Influence of CuO nanoparticle on palm oil based alkyd resin preparation and its antimicrobial activity

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Abstract. An alkyd resin has been synthesized from palm oil that reacted with glycerol and phthalic anhydride by alcoholysis-polyesterification process and co-catalyzed by CuO nanoparticle. The CuO nanoparticle was pre-prepared in the glycerol via sol gel method, which creates a new reaction condition for resin preparation. The resins were characterized by fourier transform infrared spectroscopy (FTIR), where a new ester linkage bond (C-O-C) was noticed for resin sample. The antimicrobial activity and the curing behaviour of the resin were determined by Kirby-Bauer and differential scanning calorimeter technique. It was found that, the addition of CuO speeded up the reaction rate and played antimicrobial role. Moreover, it shortens the reaction time of alcoholysis and polyesterification process.

1. Introduction
In recent years, intensive research on the development of polymers from renewable resources has been triggered due to the environmental concerns [1]. Vegetable oils are one of the most favourable options to use for polymer development. This is due to its desirable properties such as cheap, ready availability and biodegradable [2, 3]. Alkyd resin, oil modified polyester which widely applied in paint, varnishes, lacquers, adhesive, composite making etc. [4-6] Alkyd is a mixture comprised of polyol, dicarboxylic acid or anhydride, and fatty acids. The common used polyol and diacid component in alkyd preparation was glycerol and phthalic anhydride respectively [7]. Synthesis of alkyd involved a two-step process, Alcoholysis-polyesterification reaction, the first process which is known as alcoholysis referred as “monoglyceride process” [8]. This reaction consists of triglyceride (TG) and glycerol, which yield required amount of monoglyceride (MG) for later polyesterification process in alkyd synthesis. Simple Brönsted base catalyst commonly is used to conduct the reaction at 240-270 °C. Two kinds of catalyst system which practically used, homogeneous catalyst (Ca(OH)2, KOH and NaOH) and heterogeneous catalyst (MgO, CaO, ZnO/alumina, calcium acetate and calcium carbonate). Homogeneous catalysed processes yield usually 40-60% of MG [9, 10] whereas the heterogeneous catalysed reaction yield 32-39% of MG [11]. Obtaining high yield of MG (at least > 40%) is important for the homogeneity of the reaction mixture and proceed to polyesterification [12]. Monoglycerides and diglycerides generated during alcoholysis take part in polymerization with diacid component. Furthermore, the reaction period required in acquiring maximum MG yield of heterogeneous catalysed is longer compared to homogeneous catalysed reaction. Lowering the
alcoholysis period is crucial to yield a low cost process. Ferretti, et al. [9] used MgO heterogeneous catalyst in MG preparation and found that ~77% of MG was achieved after two hours of reaction. However, the utility of MgO in polyesterification has not been explored. It is well known that, nanosize particle with high surface area is a promising catalyst. Thus, the combination of nanosize catalyst in homogeneous catalysis system can induce a novel catalyst system for alkyd resin preparation. Apart from that, remaining of nano-catalyst in the matrix after polyesterification can act as a property enhancing agent. However, the catalyst act as an antimicrobial agent is not reported yet. In recent years, metal oxide nanoparticle such as zinc oxide (ZnO) [13], titanium dioxide (TiO₂) [14], copper oxide (CuO) [15] has raised the attention as antimicrobial agents as they exhibits good antimicrobial property with minimum concentration [16] and considered as toxic free material [17]. Among them, CuO attracts the most attention due to its catalytic reactivity and low cost [18, 19]. Usually, the inclusion of nanoparticle into polymer was through mechanical mixing technique [13, 15, 20]. Delgado, et al. [15] used copper (Cu) and CuO nanoparticles as antimicrobial agent in polypropylene. They found that, CuO possessed better antimicrobial property than Cu alone. Ebrahimiasl, et al. [13] also incorporated ZnO nanoparticle in polypyrrole/chitosan as antimicrobial agent where it effectively against all the studied bacteria. Our attempt is to study the combined system comprised of liquid bases and CuO nanoparticle in palm oil based alkyd preparation. Oil palm tree is one of the most planted agriculture crop in Malaysia and Malaysia is one of the top palm oil producers in the world [21, 22]. In the present study, a novel catalyst system comprising with NaOH and CuO nanoparticles has been studied for alkyd preparation. The CuO nanoparticle was synthesized in glycerol and the antimicrobial property of nanoparticle included resin has been inspected.

2. Experimental section

2.1. Materials

Copper (II) chloride salt (CuCl₂·2H₂O), hydrazine monohydrate (64%), ethanol (99.9%), anhydrous methanol, sodium hydroxide, Methyl ethyl ketone peroxide (MEKP), cobalt octoate, glycerol, dimethyl sulfoxide (DMSO), copper (II) oxide (97%), copper (I) oxide (99.99%), *Escherichia coli* (ATCC 8739), *Pseudomonas aeruginosa* (ATCC 9027), *Staphylococcus aureus* (ATCC6538) and *Salmonella sp.* (ATCC 14028) were obtained from Sigma-Aldrich, Malaysia and used without further purification. Refined palm oil was provided by Malaysian Palm Oil Board (MPOB), Malaysia.

2.2. Preparation of CuO nanosol

The CuO nanosol was prepared by sol-gel method at ambient condition [18, 23-25]. Initially, the precursor was prepared by dissolving vital amount of CuCl₂·2H₂O in 44 mL of glycerol. The reducing agent solution at 7.060 mM was ready by mixing with ethanol. Then, ~6 mL of reducing agent was injected into the precursor solution and stirred for 10 h. The concentration of copper precursor in the solution was maintained in the range of 100–300 mg/L and used for current study.

2.3. Preparation of alkyd resin

Alkyd was prepared by alcoholysis-polyesterification reaction involving palm oil, glycerol and phthalic anhydride. Initially, 100g of oil was heated to 240 °C and subsequently added 22.2 g of glycerol into the oil with constant stirring and inert condition. Afterward, 0.3 g of NaOH was introduced into the mixture. The end point of alcoholysis reaction was determined by methanol solubility test[26]. After the end point acquired, the reaction mixture was cool down to 140 °C. Then, fine phthalic anhydride (38.7 g) was supplied into the system to kick start the polyesterification reaction and the reaction was controlled under 240 °C and inert condition. During polyesterification reaction, acid value (AV) followed ASTM D 1639-90 was used to monitor the reaction progress [27]. The reaction mixture was quenched to room temperature when the AV reached ~ 10. For the preparation of alkyd resin catalysed by combined system, pure glycerol was substituted by the CuO nanosol in several concentrations, i.e. 0, 100, 200 and 300 mg/L and labelled as A0, A100, A200 and A300, respectively.
2.4. *Calculation of extent of reaction*

The acid value of in-process samples was withdrawn and determined by titrating method. The extent of the reaction, $P$ with respect to the acid value was calculated using the following equation\[28, 29\]:

$$P = \frac{(C_0 - C_t)}{C_0}$$  \hspace{1cm} (1)

where $C_0$ is the initial acid value and $C_t$ is the acid value at time, $t$ of the reaction.

2.5. *Fourier transform infrared spectroscopy (FTIR)*

The structural information of the sample was attained by FTIR Spectrometer, Imprestige–21 model, Schimadzu Co., Japan, equipped with an attenuated total reflectance (ATR) device in the wave number range 500–4500 cm$^{-1}$ and resolution 4 cm$^{-1}$. The FTIR spectra were taken in a transmittance mode.

2.6. *Antimicrobial test*

The antimicrobial property of alkyd samples synthesized by A0 and A200 catalyst system was examined by Kirby–Bauer Method [30]. A number of microorganisms, such as Escherichia coli (ATCC 8739), Pseudomonas aeruginosa (ATCC 9027), Staphylococcus aureus (ATCC6538) and Salmonella sp. (ATCC 14028) was used. The cultures were maintained in a nutrient broth and subcultured at regular intervals. The samples were prepared (10 mg/mL) using 0.5% DMSO. The microbial cultures in nutrient agar plates were inoculated using spread plate technique and cork borer was used to make the hole on the agar. The samples (10 mg/mL) were loaded in the hole and incubated at 32.5 °C for 24 h. A blank sample was prepared separately as control. The diameter of the inhibition zone after 24 h incubation was measured.

2.7. *Differential scanning calorimeter (DSC) measurement*

The curing of the resin was monitored by DSC (model-TA-Q1000), under nitrogen purge gas. Prior to that, 1 g of resin was mixed with 0.04 g of MEKP and 0.02 g of cobalt octoate. The mixture was agitated manually and heated at 65 °C for 15 min. Thereafter, ~5 g of the mixture was put into a DSC sample pan and covered with an aluminum lid and closed tightly under pressure. The sample pan was placed in the DSC sample cell at ambient temperature, and an empty pan was used as reference cell. The DSC scan started from room temperature to 400 °C at 10 °C/min.

3. *Results and Discussion*

3.1. *Preparation of alkyd resin*

Methanol solubility method has been used to inspect the end point of alcoholysis reaction. Figure 1 exhibited the required time for end point of each catalyzed reaction. It can be seen that, combined catalyst system (A100, A200 and A300) significantly lowered the reaction period. Among them, A200 exhibited shortest reaction period. Beyond the 200 mg/L CuO limits, no significant performance was noticed. End point determination is important to control the alcoholysis reaction time, to avoid the intensification of polyglycerols formation [26].

Figure 2 exhibited the extent of reaction of different catalysed reactions. As seen, the extent of reaction increased as the reaction proceeded. It is noticed that, the early stage of reaction rate was faster than that of later stages. Comparable experiment curve were also reported elsewhere [27, 31-33]. These changes in extent of reaction during polyesterification is due to the different reactivity of primary and secondary –OH group in glycerol [34]. It is well known that, primary –OH react faster than that of secondary –OH. Thus, the fast reaction rate during early stage might be due to primary –OH, whilst secondary –OH at later stage [31]. In addition, 3D network in alkyd might be formed during later stages of the reaction. This might be due to alkyd chains cross-linking formation as the viscosity of the resin increased [35].

Apart from that, CuO addition is significantly affect the reaction during the early stage of the reaction. It can be seen that the initial reaction rates of combined system (A100, A200 and A300) are
significantly higher compared to A0. The initial rates of A200 and A300 were almost alike. In addition, A200 possessed earliest equilibrium (60 min) compared with others (Figure 2). To this, A200 system has been designated as optimum.

3.2. IR analysis of alkyd resin
Figure 3 illustrated the FTIR spectra of oil and alkyd resin. It can be seen that, the oil spectrum was significantly different compared to alkyd. A wide band was observed at 3550-3200 cm$^{-1}$ which assigned to O-H stretching in oil spectrum (Figure 3, i) [21, 36-40]. A characteristic absorption was detected at 3050-2800 cm$^{-1}$ assigned to C-H stretching [41, 42]. The absorption bands at 1750-1720 cm$^{-1}$ was endorsed to C=O. The C-O-C stretching in oil was noticed in the range of 1250-1050 cm$^{-1}$ [43]. The C-H bending was observed at 1470-1440 cm$^{-1}$. Additionally, an characteristic peak at 722 cm$^{-1}$ was noticed might be due to the existence of unsaturation in fatty acid [44].

Figure 1. End point determination of alcoholysis for different catalyst system

Figure 2. Progress of extent of reaction for different catalyst systems at polyesterification process (■A0, ●A100, ▲A200 and ▼A300).
The existence of ester linkages and other distinguish peaks in alkyd spectra was noticed (Figure 3, ii and iii). A new characteristic peak of C-O-C stretching at 1300-1250 cm\(^{-1}\) was appeared [33], which absent in oil spectrum. The C=O stretching of alkyd has shifted from 1748 cm\(^{-1}\) (oil’s spectrum) to 1735 cm\(^{-1}\). The C-H bending of aromatic ring of phthalate was visualized at 743 cm\(^{-1}\) [42]. It ensured the formation of alkyd resin [27, 41]. It is noticed that, the stretching frequencies of A0 (Figure 3, ii) and A200 (Figure 3, iii) samples were alike. Though, a slight shifts of C-O-C stretching (1270 cm\(^{-1}\) to 1266 cm\(^{-1}\)) and C-H bending of aromatic ring (743 cm\(^{-1}\) to 735 cm\(^{-1}\)) were detected. This phenomenon might be due to the interaction between polymer and nanoparticle [45].

3.3. Antimicrobial study

Figure 4 showed the antimicrobial property of A0 and A200 towards microorganism. The property of antimicrobial was determined based on the inhibition zone measurement. The inhibition zone of A200 sample were 23, 25, 15 and 40 for *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Salmonella sp.*, respectively, while A0 sample did not display any inhibition zones, indicating A200 have better antimicrobial property than A0. However, the bactericidal mechanism of nanoparticle toward microorganism is unknown. The disruption in the bacterial cell wall which resultant the cell death might be due to the binding between nanoparticle and the bacterial cell wall. Apart from that, the linkage can also form between nanoparticle with electron donor group like sulphur and nitrogen from bacterial molecule [46-48]. In addition, the bacterial cell metabolism and function like permeability and respiration might be disturbed by the copper-peptide linkage formed, which resultant the death of cell [48, 49]. In overall, the reduction rate of Gram negative bacteria is higher than Gram positive, due to their slimmer wall, which allow the easy absorption of the ions into the cell [50, 51].

![Figure 3. FTIR spectra of (i) oil, (ii) A0 and (iii) A200.](image-url)
3.4. Curing behavior

The DSC scans of the cure schedule for sample A0 and A200 were shown in Figure 5. A range of maximum cure temperature from 250 to 385 °C is depicted for the samples. The exothermic peak of sample A0 and A200 were 335 and 315 °C, respectively. It appears that CuO nanoparticles have an influence on the total heat released by the samples. Samples A200 have smaller exothermic heat compared to A0. The result obtained was in agreement with Ghaemy, et al. [52], Macan, et al. [53], which reported that nanoparticles able to lower the exothermic heat during the curing. This phenomenon occurred due to the absorption some of the heat by the nanoparticle [52]. Therefore, the presence of CuO nanoparticle in the alkyd resin can enhance the curing properties.

4. Conclusion
Palm oil based alkyd resin has been synthesized using the novel combined system. The addition of nanoparticle into the NaOH catalytic system improved the alcoholysis-polyesterification process performance. The antimicrobial activity of A200 was better than A0. The curing property of resin was improved by CuO nanoparticle via lowering the exothermic heat of the reaction. Therefore, it is evidenced that CuO nanoparticle can worked as co-catalyst for resin preparation simultaneously served as antimicrobial agent for alkyd.

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