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γ -Ray Pre-Irradiated Grafting of Polytetrafluoroethylene Film Membrane

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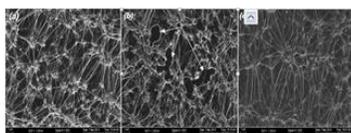
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Graphical abstract



Abstract

The changes induced by γ -ray pre-irradiated grafting of polytetrafluoroethylene (PTFE) with alkalamines such as Monoethanolamine (MEA), Diethanolamine (DEA) and Methyl-diethanolamine (MDEA) solvents were investigated. Samples of the commercially available fluoropolymer, i.e. PTFE film membranes were irradiated with ^{60}Co source γ -radiation with absorbed doses of 30 to 90 kGy. Effects of the grafting conditions of the amines onto the pre-irradiated PTFE, such as grafting time, reaction temperature and pre-irradiation doses on the resulting grafting yield are reported. The grafted PTFE was characterized by the FT-IR spectroscopy and FESEM. The gravimetric analysis showed that the maximum grafting yield obtained is 2.9% for the 30 kGy irradiated MDEA grafted PTFE (MDEA-g-PTFE) at 10 min grafting time. However, at 60 min grafting time the maximum grafting yield reduced to 1.05% for the same sample. Consequently, therefore, for the low dose γ -ray pre-irradiated samples, the effects of applied dose and grafting time were found to be remarkably insignificant.

Keywords: Amines; grafting; PTFE membrane; γ -ray irradiation

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1.0 INTRODUCTION

Fluoropolymers are a broad grouping of polymers with Fluorine as the main constituent either as a single or more atoms present with other monomers. Fluoropolymers such as polytetrafluoroethylene (PTFE), Teflon AF, Perfluoroalkoxy (PFA) and hexafluoropropylene (FEP) are known for their chemical stability and mechanical strength as the backbone of such fluoropolymers are formed of extremely strong carbon-carbon and carbon-fluorine bonds of 607 kJ/mole and 552 kJ/mole respectively [1]. This bond strength determines the further properties of the polymer, which categorizes the material to be the most chemically stable of all polymers. It also presents excellent thermal resistance. PTFE among the other fluoropolymers is regarded as the most stable fluoropolymer.

PTFE is a member of the fluoropolymer family with a superior property such as high chemical, mechanical stability, high resistance to plasticization, highly hydrophobic and organophobic [2]. In addition, PTFE has shown no sign of aging upon its application [3]. Thus, PTFE membrane has been used for a wide applications in separation technology; For instance, the hydrophobic property of PTFE membrane is exploited for Membrane Distillation (MD) in a desalination plant, its thermal resistance property for electrolyte membranes for fuel cell applications [4, 5] for ion exchange membrane [6], biocompatibility property for medical applications, its permeable properties exploited in a membrane gas contractor [3], and the high permeability property for gas separation membrane.

The high chemical inertness of the material makes it difficult to attempt any sort of improvement by means of chemical reactions. This particular fact sets limits to its application as a membrane for gas separation purposes. Modification of the membrane is then recommended specifically by the use of external high energy source [7]. Thus, activation of the PTFE polymer by the use of high energy source such as γ -ray radiation or electron beam radiation will lead to the creation of active sites and radicals [8, 9]. These active sites generated serve as grafting centers in the membrane matrix which can possibly accommodate the grafting of amine solvents on its membrane matrix. Besides the generation of active sites such as radicals, PTFE was reported to have improved its radiation resistance on the mechanical properties by crosslinking and grafting [2].

The radiation treatment of polymeric materials brings change in chemical resistance, thermal stability, surface properties and other characteristics [10]. This is caused due to the ionizing ability of the irradiation treatment. However, the overall change may depend upon the nature of the material, the dose rate applied, and the energy associated with the radiation [2, 11].

In general, radiation grafting can be carried out in either of three different techniques: pre-irradiation, peroxidation and mutual or simultaneous irradiation techniques [7, 12]. In the pre-irradiation technique, the backbone of the polymer is irradiated first in an inert gas medium or vacuum to form active sites such as free radicals and then treated with a monomer solution that to be grafted to [13]. In the peroxidation grafting method, the

polymeric membrane is subjected to high energy irradiation in the presence of air or oxygen as a result hydroperoxides or diperoxides are formed [14]. These peroxy groups are then treated with a monomer at high temperature to deactivate or decompose the radicals initiating grafting. On the other hand, with the mutual or simultaneous irradiation technique, the polymeric membrane and monomer solution are irradiated simultaneously to form free radicals and subsequent addition oxidation.

In this study, as the first attempt the pre-irradiated technique was employed to investigate the degree of grafting, the influence of the grafting conditions such as reaction time, reaction temperature and the applied dose during the pre-irradiation treatment. The best technique of radiation-induced grafting is the pre-irradiation technique. In this method, the ionizing radiation will create excited radicals on the backbone of the polymer. When the sample is immersed into the amine solution, the grafting reaction is initiated. The extent of grafting may be monitored by reaction time, radiation dose and the composition of graft solution [6]. There is no handling of expensive and poisonous initiators, and the monomer, which is to be grafted, is not subjected to irradiation but only to reactive sites on the irradiated polymer membrane. Bozzi *et al.* [15] reported that the common feature of the grafted PTFE films is the fairly homogeneous distribution of the active sites throughout the bulk of the film.

2.0 EXPERIMENTAL

2.1 Materials

Pristine PTFE film membranes were purchased from Merck Millipore Co. (FGPL29325) with pore size and porosity of 0.22 μm and 70% respectively. The amine solvents such as Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA) were also supplied by Merck Co. and used as received.

2.2 Grafting

The PTFE film of 127 μm thickness is first pre-irradiated by ^{60}Co source γ -ray at MINTech (Malaysian Nuclear Agency), and consequently active sites such as free radicals or ions are generated due to the breakage of the bonds and then immersed or soaked in pure amine solution. In order to investigate thoroughly, the γ -ray dose applied is varied throughout the experiments, i.e., identical samples are treated with varying doses of 30, 50, 70 and 90 kGy, while all other conditions are kept constant. Further, the samples are immersed in a sufficient amount of pure amine solvents for identical reaction time and grafting temperature. Again during the grafting step, it's crucial

to determine which amine group has the highest affinity to attach itself to the activated PTFE film which can possibly result in appreciable grafting yield. Since the three selected amines belong to different classes of amine functional group, such as primary, secondary and tertiary amine groups, these amines are expected to react differently leading to different values of grafting yield. The extent of grafting yield may differ, but the same functional group (-NH) is expected to react with the active sites within the membrane matrix. The immersed PTFE films are removed after the required time and drying in a vacuum dryer for 24 hours, until the material gives constant weight. The grafting step of the PTFE membrane is shown in Figure 1.

The Degree of Grafting (DOG) was determined by the simple method of gravimetric analysis computing the increase in weight of the membrane before and after grafting which is given according to the following equation:

$$DOG(\%) = \frac{w_g - w_o}{w_o} \times 100 \quad (1)$$

where w_g and w_o are sample weights after and before grafting, respectively [16, 17].

2.3 Characterization

The pristine and grafted PTFE membrane were characterized by the Field Emission Scanning Microscope VP-FESEM (Model SUPRA 55VPCarl Zeiss AG, Germany) for the study of the surface morphology, and Fourier Transform-Infrared Spectroscopy FT-IR (Model Spectrum One/BX, Perkin Elmer Inc.) to determine the constituents composition of the polymeric membrane material. The characterization tests were performed on the given pristine and grafted PTFE membrane samples. FESEM can also quantify the constituent members of the polymeric material and determine their atomic and weight percent, based on the characteristic X-rays generated, which will in turn gives information about the surface structure and morphology of the sample material. The characteristic X-ray generated are used for identification of different elements present in the specimen by energy dispersive spectrometer (EDS), which is an integral part of the FESEM used. Images of high magnification and ultra high resolution can be produced at different sample points. For more precise determination of the constituent present within the polymeric membrane material, FT-IR were also used as characterization tool, which uses infrared portion of the electromagnetic spectrum to characterize the material as molecules absorb specific IR frequencies that exactly match the frequency of the chemical bonds present in the molecular structure. The data processing technique (Fourier Transform) converts the raw data into FTIR spectrum.

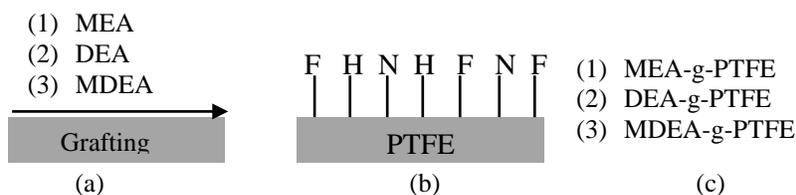


Figure 1 Grafting steps: (a) The grafting of γ -ray irradiated PTFE film, (b) and (c) amine

3.0 RESULTS AND DISCUSSION

3.1 Establishing Exudation Technique

The pristine PTFE film membrane was first characterized using Field Emission Scanning Electron Microscope (FESEM) and Fourier Transform-Infrared spectroscopy (FT-IR), to confirm and set the basis for comparison. The grafting of γ -ray pre-irradiated PTFE with amine solvents such as MEA, DEA and MDEA, conducted by immersion of γ -ray pre-irradiated samples in amine solutions at 80°C. However, the grafting reaction time was varied to study the effect of time on the grafting yield i.e. at 10 min and at 60 min. The grafted samples with 30 kGy irradiated dose were also characterized by FESEM and FT-IR to visualize the changes brought by the γ -ray irradiation and subsequent grafting.

3.2 FESEM Analysis

The Scanning Electron Microscope (SEM) images for pristine and grafted PTFE is presented in Figure 2 and Figure 3 respectively. As it can be observed that the pristine PTFE is composed of thin interconnected fibrils, joining at the node points. These thin fibrils are arranged in an irregular fashion leading to high porosity. These fibrils are generated due to the stretching procedure applied during the casting operation; the length and direction of the fibrils relate to the magnitude and direction of applied force during the stretching operation of membrane casting [18].

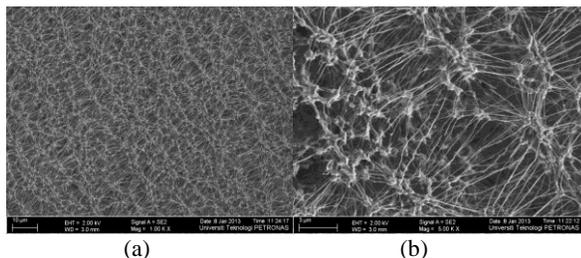


Figure 2 SEM images for pristine PTFE film membrane (a) 1.0 KX and (b) 5.0 KX magnifications

The γ -ray irradiated with 30 kGy dose and grafted membranes were also characterized by the field emission SEM, for which their respective SEM images are shown in Figure 3. Comparing these images of grafted PTFE with pristine PTFE images, we can observe there are changes in size at the node points, breakdown of some thin fibrils as shown in Figure 3(b). This can be explained that the changes in the size of nodes indicate that possible active surface, i.e. the active grafting site. Though the breakdown of fibrils are observed in the three samples, however, in the case of DEA grafted PTFE (DEA-g-PTFE sample), which lead to an island of pores. This is due to the occurrence of chain scission and ion erosion during grafting [19], thus the thin fibrils seen broken, instead of generation of active sites, it led to scission of fibrils. Furthermore, the composition of surface of the grafted membrane was also quantified by energy dispersive spectrometer and presented in Table 1. This also confirms that the grafting was obvious, as shown in the Table 1, the weight and atomic ratio of fluorine to carbon, in all the grafted samples have reduced. For pristine PTFE, the F:C weight ratio was obtained to be 2.51, however, the F:C weight ratio for grafted PTFE membranes were decreased to 2.46, 2.17 and 2.23 for

MEA-g-PTFE, DEA-g-PTFE, and MDEA-g-PTFE, respectively.

3.2 FT-IR Spectra

Infrared spectra of the irradiation grafted PTFE show, in addition, to the bands of pristine PTFE polymer; there are bands of fluoride and carboxylic end groups. The band at 2348 cm^{-1} is a combination of band associated with CF_2 backbone. The group frequency, wave number (cm^{-1}) for C-F stretch is in the range 1400-1000, which is exhibited as peaks in the spectra for the pristine PTFE.

Table 1 Compositional analysis of grafted PTFE membrane

Element	Weight %			
	Pristin	MEA-g-PTFE	DEA-g-PTFE	MDEA-g-PTFE
C	28.46	27.97	30.48	29.41
F	71.54	68.81	66.11	65.44
N	-	0.36	1.21	1.82
H	-	2.86	2.2	3.33
O	-	0	0	0
Total	100	100	100	100

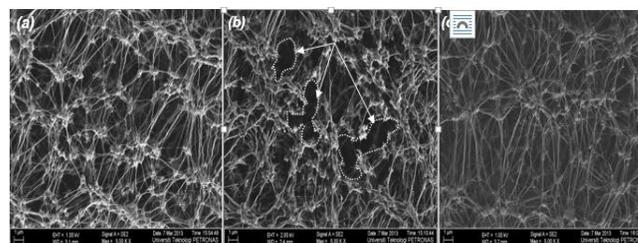


Figure 3 SEM images for amine grafted PTFE membrane. (a) MEA-g-PTFE, (b) DEA-g-PTFE, (c) MDEA-g-PTFE

The assignment of amine and amino compound group frequencies at the amino-g-PTFE membrane requires the understanding of the functional groups used. For primary amino functional groups such as MEA, its functional group is identified as N-H bend which is assigned to bands of 1650-1590 and C-N stretch for the bands 1090-1020 [20] for which only weak or no peak are observed at these range for the MEA grafted PTFE (MEA-g-PTFE). For secondary amines, N-H bend 1650-1550, and C-N stretch at 1190-1130 [21]. At these ranges only weak peaks are observed for the DEA-g-PTFE film membrane. For the tertiary amines, the only assigned wave number range is 1340-1250, for C-N stretch [20]. For the tertiary amine used in the analysis, MDEA grafted PTFE (MDEA-g-PTFE) has detected a peak at these ranges, which confirms the attachment of nitrogen atoms at the activated PTFE film.

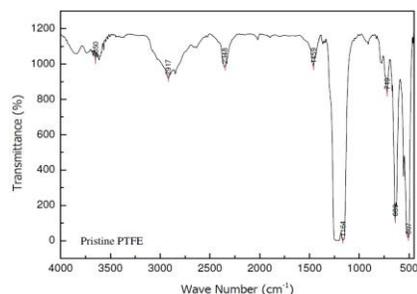


Figure 4 FTIR Spectra for Pristine PTFE membrane

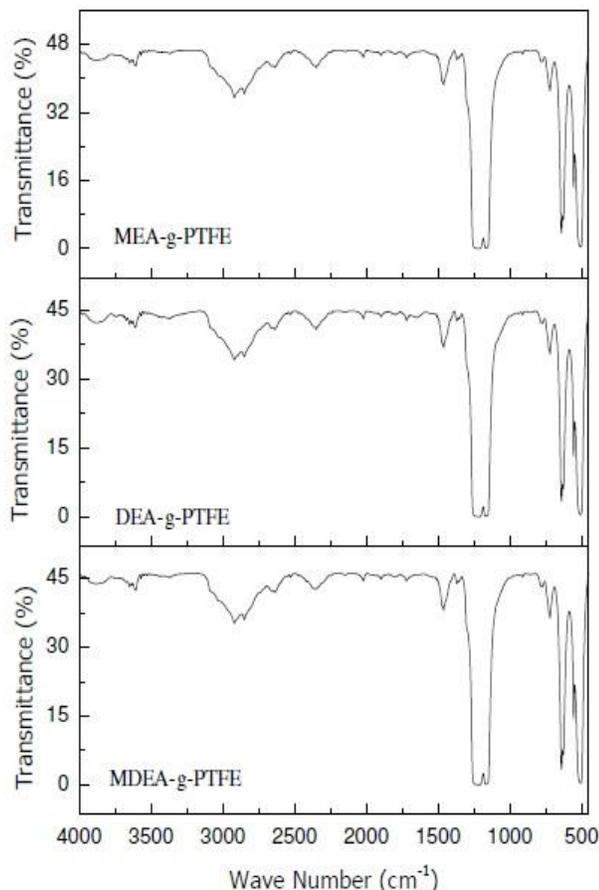


Figure 5 FT-IR Spectra for amine grafted PTFE: (a) MEA-g-PTFE, (b) DEA-g-PTFE, and (c) MDEA-g-PTFE

3.3 Effect of γ -ray Dose

The degree of grafting of different amines (MEA, DEA, and MDEA) onto the PTFE at 80°C and 10 min grafting reaction time versus irradiated dose is shown in the Figure 6. From the figure, regardless of the low percentage grafting yield, it can be seen that the grafting has taken place. However, the trend of the line showed slightly different transmission (%) for different grafting materials. The reason behind the low grafting yield is mainly restricted to the grafting employed, where only the PTFE

films were subjected to γ -ray irradiation. In the case of MDEA-g-PTFE, the degree of grafting didn't increase coincidentally with the increase of doses from 30 kGy upto 70 kGy. This is due to the high molecular weight of MDEA and the low dose applied to the PTFE films which might not have resulted in appreciable active sites in the membrane matrix. Thus, the resulting degree of grafting was obtained as low as 0.3% at 70 kGy. However, in the case of MEA-g-PTFE and DEA-g-PTFE, when the dose increased from 30 kGy to 50 kGy, an increase in percentage yield was observed, but with an increase in dose beyond 50 kGy, the grafting yield decreases. However, the method restriction still holds the main reason behind the low grafting yield obtained, as only the PTFE was subjected to γ -ray irradiation. This is going to be further justified with Electron Spin Resonance (ESR) to quantify the type and quantity of radicals generated upon irradiation on PTFE sample alone [22]. As the polymer is fully fluorinated, the low grafting yield is related to the crystallinity of the polymer, this further justified, for both PTFE and FEP, reported to have low grafting yield when compared with the partially hydrogenated polymers [23].

3.4 Effect of Grafting Reaction Time

In order to determine the effect of reaction time on the percentage grafting yield, identical PTFE samples were pre-irradiated at typical treatment conditions, and the grafting reaction time was kept for 60 minutes. The grafting temperature is maintained at 80°C throughout the experiments. Comparing Figure 6 and 7, one can see the effect of grafting time on the percentage grafting yield. It is observed that the trend lines behaved differently for different conditions adopted. Though still there is not appreciable gain in the grafting yield, but there are remarkable changes in the trend line plus the grafting yield didn't result in identical values to that of 10 min grafting time. Since the grafting time has significant impact on the grafting yield, further work such as grafting at dose rate, its respective permeabilities to CO₂ and N₂ will be carried out after determining the optimum grafting time.

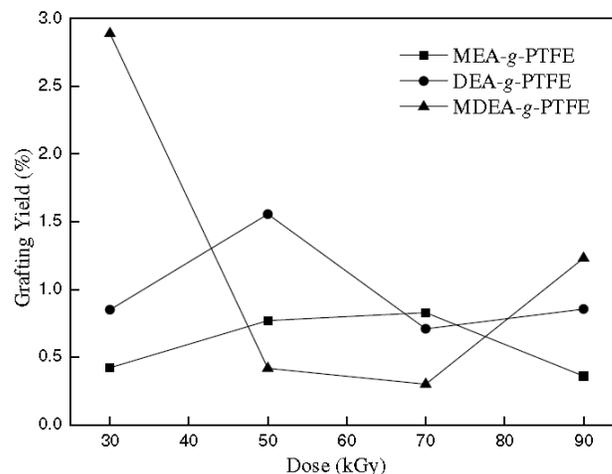


Figure 6 Effect of γ -ray dose on the grafting yield of PTFE at 80°C and 10 min reaction time

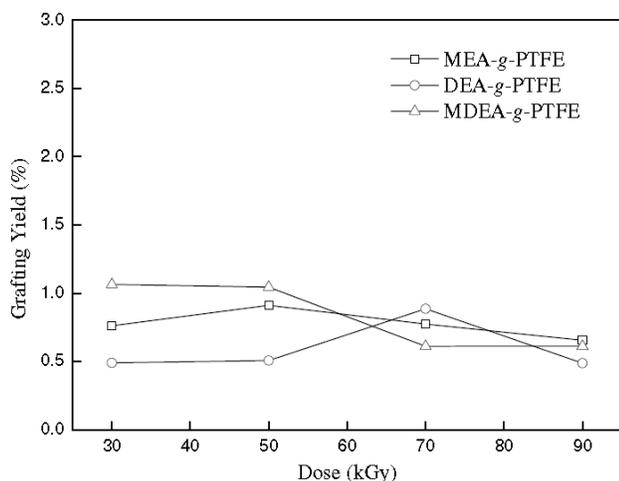


Figure 7 Effect of γ -ray dose on the grafting yield of PTFE at 80°C and 60 min reaction time

3.5 Effect of Grafting Solvents

The solvent used for the study, has also an influence over the resultant grafting yield. This is demonstrated due to the fact that the concentration or the quantity of the functional groups present in the solvent used. The amines used in this study were selected from different amino groups with different molecular weights and the concentration. However, studying this effect independently may not result to a clear conclusion which may need the thorough understanding of the other factors associated, as shown in Figure 6 and Figure 7. The grafting yield obtained for the different amines used and at the different reaction time had resulted in nonlinear relationship which is in agreement with the literature reported [24, 25].

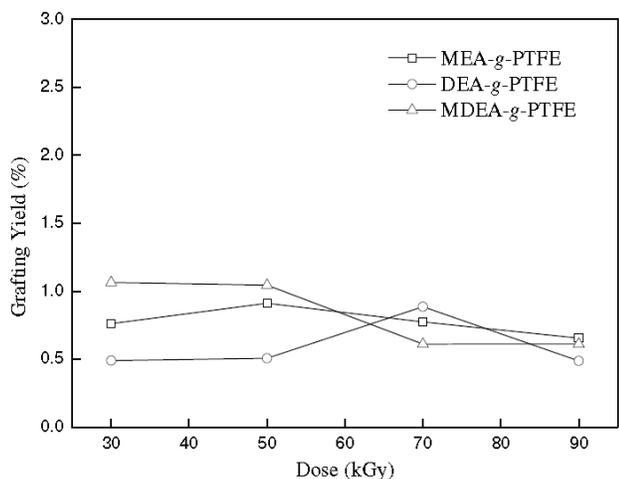


Figure 7 Effect of γ -ray dose on the grafting yield of PTFE at 80°C and 60 min reaction time

4.0 CONCLUSION

The PTFE samples were irradiated by 60Co source γ -ray with varying doses, leading to activated surface. The subsequent grafting was carried out by immersion in different types of amines at 80°C for 10 and 60 minutes. The characterization was

conducted for both the pristine PTFE and the grafted PTFE using the SEM and FT-IR. Effects of applied dose, grafting time, and grafting solvents on the resultant grafting yield were studied for different amine solvents such as MEA, DEA and MDEA. The results confirm slight change in grafting yield (less than 3%) was obtained.

This work is ongoing to elucidate the effect of grafting conditions on the rate of CO₂ capture. It is believed that if the amines are incorporated in the polymeric membrane matrix, the separation properties of the membrane will be enhanced. This can be achieved either by grafting or crosslinking on to the PTFE membrane.

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