

The Effectiveness of TBAF/DMSO in Dissolving Oil Palm Empty Fruit Bunch-Cellulose Phosphate

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Abstract—Oil Palm Empty Fruit Bunch (OPEFB), a waste from Oil Palm tree is the most waste products which can be found abundantly on earth that leads to contamination. Cellulose Phosphate (OPEFB-CP) which is derived from the process known as phosphorylation possesses good attribute to be diversified in bone graft functioning as natural polymer. Sol-gel process is chosen to produce porous bone scaffold where it is essential to the OPEFB-CP to get dissolved before reacting with coupling agent. The main problem for the natural polymer is, it cannot be melted or easily dissolved in any common or cheap solvents to be applied in various potential application. This paper will discuss specifically in dissolving the natural polymer by using Tetrabutyl Ammonium Fluoride (TBAF) in Dimethyl Sulfoxide (DMSO) and analyzing results from FTIR. TBAF will be added into DMSO and heated and evenly stirred beginning at the lowest temperature, 60°C and OPEFB-CP was added to the mixture solution until clear solution is produced. The characterization of cellulose solution from FTIR showed obvious different pattern with solid OPEFB-CP that proved cellulose was completely dissolved in mixture of TBAF/DMSO solution. FTIR results show no peak at wavenumbers 2385cm⁻¹ but still remain two other peaks at wavenumbers 1377cm⁻¹ and 1021cm⁻¹. The observation obtained from the experimental works also concluded that the dissolution rate of cellulose is linear with the temperature increase starting from 60°C with changes in the solution color.

Index Terms—Oil Palm Empty Fruit Bunch-Cellulose Phosphate (OPEFB-CP), TBAF, DMSO, natural polymer, FTIR

I. INTRODUCTION

Polysaccharides are polymeric carbohydrate molecules where cellulose and chitin are examples of structural polysaccharides. Cellulose is said to be the most abundant organic molecule on earth [1], [2] and has many uses in the paper and textile industries. Malaysia possesses more than 4.69 million hectares land of oil palm tree and has produced 17.73 million tons of palm oil annually [3], with the latest estimation of more than 15 million tons of residues from trunks, fronds and empty fruit bunch which were generated from palm oil industry [4].

Oil constitutes for only about 10% of the palm production while the rest is biomass [5], [6]. Derivatives

from oil palm residues such as empty fruit bunch which are carboxymethylcellulose (CMC), Cellulose Acetate (CA) and Cellulose Phosphate (CP) have great potential to be used as biomaterials [2]. Phosphorylation process is expected to enhance the cellulose bioactivity as the natural cellulose from oil palm residues are lacking in osteoinduction (the ability to induce bone formation). Phosphorylated cellulose is able to encourage the formation of calcium phosphate that satisfactorily creates bonding at the interface between hard tissue and biomaterials.

This paper will be discussing specifically in dissolving the OPEFB-CP, which is the natural polymer used in the research, with solution mixture of TBAF/DMSO.

II. CELLULOSE SOLVENTS

Cellulose is an organic compound of homopolysaccharide with the formula (C₆H₁₀O₅)_n, degree of polymerization (DP) of the macromolecule which can vary from 100 to 20,000 depending on the source [7], [8]. It is formed from linearly connecting D-glucose units condensed through the β (1-4) glycosidic bond as shown in Fig. 1 [9]. This natural polymer is insoluble in water because cellulose possesses a high crystalline structure due to the presence of extensive intra- and intermolecular hydrogen bonding [10]-[14].

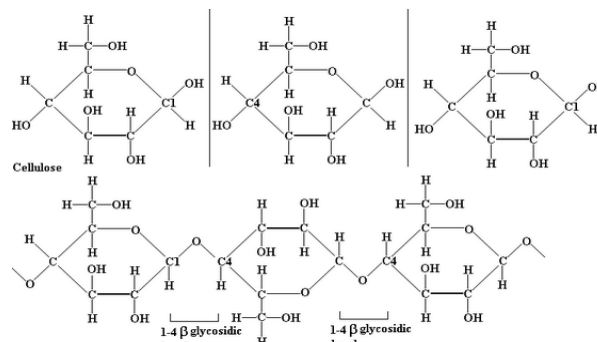


Figure 1. Cellulose structure [9]

OPEFB-CP as natural polymer used in this paper needs to be completely dissolved in any possible liquid in order to create the crosslinking bonding with glass materials. Polymer/glass hybrids are usually synthesized by the sol-gel process, where the polymer is introduced earlier in the process so that the inorganic (silica) chains are formed

method [2]. TBAF and DMSO are bought from BGOilchem, which is used directly in the lab as received from supplier. All the experimental work was done at School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia.

B. OPEFB – CP Dissolution

The ratio of TBAF/DMSO mixture is the same as obtained from Heinze *et al.* [30]-[32] also from other publication [33]. For the dissolution of OPEFB-CP, TBAF was measured at 6.6g while DMSO at 33g and both solutions were mixed in a beaker. Then, the mixture was heated at temperature started from 60°C, 70°C, 80°C and 100°C and evenly stir with magnetic stirrer, respectively. 1g of OPEFB-CP was added into the mixture, maintain the temperature and evenly stir until clear solution is formed showing that the cellulose is completely dissolved in TBAF/DMSO. Cover the beaker with parafilm cover to avoid excess condensation.

V. RESULT AND DISCUSSION

OPEFB-CP, the cellulose source in this research, is proven to completely dissolve in mixture solution of TBAF/DMSO. Analysis from FTIR showed obvious different pattern when compared to the solid OPEFB-CP with OPEFB-CP solution.

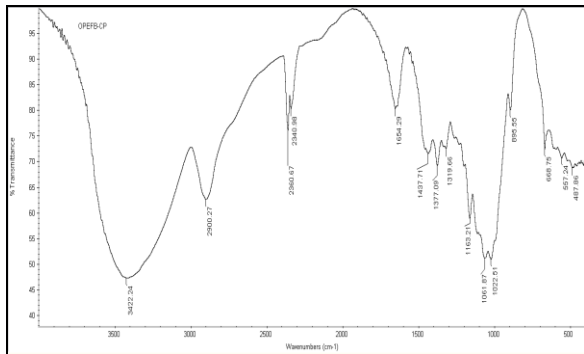


Figure 4. FTIR spectra for OPEFB-CP (solid form)

From Fig. 4, after phosphorylation process, new peaks of cellulose phosphate characteristics arose; the vibration bands of P=O at 1377cm⁻¹, P-H at 2385cm⁻¹ and C-O-C at 1021cm⁻¹ [34]. The same figure shows three peaks having similar spectrum number as stated by previous researcher [35], at vibration numbers 2360.67cm⁻¹, 1377.09cm⁻¹ and 1022.51cm⁻¹.

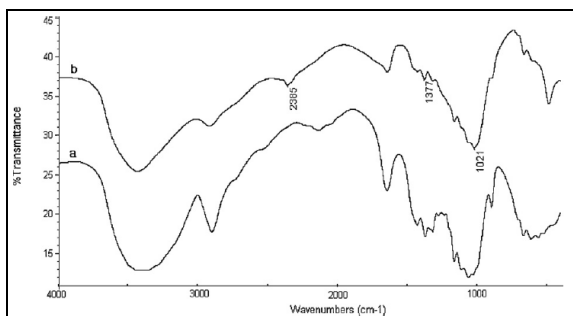


Figure 5. FTIR spectra of (a) native OPEFB-MCC and (b) OPEFB-CP with DS=2.2 [34]

Fig. 5 showed FTIR result from W. D. Wan Rosli and his co-workers [34] depicted FTIR spectra of native OPEFB-MCC and OPEFB-CP with DS=2.2. It can also be seen that the solid OPEFB-CP (as referred to Fig. 4) synthesized from phosphorylation process, with the same peaks as shown in Fig. 5 (b) [34].

The FTIR spectra of phosphorylated samples (Fig. 6) showed the sharp peak at 1383cm⁻¹ can be attributed to P=O stretching, indicating the presence of a phosphate ester [36], [37] which noted the identical result as obtained by the author as referred to Fig. 4.

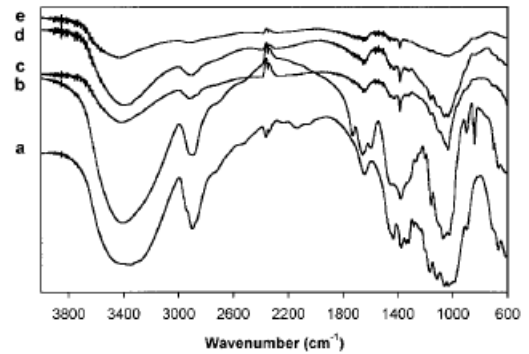
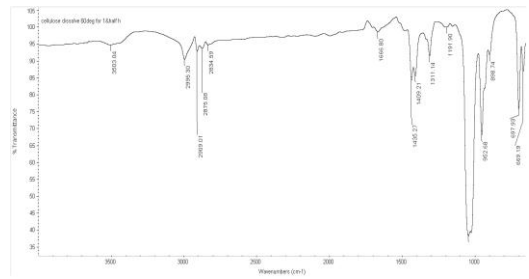
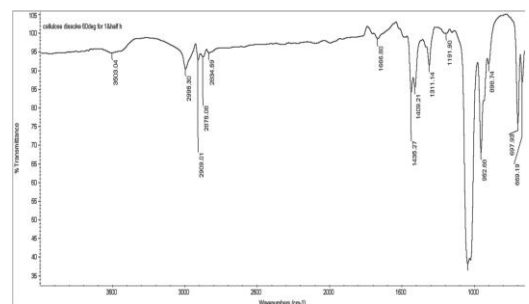


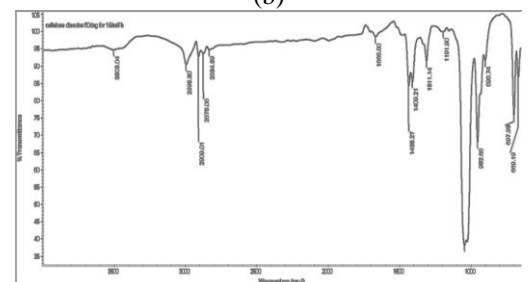
Figure 6. FTIR Spectra of (a) unmodified microcrystalline cellulose Avicel, (b) amorphous cellulose, and cellulose phosphates with varying DS values: (c) 0.4, (d) 0.8, (e) 1.4 [38]



(a)



(b)



(c)

Figure 7. OPEFB-CP dissolved at 60°C with different in time parameter

Fig. 7 (a), (b), and (c) are FTIR results with wave vibration number of OPEFB-CP in a solution formed after fully dissolved in TBAF/DMSO. The graph wave shows two peaks disappeared which are at vibration numbers 1377.09cm^{-1} and 2360.67cm^{-1} , but at peak number 1022.51cm^{-1} , the vibration number remains unchanged.

TABLE I. DIFFERENT PARAMETER (TEMPERATURE) IN DISSOLVING OPEFB-CP IN TBAF/DMSO

Temperature (°C)	60°C	70°C	80°C	100°C
Time (minutes)	240	180	90	30

Table I shows the effects of dissolving OPEFB-CP in different temperature, one of the parameter used in the experimental work. It can be seen that the higher temperature applied to dissolve the OPEFB-CP, the shorter time consumed. From the experiment observed, the color of the cellulose solution will change from light brown to dark black as the temperature increases.

VI. CONCLUSION

Oil Palm Empty Fruit Bunch-Cellulose Phosphate (OPEFB-CP) was successfully dissolved in solution mixture of Tetrabutyl Ammonium Fluoride (TBAF) / Dimethyl Sulfoxide (DMSO) without prior chemical modification or any pre-treatment. This is the simplest way in dissolving cellulose which is done perfectly in room environment without long time consuming and unnecessarily done in high temperature because the hydrogen bonding could be distracted at temperature as low as at 60°C.

VII. FUTURE RECOMMENDATION

There is several future recommendations suggested for further improvement of this research in the future such as to dissolve the natural polymer with different type of potential solvents, comparing the results and figure out which solvents is the most effective. The research can be expanded by making a detail analysis of the polymer dissolution in terms of their temperature and time with its Degree of Substitution (DS) or Degree of Polymerization (DP). Finally, from the experiment done in this paper which is dissolving the natural polymer in mixture solution of TBAF/DMSO, there was an obvious color changing with the rise of temperature. These findings should be investigated thoroughly and discussed in details in the next publication to know the reasons behind the observation.

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