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Effect of Ionizing Radiation on the Properties of Some Synthesized Polyurethanes.

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ABSTRACT

Polyurethanes (PUs) were synthesized based on methylene diphenyl diisocyanate (MDI) as diisocyanate and castor oil (CO) or polytetrahydrofuran (PTHF) as polyol together, in the presence of 1,4-butanediol (BDO) and ethanolamine (ETA) as chain extender with molar ratio 1:0.5:0.5. The synthesis was performed by one shot casting technique. The changes in physico-chemical as well as chemical properties were followed according to the increase in gamma irradiation dose in the range from 100 kGy to 600 kGy. Moreover, FT-IR measurements were performed to confirm a complete reaction between components and formation of PUs. The thermal properties, swelling characteristics, cross-linking density , tensile strength and hardness were improved as the irradiation dose was increased, while elongation at break was decreased.
Keywords: gamma irradiation; cross-linking; polyester, ether urethane; thermal and mechanical properties.

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INTRODUCTION

The radiation curing being applied to polymer processing comprise too many different radiation types and sources used [1-5]. Currently, the most prevalent applications are the modification of many plastic and rubber products, mainly cross-linking of cable jackets, heat-shrinkable plastic pipe, plastic tubing and film, foam and pellets, and partial curing of rubber sheet for automobile tires [6]. Cross-linking by radiation has the advantage over chemical cross-linking that no chemicals are added, speed, and therefore, no by-products are generated[7]. These by-products can be detrimental for biomedical and food-packaging applications. In addition, radiation cross-linking can be performed at ambient temperature whereas chemical systems needs heating [8].Polyurethanes are one of the most versatile class of polymers ever invented [9] and most useful commercial classes of polymers that are widely used in both industry and everyday life, PUs have a wide range of applications such as coatings, foams, adhesives, membranes, textiles, elastomers and rubber adhesion promoters [10].Polyurethanes exhibit a broad range of physicochemical and mechanical properties, due to their structural diversity. They consist of a hard (HS) and soft segments (SS) connected by means of urethane linkages, which either mix or segregate depending on chemical composition and produce phase mixed or phase separated morphologies due to their immiscibility. In phase separated, HS provide physical cross-links within the SS matrix [11,12].Polyurethanes are qualified as materials possessing excellent radiation stability. However, depending on the molecular architecture and composition, the radiation resistance of PUs differs significantly [13].Irradiation is known to produce changes in the bulk of polymers such as scission, cross-linking and oxidation of polymer chains[14],including PUs. In the reported work, we focused on the quantification of the effects of gamma irradiation on the properties of PUs through a diverse array of characterization techniques. The material was irradiated at doses (100, 250, 400 and 600 kGy) in an air atmosphere at room temperature.

MATERIALS AND METHODS

All chemical reagents were of analytical grade, MDI (the molecular formula is $C_{15}H_{10}N_2O_2$, molar mass 250.25 g/mol).The BDO ($C_4H_{10}O_2$, molar mass 90.12 g/mol) and ETA (C_2H_7NO, molar mass 61.08 g/mol) both used as chain extenders. The polyether polyol was PTHF $H(C_4H_8O)nOH$, molar mass 1000 g/mol) all chemicals above were procured from Merck KGaA, Germany. The polyester polyol CO ($C_{57}H_{104}O_9$, molar mass 933.61 g/mol). Dichloromethane (CH_2Cl_2)used as a solvent, (molar mass 84.93 g/mol) were purchased from El-Gomhouria company for Trading Chemicals and Medical Appliances, Pharmaceutical Chemicals Group, Egypt. Stannous Octoate $Sn(C_8H_{15}O_2)_2$, molar mass 405.12 g/mol was used as a catalyst and provided by Sigma-Aldrich.

Polymer synthesis

Generally, polymers with urethane or urea linkages were based on three component systems consisting of: (1) a diisocyanate (DI) generating HS (MDI); (2) a macrodiol (MD) generating SS like polyester polyol (CO) or polyether polyol (PTHF); (3) chain extender like diol (BDO), or diamines as (ETA).In all cases the molar ratio of DI:CE:MD was 1:0.5:0.5. All PUs were prepared by using a one-step bulk polymerization procedure. MDI was used as received, polyols and chain extender were dried at 80 °C under vacuum for 24 h before use to ensure the elimination of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Macrodiols (CO) or (PTHF), chain extender (BDO or ETA) and stannous octoate (0.03 wt% of total solid) as a catalyst were placed in a 250 ml polypropylene beaker with stirring. MDI was weighed into a wet tarred 50 ml polypropylene beaker and quickly poured into the macrodiol while rapidly stirring with a stainless steel spatula under the nitrogen blanket. After stirring for 30 seconds, the viscous polymer was poured in a silica mold and complete polymerization at 50 °C for 100 h in an oven. Then the samples were transferred to roll mill mixer for 10 minutes to get rid of trapped bubbles during the casting process. To insure sufficient homogeneous mixing, the samples were subjected to hot press; compression molded into 1 mm plates at 175 °C for 45 min at pressure 9000 psi, and then cooled down in 10 min to room temperature. The resulting PUs samples were about 1 mm thickness. The formula, symbols, HS and SS for polymers are presented in table. 1. The HS and SS contents were calculated using equations (1) and (2) respectively.

Gamma Irradiation

Irradiation was 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), Egypt. The samples were irradiated at doses to 100, 250, 400, and 600 kGy in the air, at a dose rate 5 kGy/h.

$$\text{Hard segment content } (wt\%) = \frac{W_{DI} + W_{CH}}{W_{DI} + W_{MD} + W_{CH}} \times 100\% \qquad (1)$$

Soft segment content (wt%) = 1 - hard segment content (wt%) $\qquad$ (2)

W_{DI}: weight of MDI
W_{MD}: weight of polyol
W_{CH}: weight of chain extender

Table. 1. Formula, symbols, HS and SS for PU samples

Designation	Composition	Molar ratio	Hard segment content (wt %)	Soft segment content (wt%)
MCB	MDI-CO-BDO	1:0.5:0.5	48.66	51.34
MTB	MDI-PTHF- BDO	1:0.5:0.5	37.1	62.9
MCE	MDI-CO-ETA	1:0.5:0.5	47.4	52.6
MTE	MDI-PTHF- ETA	1:0.5:0.5	35.93	64.07

Characterization techniques

Fourier transforms infrared (FT-IR) spectroscopy

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

Thermo gravimetric analysis

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

Tensile testing

Mechanical testing was carried out at room temperature by the tensile testing machine (Mecmesin,-United Kingdom) MultiTest 25-I model. Samples were cut out from the sheets in dumbbell-shape using a steel die of standard width (4 mm) with 1 mm thickness. A benchmark of 1.5 cm and crosshead speed 500 mm / min was made on working part of each test specimen for elongation estimation.

Hardness measurements

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

Swelling measurements:

All samples of known weight immersed in dichloromethane at room temperature for 72 h. The samples were removed from the solvent, blotted quickly to remove the attached solvent on the sample surface and weight again. The vacuum oven was preheated to 60$^{°}$C and the swollen samples were dried until a

constant weight was obtained. This procedure was repeated four times for each sample. The swollen polymers are calculated according to the following equation:

$$S = \frac{W_s - W_o}{W_o}$$ (3)

where

W_s is the weight of the swollen gel
W_o is the original weight of sample before swelling

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.

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

Where

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. Parameter G_e depends on the degree of cross-linking. The average molecular weight.between cross-links Mc, which is directly related to the crosslink density, can be estimated from the value of Ge as follows:

$$Mc = A_o \rho RT/G_e$$ (5)

Mc is the average molecular weight of the polymer between cross-links, A_o is the a 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.

RESULTS AND DISCUSSION

FT-IR spectroscopy

Table. 2. Infrared characteristic absorption peaks for polyols and hard segment

S.NO.	Main assignments of absorption beaks	CO	PTHF	BDO	ETA	MDI
1	v (OH) (cm^{-1})	3411	3467	3345	-	-
2	v (NH$_2$) (cm^{-1})	-	-	-	3377	-
3	v (NCO) (cm^{-1})	-	-	-	-	2274
4	v (C=O) (cm^{-1})	1744	-	-	-	-
5	v_s(CH$_2$) (cm^{-1})	2927	2940	2940	2952	-
6	v_{as}(CH$_2$) (cm^{-1})	2855	2856	2874	2881	-
7	v (C=C) (cm^{-1})aromatic	-	-	-	-	1522
8	v (C-H) (cm^{-1})aromatic	-	-	-	-	3031
9	v_s(C-O-C) (cm^{-1})ether	-	1113	1052	-	-
10	δ (NH) (cm^{-1})	-	-	-	1585	-
11	v (C-N) (cm^{-1})	-	-	-	1067	-
12	δ (OH) (cm^{-1})	-	-	-	1326	-

v stretching vibration v_s symmetric stretching vibration
v_{as}asymmetric stretching vibration δ deformation/ bending

The FT-IR spectra absorption bands in (Figs.1- 3) are listed in the (Table 2 and 3). From (Table 2) the characteristic band for (OH stretching vibration) appears in PTHF, CO and BDO at (3467cm^{-1}, 3411cm^{-1}and 3345cm^{-1}), and at 1326cm^{-1}(bending) for ETA. The characteristic peak for CO at 1744 cm^{-1} for (C=O stretching). On the other hand, the peak at 1113cm^{-1} and 1052cm^{-1} are assigned for (C—O—C stretching vibration)in PTHF and BDO respectively. The peak at 3377cm^{-1} is assigned for (NH stretching vibration) and at 1585cm^{-1} for (NH

bending vibration). The peak at 2274cm^{-1} is assigned for (N=C=O) in MDI. The FT-IR spectra absorption peaks for PUs are shown in (Fig. 3) and (Table 3). From the data in the (Table 3), it follows that there is a common feature in all spectrum. Firstly the disappearance of (N=C=O) band, secondly the appearance of NH cm^{-1}at 3316-3283 cm^{-1} which are evidence for a complete reaction between the three components constitutes PUs. Moreover, the appearance of the absorption peak at 1522cm^{-1} assigned for C=C aromatic ring stretching in MDI and (C-O-C) for PUs ester at 1051cm^{-1} and at 1088cm^{-1} for polyether urethanes. Generally, the peaks of PUs are mostly similar except the bands characteristic the CH$_2$ (asymmetric vibration) appears only in PUs ester (MTB and MTE).

**Table. 3. Infrared characteristic absorption peaks to final Pus**

S.NO.	Main assignments of absorption beaks	MCB	MCE	MTB	MTE
1	v (NH) (cm^{-1})	3316	3303	3292	3283
2	vs (CH$_2$) (cm^{-1})	2922	2925	2928	2929
3	vas(CH$_2$) (cm^{-1})	-	-	2855	2858
4	v (C=O) (cm^{-1})	1712	1706	1713	1711
5	v (C=C) (cm^{-1})	1520	1521	1522	1521
6	δas(CH) (cm^{-1})	1417	1419	1431	1408
7	vs (C-O-C) (cm^{-1})	1051	1052	1086	1088

v stretching vibration $v_s$symmetric stretching vibration
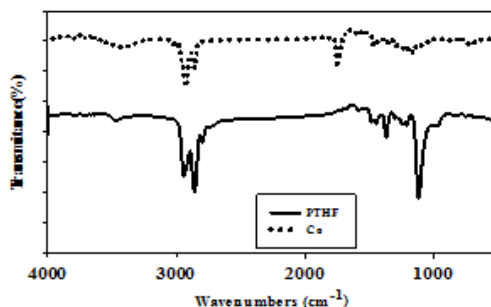
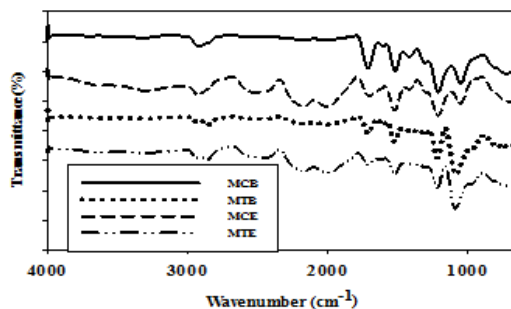v_{as} asymmetric stretching vibration δ_{as} asymmetric bending vibration
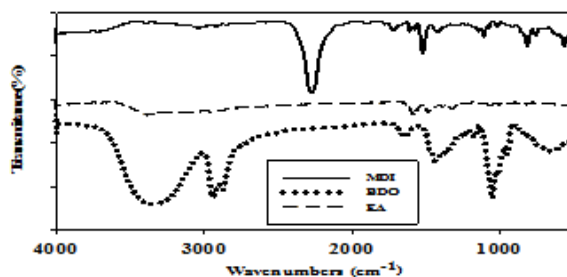
Figure (1) FTIR spectra of hard segments

Figure (2) FTIR spectra of polyol


Figure (3)FTIR spectra of synthytized PUs

Thermal properties

Thermal stability of the specimens under investigation namely polyesterurethanes (MCB, MCE) and polyetherurethanes (MTB, MTE) can be estimated via monitoring the change in weight loss or more accurately a via temperature peaks of weight derivative of the first degradation step (Dr-TGA) with the increase of temperature. Figure 4 describes the relation between weight derivative dw/dt with temperature.

The temperature of first significant weight. Derivative peaks of specimens are listed in (Table 4). From the listed data, it noticed that the temperature peak corresponding polyester urethanes (MCB and MCE) are higher than polyether urethane (MTB and MTE) which indicates higher thermal stability. This is may be due to the NH- carbonyl hydrogen bonding is more strong than NH – oxygen bonds in addition to the percentage of HS in polyesterurethane is higher than polyetherurethane. Also it was observed that chain extended specimens with ETA (MCE and MTE) have higher temperature peak than that chain extended with BDO (MCB and MTB) due to introduction of urea linkage in case of ETA which is stronger than urethane linkage specimen . The exception is in the case of PTHF polyether in which MTB is higher than MTE, However the temperature of start peak of MTE is higher than MTB. Also from the table it's clear that the irradiated samples at 400 KGy have higher temperature peaks than un-irradiated one for all samples under investigation due to radiation-induced between the molecular chains via methylene group of isocyanate and also between soft segments of adjacent chains via linkage of free radical produced during irradiation process.
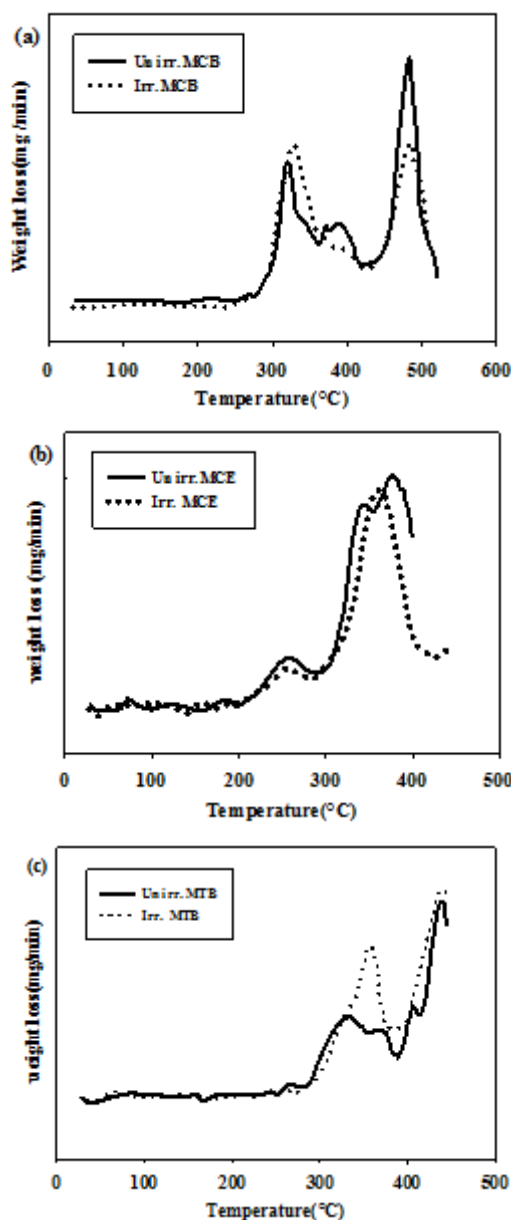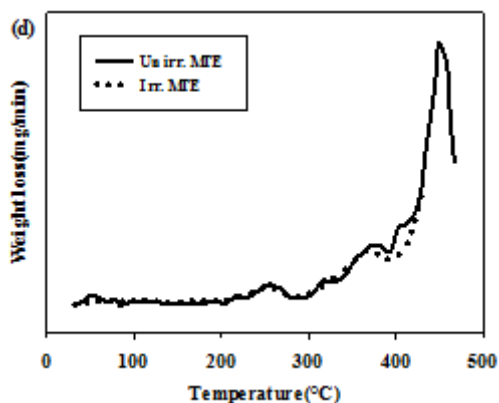
Fig.4. DTG curves for un-irrdiated and irradiated PUs

Table.4 Thermal parameters of first decomposition stages for PUs for Un-irradiated and irradiated samples

Polymer	Un-irradiated						
	T_i (°C)	T_P (°C)	T_e(°C)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$T_{25\%}$(°C)	$T_{30\%}$(°C)
MCB	269	308	334	219	305	340	354
MTB	280	328	379	288	310	351	371
MCE	292	328	345	264	310	350	361
MTE	304	309	397	261	335	389	403
Irradiated 400 kGy							
	T_i(°C)	T_P (°C)	T_e(°C)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$T_{25\%}$(°C)	$T_{30\%}$(°C)
MCB	264	313	371	291	304	330	344
MTB	270	348	376	295	321	353	363
MCE	301	350	409	256	306	344	355
MTE	285	353	385	271	325	371	395

T_i, initial decomposition temperature; T_e, end decomposition temperature: T_p, peak temperature: $T_{5\%}$, $T_{10\%,}$ $_{T25\%}$, $T_{30\%}$ weight. Losses obtained from TGA

Tensile properties

Figure 5 describes the relation between the irradiation dose and tensile strength for PUs samples. From the (Fig.5) it's noticed that the tensile strength of PU based on CO polyol has higher value than that based on PTHF. This is accordance with the fact that the PU based polyester polyol is stronger than polyether polyol. This phenomenon is due to that urethane N—H ester carbonyl hydrogen bonds are stronger than urethane N—H ether oxygen bonds. [15]. It is also well known that ether linkages have a higher flexibility and lower cohesive energy (1.00 kcal/mol) than ester linkages (2.90 kcal/mol) [16]. Consequently, it is anticipated that the introduction of ether linkages leads to enhanced flexibility and reduces the tensile strength of polyurethane elastomers [17].On the other hand, the chain extended replays an important role depends on the type of linkage, e.g. urethane linkage or urea linkage. The urea linkage due to an introduction of ETA induce is higher TS than urethane linkage on using BDO. Also, it's emphasized that the tensile strength significantly affected by irradiation doses.

On the other hand, elongation at break (Fig.6) is significantly affected due to increase cross-linking density with irradiation dose where the elongation is the highest value for unirradiated samples then decrease continuously up to 600 kGy. The elongation is more sensitive toward the change in polymer morphology (e.g. cross-links that create between the molecular chains.
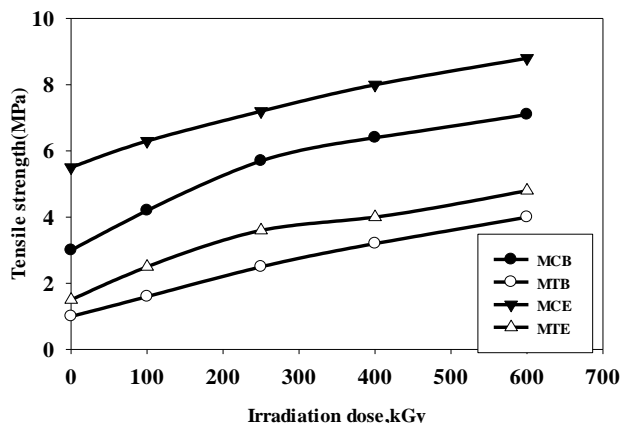
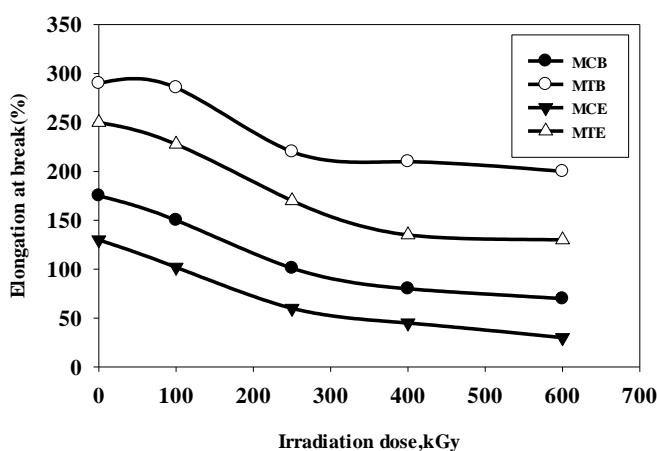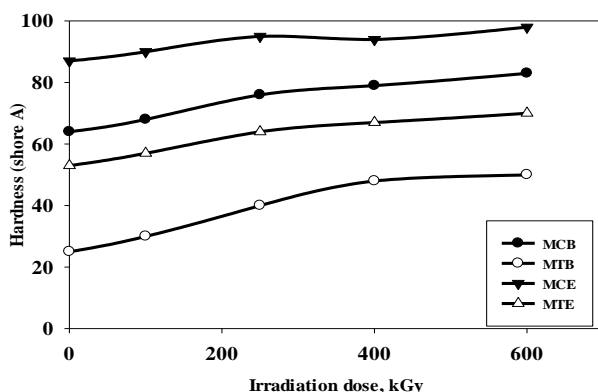**Figure (5) Effect of irradiation dose on Tensile strength of PUs**

Figure (6) Effect of irradiation dose on elongation at break of PUs

Hardness

The relation between hardness (shore A) and irradiation dose for the different type of PUs are represented in (Fig.7). The figure shows that the PU based on CO is higher than PTHF and that chain extended with ETA is higher than BDO which is in accordance with TS data. Also, it's observed that there is an increase in hardness value with increase irradiated dose for all samples under investigation.

Figure(7) Effect of radiation dose on the hardness of PUs

Swelling properties

Unlike tensile stress at a given elongation, there is no direct proportionality between swelling and Mc (the molecular wt. between cross-links). The amount of swelling cannot, however be a very much influenced by the degree of cross-linking. Instead, it depends mainly on the chemical structure of the polymers and on the solvent, therefore swelling data at best rough estimation of cross linking density. However for a particular

solvent and polymer the decrease in swelling after curing is an indication of increasing cross linking density. For different polymers, the chemical structure of the polymer as well as the cross linking densities are contribute to the amount of solvent absorbed (Fig.8) describes the relation between swelling number and irradiation dose for PUs samples. From the figure it appears that the amount of swelling absorbed decrease for all sample as the irradiation dose increases and the amount of swelling is arranged in the descending order as follows MTB, MTE,MCB and MCE. Because of different polymer structures, this order dose not necessary means that the cross-linking density is decreased in the same sequence, however the results give us an information about the response of each polymers toward irradiation process, in which increasing irradiation dose decrease the amount of swelling no for all samples under investigation.
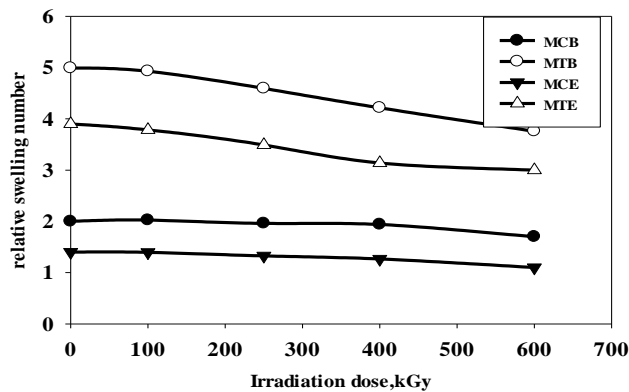

Figure (8) swelling number

Tensile stress at 100% elongation (M$_{100\%}$):

The relation between tensile stress at a given elongation and Mc^{-1} is given by the following eq[18].

$$F = \rho RT \, Mc^{-1} A_o \, (\lambda^{-2} - \lambda^{-1}) \tag{6}$$

ρ is the polymer density, R is the gas constant, T is the absolute temperature, A_o is the cross-sectional area and λ is the elongation, Mc^{-1} is the reciprocal of molecular weight between cross-links. When ρ, R, T and λ are constant, then the stress at a given elongation (M$_{100\%}$) is proportional with Mc^{-1} , therefore the tensile stress at given elongation is largely independent on the chemical constitution of polymers and the nature of cross-links.

From (Fig.9), it follows that tensile stress of PUs at 100% is lower than polyester urethanes (MTB and MTE < MCB and MCE). Also, it is noticed that MCE samples breaks before reaching 100% at higher irradiation dose than 100 kGy whereas MCB breaks at less than 100% at doses higher than 250 kGy Also one may observed that the M100% values for ETA samples is higher than BDO samples. These results are in accordance with the swelling number and hardness values.
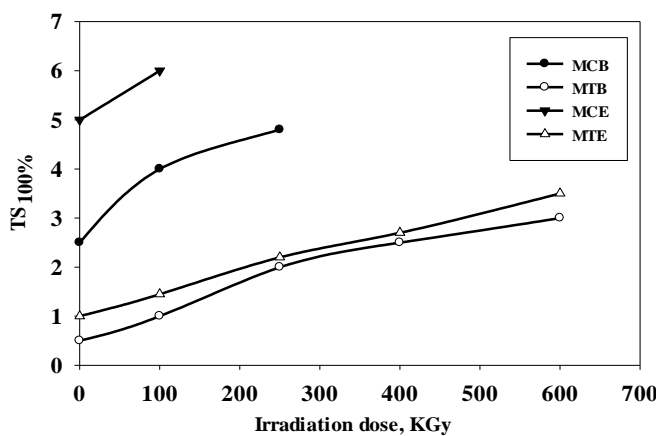

Figure (9) Tensile stress at 100% elongation

Determination of cross-linking density

The crosslinking density $1/M_c$ is calculated based on equation (4), (5), and the results of $1/M_c$ against irradiation dose are plotted in (Fig.10). From the figure, it is observed that $1/M_c$ value for PUs based CO polyol is higher than PTHF polyol and that contain chain extended with ETA is higher than BDO. The explanation is mentioned earlier in discussions of swelling, hardness and thermal properties. The results of $1/MC$ are confirmation of the data obtain with the other properties.
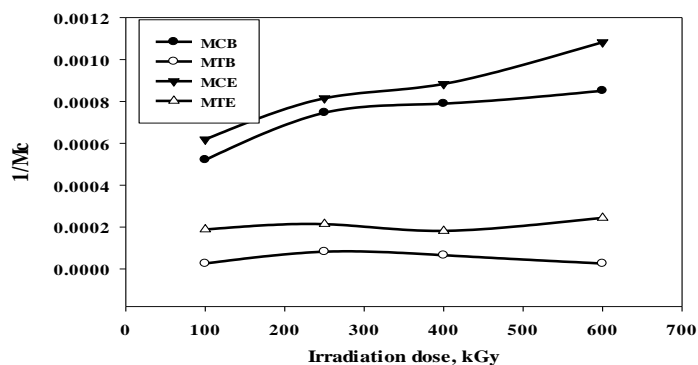

Figure (10). cross-linking density

CONCLUSION

From the results obtained in this work one may conclude that:

FT-IR measurements proofs complete reaction between polyurethane ingredients through the disappearance of (N=C=O) absorption bands and appearance of (NH stretching vibration) in all polyurethanes final products. The effect of irradiation dose on the various properties such as tensile strength, thermal properties, swelling characteristics, hardness, cross-linking density was found to improved. On the other hand, elongation at break decreased on irradiation. Also, it is noticed that polyester urethanes have superior properties over polyether urethanes and using ethanolamine is better than BDO as a chain extender.

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