Production of cellulose phosphate from oil palm empty fruit bunch: Effect of chemical ratio

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Abstract.
Cellulose phosphate was synthesized from oil palm biomass residue that has the potential to represent a considerable added value product for the oil palm biomass utilization. Cellulose phosphate (CP) is prepared via a phosphorylation process using the \( \text{H}_3\text{PO}_4/\text{P}_2\text{O}_5/\text{Et}_3\text{PO}_4/\text{hexanol} \) sequence using oil palm empty fruit bunch microcrystalline cellulose (OPEFB-MCC) as the starting material. Various factors affect its synthesis; one of which is the subject of this investigation is the orthophosphoric acid (\( \text{H}_3\text{PO}_4 \)) to triethylphosphate (\( \text{Et}_3\text{PO}_4 \)) ratio which have the capability to increase the phosphorus content of CP. It is believed that during this reaction, the esterification of the free hydroxyl groups of the cellulose occurred. The \( \text{H}_3\text{PO}_4/\text{Et}_3\text{PO}_4 \) ratios applied were 0.16, 1.00, and 1.84. The effect of the \( \text{H}_3\text{PO}_4/\text{Et}_3\text{PO}_4 \) ratio on phosphorus content, yield, water swelling and molecular structure of CP are discussed.

Keywords: cellulose phosphate; oil palm empty fruit bunch microcrystalline cellulose; \( \text{H}_3\text{PO}_4/\text{P}_2\text{O}_5/\text{Et}_3\text{PO}_4/\text{hexanol} \) sequence; \( \text{H}_3\text{PO}_4/\text{Et}_3\text{PO}_4 \) ratio; phosphorus content

1. Introduction
In 2011, Malaysia had 4.908 million hectares of oil palm plantation, which covers approximately 73% of the Malaysia's agricultural land [1]. Despite the obvious benefits, for 2005 alone, an estimated 56 million tons of oil palm biomass are generated in Malaysia and annual production is expected to increase in line with the growing worldwide demand for palm oils [2]. At present, there is a massive quantity of oil palm biomass residue still perceived as waste by-products. However, despite this issue, oil palm biomass are now being utilized as an alternative towards economically useful. Later effort, oil palm empty fruit bunch (EFB) is now viewed as feasible alternatives to sources of fibers, which can be converted into paper making pulp that would have good printing properties and a good formation within papermaking, yet to be extensively commercialized.

Preferably, a solution that utilizes these plentiful by-products to replace wood sources should be realized. This will be a positive impact towards a more sustainable development. Oil palm biomass residue is a reliable resource because of its availability, continuity, non-hazardous biodegradable material [3], and do not compete its food production in terms of land destination [4]. Furthermore, oil palm fibers are versatile, stable, and can be processed into various dimension grades to fit specific applications.
Realizing the potential of this oil palm biomass, recently, there have been numerous ongoing efforts to increase profits from oil palm biomass fiber by producing fuel and biobased chemicals, with an emphasis on its major component, cellulose. Cellulose such an important material is among the potential output of use for industrial exploitation and can represent a considerable value added product for the oil palm biomass utilization.

Currently products made from lignocellulosic biomass feedstock represent only minor fraction of the chemical industries product, however, the interest in the bio-based products has increased because of the rapidly rising barrel cost, an increasing concern about the environment issue and the depletion of the fossil resources in the near future [4].

Besides oil palm biomass, cellulose can be produced from others lignocellulosic biomass and some potential feedstocks including wood waste such as timber residues from saw mills, agriculture waste, such as straw and corn stover, grasses such as miscanthus and algae [4]. For industrial, most of the cellulose fiber derived from wood (softwood and hardwood) and relatively small amount in volume of non-woody fibre, which mainly from bagasse, bamboo, jute, ramie, hemp, flax and cotton. Nevertheless, non-woody fibers are important particularly in the developing world to reduce the spent on importing costly wood pulp and in advantages since non-woody fibers produce an annual crop with higher yield than wood [5].

There are great numbers of potential uses of cellulose within different industries. Until now, cellulose is the major constituent in the production of material in some of the largest industries in particular in pulp, paper, and textile industries, and expected will continue to be so in the future. However, the limited usage of pure cellulose has led to develop a number of cellulose surface modification strategies to enrich several key properties and characteristic of cellulose fibers that do not exist in the parent cellulose [6]. Chemical modification via etherification and esterification of polysaccharides are interesting routes represent the most versatile transformations for preparing new types of polymers based on polysaccharides, with advances in performance and application [7]. The unique characteristic of cellulose obtained from cellulose modification (cellulose derivatives) therefore accord it more advantages for the application purpose.

For example, the incorporation of cellulose into phosphate group alters the significance of cellulose application by endowing the material advantageous phosphate characteristics. Specific effect may thus be obtained by the phosphate group are the reduction in the flammability of the material and an increase in ion exchange capability [8, 9]. Flame resistance provides an advantage to cellulose phosphate especially for utilization in the manufacturing of textile and paper. This property has an adequate capability to execute thermal insulation of materials resulting in increased material protection upon exposure to sufficient heat. Cellulose phosphate is also identified as a cation-exchange material [9, 10]. The ion-exchange capability of phosphate advances the application of cellulose phosphate as an absorbent material. With this property, cellulose phosphate constituent a very important part of the world market as an absorbent material.

Significant improvements in surface properties and functionalities will be possible, allowing the development of many more new products that could replace a wide range of material because of their biocompatibility, biodegradation and non-toxicity [11]. Furthermore, the usage of cellulose and its derivatives in a diverse array of other applications, such as biosensors, bioengineering, pharmaceutics, smart and responsive material with polysaccharides and thus continue to grow on a worldwide basis [6]. Moreover, cellulose phosphate from oil palm empty fruit bunch can be classified as a value added biomaterial [12-14], that can provide benefits and extend well beyond discipline, which is the key to exploiting the full potential of oil palm biomass residue.

In the previous study, it has been shown that cellulose phosphate (CP) can be successfully synthesized from oil palm empty fruit bunch (OPEFB) [12, 13]. However, for the intent of application purposes, a higher degree of OPEFB-CP substitution should be achieved. The objective of this study is to investigate the effect of orthophosphoric acid (H₃PO₄) to triethylphosphate (Et₃PO₄) ratio in cellulose phosphate synthesis from OPEFB. For this purpose, OPEFB first has to be converted to pure cellulose pulp by a pulping process followed by an environmentally bleaching process using a totally
chlorine free (TCF) bleaching sequences to eliminate the remaining lignin that gives a brownish color to the pulp. Microcrystalline cellulose (MCC) is prepared via a hydrolysis process of the TCF pulp. Various characterizations of the resulting CP were carried out.

2. Materials and Methods

2.1. Preparation of microcrystalline cellulose
OPEFB cellulose was prepared using the environmentally benign process as described by Wan Rosli et al. (2003) [15] and Leh et al. (2008) [16]. The procedure involved water prehydrolysis of the OPEFB, which was then followed by soda pulping. The unbleached pulp was afterwards bleached using a TCF sequence of oxygen (O), ozone (Z) and peroxide (P) to a Kappa no. of 1.4. The resultant (OZP) bleached pulp was later hydrolyzed to microcrystalline cellulose (MCC) with 2.5 M HCl while maintaining a solid to liquid ratio of 1:20 and refluxing at 105 ± 2 °C for 15 min. After hydrolysis, the material was thoroughly washed with distilled water before air-drying. Powdered OPEFB-MCC was then obtained by grinding the sample in a ball mill, and was subsequently kept in a desiccator over phosphorous pentoxide before further use [12].

2.2. Synthesis of cellulose phosphate
4.0 g of MCC powder was swollen consecutively in distilled water, ethanol and hexanol for 24 hours to activate the cellulose surface. Phosphorylation reaction was carried out in the four-neck round bottom flask equipped with a nitrogen inlet, a condenser, a thermometer, and a mechanical stirrer. MCC was then dispersed in 29 mL 1-hexanol. Then a solution of 50 g phosphorus pentaoxide (P$_2$O$_5$) in various ratios of H$_3$PO$_4$ to Et$_3$PO$_4$ was added portion wise to the suspension. The reaction was allowed to proceed under constant stirring and a nitrogen atmosphere at 50 °C for 72 h. After chemical treatment, modified MCC were rinsed with hexanol, ethanol, and then extraction against distilled water to remove excessive reagents. The resulting yield was then dried at room temperature.

2.3. Characterization method

2.3.1. Determination of phosphate content
Quantification of phosphorous requires its conversion into dissolved orthophosphate. This is then followed by colorimetric determination of the dissolved orthophosphate. A sulfuric acid-nitric acid mixture was used as oxidants for the Kjeldahl digestion procedure to oxidize organic matter and thereby release phosphorus as orthophosphate. Phosphorus concentration was determined spectrometrically at 880 nm by the ascorbic acid colorimetric method.

2.3.2. Water sorption
For water sorption measurement, 10 mg of samples was allowed to hydrate in excess distilled water at room temperature in centrifuge polyethylene tubes. After centrifugation at 4000 rpm for 10 min following removal of the excess water, the samples were then periodically weighed several times. Water sorption as expressed by % swelling was determined via the difference of weight before and after swelling.

2.3.3. Differential Scanning Calorimetry (DSC)
DSC thermograms were obtained using a Perkin Elmer DSC6 with approximately 10 mg of material in sealed aluminium pans that were heated from ambient temperature to 300 °C at a heating rate 10 °C/min under nitrogen atmosphere.
2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was performed using a Nicolet Avatar 360 under transmission mode from 400 to 4000 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution, using the potassium bromide (KBr) method.

3. Results and discussion

Fig. 1 shows the FTIR spectra between MCC and its phosphorylated form. After phosphorylation, a few peaks that were earlier present in the MCC spectrum disappeared and concurrently the appearance of several new bands which are attributed to the phosphate group. New absorption peaks which characterized CP were indicated by the vibration bands of PO\(_4\) at 1027 cm\(^{-1}\), P=O at 1377 cm\(^{-1}\), and P-H at 2360 cm\(^{-1}\) (Fig. 1 b, c, d) [17]. Although the reaction was carried out under different H\(_3\)PO\(_4\)/Et\(_3\)PO\(_4\) ratio it seemed that each phosphorylated sample showed similar changes in absorption peaks. The resulting spectrums suggest that cellulose phosphate (CP) was successfully synthesized from oil palm empty fruit bunch via MCC and the molecular structures of the derived CP products are probably comparable.

The effect of the H\(_3\)PO\(_4\)/Et\(_3\)PO\(_4\) ratio on the phosphorus content, yield and water swelling of the cellulose phosphate are shown in Table 1. It can be seen that by varying the H\(_3\)PO\(_4\)/Et\(_3\)PO\(_4\) ratio significantly influenced the phosphorus content and percentage yield of CP. As the H\(_3\)PO\(_4\) concentration increases, the phosphorus content of the samples also increases, but it was the opposite for the percentage yield. These results suggest that by increasing the concentration of the H\(_3\)PO\(_4\), it will enhance the substitution reactivity of the hydroxyl groups to the phosphate group in anhydroglucose units of the cellulose molecules, thus increasing the phosphate content.

On the contrary, it seems that as the phosphorylation process progresses, degradation of MCC also took place resulting in less CP (yield) was obtained. This indicates that there was probably a competitive reaction between the phosphorylation and hydrolysis of the resulted product from the reaction [9]. Our previous study [12, 13] showed that the phosphorylation process is affected by the duration and temperature of the reaction, while in this study it is shown that the phosphorylation process is also sensitive to the H\(_3\)PO\(_4\)/Et\(_3\)PO\(_4\) ratio.

![FTIR spectra](image)

Fig. 1: FTIR spectra of (a) MCC and CP with H\(_3\)PO\(_4\)/Et\(_3\)PO\(_4\) ratio (b) 0.16 (c) 1.00 (d) 1.84
Table 1: Effect of H$_3$PO$_4$/Et$_3$PO$_4$ ratio on phosphorus content, yield and water swelling of CP

| H$_3$PO$_4$/Et$_3$PO$_4$ | P (%)  | Yield (%) | Swelling (%) |
|--------------------------|--------|-----------|--------------|
| 0.16                     | 10.34  | 72.17     | 172          |
| 1                        | 12.80  | 62.44     | 468          |
| 1.84                     | 20.66  | 45.56     | 1142         |

Macroscopically, the water swelling ability of CP was significantly higher compared to MCC (3%). This observation indicates that CP swells considerably in water with the higher the phosphorus content, the higher is the swelling ability. This was possible due to the incorporation of the phosphate group within the MCC which formed an ion exchange material.

The solubility of cellulose was relatively low in a many types of solvent; this is due to the hydrogen bonding between cellulose molecules and the crystalline region of molecular structure [18]. However, after the phosphorylation, the solubility of the resulted product increases. This is because of the substitution of the hydroxyl group with the phosphate group in the cellulose molecule. The presence of a larger group of phosphate as compared to the hydroxyl group in the cellulose molecule distracts the arrangement of crystalline pattern in the molecular structure. In this process, the phosphate group inside the cellulose granules would be able to create a repulsive force that might enhance inter- and intramolecular space and allow more water molecules to be absorbed. As a consequence, the phosphorylation process changed the molecular structure of the amorphous region and increased the swelling ability of modified cellulose in water.

To confirm this explanation, the crystallinity and thermal stability of MCC and CPs were examined using differential scanning calorimetry (DSC). According to the results (Fig. 2), what is observed could have been the phenomena related to the morphological changes of the MCC and CPs molecular structure. DSC curves of MCC and CP illustrate that phosphorylation strongly influence cellulose thermal degradation behavior. The first endothermic peak was observed at ca. 85 ºC due to evaporation of adsorbed water in the samples. Results indicated that CP has a higher water holding...
capacity as observed from the area of evaporation peak of CP which is slightly bigger compared to MCC itself. This results support the water swelling ability of the CP as discussed earlier. The additional exothermic peak of CP observed at ca. 180 °C appears to be mainly due to the thermal decomposition point of phosphate group [19, 20].

Results also indicate that part of the crystalline region of MCC molecule was transformed to the amorphous region, which can be observed as a Tg. When the phosphate group was introduced to the MCC as a main chain, Tg can be observed in the CPs thermograms around 162°C which is not present in the MCC thermogram (Fig. 2). The Tg value for each sample showed no large difference among them even though the H3PO4/Et3PO4 ratio and the phosphate content of each sample were different. From this result, we can conclude that the Tg value for each sample was not affected by the H3PO4/Et3PO4 ratio and the value of DS.

4. Conclusion
The FTIR analysis for CPs confirm the existence of a phosphate group. The results obtained illustrates that the synthesis of cellulose phosphate from OPEFB-MCC had been significantly influenced by the H3PO4/Et3PO4 ratio. Experiment data demonstrated that phosphorus content, yield and water swelling ability of CP change variably with increasing of H3PO4/Et3PO4 ratio. As the phosphate group was incorporated into the MCC chain, the formation of an amorphous region and the water swelling ability of the modified MCC also were observed. The OPEFB-CP synthesized from oil palm fruit bunch fibers has the potential to be utilized to generate more advanced materials in various biomaterial applications.

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