

Modification of Cellulose by Polymethyl Methacrylate Grafting for Membrane Applications

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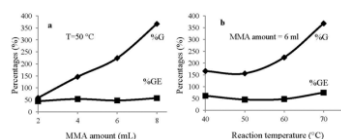
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Graphical abstract



Abstract

Cellulose is a renewable resource that receives attention from researchers due to its potential as a raw material for the production of biofuels and new composite materials. In this study, cellulose extracted from pineapple (*Ananas Comosus*) leaves was grafted with polymethyl methacrylate in order to prepare a hydrophobic cellulose for the membrane applications. The grafting of cellulose from the pineapple leaves was carried out by alkali treatment and the cellulose was grafted with PMMA at a concentration of 6 ml/g and a temperature of 60 °C for 5 hours by radical polymerization via direct oxidation of Ce (IV) ions. After polymerization process completed, the homopolymer or excess PMMA was extracted from the grafted product in acetone for 24 hours. The cellulose and grafted products were analyzed and compared by Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffractometer (XRD), Variable Pressure Scanning Electron Microscope (VP-SEM) and surface area analyzer (BET). FTIR shows the presence of additional peak from cellulose spectrum at 1736 cm^{-1} attributed to the ester carbonyl group (C=O) from PMMA, XRD indicates the declination of crystallinity index, VPSEM displays a rough surface compared to a smooth cellulose surface and the increment of diameter, while BET gives a 200 % higher surface area to prove that PMMA was successfully grafted on the extracted cellulose which specially named as Cell-g-PMMA. Cell-g-PMMA will further be filled into the ENR/PVC matrix to develop a hydrophobic composite membrane for oil-water separation.

Keywords: PMMA grafting; cellulose modification; hydrophobic membrane; pineapple leaves; characterization

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1.0 INTRODUCTION

Membrane separation processes offer many advantages in terms of less energy requirement, environmental friendly, easy to operate and use compact equipment compared to the conventional method [1, 2]. Polymeric membranes are the most common ones used in the separation processes because all polymers can be used as barrier or membrane material [1]. Polymers that commercially used as membrane are polypropylene (PP), polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), polysulfone (PS), and polyethersulfone (PES) due to their porosity, thermal and mechanical properties [3]. Ta *et al.* (2010) [4] stated that membrane technology is an attractive method to treat the effluents from industries because it is effective and capable to meet to the stringent regulation of waste water disposal set by the government. However, membrane is quite specific to certain waste water depending on the compounds and composition of the waste water.

Cellulose has unique characteristics such as fine cross section, water absorbency, high in strength and durability, high thermal stability, biocompatibility and yet relatively low cost compare to other renewable material. However, there are some disadvantages for application of cellulose such as poor solubility

in common solvent, poor crease resistance, low thermoplasticity and poor dimensional stability, high hydrophilicity and lack of antimicrobial properties [5]. Physical and/or chemical modification can be carried out to improve the properties of the cellulose for desired applications. Grafting copolymerization could be carried out to stabilize the structure of cellulose and reduce the hydrophilicity. Figure 1 shows the schematic diagram of the grafting copolymerization between cellulose and polymer. Many researches have been conducted to graft polymer on cellulose using different polymer such as polycaprolactone [6, 7, 8], polyvinyl alcohol [9], oligo-ester chain [10], acrylic monomers [11], methyl methacrylate [12], acrylamide [13] and acrylonitrile [14]. The grafted cellulose exhibited various properties according to the grafted polymer.

Polymerization reactions using hydrophobic monomer of acrylonitrile and methyl methacrylate decrease the ability of cellulose to absorb moisture and increase water retention value. In this study, methyl methacrylate as polymer source which will be grafted on the cellulose extracted from PALF (cell-g-pmma) and characterized. The grafting procedure involves radical polymerization via direct oxidation of Ce (IV) ions. The cell-g-pmma will be blend with the membrane matrix to develop a hydrophobic membrane for oil and water separation.

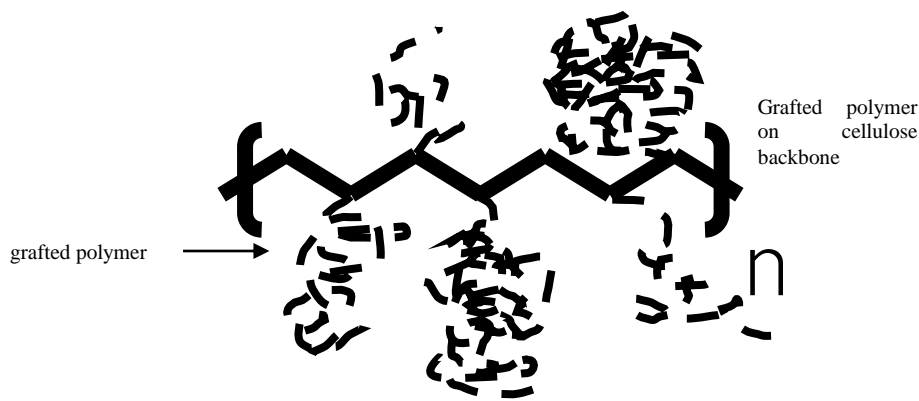


Figure 1 Illustration of polymer grafted on cellulose

2.0 MATERIAL AND METHODS

2.1 Material

Pineapple leaves were collected and gathered from Bera (Pahang, Malaysia). The chemicals reagents used for this research were sodium chlorite (NaClO_2), ceric ammonium nitrate, $\text{H}_8\text{CeN}_8\text{O}_{18}$ (CAN) and methyl methacrylate, $\text{C}_5\text{H}_8\text{O}_2$ (MMA) purchased from Sigma-Aldrich while nitric acid-65% concentration (HNO_3), sodium hydroxide (NaOH), acetic acid and acetone were from SYSTERM. MMA was purified from inhibitor by separation technique using alumina column chromatography. All chemicals are reagent grade except NaClO_2 (technical grade).

2.2 Isolation of α -cellulose from Pineapple Leaves Fibers (PALF)

The fresh pineapple leaves were cleaned and the spiny margin was discarded. Next the leaves were chopped into approximately $1\text{ cm} \times 1\text{ cm}$ pieces and soaked for 3 days in stagnant water. During the process, water was changed frequently. Then, the leaves were dried under sunlight for a few days. The dried leaves were then ground at 5800 rpm by a BH Chopper grinder (FFC-23) and dried at 105°C in Universal Memmert Oven (model UFB400) until the mass was constant.

The isolation of α -cellulose was adapted from Sheltami *et al.* (2012) [15]. Firstly, the leaves sample was treated with 4% NaOH for 2 h. Bleaching treatment was carried out using buffer solution containing 1.7 w/v% NaClO_2 at pH 4.5 and 125°C for 4 h. The total reaction sample to solution was repeated twice. After each treatment, the samples were washed with distilled water.

2.3 Graft copolymerization

The experimental for graft copolymerization was based on the work done by Kumar *et al.* (2011) [13]. Grafting reaction was carried out in 250 mL, three-necked flask equipped with a reflux condenser, hot plate with magnetic stirrer, N_2 gas inlet system and immersed in water bath which the temperature was kept constant. Cellulose was dispersed in a definite volume of an aqueous HNO_3 (0.1 v/v%; 50 mL) with constant stirring.

The desired temperature of 20°C to 60°C was monitored by a thermometer. Then, a freshly prepared solution of 10 mL HNO_3 (0.1 v/v%) with CAN (0.55 g) was added into reaction flask and stirred for about 10 min. After that, MMA (6-8 mL)

was added and stirred homogeneously for 5 hours. The reaction was conducted under N_2 gas atmosphere.

The solid or grafted product was washed with distilled water and dried in oven at 60°C for 24 h until constant mass obtained. The homopolymer (ungrafted PMMA) was removed from the product by immersing in acetone for 24 h at ambient temperature. The sample was filtered and the cake, which was the grafted product (cell-g-pmma), was dried to a constant mass. Determination of percentage grafting (% G) and percentage grafting efficiency (% GE) was calculated by the following equations:

$$\%G = \frac{\text{final cellulose weight} - \text{initial cellulose weight}}{\text{initial cellulose weight}} \times 100\% \quad (1)$$

$$\%GE = \frac{\text{final cellulose weight} - \text{initial cellulose weight}}{\text{total weight after reaction} - \text{initial cellulose weight}} \times 100\% \quad (2)$$

2.4 Characterization

The Fourier Transform Infrared Spectrum (FTIR) was measured to investigate possible changes of functional group between α -cellulose and cell-g-pmma using a Perkin-Elmer spectrometer (Spectrum GX) in the range of $4000\text{--}500\text{ cm}^{-1}$. The sample was ground with mortar and pestle, then mixed with KBr and pressed to become thin transparent pellets.

The crystallinity index of the samples, X_c , was calculated by using equation (3) [16]. I_{002} and I_{am} are the intensities peak of crystalline and amorphous material respectively;

$$X_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (3)$$

The thermal stability of the samples was evaluated by thermogravimetric analyzer (Mettler Toledo model TGA/SDTA851e). This analysis was carried out in temperature intervals 25°C – 600°C at $10^\circ\text{C}/\text{min}$ heating rate. Thermogram obtained which represent weight loss and its derivatives (DTG) as function of temperature were analyzed.

An Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020) by Micromeritics Instrument Corporation were carried out to determine N_2 adsorption of the samples. The amount of gas adsorbed and desorbed at a given pressure allows determining the surface area, pore volume, and pore size

distribution [17, 18, 19] Brunauer, Emmett and Teller (BET) theory were used to calculate specific surface area at the rate of 10°C/min. The cell-g-pmma samples were degassed at 363.15 K with heating rate 10°C/min.

The morphology of the sample was studied by Leo 1450 VP variable pressure scanning electron microscopy (VPSEM) (United Kingdom) with an accelerating potential of 15 kV. The samples were sputter coated with gold prior to analysis.

3.0 RESULTS AND DISCUSSION

3.1 Effect of MMA amount and reaction temperature

Figure 2 shows the effect of MMA amount and reaction temperature on the percentage of grafting yield (% G) and grafting efficiency (% GE). The reaction temperature was fixed

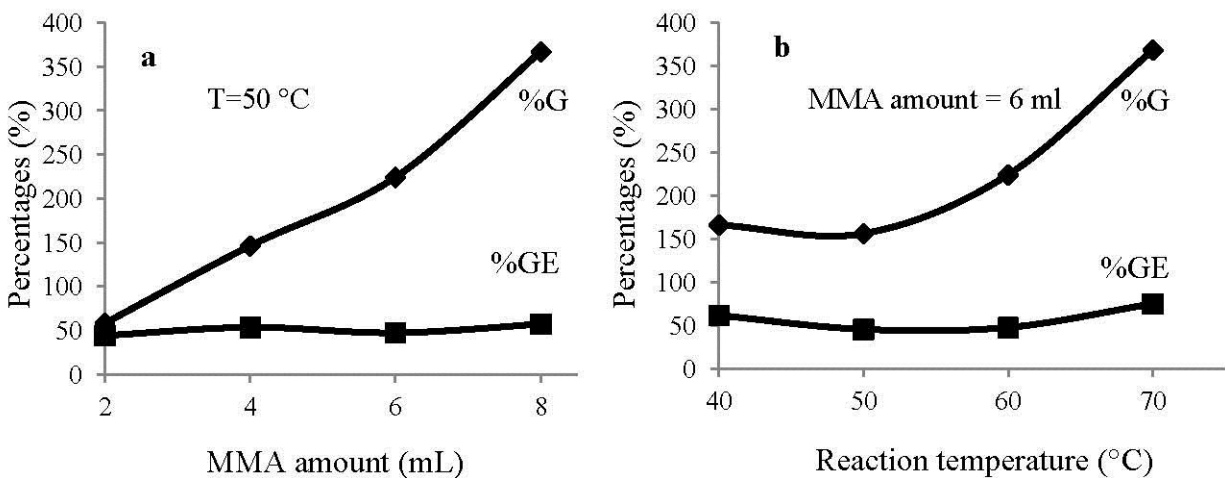


Figure 2 Percentage grafting (% G) and percentage grafting efficiency (% GE) of PMMA onto cellulose based on (a) MMA amount (mL) (b) Reaction temperature (°C)

3.2 Characterization

Figure 3 shows the FTIR spectra of cellulose extracted from PALF and (b) polymethyl methacrylate grafted on cellulose (cell-g-pmma). Based on the spectra, broad absorption of hydroxyl group (OH) at about 3350 cm^{-1} was observed in cellulose sample. The intensity of the OH group was reduced on the grafted product (cell-g-pmma) indicates the involvement of the group for grafting copolymerization. The same finding was observed by Kumar *et al.* (2011) [13], Roy *et al.* (2008) [5].

On the other hand, The FTIR spectra of cell-g-pmma showed additional peaks at about 1736 cm^{-1} wavenumber which referred to stretching vibration of carbonyl group of ester, C=O belongs to MMA [20,12]. The wavenumber at 2997 cm^{-1} indicates vibration of methyl-stretching and this statement is augmented by the present of 1451 cm^{-1} and 1387 cm^{-1} band for methyl-bending vibration, therefore proving the formation of cell-g-pmma.

The determination of X_c (crystallinity Index) by the XRD peak height method has been developed by Segal and coworkers. This method was proposed as empirical measurement to allow rapid comparison of cellulose samples and useful for comparing

at 50°C for Figure 2(a) and MMA amount was fixed at 6 mL for Figure 2(b). Figure 2(a) indicates that the % G increased with amount of MMA and reached the maximum value of 367 % at 8 mL MMA amount. However, the % GE that shows the actual amount of MMA grafted on the cellulose was almost constant despite the increment of MMA amount. This is due to the fact that the amount of OH functional group on the cellulose was almost the same and Ce (IV)-initiated graft polymerization onto cellulose occurs at OH group preferably at $\text{C}_2\text{-C}_3$ glycol unit rather than C_6 primary hydroxyl [13]. The grafting copolymerization of MMA onto cellulose has been determined at a range of temperature ($40\text{-}70^\circ\text{C}$) and other variables were kept constant. Figure 2(b) revealed that % G and % GE were almost constant at the reaction temperature of $40\text{-}50^\circ\text{C}$ but started to increase from 60°C . The effective temperature was recorded at 70°C (368 %). The grafting was efficient at the high temperature specifically higher than 70°C in order for the chemical bonding of OH-group and MMA to occur.

the relative differences between samples [28]. Figure 4 presents the XRD patterns of (a) polymethyl methacrylate (PMMA) (b) cellulose and (c) cell-g-pmma. PMMA has an amorphous structure, cellulose has a crystalline structure of about 65 % crystallinity index indicated by a high peak at 22.8° , and the grafted product, cell-g-pmma, was the combination of both but indicated a shifted crystalline peak at 18.0° . From the peak obtained it can be indicated that PMMA was change the crystal phase of the cellulose. The high peak (002) was shifted due to attachment of PMMA on cellulose crystallographic phase. The cellulose-binding domains, (in this case PMMA) penetrate the fibers and preferentially bind to the edge of cellulose microfibrils [29].

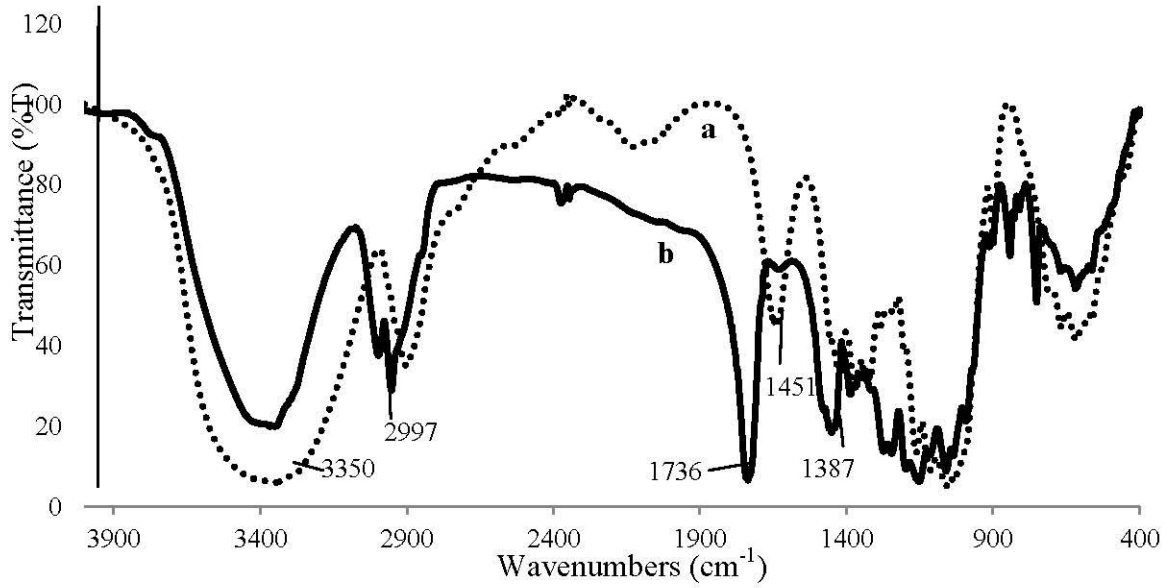


Figure 3 FTIR spectra of (a) cellulose and (b) cell-g-pmma (% G = 224 %; % GE = 47 %)

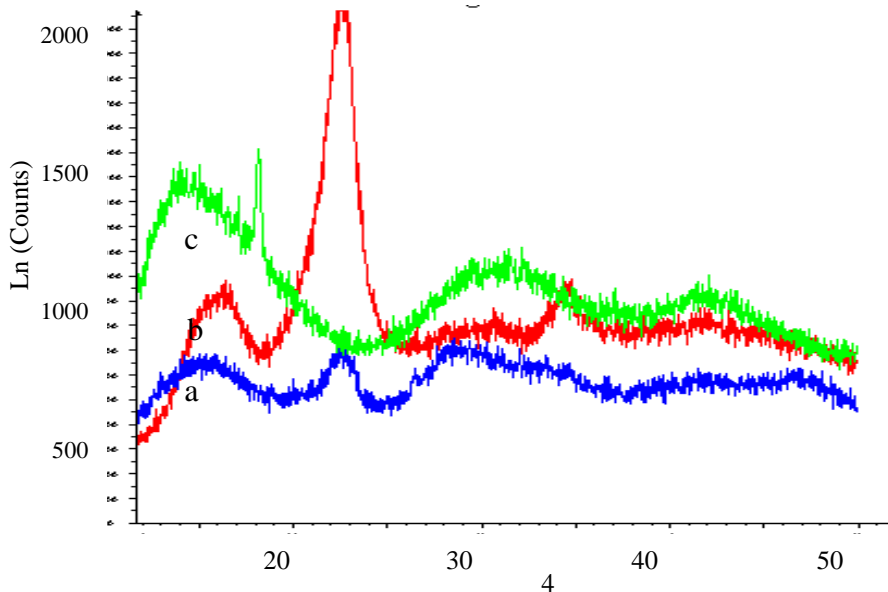


Figure 4 DTG curves of (a) cellulose and (b) cell-g-pmma (% G = 224 %; % GE = 47 %) and (c) cellulose-g-pmma (% G = 224 %; % GE = 47 %)

Based on the literature, it has been established that the degradation of cellulose only can take place from 200°C [11][30]. The thermal stability of the sample above this temperature is decreased gradually and degradation of fiber cellulose and polymethyl methacrylate are examined through thermogram of TGA and DTG curve as shown in Figure 5.

In TGA curve, all the samples show the same pattern of decomposition curves. The cell-g-pmma shows the intermediate mass loss which agreed to the % GE showing that MMA content was almost half of the mass of the cellulose (47 %). Cellulose decomposition curve shows that at the maximum temperature of 600°C, there was about 20 % of residual mass. Cell-g-pmma is a mixture of cellulose and

PMMA. The residual mass of the sample is about 10 % obtained at maximum temperature of 600°C. There are no residual mass obtained for PMMA samples at 600°C in TGA curve. This is due to the degradation of PMMA started slowly at 220°C and completely at the temperature higher than 305°C [24].

Cellulose and PMMA occurred at temperature of 355°C and 370°C, respectively but the maximum degradation temperature of cell-g-pmma was found out to be 380°C. Thus, grafting modification had increased the thermal stability of the product.

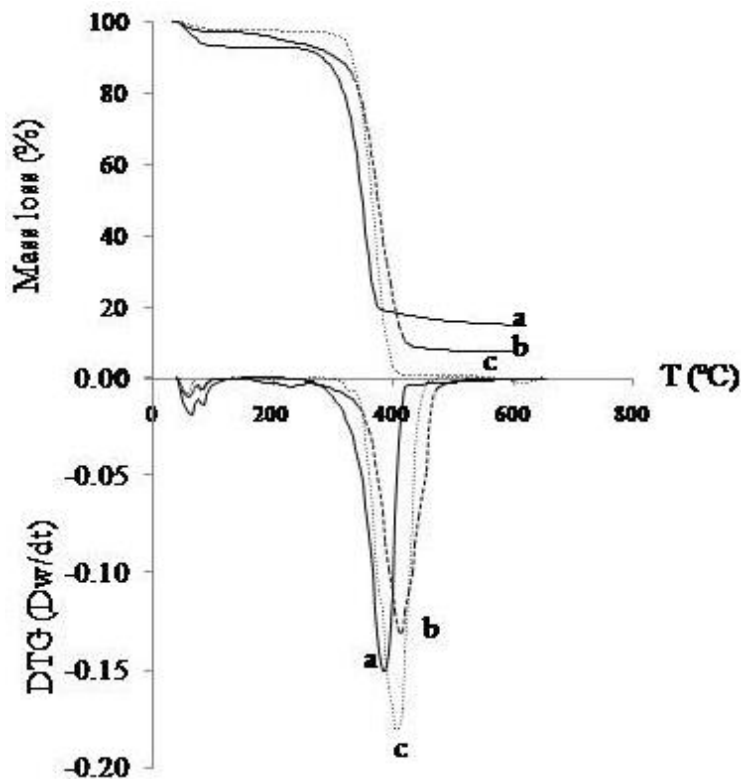


Figure 5 TGA and DTG curves for cellulose (a) cell-g-pmma (%G= 224%; %GE= 47%) (c) PMMA

N₂ adsorption-desorption isotherm was carried out at 77 K to study the effect of chemical modified (grafting) on pore structure (Figure 6). The isotherm plot of the sample show that it follow type IV isotherm behavior which mean that this adsorption-desorption occur at multiple layer. Table 1 summarized the specific surface area, pore volume and pore

size. The specific surface area, pore volume and pore size of cell-g-pmma were higher than those of cellulose. The BET surface area of cell-g-pmma was about 200 m²/g higher than cellulose. This improvement due to polymethyl methacrylate chain which grafted on cellulose backbone gives additional surface area and pores to the sample.

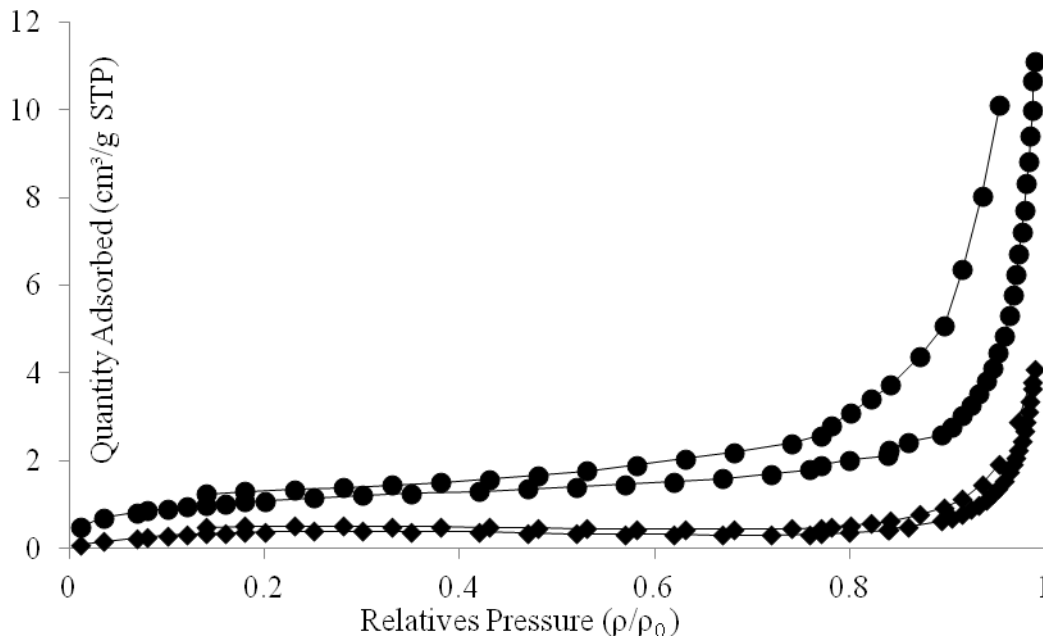


Figure 6 N₂ adsorption-desorption isotherms for cellulose (♦) and cell-g-pmma (%G= 224%; %GE= 47%) (●)

Table 1 Specific surface area, pore volume and pore size

Description		α -cellulose	cell-g-pmma
Surface area (m ² /g)	BET Surface Area	1.37	3.84
	t-Plot Micropore Area	-	7.7×10 ⁻³
	t-Plot External Surface Area	1.71	3.83
Pore volume (cm ³ /g)	Adsorption total pore volume	4.82×10 ⁻³	1.45×10 ⁻²
	Desorption total pore volume	4.46×10 ⁻³	1.56×10 ⁻²
	t-Plot micropore volume	-	6.00×10 ⁻⁵
		1.70×10 ⁻⁴	
Pore Size (Å)	Adsorption average pore width	1.41×10 ²	1.51×10 ²
	Desorption average pore width	1.30×10 ²	1.63×10 ²

(±0.03g weight from both samples was used to carry out this analysis. The cell-g-pmma which has been choosing is from t= 5h, T= 60°C, 6 mL mma monomer and 0.1% HNO₃ concentration).

VPSEM were carried out and as illustrated in Figure 7 (a & c) for α -cellulose and (b & d) for cell-g-pmma with 300× and 5k× magnification respectively. The images obtained clearly exhibit that the surface of the samples has been changes. The weight of α -cellulose was similar with a diameter

of 4.5 μ m. When, PMMA was grafted onto the cellulose, the surface became rougher and the deposit of grafted polymer can be seen. The weight of cell-g-pmma was similar with a diameter of 9.95 μ m. PALF increases after grafting modification by methyl methacrylate.

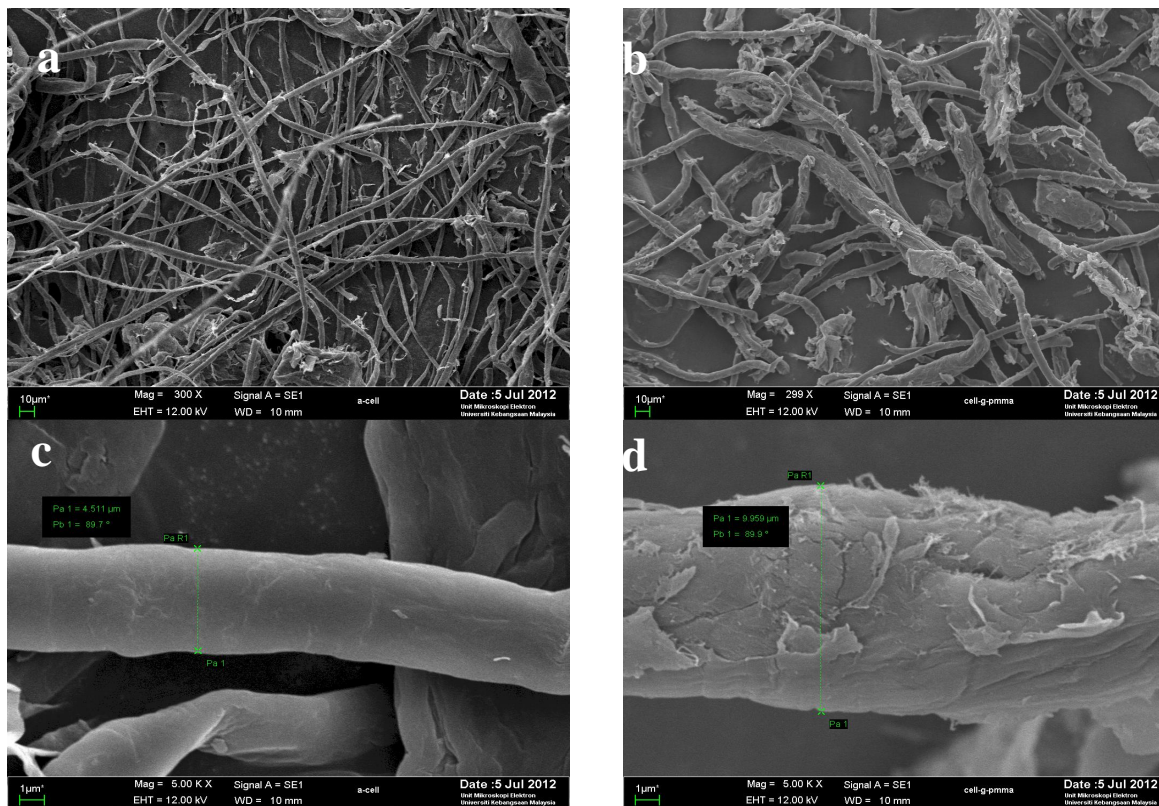


Figure 7 (a) α -cellulose and (b) cell-g-pmma at 300× magnification (c) α -cellulose & (d) cell-g-pmma at 5k× magnification

4.0 CONCLUSION

α -cellulose from PALF was successfully modified with PMMA by grafting copolymerization via Ce (IV) ion radical polymerization at reaction condition as stated before. Significantly, the modification reaction was best conducted at

temperature more than 70°C but the amount of monomer must be more than half of the amount of the cellulose. FTIR spectrum proved grafting polymerization was successfully done with the appearance of new peaks at 1736 cm⁻¹ (ester carbonyl, C=O) and decreasing intensity of OH band at 3350 cm⁻¹. TGA and DTG thermogram shows that thermal stability of cellulose

increased due to modification. BET surface area increased apparently to 200 % after modification of cellulose with PMMA. N₂ adsorption isotherm shows that grafting modification improved surface area and porosity of cellulose. VPSEM micrograph revealed formation of roughness surface and increasing of cellulose diameter due to deposition of grafted polymer (PMMA). Hence, we can conclude that the grafting of cellulose to improve its properties was successfully done.

Acknowledgement

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