Better Understanding of the Polymeric Irradiation Using Physico-Electrochemical Characteristics

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Research Article

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Abstract

Poly (ester-urethane) urea (PEUU) based on ethanolamine as a chain extender contain hydroxyl and amino groups was chemically synthesized using 1,1'-methylenebis(4-isocyanatobenzene) MDI diisocyanates, and castor oil. One step polymerization procedure has been used to complete the PEUU formation and this polymeric target was irradiated with different doses (100, 250, 400 and 600 kGy) of gamma-rays. A full physico-electrochemical characterization package was performed on the solid surfaces, radiated vs non-irradiated, for the better understanding of the structure changes. To that end, Fourier transform infrared spectroscopy (FTIR), and the morphological features were characterized by the scanning electron microscope (SEM). Thermal stability was investigated using the differential scanning calorimetry (DSC), while the crystallinity and electrochemical properties were explored by the X-ray diffraction (XRD), and cyclic voltammetry (CV), respectively. Eventually, swelling, crosslinking density, mechanical strength, water absorption and contact angle measurements were discussed. Ultimately, the crosslinking density was discovered to be irradiated dependent. Worth mentioning here, this kind of study is recommended as a protocol that could be applied on other polymeric targets exposed to electromagnetic radiations.

Introduction

Segmented polyurethane–urea linear block copolymers are consisted of two incompatible blocks alternating "hard" and "soft" segments along their macromolecular chain due to their two-phase morphology, formed by the reaction of diisocyanate and diamine extender which yields a urea linkage, while the soft segment is made up from the polyol [1-4]. From the structural point of view, segmented PUU could be further distributed into polyether polyol-based and polyester polyol-based PUU [5, 6]. The use of natural plant oils to replace the use of petroleum oils for the development of polymers has attracted much attention, this is attributed to widespread availability, ease of chemical modification of their backbone, low cost and highly promising applications in several fields [7]. Among natural plant oils, castor oil represents a promising raw material and can be used directly as a starting material for the synthesis of polyurethanes or polyurethane-urea [8]. The major constituent of castor oil, ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid), is the hydroxyl-containing fatty acids [9]. Due to their significant biocompatibility and biodegradability, the polyurethanes-based castor oils have been used in biomedical applications such as wound dressing, bio-adhesives, bone tissue engineering, and drug delivery systems [10-14]. It is known that the PUU properties are strongly deponent on the type of the diisocyanate, polyol and chain extender, reaction conditions, degree of microphase separation, hydrogen bonding properties, copolymer structure, hard and soft phases content. Accordingly, the PUU exhibited excellent properties of high elasticity, huge tensile strength and extra toughness [15-19]. Thus, the PUUs are among the most important polymeric materials gained considerable attention in the last decades, exhibiting functional properties that make them convenient to be exploited in many different fields whether industries or everyday life such as coatings and paints, footwear, textile, elastic fibers, electronics, machinery, biomedical applications like drug delivery, biomedical therapies, biological and membrane science, as well as, many of the

3

biomedical devices such as insulation for prosthetic heart valves, pacemakers, blood pumps, and vessels [20-22]. Insulation is an important property of PUU and it is the major focus nowadays because of their chemical constituents yet highly promising applications [6]. Ionizing radiation can be used to improve the properties of polymers, change the physical and mechanical properties [23]. Radiation can increase polymerization reaction, initiation of the polymerization process as well as cross-linking [24, 25]. Radiation crosslinking is one of the most important research fields of radiation polymerization and has been great development since Charles [26] found polyethylene radiation effect and predicted these radiation effects can be used in industrial applications. Radiation crosslinking (RC) is one of the approaches of physical functionalization of synthetic polymers [27]. The RC leads to detaching hydrogen atoms from the surface of polymer chain because of the effect of high-energy radiation, and usually the RC is taking place in a solid phase and in a direct contact with the target polymeric surfaces. Hence the RC has the advantage over the other chemical crosslinking that no catalysts or other additives are needed, and therefore, no by-products are generated, no heat treatment, and the formation of crosslinks in the solid state and complete control of density of crosslinking [28, 29]. Here, we have synthesized ETA-based PEUU elastomer, and we studied the effect of γ-irradiation with different doses on the physico-electrochemical properties of the PEUU. Understanding the radiation influence on the polymer features changed was achieved.

Materials and methods

Chemicals and reagents

1,1'-Methylenebis(4-isocyanatobenzene), (MDI, Mw 250.25 g/ mole), Ethanolamine (ETA, Mw 61.08 g/ mole), and Castor oil (CO, Mn= 933.61 g mole/mole) were purchased from Merck, Germany. Tin(II) 2-ethylhexanoate was used as a catalyst and it has been provided by

Sigma-Aldrich. Dichloromethane (DCM) was purchased from El-gomhouria for trading pharmaceuticals, chemicals & medical appliances, Egypt.

Synthesis of Poly(ester-urethane) urea (PEUU)

Co-based polyurethane Urea (PUU) was synthesized according to previous reports **[30, 31]**. CO - MDI - ETA was synthesized by a typical one step polymerization procedure as is shown in **Scheme 1** and their feed ratios were 1:0.6:0.4. Briefly, three solutions were placed in 250 ml polypropylene beaker, stannous octoate (0.03 wt%, with respect to the reactant) was added to the solution as a catalyst and stirred vigorously. The resulting viscous (PEUU) was then poured into a silica mold and heated at 50 °C for 100 h in an oven to obtain a complete polymerization. Then, the samples were conveyed to a roll mill mixer for few minutes to remove air bubbles through the casting process. Finally, the product was undergone to hot press, and compression molded into 1 mm plates at 175 °C for 45 min at pressure of 62.05 MPa, and then cooled to room temperature. The composition, sample code, HS and SS content for PEUU are presented in **Table 1**. The HS and SS contents are calculated using equation (1) and (2) respectively.

Irradiation of the samples

Poly(ester-urethane) urea films were irradiated by gamma-rays at doses 100, 250, 400 and 600 kGy with a dose rate 5kGy/h. The irradiation process was performed at ambient room temperature (25°C), where a cooling system was used in the irradiation chamber to avoid heating of samples during irradiation. Gamma-irradiation was carried out using Cobalt-60 gamma cell source available in National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority of Egypt (AEAE), Cairo, Egypt.
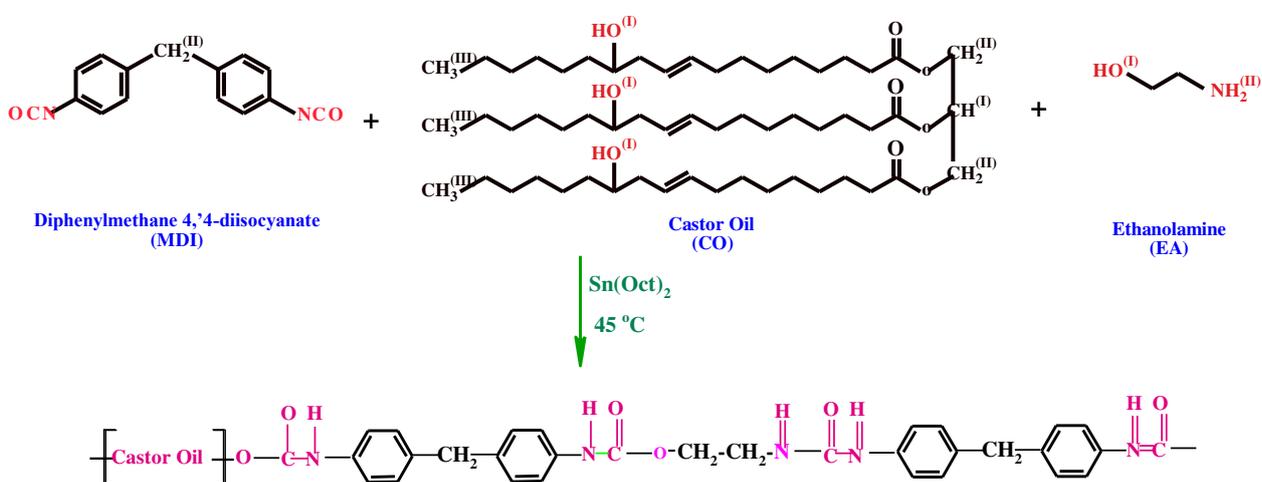
$$\text{Hard segment content (wt \%)} = \frac{W_{MDI} + W_{CO}}{W_{MDI} + W_{CO} + W_{CH}} \qquad \textbf{(1)}$$

$$\text{Soft segment content (wt \%)} = 1 - \text{hard segment content (wt \%)} \qquad \textbf{(2)}$$

WMDI: weight of MDI

WCO: weight of polyol

WCH: weight of chain extender

Scheme 1. The reaction scheme of the PEUU.

Physico-chemical characterization

- The FTIR spectra were collected in the range of 4000-400 cm^{-1} at room temperature, utilizing 64 scans at 4 cm^{-1} resolutions.

- Differential Scanning Calorimetry (DSC) analysis was performed using the Q20 V24.10 Build 122(USA), whereas approximately 6 mg of the sample was measured,

6

temperature range from 0-400 °C at a heating rate of 10 °C/ min, under the nitrogen flow of 40 ml/min.

- X-ray diffraction (XRD) analysis was performed using Shimadzu XRD6000 Japan, operating with nickel filtered, *Cu-K* target, voltage 40kV, current 30mA, and scan speed 8deg/min.

- Electron microscopic images using the scanning electron microscope (SEM, JEOL, JXA-840A) was captured at an accelerating applied potential of 15 keV.

- The cyclic voltammetric measurements were carried out using a computer-controlled Gamry potentiostat/galvanostat/ZRA G750 (Gamry, Pennsylvania, USA).

Mechanical measurements

Mechanical testing was performed by the tensile testing machine (Mecmesin, UK, MultiTest 25-I model). Five samples were cut out from the polymeric sheets in a dumbbell-shape using a steel die of standard width (4 mm) with 1 mm thickness. A benchmark of 1.5 cm and crosshead speed of 500 mm /min was set for carrying out each part of the test specimen for elongation estimation.

Swelling measurements

All Specimens of known weight were immersed in DCM solvent for 72 h at 25℃. Subsequent to this, the swollen samples were removed from the DCM and weighed again before being placed in a vacuum oven. The vacuum oven was preheated to 60℃ and the swollen samples were dried until a constant weight was achieved. This procedure was repeated four times for each sample. The swollen polymers were calculated according to the following equation:

$$\text{Swelling ratio} = W_s + W_i/W_i \qquad \qquad (3)$$

Where W_s is the weight of the swollen gel and W_i is the initial polymer weight.

Cross linking density measurements

It has been shown that the true stress in simple extension can be considered as a sum of two contributions as follows:

$$\sigma = \sigma_o(\lambda) + Ge\ (\lambda^2 - \lambda^{-1}) \qquad \qquad (4)$$

σ is the true stress, λ is the extension ratio, the value of σ_o depends on the chemical nature of the rubber but not on the crosslink density. Ge depends on the degree of cross-linking. The average molecular weight between cross-links M_c, which is directly related to the crosslink density, can be estimated from the value of Ge as follows:

$$Mc = A_o \rho RT/Ge \qquad \qquad (5)$$

M_c is the average molecular weight of the polymer between crosslinks, A_o is the a prefactor equal to 1, ρ is the polymer density, R is the gas constant equal to $8.3 \times 10^6\ cm^{-1}\ pa\ mol^{-1}$, T is the absolute temperature [32, 33].

Water absorption measurements

The water absorption testing was determined as previously described [34]. The samples were first cut into 1 cm × 1 cm square shapes and weighed. Next, samples were placed in an oven of 50 ºC for 24 h. Then the samples were transferred into a desiccator and cooled to room temperature. Eventually, the samples were immersed in boiling deionized water for 30 min. cooling for 15 min until the water in the surface of the samples was dried up with filter paper, the weight of the samples was measured again and recorded. The absorptivity (W_m) was finally calculated from the equation:

$$\text{Water absorption } (W_m) = \frac{m_2 + m_1}{m_1} \times 100 \, \% \tag{6}$$

Where m_1 is the weight of samples before soaking in water and m_2 is the weight of samples after absorbing water.

Contact angle measurements

The contact angle was measured after 10s by dropping a water drop on the PEUUs surface. Three samples of each material were measured and three measurements were carried out for each sample, and the angle between the liquid surface and PEUUs was then calculated using Image-J program.

Results and discussion

The FTIR spectra of pristine (un-irradiated) and the irradiated polyurethane-urea solid surfaces were exposed to gamma irradiation at various doses from 0 to 600 kGy, as illustrated in **Figure 1**, and frequencies for characteristics peaks are tabulated in **Table 2**. The characteristic absorption at 2267cm^{-1} (N=C stretching) of the -NCO group is disappeared, indicating that all the isocyanate groups are incorporated into the copolymerization, and complete formation of PEUU [35, 36]. The absorbance peaks of (N-H stretch) for urethane and urea groups were observed in all FTIR spectra. Meanwhile, C=O stretch of ordered C=O···H-N in the urethane and urea groups indicated the successful chain extension and displayed effect which increased with increasing the hard segment content by urea groups, this has been identified in all curves (PEUU$_0$ to PEUU$_{600}$) [37]. In addition, the two FTIR bands were observed between 2922 and 2852 cm^{-1} which are attributed to symmetric and asymmetric stretching of the C–H bond [38]. After irradiation for different doses of γ-ray, minor shifts in frequencies toward higher or lower wave number for some of the

9

characteristic vibration peaks of PEUU were observed. The frequency changes to lower or higher is found to be dependent on the dose of radiation. Hence, irradiated PEUU samples may have formed stronger bonds due to gamma doses than bonds of pristine PEUU [39].

Mechanical properties

Mechanical properties of PEUU are extremely important for its polymeric performance, particularly in biomedical application. Therefore, changes in mechanical features such as tensile strength, elongation, hardness and modulus have been investigated and plotted in the **Figure 2**. As a function of the gamma ray doses, the tensile strength values **Figure 2A** were increased gradually when the ionization radiation doses were increased. Based on the radiation doses (0,100, 250, 400 and 600 kGy), strength values (4.5± 0.14, 5.6 ± 0.16, 6.15 ± 0.21, and 6.85 ± 0.07) were obtained, respectively. On the other hand, 600 kGy exhibited the highest tensile strength as it reached the value 8.35 ± 0.22. This indicates that, irradiation of the PEUU surfaces using the γ-rays led to the formation of cross-links between the polymer chains [40]. On the other hand, elongation at break **Figure 2B** which is the measure of a materials ductility was markedly decreased after the irradiation, where the elongation reached the maximum value at zero-irradiation then decreased continuously up to 600 kGy. Elongation at break is more sensitive towards the change in polymer morphology. Once again, the increase in tensile strength and decrease in percentage elongation at break could be attributed to the formation of crosslinking at the amorphous phase. Formation of cross-links impacted the rigidity of the material and reduced the elongation at break upon irradiation. All these finding were in accordance with what has been obtained by Bailey et al. [40, 41].

Figure 2 (C and D), showed the Young's modulus and hardness vs. different radiation doses and the non-irradiated PEUU. A continuous increase in the Young's modulus (4.75 ± 0.75, 11 ± 1.01, 26 ± 1.02, 38.5 ± 1.53, 57.5 ± 2.48 MPa) was observed with the increase. On the other

side, the hardness was increased slightly with irradiation dose, the non-irradiated sample showed the lowest hardness value (77 ± 2 MPa) and increased very slowly with 100, 400 and 600 kGy (79.5 ± 1.5, 96 ± 3.9 and 101 ± 5.1) while with the 250 kGy the highest value (93 ± 3.02) was obtained.

Morphological characterization using the electron microscopy (SEM)

Changes in the surface morphology of the PEUU was studied before and after irradiation. Hence, scanning electron microscopy (SEM) images were conducted on the pristine (0 kGy) and gamma irradiated (600 kGy), as shown in **Figure 3**. As result, the surface of PEUU appeared to be very rough before the irradiation, while the irradiated surfaces were smoother break, which may be attributed to the formation of the crosslinking by the irradiation process. The increase in the smooth-surface by gamma ray could be correlated to the formation of oxidation on the surface of the irradiated PEUU, which, in turn, modified the properties of irradiated sample [**42, 43**].

Differential Scanning Calorimetry (DSC) Analysis

The thermal properties of PEUU activated by different gamma ray doses were determined by the DSC analysis, as shown in **Figure 4**. The glass transitions temperature (T_g) of hard segment and melting transition temperature (T_m) of soft segment are represented in **Table 3**. The T_g values of the hard segment were observed from 53 to 74 °C for all PEUU samples with unsettled changes in the T_g when the samples were irradiated. This is accredited to branching and chain separation achieved by the irradiation process, which in turn leads to increase the free volume of the samples [**44**]. In a strong agreement with what has been reported by Fox and Gibbs [**45, 46**] where they stated that the chain ends introduced an additional free volume that allowed the T_g to decrease by means of decreasing the chain

length. Furthermore, branching affected the T_g value to decrease by limiting chain packaging and generating free volume **[47-49]**. A higher temperature endotherm observed above 200°C reflected the melting point of hard microdomains **[50, 51]**. Also, the melting points T_m values of the hard domain for all PEUU samples were observed from 315 to 318°C. With increasing the irradiation doses, the melting temperature increase in a non-linear pattern, whereas the flexible hydrocarbon chain in the backbone may play a role in this finding **[52]**.

X-ray diffraction (XRD)

Since the XRD is the principal technique to assess the degree of crystallinity in polymers, crystallinity phase of all PEUU surfaces were studied, as shown in **Figure 5**, and **Table 4**. The XRD diffractograms for the non-irradiated and irradiated PEUU disclosed the crystallinity degree which is evidenced by the sharp diffraction peaks allocated at several 2θ values, where $PEUU_0$ ($2\theta =20.46°$), $PEUU_{100}$ ($2\theta =20.84°$), $PEUU_{250}$ ($2\theta =20.4°$), $PEUU_{400}$ ($2\theta =20.12°$), and the $PEUU_{600}$ ($2\theta =20.32°$). This indicates that the crystallinity of PEUU elastomers is provided by the soft segments and is related to a certain degree of structural ordering [**53**]. On the other hand, as the crystallite size is another important parameter could be fetched out the XRD analysis, the crystalline size of the PEUU surfaces were calculated by cherrer's equation [**54**]. As can been seen in Table 3, there is no significant changes in the crystalline size of PEUU after the irradiation, whereas the crystalline size average was about 12 Å, expect the last sample ($PEUU_{600}$) with a value of 13 Å. These results confirm that, gamma irradiation had no effect on the materials crystalline size.

Swelling and Crosslink density

Basically, swelling study gives an indication of the extent of crosslink density in polymer chains [57]. The swelling value is usually decreases with the increase of crosslink density [58]. Here, the impact of gamma rays on the swelling behavior of PEUU were measured in dichloromethane at 25 $^{\circ}$C and calculated based on equation (3), the swelling values irradiation-doses curve were represented **Figure 6**, (Black line). As a result, the decrease in the swelling rate was dependent on the intensity of gamma irradiation doses. Therefore, the pristine PEUU surfaces the highest swelling degree (1.72 g\g), while the lowest swelling degree (0.956 g\g) was accomplished by highest irradiation dose 600 kGy. This is an evidence that the activation of PEUU surfaces with gamma ray led to the formation of crosslink density between the polymer chains, accordingly the swelling capacity of the treated surfaces were reduced. The degree of crosslink density 1/Mc against irradiation dose is calculated based on equation (4), (5), and the results are plotted in **Figure 6**, (Blue line).

Water uptake performance

In order to study the ability of water uptake during the network formation, degree of water absorption of the PEUU was measured for the irradiated samples while the pristine sample was considered as the positive control. The values calculated based on equation (6) as shown in **Table 5**, all PEUU irradiated surfaces absorbed volumes of water with a large degree of variation in the water absorption capability. The pristine PEUU, as the control, exhibited the maximum volume followed by a decrease in the water content with increasing irradiation dose. The water uptake occur as a result of swelling (water uptake of the polymer matrix material) or hydration (entry of water into accessible spaces into the porous matrix) [59].

13

Hence, the irradiated PEUU surfaces exhibited a resistance of water absorption with increasing crosslink density between polymer chains.

Contact angle

In order to evaluate the surface hydrophilicity of the PEUU films after exposed to gamma rays, water contact angles were measured and presented in **Figure 7**. As a result, water contact angle was increased from 0 to 250 kGy, and then reduced with irradiation dose 400 and 600 kGy to 69.7±3.07 and 72.7±1.6, respectively. According to the formation of cross-linking between polymer chains, the contact angle was increased and the hydrophilicity was decreased at the lower doses 250 and 400 kGy. Moreover, a notable reduction of the contact angle values was observed with 400 and 600 kGy, this might be attributed to the free radicals produced upon radiolysis with oxygen and/or surface degradation [60, 61].

Electrochemical characterization

Electrochemical properties of the target polymers were studied here using the cyclic voltammetric technique, as shown in **Figure 8**. Reduction-oxidation of a standard redox probe ([Fe (CN)6]$^{3-/4-}$) was used for the electrochemical evaluation. Basically, generation of oxidation faradaic current (Positive electric current on the Y-axis), and/or generation of reduction faradaic current (Negative electric current on the Y-axis) means that there is an electron transfer taking place at the conducted interface. The higher the current, the fast the electron transfer. However, blocking the generation of such faradaic current designates that there an insulating interface. From the obtained result, a complete blocking of Faradaic current was accomplished by using the PEUU, either the irradiated or the non-irradiated. This finding is a strong evidence that the insulating electric feature is there for the PEUU, and it was not affected by the irradiation even at the highest dose.

Conclusions

PEUU elastomers were successfully synthesized using ethanolamine as a chain extender, the hard segment constituted of 1,1'-methylenebis(4-isocyanatobenzene) was formed by the castor oil as a soft segment. FTIR spectra confirmed the formation of the urethane-urea group. Cross-linking by gamma irradiation, at different doses, affected the thermo-mechanical properties of the PEUU but did not show any effect on the electrical performance of the irradiated surfaces. Diffraction patterns demonstrated the crystalline phase segments. The prominent effect with crosslink density was determined by swelling measurements, further information was obtained by water absorption and contact angle. Eventually, this study provided a wide over view on the effect of electromagnetic radiations on the physico-electrochemical properties of synthetic polymers. This will support a better understanding of the polymer future applications.

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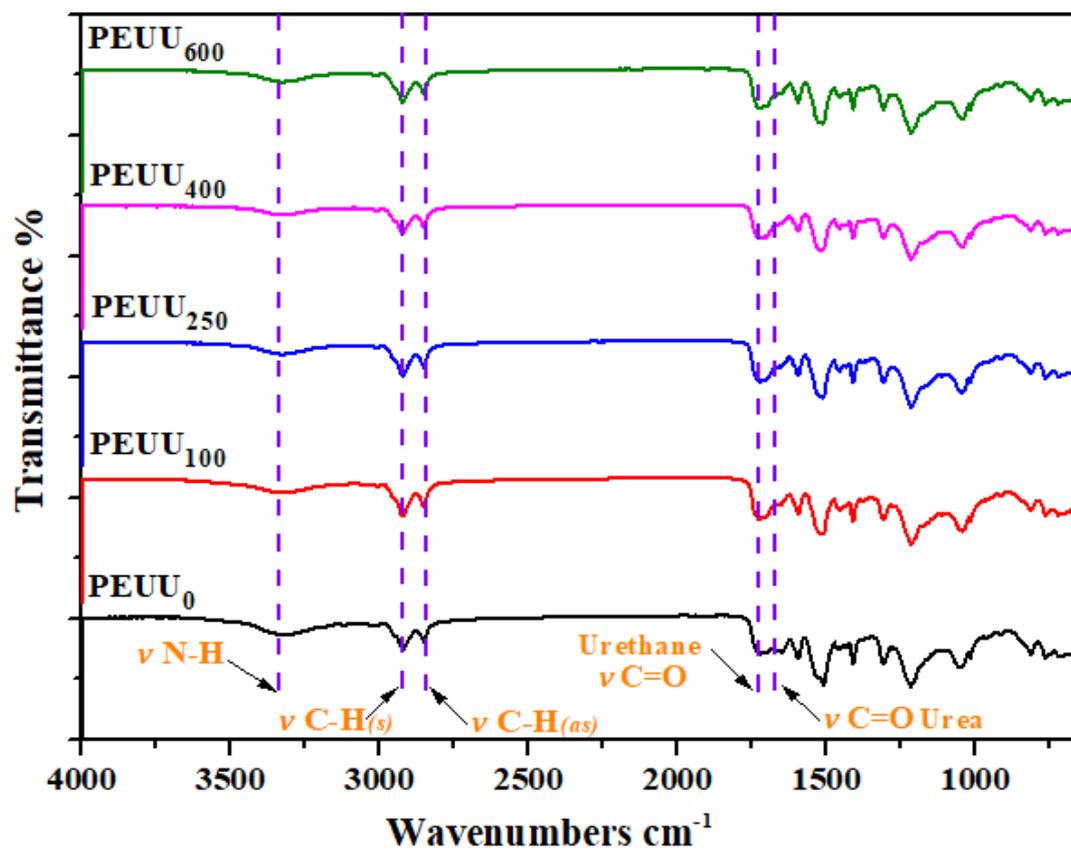
Figure 1. FTIR spectra of pristine and gamma-irradiated PEUU with different gamma radiation doses (0,100,250,400,600 kGy)
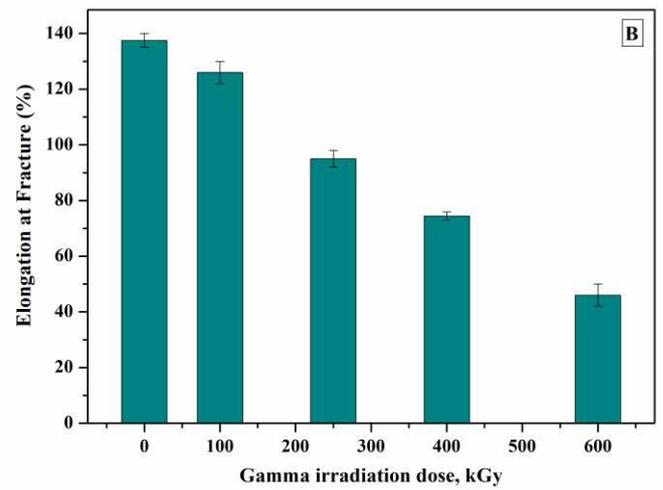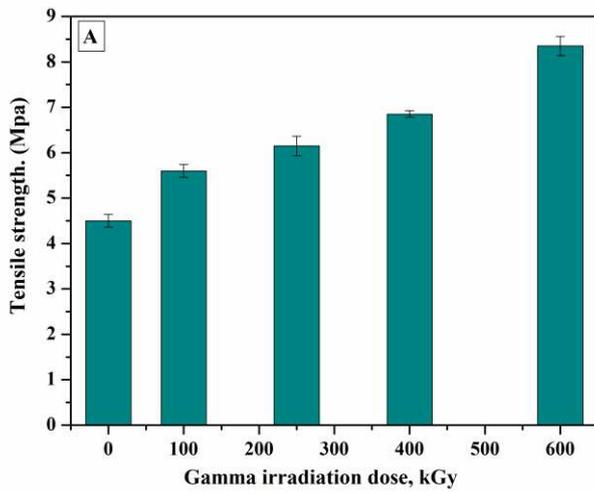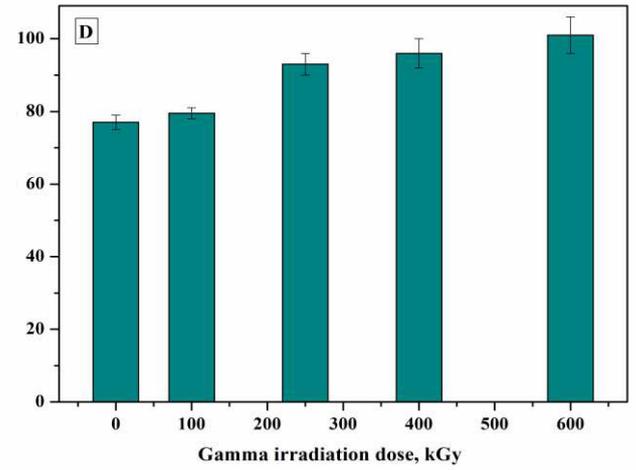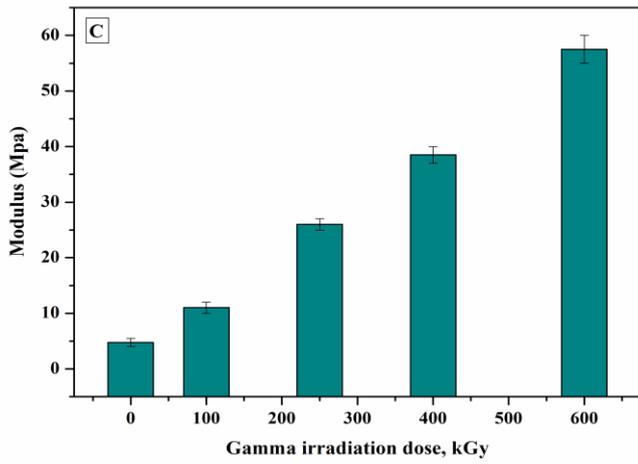
Figure 2. Mechanical properties of non-irradiated and irradiated samples (A) Tensile strength, (B) Elongation, (C) Modulus and (D) Hardness.
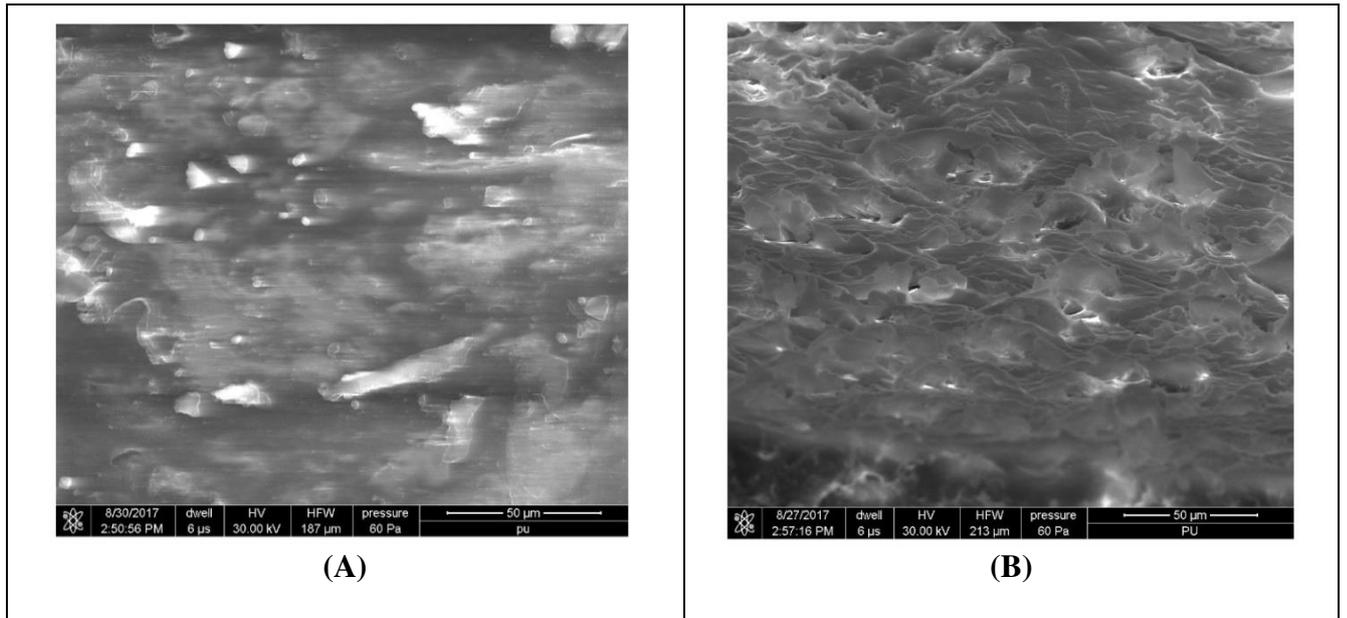
Figure 3. SEM photographs of: (A) non-irradiated, (B) 600 kGy -irradiated PEUU solid surfaces.
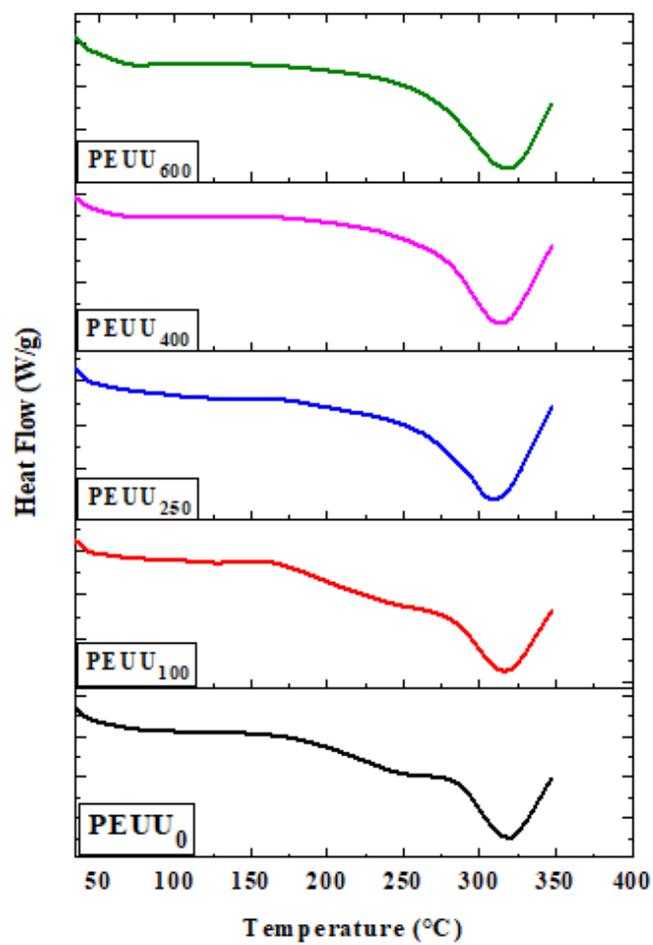
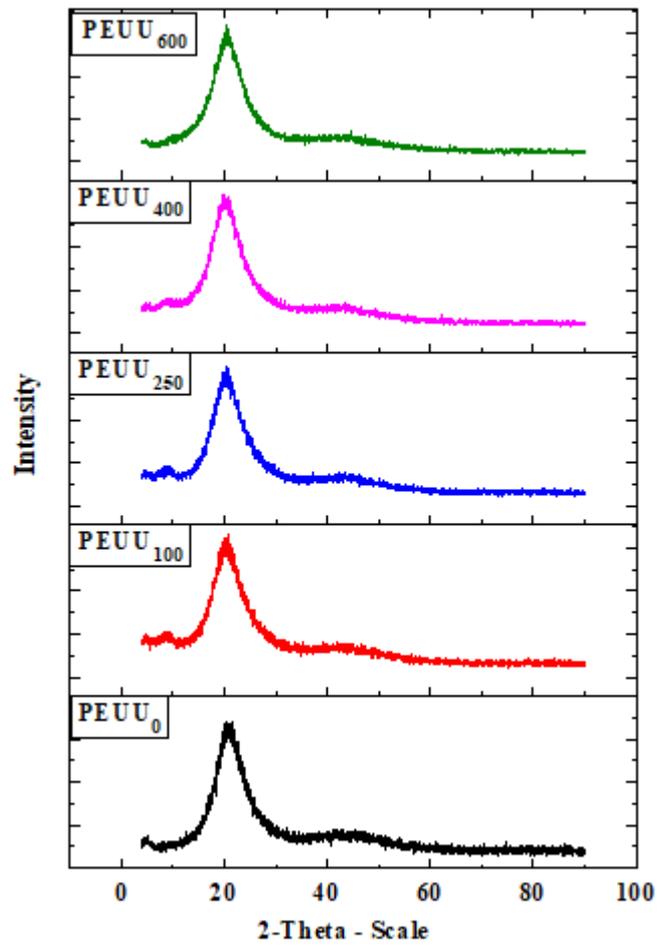**Figure 4.** DSC curves of the non-irradiated and irradiated PEUU samples

22

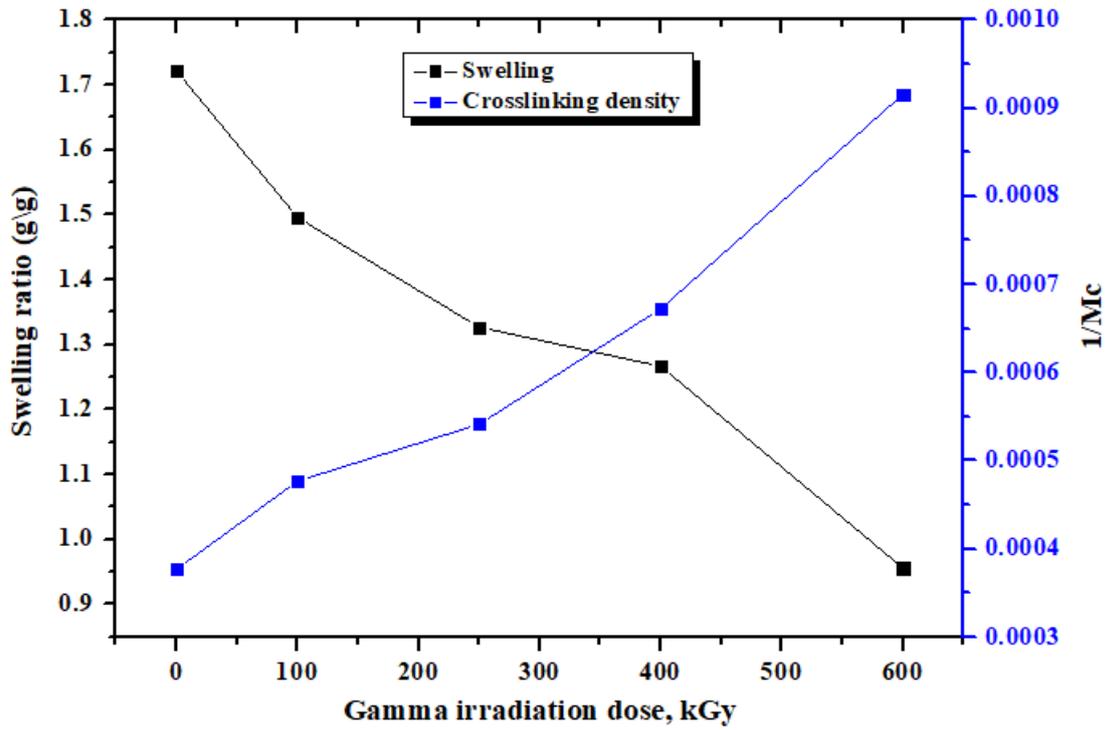**Figure 5.** XRD diffractogram of the non-irradiated and irradiated PEUU samples.

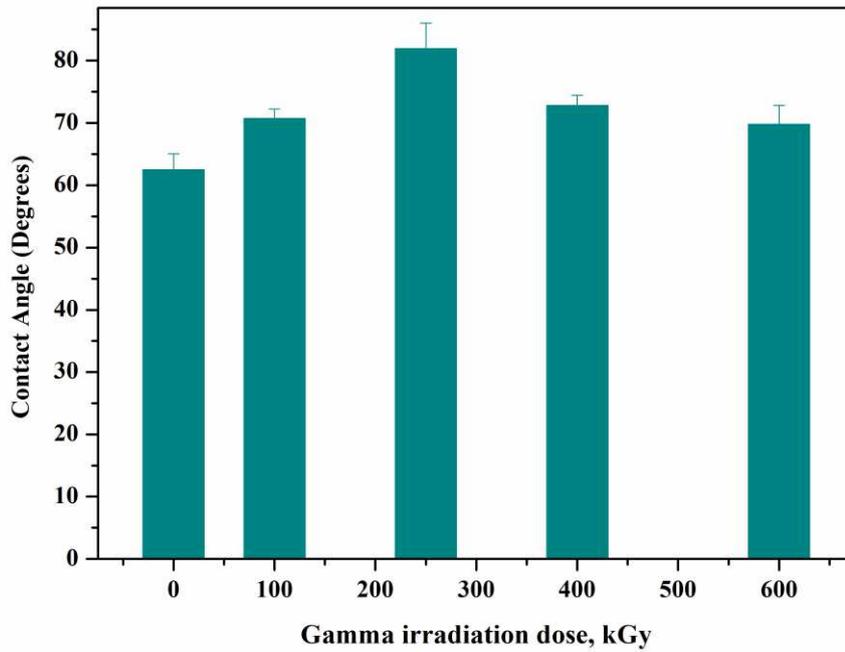**Figure 6.** Swelling ratio and crosslink density of the non-irradiated and irradiated PEUU samples.

Figure 7. Contact angle measurements for the non-irradiated and irradiated PEUU samples.

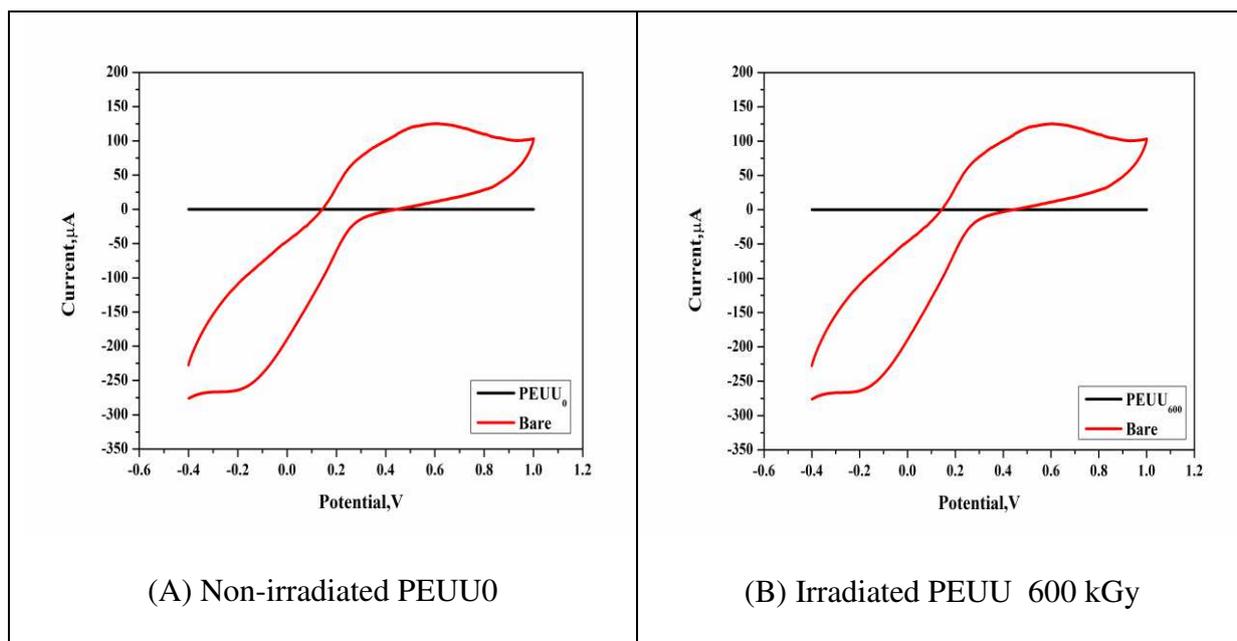(A) Non-irradiated PEUU0 | (B) Irradiated PEUU 600 kGy

Figure 8. Cyclic voltammetric measurements of FCN redox reactions of graphite solid electrode (the positive electrode), and non-irradiated and irradiated PEUU 600 kGy surfaces. The voltammetric measurements were conducted in KCl (0.1 M) containing 1 mM of the standard redox probe which is the $[Fe (CN)6]^{3-/4-}$.

Tables

Sample	Composition	Molar ratio	S.S.(mass%)	H.S.(mass%)
PEUU	MDI:CO:ETA	1:0.6:0.4	54.99	45.01

Table.1. Composition of the synthesized Poly (ester-urethane) urea.

	Absorption frequency from FTIR spectra (cm^{-1})				
γ radiation dose (kGy)	v N-H	v C-H(s)	v C-H(as)	v C=O (Urethane)	v C=O (Urea)
PEUU$_0$	3323.27	2922.63	2853.08	1725.26	1651.92
PEUU$_{100}$	3324.79	2923.29	2852.19	1724.64	1652.55
PEUU$_{250}$	3325.49	2923.64	2853.39	1726.91	1652.89
PEUU$_{400}$	3327.92	2924.02	2854.09	1727.29	1654.01
PEUU$_{600}$	3329.95	2925.32	2855.40	1727.62	1655.26

Table 2. Values of vibration frequencies from FTIR spectra of PEUU before and after irradiation.

Sample	Peak $T_{g(HS)}$ (°C)	Peak $T_{m(HS)}$ (°C)
PEUU$_0$	53	315
PEUU$_{100}$	56	317
PEUU$_{250}$	55	309
PEUU$_{400}$	53	313
PEUU$_{600}$	74	318

Table 3. Data obtained from the DSC analysis of the non-irradiated and irradiated PEUU samples.

Sample	2θ	Crystalline Size (Å)
PEUU$_0$	20.46°	12
PEUU$_{100}$	20.84°	12
PEUU$_{250}$	20.4°	12
PEUU$_{400}$	20.12°	12
PEUU$_{600}$	20.32°	13

Table 4. Data obtained from the XRD scans of the non-irradiated and irradiated PEUU samples

Sample	PEUU$_0$	PEUU$_{100}$	PEUU$_{250}$	PEUU$_{400}$	PEUU$_{600}$
Water absorption W_m (%)	5.21	3.93	3.12	1.75	1.40

Table 5. Comparison of water absorption of PEUU before and after irradiation.