

GRAFTING COPOLYMERIZATION OF OZONATED POLYPROPYLENE WITH POLY(ACRYLIC ACID) : AS CATIONIC EXCHANGER

Intan Parapak¹, Oka Ratnayani¹, Manuntun Manurung^{1,2}, James Sibarani^{1,2*}

¹Department of Chemistry, Faculty of Mathematics and Science, Udayana University, Badung-Bali, Indonesia

²Magister Program of Chemistry, Faculty of Mathematics and Science, Udayana University, Badung-Bali, Indonesia

*Email : james_sibarani@unud.ac.id

ABSTRACT: Copolymer grafting of polypropylene-g-poly(acrylic acid) (PP-g-PAA) as cationic exchanger has been prepared by 'grafting from' method of poly(acrylic acid) (PAA) onto ozonated polypropylene film with variation of ozonization time. The percentage of grafting was determined by gravimetric method. The percentage of grafting was influenced by the variation of ozonization time where the maximum percent grafting of 175% obtained on 60 minute of ozonization time. The PP-g-PAA copolymers obtained were characterized using Fourier Transform Infrared (FTIR) and Laser Induced Breakdown Spectroscopy (LIBS). The graft copolymerization process was confirmed by the existence of new absorption peaks at 1708.33 cm^{-1} and 3188.33 cm^{-1} assigned to -C=O and -OH respectively. The increasing of the emission intensity of C, H and O atoms as the percentage of grafting based on LIBS spectroscopy signifies that PAA has been successfully grafted on PP films. The characterization of the PP-g-PAA films were conducted by measuring water uptake capability and cation exchange capacity toward Cu^{2+} . The two characteristics were increasing as the percentage of grafting. The cation exchange capacity of the graft copolymer was 1.5547 meq/g.

Keywords: Cationic exchanger; Graft Copolymerization; Polypropylene; Poly(acrylic acid)

ABSTRAK: Penukar kation polipropilen-g-poli(asam akrilat) (PP-g-PAA) telah dibuat melalui kopolimerisasi *grafting* dengan teknik "*grafting-from*" poli(asam akrilat) (PAA) pada film polipropilen terozonasi dengan variasi lama waktu ozonisasi. Jumlah PAA yang *tergrafting* pada film PP (persen *grafting*) dihitung menggunakan metode gravimetri. Dari hasil penelitian diperoleh bahwa persen *grafting* dipengaruhi oleh variasi waktu ozonisasi dan persen *grafting* tertinggi diperoleh pada lama ozonisasi selama 60 menit dengan persen *grafting* sebesar 175%. Untuk mengevaluasi terbentuknya kopolimer PP-g-PAA dilakukan karakterisasi menggunakan *Fourier Transform Infrared* (FTIR) dan *Laser Induced Breakdown Spectroscopy* (LIBS). Berdasarkan data spektroskopi FTIR, munculnya puncak-puncak serapan baru pada bilangan gelombang 1708.33 cm^{-1} (-C=O) dan 3188,33 cm^{-1} (-OH) serta adanya peningkatan intensitas emisi atom C, H dan O seiring pertambahan persen *grafting* berdasarkan spektroskopi LIBS menandakan bahwa PAA telah berhasil *tergrafting* pada film PP. Karakterisasi film PP-g-PAA dilakukan dengan menguji daya serap air dan kapasitas pertukaran kation terhadap logam Cu^{2+} . Berdasarkan hasil penelitian, semakin tinggi persen *grafting* maka semakin tinggi daya serap air dan kapasitas pertukaran ion logam Cu^{2+} tertinggi adalah sebesar 1,5547 meq/gram.

Kata kunci: Kopolimerisasi *grafting*; Penukar kation; Polipropilen; Poli(asam akrilat).

1. INTRODUCTION

We live in an era of polymers where fibers, plastics, adhesives, rubber, and coating materials are familiar. That is part of the amazing chemistry of polymers [1]. Polymers play a big role in human life and are widely used in everyday life, for example materials or stuff that are made of plastic. Nowadays, the use of polymers have become prevalent. One of the most commonly used polymers is polypropylene (PP). Polypropylene is a hydrophobic, corrosion-resistant thermoplastic polymer made from cheap, easy to obtain and has good strength and stiffness that can be widely used in industries [2].

The awareness of plastic waste processing into a product with benefits that can be used by all layers of society is increasing so that increasing polypropylene waste can be utilized in various fields, for example as an cationic exchanger. Utilization of polypropylene waste can be done by modifying the polypropylene surface in order to have high adhesion power so that it can interact with other materials and facilitate its application in various fields according to its usefulness [2].

One of effective method for producing the desirable properties of polypropylene is by grafting technique. The technique of grafting has several advantages, one of which is polypropylene can be functionalized in accordance with properties possessed by monomers without affecting the basic structure and chemical properties of polypropylene [3]. There have been many reports about cationic exchanger membrane by using grafting technique. Modification of a polymer by grafting technique involves the formation of an active site of free radical or ions prior to a monomer or a parent polymer. The formation of active sites in the grafting process is done by the technique of "grafting-from", where the formation of active sites begins in the polymer. The grafting technique has been utilized, among others, to alter the properties of polymers

with the aim of enhancing metal adhesion and metal oxides [4], immobilization of enzymes in polymers [5], giving polymer sensitivity to temperature changes [6], provides polymer sensitivity to the changes of pH [7], catalytic properties [8], ion exchange properties [9], providing antioxidant and antibacterial properties [10].

The rise of various studies of ion exchange membranes and the success of polymer modification and the availability of a variety of standard modification methods are the basis of ideas in the use of polypropylene as cationic exchanger. A cationic exchanger membrane is carried out by polymerization of copolymerization technique of "grafting-from" polypropylene with acrylic acid monomer (AA) by free radical reaction. This product is particularly useful for cationic exchanger in order to attract heavy metals and harmful cations [9].

To obtain poly(acrylic acid) copolymers on polypropylene (PP) with high percentage of grafting and high ion exchange capacity, a study is needed to determine the effect of several variables on the percentage of grafting such as ozonation reaction time, monomer concentration, and reaction time of copolymerization. The effect of ozonation reaction time on percentage of grafting, water absorption, and membrane ion exchange capacity were also observed.

2. EXPERIMENTAL

Materials

Transparent polypropylene plastic sheets (100 μm in thickness) commercially available, monomer acrylic acid (AA) was purchased from Sigma Aldrich. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, K_2HPO_4 , KH_2PO_4 were purchased from Bratachem Chemical Indonesia.

Ozonization of PP Sheet

The plastic sheets were cut into 2.5 x 2.5 cm and then refluxed with acetone

using sokhlet for 8 hours at 57°C. Then the plastic was dried in an oven with a temperature of 50°C for 1 hour. The PP plastic sheet was placed into an Erlenmeyer and ozonized by flowing ozone generated from commercial O₃ generator with variation of time of 30, 60, 120, and 240 minutes.

Grafting Copolymerization of PP-g-PAA

The grafting copolymerization was carried out by immersing the ozonated plastic sheet into 10 mL of 20% acrylic acid monomer solution. The solution was bubbled with nitrogen gas for 30 minutes and heated in an oil bath at 80°C for 2 hours. The PP-g-PAA obtained was cleaned with warm water and dried on vacuum. Percent grafting of the PAA was calculated by :

$$\text{Percent grafting (\%)} = \frac{W - W_0}{W_0} \times 100\%$$

Where W is the weight of PP-g-PAA film and W₀ is the weight of PP. The characterizations were conducted by Fourier Transformation Infra Red (FTIR) (IRPrestige-21 Shimadzu) and Laser Induced Breakdown Spectrometer (LIBS) (Insight Photon Machines).

Determination of Water Uptake

PP-g-PAA films with various percent of grafting are immersed in water for 24 hours at room temperature (28°C). Then the film was removed and the excess water removed with filter paper. The water uptake is calculated based on the following formula [11]:

$$\text{Water uptake (\%)} = \frac{W_1 - W_0}{W_0} \times 100\%$$

Where W₁ is the weight of PP-g-PAA film after soaked in water (g) and W₀ is the dry weight of PP-g-PAA before immersing in water (g).

Determination of Cation Exchange Capacity

The PP-g-PAA copolymer was inserted into a 50 mL Erlenmeyer containing 20 mL of 250 ppm Cu²⁺ solution in buffer with pH of 7 and stirred for 1 hour. The remaining concentration of Cu²⁺ ions in the solution was determined using AAS. The absorption capacity of Cu²⁺ ions was expressed in meq/g, as is the following formula:

$$\text{Absorption Capacity (meq/g)} = \frac{(C_1 - C_2) \times 2000 \times V}{\text{Ar Cu} \times W_1}$$

Where C₁ is the initial Cu²⁺ concentration (ppm), C₂ is the residual Cu²⁺ concentration (ppm), V is the volume of Cu²⁺ (mL), and W₁ is the weight of PP-g-PAA (g).

3. RESULTS AND DISCUSSION

Effect of Ozonation Time on Graft Copolymerization

In this study, the ozonation time is very important in determining the amount of peroxide as the active center which will break to form radicals so that the expected number of percent of grafting will increase. The effect of ozonation time on the percent of grafting on copolymer PP-g-PAA is shown in Figure 1.

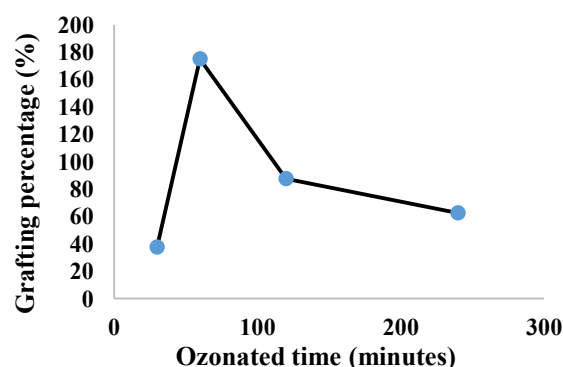


Figure 1. Effect of ozonation time on percent grafting of poly(acrylic acid)

It is seen that the optimum grafting percentage occurs in PP with a 60 minute ozonation time. At 30 minutes of ozonation time, the percentage of grafting increased but not significant because with the amount of free radical (active sites)

Table 1. Characterization of PP, Ozonated PP, and PP-g-PAA using FTIR

Functional Group	Wavenumber (cm ⁻¹)					
	PP	Ozonated PP	PP-g-PAA (30 min)	PP-g-PAA (60 min)	PP-g-PAA (120 min)	PP-g-PAA (240 min)
C-H	2721.56	2721.56	2721.56	2721.56	2721.56	2721.56
CH ₂	1467.83	1467.83	1450	1467.83	1467.83	1467.83
CH ₃	1365.60	1365.60	1375	1365.60	1365.60	1365.60
C-O	-	1291.66	1250	1290	1298.09	1290
C=O	-	-	1708.33	1708.33	1700	1708.93
O-H	-	-	3188.33	3188.33	3190.26	3190.26

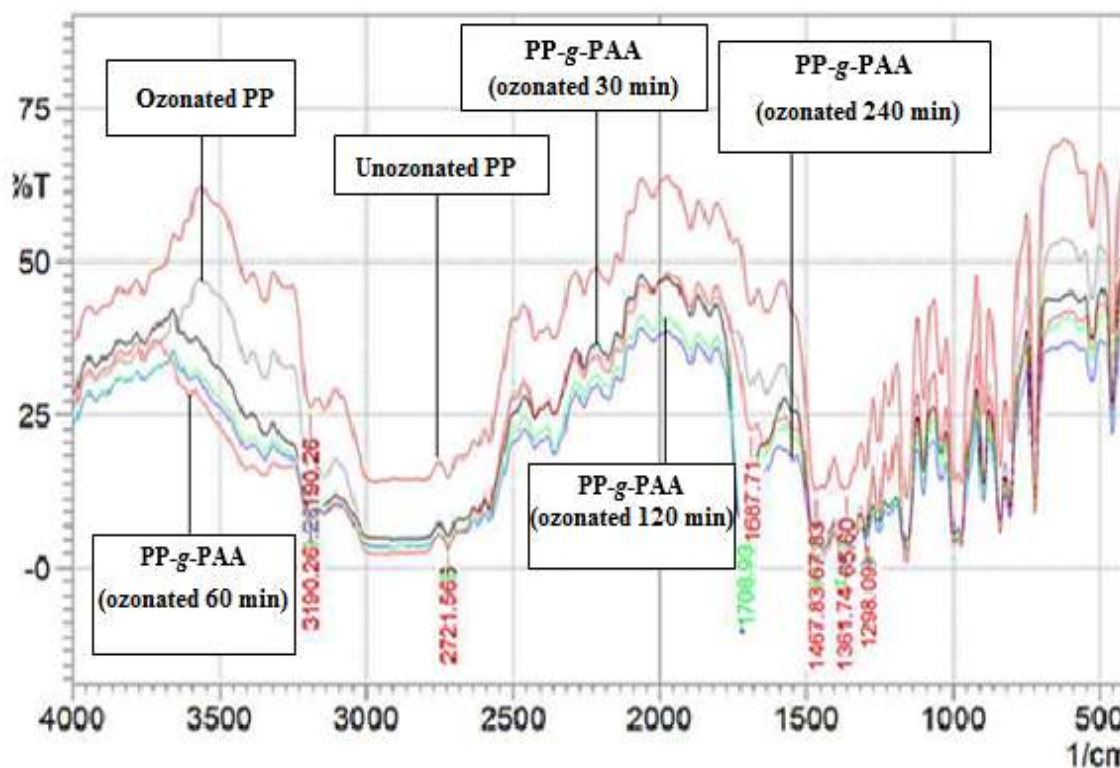


Figure 2. FTIR spectrums of bare PP (red), ozonated PP (grey), PP-g-PAA ozonated 30 min (black), PP-g-PAA ozonated 60 min (light red), PP-g-PAA ozonated 120 min (green), PP-g-PAA ozonated 240 min (light blue)

which was small so intensity of intermolecular collision of AA monomer is also small so the propagation rate of polycrystalline homopolymer poly(AA) becomes slow and leads the chain of poly homopolymer (AA) that grafted on PP to be short. The 60 minutes of ozonization time was the optimum ozonization time with the highest percentage of grafting was 175%. At a longer ozonization time, the rate of elongation of the homopolymer chain will increase so that it can be concluded that at the 60 minutes of ozonization time the propagation rate of the homopolymer chain of poly (AA) was very rapid, resulting in radically homopolymer poly(AA) which is grafted onto the active side of the polymer PP become long. This shows that the PAA can be grafted on the surface of an ozonated PP film. At a longer ozonation time at 120 minutes and 240 minutes there was a decrease in percentage of grafting. This is caused by too long ozonation time resulting the formation of radical long-chain poly(AA) homopolymer. This is evidenced by the very high viscosity of the solution (so thickened) that the radical homopolymer poly (AA) will be difficult to join the active side of the PP due to the very slow radical homopolymer movement so that only a small amount of poly(AA) was grafted onto the PP.

Homopolymerization is characterized by the presence of viscous fluid in the copolymer mixture. The considerable time difference of ozonation will give a different percentage of grafting. The best ozonation time for each grafting system is not always the same. It is highly dependent on various factors such as the solvent type and the polymeric material.

Characterization of PP-g-PAA Copolymer with FTIR

To determine the occurrence of grafting on PP film, the testing of infra red absorption wave was conducted using FTIR. The formation of copolymer PP-g-PAA can be evaluated by comparing the FTIR spectra of unozonated PP and

ozonated PP with PP-g-PAA with various ozonization times. The FTIR spectral function groups are shown in Table 1.

In Table 1 and Graphic 1, it is seen that PP film spectra before ozonization shows absorption with a strong peak. This shows the basic structure of a simple and linear nonpolar polymer. The strong absorption band of this film was seen in the area of 2721.56 cm^{-1} which is the vibration of CH groups and in the 1467.83 cm^{-1} region which is the vibration of the methylene group (-CH₂-), whereas in the wave number 1365.60 cm^{-1} is the vibration of the methyl group (-CH₃-). These absorption bands are typical absorption for polypropylene. If the spectrum was compared with the ozonated PP film and the PP-g-PAA, then it can be seen that there was a significant difference in the absorption spectrum. The new absorption bands appearing on the absorption spectrum of ozonated PP include the emergence of CO group vibrations at wave numbers 1291.66 cm^{-1} , vibration of -C=O groups at wave numbers 1708.33 cm^{-1} and vibration of -OH groups at wave numbers 3188.33 cm^{-1} . The emergence of new (additional) absorption bands from the Poly(Acrylic Acid) proves that AA has been grafted on the PP film. As the PP film ozonation time increases, it can be seen that the emerging spectral absorption for vibration of the -C=O, -C-O and -OH groups was getting stronger. This indicates that poly(acrylic acid) has been grafted onto PP film. Pure PP film spectra, PP ozonation film, and PP-g-PAA with various variations of ozonization time have some similar absorption. This indicates that the PP film modification will still provide the same infrared spectrum and the grafting process will not affect the absorption peak in pure PP film. This suggests that grafting techniques with the ozonation process as an active site builder will not affect the original structure of the PP film.

Characterization of PP-g-PAA Copolymer with LIBS

To determine the occurrence of grafting on PP film, the quantitative analysis of elements that C, H, and O on PP-g-PAA has done using Laser Induced Breakdown Spectroscopy (LIBS). This analysis in this study is to determine the level of elements present in the sample expressed by the intensity of emissions. The formation of PP-g-PAA grafting copolymers can be evaluated by comparing the emission intensity of C, H, and O at a pure PP film with the emission intensity of C, H, and O at ozonated PP film and PP-g-PAA with various ozonization time. C, H, and O elements in pure PP film, ozonated PP film, and PP-g-PAA with various time of ozonization have different emission intensity values.

From Graphic 3-5, it is seen that the emission intensity of C, H and O at 60 minutes is the highest emission intensity compared to 30 minutes, 120 minutes and 240 minutes of ozone time. This is due to the amount of PAA that is grafted on a 60-minute ozonated PP film was the highest. The emission intensity of C, H and O atoms increases when the PP film was ozonated means that there have been active sides on the PP film through the ozonization process. The higher the percentage of grafting, the emission intensity of C, H and O atoms increases. The emission intensity of C, H and O atoms based on percentage of PP-g-PAA grafting at various time variations of ozonation.

Water Absorption Capacity of PP-g-PAA Copolymer

The grafting copolymerization of AA to the PP film matrix could change the surface of PP film which was previously hydrophobic to be hydrophilic by the presence of AA which is grafted on the PP film so it has the ability to absorb water. Water absorption of PP-g-PAA after soaked in aquades for 24 hours can be seen in Figure 6 as a function of percent grafting.

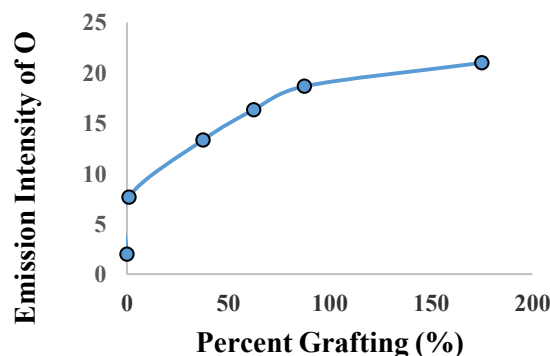


Figure 3. Effect of percent grafting of poly(acrylic acid) on intensity of oxygen

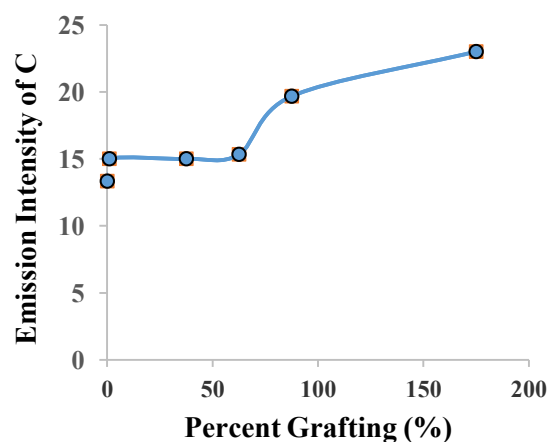


Figure 4. Effect of percent grafting of poly(acrylic acid) on intensity of carbon

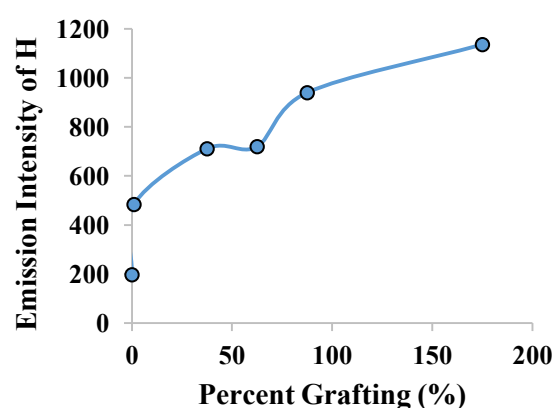


Figure 5. Effect of percent grafting of poly(acrylic acid) on intensity of hydrogen

Based on the graphic 6, it can be seen that the water absorption of PP-g-PAA increased with the increasing number of AA that grafted on PP film. At 37.5% grafting rate, water absorption of PP-g-PAA film was not too significant because

AA was grafted on PP film was still too small. While the percentage of grafting 175% was the optimum water absorption with a water absorption percentage of 212.5%. At a high percentage of grafting, water that can be adsorbed by PP film will be higher. This relates to the molecular structure of the carboxylate group present in the PP-g-PAA film. The carboxyl group (R-COOH) derived from poly(acrylic acid) was responsible for the water absorption process. This is due to the carboxyl group having the ability to bind water molecules by forming hydrogen bonds between carboxyl groups with water molecules. In the percentage of grafting 87.5% and 62.5% there is a decrease in water absorption percent. This was caused by the amount of AA that grafted on PP film decreased so that there was a decrease in the percent water absorption. The more carboxyl (R-COOH) groups attached to the PP film, the more hydrogen bonds were formed so the water absorbed by the PP film will be higher. Before grafting, the PP film was hydrophobic and has a smaller density than water, which is 0.905 g/cm^3 [2]. After grafting copolymerization, the PP-g-PAA becomes hydrophilic and has a larger density than water and forms canals that are capable of transferring protons (H^+).

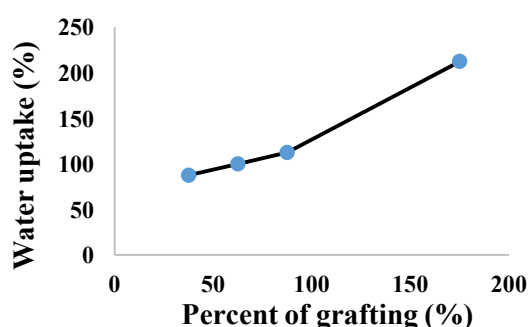


Figure 6. Effect of percent grafting of poly(acrylic acid) on water uptake of PP-g-PAA

The inclusion of water molecules into the PP-g-PAA polymer matrix will increase the pore size of film and film thickness due

to swelling. This water absorption ability was expected to contribute positively to ion exchange capacity. In this study, the water absorbance capacity obtained was greater than the percentage of grafting. This proved that the surface of the original film was hydrophobic has turned into hydrophilic after grafted with PAA. This water-binding ability is demonstrated by the development of the membrane in water which is strongly influenced by the crystallinity, the matrix of the polymer membrane, and the number of hydrophilic groups.

The exchange capacity of PP-g-PAA membrane cations on Cu^{2+} ions can be done by reacting PP-g-PAA film with Cu^{2+} solution as a function of percent grafting. The Cu^{2+} ion exchange test was performed on PP-g-PAA film with various percentage of grafting at pH 7. In this study, first PP-g-PAA film was added into Cu^{2+} solution at 250 ppm and then stirred for 1 hour. Moments after the reaction, the white-colored PP-g-PAA film turned light blue. This proved that PP-g-PAA film has absorbed Cu^{2+} ions. Based on Table 2, the highest ion exchange capacity of Cu^{2+} was in PP-g-PAA with a time of 120 minutes of ozonation. The PP-g-PAA membrane uptake of large size of Cu^{2+} ions was due to the ability of the carboxyl groups present in AA capable of forming a stable chelate complex with Cu^{2+} ions.

The capacity of the exchange of Cu^{2+} ions in PP-g-PAA with ozone time variations was not significant due to the amount of PAA attached to the PP film slightly so that the ability of the carboxyl groups present in AA capable of forming a stable chelate complex with Cu^{2+} ions was also small. In addition, the active sides formation of PP with an ozone time of more than 120 minutes does not occur anymore because all possible sides of peroxide on PP surfaces were already oxidized so that the number of PAAs that were grafted on the PP was small. The high density active sides on PP cause difficulties of Cu^{2+} ions to fill the active side of the PAA chain to exchange with H^+ . Small

Table 2. Cation Exchange Capacity of The PP-g-PAA on Cu²⁺

Grafting percentage (%)	Initial concentration of Cu ²⁺ (mg/L)	Residual concentration of Cu ²⁺ (mg/L)	Absorbed concentration of Cu ²⁺ (mg/L)	Capacity of the exchange of Cu ²⁺ (mek/g)
37.5	250	3.0811	246.9189	1.5541
62.5	250	3.1006	246.8994	1.5540
87.5	250	2.9963	247.0037	1.5547
175	250	3.0102	246.9898	1.5546

amount of Cu²⁺ ions which exchange with H⁺ results the insignificant of Cu²⁺ ion exchange capacity.

The insignificant Cu²⁺ ion exchange capacity can also be caused by high PP density causing PP matrix did not swelled so that the ability of PP-g-PAA to absorb Cu²⁺ was limited or did not followed the improvement of grading percent of grafting although PP-g-PAA has high ability to absorb water. Otherwise, the Cu²⁺ ion exchange capacity which did not followed the percentage of grafting can be caused by the pH of the pH 7 solution where in the pH 7, the intercellarboxylic hydrogen bond was still difficult to break down (still dominant). The hydrogen bond will break at an alkaline atmosphere or a pH of more than 7. This results in insignificant result of Cu²⁺ ions exchange capacity and the PP-g-PAA swelling capability was also limited.

4. CONCLUSION

The time of ozonization of the cation exchange membrane through the grafting copolymerization of PAA on the PP film was obtained at the time of ozonization of PP for 60 minutes. Furthermore, the ion exchange capacity of the PP-g-PAA copolymer as the highest cation exchange of Cu²⁺ was 1.5547 meq/gram.

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