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Creep Behavior of Linear Low-Density Polyethylene Films

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Abstract

The Creep of biaxially-orientated linear low-density polyethylene (LLDPE) non-crosslinked and crosslinked with β-irradiation was studied as a function of the draw ratio and irradiation dose. The creep results have shown an increase in the creep strain after the polymer irradiation with a dose below 4 Megarad (MR) in comparison with a non-irradiated film. This increase corresponds 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.

Key words: polyethylene films, orientation, β-irradiation, crosslinking, creep.

Introduction

Biaxially-oriented polyethylene films are widely used in the packaging industry. These films are extensively used for flexible packaging of a broad 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.(10)

There are several processes for the production of oriented films, among them 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) that takes place below the melting point is the most important difference between this process and the well-known blown process. During the winding of 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 constituting the inner layers of the reel cannot release its elastic deformation because the outer layers compress it. It has been found that when the film is kept under stress without a possibility to release its deformation, wrinkling takes place in the film, making it unsuitable for subsequent use. This phenomenon is caused by the viscoelastic behavior of the polymer, which can be characterized by the creep and stress relaxation. Therefore, the study of viscoelastic properties and the morphology of oriented films is necessary from both scientific and technological viewpoints.

A potential problem associated with the long-term use of polyethylene is its tendency to "creep", that is, to deform gradually under sustained load. It is especially prevalent in polyethylene with modest levels of crystallinity.(7) The poor creep performance of polyethylene can exclude it from a wide range of applications. During orientation, considerable structural changes in polyethylene occur, e.g. its transformation from the spherulitic into the fibril structure.(7-8)

Earlier, the influence of irradiation (mainly γ) on the creep behavior of polyethylene was studied by.(6, 13, 1, 12, 3, 4) The results for ultra-high molecular weight polyethylene manifest a decrease in the creep strain with the growth of the irradiation dose. Ward with coauthors (1986, 1994, 2003) studied the influence of β-irradiation on the creep behavior of uniaxially oriented polyethylene film. The influence of the morphology on creep behavior of melt-extruded polyethylene films was investigated by.(14) However, the creep behavior of

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biaxially oriented linear low-density polyethylene (LLDPE) films has not been studied in- depth yet. There are no data concerning creep behavior of crosslinked LLDPE films biaxially stretched below the melting point.

The main goal of the present research is to investigate the creep behavior of non-oriented and biaxially oriented LLDPE films crosslinked by β-irradiation at the temperatures below the melting point.

Experimental

In the present study, a linear low-density polyethylene (LLDPE) films non-crosslinked and crosslinked by electron beam bombardment were investigated. The 15 micron-thick film with the density of 0.922 gr/cm^3 was stretched using a double bubble technology. The orientation ratio was 1:5 in MD and 1:5.2 in TD direction. The orientation temperature was 109oC. The film was irradiated post-production using an electron beam of varying doses. Besides, the creep behavior of a non-oriented 0.4 mm thick polyethylene (after the 'first bubble') was also studied.

Creep tests were carried out using a creep tester developed in the laboratory of viscoelasticity of the Department of Materials Science at the Ben-Gurion University of the Negev. A sample with the gage length 100-120 mm and width 25 mm was placed in special grips in the air atmosphere 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 maintained within ±0.2oC. The creep strain was monitored by the displacement of the bottom grip using a special precision-positioning system and the MATLAB program (toolbox data acquisition). The calibration of the measuring system was carried out by the Model 2000 comparator (Satec Inc., USA) with the accuracy of ±0.5 microns on the length of 25 mm.

A Mettler DSC822 apparatus (Differential Scanning Calorimeter) was used with a heating rate of 10ºC/min. The X-ray diffraction patterns of the films were recorded with a Philips X-ray diffractometer (type PW-1130) using Co-Kα radiation and a Fe-filter within the angular range 2θ = 11º – 40º, at the scanning rate 2o/min, and operating voltage of 40 kV and current of 30 mA.

Results and discussion

The creep experiments were carried out at room temperature (25ºC ± 1ºC) and at elevated temperatures (50ºC, 60ºC, 65ºC, 75ºC and 90ºC). Oriented samples are less liable to creep than isotropic ones: the total strain corresponding, e.g. to the test time of 100 s, increased from 2% for an oriented film to 50% for non-oriented polyethylene at the same test conditions (Figure 1). The fast increase in the strain was observed during the initial 20-100 s, then the strain of non-oriented and oriented samples grows within a negligible margin (Figure 2). An increase in the test temperature from the room temperature to 75ºC leads to the growth of the strain both in non-oriented PE and in biaxially oriented PE by an order of magnitude (Figure 3).

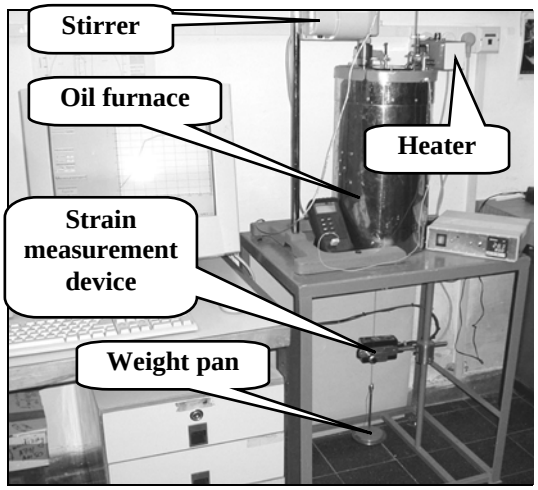


Figure 1. A view of the creep tester

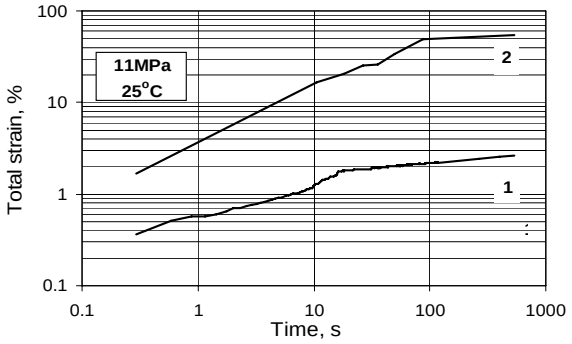
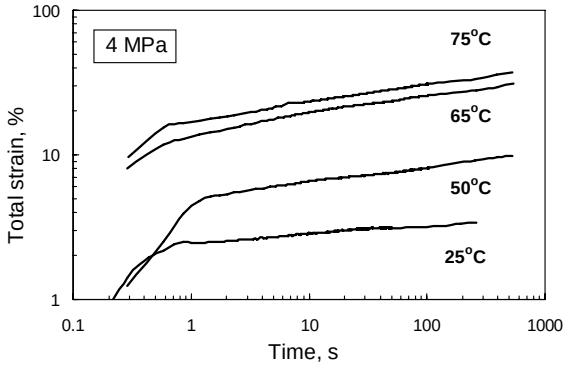
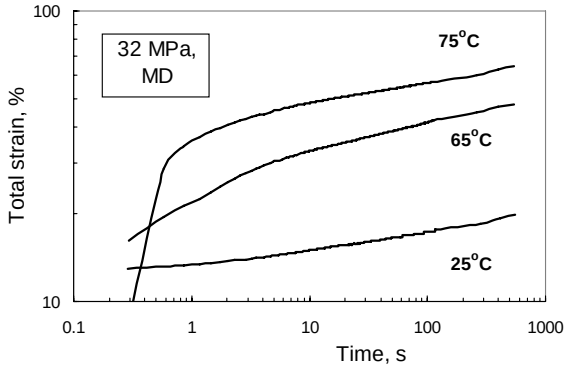


Figure 2. Creep behavior of non-oriented polyethylene and biaxially-oriented film (2) at room temperature under the stress of 11 MPa



(a)



(b)

Figure 3. Creep behavior of non-oriented 0.4 mm thick polyethylene (a) and biaxially- oriented 15 μm thick film (b) at different temperatures. Stress, MPa: 4 (a) and 32 (b).

The drastic increase in the strain at the very initial period of time observed in Figure 2, 3 is connected with the neck formation on the gage of the sample. It is known that the strain is a sum of three components: the instantaneous elastic strain proportional to the elastic modulus; the delayed elastic strain and the Newtonian component, which reflects the viscous flow of the polymer. After a critical time t_c the deformation increases rapidly, and a neck develops. The neck rapidly propagates along the sample until it covers the whole gage. After that the creep strain increases slowly during a long period of time.

The effect of the draw ratio can be observed in Figure 4 At the room temperature, we do not see any difference between the creep behavior of films cut out in the machine and transverse directions. However, at 75ºC, in the machine direction, the film showed a smaller strain (a higher creep resistance) as compared to that in the transverse direction (Figure 4).

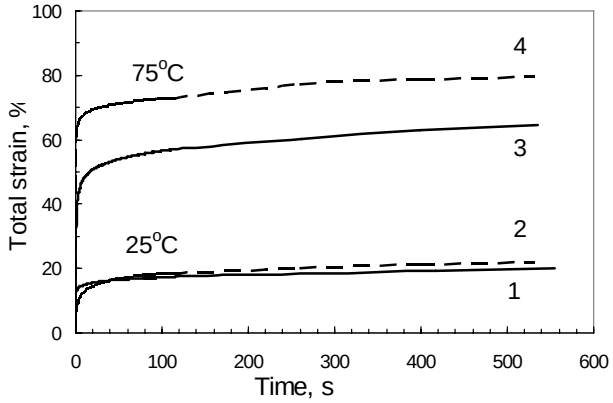


Figure 4. Creep behavior of biaxially-oriented film cut out in MD (1, 3) and TD (2, 4) at room and elevated temperatures under the stress of 32 MPa.

Crosslinked films showed also a fast growth of the strain in the first 1-100 s and then a slow increase in the strain during a very long period of time. In Figure 5, e.g., one can observe such behavior of the film crosslinked with an irradiation dose of 4 MR up to the test time of 10^6 s. The irradiation increases the strain of the films in comparison with the creep behavior of non-crosslinked film both at room temperature and at elevated temperatures (Figure 6, 7). This result is contrary to the results obtained in previous investigations.[6, 9, 11, 12] where the creep behavior of polyethylene crosslinked by γandβ-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.

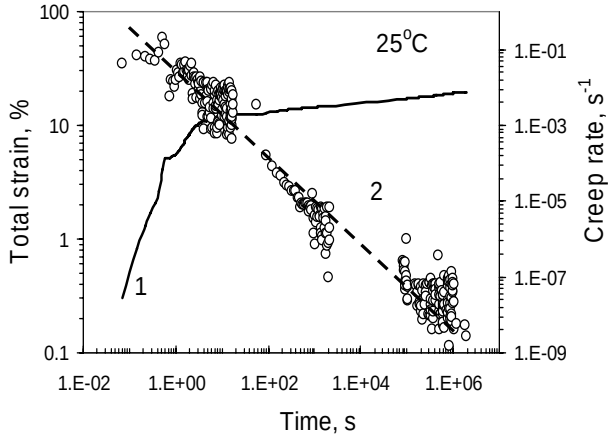
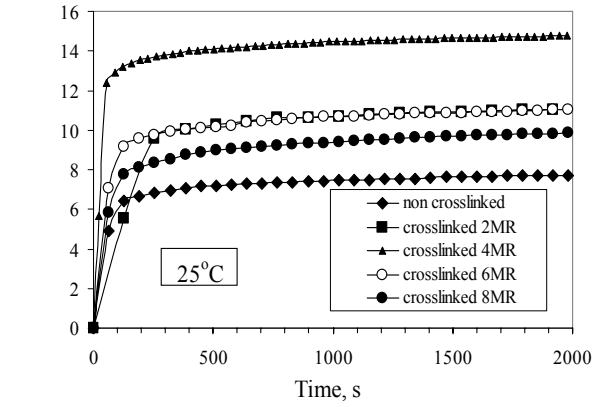
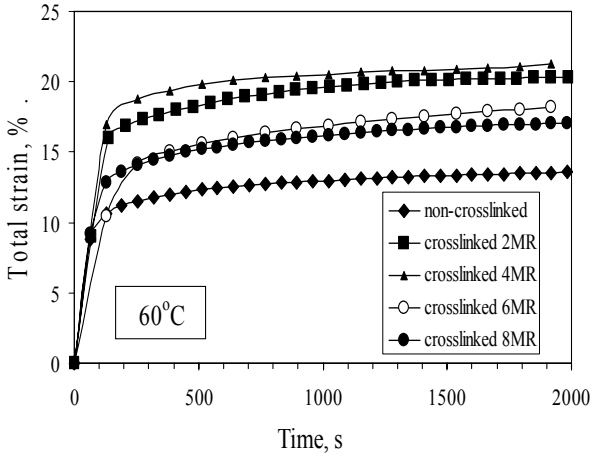


Figure 5. Typical creep curve (1) and creep rate (2) vs. time for a crosslinked film (25°C, 16 MPa, the irradiation dose of 4 MR).



(a)



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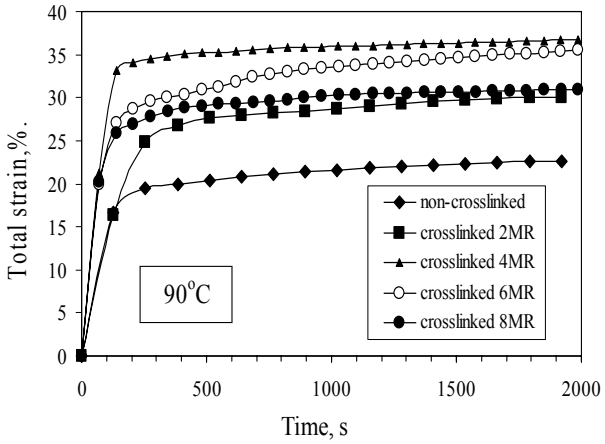

(c)

Figure 6. Typical creep curves of films crosslinked by various irradiation doses at 25°C (a), 60°C (b) and 90°C (c) under the stress of 16 MPa.

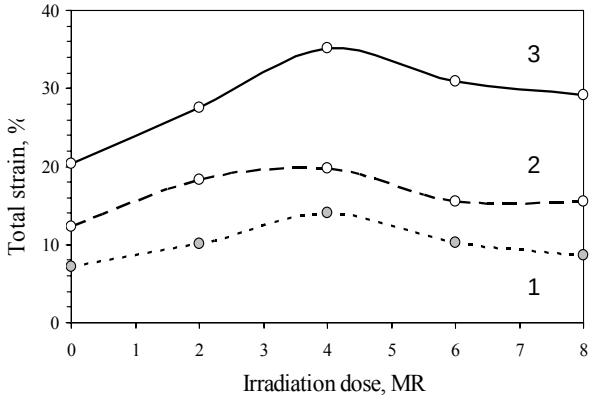

Figure 7. Effect of the test temperature and irradiation dose on the total strain of biaxially-oriented crosslinked films. The test temperature, °C: 25 (1), 60 (2) and 90 (3), 16 MPa; the total strain corresponds to the time of 500 s.

We have attempted to explain the strain increase at the oriented film irradiation with relatively small doses from the viewpoint of morphological changes taking place in the film during the irradiation. Indeed, when the film passes through an irradiation zone, it is subjected to extremely high temperatures. In order to prevent the film from melting, it is passed through a chilled roll. Nevertheless, a slight increase in the film temperature was observed. We assume that this temperature increase causes the partial disoreintation in the oriented amorphous phase. From another viewpoint, the chilled roll prevents the film from heating to temperatures that can affect the crystalline phase. Therefore, after the irradiation even with a 4 MR dose, the film loses some of its orientation, and amorphous molecules partially recoil.

The apparent creep activation energy E_c calculated by the Arrhenius method amounts to 15 kJ/mole for non-irradiated films and 23, 30, 25 and 13 kJ/mole for films crosslinked by irradiation doses of 2, 4, 6 and 8 MR, respectively, (Figure 8). One can see an increase in the apparent activation energy with the irradiation dose followed by a decrease when the dose exceeds 4 MR. This result correlates with the phenomenon of creep strain increase when the dose increases followed by strain decrease when the dose exceeds 4 MR.

In Figure 8, one can also observe a slight decrease of the melting enthalpy of the crosslinked film obtained by DSC measurements. On the other hand, the melting temperature of the LLDPE film remained the same as it was following the

orientation (118ºC). As mentioned earlier, the orientation causes an increase in the melting enthalpy due to a high orientation of the amorphous phase.(2) Here, following the irradiation, some of this apparent crystallinity disappears. We should mention that no influence of heating on the crystalline phase during the irradiation has been observed. These DSC results prove the above assumption concerning the disorientation of the amorphous phase after the passage through the irradiation zone.

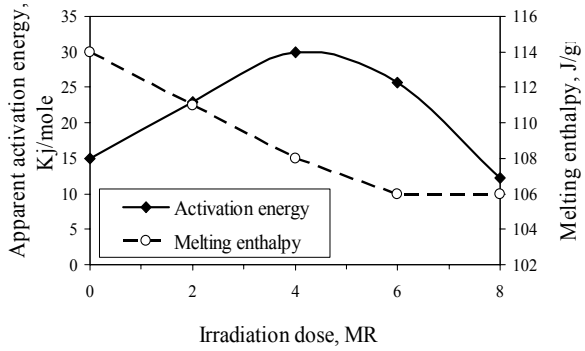

Figure 8. Apparent activation energy of the creep process and melting enthalpy of crosslinked oriented polyethylene as a unction of the irradiation dose.

Another proof of the disorientation of the amorphous phase can be obtained from an X-ray diffractogram (Figure 9). One can see that the crystalline phase both in the non-crosslinked sample and in an irradiated sample is almost unaffected, while the oriented amorphous halo has decreased after crosslinking.

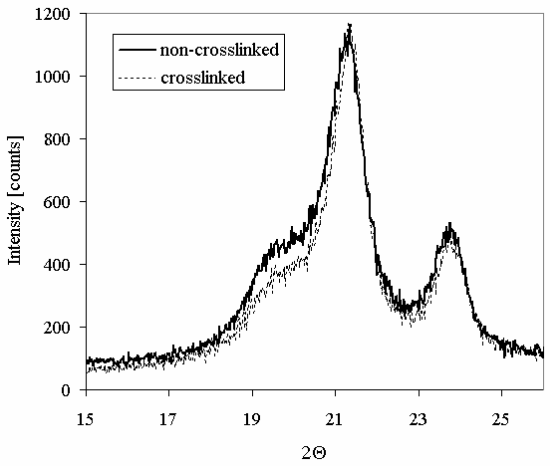

Figure 9. X-ray diffractogram of non-crosslinked and crosslinked oriented LLDPE films.

Conclusions

Draw ratio influences the creep behavior of oriented films only at elevated temperatures. For instance, at 75ºC, the sample loaded along the machine direction with the draw ratio of 1:5 shows a higher creep resistance in comparison with that loaded along the transverse direction with the draw ratio of 1:5.2.

Higher creep strain of films irradiated with relatively low doses was observed because of the partial disorientation of the molecules in the oriented amorphous phase. The heating of the film during the irradiation caused this disorientation. DSC and X-ray analysis demonstrated the disorientation in the amorphous phase. The irradiation of film with doses above 4MR caused a decrease in the creep strain.

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