Synthesis of Polyurethane Elastomers by One-shot Technique and Study of Different Polyol Types and Hard Segment Content After Exposure to γ-Irradiation

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Abstract: In the present study, a series of polyurethane elastomers (PUEs) are developed via a one-shot technique, with the aid of an internal mixer, followed by the compression molding of the samples. Bis(4-isocyanatophenyl)methane (MDI) is used with various ratios; of 1,4-butanediol (BG) as a hard domain, whereas the soft domain is based on two classes of polyols of different number of -OH groups; castor oil (CO) as a polyester and poly(tetramethylene ether) glycol (PTMO) as a polyether. The obtained PUEs films are irradiated with gamma radiation from a ^{60}Co source in air at doses that ranged from 100 kGy to 600 kGy at room temperature and a dose rate of 5kGy/h. The samples are characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mechanical testing. The formation of the PUEs is confirmed via disappearance of the NCO peak in the FT-IR spectrum and which demonstrates that MDI has reacted completely. TGA and DSC results have shown that the thermal resistance, glass transition temperature (T_g) and the melting point (T_m) have increased with increasing BG content and irradiation dose. It has been found also that the PUEs samples based on polyester polyol are more superior than the ones based on polyether polyol. The mechanical tests of the polyester-based PUE's shown that their tensile strength, hardness modules rise and the elongation at break decrease with increasing both BG and crosslinking density contrariwise of polyether-based PUEs. Moreover, the crosslinking density that formed upon increasing irradiation dose has shown the same results.

Keywords: Polyurethane elastomers, synthesis, gamma irradiation, hard segment content, thermal and mechanical properties

1 Introduction

Polyurethane (PU) is one of the most versatile classes of materials that opened the way to a new type of high-performance polymers that are used in different applications such as coatings, adhesives, elastomers, fibers, electronics, foams, and biomaterials. Based on a simple poly addition reaction, polyurethanes were proved to be very versatile polymers [1]. The group of these materials, the polyurethane elastomers (PUEs), is one of the six main synthetic materials which belong to polymeric materials that have both properties of rubber and hard plastic. It has high strength of plastic as well as elasticity and toughness of rubber[2,3], which can be molded, injected, extruded and recycled [4]. PUEs are structurally considered as multi block copolymers [5] consisting of an alternating flexible component or macrodiol, called soft segment, and a stiff component derived from the diisocyanate and a chain extender, called hard segment [6] .The segment structure, weight fraction, molecular mass, segment ratio, crystallinity, polydispersity, method/polymerization procedure used during the synthesis (one or two-step i.e., prepolymer method), processing conditions, and crosslinking, in either phase (hard or soft), influence phase separation, and consequently the mechanical properties of PUE's [7, 8]. In addition, formation of hydrogen bonding between urethane linkages, also strongly influences PUEs phase

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separation [9]. Due to their advantageous properties like, biocompatibility, bio-stability, process ability and broad range of mechanical properties such as flexibility, toughness, durability and tensile strength, these polymers have become the choice for a wide variety of biomedical application [10,11], including external applications as catheters, padding and bedding, cardiovascular applications, nerve guides bone tissue engineered substrates, artificial organs [12], tissue replacement and augmentation, breast implantation, and wound dressings and adhesives [13,14,15]. However, its composition, phase separation, and thus, structure must be adjusted to satisfy the stringent conditions of medical applications. It is now well-recognized that we witness a golden age of innovation with novel materials, with discoveries important for both basic science and device applications, smart materials consider one of the most material used in quantum computation. Materials by design and the exciting role of quantum computation/simulation [16] such as silicon as a material gains ground in quantum-computing race [17], shape memory polymer of polyurethanehas myriad of advanced applications in different fields from daily life uses like textile to biomedicals. These applications include artificial organs like muscles, smart catheter, drug-delivery systems, biosensors, auto-repairing automobile parts, smart textile, self-healing materials, smart suture, quantum computing [18,19,20] and so on. Moreover, one of the main information processing is magnetic resonance imaging (MRI) which is the most powerful diagnostic tools, has emerged as a versatile platform to monitor the delivery efficiency of drug [21,22]. Super paramagnetic iron oxide (SPIO) nanoparticles are used to improve the imaging resolution of MRI,because of its excellent super paramagnetic properties [23]. Hence, SPIO can be loaded with polyurethane, as a nano vehicles, for multifunctional drug delivery and MRI applications [24]. On the other hand, polyurethane sponge is used as a carbon source developed by N-doped carbon nano materials and as a good probe for cellular imaging [25].

When PUs are appointed in the manufacture of medical devices that are implanted, it is critical for the final product to be sterilized before use. Sterilization processes, like ethylene oxide, dry steam, heat, and high energy irradiation can have unfavorable effects on medical grade polymers, such as, extensive material degradation, and plastic deformation. Moreover, sterilizing techniques can act either physically or chemically leading to alterations of the structure, or function of macromolecules, which can result in oxidation, chain scission, cross-linking, melting and hydrolysis [26,27]. Polyurethanes are qualified as materials having excellent radiation stability. However, depending on the molecular architecture and composition, radiation resistance of polyurethanes differs significantly [28].

Ionizing radiation has been found to be widely applicable in modifying the structure and the properties of polymers, and can be used to tailor the performance of either bulk materials or surfaces. Radiation cross-linking modification of polyurethanes is one of the most important aspects [29], but few papers have published, concerning the effects of ionizing radiation on PUs, either with gamma irradiation or electron beam irradiation [30]-[39], and mainly in the last decade, for the latter. Gamma radiation effects on polyurethanes were investigated by Pierpoint et al.[36] who observed that polyurethanes are more resistant to high-energy radiation than other polymers due to the presence of aromatic rings. However, the effects of irradiation on the microstructure are complex and closely related to the chemical composition, irradiation environment, and the absorbed dose [40]. The objective of this study is to quantify the effect of chemical soft segment constructions that has been investigated by choosing two types of polyols, polyester and polyether, and clarify the role of the hard segment chemical construction in physical and mechanical properties of the elastomers, which has been studied with changing the molar ratio of the chain extender. This study is also concerned with the effects of irradiation on the properties of PUEs, the radiation has been used in crosslinking of PUEs at room temperature.

2 Experimental procedure

2.1 Raw materials

Bis(4-isocyanatophenyl) methane (MDI), Butylene glycol (BG, 99.8%), poly (tetramethylene ether) glycol (PTMO, $Mn= 1000$ g mole^{-1}) were purchased from Merck KGaA, Germany. Castor oil (CO, $Mn= 933.61$ g mole^{-1}) (hydroxyl value = 180 mg KOH/g), Dichloromethane (DCM) as a solvent were obtained from El-Gomhouria Company for Trading Chemicals and Medical Appliances, Pharmaceutical Chemicals Group, Egypt. Tin2-ethylhexanoate ($Sn(Oct)_2$, > 9%) is used as the catalyst and provided by Sigma Aldrich.

2.2 Preparation of PUEs

All PUE samples are prepared by using a one-step bulk polymerization procedure. MDI is used as received; polyols and chain extender are dried at 80 °C under vacuum for 24 h before use to ensure the elimination of all air bubbles and water vapors that may interfere with the isocyanate reactions. Macrodiols (CO) or (PTMO), chain extender (BG) and Tin2-ethylhexanoate (0.03 wt% of total solid) as a catalyst are placed in a 250 ml polypropylene beaker with stirring. MDI is weighed into a wet tarred 50 ml polypropylene beaker and quickly poured into the macrodiol while rapidly stirred with a stainless steel spatula under the nitrogen blanket. After stirring for 30 seconds, the viscous polymer is poured into

a silica mold and complete polymerization at 50 °C for 100 h in an oven. Then the samples are transferred to roll mill mixer for 10 minutes to get rid of trapped bubbles during the casting process. To ensure sufficient homogeneous mixing, the samples were subjected to hot press; compression molded into 1 mm plates at 175 °C for 45 min at pressure 62.05 Mpa and then cooled down in 10 min. to room temperature. The resulting PUEs samples are about 1 mm thickness. The composition, sample code, HS and SS content for polymers are presented in Table (1). The HS and SS contents are calculated using equations (1) and (2) respectively.

2.3 Irradiation of the samples

Polyurethane films are irradiated in the presence of air at room temperature with doses 100, 250, 400 and 600 kGy at dose rate 5kGy/h. The irradiation process is carried out using Cobalt-60 gamma cell source (manufactured by the Atomic Energy Authority of Canada) established at National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority of Egypt (AEAE), Cairo, Egypt.

$$hard segment content (wt\%) = \frac{W_{MDI} + W_{BG}}{W_{MDI} + W_{MD} + W_{BG}} \quad (1)$$

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

Where
W_{MDI}: weight of MDI,
W_{MD}: weight of polyol,
W_{BG}: weight of chain extender.

Table 1: Composition, sample code, HS and SS for PUEs samples

Sample code	composition	Molar ratio	H.S.(mass%)	S.S.(mass%)
PU1-CO	MDI-CO-BG	1:0.4:0.6	54.99	45.01
PU2-CO	MDI-CO-BG	1:0.3:0.7	62.65	37.35
PU3-PTMO	MDI-PTMO-BG	1:0.4:0.6	43.18	56.82
PU4-PTMO	MDI-PTMO-BG	1:0.3:0.7	51.06	48.94

2.4 Characterization

2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of the prepared samples are obtained using a Thermo Scientific IS10 FT-IR spectrometer (USA). Spectra accumulate in the spectral range of 4000-400 cm^{-1} at room temperature, utilizing 64 scans at 4 cm^{-1} resolution. All spectra are obtained in the transmittance mode.

2.4.2 Thermogravimetric Analysis (TGA)

Thermal decomposition of PUs is assessed by (DTG-60H, Shimadzu, Japan). Temperature range of (0-350°C) at a heating rate of (10°C min^{-1}) under the nitrogen atmosphere at a flow rate of (40 ml min^{-1}). The samples (6-10 mg) are carried out in the standard platinum pan with referent pan empty Alpha-Alumina.

2.4.3 Differential Scanning Calorimetry (DSC)

Thermo Analysis DSC Q20 V24.10 Build 122(USA).The samples (5-10 mg) are sealed in aluminum pans with referent Tzero cell and purged with nitrogen gas at a scanning rate of (50 ml min^{-1}), the samples are heated from room temperature to 350°C, experiments are carried out at a scanning rate of (10°C min^{-1}). The instrument is calibrated using standard indium. Data processing is performed with Universal Analysis 2000, version 4.5 A, by TA Instruments.

2.4.4 Tensile tests

Mechanical testing is carried out at room temperature by the tensile testing machine (Mecmesin, UK) MultiTest 25-I model. Five samples are cut out from the 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 is set for carrying out each part of the test specimen for elongation estimation.

2.4.5 Hardness measurements

The hardness of samples is measured by using durometer type A (Model 306L) instrument is from Pacific transducer corp. Los Angeles, USA. The test specimens are carried out at room temperature, according to ASTM D2240, standard procedure.

2.4.6 Crosslinking density measurements

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

$$\sigma = \sigma_0(\lambda) + Ge(\lambda^2 - \lambda^{-1}) \quad (3)$$

Where σ is the true stress, λ is the extension ratio, the value of σ_0 depends on the chemical nature of the rubber but not on the crosslink density. Parameter Ge depends on the degree of cross-linking. The average molecular mass between cross-links M_c, which is directly related to the crosslink density, can be estimated from the value of Ge as follows:

$$M_c = \frac{A_0 \rho RT}{Ge} \quad (4)$$

M_c is the average molecular mass of the polymer between cross-links, A_0 is the prefactor equal to 1, ρ is the polymer density, R is the gas constant equal to 8.3×10^6 cm^{-1} pa mol^{-1}, T is the absolute temperature.

3 Results

3.1 Fourier transforms infra-red spectroscopy (FT-IR)

FT-IR spectroscopy is a powerful method to investigate the groups characteristic in the hard/ soft segment and final PUEs. Fig. (1), shows the FT-IR spectra for the neat reagents and the final product. As well as, their chemical structure and the most important groups on MDI, BG, CO and PTMO reagents. Fig. (1a) and b of the components that build the hard segment content presents, in detail, a strong band at approximately 2274 cm^{-1} assigned to NCO groups [41,42], and the stretching vibration peak of the benzene ring C=C group at 1522 cm^{-1}, Fig. (1b) shows the band at about 3345cm^{-1} assigned to OH group. Fig. (1c) and Fig. (1d) of the CO and PTMO as a soft segment shows the band at 3411cm^{-1}, 3467cm^{-1} ascribed to OH groups, 2927 cm^{-1}, 2940 cm^{-1} symmetric CH$_2$ group, 2856 cm^{-1}, 2857 cm^{-1} asymmetric CH$_2$ stretching group, respectively. The C=O ester group of CO in Fig. (1c) is observed at 1744 cm^{-1} and the C-O-C ether group of PTMO at 1113 cm^{-1}. Fig. Fig. (1e), presents the four PUEs samples synthesized. It shows presence of N-H groups at about 3361-3311 cm^{-1}, and 3291 - 3295 cm^{-1} for all samples PU1-CO - PU2-CO and PU1-PTMO - PU2-PTMO, while carbonyl group C=O stretching at 1710 - 1708 cm^{-1} and 1711-1709 cm^{-1} respectively. The two samples PU1-PTMO and PU2-PTMO exhibited the characteristic absorption peaks at 2859-2865 cm^{-1}, while asymmetric CH$_2$ does not appear in PU1-CO and PU2-CO, and in contrast, 2930-2931 cm^{-1} of symmetric CH$_2$ is observed in PU1-CO and PU2-CO at 2923-2924 cm^{-1}. The absence of characteristic N=C=O peak at approximately 2274 cm^{-1} Fig. (1a) and the appearance of N-H peak Fig. (1e) indicates, a complete conversion of the isocyanate terminations in MDI reagent in Fig. (1a), an into urethane groups [42] .

3.2 Thermal properties

3.2.1 TGA analysis

TGA exhibited the thermal stability of the PUEs. Two successive mass loss processes for all the samples are observed. The first step could be attributed to the degradation of hard segments of the PUEs, and is commonly related to urethane break bonds, occurring between (250-350°C). The second step could be related to

(a)

(b)

(c)

(d)

(e)
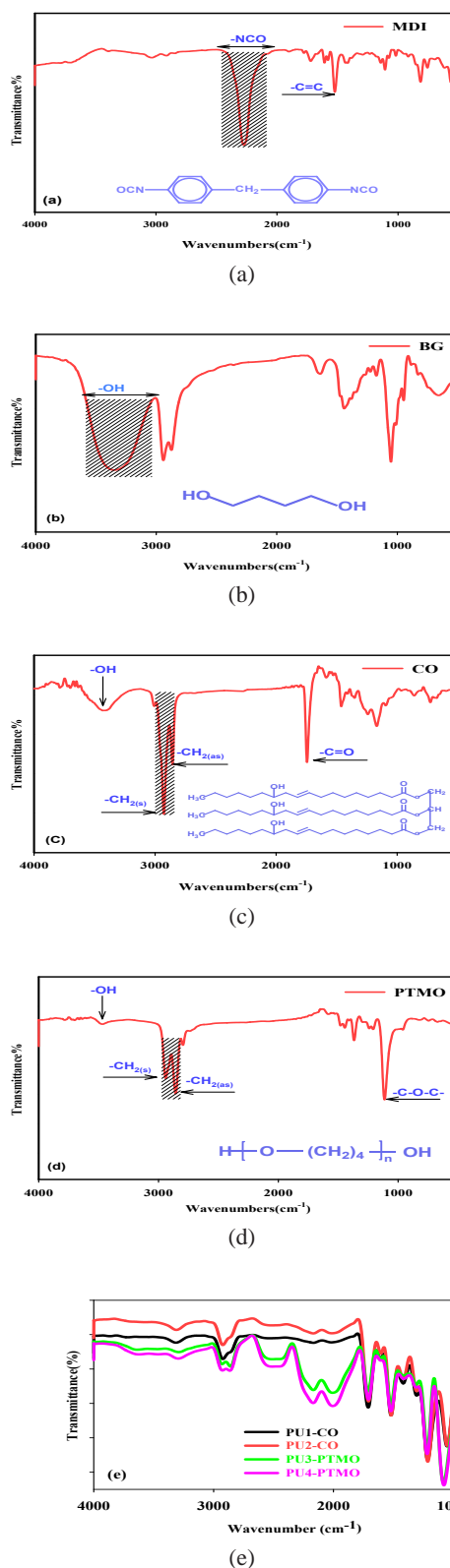
Fig. 1: FT-IR spectra of reagents: (a) MDI (b) BG (C) CO (d) PTMO and final PUEs (e).

the degradation of the soft segment, and this event is situated in the range of (350-500°C) [41,43]. According to the data obtained from Fig. (2), and Table (2), the thermal stability of the samples based on polyester polyol that is represented in CO (PU1-CO , PU2-CO) is higher than in the samples based on polyether polyol which is represented in PTMO (PU3-PTMO , PU4-PTMO). This phenomenon is related to the polar nature of esteric bonds, another reason may be due to the presence of three isocyanate reactive groups in CO (three OH) while PTMO contains only two isocyanate reactive groups (two OH). Accordingly, polyester urethane is more bonding than polyether urethane. Polyester based PUEs are more stable than the samples obtained with the polyether polyol.

In each sample of PUEs as shown in Table (2), the peak temperature increases from 310.05°C to 314.54°C and from 305.81°C to 310.5°C. The increase in the thermal stability is related to the increase of molar ratio of BG that lead to increasing the content of hard segment, and more hydrogen bonding formed between molecular chains as a result, leading to significant phase ordering, and possibly, crystallinity occurred [44], thus it is difficult to separate each exact degradation temperature due to possible over lapping of each degradation phenomenon. The presence of biphenyl groups on the main chains of MDI in PUEs, which exhibit thermal stability is another reason [45]. This means that higher thermal stability for specimens contains an excess of BG.

When the samples are irradiated by gamma irradiation at 400 kGy, higher thermal stability is obtained. From the previous DTG curves, the thermal decomposition of two steps hard and soft segments have improved. This is due to the increase of the crosslinking by γ-irradiation between the molecular chain via methylene group of isocyanate [46], and also between the soft segments of adjacent chains via linkage of free radical produced during irradiation process, in this case γ-irradiation cross linking dominates in the soft segment, where the cross linking is believed to be most efficient in the soft phase [46,47]. The radiation cross linking of PUEs is improved at the dose used, as it has the density of cross linking and hence have has resistance.

Table 2: TGA data of synthesized PUEs for Non-irradiated and irradiated samples
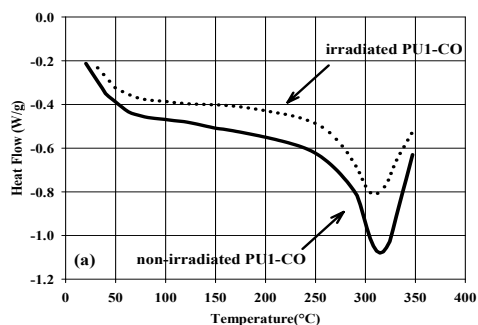
Sample Code	Non-irradiated		Irradiated 400 kGy	
	$T_{d(HS)}$(°C)	$T_{d(SS)}$(°C)	$T_{d(HS)}$(°C)	$T_{d(SS)}$(°C)
PU1-CO	310.05	462.5	313.32	467.77
PU2-CO	314.54	470.62	318.67	474.99
PU3-PTMO	305.81	424.84	321.68	429.85
PU4-PTMO	310.5	433.89	328.84	436.49

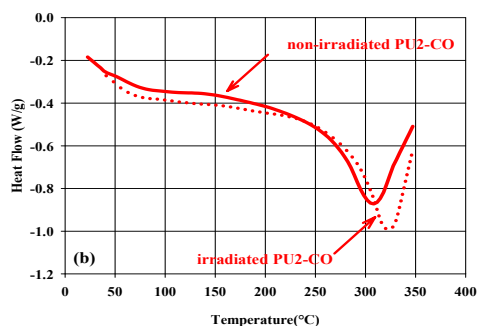$T_{d(HS)}$, decomposition temperature of hard domain
$T_{d(SS)}$ decomposition temperature of soft domain
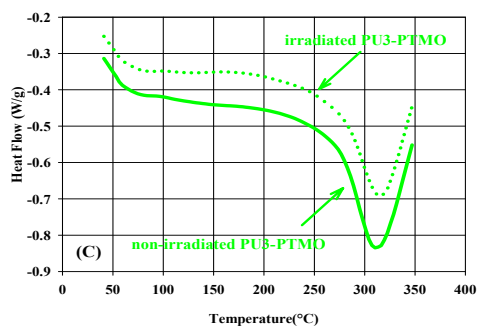
(a)

(b)

(c)

(d)
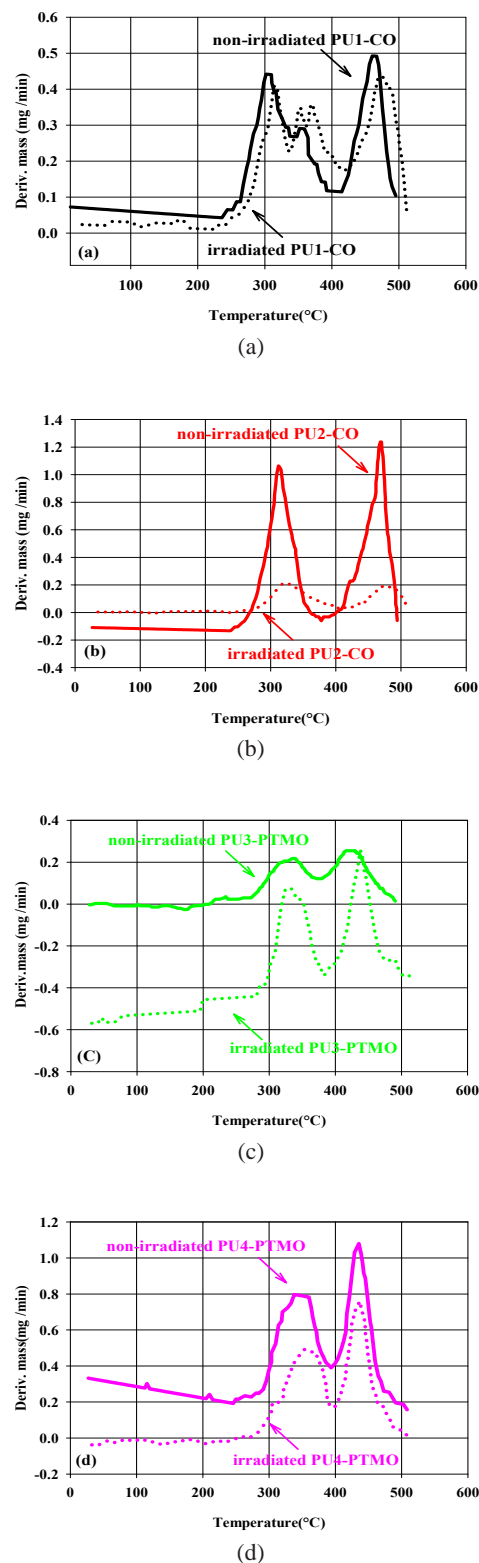
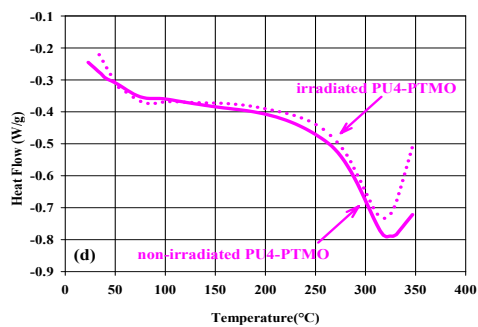**Fig. 2:** DTG curves for Non-irradiated and irradiated PUEs.

(a)

(b)

(c)

(d)

**Fig. 3:** DSC curves for Non-irradiated and irradiated PUEs.

Table 3: DSC data of synthesized PUEs for Non-irradiated and irradiated samples
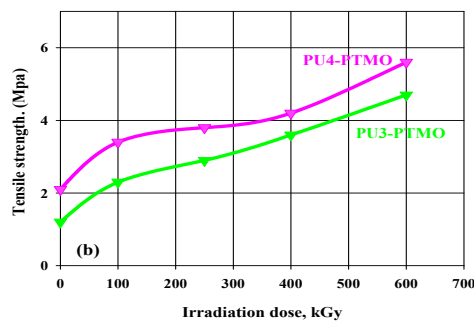
Sample Code	Non-irradiated		Irradiated 400 kGy	
	$T_{g(HS)}(°C)$	$T_{m(HS)}(°C)$	$T_{g(HS)}(°C)$	$T_{m(HS)}(°C)$
PU1-CO	55	311	61	315
PU2-CO	61	312	63	320
PU3-PTMO	50	309	64	316
PU4-PTMO	68	317	69	319

$T_{g(HS)}$ glass transition temperature of hard domain

$T_{m(HS)}$ melting temperature of hard domain
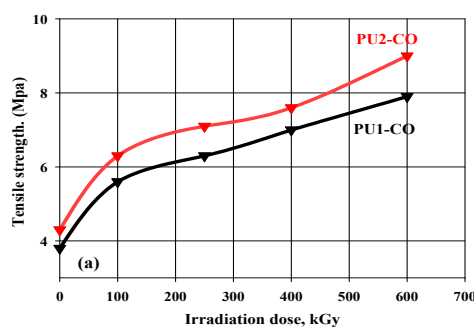
(a)

(b)

Fig. 4: Tensile Strength of PUEs based on (a) CO and (b) PTMO.

3.2.2 DSC analysis

DSC thermograms and corresponding data for all samples are shown in Fig. (3), and listed in Table (2). It is clear that there are different endothermic peaks corresponding to different phase transition for PUEs [48]. In these samples there are two transitions in each thermogram, including a glass transition temperature Tg(HS) and a melting point Tm(HS) of hard segment. Thermograms of the tested materials differ depending on the ratio of the chain extender in their manufacture. The Tg and Tm of the hard segment increase due to the increase of the molar ratio of BG. The Tg increases due to the increase of HS content,[49], this is due to the increase of the HS length that allows HS to segregate and according to Seymour
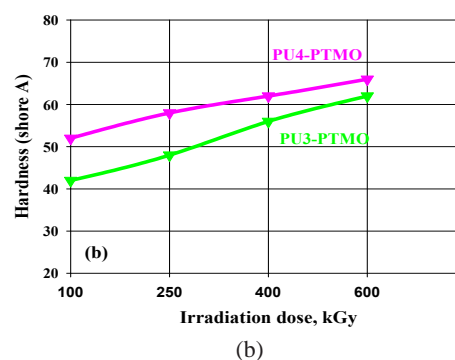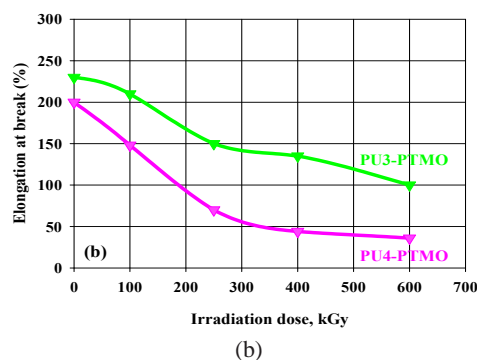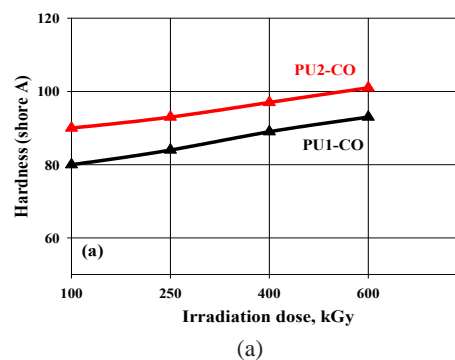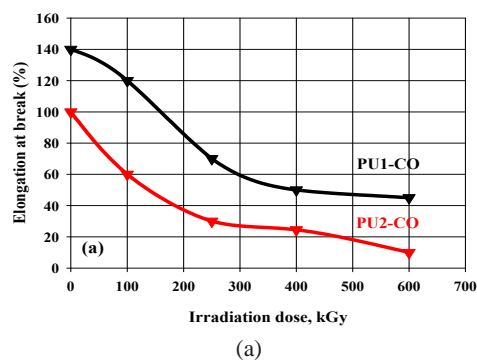
**Fig. 5:** Elongation at break of PUEs based on (a) CO and (b) PTMO.

Fig. 6: Hardness of PUEs based on (a) CO and (b) PTMO.

and Cooper's studies [50,51], the increase in temperature endotherm transition Tg(HS), may attribute, by phase segregated structure of the large ordering of HS domains. In addition, the increase of methylene group content due to increasing BG used, favors the formation of more ordered structures, that lead to increased Tm values of hard segment. Based on these criteria, the breaking up of the greater ordered hard-segment-domains, or the melting of micro crystalline ones are present in the polymer [52, 53]. In Fig.(3), the changes in glass transition, and melting point by gamma rays can be seen. Hard segment glass transition, and melting point increased with dose. This increase is induced by crosslinking of the chains. Namely, the high crosslinkage reduces the chain mobility which results in high T_g and T_m [54,55].

3.3 Tensile properties

The effect of changing chain extender BG ratios and polyol type on the properties of PUEs based on CO and PUEs as well as PTMO at different irradiation dose (100-600kGy) are illustrated in Fig. (4). According to the figure, it is obvious that increasing BG ratio increases the tensile strength. The increase in BG ratio leads to the increase of hard segment on the expense of soft segment

content, thus hydrogen bonding increases between molecular chains. Moreover, the values of TS obtained for non-irradiated and irradiated polyurethanes based on CO polyol are higher than the values of TS of the polyurethanes based on PTMO polyol. This is due to the degree of segregation between hard and soft segment, which is less pronounced in polyester urethane than in polyether urethane, as phase mixing in polyester urethane is higher than in polyether urethane, due to the stronger linkage of NH ester carbonyl hydrogen bonds than NH oxygen bonds, in ether. This leads to better properties of the polyester than polyether urethane [56,57]. In addition, it is noticed that increasing irradiation dose increases TS values up to 600 kGy, this is attributed to the crosslinking between PUEs chains, the crosslinking process may take place by liberation of two hydrogen atoms from two adjacent chains, the reaction extends to finally yield specimen with three dimensional networks the mechanism of hydrogen liberation process is activated by using ionizing radiation proposed by Shintani and Nakamura [32]. On the other hand, elongation at break Fig. (5), is significantly affected by increasing both irradiation dose and BG ratio that reduce the elongation at break. Also, it can be seen that the elongation values of polyether urethane are higher than that of polyester urethane at the same irradiation dose and BG ratio due to

(a)

(b)
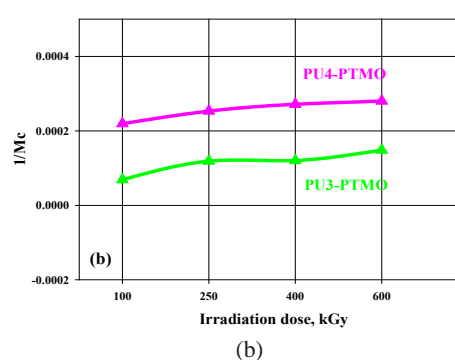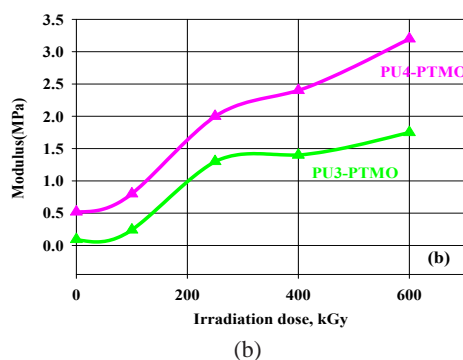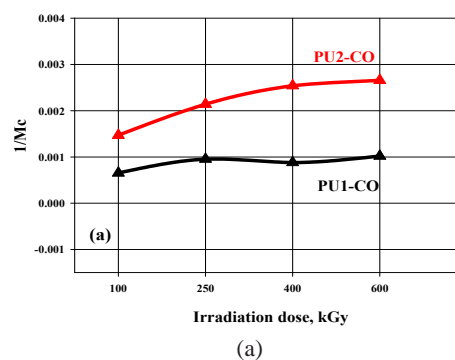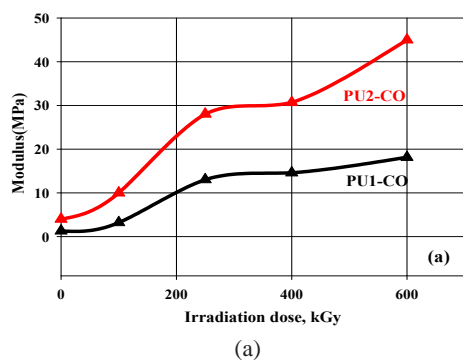
Fig. 7: Modulus of PUEs based on (a) CO and (b) PTMO.

(a)

(b)

Fig. 8: Cross-linking density of PUEs based on (a) CO and (b) PTMO.

the stronger linkage in the polyester urethane than in polyether urethane as previously discussed.

3.4 Hardness

The samples for studying Shore A hardness are illustrated in Fig. (6). On the basis of the analysis of the result, it is possible to conclude that the hardness properties depended on several parameters, such as the content of hard segment, polyol type and irradiation dose. In each series, increasing BG and irradiation dose result in increasing the hardness, and PUEs based on CO is higher in hardness than PTMO which is in accordance with TS data.

3.5 Modulus of elasticity

The obtained Modulus properties for the investigated samples of PUEs are given in Fig. (7). As these Figures illustrate, the modulus increases slightly up to 100 kGy, followed by a sudden increase up to 250 kGy for the two BG ratios. Afterwards, the increase is the highest, reaching up to 600 kGy at the highest BG ratio whereas the other ratios tend to level off. This trend is applied to both CO and PTMO polyol, so the modulus value of the

CO containing polyurethane is extremely different from the modulus value of PTMO polyol.

3.6 Determination of cross-linking density

The cross linking density is a term of $1/M_c$ and calculated according to eq. (3 and 4) [58]. Based on the mechanical properties, as shown in Fig. (8), a noticeable increase in $1/M_c$ values upon irradiation for the highest BG ratio is observed, while a slight increase for the other lower ratios is shown. Also, it is observed that the value of $1/M_c$ of CO urethane is very high compared to PTMO urethane at each particular ratio and irradiation dose. The results of $1/M_C$ are a confirmation of the data obtained with the other properties.

4 Perspective

PUEs are successfully synthesized from the aromatic diisocyanate (MDI), aliphatic diols (BG), polyester polyol (CO), and polyether polyol (PTMO). Effect of the polyol type, chain extender content, and gamma irradiation used on the structure as well as some physico-chemical, and

mechanical characterization of PUEs are investigated. FT-IR measurements prove a complete reaction between polyurethane ingredients, through the disappearance of (N=C=O) absorption bands, and the appearance of (NH stretching vibration) in all polyurethanes final products. The mechanical properties, such as, tensile strength, hardness, modules, and cross linking density increased in accordance, with the increase of both BG, and irradiation dose, while elongation at break decrease. Also, the thermal stability, glass transition temperature, and the melting point improve with chain extender, and irradiation dose. On the other hand, PUEs resulted from CO possess better properties than the ones based on PTMO.

Acknowledgement

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