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Green Adhesive-Using Glyoxalated Lignin and Hydrogenated Resin as Ecologically Safe Wood Adhesive for Interior Plywood

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Abstract

Petroleum-based adhesive such as urea formaldehyde and phenol formaldehyde resin dominates adhesive market which releases formaldehyde and VOC to the environment. The purpose of this study is to develop an adhesive based on isocyanate in combination with compounds from renewable sources like lignin, protein and starch. Adhesive formulation was developed by incorporation of hydrogenated resin, corn starch/PVOH emulsion with glyoxalated lignin (GL) and evaluation properties of the adhesive with plywood of inferior grade. Different concentrations of hydrogenated resin and corn starch emulsion were incorporated with GL to carry out the study. In order to evaluate the quality of the adhesive, 12 mm plyboard was manufactured and physical and mechanical properties was investigated. The optimum adhesive formulation, hot pressure conditions like temperature, pressure and time was optimized. The result showed that GL, hydrogenated resin, corn starch and PMDI having weight ratio 50:2:10:10, resulted in the highest water resistance when hot pressure temperature was 145–150 ^{o}C. Both water resistance and glue shear strength of plywood bonded with adhesive remained same when the hot press time was 12–16 min for 12 mm plywood. In order to evaluate the mechanical properties of the plywood, static bending strength and tensile strength was carried out. The mechanical properties of the plywood with unmodified lignin showed inferior mechanical properties then the modified. Bonding strength increases on addition of PMDI. The overall work has indicated that an ecologically safe wood adhesive can be prepared for wood-based panel products from renewable resources for bonding inferior-grade plywood.

Keywords: *glyoxalated lignin, PMDI, corn starch emulsion, hydrogenated resin, ecologically safe wood adhesive*

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INTRODUCTION

Since formaldehyde has been classified as carcinogenic to human[1], the requirements of urea–formaldehyde resins have become stricter and an urgent need for a reduction of its content and emission from wood-based materials and adhesives occurred. E0 (known as F***) class means formaldehyde emission below 3 mg/100 g while that for Super E0 (also known as F****) is below 2 mg/100 g[2]. There are several approaches to overcome that problem:

1. Development of adhesives based on renewable resources, e.g. soy proteins[3], tannins[4];
2. Replacement of formaldehyde-emitting adhesives namely urea–formaldehyde with other types of adhesives (e.g. polyurethanes);

3. Addition of formaldehyde scavengers to the glue formulation (e.g. liquefied wood[5] urea which is used in industry up to date);
4. Adhesive reformulating and/or partial substitution of formaldehyde with other aldehydes.

In literature, there are some reports on the application of succinaldehyde or propionic aldehyde in adhesives[6]. In the proposed solution, formaldehyde was replaced by glutaraldehyde-an industrial aldehyde used as a disinfecting agent or proteins-crosslinking agent (Kupec *et al.* 2003)-so that urea–glutaraldehyde (UGA) adhesive was obtained. However, it must be stressed that glutaraldehyde is less toxic than formaldehyde. Glutaraldehyde LD50 value (oral, rat) is 1470 mg/Kg (Sigma-Aldrich 2008), while that for formaldehyde is 100 mg/Kg[7] Also, since it is known that nanoparticles may greatly improve adhesive interactions with a substrate[8], the prepared UGA mix was blended with Al_2O_3 nanopowder[7-9]. The approach allowed for the development of a cold setting formaldehyde-free urea-based adhesive for wood bonding. API adhesive belongs to nonformaldehyde adhesives and solves formaldehyde release completely. However, API adhesive has its disadvantage, for instance, high viscosity, short working life, high cost and so on. All these factors have limited the application of API adhesive[8-11]. Here, we researched utilization of corn starch's esterification and then manufactured an API adhesive. This API adhesive was of no poison, no environmental pollution, low cost, long working life, low apparent viscosity, and good prepressing performance. In addition, it has excellent weather resistance, water resistance and resistance to high temperature[10-14]. All of the above performance is because of esterified corn starch emulsion itself. API adhesive is used in the production of plywood, block board and three layers composite flooring board and all of these experiment results were excellent[11-16].

MATERIALS AND METHODS

The alkaline lignin and maize starch used as a starting material for the glyoxalation reaction was purchased from the local market. Glyoxal (40%) and sodium hydroxide, PVA and pMDI used for this research work were procured from Merck/sigma Aldrich. Hydrogenated resin was procured from DKS Comp.

Adhesive Synthesis

Part – I

The glyoxalation reaction was carried out in the laboratory by taking three necked round bottom flask fitted with reflux condenser and thermometer. The alkaline lignin was dissolved with 30% caustic solution inside the round bottom flask under stirring for 20 to 30 min till the solution became uniform. The above mixture was heated upto 45–50 °C under stirring. The glyoxal 40% was added slowly under stirring (Molar ratio of G/L = 2.0 and NaOH/L = 0.5). The reaction was continued for 12 h at 50 °C.

Part-II

150 g corn starch, 2 g hydrogenated resin, 2 g PVA with 250 ml water emulsion was prepared.

Blending of Glyoxalated Lignin with Hydrogenated Resin, Corn Starch and pMDI

Part-II material was added to the above part-I reaction mixture and the raction was continued at the temperature 50–60°C for another one h. Polymeric 4,4'diphenyl methane diisocyanate (pMDI) was added and mixed for 30 min to prepare the non-formaldehyde-based, ecological safe adhesive for manufacture of plywood. The adhesive was taken for rheological properties study and bonding properties. The optimum adhesive formulation, hot pressure conditions like temperature, pressure and time was optimized.

Adhesive Mix Preparation

(1) Best formulation of GL–Corn starch Adhesive in the highest water resistance:

Glyoxalated lignin	:	50 parts
Corn starch	:	10
pMDI	:	10
Hydrogenated resin	:	2
Water soluble polymer:		30
Polyvinyl alchol	:	2

Extender: 4–5 parts

Plywood Manufacture

Nine ply plywood was manufactured by taking Gurjan (*Dipterocarpus*) species as core, face and back veneer of size 2′X2′ and 12 mm thickness. Each adhesive mix was applied on the veneer and conditioned for moisture content up to 14% with a roller coaster at a spread rate of 300–350 g/m^2 on both sides basis.

Pressing Conditions

Curing of resin by application of pressure may be effected at room temperature or may be accelerated by simultaneous heating at high temperature during application of pressure as shown in Table 1.

Table 1: *Pressing Conditions for Resin Curing.*

Parameters	Cold pressing	Hot pressing
Pressure	12 Kg/cm^2	14 Kg/cm^2
Temperature	NA	140°–150 °C
Time	30 min	12 min

Gel Time and Pot-Life Measurements

A glass test tube with 10 g of the glue was immersed in boiling water. The glue was being mixed with a glass rod until gelation occurred. Measurement was made in triplicate. Pot-lives were determined on viscosity basis.

Determination of Storage Life

The storage life is a test of the shelf life of resin under ambient conditions. Resin was first stored at ambient room temperature. Viscosity of the resin was checked every day.

Determination of Resin Solubility

A mass of 10 g resin was weighed into a 100 ml conical flask. The balance was tarred and then water was added slowly into the flask. The flask was shaked and observed for the precipitation of whole particles and sediments. Weight of water was recorded when the precipitate was found to be observed. The water tolerance of the resin is expressed as the ratio of parts of water W1 to one part of resin W_2 or W_1/W_2.

Adhesive Bond Assessment

The manufactured plywood was tested in boiling water resistance and boiling waterproof plywood. Glue shear strength, résistance to microorganism, tensile strength, percentage of wood failure and static bending strength etc. were tested as per IS:1734/1983 for assessment of bond quality.

Mechanical Properties Study

Physico-mechanical properties of the plywood has been carried as per IS:1734.

RESULTS AND DISCUSSION

Gel Time

From the data shown in Table 2 it is clear that reactivity of the adhesive is high-even at ambient temperature gellation occurred in 43–62 min without any hardener. Average physical and mechanical properties of plyboards are summarized in Table 3.

Table 2: *Properties of Resin.*

Gel time at 100°C (min)	Flow time (B4 cup) (sec)	Solid content (%)	Water tolerance	pH
588	21	48.50	1:7	7.2

Table 3: Physico-mechanical Properties of the Plywood.

Sl. No.	Static bending				Tensile strength, N/mm^2	
	MoR, N/mm^2		MoE, N/mm^2			
	Along	Across	Along	Across	Along	Across
1	49.46	28.24	4785	2862	29.64	16.22

Effect of Hot Press Temperature on the Mechanical Properties of the Board

Effect of hot press temperature on the mechanical properties of the board has been studied randomly. The average MOR, MOE and tensile strength increased significantly at 145–150 °C then below and higher temperature at the pressure 14 Kg/cm^2 (Table 4).

Effect of Hot Press Time on the Mechanical Properties of the Board

Effect of hot press time on the mechanical properties of the board has been studied randomly. The average MOR, MOE and tensile strength increased significantly at 12–15 min then below and higher temperature at the pressure 14 Kg/cm^2.

Table 4: Board Pressing Conditions.

<table>
<tr><th>Parameters</th><th>Cold pressing</th><th>Hot pressing</th></tr>
<tr><td>Pressure</td><td>12 Kg/cm^2</td><td rowspan="3">14 Kg/cm^2
150 °C
15 min</td></tr>
<tr><td>Temperature</td><td>NA</td></tr>
<tr><td>Time</td><td>30 min</td></tr>
</table>

Effect of Core Adhesive Coverage on the Mechanical Properties of the Board

The average MOR, MOE and tensile strength increased significantly at 250–350 g/m^2, then below and higher coverage (Table 5).

Table 5: Composition of the Adhesive Mix Used to Prepare 7 Ply Plies (1.2 mm Thickness).

Adhesive mix		Board parameters for 7 ply plywood	
Component	**Parts by weight**	**Characters**	**Board parameters (mm)**
Adhesive	200	Number of plies	7
Extender	10	Face longitudinal	1.0
Insecticide (GLP)	0.5	Cross band (cross grain glued)	2.2
		Long core (longitudinal grain	2.2
		Cross band (cross grain glued)	2.2
		Long core (longitudinal grain	2.2
		Cross band (cross grain glued)	2.2
		Back (longitudinal grain)	1.0

Effect of Moisture Content on the Mechanical Properties of the Board

The average MOR, MOE and tensile strength increased significantly at moisture content of the veneer in between 6–8% then below and higher moisture content.

Effect of Extender on the Mechanical Properties of the Board

The purpose of using extender in adhesive system was to improve some properties of adhesive, decrease the cost and endowed its some new functions. In the course of bonding, extender can fill up small opening of glued materials; meanwhile, it can also prevent outer layer starved glue lines because of adhesive permeating excessively. Bonding experiment of wood-based panels above proved that it was feasible in the production of plywood.

CONCLUSION

The present study on the use of GL–Corn starch and hydrogenated resin with PVA to prepare a natural wood adhesive shows that plywood bonded with above adhesive showed comparable mechanical properties to the panels made with the commercial

UF resins. The study demonstrates that formaldehyde-free and environment friendly GL–Corn starch/pMDI based adhesive could be used for making plywood and panel products at press equal to 12–14 Kg/cm^2, temperature 1145–50°C. Formaldehyde emission content in bonding product as per national standard was used in room that had obvious social benefit.

REFERENCES

1. Ballerini A, Despres A, Pizzi A (2005) Non-toxic, zero emission tannin-glyoxal adhesives for wood panels.*Holz als Roh-und Werkstoff*. 2005; 63(6): 477–8p.
2. Dziurka D, Łecka J. The effect of introducing acrylic emulsions grafted with acetoacetyl groups on the properties of particleboards. *J Appl Polym Sci*. 2004; 91: 2256–64p. IFT. *EN 205—Test methods for wood adhesives for non structural applications—Determination of tensile strength of lap joints*. Rosenheim, Germany: IFT; 2005.
3. IARC. *IARC classified formaldehyde as carcinogenic to humans. Press Release No. 153*. France: International Agency for Research on Cancer; 2004. Available from: http://www.iarc.fr/en/media-centre/pr/2004/pr153.html
4. Japanese Industrial Standards. *JIS A 5905: 2003*. Japan: Japanese Standards Association; 2003.
5. Kupec J, Charvátová K, Navrátil M, *et al*. Effect of cross-linking waste protein with dialdehydes on its biodegradation under anaerobic conditions. *J Polym Environ*. 2003; 11: 93–100p.
6. Kumar R, Choudhary V, Mishra S, *et al*. Adhesives and plastics based on soy protein products. Ind Crops Prod. 2002; 16: 155–72p.
7. Mansouri HR, Pizzi A. Urea-formaldehyde-propionaldehyde physical gelation resins for improved swelling in water. *J Appl Polym Sci*. 2006; 102: 5131–6p.
8. Medved S, Šega B, Kunaver M, *et al*. Liquefied wood as formaldehyde scavenger for wood-based panels. *Proceedings of the International Panel Products Symposium*; 2009 Sep 16–18; Nantes, France. 61–9p.
9. National Technical Information Service, formerly U.S. Clearing House for Scientific & Technical Information. *ADA125- 539*. Springfield, VA 22161: NTIS; 2005.
10. Umemura K, Inoue A, Kawai S. Development of new natural polymer-based wood adhesives I: dry bond strength and water resistance of konjac glucomannan, chitosan and their composites. *J Wood Sci*. 2003; 49: 221–6p.
11. Wang S, Pizzi A. Succinaldehyde induced water resistance improvements of UF wood adhesives. *HolzRoh-Werkst*. 1997; 55: 9–12p
12. Zhai LL, Ling GP, Wang YW. Effect of nano-Al_2O_3 on adhesion strength of epoxy adhesive and steel. *Int J Adhes Adhes*. 2007; 28(1–2): 23–8p.
13. Pizzi A. Theory and practice of the preparation of low formaldehyde emission UF adhesives.
14. *Holzforschung*. 1994; 48(3): 254–61p.
15. Zhang LT. *Carbohydrate Chemistry*. Beijing, China: Light Industry Publisher; 1984.
16. Kou XC, Zheng WZ. Water soluble polymer accelerates to stability and film-forming properties of starch adhesion agent. *Chinese Adhesive*. 1991; 13(5): 35–8p. Shi J, Wei S. Isocyanate Adhesive with Esterified Corn Starch Emulsion as main agent. *Electronic Journal of Biology*. 2007; 3(2): 35–41p.