

Evaluation of Melamine-Modified Urea-Formaldehyde Resin for Plywood Flooring Adhesive Application

Avaliação da resina da Uréia-Formaldeído Modificada por Melamina para Aplicação como Aderente de Madeira Compensada em Assoalho

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Uma resina de uréia-formaldeído modificada por melamina (MUF) como adesivo de madeira compensada para assoalho, foi sintetizada em laboratório com uma relação molar de 1,48 de formaldeído/(uréia + melamina). As características físicas da resina MUF incluindo sólidos não voláteis, peso específico, pH, formaldeído livre e viscosidade, etc., foram determinadas. A resina MUF foi aumentada com farinha de cones de pinheiro e NH_4Cl . A mistura continha aproximadamente 39% de sólidos de resina, 55,8% de sólidos totais e 44,2% de água. O tempo de mistura gel com o catalisador foi de 1,9 minutos a 100 °C. Foram feitos painéis de compensado em laboratório com o adesivo, usando-se madeiras coreanas. Os painéis de compensado foram testados para tensão de cisalhamento depois de submersos em água a 60 °C como método de envelhecimento, também para o módulo de ruptura, emissão de formaldeído e abrasão de superfície de acordo com os procedimentos KS F 3101 e KS F 3114. O resultado do teste mostrou que era possível usar a resina MUF para a aplicação da produção de compensado para assoalho Ondol.

Palavras-Chave: mistura adesiva, assoalho de madeira compensada, propriedades físicas e mecânicas.

Abstract

A melamine-modified urea-formaldehyde (MUF) resin, as a plywood flooring adhesive, was synthesized in the laboratory with a formaldehyde/(urea + melamine) mole ratio of 1.48. The physical characteristics of the MUF resin including nonvolatile solids, specific gravity, pH, free formaldehyde, and viscosity, etc., were determined. The MUF resin was mixed with an extender, pinenut flour and NH_4Cl . The mixture contained approximately 39 percent resin solids, 55.8 percent total solids, and 44.2 percent water. The mixture gel time with the catalyst was 1.9 minutes at 100°C. Laboratory plywood panels with the MUF resin adhesive mixture were made using Korean wood species. The plywood panels were tested for tension shear strength after 3-hour soak (60°C water) aging method, modulus of rupture, formaldehyde emission, and surface abrasion according to the procedures of KS F 3101, and KS F 3114. The test results showed that the MUF resin can be used for Ondol plywood flooring production.

Keywords: adhesive mix, plywood flooring, physical and mechanical properties

INTRODUCTION

Wood flooring is classified into solid wood flooring, laminated flooring and plywood flooring. Laminated flooring is made up of a core layer of high-density fiberboard and a face layer of a decorative paper, impregnated with melamine resin under high temperature and pressure (OH, 2010). Plywood flooring consisted of a face layer of wood veneer on plywood. The top side covering on the Korean plywood flooring is generally made from a layer of less than 2mm decorative wood veneer finished with a urethane type coating. Plywood flooring is comparable to solid wood flooring, and better than laminated flooring. The advantage of plywood flooring is

its natural texture, durability to heat and water, and ecological friendliness. Plywood flooring offers warmth and beauty, and there are more colors and species of wood available than ever before. Plywood flooring is used widely in residential, commercial and public buildings (NWEA, 2009).

Plywood flooring with tongues and grooves is easily installed on floors without additional tightening elements. In Korea, plywood flooring is used as a covering of an under floor heating system, known as an Ondol plywood flooring board. Korean Ondol plywood flooring board is well known internationally, and exported widely to the world. In 2005, in Korea, the production of wood flooring was 8.1 million m^2 , of which

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4.1 million m² was Ondol plywood flooring (PARK, 2007). The world production of wood flooring is expected to increase steadily over the next decade (NWFPA, 2009; PARK, 2007).

Melamine-modified urea-formaldehyde (MUF) resin is used widely for manufacturing engineered wood products, such as plywood, wood flooring board, particleboard and fiberboard, owing to its excellent glue-line durability and water resistance. MUF resin can be synthesized easily by adding melamine to urea-formaldehyde resins due to the similarity of the molecular structure, such as the amine group between melamine and urea. MUF resin with low melamine content showed relatively good panel performance, such as heat and water resistance, and can reduce the production cost of adhesives due to the high cost of melamine (OH, 1999; HSE, 2009).

A resin adhesive mix is used as a binder for the manufacture of plywood (Oh and Sellers, 1999; SELLERS JUNIOR, 1985). The MUF resin is normally mixed with an extender, filler, catalyst (e.g., ammonium chloride) and water to accelerate cure rate and develop glue-line strength. The extender and filler content in the dispersion comprises 10 to 20 percent of the total adhesive mix solids.

In Korea, *Pinus densiflora* Siebol et Zuccarini, *Pinus rigida* Miller, and *Quercus acutissima* Carruthers are the main tree stands and commercially important species. Wood composite manufacturers located in Korea use these species as a raw material.

This study evaluated the laboratory-synthesized MUF resin for Ondol plywood flooring applications. A MUF resin was formulated for bonding plywood using Korean wood species. Comparisons were made among plywood manufactured with different species.

MATERIAL AND METHODS

MUF Resin synthesis

MUF resin was formulated in the laboratory with a formaldehyde/(urea + melamine) mole ratio of 1.48 (melamine content of 5 percent based on resin solid) (Table 1). The general synthesis procedure of the MUF resin was similar to that outlined previously by Oh (1999). The formaldehyde solution (37% conc.) was first charged to a stirred reactor, and adjusted to pH 7.5. The urea aliquot was first added to the heated reactor at 80°C. After the first urea

addition was completed, the polymerization reaction was carried out at pH 5.0. For the next step, melamine was added slowly and reacted by increasing the pH to about 8.5. The second urea aliquot was then added. The reaction temperature was maintained until the desired viscosity by Gardner-Holdt viscosity. The resulting resin was cooled to room temperature, and stored until property analysis and use. To calculate the targeted resin solids levels, the charged urea and melamine solids values were taken as such and formaldehyde-derived solids were taken as the methylene group (CH₂) values, which were obtained by multiplying the charge weights by a factor of 14/30.

MUF resin analysis

The resin solid content was determined by heating 1 g of resin on an aluminum pan at 125°C for 2h. The specific gravity was measured using a specific gravity meter (Troemner Co., Philadelphia, PA). After calibrating the pH meter (Mettler-Toledo Ltd, Beaumont Leys, Leicester, England), pH was measured at 25°C. The gel time was measured using a Sunshine gel timer (Philadelphia, PA) at 100°C. The free formaldehyde content was measured using the hydroxylamine hydrochloride method (WALKER, 1964). The viscosity of the laboratory-synthesized MUF resin was measured using a Brookfield Viscometer (Stoughton, MA), Model RVE, spindle number 1 and 2 at 2.09rad/s (20rpm) rotation (Table 2).

Plywood manufacture

Plywood panels were made using three Korean species veneers supplied by a commercial plywood manufacturing company in Korea. Laboratory plywood panels were similarly manufactured according to the procedure reported previously by Oh and Sellers (1999). Plywood panels were then manufactured using the processing parameters listed in Table 3. The adhesive spread was applied with a roller coater.

Plywood performance test

Of the eight plywood panels bonded with the MUF resin mix, four panels were used for the mechanical property tests and the other four panels were used to measure the surface abrasion and formaldehyde emission. The test specimens were cut, and property tests were performed for tension shear strength, modulus of rupture (MOR), and formaldehyde emission

Tabela 1. Cargas de síntese e propriedades da resina de laboratório MUF.**Table 1.** Synthesis charges and properties of laboratory MUF resin.

MUF resin synthesis		MUF resin properties	
Ingredient	Amount (mole)	Properties	MUF resin
Formaldehyde	5.01	Solid content	50 %
Urea	3.26	Specific gravity	1.2
Melamine	0.11	pH	7.9
Water	14.23	Free formaldehyde	0.32 %
		Viscosity	350 mPa.s

Tabela 2. Ingredientes da mistura de adesivos de compensado e características da mistura.**Table 2.** Plywood adhesive mix ingredients and mix characteristics.

Mix ingredient	Amount (%)	Mix characteristics	Amount (%)
MUF resin (50%)	78	MUF resin solids	39
NH ₄ Cl (15%)	4	Extender solids	13.5
Wheat flour	15	Filler solids	2.7
Pinenut flour	3	NH ₄ Cl solids	0.6
		Total mix solids	55.8
Total	100	Total mix water	44.2

Wheat flour and Pinenut flour estimated at 10 percent moisture content.

Tabela 3. Parâmetros de manufatura de compensado de laboratório utilizados neste estudo.**Table 3.** Laboratory plywood manufacturing parameters used in this study.

Veneer dimensions	300 by 300 by 2.1 mm
Veneer moisture content	4 to 6%
Plywood panel	3-ply
Resin application rate	171 g/m ² single glueline basis
Cold press time	5 min
Cold & hot press pressure	1.03 MPa, 1.37 MPa
Hot press temperature	125°C
Hot press time	4 min
Total assembly time	30 min
Replication	8 boards (total of 24 panels)

in accordance with the KS F 3101 (KSA 2006). The parallel MOR results were obtained in a static bending test. The tension shear strength of each specimen was recorded, and wood failure over the sheared area was estimated visually after drying the specimen. The abrasion test for the unfinished surface specimens was measured from the specimen weight difference between initial weight and weight after 500 revolutions of an abrasion disc on the specimen surface according to the procedure, KS F 3114 Plywood for flooring (KSA 2000).

Statistical analysis

The panel property test results were analyzed using the Statistical Analysis System (SAS) programming package (SAS INSTITUTE, 1994). The wood failure values (percent) are not normally distributed. Therefore, the wood failure values were converted to a normal distribution by an arcsine transformation (degree) prior to analysis (Oh *et al.*, 1997). The analysis of variance (ANOVA) was used to determine the

differences within each panel type. Significant differences (0.05 levels) were further compared using a t-test for Least Significance Differences (LSD) from the SAS program (STEEL AND TORRIE, 1980).

RESULTS AND DISCUSSION

MUF resin properties

The MUF resin made in this study showed very low free formaldehyde contents of 0.32 percent. Generally, for industry uses some of the second urea reacted with the residual free formaldehyde present in the reaction mixture, resulting in very low free formaldehyde content in the resin (LEE AND OH, 2010; SELLERS JUNIOR, 1985). The resin viscosity was 350mPa.s, which is suitable as an adhesive mix (SELLERS JUNIOR, 1985). The resin had a solid content of 50 percent, specific gravity of 1.2, and a pH of 7.9 (Table 1). All the tested properties of the resin were in the acceptable range for bonding plywood.

The MUF adhesive mix contained 39 percent MUF resin solids, 13.5 percent extender solids, 2.7 percent filler solids, 0.6 percent NH₄Cl solids (catalyst), and 44.2 percent water (Table 2). The mix gel time with the catalyst was 1.9 minutes at 100°C. The storage of the MUF resin mix has very limited working life due to the addition of catalyst and curing period was 24 hours at room temperature.

Plywood performance test

The shear strength range for all plywood samples after 3-hour soak in 60°C water ranged from 887 to 1125 kPa (Table 4). The LSD test results showed that the plywood made from

Quercus acutissima had significantly (0.05 level) higher shear strength than the plywood made from *Pinus densiflora* and *Pinus rigida*. In addition, the plywood made from *Pinus densiflora* and *Pinus rigida* did not significantly differ from each other in shear strength. Specific gravity was the major factor influencing shear strength and wood failure (SELLERS JUNIOR, 1985).

The wood failure values for all plywood samples after a 3-hour soak in 60°C water ranged from 80 to 88 percent (Table 4). The LSD test results showed that the plywood made from *Quercus acutissima* had significantly (0.05 level) higher wood failure results than the plywood made from *Pinus densiflora* and *Pinus rigida*. The plywood made from *Pinus densiflora* and *Pinus rigida* did not significantly differ from each other in wood failure. The average test values exceeded the minimum requirement for 50 percent wood failure and 600 kPa shear strength for the Korean Standard KS F 3101, interior panel (KSA, 2006).

The MOR range for all plywood panels was 40.2 to 47.7 MPa (Table 5). The LSD test results showed that the MOR differed significantly (0.05 level) according to the plywood type. The plywood made from *Quercus acutissima* had a higher MOR value than that of other panel types. This difference can probably be related to the species used to produce veneers with plywood. These MOR values were higher than the minimum performance (8MPa, commercial use) of NALFA/ANSI LF-01-2008 for laminate flooring (NALFA, 2007).

The surface abrasion resistance values for all plywood samples ranged from 0.0109 to 0.0300 percent (Table 5). The LSD test results showed that abrasion did not differ significantly

(0.05 level) according to the plywood type. The plywood made from *Quercus acutissima* showed a lower abrasion value than that of the other panel types. Abrasion represents the resistance of wood to wear and marring, and is a very important factor for wood flooring applications. The test results obtained in this study probably related specific gravity of veneer and showed good performance. These abrasion values were lower than the minimum 0.15% for the Korean Standard KS F 3101 (2006).

The formaldehyde emission range for all plywood panels ranged from 0.3 to 0.4 mg/L (Table 5). The LSD test results showed that there were no significantly (0.05 level) differences in formaldehyde emission regardless of the plywood type. These formaldehyde emission values were equal or lower than the maximum 0.4 mg/L (SE₀) for the Korean Standard KS F 3101 (KSA, 2006).

CONCLUSIONS

MUF resin and Korean wood species veneers were used as binder and raw materials for Ondol plywood flooring application. The performance test evaluation of the plywood samples showed that the panel properties differed significantly according to the plywood type. However, all plywood panel types showed good physical and mechanical properties for Ondol plywood flooring applications.

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Tabela 4. Força de cisalhamento e colapso da madeira após envelhecimento em água a 60°C por três horas.

Table 4. Plywood shear strength and wood failure after 3-hour soak in 60°C water aging method.

Plywood type	Specific gravity of plywood	Shear strength (kPa)	Wood failure (%)
<i>Pinus densiflora</i> (I)	0.53	931 (19.4) ab	84 (2.7) b
<i>Pinus rigida</i> (II)	0.52	887 (22.7) b	80 (4.4) b
<i>Quercus acutissima</i> (III)	0.64	1125 (18.7) a	88 (3.1) a

The shear strength and wood failure values given represent an average of 16 specimens (4 panels x 4 specimens per panel). Specific gravity measured at 12% MC and volume at 12% MC. Values in parentheses are coefficients of variations. LSD means with the same letter are not significant different (0.05 level).

Tabela 5. Resultados do teste de madeira compensada colada com resina MUF neste estudo.

Table 5. Test results of plywood bonded with MUF resin in this study.

Plywood type	MC (%)	MOR (MPa)	Abrasion (%)	Formaldehyde emission (mg/L)
<i>Pinus densiflora</i> (I)	7.5	42.4 (18.9) b	0.0119 (16.9) a	0.3 (11.5) a
<i>Pinus rigida</i> (II)	7.9	40.2 (23.1) b	0.0300 (8.0) a	0.4 (10.3) a
<i>Quercus acutissima</i> (III)	8.2	47.7 (17.4) a	0.0109 (12.4) a	0.3 (9.1) a

Each value of MOR and Abrasion represents an average of 8 test specimens (4 panels x 2 specimens per panel). Values in parentheses are coefficients of variations. LSD means with the same letter are not significant different (0.05 level).

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