Brominated Phenol–Formaldehyde Resin as an Adhesive for Plywood

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ABSTRACT: A brominated phenol–formaldehyde resin was investigated as a plywood adhesive to study the effect of bromine on the physical and flammability properties of this resin. The results of these studies showed that brominated phenol–formaldehyde resin of 10% bromine content by weight of the phenol–formaldehyde resin was suitable to be used as a plywood adhesive. The optimal compressing temperature and compressing time were 110°C and 30 min, respectively. The prepared plywood obtained from the optimal condition gave a high shear strength, good flame retardancy, and good resistance to both hot and cold water.
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Key words: adhesives; synthesis; resins

INTRODUCTION

The demand for wood is increasing but the supply is unable to keep pace with it. Additionally, the decline of the size of available logs and economics led to the need to recover a higher percentage of usable material from forest resources. New sources of wood supplies have to be exploited so as to maintain the industries where wood is the starting material. From this point of view, softwood, small, and low-quality trees are used as effective substitutes for wood-panel industries, especially plywood, fiberboard, and particleboard.[1,2]

Plywood has been defined as a product of balanced construction made up of veneers assembled by gluing. The greatest volumes of wood adhesives or binder for structural applications are thermosetting phenol–formaldehyde (PF) or urea–formaldehyde (UF) polymers or their derivatives.[3–5] Synthetic resin glues such as urea–formaldehyde, poly(vinyl acetate), melamine formaldehyde, and PF have been commonly used as glue in plywood manufacturing. Phenolic resins posses many good properties such as heat, chemical, and moisture resistance. Phenolic resin can be classified into two classes: novolaks and resoles. Plywood manufacture involves the adhering of three or more layers of wood with phenolic resin under heat and pressure. The resin generally is combined with fillers and diluents to control wetting and to avoid substrate penetration. Phenolics are considered to have moderate nonflammability characteristics. However, early investigators found that various simple materials could be used to improve the fire retardancy of phenolic resins. Halogen compounds can improve the flame retardancy of phenolic resin. The mechanisms of bromine for the enhancement of flame retardancy are the redirection or termination of chemical reactions involved in combustion and the evolution of heavy bromine-containing gases, which tend to protect the condensed phase by inhibiting the access of oxygen and the transfer of heat.[6]

Brominated PF resin was prepared by the bromination of the PF resin according to Antony and Pillai's work[7] through the *ortho/para* position available after polymerization. The chemical equation of bromination of PF resin is shown in Scheme 1. There is much research that has studied the flame retardancy of phenolic resin and its derivatives.

Anthony and Pillai[7] studied phenolic resins with improved/altered thermal stability and flame retardancy. These phenolic resins were prepared by introducing flame-retardant elements such as phosphorus and bromine at the monomer stage, followed by condensation with formaldehyde and hexamethylene tetramine. The thermal stability of products was evaluated using thermal gravimetric analysis (TGA) and limited oxygen index (LOI) techniques. The results showed that the addition of phosphorus to PF resin at the monomer stage enhances its thermal stability and flame retardancy.

In this research, plywood from rubber wood veneer with brominated PF resin was prepared. Three-layer plywood was fabricated and tested under normal and vigorous conditions. The effects of the bromine content on the flammable and mechanical properties were investigated.

EXPERIMENTAL

Materials and chemicals

The wood veneer in this research was all rubber wood, obtained from the wood industry. The dimension of the

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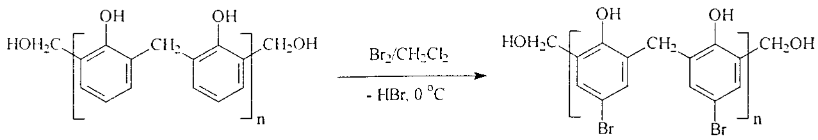

Scheme 1 Bromination of PF resin.

veneer was 3 × 130 × 130 (thickness × width × length) and its color was light brown. Phenol and bromine solutions were purchased from Fluka (A Sigma-Aldrich Co., Buchs, Switzerland). Sodium hydroxide, methylene chloride, acetone, and hydrochloric acid were provided by Merck (Germany). The formaldehyde solution was bought from Lab Scan Co., Ltd. (Thailand).

Apparatus and equipment

The compression molder was a product of the Lab Tech Engineering Co., Ltd. X-ray fluorescence was done on a Model E.D.2000 of the Oxford Co. The nuclear-magnetic resonance spectrometer was a Model ACF 200 MHz of Bruker, Switzerland. The infrared spectrophotometer was a Model Impact 410 of Perkin–Elmer. The testing shear strength machine was a product of Ottto Wolpert-Werke G.m.b.H. Ludwigshafen amRh. The LOI machine was a product of Polymer Laboratories.

Preparation of wood veneer

The size of the rubber wood veneer was determined using an electric saw and the surface was polished by sandpaper to remove the woolly fiber and to smooth the surface. The veneer sheets were dried by a dryer to control the moisture content at 1.0 ± 2.5%

Preparation of synthetic adhesives

PF resin

Phenol 50 g, 100 mL 37% aqueous formaldehyde, and 6 mL of 40% sodium hydroxide were placed in a 250-mL three-necked flask fitted with a mechanical stirrer and reflux condenser. The reaction was heated under constant stirring at 80–90°C for 60–75 min. The reaction was stopped by cooling and the pH was adjusted to 7–8.

Brominated phenol-formaldehyde (BrPF) resin

PF was brominated to obtain BrPF resin. One hundred grams PF and 100 mL dichloromethane were place in a 500-mL round-bottom flask kept in an ice bath and then 50 mL of bromine (1, 5, 10, and 15% wt of PF) in dichloromethane was added dropwise with vigorous stirring. Finally, dichloromethane was removed to obtain BrPF.

Characterization of BrPF resin

BrPF resin was characterized using X-ray fluorescence (XPF), infrared (IR) spectrophotometry, and nuclear magnetic resonance (NMR).

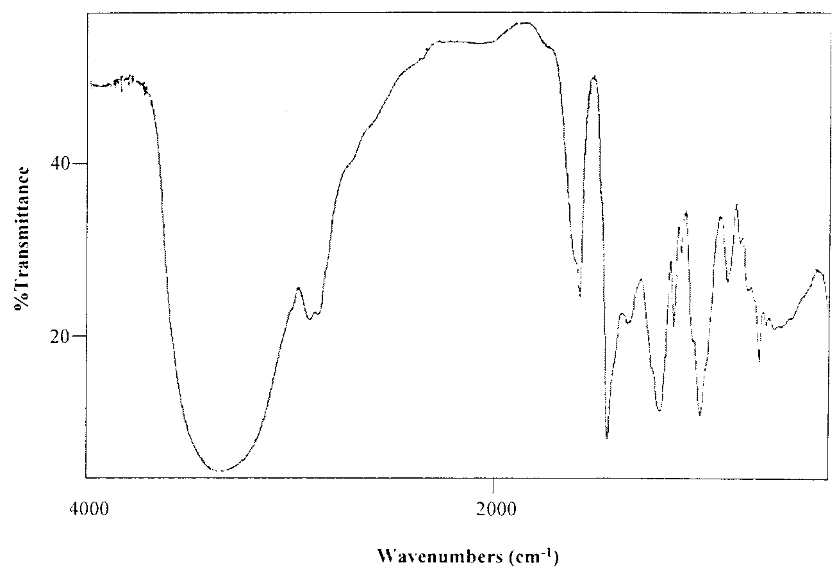

Figure 1 IR spectrum of BrPF resin.

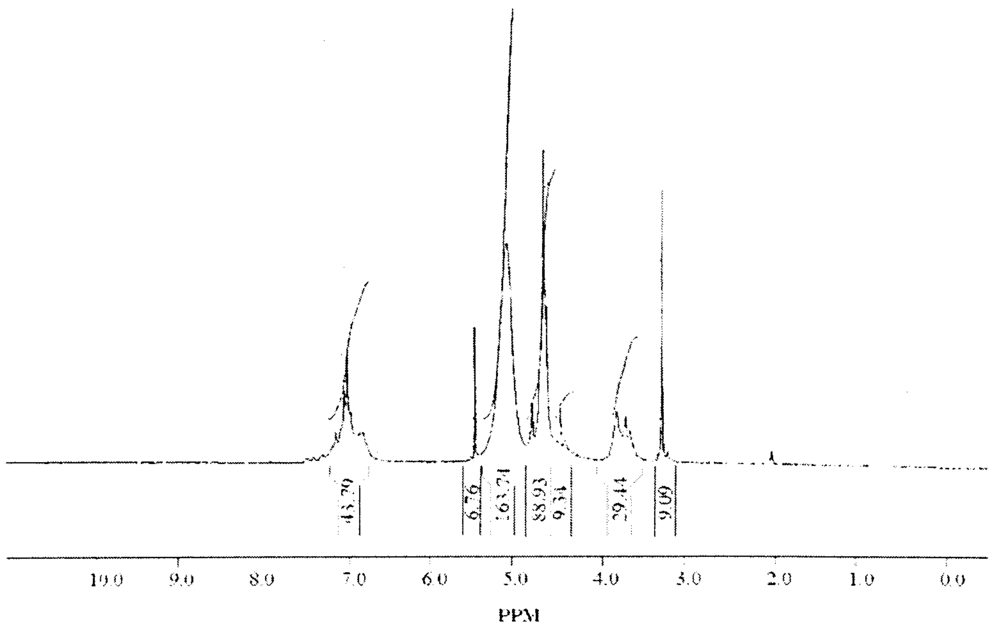

Figure 2 ^{1}H-NMR spectrum of BrPF resin.

Preparation of plywood

The adhesive was brushed onto the surface of the veneer by the following equation; weight of the adhesive = 220 g × area of the veneer (m^2). Three plies of glued veneer were alternatively laid and then a hot-press process at 1400–1600 psi was applied at various times and temperatures. After the hot-press process, the plywood was cooled and then the finish product was trimmed to precise sizes.

Factors affecting plywood properties

The plywood was prepared as follows: compressing temperature of 120°C, 30 min, and pressed pressure of 1400–1600 psi. The bromine content, compressing time, and temperatures were varied at 0, 1, 5, 10, and 15% wt of PF, 10, 20, 30, and 40 min, and 100, 110, 120, 130, and 140°C, respectively.

Testing

The properties of the rubber wood plywood were measured by following the test methods; the moisture content and the strength property of the adhesive by shear were determined according to TISI 178-2538,[8] which has a moisture content range of 7–15. The minimum oxygen concentration support combustion of plywood (LOI value) was performed using the procedure of ASTM D2863-91.[9] Moreover, the resistance to cold water (27 ± 2°C, 16–24 h) and hot water (95°C, 72 h) of the plywood was investigated.

RESULTS AND DISCUSSION

The effects of various parameters on the processing conditions and mechanical properties of rubber wood plywood using the PF resin and the BrPF resin as the plywood adhesive were investigated.

Preparative and characterization of BrPF resin

BrPF resin was synthesized from the bromination of PF resin and characterized by IR spectroscopy, NMR, and XRF. The IR spectrum of BrPF (Fig. 1) shows carbon bromine bonds at 740 cm^{-1} and their absence in the IR spectrum of PF (data not shown). NMR of BrPF is shown in Figures 2 and 3.

The ^{1}H-NMR spectrum (Fig. 2) of BrPF revealed signals at δ_H of 7.09, 6.98, 6.95, 6.90, and 6.78 ppm, which all corresponded to protons in the benzene ring. Moreover, signals at δ_H of 5.50 and 5.12 referred to phenolic protons, which were affected by the presence of bromine at the *para* position. The ^{13}C-NMR spectrum of BrPF (Fig. 3) shows the same spectrum of PF (data not shown) but a signal that referred to *para*-free sites on the phenolic resin (δ of 116.1, 115.8, and 115.6) was decreased due to the displacement of the bromine atom through the *para* position.

The bromine content was determined using XRF. The XRF graphs of the PF and BrPF resins are shown in Figure 4. The results of the characterization are shown in Table I. Figure 4(a) shows PF with an absence bromine (the bromine content was 0%). For the BrPF resins, the intensity of bromine was increased accordingly when the amount of the bromine concen-

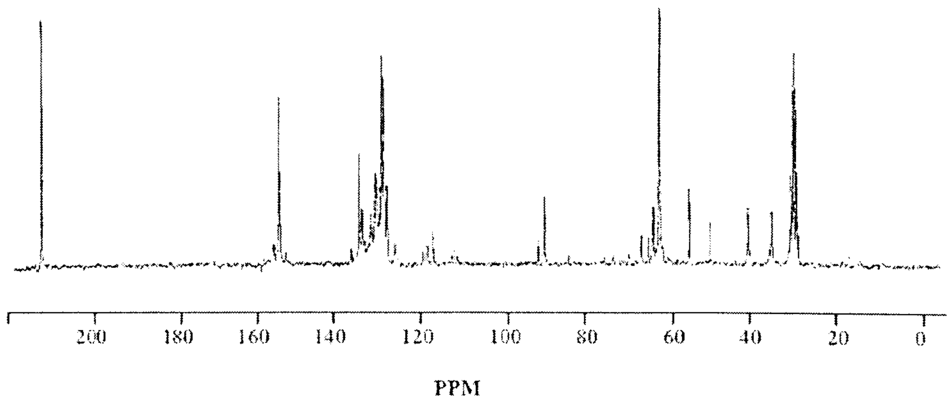

Figure 3 ^{13}C-NMR spectrum of BrPF resin.

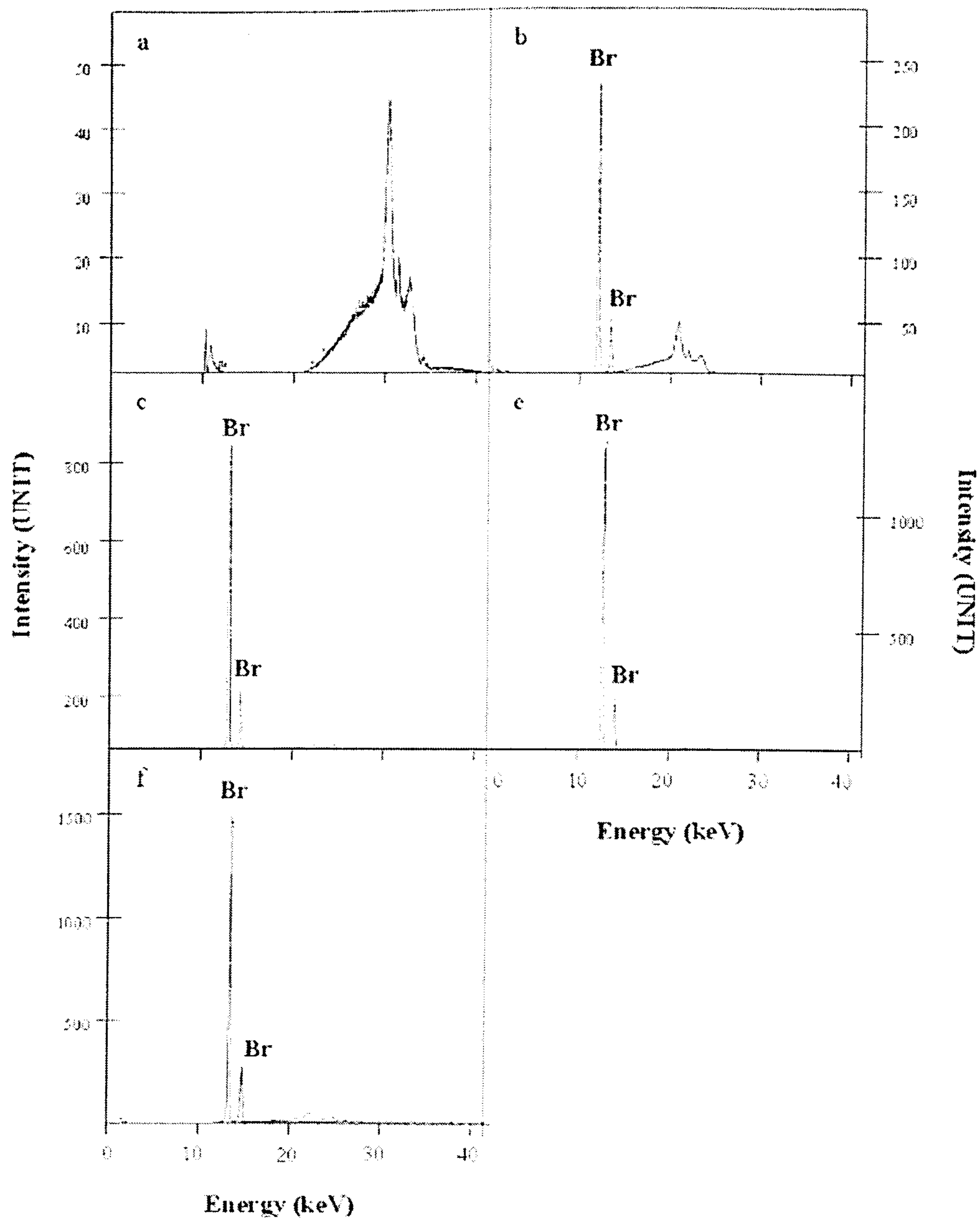

Figure 4 ^{13}C-NMR spectrum of BrPF resin.

TABLE I
Bromine Content and LOI of BrPF Resin

Sample	Bromine content (%)	LOI value (%)
PF	0.00	28.10
Br1	12.93	29.33
Br5	41.32	33.00
Br10	75.53	35.70
Br15	84.36	38.80

Where Br1 is bromine 1% by wt of PF; Br5, bromine 5% by wt of PF; Br10, bromine 10% by wt of PF; and Br15, bromine 15% by wt of PF.

tration was increased [Fig. 4(b–e)]. The LOI of all the samples was studied. The results are shown in Table I. The LOI value was increased when the amount of bromine increased in the BrPF. This phenomenon indicated that the flame-retardant property is dependent on the amount of bromine. The flame-retardant effect on BrPF could result from the vapor phase, which was generated from the decomposition when the bromine concentration in the prepared BrPF resin was increased.

Effect of bromine content of BrPF resin on the properties of plywood

BrPF was used for the preparation of plywood to increase the flame retardancy of the plywood. The moisture, shear strength, and LOI values of the plywood containing BrPF as an adhesive are shown in Table II. It is indicated that the addition of bromine into PF increased the flame retardancy of the plywood. At Br10 of the BrPF resin, the LOI value was increased approximately three times compared to plywood, which contained PF as an adhesive.

The moisture of the plywood samples was controlled between 10 and 12% and was not significantly different from that of the untreated plywood. These moisture content values of the tested samples were in the range of the TISI 178-2538 standard. The shear strength of all the samples is also shown in Table II. The shear strength of the plywood increased with an increasing amount of bromine content in the BrPF resin. This result might be due to the reaction site of the PF resin, which was an oxymethylene group (—CH_2OH groups). Thus, when heating polymerized the PF resin, the resin would form a long-chain polymer, with oxymethylene groups at the end of the PF resin chain forming covalent bonds with wood. The methylated adhesive with hydroxyl groups of cellulose or lignin formed covalent oxymethylene bridges. The reactive site of the BrPF resin was a hydroxyl group (—OH group), which was replaced with an oxymethylene group and the substitute Br affected the aromatic ring by resonance of the Br element. When heating the polymerized BrPF resin, the polymer was formed and most of the oxymethylene groups formed covalent bonds with the wood. As a result, the Br content of the BrPF resin increased, the shear strength of the plywood increased significantly, and the shear strength of the plywood using the BrPF adhesive was better than was the shear strength of the plywood using the common PF adhesive.

Moreover, the LOI values of the plywood were increased accordingly with an increasing amount of the bromine content of the BrPF resin, as shown in Table II. This result suggested that BrPF appears to be principally effective in the ignition of plywood, by blocking the access of oxygen from the flame to retard the combustion reaction. It was necessary for the burning process to be progressed through the decomposition of the plywood and to release bromine-containing compounds into the gaseous phase. All the above processes would lead to flame retardancy.

The viscosity of the BrPF resins was considered. The results indicated that the viscosity of the BrPF resin increased with an increasing amount of the bromine content. Unfortunately, the BrPF resin with a high viscosity was not suitable for use with the plywood adhesive although it showed significant flame retardancy. Therefore, the bromine content at 10% wt of the PF resin (Br10) was used for all the following experiments.

Effect of compressing time on the properties of plywood

Compressing time was one of the major factors which were considered. Br10 at a pressure of 1400–1600 psi and a compressing temperature of 120°C was used.

TABLE II
Effect of Bromine Concentration in BrPF Resin on the Properties of Plywood

Bromine concentration in BrPF resin (% wt of PF)	Properties		
	Moisture content (%)	Shear strength (N/cm^2)	LOI value (%)
0 (PF)	11.96 ± 0.36	186.93 ± 2.66	24.63 ± 0.05
1	10.59 ± 0.09	192.93 ± 0.02	24.79 ± 0.29
5	11.03 ± 0.47	249.83 ± 7.38	26.15 ± 0.13
10	10.72 ± 0.10	275.07 ± 4.19	27.23 ± 0.08
15	10.99 ± 0.52	309.50 ± 3.38	27.85 ± 0.11

TABLE III
Effect of Compressing Time on the Properties of Plywood

Compressing time (min)	Properties		
	Moisture content (%)	Shear strength (N/cm^2)	LOI value (%)
10	10.51 ± 0.05	88.24 ± 7.67	27.18 ± 0.02
20	10.56 ± 0.02	127.48 ± 0.99	27.22 ± 0.02
30	10.97 ± 0.51	280.27 ± 1.53	27.22 ± 0.01
40	11.35 ± 0.00	285.73 ± 0.98	27.23 ± 0.00

The effects of the compressing time on the properties of plywood are shown in Table III.

Table III, shows that the moisture content of the plywood was between 10 and 11%. The moisture content was within the range of the TISI 178-2538 standard. The shear strength of the plywood at different compressing times is also shown in Table III. The results indicate that the longer is the compressing time the greater are the shear strength values. The effect might be due to the longer compressing time allowed for the curing process to be complete. For LOI values of the plywood, the effect of the compressing time did not have an impact on the flammability behavior of the plywood.

Effect of compressing temperature on the plywood properties

Br10 resins were used to study the effect of the compressing temperature against the properties of the plywood. The results are shown in Table IV.

The plywood, which was prepared at various compressing temperatures of 100–140°C, had a moisture content between 9 and 10%. The effect of the compressing temperature showed that there was no significant difference in the flame retardancy (see Table IV).

In the case of the shear strength, the lower compressing temperature shows a lower shear strength value. Thus, the lowest shear strength is at a compressing temperature of 100°C. Considering the shear strength property of the plywood and the compressing temperature, the results suggested that at a temperature above 110°C the increase of the shear strength was insignificant; it might reach the maximum value in this system.

Resistance of plywood to cold water and water containing BrPF resin as the adhesive

Plywood containing of Br10 as the adhesive with a compressing time 30 min, compressing temperature of 110°C, and pressure of 1400–1600 psi was tested for its resistance to cold and hot water. It was immersed in cold and hot water and compared with the plywood that used PF as the adhesive. The results are shown in Table V.

The moisture content of the plywood using PF resin was 11.96%. When it was immersed in cold and hot water, the moisture was increased to 13.62 and 13.75, respectively. The moisture content of Br10 also increased from 10.27 to 12.59% in cold water and increased to 13.75% in hot water. These results suggest that the moisture content resistance of Br10 and PF are similar.

The shear strength and LOI value of the plywood when immersed to cold and hot water were investigated. The results show the decreasing of the shear strength and the LOI value with both plywoods containing PF and Br0 as the adhesive. However, both properties of the Br10 plywood were higher than those of the PF plywood.

CONCLUSIONS

In these studies, BrPF resins were synthesized from the bromination of PF resins. The BrPF resins were characterized by spectroscopy techniques.

TABLE IV
Effect of Bromine Concentration in Br10 Resin on the Pproperties of Plywood

Compressing temperature (°C)	Properties		
	Moisture content (%)	Shear strength (N/cm^2)	LOI value (%)
100	10.02 ± 0.01	158.42 ± 11.22	27.16 ± 0.04
110	9.64 ± 0.08	266.97 ± 0.32	27.17 ± 0.035
120	9.38 ± 0.10	302.59 ± 0.38	27.17 ± 0.003
130	10.03 ± 0.02	292.69 ± 6.37	27.16 ± 0.00
140	9.37 ± 0.09	305.26 ± 7.05	27.15 ± 0.03

TABLE V
Results of the Resistance Effect of Bromine Concentration in Br10 Resin on the Properties of Plywood

Samples	Properties		
	Moisture content (%)	Shear strength (N/cm^2)	LOI value (%)
PF	11.96 ± 0.36	186.93 ± 2.66	24.63 ± 0.05
PF in cold water	13.62 ± 0.00	141.29 ± 0.94	24.08 ± 0.05
PF in hot water	13.75 ± 0.00	114.81 ± 6.56	24.03 ± 0.03
Br10	10.72 ± 0.10	275.07 ± 4.19	27.23 ± 0.08
Br10 in cold water	12.59 ± 0.04	243.12 ± 2.67	25.90 ± 0.06
Br10 in hot water	13.75 ± 0.01	218.59 ± 1.14	25.59 ± 0.07

The manufacture of plywood from rubber wood veneer using BrPF resin as an adhesive appears to be technically feasible. The plywood preparation meets the industry-level requirements for commercial plywood. The optimum conditions for the plywood preparation were as follows: 10% of bromine content, compressing time of 30 min, and compressing temperature of 110°C. Under these conditions high-performance plywood was achieved with the highest shear strength and high LOI value, which indicated high flame retardancy and high resistance to cold and hot water. It could be concluded that the BrPF resin can be used as an effective adhesive for rubber wood veneer plywood.

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