Formation Thin Film Nanofibre Of Polyacrylic Acid (PAA) -Carboxymethylcellulose (CMC)-Polyethylene Oxide (PEO) using electrospinning technique

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***Abstract*— Formation of thin film nanofibre of PEO-CMC-PAA was conducted via electrospinning technique. Three different solutions were prepared namely PAA-ethanol, PEO-water-ethanol and CMC-water before vigorously mixed together forming polymer blend solution. Viscosity and conductivity were measured before electrospinning. The electrospun nanofibre was characterized by using Field Emission Scanning Electron Microscope (FESEM), contact angle and Fourier Transform Infrared Spectroscopy (FTIR). The electrospun nanofibers of PAA-CMC-PEO was analyzed by using FESEM and average diameter of 400 nm was obtained by using Image J software. The contact angle measurement of electrospun nanofibers is 20.20°. Compounds of O-H, R-C=OO, RC=O, cellulose, CH_3 and C-O-H were obtained in polymers solution and electrospun nanofibers via Fourier Transform Infrared Spectroscopy. This study contributes a promising approach to fabricate an electrospun nanofiber from the blended polymer of PEO-CMC-PAA.**

***Keywords*— Electrospinning, Polyethylene oxide, Polyacrylic acid, Carboxymethylcellulose, blend polymer, electospun nanofiber**

I. INTRODUCTION

Electrospinning is a method producing nano size of polymer fibers with low manufacturing cost and it is only a simple process. It is the versatile technique to fabricate whether organic or inorganic nanofibers with certain wavelengths, uniform diameter and diverse composition by controlling the uses of electrostatic force [1]. Several roles of electrostatic force in electrospinning technique is to help in the formation of fiber including it used to substitute and replace the conventional mechanical force such as pneumatic and hydrostatic to form jet. It is also used to minimize the size of fiber [13]. The subject concerning polymer nanofibers formed by electrospinning technique has to become a great interest for several years. This technique widely used in many applications nowadays [2]. Parameters affecting electrospinning is divided into three which are solution parameters, process parameters, and ambient parameters. Table 1 shows the parameters affecting the electrospinning. The method has been broadly applicable in another field such as photocatalyst, sensors, an antibacterial scaffold for tissue engineering and others. In the electrospinning practice, steep voltage is given a polymer droplet suspended at the tip of a syringe needle. Charge has build up on this droplet that will elongates and produce a Taylor cone as immediately as this charge overcomes the surface tension of the solution [1]. In order to generate the electrospinning process, the Direct current (DC) voltage should be more than ten kV. Polymers usually are dissolves in some solvents first before electrospinning process occurs to produce polymer solution [14].

Table 1: Parameter affecting diameter of fiber

Parameters	Effect on fiber morphology	References
1)Solution Parameters Viscosity	Increase in viscosity will increase the diameter of fiber produced and formation of low beads.	[2],[16]
Polymer concentration	Relationship of polymer concentration and fiber diameter is directly proportional. Increasing in the polymer concentration will increase the fiber diameter produced.	[17]
Molecular weight of polymer	The heavier the weight of polymer, the smaller the number of beads formed.	[18]
Conductivity	The higher the conductivity of the polymer solution, the smaller the diameter of nanofibers.	[19]
Surface Tension	Surface tension influences the stability of the jet. The higher the surface tension exists, the more unstable jet will form.	[20]
2)Processing parameters Applied voltage	The higher the voltage applied, the smaller the diameter of the fiber	[18]
Distance between the tip to collector	Bead produced if the distance is too small or too big. Perfect distance between tip of needle to collector is required in obtaining the uniform fiber.	[21]
Flow rate	Increasing in flow rate will result in the production of beads. In the other hand, a decrease of flow rate will decrease the fiber diameters	[20]
3)Ambient parameters Humidity	Circular pores on the fiber produced if the humidity is high.	[22]
Temperature	Small diameter of nanofiber produced if the temperature is high.	[23]

Carboxymethylcellulose is derivative of cellulose which is a hydrophilic compound that has the capability to produce very viscous solution and it can be dissolved in water [5]. Carboxymethylcellulose is a polyelectrolyte compound that produced from cellulose under controlled condition [8]. Cellulose is one of the examples of a natural polymer under polysaccharides which degradable. Cellulose is one of the most plentiful polysaccharides and easily obtained because it is a natural polymer. Carboxymethylcellulose does not soluble in many solvents and not easily to be used in electrospinning method because of its intrinsic chemistry. Many researcher used polyethylene oxide and carboxymethylcellulose in their research but there are no researcher has been produced a film that contain carboxymethylcellulose blend with polyacrylic acid and polyethylene oxide polymer solution. Polyacrylic acid is a weak anionic polyelectrolyte compound that is used in many applications such as biomedicine, drug delivery, paint industry, as a cleaning

agent, dentistry and hair styling products [6-7]. Polyelectrolyte base on the IUPAC definition is defines as the polymer that comprises of macromolecules where a large portion of the constitutional unit contains ionic or ionisable groups or both. The polyelectrolyte can be divided into two types which is weak and strong electrolyte. The strong polyelectrolyte is defined as the polymer that has a strong acidic or basic group that is stay ionized at pH condition. The weak polyelectrolyte is the polymer that has molecules such as carboxyl group or amide group or others that will react with the solvent and changing in the charge base on the change in pH. Polyacrylic Acid can be dissolved in tetrahydrofuran, ethanol, methanol and water [11]. Polyacrylic acid is very hydrophilic polymer [10]. Electrospinning of polyacrylic acid producing nanofiber that widely used in the sensor application. There is some research regarding electrospinning that combining polyacrylic acid and polyethylene oxide but applicable for different application. The electrospinning of polyethylene oxide and polyacrylic acid has been performed for vaginal therapies application [9].

Polyethylene oxide is one of biodegradable material that is nontoxic and flexible because of its high thermal stability. Polyethylene oxide is a semi crystalline state polymer and one of the biodegradable synthetics polymers [12]. Polyethylene oxide is broadly used in electrochemical, optoelectronic and photonic application. Polyethylene oxide is used in many application including pharmaceutical, food and cosmetics because it has been approved in safety for various purpose. It is also an effective ion conductive polymer. Polyethylene oxide is used for the spinning solution in the blend with natural derivative polymer like carboxymethylcellulose. The present of polyethylene oxide will increase the electrospinnability of the polymer like carboxymethylcellulose that cannot be electrospun by itself. Polyethylene oxide is the compound that can be dissolved in many type of solvent including chloroform, ethanol, di-methyl formamide and water [12]. The chosen solvent is important in the preparation of blend because blend of these three polymer cannot be achieve as some of these three polymer cannot be dissolve in the solvent that the other polymer can dissolve. The objective of three polymer solutions created at different solvent system is because to avoid sedimentation and agglomeration when the phase changes occur. It is hard to mix these three polymer solution because carboxymethylcellulose only can be dissolve in water and di-methylformamide. Polyethylene oxide has a great function as it is the agent of the carboxymethylcellulose to be dissolve in polyacrylic acid solution without agglomeration occurs. There are no researcher has performing the electrospinning of three polymer blend solution of PAA-CMC-PAA. This study is significant to determine the polymer blend solution of three polymer of different structure could be electrospinning or not. This research generally studying the electrospinning technique to fabricating nanofiber from polymer blended solution.

The objective of this research is to electrospin the polymer blend solution that consists of polyacrylic acid, polyethylene oxide and carboxymethylcellulose. On the other hand, other objective is to characterize the PEO-CMC-PAA film.

II. METHODOLOGY

A. Materials

Polyacrylic acid (PAA, molecular weight M= 450,000 g/mol) and Polyethylene oxide (PEO, molecular weight=5,000,000 g/mol) purchases from Adrich Chemistry, Carboxymethylcellulose (CMC grade THH) from Waris Nove Sdn Bhd were used to prepared the polymer blend solution. The solvent used were ethanol absolute and distilled water.

B. Preparation of Polymer blend solution

Blend polymer solution is prepared by mix all three pure polymer solutions to each other after done preparing all three pure polymer solutions. There are three pure polymer solutions which are CMC solution, PEO solution and PAA solution.

i) Preparation of CMC solution

0.2% w/w CMC solution was prepared by firstly heating the distilled water at temperature 50 to 60 C°. CMC was added into the solvent and vigorously stirred about 30 minutes. CMC solution is allowed to be cooled at room temperature before mixed with other two polymers to form blend polymer solution.

ii) Preparation of PEO solution

Ethanol was heated at temperature 70 C° before added 0.6% w/w Polyethylene Oxide into the solvent. Water was added into the solution after PEO-ethanol solution was completely mixed. Ethanol-water ratio is 8:2. PEO solution was allowed to be cooled at room temperature before preparing polymer blend solution.

iii) Preparation of PAA solution

94% w/w of Ethanol solvent was heated at temperature 40C°and measured by using thermometer. 6% w/w was added into the heated solvent and vigorously stirred about 1 hour.

iv) Preparation of PAA-CMC-PEO solution

CMC solution was added into PEO solution and vigorously stirred about 30 minutes. The formation of CMC-PEO solution was produced to prevent agglomeration of CMC when blending it with PAA solution. It is because CMC naturally does not dissolve in ethanol. The mixture of blended polymer solution was formed with the ratio of PAA solution, PEO solution, CMC solution 68:21:11. Fig. 1 shows the illustration of PAA-CMC-PEO polymer blend solution preparation.

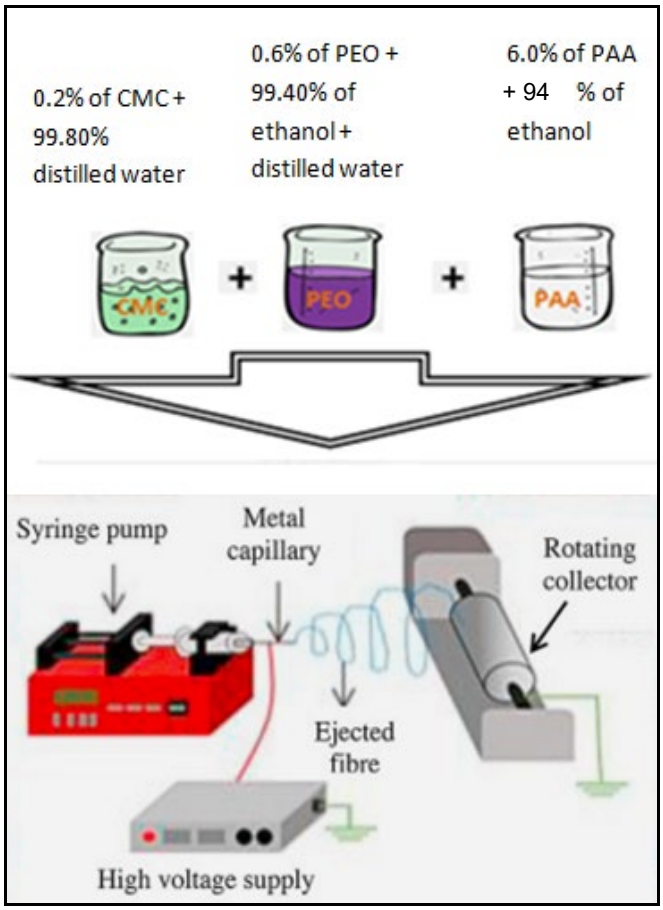

Fig 1: Illustration of polymer blend preparation

C. Viscosity and Conductivity test

The viscosity and conductivity tests were measured before performing electrospinning experiment. Viscosity of polymer blend solution of PAA-CMC-PEO was determined by using Fann

Viscometer Model 35A at temperature 25C°. Newtonian viscosity obtained in unit centipoises (cP) by adjusting the rotor-bob-torsion R1-B1—F1 setting with the speed of 300 rpm. The conductivity of PEO solution, PAA solution, CMC solution and PAA-CMC-PEO solution were measured by Mettler Toledo Conductivity meter. Both conductivity and viscosity test measured three times to obtain average value.

D. Electrospinning

3ml of polymer solution was extruded through 5ml blunt-needle syringe. Aluminium foil was used as a collector and the distance between the tip and the collector was 8 cm. Electrospinning experiment was conducted at room temperature and the applied voltage used was 15 kV. The flow rate used was 2ml/hr. The electrospun nanofiber was dried in the incubator about 2 hours.

E. Characterization of electrospun nanofibre

i)Field Emission Scanning Electron Microscope (FESEM)

PAA-CMC-PEO film is sputter coated with Au/Pd under high vacuum and morphology was observed by using Field Emission Scanning Electron Microscope (FESEM) Fei Quanta 450 Feg at accelerated voltage of 15kV. The diameters of electrospun nanofibers were analyzed by using Image J software.

ii) Contact Angle

The hydrophilic properties of electrospun nanofiber of PAA-CMC-PEO were determined by VCA Optima XE Contact Angle Measurement. PEO, CMC, PAA conventional films were prepared by casting method. Each of the pure polymer solution was cast into aluminium foil. The casting films were dried by using hair dryer for two hours. The hydrophilic properties of conventional pure polymer films were compared to electrospun nanofiber PAA-CMC-PEO. The volume of distilled water used to hit the surface of the films was 10µL. The contact angle of the films was determined by AUTOFAST calculation.

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iii) Fourier Transform Infrared Spectroscopy (FTIR)

The functional group of electrospun nanofibers and polymer solutions were studied by using Fourier Transform Infrared Spectroscopy (FTIR) Perkin Elmer at a range of 4000 cm^{-1}- 400cm^{-1} with 4 cm^{-1} resolution. Electrospun nanofiber was analyzed by comparing the electrospun nanofiber with PEO solution, PAA solution, CMC solution and PAA-CMC-PEO polymers solution.

III. RESULTS AND DISCUSSION

A. The viscosity of the polymer solution

Base on the table 2, the higher the speed used to test the viscosity of the solution, the higher the value of viscosity. However, only the viscosity reading at 300rpm is used to obtain the Newtonian viscosity. The viscosity of PAA-CMC-PEO polymer solution is 195.3centiPoise (1.95 Poise). The best viscosity for electrospinning of polymer solution should not be more than20 poise (2000 centipoise) and should not less than 1 Poise (centipoises) [2]. The value is acceptable as it is in the range of 1Poise to 20 Poise. High viscosity solution has a tendency to form a continuous jet and producing electrospun nanofibers [24]. There is no continuous jet produced if the viscosity is too low. The difficulty in the ejection of jet occurs when the polymer solution has very high viscosity [2]. The viscosity of the blend polymer is in the range and it is suitable for electrospinning. The viscosity less than 1 poise will end to the formation of beads fibers because the fluid jets is rupture into small droplet and the fiber could not be occurs.

Table 2: Viscosity reading

Speed (rpm)	Reading (centi Poise)
3 rpm	5.67 ± 1.16
6 rpm	9.67 ±0.58
100 rpm	86.3 ± 1.53
200 rpm	140.3±0.58
300 rpm	195.3 ±1.53

B. The conductivity of the polymer solution

Base on Table 3, it is clearly shown the conductivity value of pure polyethylene oxide has the highest value of conductivity which is 2160 ± 20 µS/cm compared to other type of pure polymer although only 0.6% of PEO used during the preparation of blend polymer. The conductivity values of pure carboxymethylcellulose is242±3.21 µS/cm and the conductivity of pure polyacrylic acid is567±13.65 µS/cm**.** High conductivity value in polyethylene oxide solution due to the ultrahigh molecular weight of polyethylene oxide. High molecular weight of polymer intended to increase the ionic conductivity of polymer electrolyte membrane [16]. The chemical nature of CMC affecting the charge density of solution in ejected jet and fabricate the thinner diameter of the electrospun nanofibers [8]. Other studies propose that the conductivity of the prepared solution should be in the range of. 1µS/cm to 10 mS/cm [14]. The lowest conductivity of pure polymer is pure carboxymethylcellulose polymer solution and second lower is polyacrylic acid polymer solution. Both carboxymethylcellulose and polyacrylic acid are polyelectrolyte polymer [7-8]. The molecular weight of polymer is influence the conductivity of the polymer solution. The blend polymer solution is the highest compared to three other pure polymer solution. In this study, all the values of conductivity obtained were within the suggested range. By putting carboxymethylcellulose pure polymer solution as the reference because has a lowest conductivity, the blend polymer solution has increase the conductivity about 94%.

Table 3: Conductivity reading

Polymer	Conductivity reading (µS/cm)
Pure PEO	2160±20
Pure CMC	242±3.21
Pure PAA	567±13.65
Polymer blend PAA-CMC-PEO solution	3887±15.27

C. Electrospinning

Electrospinning is the process of fabricating nanofibers. The collector used in the experiment is aluminium foil. Fig. 2 shows the electrospun nanofiber of PAA-CMC-PEO.

Fig 2: Nanofiber produced after electrospinning

D. Contact Angle

Fig. 3 (a), (b), (c) and (d) show the contact angle of polymer films. Fig. 3 (a) defined as the contact angle of pure acrylic acid mixed with ethanol, Fig. 3(b) shows the contact angle of pure polyethylene oxide mixed with ethanol and distilled water whereas Fig. 3(c) shows the contact angle of pure carboxymethylcellulose mixed with distilled water. Fig. 3 (d) shows the contact angle of electrospun nanofibers of PAA-CMC-PEO. The contact angle of polymers was described in Table 4.

Table 4: Contact angle measurement of polymers film

Polymers film	Contact angle
PAA-Ethanol conventional film	34.90º
PEO-Distilled Water - ethanol conventional film	47.70º
CMC-Distilled water conventional film	64.90º
PAA-CMC-PEO electrospun nanofibers	20.20^0

Pure polyacrylic acid film is the most hydrophilic compared to other two polymer tested because has the lowest value of contact angle followed by polyethylene oxide film and carboxymethylcellulose film. Polymer blend film has high wettability properties and more hydrophilic than three pure polymer film. All polymers that had been tested are hydrophilic because the values are less than 90^0 but the most hydrophilic film is the one that has the lowest contact angle value. The highest wettability film is PAA-CMC-PEO blend polymer film followed by pure polyacrylic acid film. High wettability defined film has high hydrophilic properties. Three conventional films of PEO-ethanol-water, PAA-ethanol, and CMC-water shows the hydrophilic properties but the electrospun nanofiber of PAA-CMC-PEO producing more hydrophilic than conventional film.

The research performed by (Akbar Esmaeili et al, 2017) has a value of contact angle of 58.9º. However, the research of (Akbar Esmaeili et al, 2017) is a 3% polymer concentration the mixture of polyethylene oxide (PEO) - chloroform and thermal carboxymethylcellulose (TCMC) – Dimethylformamide (DMF). There are no researches that combine the blend of PAA-CMC-PEO polymers. In comparison, the blend polymers of PAA-CMC-PEO is much better as it has low value defined it has high wettability properties compared to TCMC-PEO film.

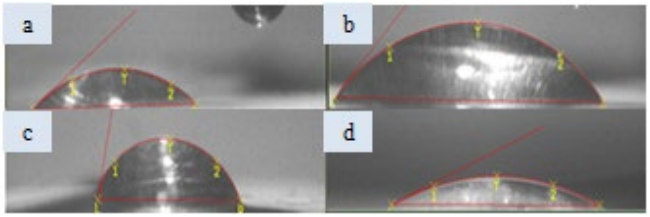

Fig 3: Contact Angle measurement for (a) PAA conventional film;(b) PEO conventional film; (c) CMC conventional film; (d) Electrospun nanofibers PAA-CMC-PEO

E. Field Emission Scanning Electron Microscope

SEM image in Fig. 4 also depicted the uniqueness and difference in diameter fibers of polymer blend solution. Smooth nanofibers has been produced. The nanofiber produced has a wide range of diameter because the flow rate used during electrospinning is quite high resulted to the incomplete drying between the tip of the needle and the collector. The electrospinning process also sometime producing receding jets and cone jet which affected the wide range of fiber diameter. Receding jet is an unstable jet. Carboxymethylcellulose is polyelectrolyte polymer that can cause an increasing in the charge density of solution during electrospinning. The increasing in the charge density will produce a strong elongation force that influence in the fabrication of straight electrospun nanofibers. The thicker diameter of nanofiber produce resulted from the restrain properties of polyethylene oxide polymer. Fig. 4(a) and Fig 4(b) are the image of the same polymer blend electrospun nanofibers at different magnification.

Fig. 5 shows the distribution of diameter for electrospun nanofibers average fiber diameter. The diameter of electrospun nanofibers were measured by using ImageJ and data was summarized. The average size of polymer blended nanofibers is 400 ± 65 nm. The short distance between the tip to the collector used resulting the large diameter of the polymer blended electrospun nanofibers produced. According to this result, the first objective of this study was achieved with the average diameter of electrospun nanofiber is 400 ±65 nm.

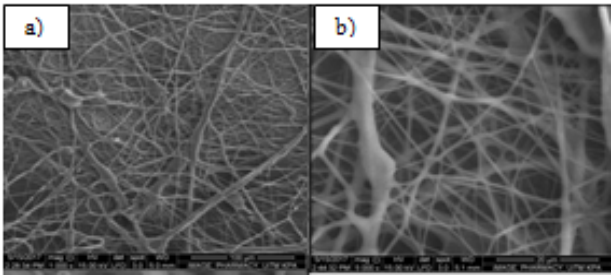

Fig 4:(a) PAA-CMC-PEO blend polymer nanofibers at 500 magnification, (b) PAA-CMC-PEO blend nanofibers at 5000 magnification

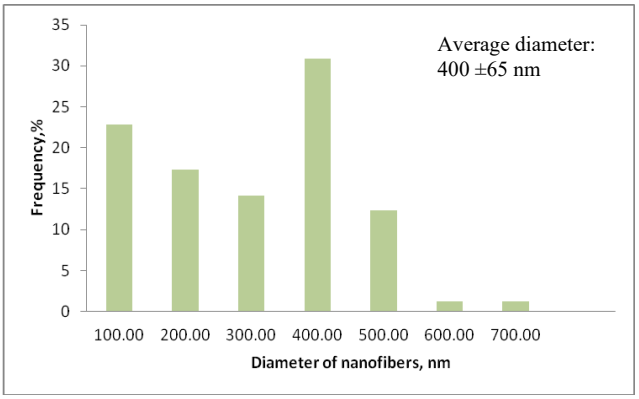

Fig. 5: Average diameter of nanofibers for polymeric composite of PAA-CMC-PEO

F. Fourier Transform Electron Spectroscopy(FTIR)

Fig. 6 shows the FTIR spectra of CMC powder, PEO powder, PAA powder, Polymer blend of PAA-CMC-PEO solution before electrospinning and PAA-CMC-PEO electrospun nanofibers after electrospinning. FTIR was used to study the functional group and determining any possible interaction between CMC, PEO and PAA.

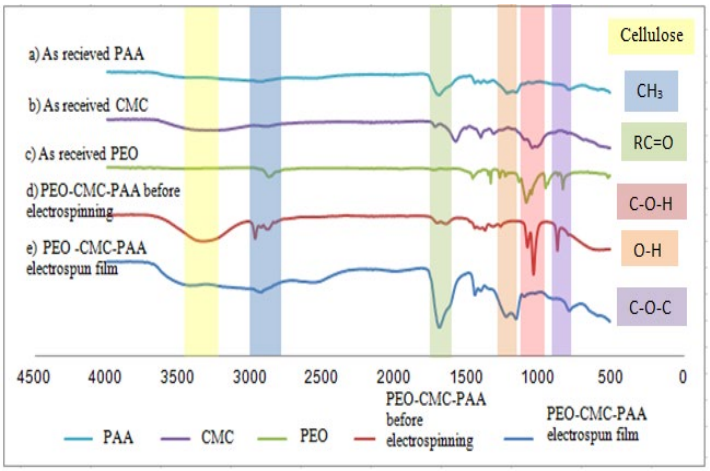

Fig 6: FTIR spectrum of (a) PAA powder, (b) CMC powder, (c) PEO powder, (d) PAA-CMC-PEO polymer blended solution before electrospinning, (e) Electrospun nanofiber PAA-CMC-PEO after electrospinning

In the spectrum of PAA, the main characteristic peaks of PAA appeared as a strong peaks at 1699.56 cm^{-1}, and at 1365 cm^{-1} which were attributed to RC=O stretching vibration and OH stretching vibration respectively. The intensity of absorption band at 1698 cm^{-1} in the electrospun film of PEO-CMC-PAA is higher compared to PAA. The absorption band shows the present of PAA in the PAA-CMC-PEO electrospun film. The characteristic peaks of PAA appeared in the spectrum of PAA-CMC-PEO electrospun film at 1270 cm^{-1} represents the OH stretching vibration. In the spectrum of CMC, the peak at 3268 cm^{-1}exist assigned to the

cellulose type that present in CMC polymer. The intensity of absorption band at 3350 cm^{-1} in the spectrum of PAA-CMC-PEO solution before electrospinning is higher compared to the spectrum of CMC which was attributed to the present of CMC in the polymer blended solution. CMC is fully evaporated during electrospinning experiment resulted to the no peak of cellulose type at PAA-CMC-PEO electrospun film. The absorption peak at 1054 cm^{-1}, 1094 cm^{-1} and 1044 cm^{-1} which assigned C-O-H present in CMC, PEO, and PAA-CMC-PEO spectra. In the spectrum of PEO, the main characteristic of PEO appeared at 2878 cm^{-1} and 876 cm^{-1} represent CH_3 and C-O-C absorption complex of PEO. The characteristic peak of PEO in PEO-CMC-PAA solution before electrospinning spectrum shows the C-O-C stretching vibration at the peak of 796cm^{-1}. On comparing the spectra of PEO and the PAA-CMC-PEO solution before electrospinning, the intensity was higher in the PAA-CMC-PEO solution at the peak of 2886 cm^{-1}. The composition of PAA in the electrospun film is the highest compared to two others polymer resulted to the high intensity of the FTIR spectrum of PAA.

IV. Conclusion

Electrospun nanofiber of PAA-CMC-PEO was successfully produced via electrospinning technique. Viscosity of polymer blended solution was 195.3centiPoise. The viscosity of the polymer blended solution was suitable as it producing no bead fibre after observed by using Field Emission Scanning Electron Microscope (FESEM). The conductivity of PAA-CMC-PEO blended solution was 3887±15.27 µS/cm. The average diameter of electrospun nanofibers is 400 nm ± 65. The characterization by using contact angle of electrospun nanofibers shows the hydrophilic properties was 20.20°. It shows high wettability surface of nanofibers. The present of OH, C-OH, C-O-C and RC=O in the FTIR characterization proven that the electrospun nanofiber is hydrophilic. In conclusion, both objectives were achieved.

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