eProceedings Chemistry 4 (2019) 62-69

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

Synthesis of Grafted Cellulose with Methacrylate Homopolymer for Copper Removal

Ayu Fatini Yusop and Khairil Juhanni Abd Karim*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
**Corresponding Author: juhanni@kimia.fs.utm.my*

Article history:
Received 15 June 2019
Accepted 14 July 2019

GRAPHICAL ABSTRACT

Blended cellulose and PHEMA rafted cellulose

ABSTRACT

Cellulose is one of the most abundant natural polymers on Earth. Nevertheless, one of the drawbacks of cellulose is it does not soluble in many common solvent such as distilled water, methanol, and dimethyl sulfoxide (DMSO). The main purpose of this study was to synthesis cellulose-g-PHEMA via the “grafting onto” method on the blended cellulose from Whatman filter paper with poly(2-hydroxyethyl methacrylate) (PHEMA). PHEMA was synthesized from its monomer, HEMA by Reversible Addition-Fragmentation Chain-transfer (RAFT) polymerisation carried out at 80°C for 24 hours. The solubility of blended cellulose, PHEMA, and cellulose-g-PHEMA were tested in distilled water, methanol and DMSO. For swelling test, solvent used is deionized water while copper removal testing required immersion of blended cellulose, PHEMA, and cellulose-g-PHEMA in copper (II) sulphate solution for 2 to 6 hours range. In this study, PHEMA was synthesized by RAFT polymerisation with 63.78% of monomer conversion. For the esterification, blended cellulose was grafted with PHEMA by 39.72% of grafting and 33.10% of efficiency of polymerisation. Then, cellulose-g-PHEMA synthesized for 5 hours showed better swelling ability than the blended cellulose. The modification of blended cellulose with synthetic polymer, PHEMA, showed some differences in the physical properties in terms of solubility and swelling, thus also expected to show some influence in the copper removal test.

Keywords: cellulose, RAFT polymerisation, poly(2-hydroxyethyl methacrylate), RAFT agent, copper removal

1. INTRODUCTION

Polymers are large molecules made by repeating units which are monomers that linked together covalently. It has been used widely where it is used as homeware, agriculture, toiletries, sanitary products and materials for health care. Before synthetic polymer had been developed, all of the materials are made from natural polymer at first. Cellulose is one of the natural polymer which can easily be found on Earth as it exists in large amount [1, 2]. It is actually a polysaccharide composed of a linear chain of β-1,4 linked D-glucose units . This polysaccharide can be classified as carbohydrate which is a suitable polymer to be used as the backbone for the grafted polymer as it is linear in chain and have reactive primary hydroxyl group. Poly(2-hydroxyethyl methacrylate) (PHEMA) is used as the homopolymer when it is grafted onto the reactive hydroxyl group of cellulose in this study. PHEMA is a synthetic polymer made of its monomer, 2-hydroxyethyl methacrylate (HEMA) by the conversion of alkene group [3]. The allyl bond, C=C in HEMA is converted to alkyl, C-C covalently to make a nontoxic and useful polymer, PHEMA.

Currently, there are three methods used for the conversion of HEMA; free radical polymerisation, anionic polymerisation, and controlled/living radical polymerisation [4]. The focus of this study was to perform a controlled radical polymerisation called the Reversible Addition-Fragmentation Chain-transfer (RAFT) polymerisation. The method is widely used in the industries as it is simple and also inexpensive. RAFT polymerisation can be applied in widely range of monomers with the help of RAFT agent. The RAFT agent help to make the reaction easier and controllable than other methods that is available for this polymerisation. This RAFT polymerisation is also chosen for the method to synthesis PHEMA as it can narrow the polydispersity and predetermined the chain length [1, 5].

Copolymerisation is a method of modification for the natural and synthetic polymer. There are four types of copolymerisation which are random, block, alternate and graft copolymerisation. The graft copolymerisation was done by using “grafting onto” method by esterification to prepare the cellulose-g-PHEMA (Figure 1). “Grafting onto” method is when the grafting is done between the homopolymer with the targeted site on the backbone of the other polymer. Homopolymer, PHEMA is first synthesis to get a polymer with a reactive site, R group of RAFT agent that will react with the active site of hydroxyl group on cellulose backbone.

Testing done for the application of cellulose-g-PHEMA are solubility, swelling and copper removal. All of this testing is to determine the ability of blended cellulose and cellulose-g-PHEMA. Copper is needed to be removed from the industrial waste streams because it is dangerous for human health and environment. High uptake of copper lead to kidney and liver damage as well as death. Reduction of ecosystem, plant and animals reproduction rate decreasing are the impact of high concentration of copper in the environments such as soil, river and air [6].

Cellulose is insoluble in any solvent due to its crystalline structure. Besides, the application of cellulose is limited to paper-based industries or any application of giving structure to the product. By making it soluble in common solvent especially water, cellulose can be more useful in the future chemistry industries.

Moreover, free radical polymerisation which can be used as the method to synthesis PHEMA is difficult to control and the desired product might not be able to be obtain easily. So, RAFT polymerisation is used to have a good polymerisation of HEMA and able to control the polymerisation to get the desired products.

Furthermore, copper is dangerous for environment and human health. Removal of copper from industrial waste stream helps to decrease the concentration of copper and even reducing the risk of plants, animals as well as human to get sick because of high uptake of copper. Thus, cellulose-g-PHEMA is tested to be adsorbent to remove copper from the solution.

For this study, the main aim is to synthesis new copolymer, cellulose-graft-PHEMA using “grafting onto” method. The objectives of this study are to synthesis poly(2-hydroxyethyl methacrylate) (PHEMA) by RAFT polymerisation and characterize the synthesized PHEMA by Attenuated Total Reflectance (ATR) spectroscopy as well as Nuclear Magnetic Resonance (NMR) spectroscopy,to modify cellulose with PHEMA by “grafting onto” method and the characterization of blended cellulose and cellulose-g-PHEMA by ^{13}C solid Nuclear Magnetic Resonance (NMR) spectroscopy, to test the solubility and swelling of blended cellulose, PHEMA, and cellulose-g-PHEMA in different solvent according to time and to apply the cellulose-g-PHEMA as absorbent for the copper removal by UV-Visible spectroscopy.

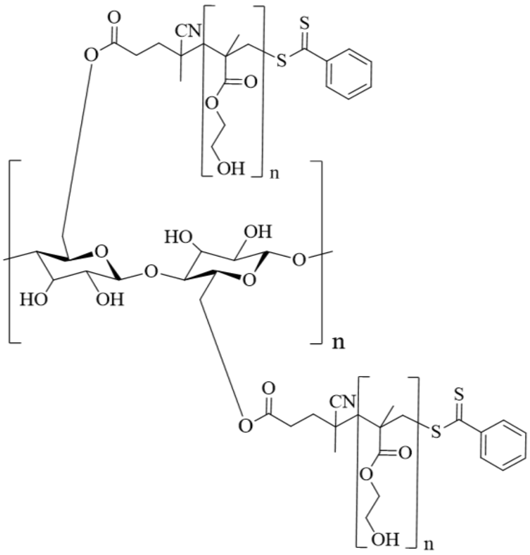


Figure 1. Chemical synthesised structure of cellulose-g-PHEMA

2. EXPERIMENTAL

Ten pieces of the Whatman filter paper was put into a clean and dry blender. After that, blending was done for 30 seconds per cycle. The blending was done for five to six cycles until the filter paper become cotton wool-like material. The blended filter paper was then store in a dry reagent bottle.

The monomer, HEMA was purified by passing through an activated-alumina packed column to remove the inhibitor. The procedure started with packing a small burette with cotton wool followed by activated alumina and attached to a retort stand. The HEMA was then filled up through a filter funnel which allowed to flow into the burette gravitationally. Purified HEMA was collected in a labelled reagent bottle, sealed and keep in the refrigerator below 10°C. The monomer was then analysed by ATR and ^{1}H NMR spectroscopy.

HEMA (2 mL), CPADB (0.0459 g) and ACPA (0.0046 g) were put in a 100 mL two-necked round bottom flask and dissolved in tetrahydrofuran (THF) (15 mL) with the ratio of 100:1:0.1 respectively. Then, the mixture was degassed by the nitrogen gas for the first hour before placing the flask into the preheated oil bath (80°C) for 24 hours for the polymerisation to occur. After 24 hours reaction, the flask was cooled in the ice bath with exposure to the air. To precipitate the polymer in the mixture, the mixture was added dropwise into cold distilled water, decanned and repeated until the mixture become saturated in cold distilled water. The mixture after cooling, crude solution containing the monomer, RAFT agent, initiator as well as the polymer and the resultant solid obtained were dried as well as being weighed before being analysed by ATR and ^{1}H NMR spectroscopies.

The characterization of blended cellulose was done by ^{13}C solid NMR spectroscopy. Then, the blended cellulose (0.3333 g) was soaked in sodium hydroxide (NaOH) for 24 hours. When the cellulose was ready and become swollen, the cellulose was washed with methanol until it become neutral and places in a three-neck round bottomed flask. The mixture of DCC (0.5000 g) and PHEMA (0.4000 g) which already dissolved in the methanol as solvent was then added into the cellulose solution dropwise with the rate of 1 drop per 30 seconds. Then, the DMAP (0.6666 g) was added and the mixture was degassed by the nitrogen gas for 60 minutes before placing the flask into the preheated oil bath (80°C) for 5 hours for the polymerisation to occur. After that, the solution then exposed to air and cooled in the ice bath. The resultant solid was then dried in open air and weighted before being analysed by ^{13}C solid NMR spectroscopy.

The tests were done with the blended cellulose, PHEMA and cellulose-g-PHEMA. All of the compounds were soaked in distilled water, methanol, dimethyl sulfoxide (DMSO) and being observed for 24 hours. The changes observed were recorded in table form.

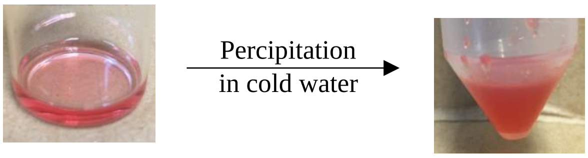
For the swelling test, blended cellulose, PHEMA and cellulose-g-PHEMA was put in an empty tea bag each and soaked in excess deionized water at room temperature for a range of time from 10 minutes to 60 minutes. After that, the tea bag with the swell cellulose was dried and weighed. The difference in weight of cellulose before and after soaked in the deionized water was calculated.

Copper (II) sulphate solution was prepared by adding 24.96 g of copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) powder into a 100 mL of volumetric flask. 5 mL of the $CuSO_4.5H_2O$ solution was added into 10 different vial and 0.01 g of blended cellulose was added into the vial. Then, the vial was put on the orbital shaker for 6 hours' time range. 2 mL of the solution was pipetted for every 2 hours and put into new vial. This procedure was repeated by using PHEMA and cellulose-g-PHEMA as the absorbents. The before and after solution was analysed using the UV-Vis spectrophotometer to determine the absorbance of copper in the solution.

3. RESULTS AND DISCUSSION

3.1. Synthesis of PHEMA by RAFT Polymerisation

In this study, poly(2-hydroxylethyl methacrylate) (PHEMA) is successfully synthesized by Reversible Addition-Fragmentation chain-transfer (RAFT) polymerisation. The purified monomer is mixed with the 4-cyano-4(phenylcarbonothioylthio)pentanoic acid (CPADB) as the RAFT agent and 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as the initiator in tetrahydrofuran (THF) which act as the solvent. In this experiment, the ratio used for monomer to RAFT agent to initiator is 100:10:1. HEMA, CPADB and ACPA were mixed in tetrahydrofuran (THF) and the mixture was purged by nitrogen gas for one hour to put it into the inert condition. Degassing by using nitrogen gas was to remove oxygen in the solution before placing the mixture in a preheated oil bath held at a temperature of 80°C for 24 hours [7]. The crude solution containing monomer, initiator, RAFT agent and polymer (Figure 2(a)) was then cooled by immersing in an ice bath. The solution was exposed to air to allow oxygen to enter the flask. The polymer is then precipitated in cold distilled water and dried to the air. After the polymerisation, the crude solution was dropped drop-wise into cold distilled water to precipitate out the PHEMA. Since PHEMA is not soluble in water, it is easily to precipitate out the PHEMA from the solvent and the monomer. The resultant PHEMA was in the form of gel (Figure 2(b)). This was because the chain of PHEMA obtained is short, thus it cannot be clumped into the form of powder or beads [8].



(a) (b)

Figure 2. Physical appearance of (a) crude solution of poly(2-hydroxyethyl methacrylate) after 24 hours reaction in THF at 80°C and (b) pure poly(2-hydroxyethyl methacrylate) after precipitation in cold distilled water

When the PHEMA chains is short, the less it will tangle with each other. This caused the gel form of PHEMA obtained since the weakly bonded PHEMA chains were easily to be separated from each other. Results of ATR and NMR spectroscopy are shown in Figure 3(A), 4 and 5. The conversion percentage for the polymer is calculated and determined from the NMR spectrum of crude mixture. The integral of e_m and e_p were used as both of the proton environment are not changing before and after polymerisation. From this calculation, the conversion of HEMA to form PHEMA was 63.78%. The ratio of HEMA to CPADB to ACPA was shown to be 100:1:0.1, thus equivalent to 100 unit of monomer is polymerized. At 63.78%, it indicated that only 63 unit of HEMA was polymerized into PHEMA.

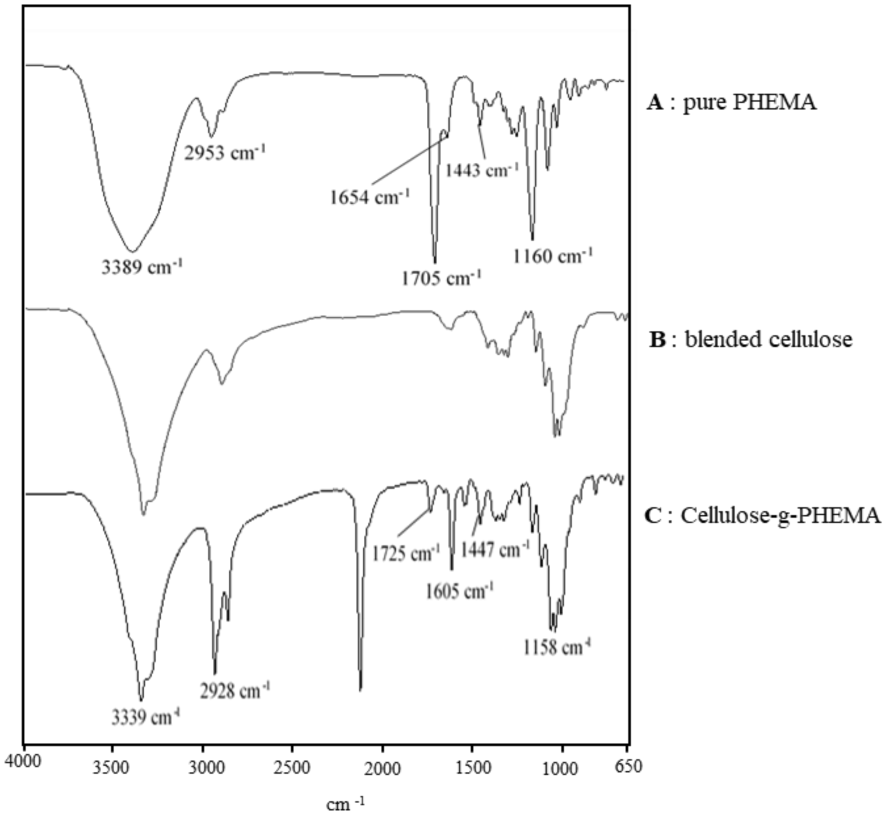


Figure 3. ATR spectrum for (A) pure PHEMA synthesized for 24 hours at 80°C, (B) blended cellulose from Whatman filter paper and (C) synthesised cellulose-g-PHEMA

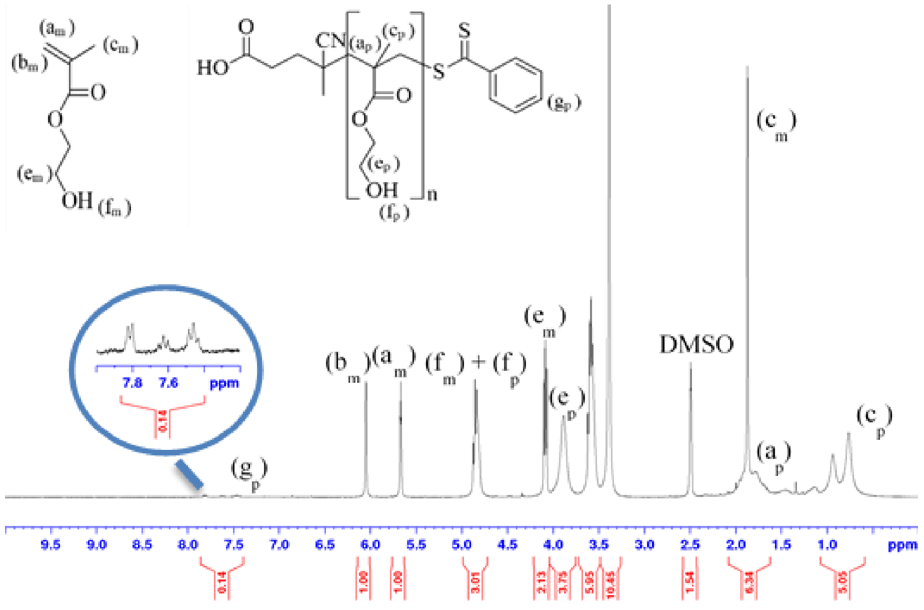


Figure 4. ^{1}H NMR spectrum for crude PHEMA reaction mixture in deuterated DMSO

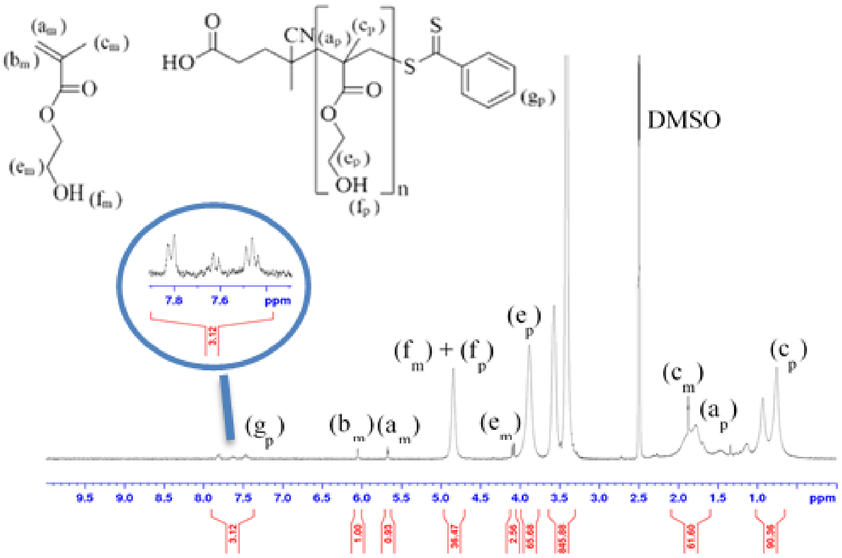


Figure 5. ^{1}H NMR spectrum for pure PHEMA in deuterated DMSO

3.2. Synthesis of Cellulose-grafted PHEMA

The cellulose used in this study was from Whatman brand filter paper which is blended to obtain blended cellulose. At first, the blended cellulose is soaked in the 8 wt % of sodium hydroxide (NaOH) for 20 hours to make the hydroxyl group accessible on the surface of the cellulose. This was to ensure the reaction occurs at the targeted primary hydroxyl groups which are reactive as the cellulose's backbone is insoluble due to its crystalline structure. The PHEMA was then mixed with the *N,N'*-dicyclohexylcarbodiimide (DCC) which acts as the coupling reagent before introduction of the cellulose solution at 80°C for 5 hours. This method was done under inert condition with the help of dimethylaminopyridine (DMAP) as catalyst. The synthesized copolymer was characterized and confirmed by the ATR (Figure 3) and solid ^{13}C NMR spectroscopy (Figure 6).

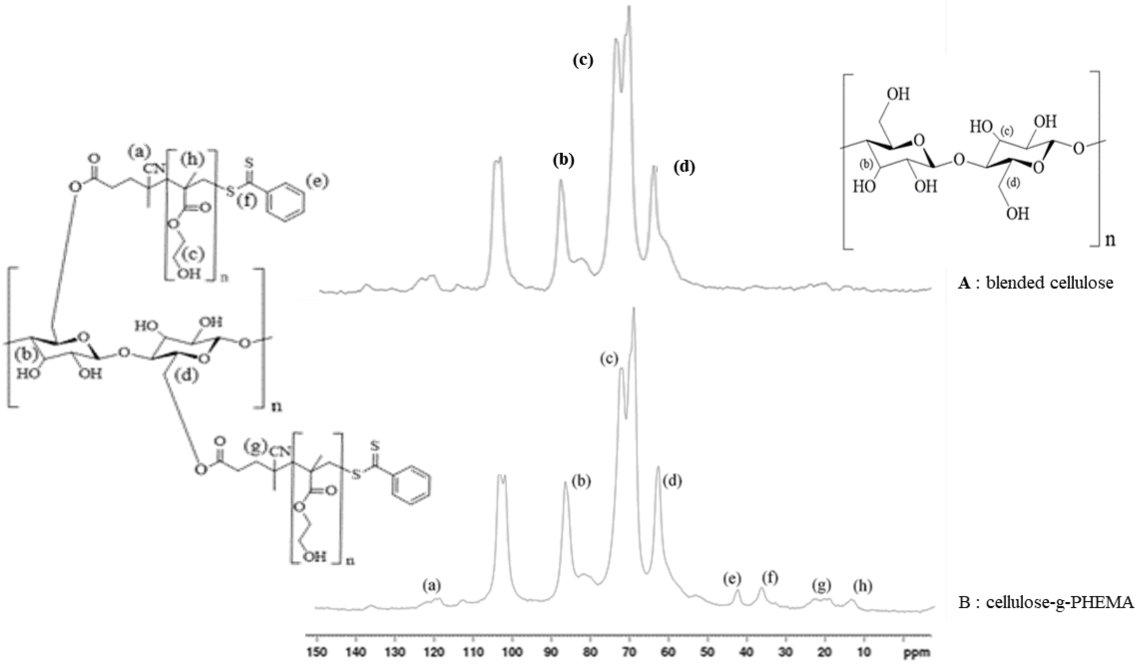


Figure 6. ^{13}C solid NMR spectrum for (A) blended cellulose and (B) cellulose-g-PHEMA

The study found that the cellulose was grafted and the "grafting onto" method was successful to synthesis cellulose-g-PHEMA. The percentage of grafting is 39.72% whereas the efficiency percentage is 33.10%. Even though the grafting percentage is not high, but it is enough for the next step in this study which are solubility, swelling and copper removal test. PHEMA in different solvents was done. The solvents used were distilled water, methanol, and dimethyl sulfoxide (DMSO).

3.3. Solubility and Swelling Tests

Testing on the solubility and swelling was done for PHEMA, cellulose and cellulose-g-PHEMA. All of the compounds were soaked in different solvents for 5, 8 and 24 hours and the results are tabulated (Table 1).

Table 1. Solubility and swelling of cellulose, PHEMA and cellulose-g-PHEMA in distilled water, methanol and dimethylsulfoxide (DMSO) at different time.

Solvent	Time	Blended cellulose	PHEMA	Cellulose-g-PHEMA
Distilled water	5 hours	#	X	#
	18 hours	#	X	#
	24 hours	#	X	#
Methanol	5 hours	#	/	#
	18 hours	#	/	#
	24 hours	#	/	#
DMSO	5 hours	#	/	#
	18 hours	#	/	#
	24 hours	#	/	#

The study found that cellulose was not soluble in water or any other common solvents because of its crystalline structure. This structure is caused by the intermolecular hydrogen bonding which make the molecules to stack themselves side by side with each other and form a linear polymer [9]. This explained the insolubility of cellulose even though cellulose contained numerous of hydroxyl group (-OH). Figure 7 illustrated the structure of cellulose and its crystallinity with the present hydrogen bonding.

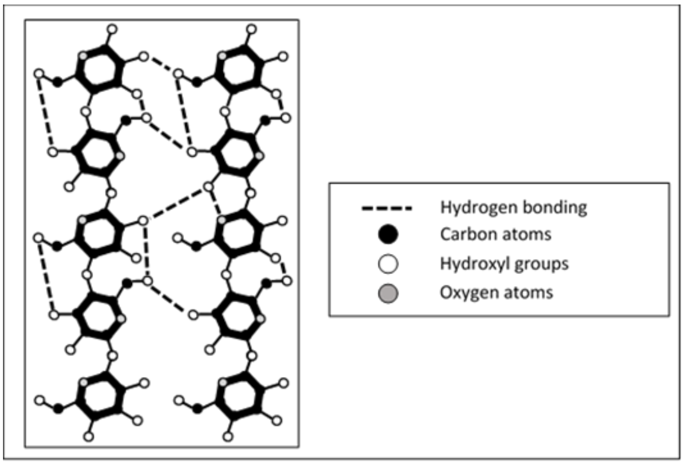


Figure 7. illustrated the structure of cellulose and its crystallinity with the presence of hydrogen bonding

From Table 1, the experiment showed that cellulose is absolutely not soluble in water or any common solvent. This proved the theory of previous studies for the insolubility of cellulose. By modification of cellulose by grafting it with PHEMA which is more likely to be hydrophilic polymer and has high water content, this grafted cellulose become more flexible in most common solvent.

However, cellulose-g-PHEMA did not showed any positive reaction of the solubility. It is still not soluble in distilled water, methanol and DMSO just like blended cellulose. This was possible due to the low amount of PHEMA attached to the cellulose backbone. The other reason was the reaction of hydroxyl group of PHEMA with another PHEMA molecule which can be the crosslinked of the cellulose chains. This resulted in the cellulose backbone becoming more rigid and the amorphous region in the cellulose become crystalline. This crystalline structure of rigid cellulose make it become more hydrophilic than before the grafting method.

Swelling of the cellulose, PHEMA and cellulose-g-PHEMA is determined and the result showed that cellulose-g-PHEMA have better ability to swell than blended cellulose (Table 2). This is caused by the modification made by PHEMA which is attached onto the cellulose tend to have high water intake properties. Thus, the swelling of cellulose-g-PHEMA is higher than cellulose. This improvement indicated that cellulose was grafted with PHEMA which can be widely applied in the industries. The graph in Figure 14 showed the significant different of the degree of swelling for blended cellulose and cellulose-g-PHEMA

Table 2. Degree of swelling for blended cellulose, PHEMA and cellulose-g-PHEMA.

Compound	Time taken (minutes)	Weight of dry compound	Weight of wet compound	Degree of swelling
Blended cellulose	10	0.050	0.178	2.56
	20	0.050	0.196	2.92
	30	0.050	0.211	3.18
	40	0.050	0.243	3.28
	50	0.050	0.254	3.66
	60	0.050	0.278	4.02
Cellulose-g-PHEMA	10	0.050	0.140	0.78
	20	0.050	0.167	1.24
	30	0.050	0.189	2.12
	40	0.050	0.218	2.96
	50	0.050	0.264	4.12
	60	0.050	0.289	4.94

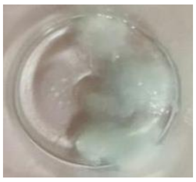
3.4. Copper removal testing of blended cellulose, PHEMA and cellulose-g-PHEMA

Copper removal test was done using copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$) as the solution. 0.001 M of $CuSO_4.5H_2O$ was prepared by dilution of 24.96 g of copper powder in 100 ml volumetric flask. A fixed weights of blended cellulose, PHEMA and PHEMA grafted cellulose was immersed into 5 mL of the copper (II) sulphate solution and 2 mL of the solution is taken every 2 hours for 6 hours time range. Then, the taken solution is analysed with UV-Vis spectrophotometer.

However, the UV-Vis showed no readings of the solution thus the spectra cannot be obtained. This is because of the small particles of blended cellulose and cellulose-g-PHEMA are dispersed in the copper (II) sulphate solution. The particles in the solution scattered the light from UV radiation which resulted error of using the UV-Vis spectrophotometer.

The study found that cellulose-g-PHEMA was a better adsorbent for copper removal from the physical observation of the resultant samples. This was due to the bright blue colour of the cellulose-g-PHEMA than the blended cellulose after 2, 4 and 6 hours immersion in the copper (II) sulphate solution as shown in Table 3.

Table 3. Physical appearance of blended cellulose and cellulose-g-PHEMA after 2,4, and 6 hours immersion in the copper (II) sulphate solution.

Time immersed in copper (II) sulphate solution	**2 hours**	**4 hours**	**6 hours**
Blended cellulose			
Cellulose-g-PHEMA			

4. CONCLUSION

As the conclusion, PHEMA was synthesized by using the RAFT polymerisation with ACPA as the initiator and CPADB as the RAFT agent from this experiment. The 63.78% conversion of HEMA to PHEMA proved the success of RAFT polymerisation of HEMA. In addition, cellulose-g-PHEMA was synthesized via “grafting onto” method with DCC and DMAP used as coupling reagent and catalyst respectively. The grafting percentage of 39.72% with 33.10% of efficiency showed that PHEMA was successfully grafted onto cellulose backbone. Other than that, all the samples afforded the same reaction when soaked in the solvents. This indicated that the cellulose-g-PHEMA were not soluble in the solvents which were distilled water, methanol and DMSO. As for the swelling test, cellulose-g-PHEMA synthesized for 5 hours showed better swelling ability than the blended cellulose. Result of the copper removal test was done for suggested potential of cellulose-g-PHEMA to remove copper from solution. This give opportunity for applying this cellulose-g-PHEMA for further study for uses in the variety of industries such as for medical application, optical industries, adhesive application or any other suitable industries. This cellulose-g-PHEMA should be used in further studies of its applications. Other than the agriculture industry, cellulose-g-PHEMA might be able to be used in medical or automotive industries. It was also recommended to change the sources of cellulose and modify the cellulose to be cellulose acetate or ethyl cellulose before being grafted with the PHEMA. This can change the properties of the cellulose and the grafted cellulose because some modified cellulose was soluble in certain solvent.

REFERENCES

[1] Roy, D., Semsarilar, M., Guthriea, J. T., & Perrier, S., (2009) Cellulose Modification by Polymer Grafting - A Review. Chem Soc Rev, 38(7), 2046-2064

[2] Hiltunen, M., (2013) Cellulose Based Graft Copolymers Prepared via Controlled Radical Polymerization Methods, 1-54.

[3] Paterson, S. M., (2011) The Synthesis of PHEMA-based Materials for Tissue Engineering Applications. 1-184.

[4] Lizundia, E., Meaurio, E., & Vilas, J. L., (2016) Grafting of Cellulose Nanocrystals. 61-113.

[5] Volynets, B., Nakhoda, H., Abu Ghalia, M., & Dahman, Y., (2017) Preparation & Characterization of Poly(2-Hydroxyethyl Methacrylate) Grafted Bacterial Cellulose using Atom Transfer Radical Polymerization, Fibers & Polymers, 18(5), 859-867.

[6] Okieimen, F. E., Sogbaike, C. E., & Ebhoaye, J. E., (2005) Removal of Cadmium & Copper Ions from Aqueous Solution with Cellulose Graft Copolymers. Separation & Purification Technology, 44(1), 85-89.

[7] Kenji, S., Kohzoh, S., Etsuo, S., Kenji, A., Kiyoshi, N., & Tamao, H., (1997) Degassing Effect in Water-Sterilizing Effect, RF Superconductivity, 655-661.

[8] Kessler, M. R., (2008) Self-healing Composites. 650-673.

[9] Oh, S. Y., et al., (2005) Crystalline Structure Analysis of Cellulose Treated with Sodium Hydroxide & Carbon Dioxide by Means of X-Ray Diffraction & FTIR Spectroscopy. Carbohydrate Research, 340(15), 2376-2391.