



## Original Article

## Gamma irradiation-induced grafting of 2-hydroxyethyl methacrylate (HEMA) onto ePTFE for implant applications

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## ABSTRACT

The extreme hydrophobicity of expanded polytetrafluoroethylene (ePTFE) hinders bone-tissue integration, thus limiting the use of ePTFE in medical implant applications. To improve the potential of ePTFE as a biomaterial, 2-hydroxyethyl methacrylate (HEMA) was grafted onto the ePTFE surface using the gamma irradiation technique. The characteristics of the grafted ePTFE were successfully evaluated using attenuated total reflectance Fourier transform infrared (ATR-FTIR), field-emission scanning electron microscopy (FESEM)/energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS). Under the tensile test, the modified ePTFE was found to be more brittle and rigid than the untreated sample. In addition, the grafted ePTFE was less hydrophobic with a higher percentage of water uptake compared to the untreated ePTFE. The protein adsorption test showed that grafted ePTFE could adsorb protein, which was denoted by the presence of N peaks in the XPS analysis. Moreover, the formation of the globular mineral on the grafted ePTFE surface was successfully visualized using the FESEM analysis, with a ratio of 1.94 for Ca:P minerals by the EDX. To summarize, the capability of the modified ePTFE to show protein adsorption and mineralization indicates the improvement of the polymer properties, and it can potentially be used as a biomaterial for implant application.

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## 1. Introduction

In the last few decades, polymers have widely been used in biomaterial applications, especially as medical implants [1]. The versatility of polymers contributes to their various functions, such as in vascular grafting, catheters, bone cement, and soft-tissue reconstruction [2]. These applications are possible due to their surface characteristics, such as hydrophilicity, porosity, crystallinity, and crosslinking density [3]. However, most of the manufactured polymers do not possess the desired characteristics for medical applications in their original state; hence, to address this issue, the search for an ideal implant material has been continuous. Therefore, modification is needed to optimize specific surface properties. One of the alternatives to enhance the properties of polymers and introduce new functionalities is through irradiation-induced grafting techniques.

Expanded polytetrafluoroethylene (ePTFE) is used in this study due to its special properties, such as its porous structure, good dielectric properties, excellent mechanical properties, and high resistance to chemicals [4]. Nevertheless, ePTFE possesses very high hydrophobicity and inert properties [4]. It is well known that, for an artificial membrane, a polymer with an extreme hydrophobicity or hydrophilicity can hinder interaction between fluids surrounding living tissues. Thus, this property limits the use of ePTFE for the intended applications, such as facial implants, which require good bone-tissue integration [5].

In addition, the response/interaction of the biomaterial after it has been implanted depends on the nature of the implant material. The response of polymers in biological living tissue can be influenced by various variables, such as surface chemical properties, the topography [6], and the mobility of the surface molecules. Advance development in surface treatment has been made to alter the chemical and physical properties of polymer surfaces without affecting the overall polymer properties. Previous studies have demonstrated successful grafting of ePTFE using various techniques, such as plasma [7], chemical treatment [8], and radiation

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[9]. Acetic acid [10] and monomers, such as acrylic acid [11] and methacryloyloxyethyl phosphate (MOEP) [12], have been proven to result in the successful grafting of the ePTFE surfaces, thus changing the initial properties of the polymer.

In the current study, 2-hydroxyethyl methacrylate (HEMA) was chosen as the grafted monomer. Moreover, HEMA is a hydrophilic monomer, which is nontoxic and possesses the properties of hydrogels [13]. Numerous studies have been done on poly(HEMA) (pHEMA) hydrogel for medical applications due to its biocompatibility and physicochemical properties, which are similar to those of living tissues [14–16]. Previous studies had demonstrated successful grafting of HEMA onto chitosan [17], polypropylene, and low-density polyethylene [18]. Due to their properties and compatibility, HEMA has been used as a grafted monomer by introducing hydrophilic groups onto the hydrophobic surface of ePTFE.

In the present study, the grafted ePTFE was evaluated using various characterization techniques, including attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FESEM) with energy dispersive X-ray (EDX), contact angle measurement, and tensile strength testing using a universal test machine. In addition, *in vitro* studies were performed to evaluate the biocompatibility of modified ePTFE to be used as implants in the human body.

Theoretically, when a biomaterial is successfully implanted in the human body, the formation of an apatite layer on the surface of an implant will be observed [19]. This fundamental understanding is applied in the simulated body fluid (SBF) study, where an SBF solution is used to mimic the solution in the human body. This *in vitro* testing method was performed to evaluate the viability of ePTFE as an implant in the human body. In this method, after immersing the grafted membrane in the SBF solution, the formation of CaP minerals indicates the interaction between ePTFE and bone tissue [20]. Next, the adsorption of protein onto the ePTFE and the grafted membrane was observed to evaluate the ability of the membrane to adsorb proteins when implanted in the body. The interaction of proteins with an implant is important because the adsorption process occurs directly after the material is implanted in living tissue [21].

## 2. Materials and methods

### 2.1. Materials

The ePTFE membranes (trade name: Zeflour; thickness: 0.22 mm) were obtained from the Pall Corporation. For decontamination purposes, the membranes were pretreated with hot methanol (40 °C) overnight before drying in a desiccator jar until a constant weight was achieved. For the grafting procedure, the chemicals were purchased from different suppliers: methanol from MERCK, HEMA (chemical structure shown in Fig. 1) from Sigma Aldrich, and ammonium iron (II) sulfate hexahydrate (Mohr's salt) from Honeywell Riedel-de Haen. For the protein adsorption study, the chemicals were obtained from various sources: bovine serum albumin (BSA; 96%–99%) from Sigma, NaCl (>99%) from JT Baker,

and  $\text{KH}_2\text{PO}_4$  (99%) and  $\text{Na}_2\text{HPO}_4$  (99%) from MERCK. The chemicals for the preparation of the SBF ( $1.5 \times$  SBF) were obtained from different sources: NaCl (>99%) and HCl from JT Baker;  $\text{NaHCO}_3$  ( $\geq 99\%$ ),  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  ( $\geq 99\%$ ), and  $\text{Na}_2\text{SO}_4$  (99%) from MERCK; KCl (99.8%) from System Chemicals;  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (99%) and  $\text{CaCl}_2$  (97%) from R&M; and tris-hydroxymethyl aminomethane (99.8%) from Acros Organic. Deionized water was used in the preparation of a  $1.5 \times$  SBF solution according to the procedure reported by Kokubo and Tadama [22].

### 2.2. Grafting procedure

Various concentrations of HEMA (2, 10, 20, and 30 w/v%) were used throughout the experiment by adding 20 mg of Mohr's salt. The ePTFE was cut into dimensions of  $10 \times 15 \text{ mm}^2$  (weight 1.6–2.1 mg), and for the tensile test, the membrane was cut into a dumbbell shape (14 mm gauge length and 2 mm width). The prepared ePTFE was immersed in the monomer solution. All test tubes were covered with parafilm and degassed with nitrogen for 15 min to purge the oxygen from the solution, which can inhibit the grafting process. The sealed test tubes were irradiated by gamma-rays at 25 °C with radiation doses (2, 5, 10, and 20 kGy) at a rate of  $1.767 \text{ kGyh}^{-1}$  using gamma cell 220 Excel (MDS Nordion). Following the irradiation process, the samples were washed with hot methanol at 40 °C and were further washed with deionized water to remove any homopolymer (gel) or unreacted monomer that only physically grafted onto the ePTFE surfaces [11]. The ePTFE was then left in deionized water overnight. The sample ePTFE grafted with HEMA (ePTFE-g-HEMA) was dried in the desiccator jar until a stable weight was achieved. Each parameter was recorded in triplicate. The sample grafted with HEMA was labeled HEMAd(*m*) (where *d* refers to the dose and *m* refers to the concentration of the monomer). For instance, the sample irradiated at 2 kGy and grafted in a 10% concentration of HEMA was labeled HEMA2(10).

### 2.3. Protein adsorption study

The PBS solution was prepared by dissolving NaCl,  $\text{KH}_2\text{PO}_4$ , and  $\text{Na}_2\text{HPO}_4$  in 800 mL of deionized water at  $36.5 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$  in a plastic beaker [23]. After all of the reagents dissolved, 200 mL of deionized water was added. The pH of the solution was measured at all times during the preparation of the PBS solution. The dissolved reagent was adjusted to a pH of 7.4 using NaOH and HCl. The untreated and grafted samples were immersed in a 15 mL PBS solution containing 1 mg of BSA for 1 h at 37 °C. The samples were then washed with deionized water and dried in the desiccator jar until a stable weight was achieved.

### 2.4. Simulated body fluid study

The untreated and grafted samples were immersed in the  $1.5 \times$  SBF solution, which was prepared following the procedure reported by Kokubo and Tadama [22] at 36.5 °C for two weeks. The  $1.5 \times$  SBF solution was changed at intervals of every three days and no change in the pH was observed throughout the study. After two weeks, the samples were removed and dried in the desiccator jar until a constant weight was achieved. The deposition of the CaP minerals onto the ePTFE surfaces was measured by the increase in the sample weight, and the samples were further analyzed using ATR-FTIR, XPS, and FESEM/EDX.

### 2.5. Characterization

The grafting yield obtained for the sample was determined by measuring the weight changes of the samples before and after the

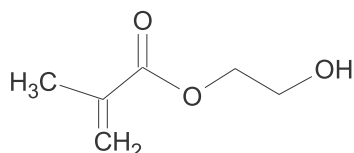


Fig. 1. Chemical structure of 2-hydroxyethyl methacrylate (HEMA).

sample was grafted with HEMA (ePTFE-g-HEMA) using the electronic balance (Entris 224i-1s). The grafting yield was calculated using the following formula:

$$\text{Grafting yield (\%)} = \left[ \frac{(W_f - W_i)}{W_i} \right] \times 100\%, \quad (1)$$

where  $W_f$  is the weight of sample ePTFE-g-HEMA, and  $W_i$  is the initial weight of the sample. The average and standard deviation are reported in triplicate.

Water uptake was measured by immersing the ePTFE samples (grafted and untreated) in deionized water for 24 h. The samples were then removed and weighed. Excess water on the ePTFE sample surfaces that may affect the weight of the water absorbed in the ePTFE were blotted using filter paper. The water uptake was calculated using the following formula:

$$\text{Water uptake (\%)} = \left[ \frac{(W_s - W_d)}{W_{pHEMA}} \right] \times 100\%, \quad (2)$$

where  $W_s$  is the weight of the swollen sample (ePTFE/grafted ePTFE immersed in deionized water),  $W_d$  is the weight of the dry sample, and  $W_{pHEMA}$  is the mass of pHEMA on the grafted ePTFE. The average and standard deviation are reported in triplicate.

The contact angle measurement was determined using an automated angle goniometer machine (Rama Hart) as previously described [10]. The samples were placed on a Teflon stage, and 5  $\mu$ L of deionized water was dropped onto the sample surface using a 50  $\mu$ L glass flat-tip syringe. Five measurements were taken for each sample, and the average and standard deviation were reported accordingly.

Both ATR-FTIR spectroscopy and XPS were used to analyze the chemical composition of the surface. In this analysis, ATR-FTIR (model PerkinElmer Spectrum BX) with a resolution of 8  $\text{cm}^{-1}$  and a wavenumber between 4000  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  were used. The XPS analysis was performed on the samples using the Kratos model Axis Ultra DLD equipped with an Al  $K_{\alpha}$  source (1486.6 eV). Survey scans were carried out at 1200-0 eV with 1.0 eV steps at the pass energy of 160 eV, while narrow scans were performed at 0.1 eV at the pass energy of 20 eV. The binding energy of the sample was corrected based on the C-F value of 292 eV [24]. VISION software was used to plot the data, fit the curve for the high-resolution spectra, and calculate the atomic concentration in the sample. The refinement of the peak was performed based on previously published work [11]. The grafting extent was determined from an XPS carbon narrow scan using the following formula (3) as previously described [25]:

$$\text{Graft extent (\%)} = \left[ \frac{(\text{Carbon}_{All} - \text{Carbon}_{C-F})}{\text{Carbon}_{All}} \right] \times 100\%, \quad (3)$$

where  $\text{Carbon}_{All}$  is the percentage concentration of all carbon bond components present in the sample, and  $\text{Carbon}_{C-F}$  is the percentage of the carbon-fluorine bond.

In this study, the FESEM/EDX analysis from the Merlin compact model was performed on the sample under a high vacuum with the standard mode voltage at 3 kV. The samples were coated with platinum for 5 min until a 15 nm thick layer formed before the analysis to make the material conductive. Magnifications of 1kX, 5kX, and 10kX were taken for the morphology analysis of the samples.

The tensile test was performed on samples using a universal tensile machine (Instron 5567) at a displacement rate of 10  $\text{mm min}^{-1}$  under a 50 N load. The measurements for Young's

modulus,  $E$  (MPa), the elongation at break (percentage of tensile strain), and the ultimate tensile strength (UTS; maximum tensile strength in MPa) were taken for at least five readings. The reported values were the average  $\pm$  the standard deviation.

## 2.6. Statistical analysis

The statistical analysis of the quantitative results was conducted between two independent samples for analysis of the mechanical properties and water contact angle. The reported values were the average  $\pm$  the standard deviation of five replicate samples. A  $t$ -test was performed on the means between the two groups for a specific comparison. The statistical significance of the means was based on  $p$ -values of  $< .05$ .

## 3. Results and discussion

### 3.1. Effects of grafting parameters

The grafting yield (measured by increased weight) of the sample after irradiation in the presence of the monomer is the initial indicator of successful grafting. In this study, the grafting yield is observed to vary with changes in radiation doses and monomer concentrations (Table 1). For instance, at similar monomer concentrations (10 v/v%), the HEMA2(10) sample (irradiated at 2 kGy) only resulted in a 13% graft yield, whereas the HEMA5(10) sample (irradiated at 5 kGy) produced a higher graft yield at 60%. This indicates that the grafting yields are affected by the radiation dose. This can be explained by the volume of radicals; by increasing the radiation dose, the radicals that are involved in the grafting reaction also increase. The concentrations of monomer also influence the grafting yield because the increase in the concentration of HEMA most likely results in a higher diffusion of the HEMA concentration in the grafting region [16].

The results of the present study have shown that the grafting yield after exposure to radiation increased in a dose-dependent manner. A similar trend was observed in the previous study on radiation-induced grafting of HEMA onto polypropylene, where a better grafting yield was obtained at a higher dose (76% for 40 kGy) using the pre-irradiation method [26]. In a past study, Nasef demonstrated that the radiation dose influences the grafting yield, where the highest grafting yield (60%) was obtained when the PTFE membrane was irradiated at 30 kGy with a 40 v/v% monomer concentration [27]. It was believed that the grafting reaction occurs initially at the surface of the sample and progresses inwards as the grafting zone is swollen by the monomer solution. This reaction is called the grafting-front mechanism [28,29].

In the present study, a dose of 2 kGy at a 30% concentration of HEMA is determined as the optimal parameter. The results show that a high graft yield (56%) was produced for the HEMA2(30) sample. Although the highest grafting yield (~358%) was observed for the HEMA5(30) sample, this condition is not considered the optimal parameter because the high grafting yield was attributed to the presence of a large volume of insoluble homopolymers that cannot be eliminated via the washing process. In addition, the grafted ePTFE was observed to be very hard and brittle. Further increases in HEMA concentrations (40, 50, and 60 v/v%) when ePTFE membranes were irradiated at 2 kGy also resulted in further homopolymer formation, thus hindering the diffusion of HEMA onto ePTFE (data not shown). A past study stated that the reaction of monomers that occur at the primordial phase of the reaction prevented them from diffusing to the active sites of the polymer chain, causing the grafting reaction to be extremely concentrated [30].

The ePTFE membrane was observed to become less hydrophobic after it was grafted with HEMA. A significant decrease in

**Table 1**  
Characterization of ePTFE and grafted ePTFE membrane after gamma irradiation.

Sample	Dose (kGy)	Monomer concentration (%)	Grafting yield (%)	Water uptake (%)	Contact angle (°)
ePTFE	–	–	–	0	114 ± 2
HEMA2(2)	2	2	11 ± 2	200 ± 10	100 ± 4
HEMA2(10)	2	10	13 ± 2	250 ± 28	102 ± 10
HEMA2(20)	2	20	36 ± 5	125 ± 13	91 ± 1
HEMA2(30)	2	30	56 ± 3	117 ± 65	79 ± 1
HEMA5(2)	5	2	5 ± 0	200 ± 33	102 ± 5
HEMA5(10) <sup>a</sup>	5	10	60 ± 6	219 ± 13	–
HEMA5(30) <sup>a</sup>	5	30	358 ± 62	30 ± 8	–

<sup>a</sup> Samples became physically hard and highly brittle.

the water contact angle was observed ( $p = .001$ ) from 114° for untreated ePTFE to 79° for the HEMA2(30) sample (graft yield of 56%). Hidzir et al. reported a similar trend in which a reduction in the water contact angle was observed after ePTFE was grafted with acrylic acid (water contact angle of 92° and 40% graft yield) [11]. The result of the water contact angle in the current study correlates well with the water uptake study and the obtained grafting yield. High water uptake (100%–250%) was recorded for pHEMA-g-ePTFE compared to the untreated ePTFE (0%). In addition, water uptake obtained in this study was higher than that previously reported by Nizam et al. (2005), where about 75% of the water uptake swelling was reported when the pHEMA hydrogel was prepared at a dose of 50 kGy [31]. The high water uptake and decrease in the water contact angle in the current study could be attributed to the hydrophilic component of HEMA, which became hydrogel after irradiation, which increases the ability of the grafted sample to sustain the water uptake [32].

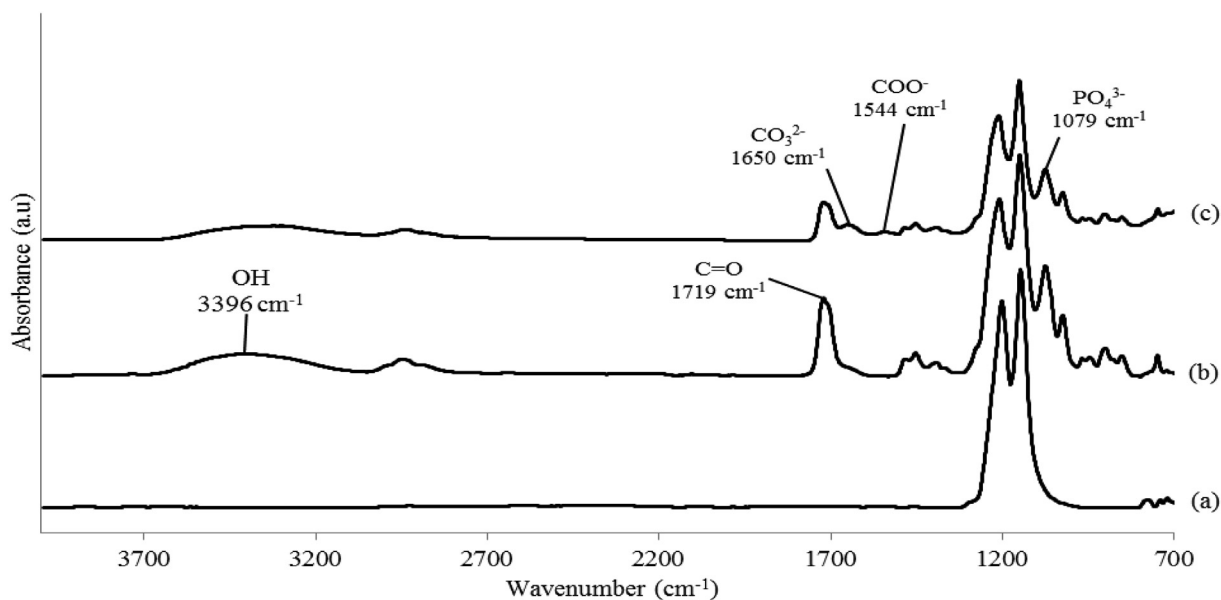
### 3.2. Chemical composition of the membrane

The spectrum of untreated ePTFE (Fig. 2a) displays the main characteristic asymmetric  $\text{CF}_2$  stretch at 1201  $\text{cm}^{-1}$  and the symmetric  $\text{CF}_2$  stretch at 1147  $\text{cm}^{-1}$ . After irradiation-induced grafting of HEMA onto ePTFE was performed, two noticeable additional peaks were observed on the HEMA2(30) sample (Fig. 2b). These

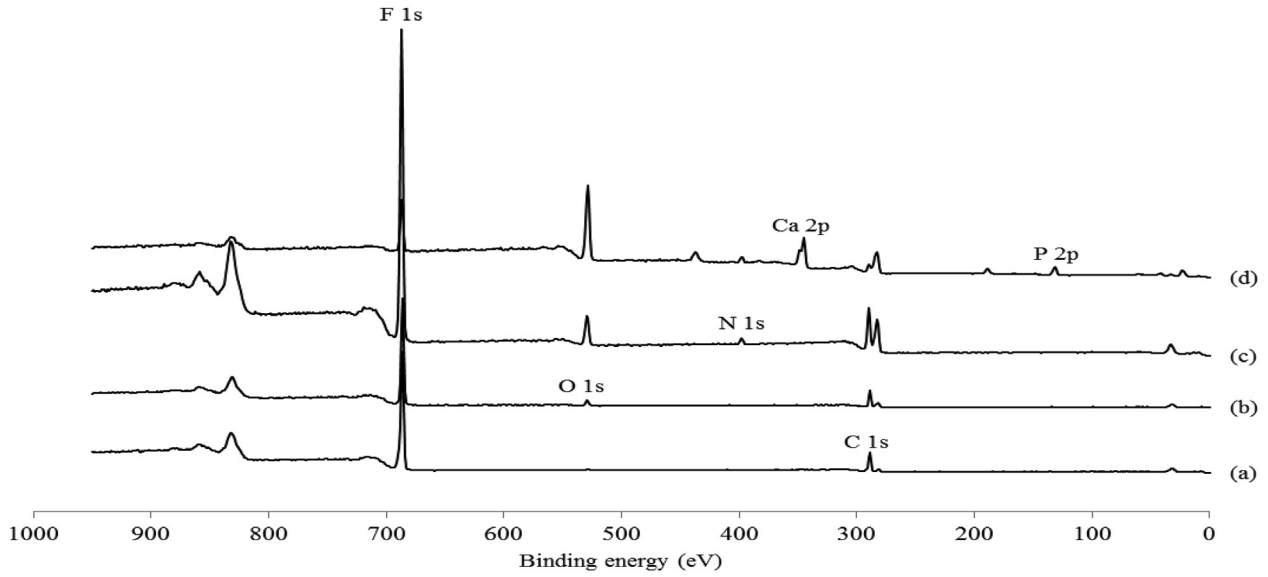
two peaks represent the carbonyl band of carboxylic acid at 1719  $\text{cm}^{-1}$  and the broad band of the O-H stretching vibration at 3396  $\text{cm}^{-1}$  [33]. In addition, a C-H stretching vibration is observed at 2800 to 3000  $\text{cm}^{-1}$ .

The XPS survey scans show only carbon and fluorine peaks present in the untreated ePTFE sample (Fig. 3a), whereas an additional oxygen peak is observed for the modified sample HEMA2(30) (Fig. 3b). The additional peaks present on the HEMA2(30) sample (Fig. 3b) indicate the successful introduction of HEMA grafted onto the ePTFE backbone chain. Furthermore, a high resolution of XPS (Fig. 4b) clearly indicates the presence of four carbon components (i.e., COO at 288.5 eV, C-O at 286.5, C-CO at 285.5, and C-C at 284.5 eV), which correlate well with the chemical structure of HEMA (Fig. 1) compared to untreated ePTFE (Fig. 4a). Similar peaks were also observed in a previous study on HEMA grafted onto polyethylene [34].

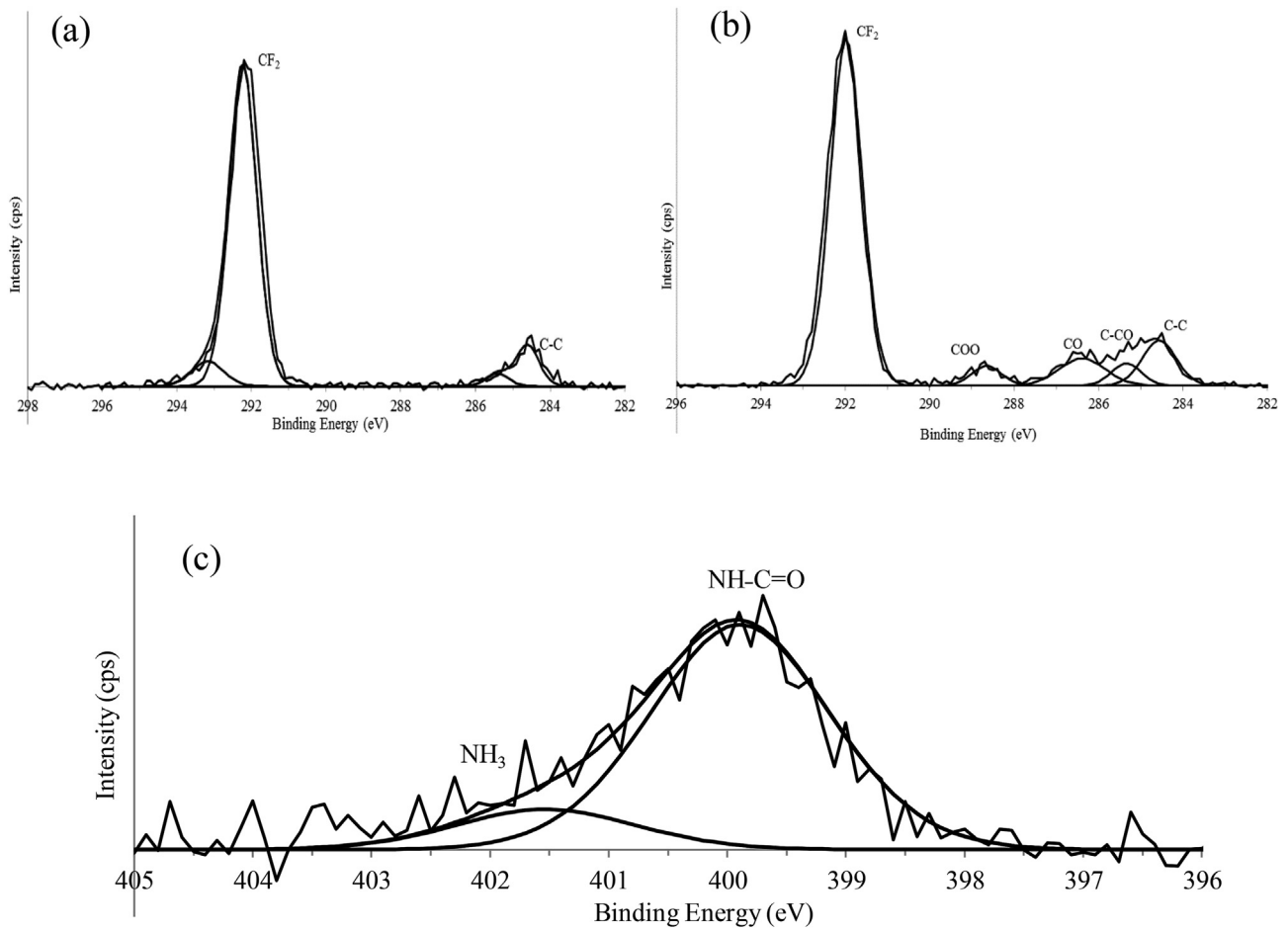
The grafting process that took place was also proven by the weight composition analysis using EDX. The results (Table 2) show the presence of carbon and fluorine elements in untreated ePTFE, whereas additional oxygen (7% weight) is observed for the HEMA2(30) sample. In addition, the carbon percentage was observed to increase from 26% for untreated ePTFE to 42% for the HEMA2(30) sample. The results from the EDX analysis correlate with the results from the FTIR and XPS analyses, indicating the successful grafting of HEMA onto the ePTFE membrane.



**Fig. 2.** FTIR spectrum for (a) untreated ePTFE, (b) sample HEMA2(30), and (c) sample HEMA2(30) [after 2 weeks in SBF solution].



**Fig. 3.** XPS survey scan for (a) untreated ePTFE, (b) sample HEMA2(30), and (c) sample HEMA2(30) [after 1 h in protein BSA], and (d) sample HEMA2(30) [after 2 weeks in SBF solution].



**Fig. 4.** XPS narrow scan for (a) C 1s for untreated membrane, (b) C 1s for grafted sample HEMA2(30), and (c) N 1s for sample HEMA2(30) after BSA adsorption.

**3.3. Mechanical properties**

The mechanical properties of untreated and grafted ePTFE are

shown in [Table 3](#). Young's modulus for the HEMA2(30) sample increased significantly compared to that of untreated ePTFE ( $p = .002$ ). In contrast, both the UTS and elongation percentage of

**Table 2**  
Energy dispersive X-ray (EDX) analysis for ePTFE and grafted ePTFE.

Sample	Element (wt%)						
	C	F	O	Ca	P	Mg	Na
ePTFE	26	74	—	—	—	—	—
HEMA2(30)	41.7	51.1	7.2	—	—	—	—
HEMA2(30) [2 weeks in 1.5 × SBF]	9.4	1.6	37.8	32.5	16.7	1.5	0.5

the HEMA2(30) sample decreased by approximately half from that of the untreated ePTFE ( $p = .002$ ;  $p = .0003$ , respectively). These results indicate that the grafting process could lead to embrittlement of the sample due to either physical or chemical changes in the process [11]. This is due to the exposure of fluoropolymers to gamma radiation that can result in defluorination, oxidation, crosslinking, and chain scission [35]. In addition, the grafted sample was observed to become stiffer and more rigid compared to the untreated ePTFE. The result obtained in this study was similar to the result obtained by Hidzir et al. [11] for the graft of acrylic acid onto ePTFE (grafting yield 36%) with Young’s modulus equal to  $81 \pm 8$  MPa and an elongation of  $45\% \pm 7\%$ .

**Table 3**  
Mechanical properties for ePTFE samples.

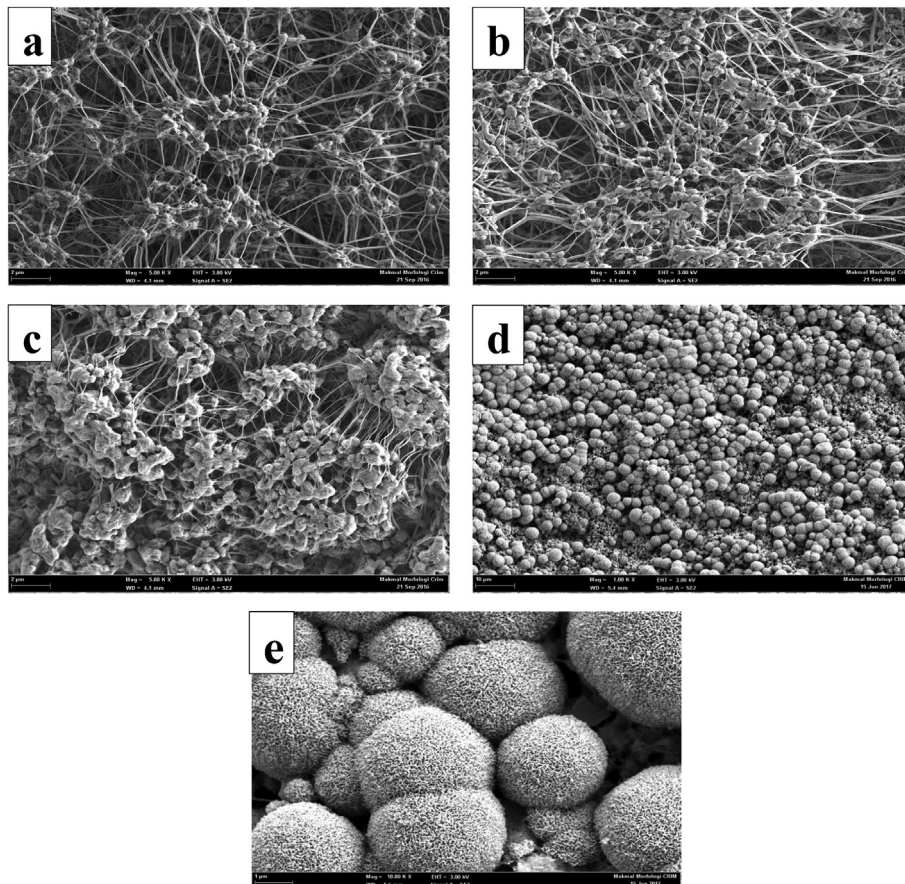
Sample	Young’s modulus, $E$ (MPa)	Ultimate tensile strength (UTS) (MPa)	Elongation at break (%)
ePTFE	$21 \pm 2$	$11 \pm 1$	$144 \pm 27$
HEMA2(30)	$110 \pm 28$	$5 \pm 1$	$46 \pm 7$

3.4. Membrane morphology

The morphology of the untreated ePTFE membrane is observed to contain fibrils interconnecting the nodal region (Fig. 5a). The fibrils are approximately 1.5  $\mu\text{m}$  long and 0.12  $\mu\text{m}$  wide [7]. Fig. 5b and c illustrate the morphology of the grafted ePTFE for the HEMA2(2) (11% graft yield) and HEMA2(30) samples (56% graft yield), respectively. For the grafted ePTFE, more islands and fewer fibrils are formed as the monomer concentration increases. These observations are consistent with the previous report by Hidzir et al., where the authors stated that the low number of fibrils observed for the grafted ePTFE is a result of the graft copolymer covering some parts of the fibril regions [7].

3.5. In vitro studies

In the current study, two *in vitro* testing methods were conducted, namely, the protein adsorption test and the SBF test. These studies were performed to evaluate the biocompatibility of the modified ePTFE to be used as implants in the human body. A protein adsorption study was performed on both untreated ePTFE and



**Fig. 5.** FESEM image for (a) untreated ePTFE, (b) sample HEMA2(2), (c) sample HEMA2(30), (d) sample HEMA2(30) [after 2 weeks in SBF] for 1kX magnification, and (e) sample HEMA2(30) [after 2 weeks in SBF] for 10kX magnification. Fig. 5 (a)–(c) were taken at 5kX magnification.

grafted ePTFE. The results demonstrate the presence of N 1 s peaks (2%) at 400 eV in the XPS survey scan (Fig. 3c) for the HEMA2(30) sample, whereas N 1 s peaks are not observed for the untreated ePTFE sample after the protein adsorption study (data not shown). The XPS narrow scan for the grafted ePTFE (sample HEMA2(30); Fig. 4c) detects two N peaks (i.e., NH<sub>3</sub> and NH-C=O at 401 eV and 400 eV, respectively). In comparison, Suzuki et al. illustrated that the grafted ePTFE with MOEP as a monomer was also able to adsorb protein with 12% N 1 s peaks [21]. Overall, this protein adsorption study showed that grafted ePTFE was able to adsorb protein, which was indicated by the presence of N peaks in XPS compared to untreated ePTFE.

A weight increase (35%) was observed for the HEMA2(30) sample after the SBF immersion, which indicated possible mineral formation on the grafted ePTFE. This result correlates with the FTIR analysis, which shows a broader band for the HEMA2(30) sample at 1079 cm<sup>-1</sup>, which corresponds to a phosphate vibration mode by hydroxyapatite (HA), and another band at 1650 cm<sup>-1</sup>, corresponding to the carbonate vibration (Fig. 2c) [36]. Additionally, the carboxylic acid peak from the carbonyl group decreases at 1720 cm<sup>-1</sup>, and the carboxylate peak from the carbonyl group rises at 1544 cm<sup>-1</sup> and 1650 cm<sup>-1</sup>. The mineral formation on the grafted ePTFE is further supported by the FESEM analysis (Fig. 5d and e), which shows the formation of minerals with a globular structure after being immersed in the SBF solution. A similar porous globular structure has been observed previously by Hidzir et al., which indicates the formation of minerals on the grafted ePTFE [37]. The EDX analysis (Table 2) performed on the HEMA2(30) sample indicates the presence of mineral formation with the detection of Ca, P, Mg, and Na, with a Ca to P ratio of 1.94. An apatite formation was also confirmed through the XPS survey scan (Fig. 3d) with the presence of peak energy at 131 and 345 eV, which corresponds to Ca 2p and P 2p. The Ca to P ratio was found to be 1.68 for the HEMA2(30) sample after two weeks in SBF, which is slightly higher compared to the previous study using the acrylic acid grafted ePTFE [37] with the ratio of 1.49. These results proved that grafted ePTFE, (i.e., sample HEMA2(30)) was able to induce mineralization in the SBF solution.

#### 4. Conclusion

This study demonstrated the success of grafting HEMA onto ePTFE using the gamma radiation method. This process altered the initial properties of the ePTFE membrane, thus improving its potentiality as a biomaterial. The ePTFE became less hydrophobic after it was grafted with HEMA. This is useful because hydrophilicity is one of the desirable characteristics of biomaterial as a medical implant. Furthermore, the grafting yield was dependent on the radiation dose and the concentration of HEMA. Through *in vitro* studies, it was concluded that the grafted membrane was viable as biocompatible material and has the potential to be used as an implant in the human body. However, due to the exposure of fluoropolymers to gamma radiation, the grafted sample was more brittle and rigid compared to the untreated ePTFE. Therefore, for future work, it is suggested to consider investigating the most optimal parameters that ensure that a modified ePTFE with more durable mechanical properties can be manufactured. In conclusion, the results of this study provide new insight into the potential of ePTFE-g-HEMA as a biomaterial, especially in implant applications.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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