

Effects of γ -irradiation on the Mechanical and Relaxation Behaviour of High and Low Density Polyethylene.

S.A. Mansour

*Department of Physics, Faculty of Science, Suez Canal University,
Ismailia, Egypt*

The effect of different doses of γ -irradiation on the mechanical and relaxation properties of High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE) were studied. It was found that HDPE is more susceptible than LDPE to the influence of radiation. Recognizable differences are observed for all parameters between the unirradiated and irradiated cross-linked polyethylene. Existence of a relaxation mechanism within the first 200 s is reported. The shear modulus for all samples is also obtained and discussed. These data are used to calculate the strain energy density using the equation proposed by Blatz et al (1974 Trans. Soc. Rheol. 18 145-61), based on the n -measure of Sethe. It was found that the n -measure is still a material constant for both types and independent of γ -irradiation dose.

Introduction

Polyethylene is a widely used commodity thermoplastic. It is commercially available in different grades, such as (LDPE), Linear Low Density Polyethylene (LLDPE), (HDPE), and Ultrahigh Molecular Weight Polyethylene (UHMWPE).

High-energy radiation has unusual chemical effects on polymers in the solid state, inducing cross-linking, and chains scission by radical reaction [1]. Cross-linking has been widely used for improving physical properties of polymer materials. However, radiation-induced chain scission results in degradation of polymer materials. The carbonyl and double bonds concentration increased with the increase in radiation dose when polyethylene was γ -irradiated in air [2].

Irradiation produced further crosslinking in amorphous regions plus extensive chain scission of taut tie molecules and led to increase the crystallinity and crystal perfection [3]. Although increasing crystallinity leads to increasing modulus and hardness, it may also lead to increasing brittleness and fatigue wear [4].

The present work is devoted to study the mechanical and relaxation properties of HDPE and LDPE before and after γ - irradiation to different doses.

It is of the interest of the present work to calculate the n-measure and its dependency on the polymeric materials, (LDPE) and (HDPE) exposed to different γ - doses.

Blatz et al. [5] showed that it is possible to represent the stress-strain behavior of several polymer materials by a very simple stress-strain relation in which the strain is based on the n- measure, with n being adjusted for the fit to the material appropriate data. According to Blatz et al, the true stress-strain extension ratio, σ , under simple tension conditions is given by a simple form, in which the strain is based on the n measure considered by Sethe [6] as follows:

$$\sigma = \frac{2G}{n} (\lambda^n - \lambda^{-n/2}) \quad (1)$$

Where σ is the true stress, G, is the shear modulus, and λ is the extension ratio. This equation, σ , is derived from the strain energy density equation, W, which is given by

$$W = (2G/n^2) (\lambda^n + 2\lambda^{-n/2} - 3) \quad (2)$$

The shear modulus and the parameter n for all samples are calculated. The strain energy density behavior is studied at room temperature.

Experimental Technique

Polyethylene films of low and high density with thickness' 0.066 cm and 0.145 cm respectively were provided by EL- Sherief for plastics industry, Cairo, Egypt. The irradiated samples were obtained by exposing unirradiated samples to different gamma exposure doses of 2, 4, 6, 8, and 10 Mrad, using Co - 60 cell- 200 of Atomic Energy of Canada. The samples were prepared as strips of approximate dimensions $2 \times 0.2 \times 0.066 \text{ cm}^3$ for LDPE and $2 \times 0.2 \times 0.145 \text{ cm}^3$ for HDPE. A digital force gauge (Hunter Spring - ACCU Force II, 0.01N resolution) was used for the mechanical measurements. The length resolution was 0.01 cm. The strain rate during measurement was fixed at 2%/sec. All measurements were performed at room temperature ($23 \pm 1 \text{ }^\circ\text{C}$). From the stress - strain curves, the following properties were calculated: Young's modulus (percentage error, P.E. \approx 12%), ultimate tensile strength (P.E. \approx 10 %), strain to break, ϵ , and ductility (P.E. \approx 2 %) for all samples, before and after irradiation. The stress relaxation was carried out under 10 % extension ratio. The decay of stress as a function of time was automatically recorded on a chart paper.

Results and Discussion

Figure (1) shows the effect of different γ -irradiation doses on the true stress-strain behavior of HDPE and LDPE. The deduced parameters, such as Young's modulus, ductility percent, strain to break, ϵ , and tensile strength are shown in Figs. (2) and (3), for LDPE and HDPE exposed to different doses of γ -irradiation. For (LDPE), it is observed that, Young's modulus is increasing as, the γ -dose increases up to 6 Mrad. This may manifest the role of γ -irradiation crosslinking. The stress-strain curve for HDPE at 10 Mrad shows a brittle fracture, which takes place after approximately 10 percent elongation.

One may suggest that the HDPE underwent some deterioration, probably due to very high densities of crosslinking and chain scission induced by irradiation to 10 Mrad. All the samples show fracturing at a tensile strain, (Fig. 3), occurs at around 210 - 360 % for the LDPE and 540 - 780 % for HDPE.

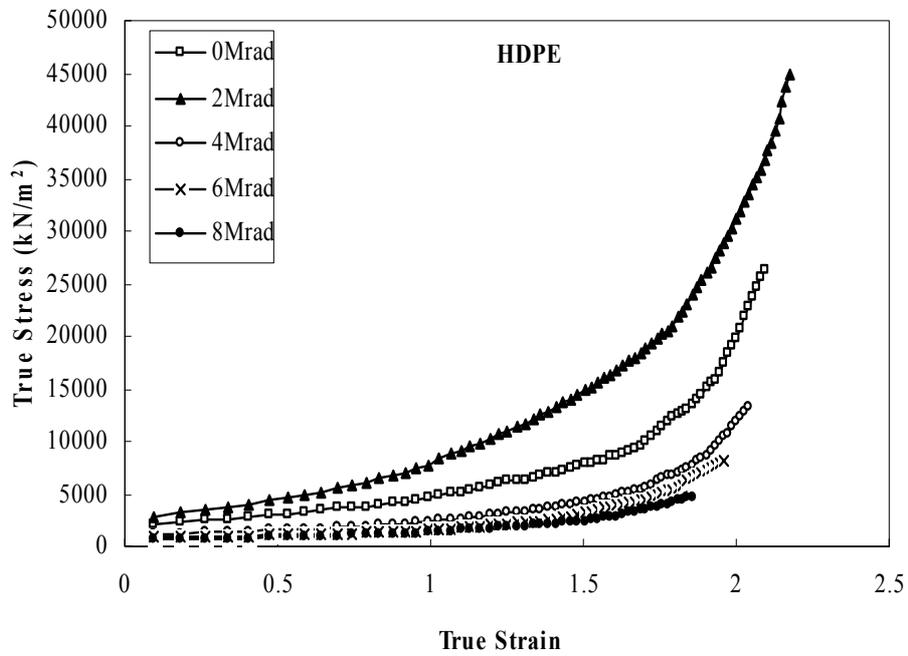
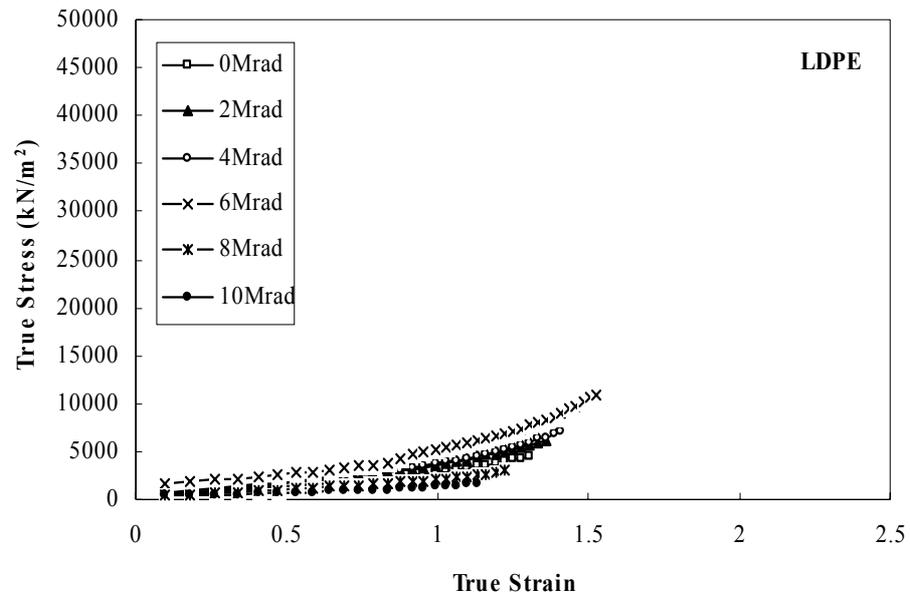


Fig (1) The true stress-strain behavior for all samples.

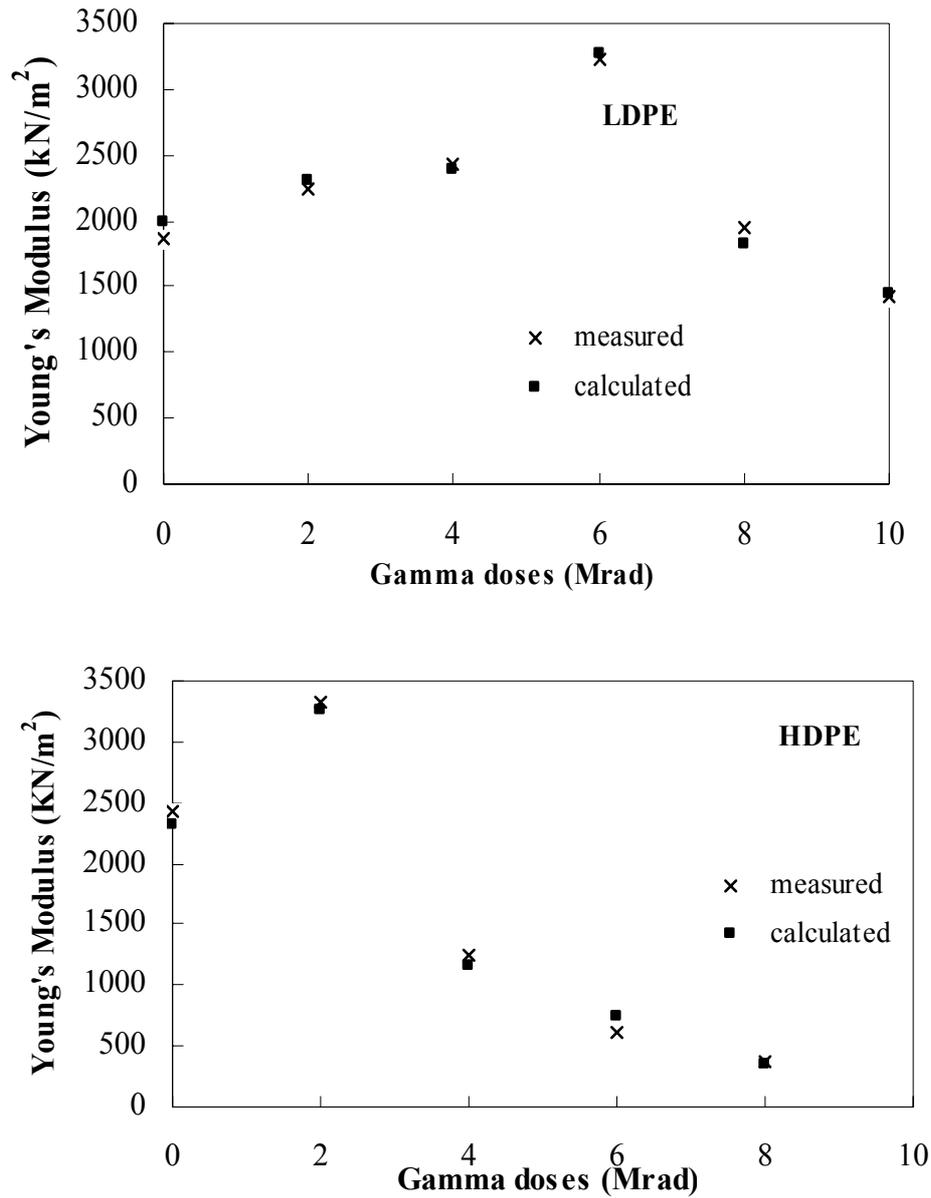


Fig (2): The measured and calculated of the Young's modulus, E, as a function of different γ -irradiation doses.

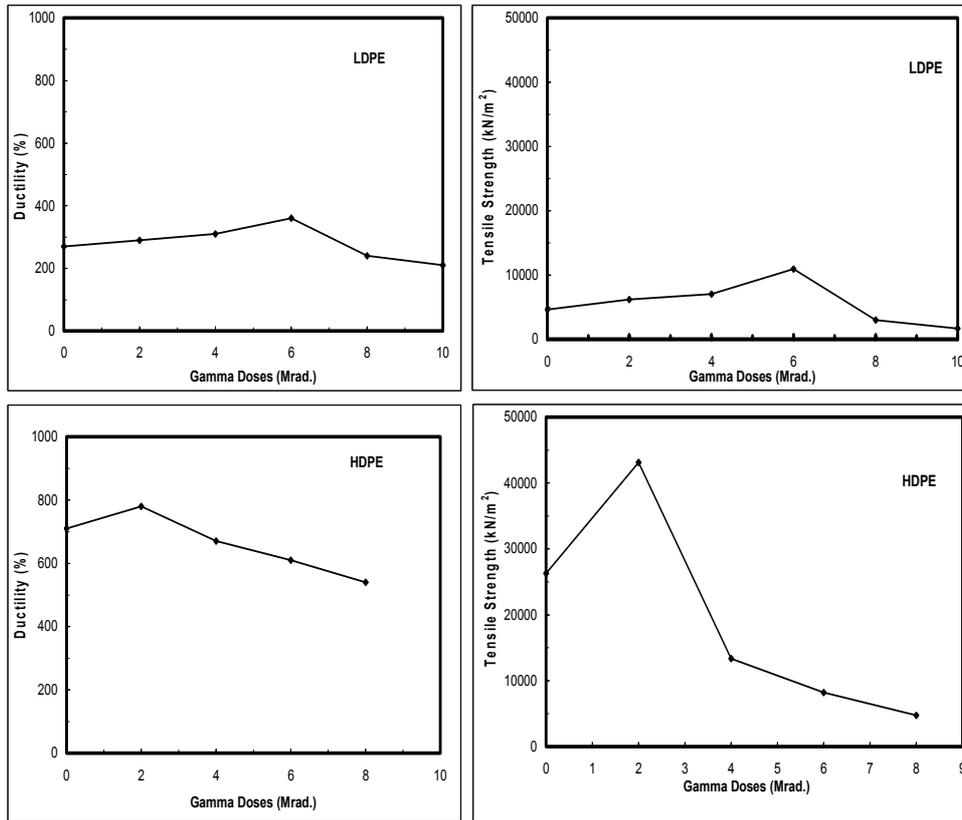


Fig. (3): The tensile strength and ductility at different γ -irradiation doses.

From the slope at low strains, of the respective stress-strain curves, the Young's moduli for the two types of samples at different doses can be determined (Fig. 2).

On the other hand, Eqn. (1) may be represented in a differential form as follows,

$$\frac{d\sigma}{d\varepsilon} = 3G + 3G\left(\frac{n}{2} - 1\right)\varepsilon \quad (3)$$

where ε is the strain, from which the modulus G ($E = 3G$, where E is the calculated Young's modulus) and n are obtained, Table (1).

Table (1): The calculated n, G, and strain to break (ε %) values

for LDPE and HDPE

γ - dose (Mrad)	LDPE			HDPE		
	n	G (KN/m ²)	ϵ (%)	n	G (KN/m ²)	ϵ (%)
0	1.71	5951.70	270	1.21	6967.80	710
2	1.64	6925.80	290	1.36	9747.00	780
4	1.60	7180.50	310	1.23	3468.00	670
6	1.60	9786.60	360	1.27	2219.19	610
8	1.60	5448.60	240	1.13	1081.50	540
10	1.42	4307.1	210			

It was found that, the n- measure was always a material constant, and is independent of γ -irradiation. The average value for LDPE and HDPE were $n = 1.6 \pm 0.15$ and $n = 1.24 \pm 0.10$ respectively. In our experiments the percentage errors of the parameters n and G were less than 10 %.

The experimentally measured Young's moduli as a function of γ -doses for LDPE and HDPE are shown in Fig. (2), in comparison with those calculated from Eqn. (3). It can be seen that a good agreement with the measured values is obtained. The stress-strain curve for LDPE shows that, at low doses, (2,4, and 6 Mrad.) one observes less deformation due to cross-linking which tends to increase the amorphous state. In other words, the γ -irradiation at doses up to 6 Mrad changes the sample from soft and tough to hard and tough state due to the increase of cross-linking at low doses. At higher dose, the sample is becoming hard and weak (i.e. brittle). It can also be seen that the high crosslinking for LDPE and HDPE of the same value of Young's modulus has occurred at doses 6 and 2 Mrad respectively.

Figure (3) represents the tensile strength and ductility for LDPE and HDPE sample at different γ -irradiation doses. These curves show, in general, the tensile strength and ductility for LDPE are always lower than those of the HDPE at the same γ -doses are. This means that, the HDPE samples are more hard and ductile. Also, crosslinking predominates over degradation up to higher exposure dose, up to 6 Mrad in the case of LDPE and up to 2 Mrad in the case of HDPE.

The calculated strain energy density W, for the investigated samples of LDPE and HDPE at different doses of γ -irradiation are shown in Fig. (4). It is noticed that LDPE and HDPE exhibit higher values of W upon stretching at 6 and 2 Mrad respectively. From this figure one may conclude that W increases with increase the crosslinking. In addition, a decrease in toughness or an increase in brittleness by formation of highly dense crosslinks should be taken into consideration.

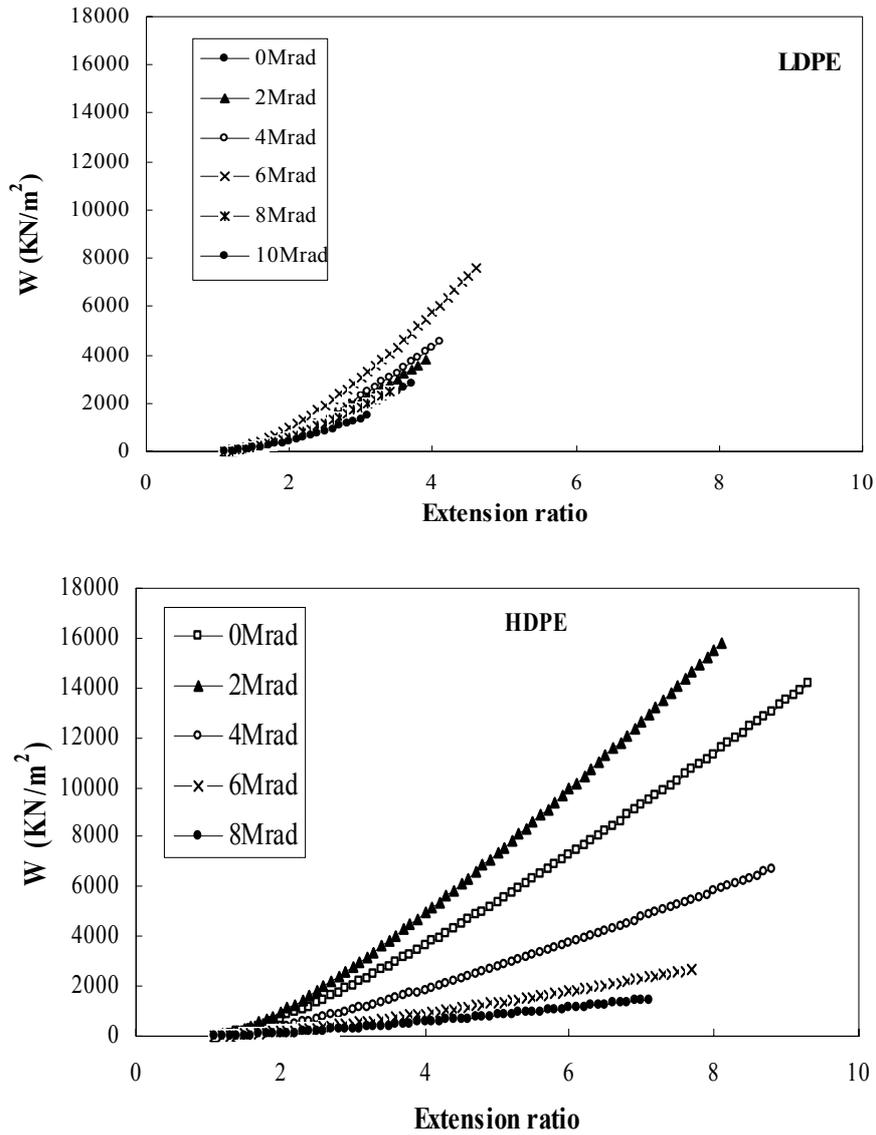


Fig (4): The calculated strain energy density, as a function of extension ratio.

Figure (5) shows the change of the strain energy density, W , with the γ -doses for the two types of PEs at constant extension ratio of 2.5. Comparison of this figure with Fig. (2) shows that the behavior of both E and W with γ -doses is almost the same. This indicates that as the Young's modulus increases the stored energy also increases.

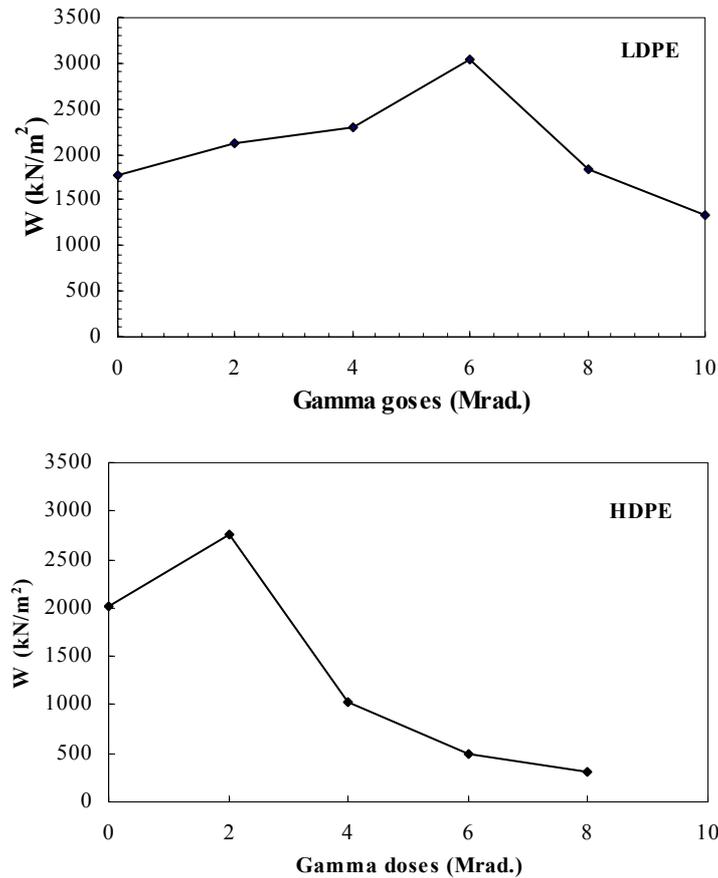


Fig (5): The calculated strain energy density at different doses of γ -irradiation.

Measurements of the relaxation time may indicate the degree of interaction between the macromolecules of polymeric chains. Long relaxation times indicate higher degrees of interaction while short relaxation time indicates smaller degrees of interaction. Stress relaxation measurements were performed and are shown in Fig. (6) for LDPE and HDPE at different irradiation doses. The stress relaxation curves were fitted to the following equation

$$\sigma(t) = \sigma_0 e^{-\frac{t}{\tau}}$$

where $\sigma(t)$ and σ_0 are the true stresses at time = t and 0, respectively, and τ is the relaxation time. The calculated relaxation times are presented in Fig. (7).

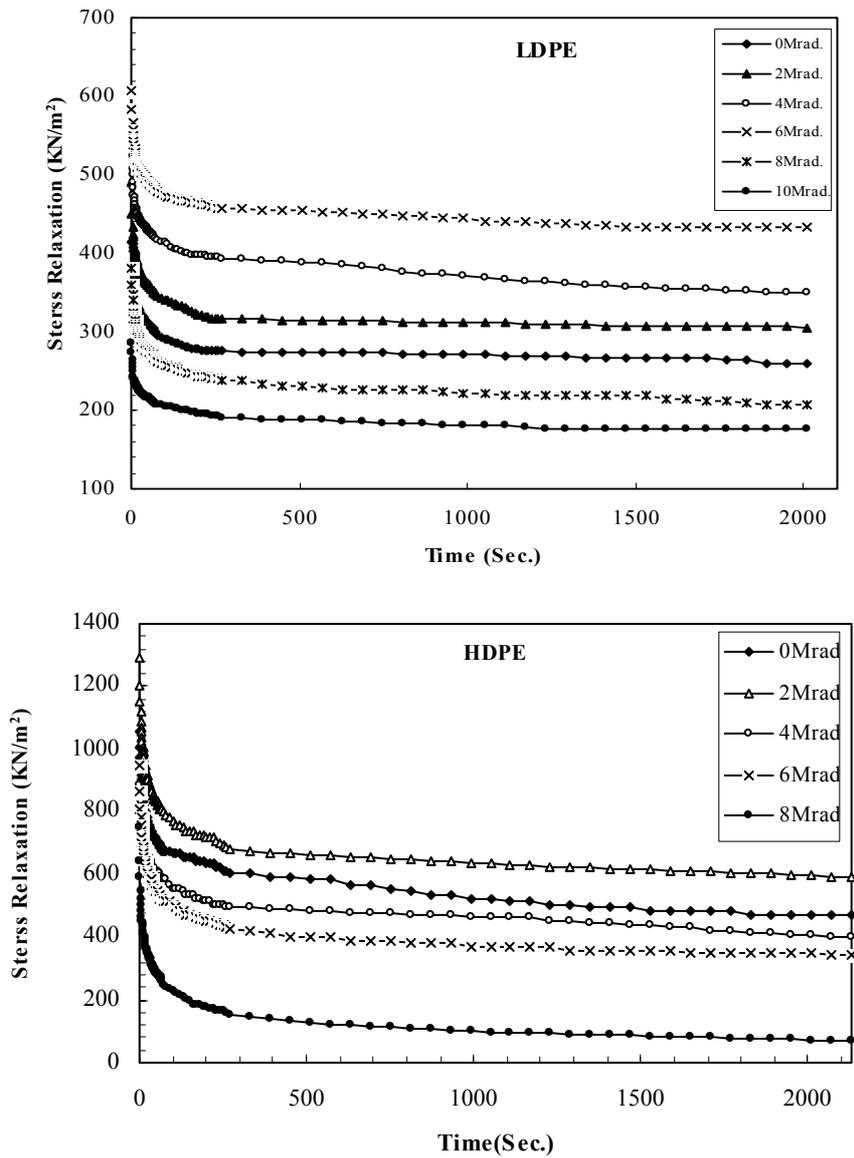


Fig (6): the stress relaxation measurements for all samples exposed to different γ -irradiation doses.

These curves show that, as expected, the intermolecular interactions between chains in HDPE are higher than that in case of LDPE. These data agree well with the obtained results of stress-strain behavior.

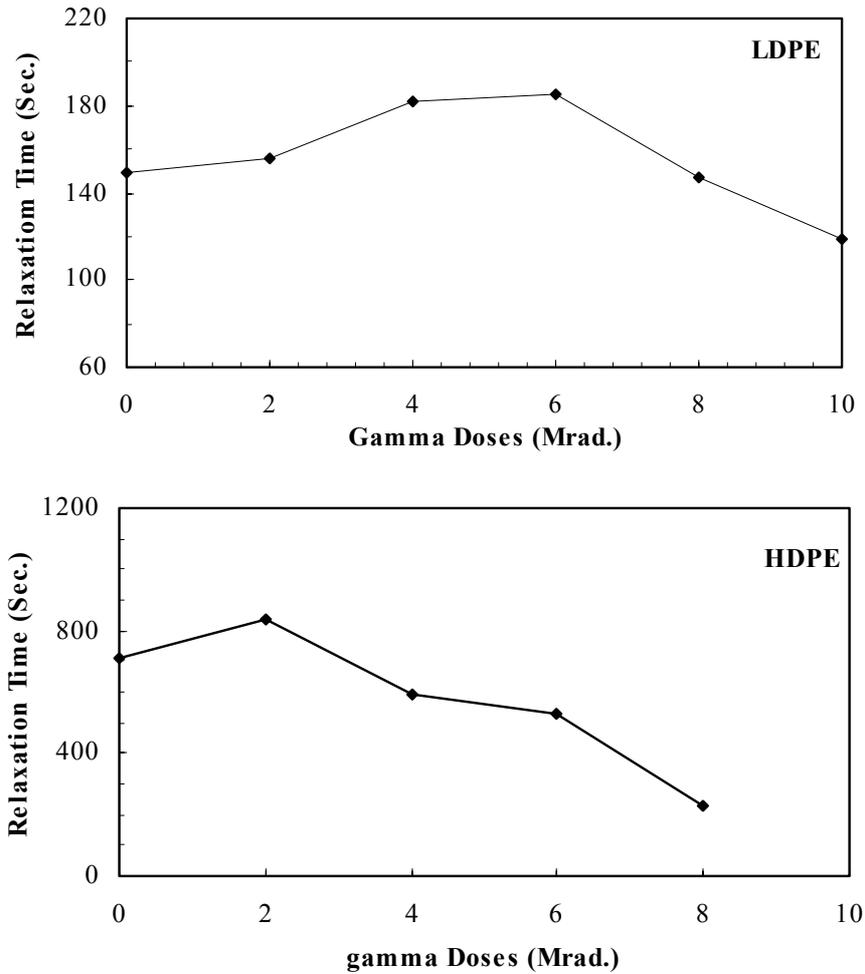


Fig (7): The calculated relaxation times for all samples before and after irradiation.

Conclusions

It was found that HDPE is more susceptible than LDPE to the influence of high-energy irradiation. Recognizable differences are observed for all parameters between the unirradiated and irradiated cross-linked polyethylene. On the basis of the obtained results, one may conclude that the measured data fits, quite satisfactorily, the equations proposed by Blatz et al at low extension. Since n is always dependent on materials, it is a material as well as a kinematics parameter for LDPE and HDPE. The calculated values of G show that it depends on the type of polyethylene and γ -doses. From the strain energy

density calculations one may conclude that the higher the polyethylene density the higher the strain energy density due to the increased crosslinking density. The stress relaxation data confirm fairly well the obtained parameters of the measured stress- strain data.

Acknowledgement

The author would like to express his deep gratitude to Prof. MY EL-Ashry, Dean of the Faculty of Science, and Dr A M Y EL-Lawindy for his interest and fruitful comments on the discussion of the experimental data.

References

1. Charlesby A, "Irradiation effects on polymers", Edt. Clegg CW, Collyer AA, Amsterdam:Elsevier,. Ch2 (1991).
2. Ikada Y, Nakamura K., Ogata S., Makino K., Tajima K., Endoh N., Hayashi T., Fujita S., Fujisawa A., Masuda S., Oonishi H. J of Polym. Sci.: A: Polym. Chem., **37**, 159 (1999).
3. Washen F, Mckellop HA, Salovey R. J. of Polym. Sci.: B: polymer physics, **34**, 1063 (1996).
4. Mckellop H.A., in total Hip Revision Surgery, Galante J.O., Rosenberg A.G., and Callaghan J. J.(eds.), Raven Press, New York, p. 211995.
5. Blatz P J, Sharda S C and Tschoegl N W: Trans. Soc. Rheol. **18**, 145(1974).
6. Sethe B R, "Second Order Effects in Elasticity, Plasticity and Fluid Mechanics", Edt. M Reiner and D Abir (New York: McMillan) p. 162 (1964).