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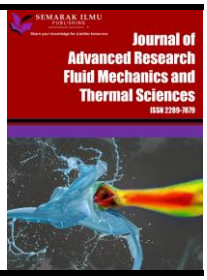

Thermal and Degradation Analysis of Electrospun Polyurethane Prepared using Radiation Induced Grafting

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ABSTRACT

Polyurethane (PU) membranes was prepared using electrospinning followed by modification with 2-hydroxyethyl methacrylate (HEMA) by radiation-induced grafting (RIG) copolymerization method via electron beam. The lack of knowledge of polymer properties of PU-based membrane prepared using RIG method need for dedicated study. Thus, the effect of thermal stability, in vitro degradation, water uptake analysis, and surface morphology after 84 days' incubation times toward grafted PU-g-poly(HEMA) membrane was evaluated for the first time using thermal gravimetric analysis (TGA), analysis of mass, percentage of water uptake and Scanning Electron Microscope (SEM), respectively. Based on the DTGA curves, the electrospun PU exhibits two-stage of deposition. After grafted with HEMA, the first stage of decomposition was shifted to the lower temperature, and the second stage of decomposition was shifted to a higher temperature. At 500 °C, PU grafted with HEMA leaves residue about 3.526% more elevated in value than original material of PU, which is 1.151%. Degradation test showed that a higher percentage degree of grafting was lowering the percentage of weight loss. SEM images supported the morphology observation shows no noticeable changes such as cracked or eroded has occurred. In conclusion, electrospun PU grafted with HEMA was improved its thermal stability, stable in swelling properties and was found competent to degrade slowly in phosphate buffer saline (PBS). The results show that PU-g-poly(HEMA) exhibits better thermal stability than pure poly(HEMA) and the amorphous regions give the polymer toughness and could be up-and coming candidates for tissue engineering including artificial blood contracting medical devices.

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1. Introduction

Polyurethane (PU) is a polymer that consisted of the hard segment and soft segment that led to the desirable elasticity, biocompatibility and stability [1]. Therefore, PU has been widely used in the form of coating, injection moulding and biomedical devices [2-4]. In the part of biomedical devices, available off-the-shelf material (scaffolds) was highly recommended to ensure no waiting time for the late stage of patient [5]. In overall, there are two methods used to modify a scaffold either using physical method or chemical method. Polymer blending is one of the most common physical methods to modify scaffolds. By mixing two or more polymers, biocompatibility and biodegradability of the scaffolds will be changed. For example, thermoplastic PU is blended with polyvinylidene fluoride (PVDF) then undergoes electrospinning. The result of mixing the polymer produces high ionic conductivity and good mechanical strength [6-8]. Another previous research by Sharhan *et al.,* [9] conducted physical blending of poly (3-hydroxylbutyric acid) with poly (vinyl acetate) (PHB/PVA). That study indicated that the polymer blending improved the thermal stability of poly (3-hydroxylbutyric acid) component. However, the crystallization rate decreased after the blending process [10]. Apart from blending polymer with polymer, there were also studies conducted on using natural fibres reinforcing polymer by adding polylactic acid (PLA) with hemp, bamboo, and jute fibre, producing natural fibres reinforced composite with improvement in tensile strength [11-13]. This modification also one of promising alternatives for biodegradable hybrid composites for good mechanical and physical characteristics [14]. This matter should be put into limelight as waste should be considered as a problem. Implementing a technology such as using waste as energy, waste-to-energy (WtE) is one of ways to overcome this will retain the sustainability that we strive to achieve in this circular economy nowadays [15].

Modification using chemical method is also known as graft copolymerization. The graft copolymerization can be classified into four categories; by using chemical initiators, photo initiators, plasma treatment and high energy radiation. Graft copolymerization by chemical initiators usually uses initiator which is a source of chemical species to react with monomer for formation of free radical [16-18]. Chemical synthesis undeniably the simplest method and able to produce in big quantity of stable products [19]. For example, PU is grafted with HEMA and HEA initiated using ceric ion [20]. The disadvantage of this method is that it will give exposure of toxic chemical to human body. Photo initiators method usually uses ultraviolet (UV) radiation [21]. An example, PCL is grafted with collagen using UV radiation [22]. Plasma treatment involves reacting plasma that contains electron or ions to produce cleavage [22-25]. Usually, this method only produces surface free radical due to low radiation energy. Among all, high energy radiation or also called as radiation-induced copolymerization is the best method. It can be divided into gamma radiation and electron beam radiation [26,27]. Radiation-induced grafting (RIG) was suggested as the fast technique, green method and clean process without the need of chemical initiator or reducing agents [28]. It can also sterilize the PU scaffolds [29]. Gamma irradiation also favoured in other synthesis such as in producing nanoparticles as this method is easy, less cost required, limiting waste by-products and require no chemical initiator that could be hazardous or harmful [19]. Different doses also proven to effect production such as the product sizes, but nevertheless, gamma synthesis product able to outstand the production from chemical synthesis [19]. With this method, the degree of grafting of monomer on it can be controlled [30]. PU was chosen due to its biocompatible, biodegradable and widely used in biomedical applications. Poly (HEMA) is hydrophilic monomer which is hemocompatible and non-specific protein adsorption. Combination of PU and poly (HEMA) using RIG is the suitable candidate for enhanced hydrophilic properties [31]. However, the lack of information on the thermal and degradation analysis of materials after RIG process need to be observed. Because

of it, investigation on thermal and degradation analysis toward the grafted surface PU needs to evaluated for future suitable usage. Therefore, in this paper the analysis was conducted by using thermal analysis, in vitro degradation, surface morphology observation and water absorption ratio.

2. Methodology

2.1 Materials and Methods

2.1.1 Materials

PU pellet that is known as Selectophore^{TM}, as well as HEMA were purchased from Sigma Aldrich. Tetrahydrofuran (THF, 99.5% purity) and N,N-dimethylformamide (DMF, 99.5% purity) was used as a solvent in fabrication procedure was supplied by Merck. Phosphate buffer saline was supplied by Invitrogen in medical grade. All of these materials were used without further purification.

2.2 Methodology

2.2.1 Preparation of electrospun polyurethane

The electrospinning process starts with the preparation of the PU solution. The PU pellet was solubilized in DMF and THF (1:1 ratio) with continuous stirring for 12 hours at room temperature with concentration of 10wt%. The electrospinning process is set-up using a horizontal layout. The spinneret consists of a syringe to hold the polymeric polyurethane solution which is connected with steel needle with an internal diameter of 0.7mm (22G). A syringe pump, a high voltage supplies in the 20 kV range and a static aluminium plate as the collector. The electrospun fibers fabricated was dried in oven for 3 days at 60 °C.

2.3 Radiation-Induced Grafting Polymerization Method

Electrospun PU fabricated by electrospinning process was cut into 5x3 cm each. 10 wt% HEMA monomers were prepared by dissolving it in water. Then, PU fibers were entirely soaked in HEMA monomer solution in 50 ml closed bottles for overnight. Samples were taken out, and excess solution was dried with filter paper by applying gentle pressure. PU fibers then were placed in polypropylene plastics and sealed using the vacuum pump. The prepared samples were arranged on a tray covered with ice and were radiated under an Electron Beam Accelerator at a radiation dose 50 kGy with the acceleration voltage of 1 kV under 1.0 x 10^{-4} Pa. After reaction completed, the scaffolds were peeled off and thoroughly washed (three times) and were dried in an oven (60 °C) for three days. The monomer concentration was varied from 2wt%, 4wt%, 6wt%, 8wt% and 10wt% in order to study the effect of degradation towards scaffolds.

2.4 Characterization

2.4.1 Thermal gravimetric analysis

Thermal analysis was done to investigate the thermal stability of the unmodified and modified surface scaffolds. This analysis was measured using TGA Instrument (TGA 55, Perkin Elmer, USA). All the samples were investigated under nitrogen gas with a flow rate of 20 mL/min and were gradually heated from 30 °C to 600 °C at the rate of 10 °C/min by following the previous researcher [15].

2.4.2 In vitro degradation test

In vitro degradation test was conducted to determine the degradation of polymer for 84 days (ASTM D6691-09) [32]. All electrospun scaffolds were cut into 1cm x 1cm in size and immersed into phosphate buffer saline media (PBS) without an addition of 1% of penicillin and streptomycin as anti-fungal as well as anti-bacterial agents. Polymer samples were each incubated in 1ml of a medium, in duplicate at 37 °C in a non-CO_2 incubator. The media was changed with new prepared media for each sample in every 3 days. Percent degradation was calculated using Eq. (1).

$$\text{Percent Degradation (\%)} = \frac{W_f - W_o \times 100}{W_o} \quad (1)$$

where, W_f and W_o are the weight of the dry scaffolds after 84 days and before incubation with PBS [32]. The topological surface observation was carried out on the dried scaffolds after 84 days by SEM instrument following the technique mentioned in SEM analysis.

2.4.3 Scanning electron microscopy analysis

The surface morphology of electrospun PU and electrospun PU-g-poly(HEMA) before and after incubated with PBS were observed using SEM (JSM-6701F, JOEL, USA) at 2000x magnification. All samples investigated were coated with platinum prior to analysis for 60 seconds by auto fine coater (JFC-1600, JOEL, USA).

2.4.4 Water absorption ratio measurement

The water adsorption ratio was an analysis to measure how much water was taken by scaffold in certain period of times. The water adsorption ratio of the modified surface of electrospun fibers was evaluated after immersion in the distilled water for around 1 hour at room temperature. The scaffolds were taken out from the solution and wiped gently with filter paper before being weight. The total water adsorption ratio was calculated using Eq. (2).

$$\text{Water adsorption ratio (\%)} = \frac{W_f - W_i \times 100}{W_i} \quad (2)$$

where, W_f and W_i are referred to the weight of the wet and dry condition of the scaffolds [33].

3. Results

3.1 Thermal Stability of the Electrospun PU-g-poly (HEMA) Scaffolds

Figure 1 shows the TGA curves of electrospun PU fiber, poly (HEMA) and electrospun PU-g-poly(HEMA) and it was found that electrospun PU remained stable up to 200°C, and only 0.75% of percentage weight loss (0.046 mg) occurred. Meanwhile, poly (HEMA) showed 4.25% reduce in percentage weight (1.597 mg), with about 1.03% percentage of weight loss (0.0723 mg) evaluated on modified surface PU-g-poly(HEMA) 28.9% DG below the temperature of 200°C. The first stage degradation was due to the evaporation of non-bonded water and volatile compounds [34]. Higher percentage of weight loss on poly (HEMA) compared to electrospun PU and modified surface scaffolds were due to hydrophilic nature of poly(HEMA).

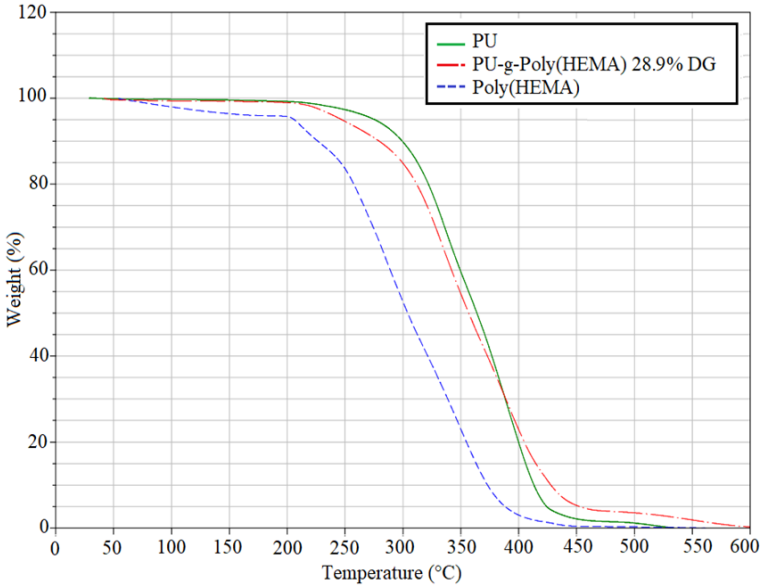


Fig. 1. TGA thermograms for electrospun PU, electrospun PU-g-poly(HEMA) and pure poly(HEMA)

Based on TGA curves, the onset temperature for electrospun PU, poly(HEMA) and PU-g-poly(HEMA) started at 213.78, 199.91 and 205.51 °C, and the endset temperature were 451.29, 429.87 and 466.44 °C, respectively. At 500 °C, there were only 0.258% residue left for poly(HEMA), 1.151% and 3.526% residue left for PU and PU-g-poly(HEMA) 28.9% DG, individually. DTGA curves show the maximum temperature (T_{max}) of the materials (Figure 2). The electrospun PU exhibit two stages of decomposition, which occurred at 337.58 and 385.88 °C. The low temperature stage of PU is due to decomposition of hard segments which is initially associated with scission of the urethane linkages with the emission of carbon dioxide [35,36]. This result is also supported by Goel et. al, where it is indicated that the decomposition of urethane bonds tends to produce its origin compound (polyols and di-isocyanates) or to amines, olefins, and carbon dioxide (CO_2) [37]. The higher temperature stage is due to the cleavage of soft segments chain that corresponds to the efficient disintegration of hydrocarbon polymer backbone.

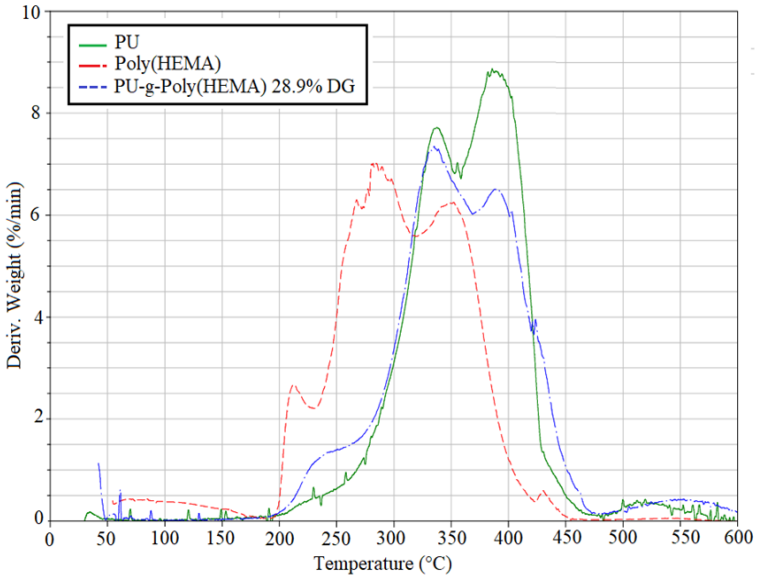


Fig. 2. DTGA thermograms of electrospun PU polymer, electrospun PU-g-poly(HEMA) and pure poly(HEMA)

These results are also supported by Cervantes-Uc *et al.,* [38], who was conducted research using TGA/FTIR for predict the segmented of aliphatic polyurethane and claimed that aromatic isocyanate is less stable than aliphatic ones. Cervantes-Uc and teams also evaluated the mechanism of PU and reported that the presence of CO_2 is due to decomposition of urethane group hard segment. The C-H stretching vibration was claimed related to methylene group from cyclohexyl and butanediol. The O-H stretching vibration is from water or hydroxyl terminated compound. Besides, N-H stretching vibration is coming from either urea or amine group. Meanwhile, poly(HEMA) produced two stages of decomposition temperature which refer to decomposition to monomer segments and decomposition of other various ester chain segments [39]. These two stages of decomposition mentioned by Acevedo *et al.,* [39] was supported by Demirrelli *et al.,* [40] where further suggestion was reported that HEMA is the main product of the first stage. In this stage, (Ambient temperature to 340 °C), 2-isopropenyloxy-ethyl methacrylate is another important product with additional of minor product such as ethylene glycol, methacrylic acid and dioxolane compound. At the second stage (340 to 400 °C), 2-isopropenyloxy-ethyl methacrylate is the main product of the degradation.

After grafting HEMA monomer into electrospun PU surface, the first degradation peak was shifted to lower temperature 335.33 °C. This condition ascribed to the combined effect of PU and HEMA, most probably due to decarboxylation of grafted poly (HEMA) on grafted electrospun PU. The second peak showed an improvement where the second maximum temperature was shifted to higher temperature (389.31°C). This observation provided the quantitative evidence that HEMA monomer was grafted on the PU surface, which improved the thermal stability and density of the electrospun PU. It has been reported by Goel *et al.,* [37], where poly (arylic acid) was grafted on PU foam using gamma radiation. The result of this new combination has yield stable structure where the second maximum temperature peak on poly (acrylic acid) grafted PU shows the overall changes in the thermal conductivity and density [37]. Some other literature also supported this finding [41,42]. The summary of thermal stability of all materials is shown in details in Table 1.

Table 1
The summary of thermal stability of electrospun PU, Poly(HEMA) and electrospun PU-g-poly(HEMA)

Samples*	Onset and Endset temperature (°C)		Max. degradation temperature (T_{max}) (°C)		Decomposition rate		Residue at 500°C (%)
	Onset T_{max}	Endset T_{max}	First T_{max}	Second T_{maxs}	At 300°C (%)/(°C)	At 500°C (%)/(°C)	
A	213.78	451.29	337.58	385.88	0.2994	0.0023	1.151
B	199.91	429.87	284.40	348.97	0.1752	0.0005	0.258
C	205.51	466.44	335.33	389.31	0.2829	0.0071	3.526

*A=Polyurethane, B=poly(HEMA), C=PU-g-poly(HEMA)

With respect to the PU material and HEMA monomer, poly(HEMA) grafted on electrospun PU surface became more thermally stable. These results were confirmed by evaluation on prolonged degradation time and reduced weight loss. The weight loss percentage of PU-g-poly(HEMA) was 95.44% while PU produced 98.1%, which means modified surface electrospun PU is more thermally stable. As conclusion, after RIG process, PU maintained its thermal stability when polymerized with HEMA and PU-g-poly(HEMA) successful produced good thermal stability of electrospun fibre.

3.2 In Vitro Degradation Behavior of PU-g-poly(HEMA) Scaffolds

Degradation of the porous material have been widely conducted in order to determine that the residual solvent was toxic or not towards cells. Figure 3 shows the weight loss profile of electrospun PU and modified surface with 28.9% percentage degree of grafting of HEMA. Based on the graft, it

can be seen that electrospun PU is biodegradable and weight loss occurred on pure material without surface modification in around 14.2%. By introducing 28.9% percentage degree of grafting, percentage weight loss of modified surface scaffolds became reduced. It was found that by increasing the percentage of modification, the scaffolds became more stable, lowering the ability to degrade. This situation is due to the effect of modification technique where the radiation successfully cross-linked those polymers and bound it with stronger hydrogen bonding. The same decreasing trend can be observed on She's *et al.,* [43] study where they reported that the effect of porosity on polymer degradation. However, different solutions were used which is 0.01M of hydrochloric acid and 0.14M of sodium chloride to accelerate that degradation test [43].

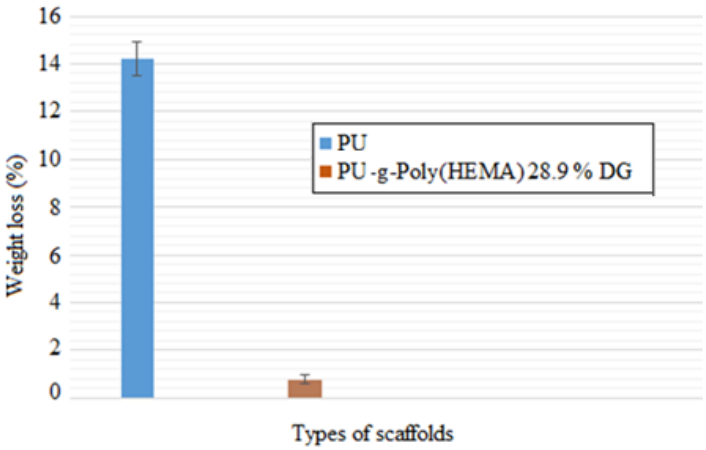
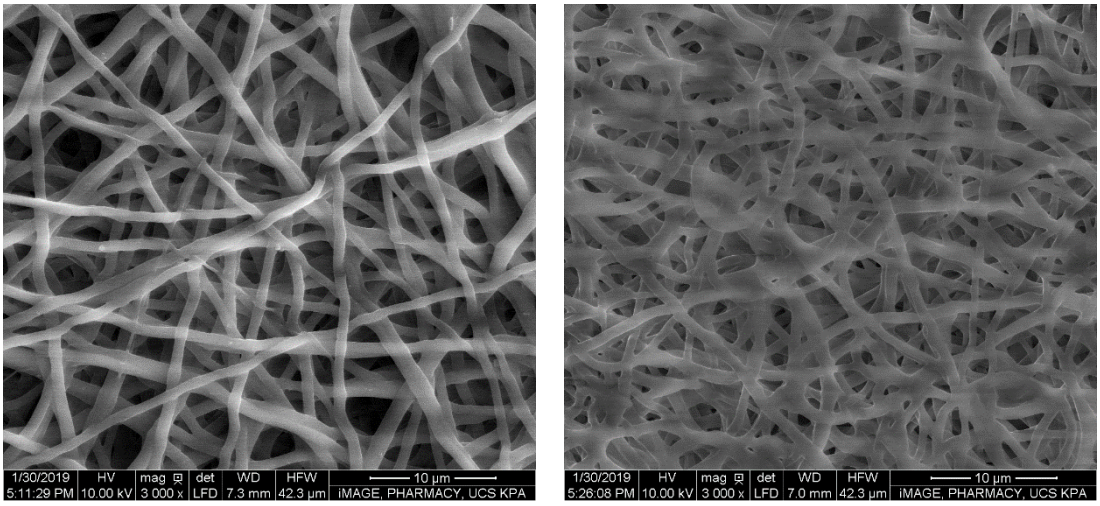


Fig. 3. The weight loss profile of PU and PU-g-poly(HEMA) scaffolds after 84 days incubation periods in PBS

Besides, in case of PLA scaffolds prepared by Barbeck *et al.,* [44], it was revealed that formation of crack was clearly visible after 8 weeks. Thus, the morphology observation towards the surface of biodegradable materials is essential to evaluate the condition of the fibrous scaffolds. This condition can be confirmed by observing the surface of electrospun materials after being incubated in PBS for 84 days using SEM instrument (Figure 4). It can be seen that electrospun PU and modified surface PU maintained its fibrous structures without obvious changes such as cracked or eroded surfaces, showing that PU and PU-g-poly(HEMA) scaffolds are stable in swelling properties and have regular degradation time. As conclusion, electrospun PU fiber and modified surface scaffolds was found to be able to degrade slowly in PBS. However, the percentage of weight loss reduced as the function of DG. Thus, it was confirmed that PU and PU-g-Poly(HEMA) produced good biodegradation property and this new biomaterial was expected to be useful for further biodegradable tissue scaffolds in biomedical aspects.



(a) (b)

Fig. 4. The SEM images of in vitro degradation of electrospun scaffold for 84 days incubation periods. (a) electrospun PU (b) electrospun PU-g-Poly(HEMA) 28.9% DG

3.2.1 Water absorption ratio analysis

All the electrospun PU fibers demonstrated rapid water absorption and reach the equilibrium water uptake within 10 minutes. Table 2 shows the summary of average weight of water taken by electrospun PU and modified surface electrospun PU with 28.9% percentage degree of grafting (DG) of HEMA in 30 minutes. Based on the results from the table, the water uptake capacity of modified surface was decreases with increasing percentage grafting of HEMA. The reason of this situation can be related with the morphology of electrospun fiber before and after modification. Electrospun PU has morphology of porous structure, therefore, this material has the ability to trap some amount of water as physical interaction. By grafting of HEMA on the PU surfaces with high percentage of DG, the hydrophilicity of modified electrospun PU was improved. However, radiation-induced grafting process increased the average fiber diameter of electrospun fiber.

Table 2
The summary of water uptake percentage of electrospun PU and PU-g poly(HEMA) with different percentage of DG

Samples	Weight (%)	Weight (%)	Weight (%)	Average Weight (%)
PU	142.86	178.57	161.90	161.11 ± 17.86
PU-g-poly(HEMA) 28.9% DG	58.00	62.25	57.75	59.33 ± 2.06

Besides, high percentage degree of grafting produced high potentials for homo-polymerization and pore blockage. Thus, the average weight of water uptake reduced with increasing percentage degree of grafting of HEMA. These findings were supported by Mombini *et al.,* [45], which reported that by increasing the carbon nanotubes contents in PVA-CS scaffolds, it will lead to decrease in the water uptake ability of scaffolds. The reason of these trends is due to the gradual increase of crosslinking density [46]. Although the water uptake was decrease on the function of DG, electrospun PU still had not stop to absorb water in response to its porous structure. This reason was supported by previous study, which reported that scaffolds were made of nanofibers and irradiated with the same dose resulted in higher water uptake compared to same materials prepared in form of films casting [27]. The water uptake also depends on the temperature, where the tested materials of hydrogel nanofiber and PCL nanofibers reduced its water uptake at higher temperature [47]. Besides,

the water uptake also depends on the pH of solutions [48]. As conclusion, the desirable water uptake ability indicates that the electrospun PU and electrospun PU-g-poly(HEMA) scaffolds can provide an excellent platform for cell growth and proliferation where the nutrients needed can easily flow and reach the desired locations. Thus, this property is important and could have advantages in tissue engineering applications.

4. Conclusions

The thermal degradation of poly(HEMA) grafted PU–based electrospun fibers was found to produce two stage of decomposition where the first and second stage are related to decomposition of hard segments and soft segments, respectively. The first degradation peak was shifted to lower temperature attributed to combination effect of PU and HEMA. With respect to PU-based electrospun fiber and poly(HEMA), poly(HEMA) grafted PU-based electrospun fibers was became more thermally stable. It was confirmed on prolonged degradation time and weight loss percentage. Besides, the thermal degradation results were in good agreement with in vitro degradation study, where the grafted electrospun PU fibers reduced the percentage of weight loss in PBS compared to raw PU-based electrospun fibers. Meanwhile, water uptake demonstrated that water absorption reduced with the increasing in DG as fiber diameter increased after poly(HEMA) was grafted into electrospun fibers.

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