Synthesis of Phenol Formaldehyde Resin with Paraformaldehyde and Formalin

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Abstract. Phenol and formaldehyde are the well-known raw materials used in synthesizing Phenol Formaldehyde (PF) resin. PF resin has been used extensively in various applications including molding and composite laminate industries. This study focused on the synthesizing PF resin using formalin and/or paraformaldehyde for laminate application and assess the physical properties, mechanical properties and fracture toughness of the resins. The density, dynamic viscosity, solid content, gel time, flexural properties, tensile properties and fracture toughness of the synthesized resins were evaluated upon varying the formalin content from 0% to 40% (w/w) in the synthesis process. The result shows that addition of 40% w/w formalin in the PF resin synthesis had increased the fracture toughness and decreased the flexural strength and modulus properties of PF by 97.14% and 97.60% respectively. The tensile stress value was also reduced by 67.80% when the 40% w/w of formalin was added. However, the PF resins that produced by adding formalin up to 20% w/w in the PF resin synthesis, still maintained their flexural and tensile properties within the acceptable range required by EN438 standard for decorative high-pressure laminate (HPL) application. This work shows that paraformaldehyde enhanced the mechanical properties of PF laminate resin compared to formalin.

Keywords: Phenol formaldehyde, paraformaldehyde, formalin, laminate resin, mechanical properties

1. Introduction

Phenol formaldehyde (PF) resin is a polymer condensate obtained from the condensation reaction between phenol and formaldehyde in the presence of an alkaline catalyst [1-7]. PF resin is usually synthesized with formaldehyde (liquid formalin) instead of paraformaldehyde (powder) [2, 7, 8-12].
According to Pilato [13] and Gardziella et al. [4], liquid formaldehyde has higher chemical reactivity due to the availability of free formaldehyde which led to complete reaction process to form methylol phenols compared to the big polymer molecules in paraformaldehyde. The structure of various chemicals involved are shown in Figure 1 (a), (b) and (c) [14]. Formalin in aqueous solution is formed from the dissolution of formaldehyde (gas form) which is then chemically combined to form methylene hydrate (OH-CH₂-OH) [14].

![Figure 1: Formaldehyde Chemical Structure; a) in gas as formaldehyde, b) in aqueous formaldehyde, Formalin, b) in solid powder, Paraformaldehyde with (n=4) [14]](image)

Synthesis of thermoset resin is an exothermic process [13, 15, 16] where, heat is released during the reaction. Using paraformaldehyde as reactant in the synthesis process requires more energy (more heat released) to depolymerize the big molecules of paraformaldehyde [14]. The uncontrolled heat released during the synthesis period will lead to runaway reaction and explosion [17]. Therefore, it is much safer to use formalin in the phenol formaldehyde resin because it will reduce the amount of heat generated during the reaction.

However, using formalin in the synthesis of PF resin requires longer synthesis time in order to remove water and make the resin more viscous. High water content will lead to the formation of voids within the cured resin structure due to the evaporation of water. These voids create defects on the cured resin and affect the mechanical properties [5, 9, 13]. Based on previous work, the viscosity that is usually used in laminate resin synthesis is 400 - 500 cP [18]. To illustrate, Shafizadeh et al. [8] required nine hours to produce 900 cp PF resin, whilst Zhang et al. [11] required three hours to produce PF resin with viscosity of 150 cp. Lin and Lee [12] required more than three hours to produce PF resin with viscosity of 142 cp. Another group of researchers performed tests using paraformaldehyde to synthesize viscous PF resin at a much shorter period, e.g Cardona & Sultan [5] spent three hours to produce PF resin with a viscosity of 2000 cP and Cui et al. [19] needed two hours to produce PF resin with viscosity value of 900cP. All of these studies indicated that phenol and base-catalyst that were available and used in the PF resin synthesis provided sufficient water to activate paraformaldehyde; therefore, excess water, i.e. use of formalin, is not practical.

During the PF resin synthesis process, water will be generated via the condensation reaction. This water needs to be removed to maintain the solid content in the PF resin after post curing is within the range of 75-80% by weight [18 - 21].

Most research had focused on the use of either paraformaldehyde or formalin in the production of PF resin [8, 11-13, 15, 16, 19], none had compared the properties of the PF resin produced using both. Therefore, in this study formalin was added to paraformaldehyde to produce PF laminate resin. The aim is to investigate the effect of using the heterogeneous mixture of formaldehyde on the physical and mechanical properties of PF laminate resin produced.

2. Materials and Methods

Phenol was purchased from Malayan Adhesive & Chemical Sdn. Bhd, (Kuala Lumpur, Malaysia) with the molecular weight of 94.11 g/mol and is 95% pure. Industrial grade paraformaldehyde (molecular weight = 30.03 g/mol, purity of 92%) was purchased from Chang Chun Plastics Co. Ltd. China. Formalin (37% purity), sodium hydroxide (NaOH) pellets were purchased from Merck, Malaysia. Silicon oil (Merck) was used as bath in the phenol formaldehyde resin synthesis. Aqueous solution of NaOH (40% by weight) was prepared from the NaOH pellets for the phenol formaldehyde resin synthesis as the base catalyst.
2.1 Synthesis of Liquid Phenol Formaldehyde (PF) Laminate Resin

PF laminate resin was prepared by reacting phenol (P) and formaldehyde (F). The formaldehyde used is formalin with 37% purity and/or paraformaldehyde with 92% purity. The initial set ratio and synthesis period was referred to previous studies [5, 10, 22-24]. The experiments were further screened using rheological analysis to identify the best processing time and synthesis temperature. The results of the mechanical properties of the produced and cured laminate resin were used to select suitable mixing ratio for phenol formaldehyde reaction. The ratio of P to F found is 1.00:1.50 and this ratio is used as the production composition.

The synthesis process was conducted as described in the literatures [5, 25, 26]. The speed of the rotary evaporator used to synthesize the PF resin is ±150.00 rpm. The dynamic viscosity of phenol formaldehyde was measured using Brookfield Viscometer (DV2T) with LV-04(64) spindle rotated at 200 RPM.

The amount of formalin added based on the total formaldehyde content (paraformaldehyde and formalin) was varied between 0% w/w formalin up to 40% w/w formalin. Table 1 shows the set conditions for PF resin production.

Table 1: Set Conditions for Synthesis of Phenol Formaldehyde (PF) Resin

| Formalin Content (%) | Synthesis Temperature (°C) | Synthesis Period, t (min) | Set Viscosity, cP |
|----------------------|-----------------------------|---------------------------|-------------------|
| 0.00                 | 60 ; 80                     | 40 ; 20                   | ~500              |
| 10.00                | 60 ; 80 ; 60                | 60 ; 60 ; 60              |                   |
| 20.00                | 60 ; 80 ; 60                | 60 ; 60 ; 60              |                   |
| 30.00                | 60 ; 80 ; 60                | 60 ; 60 ; 80              |                   |
| 40.00                | 60 ; 80 ; 60                | 60 ; 60 ; 80              |                   |

The curing mixture and the process to produce PF laminate resin was adapted based on work done by Starks [27]; Cardona & Moscou [3] and Cardona & Sultan [5]. After adding the catalyst to the resins and mixing, the resins were poured into a mold with a dimension of 18 cm (length) by 11 cm (width) by 0.4 cm (thick). The PF laminate resin were initially cured at room temperature for 12 h, followed by post-curing in the oven at 80 °C for 10 hours. The physical properties of the PF laminate resin and the mechanical properties of the cured PF laminate resin were assessed.

2.2 Characterization of Phenol Formaldehyde (PF) Laminate Resin

The analysis of phenol formaldehyde (PF) laminate resin is comprised of the physical properties of PF laminate resin and mechanical test of cured laminate PF resin.

2.2.1 Physical Properties

The physical properties of the synthesized resin such as density, gel time and total solid content were assessed. The density of phenol formaldehyde resin is measured by weighing resin in 25ml of volumetric flask grade A. The mass of the resin is then measured for several times in the different volumetric flasks.

Total solid content (TSC) was determined by drying the PF laminate resin based on method described by Atta-Obeng [28]. The petri dish was heated up in the oven at 80°C for 24 hours. The mass of resin was weighed before and after drying. The processes of weighing and drying is iterated until a constant mass is obtained. The total solid content percentage is determined as Equation 1.

\[
\text{TSC} (%) = \frac{\text{Mass before drying} - \text{Mass after drying}}{\text{Mass before drying}} \times 100
\]  

(1)

The gel time of the resin was tested based on method described by Ashaari et al. [29] and Hoong et al. [30]. A weighed amount of phenol formaldehyde resin was filled into a test tube and dipped into
in a water bath at 90 ± 2 °C and stirred with a glass rod. The gel point of the resin is identified when the glass rod is stuck in the resin. The time required for the formation of gel state is known as the gel time.

2.2.2 Mechanical Properties of Cured Phenol Formaldehyde (PF) Laminate Resin

The cured PF laminate resin were tested for their tensile and flexural properties based on ASTM D638 and ASTM D7264 methods, respectively as the first screening of their mechanical strengths. Five samples from each prepared cured laminate resin were cut using vertical saw machine (metabo®, BAS 260 swift) into a rectangular shape with a dimension of 180 mm by 20 mm as illustrated in Figure 2 (a) for tensile test and a dimension of 180 mm by 25 mm as shown in Figure 2 (b) for flexural test. In total, 25 samples were prepared each for tensile and flexural tests.

![Figure 2](image)

**Figure 2**: Schematic diagram of specimen size for (a) tensile test (b) flexural test

Fracture toughness or critical stress intensity factor, $K_{IC}$ (unit) of the cured laminate resins were evaluated and calculated using Equation 2 [5, 31-34].

$$K_{IC} = \frac{f \cdot a \cdot F}{\sqrt{h \cdot w}}$$

Here, $F$ is load at break (N), $h$ (mm) is thickness of the specimen, $w$ (mm) is width of the specimen, $a$ (mm) is notch length and $f$ is the geometry factor. Notched value is maintained so that $\frac{a}{w} \approx 1.0$ [31, 33] and the geometry factor, $f$ is equal to 1.1 since the width of the samples were not infinite as stated by Dharmarajan & Vipulanandan [31].

3. Results and Discussions

The physical properties of synthesized PF laminate resins and the mechanical properties of the cured laminate resin were evaluated and compared.

3.1 Physical Properties of Phenol Formaldehyde (PF) Laminate Resin

The assessed physical properties of the produced phenol formaldehyde (PF) laminate resin include the density, dynamic viscosity, total solid content (TSC) and also gel time as shown in Figure 3 (a) and (b). The measurements of dynamic viscosity were done at room temperature.
Figure 3: Plots of the (a) viscosity values (cP) and solid content (%), (b) density (g/cm³) and gel time (minutes) against Formalin content in the Phenol Formaldehyde (PF) laminate resins.

The effect of adding formalin to the paraformaldehyde in the PF laminate resin synthesis are presented in Figure 3 (a) and (b). It shows that all four parameters were affected when the content of formalin is increased in the PF resin mixture. To illustrate, the viscosity, density and total solid content of the PF resins were reduced when the formalin content was increased. On the other hand, the gel time was increased with an increase in formalin content. Increasing the amount of formalin into the mixture will increase the free water content which made the solution much thinner, less dense and has lower solid content. With this excess water, longer time was required to increase the viscosity of the liquid to reach the gel consistency. Increasing the percentage of formalin used in the synthesis from 40% w/w, will reduce the density and TSC of the PF resin from 1.37 g/cm³ to 1.30 g/cm³ and 84.16% TSC to 65.70% TSC, respectively. The viscosity value was also reduced from 420cP to 385cP. While, for the gel time of the PF resin, when the percentage of formalin is increased, the gel time increased from 30 minutes to 130 minutes.

3.2 Mechanical Properties of Cured Phenol Formaldehyde (PF) Laminate Resin

The mechanical properties of the cured PF laminate resin based on the flexural and tensile strengths data. The fracture toughness was calculated and analyzed to evaluate the brittle fracture of the sample when a crack is present [34, 35].

3.2.1 Fracture Toughness, Flexural and Tensile Strength Analysis

Fracture toughness or critical stress intensity factor, $K_{IC} \text{ (MPa.m}^{1/2})$, for the cured PF laminate resin was evaluated. The calculated values for fracture toughness is presented in Figure 4.
Fracture toughness of the prepared cured laminate resins samples were increased as the formalin content was increased. The cured PF laminate resin that has the highest fracture toughness was the resin produced with 40% w/w formalin. The increased in fracture toughness between resin produced without formalin and with 40% w/w formalin was about 18%. The fracture toughness value was increased from 3.13 MPa.m\(^{1/2}\) to 3.68 MPa.m\(^{1/2}\), respectively.

The result of the flexural and tensile analyses of cured PF laminate resins is presented in Figure 5 (a) and (b). Figure 5 (a) is a plot of mechanical flexural properties of PF composite laminate with addition of formalin. With the formalin content of 40% w/w, the flexural strength and modulus of the cured PF laminate resin were reduced from 1051.68MPa (without formalin) to 29.79MPa and from 55707.68MPa (without formalin) to 1335.41MPa. Reduction of the flexural modulus value reflects the decreased of the stiffness of the resin samples [36, 37].

Figure 5 (b) is a plot of the tensile stress and tensile strain of the cured laminate resin. It is observed that the tensile value was decreased from 1419.91MPa (without formalin) to 457.19MPa 40% (w/w) was added. The tensile strain also shows similar profile i.e. tensile strain value was decreased with the increasing of formalin content from 0% to 40% (w/w).

The resin that was synthesized using 40% (w/w) formalin content has higher fracture toughness factors compared to that prepared without formalin. In general, product with higher fracture toughness will be less brittle [5]. However, in this study, it was found that product with higher fracture toughness is more brittle, i.e. weaker as presented in Figure 5 (b). The most probable cause that leads to this discrepancy is the high water (liquid) content and lower total solid content that present in the resin mixture. Ngo et al. [38] also observed similar trend when they mixed their resin mixture with bio-oil.

Figure 5 (a) and (b) shows the effect of adding formalin to the PF resin mix on the flexural strength and modulus as well as the tensile stress and strain of the cured PF resins. From the graph, it can be deduced that, to produced cured PF resin laminates that can sustain up to 80 MPa force load, the maximum content of formalin added should be ≥ 20% w/w. As for flexural modulus, the minimum load requirement for the High-Pressure Laminate class is ≥9000 MPa. Based on Figure 5(b), the maximum amount of formalin to be added shall be 20% w/w. For tensile stress, all samples exceeded the HPL standard requirement, which is ≥60MPa.
4. Conclusions

The mechanical properties as well as the physical properties of PF laminate resin synthesized with different content of formalin and paraformaldehyde were evaluated. Mixing paraformaldehyde with formalin in the PF laminate resin lead to the following conclusions:

1. The physical properties of PF laminate resins were proportionally dependent on the content of formalin and paraformaldehyde.
2. The flexural and tensile properties of the cured PF laminate resin with addition of 20% (w/w) formalin is still within the HPL standard requirement.

References

[1] Kopf P W 2002 Encyclopaedia of Polymer Science and Technology vol 7, pp 322
[2] Poljansek I and Krajnc M 2005 Acta Chimica Slovenica 52 238
[3] Cardona F and Moscou C 2009 Proc. of the 20th Australasian Conference on the Mechanics of Structures and Materials pp 317 (Taylor & Francis)
[4] Gardziella A, Pilato L A and Knop A 2013 Phenolic resins: chemistry, applications, standardization, safety and ecology (New York: Springer) chapter 3 pp 83
[5] Cardona F and Sultan M T H 2016 BioResources 11 pp 965
[6] Asim M, Saba N, Jawaid M, Nasir M, Pervaiz M and Alothman O Y 2018 Current Analytical Chemistry 14 pp 185
[7] Younessi-Kordkheili H and Pizzi A 2018 European journal of wood and wood products 76 pp 871
[8] Shafizadeh J E, Guionnet S, Tillman M S and Seferis J C 1999 Journal of Applied Polymer Science 73 pp 505
[9] Bajia S C, Swarnkar P, Kumar S and Bajia B 2007 Journal of Chemistry 4 pp 457
[10] Christjanson P, Pehk T and Paju J 2010 Proc. of the Estonian Academy of Sciences 59 pp 225
[11] Zhang W, Ma Y, Wang C, Li S, Zhang M and Chu F 2013 Industrial Crops and Products 43 pp 326
[12] Lin W S and Lee W J 2018 European journal of wood and wood products 76 pp 297
[13] Pilato L 2010 Phenolic resins: a century of progress (New York: Springer) pp 121
[14] Kiernan J A 2000 Microscopy today 8 pp 8-13.
[15] Gabilondo N, Larranaga M, Pena C, Corcuera M A, Echeverria J M and Mondragon I 2006 Journal of applied polymer science 102 pp 2623
[16] Hu X M, Zhao Y Y and Cheng W M 2015 Polymer Composites 36 pp 1531
[17] Strauss C R and Varma R S 2006 Microwaves in green and sustainable chemistry. In Microwave Methods in Organic Synthesis (Springer, Berlin, Heidelberg) 266 pp 199
[18] Gillern M F, Oita K, Teng R J and Tiedeman G T 1981 (Washington DC US Patent and Trademark Office) US Patent No 4,264,671
[19] Cui Y, Hou X, Wang W and Chang J 2017 Materials 10 pp 668
[20] Fleckenstein M, Biziks V, Mai C and Militz H 2018 European journal of wood and wood products 76 pp 843
[21] Taverna M E, Ollearo R, Morán J, Nicolau V, Estenoz D and Frontini P 2015 BioResources 10 pp 8325
[22] Niederhauser W S and Miller M W 1944 US Patent No 2,357,798
[23] Shafizadeh J E and Seferis J C 2000 Proceedings of the International Committee on Composite Materials pp 1285
[24] Turunen M, Alvila L, Pakkanen T T and Rainio J 2003 Journal of Applied Polymer Science 88 pp 582
[25] Cardona F, Kin-tak A L, Fedrigo J and Bataillon P E 2011 Journal of Applied Polymer Science 123 pp 1231
[26] Wexler A 1976 Journal of Research of the National Bureau of Standards 80 pp 775
[27] Starks C M 1980 (Washington DC US Patent and Trademark Office) U.S. Patent No. 4,200,706.
[28] Atta-Obeng E, Via B, Fasina O, Auad M and Jiang W 2013 International Journal of Composite Materials 3
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