COMPARISON OF THE ELASTOMERIC PROPERTIES OF PROPYLENE BASED ELASTOMERS (PBE’S) AND ETHYLENE-OCTENE (E/O) ELASTOMERS

P. DIAS¹, A. HILTNER¹, E. BAER¹, P. ANSEMS², AND S. CHUM²

¹Center for Applied Polymer Research (CAPRI) and Department of Macromolecular Science and Engineering
Case Western Reserve University, Cleveland, OH 44106
²Polyolefins and Elastomers R&D
The Dow Chemical Company
Freeport, TX 77541

Abstract

The time-dependent elastic properties of a new propylene based elastomer (PBE) product family made with propylene-ethylene copolymers are investigated. Although these materials show some degree of permanent set upon initial tensile deformation, the materials created as a result of a tensile “conditioning” process exhibit almost complete instantaneous strain recovery after a long period of stress relaxation. The stress relaxation and subsequent strain recovery behavior of the new PBE’s are compared to that of elastomeric metallocene propylene-ethylene and ethylene-octene copolymers [3].

Introduction

The Dow Chemical Company recently developed a new catalyst which allows copolymerization of propylene with various alpha-olefin comonomers over a broad range of compositions in isotactic fashion and with high molecular weight. These copolymers exhibit relatively narrow molecular weight distribution and unique micro-molecular structures. These new copolymers showed a continuum of properties. Based on comonomer content, the propylene-ethylene copolymers were classified into 4 types to reflect the structure-property relationships. The lowest crystallinity Type I P/E with more than 15 mole % ethylene, corresponding to less than 18 wt % crystallinity, exhibited elastomeric properties with uniform deformation and high recovery from large strains. [1]

The elastomeric behavior of Type I P/E is novel. Elastomers based on copolymers of ethylene and propylene are usually ethylene rich, for example EP and EPDM. [2] The scope of this paper is to explore in detail the time dependent elastic properties of Type I P/E and to compare it with elastomeric ethylene-octene copolymer and metallocene P/E and

Experimental

The three resins used in this study were supplied by The Dow Chemical Company. The new PBE copolymer contained 19.4 mole % ethylene with 13 wt. % crystallinity calculated from density. It had a weight average molecular weight of 2.6 x 10⁵ g/mol. This material was designated P/E19.4. The metallocene P/E contained mole % ethylene with 13 wt. % crystallinity, had an average molecular weight of 1x10⁵ g/mol, and was designated mP/E-B. The ethylene-octene copolymer contained mole % ethylene with 12 wt. % crystallinity, had an average molecular weight of 1x10⁵ g/mol, and was designated EO86.

Films 0.5 mm thick were compression molded from pellets into plaques as described previously [1]. The plaques were aged for 7 to 12 days at ambient temperature. The density was measured according to ASTM D1505-85 using small pieces cut from stretched microtensile specimens. An isopropanol-water density gradient column with a range of 0.8-1.0 g cm⁻³ was used. The reported density is the average from at least 3 specimens.

A: Conditioning

Microtensile specimens were cut from the plaques according to ASTM 1708. The specimens were cyclically loaded and unloaded in uniaxial tension to 600% strain (133.8 mm) with an Instron 1123 at a crosshead speed of 22.3 mm min⁻¹ (100 % min⁻¹ for the as-cut microtensile specimen). The initial cycle is labeled “conditioning cycle”. Following the conditioning cycle, samples were removed from the Instron and placed aside for 24 hours. After this 24 hour period two different types of experiments were performed on the conditioned polymers: a cyclic experiment and a stress relaxation-recovery experiment.

B: Cyclic Behavior

After 24 hours following the conditioning cycle, specimens were subsequently re-stretched to the same
crosshead displacement with the same crosshead speed as the conditioning cycle. This is referred to as the “first cycle” of the conditioned material.

C: Stress Relaxation-Strain Recovery

Samples were conditioned according to the procedure described above in section A and set aside for 24 hours. Rectangular specimens were cut from the “conditioned” tensile specimens and reloaded into the Instron. The sample length and stretching speed were varied to obtain a stretching time of about 1s. The maximum speed used was about 1000 mm/min. Reference lines were drawn on the center of the specimens to obtain the draw ratio, which is defined as the ratio of the length after loading to the initial length. The deformation was recorded with a video camera and telescopic lens attachment.

The stress relaxation response was measured in uniaxial extension. The stress was recorded continuously beginning approximately 10s after stretching in order to avoid initial instabilities. After the specimen relaxed for a period of 1 hour, the lower grip was opened and the sample was released. Strain recovery was recorded on videotape during grip release and for period of 10 min after release. [5] Measurements were made by computer using BioScan Optimas v2.3 image analysis software starting 1s after release.

Results and Discussion

Cyclic Behavior

The condition cycles and the effect of conditioning on the first cycle behavior of P/E19.4, mP/E-B and EO86 is shown in Figure 1. The samples were conditioned to a crosshead displacement of 133.8 mm, or 600%. The initial loading and unloading cycle is designated as the “conditioning cycle”, and the subsequent cycle is the “first cycle”. [3] During the first cycle, the specimens are taken to the same crosshead displacement as the conditioning cycle. Specimen gage length changes as a result of conditioning. Therefore, the strain during the first cycle is less than during conditioning. As a result of the relatively lower recovery in mP/E-B during the conditioning cycle it stretches out to a lower strain than the other elastomers during the first cycle.

There was a considerable change in the stress response between the conditioning cycle and the first cycle in all the three elastomers. Conditioned P/E19.4 exhibits the greatest amount of strain hardening, and has a stress response that is much greater than that of EO86 and mP/E-B. The structural changes resulting from the conditioning cycle are reported in a previous paper. [3]

Stress Relaxation: Conditioned Materials

The normalized stress relaxation curves for conditioned elastomers at different applied strains are shown in Figures 2a and 2b. The stress relaxation of EO86 is logarithmic with respect to time, whereas the rate of stress relaxation curves of the propylene copolymers decreases with time. The rates of relaxation of the copolymers are compared at draw ratios of \( \lambda \approx 1.30 \) in Figure 2a and \( \lambda \approx 1.70 \) in Figures 2b. The rate of stress relaxation was lowest in P/E19.4 at both low and high draw ratios.

The effect applied deformation on the time dependent rubber modulus of conditioned P/E19.4 is shown on an isochronal plot in Figure 3a. Values for stress were extracted from stress relaxation curves at various levels of applied deformation at 10s, 100s, and 1000s. The modulus was defined by the following equation resulting from the simple theory of rubber elasticity:

\[
E(\lambda) = \frac{3\sigma}{\lambda - \lambda^{-2}}
\]

where \( \sigma \) is the tensile stress and \( \lambda \) is the applied draw ratio during relaxation [4]. The modulus of P/E19.4 and mP/E-B did not depend on applied deformation if the draw ratio was about 1.8 or less, and the polymers exhibited linear stress relaxation. The modulus of conditioned EO86 was independent of applied deformation up to a draw ratio of about 1.4.

Strain Recovery after Stress Relaxation: Conditioned Materials

A comparison of the strain recovery in P/E19.4 and mP/E-B is shown in Figure 4a. P/E19.4 is compared to EO86 in Figure 4b.

Percent strain recovery is defined by:

\[
%\text{Recovery} = 100 \left[ 1 - \frac{\lambda_t}{\lambda_o} \right] = 100 \left[ 1 - \frac{l - l_o}{l_i - l_o} \right]
\]

where \( \lambda_t \) is the draw ratio at a given time during recovery and \( \lambda_o \) is the draw ratio during stress relaxation. [5,6,7]

The recovery after 1s was defined as instantaneous recovery. The recovery after 10 min was defined as delayed recovery.

After a period of 1 hour of stress relaxation, instantaneous strain recovery for P/E19.4 was about 95%, and was independent of the level of applied deformation. In mP/E-B, the instantaneous recovery was about 85%. In EO86 the instantaneous recovery was about 85%.
Conclusions

The cyclic tensile behavior of the three elastomers is considerably changed after the conditioning process. The first cycle behavior of conditioned P/E19.4 is marked by much greater stress response than mP/E-B and EO86. Furthermore, it has less permanent deformation from the conditioning cycle than metalloocene P/E of comparable density and crystallinity.

The instantaneous strain recovery of conditioned P/E19.4 after one hour of stress relaxation P/E19.4 was almost complete, and significantly greater than in mP/E-B and EO86.

Acknowledgment

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References

Figure 1: Conditioning curves (dashed lines) and first cycles (solid lines) of P/E19.4, mP/E-B, and EO86

Figure 1

Conditioning curves (dashed lines) and first cycles (solid lines) of P/E19.4, mP/E-B, and EO86 at T= Ambient Conditioning Strain = 600% 24 hours after conditioning Conditioned Samples

Figure 2:

Figure 2a

Normalized stress relaxation of P/E19.4, mP/E-B, and EO86 at T= Ambient Conditioning Strain = 600% 24 hours after conditioning Conditioned Samples

Figure 2b

Figure 3:

Isochronal plots for P/E19.4, mP/E-B, and EO86 at a: $\lambda = 1.30$ and b: $\lambda = 1.70-1.80$

Figure 3a

Figure 3b

Figure 3c
Figure 4: Strain recovery after one hour of stress relaxation

a: Strain recovery of P/E19.4 (circles) and mP/E-B (squares) at various draw ratios

b: Strain recovery of P/E19.4 (circles) and EO86 (squares) at various draw ratios