Viscoelastic Properties of Crosslinked LLDPE Films Biaxially Oriented at Temperatures Below Melting Point

A. L. Bobovitch,[1] Y. Unigovski,[2] E. M. Gutman,[2] E. Kolmakov,[2] S. Vyazovkin[3]

[1]*Syfan Saad (99) Ltd., Kibbutz Saad, D.N. Hanegev, 85140, Israel*
[2]*Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel*
[3]*Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama*

Received 29 November 2005; accepted 3 June 2006
DOI 10.1002/app.25148
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Creep and stress-relaxation of linear low-density polyethylene (LLDPE) crosslinked with β-irradiation was studied as a function of irradiation dose. It was shown that both storage modulus and α-relaxation are influenced by irradiation. An influence of relatively low gel content on stress relaxation was detected. However, the creep results showed an increase of the creep strain when the polymer is irradiated with a dose below 4 Megarad (MR) in comparison with a nonirradiated film. This increase corresponded to the disorientation in the amorphous phase, which takes place as a result of the film heating during irradiation. This disorientation was demonstrated by differential scanning calorimetry (DSC) and X-ray analysis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3718–3723, 2007

Key words: polyethylene films; orientation; β-irradiation; crosslinking; stress relaxation; creep

INTRODUCTION

Biaxially oriented polyethylene films are a widely used product in the packaging industry. These films are extensively used for flexible packaging of a wide spectrum of products. They provide a very good combination of physical and mechanical properties, which meet the demands and technical requirements of the packaging industry.[1]

There are several processes for the production of oriented films. One of them is biaxial orientation by the double-bubble process, or tubular orientation process. During this process the primary extruded tube is quenched, reheated to a temperature below the melting point, and then simultaneously oriented in both machine direction (MD) and transverse direction (TD). The stretching (orientation), which takes place below the melting point, is the most important difference between this process and the well-known blown process.

In order to improve the mechanical problems of the film at elevated temperatures, the crosslinking method is usually applied. One of the best-known crosslinking processes is the irradiation of the film by β-irradiation. Crosslinking provides the possibility to increase the temperatures during film shrinkage and to achieve better shrinkage of the film over the item being packed.

During winding of the films at various stages of the technological process, stress is applied to the film in order to wind it smoothly. When the film is wound into reels, the film comprising the inner layers of the reel cannot release its elastic deformation because the outer layers compress it. It was found that when the film is kept under stress with no possibility to release its deformation, wrinkling takes place in the film, making it impossible for subsequent usage. This phenomenon is caused by viscoelastic behavior of the polymer, which can be characterized by stress relaxation and creep. Therefore, the study of the morphology and viscoelastic properties of oriented films is necessary from both a scientific and a technological viewpoint.

Stress-relaxation has been studied in a number of oriented structures. For example, mechanical relaxation in uniaxial-oriented linear low-density polyethylene (LLDPE) was studied by Chong et al.[2] Chow and Van Laeken[3] and Hawthorne[4] explained stress relaxation in oriented PET films. They studied relatively thick films (76 and 33 μm, respectively), which were oriented at a temperature above glass-transition temperature.

Baumgartel and Winter used dynamical mechanical thermal analysis (DMTA) in order to determine discrete and continuous relaxation time spectra.[5] A DMTA study of polyethylene nanophthalate (PEN) film was carried out by Gillmor and Greerer.[6]

Correspondence to: A. L. Bobovitch (arthurB@syfan.co.ie).

Journal of Applied Polymer Science, Vol. 103, 3718–3723 (2007)

In our previous studies we investigated the viscoelastic behavior of biaxially oriented polyolefin films from the viewpoint of the relaxation time spectrum.[7,8] The relaxation time spectrum of crosslinked polyethylene films has been studied as well.[9]

The influence of irradiation (mainly γ) on the creep behavior of polyethylene has also been studied.[10–12] The creep behavior of ultra-high-molecular-weight polyethylene (UHMWPE), nonirradiated and irradiated with γ-irradiation, has been studied extensively.[13–15] These results manifest a decrease in the creep strain with growth of the irradiation dose.

The creep behavior of polyethylene films has been studied by several researchers. Ward and coauthors studied the influence of β-irradiation on the creep behavior of uniaxially oriented polyethylene film.[16–18] The influence of morphology on creep behavior of melt-extruded polyethylene films was investigated by Zhou and Wilkes.[19] However, the creep behavior of biaxially oriented linear low-density polyethylene (LLDPE) films has not yet been studied in depth. There are no data concerning creep behavior of crosslinked LLDPE films biaxially stretched below melting point.

The main goal of the present research is to investigate the influence of irradiation on both creep and stress-relaxation of crosslinked LLDPE films biaxially oriented at temperatures below melting point.

EXPERIMENTAL

In the present study a linear low-density polyethylene (LLDPE) film crosslinked by electron beam bombardment was investigated. The thickness of the film was 15 μm and the film density 0.922 gr/cm^3. The film was produced from LLDPE of Melt Index 1 (190°C/2.16 kg) and octene comonomer type. The film was stretched using double-bubble technology. The orientation ratio was 1:5.2 in both MD and TD. The orientation temperature was 109°C. The film was irradiated post-production using an electron beam of varying doses. The accelerating voltage of 150 keV was applied. The film passed on a chill roll in order to prevent heating. The temperature of the film was measured with infrared thermometer Model 610LC ex. CE.

Dynamic-mechanical tests were conducted using a dynamic mechanical and thermal analyzer (DMTA, Model MKII, Polymer Laboratories Ltd, Loughborough, U.K.). The samples were tested at a frequency of 1, 3, and 10 Hz, and within a temperature range from −50°C to 130°C, at a heating rate of 0.5°C/min, under a constant tensile load of 0.2 N. The length and the width of the specimens were 20 and 5 mm, respectively. Samples were tested in the tension mode longitudinally (along the extrusion direction).

Creep tests were carried out using a creep tester developed in our laboratory (Ben-Gurion University). A sample of length 120–130 mm and width 25 mm was placed in special grips into a copper tube of a thermostat-controlled silicon oil furnace. The test temperature was stabilized using a digital controller and an oil stirrer, and was maintained within ±0.2°C. Measurements were carried out at a constant load of 6 N at temperatures of 23, 60, and 90°C. The creep strain was calculated in real time from the displacement of the bottom grip using a special precision-positioning system and the MATLAB program (toolbox data acquisition). The signal proportional to the displacement of the sample and to the angle displacement of the precision multiturn potentiometer was monitored by the sound blaster (card) of computer. Calibration of the measuring system was carried out by the Model 2000 comparator (Satec Inc.) with accuracy of ±0.5 μm on the length of 25 mm.

Gel content in the crosslinked films was determined by extraction in xylene at 138°C during a 12 hour period. A Mettler DSC822 apparatus (Differential Scanning Calorimeter) was used with a heating rate of 10°C/min. The X-ray diffraction patterns of the coextruded film were recorded with a Philips X-ray diffractometer (type PW-1130) using Co K_α radiation and an Fe filter at an angular range 2θ = 11–40°, a scanning rate 2°/min, and an operating voltage of 40 kV with 30 mA current.

RESULTS AND DISCUSSION

The DMTA study of crosslinked films showed an increase in the storage modulus (E') at low temperatures below (−30°C) when the irradiation dose achieved 6 MR (Fig. 1). The increasing modulus as a result of irradiation can also be observed at higher temperatures.

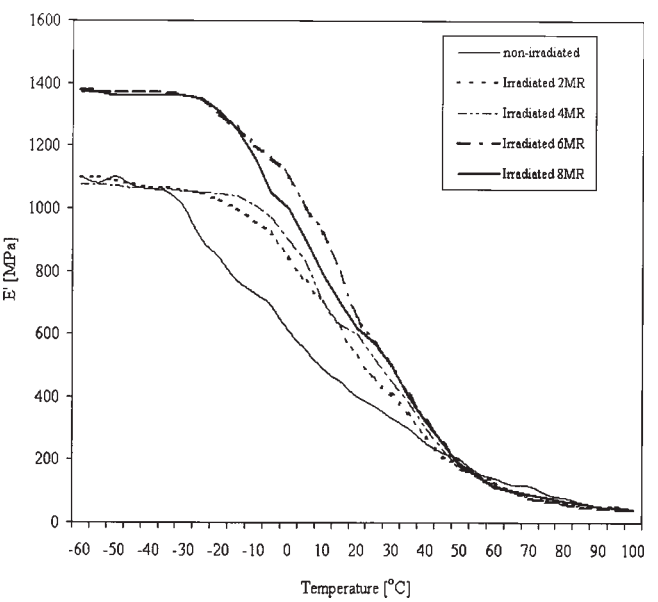

Figure 1 Storage modulus (E') as a function of irradiation dose.

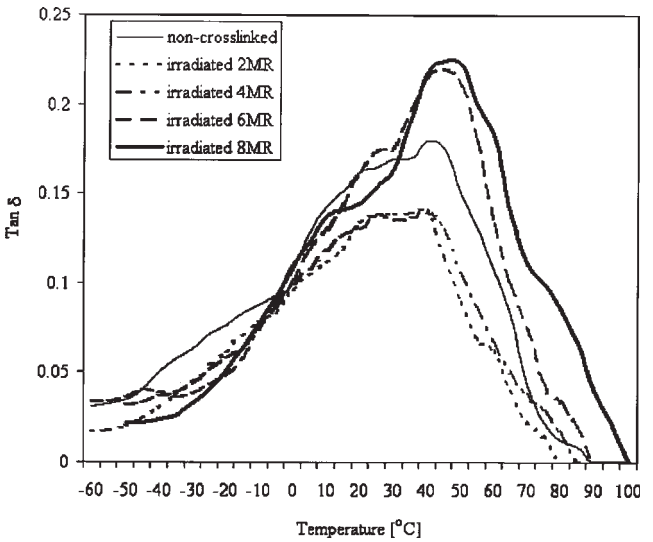

Figure 2 Tan δ as a function of irradiation dose.

Above 50°C, values of E' detected in all films are almost identical. Here one can also see that irradiation at 2 MR significantly affects only the storage modulus.

One can see that tanδ (Fig. 2) shows a shift of the peak to higher temperatures when the irradiation dose increases. It is important to note that we associate α-relaxation with the relaxation of amorphous molecules that are close to the crystalline part of the polymer. Taking into account the fact that no difference in T_m of the crystalline phase was detected with the increase of irradiation dose and only a slight change in melting enthalpy was observed by DSC (Fig. 3), we can assume that the irradiation does not affect the crystalline phase. Also, our previous results on stress-relaxation of crosslinked films[8] did not show an effect of crosslinking on the crystalline phase. So the increase of α-transition temperature also proves that the mobility of the molecules decreases with the increase of the irradiation dose. An additional confirmation of the decreasing mobility is the fact that β-transition was almost undetectable in irradiated films.

Since the plot of the logarithm of frequencies versus $1/T$ shows good linearity in the limited frequency range used in this study, the apparent activation energy E_a of the α-relaxation process can be described by the Arrhenius equation as follows:[20,21]

$$f = f_0 \exp\left[\frac{-E_a}{RT}\right] \quad (1)$$

where f_0 is a preexponential factor designating the relaxation time at $T \to 0$ and R is the gas constant.

The influence of irradiation dose on the gel content and the apparent activation energy of the relaxation process is presented in Figure 4. In fact, the transition that was measured (Fig. 2) is actually the superposition of α and β relaxations, and β is suppressed by crosslinking. Therefore, the change in apparent activation energy with crosslinking may reflect the shifting balance of α versus β relaxation contributions to the merged transition.

It was observed that the gel content in the polymer is very low after irradiation with 2 MR and increases dramatically after irradiation with higher doses. The most significant decrease in apparent activation energy was observed with the first 5% gel content. This result correlates with the effect of low irradiation dose on storage modulus, and is an additional strengthening of the assumption that the initial crosslinking (even at 5%) of gel content affects the material more that the following dramatic increase of gel content as a result of the increased irradiation dose.

The creep experiments were carried out at room temperature (23°C ± 1°C) and at temperatures of

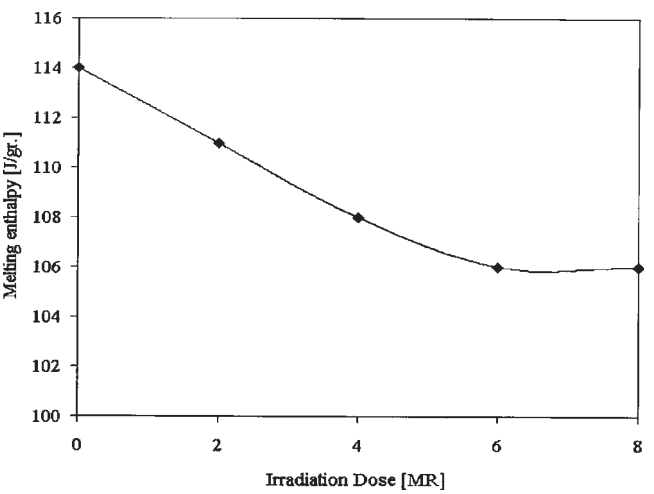

Figure 3 Melting enthalpy of crosslinked oriented polyethylene as a function of irradiation dose.

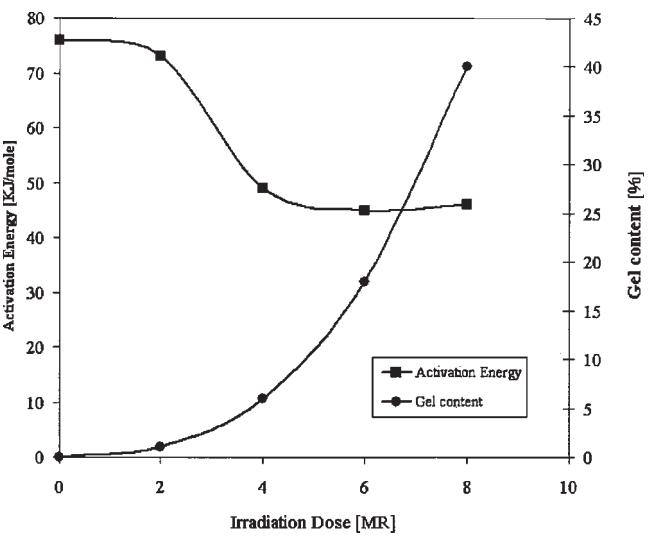

Figure 4 Activation energy of α-transition and gel content as a function of irradiation dose.

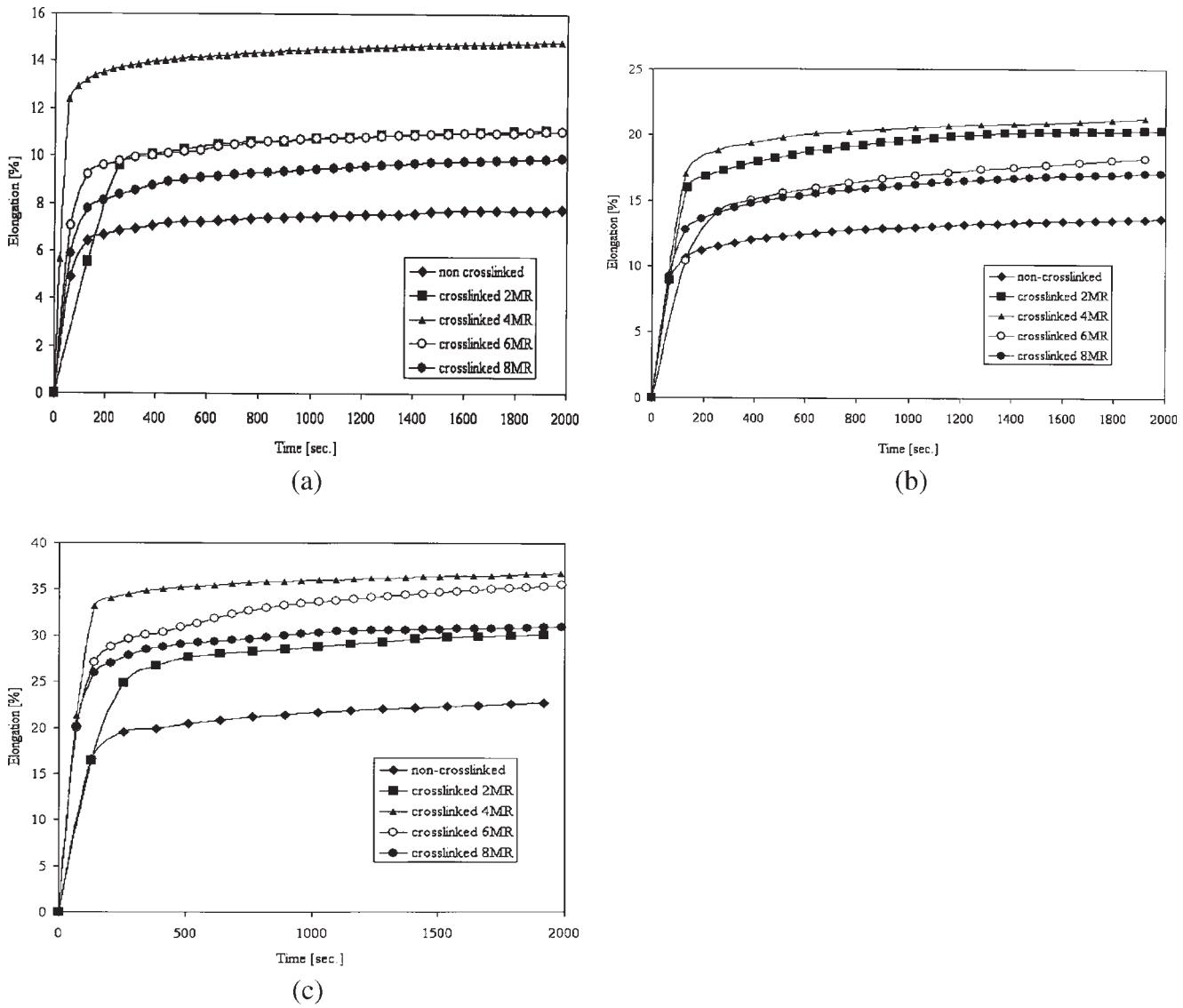

Figure 5 Creep of films crosslinked with varying irradiation doses at (a) 23°C; (b) 60°C; (c) 90°C.

60°C and 90°C. One can see the results of the creep tests in Figure 5. At each temperature, the irradiation increases the strain of the films in comparison with the creep behavior of noncrosslinked film. This result is contrary to the results obtained in previous investigations,[12,15,17,18] where the creep behavior of polyethylene crosslinked with γ- and β-irradiation was studied. However, in our case, when the dose is above 4 MR, a decrease in the creep-strain values can be observed. This is in agreement with previously published results.

We have attempted to explain the strain increase when oriented film is irradiated with relatively small doses, from the viewpoint of morphological changes taking place in the film during irradiation. Indeed, in order to prevent the film from melting during the irradiation process, it is passed through a chill roll. Nevertheless, a slight increase in film temperature was observed. Using an infrared thermometer, we detected the film temperature of about 50°C immediately after irradiation while the ambient temperature (the temperature of the film before irradiation) was 27°C. We assume that the temperature of 50°C is relatively low in order to affect the crystalline phase, but from the other side this temperature causes the partial relaxation and disorientation in the oriented amorphous phase. Therefore, the film after irradiation with even a 4 MR dose lost some of its orientation, and amorphous molecules partially recoiled. However, the quantity of gel in the film is not high enough (only 5%). Therefore, ultimately the ''loosened'' orientation enables a higher ability of the material to undergo creep.

Indeed, DSC measurements of the crosslinked film demonstrated a slight decrease of the melting enthalpy (Fig. 3). On the other hand, the melting tem-

perature of the LLDPE film remained the same as it was following orientation (118°C). As mentioned above, the orientation causes an increasing of the melting enthalpy due to the high orientation of the amorphous phase.[7] Here, following irradiation, some of this apparent crystallinity disappears. We must mention that no influence of heating on the crystalline phase during irradiation has been observed. These DSC results strengthen the assumption made above concerning the disorientation of the amorphous phase after passage through the irradiation zone.

Another idea about disorientation of the amorphous phase can arise from the interpretation of an X-ray diffractogram (Fig. 6). One can see that the crystalline phase both in the noncrosslinked sample and in an irradiated sample is almost unaffected, while the oriented amorphous halo has been decreased after crosslinking.

So one can conclude that at low irradiation doses the amorphous chains relaxation or disorientation predominates over the crosslinking effect, which leads to an increase in creep strain. The important point here is that the heating during irradiation with an electron beam is one of the differences compared to γ-irradiation. This can be the reason for the contradiction in our results with those received previously. Another reason for the contradictory results can be the high orientation of amorphous phase that was done below melting point and the ability of the amorphous molecules to undergo relaxation at temperatures close to 50°C.

In order to estimate the apparent activation energy of creep, the creep rate at 1900 sec was considered. Since the plot of the logarithm of the creep rate versus $1/T$ shows good linearity (the correlation coefficients vary in the range of 0.97–0.99) in the limited

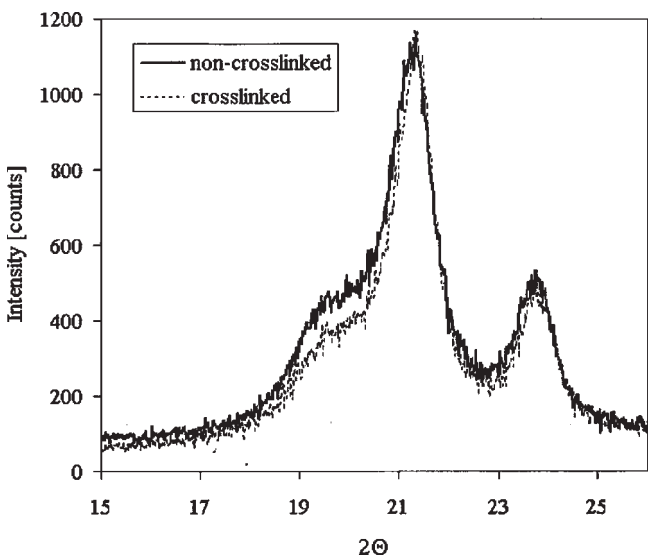

Figure 6 X-ray diffractogram of noncrosslinked and crosslinked oriented LLDPE films.

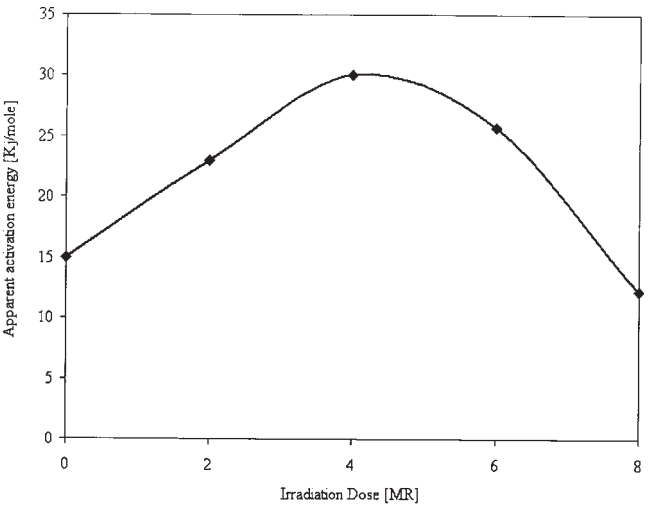

Figure 7 Apparent activation energy of creep as a function of irradiation dose.

temperature range used in this study, we can calculate the apparent activation energy of creep E_c by the Arrhenius equation as follows:

$$\varepsilon = \varepsilon_0 \exp\left[-\frac{E_c}{RT}\right] \tag{2}$$

here ε is the minimum creep rate and ε_0 is the preexponential factor.

The E_c values amount to 15 kJ/mole for nonirradiated film and 23, 30, 25, and 13 kJ/mole for films crosslinked by irradiation doses of 2, 4, 6, and 8 MR, respectively, (Fig. 7). One can see the increase in the apparent activation energy with irradiation dose followed by a decrease when the dose exceeds 4 MR. This result correlates with the phenomenon of creep strain increasing observed when the dose increases are followed by decreasing strain when the dose exceeds 4 MR.

CONCLUSIONS

Irradiation affects stress-relaxation in LLDPE. The shift of the modulus to higher values has been observed even when the gel content in the polymer is very low. This effect of low gel content is in agreement with the results found in previous investigations. The low mobility of the crosslinked molecules causes the shift of α-relaxation to higher temperatures. A decrease in the apparent activation energyofrelaxation as a result of crosslinking has been observed.

The higher creep strain of film irradiated with relatively low doses was observed because of the partial disorientation of the molecules in the oriented amorphous phase. Heating of the film during irradiation caused this disorientation. DSC and X-ray anal-

yses demonstrated the disorientation in the amorphous phase. The irradiation of film with doses above 4MR caused a decrease of the creep strain.

The authors are grateful to L. Dorfman, Y. Frolov, A. Jarashneli, and Dr. V. Kasiyan (Ben-Gurion University of the Negev) for kind assistance with the creep and X-ray experiments.

References

1. Osborn, K. R.; Jenkins, K. R. Plastic Films, Technomoc Publishing Company: Lancaster, PA, 1992.
2. Chong, C. L.; Leung, W. P.; Hg, H. C. J Appl Polym Sci 1986, 32, 5883.
3. Chow, T. S.; Van Laeken, A. C. Polym 32, 1991, 1798.
4. Hawthorne, J. M. J Appl Polym Sci 1981, 26, 3317.
5. Baumgartel, M.; Winter, H. H. Rheol Acta 1989, 28, 511.
6. Gillmor, J. R.; Greerer, J. J Plast Film and Sheeting 1999, 15, 37.
7. Bobovitch, A.; Gutman, E. M.; Henning, S.; Michler, G. H. J Appl Polym Sci 2003, 90, 3424.
8. Bobovitch, A.; Gutman, E. M.; Henning, S.; Michler, G. H. Mater Lett 2003, 57, 2579.
9. Bobovitch, A.; Gutman, E. M.; Henning, S.; Michler, G. H.; Nir, Y. J Plastic Film and Sheeting 2002, 18, 169.
10. Ward, I. M.; Wilding, H. A. J Polym Sci, Polym Phys Ed 1984, 22, 561.
11. Marin, J.; Criesacher, D. B. J Appl Polym Sci 1963, 7, 133.
12. Birkinshaw, C.; Buggy, M.; Daly, S.; O'Neill, M. J Appl Polym Sci 1989, 38, 1967.
13. Deny, M.; Latour, R. A.; Ogale, A. A.; Shalaby, W. S. J Biomed Mat Res 1998, 40, 214.
14. Ikada, Y.; Nakamura, S.; Ogata, K.; Makino, T. K.; Endoh, N.; Kayashi, I.; Fujita, S.; Fujiseena, A.; Masudee, S.; Oonishi, H. J Polym Sci Pt A: Polym. Chem 1999, 32, 159.
15. Sangster, D. F.; Barry, D. B. J Appl Poly Sci 1991, 42, 1385.
16. O'Connel, P. A.; Banner, M. J.; Duckett, R. A.; Ward, I. M. J Appl Polym Sci 2003, 89, 1663.
17. Rasburn, J.; Klein, P. G.; Ward, I. M. J Polym Sci, Part B: Polym. Phys 1994, 32, 1329.
18. Klein, P. G.; Ladizrsky, N. H.; Ward, I. M. J Polym Sci, Part B, Polym Phys 1986, 24, 1093.
19. Zhou, H.; Wilkes, G. L. Polym 1998, 39, 3597.
20. Ryabov, Ya.E.; Nuriel, H.; Marom, G.; Feldman, Yu. J Poly Sci, Pt B: Polym Phys 2003, 41, 217.
21. Jeong Y. G.; Jo, W. H.; Lee, S. C. Polym 2004, 45, 3321.