Manufacturing of BWP-Grade Plywood from Resin Adhesive Using Animal Protein (Glue) by Partial Replacement of Phenol

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Abstract
This paper presents the development of plyboard using phenol–glue–formaldehyde (PGF) resin and their basic mechanical properties. Phenoplast and aminoplast-based resins is the important adhesive for the manufacturing of boiling water proof (BWP) 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 and soya etc. are used as partial substitution of phenol. Development of bio-based phenol–animal protein formaldehyde resin as exterior grade binder is not only cost effective but is noncorrosive also. Here about 30% of phenol was substituted by animal protein and optimized. The experimental results (as per IS: 1734 - 1983) of the physic-mechanical properties like surface finishing, tensile strength, internal bond strength, density, screw withdrawal and glue shear strength etc. of the ply board 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, veneer, plyboard, resin*

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INTRODUCTION

Plywood is a universal material in the field of construction and is progressively being used in building and furniture industries along with particle board and block board. It is widely being used in making cabinets, decorative wall paneling and partition walls. The more efficient synthetic resin adhesive had led to the development of weather-resistant plywood which are extensively used for exterior applications viz. building construction, concrete shuttering. It is also having an extensive application in construction of railway carriage, bus bodies and ships. Moreover, plywood has a tremendous export potential with continuously being exported to countries like Japan, Middle East, and West Asia. There is a greater awareness of the need for materials in an expanding global population and increasing affluence. 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 serve a great role 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, soya-based adhesive have limited applications[2].

Cross-linking agents 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 repellant properties increases[7, 12]. Animal glue is available in defatted semisolid 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 resistant 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 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 average molecular weight of animal glue has a wide range of 20,000–250,000. The higher the molecular weight, higher the gel strength[14, 16].

Usually the pH value of animal glue solution vary in the range of 6.5–7.4 and the solubility of animal glue is highly pH-dependent[14, 16]. In a natural and alkaline medium, around 90% protein can be dissolved. The solubility of this protein decreases gradually and it is 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) having 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 requires raw materials are almost entirely petroleum based. Among them, phenol formaldehyde (PF) resins 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 and the current consumption rate, the worldwide 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, noncorrosive, nonpetroleum-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 a 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. For particles, a smaller percentage of fine fractions lowered the strength properties of composites as stated by Hill and Wilson[19]. The strength loss was due to relatively larger surface area (up to 88% increased surface area) of the fine materials. However, most studies have not focused on the property enhancement of a multifiber layer system for agro-based medium-density fiberboard (MDF). Indian Plywood Industries Research & Training Institute has also done a lot of work on impregnated jute for making composite along with wood veneer as done by Naha *et al.*[20].

EXPERIMENTAL METHOD

Materials

1. Phenol (C_6H_5OH): 99%.
2. Formalin (HCHO) having formaldehyde content 37%.
3. Sodium Hydroxide (NaOH) of Commercial Grade.
4. Animal protein: Animal protein of different quality is available in the market in the form of flake (Trade name siris) cost Rs. 60–100 depending upon the quality. It is sparingly soluble or insoluble in cold water but is highly soluble in water at a temperature 60ºC and above 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, warmed at a temperature 80±2 ºC (pH of the solution is 9.8) and finally the animal protein in the form of flake was added to the alkaline solution.

After stirring for about 40 to 50 min, a clear homogeneous solution was prepared (pH of the solution was 9.6). This was due to base-catalyzed hydrolysis of animal protein and was optimized at 90 ºC temperature because after 80 ºC change in viscosity was really negligible (Table 1).

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

Exp. No.	pH of solution	Temperature (ºC)	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 by 5% (W/V) caustic soda solution in the resin kettle warmed at a temperature of 90±2ºC and finally the animal protein in the flake form was added to the alkaline solution. After stirring for about 40–50 min, a very thin, clear homogeneous solution was prepared.

This was due to base-catalysed hydrolysis of animal protein. The temperature of the solution was cooled up to 40ºC. After that phenol was added in the reaction mixture followed by formalin. The temperature of the mixture was increased up to 60ºC by slow supply of heat up to 70ºC and the temperature source was cut off gradually.

The temperature increased slowly and finally it was kept at 90ºC. The cooking was continued till the mixture made clear cold water cloudy and the flow time of hot liquid was 14 in a B_4 cup (Table 2).

Table 2: *Preparation of Phenol Animal Protein and 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 (ºC)	90	90	90	90
Condensation time (min)	45-50	45-50	45-50	45-50
Flow time in B4 cup at room temperature (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

Glue Formulation

The glue for plywood adhesives were prepared by mixing pre-impregnated glass fiber (PGF) resin with coconut shell flower (CSF) as filler in a glue mixture machine for 20 min for proper mixing of resin and filler at a ratio (weight in Kg) of PGF resin: CSF = 100 : 8

Spreading of Glue in Glue Spreader

The prepared glue was taken in spreader roller and the core veneers were passed through the spreader roller to make both side glued 30 g/sq. ft.

Manufacture of Plywood

1. Air dried core and face veneer was cut according to the desired size.
2. Individual jute felt has been compressed in cold press at pressure 12 $Kg.cm^2$ for 10 min to minimize the thickness.
3. Veneer (face core and face) were assembled as per opposite grain direction of wood veneer as required.
4. Plywood having various thicknesses was prepared at different specific pressure, temperature 135–140ºC and for a time of thickness of plywood + 2 min. The detail of plywood construction is given in Table 3.

Table 3: *Details of Plyboard Construction.*

Thickness (mm)	No. of ply	Veneer Assembly
6	5	Face (0.5 mm)—2 nos. Glue core (2.5 mm)—2 nos. Unglued core (2.5 mm)—1 nos.
12	7	Face (0.5 mm)—2 nos. Glue core (2.5 mm)—3 nos. Unglued core (2.5 mm)—2 nos.

Thereafter, plyboard were trimmed, sanded and taken for study of physic-mechanical properties.

Testing

Different physic-mechanical properties of plyboard have been studied as per relevant Indian Standards[21, 22].

Test parameters for moisture content, density, water absorption and cyclic test were also studied.

Static Bending Strength

Mechanical testing for evaluating of static bending strength such as modulus of rupture and modulus of elasticity of each sample were carried out as per IS: 1734-1983 (Part 11).

Tensile Strength

Tensile strength perpendicular and parallel to the grain were conducted in 10 Ton

UTM in tension mode and were calculated as per IS: 1734-1983 (Part 9).

Compressive Strength

Compressive strength evaluated at elastic limit was conducted in 10 Ton UTM in compression mode and were calculated as per IS: 1734–1983 (Part 10).

RESULTS AND DISCUSSION

Plyboard of different thickness have been manufactured by using the wooden glue core and face veneer whose data are depicted in Table 3**.** The mechanical properties of different composition are given in Tables 4–9.

Table 4: *Water Absorption Properties of 6 mm Thick Plyboard.*

Sample no.	Moisture content (%)	Density (Kg/mm^3)	Water absorption (%)
1	6.3	810	10.16
2	6.6	813	10.66
3	6.5	817	10.74
4	6.3	808	10.34

Table 5: *Physical and Mechanical Properties of 6 mm Thick Plyboard.*

Sample no.	Modulus of rupture (N/mm^2)	Modulus of elasticity (N/mm^2)	Tensile strength (N/mm^2)
Along the grain			
1	64.86	9302	46.31
2	68.19	9729	47.14
3	61.05	9004	46.81
4	63.35	9087	45.54

Table 6: *Physical and Mechanical Properties of 6 mm Thick Plyboard.*

Sample No.	Modulus of rupture (N/mm^2)	Modulus of elasticity (N/mm^2)	Tensile strength (N/mm^2)
	Across the grain		
1	60.33	6204	43.12
2	65.34	6645	43.56
3	50.21	6952	42.99
4	56.12	6296	42.45

Test was done in digital universal testing machine of 10 Ton capacity with two interchangeable load cell having capacity 1 KN and 10 KN.

Table 7: *Water Absorption Properties of 12 mm Thick Plyboard.*

Sample no.	Moisture content (%)	Density (Kg/mm^3)	Water absorption (%)
1	7.89	867	11.4
2	7.67	877	11.6
3	7.43	807	11.2
4	7.67	804	11.8

Table 8: *Physical and Mechanical Properties of 12 mm Thick Plyboard.*

Sample no.	Modulus of rupture (N/mm^2)	Modulus of elasticity (N/mm^2)	Tensile strength (N/mm^2)
	Along the grain		
1	62.22	6875	44.98
2	57.27	6889	44.45
3	58.67	7598	43.66
4	57.55	7567	44.65

Table 9: *Physical and Mechanical Properties of 12 mm Thick Plyboard.*

Sample no.	Modulus of rupture (N/mm^2)	Modulus of elasticity (N/mm^2)	Tensile strength (N/mm^2)
	Across the grain		
1	47.22	5551	42.64
2	49.14	6176	44.53
3	47.21	5947	41.27
4	45.65	6377	42.49

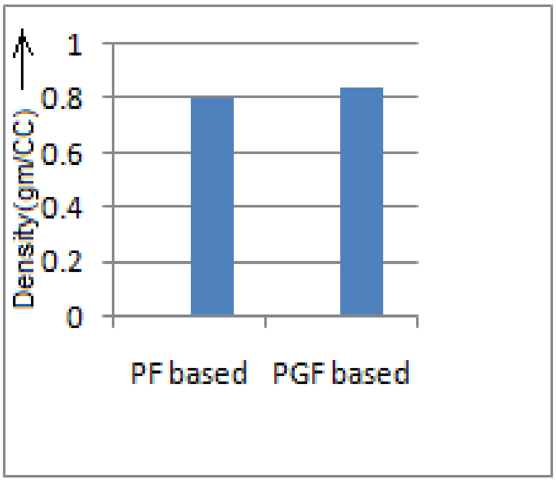

Fig. 1: *Average Densities of PF and PGF-Based 12 mm Thick Plyboard.*

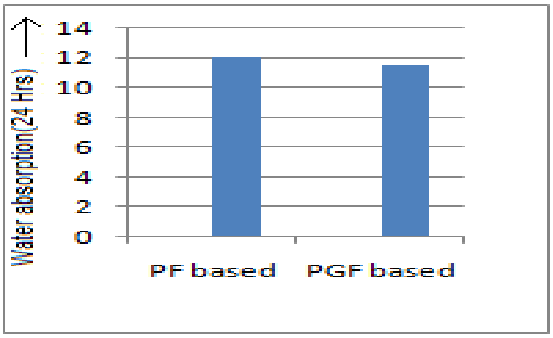

Fig. 2: *Average Water of PF and PGF-Based 12 mm Thick Plyboard.*

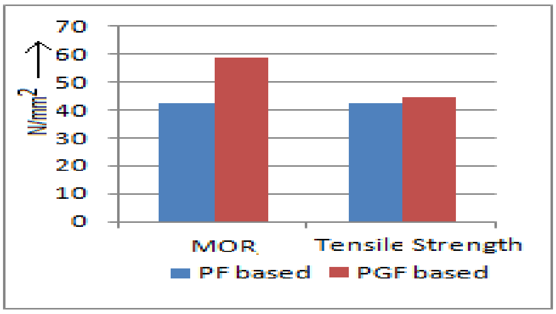

Fig. 3: *Average MOR and Tensile Strength of PF and PGF-Based 12 mm Thick Plyboard.*

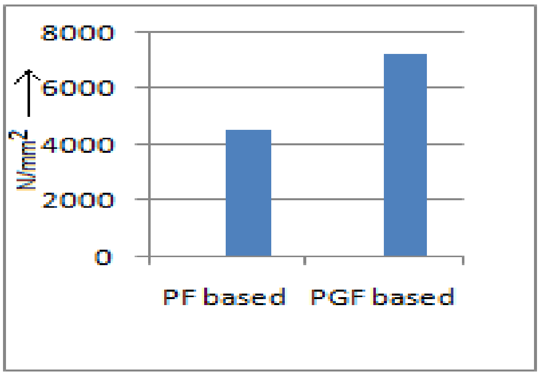

Fig. 4: *Average MOE of PF and PGF-Based 12 mm Thick Plyboard.*

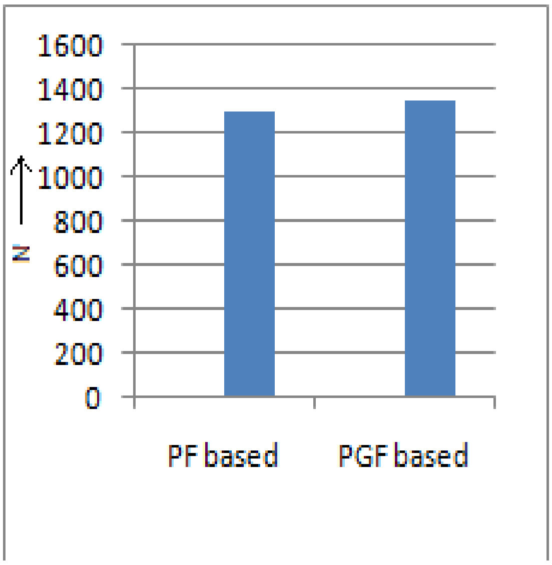

Fig. 5: *Average Glue Shear Strength of PF and PGF-Based 12 mm Thick Plyboard.*

From the study, it can be inferred that no appreciable change was observed in glue shear strength. From Table 10, it has been observed that there is no change in water absorption and density as compared to traditional plywood**.** From Figures 1–5, the higher values of static bending strength and tensile strength were obtained in the range of 60–70 N/mm^2 and 40–47 N/mm^2, respectively.

From the comparative study, traditional plyboard and plyboard manufactured by using modified PGF resin adhesive were tested as per IS: 303–2003, it has been observed that there is no appreciable change in bond quality and mechanical properties of the plyboard manufactured and results conforms as per BWR grade as depicted in Table 10 and 11.

Table 11: *Glue Shear Strength of 6 mm and 12 mm Plyboard.*

Used resin	No. of sample	Resistance to water after three cycle	Glue shear strength in dry state (N)	
			6 mm plyboard	12 mm plyboard
PGF	1	No delamination	1379	1336
	2	No delamination	1345	1367
	3	No delamination	1387	1349

Table 10: *Comparative Physico-mechanical Properties of PF Resin-Based Plywood with Modified PGF Resin-Based Plywood.*

Test performed	PF-based plywood	PGF-based composite
Thickness (mm)	12.0	12.0
Density (gm/cc)	0.798	0.838
Water absorption (24 h, %)	12.0	11.5
MOR (N/mm^2)	42.6	58.92
MOE (N/mm^2)	4500	7232
Tensile strength (N/mm^2)	42.6	44.43
Glue shear strength (Dry State, N)	1300	1350
Thickness swelling (%)	3.0	3.0
Compressive strength (MPa)	25.0	22.8

It may be concluded that, i) from the point of view of physico-mechanical strength properties of plywood by using bio-based PGF resin adhesive, it achieved better bond quality indicating 25–30% replacement of phenol by animal glue for the preparation of PGF resin which is 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 lowered 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 plyboard is necessary in future.

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