

EVALUATION OF PHENOL FORMALDEHYDE RESIN SYNTHESIZED FROM SUGARCANE BAGASSE BIO-OIL UNDER OPTIMIZED PARAMETERS

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Abstract

Bio-oil from biomass is considered as a potential substitute to partially replace phenol in the preparation of phenol formaldehyde resin as replacement to the commercial phenol which high in cost. However, the percentages of bio-oil substitutions need to be determined to ensure that the performance is good as the commercial ones. The aim of this research is to identify the optimum conditions for synthesizing phenol formaldehyde resin (PF) and determines the percentages of bio-oil substitutions by manipulating the synthesizing variables such as formaldehyde to phenol (F/P) catalyst ratio (NaOH/P), catalyst ratio and duration using one-factor-at-time method. The effect of each manipulated variables on shear strength was compared to the Chinese National Standard for PF resin shear strength. Bio-based phenolic resins are synthesized using the optimum conditions by replacing 10, 20, 30 and 40% of phenol with bio-oil from the pyrolysis of sugarcane bagasse. The results obtained shown that the optimum conditions to synthesize phenol formaldehyde resin is at F/P molar ratio of 2.0, catalyst ratio of 0.6 and duration of 3 hour. The results of bio-based phenolic resins bonding performance shows that substitution percentage of bio-oil up to 20% at most gives good performance compared to the pure PF resin.

Keywords: Bio-oil, Phenol formaldehyde (PF) resin, Pyrolysis, Sugarcane bagasse.

1. Introduction

Phenolic resins are thermosetting polymers that are formed from the condensation of petroleum-based phenol and formaldehyde [1]. Resoles resin is the most common adhesive used especially in plywood industry. However due to the fluctuation of oil price, the price of phenol is also affected which constrained the application of PF resin [2].

Utilization of lignocellulose biomass such as rice husk, empty palm fruit bunch, sawdust, bagasse and grasses seems like a good alternative for the production of bio-based adhesive as it contains high amount of pyrolytic lignin and is inexpensive [3]. Previous researches show that agricultural waste is an excellent element for the synthesis of bio-based adhesive [3, 4]. Lignocellulose materials can be converted into bio-oil by thermochemical methods, such as pyrolysis and liquefaction. In this study, pyrolysis process is chosen because previous studies have shown that pyrolysis method gives the highest yield of bio-oil [5, 6].

Lignocellulosic biomass consists of cellulose, hemicelluloses, lignin and a small number of other substances. It has a variety of conversion methods, various final products and a wide range of uses. It is good for manufacturing fuels, chemicals, materials and food. Renewable biomass can help settle the problem of material shortages and address concerns about the use of non-renewable fossil fuels. [7].

In this study, sugarcane bagasse was used as biomass feedstock to extract bio-oil by using pyrolysis method. The bio-oil obtained will be further optimized into adhesive. Most studies about bio-oil have emphasized its usage in transportation, fertilizers, agrichemicals and food flavourings [8]. However, to date there have been scarce of study on the synthesis of adhesive using whole bio-oil. Sugarcane bagasse is a sustainable alternative that can be used as a partial replacement of phenol from petrochemicals due to high content of lignin which is about 12 to 18% [9].

Previous studies have shown that in resin synthesis, only 20% of phenol formaldehyde resin can be replaced by bagasse lignin. The performances of the resin were good and passed the relevant international standard specifications for interior-grade panels [3]. Pyrolytic lignin in sugarcane bagasse is believed can be used to be substituted for phenol in the preparation of phenol formaldehyde resin as it has quite similar structure as phenol [10]. A few researches on the substitution of phenol using pyrolysis oil for the preparation of phenol formaldehyde resin have been conducted. The most recent research on synthesizing phenol formaldehyde resin using bio-oil extracted from palm kernel shell (PKS) and *Leucaena* sp. Wood shown that the best operational conditions were found at temperature of 85 °C, catalyst loading of 0.5 and within 60 minutes of resinification process [11]. However, in the meantime there are not many studies focusing on the optimization and production of bio-based phenol formaldehyde resin using bio-oil extracted from sugarcane bagasse which is the main target of this paper.

2. Materials and Method

2.1. Feedstock

Sugarcane bagasse as raw material was collected along roadside of Jitra, Kedah, Malaysia at coordinate of (6.2644° N, 100.4202° E). Sugarcane bagasse was dried in oven at temperature 80 °C and was grinded in a cutting mill and sieved to obtain

a particle size in the range of 4.0 to 6.0 mm [12]. The shear strength test of PF resin was done on plywood planks. Plywood was acquired from local plywood factory in Jitra. The dimension of the plywood was (277 mm × 27 mm × 4 mm). Pure Zeolite Socony Mobil-5 or known as ZSM-5 zeolite used in this research was purchased from Malaysia Chemical Exporters. ZSM-5 zeolite is a high acidity catalyst which comes in pellets form with diameter about 0.2 to 0.3 cm.

2.2. Catalytic bed reactors

Bio-oil was extracted using catalytic pyrolysis process at temperature 500°C which was executed in a catalytic bed reactor as depicted in Fig. 1. The operating conditions for the pyrolysis process were selected based on the optimal results done from previous research [12, 13].

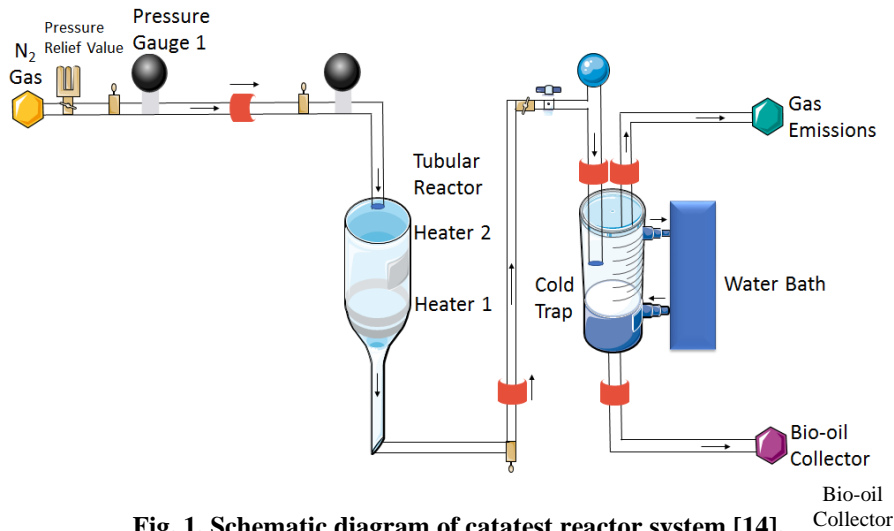


Fig. 1. Schematic diagram of catalytic reactor system [14].

2.3. Optimization of phenol formaldehyde resin using one-factor-at-time method

One-factor-at-time or known as OFAT method is used in experiments which involve the testing of factors one at a time instead of multiple factors simultaneously [15]. In this experiment OFAT method will be applied where first of all phenol formaldehyde resin were prepared in 500 mL round flask by using batch polymerization process. The F/P molar ratio, NaOH/P molar ratio and duration were manipulated. In the first step, sodium hydroxide as alkaline catalyst was mixed with 15 mL of water. Then phenol and formaldehyde were added into the mixture and heated up to 80°C for 1h with continuous stirring. The solution was rapidly cooled to 65°C to yield phenol formaldehyde resins.

Each parameter was manipulated by using one-factor-at-time method. The most optimum conditions for the preparation of PF resin were determined by identifying the bonding strength using universal testing machine and compared with the Chinese National Standard [16]. The optimum conditions were used in the preparation of bio-based phenol formaldehyde resin.

2.4. Preparation of bio-based phenol formaldehyde resin bonding strength

Plywood panel with size of 277 mm × 27 mm × 4 mm were constructed for the shear strength test [16]. A total of nine plywood panels were prepared for the testing process. The ends of the two plywood panels were joined together with the bio-based PF resin. Figure 2 shows the dimension of the plywood. The plywood panels were bonded together to a thickness of 8 mm. The lap area of the plywood bonded with the resin is 810 mm² with press pressure, temperature and duration of 0.2 N/mm², 120°C, and 15 min, respectively according to previous work [17]. The tensile shear strength of the plywood bonded with the resin was determined according to the Chinese National standard, GB/T 14732-2006 [16].

The resin specimens were divided into two subgroups prior to the testing. The first subgroup was tested in the dry state where the plywood was exposed to standard climate of 82% relative humidity and temperature 28°C for 7 days. The second subgroup of plywood was immersed in cold water at 22°C for 24 h. The tensile shear tests were carried out using the Universal Testing Machine after all the pre-treatments were finished according to previous work [18]. The speed for the pulling force exerted on the plywood was 1 mm/min. The pressure was applied until a break or separation happened on the surface of the plywood.

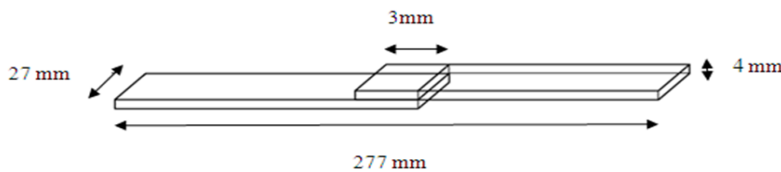


Fig. 2. Dimension of the plywood.

3. Result and Discussion

Optimization of Shear Strength

The optimization of shear strength was executed in terms of the F/P molar ratio, catalyst ratio (NaOH/P) and duration. The optimization value was applied based on the optimal data range for the preparation of PF resin from previous work [17]. Figure 3 indicates the impact of F/P molar ratio on the shear strength of PF resin. In this process F/P molar ratio is manipulated at three different ratios which were molar ratio of 1.8, 2.0 and 2.2 while catalyst ratio and duration was kept constant at 0.5 and 2 h respectively. The results gained shows that the highest shear strength recorded was at F/P molar ratio of 2.0 which was 1.8 MPa. The result achieved was in accordance with previous research which claimed that the best shear strength was gained from F/P molar ratio of 2.0 [19]. However, the shear strength of previous research was 1.04MPa which was a bit different from the result of this research. These may be due to different types and methods used for the preparation of the feedstocks. The F/P molar ratio will be kept constant at 2.0 for next optimization process which was effect of catalyst ratio.

Figure 4 shows the effect of catalyst ratio (NaOH/P) on the shear strength of PF resin. In this process catalyst molar ratio is manipulated at three different ratios which were molar ratio of 0.5, 0.6 and 0.7 while F/P molar ratio and duration was

kept constant at 2.0 and 2 h respectively. The results achieved shows that the highest shear strength recorded was at catalyst ratio of 0.6 which was 2.83 MPa. Significant increase of shear strength was observed at catalyst ratio of 0.6. The result gained shows some similarities with previous research which showed that catalyst ratio shows significant effect on shear strength at range of molar ratio of 0.5 to 0.6 [20]. For the next optimization process which was effect of duration, the F/P molar ratio and catalyst ratio of 2.0 and 0.6 respectively were kept constant.

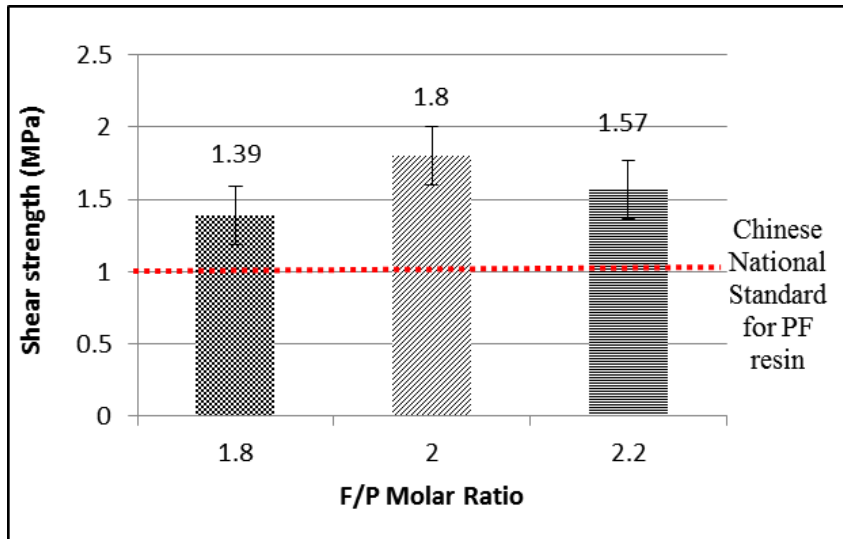


Fig. 3. Effect of F/P molar ratio on shear strength.

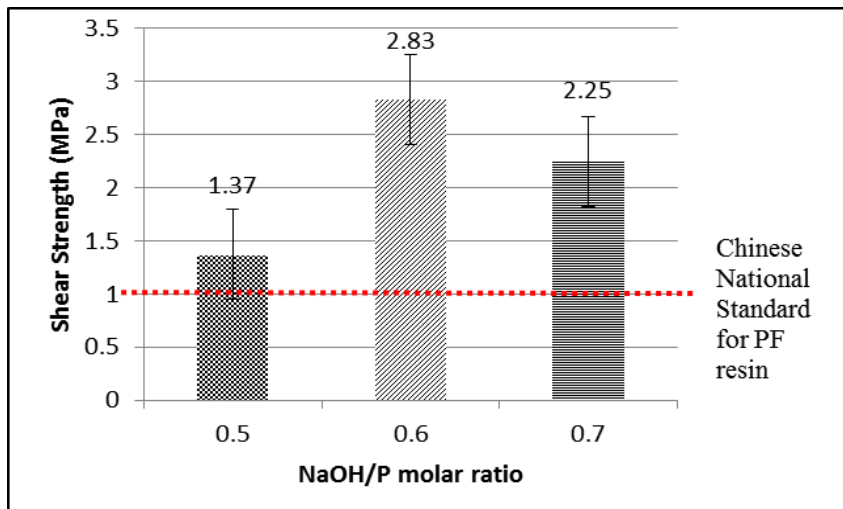


Fig. 4. Effect of catalyst ratio on shear strength.

Figure 5 portrays the effects of duration on the shear strength of PF resin. The duration is manipulated at three different durations which were 1 hr, 2 hr and 3 hr. The results gained shows that the highest shear strength was at duration of 3 hr.

The results indicate that the shear strength increase as time increase from 1 hr to 3 hr and then deteriorate when increasing the time to 4 hr. Further increasing the duration to 4 hr resulting in wood ruptures which also known as wood failure. The finding is not consistent with previous research maybe because of different feedstocks, characterizations and methods of preparation [21, 22]. Hence from the overall optimization process, the optimum state for the preparation of PF resin were at F/P molar ratio of 2.0, catalyst ratio 0.6 and duration 3 hr. These conditions are applied in the preparation of bio-based PF resin.

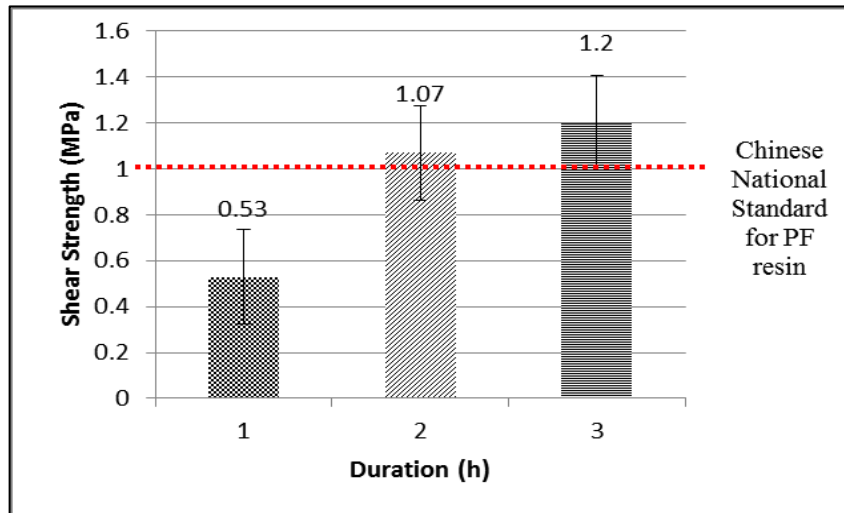


Fig. 5. Effect of duration on shear strength.

Table 1 shows the effect of substitution level of bio-oil with phenol formaldehyde resin in the preparation of bio-based PF resin on the dry and wet shear strength of the resin which was being compared with the Chinese National Standard of shear strength for PF resin. The modified resin includes the degree of bio-oil substitution (10-40 wt. %). The effects of bio-oil substitution on the performances of strength of the plywood were investigated. The results show that the dry bonding strength of the resins appeared to be varied from 1.40 MPa to 0.89 MPa depending on the level of bio-oil substitution.

As can be seen from the results, dry bonding strength of bio-based PF resins satisfy the requirement of the Chinese National Standard (GB/T 14732-2006, ≥ 1.00 MPa) up to 20% substitution of bio-oil only. This result is consistent with the data gained from previous research which showed that only up to 20% of PF resin can be replaced by bagasse lignin in the synthesis of bio-based PF resins [3]. Further increment of bio-oil substitution leads to decrement of bonding strength. On the other hand, for wet bonding strength of bio-based PF resins none of the resins fulfil the requirement of Chinese National Standard (GB/T 14732-2006, ≥ 0.70 MPa). The water resistance of bio-based PF resins was weaker than PF resin because of reactivity of lignin was lower compared to phenol which supports the statements of another research [23]. Overall it can be concluded that the substitution of bio-oil extracted from sugarcane bagasse can be used up to 20% for the substitution of phenol in the synthesis of bio-based PF resin.

Table 1. Effect of bio-oil substitution with PF resin on shear strength.

| Adhesive | Plywood performances | |
|-----------|----------------------------|----------------------------|
| | Dry bonding strength (MPa) | Wet bonding strength (MPa) |
| PF | 1.65 | 0.86 |
| 10% BPF | 1.40 | 0.67 |
| 20% BPF | 1.08 | 0.35 |
| 30% BPF | 0.88 | 0.29 |
| 40% BPF | 0.89 | 0.34 |
| GB/T14732 | >1.00 | >0.70 |

4. Conclusion

The optimum conditions for the preparation of PF resin were at F/P molar ratio of 2.0, catalyst ratio (NaOH/P) of 0.6, and duration of 3 h where these conditions were applied next in the preparation of bio-based PF resin. Based on this study, it had been proven that the replacement of commercial phenol with bio-oil derived from pyrolysis of sugarcane bagasse for the preparation of phenol formaldehyde (PF) resin can be achieved at certain rate of substitution. The results for dry bonding strength of bio-based PF resins satisfy the requirement of the Chinese National Standard up to 20% substitution of bio-oil only. The results gained were consistent with previous research [3]. However, for the wet bonding strength results of bio-based PF resins none of the resins fulfil the requirements of Chinese National Standard. Bio-based PF resins are considered to be environmentally friendly adhesives with significantly lower contamination and formulation costs compared to petroleum-based types. Research on formaldehyde emission from conventional thermosetting resins which is also one of negative aspects in production of adhesive can be investigate and improve further in the future.

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