Ciência Florestal, Santa Maria, v. 25, n. 2, p. 515-521, abr.-jun., 2015
ISSN 0103-9954 DOI: 10.5902/1980509818471

EVALUATION OF RAPESEED STALK PARTICLEBOARD BONDED WITH LABORATORY-MADE UREA-FORMALDEHYDE RESIN

AVALIAÇÃO DE AGLOMERADO DE CAULE DA COLZA COLADO COM RESINA UREIA-FORMALDEÍDO PRODUZIDA EM LABORATÓRIO

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ABSTRACT

Brassica napus L. (rapeseed) stalk was used as a possible raw material for particleboard. A urea-formaldehyde resin was synthesized in the laboratory with resin solids at 50% content as a particleboard binder. The physical characteristics of the synthesized urea-formaldehyde resin were analyzed for solid content, specific gravity, viscosity, gel time, pH, and free formaldehyde content. The laboratory particleboards were made using rapeseed stalk and wood particles based on a rapeseed stalk oven dry weight of 0, 23, 48, 73, and 100% with UF resin. The physical and mechanical properties of the particleboards were tested according to the ASTM D 1037-99 procedure. The internal bond, bending strength and screw-holding properties of the particleboards made using the urea-formaldehyde resin decreased gradually with increasing rapeseed stalk content. However, the acceptable physical and mechanical properties of all the particleboards demonstrated that rapeseed stalk is a suitable raw material for particleboard manufacture.
Keywords: *Brassica napus* L. (Rapeseed); Agricultural stalk; Urea-formaldehyde resin; Particleboard.

RESUMO

O caule de *Brassica napus* L. (colza) foi usado como matéria-prima para fabricação de chapas aglomeradas. A resina à base de ureia-formaldeído foi sintetizada em laboratório com 50% de teor de sólidos como agente ligante. As características físicas da resina de ureia-formaldeído sintetizada foram analisadas com base no teor de sólidos, massa específica, viscosidade, tempo gel, pH e teor de formaldeído livre. Os aglomerados foram feitos em laboratório, usando o caule da *Brassica napus* e partículas de madeira com base de caule da mesma espécie, no peso seco nas proporções de 0%, 23%, 48%, 73%, e 100% e resina de ureia-formadeído. As propriedades físicas e mecânicas dos aglomerados foram testadas de acordo com procedimentos da norma ASTM 0 1037-99. A ligação interna, a resistência à flexão e as propriedades de retenção de parafusos nos aglomerados, usando a resina ureia-formaldeído reduziram gradualmente com o aumento da proporção do caule da colza. No entanto, as propriedades físicas e mecânicas aceitáveis de todos os aglomerados demostraram que o caule da colza é matéria-prima adequada na manufatura de aglomerados.
Palavras-chave: *Brassica napus* L. (colza); resíduo agrícola; resina ureia-formadeído; aglomerado.

INTRODUCTION

Urea-formaldehyde (UF) resin is extensively used as a binder adhesive for the production of wood-based panels such as medium density fiberboard, particleboard (PB) and hardwood plywood for interior uses. UF resin is an excellent adhesive with features such as virtually colorless glue lines, low price, mold and fungi resistance, and ease of handling (e.g.; mixing, applying and cleaning). UF resin can be successfully bonded with most species of wood in many combinations (SELLERS, 1985). However, formaldehyde emission is the main disadvantage property of the

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Recebido para publicação em 24/02/2013 e aceito em 3/09/2013

UF resin. The lower formaldehyde/urea (F/U) molar ratio, the lower the content of free formaldehyde in the UF resin. The formaldehyde emission of UF resin has been declining as a result of new resins and resin technologies (Dunky, 1998).

During the UF resin synthesis, chemical condensation reactions between formaldehyde and urea occur to form a polymer, and three reaction steps are involved (PIZZI and MITTAL, 1994). The first step is the addition reaction of urea and formaldehyde under mild alkaline condition of pH 7.4 to produce methylol ($-CH_2OH$) compounds (mono-, di- and trimethylolurea). The starting mole ratio of formaldehyde to urea is about 2.0 or slightly above. This step is usually completed in less than 10 minutes at 70~80°C. The second step is the condensation of the methylol units with the elimination of water. The polymerization reaction involves the formation of methylene ($-CH_2-$) bonds, and proceeds to reach the desired viscosity. As this polymerization reaction continues, the free formaldehyde content in the solution increases. This step is always acid catalyzed and completed by applying heat at 90°C. In the final step, the pH of the reaction mixture is raised to 7~8 to stop the polymerization reaction. A second charge of urea is added to the resin in order to reduce the level of the free formaldehyde content. Free formaldehyde in the resin reacts with this second urea. Therefore, the final mole ratio of formaldehyde to urea reaches around 1.1~1.2 in order to keep very low formaldehyde emission for PB binder adhesives (PIZZI and MITTAL, 1994).

PB is a wood-based panel product used widely in the manufacture of furniture, cabinets, interior wall, and floor underlayment in home construction. The production of PB has increased with the increase of the world population and the economic development. The global consumption of PB was 97.5 million m^3 in 2010 according to the Food and Agricultural Organization of the United Nations (FAO, 2011). Wood particles come from planer shavings, edgings, sawdust, other process residues, and small diameter logs from thinning (ROWELL et al., 1997).

On the other hand, PB can be easily manufactured by use of flax residues and other agricultural residue, such as straw and cotton stalks (BOWYER and STOCKMANN, 2001). Sustainable agricultural wastes are potentially alternative renewable sources of raw materials for the manufacturing of reconstituted bio-based panel products. The widespread availability of agricultural wastes has spurred new profit in using agricultural fibers for worldwide panel industries because of their environmental and profitable advantages (ROWELL et al., 1997). For utilizing other agro-based residues for panel products, many global researchers have examined a wide variety of sustainable renewable agricultural fibers such as particles and fibers of sugar cane bagasse, banana stem, kiwi branch, coffee husk, corn stalks, cotton stalks, rice husk, rice straw, and kenaf (ROWELL et al., 1997).

Brassica napus L. (rapeseed), which grows to approximately 80~130 cm tall, is widely grown for the production of animal feed from leaves, vegetable oil for human consumption and biodiesel from seeds. Rapeseed was the third leading source of vegetable oil in the world in 2000. Leading producers of rapeseed include the European Union, China, Canada, United States, Australia, and India (FAO, 2011). Worldwide production of rapeseed increased sixfold between 1975 and 2007. In 2009, the world production of rapeseed was 57.3 million metric tonnes (FAO, 2011). Rapeseed stalk can be used as an alternative fiber resource for commercial production of glued wood-based panel.

The purpose of this study was to evaluate the properties of PB made from wood particles and rapeseed stalks. A UF resin was synthesized in the laboratory as a PB binder. The physical and mechanical properties of PB were compared with those of panels made with different contents of rapeseed stalks.

MATERIALS AND METHODS

UF resin synthesis

UF resin was formulated in the laboratory with a target resin solids level of 50 % and a F/U mole ratio of 1.15. To calculate the targeted resin solid levels, the charged urea solid value was taken, and the formaldehyde-derived solids were taken as the methylene group (CH_2) values, which were obtained by multiplying the charge weights by a factor of 14/30 (OH, 1999). The general procedure was similar to that outlined by OH and LEE (2004). Firstly, 730.4 g of formaldehyde (F) solution (37% conc.) was charged into a stirred reactor that was heated to 50°C. After the pH was adjusted to 7.7 with a 6% sodium hydroxide solution, 269.8 g of urea (U_1) was added to bring the initial F/U_1 mole ratio to 2.0 over a period of 10 min while the reaction temperature was held at 70~80°C with the heating control of the exothermic reaction. After the reaction temperature was increased gradually to 90°C, the pH of the reaction mixtures was decreased to 5.2 by using 8% sulfuric acid solution. This reaction temperature was maintained until the resin was polymerized in approximately 25 min. When the reaction mixture had reached the desired viscosity, the pH was increased to pH 7.3 by adding 6% sodium hydroxide solution in order to end the polymerization reaction, and 199.8 g of the second charge of urea (U_2) was added to give a final F/(U_1+U_2) mole ratio of 1.15. The resin synthesis was completed by cooling to room temperature.

UF resin analysis

The viscosity of the UF resin was measured using a Brookfield RVF viscometer, spindle number 1 at a rotation of 2.09 rad/s (20 rpm). The free formaldehyde content was measured using the hydroxylamine hydrochloride method (WALKER, 1964). After the pH meter was calibrated with standardized buffer solutions, the pH was measured at 25°C. The gel time required for the UF resin to harden was measured in a test tube at 100°C, and the specific gravity was determined at 25°C. The resin solids level was determined by heating 1 g of UF resin on an aluminum pan at 105°C for 3 h and the following formula was used:

$$\text{Resin solid level (\%)} = \frac{\text{sample weight after 3h}}{\text{initial sample weight}} \times 100$$

PB manufacture

Brassica napus L. (rapeseed) stalks were collected from the Gyeongsan region of Korea. The rapeseed stalks particles (12~3.5 mesh) were dried to a 4~5 % moisture content prior to use. The determinations of cold water extractive and ethanol-benzene extractive of the rapeseed stalk were carried according to TAPPI T 207 OM-88 and TAPPI T 204 OM-88 (1992) test methods, respectively. The lignin and ash contents of the rapeseed stalk were determined according to TAPPI 222 OM-88 and TAPPI T 211 OM-85 (1992) test methods, respectively. Wood particles, which consisted of 60% *Populus alba* x *glandulosa* (hybrid poplar) and 40% *Pinus densiflora* (red pine) for the core layer, were obtained from a commercial PB plant in Korea. Table 1 shows the experimental design of the PB made in this study. To obtain a better mixture of wood particles and rapeseed stalks, the two particle types were hand-mixed and blended with the laboratory synthesized UF resin in a rotary drum blender. The liquid UF resin was applied with an air spray system at 172 kPa (25 psi). Single-layer homogeneous PBs were then manufactured using the processing parameters shown in Table 2.

PB performance test

Of the nine PB panels from each board type, five panels were used for physical and mechanical property tests and four for the screw-holding property tests. The test specimens were cut from boards and conditioned to equilibrium at a temperature of 20°C and 65% relative humidity before the test. The internal bond (IB), modulus of elasticity (MOE), modulus of rupture (MOR), and screw-holding properties were determined in accordance with the American Society for Testing and Materials (ASTM) procedure D 1037-99 (2002). The panel water absorption and thickness swelling properties were observed after the 2-h and 24-h soaking tests. The face screw-holding test was performed using 2.5-cm thick PBs, which were made of four 6-mm thick PBs glued together.

Statistical analysis

The panel property test results were analyzed using the Statistical Analysis System (SAS) programming package (SAS, 1998). One-way analysis of variance (ANOVA) in a completely random design with subsampling was used to determine the differences within each panel type. Significant differences ($P<0.05$) were further compared using a t test for the least significant differences (LSDs) from the SAS programming (STEEL and TORRIE, 1980). The effect of wood/rapeseed stalk composition on PB properties was also examined by regression analysis.

RESULTS AND DISCUSSION

UF resin properties

The properties of UF resin are important parameters for their application in PB manufacture. The synthesized UF resin viscosity was 180 mPa·s, which was suitable for resin spray application with a

TABLE 1: Experimental design of the particleboards.
TABELA 1: O desenho experimental dos aglomerados.

Board type	Rapeseed stalk	Wood particles
	--- (%) ---	
1	0	100
2	23	77
3	48	52
4	73	27
5	100	0

TABLE 2: Particleboard manufacturing parameters.
TABELA 2: Parâmetros da fabricação do aglomerado.

Panel dimensions	250 by 250 by 6.3 mm
Mat moisture content	8 to 9%
Wax & resin solids loading	1 & 8%, respectively, based on oven-dry wood weight
Target board density	700 kg/m^3 objective
Catalyst	None
Resin flow rate	130 mL/min
Hot press temperature	170^{o}C
Hot press times	4 min
Replication	9 boards per condition (total of 45 boards)

compressed air sprayer (Table 3). Viscosity reflects the resin flow on wood particles under hot-pressing conditions. Resin flow is therefore a determining factor in the manufacture of good PB. As expected, the resin produced in this study had very low free formaldehyde content (0.4%). Free formaldehyde content is an important parameter for plant hygiene and board emission quality. The resin had a pH of 7.6, solid content of 50.4%, and specific gravity of 1.19. Typically, aqueous UF 50~65% solid solutions are usually suitable for bonding PB. The gel time of the UF resin was 32.1 min (at 100^{o}C), which was relatively long due to the absence of any catalyst addition in the resin. In general, the gel time indicates the resin stability and cure speed in actual operations. Boards, which are bonded with UF resin below the F/U mole ratio of 1.15, will show poor strength properties, albeit of very low formaldehyde emission (PIZZI and MITTAL, 1994).

TABLE 3: Physical properties of the synthesized UF resin.
TABELA 3: Propriedades físicas da resina de ureia-formladeído sintetizada.

Property	Unit	UF resin
Solid content	%	50.4
Specific gravity	--	1.19
pH	--	7.6
Gel time (at 100^{o}C)	min	32.1
Viscosity	mPa·s	180
Free formaldehyde	%	0.4

Characteristics of rapeseed stalk

Table 4 lists the properties of the rapeseed stalk. The cold water extractive, ethanol-benzene extractive, and lignin contents of rapeseed stalk were 11.2%, 5.6% and 15.3%, respectively. The ash content and pH of rapeseed stalk were 9.8% and 6.1, respectively. Rapeseed stalks have lower lignin and higher ash content than common wood species. The chemical composition of rapeseed fibers probably influence the physical and mechanical properties of board (ROWELL et al., 1997)

PB performance test

The PB densities in this study ranged from 684 to 708 kg/m^3 (Table 5). ANOVA results showed that the panel density was significantly ($P<0.05$) affected by board type. LSD test showed that the panel density was significantly ($P<0.05$) affected by rapeseed stalk particle content, with board type 1 (100% wood particles) being denser than board type 5 (100% rapeseed stalk). Panel density variation may be considered to be due to difference between wood and rapeseed stalks. However, the panels of board types 2, 3, 4, and 5 had equivalent densities, showing that panel density was relatively constant regardless of the content of rapeseed stalk.

The IB range for all panels was 0.47 N/mm^2 to 0.90 N/mm^2 (Table 5). In general, the IB value decreased with increasing rapeseed contents. The LSD test showed that IB was significantly affected

TABLE 4: Characteristics of rapeseed stalk.
TABELA 4: Características do caule da colza.

Property	Unit	Rapeseed stalk
Cold water extractive	%	11.2
Ethanol-benzene extractive	%	5.6
Lignin	%	15.3
Ash	%	9.8
pH	--	6.1

TABLE 5: Performance test results of the PBs made from rapeseed stalk.
TABELA 5: Resultados do desempenho do ensaio sobre os alomerados feitos do caule da colza.

Board type	Panel density	IB	MOE	MOR	Face screw-holding	Thickness swelling		Water absorption	
						2-h	24-h	2-h	24-h
	(kg/m^3)	------- (N/mm^2) -------			N	--------------- (%) ---------------			
KS type 8.0	500 ~ 800	0.15	1600	8.0	500	NS	NS	NS	NS
1	708 (0.9) A	0.90 (4.3) A	2577 (11.8) A	16.5 (10.2) A	1012 (2.1)A	10.3 (4.3) D	32.7 (5.7) D	10.8 (7.2) D	66.1 (5.2) D
2	704 (1.3) AB	0.70 (7.6) B	2210 (9.3) B	14.0 (12.3) B	854 (4.6)B	11.2 (11.5) C	35.8 (8.6) C	12.9 (6.8) C	72.3 (6.5) C
3	695 (1.1) AB	0.66 (9.3) C	2069 (11.5) C	12.9 (10.6) C	831 (5.2)C	13.3 (6.7) B	43.9 (9.1) BC	14.5 (9.2) B	80.2 (5.9) B
4	689 (0.8) AB	0.59 (11.5) D	1959 (15.1) C	12.6 (9.8) C	827 (7.3)C	13.5 (10.2) B	44.5 (11.7) B	14.8 (10.7) B	81.7 (8.6) B
5	684 (0.7) B	0.47 (14.3) E	1798 (7.6) D	11.7 (8.3) D	802 (3.8)D	14.7 (6.8) A	50.3 (4.6) A	16.1 (8.4) A	90.4 (5.6) A

Where in: Values in parentheses are coefficients of variations. IB values represent an average of 15 test specimens. Each value of MOE, MOR, thickness swelling and water absorption represents an average of 10 test specimens. Face screw-holding values represent an average of 3 test specimens. Means with the same letter are not significantly different (0.05 level). NS: Not specified by the rapeseed stalk particle content, which suggests that rapeseed stalk particles require a larger resin loading to obtain the same IB as wood particles. Previous research reported that increasing resin loading generally improved the panel's physical and mechanical properties (OH, 2010). However, the panels exceeded the minimum strength requirements (0.15 N/mm^2) for IB, according to Korean Standard KS F 3104 for PB type 8.0 (KSA, 2006).

The MOE ranged from 1798 N/mm^2 to 2577 N/mm^2 (Table 5). LSD test showed significant differences for MOE among board types. Also, the result of the regression analysis test (Table 6) showed significant differences in MOE for wood/rapeseed stalks ratio.

The MOR range for panels produced in this study was between 11.7 N/mm^2 and 16.5 N/mm^2 (Table 5). The results of regression analysis test showed significant differences in MOR for wood/rapeseed stalks composition (Table 6). This suggests that wood/rapeseed stalks ratio had an adverse effect on the flexural strength properties. Similar findings were previously reported for castor stalks and cotton stalks in which the MOR decreased with increasing the amounts of castor stalks and cotton stalks in PBs, respectively (GRIGORIOUS and NTALOS, 2001; GULER and OZEN, 2004). However, the panels exceeded the minimum MOR strength requirements (8.0 N/mm^2) according to the Korean Standard KS F 3104 for PB type 8.0 (KSA, 2006).

The face screw-holding for all panels ranged from 802 N to 1012 N (Table 5). There was a significant difference in face screw-holding for wood/rapeseed stalks ratio (Table 6). However, the panels exceeded the minimum strength requirements (500 N) for face screw-holding, according to Korean Standard KS F 3104 for PB type 8.0 (KSA, 2006).

The thickness swelling range for all panels was 10.3 to 14.7 % for the 2-hour test and 32.7 to 50.3 % for the 24-hour test (Table 5). The results of regression analysis test showed significant differences in thickness swelling for wood/rapeseed stalks ratio (Table 6).

The water absorption for all panels ranged from 10.8 to 16.1 % for the 2-hour test and 66.1 to 90.4 % for the 24-hour test (Table 5). The results of regression analysis test showed significant differences in water absorption for wood/rapeseed stalks ratio (Table 6). Dimensional stability test results showed that the thickness swelling and water absorption of the panel increased with increasing rapeseed stalk content. This difference may be attributed to relatively lower lignin content of rapeseed stalks, resulting in their high porosity (Table 4). The results are in agreement with the results previously reported in the literature. Similarly, GRIGORIOUS and NTALOS (2001), and GULER and OZEN (2004) were also reported that thickness swelling and water absorption increased with the increasing of the content of castor stalks and cotton stalks in PBs, respectively.

CONCLUSIONS

Rapeseed stalks were used as a raw material for PB manufacture. The performance test evaluation showed that the mechanical properties of the resulting PBs decreased gradually with increasing the rapeseed stalk content. On the other hand, the dimensional stability test results of PBs increased with the increasing of the amount of

TABLE 6: Analysis of the effect of wood/rapeseed stalks composition on PB properties
TABELA 6: Análise do efeito da composição madeira/caule colza em aglomerado propriedades

Properties	Linear regression	r^2
IB	0.85 - 0.0039x	0.96
MOE	2473.4 – 7.18x	0.95
MOR	15.66 – 0.043x	0.89
Face screw-holding	951.1 – 1.75x	0.81
24-h Thickness swelling	32.87 + 0.17x	0.96
24-h Water absorption	66.82 + 0.231x	0.98

Where in: r^2 = coefficient of determination rapeseed stalk. Nevertheless, all boards made in this study showed good physical and mechanical properties. The study results demonstrate that rapeseed stalks are a suitable raw material for PB manufacture.

Finding these, alternative and valuable fiber applications of rapeseed stalks have the potential to alleviate regional wood fiber shortages from a global perspective.

ACKNOWLEDGEMENTS

The research was supported by Yeungnam University Research Grants in 2011.

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