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Study on Liquefaction of Walnut Shell and its Application to Phenol-Formaldehyde Resin Adhesives

ZHENG Zhi-feng[1], ZOU Ju-chun[1], ZHANG Hong-jian[1], GU Ji-you[2], MA Tian-qi[1]
(1. Faculty of Wood Science and Technology, Southwest Forestry College, Kunming 650224, China;
2. College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, China)

Abstract: The liquefaction of walnut shell by using sulfuric acid as a catalyst in phenol was investigated under different ratio of walnut shell to phenol, content of catalyst, reaction time and reaction temperature. Results showed that walnut shell was rapidly liquefied under the conditions. With processing of the liquefaction, the amount of residue and free phenol decreased. The range of molecular weights of the resultants dramatically decreased in the initial stage of liquefaction, too. Comparing to the conventional PF resin adhesives, the liquefied walnut shell/phenol/formaldehyde cocondensed (WPF) resin adhesives were acceptable for plywood.

Key words: walnut shell; phenol; liquefaction; phenol-formaldehyde resin adhesives
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It has been found that liquefaction is one of the useful methods for utilization of biomass[1-2]. In this paper, the objective is to transform walnut shell into phenol-type adhesives by thermochemical liquefaction in the presence of phenol with sulfuric acid catalyzed.

1 Experimental

1.1 Materials

Walnut (Juglans Sigillata Dod) shell meal (>100 mesh) was dried to a constant weight and kept in a desiccator before use. The composition of walnut shell is lignin 53.81%, cellulose 22.06%, hemicelluloses 19.90%, and ash 1.46% on a dry weight basis[3].

1.2 Liquefaction reaction of walnut shell

A mixture of walnut shell, phenol and the sulfuric acid catalyst solution were heated in a three-flask reactor at definite temperature under constant stirring and reflux. The resulting mixture was cooled and poured into dioxane-water (V/V, 8/2) solution after liquefaction. The diluted solution was filtrated under reduced pressure. The dioxane-water insoluble residue was dried to a constant weight and calculated for the percent of residue. Molecular weight distribution profiles of the resultant were monitored by a GPC system. Free phenol content (UFP) was determined according to GB/T 14074.13—1993.

1.3 Preparation and determination of the adhesives

After liquefaction, NaOH solution was added into the liquefied products to maintain the value of pH 10~11. Then the calculated amount of formalin (37% aqueous solution) was added to have a cocondensation reaction at 85~95℃ under reflux with total reaction time of 5~6 h. The general procedure for synthesis of conventional phenol formaldehyde resin was followed for comparison. The bond properties of the adhesives were measured according to GB/T 17657—1999.

2 Results and discussion

2.1 Effects of various reaction parameters

Table 1 shows the effect of various reaction parameters on the liquefaction of walnut shell in the presence of phenol, using sulfuric acid as catalyst. From the table, the amount of walnut shell residue remaining, the molecular weight and its polydispersity (M_w/M_n) of resultants after liquefaction reduces considerably with the processing of liquefaction. But a reduction in the unreacted free phenol was happened too, especially in the initial stage. This might be due to the nature of reactivity of phenol[4]. In the initial stage of liquefaction, the amount of residue and molecular weight of resultants reduce quickly. But there is some walnut shell residue remaining in the solution, and the molecular weight and its polydispersity change a little, especially after 120 min.

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作者简介: 郑志锋 (1975年生), 男, 讲师; E-mail: zhengzhifeng666@163.com

Tab. 1 The effect of various reaction parameters on the liquefaction of walnut shell

S/Ph	H_2SO_4 %	Time min	Temp ℃	Residue %	UFP %	M_w	M_n	M_w/M_n
Effect of walnut shell/phenol ratio								
1/2	3	60	120	26.49	8.40	945	757	1.25
1/3	3	60	120	19.08	17.40	929	809	1.15
1/5	3	60	120	6.60	32.31	706	678	1.04
Effect of H_2SO_4 concentration								
1/3	2	60	120	20.79	17.32	974	832	1.17
1/3	3	60	120	19.08	17.40	929	809	1.15
1/3	4	60	120	10.48	12.67	940	806	1.17
Effect of reaction time								
1/3	3	5	120	48.84	41.71	1030	884	1.17
1/3	3	10	120	25.88	36.10	994	855	1.16
1/3	3	30	120	22.21	28.33	963	832	1.16
1/3	3	60	120	19.08	17.40	929	809	1.15
1/3	3	120	120	15.62	10.25	919	802	1.15
Effect of reaction temperature								
1/3	3	60	100	28.86	21.94	979	846	1.16
1/3	3	60	120	19.08	17.40	929	809	1.15
1/3	3	60	150	9.39	14.33	990	814	1.22

2.2 Properties of the adhesives

Table 2 represents properties of the pine polywood for concrete form bonded with WPF adhesives compared to the conventional PF adhesives.

Tab. 2 Properties of plywood for concrete form bonded with adhesives

Items		Standard value	PF	WPF
MOR (MPa)	Longitudinal	≥24	41	40.6
	Horizontal	≥20	31.5	27.6
MOE (MPa)	Longitudinal	≥5000	5442	5461
	Horizontal	≥4000	4314	4299
Bond Strength (MPa)		≥0.7	1.20	1.33
Wood failure (%)		—	95%	90%

From Table 2, WPF adhesives can be successfully applied to bonding the plywood for concrete form.

3 Conclusions

(1) Walnut shell was easily liquefied in phenol by using sulfuric acid as the catalyst.

(2) The properties of WPF resin adhesives were close to those of the conventional PF resin adhesives. WPF resin adhesives were acceptable for plywood.

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核桃壳液化及其产物在酚醛树脂胶粘剂中的应用研究

郑志锋[1]，邹局春[1]，张宏健[1]，顾继友[2]，马天旗[1]

（1. 西南林学院木质科学与装饰工程学院，云南 昆明 650224；

2. 东北林业大学材料科学与工程学院，黑龙江 哈尔滨 150040）

摘 要：采用硫酸催化剂，考察了核桃壳与苯酚重量比、浓硫酸加入量、液化时间和温度对核桃壳液化的影响。研究结果表明核桃壳容易液化，随着液化的进行，核桃壳残渣率和游离酚含量降低，液化反应初期产物的分子量也迅速降低；核桃壳液化产物/苯酚/甲醛共缩聚树脂胶粘剂（WPF）与传统酚醛树脂胶粘剂（PF）的对比表明，WPF可作为胶合板用胶粘剂。

关键词：核桃壳；苯酚；液化；酚醛树脂胶粘剂

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