Macromol. Symp. **2004**, *214,* 241-250

Technology and Stress Relaxation of Biaxially Oriented Polyolefin Shrink Films

Arthur Bobovitch,[1,2] *Yakov Unigovski,*[2] *Albert Jarashneli,*[2] *Emmanuel M. Gutman*[2]

[1] Syfan Saad (99) Ltd., Israel

[2] Dept. of Materials Engineering, Ben-Gurion University of the Negev, Israel

Summary: In the present study the influence of the heating rate on the stability of the double bubble technological process was investigated. It was shown that increasing the heating rate decreases the stability of the process and causes the lower elongation of the films produced. The morphological transformations of linear low density polyethylene (LLDPE) film were explained using X-ray and transmission electrom microscopy (TEM) methods. The stress relaxation behavior of co-extruded LLDPE/ethylene-vinyl-acetate (EVA) film was studied using the relaxation time spectrum approach. The influence of vinyl-acetate (VA) content in EVA copolymers on the relaxation time spectrum was observed.

Keywords: morphology; polyolefin film; relaxation time spectrum; stress relaxation

Introduction

Polyethylene (PE) films are widely used in the packaging industry. These films are extensively used in 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. The first films produced by "double-bubble" technology were made from PVC, but today, the trend is to leave PVC for polyolefins like polyethylene, polypropylene, ethylene-vinyl-acetate. The main reasons for this trend are: toxicity of the degradation products of PVC (mainly HCl) and lack of the approval for plasticisers, that are an important part of PVC based formulations, to be in contact with food.

The most widely used packaging technique associated with PE films is the shrinkage method. In this method the film wraps the packaged item, producing a bag. This bag is introduced into a

DOI: 10.1002/masy.200451017

heated tunnel. If the film is oriented it shrinks and wraps the item smoothly. There are several processes used for the production of these oriented films. One of the best known is biaxial orientation by the "double-bubble" process or tubular orientation process. In this process the primary extruded tube is quenched, reheated to a temperature below the melting point, and then oriented in both machine direction (MD) and transverse direction (TD) simultaneously. The advantage of this technique is the resulting balanced properties of the film in both directions[1]. Biaxially oriented films possess exceptional clarity, superior tensile properties, improved flexibility and toughness, improved barrier properties and the unique property of engineering shrinkability[2].

The production lines for the double bubble process have changed over the past fifteen years. The first production lines were equipped with water stream heating ovens, but recently IR ovens have been introduced. These ovens increase the heating capacity of the lines but cause problems with the stability of the second bubble. The present work describes a way in which the stability of the second bubble can be increased.

Despite its technological advantages, the double-bubble process has not been studied in depth from the viewpoint of morphological transformations taking place with the polymer during production. One of the goals of this study is to describe the transformations taking place within the polymer at different stages of the technological process. An understanding of this behavior should lead to improvement of technological parameters as well as to better materials choice during construction of film formulations.

During different production stages (slitting, folding etc.) the film is stressed, usually below the yield point. The behavior of the stressed film inside the rolls can be characterized by stress-relaxation. The film is under stress, it is deformed but cannot relax its deformation, which is constant. Hence, a study of the stress-relaxation process, which is usually characterized by relaxation time spectra, is of interest from both scientific and technological viewpoints.

Relaxation time spectra are of fundamental interest.

$$H(\tau) = -[dE(t)/d\ln t]_{t=\tau} \quad (1)$$

where H (τ) is the relaxation time spectrum and E(t) is the relaxation modulus. It is often used to discuss the molecular theory of materials and their morphology [3]. Some authors have investigated the relaxation time spectra of crosslinked materials. Fedors et al [4] investigated the stress-relaxation behavior of (EVA) cross-linked to different gel contents. They tried to explain long-term relaxation behavior using the stress-relaxation tests at different temperatures, but no conclusions about the influence of crosslinking density on morphology and relaxation behavior of the polymer were reached. Gotlib and co-authors [5-7] explained relaxation processes in crosslinked polymer networks. They investigated the influence of interchain motion and friction on the relaxation process. The models of segment relaxation were also studied. The morphology of crosslinked polymers was however not discussed. It is not clear what the influence is of varying degrees of crosslinking on the relaxation time spectrum.

In our previous work we investigated the morphology and stress relaxation of composite films with polypropylene in the outer layers and with LLDPE in the skin layer. The morphology and stress relaxation behavior of crosslinked LLDPE films was also studied [8-10]. In the present paper we will discuss the relaxation behavior of the film coextruded with LLDPE and EVA. These films are often used in paper products packaging (journals, envelopes, etc.) In these applications lower shrinkage forces are required in order not to destroy the packed item.

Experimental

In order to investigate the influence of the heating rate on the stretching process and on the properties of the final films a sheet from LLDPE (density 0.920g/cm^3 and melt flow index (MFI) 1) with average thickness of 375 microns was extruded. The films were produced by stretching the extruded sheets at a KARO IV laboratory stretcher produced by Brueckner, Germany. The films were stretched simultaneously in MD and TD. The orientation ratio was 1:5 in each direction. The different heating rates were applied. The mechanical properties of the films with the thickness of 15 microns, achieved after biaxial stretching, were tested according to ASTM D 1894 using a LLOYDS LRX tensile tester. Differential scanning calorimetry (DSC) at different heating rates was used to determine the influence of heating rate on polymer morphology.

X-ray diffraction was used to investigate the morphological transformation in LLDPE during the double bubble process. The X-ray diffraction patterns of the extruded sheet of 0.375 mm polyethylene were recorded at different temperatures with a Philips X-ray diffractometer (type PW-1130) using Co K_α radiation and a Fe – filter at the angular range 17 – 40°, scanning rate 2°/min, an operating voltage of 40 kV and a current of 30 mA. In order to carry out the X-ray experiments at elevated temperatures a special unit was designed (Figure 1).

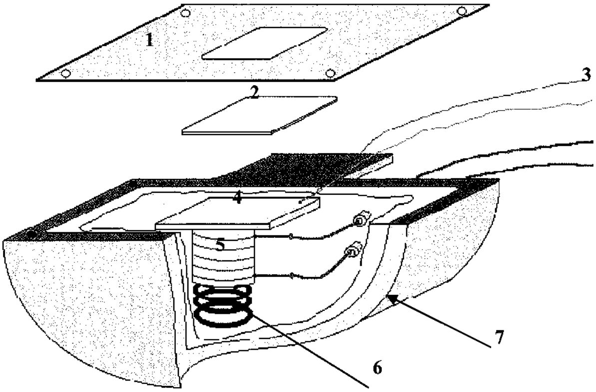

Figure 1. Specimen's holder specially designed to carry out X-ray experiments at elevated temperatures: 1 – cover, 2 – specimen, 3 – thermocouple, 4 – ceramic platform, 5-heater, 6 – spring, 7 – isolation.

Samples for transmission electron microscopy were first stained in RuO_4 for several days. Ultrathin sections (60 nm) were prepared at room temperature, using a diamond knife with a LEICA Ultramicrotome. TESLA BS 500 TEM was operated.

In order to investigate the stress-relaxation behavior a five-layer co-extruded crosslinked film was used. The structure of the film was LLDPE/EVA/LLDPE/EVA/LLDPE. The thickness of each EVA layer was 20 %, the thickness of LLDPE skin layers was 10 % and the thickness of LLDPE core was 40 %. The total film thickness was 15 microns. The EVA copolymers with VA contents

4 %, 12 % and 19 % were used.

For the stress relaxation measurements, samples with 6 mm width were carefully cut from the film. The experiments were carried out with Zwick 1405 tensile tester with a 10 N load cell.

Results and Discussion

Morphology transformations during the double-bubble process

The morphology transformation of any semicrystalline polymer during the double-bubble process can be presented by Figure 2.

After extrusion the melt is quenched with water, preventing spherulitic structure formation. Lamellae with different thicknesses can be observed (Figure 3). The quenched polymer is then reheated to below the melting point. The crystallinity of the polymer decreases. Figure 4 shows that, after heating to 80 °C, the polyethylene peak in the X-ray diffraction pattern decreases dramatically.

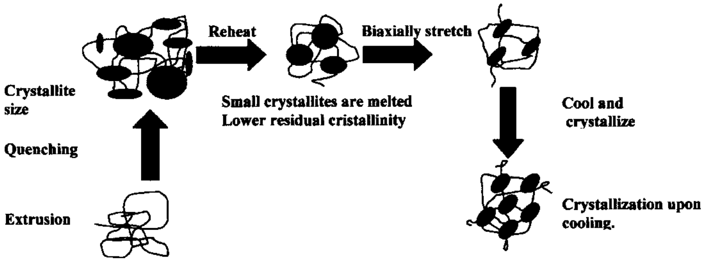

Figure 2. Morphology transformations in a semicrystalline polymer during the double-bubble process

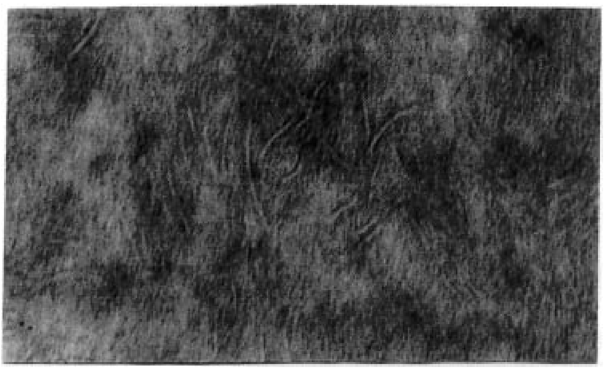

Figure 3. TEM photograph of the quenched LLDPE (X 120,000)

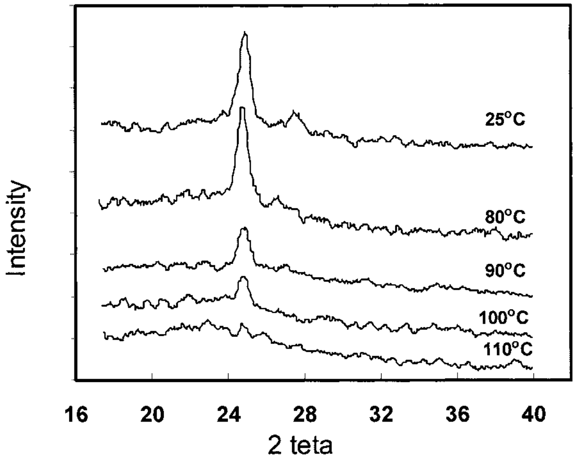

Figure 4. X-ray diffraction patterns of LLDPE as a function of temperature

After reheating to temperatures below the melting point the polymer is stretched in both MD and TD simultaneously, with the same orientation ratio. The lamellae structure transforms into fibrilious-like with the fibrila oriented at about 45 ° between MD and TD.

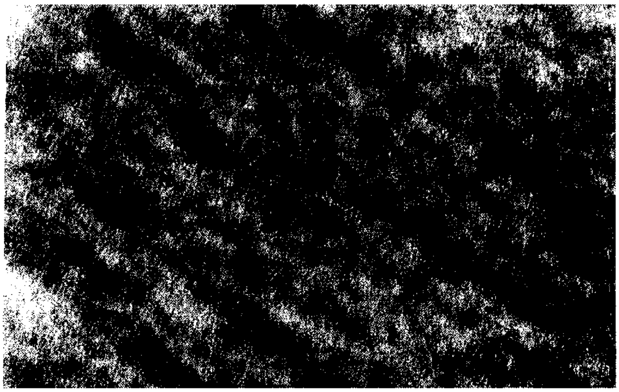

Figure 5. TEM photograph of biaxially oriented LLDPE film (X 120,000).

Influence of the heating rate on the process and on the film properties

As has been mentioned, the first production lines for the double-bubble process were equipped with a hot water steam-based oven. As technology developed, these ovens were later substituted by IR-based ovens. The main reason for this was to provide quicker heating and increased output. The heating rate in an IR-oven is about three times higher than the heating rate in a water/steam oven. It was however observed that with the IR-oven the bubble stability was decreased and the film became less elastic. In order to stretch LLDPE biaxially the polymer has to be heated to a specific orientation temperature. DSC measurements showed that with an increasing heating rate the melting curve of the polymer is sharper [11]. This means that the window of orientation temperatures becomes narrower with increasing heating rate. Indeed, when the heating rate is high, a small temperature change will cause significant change in the polymer crystallinity.

In order to understand the influence of the heating rate on the stretchability of LLDPE, ten samples were stretched biaxially at different heating rates and the number of broken samples was calculated. When the heating rate reached 12 °C/min the number of unsuccesfull tests was more than 60 %. Any further increase in the heating rate resulted in it being impossible for LLDPE to be stretched; 100 % of samples were broken after stretching.

The influence of the heating rate on mechanical properties of a LLDPE film is shown in Figure 6. With an increase in heating rate the ultimate tensile stress increases and elongation decreases dramatically.

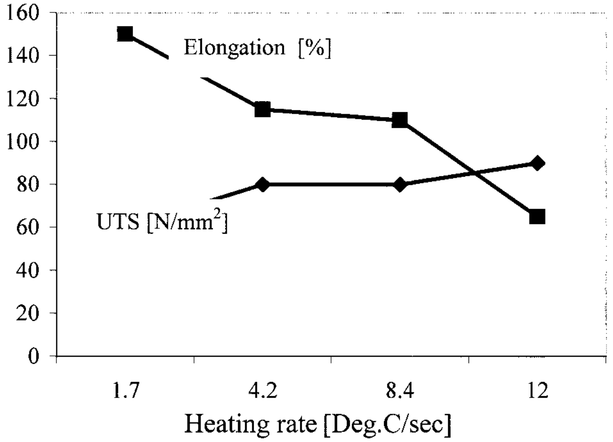

Figure 6. An influence of heating rate on ultimate tensile stress (UTS) and elongation of LLDPE-film

Stress-relaxation of co-extruded LLDPE/EVA film

Relaxation time spectra of the LLDPE/EVA co-extruded films, containing EVA with different VA content, are shown in Figure 7.

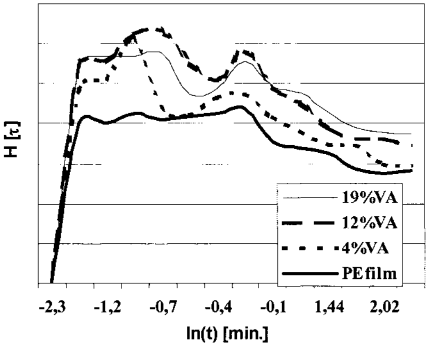

Figure 7. Relaxation time spectra of LLDPE/EVA co-extruded films

Two main peaks can be observed in each spectrum. At *ln(t)* = – 0.3 the peak corresponds to the crystalline phase of the polymers and the peak at about *ln(t)* ≈ – 0.8 corresponds to the crosslinked amoprphous phase[9]. One can see that the difference between the relaxation of the amorphous and of crystalline phases clearer when EVA copolymers are included in the formulation. Higher peak intensity in the relaxation time spectra of co-extruded LLDPE/EVA, in comparison with the spectra of LLDPE film, means that the observed decrease in stress was more significant in the co-extruded film than in the LLDPE film. Hence, the remaining stresses in co-extruded film will be lower that in LLDPE film.

Conclusions

The morphology transformation of LLDPE during the double-bubble process was investigated and explained. It was shown that the morphology of the oriented film is fibril-like, with the fibril orientation at 45 degrees between MD and TD. It was also shown that the heating rate influences the stability of biaxial orientation as well as the properties of the film; the higher the heating rate the worse the process stability and the lower the elongation of the films produced.

The study of relaxation time spectra of crosslinked LLDPE film and crosslinked coextruded LLDPE/EVA film shows two main peaks, corresponding to crystalline and to crosslinked amorphous phases. The difference in relaxation of these two phases is clearer in coextruded films. Practically, that means that the coextruded LLDPE/EVA films have to be suspended between different technological stages (extrusion, slitting, centerfolding) for the same time periods as LLDPE film in order to relax internal stresses. The observed relaxation behavior of coextruded LLDPE/EVA film (higher peaks on relaxation time spectra) can provide the worse performance of this film during its winding (wrinkling during suspension time). It is for this reason that it is recommended that the tension during winding of this co-extruded film be decreased.

[1] K. R. Osborn, K. R. Jenkins, in: *"Plastic Films"*, Technomic Publishing Co., Lancaster, PN 1992.
[2] C. J. Benning, in: *"Plastic Films For Packaging"*, Technomic Publishing Company, Lancaster, PN 1983.
[3] C. Friedrich, H. Braun, J. Weese, *Polym. Eng. Sci.* **1995**, *35*, 1661.
[4] R. F. Fedors, S. Y. Chung, S. D. Hong, *J. Appl. Polym. Sci.* **1985**, *30*, 2551.
[5] Yu Ya Gotlib, *Pure & Appl. Chem.* **1981**, *53*, 1531.
[6] Yu Gotlib, G. Golovachev, *Journal of Non-Crystalline Solids* **1994**, *172*, 850.
[7] A. A. Gurtovenko, Yu Ya Gotlib, *Macromolecules* **1998**, *31*, 5756.
[8] A. Bobovitch, E. M. Gutman, S. Henning, G. H. Michler, *J. Applied Polymer Sci.* (accepted).
[9] A. Bobovitch, E. M. Gutman, S. Henning, G. H. Michler, *Materials Letters* **2003**, *57/16-17*, 2579.
[10] A. Bobovitch, E. M. Gutman, S. Henning, G. H. Michler, Y. Nir, *J. of Plastic Film & Sheeting* (in press).
[11] V. B. F. Mathot, in: *"Calorimetry and Thermal Analysis of Polymers"*, Hanser Publisher, Munich, Vienna, New York 1994.