



Physico-mechanical properties of resol phenolic adhesives derived from liquefaction of oil palm empty fruit bunch fibres



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ABSTRACT

Utilization of oil palm empty fruit bunch (EFB) fibres in the production of phenolic (PF) resin is an alternative way to reduce the dependency of petroleum-based phenol. In this study, resol-type phenolic resin was synthesized from oil palm EFB fibres via liquefaction process using phenol and sulfuric acid, followed by resinification reaction with formaldehyde in alkaline condition. The increase of the ratio of formaldehyde/liquefied EFB (F/L_{EFB}) results in the increase in the viscosity and molecular weight of the produced PF resin. The obtained FTIR spectra confirmed that the chemical functionalities of the produced PF resin are almost similar to that of commercial PF resin. The NMR analyses indicated that the phenol para position was favoured for the reaction over the ortho position in both commercial resin and resin synthesized due to the existence of steric hindrance effect from the hydroxyl phenol and phenol derivatives of liquefied EFB. The shear strength of the produced PF resins is fulfilling the requirement as specified in JIS K-6852.

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1. Introduction

Thermosetting resins play a vital role in various industries due to their excellent properties including modulus, strength, durability, thermal and chemical resistance (Raquez et al., 2010). Phenolic resins (PF) remain of high commercial and industrial interest despite the emergence of new thermosets and high performance polymers (Langenberg et al., 2010). PF resins are widely used as an adhesive for wood-based panels and other engineering products (Schmidt and Frazier, 1998). However, there are concerns regarding the chemicals used in the production of phenolic resins, i.e., phenol and formaldehyde, which are expensive and harmful, leading to increasing interest for alternatives derived from lignocellulosic biomass (Jang et al., 2011).

PF resins are produced via polycondensation of phenol with formaldehyde. It is the first synthetic polymer developed commercially in 1908 (Pizzi, 2003). It can be divided into two types, i.e. novolac and resol. Chemical properties of PF depend on various key factors, such as formaldehyde to phenol molar ratio and catalyst, during the synthesis process. Acid catalysis produces

thermoplastic phenolic resins called novolacs, while resol type PF resins are produced in the presence of alkaline catalysts. Resol PF is classified as thermosetting resins because it is sensitive to heat (Pan, 2011). There are three differences between the reaction of formaldehyde with phenol in acidic and alkaline conditions. The first one is the rate of aldehyde attacks on phenol, second is the subsequent condensation of phenolic alcohols, and third is in the nature of the condensation reaction (Pizzi, 2003).

Lignocellulosic biomass is well recognized as the world's most abundant and promising material to substitute petroleum-based chemicals due to its similarity in chemical structure. It comprises three main components i.e. cellulose, hemicelluloses and lignin. Over the past decade, several attempts to use lignocellulosic biomass such as wood (Kunaver et al., 2010), bark (Yuan et al., 2009), lignin and tannins (Vázquez et al., 2012) have been done to reduce the consumption of petroleum-based phenol in the production PF resins. By the utilizing of biomass, the issues related to petroleum sustainability can be prevented and bio-products which meet the needs of the present generation without compromising the needs of future generations can be obtained. Apart from the fluctuation of petroleum prices, there are also other problems that arise, such as the management of waste from wood and agricultural industries. Utilization of these wastes to produce high-value products is capable to reduce the impact of pollution on the

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environment and also enhance the well-being of future development (Langenberg et al., 2010).

Malaysia is one of the world largest plywood manufacturers, which consumes great amount of PF adhesives. Hence, the introduction of phenolic derivatives from lignin in biomass for the preparation of phenolic resins can help reduce the dependency on petroleum-based phenol. One of the most important agricultural industries in Malaysia is palm oil refinery. According to the Malaysian Palm Oil Board (MPOB), palm trees were cultivated on 5.2 million hectares in 2013. After palm oil extraction process, waste by-product such as empty fruit bunch (EFB), amount to 70–80 million tons per annum (MPOB, 2013). Therefore, several approaches have been developed to utilize EFB fibres for value added products, such as pulp (Jiménez et al., 2009), composite board (Chai et al., 2009), activated carbon (Alam et al., 2009), bio-oil (Fan et al., 2011), bio-adsorbent (Sajab et al., 2013), etc.

The aim of this work is to study the utilization of oil palm EFB fibres to produce resol-type PF resins adhesive for plywood application. The EFB fibres were liquefied using phenol as a liquefying reagent in the presence of sulfuric acid as a catalyst and then reacted with formaldehyde under alkaline condition to produce resol PF resin at a moderate temperature. The produced PF resin was applied on plywood to study the shear strength of the products.

2. Experimental

2.1. Materials

Oil palm EFB fibres were purchased from Szetech Engineering Sdn. Bhd. The commercial phenolic (PF Com) resin used as a comparison in this study and industrial grade phenol was supplied by Malayan Adhesives and Chemicals (MAC) Sdn. Bhd. Analytical grade sulfuric acid (98%), methanol, formaldehyde (37%), NaOH, pyridine, and acetic anhydride were purchased from Sigma-Aldrich. All chemicals were used without purification.

2.2. Liquefaction of EFB fibres

The liquefaction of EFB fibres was conducted according to method reported previously with modification (Ahmadzadeh et al., 2009; Zakaria et al., 2014). Firstly, the EFB fibres were dried in an oven at 105 °C for 24 h. After that, liquefaction of the EFB fibres was carried out at weight ratio of phenol to EFB (P/E) 3:1 in the presence of sulfuric acid (3% based on phenol weight) as the catalyst. This reaction was conducted at 150 °C for 120 min in an oil bath. The liquefied mixture was then diluted in 400 ml methanol and filtered with filter paper (Whatman No. 1) to separate the un-liquefied fractions. Evaporation with rotary evaporator was conducted to recover the methanol added.

2.3. Resin synthesis

Resinification was carried out by mixing the liquefied EFB (L_{EFB}) mixture and formaldehyde in a round bottom flask at different weight ratios of formaldehyde to L_{EFB} (1.8:1, 2.0:1, and 2.2:1) under alkaline condition. Alkaline condition in the reaction was controlled by two steps addition of 40% aqueous NaOH. The first addition of NaOH (0.5 g) is to neutralize the acid catalyst added during the liquefaction process and the second addition of NaOH (4.5 g) is to maintain the reaction in alkaline condition. The temperature was set at 65 °C for the first 60 min and then increased to 85 °C after the second addition of NaOH solution for another 120 min. After the reaction completed, the product (designated as PF 1.8, PF 2.0 and PF 2.2) were cooled to room temperature and kept in the refrigerator for further characterization.

2.4. Characterizations

The Fourier Transform IR (FTIR) spectra of the PF samples were recorded using a Perkin-Elmer FTIR-ATR spectrometer with a resolution of 1 cm^{-1} . The chemical shifts of the PF produced were characterized with a liquid-state ^{13}C Carbon Nuclear Magnetic Resonance (^{13}C NMR) (advance 111, 600 MHz, Bruker) in DMSO-d_6 . The molecular weight of the PF Com and PF produced were analyzed on Gel Permeation Chromatography (GPC) (RI detector at 30 °C; UV detector 254 nm; PSS SDV column at 30 °C) using THF as the eluent with flow rate of 1 ml/min. Before GPC analysis, the PF resins were acetylated with 1:1 pyridine and acetic anhydride. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo (SDTA 851e) thermal analyzer. Approximately 15 mg of PF resin was placed in a 30 μl aluminium crucible and subjected to heating in a nitrogen atmosphere at a heating rate of 10 °C/min from 25 to 600 °C.

2.5. Shear strength

Shorea sp. plywood was used as wood testing panel. The sample was cut into strips (90 mm \times 25.4 mm \times 2.5 mm) and conditioned at 23 ± 1 °C for at least seven days before used. After that, the PF Com and PF produced were spread on one side of the sample at amount of 0.035 g/cm^2 (on solid basis) in an area of 25.4 mm \times 90 mm. Then, the adhesives coated plywood sample was overlapped with uncoated plywood with the length direction parallel to the wood grain. The resulting two layered panel was then clamped with G-clamp for three days and followed by conditioning at temperature of 23 ± 1 °C at a relative humidity of 50% either for seven days, or until they attain a constant mass, whichever is the longer period. The evaluation of bonding strength was carried out according to Japanese Industrial Standard (JIS K-6852) using a Universal Testing Machine (Testometric M500-50CT) until failure at a force of 9.7 MPa of shear area per minute (approximately 1.3 mm/min crosshead speed).

3. Results and discussion

3.1. Characterizations of the PF resin

The physical properties of the PF produced from the liquefied EFB are shown in Table 1. The pH value of the PF resin is lower as compared to the PF Com resin. This may be attributed to the presence of residual H_2SO_4 , which was used as a catalyst during the liquefaction process has reduced the pH of the resinification mixture. The solid content of each PF resin produced is almost similar, but slightly lower than that of the commercial PF resin, which may probably due to the existence of urea in the commercial PF resin (Zhao et al., 2010). Meanwhile, the viscosity and molecular weight of the PF produced resins is higher as compared to the commercial PF resin. The results show that the amount of formaldehyde used in the reaction has influenced the viscosity and molecular weight of the PF produced tremendously. It is well known that resin viscosity and molecular weight of PF resin are influenced by non-volatile chemicals, temperature and F/P ratio (Haupt and Sellers, 1994). Higher formaldehyde content might result in the increase of viscosity for each resin produced because higher content of formaldehyde tends to speed up the polymerization process. Besides, the presence of larger molecule in the liquefied EFB in the resin also will increase the viscosity and molecular weight of the PF resin Fig. 1.

3.2. Chemical functionality analysis by FTIR

Fig. 1 illustrates the FTIR spectra of the PF Com and PF samples produced using different ratios of F/ L_{EFB} (PF 1.8, PF 2.0 and PF 2.2).

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