	160	14	15	83.94	84.62	82.64
5	3	170	12	5	86.02	86.63	84.76
6	3	180	10	10	84.06	84.67	81.27
7	5	160	14	10	93.96	94.27	90.21
8	5	170	10	15	95.97	96.72	92.03
9	5	180	12	5	95.55	96.21	91.96

Tab.5 Range analysis table of orthogonal experimental

No.	Antibacterial agent content (%) A	Hot-pressing temperature (°C) B	Hot-pressing pressure (MPa) C	Hot-pressing time (min) D
Mean inhibition rate of S. aureus t1	74.600	84.073	84.783	85.297
t2	84.673	85.983	85.150	84.660
t3	95.160	84.377	84.500	84.477
R	20.560	1.910	0.650	0.820
Optimal level	A3	B2	C2	D1
Sequence	A > B > D > C			
Mean inhibition rate of E. coli t1	74.523	84.070	84.903	85.387
t2	85.307	86.277	85.437	84.807
t3	95.733	85.217	85.233	85.370
R	21.210	2.207	0.534	0.580
Optimal level	A3	B2	C2	D1
Sequence	A > B > D > C			
Mean inhibition rate of salmonella t1	71.860	81.007	81.157	82.297
t2	82.890	83.437	82.707	81.677
t3	81.400	81.707	82.287	82.187
R	19.540	2.430	1.550	0.630
Optimal level	A3	B2	C3	D1
Sequence	A > B > C > D			

Tab.6 Variance analysis results of *S. aureus* antibacterial performance

Sources of variation	Sum of squared deviations S	Degrees of freedom f	S/f	F	Obviousness
A	634.156	2	3.950	3.110	*
B	6.321	2	0.039		
C	0.637	2	0.004		
D	1.111	2	0.007		
Total	642.22	8			

Tab.7 Variance analysis results of *E. coli* antibacterial performance

Sources of variance	Sum of squared deviations S	Degrees of freedom f	S/f	F	Obviousness
A	674.860	2	3.951	3.110	*
B	7.308	2	0.043		
C	0.432	2	0.003		
D	0.654	2	0.004		
Total	683.25	8			

rial ratio, the secondary is hot-pressing temperature, the third is hot-pressing time and the last one is hot-pressing pressure. The primary factor that impact antibacterial ratio of salmonella is antibacterial agent mass fraction, the secondary is hot-pressing temperature, the third is hot-pressing pressure and the last one is hot-pressing time. Under the condition of 3wt% Tetra-needle like ZnO whiskers antibacterial agent, hot pressing pressure 12 MPa, hot pressing temperature 170 °C, hot pressing time 5 min, material has the best antibacterial performance of E. coli. Under the condition of 3wt% antibacterial agent, hot pressing pressure 14 MPa, hot pressing temperature 170 °C, hot pressing time 5 min, material has the best antibacterial performance of Salmonella. While the condition of C_2 and C_3 has no much different on antibacterial rate of Salmonella, for the purpose of save energy so determine the optimal process condition is 3wt% antibacterial agent, hot pressing pressure 12 MPa, hot pressing temperature 170 °C, hot pressing time 5 min. Under these conditions, the antibacterial ratio of *S. aureus*, *E. coli* and *Salmonella* is 96.03, 96.98 and 92.33% respectively.

To verify the range analysis results in Tab.5, variance analysis of the orthogonal experimental was developed, and the results are shown in Tab.6 - 8. From the three table we can learn that, $F_A > F_{0.10}(2,2) = 3.11$, at the level of 0.10 antibacterial agent content is the main influence factor to *S. aureus*, *E. coli* and *Salmonella* survival ratio.

4. Conclusion

In this work, main factors that affect the flame retardant properties and regression model of limiting oxygen index were achieved by response surface analysis.

By solving the regression equation we got the optimal process condition, 49.5wt% peanut shell, 4.4wt% ammonium polyphosphate, 14.2wt%

Tab.8 Variance analysis results of *Salmonella* antibacterial performance

Sources of variance	Sum of squared deviations S	Degrees of freedom f	S/f	F	Obviousness
A	575.893	2	3.906	3.110	*
B	9.388	2	0.064		
C	3.856	2	0.026		
D	0.679	2	0.005		
Total	589.82	8			

flame retardant agent. Under these conditions, limit oxygen index of material is 32.78%.

Single factor analysis of antibacterial agent content, range and variance analysis of orthogonal experiments were developed and achieved the optimal process condition. When 49.5wt% peanut shell, 4.4wt% ammonium polyphosphate, 14.2% flame retardant agent, 3wt% antibacterial agent, material has perfect flame antibacterial performance and the antimicrobial ratio of *Staphylococcus aureus, Escherichia coli, Salmonella* antimicrobial is 96.03, 96.98 and 92.33% respectively. When hot-pressing temperature 170 °C, hot pressing pressure 12 MPa, hot pressing time 5 min, material has perfect retardant performance and the limiting oxygen index is 32.7%.

In this study, abandoned peanut shells are used to make the household fill material, and the product has the characteristics of light weight, good resilience and so on. On the one hand it can make full use of abandoned peanut shells and expand the application field of peanut shells; On the other hand it can reduce the pollution on the environment caused by TPU, and has good economic benefits and market potential.

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