International Journal of Polymer Science
Vol. 1: Issue 1
www.journalspub.com

Environment Friendly, Exterior Grade Resin Adhesive from Phenol-Animal Glue Formaldehyde (PGF)

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Abstract

Phenoplast and aminoplast based resins are the important adhesive for the manufacturing of marine grade, shuttering and moisture resistance plywood. Environmental concerns and higher cost of petroleum based resins have resulted in the development of technologies to replace phenol partially by biomaterials for the manufacturing of resin adhesive. Natural bio-based materials such as tannin, CNSL (cardanol), lignin soya etc. are used as partial substitution of phenol. This paper presents the development of phenol-animal glue formaldehyde resin as exterior grade binder. Here about 30% phenols were substituted by animal glue and optimized. The different physico-mechanical properties as per standard are quite satisfactory. This technique for the production of bio based wood adhesive is cost effective, eco-friendly and could be an ideal solution of petroleum based non-biodegradable resin adhesives.

Keywords: *Adhesive, glue, plyboard, resin, veneer*

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INTRODUCTION

Proteins have been used since many years as wood adhesives[1], mainly bio-based protein. Protein wood adhesive can be divided into plant protein[2–5] adhesive and animal protein[6,7] adhesive. In the present scenario these two types of proteins serves a great roll for the manufacturing of resin adhesive. The use of soya based adhesive is not new in the plywood panel industries[3,8,9]. About 9.0 million tons of soya beans are produced in India[1]. The early soya based adhesives were made by extending the protein with amino resin[10,11]. Soya based glues were popular in the early 20th century and worked well in plywood panels. Due to poor water resistance of soya based adhesive have limited applications[2]. Cross linking agent that can be used for alkaline soya[12] dispersion are soluble copper, chromium, zinc salt or aliphatic epoxies[13]. Epoxies are active hardening agents for alkaline soya glue and yield products with improved strength and durability but are expensive. An aqueous solution of polyamido amino epichlorohydrin could be used as cross linking agent for soya protein and consequently strength and water repelant properties increases[12,7] Animal glue is available defatted semi-solid form called siris. It is a protein derived from the simple hydrolysis of collagen, which is the principal protein constituent of animal hide, connective tissue and bones. Collagen, animal glue, and gelatin are very closely related as to protein and chemical composition. Gelatin is considered to be hydrolyzed collagen: $C_{102}H_{149}0_{38}N_{31}+ H_2O = C_{102}H_{151}O_{39}N_{31}$[14]. The protein in animal glue is globular protein, reactive and highly water soluble. On the basis of understanding of the adhesive mechanism of mussel protein

which serves as a strong and water resistance adhesive, cyst amine was successfully grafted into SPI by amide linkages[15].

The main component of animal protein is amino acid having reactive functional groups which can potentially react with other aqua based compatible cross linking adhesives. The main components of animal protein in the form of amino acids are of 51.29% carbon, 6.39% hydrogen, 24.13% oxygen, and 18.19% nitrogen. There may be minor variations in the composition of collagens from different sources, as well as in the composition of animal glues imparted by variations in processing techniques; however, the composition of glues having widely varying case histories are still very similar. The weight average molecular weight of animal glue has a wide range from 20,000–250,000. The higher the molecular weight, higher is the gel strength[14,16].

Usually the pH value of animal glue solution vary in the range of 6.5 to 7.4 and the solubility of animal glue is highly pH[14,16] dependent. In a natural and alkaline medium around 90 percent protein can be dissolved. The solubility of this protein decreases gradually and very low at pH (3–5). Animal protein is very compact structure where the polyamide long chains are held together by disulphide bonds, hydrogen bonds. The protein in animal glue mainly contains many reactive side chain amino acid group (about 30% of total amino acid) have the ability to form cross linking during thermosetting polymer growth with suitable cross linking agent. Presently used adhesives for plywood and composite material productions are mainly synthetic resin[10,17] for which required raw materials are almost entirely petroleum based. Among them phenol formaldehyde resin have been well accepted for the manufacture of plywood and composite product. In PF resin one of the main components is phenol, having high cost which directly influences the cost of adhesive as well as the composite materials also. As with demand the current consumption rate, the world wide petroleum reserves have been estimated to last only for next 40 years or less[18]. Higher price, corrosive and intermittent shortage of phenol has encourage the scientist to search for available alternative of phenol which have low cost non corrosive non-petroleum based chemical for partial replacement of phenol for the manufacturing of resin adhesive. Natural products like lignin, tannin, CSNL etc. are often used as partial replacement of phenol for the manufacturing of resin adhesive in plywood panel industry. Poor water resistance and bonding strength are the main problems of animal protein. To make this protein as good alternative animal protein needs to be modified before being used partially with PF resin preparation. Formaldehyde is also an important protein modifier. It first denatures the native protein and cross link thus resulting in enhancement of water resistance property.

RESEARCH METHODOLOGY

Materials

1. Phenol (C_6H_5OH) - 99%.
2. Formalin (HCHO) having Formaldehyde content 37%.
3. Sodium Hydroxide (NaOH) of Commercial Grade
4. Animal glue: Animal glue of different quality is available in the market in the form of flake trade name siris cost Rs. 60 to 100 depending upon the quality shown in Figure 1. It is sparingly soluble or insoluble in cold water but water at a temperature 60^0C and above is highly soluble in water but the solution is heterogeneous type.

Disruption of Animal Glue

To make the homogeneous solution an aqueous solution of 5% (W/V) caustic soda solution was taken, wormed at a

temperature 80±2^{0}C (pH of the solution is 9.8) and finally the animal protein in the flake from is added to the alkaline solution. After stirring about 40 to 50 min a clear homogeneous solution is prepared (pH of the solution is 9.6) (Table 1). This is due to base catalyzed hydrolysis of animal protein and was optimized at 90^{0}C temperature because after 80^{0}C change in viscosity is really negligible shown in Figure 2.

Fig. 1: *Picture of Animal Glue.*

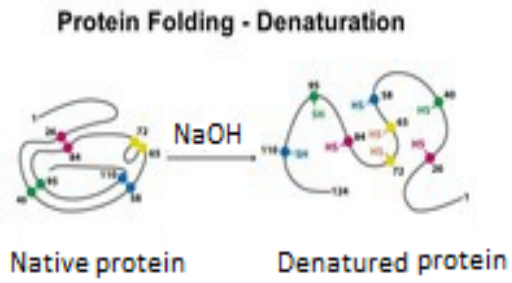

Fig. 2: *Picture of Denature Animal Glue.*

Table 1: *Viscosity of Animal Glue at Different Temperature and Fixed pH.*

Exp. No.	pH of solution	Temperature (°C)	Viscosity (cP)
1.	9.6	60	900
2.	9.6	65	820
3.	9.6	70	730
4.	9.6	75	610
5.	9.6	80	590
6.	9.6	85	586
7.	9.6	90	582

Preparation of Phenol Animal Protein and Formaldehyde Adhesive

To make the adhesive water was added followed 5% (W/V) caustic soda solution in the resin kettle wormed at a temperature 90±2°C and finally the animal protein in the flake from is added to the alkaline solution. After stirring about 40 to 50 min a very thin, clear homogeneous solution is prepared. This is due to base catalysed hydrolysis of animal protein. The temperature of the solution was cooled up to 40°C. After that phenol is added in the reaction mixture followed by formalin. The temperature of the mixture was increased up to 60°C by slowly supply of heat up to 70°C the temperature source was cut off gradually temperature increased slowly ay finally it was kept at 90°C. The cooking was continued till the mixture make clear cold water cloudy and the flow time of hot liquid was 14 in a B_4 cup.

Table 2: *Preparation of Phenol Animal Protein Formaldehyde at Different Proportion.*

Materials	Composition A	Composition B	Composition C	Composition D
Water (g)	50	60	50	60
Caustic Soda (g)	5	5	5	5
Animal protein (g)	20	30	20	30
Ph	9.6	9.6	9.6	9.5
Phenol (g)	100	100	100	100
Formaldehyde (g)	150	150	180	180
Temperature (^{0}C)	90	90	90	90
Condensation time (min)	45–50	45–50	45–50	45–50
Flow time in B4 cup at room temp (sec)	22.47	21.22	22.03	20.66
Solid content (%)	45.46	41.84	43.22	39.48
Pot life (days)	25	29	32	36

Curing of the PGF Resin Adhesive

The viscous liquid of PGF resin is taken in a bi-oriented polypropylene (BOPP) film (M.P. >200°C) and dried in open assembly up to a moisture content 10–12%. A looks like a semisolid layer of thickness approximately 3 mm. The whole system is cured at a temperature 140°C and pressure 10 Kg/cm^2 for 6 min. After removal of BOPP film a brown black hard mass solid of thickness 2.5 mm (average) is prepared. The physic-mechanical properties like tensile strength and flexural strength swelling test are done as per specification and the results are given in Tables 1, 2 and 3, respectively.

Table 3: *Tensile and Flexural Strength of Composite.*

Nature of material	Phenol: Animal glue	Av. tensile Strength (MPa)	Elongation at break (mm)	Flexural Strength (MPa)
Cured polymer	100:00	55	1.85	22.2
	90:10	53	1.94	24.5
	80:20	52	2.00	24.9
	70:30	50	4.92	33.8

(Thickness 2.55 ± 0.25 mm.)

**Av. tensile strength is obtained from three samples, Tests were done by Tensometer. Make: Kudal instrument, Bangalore, India.*

Table 4: *Water Absorption Test and Av. Thickness Swelling.*

Nature of material	Phenol : Animal glue	After 2 h (%)	After 24 h (%)	Av. Thickness swelling (%)
Cured polymer	100:00	7.15	9.12	4.82
	90:10	7.30	9.15	4.89
	80:20	7.50	9.36	4.95
	70:30	7.80	9.80	4.95

Testing

Different physico-mechanical properties of board have been studied as per relevant Indian standards[19,20]. Test parameters for moisture content, density, water absorption and tensile strength were also studied (Table 4).

RESULTS AND DISCUSSION

The resins prepared in different composition have high tack with comparable solid content and good pot life as well as low cost also.

The IR spectrum of native animal protein, denature protein in worm caustic solution and resin showed an interesting result which indicate that the denature animal protein is highly compatible with phenol and formaldehyde in aqueous medium undergo cross linking, produce high strength adhesive for plywood, panel industry.

FTIR Analysis of PGF Resin

The infrared (IR) spectrum of animal glue, denatured protein of animal glue solution and the resin prepared from phenol animal glue formaldehyde are given in Figure 3,4 and 5, respectively. It was found that the sharp peak at 3325–3330 cm^{-1} in the IR spectrum of Figure 3 due to the N-H stretching of $–CONH_2$ in protein. The special characteristic peaks of protein amide-I(C=O stretching vibration in amide group) at 1650 cm^{-1} and amide-IV (N-H plane bending vibration in amide groups) at 1535–1537 cm^{-1} is shown by Figure 3 has been reduced to 1635 and 1515 cm^{-1} is shown by Figure 5. The sifting of amide bonds may be due to the hydrolysis of amide linkage in animal protein by the alkali at elevated temperature. The alkali based hydrolysis of amide produce primary amine which is supported by the N-H bending frequency at 1575–1631 cm^{-1}. Also from Figure 5 the

IR spectrum the single broad peak at 3264 cm^{-1} indicates the stretching vibration of –OH functional group in PGF resin. Presence of all these groups $–NH_2$, -CONH and –OH (supported by IR) strongly support about the presence of Hydrogen bond between phenol and protein. The sharp peak at 1152 cm^{-1} indicates the presence of methylene ether bridge (C-O-C) in the polymer chain. Also the peak at 1631 cm^{-1} is due to secondary amide C=O stretching animal protein. The physic-mechanical strength properties like flexural and tensile strength of board by using bio based PGF resin adhesive achieve better bond quality as shown in Figure 6 and 7.

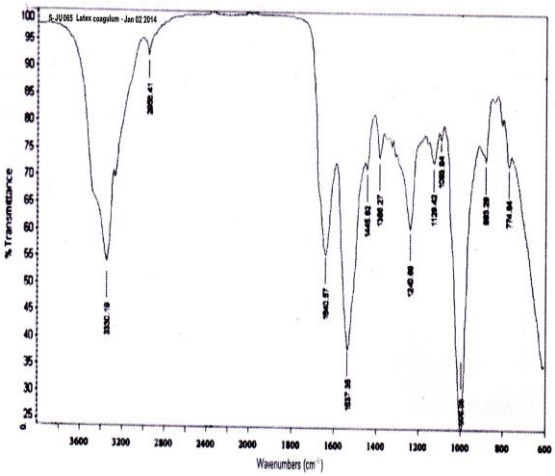

Fig. 3: *Infrared Spectrum of Animal Glue.*

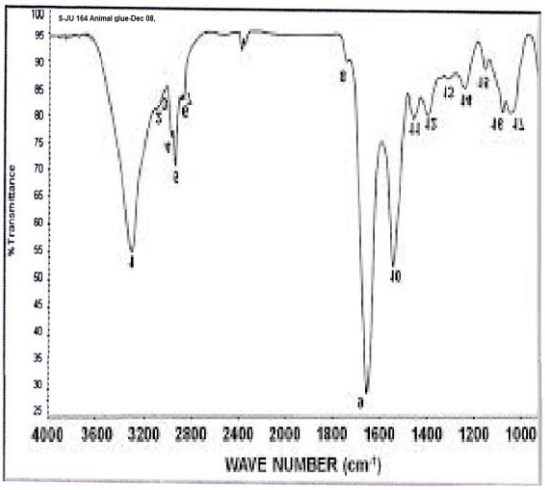

Fig. 4: *Infrared Spectrum of Denatured Animal Glue.*

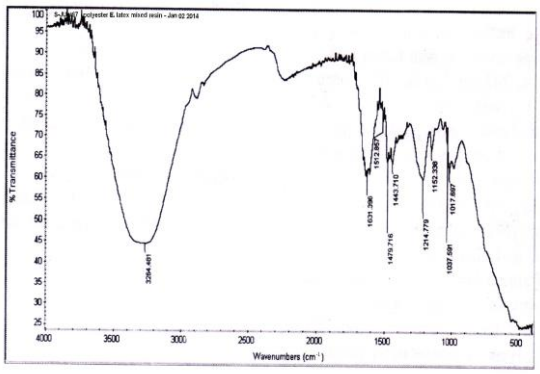

Fig. 5: *Infrared Spectrum of PGF Resin.*

Thickness of the board 2.5 mm

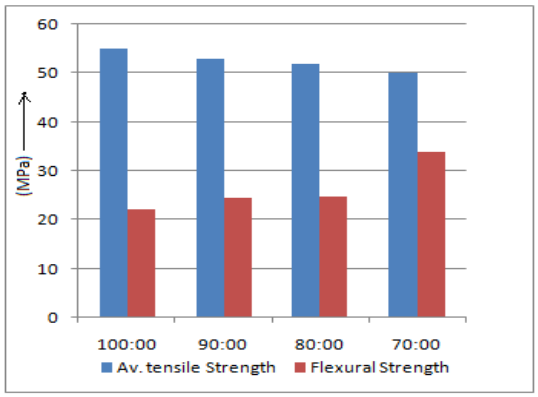

Fig. 6: *Av. Tensile Strength (MPa), Flexural Strength (MPa) of Board.*

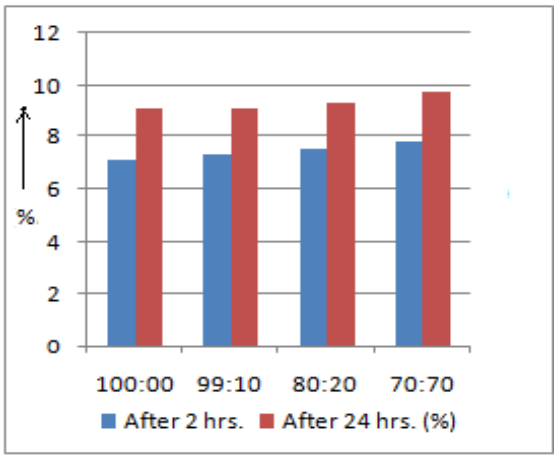

Fig. 7: *Av. Tensile Strength (MPa), Flexural Strength (MPa) of Board.*

CONCLUSION

It may be concluded i) from the point of view of physic-mechanical strength properties of board by using bio based PGF resin adhesive achieve better bond quality indicate 25–30 percent

replacement of phenol by the animal glue for the preparation of PGF resin will be good as a suitable binder for exterior grade plywood. ii) from the economic point of view that about 25–30% replacement of phenol not only lower the cost of resin adhesive as well as it could be an ideal solution of traditional PF resin in future. Finally, the PGF based adhesive contains nitrogen in animal glue which has good fire retardant properties. So, study of the fire retardant property of the ply board is necessary in future.

ACKNOWLEDGEMENT

The authors express their gratitude to ICAR, New Delhi for the financial assistance for this project as well as to Dr. A. Day, Principal Scientist, of NIRJAFT, Kolkata for time to time discussion, guidance and encouragement throughout the whole project.

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