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Strain Hardening in Uniaxial Elongation vs. Temperature for Random Copolymer Melts with High Comonomer Content

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Abstract. Two metallocene-catalyzed random copolymers with a polyethylene backbone and octene comonomer content of 20 wt% and 38 wt% were tested in uniaxial extensional flow at different temperatures. Sparse LCB was detected in both melts with these measurements. The strain hardening parameter at the lowest strain rate was found to be greater for EO3, the material with the smaller degree of LCB. The temperature dependence of the strain hardening parameter was also greater for EO3 than for EO1. These trends may be related to the two model parameters used by Wagner and coworkers representing branch content and the maximum tube diameter contraction.

Keywords: random copolymers, strain hardening, temperature dependence, uniaxial extension.
PACS: 61.25.hk

INTRODUCTION

The extent of sparse long chain branching in metallocene-catalyzed random ethylene-α-olefin copolymers is known to go down with increasing comonomer content[1] and become progressively harder to detect. In general, even small levels of long chain branching lead to strain hardening in extensional flow; but this may be associated with a variety of other features such as a broad molecular weight distribution or a high molecular weight tail. Various characterization techniques have been proposed to detect small levels of long chain branching in copolymers with less than 20 wt% of comonomer[2-6]. The object of this paper is to present experimental results on the transient uniaxial extensional viscosity for a metallocene-catalyzed random ethylene-octene copolymer melt with much higher comonomer content -- 38 wt% octene, for which the zero shear viscosity and the vanGurp-Palmen plot[7] from dynamic moduli do not indicate long chain branching and also the molecular weight distribution is not broad. In addition, the temperature dependence of the strain hardening parameter has been compared for two different random copolymers.

EXPERIMENTAL

Materials. Two different metallocene-catalyzed ethylene-octene random copolymers were selected in this study. Engage 8480 (EO1) contains 20 wt% octene and melts at 98°C while Engage 8100 (EO3) contains 38 wt% octene and melts at 48°C. Detailed characterization of these materials has been reported[8]; in particular, sparse LCB was detected in EO1 but not in EO3 from vanGurp-Palmen plots.

Procedures. The transient extensional flow tests were performed on the Rheometrics Melt Elongational (RME) Rheometer at two different temperatures, 120°C and 150°C and up to Hencky strains of 3 over strain rates of 0.01 s^{-1} to 1 s^{-1}. All experiments were performed under a nitrogen blanket. Spacer pins were used to avoid spurious observations of strain hardening, reduce the noise observed at the short times, and also prevent the material from deforming before the test, or prematurely squeezing the material onto the air table. Experimental procedures were

verified with tests on a linear polypropylene known not to strain harden at 180°C. No strain hardening was observed for this polymer melt, which is consistent with published results[9]. It was observed for several of the tests, that the extensional viscosity plot would not fall atop the $3\eta_0^+$ curve. A corrected strain hardening parameter was calculated after dividing the observed strain hardening parameter by a base value or vertical offset between the extensional viscosity data before the strain hardening began and the $3\eta_0^+$ curve.

RESULTS AND DISCUSSION

Transient extensional viscosity curves of EO1 and EO3 have been presented in Figure 1 (a,b). The random copolymer melt with 38 wt% comonomer, EO3 showed distinct strain hardening at both 120°C and 150°C. The strain hardening ratio (with respect to $3\eta_0^+$) was greater at 120°C and also declined more gradually with strain rate at this temperature. The strain hardening parameters for both materials are presented in Figure 2 (a,b). The maximum value of strain hardening ratio was 3.7 at 120°C compared to 2.8 at 150°C. These values were greater than the strain
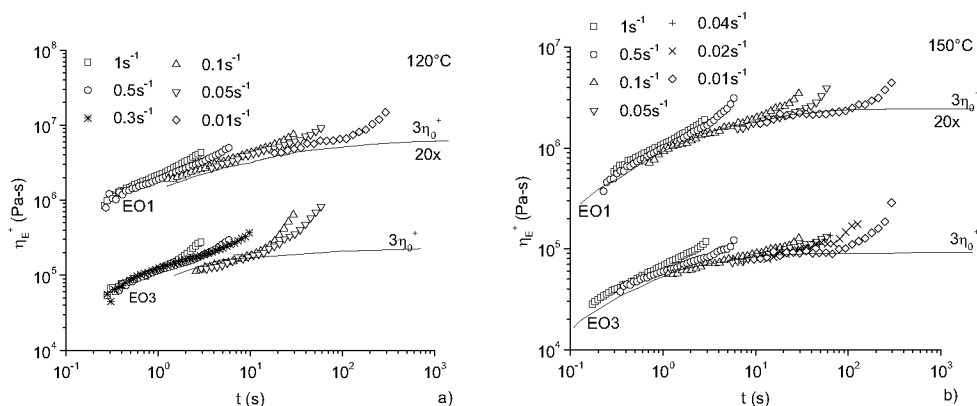

FIGURE 1. Extensional viscosity plots of EO1 and EO3 at (a) 120°C and (b) 150°C.
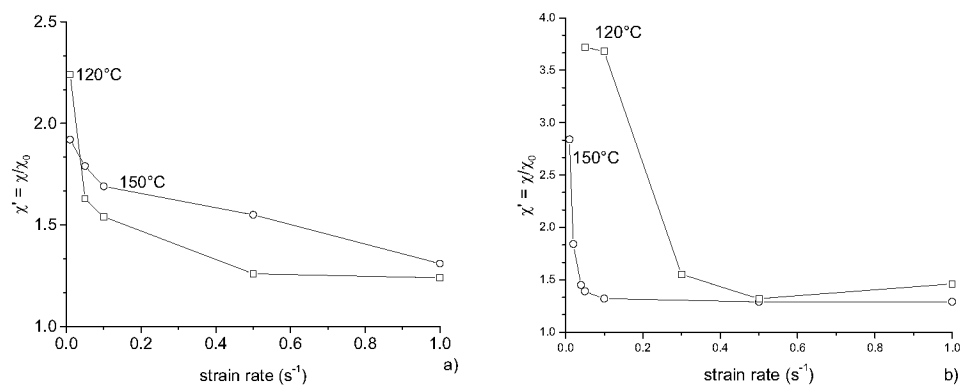

FIGURE 2. Corrected strain hardening parameter plotted against strain rate 120°C and 150°C for (a) EO1 and (b) EO3.

hardening ratios of 2.24 at 120°C and 1.92 at 150°C observed for another random copolymer melt with (lower) 20 wt% comonomer. The steady state creep compliance values were very close for these two copolymer melts, ruling out differences in high molecular weight components. In addition, the molecular weight distributions were very similar[8] and not broad. This would indicate that EO3 must contain sparse LCB even though the vanGurp-Palmen plots failed to show its presence. A different construction based on linear viscoelastic data such as the weighted relaxation spectrum[10] -- $\lambda H(\lambda)$ vs. λ is revealing and is presented in Figure 3. The weighted relaxation spectrum for EO3 showed two distinct peaks – one associated with the backbone at 4.641s and another associated with long chain branches at 0.215s. The weighted spectrum for EO1 shows a broad, lopsided peak at 5.88s, with a slight shoulder at 0.077s. The two sets of relaxation times may be associated with the backbone and the branches respectively.

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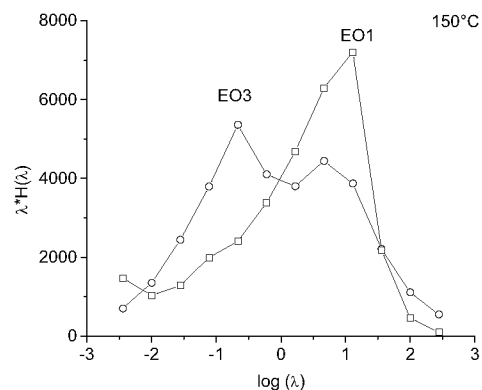
FIGURE 3. Weighted relaxation spectrum for EO1 and EO3 at 150°C.

Wagner and coworkers[11] have modeled tree-type and heavily branched polymers using a variation of the tube model with convective constraint release. This model has two nonlinear parameters, one related to the branching content (1<β<2) and the other related to the maximum tube diameter contraction (f^2_{max}) during stretching flows. Greater branching content as well as greater tube contraction lead to a greater extent of strain hardening. Since the EO systems presented in this paper are sparsely branched, the branching content parameter β should be considerably lower (closer to 1) than that for tree-type branched systems and this parameter is independent of temperature. However, our results indicate that the maximum tube diameter contraction parameter should be larger for EO3 and should have a greater dependence on temperature than for EO1.

CONCLUSIONS

Transient extensional viscosity measurements on two different random copolymer melts showed significant strain hardening for both melts, indicating the presence of sparse LCB in both even in the case where vanGurp-Palmen plots did not detect it. Indeed the strain hardening parameter at the lowest strain rate was found to be greater for EO3, the material with the smaller degree of LCB. The temperature dependence of the strain hardening parameter was also greater for EO3 than for EO1. These trends may be related to the two model parameters used by Wagner and coworkers[11] representing branch content and the maximum tube diameter contraction.

ACKNOWLEDGMENTS

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