

Modification of PTFE Flat Sheet Film *via* Radiation Induced Grafting Polymerization with Acrylic Acid

(Modifikasi Filem Kepingan Rata PTFE melalui Kaedah Pempolimeran Cangkuk Sinaran dengan Asid Akrilik)

FAEZEAH ABD GHANI, KHAIDZIR HAMZAH*, NOR HASIMAH MOHAMED & WAN NORHARYATI WAN SALLEH

ABSTRACT

Polytetrafluoroethylene (PTFE) flat sheet film was modified with acrylic acid (AAC) by radiation induced grafting polymerization (RIGP) method using electron beam. The adsorbed doses were varied from 10 to 50 kGy, time of grafting from 1 to 3 h and monomer concentration and temperature were kept constant at 30 wt. % and 40°C. The degree of grafting (D_g) and equilibrium degree of swelling (EDS) of the grafted films were then determined. The films were further characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), atomic force microscope (AFM), X-ray diffraction (XRD), and optical water contact angle. D_g within the range of 17% to 210% were obtained for doses from 10 to 50 kGy within time of grafting from 1 to 3 h. The grafted film (PTFE-g-AAC) showed increased hydrophilicity leading to an increase in EDS. The successful grafting process was confirmed by FTIR results that showed characteristics peaks for carbonyl and hydroxyl group and a decrease in crystallinity for the PTFE-g-AAC film. SEM images showed that PTFE-g-AAC films had less fibrillar compared to PTFE film and was consistent with the decrease in roughness for the PTFE-g-AAC film. This study indicated that modifying PTFE film by grafting AAC could significantly improve the hydrophilicity of PTFE film. The PTFE-g-AAC films has potential as a heavy metal adsorbent as it can remove at least 75% of Fe ion and 50 % of Pb ion from competitive media.

Keywords: Acrylic acid; adsorbent; polytetrafluoroethylene; radiation grafting

ABSTRAK

Filem kepingan rata politetrafluoroetilena (PTFE) telah diubah suai dengan asid akrilik (AAC) melalui kaedah pempolimeran cangkuk sinaran (RIGP) menggunakan alur elektron. Dos terserap diubah daripada 10 sehingga 50 kGy, masa cangkukan dari 1 sehingga 3 jam manakala kepekatan monomer 30% pada suhu 40°C. Darjah pencangkukan (D_g) dan darjah keseimbangan pengembangan (EDS) filem ditentukan. Seterusnya filem dianalisis menggunakan spektroskopi transformasi Fourier inframerah (FTIR), mikroskopi pengimbas elektron (SEM), mikroskopi tenaga atom (AFM), pembelauan sinar-X (XRD) dan sudut sentuhan optik. Keputusan diperoleh menunjukkan D_g berada pada julat antara 17% sehingga 210% untuk dos 10 hingga 50 kGy pada masa cangkukan antara 1 sehingga 3 jam. Filem yang dicangkuk (PTFE-g-AAC) menunjukkan peningkatan sifat hidrofilik yang memberi kesan kepada peningkatan EDS. Keberhasilan pencangkukan dapat disahkan melalui FTIR iaitu kewujudan puncak bagi kumpulan berfungsi karbonil dan hidroksil serta penurunan sifat hablur filem PTFE-g-AAC. Imej SEM membuktikan filem PTFE-g-AAC mempunyai kurang fibril berbanding filem PTFE dan konsisten dengan penurunan darjah kekasaran untuk PTFE-g-AAC. Kajian ini menunjukkan dengan mengubahsuai filem PTFE dengan AAC secara pempolimeran cangkuk sinaran dapat meningkatkan sifat hidrofilik filem PTFE. Filem PTFE-g-AAC mempunyai potensi sebagai penjerab logam berat sebagaimana ia dapat menyingkirkan 75% ion Fe and 50% ion Pb daripada media yang kompetitif.

Kata kunci: Asid akrilik; pengrahan radiasi; penjerab; politetrafluoroetilena (PTFE)

INTRODUCTION

Polytetrafluoroethylene (PTFE) has been widely known as one of fluorocarbon polymers that has strong bonds exist between fluorine and carbon atoms. This specific molecular structure gives PTFE good combination of chemical, physical, and electrical properties (Qian et al. 2016). Due to low PTFE surface energy, its surface properties such as hydrophilicity, adhesivity and printability tend not to meet the requirements for industrial applications (Sun et al. 2018). In order to tackle these drawbacks, various

enhancements have been made to modify its surface properties such as crosslinking (Wang et al. 2019), laser ablation (Qin et al. 2019) and (Yin et al. 2018), atomic layer deposition (Krumpolec et al. 2016), co-deposition (Li et al. 2019) and (Song et al. 2017), plasma treatment (Cheng et al. 2019) and radiation induced grafting polymerization (López et al. 2019; Park et al. 2016a).

RIGP is an advantageous method of modifying base polymers because grafting may result in the superimposition of properties related to the backbone and grafted chain.

However, PTFE films will undergo degradation by exposure to radiation hence the tolerance dose has been reported to be between 5 and 60 kGy, depending on the irradiation condition (Martínez et al. 2018). By using the right choice of monomers with exclusive functional group, new molecular functionalities can be impregnated onto base polymer by RIGP (Taimur et al. 2018). Figure 1 shows the mechanism of RIGP of polymer by pre-irradiation method. Briefly, the trunk polymer PTFE was irradiated by electron beam in vacuum or inert gas to produce stable free radicals. These stable free radicals were then reacted with monomer within the required time.

There are numerous variety of graft copolymers that can be formed by RIGP. The monomer used for grafting will determine the type of copolymer formed. The classification is either neutral or ionic copolymer. Examples of neutral monomers are perfluoroacrylate and acrylamide (Magaña et al. 2015). Ionic copolymer may be divided into anionic, cationic and bipolar. Example for anionic monomers are polystyrene-divinylbenzene (PS/DVB) (Kaltz et al. 2018) and glycidyl methacrylate (GMA) followed by reaction with triethyl amine (Mahmoud et al. 2016). Meanwhile acrylic acid (Jiang et al. 2019), poly(sodium 4-styrenesulfonate) (PSS) (Chen et al. 2018) and GMA followed by reaction with sodium sulphite (Shin et al. 2017) resulted in cationic copolymer. Example of bipolar monomer is GMA then followed by reaction with amino acid (Selin & Emik 2018).

There are two types of monomers; functionalized monomers and non-functionalized monomers. Functionalized monomers are the monomers that provide the desired properties when copolymerized on polymer substrate. As an example, perfluoroethyl alkyl acrylate produces highly fluorinated graft side chains which result

in a very hydrophobic copolymer (Gengec et al. 2016) while acrylamide results in hydrophilic copolymer (Sh et al. 2018). Meanwhile, non-functionalized monomers are another option to subject the copolymer to post grafting reaction where side chain is chemically converted to give desired functionality. GMA is one of the examples that produces epoxy functional side chain groups (Kim & Lee 2017). The epoxy group can then be reacted with other materials including imidazole (Selambakkannu et al. 2018), ammonium 12-molybdophosphate (AMP) (Seko et al. 2018) and amines (Gao et al. 2017).

Functionalized monomers that offer carboxylic group to the trunk polymer will modify the hydrophilic properties of the graft PTFE copolymer. The electronegative carboxyl and hydroxyl group anchored on the film surface will lead copolymer to become potential metal ion adsorbent (Wang et al. 2018). In this study, acrylic acid (AAC) was chosen as the grafting monomer to introduce carboxylic acid groups onto the surface of PTFE film *via* radiation grafting. The effect of radiation dose and time of grafting on D_g and swelling behaviour were investigated through various characterization techniques including FTIR, SEM, AFM, XRD and optical water contact angle measurement. Moreover, the efficacy of the grafted sample was discovered for the removal of metal ions from aqueous media.

MATERIALS AND METHODS

MATERIALS

PTFE polymer in the form of aqueous dispersion (FR301B) was purchased from 3F New Materials Co., Ltd., Shanghai, China. Ethylene glycol (6207) additive was supplied by

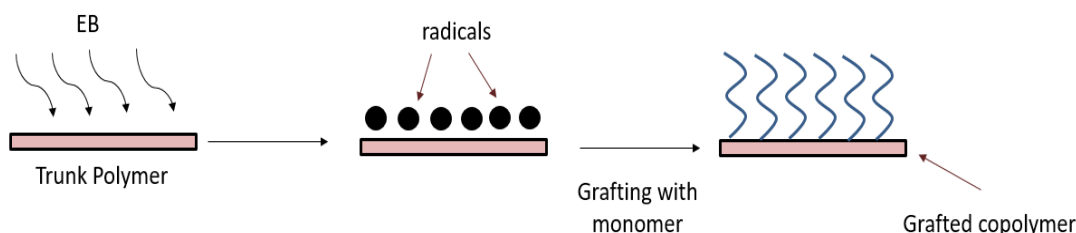


FIGURE 1. Mechanism of radiation induced grafting polymerization of polymer by pre-irradiation method

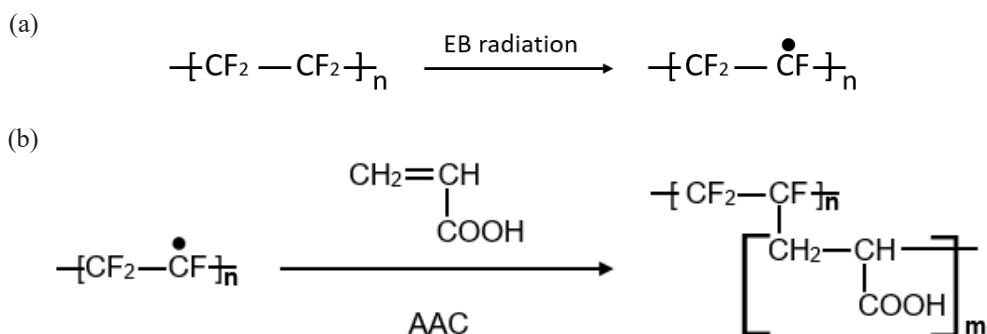


FIGURE 2. Reaction schemes for (a) preirradiation step (represent radical) and (b) the preparation of PTFE-g-AAC

Merck. Sodium benzoate (144.11) salts was provided by Riedel-de-Haen. AAC and methanol were purchased from Merck and used without purification. Cations standard solutions 1000 ppm (BDH Chemicals) were obtained from Bahagian Alam Sekitar (BAS) Agensi Nuklear Malaysia.

PREPARATION OF PTFE FLAT SHEET FILM

PTFE flat sheet film was prepared by casting and sintering technique as described in the previous study (Ghani et al. 2017). Briefly, sodium benzoate was dissolved in the mixture of PTFE and ethylene glycol solution and then casted on glass plate. The film was then sintered at 385°C in an oven and was leached by immersing in hot water. The resulted PTFE flat sheet film was used as substrate for irradiation and grafting process.

PREPARATION OF RADIATION INDUCED GRAFT POLYMERIZATION OF PTFE FLAT SHEET FILM

Irradiation of PTFE Flat Sheet Film PTFE flat sheet film was cut into 2.5 cm × 2.5 cm sized pieces. The film was then washed with acetone and dried in a vacuum oven (1 torr) at 50°C for 1 h. PTFE film was purged with nitrogen gas in polyethylene bag and sealed. The film was placed on dry ice and irradiated with an electron beam (EB). Parameters of the EB and irradiation conditions are given in Table 1. After irradiation, the film was quickly stored at -80°C.

TABLE 1. Electron beam parameters and irradiation conditions of PTFE flat sheet film

Irradiation parameter	Conditions
Energy	2 MeV
Current	3 mA
Dose	10-50 (10,20,30,40,50) kGy
Dose per pass	10 kGy
Atmosphere	Nitrogen

Copolymerization of PTFE with AAC AAC monomer solution was prepared by adding 30 wt. % of AAC to distilled water. The monomer solution was stirred at room temperature with magnetic stirrer for 10 min followed by stirring with high speed homogenizer for 15 min and de-aerated with nitrogen gas. The monomer was sucked into an evacuated glass ampoule in which the irradiated PTFE film was transferred. The glass ampoule was placed in water bath to initiate graft polymerization of AAC onto PTFE film. The grafting reaction was then allowed to react from 1 to 3 h at 40°C. After the reaction, the grafted film was recovered from the ampoules and washed repeatedly with hot water and methanol to remove homopolymer. The grafted film was dried overnight at 40°C. D_g was calculated by gravimetric method using (1):

$$D_g(\%) = (W_g - W_o) / W_o \times 100 \quad (1)$$

where W_o and W_g represent the weights of initial and grafted film, respectively. The PTFE grafting reaction is schematized in Figure 2.

POTENTIAL ADSORPTION STUDY OF PTFE-G-AAC FILM

Metal ions adsorption of the grafted PTFE films were performed by batch adsorption to study the potential use as an adsorbent of heavy metal. Several cations which commonly exists in waste water were selected namely cadmium (Cd), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), zinc (Zn) and zirconium (Zr). Fifty mg of adsorbent weight were soaked in 20 mL cation solution with 10 ppm of metal solutions for 4 h at pH6. The experiment were carried out at room temperature. Cations concentration were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Perkin-Elmer NexION 350× (United States). The removal efficiency was calculated by the following equation:

$$\text{Removal efficiency (\%)} = (C_o - C_e) / C_o \times 100 \quad (2)$$

where C_o and C_e are initial and final cations concentrations, respectively.

CHARACTERIZATION OF PTFE-G-AAC FILM

The grafting monomers was confirmed by ATR-FTIR Tensor II, Bruker (United State). The spectra were measured in a wavenumber range 4000-500 cm^{-1} . Crystalline structures of the grafted PTFE (PTFE-g-AAC) film was analysed by XRD Panalytical X'Pert Pro MRD (Netherlands) equipped with a Cu $K\alpha$ radiation source (40 kV, 30 mA). The sample was scanned in the range of diffraction angle 2θ from 5° to 90°. Crystallinity index (CrI) was calculated using the intensity values corresponding to the diffraction of the crystalline structure and the amorphous fraction following Segal method (Singha et al. 2014).

$$\text{CrI (\%)} = (I_{100} - I_{\text{am}}) / I_{100} \times 100 \quad (3)$$

where I_{100} is the intensity of the crystalline peak at the maximum; and I_{am} is the intensity at the minimum. The changes in terms of hydrophilicity of PTFE-g-AAC film were assessed based on the measurement of the static contact angle of water using Attension Optical Tensiometer Contact Angle Meter (Theta, Biolin Scientific., Stockholm, Sweden) at 25°C and at 40-50% relative humidity. The average of five measured values for each sample were taken as its optical contact angle. EDS was determined gravimetrically. The PTFE-g-AAC film was immersed in distilled water for 24 h at room temperature. The sample was removed from the distilled water and filter paper was used to remove any surface water before the weight of sample was determined. The EDS was calculated using the following equation:

$$\text{EDS (\%)} = (W_s - W_g) / W_g \times 100 \quad (4)$$

where W_g and W_s represent the weights of the initial and swollen grafted PTFE flat sheet films. The surface topography of the PTFE and PTFE-g-AAC films were studied using a SEM Phenom, G2 Pro (Eindhoven, The Netherlands). Surface roughness of the PTFE films were analysed at room temperature by AFM JPK NanoWizard II (Germany) in $5 \mu\text{m} \times 5 \mu\text{m}$ scanning field.

RESULTS AND DISCUSSION

EFFECT OF IRRADIATION DOSE AND GRAFTING TIME ON D_g

The radiation induced grafting of AAC onto PTFE film was carried out at two different conditions: irradiation dose from 10 to 50 kGy on D_g ; and grafting time from 1 to 3 h. Figure 3 shows the D_g obtained with different irradiation dose and grafting time. It can be seen that the D_g increases gradually with increasing irradiation dose and time of grafting. At 2 h of grafting, D_g increased from 36% to 98% when the irradiation dose increased from 10 kGy to 50 kGy. This can be explained by the fact that with increasing irradiation dose, the production of radicals on the PTFE film increased. Thus, more radicals were available to take part in the grafting polymerization reaction hence the increase in D_g . This results is supported by Hegazy (2012) that grafted AAC onto non-woven polypropylene sheet. Meanwhile at 10 kGy, D_g increased from 16% to 57% when the grafting time increased from 1 to 3 h. As the time of grafting increased, the number of monomer molecules that diffused onto PTFE chains increased. Furthermore, the monomer also reacted with grafted AAC to form longer chains thus resulted in higher D_g . Similar trend was reported

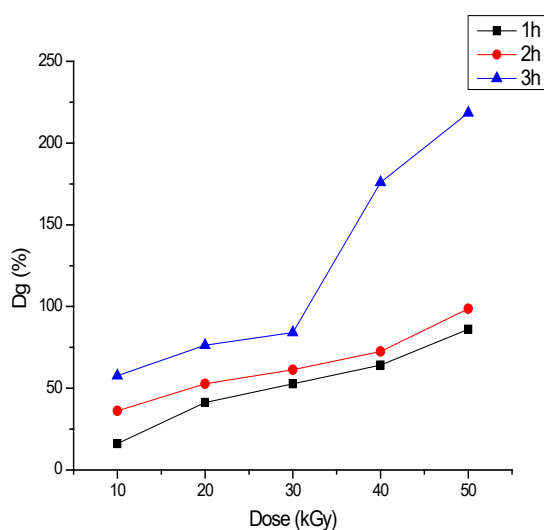


FIGURE 3. Effect of irradiation dose and grafting time on D_g

for grafting of poly(methyl methacrylate) and poly(vinyl imidazole) onto PTFE films (López et al. 2019).

FTIR ANALYSIS OF PTFE-G-AAC FILM

Figure 4 indicates FTIR spectra of the PTFE and PTFE-g-AAC films. FTIR spectra for PTFE film shows strong absorption bands at 1200 cm^{-1} and 1146 cm^{-1} due to stretching vibrations of CF_2 in PTFE film. New bands were observed in the FTIR spectra for PTFE-g-AAC film. Most noticeably, peak at 1712 cm^{-1} which is assigned to carbonyl band $\text{C}=\text{O}$ of the carboxylic acid. Furthermore, the PTFE-g-AAC film displays a very broad band at $3000\text{-}3750 \text{ cm}^{-1}$ attributed to O-H stretching vibration, while a C-H stretching vibration observed at $2850\text{-}2970 \text{ cm}^{-1}$ and the C-H bending vibration at 1470 cm^{-1} . These new bands observed after grafting confirmed the successful introduction of AAC onto PTFE flat sheet film. Similar findings was reported by Essawy et al. (2017).

CRYSTALLINITY ANALYSIS OF PTFE-G-AAC FILM

XRD analysis of PTFE and PTFE-g-AAC films were performed to clarify the changes in their crystallinity as presented in Figure 5. The PTFE film shows an intense peak centered at 17.9° corresponding to the diffraction from (1 0 0) planes with a spacing of 4.9 \AA in semicrystalline PTFE that consists of lamellar crystal. It can be seen that the intensity of the PTFE-g-AAC diffractogram, representing the crystallinity decreases after grafting polymerization with AAC. This decrement is also proven by the decrease of CrI from 99.8% for PTFE to 98.6% for PTFE-g-AAC film. This is due to the dilution of the crystalline region of PTFE by incorporation of grafting polymerization hydrophilic AAC chains. This finding is supported by Moawia et al. (2016). The interaction of the hydrogen bond

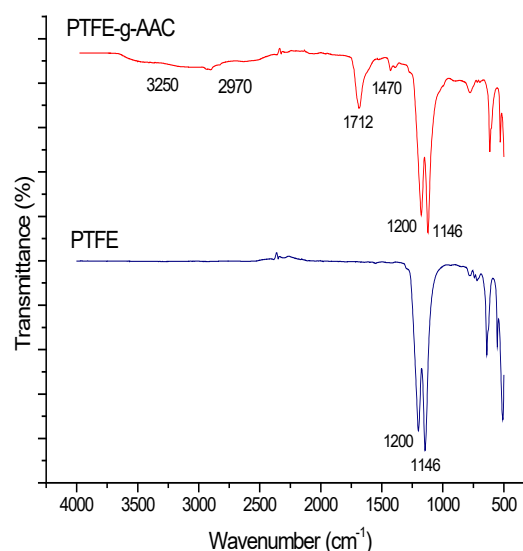


FIGURE 4. FTIR-ATR spectra of PTFE and PTFE-g-AAC flat sheet film

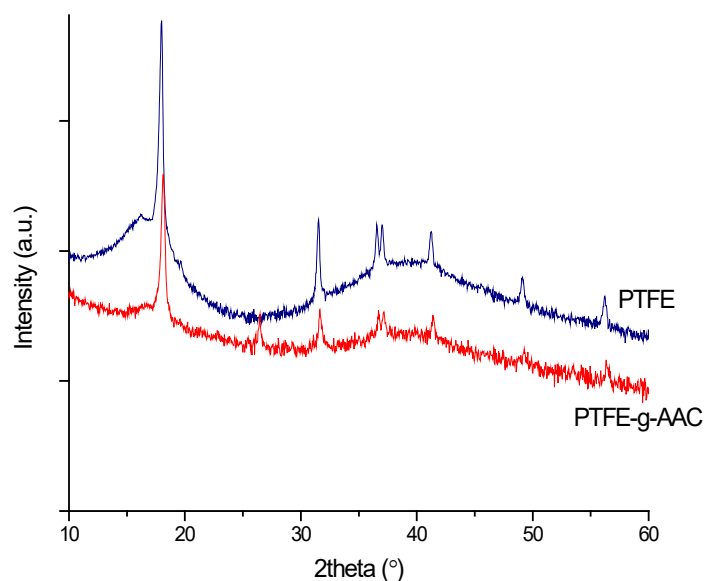


FIGURE 5. XRD diffractogram of the PTFE and PTFE-g-AAC flat sheet film

that exist in COOH groups of AAC thus enhanced the permeability of water throughout the amorphous layer of the film as supported by Wang et al. (2010). Furthermore, the diffraction peaks display a noticeable right-shift after grafting polymerization with AAC. This indicates that the unit cell parameters or interlayer space of PTFE was slightly expanded due to AAC grafting polymerization as supported by Xu et al. (2012).

PTFE film is super-hydrophobic. This is due to the fluorine atoms in the external layer of the chemical structure $[-(\text{CF}_2-\text{CF}_2)-]$ that possessed high electronegativity and have strong interaction with carbon. After grafting polymerization with AAC, the contact angle was reduced to 104° . This decrement was due to the existence of hydrophilic group such as carboxyl and hydroxyl group in PTFE-g-AAC film. This findings was supported by Yang et al. (2013) that modified PVDF films by radiation induced grafting.

HYDROPHILICITY ANALYSIS OF PTFE-G-AAC FILM

The hydrophilicity of PTFE and PTFE-g-AAC film are presented in Figure 6. The optical water contact angle of PTFE film is 147° , which is greater than 90° , indicating

SWELLING BEHAVIOUR OF PTFE-G-AAC FILM

Figure 7 indicates the increase in the EDS of PTFE-g-AAC film with increasing D_g . This is due to the increase of the

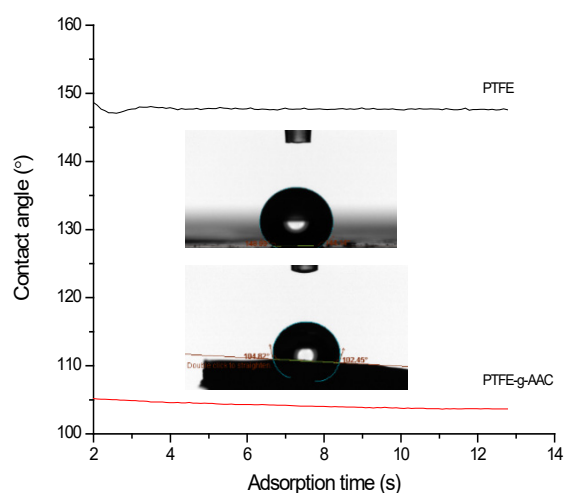


FIGURE 6. Curve of optical contact angle of PTFE and PTFE-g-AAC subjected to adsorption time. The inserts in the middle are the photographs of the water droplet on the films

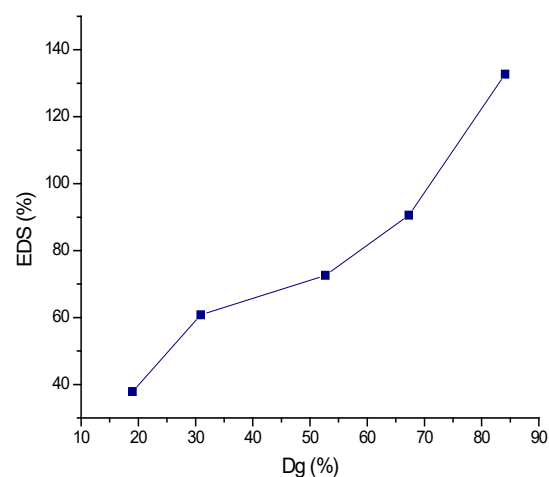


FIGURE 7. Equilibrium degree swelling as a function of degree of grafting D_g

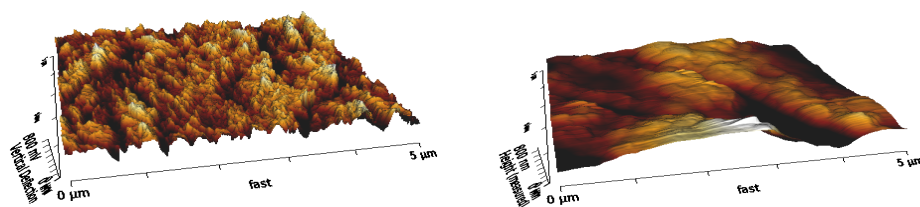


FIGURE 8. AFM images and surface roughness parameter of (a) PTFE and (b) PTFE-g-AAC flat sheet films [Ra: average roughness, Rt: peak to valley roughness, Rq: RMS roughness]

hydrophilic groups introduced into the grafted film with the increase of D_g . Moreover, the crystalline-amorphous changes in the film were another important factor influencing the water uptake. Once the crystallinity of the grafted film decreased, the water molecules could easily penetrate the non-crystalline region. As a result, the water uptake increased with an increasing grafting level and decreasing crystallinity. These results suggested that the degree of swelling depends mainly on the degree of grafting, amount of the hydrophilic groups in the PTFE-g-AAC film. Similar trend was reported by Abdel et al. (2014).

SURFACE ROUGHNESS ANALYSIS OF PTFE-G-AAC FILM

Figure 8 presents the AFM images and surface roughness parameter for the PTFE and PTFE-g-AAC films. It showed that the average roughness (R_a) decreased from 102.2 nm to 88.17 nm. The root mean square roughness (R_q) showed similar trends which was slightly down from 125.5 nm to 111.7 nm. These results are supported by Wu et al. (2019) that stated hydrophilic side chains could decrease the roughness of the surface. Furthermore, these changes of roughness parameters agree well with changes of hydrophilicity of the films, proposing that hydrophilicity may play a vital role in the surface roughness of the films. This findings is supported by Li et al. (2018) that enhancing water permeability of polyvinylidene fluoride membranes with carboxylated nanodiamonds. Interestingly, the peak

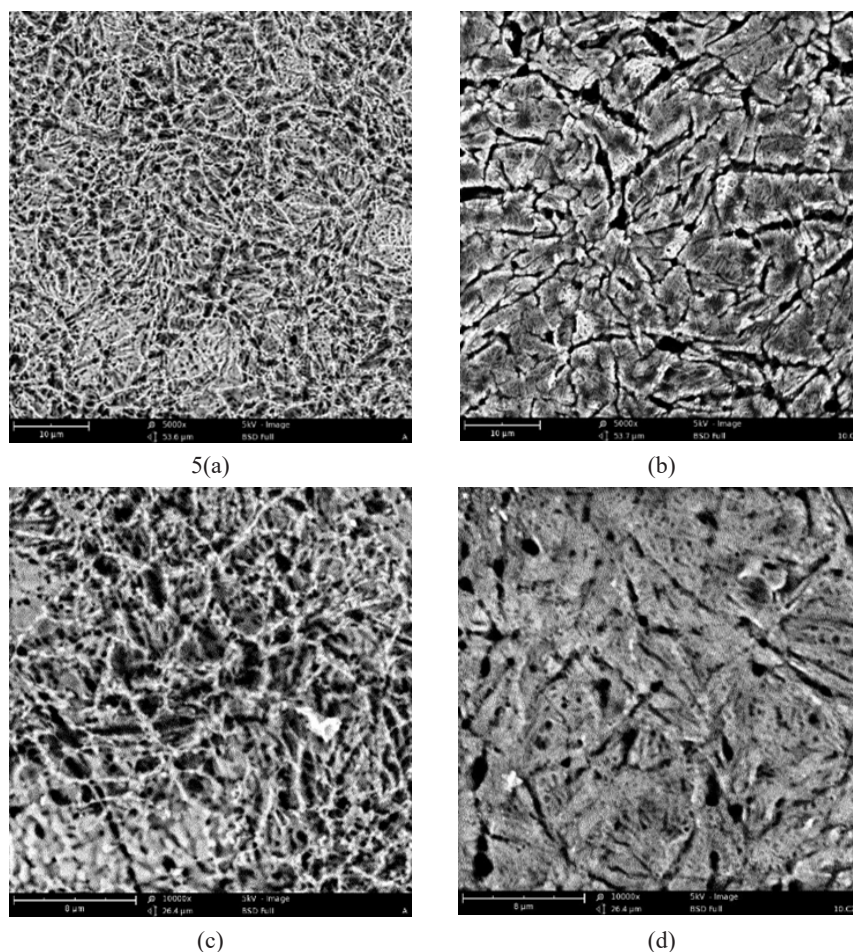


FIGURE 9. SEM images of the surface of (a) PTFE (b) PTFE-g-AAC at 5000 magnification; (c) PTFE (d) PTFE-g-AAC at 10000 magnification

to valley roughness (R_v) increased from 738.8 nm to 862.6 nm after PTFE film grafted with acrylic acid.

MORPHOLOGY OF PTFE-G-AAC FILM

The surface morphology of the PTFE and PTFE-g-AAC were examined by SEM as presented in Figure 9. The PTFE film was observed to contain fibrils interconnecting nodal region in the matrix (Figure 9(a) and 9(c)). The fibrils connecting the islands were randomly oriented in the film. This findings was supported by Hidzir et al. (2015) that grafted acrylic acid-co-itaconic acid onto ePTFE. Figure 9(b) and 9(d) shows less fibrillar regions meanwhile the islands region are clearly discernible correspond to grafting polymerization of AAC compared to Figure 9(a) and 9(c). This findings was consistent with Mohd et al. (2012) that grafting AAC onto expanded PTFE films.

ADSORPTION POTENTIAL STUDY OF PTFE-G-AAC FILM

A preliminary study was done to investigate the potential use of the PTFE-g-AAC film as heavy metal adsorbent in competitive media. Several metal ions which commonly exist in waste water were selected namely Cd, Fe, Ni, Pb, Zn and Zr. Figure 10 shows the removal efficiency of the grafted film towards metal ions. Obviously, the PTFE-g-AAC films show highest removal efficiency for Fe (75.8%) followed by Pb (53.1%) and Cu (33.9%). While only 20-25% for Cd and Zr, and below 10% for Ni and Zn ions can be removed by PTFE-g-AAC films. Therefore, the removal efficiency observed can be ordered in the following way: Fe > Pb > Cu > Zr > Cd > Zn > Ni.

There are some factors that could contribute for this selectivity of adsorption such as the size of the hydrated ion, hydrated-free energy, activity and electronegativity of

TABLE 2. Ionic properties, free energy of hydration and electronegativity of the metal ions

Metal ions	Ionic radius (\AA) ^a	Hydrated radius (\AA) ^b	Hydration-free energy (kJ/mol) ^a	Electronegativity ^c
Cd	0.95	4.26	-1755	1.83
Cu	0.73	4.19	-2010	1.87
Fe	0.78	4.28	-1840	1.90
Ni	0.69	4.04	-1980	1.33
Pb	1.18	4.01	-1425	1.69
Zn	0.74	4.30	-1955	1.65
Zr	0.72	-	-6790	1.91

^a The ionic radius and the hydration-free energy were obtained from Marcus (1994) ^b The hydrated radius was obtained from Nightingale (1959) ^c The electronegativity was obtained from Pauling (1960)

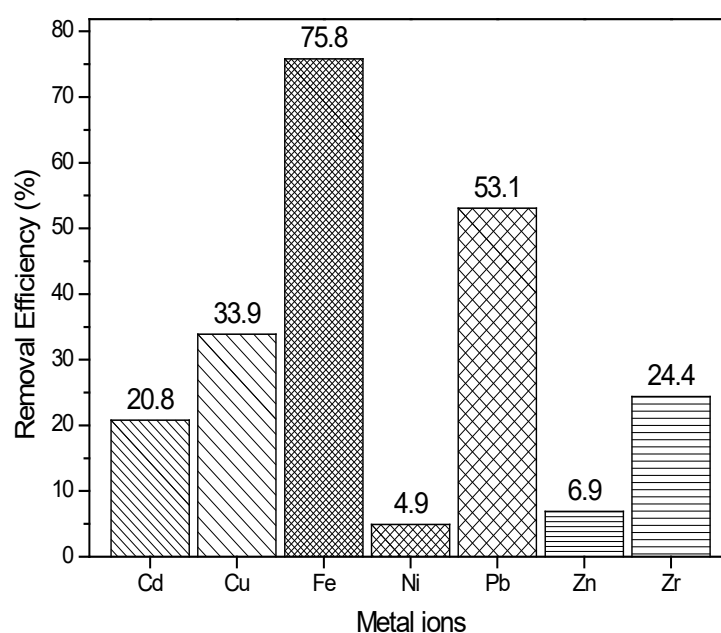


FIGURE 10. Removal efficiency of PTFE-g-AAC film towards metal ions

the metal ions (Jain et al. 2016; Liu et al. 2018). The hydrated radius, free energy of hydration and electronegativity data are shown in Table 2. The order of the hydrated radius is $Zn > Fe > Cd > Cu > Ni > Pb$ and the free energy of hydration is $Zr > Cu > Ni > Zn > Fe > Cd > Pb$. Meanwhile, the order of heavy metal reactivity is $Zn > Fe > Cd > Ni > Pb > Cu$ and electronegativity is $Ni > Cu > Pb > Fe > Cd > Zn > Zr$. The affinity of the metal ions is dependent on the electronegativity and the size of the hydrated ion. The smaller the radius and higher electronegativity lead to the higher affinity (Park et al. 2016b). Meanwhile, higher hydration of free energy may cause the metal ion to remain in the aqueous hence reduced the possibility of being adsorbed. According to the order of the hydrated radius, electronegativity and free energy hydrated, Pb should be the most favorable ion to be adsorbed. Nevertheless, it is noted that the removal efficiency of Fe is higher than Pb that may be due to reactivity of the Fe ion is higher than Pb. The adsorption of metal ions is probably due to hydroxyl and carbonyl groups present in the PTFE-g-AAC film which endowed it with strong affinity towards metal ions and form complexes, consistent with Xu et al. (2019).

CONCLUSION

This study has demonstrated the successful radiation induced grafting polymerization of AAC onto PTFE flat sheet film. The D_g was found to be dependent on the irradiation dose and the time of grafting. The higher the irradiation dose and longer reaction time, the higher the D_g . The surface of PTFE-g-AAC films showed significant changes from hydrophobic surface to hydrophilic surface that was demonstrated by optical water contact angle and swelling behaviour. XRD, ATR-FTIR, SEM and AFM were able to demonstrate the overall physicochemical changes including crystallinity, functional groups, morphology and surface roughness the film. In addition, PTFE-g-AAC film has the potential to be an adsorbent for metal ion removal from aqueous solutions. It was shown that at least 75% of Fe ion can be removed in competitive media.

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- Faezeah Abd Ghani & Wan NorHaryati Wan Salleh
Advanced Film Technology Research Centre (AMTEC)
Universiti Teknologi Malaysia
81310 Skudai, Johor Darul Takzim
Malaysia
- Faezeah Abd Ghani, Khaidzir Hamzah* & Wan NorHaryati Wan Salleh
UTM-MPRC Institute for Oil and Gas
Universiti Teknologi Malaysia
81310 Skudai, Johor Darul Takzim
Malaysia
- Khaidzir Hamzah*
Faculty of Chemical and Energy Engineering (FCEE)
Universiti Teknologi Malaysia
81310 Skudai, Johor Darul Takzim
Malaysia
- Nor Hasimah Mohamed
Radiation Processing Technology Division
Malaysian Nuclear Agency
43000 Kajang, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: khaidzir@utm.my

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