

Morphology and Stress Relaxation in Oriented Polyolefin Shrink Films

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Received 27 August 2002; accepted 4 May 2003

ABSTRACT: Morphology and stress relaxation of oriented polyolefin films has been studied. The influence of orientation on morphology of the films has been investigated using X-ray, DSC, and TEM. The relaxation time spectrum of oriented films has been investigated. It was shown that relaxation time spectrum of composite film can be pre-

dicted if one knows the relaxation time spectrum of each component in the film. An influence of irradiation on relaxation behavior of polyethylene film was shown as well. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3424–3429, 2003

Key words: relaxation time; spectrum; polymer films

INTRODUCTION

Packaging began when early man needed some way of carrying items from one place to another. Large solid objects could be carried unpacked, but liquids and powders require some form of container. Thus began the first and most fundamental function of the packaging: containment of the product. Because some of these packaged items were not consumed all at once, some way of dispersing part of the contents and preserving the rest for later use was needed, leading to the second and third basic package functions: dispersing and protection.

The other major package functions appeared when commercial transactions began. The sale of a product was facilitated by the use of package to standardize the amount of product sold. If several identical items in a single transaction, packaging provided a way of assembling these products. In modern marketing, display and communication have become highly important function.¹

Polyethylene film is a widely used product in 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 total consumption of polyethylene film in the packaging industry of USA was 5800 million pounds in 1989.¹ In the last years there is a trend to substitute some packaging films, for example, elasticized PVC

films, by polyethylene ones. This fact, in addition to the growing market of polyolefin films, makes the polyethylene films the most important product in the worldwide packaging industry.

The mostly used packaging technique when talking about the films is the shrinkage method. In this method the film wraps the packaged item, producing the bag. This bag is introduced into the tunnel with the high temperature. If the film is oriented it shrinks and wraps the item smoothly. There are several processes 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. Although stretching occurs simultaneously in the MD and TD, the forces for each are controlled separately. The MD force is applied by the differential speed between the two sets of nip rolls that contain the bubble. The TD force is applied by the air pressure introduced into the tube. To minimize thickness variations, cooling air is often used on the outside of the inflating tube to shift the stretching to the thicker sections of the tube.

The advantage of this technique is the homogeneous 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

Molecular orientation during stretching takes place in the following manner: below their melting point (or glass transition temperature in the case of amorphous

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polymers) polymer chains are rigid. At higher temperatures they become more flexible and are able to unfold as stress is applied. If a mass of randomly coiled and entangled chains is at temperature high enough when stress is applied, as in biaxially stretching, the polymer chains disentangle, unfold, and straighten, and slip past their nearest neighbor.

There are three rheological components to this process: first, the instantaneous elastic deformation caused by bond deformation or bond stretching, which is completely recoverable when the stress is released; second, the molecular alignment deformation caused by uncoiling, which results in a more linear molecular arrangement parallel to the surface and which is frozen into the structure when the material is cooled; and third, the unrecoverable viscous flow caused by molecules sliding past one another. The secondary, is the major component of the stretching process.²

The investigation of the shrinkage as a function of the materials and working conditions should be very important for the better understanding of the process, for the right choice of working conditions and for the development of the new films.

The thermal shrinkage of different films has been investigated³⁻⁷ to understand the behavior of different polymers in different conditions (shrinkage temperature, time). The shrinkage is usually measured by placing the specimens in an oil or water bath at high temperatures. On the one hand, thermomechanical analysis (TMA) is a very popular method to obtain the thermal shrinkage under a constant heating rate.

The stress relaxation process is important when talking about oriented films. The film after production is stressed, and the stress relaxation that takes place can influence morphology and the properties. Because of the sensitivity of the film to the temperature the dependence of stress relaxation on the temperature is of the special interest. It can be important talking about the right condition of film storage before using. The most important characteristic of stress relaxation is relaxation time spectrum.⁸ It is often used when discussing the molecular theory of materials and their morphology.⁹ The molecular weight dependence of the relaxation time spectrum has been investigated by Jackson et al.¹⁰ According to them, the high molecular weight causes the increasing entanglement, and this changes the relaxation time spectra.

Attalla et al.¹¹ investigated the influence of morphology on stress-relaxation of polypropylene. They showed that the relaxation behavior of isotactic polypropylene in the range of temperatures of -20 and 40°C is strongly influenced both by crystallinity and morphology. The increase in crystallinity and/or size of crystalline aggregates increases the value of relaxation modulus and affects both the peak location and the shape of the spectrum of relaxation times.

Some authors investigated the relaxation time spectra in crosslinked materials. Fedors et al.¹² investigated stress-relaxation behavior of ethylene-vinyl-acetate (EVA) crosslinked to different gel content. 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 have been done. Edward and O'Donnell¹³ introduced the model for stress-relaxation in entangled polymer melts. In terms of this model the tightening of entanglements appears to be important in lightly crosslinked polymers or in polymers in which the intermolecular interactions are heterogeneous due to copolymerization or limited crystallinity, but not in amorphous homopolymers in which the entanglements are expected to be more homogeneous.

Gotlib and coauthors¹⁴⁻¹⁶ explained relaxation processes in crosslinked polymer networks. They investigated the influence of interchain motion and friction on relaxation process. The models of segment relaxation have been studied as well. However, there is no relation with the morphology of crosslinked polymers in this work. It is not clear what the influence is of different crosslinking degree on relaxation time spectrum.

The stress-relaxation and creep processes have been studied in a number of oriented structures. For example, Chow and Van Laeken¹⁷ and Hawthorne¹⁸ explained stress relaxation in oriented poly(ethylene terephthalate) (PET) films. They studied relatively thick films (76 and 33 μm , respectively), which have been oriented at the temperature above glass transition temperature. Shimosaki and Sargent¹⁹ investigated the relaxation behavior of uniaxially hot drawn polypropylene. They investigated the temperature influence of relaxation process. So there are still no data about the stress relaxation process and relaxation time spectrum in highly oriented semicrystalline polyethylene films. The influence of the structure of composite films on relaxation time spectrum has not been studied as well.

The main goal of this work is to investigate the morphology and stress-relaxation behavior of biaxially oriented films produced by double bubble process.

EXPERIMENTAL TECHNIQUES

Materials

In the present study a number of different polyolefin films were investigated to understand stress-relaxation mechanisms. A number of different films have been investigated: monolayer linear low-density polyethylene (LLDPE) film produced from polyethylene with melt flow index (MFI) 1, the same film

crosslinked with β -irradiation, monolayer film produced from polypropylene random copolymer (CPP) with MFI 2, composite multilayer film with the CPP skin layers and LLDPE core layer. The average thickness of the films investigated was 15 μm .

Mechanical properties

Mechanical properties of the different films were tested with a Lloyds LRX testing machine according to the ASTM-1984 method.

The 6-mm width specimens for the stress-relaxation were precisely cut from the biaxially oriented films produced by double-bubble technology. Sample thickness was 15 μm .

Stress-relaxation behavior was studied with Zwick 1405 tensile tester with the special program for stress-relaxation and creep tests. A 10-N load cell was used in this study.

The stress-relaxation was investigated at room temperature.

Morphology investigations

X-ray diffraction and DSC (Differential Scanning Calorimetry) were used for the characterization of morphological features of polymer films as a result of orientation. The specimens from these tests will be prepared as from the films as from the polymers before orientation to investigate an influence of orientation on the morphology of the polymers.

Samples for transmission electron microscopy were stained in RuO_4 for several days. An ultrathin section (80 nm) was prepared at a room temperature using a diamond knife with a LEICA Ultramicrotome. For morphology investigations, the stained sections were transferred to a TESLA BS 500 TEM operated at 90 kV accelerating voltage.



Figure 1 Morphology of the primary extruded PE tube before orientation, showing thin lamellae with no spherulitic superstructure ($\times 66,000$).

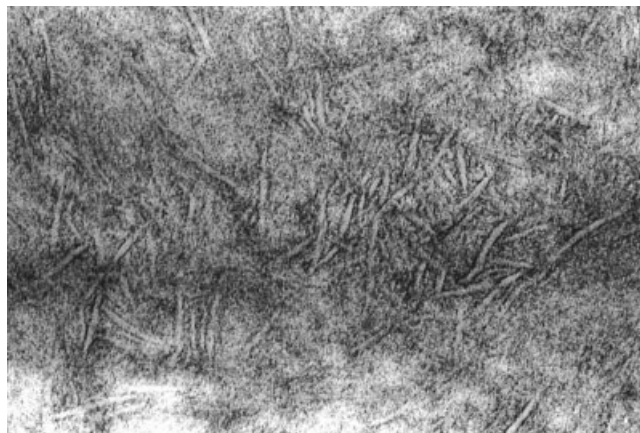


Figure 2 The morphology of the PE core in the primary extruded PP/PE/PP tube, showing thicker lamellae than in Figure 1 ($\times 66,000$).

RESULTS

Electron microscopy results

The TEM micrograph of the LLDPE tube before orientation is shown on Figure 1, and the morphology of the PE in the core of PP/PE/PP extruded tube is shown on Figure 2.

Figure 3 shows the lamellar structure of the biaxially oriented PE film. One can see the specimen topography, which is similar to machine direction (MD).

X-ray and DSC investigations

Figure 4 demonstrates the X-ray data obtained by us from two samples.

The first one is polyethylene before orientation, the second one is an oriented film. One can see the differences in the X-ray diffraction spectra of these samples. There is a growth of the peak corresponding to amor-

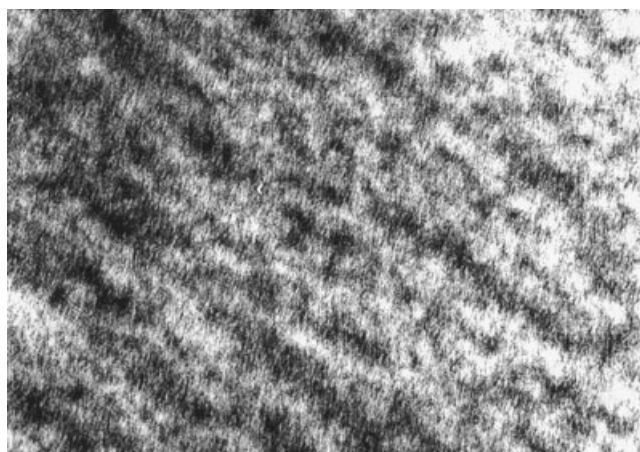


Figure 3 The lamellar structure of biaxially oriented PE film ($\times 66,000$).

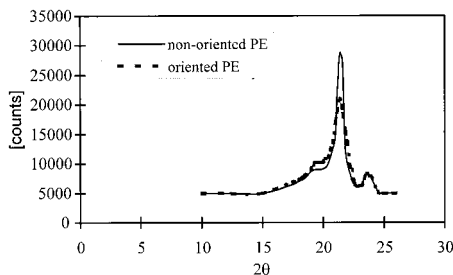


Figure 4 X-ray spectra of oriented and nonoriented PE.

phous scattering (19.5°) and a lowering and widening of the peak (21.4°) corresponding to the reflection from the [110] plane of the crystalline lattice.²⁰

DSC results obtained from the oriented and nonoriented films are shown on Figure 5. One can see a decrease of the polyethylene melting temperature after orientation. The increasing of the melting enthalpy was observed as well.

Mechanical properties and stress relaxation

Tensile tests carried out in both machine and transverse directions demonstrated that the mechanical properties of the oriented film are slightly differ in these directions. The values of ultimate tensile stress in MD and TD are of 110 N/mm² and 115 N/mm², respectively, and the strain values in these directions are of 135 and 130%, respectively. Nevertheless, the difference in stress–relaxation curves measured in MD and TD is very clear (Fig. 6). Relaxation time spectrum has been calculated according to eq. (1).

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

where $H(\tau)$ is the relaxation time spectrum, E is Young’s modulus, t is time.

Figure 7(a)–(c) shows the relaxation spectrum $H(\tau)$ of different polyolefin films in both MD and TD.

The spectra for samples tested in TD show higher relaxation intensity at short times. This fact can be corresponded to the difference in polymer structure²¹

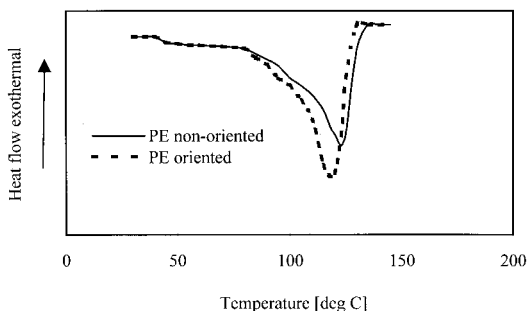


Figure 5 DSC of oriented and nonoriented PE.

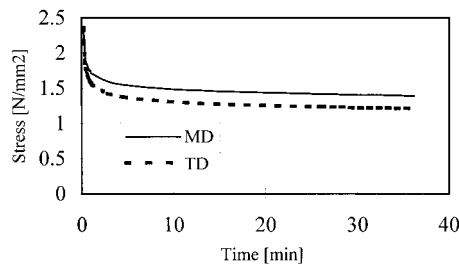


Figure 6 Stress–relaxation curves of the oriented polyethylene film (MD—machine direction, TD—transverse direction).

in two directions caused by different deformations. The difference in deformations is a result of the slightly different orientation ratios in MD and TD.

We assumed that the relaxation time spectrum of the laminate composite film can be predicted by measuring the spectrum of each component and the “rule of mixture for composites” can be used.

$$H_c(\tau) = mH_1(\tau) + (1 - m)H_2(\tau) \tag{2}$$

where, $H_c(\tau)$ is the relaxation time spectrum of composite material, $H_1(\tau)$ and $H_2(\tau)$ are the relaxation time spectra of the components 1 and 2, m is the fraction of component 1.

So, for the composite film with 10% of CPP in each skin layer and 80% of LLDPE in the core layer, eq. (2) can be written as

$$H_c(\tau) = 0.2H_{CPP}(\tau) + 0.8H_{PE}(\tau) \tag{3}$$

Figure 8 shows predicted and measured relaxation time spectra of the composite film. One can see good agreement between measured and calculated relaxation time spectra.

The stress–relaxation behavior of crosslinked polyethylene film has been investigated as well. The films were crosslinked using electron beam bombardment. The different doses were applied to achieve different amounts of crosslinking. The results of stress relaxation tests are shown in Figure 9.

DISCUSSION

Morphology development in oriented films

Morphology development in the oriented film can be understood from TEM microphotographs. One can see no spherulitic structure in the primary extruded PE tube (Fig. 1). This can be explained by the high cooling rate caused by the quenching of the extruded tube. The lamellae in the core of the three-layer tube (Fig. 2) are somewhat thicker. This occurs because of the lower cooling rate on the internal layer. The orienta-

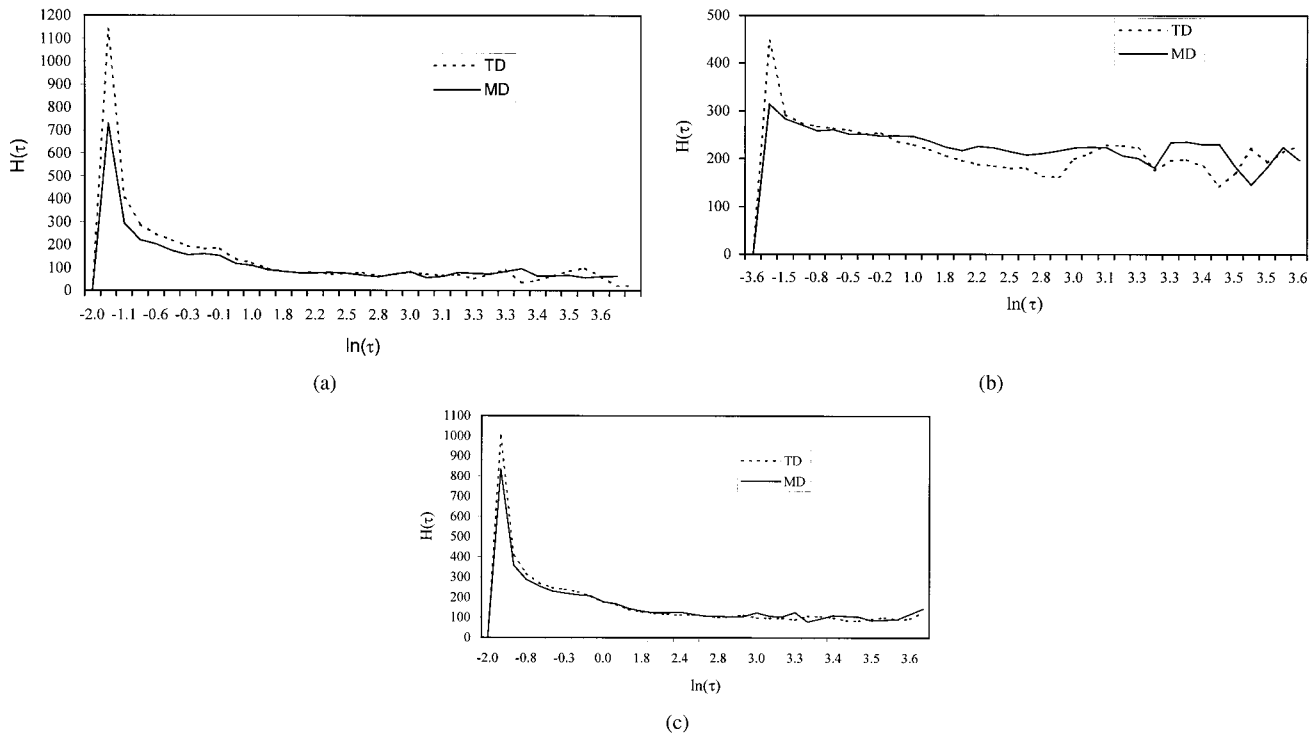


Figure 7 Relaxation time spectra of different films: (a) PE film; (b) CPP film; (c) composite CPP/PE/PP film.

tion process influences the lamellar structure of polyethylene (Fig. 3). The lamellae are oriented in the same direction. Lamellar oriented in the direction of about 50 degrees to MD appear as well.

X-ray results provide the possibility to estimate the differences in crystallite sizes t (perpendicular to the hkl plane) using the following equation used in investigation of semicrystalline PET:

$$t = \frac{0.89\lambda}{B\cos\theta_{hkl}} \quad (4)$$

where B is a half-width of [hkl] scan, λ is the wavelength of X-rays, and θ_{hkl} is the Bragg angle for this plane. Taking into account the obtained fact that the half-width of the peak corresponding to the [110]

plane increased by a factor of 2 after orientation, one can conclude that the crystallite size perpendicular to the [110] plane has been decreased by a factor of 2. In addition, one can assume that orientation leads to a more stressed crystalline structure.

The growth of the "amorphous" peak shows orientation in the amorphous phase. This orientation can cause an additional ordering. In fact, the DSC results (Fig. 5) show the growth in degree of crystallinity from 32% before orientation to 39% after orientation. This phenomenon can be explained by additional apparent crystallinity caused by orientation in the amorphous phase. The lowering of the melting point from 123°C before orientation to 118.5°C after orientation can be explained by the stresses within the crystals and by the decrease of the lamellar thickness after orientation.

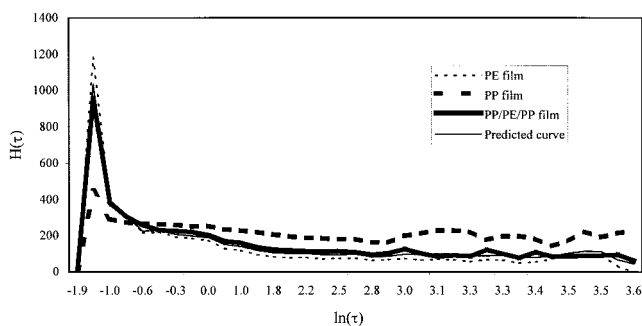


Figure 8 Measured and predicted relaxation time spectra.

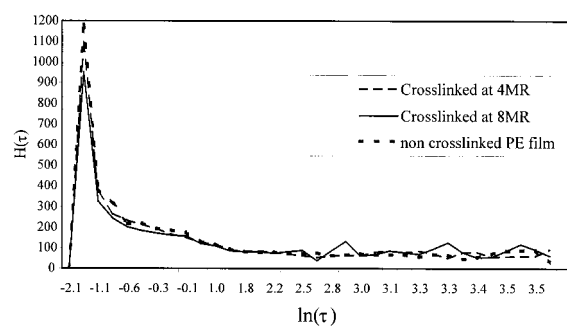


Figure 9 Relaxation time spectra of crosslinked films.

Stress relaxation

It was shown that, despite the slightly different mechanical properties, the stress-relaxation experiment provides the possibility to detect the differences in orientation in both directions clearly. The relaxation intensity of the material at short times is differing in MD and TD. So, even if the deformations induced into the material during production are only slightly different in different directions, the stress-relaxation technique is the very sensitive tool to detect these differences. Therefore, one can conclude that stress-relaxation technique is more sensitive than usual tensile tests when it is necessary to detect the differences in the properties as a result of slightly different processing conditions. Relaxation intensity of the polyethylene film is higher than the relaxation intensity of CPP film. This can be corresponded to the higher amount of amorphous phase in LLDPE and by higher mobility of the molecules in amorphous phase.

There is a good agreement between predicted and measured values of the stress-relaxation of the composite film. The role of mixtures calculation allows to predict the relaxation behavior of the composite film when the behavior of the polymers in skin and core layers is known; however, there is still a question if this phenomenon depends on adhesion quality between the layers.

One can see the appearance of longer relaxation times in the spectrum of highly crosslinked polyethylene. The phenomenon can be explained by lower mobility of the molecules or molecular segments in amorphous phase with increasing of crosslinking degree. The study of this phenomenon will be continued at elevated temperatures in further investigations.

CONCLUSIONS

1. Orientation influences both crystalline and amorphous phases. This was confirmed by TEM, X-ray and DSC results.
2. An additional ordering of the amorphous phase as a result of orientation was proved by growth

of "amorphous" peak in X-ray diffraction and by increasing of the crystallinity degree calculated from DSC analysis.

3. The stress-relaxation technique is more sensitive tool than usual tensile test.
4. It has been shown that the relaxation behavior of the laminate composite film can be predicted if one knows the relaxation behavior of the components.
5. The study of the crosslinked films showed the appearance of longer relaxation times in the spectrum that can be explained by lower mobility of the crosslinked molecules.

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