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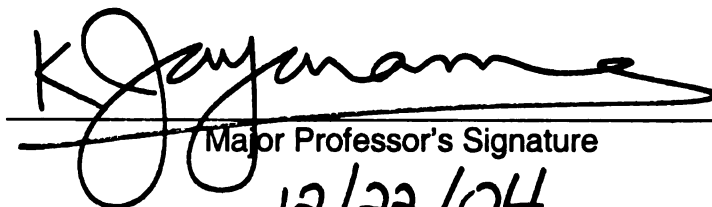
**NONLINEAR RHEOLOGY AND STRAIN RECOVERY
OF SHORT CHAIN BRANCHED
POLYOLEFIN ELASTOMERS AND
THERMOPLASTIC OLEFIN BLENDS**

presented by

BHASKAR PATHAM

has been accepted towards fulfillment
of the requirements for the

Doctoral degree in Chemical Engineering and
Materials Science



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ABSTRACT

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The effects of varying short chain branch density (SCB) on the melt rheology of three ethylene-octene random copolymers have been investigated. In particular, the strain-hardening behavior in extensional flow and recovery following nonlinear shear creep has been evaluated.

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Polyolefin elastomers are random copolymers having a polyethylene backbone with the higher olefinic comonomer incorporated as short-chain branches. These random copolymers are widely used as polymer modifiers for thermoplastic materials such as polypropylenes, resulting in thermoplastic olefin (TPO) blends. This thesis addresses the nonlinear rheological behavior of the elastomers and then of the TPO blends.

The effects of varying short chain branch density (SCB) on the melt rheology of three ethylene-octene random copolymers have been investigated. In particular, the strain-hardening behavior in extensional flow and strain recovery following nonlinear shear creep has been evaluated. The zero-shear viscosity followed trends in the backbone molecular weight closely. While the three copolymers were indistinguishable in linear viscoelastic creep and recovery, recovery following nonlinear shear creep decreased progressively with increasing SCB density. This reveals that the extent of rapid chain equilibration that occurs over Rouse time scales at higher strains was progressively lower with increasing SCB density. Strain hardening in uniaxial extensional flow was observed for all three copolymers. At strain rates below the primitive chain equilibration rates, strain hardening increases progressively with increasing SCB density. At higher rates,

upon onset of primitive chain stretch, the strain hardening behavior for the three melts merges.

Two thermoplastic olefin (TPO) blends were characterized in the context of injection molding; the surface morphology of injection molded tensile bars with these materials showed surface defects or flow marks to different extents. The flow marks were traced to different degrees of strain recovery in the dispersed phases of the two blends. This recovery occurred over injection molding timescales of the order of a few seconds. Strain recovery after shear creep was higher in the blend that displayed more severe flow marks in injection molding; the corresponding elastomer by itself also showed a greater extent of creep recovery. The quick strain recovery in the elastomer must be associated with elastic stresses rather than interfacial tension.

A new experimental apparatus was assembled to study strain recovery after elongation of a model elastomer suspended in a less viscoelastic medium at room temperature. Small drops of well-characterized elastomers suspended in a matrix fluid of lower viscosity and elasticity, are stretched rapidly without wall effects in this setup; the stretch ratio of the drops is then recorded over time. Preliminary results confirm significant recovery over a few seconds. Exploration of the full range of parameters with this setup is left for future work.

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To my parents
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E_a Flow activation energy

$G(t)$ Relaxation modulus

$G(t, \gamma)$ Strain-dependent nonlinear stress relaxation modulus

G' Dynamic storage modulus

G'' Dynamic loss modulus

$G^0(t)$ Linear viscoelastic stress relaxation modulus

G_i weighting factor for discrete relaxation spectrum

G_N^0 Plateau modulus

I_1 First invariant of Finger tensor

I_2 Second invariant of Finger strain tensor

$J(t)$ Shear compliance

$J_e(t)$ Elastic compliance

NOMENCLATURE

J_e^0	Linear equilibrium compliance
J_{inst}	Compliance associated with instantaneous deformation during creep
$a_T(t)$	Time-temperature shift factor
B	Minor axis of the drop
$\underline{C}_t^{-1}(t')$	Finger strain tensor
Ca	Capillary number
D	Drop deformation parameter defined for small deformations
$D_{stretch}$	Stretch ratio of the drop defined for large deformation
De	Deborah number
$E(t)$	Elastic modulus
E_a	Flow activation energy
$G(t)$	Relaxation modulus
$G(t, \gamma)$	Strain dependent nonlinear stress relaxation modulus
G'	Dynamic storage modulus
G''	Dynamic loss modulus
$G^0(t)$	Linear viscoelastic stress relaxation modulus
G_i	weighting factor for discrete relaxation spectrum
G_N^0	Plateau modulus
I_1	First invariant of Finger tensor
I_2	Second invariant of Finger strain tensor
$J(t)$	Shear compliance
$J_e(t)$	Elastic compliance

J_e^0	Linear equilibrium recoverable compliance
J_{inst}	Compliance associated with instantaneous deformation during creep
$J_r(t)$	Recoverable compliance
k	Drop / matrix viscosity ratio
K	Drop / matrix elasticity ratio
K	Pre-exponential factor for power-law dependence of shear viscosity on the shear rate
L	Major axis of the drop
L	Length of the semi-hyperboloidal converging die
M	Molecular weight
M_{br}	Molecular weight of the branch
M_c	Critical molecular weight for entanglements
M_e	Entanglement molecular weight
M_N	Number average molecular weight
M_W	Weight average molecular weight
n	Exponent for power-law dependence of shear viscosity on the shear rate
r	radial direction
R	Instantaneous radius of the drop during deformation or recovery
R_B	Radius of the rheometer barrel
R_e	Exit radius of the semi-hyperboloidal converging die
R_{eq}	Equilibrium spherical radius of drop
t	Time
t_{max}	Time at which creep stress is removed

t_{res}	Residence time of the melt within the semi-hyperboloidal die
V_P	Piston velocity for testing in the pressure driven rheometer
$\bar{\eta}_{eff}$	Effective viscosity of a two phase drop / matrix system or emulsion or
$\bar{x}$	Number average x-direction length of the dispersed phase
z_E	principal axis
Z	Entanglement density in a polymer chain
Z_{bb}	Backbone entanglement density
$\sigma(t)$	Stress tensor
Greek	
$\tau(t)$	Shear stress
χ	Characteristic relaxation time determined from shear creep experiments
χ	Drop shape factor or drop / matrix interaction parameter
ϵ_H	Hencky strain
$\dot{\epsilon}$	Extensional strain rate
γ	Shear strain
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_{\infty}$	Shear rate at long time viscous response during shear creep
γ_0	Instantaneous shear strain imposed during stress relaxation
$\gamma_r(t')$	Recoverable shear strain
Γ	Interfacial tension between dispersed phase and matrix
$h(\gamma)$	Shear strain damping function
η^+	Linear startup shear viscosity
η'	Dynamic viscosity
η''	Dynamic complex viscosity
η_0	Zero-shear viscosity

$ \eta^* $	Complex viscosity
η_{eff}	Effective viscosity of a two phase drop / matrix system or emulsion or blend
η_E	Extensional viscosity
λ_i	Discrete relaxation times in the relaxation spectrum
$\mu^0(t)$	Linear viscoelastic memory function
$\underline{\sigma}(t)$	Stress tensor
$\tau(t)$	Shear stress
τ_1	Characteristic relaxation time determined from shear creep experiments
$\tau_{11} - \tau_{22}$	Extensional stress
τ_d	Tube disengagement or reptation time
τ_R	Equilibration or Rouse time
τ_w	Wall shear stress
ω	Frequency
Special	
$G(t, \gamma)$	Strain dependent nonlinear stress relaxation modulus
$h(\gamma)$	Shear strain damping function
ΔP	Pressure drop
ΔP_{en}	Entrance pressure drop

such as butene (C-4), or hexene (C-6). The metallocene catalyst structure facilitates homogeneous incorporation of the comonomer throughout the polymer chain, and a narrow distribution of comonomer type [Schanabish et al. (1994)]. The higher-olefin comonomers are incorporated as short-chain branches (SCB) on a polyethylene backbone, as **PROBLEM STATEMENT**. Depending on the short-chain branch (SCB) density (i. e., comonomer content), these random copolymers show a whole range of structures, ranging from LLDPE at low SCB densities to elastomeric at high SCB densities [Bensason et al., (1996), Shan and White (2004)].

MOTIVATION

Such polyethylene copolymer elastomers (having high SCB density) or polyolefin Blending of polymers to improve material properties offers an effective alternative to synthesis of new materials. Rubbers are blended with thermoplastics to modifiers. For example, ethylene-octene (EO) random copolymer elastomers have improved the impact strength and low temperature properties of the thermoplastic material. Recently established thermoplastics as polymer modifiers or blends for polypropylene (PP). Crosslinked rubber however is difficult to process and not amenable to recycling. A Blends of polypropylene (PP) and ethylene-octene (EO) elastomers are now widely used special class of materials known as thermoplastic elastomers offers an attractive alternative to rubbers. Thermoplastic elastomers are not crosslinked, but instead have and are processed via high-speed injection molding and thermoforming. Blends reversible bonding, in the form of hydrogen bond forces, which makes them rubber-like containing polyolefin elastomers dispersed in a thermoplastic matrix are known as at room temperature, while the absence of cross links imparts thermoplastic-like thermoplastic olefin (TPO) blends. Polyolefin elastomers are also employed "neat" (i.e., characteristics in the melt state [Morris (1979), Coran (2001)]. Such reversible bonding by themselves, without adding them to another polymer) for rapid blow-molding and is usually achieved via copolymerization. Block copolymers as well as random thermoplastic applications. copolymers have been used widely as polymer modifiers.

Given the wide range of applications of these elastomers, their melt rheology is The advances in the field of metallocene catalysis have brought about the advent obviously of great interest. Nonlinearities in rheological behavior are very sensitive to of a new class of random copolymers of polyethylene with a higher olefin comonomer

such as butene (C-4), or hexene (C-6), or octene (C-8). The metallocene catalyst structure facilitates homogeneous incorporation of the comonomer throughout the polymer chain, and a narrow distribution of comonomer type [Sehanobish et al. (1994)]. The higher-olefin comonomers are incorporated as short-chain branches (SCB) on a polyethylene backbone, as shown schematically in Figure 1.1. Depending on the short-chain branch (SCB) density (i. e., comonomer content), these random copolymers show a whole range of structures, ranging from LLDPE at low SCB densities to elastomeric at high SCB densities [Bensason et al., (1996), Shan and White (2004)].

The effectiveness of these polyethylene copolymers elastomers as polymer modifiers. Such polyethylene copolymer elastomers (having high SCB density) or polyolefin elastomers are a new class of thermoplastic elastomers, and are very effective polymer modifiers. For example, ethylene-octene (EO) random copolymer elastomers have quickly established themselves as polymer modifiers of choice for polypropylene (PP). Blends of polypropylene (PP) and ethylene-octene (EO) elastomers are now widely used for internal as well as external automotive applications such as dashboards and bumpers – and are processed via high-speed injection molding and thermoforming. Blends containing polyolefin elastomers dispersed in a thermoplastic matrix are known as thermoplastic olefin (TPO) blends. Polyolefin elastomers are also employed “neat” (i.e., by themselves, without adding them to another polymer) for several blow-molding and thermoforming applications. Involving rapid evolution of TPO elastomers has been studied in our laboratory [Patham et al. (2004a), Patham et al. (2004b)]. Given the wide range of applications of these elastomers, their melt rheology is obviously of great interest. Nonlinearities in rheological behavior are very sensitive to

the polymer chain architecture. The effects of polymer molecular weight distribution, and sparse as well as profuse long-chain branching on the rheology of polymer melts have all received different degrees of attention by several researchers in the past [Graessley (1992), Ferry (1980), Kasehagen and Macosko (1998), Gabriel and Munstedt (2003)]. A less understood aspect of polyolefin random copolymers that warrants further investigation is the effect of short-chain branching density on the melt rheology of these copolymers, especially at high SCB densities.

The effectiveness of these polyethylene-copolymer elastomers as polymer modifiers is in great part governed by the microstructure of the resulting thermoplastic olefin (TPO) blends. Microstructure of the blend is especially important when the TPO blends are employed for non-painted external automotive parts such as car bumpers. The evolution of such microstructure is governed by the properties of the thermoplastic matrix, the elastomeric dispersed phase, the interfacial tension, the deformations and the rates of deformation imposed on the blend during processing. The final blend microstructure as well as physical properties of the product are governed by recovery following such deformations. It is therefore important to understand the factors driving blend recovery in these systems, especially under high-rate processing conditions.

An interesting problem involving rapid evolution of TPO blend microstructure has been studied in our laboratory [Patham et al. (2004a), Papworth (2001)] over the last few years. TPO parts injection molded at high-rates develop surface gloss defects called flow-marks. This phenomenon is associated with a flow transition at the advancing melt

front from stable symmetric fountain flow to unstable, oscillating, asymmetric flow. Frequency of flow-marks on the surface of the TPO part is therefore governed by how unstable the melt front is. Recently conducted analyses of surface microstructure associated with the flow-mark regions in our laboratory reveal high degrees of recovery of extensional strains in the elastomeric dispersed phase. Greater extents of recovery result in greater surface contrast, and more severe gloss defects. Such recovery usually occurs within the injection-molding timescales of the order of a few seconds, and cannot be attributed to interfacial tension alone. It is therefore essential to relate the frequency and severity of these surface defects to the nonlinear rheology of the TPO blends and the components.

The elasticity of the melts has been assessed using nonlinear shear creep-recovery measurements, and the strain hardening behavior in extensional flows has been studied. The flow-mark phenomenon presents the need to systematically investigate the role of component rheology and flow kinematics in the manifestation of elastic effects during recovery. While interfacial tension driven recovery in drops and blends has been widely studied [Tucker and Moldenaers (2002), Gramespacher and Meissner (1995, 1997), Vinckier et al. (1999a, 1999b), Cohen and Carriere (1989)], the understanding of elastic effects during recovery is not very well developed. In particular, model systems in which the drop phase is much more viscous and elastic as compared to the matrix are attractive due to their similarity to TPO blend systems.

This thesis addresses three specific research problems motivated by the scenario described above. These problems are associated with polyolefin elastomers and TPO blends and focus on nonlinear rheology and strain recovery.

marks when molded at the same rate. The different degrees of surface defects or flow

RESEARCH PROBLEM 1

the degrees of strain recovery in the dispersed phases of the two blends. Surface microstructure following injection molding of TPO blends has been

analyzed. *To investigate the interrelationships between short-chain branching density in ethylene- α -olefin elastomers and their nonlinear melt rheology*

components, as assessed from nonlinear shear creep-recovery and extensional strain hardening, are found to be

important. In this study the effect of short chain branching density on the nonlinear melt

rheology of polyolefin elastomers has been investigated with three carefully chosen metallocene based ethylene-octene random copolymer elastomers of low polydispersity.

In particular, the elasticity of the melts has been assessed using nonlinear shear creep-

recovery measurements, and the strain hardening behavior in extensional flows has been

studied. Trends in linear viscoelasticity and nonlinear rheology have been carefully

evaluated to contrast them with those obtained in the presence of long-chain branching or

high molecular weight tails. this work aims at gaining an understanding of the effect of

drop and matrix viscosities and elasticities as well as flow conditions on the extent of

RESEARCH PROBLEM 2

effects. A new experimental apparatus has been assembled in our laboratory to study strain recovery after elongation of a stretch lamina suspended

in a liquid. *To study the effect of polyolefin elastomer and TPO blend rheology on the evolution of blend morphology in high-rate processing operations.*

viscosity, are stretched rapidly without wall effects in this setup; the stretch ratio of the sample is then recorded

over time. In this study, two thermoplastic olefin (TPO) blends have been rheologically

characterized in the context of the flow-marks associated with high-speed injection

molding. The two TPO blends displayed different frequencies and severity of flow-

marks when molded at the same rate. The different degrees of surface defects or flow marks were traced to different degrees of strain recovery in the dispersed phases of the two blends. Surface microstructure following injection molding of TPO blends has been analyzed based on the melt rheology of the blends as well as their components. The nonlinear melt rheology of the blends as well as their components, as assessed from nonlinear shear creep-recovery and extensional strain hardening, are found to be important parameters governing the blend recovery behavior.

RESEARCH PROBLEM 3 *Two aspects. Firstly, it summarizes the prior studies on rheological characterization of polyolefins, and the current understanding of the relation. To evaluate the fluid and flow parameters governing elastic effects during recovery of elastomeric drops in suspension. Critical analysis of deformation and recovery behavior of drops suspended in a sea of matrix.*

The final aspect of this work aims at gaining an understanding of the effect of drop and matrix viscosities and elasticities as well as flow conditions on the extent of recovery driven by elastic effects. A new experimental apparatus has been assembled in our laboratory to study strain recovery after elongation of a model elastomer suspended in a less viscoelastic medium at room temperature. Small drops of well-characterized elastomers suspended in a matrix fluid of lower viscosity and elasticity, are stretched rapidly without wall effects in this setup; the stretch ratio of the drops is then recorded over time. Preliminary results confirm significant recovery over a few seconds. Exploration of the full range of parameters with this setup is left for future work.

Figure 1.2. summarizes the main thrusts of this work. Some aspects of this work, such as the phenomenological modeling of recovery behavior are still in the formative stages, and will be carried out in future.

In Chapter 5, thermoplastic olefin (TPO) blend microstructures associated with **ORGANIZATION OF THESIS** interpreted in terms of the rheology of the blends as well as their components. [Pathan et al. (2002b, 2004a)].

In Chapter 2, a detailed background is presented, in which several aspects mentioned in the foregoing are elaborated, to place the current study in perspective. The background broadly covers two aspects. Firstly, it summarizes the prior studies on rheological characterization of polyolefins, and the current understanding of the relationships between rheology and molecular architecture. The second aspect involves a summary of experimental studies and theoretical analyses of deformation and recovery behavior of drops suspended in a sea of matrix.

The principal conclusions and recommendations for future work are laid out in Chapter 6. One of the important methods of characterization of several materials involved in these studies was extensional viscosity at a high extensional strain and high strain rates. For this purpose we applied a technique involving lubricated skin-core flow of the test material through converging dies of special profiles. The experimental aspects of these measurements and other rheological characterization techniques employed are laid out in Chapter 3 [Pathan and Jayaraman (2002a)]

The experimental results on interrelationships between the molecular architecture, particularly short-chain branching and the linear and nonlinear rheology of the ethylene-

octene elastomers are presented in Chapter 4, along with interpretation of the trends in the light of reptation model for polymer melts. [Patham and Jayaraman (2004b, 2004c)]

In Chapter 5, thermoplastic olefin (TPO) blend microstructures associated with high-speed injection molding are interpreted in terms of the rheology of the blends as well as their components. [Patham et al. (2002b, 2004a)].

In Chapter 6, the experimental methodology - for recording and identifying the elastic phase of recovery of an elastomeric drop suspended in a matrix of lower viscosity and elasticity following rapid high strain extensional deformations - is laid out. Preliminary results from this experiment are encouraging and offer new areas to be investigated in future.

The principal conclusions and recommendations for future work are laid out in Chapter 7.

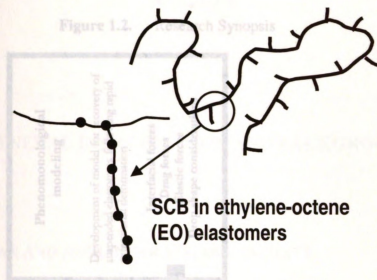


Figure 1.1. Short-chain branching in polyolefin random copolymers

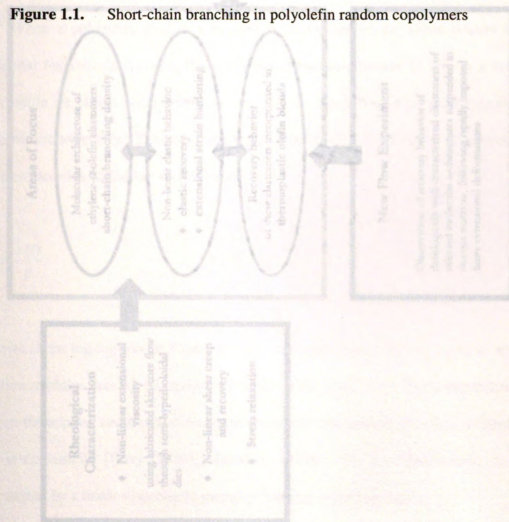
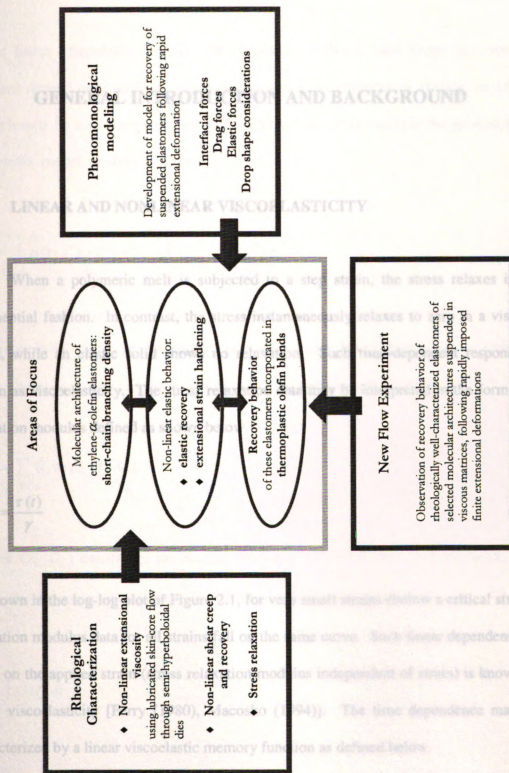


Figure 1.2. Research Synopsis



Chapter 2.

$$\mu(t) = -\frac{dG(t)}{dt} \quad (2.2)$$

In the linear viscoelastic regime, the relaxation modulus (and hence the memory function) depends on the time t after the onset of the deformation. The critical strain results by a summation of all small deformation. This results in the general linear viscoelastic model, as shown below

GENERAL INTRODUCTION AND BACKGROUND

2.1. LINEAR AND NONLINEAR VISCOELASTICITY

$$\tau(t) = \int_0^t \mu(t-t') \gamma(t') dt' = \int_0^t G(t-t') \dot{\gamma}(t') dt' \quad (2.3)$$

When a polymeric melt is subjected to a step strain, the stress relaxes in an exponential fashion. In contrast, the stress instantaneously relaxes to zero in a viscous liquid, while an elastic solid shows no relaxation. Such time-dependent response is known as viscoelasticity. The stress relaxation data may be interpreted in the form of a relaxation modulus defined as shown below.

$$G(t) = \sum G_i \exp(-t/\lambda_i) \quad (2.4)$$

$$G(t) = \frac{\tau(t)}{\gamma} \quad (2.1)$$

The set (λ_i, G_i) constitutes the discrete relaxation spectrum of the polymer melt. The

As shown in the log-log plot of Figure 2.1, for very small strains (below a critical strain), relaxation modulus data for all strains fall on the same curve. Such linear dependence of stress on the applied strain (stress relaxation modulus independent of strain) is known as linear viscoelasticity [Ferry (1980), Macosko (1994)]. The time dependence may be characterized by a linear viscoelastic memory function as defined below.

$$\eta_0 = \int_0^\infty G(t) dt \quad (2.5)$$

$$\mu(t) = -\frac{dG(t)}{dt} \quad (2.2)$$

When loaded in shear or extension, polymer melts exhibit an instantaneous deformation similar to an elastic solid, followed by a continuous time-dependent deformation known as creep. Creep data may be interpreted using a creep compliance, as defined below. In the linear viscoelastic regime, the relaxation modulus (and hence the memory function) depend only on time, and therefore any larger deformation (below the critical strain) results by a summation of all small deformation. This results in the general linear viscoelastic model, as shown below

$$J(t) = \frac{t}{\eta_0} + \sum_{i=1}^n \frac{G_i}{\lambda_i} \exp(-t/\lambda_i) \quad (2.6)$$

The creep response for melts is schematically shown in Figure 2.2. At long times, a steady state is reached. In the linear viscoelastic regime, since strain is

$$\tau(t) = \int_0^t \mu(t-t') \dot{\gamma}(t') dt' = \int_0^t G(t-t') \dot{\gamma}(t') dt' \quad (2.3)$$

linear with stress, the strain vs. time data collapse onto a single $J(t)$ curve. The response

The exponential decay of the relaxation modulus may be modeled using a series of relaxation times λ_i and weighting constants G_i as shown below,

$$G(t) = \sum_{i=1}^n G_i \exp(-t/\lambda_i) \quad (2.4)$$

The set (λ_i, G_i) constitutes the discrete relaxation spectrum of the polymer melt. The area under the stress relaxation curve yields the zero-shear viscosity of the melt.

$$\eta_0 = \int_0^{\infty} G(t) dt \quad (2.5)$$

Alternatively, when loaded in shear or extension, polymer melts exhibit an instantaneous deformation similar to an elastic solid, followed by a continuous time-dependent deformation known as creep. Creep data may be interpreted using a creep compliance, as defined below.

$$J_e(t) = \frac{\gamma(t)}{\tau_0} \quad (2.9)$$

$$J(t) = \frac{\gamma(t)}{\tau_0} \quad (2.6)$$

In the linear viscoelastic regime, if steady state is achieved in creep, then the equilibrium creep recovery is a direct measure of J_e^0 .

The creep response for melts is schematically shown in Figure 2.2. At long times, a steady rate of straining $\dot{\gamma}_\infty$ is attained. In the linear viscoelastic regime, since strain is linear with stress, the strain vs. time data collapse onto a single $J(t)$ curve. The response of the melt to creep can be decomposed into three portions: an instantaneous deformation J_{inst} , an elastic portion and a viscous portion that grows with time, as shown below.

$$\gamma = \gamma_0 \sin \omega t \quad (2.10)$$

$$J(t) = J_{inst} + J_e(t) + \frac{t}{\eta_0} \quad (2.7)$$

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (2.11)$$

J_{inst} is usually negligible as compared to the elastic and viscous portions. Thus during the steady linear creeping regime,

Such sinusoidal data are analyzed by decomposing the stress into two components – an elastic component in phase with the strain and a viscous component 90° out of phase with strain. This results in two dynamic moduli - an in-phase storage or storage modulus G' and an out-of-phase viscous or loss modulus G'' . The elasticity of the melt is assessed using the phase tangent.

$$J(t) = J_e^0 + \frac{t}{\eta_0} \quad (2.8)$$

Upon removal of the stress, the polymer melt recovers the elastic portion of the imposed deformation. The recoverable compliance is defined as shown below.

In addition, a complex viscosity may be defined, with its magnitude is given by,

$$J_r(t) = \frac{\gamma_r(t)}{\tau_0} \quad (2.9)$$

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} = \left[\left(\frac{G'}{\omega} \right)^2 + \left(G'' \right)^2 \right]^{1/2} = \left| G'' \right| \quad (2.13)$$

In the linear viscoelastic regime, if steady state is achieved in creep, then the equilibrium creep recovery is a direct measure of J_e^0 .

Another distinguishing characteristic of the linear viscoelastic regime of

Linear viscoelastic or small strain material functions are also assessed using dynamic testing, in which sinusoidal oscillations with small strain amplitude are imposed on the melt sample.

$$\gamma = \gamma_0 \sin \omega t \quad (2.10)$$

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (2.11)$$

Such sinusoidal data are analyzed by decomposing the stress into two components – an elastic component in phase with the strain and a viscous component 90° out of phase with strain. This results in two dynamic moduli - an in-phase elastic or storage modulus G' and an out-of-phase viscous or loss modulus G'' . The elasticity of the melt is assessed using the phase tangent.

$$\tan \delta = \frac{G''}{G'} = \int_0^\infty 3G(t) dt = 3\eta_0 \quad (2.12)$$

In addition, a complex viscosity may be defined, with its magnitude is given by,

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} = \left[\left(\frac{G'}{\omega} \right)^2 + \left(\frac{G''}{\omega} \right)^2 \right]^{1/2} = \frac{|G^*|}{\omega} \quad (2.13)$$

$$G(t, \gamma) = \frac{\tau(t, \gamma)}{\gamma} \quad (2.17)$$

Another distinguishing characteristic of the linear viscoelastic regime of deformation is that normal stresses in shear are not of importance. Also, the type of deformation, e.g., shear versus uniaxial extension, is not important. For tensile deformations, a tensile modulus may be defined as shown below.

In shear, nonlinear behavior is characterized by shear thinning and normal stresses. Nonlinear effects are also evident in the time dependent startup shear viscosity.

$$E(t) = \frac{(\sigma_{11} - \sigma_{22})(t)}{\epsilon} \quad (2.14)$$

defined as shown below.

For small strains, however,

$$\eta(t, \gamma) = \frac{\tau(t, \gamma)}{\gamma} \quad (2.18)$$

$$E(t) = 3G(t) \quad (2.15)$$

At the lowest shear rates, $\eta^*(t, \dot{\gamma})$ is independent of shear rate, and shows a monotonic and by consequence, the viscosity in extension would be three times the zero-shear viscosity.

decreases at comparable times, and an overshoot appears in the transient. Even at high shear rates, however, $\eta^*(t, \dot{\gamma})$ at small times does not depart from the

linear viscoelastic response. Thus nonlinear effects occur only when both the strain rate $\dot{\gamma}$ and the strain γ are large. These effects are schematically shown in Figure 2.3.

At strains larger than a critical strain, the relaxation modulus is no longer independent of strain. Strain hardening is the upward deviation from the Trouton's rule.

$$G(t, \gamma) = \frac{\tau(t, \gamma)}{\gamma} \quad (2.17)$$

$$\frac{\eta_E^+(t, \dot{\gamma})}{\eta_0^+} = 3 \quad (2.19)$$

Such strain dependence of the relaxation modulus at high strains is also schematically shown in Figure 2.1. This behavior is known as nonlinear viscoelasticity.

In shear, nonlinear behavior is characterized by shear thinning and normal stresses. Nonlinear effects are also evident in the time dependent startup shear viscosity, defined as shown below.

The advent of Dow's INSITE[®] constrained geometry catalyst technology has

$$\eta^+(t, \dot{\gamma}) = \frac{\sigma_{12}(t, \dot{\gamma})}{\dot{\gamma}} \quad (2.18)$$

synthesize linear low-density polyethylenes (LLDPE) with narrow molecular weight distributions [Schanabish et al. (1994)]. These catalysts also

facilitate incorporation of higher olefin comonomers in a highly homogeneous fashion

At the lowest shear rates, $\eta^+(t, \dot{\gamma})$ is independent of shear rate, and shows a monotonic increase to the linear viscoelastic zero-shear viscosity. As the shear rate increases, $\eta^+(t, \dot{\gamma})$ decreases at comparable times, and an overshoot appears in the transient.

Even at high shear rates, however, $\eta^+(t, \dot{\gamma})$ at small times does not depart from the

linear viscoelastic response. Thus nonlinear effects occur only when both the strain rate $\dot{\gamma}$ and the strain $\gamma = \dot{\gamma}t$ are large. These effects are schematically shown in Figure 2.3.

In extension, strain hardening, schematically shown in Figure 2.4, is observed at high strains. Extensional strain hardening is the upward deviation from the Trouton's rule, and this has been widely investigated. With increase in comonomer content, there is progressive decrease in the density, crystallinity and melting point of the copolymer [Bensason et al. (1996)]. More importantly, increasing comonomer content $\frac{\eta_E^+(t, \dot{\epsilon})}{\eta_0^+(t)} = 3$ (2.19) fundamental changes in the crystalline microstructure of the copolymer. Four

distinct microstructures have been identified with increasing comonomer content. Such deviations typically occur above extensional strains of 1.0. Materials with densities greater than 0.93 g/cc (very low comonomer content) exhibit lamellar morphology with well developed spherulites typical of high density polyethylenes (HDPE); (Type III)

2.2. RHEOLOGY AND MOLECULAR ARCHITECTURE OF POLYOLEFINS

spherulites; typical of conventional linear low density polyethylenes (LLDPE); (Type II)

Copoly. The advent of Dow's INSITE[®] constrained geometry catalyst technology has made it possible to synthesize linear low-density polyethylenes (LLDPE) with fairly narrow molecular weight distributions [Sehanobish et al. (1994)]. These catalysts also facilitate incorporation of higher olefin comonomers in a highly homogeneous fashion resulting in ethylene- α -olefin copolymers with a fairly narrow comonomer distribution, independent of the molecular weight. The higher olefin comonomers are incorporated in the form of short-chain branches (SCB) – butene (C4) comonomer is present in the form

of ethyl (2-carbon) branches, octene (C8) comonomer is present in the form of hexyl (6-carbon) branches, and so on.^[41]

Such ethylene- α -olefin random copolymers offer a broad variety of structures and physical properties depending on the comonomer content or short-chain branch (SCB) density, and this has been widely investigated. With increase in comonomer content, there is progressive decrease in the density, crystallinity and melting point of the copolymer [Bensason et al. (1996)]. More importantly, increasing comonomer content results in fundamental changes in the crystalline microstructure of the copolymer. Four distinct microstructures have been identified with increasing comonomer content [Bensason et al. (1996), Minick et al. (1995)] – (Type IV) Materials with densities greater than 0.93 g/cc (very low comonomer content) exhibit lamellar morphology with well developed spherulites typical of high density polyethylenes (HDPE); (Type III) Copolymers with densities between 0.93-0.91 g/cc have thinner lamellae and smaller spherulites, typical of conventional linear low density polyethylenes (LLDPE); (Type II) Copolymers with densities between 0.91-0.89 g/cc have a mixed morphology of small lamellae and bundled crystals or very small spherulites; and (Type I) copolymers with densities less than 0.89 g/cc (high comonomer contents) have no lamellae or spherulites, and may have bundles crystals or granular nonlamellar morphology. The combined observations from melting behavior, microstructure assessment, and tensile testing show the transition from semicrystalline behavior typical of conventional LLDPEs at low comonomer content to an essentially elastomeric behavior at high comonomer contents,

linear entangled melts shows a 3.4 power law dependence on the molecular weight of the

corresponding to densities lower than 0.9 g/cc [Benson et al. (1996), Minick et al. (1995), Shan and White (2004)].

the critical entanglement molecular weight ($M \gg M_e$; $M_e = 2M_c$), the linear equilibrium recoverable shear compliance J_e^0 is independent of the molecular weight.

The versatility of structures achievable with ethylene- α -olefin copolymers has led to their broad applicability in polymer processing – both in “neat” form as well as in the form of polymer modifiers for thermoplastics such as polypropylenes. Therefore the rheology of these copolymers is of great interest.

viscoelastic response of entangled, linear and nearly monodisperse polymer melts is described well by the Doi-Edwards [(1978, 1986), Graessley (1980)] constitutive theory. This theory is based on the idea that

2.2.1. Molecular architecture effects on linear viscoelasticity and theoretical framework

by the entanglements with other chains. Doi and Edwards represent these constraints by modeling the polymer as a random coil of molecular weight M and mean

Molecular structure has profound consequences on the melt rheology in the linear as well as nonlinear regimes of deformation. In this context, experimental studies have primarily focused on the effects of polydispersity (M_w / M_n), profuse long-chain branching (LCB), and sparse LCB on the deviation of rheological behavior in comparison with a perfectly monodisperse linear polymer. Limited investigations on the effect of short-chain branching form a very small subset of this literature and will be discussed later in this section.

scales are strong functions of the polymer chain entanglement density Z , defined as shown below [see Larson et al. (2003) for a discussion of the various conventions].

The behavior of linear monodisperse polymers forms the base case with which the behavior of polydisperse and branched melts is compared. The zero shear viscosity of linear entangled melts shows a 3.4 power law dependence on the molecular weight of the

$$Z = \frac{M}{M_e} \quad (2.20)$$

polymer ($\eta_0 \propto M^{3.4}$). In linear polymer melts with molecular weights much higher than the critical entanglement molecular weight ($M \gg M_c$; $M_c \approx 2M_e$), the linear equilibrium recoverable shear compliance J_e^0 is independent of the molecular weight, and so is the plateau modulus G_N^0 [Ferry (1980), Graessley (1992)].

The molecular basis to understand the viscoelastic response of entangled, linear and nearly monodisperse polymer melts is described well by the Doi-Edwards [(1978, 1986), Graessley (1980)] constitutive theory. This theory is based on the idea that transverse motions of the polymer chain are impeded because of the constraints posed by the network formed by the entanglements with other chains. Doi and Edwards represent these constraints by modeling the polymer as a random coil of molecular weight M and mean square end-to-end distance R^2 , confined within a tube of diameter a and contour length L . Following deformation, stress relaxation proceeds first by a rapid equilibration of the chain within the distorted tube, then by a relatively slow disengagement of the chain from the tube brought about by the “reptation” of the chain parallel to its own contour. The rapid equilibration stage of stress relaxation is characterized by a Rouse timescale τ_R while the slower reptation stage is characterized by a tube disengagement time τ_d . These timescales are strong functions of the polymer chain entanglement density Z , defined as shown below [see Larson et al. (2003) for a discussion of the various conventions of defining the tube entanglement parameters],

$$Z = \frac{M}{M_e} \quad (2.20)$$

Then,

$$\tau_d \propto 3Z^3 \quad (2.21)$$

$$\tau_R \propto Z^2 \quad (2.22)$$

This theory gives correct qualitative results with regard to the dependence of zero shear viscosity on molecular weight ($\eta_0 \propto M^3$) and the molecular weight independence of J_e^0 for entangled linear systems. Deviations from such limiting behavior are observed with broader molecular weight distribution or in presence of branching.

Polydispersity does not significantly alter the dependence of η_0 on the molecular weight, the latter being a weight average molecular weight ($\eta_0 \propto M_w^{3.4}$). J_e^0 , however, is extremely sensitive to the molecular weight distribution [Struglinski and Graessley (1985)], even in linear polymers. J_e^0 has been shown to steeply increase with the presence of high molecular weight fractions [Graessley (1992)].

Branching profoundly affects the rheology of the polymers. From studies with model star and comb branched melts [Roovers and Toporowski (1987)], it is clear that the zero-shear viscosity shows an exponential dependence on the branch entanglement

density (M_{br} / M_e) and the recoverable compliance increases in direct proportion with M_{br} . The long-time relaxation processes are also governed by the branch relaxation.

In the absence of branch entanglement ($M_{br} < M_c$), the Rouse theory [Pearson and Raju (1982)] predicts that both η_0 and J_e^0 would be smaller for branched chains than for linear chains possessing the same total molecular weight.

2.2.2. Prior experimental work in linear and nonlinear rheology of polyolefins

In a detailed study on shear creep-recovery on the widely characterized IUPAC low-density polyethylenes (LDPE), Agarwal and Plazek (1977) reported that higher polydispersity M_w / M_n results in greater nonlinearity in the recovery behavior, and higher equilibrium recoverable compliances. For the three LDPE studied, the differences in recoverable compliances were more enhanced at lower creep stresses and shear strain rates. Random, profuse long-chain branching (LCB, branches much longer than the entanglement length, $M_{br} \gg M_e$) as observed in low-density polyethylenes (LDPE) however makes it difficult to separate the effects of LCB and polydispersity. Higher recoverable compliance with increasing LCB density was also recorded in random long-chain branched polybutadienes [Kasehagen and Macosko (1996)] – however, the samples with higher LCB density also possessed broader molecular weight distribution.

Extensional behavior, on the other hand, has been widely studied for several types of polyolefins – LLDPE [Munstedt et al. (1998), Bin Wadud and Baird (2000)], HDPE, [Munstedt and Laun (1981)], LDPE [Munstedt and Laun (1981)], as well as polypropylenes [Kurzbeck et al. (1999), Lanfray and Marin (1990), Fulchiron and Verney (1993)], and polybutadienes [Kasehagen and Macosko (1998)]. A recent paper by Gabriel and Munstedt (2003) provides a good summary of several prior works with polyethylenes and polypropylenes. Extensional strain hardening is very pronounced in the presence of sparse or profuse LCB. Presence of high molecular weight tail or high polydispersity also result in strain hardening. Linear polybutadienes studied by Kasehagen and Macosko (1998), as well as HDPE studied by Munstedt and Laun (1981) exhibited pronounced extensional strain hardening.

Kasehagen et al. (1998) also demonstrated that nonlinearity in extension is not governed by the degree of sparse LCB alone. They observed no correlation between the degree of sparse LCB and the degree of strain hardening. This observation is even more significant in the light of the fact that the polymers with higher degree of LCB also had greater polydispersity. Kasehagen and Macosko (1998) demonstrated that nonlinearity in extension is not governed by the degree of LCB alone. They conclude that addition of small amounts of a high molecular weight fraction can lead to greater strain hardening.

2.2.3. Rheology of short-chain branched polyolefin copolymers

Characterization of polyolefin random copolymers with short-chain branches has gained more importance with the advent of metallocene catalysts which produce polyolefin copolymers with a narrow comonomer distribution. Metallocene catalysts are also known to incorporate sparse degrees of long-chain branching [Dekmezian et al. (2002), Lohse et al. (2002), Beigzadeh et al. (2001), Kokko et al. (2000)]. Of course, sparse LCB in such copolymers cannot be detected by the standard chromatography or NMR techniques [Wood-Adams and Dealy (2000), Janzen and Colby (1999), Shroff and Mavridis (1999)] and only indirect evidence has been obtained from rheological techniques. Most commonly, very high flow activation energies which are close to that of LDPE melts [Malmberg et al.(2002), Bin Wadud and Baird (2000), Vega et al (1998), Villar et al (2001)], high zero-shear viscosities [Gabriel and Munstedt (2003), Chai (2000), Shroff and Mavridis (1999), Janzen and Colby (1999)], and thermorheological complexity [van Gurp and Palmen (1998), Vega et al. (1998)] in LLDPE melts with SCB has been attributed to the presence of sparse LCB. Using these rheological tools, Walter et al. (2000) and Villar et al (2001) have concluded that the possibility of incorporation of sparse LCB increases with decreasing comonomer content, especially at comonomer contents below 14 mol %. On the other hand, Vega et al. (1998) have shown with ethylene-hexene copolymers with exclusively short-chain branching that the flow activation energies increase with increasing SCB density.

Kalyon and Yu (1988) studied the effect of comonomer *type* or short branch length on the melt rheology of ethylene- α -olefin copolymers, by keeping the comonomer content more or less constant. With increasing SCB length, they observed a slower decay of normal stresses following cessation of steady shear flow, and a weaker dependence of strain damping functions on shear strain. The nonlinear rheology of copolymers with varying SCB density is not understood partly because variations in SCB density are often linked with changes in some other important molecular parameter such as polydispersity or sparse LCB [Gabriel and Munstedt (1999)].

In Chapter 4, we have carefully chosen three ethylene-octene random copolymer elastomers, with varying SCB density. The SCB densities have been chosen so as to obtain elastomeric materials. The molecular weights are similar, and the elastomers are all of a low polydispersity. Nonlinear shear creep-recovery and extensional strain hardening measurements have been then related to the SCB density.

2.3. FLOW INDUCED DEFORMATION OF DROPS AND ITS RECOVERY

The effectiveness of these polyethylene-copolymer elastomers as polymer modifiers is in great part governed by the microstructure of the resulting thermoplastic olefin (TPO) blends. The evolution of such microstructure is governed by the properties of the thermoplastic matrix, the elastomeric dispersed phase, the interfacial tension, the deformations and the rates of deformation imposed on the blend during processing. The

final blend microstructure as well as physical properties of the product are governed by recovery following deformations. This recovery may be driven by both interfacial tension as well as elasticity.

The blend systems of greatest relevance are obviously polymer blends in which both components are viscoelastic. But the best available connections between the theory and experiments exist for blends of Newtonian components [Tucker and Moldenaers (2002), Doi and Ohta (1991), Vinckier et al. (1999a, 1999b)], or phenomena in which non-Newtonian effects of the components are not strongly manifested [Palierne (1990), Gramespacher and Meissner (1997), Okamoto et al. (1999)]. The behavior of semi-concentrated blends is described well by droplet models [Taylor (1932, 1934), Hinch and Acrivos (1980), Stone (1994), Maffettone and Minale (1998), Maffettone and Greco (2004)]. In order to understand blend behavior, single droplet studies are an effective method, because they offer precise control of variables, and the fluid and flow parameters may be easily varied. The drop deformation and recovery behavior offers valuable insight into blend behavior. In fact for semi-concentrated blends, in which there are not sufficient mutual drop interactions, the understanding obtained from single drop may be directly extended.

In most processing operations, recovery is observed immediately following some kind of deformation. While the rate of deformation is immaterial when it comes to interfacial tension driven recovery, it would play an important role in viscoelastic recovery, if and when it comes into play. The type and extent of deformation are of

course important factors coming into play during both interfacial tension driven recovery as well as elastic recovery. Therefore, to study the relaxation of flow induced deformation, it is imperative to understand the various fluid and flow factors governing drop deformation behavior.

2.3.1. Parameters

The major variables that come into play during deformation of a Newtonian drop in a Newtonian matrix are: the equilibrium spherical size of the drop r_0 , viscosity of the drop η_d , the viscosity of the matrix η_m , the interfacial tension between the drop and the matrix fluids Γ , the principal rate of deformation G , and the non-dimensional strength of flow α . $\alpha = 0$ for simple shear flow, and $\alpha = 1$ when the flow is purely irrotational. In addition to the parameter α , the drop deformation may then be characterized by two non-dimensional parameters. The first is the viscosity ratio

$$k = \frac{\eta_d}{\eta_m} \quad (2.23)$$

The other non-dimensional parameter is the capillary number Ca , which is the ratio of viscous stresses to interfacial stresses,

$$Ca = \frac{\eta G}{\Gamma / r_0} \quad (2.24)$$

At small deformations, the drop shape may be defined by the deformation parameter shown below [Taylor (1932)]

$$D = \frac{L-B}{L+B} \quad (2.25)$$

In the above equation, $2L$ and $2B$ are the major and minor axis lengths of the drop. $D = 0$ for a spherical drop, and asymptotically reaches 1 at large deformations. At large deformations, it is more convenient to define a stretch ratio,

$$D_{stretch} = \frac{L}{r_0} \quad (2.26)$$

Viscoelastic effects bring in additional fluid constitutive parameters that may govern the drop deformation behavior. While comparing the matrix and drop viscoelasticity, it is common to define a ratio called elasticity ratio K . K may be defined as the ratio of some characteristic relaxation times of the drop and matrix respectively [Mighri et al. (1997)].

$$K = \frac{\lambda_d}{\lambda_m} \quad (2.27)$$

Alternatively, K has also been defined based on the drop and matrix dynamic storage moduli (G') evaluated at some characteristic frequency ω [Levitt and Macosko (1996)]

$$K = \left. \frac{G'_d}{G'_m} \right|_{\omega} \quad (2.28)$$

In addition, a dimensionless number, E , is involved, which may be called an elastocapillary number - the ratio of elastic and interfacial timescales [Greco (2002), Maffettone and Greco (2004)].

$$E = \frac{\text{Elastic Timescale}}{\text{Interfacial Timescale}} \quad (2.29)$$

2.3.2. Experimental Studies on drop deformation and recovery

2.3.2a. Drop Deformation

Several experimental studies and theoretical analyses have attempted to establish correlations between D , Ca , k and α . Among the experimental studies, the most comprehensive studies with Newtonian fluids were performed by Rumscheidt and Mason (1961), Grace (1971), and Bentley and Leal (1986). With the use of a computer controlled four-roll mill, Bentley and Leal were able to precisely control the flow strength α all the way from simple shear to pure extensional flow, in addition to investigating a wide range of Ca , and k .

For low viscosity ratios ($k \ll 1$), the largest steady shapes are long and slender, provided the deformation rates (or capillary numbers Ca) are very large. The flow strength α is not a key parameter here, because the drop remains oriented closer to the extensional axis of the shear flow [Rumscheidt and Mason (1969), Bentley and Leal (1986)]. When drop viscosities are much smaller than that of the matrix, the drop deformation was in fact observed to be greater than that of the macroscopic deformation experienced by the matrix [Delaby et al. (1994), Yamane et al. (1998)]. Yamane et al. observed ratios $D_d / D_m \approx 5/4$ for $k = 0.067$ in instantaneous simple shear deformations.

For high viscosity ratios ($k \gg 1$), the flow strength α is a key parameter governing the deformation of the drop. For $\alpha \leq 0.4$ (high rotational component in flow), it is very difficult to deform the drop, and almost impossible to fragment it in flow. Flows with stronger extensional components however are very effective in deforming the drop at low capillary numbers Ca [Bentley and Leal (1986)]. In contrast to the low viscosity scenario, the drop deformations were observed to be less than the macroscopic deformations imposed on the matrix [Delaby et al (1995)].

For k of $O(1)$, the trends with α are the same as those observed for $k \gg 1$ but no steady shapes are observed.

2.3.2b. Drop Breakup Considerations

Breakup of stretched filaments may occur via two mechanisms – “end pinching” or through capillary instabilities. For viscosity ratios less than 1.0, end pinching has been observed at intermediate aspect ratios (length / diameter) of 10-20 [Vinckier et al. (1998), Stone et al. (1986)] and breakup via capillary instabilities occurs in highly slender drops of aspect ratio greater than 50 [Vinckier et al. (1997)]. For viscosity ratios greater than 1.0, however, retraction without either of these instabilities has been observed up to aspect ratios of 10 [Stone et al. (1986)].

Breakup via end-pinching of the stretched filament

Based on boundary element simulations of drop breakup in viscous systems, Stone and Leal (1989), found that breakup via end pinching occurs over timescales t_{pinch} , given by the relationship

$$\frac{t_{pinch}}{\frac{\eta_m R_0}{\Gamma} \{1+k\}} \approx 25 - 75 \quad (2.30)$$

Higher magnitudes of the ratios correspond to higher viscosity ratios.

Breakup via Rayleigh instabilities

As pointed out by Stone et al. (1986), breakup of stretched filament through Rayleigh instabilities occurs at progressively higher filament aspect ratios with increasing drop / matrix viscosity ratio. When the viscosity of the drop phase is greater than 1.0, drop breakup via such instabilities is not seen up to an aspect ratio of 15.

2.3.2c. Viscoelastic Effects in Drop Deformation and Breakup

Tretheway and Leal (1999) observed that for similar drop / matrix viscosity ratios, the deformation of a viscoelastic drop relative to that of a Newtonian drop was lower. They also observed higher critical capillary numbers for breakup and larger critical deformations in the viscoelastic drop as compared to the Newtonian drops.

This is shown in the Figure 2.5 for a Newtonian and viscoelastic drop of viscosity ratio 14.5. Thus, as the viscoelastic stresses in the drop increase, its deformation decreases at a given capillary number.

The drop deformation is seen to be progressively lower relative to the global deformation imposed on the matrix fluid with increasing elasticity ratios K almost independent of viscosity ratios, as observed by Mighri et al (1997). In fact, the latter studies were performed with viscosity ratios k of $O(1)$ or less, for which experimental

results with Newtonian fluids show the droplet deformation being greater than that of the matrix.

2.3.3. Drop recovery

2.3.3a. Quiescent recovery of fibers and disks without prior deformation history

In the absence of any excess stresses within either the matrix or the drop phase, the recovery of an elongated drop is purely driven by the need to reduce the interfacial area between the two phases. The rate at which this equilibration takes place is governed by the interfacial tension Γ between the two phases (which drives the recovery) and the viscous forces (which offer resistance to recovery). In the absence of flow, the viscous forces can be represented by the Stokes law, with the viscosity being the linear zero-shear viscosity of the phases. Such quiescent recovery driven by interfacial tension is a slow process, especially in melt systems in which the zero-shear viscosity of the phases can be quite substantial. Two such instances are shown in Figure 2.6. Figure 2.6 (a) shows retraction of an imbedded fiber [Cohen et al. (1989)], and 2.6 (b) shows retraction of an imbedded disk [Rundqvist et al. (1996)] of a polymer melt in another immiscible polymer matrix. It should be noted that in both instances, the initial shape of the imbedded polymer at the commencement of recovery ($t = 0$) was not brought about by flow. The inclusions of that initial shape were simply “embedded” inside the matrix – the fiber was

made by extruding the polymer and the disk shape was obtained by compression molding. Consequently, at the commencement of recovery, there were no flow-induced forces in either the matrix or dispersed phase.

Such quiescent recovery of fibers and disks in the absence of any excess stresses can be represented using a balance between interfacial tension forces and drag forces. One such phenomenological model, shown below, was suggested by Cohen et al. (1989)

$$6\pi\chi\eta_{eff}R\frac{dL}{dt} + \Gamma\frac{dA}{dL} = 0 \quad (2.31)$$

In the above equation, R and L are the instantaneous radius and length of the drop respectively, and A is the interfacial area. χ is a hydrodynamic interaction parameter between the drop and the matrix and is a function of the instantaneous drop shape, and η_{eff} is an effective viscosity given by

$$\eta_{eff} = \frac{\eta_m + 1.7\eta_d}{2.7} \quad (2.32)$$

2.3.3b. Drop Recovery following flow-induced deformation

While many studies have focused on drop deformation and breakup, drop recovery following flow-induced deformation is a less widely investigated aspect. The

experimental studies by Bentley and Leal (1986) [also Stone (1994), Tretheway and Leal (2001)] establish the limits for drop breakup – in terms of strain rates, stretch ratios and viscosity ratios – in systems of Newtonian drops suspended in Newtonian fluids during deformation. Within these limits, if deformation is stopped, the drop will recover to its original spherical shape, provided it does not undergo Rayleigh instabilities. Of course, drop recovery in case of Newtonian systems is not a function of the rate of deformation. In viscoelastic systems however, excess elastic stresses develop in the fluid depending on the rate of deformation and the strains imposed. These elastic stresses can be substantial at deformation rates comparable to the polymer relaxation timescales, and at high strains. Studies of recovery following such rapid high-strain deformations are lacking.

One instance in which recovery was studied following high rate and high strain deformation was recovery of polyisobutylene droplet in a polydimethylsiloxane matrix following a step shear strain [Yamane et al. (1998)]. In this study, shear strains of the order of 4-5 were imposed on the system within a few seconds. The Drop / matrix (zero-shear) viscosity ratio was much less than 1 ($60 / 900 = 0.067$). The matrix was not only more viscous, but was also substantially more viscoelastic ($G'_d/G'_m = 6 / 2300 @ \omega = 10 \text{ s}^{-1}$).

During such rapid deformation, the drop was deformed into an ellipsoid flattened in the gradient direction [Also Levitt and Macosko (1996)]. Also, by virtue of the very low viscosity ratio, the drop deformed more than the macroscopic matrix deformation. During recovery, two stages were obvious, as shown in the graph reproduced in Figure

2.7. During initial stages of recovery, for up to about 10 s, the stretch ratio is almost constant. Thus the first stage involved shape change without large contraction in major axis. The second stage involved large contraction at long times. The times required for complete recovery of deformed drops to their original spherical shape became longer as the imposed strain increased. Reduction of droplet strain during the final stages of recovery could be expressed by a unique time constant given by the emulsion model of Palierne; this time constant is independent of the initial drop stretch.

Recovery of drops following extensional deformation was studied by Gramespacher and Meissner (1997) in semi-concentrated blends of polystyrene in PMMA. Both PS and PMMA are highly viscoelastic, and have long relaxation times, and show substantial creep recovery. Following extensional deformation at 0.1 s^{-1} , Hencky strains as high as 3.5 were completely recovered in the drop phase – the recovery was shown to be driven primarily by interfacial tension and required long times.

In the above two studies, even though the individual phases were viscoelastic, elastic effects apparently did not come into play during recovery. This could be because of several reasons. In the Yamane et al. (1998) study, the matrix was much more viscous and viscoelastic as compared to the drop phase. In the Gramespacher and Meissner (1997) study, the deformations were brought about at low rates, and even the matrix and dispersed phases were of comparable viscosity, which means there was substantial viscous resistance to the recovery. Also in these studies, the fluid parameters were not varied to investigate the effects of viscosity and elasticity ratios on the recovery behavior.

A finite element study by Hooper et al. (2001) offers some valuable clues to the factors governing drop recovery in viscoelastic systems. In this study, viscoelasticity was implemented using the Oldroyd-B constitutive equation. From the simulations, it was concluded that viscoelastic drops deformed in Newtonian matrices showed a rapid elastic recovery at timescales shorter than the interfacial timescale, followed by a slower interfacial tension driven recovery at long times. This has been shown schematically in Figure 2.8. As seen in this figure, the viscoelastic drop with a drop Deborah number $De_d = 1.0$ and with drop / matrix viscosity ratio $p = 2.0$ (dotted line) shows rapid initial recoil at timescales $t_r = t / t_\Gamma \ll 1.0$, implying that elastic effects result in retraction at times much shorter than the capillary timescales. This initial recovery of the viscoelastic drop is much faster than a Newtonian drop with $De_d = 0.0$ (solid line) in spite of the fact that the Newtonian drop has much lower viscosity ($p = 0.5$). In Chapter 5, rheological parameters governing rapid recovery of blend microstructure are investigated. Factors governing elastic effects during recovery of suspended elastomeric drops are studied in Chapter 6.

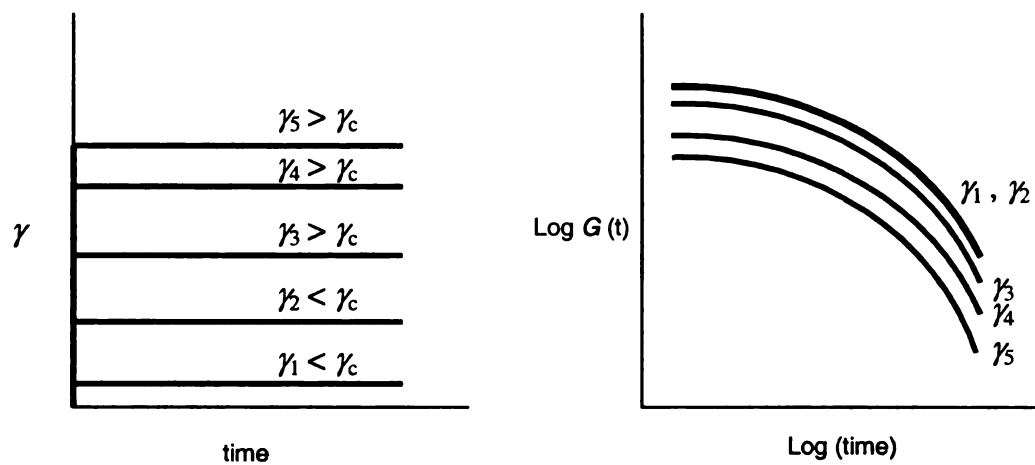


Figure 2.1. Typical flow history imposed on the polymer melt and its response during shear stress-relaxation

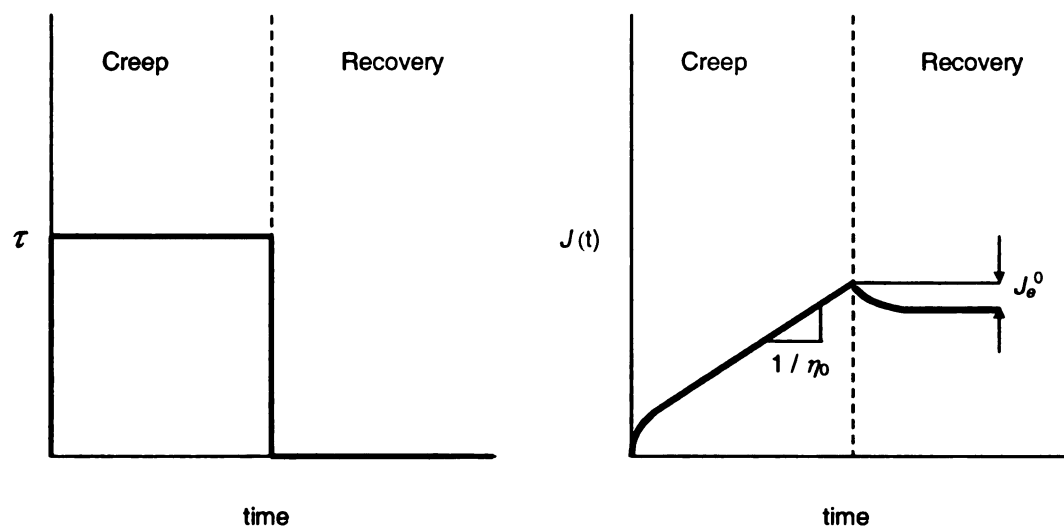


Figure 2.2. Flow history imposed on the polymer melt and its response during shear creep recovery

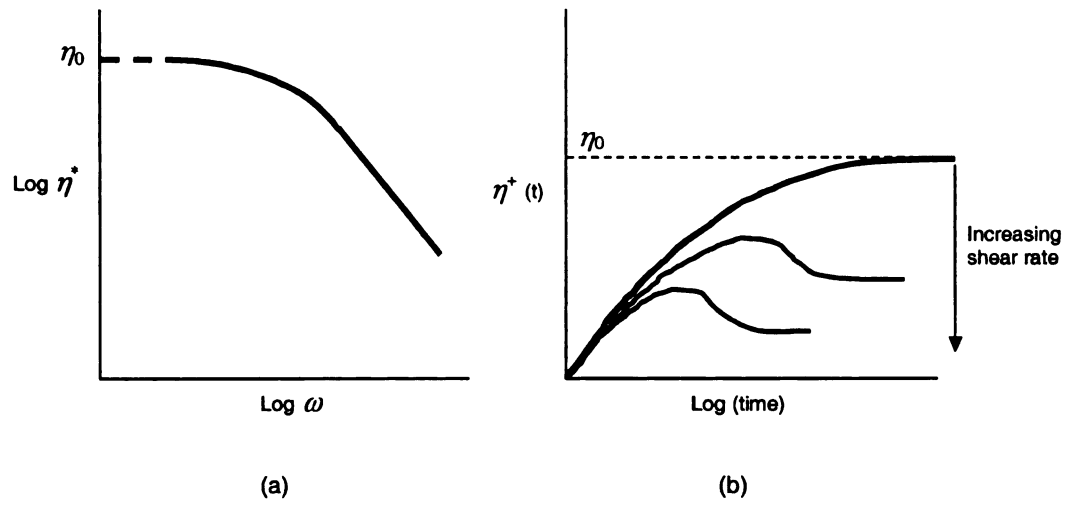


Figure 2.3. (a) Shear thinning and (b) Linear and nonlinear startup shear responses

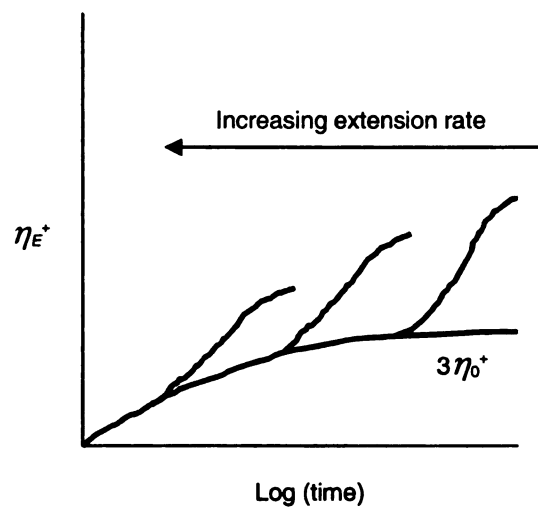


Figure 2.4. Typical linear and nonlinear responses of the polymer melt during extensional flows

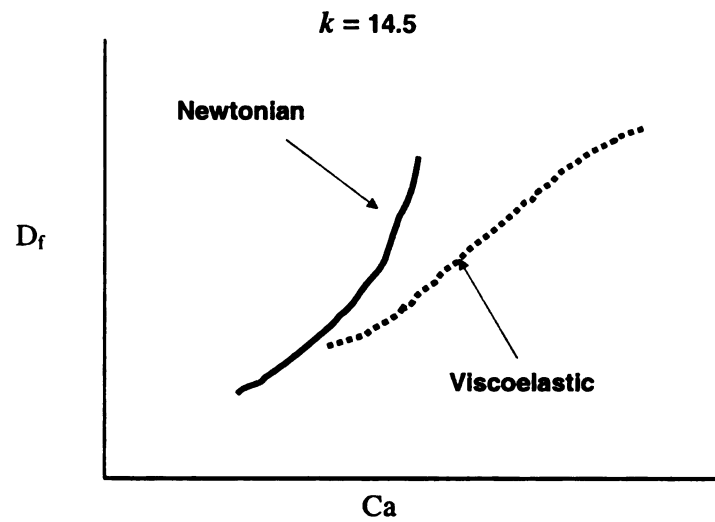


Figure 2.5. Dependence of deformation on capillary number for Newtonian and viscoelastic drops of high viscosity ratio in a Newtonian matrix

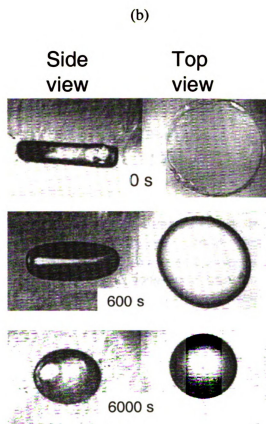
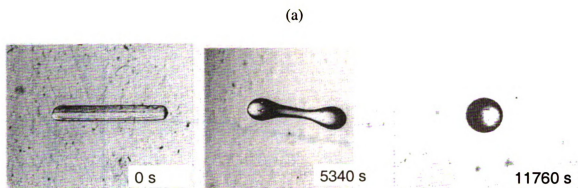


Figure 2.6. Quiescent recovery of drop deformation driven by interfacial tension: (a) imbedded fiber retraction [Cohen et al. (1989)], (b) imbedded disk retraction [Rundqvist et al. (1995)]

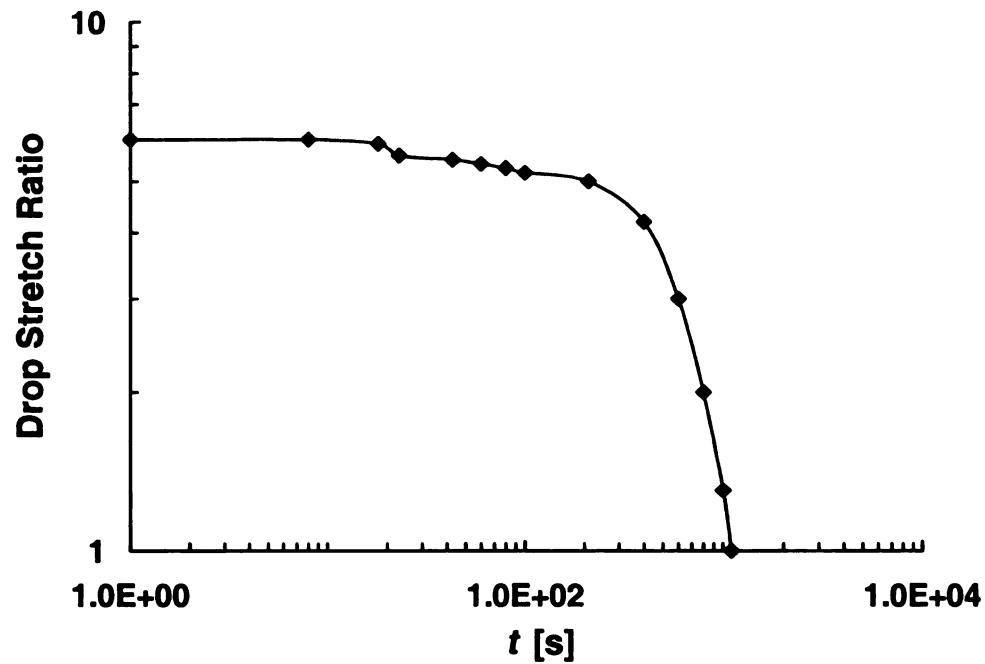


Figure 2.7. Drop relaxation following imposition of instantaneous shear strain [Yamane et al. (1998)]. Drop relaxation proceeds in two stages – the first stage involves shape relaxation to an axisymmetric spheroid, followed by retraction in length. The long time transient may be modeled using Carriere-Cohen (1989) type interfacial-drag force balances

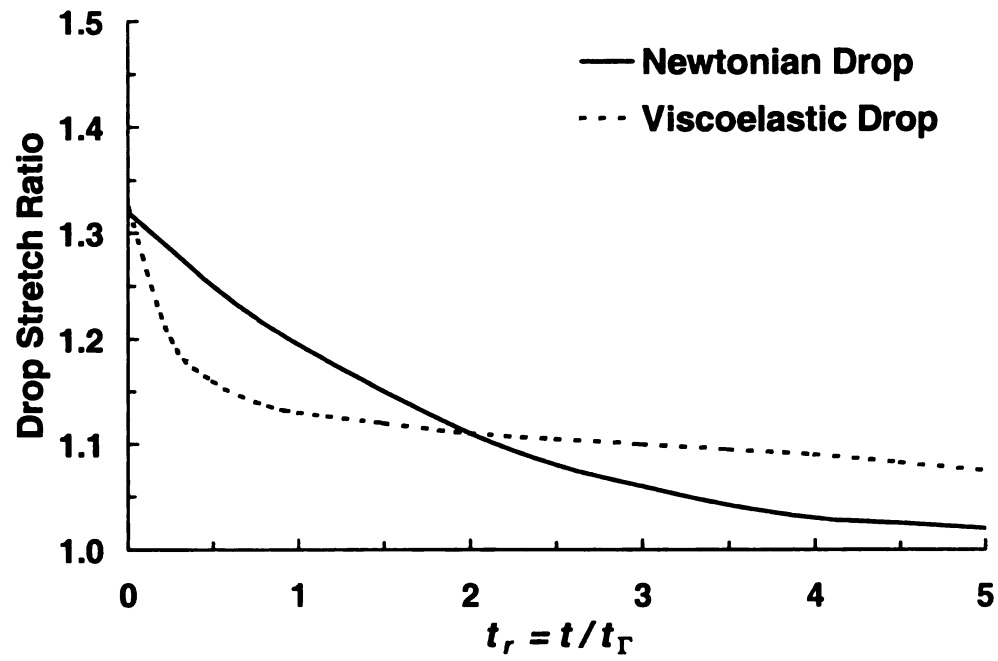


Figure 2.8. Recovery of a viscoelastic drop suspended in a Newtonian matrix following extensional deformation. The curves are predictions obtained by finite element solution of Navier-Stokes equations, with the viscoelasticity of the drop phase incorporated using Oldroyd-B model [Hooper et al. (2001)]

Chapter 3.

MEASUREMENT OF EXTENSIONAL VISCOSITY OF MELTS AT HIGH STRAIN RATES

The extensional viscosity of the melts was determined at high extensional strain rates by employing lubricated “skin-core” flow through semi-hyperboloidal dies fitted in a pressure driven rheometer (Dynisco Kayeness 6052), following an approach similar to that used by Collier et al. [Kim et al. (1994), Pendse and Collier (1996), Collier et al. (1998)]. Originally proposed by Cogswell (1978), this method was first adapted to piston driven rheometers by Everage and Ballman (1978).

3.1. METHOD

A schematic of the experimental setup is shown in Figure 3.1. The semi-hyperboloidal dies have a profile $r^2(z+a)=b$, designed to impose a fixed extensional (Hencky) strain, ϵ_H on the melt flowing through them.

$$\varepsilon_H = Ln\left(\frac{R_B^2}{R_e^2}\right) \quad (3.1)$$

In the above equation, R_B is the inlet radius of the semi-hyperboloidal die, which is the same as that of the rheometer barrel, and R_e is the exit radius of the die. For all the extensional viscosity measurements reported in the subsequent chapters, we employed a semi-hyperboloidal die designed to offer a Hencky strain of 4.88. The profile of the die is shown in Figure 3.2.

The semi-hyperboloidal die profile is designed so as to provide a constant extensional strain rate ($\dot{\varepsilon}$), over its entire length (L) for a given piston velocity (V_P).

$$\dot{\varepsilon} = \frac{V_P}{L} \exp(\varepsilon_H) \quad (3.2)$$

The length of the die was 10 mm.

In order to eliminate shear gradients (due to the presence of die walls) in the test material, the flow of test material melt was lubricated with a low viscosity “skin” made with a high MFR polyethylene (LLDPE, DOWLEX 2503). In Figures 3.3 and 3.4, the shear viscosities of some of the test “core” materials – both thermoplastics (Figure 3.3) and elastomers (Figure 3.4) have been compared with the skin material. As seen from these figures, the viscosities of the core are substantially higher than that of the skin.

This means, that with proper lubrication, most of the shear gradients and the associated pressure drop would be confined to the low viscosity skin. Consequently, almost the entire contribution to the pressure reading measured upstream of the die entrance - using a flush mounted pressure transducer - would come from the plug flow in the high-viscosity core, representative of extension in the test material. This scenario with optimum lubrication has been schematically shown in Figure 3.5 [also refer to Kim et al. (1994)].

Prefabricated skin-core billets, with a core/skin volume ratio of 70/30 to ensure adequate lubrication, were used for measurements. Skin-core billets were fabricated by inserting test polymer core rods of optimum diameter in drilled LLDPE skin rods. The skin-core billet is shown schematically in Figure 3.6. More details on sample preparation are given in Section 3.1.2.

3.1.1 Test protocol

The hyperboloidal die was mounted in the Dynisco Capillary Rheometer. Then the sample (two-layered skin-core billet) was inserted from the top end of the capillary barrel at 110°C. The temperature was then raised to 200°C over the next 20 minutes and the sample was allowed to melt and stabilize for an additional 10 minutes. The plunger ram was then introduced into the capillary barrel, and the sample was extruded through the hyperboloidal die at pre-programmed ram speeds. In lubricated flow tests, only one

ram speed was selected for every billet, while in unlubricated flow tests, several ram speeds could be run with a billet. During a test, the transient pressure was monitored in addition to the quality of the extrudate.

3.1.1a. Pressure transients during lubricated flow through the semi-hyperboloidal die

A typical transient plunger force curve for a single core/skin billet extruded at one flow rate through the hyperboloidal die is shown in Figure 3.7. The transient pressure values are calculated by dividing the transient force with the cross-sectional area of the capillary barrel ($= \pi R_B^2$, where $R_B = 0.00955$ m). When the core/skin billet is melted and then pushed by the plunger ram, initially only the LLDPE melt that is situated at the entrance of the die flows out. Once this supply of LLDPE is exhausted, the PP/LLDPE core/skin sample is pushed out of the die. Concurrently there is a sharp rise in force (hence, pressure) to a peak or a plateau. However, the pressure transients are not monotonic, as with time, there is a gradual or steep drop in force readings, which finally stabilize at a second plateau, where the pressure reading fluctuates about until all the core material is exhausted. When the core material is nearly exhausted a mixture of core and skin LLDPE flows out, and when all core material is out, a precipitous drop in pressure occurs as only some leftover LLDPE is flowing out. Thus, the lubricated flow takes longer times to reach steady state (hence only one ram rate imposed per sample billet), and also shows a non-monotonic behavior. The force readings are considered relatively stable when the range of variation is less than 3-5% over time, and this is labeled as

steady state. The force readings over this relatively stable portion of the curve are averaged for subsequent calculation of extensional viscosity.

3.1.1b. Lubricated and unlubricated flow of test materials

Better insight is obtained regarding the pressure drop truly representative of extension, when pressure drops of the test material with and without lubrication are compared. As shown in Figure 3.8, the startup pressure transients for skin-core flow measured using a flush mounted pressure transducer, located just upstream of the die entrance, were much longer than those observed for single phase unlubricated flow, and also non-monotonic. The initial peak obtained is similar in magnitude to the pressure recorded for unlubricated flow. This means it takes a finite amount of time for the skin-core flow to establish a steady interface through the length of the semi-hyperboloidal die. The initial peak or plateau at high pressure-drops is therefore indicative of shear contamination. Thus, long times are required to establish steady skin-core flow through the die. Therefore, it is the steady state at lower pressure drops which is truly representative of extension of the test polymer. Such long and non-monotonic transients were observed with the presence of slip at the capillary wall [Hatzikiriakos et al. (1997)]. Shaw (1978) also observed drop in force readings when there was elimination of wall shear stresses with the presence of a lubricant grease. The whole skin-core billet was therefore used for a single piston velocity run, to account for these long and non-monotonic pressure transients during testing. The transient force signals took longer

times to reach near steady values at low piston velocities as compared to those at higher velocities.

When compared to the unlubricated flow, the steady, “lower plateau” pressure drops were lower in skin-core flows, typically by 25 to 30%. The pressure drops in the unlubricated case is sometimes as high as 50% more than that obtained in the lubricated case. Therefore, contrary to the conclusions of Collier et al. (1996, 1998), lubricated skin-core flow is the only way to measure extensional viscosity in semi-hyperboloidal dies. Unlubricated flow has massive shear contamination.

3.1.1c. Correlation for extensional viscosity

As shown by Pendse and Collier (1996), at high Hencky strains, the following expression provides a reasonable estimate of extensional viscosity for these measurements.

$$\eta_E(\epsilon_H, \dot{\epsilon}) = \frac{\Delta P}{\dot{\epsilon} \epsilon_H} \quad (3.3)$$

ΔP is the pressure drop over the die length (with lubrication, ΔP is primarily due to extension in the test polymer). Extensional viscosities of the materials were thus measured at $\dot{\epsilon}$ ranging from 0.5 - 25 s⁻¹. At any given strain rate $\dot{\epsilon}$, the duration of

imposition of extensional flow-field t is equal to the residence time of the melt within the semi-hyperboloidal die, as defined below.

$$t_{res} = \frac{\varepsilon_H = 4.88}{\dot{\varepsilon}} \quad (3.4)$$

3.1.1d. Strain hardening parameter (χ)

The primary aim of these measurements was to understand the strain hardening behavior of the elastomer melts. The strain hardening parameter (χ) in extension was calculated with respect to the threefold linear shear stress function at matching times [Kurzbeck et al. (1999)], as shown below.

$$\chi(\varepsilon_H, \dot{\varepsilon}) = \frac{\eta_E(\dot{\varepsilon}, t = \frac{\varepsilon_H}{\dot{\varepsilon}})}{3\eta^+(t)} \quad (3.5)$$

3.2. SAMPLE PREPARATION

Due to the presence of walls in the test geometry, the contribution of shear to the pressure drop across the die is inevitable. In order to achieve pure uniaxial extensional flow through the die, shear gradients must be eliminated from the test material by

lubricating its flow with a lubricant skin composed of a very low viscosity polymer. This can be ensured in the capillary rheometer using a two-layered billet prepared by completely encapsulating the core polymer (the polymer to be tested) with a low-viscosity polyethylene skin [Pendse and Collier (1996)]. The preparation of a two-layered sample billet consisting of "core" polymer (the polymer to be tested) and a low-viscosity LLDPE polymer "skin" (which provides lubrication) is outlined below. Ideally the samples have to be prepared in the form of concentric cylindrical billets with the sample polymer placed within the skin polymer of uniform wall thickness. Several protocols were attempted for producing the two-layered (skin/core).

In one method, LLDPE rods about 9.55 mm in diameter were molded in the capillary barrel and cored with a 1/4th-inch drill (6.37 mm), before stuffing with flakes of the core sample. The flakes were obtained by first compression molding neat core polymer pellets into thin sheets and cutting them into approximately 1 mm by 1 mm bits. Air voids due to entrapment of air between the flakes could not be avoided. When the LLDPE skin/"stuffed" core was melted and pushed through the hyperboloidal die, LLDPE-rich melt and coated core melt flowed alternatively out of the die. When coated core melt flowed out, there was a sharp increase in pressure, but this was followed up by sharp decreases in pressure as soon as the LLDPE flowed out next. This pattern resulted in huge fluctuations of pressure and as such no steady value could be obtained. Surging and discontinuity in flow out of the die were other problems that were experienced.

In the second method, a compression-molded sheet was rolled up and inserted into the LLDPE cavity. Rolling did not produce very good results for the cores. The transient pressure signals fluctuated wildly in this case too, due to alternating flow of core-rich material and lubricant-rich material out of the die.

Finally, the billets were prepared from extruded rods of the two materials as laid out below.

3.2.1. LLDPE skin samples

A high MFR LLDPE, DOWLEX-2503 (purchased from Dow, MFR = 105) was employed as skin in the skin-core tests to measure extensional viscosity. In order to make LLDPE skins, the LLDPE was melted and conveyed through a single screw extruder (Brabender) at 135°C, and simply collected in hollow polycarbonate rods of appropriate internal diameter. This simple method could be employed due to the low melt temperatures and very low melt viscosity. Upon cooling, the LLDPE melt was allowed to solidify and shrink within the polycarbonate molds, yielding solid rods of diameter 9.4 ± 0.1 cm. These rods were cut to a length of 111 ± 1.5 mm and cored from one end to a diameter of 8.1 mm and a depth of 85 ± 5 mm, leaving a 25 mm length of material uncored at the other end. Thus, a wall thickness of 0.7-0.9 mm was obtained and this ensured a core: skin volume ratio of 70:30, which is considered ideal for stable core-skin flow.

3.2.2. Thermoplastic core samples

The core polymers and elastomers are much more viscous as compared to LLDPE, and also possess a higher melting point. Therefore they could not be simply collected into hollow rods, given the high pressure-drops and temperatures involved. Therefore a simple fixture was machined for attachment to the extruder outlet. It is shown in Figure 3.9. A hollow aluminum rod fixture with a flange on one end was attached to the extruder outlet, and tightened using a faceplate to prevent leaks. The thermoplastic melt at 180°C was then made to flow through this fixture at very low flow rates in order to prevent imposition of strong shear histories. When the mold was filled with the melt, it was cooled with water on the outside, ensuring no contact between the melt and water. Once cooled, the solid rod was pushed out of the mold by forcing additional melt into the mold. This way, solid PP rods 7.8 mm in diameter and a length of 95 mm were obtained.

3.2.3. Elastomer core samples

Unlike the thermoplastic samples that are rigid solids at room temperature, the elastomers are very flexible and compressible. Therefore the arrangement described above for thermoplastic samples could not be used for elastomers, since pushing solid

elastomer rod out of the mold is not feasible. Therefore an alternative arrangement was devised. An aluminum mold was made with two faces which could be attached together, each face containing a hemi-cylinder of the appropriate core radius, as shown in Figure 3.10. The two faces were attached, and the resulting mold was screwed into the extruder outlet with matching threads. The mold was then heated using a propane torch, and elastomer melt at 150°C was allowed to flow into it at very low flow rates to prevent any substantial shear deformation. When the melt had filled the mold, it was unscrewed from the extruder outlet, and allowed to cool down to room temperature. Once cooled, the screws holding the two faces of the mold were removed and the mold was dismantled to obtain an elastomer rod. During this process care was taken to discard samples which showed evidence of thermal degradation, e.g., a drastic increase or decrease in torque while being conveyed through the extruder screw, or darkening of color etc.

3.3. VALIDATION OF EXTENSIONAL FLOW MEASUREMENTS

3.3.1. Measurements with varying core / skin viscosity ratio

Using numerical simulations of core-skin flow through a planar converging semi-hyperbolic channel, Kim et al. (1994) concluded that in order to effectively reduce the pressure drop due to shear, the core / skin viscosity ratios should be ideally greater than 30 – but any viscosity ratio greater than 10 was considered to be effective in eliminating

the shear gradients in the test polymer core resulting in plug flow through the core [cf. Figure 3.5]. This implies that with proper lubrication, the pressure drop through the planar semi-hyperbolic (or in this study, axisymmetric semi-hyperboloidal) convergence should be independent of the viscosity ratios. To test the effectiveness of lubrication, two skin materials were employed. The viscosities of the skin with respect to the test polymer core at the measured deformation rates were about 1/250 and 1/600 respectively. Figure 3.11 shows the transient pressure drop growth through the semi-hyperboloidal die for skin-core flow at the same ram rate with the two skin materials. The two curves are not very different from each other, showing that the lubrication is effective in reducing the shear pressure drop through the core and the measured steady state pressure drops are indeed representative of extension in the test polymer.

3.3.2. Measurements with varying skin thickness

In core skin flow through any geometry, the interface between the core and skin attains a profile which is a function of the volumetric flow rates within the skin and core and the viscosity ratios [Kouris and Tsamopoulos (2001)]. If the core / skin volume ratio is less than 60 / 40, this would result in an unstable interface and improper lubrication through the die [Joseph et al. (1997)]. However, in addition to ensuring proper lubrication, we also have to ensure that the pressure drops may be unambiguously attributed to extension in core – or in other words they are not contaminated by shear flow of skin. In order to ensure this, extensional viscosity was estimated using skin-core

flow with two different skin thicknesses – resulting in core / skin volume ratios of 70 / 30 and 63/ 37 respectively. As seen from the startup pressure transients in Figure 3.12, for both thickness values, stable flow was attained, and the steady pressure drop was less than that obtained with unlubricated flow. But more importantly, the two steady state pressure drops are the same. This means that the pressure drop in skin-core flow is truly representative only of the core and is not contaminated by the pressure drop due to shear flow in the skin. For all the measurements reported in the subsequent chapters, the thinner skin thickness was employed to ensure enough core volume so as to avoid any core-skin instabilities.

3.3.3. Comparison with RME Data

In Table 3.1, the extensional viscosities measured using a semi-hyperboloidal die offering a Hencky strain 2 are compared with the transient extensional viscosity measured using a Rheometrics Melt Extensiometer [e.g., Schweizer (2000)]. The values obtained from the two methods are compared for two polymers at an extension rate of 1.0 s^{-1} and at a temperature of 180°C . For comparing the data, the viscosity value corresponding to a Hencky strain of 2 was extracted from the transient viscosity growth curves. For both melts, viscosity estimated from the two methods are similar in magnitude, thus giving us greater confidence in our data. While the methodology was validated using a Hencky strain 2 die, all the measurements reported in this thesis have been conducted using a semi-hyperboloidal die offering a Hencky strain 4.88.

Measurements with the Hencky strain 2 die are more difficult to perform given the low force readings due to the large exit diameter of the die. However, measurements with the Hencky strain 4.88 die were more difficult to validate with the RME data because in these rheometers, it is very difficult to obtain such high strains. On the other hand, we could not obtain polymers for which extensometer data existed at such high strains. Therefore, these measurements were checked with an approximate method based on entrance pressure drop measurements as described below.

3.3.4. Comparison with Cogswell's Estimates

The extensional viscosities measured using lubricated flow of melts through semi-hyperboloidal die offering a Hencky strain of 4.88 were compared with estimates of extensional viscosity obtained from entrance pressure drop data for flow through capillary dies using the analysis of Cogswell [Cogswell (1972, 1978), Padmanabhan and Macosko (1997), Mackay and Astarita (1997)]. For measuring entrance pressure drops, three capillary dies of diameter 1.0 mm and L/D 10, 20 and 30 respectively were employed. The pressure drops obtained for a given strain rate $\dot{\gamma}$ for flow through the three L/D dies were extrapolated to $L / D = 0$ to obtain the entrance pressure drop, as shown in the Bagley plots of Figure 3.13.

Cogswell (1972, 1978) developed the relationships laid out below by suggesting that the entrance pressure drop for at the abrupt contraction at the entrance of the

capillary die from the melt reservoir has both shear and extensional contributions. The shear viscosity was assumed to obey power law, and the extensional viscosity was assumed constant through the length of the contraction. In the converging region the flow was assumed to be locally fully developed. In our measurements of entrance pressure drop, ΔP_{en} , this sudden contraction at the die entrance was equivalent to a Hencky strain of 4.5.

$$\epsilon_{H, Capillary Die Entry} = \ln \left(\frac{Diameter of Barrel}{Diameter of Capillary Die} \right)^2 = \ln \frac{9.55^2}{1.0^2} = 4.5 \quad (3.6)$$

This equivalent Hencky strain is similar in magnitude to the Hencky strain of 4.88 offered by the semi-hyperboloidal Die. Cogswell (1972) suggested the following approximate relationships to evaluate extensional viscosity from entrance pressure drop data obtained at various strain rates. For an abrupt contraction as in a die entrance, the fluid was assumed to define its own convergence profile corresponding to a minimum pressure drop. Based on this criterion, the extensional strain rate upstream of the die entrance was given to be

$$\dot{\epsilon}_{entrance} = \frac{4}{3(n+1)} \frac{\tau_w}{\Delta P_{en}} \dot{\gamma}_{apparent} \quad (3.7)$$

In the above equation, τ_w is the wall shear stress, and n is the power law index of the shear viscosity ($\eta = K \dot{\gamma}^{n-1}$). The extensional stress is estimated as

$$\tau_{11} - \tau_{22} = \frac{3}{8} (n+1) \Delta P_{en} \quad (3.8)$$

The results of this approximate analysis and the extensional viscosities measured using lubricated skin core flow through the semi-hyperboloidal die are compared in Figure 3.14. As can be seen, the two measures of extensional viscosity overlap well with each other. Cogswell type analysis has been used in the past by other authors to validate their extensional viscosities measured using melt extensimeters [Laun and Schuch (1989), Hingmann and Marczinke (1994)].

Table 3.1. Comparison of extensional viscosities of two polypropylenes measured at 1.0 s^{-1} using lubricated skin-core flow through the semi-hyperboloidal die with η_E^+ ($\dot{\epsilon} = 1.0 \text{ s}^{-1}$, $t = \frac{\epsilon_H}{\dot{\epsilon}} = 2$) measured using Rheometrics Melt Extensiometer (University of Minnesota), both at 180°C

Polymer	RME	MSU Die
PPA	$7.0 \times 10^4 \text{ Pa-s}$	$7.41 \times 10^4 \text{ Pa-s}$
Pro-fax SD613	$1.1 \times 10^5 \text{ pa-s}$	$8.35 \times 10^4 \text{ Pa-s}$

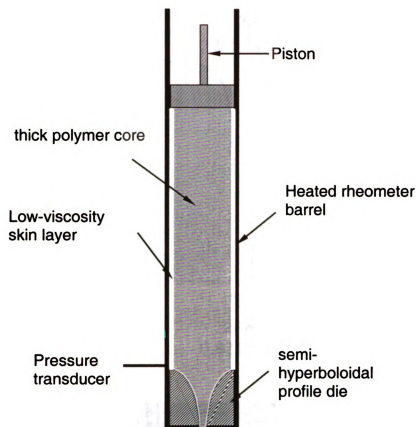


Figure 3.1. Modified capillary rheometer setup to measure the extensional viscosity of polymer and elastomer melts

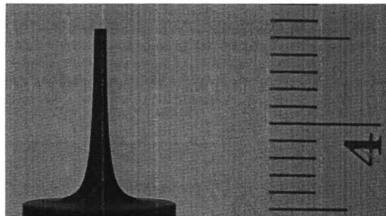
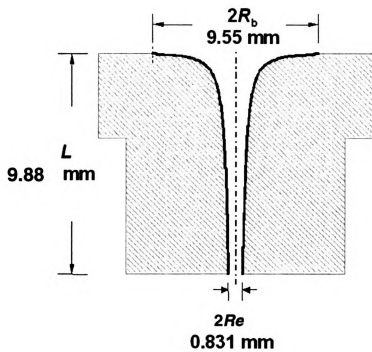


Figure 3.2. Semi-hyperboloidal profile converging die to achieve constant extensional strain rate

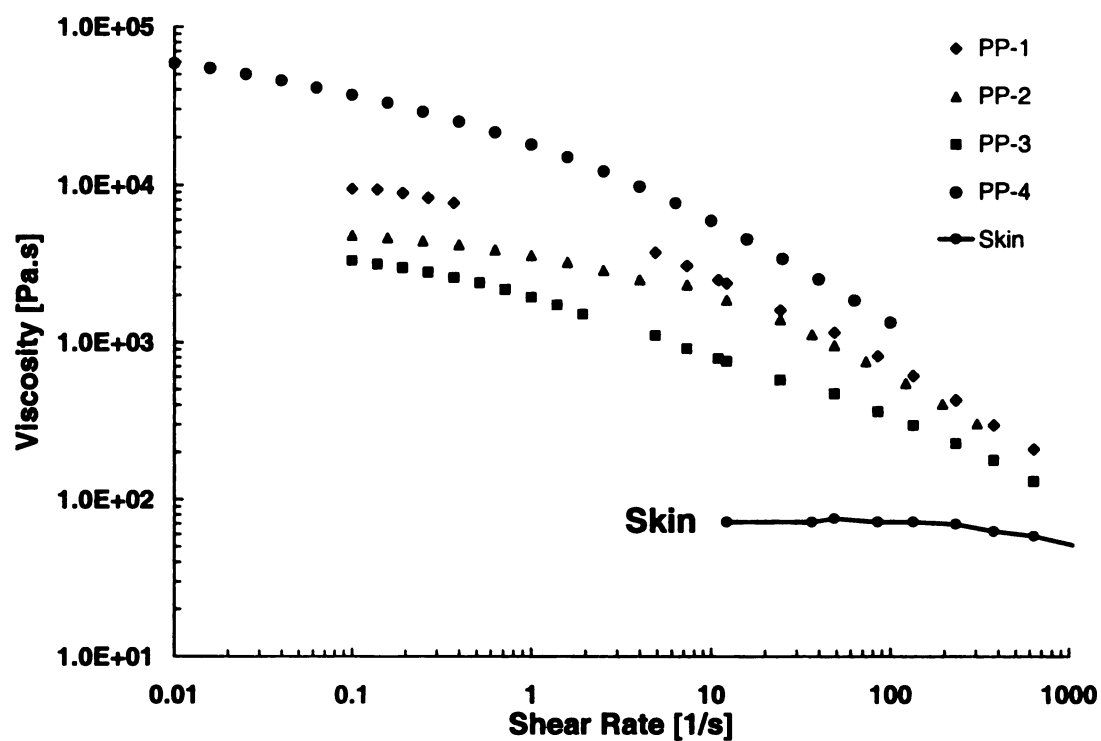


Figure 3.3. Shear viscosities of some of the thermoplastic polymer core melt samples compared with that of the LLDPE skin, at 200°C

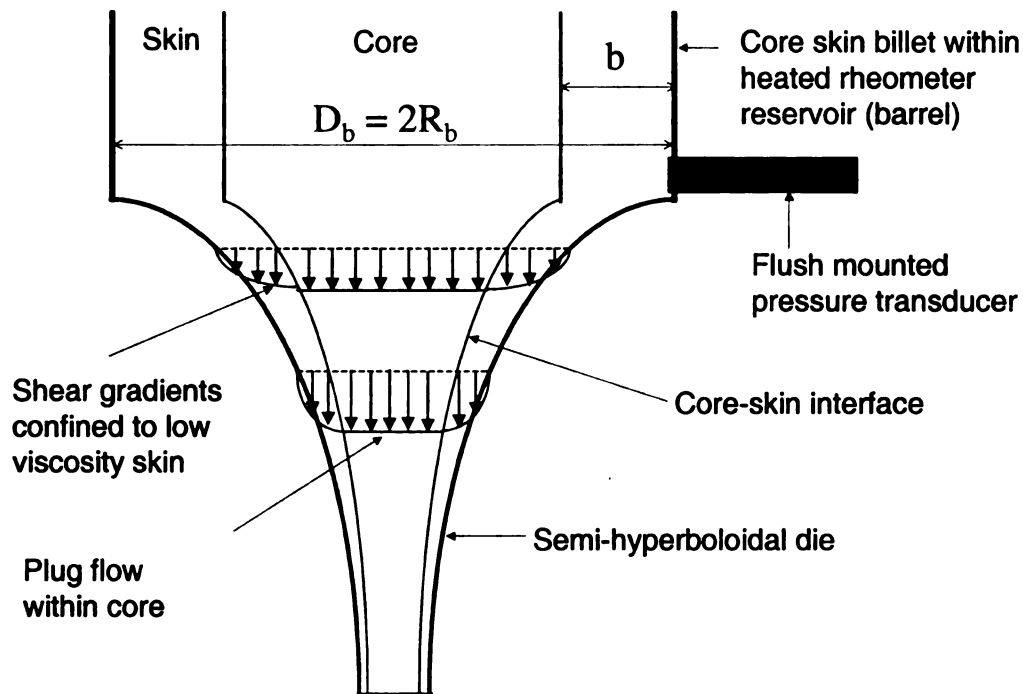


Figure 3.5. Schematic representing skin-core flow of the test material through the semi-hyperboloidal converging die, with optimum lubrication. The skin thickness, b , has been exaggerated in this figure for purpose of clarity. Typically, the skin thickness is about 14% of the reservoir (barrel) radius R_b

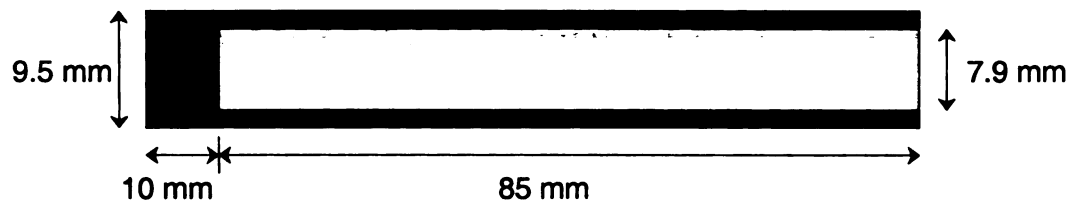


Figure 3.6. Skin-core sample for achieving lubricated flow through the semi-hyperboloidal profile converging die

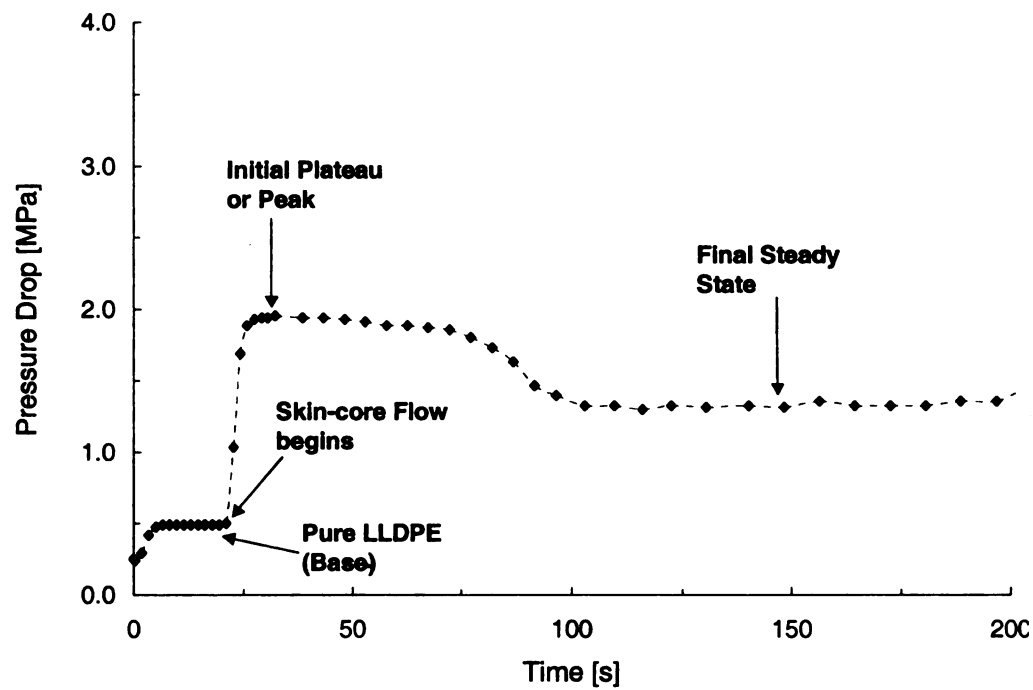


Figure 3.7. Typical startup pressure transients during the measurement of extensional viscosity using skin-core lubricated flow through the semi-hyperboloidal die

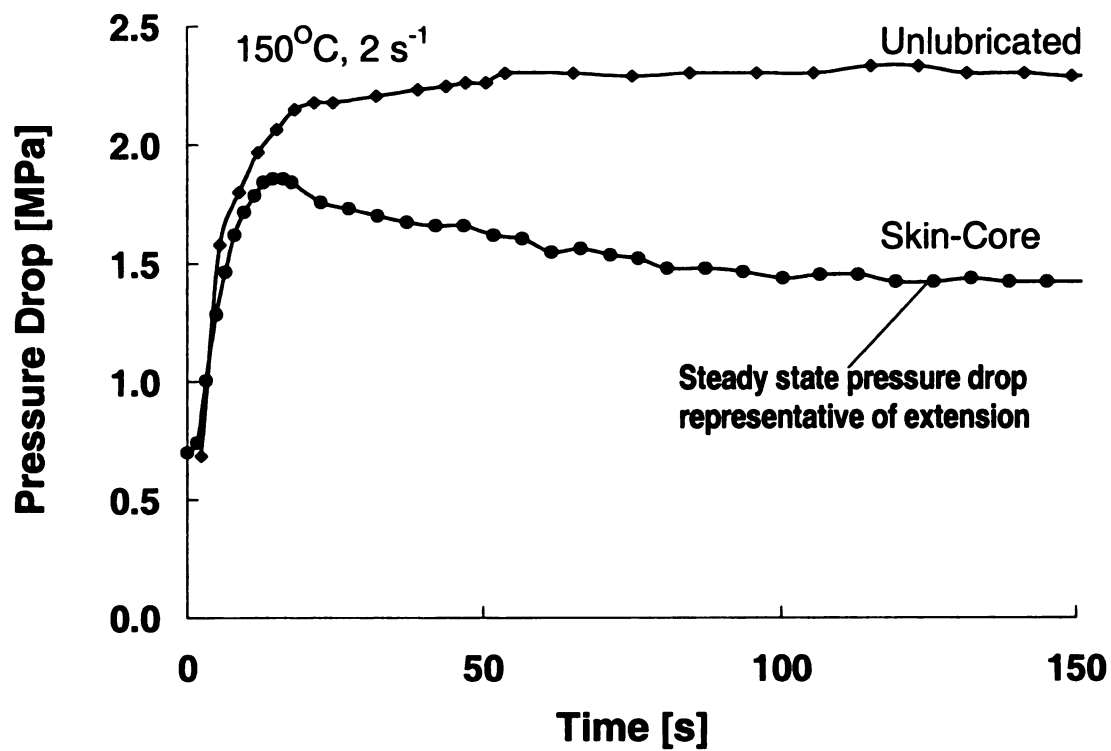


Figure 3.8. Steady state pressure drops obtained at several piston velocities using lubricated skin-core flow compared with the pressure drops obtained using unlubricated flow of the test material through the same die.

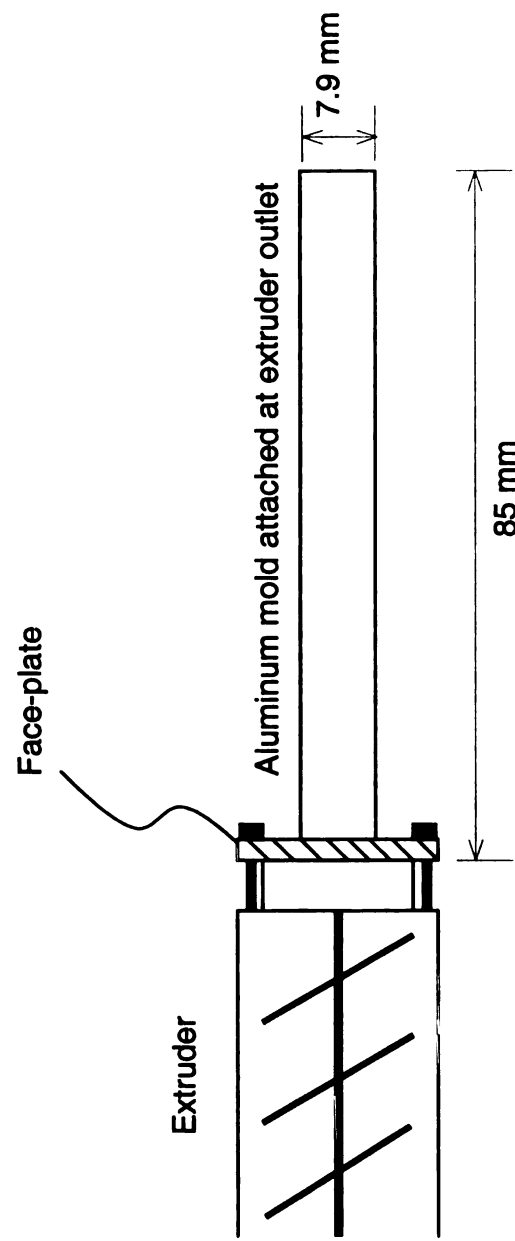


Figure 3.9. Setup for preparation of thermoplastic core samples

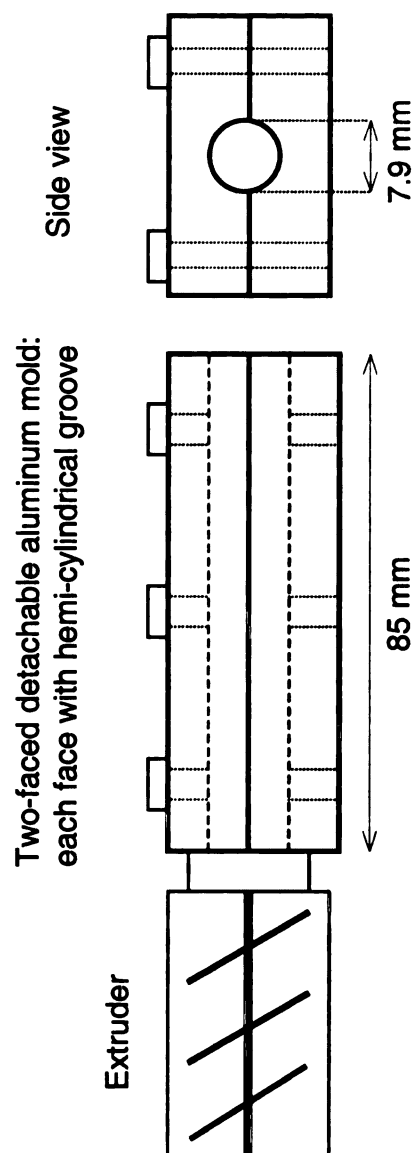


Figure 3.10. Setup for preparation of elastomeric core samples

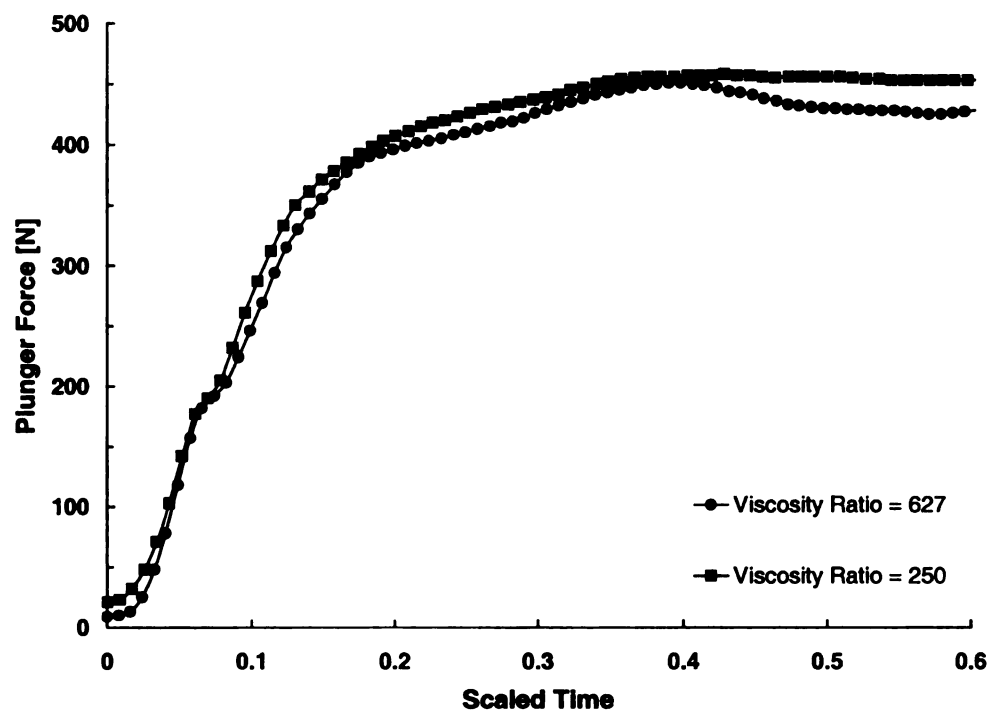


Figure 3.11. Startup pressure transients for lubricated skin-core flow through the semi-hyperboloidal die. Measurements with two different core / skin viscosity ratios, carried out at a strain rate of 1 s^{-1} and at 200°C are shown. The test material is a branched polypropylene, grade SD613 (Basell Polyolefins Inc.). Time has been scaled by the ratio sample-length / ram-rate.

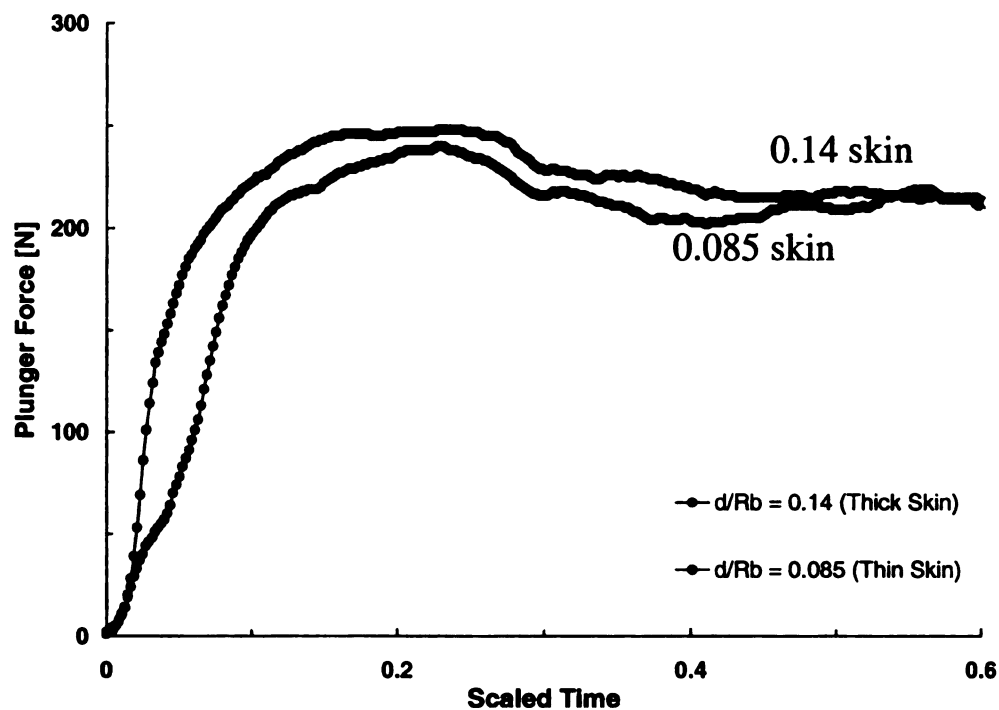


Figure 3.12. Startup pressure transients for lubricated skin-core flow through the semi-hyperboloidal die. Measurements shown above have been carried out with two different skin thicknesses resulting in core / skin volume ratios of 70/30 and 63/37 respectively. The measurements were carried out at a strain rate of 1 s^{-1} and at 200°C , for a linear polypropylene grade Pro-fax 6523 (Basell Polyolefins Inc.). Time has been scaled by the ratio sample-length / ram-rate. d/Rb , is the ratio of skin thickness and the capillary barrel radius.

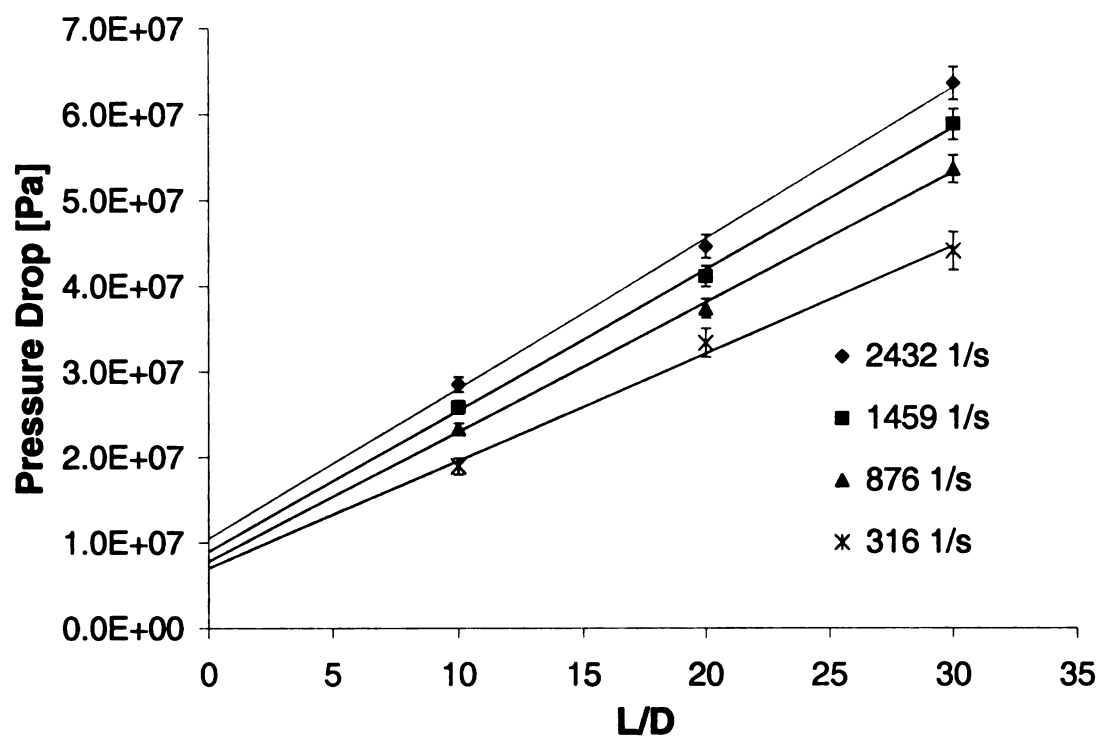


Figure 3.13. Bagley plot for obtaining ends pressure drop for shear flow through straight capillaries of diameter 1.0 mm. The material tested was an ethylene-propylene random copolymer elastomer – DOWLEX CO034 at 150°C. The entrance pressure drops were used for estimation of extensional viscosity using Cogswell analysis

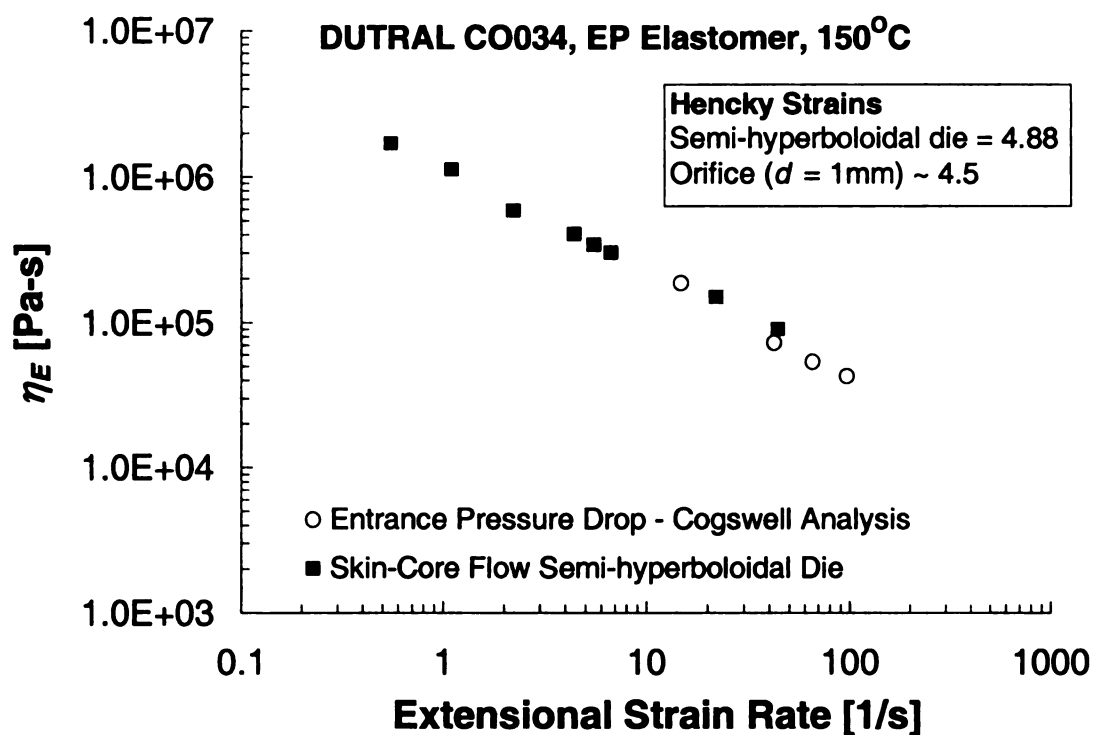


Figure 3.14. Comparison of estimates of extensional viscosity obtained from skin-core flow through the semi-hyperboloidal profile converging die and that from Cogswell analysis of entrance pressure data obtained from Bagley plots. The data were obtained on an ethylene-propylene random copolymer elastomer – DOWLEX CO034 at 150°C. The semi-hyperboloidal die offered a Hencky strain of 4.88 while the straight capillary die of 1.0 mm diameter effectively offers a Hencky strain of 4.5

Chapter 4.

MELT RHEOLOGY OF ETHYLENE-OCTENE RANDOM COPOLYMER ELASTOMERS: EFFECTS OF SHORT-CHAIN BRANCHING DENSITY

SUMMARY

The effects of varying short chain branch density (SCB) on the melt rheology of random copolymers have been investigated. In particular, the strain-hardening behavior in extensional flow and strain recovery following nonlinear shear creep have been evaluated for three different ethylene octene copolymers with octene content ranging from 20 to 40 wt % and having similar molecular weights. The rheological trends have been carefully analyzed to contrast them with those obtained in the presence of sparse long chain branching or a small high molecular weight fraction. The zero-shear viscosity followed trends in the backbone molecular weight closely, which decreases with increasing SCB. While the three copolymers were indistinguishable in linear viscoelastic creep and recovery, recovery following nonlinear shear creep decreased progressively with increasing SCB density. This reveals that the extent of rapid chain equilibration that occurs over Rouse time scales at higher strains was progressively lower with increasing

SCB density. Strain hardening in uniaxial extensional flow was observed for all three copolymers over strain rates of 1 to 7 s⁻¹ with the help of lubricated flow in semi-hyperboloidal dies. At strain rates below the primitive chain equilibration rates, strain hardening increases progressively with increasing SCB density. At higher rates, upon onset of primitive chain stretch, the strain hardening behavior for the three melts merges.

4.1. INTRODUCTION

Random copolymers are of commercial importance for use as compatibilizers and as elastomers. They can be linear or branched. Among branched copolymers, when chain entanglements are present along both the backbone and the branches, these are referred to as long chain branched; short branches are not entangled. Ethylene- α -olefin copolymers are random copolymers comprised of a polyethylene backbone and a higher olefin comonomer incorporated in the form of short-chain branches (SCB) – e.g., butene (C4) comonomer is present in the form of ethyl (2-carbon) branches, octene (C8) comonomer is present in the form of hexyl (6-carbon) branches, and so on. Increasing comonomer content or short-chain branching (SCB) density leads to progressive reduction in density, crystallinity and melting point of these copolymers. Elastomeric characteristics are enhanced with increasing SCB density, and become especially prominent with the loss of spherulitic structure at a specific gravity of 0.9 or lower [Bensason et al. (1996), Minick et al. (1995), Shan and White (2004)].

The advent of Dow's INSITE[®] constrained geometry catalyst technology has made it possible to synthesize such random copolymers with a fairly narrow molecular weight distribution [Sehanobish et al. (1994)], and also a narrow comonomer distribution. The versatility of structures achievable with ethylene- α -olefin copolymers has led to their broad applicability in polymer processing – both in “neat” form as well as in the form of polymer modifiers for thermoplastics such as polypropylenes. Therefore the rheology of these copolymers is of great interest. Recent work [] has brought up evidence of rapid recovery of the elastomer phase in injection molding of olefin blends. Hence there is a need to study the nonlinear rheology of ethylene- α -olefin copolymers having high comonomer contents.

4.1.1. OBJECTIVES

The objectives of this work were to investigate the effect of varying short chain branch density ranging from 25 to 50 branches per 1000 carbons in random copolymers on their nonlinear melt rheology including shear creep recovery from high strains and the strain hardening behavior in extensional flow. Since other molecular features such as sparse long chain branching and a small high molecular weight fraction can affect the nonlinear rheology significantly, the presence of these features has been checked with linear viscoelastic tests before studying the nonlinear rheology.

4.2. BACKGROUND

Metallocene catalysts can be used to produce copolymers with a narrow comonomer distribution and polydispersity indices of about 2. This process is also known to incorporate sparse long-chain branching [Dekmezian et al. (2002), Lohse et al. (2002), Beigzadeh et al. (2001), Kokko et al. (2000)]. Sparse LCB cannot be detected by standard chromatography or NMR techniques [Wood-Adams and Dealy (2000), Janzen and Colby (1999), Shroff and Mavridis (1999)] and only indirect evidence has been obtained from rheological techniques. Most commonly, very high flow activation energies which are close to that of LDPE melts [Malmberg et al.(2002), Bin Wadud and Baird (2000), Vega et al (1998), Villar et al (2001)], high zero-shear viscosities compared to a linear polymer of similar molecular weight [Gabriel and Munstedt (2003), Chai (2000), Shroff and Mavridis (1999), Janzen and Colby (1999)], and thermorheological complexity [van Gurp and Palmen (1998), Vega et al. (1998)] in LLDPE melts with SCB have been attributed to the presence of sparse LCB. Using these rheological tools, Walter et al. (2000) and Villar et al (2001) concluded that the possibility of incorporation of sparse LCB increases with decreasing comonomer content, especially at comonomer contents below 14 mol %.

The steady state recoverable shear compliance J_e^0 in the linear regime serves as a rheological indicator of both differences in molecular weight distribution [Ferry (1980), Graessley (1992)] and the presence of small high molecular weight fractions which are

not apparent in GPC curves [Gabriel et al. (1998)]. In a detailed study of shear creep-recovery on the widely characterized IUPAC low-density polyethylenes (LDPE), Agarwal and Plazek (1977) reported that higher polydispersity M_w / M_n also leads to greater nonlinearity in strain recovery. Random, profuse long-chain branching (LCB) as observed in low-density polyethylenes (LDPE) however makes it difficult to separate the effects of LCB and polydispersity. Higher recoverable compliance with increasing LCB density was also recorded in random long-chain branched polybutadienes [Kasehagen et al. (1996)] – however, the samples with higher LCB density also possessed broader molecular weight distribution.

The extensional viscosity of several types of polyolefins has been reported – LLDPE [Munstedt et al. (1998), Bin Wadud and Baird (2000)], HDPE, [Munstedt and Laun (1981)], LDPE [Munstedt and Laun (1981)], polypropylenes [Kurzbeck et al. (1999), Lanfray and Marin (1990), Fulchiron and Verney (1993)], and polybutadienes [Kasehagen and Macosko (1998)]. A recent paper by Gabriel and Munstedt (2003) provides a good review of the elongational flow characteristics of polyethylene and polypropylene. Pronounced strain hardening during extensional flow has been reported for melts with sparse or profuse LCB. Greater strain hardening has also been reported for systems with a high molecular weight tail or higher polydispersity. Linear polybutadienes studied by Kasehagen and Macosko (1998), as well as HDPE studied by Munstedt and Laun (1981) exhibited pronounced extensional strain hardening. Kasehagen and Macosko (1998) demonstrated that nonlinearity in extension is not

governed by the degree of LCB alone. They conclude that addition of small amounts of a high molecular weight fraction can lead to greater strain hardening.

Kalyon and Yu (1988) studied the effect of comonomer *type* or short branch length on the melt rheology of ethylene- α -olefin copolymers, by keeping the comonomer content more or less constant. With increasing SCB length, they observed a slower decay of normal stresses following cessation of steady shear flow, and a weaker dependence of strain damping functions on shear strain. The nonlinear rheology of copolymers with varying SCB density is not understood partly because variations in SCB density are often linked with changes in some other important molecular parameter such as polydispersity or sparse LCB [Gabriel and Munstedt (1999)]. While investigating the rheological trends with respect to SCB density, it is therefore important to choose the copolymers carefully.

In this study, we have characterized three carefully chosen metallocene based ethylene-octene random copolymer elastomers, with varying SCB density. The SCB densities have been chosen so as to obtain elastomeric materials. The molecular weights are similar, and the elastomers are all of a low polydispersity. Nonlinear shear creep-recovery and extensional strain hardening measurements have been then related to the SCB density.

4.3. EXPERIMENTAL

4.3.1. Materials

Three ethylene-octene (EO) random copolymer elastomers from Dupont – Dow were studied here; these were manufactured with INSITE[®] metallocene catalysts. The molecular weights of these copolymers are nearly the same and the octene content varies from 20% to 40%. The copolymer specifications and the physical properties are listed in Table 4.1. It is clear that with increasing comonomer content, the density and the melting point evaluated from differential scanning calorimetry (DSC) tests, decrease. The molecular weights and polydispersity indices for the copolymers are listed in Table 4.2 along with the short chain branch density or SCB, which was evaluated as follows. The available total weight average molecular weight was converted to the number of methylenes (CH_2) in the entire polymer chain. It might be noted here that there is one methyl (CH_3) at the termination point of the short-chain branch corresponding to every methyne (CH), at the start of the short-chain branch point along the polymer backbone.

$$\#CH_2 \text{ in entire chain} = \frac{M_w}{14.027} \quad (4.1)$$

The number of short chain branches was then calculated using the molecular weight of octene (112.22) as shown below

$$\# \text{ SCB} = \frac{M_w (\text{wt\% comonomer})}{112.22} \quad (4.2)$$

The SCB density in terms of number of SCB / 1000 Carbons in the entire polymer chain was evaluated as shown below.

$$\text{SCB Density} = \frac{\# \text{ SCB}}{\# \text{ CH}_2 \text{ in entire chain}} \times 1000 \quad (4.3)$$

The EO copolymers in this study have SCB density in the range 25-50 SCB / 1000 carbons in the polymer. These SCB densities are substantially higher than the values for copolymers studied by Kalyon and Yu (1988), around 8-12 SCB / 1000 carbons, or for the LLDPEs studied by Gabriel and Munstedt (1999).

4.3.2. Shear Rheometry

The elastomers were characterized in several shear flows on a TA Instruments Advanced Rheometer AR-2000, using 25 mm parallel disk geometry. All results in this study are reported at a reference temperature of 150°C. Dynamic testing was conducted at three temperatures, 120°C, 150°C and 200°C and a frequency range of 0.01 to 100 s⁻¹. Strain sweeps were conducted in different frequency intervals to identify the highest strain within the linear viscoelastic regime for each frequency and obtain good signals.

Master curves were obtained at 150°C using time-temperature superposition over the entire frequency range.

Linear shear creep measurements $\gamma(t \leq t_{\max})$ were carried out at low shear stresses for times ($t_{\max}$) long enough to obtain a pure viscous response (a slope of 1.0 on a log-log plot of creep compliance $J(t)$ versus time (t)); the stress was then released and the subsequent recovery $\gamma_r(t' = t - t_{\max})$ was recorded. Nonlinear shear creep was conducted at two shear stresses – 10,000 and 30,000 Pa. At 10,000 Pa, shear strains of the order of 25 were imposed in times of about 100 s. This led to a steady shear rate of about 0.5 s^{-1} . At 30,000 Pa, shear strains of about 75 were imposed in times of about 35 s, which led to a steady shear rate of about 2 s^{-1} . After removal of stresses, recovery was observed for about 1.5 hr.

Stress relaxation was recorded following imposition of shear strains (γ) ranging from 0.05 – 5. For tests at high strains, a 10% overshoot in strain was observed, and the intended strain was attained following a delay, which was never more than 0.075 s. Stress relaxation data were corrected for non-homogeneous shear in parallel plate geometry following Soskey and Winter (1984). Relaxation modulus $G(t, \gamma)$ data at high strains were used to verify time-strain separability. In addition, the linear shear stress growth coefficient, $\eta_0^+(t)$ was measured for the elastomer melts at a shear rate of 0.005 s^{-1} .

4.3.3. Extensional viscosity

The extensional viscosity of the blend components was evaluated by measuring the pressure drop in lubricated “skin-core” flow through semi-hyperboloidal dies fitted in a piston driven Dynisco Kayeness rheometer. This approach was first used with piston driven rheometers by Everage and Ballman (1978) and more recently by Pendse and Collier (1996). The semi-hyperboloidal dies have a profile given by $r^2(z+a)=b$; this is designed to impose a fixed extensional (Hencky) strain, ϵ_H on the melt flowing through the die.

$$\epsilon_H = Ln\left(\frac{R_B^2}{R_e^2}\right) \quad (4.4)$$

In the above equation, R_B is the inlet radius of the semi-hyperboloidal die, which is the same as that of the rheometer barrel, and R_e is the exit radius of the die. In this study, we employed a semi-hyperboloidal die designed to offer a Hencky strain of 4.9. The semi-hyperboloidal die profile is designed so as to provide a constant extensional strain rate ($\dot{\epsilon}$), over its entire length (L) for a given piston velocity (V_P). The length of the die was 10 mm.

$$\dot{\epsilon} = \frac{V_P}{L} \exp(\epsilon_H) \quad (4.5)$$

The flow of test material melt was lubricated with a low viscosity “skin” of a high melt flow polyethylene (LLDPE, DOWLEX 2503). Prefabricated skin-core billets, with a core/skin volume ratio of 70/30 were used for measurements. The whole skin-core billet was used for a single piston velocity run, to allow for long and non-monotonic pressure transients during testing. As shown by Pendse and Collier (1996), at high Hencky strains, the following expression provides a reasonable estimate of extensional viscosity for these measurements.

$$\eta_E (\epsilon_H, \dot{\epsilon}) = \frac{\Delta P}{\dot{\epsilon} \epsilon_H} \quad (4.6)$$

ΔP is the pressure drop over the die length (with lubrication, ΔP is primarily due to extension in the test polymer). Extensional viscosities of the blend components were thus measured at $\dot{\epsilon}$ ranging from 0.5 - 7 s⁻¹.

4.4. RESULTS AND DISCUSSION

4.4.1. Assessment of molecular architecture using linear viscoelasticity

The primary focus of this study was to evaluate the effect of varying short-chain branching density on the nonlinear shear creep recovery and extensional strain hardening

behavior of the short-chain branched ethylene-octene copolymers. As noted earlier, extensional strain hardening and enhanced recovery have been widely noted in polymers with profuse random long-chain branching or with broad polydispersity indices or with sparse long-chain branching or with small amounts of high molecular weight fraction. The latter two molecular features that are particularly relevant to metallocene catalyzed copolymers cannot be detected with standard GPC based techniques but are evident in linear viscoelastic tests. Therefore it is important to examine the linear viscoelastic data carefully before attributing the trends in nonlinear rheology to variation in SCB density. The random copolymers in this study all have polydispersity indices close to 2.0. The remaining molecular features, sparse LCB and small amounts of a high molecular weight fraction may be identified from a pronounced increase of dynamic viscosities at low frequencies, high flow activation energies, enhanced linear steady state recoverable compliances J_e^0 , and thermorheological complexity.

The shear creep compliance curves for EO3 melt at three different creep stresses ranging from 5 – 120 Pa are plotted in Figure 4.1. The creep compliance curves at 5 and 25 Pa match, but there is a noticeable departure in the creep compliance curve at 120 Pa. This indicates that linear response in creep is restricted to very low stresses for these materials. A purely viscous response is also clear at long times from a slope of 1.0 on the log-log plot. Furthermore, Figures 4.2 to 4.4 show that the elastic compliance curves $J_E(t) = J(t) - t/\eta_0$ and the recoverable compliance curves $J_r(t')$ match for a creep stress of 5 Pa confirming linear behavior at this stress level for all the three copolymer melts. Therefore linear viscoelastic parameters reported in this paper were obtained for

all the three elastomers from creep and recovery curves at 5 Pa. The steady shear rates attained in the linear viscous portion of the creep stage were $1 \times 10^{-4} \text{ s}^{-1}$ for EO1, $1.3 \times 10^{-4} \text{ s}^{-1}$ for EO2 and $1.4 \times 10^{-4} \text{ s}^{-1}$ for EO3. The zero-shear viscosities η_0 of the melts at 150°C are listed in Table 4.3.

The variation in zero shear viscosity may be understood from calculations of the molecular weight of the polyethylene backbone as shown below. First the number of pendant methylene (CH_2) in branches was calculated by taking into account the fact that for every octene, two carbons are incorporated in the backbone, thus resulting in a hexyl (six-carbon) branch.

$$\# \text{ pendant } \text{CH}_2 \text{ in branches} = 6 \times (\# \text{ SCB}) \quad (4.7)$$

$$M_{bb} = [\# \text{ CH}_2 \text{ in entire chain} - \# \text{ pendant } \text{CH}_2 \text{ in branches}] \times 14.027 \quad (4.8)$$

The backbone entanglement density was then calculated using the molecular weight between entanglements for polyethylene

$$Z_{bb} = \frac{M_{bb}}{2100} \quad (4.9)$$

Since the three copolymers have similar overall molecular weights, increasing SCB leads to lower backbone molecular weights. In fact, the zero-shear viscosity follows the same

trend as the backbone molecular weight. In other words, the zero-shear viscosity appears to be primarily governed by the backbone-backbone entanglements. This is not surprising, given the fact that the short branches do not participate in the entanglements.

The recoverable compliance curve $J_r(t')$ following linear creep at 5 Pa is plotted in Figures 4.2, 4.3 and 4.4 for EO1, EO2 and EO3 respectively. The corresponding elastic compliances obtained from the creep curves of the melts after subtracting the viscous portion from the creep compliance are also plotted in these figures. From these figures, it is also obvious that steady recoverable compliances are obtained within times comparable to the duration of creep stage. This means that creep has been carried out to times long enough to ensure that the resulting recoverable compliances are independent of duration of creep.

The linear recoverable compliance curves for the copolymer melts have been compared in Figure 4.5 and are very close together at all times. The retardation times required to attain the steady state recovery are also similar. The equilibrium recoverable compliances J_e^0 , listed in Table 4.3 are similar in magnitude. The similarity of J_e^0 for the copolymers in this study therefore rules out differences in the high molecular weight fractions among the materials. This trend is different from reported trends with random long chain branched polybutadienes, where increasing LCB fraction led to significantly larger recoverable compliance in the linear viscoelastic regime [Kasehagen et al. (1996)]. This reflects the additional long time relaxation of the entangled long chain branches.

Dynamic shear moduli evaluated at three different temperatures – 120, 150 and 200°C were used to generate master curves plotted in Figures 4.6, 4.7 and 4.8 for the three different materials with the help of time temperature superposition. The success of time-temperature superposition confirms the absence of sparse long-chain branching in all three materials [cf. Vega et al. (1998)]. The shift factors a_T were evaluated by shifting over the entire frequency range rather than just the zero-shear viscosity. The dynamic loss modulus data were used to estimate discrete relaxation spectra with 11 relaxation times which are listed in Table 4.4. This was done with the help of the NLREG code developed by Honerkaamp and Weese (1993). The discrete relaxation spectra provide good fits to the dynamic data for all the three melts as shown in Figures 4.6 to 4.8. Terminal behavior may be detected at the lowest frequencies on the dynamic moduli plots for EO2 and EO3. Among the dynamic viscosity curves presented in Figure 4.9, it is possible to estimate zero-shear viscosities from the curves for EO2 and EO3; these values are close to those determined from linear shear creep and listed in Table 4.3. Although the dynamic viscosity plot for EO1 too appears to level at lower frequencies, the zero shear viscosity could be estimated only from linear shear creep data which cover shear rates of 0.005 s^{-1} that were not accessible in oscillatory shear.

Flow activation energies (E_a) were calculated from the shift factors assuming an Arrhenius relationship.

$$a_T = \frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T_2} \right) \quad (4.10)$$

Flow activation energies range from 37 kJ/mol to 40 kJ/mol for the three materials. Vega et al. (1998) have reported similar values for a series of ethylene-hexene copolymers without LCB; they also reported substantially higher activation energies for copolymers with sparse long-chain branching. Further confirmation of the absence of sparse LCB is obtained by evaluating an index of LCB with the approach of Janzen and Colby (1999). The resulting values of the relative LCB fraction are: 6.4×10^{-7} LCB/ 10,000 Carbons for EO1 and 1.0×10^{-7} LCB / 10,000 Carbons for EO2. For EO3, an LCB fraction could not be evaluated. These values are similar to values obtained, for example, by Malmberg et al. (2002), for LLDPE without sparse long chain branching.

4.4.2. Stress Relaxation and Tube-Model Parameters

Stress relaxation experiments were conducted on the copolymer melts to estimate characteristic time scales and establish the range over which their nonlinear rheological behavior displays time-strain separability, given by the equation below.

$$G(t, \gamma) = G^0(t)h(\gamma) \quad (4.11)$$

In the above equation, $G^0(t)$ is the time dependent linear (strain independent) viscoelastic relaxation modulus and $h(\gamma)$ is the strain dependent damping function.

In the framework of tube models for polymers without branch entanglements [cf. Doi and Edwards (1978, 1986,) Graessley (1980)], there are two different mechanisms of polymer melt stress relaxation with widely separated characteristic timescales. Following very small deformations, the relaxation of stresses occurs over long times via a slow disengagement of the polymer chain from the tube brought about by “reptation” of the chain parallel to its own contour. This slow mode of relaxation is characterized by a tube disengagement or reptation timescale τ_d . The decay of stress following linear deformations may be modeled using the relaxation spectrum of the polymer (G_i, λ_i) as the summation of exponentials shown below.

$$G^0(t) = \sum_i G_i \exp(-t/\lambda_i) \quad (4.12)$$

Following large deformations however, a rapid equilibration (or retraction) of the polymer chain occurs within the distorted tube, before onset of the slower reptation process. The rapid equilibration stage is characterized by a Rouse timescale τ_R . Thus, within times τ_R , there is a finite relaxation of stress resulting in a lower relaxation modulus at the start of reptation. After the onset of reptation, the relaxation modulus decays with time in the same fashion as $G^0(t)$, leading to time-strain separability (equation 4.11) for times greater than the equilibration timescale τ_R [Takahashi et al. (1993)]. Hence the strain damping function $h(\gamma)$ is a direct measure of the fraction of

stress relaxed via the rapid equilibration of the primitive chain within the distorted tube at a given strain.

The shear stress relaxation curves for the melts have been plotted in Figures 4.10 through 4.12. Linear behavior was observed for the melts at strains of about 0.05. The linear viscoelastic relaxation modulus was also calculated from the relaxation spectra provided in table 4.4 with equation 4.12. The predicted curves of $G^0(t)$ are also plotted in the respective figures along with the experimental data. The predicted curves match well with the experimentally obtained linear viscoelastic relaxation modulus curve at low strains for all the three copolymer melts. Other relaxation modulus curves $G(t, \gamma)$ plotted in Figure 4.10 -4.12 were obtained at strains ranging from 1 to 5. The curves at higher strains as well as the linear viscoelastic modulus curve are all parallel on the log-log plot, establishing time-strain separability of nonlinear response of these melts for times greater than 1s. This would also indicate that the rapid equilibration time scale is less than 1 s for each of the copolymer melts at 150°C.

The reptation time τ_d was determined from the long-time slope on a plot of $\ln G(t, \gamma)$ vs. t , following Takahashi et al. (1993). For each copolymer, the plots of $\ln G(t, \gamma)$ vs. t for different strains were parallel at long times, leading to a single estimate for the reptation time of a given copolymer melt at 150°C. The reptation times have been listed in Table 4.3 along with estimates of the Rouse time scales. The reptation times also follow trends in the backbone molecular weight. Hence, an

approximate value for the Rouse time τ_R was estimated from τ_d and Z_{bb} with the following relation [cf. Larson et al. (2003)].

$$\tau_R = \frac{\tau_d}{3Z_{bb}} \quad (4.13)$$

The maximum strains imposed in the stress relaxation experiments were about 4-5; it is well known that the sample edge is distorted at higher strains in stress relaxation experiments functions [Takahashi et al. (1993), Kasehagen and Macosko (1998)] leading to large errors. Since much higher strains could be reached without sample distortion in nonlinear shear creep recovery experiments, strain damping functions were estimated from the nonlinear shear creep-recovery data with the K-BKZ integral constitutive equation.

4.4.3. Trends in Nonlinear Shear Creep-Recovery

The transients of recoverable strains following creep at 10,000 Pa and 30,000 Pa are compared for the three copolymer melts in Figure 4.13. During creep at 10,000 Pa, shear strains of the order of 25 were imposed in times of about 100 s. This was equivalent to a steady state creep shear rate of about 0.5s^{-1} . At 30,000 Pa, shear strains of about 75 were imposed in times of about 35 s, which was equivalent to steady state shear rate of about 2s^{-1} . These shear rates are substantially higher than the frequencies at which

terminal behavior is obtained for the copolymer melts. In contrast, during linear creep at 5 Pa, steady shear rates of about $1 \times 10^{-4} \text{ s}^{-1}$ were obtained, and the maximum strains imposed were less than 0.5. As seen in Figure 4.13, following nonlinear creep at both stresses, the copolymer with the lowest SCB density (EO1) shows the greatest initial recovery at short times and also the greatest overall recovery. The recoverable strains decrease progressively with increasing SCB density.

These trends offer a clear contrast to the recovery behavior of these melts following linear creep. While J_e^0 values for the three copolymers are close, clear trends with respect to SCB density can be seen in steady state recoverable compliances following nonlinear creep. In Figure 4.14, the steady state recoverable compliances obtained at long times during recovery have been plotted against the maximum strain imposed in the corresponding creep stage. The steady state recoverable compliances obtained following nonlinear creep are lower than J_e^0 for all three melts. Among the three copolymers, EO1 displays the least nonlinearity in terms of variation of steady state recoverable compliance with respect to creep stress or maximum imposed strain. EO3 displays the greatest nonlinearity. Variations in SCB density therefore are significant in governing the recovery following large shear deformations brought about at higher strain rates.

4.4.4. Extensional Viscosity and Strain Hardening

The range of extensional strain rates covered in this study bridge the gap between the range obtained with the RME rheometer, and the range obtained with the approximate Cogswell type die entrance pressure-drop measurements. The extensional viscosities of the copolymer melts, obtained at several extension rates and at a fixed Hencky strain $\varepsilon_H = 4.9$, are compared in Figure 4.15. The error bars in this figure indicate the variation between experimental runs at a given strain rate, and are based on triplicate measurements at the two lowest rates and duplicate measurements at the higher rates. The extensional viscosity decreases with increasing extension rates for all the copolymer melts. The extensional viscosity is progressively higher with increasing density of short-chain branches, the differences being more pronounced at lower rates.

The strain hardening parameter (χ) in extension was calculated with respect to the threefold linear shear stress function $3\eta_0^+$ at matching times [Kurzbeck et al. (1999)], as shown below.

$$\chi(\varepsilon_H, \dot{\varepsilon}) = \frac{\eta_E(\dot{\varepsilon}, t = \frac{\varepsilon_H}{\dot{\varepsilon}})}{3\eta^+(t)} \quad (4.14)$$

The fixed Hencky strain of 4.9 was translated to the residence time within the semi-hyperboloidal die at each strain rate as seen in the above equation. Thus, at every strain rate, one point along the transient extensional viscosity growth curve at $t = 4.9/\dot{\varepsilon}$ was

obtained. Extensional viscosity data in this form, along with the linear viscoelastic curve $3\eta_0^+(t)$ have been plotted for EO1, EO2 and EO3 melts in Figures 4.16, 4.17 and 4.18 respectively. The linear viscoelastic startup shear viscosity $\eta_0^+(t)$ was determined at 0.005 s^{-1} for each melt. Strain hardening relative to $3\eta_0^+(t)$ is evident at all strain rates for all the three copolymers.

The strain hardening parameter χ (equation 4.14) corresponding to $\varepsilon_H = 4.9$ has been plotted as a function of SCB density at several strain rates in Figure 4.19 for the three copolymers. Pronounced strain hardening ($\chi > 1$) that declines with increasing strain rate is clear for each copolymer. More importantly, at low extension rates, χ is a strong function of SCB density. Strain hardening is progressively higher with increasing comonomer content. The differences in χ for the three copolymers are less pronounced at higher rates. These trends in nonlinear rheology with SCB density are examined with the analysis that follows.

4.4.5. Constitutive analysis of nonlinear shear creep recovery

Nonlinear shear creep recovery data were analyzed using the K-BKZ integral constitutive equation [Kaye (1962), Bernstein et al. (1963,) and Wagner (1978)] to estimate the damping functions over a large range of shear strain. Indirect estimates of damping functions reported in the literature [Fulchiron et al. (1993), Kasehagen and

Macosko [1998]) have been obtained with startup shear experiments. The K-BKZ integral equation for stress $\underline{\underline{\sigma}}(t)$ was used as shown below. .

$$\underline{\underline{\sigma}}(t) = \int_{-\infty}^t \mu^0(t-t') h\{I_1(t,t'), I_2(t,t')\} \underline{\underline{C}}_t^{-1}(t') dt' \quad (4.15)$$

with the time dependent linear viscoelastic memory function

$$\mu^0(t-t') = \sum_i \frac{G_i}{\lambda_i} \exp[-(t-t')/\lambda_i] \quad (4.16)$$

involving the relaxation spectrum of the melt (refer to Table 4.4). The Finger strain tensor $\underline{\underline{C}}_t^{-1}(t')$ in case of shear deformation (γ) is defined as shown below.

$$\underline{\underline{C}}_t^{-1}(t') = \begin{bmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (4.17)$$

The strain damping function $h(I_1, I_2)$ is a function of the first and second invariants of the Finger strain tensor. The form of the strain damping function in shear may be chosen from the Doi Edwards form or the sigmoidal form of Fulchiron and Verney (1993) given below. The sigmoidal form offers a wider range with two adjustable parameters a and m and provided a better fit to our data.

$$h(\gamma) = \frac{1}{1 + a\gamma^{2m}} \quad (4.18)$$

Using equations 4.16, 4.17 and 4.18, the shear stress (equation 4.15) is given as shown below

$$\begin{aligned} \sigma_{12}(t) = & \int_0^t \left\{ \sum_i \frac{G_i}{\lambda_i} \exp[-(t-t')/\lambda_i] \right\} \frac{\{\gamma(t) - \gamma(t')\}}{1 + a\{\gamma(t) - \gamma(t')\}^{2m}} dt' \\ & + G^0(t) \frac{\gamma(t)}{1 + a\{\gamma(t)\}^{2m}} \end{aligned} \quad (4.19)$$

During the creep stage, the stress is fixed at a finite value ($\sigma_{12}(t \leq t_{\max}) = \sigma_{\text{creep}}$) while during recovery stage it is set to 0 ($\sigma_{12}(t > t_{\max}) = 0$). Equation 4.19 is a nonlinear Volterra integral equation of the second kind in the shear strain; this was solved for $\gamma(t)$ using successive integration, with solutions for all past times $\gamma(t')$ known [cf. Wagner and Laun (1978)]. In Figure 4.20 (a-c), the K-BKZ model predictions for creep and recovery at a creep stress of 30,000 Pa have been compared with experimental creep and creep recovery data. As seen from the figure, this procedure provides very good fits to the experimental data for all the copolymers. For each copolymer, the same magnitudes of the fitting parameters a and m gave equally good fits to creep and recovery data at a stress of 10,000 Pa. Thus this analysis gives a reliable way of obtaining damping functions at high strains.

4.4.6. Damping functions

The dependence of damping function on strain is plotted for the three copolymers in Figure 4.21; the damping function fitting parameters a and m are listed in Table 4.5. Upon inspection of this figure, it is clear that at high strains, the dependence of damping function on strain becomes progressively weaker as the SCB density (comonomer content) of the copolymers increases. The exponents m , are progressively lower with increasing comonomer contents. A weaker strain-dependence in the damping function may be interpreted as increased resistance to the equilibration of the extended primitive chains. In other words, the polymer chains become progressively stiffer as the SCB density increases.

The trends in nonlinear recoverable compliance for the ethylene-octene copolymers, together with those in strain dependence of damping function are interesting in that they offer a striking contrast to those obtained with random long-chain branched polymers. In this study, with increasing SCB density the damping function shows a weaker dependence on strain, a trend similar to that observed with increasing LCB fraction. However, the recoverable compliance progressively *decreases* with increasing SCB density. This firmly establishes that the nonlinear rheological trends for these copolymers are solely due to variations in SCB density and not due to sparse LCB. It is well understood that LCB profoundly affects the long-time relaxation phenomena of the

melt [Roovers and Toporowski (1987), Yurasova et al. (1994)] and it is these effects that must govern the increase in recoverable compliances. In the case of short-chain branched copolymers in the current study however, the long time relaxation processes are not affected by the short-chain branches, and the absence of any trend in J_e^0 further rules out differences in long time linear relaxation modes. Therefore the progressive decrease in recoverable compliances following nonlinear creep with increasing SCB density must be a consequence of the different degrees of relaxation brought about in the rapid equilibrium stage of relaxation.

It remains to relate chain equilibration phenomena to the extensional flow behavior of these copolymers. The range of strain rates employed in the extensional flow tests includes rates that are faster and slower than $1/\tau_R$, of the copolymer melts. The rate of equilibration (or retraction) of the primitive polymer chain within the deforming tube is given by τ_R^{-1} . When the deformation is imposed at rates higher than τ_R^{-1} , this results in the stretching of the primitive chain [Takahashi et al (1993)]. In Figure 4.22, the strain hardening parameter $\chi(\varepsilon_H = 4.9)$ is plotted against a Deborah number based on the Rouse time scale $De \equiv \dot{\varepsilon} \tau_R$. The strain hardening behavior for the three copolymers merges for $De > 1$, while at lower Deborah numbers, the strain hardening follows SCB density. Greater strain hardening is observed with increasing SCB at $De < 1$ because the melt is stretched slower than the rate of chain equilibration and the chain which relaxes more during this time scale will strain harden to a lesser extent. On the other hand, when the melt is stretched faster than the rate of equilibration of the primitive chain, it does not

retract within the tube, and this results in affine deformation of the chain irrespective of SCB density. This explains the merging of strain hardening curves for the three copolymers at $De \sim O(1)$ or greater.

4.5. CONCLUSIONS

Three random ethylene-octene copolymers with degrees of short-chain branching (SCB) ranging from 25 to 50 per 10 carbons and with similar molecular weights display a strong dependence of non linear shear creep recovery and elongational strain hardening on SCB. The absence of even sparse long-chain branching was confirmed with several linear viscoelastic tests. The similarity of J_e^0 for the three copolymers rules out differences in any high molecular weight fractions among them. Although the steady recoverable shear compliance values are close for strains < 0.5 , they decrease progressively with increasing SCB density at higher strains of 25 to 100. This trend must be a consequence of the different degrees of primitive chain relaxation in the rapid equilibration stage obtained at large strains with different SCB. The extensional viscosity was measured with the help of lubricated skin-core flow through semi-hyperboloidal dies over a range of strain rates broad enough to include rates that are higher and lower than the rate of equilibration of the primitive polymer chain. . At strain rates below τ_R^{-1} , the strain hardening increases progressively with increasing SCB density. At higher rates, upon onset of primitive chain stretch, the strain hardening behavior for the three melts merges.

Table 4.1. Material specifications and physical properties

Copolymers	EO1	EO2	EO3
Octene content [wt. %]	20	30	40
Specific gravity	0.902	0.885	0.870
Melting point [°C]	98	83	48

Table 4.2. Molecular architectural parameters for the EO copolymers

Copolymers	EO1	EO2	EO3
Octene content [wt. %]	20	30	40
M_w [g/mol]	129,900	127,300	127,900
M_w / M_N	2.17	2.01	1.95
SCB Density [# SCB / 1000 C]	25	37.5	50
M_{bb} [g/mol]	110,400	98,700	89,500
Z_{bb}	52.1	46.7	42.4

Table 4.3. Zero-shear viscosities and relaxation times (at 150°C) for the EO copolymers

Copolymers	EO1 [20 wt. % C8]	EO2 [30 wt. % C8]	EO3 [40 wt. % C8]
Z_{bb}	52.1	46.7	42.4
η_0 [Pa·s]	40,300	31,900	28,100
J_e^0 [Pa ⁻¹]	5.71×10^{-4}	4.57×10^{-4}	5.71×10^{-4}
$\tau_1 = \eta_0 J_e^0$ [s]	23	14.6	16
τ_d [s]	46.6	34.8	29.7
τ_R [s]	0.3	0.25	0.23

Table 4.4. Discrete relaxation spectra of the EO copolymer melts at 150°C.

λ_i [s]	G_i [Pa]		
	EO1	EO2	EO3
1.064×10^{-3}	3.095×10^5	2.510×10^5	1.918×10^5
3.342×10^{-3}	2.096×10^5	2.188×10^5	1.750×10^5
1.050×10^{-2}	1.167×10^5	1.640×10^5	1.349×10^5
3.299×10^{-2}	6.685×10^4	9.353×10^4	9.387×10^4
1.037×10^{-1}	2.978×10^4	3.755×10^4	4.413×10^4
3.257×10^{-1}	1.294×10^4	1.374×10^4	1.921×10^4
1.023×10^0	5.766×10^3	4.978×10^3	5.064×10^3
3.216×10^0	1.997×10^3	1.547×10^3	1.640×10^3
1.010×10^1	7.445×10^2	5.280×10^2	4.001×10^2
3.175×10^1	1.455×10^2	1.099×10^2	8.743×10^1
9.976×10^1	5.687×10^1	1.824×10^1	1.525×10^1

Table 4.5. Damping function fitting parameters for the EO copolymer melts

	EO1	EO2	EO3
<i>a</i>	0.045	0.2	0.525
<i>m</i>	1.125	0.7	0.5

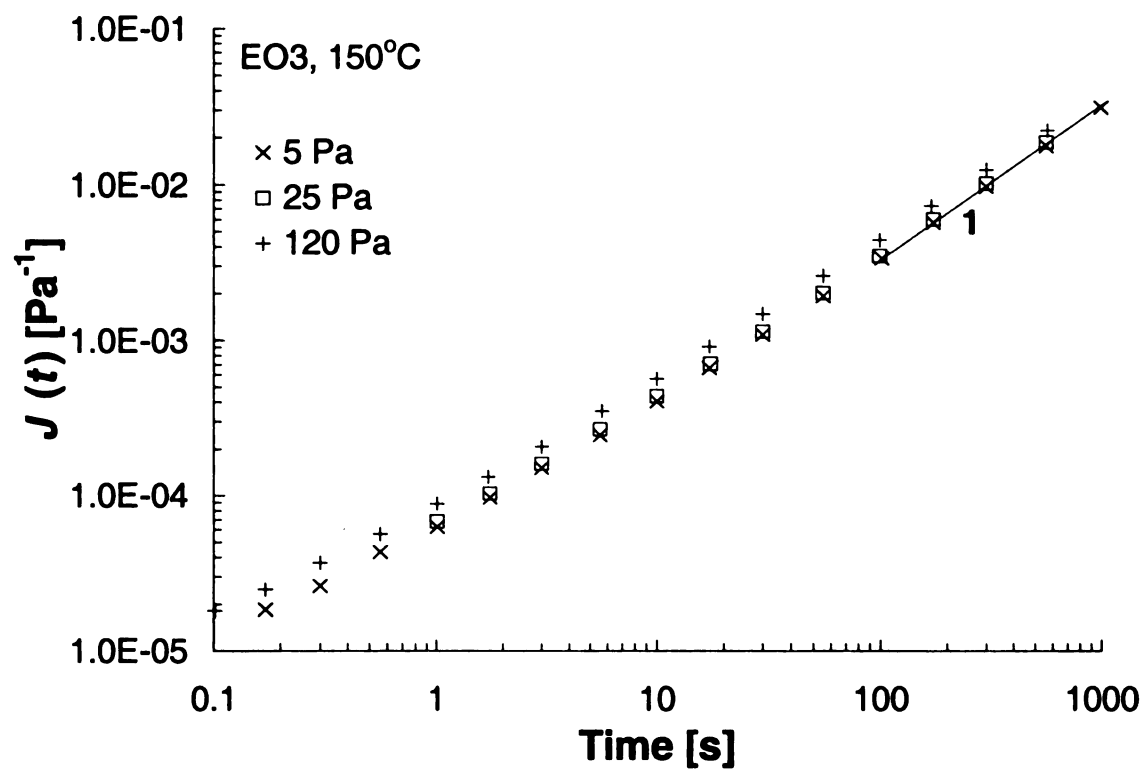


Figure 4.1. Shear creep compliance curves for EO3 at 150°C; nonlinearity is observed at 120 Pa.

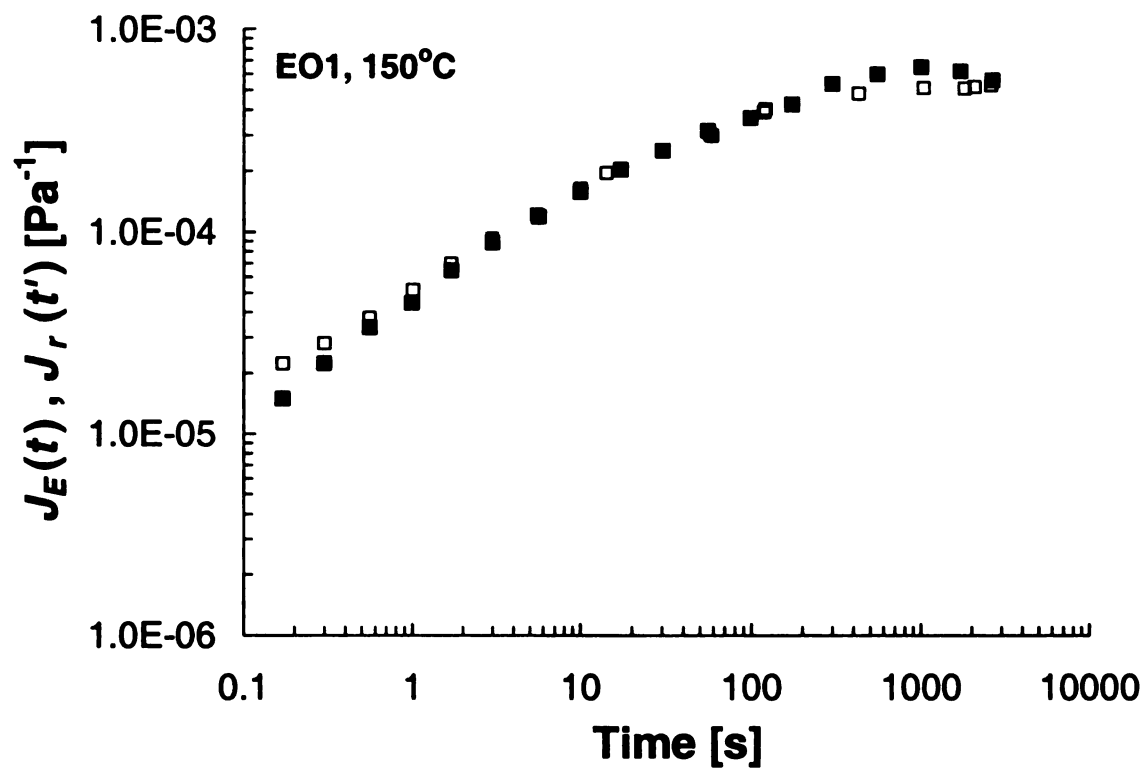


Figure 4.2. Elastic shear compliance during creep $J_E(t) = J(t) - t/\eta_0$ at 5 Pa (■) and recoverable compliance $J_r(t')$ (□) for EO1 at 150°C.

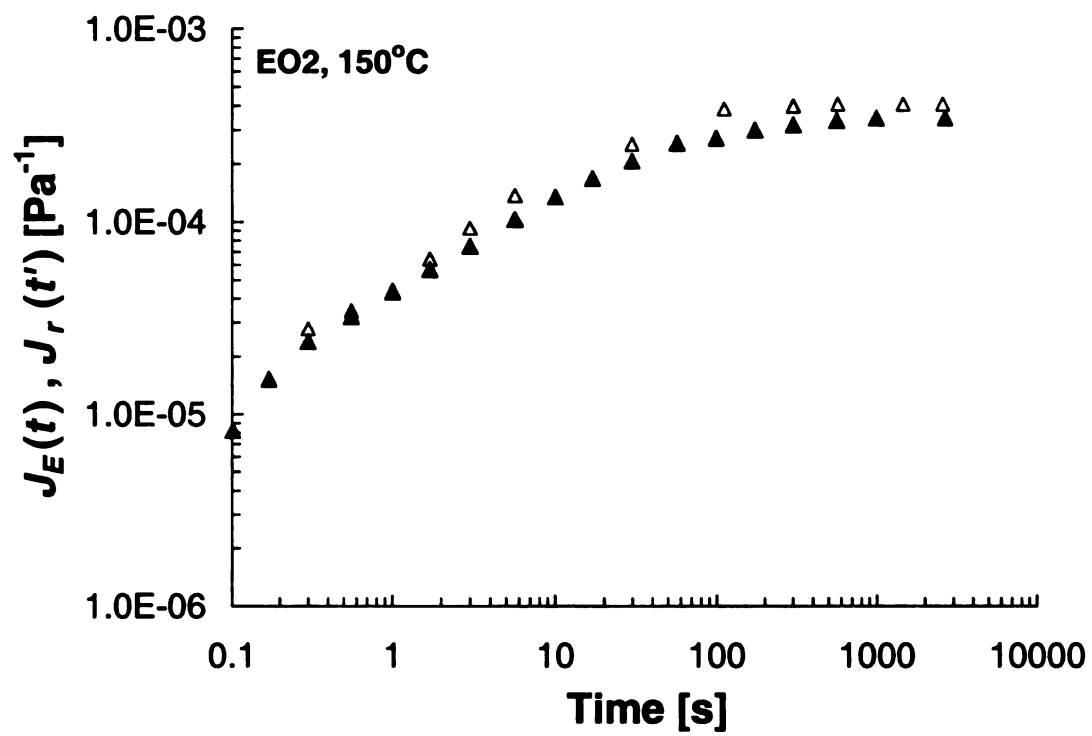


Figure 4.3. Elastic shear compliance during creep $J_E(t) = J(t) - t/\eta_0$ at 5 Pa (▲) and recoverable compliance $J_r(t')$ (Δ) for EO2 at 150°C.

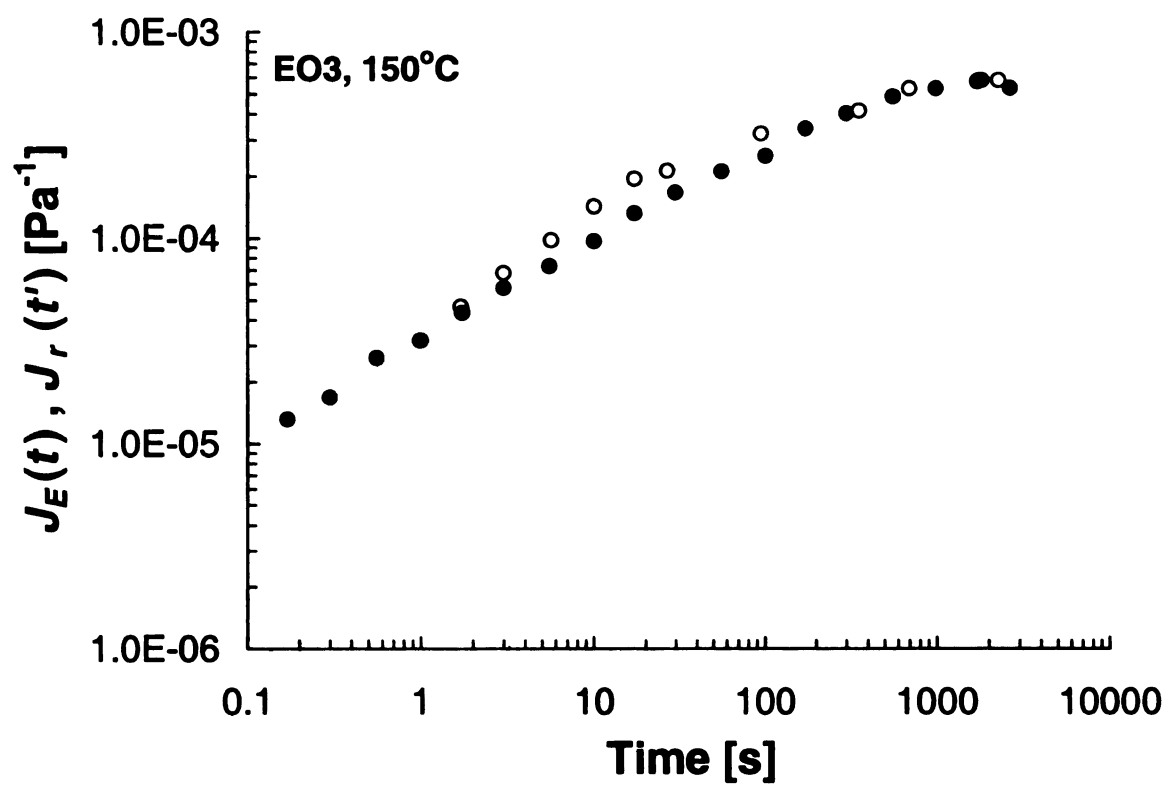


Figure 4.4. Elastic shear compliance during creep $J_E(t) = J(t) - t/\eta_0$ at 5 Pa (•) and recoverable compliance $J_r(t')$ (○) for EO3 at 150°C.

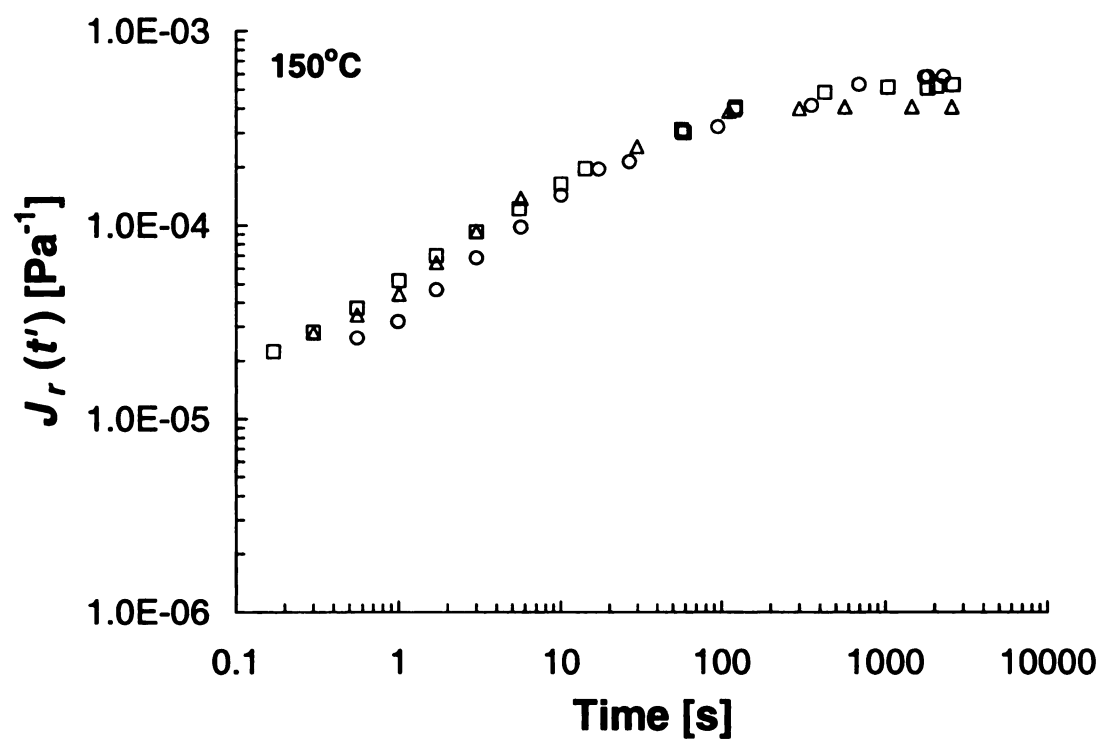


Figure 4.5. Comparison of linear shear creep recovery curves for the three EO copolymer melts at 150°C after creep at 5 Pa

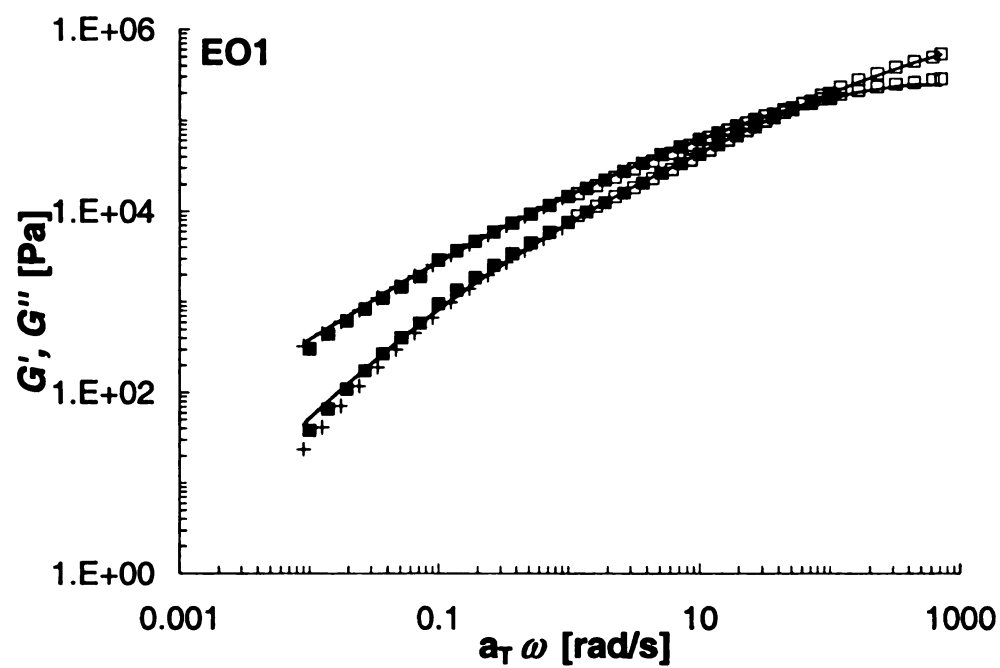


Figure 4.6. Dynamic shear moduli of EO1. Data obtained at 120°C ($\square$), 150°C ($\blacksquare$) and 200°C (+) have been shifted to the reference temperature of 150°C using time-temperature superposition. The solid lines are fits obtained with the discrete relaxation spectrum

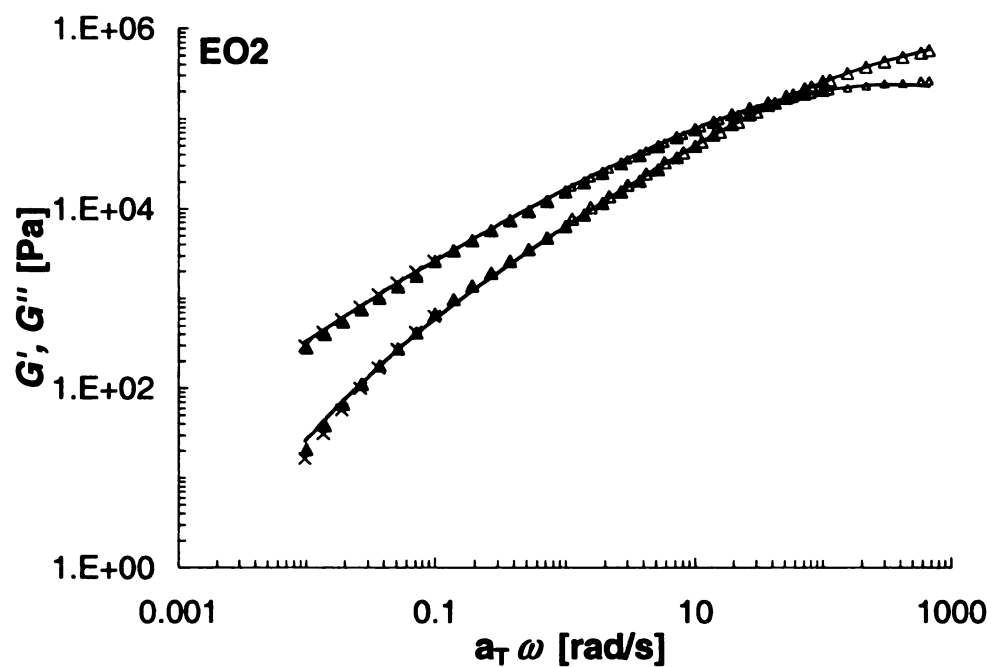


Figure 4.7. Dynamic shear moduli of EO2. Data obtained at 120°C (Δ), 150°C ($\blacktriangle$), and 200°C (X) have been shifted to the reference temperature of 150°C using time-temperature superposition. The solid lines are fits obtained from the discrete relaxation spectrum.

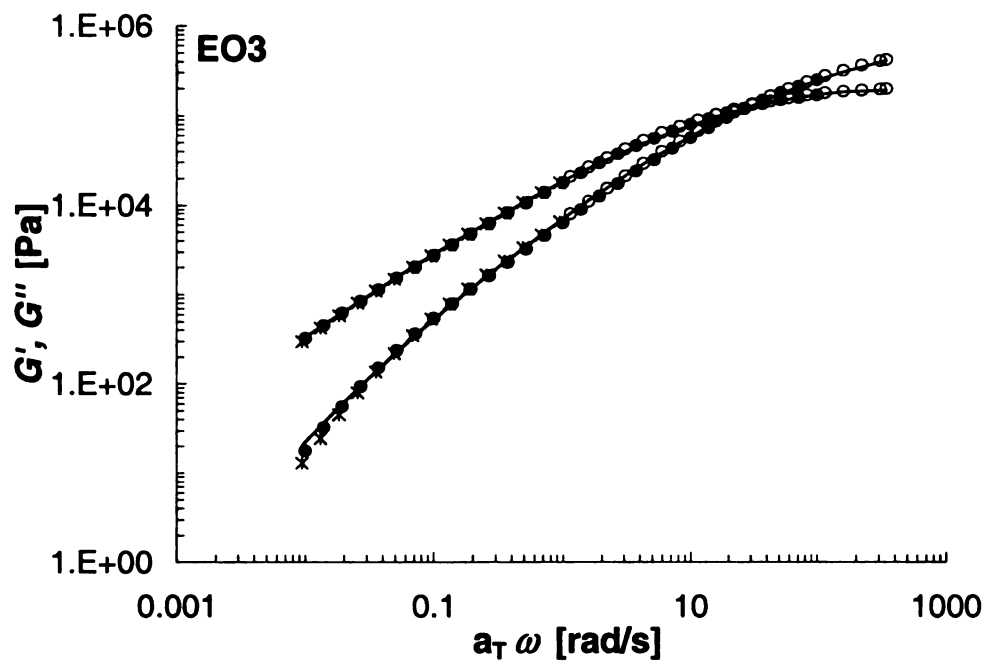


Figure 4.8. Dynamic shear moduli of EO3. Data obtained at 120°C ($\circ$), 150°C ($\bullet$), and 200°C ($\times$), have been shifted to the reference temperature of 150°C using time-temperature superposition. The solid lines are fits obtained from the discrete relaxation spectrum.

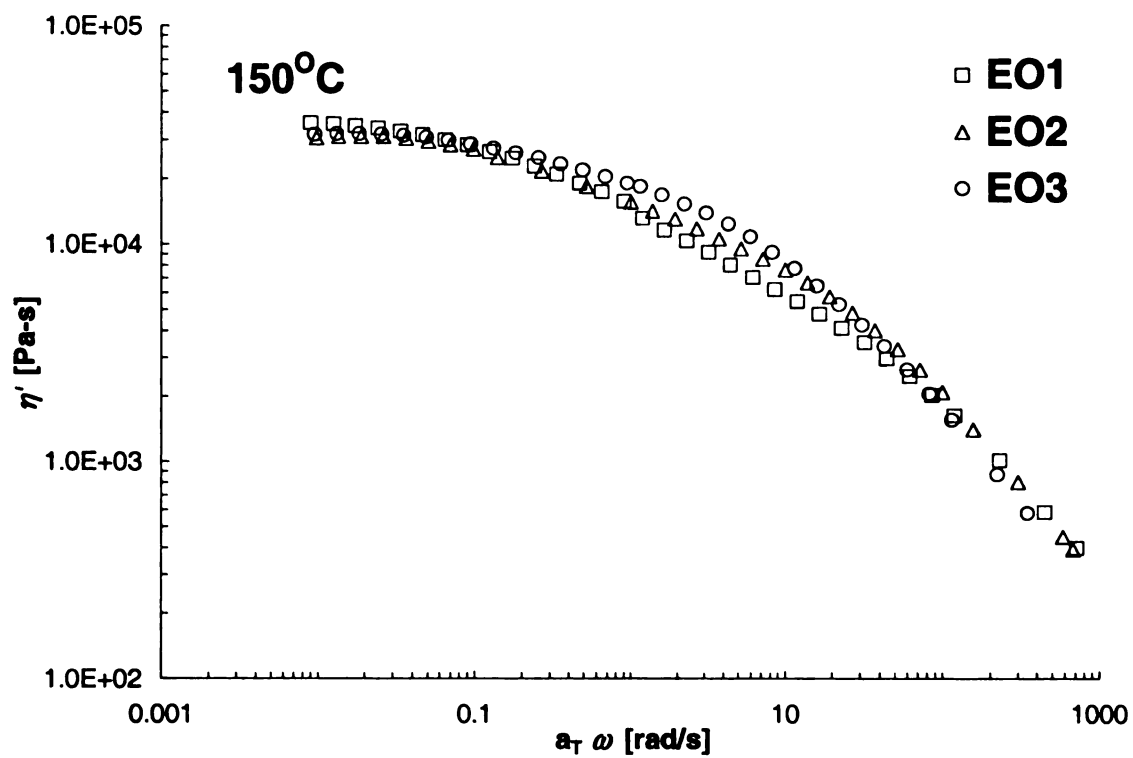


Figure 4.9. Dynamic viscosity curves for the EO copolymers at 150°C.

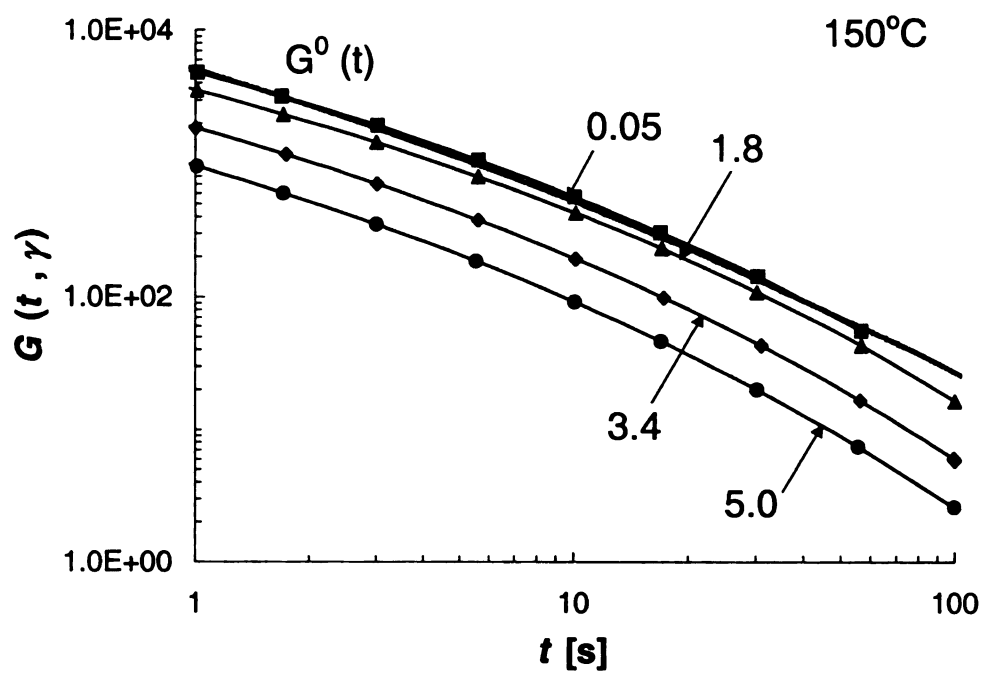


Figure 4.10. Shear stress relaxation curves for EO1 at several strains and 150°C

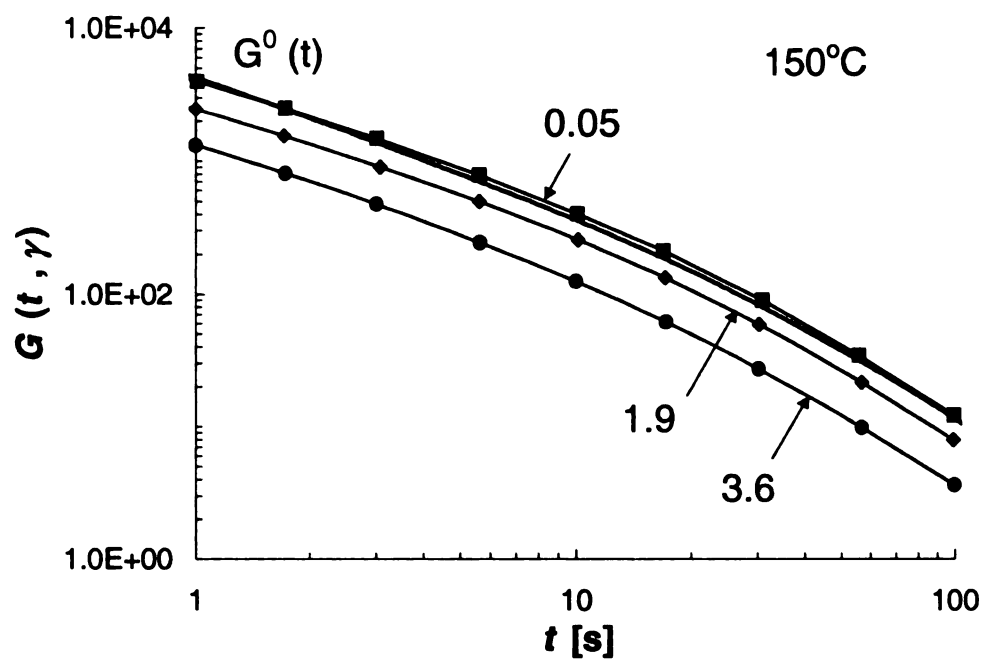


Figure 4.11. Shear stress relaxation curves for EO2 at several strains and 150°C

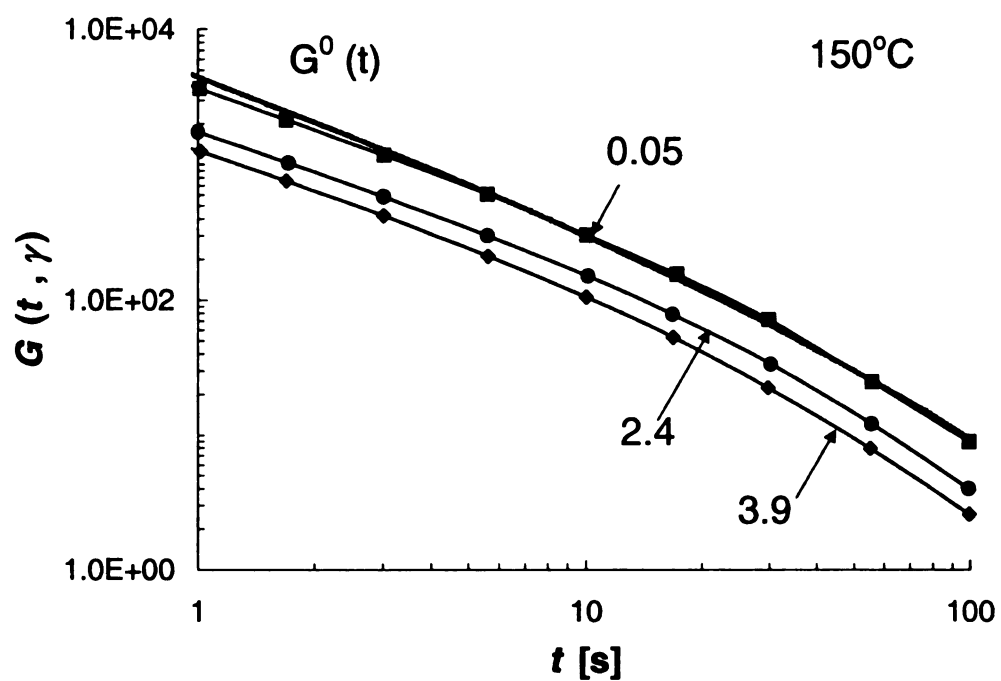


Figure 4.12. Shear stress relaxation curves for EO3 at several strains and 150°C

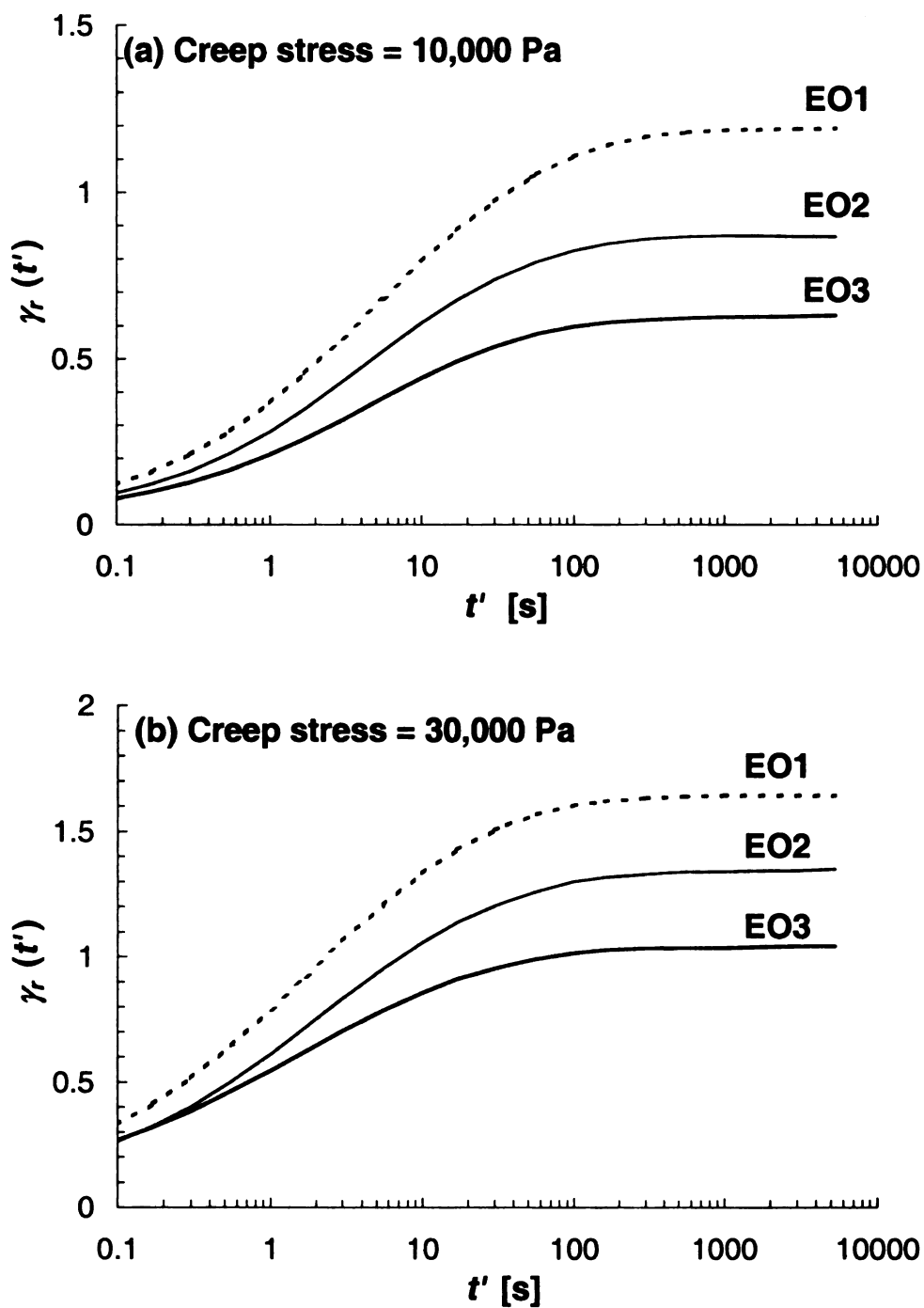


Figure 4.13. Recovery transients $\gamma_r(t')$ at 150°C for the three EO copolymers following nonlinear shear creep at (a) 10,000 Pa up to a maximum shear strain deformation $\gamma(t_{\max}) = 25$ and (b) 30,000 Pa up to a maximum shear strain deformation $\gamma(t_{\max}) = 75$

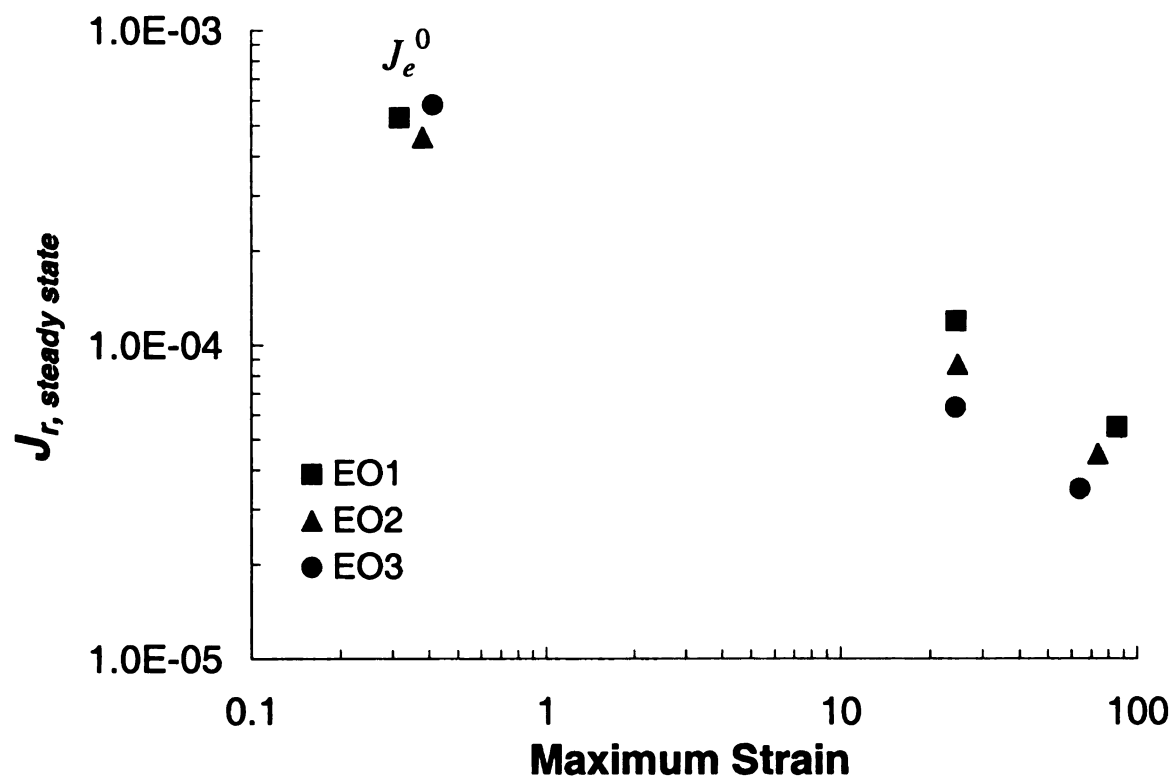


Figure 4.14. Steady recoverable compliance vs. the maximum strain imposed on the sample during creep stage, at several stresses and at 150°C. The three sets of data shown in this figure correspond to creep stresses of 5 Pa (maximum strain ~ 0.3), 10,000 Pa (maximum strain ~25) and 30,000 Pa (maximum strain ~75).

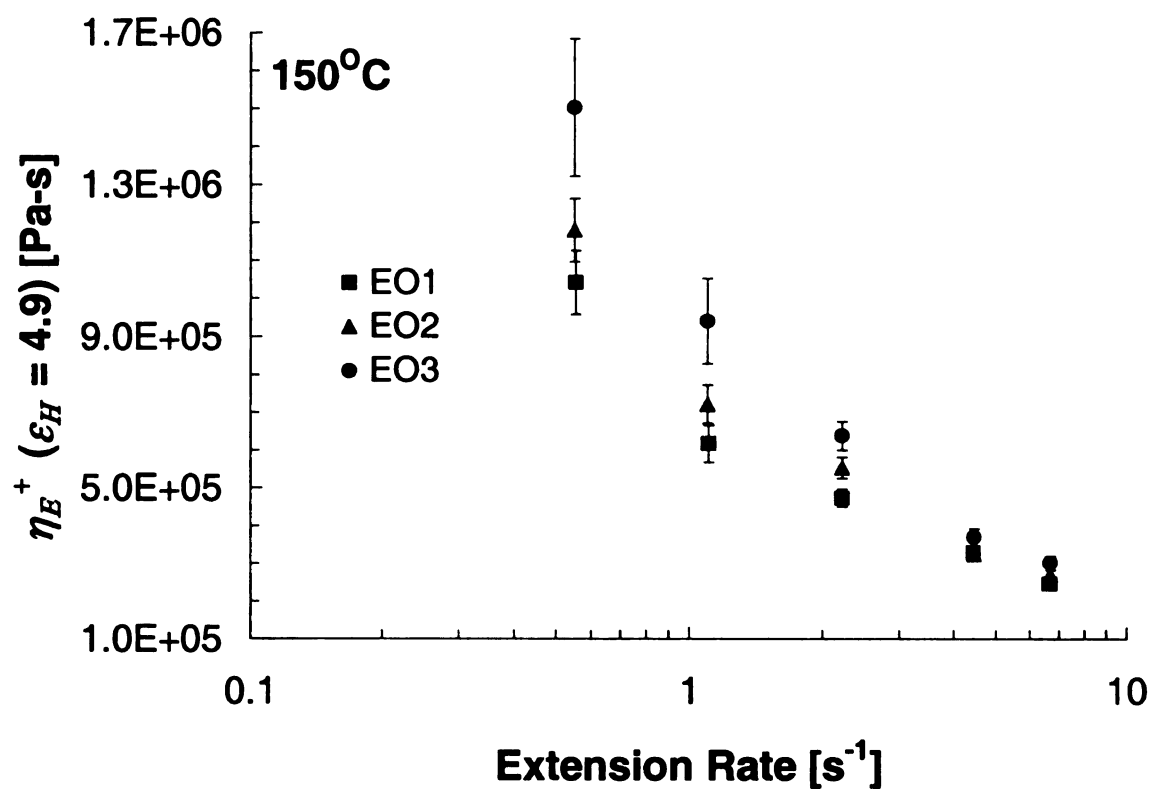


Figure 4.15. Extensional viscosity vs. extensional strain rate for the copolymer melts measured at a Hencky strain of 4.9 and at 150°C

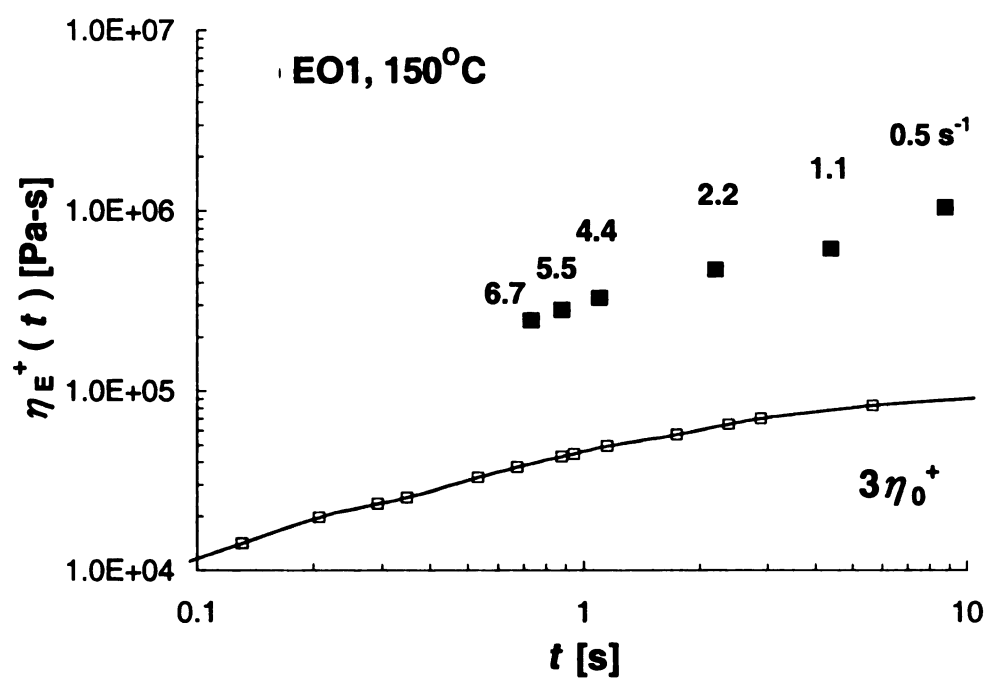


Figure 4.16. Elongational viscosity EO1 measured at 150°C and Hencky strain 4.9, plotted at equivalent times for several strain rates. The linear viscoelastic startup shear viscosity η_0^+ was measured using step shear at 0.005 s⁻¹

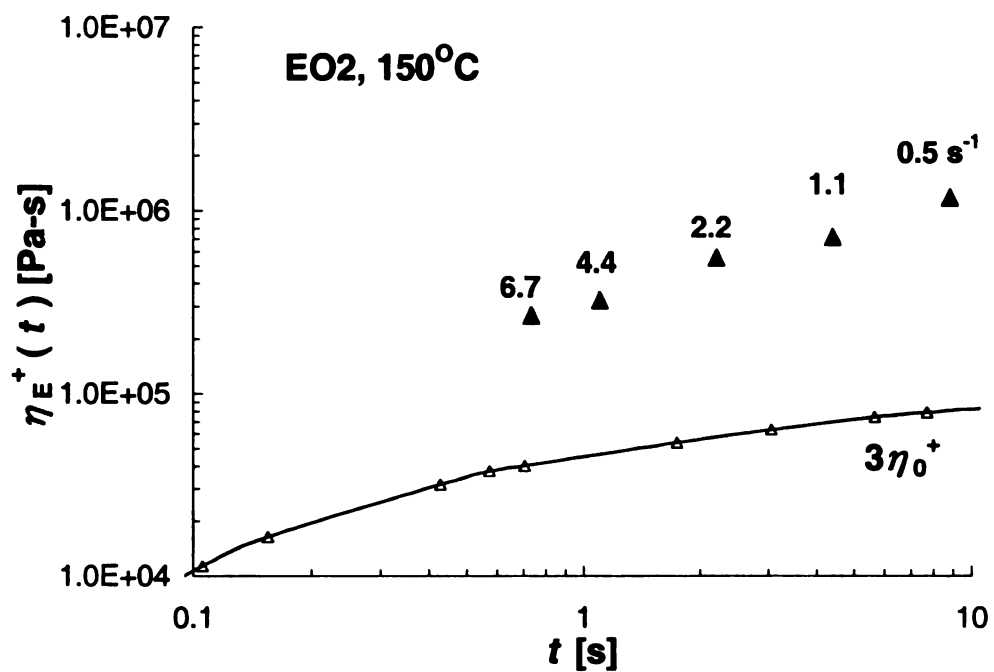


Figure 4.17. Elongational viscosity of EO2 measured at 150°C and Hencky strain 4.9, plotted at equivalent times for several strain rates. The linear viscoelastic startup shear viscosity η_0^+ was measured using step shear at $0.005 s^{-1}$

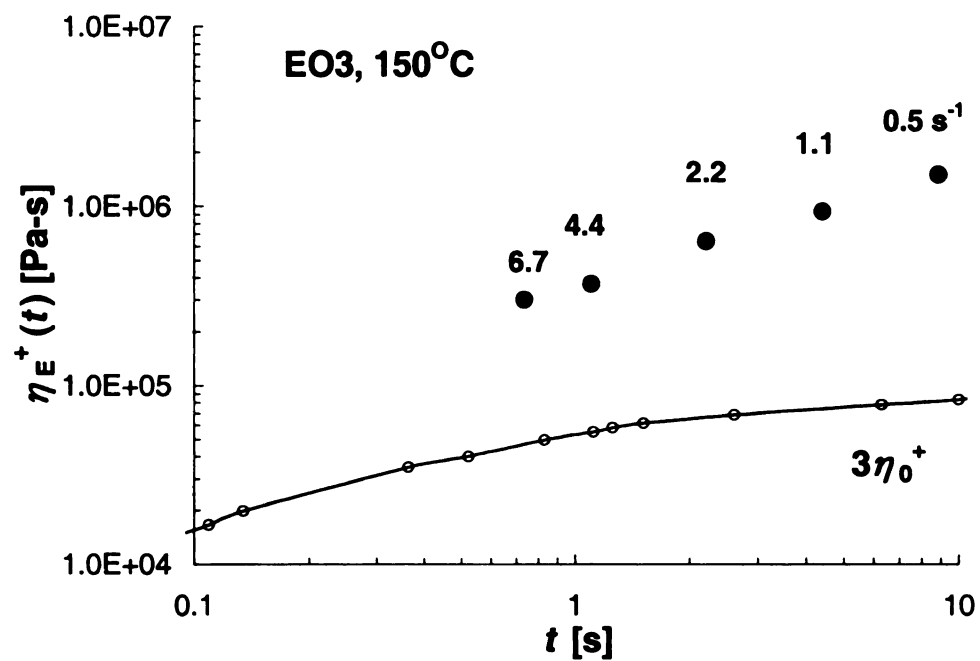


Figure 4.18. Elongational viscosity of EO3 measured at 150°C and Hencky strain 4.9, plotted at equivalent times for several strain rates. The linear viscoelastic startup shear viscosity η_0^+ was measured using step shear at 0.005 s⁻¹

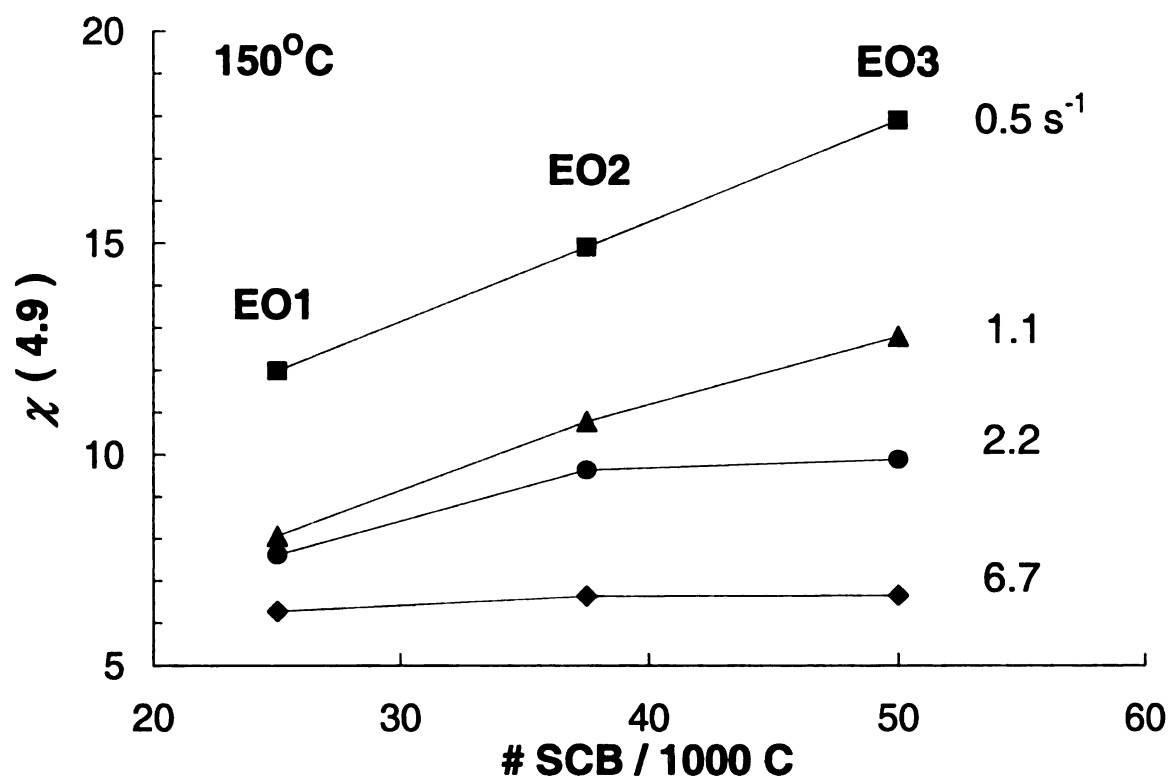


Figure 4.19. Effect of SCB density on strain hardening parameter evaluated at 150°C and at $\epsilon_H = 4.9$

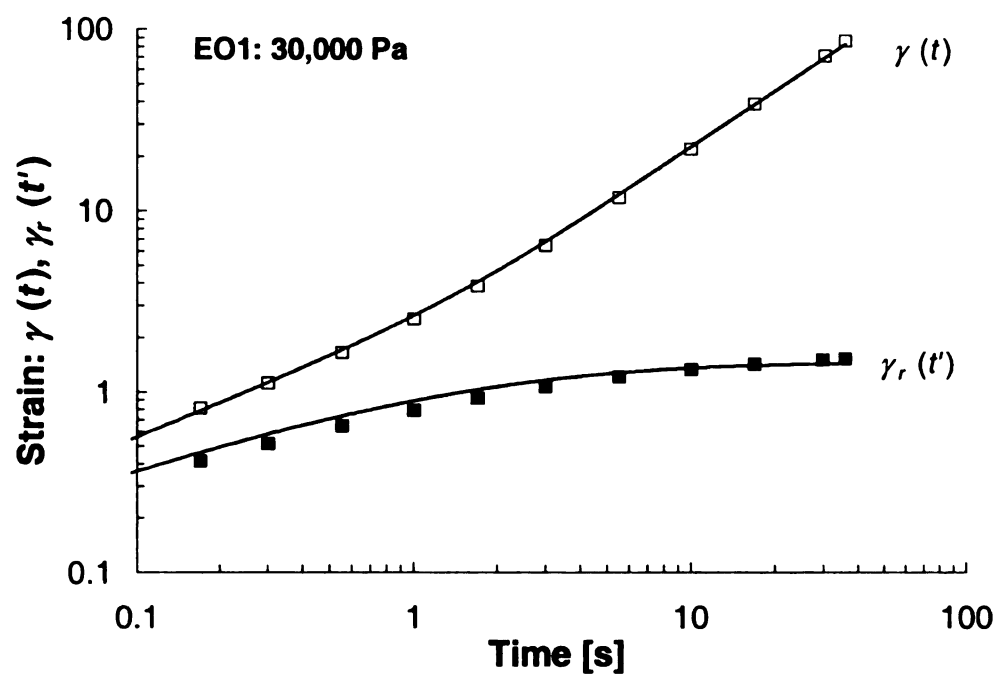


Figure 4.20a. Comparison of the KBKZ model predictions for EO1 with experimental creep and creep recovery data at 150°C with creep stress =30,000 Pa.

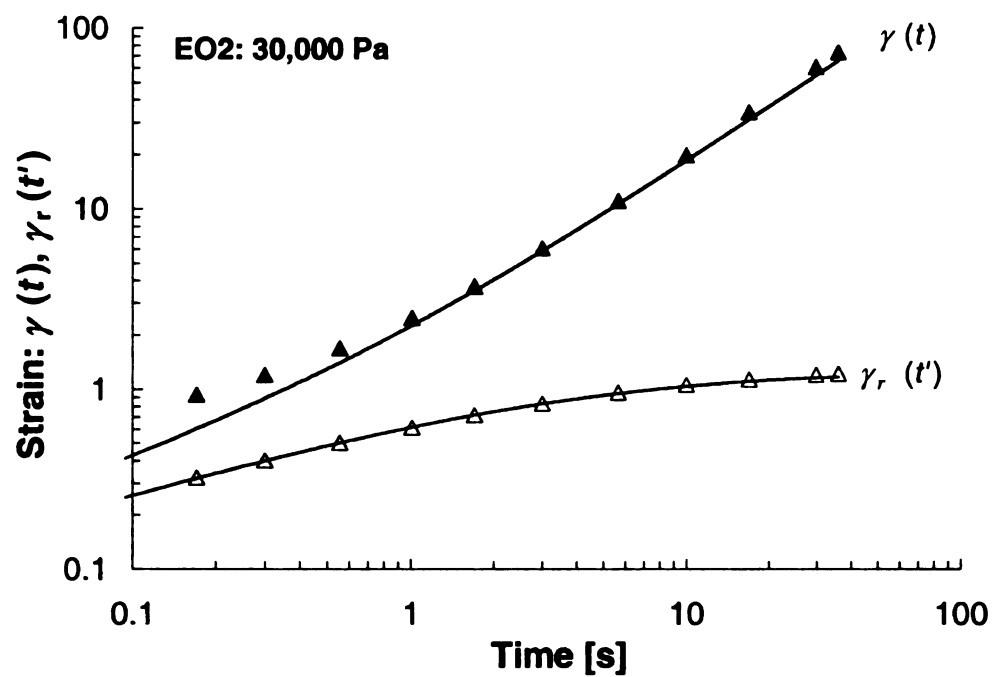


Figure 4.20b. Comparison of the KBKZ model predictions for EO2 with experimental creep and creep recovery data at 150°C with creep stress =30,000 Pa.

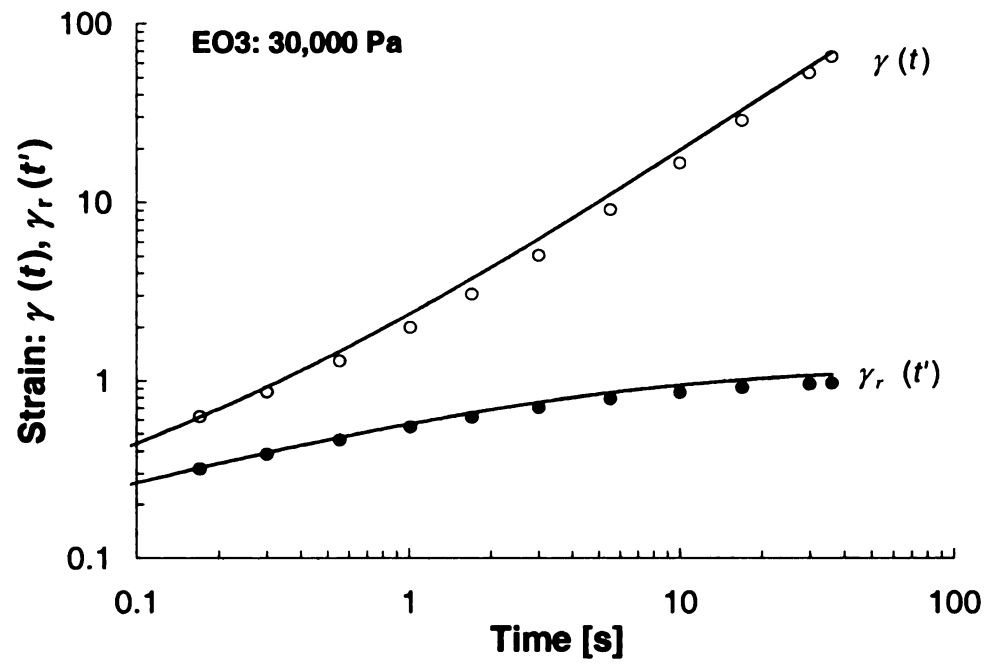


Figure 4.20c. Comparison of the KBKZ model predictions for EO3 with experimental creep and creep recovery data at 150°C with creep stress =30,000 Pa.

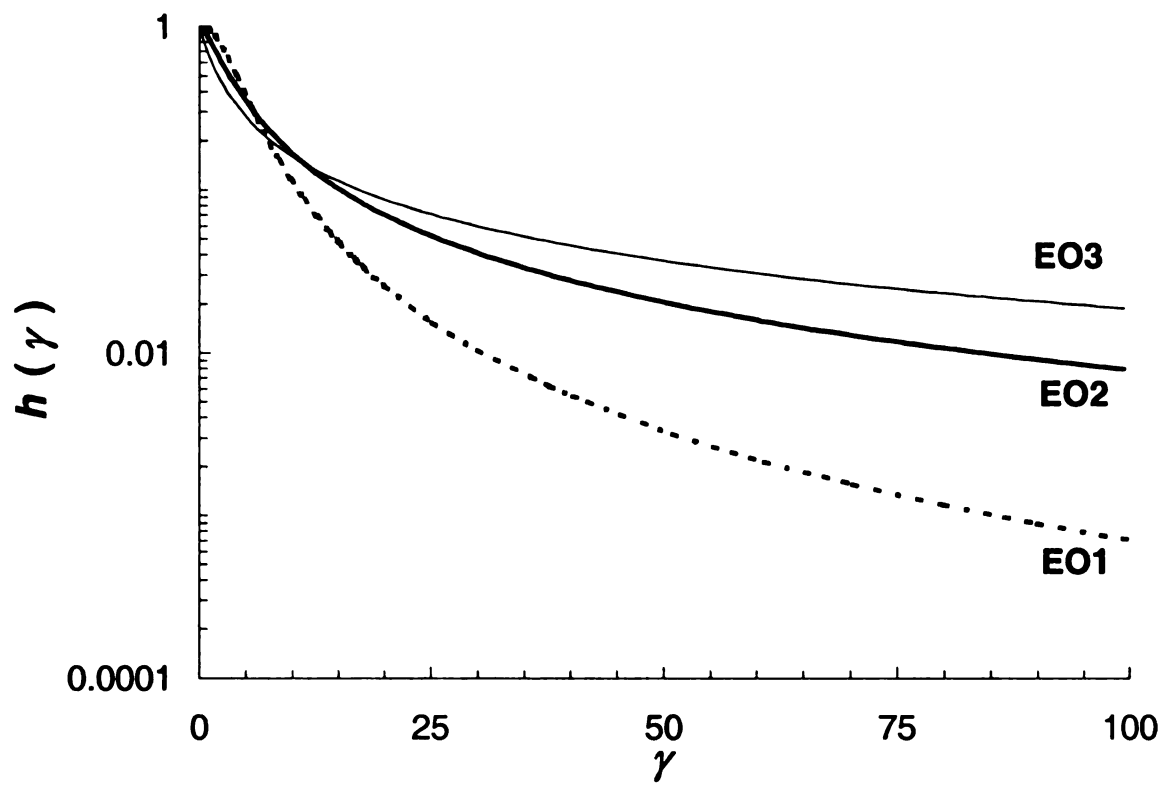


Figure 4.21. Shear strain damping functions fitted to nonlinear shear creep recovery data with the K-BKZ equation.

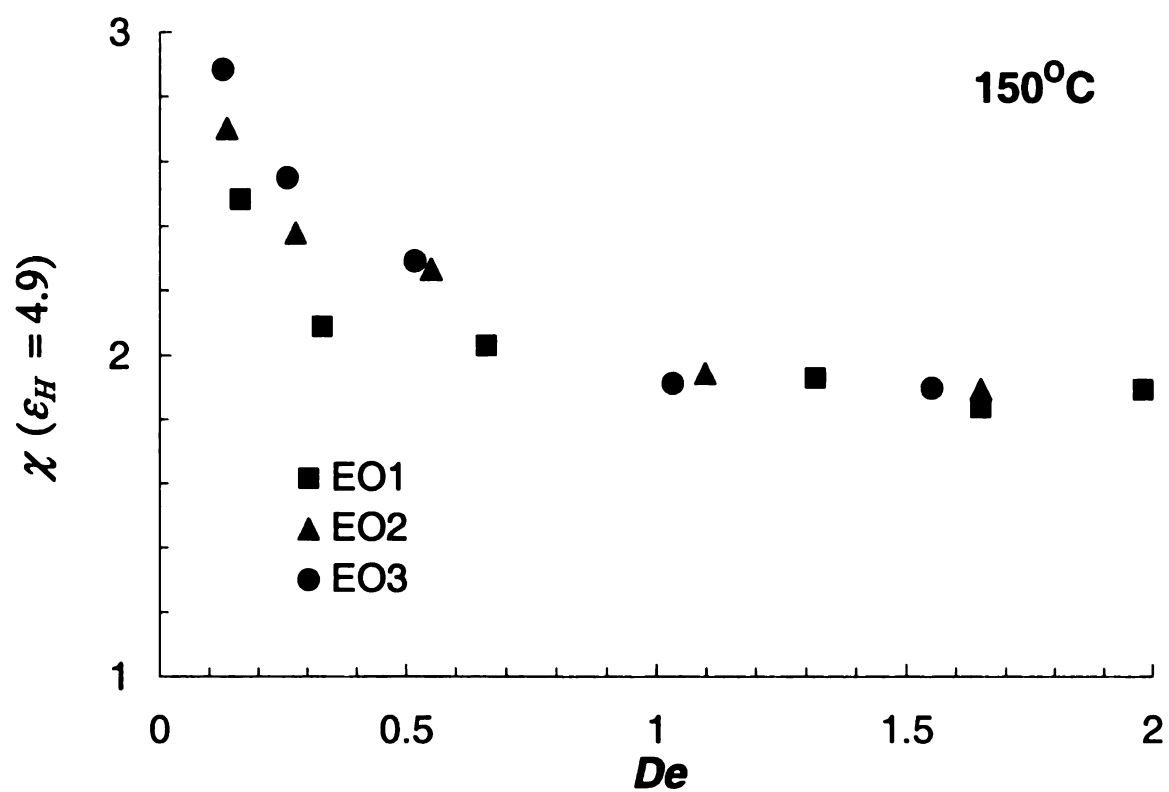


Figure 4.22. Extensional strain hardening parameter χ ($\epsilon_H = 4.9$) vs. Deborah number based on the Rouse relaxation time for the three copolymer melts at 150°C

Chapter 5.

FLOW LINES IN INJECTION - MOLDING OF THERMOPLASTIC OLEFIN BLENDS: SURFACE MICROSTRUCTURE AND NONLINEAR RHEOLOGY

This chapter has been accepted for publication in *Journal of Applied Polymer Science*, with co-authors P. Papworth, K. Jayaraman, C. Shu, and M. D. Wolkowicz.

Morphology analyses of the blends, reported in this chapter for completeness [Table 5.2, and Figures 5.15 and 5.16,] were performed by P. Papworth (2001)

SUMMARY

This chapter reports an investigation of asynchronous flow marks on the surface of injection-molded parts and short shots made from two different blends of polypropylene and ethylene-propylene random copolymer elastomers. Flow marks were observed on the surface with both blends; the spatial frequency of flow marks on the surface was greater in the blend B1 which also exhibited a greater contrast between the surface regions. The same blend was distinctly faster in the linear viscoelastic tests of

shear creep recovery and shear viscosity growth. The degree of contrast between the flow mark regions and the out of flow mark regions was traced to different degrees of strain recovery in the dispersed phases of the two blends. This recovery occurred over injection molding timescales of the order of a few seconds. Strain recovery after shear creep was higher in the blend that displayed more severe flow marks in injection molding; the corresponding elastomer by itself also showed a greater extent of creep recovery. The quick strain recovery in the elastomer must therefore be associated with elastic stresses rather than interfacial tension. Hence the nonlinear elastic recovery of the elastomer phase at short times is an important factor in governing the microstructure evolution associated with flow marks in blends of polypropylene and olefinic elastomers.

5.1 INTRODUCTION

Surface defects known as tiger stripes have been observed on injection molded parts with a variety of thermoplastic materials including neat polymers [Yokoi et al. (1994), Heuzey et al. (1997), Monasse and Mathieu (1999),] filled polymers [Mizutani et al. (2000), Hobbs (1996),] and polymer blends [Chang (1996), Hamada and Tsunasawa (1996), Grillet et al. (2002), Jayaraman et al. (2002), Papworth (2001), Edwards and Choudhary (2004)]. Tiger stripes are alternating glossy and dull bands that form perpendicular to the flow direction. In many cases, the bands are asynchronous or out of phase on opposite surfaces of the part, with a glossy region on one surface of the part located across from a dull region on the opposite surface. Asynchronous flow marks

differ from other defects in that as the injection speed is raised, they appear at shorter flow lengths while higher melt and mold temperatures delay the onset [Mizutani et al (2000), Hobbs (1996), Chang (1996)]. The dull region is termed the flow mark while the glossy region is termed “out-of-flow mark”. The contrast between these regions is an indication of the severity of the flow mark. The present chapter reports on an investigation of the microstructural differences between these regions and the material characteristics associated with both the onset and the severity of flow marks in high-speed injection molding of thermoplastic olefin (TPO) blends. These blends are dispersions of a random ethylene-propylene copolymer (EP) elastomer in a polypropylene (PP) matrix, providing toughened materials for various automotive parts including bumpers, where a uniform glossy surface finish is required.

Visual observations reported by several researchers [Yokoi et al. (1994), Monasse and Mathieu (1999), Hamada and Tsunasawa (1996), Grillet et al. (2002)] have demonstrated that flow marks are caused by a flow transition at the advancing melt front from stable symmetric fountain flow to unstable, oscillating, asymmetric flow. This non-ideal, perturbed melt flow in the mold cavity is characterized by a shift of the stagnation point from the mid plane of the channel towards one of the mold walls as shown in Figure 5.1. This also leads to flow paths of different lengths from the stagnation point to the opposing walls with the melt experiencing different strain histories on the two flow paths. This could have more noticeable effects on filled systems. Indeed, Mizutani et al. (2000) and Hobbs (1996) reported that larger filler particles and higher concentrations of the filler enhanced the contrast between the flow mark and out-of-flow mark regions.

Hamada and Tsunasawa (1996) studied the morphology of injection-molded tensile bars made with blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) and reported a similar flow transition with the flow of these PC/ABS blends too. With the help of chromic acid etching to remove ABS particles at the surface and scanning electron microscopy, they reported different phase concentrations at the surface in different regions with these blends: the glossy out-of-flow mark region was polycarbonate rich at the surface while the flow mark region displayed both components at the surface. Edwards and Choudhary (2004) have also examined variations in surface morphology of injection molded plaques from a PC/ASA (acrylonitrile-styrene-acrylate) blend and confirmed the presence of a polycarbonate rich skin in glossy regions; they attributed this in part to a lower surface energy for the PC phase. However, they observed a different type of defect that improves with increasing injection rates.

The effect of melt rheology on this phenomenon has been studied experimentally with neat melts and rigid particle filled melts by Mizutani et al. (2000). In studies with single phase polypropylene melts, they reported that higher melt viscosity and higher number average molecular weight led to more severe flow marks. In studies with filled polymers, Mizutani et al. (2000) reported that the matrix with high polydispersity led to delayed onset of the instability and to lower contrast between glossy and dull surfaces. This effect of increasing matrix polydispersity or matrix viscoelasticity was confirmed even with polymer blends by Chang (1996), who ignored the characteristics of the dispersed phase. It is worth noting here that recent numerical analysis of single-phase flow stability near the advancing melt front by Bogaerds et al. (2004) predicts that the

onset of flow marks is delayed in melts that display greater strain hardening in extensional flow. Hence there is a need to characterize the molten polymer blend and the components in extensional flow and understand the effects of the blend rheology and the dispersed elastomer rheology on the phenomenon of asynchronous flow marks.

The objectives of this study were to investigate with thermoplastic olefin blends, (1) the disperse phase morphology in flow mark regions relative to that in out-of-flow mark regions and (2) the effects of the blend rheology and of the elastomer rheology on the severity of flow marks in two different TPO blends. It will be demonstrated in this paper that the disparities in dispersed phase microstructure between the flow-mark and out-of-flow-mark regions are greater when the elastomer phase displays a greater extent of recovery on the time scale of injection molding.

5.2. EXPERIMENTAL

5.2.1. Materials

Two reactor-made TPO blends labeled B1 and B2 were studied. The matrix phase in B1 is a copolymer of polypropylene with 3 wt. % ethylene while the matrix in B2 is a PP homopolymer. The dispersed elastomer phase in B1 is a random ethylene-propylene copolymer with 35 wt% propylene while the dispersed elastomer phase in B2

is a random ethylene-propylene copolymer with 45 wt% propylene. The composition of these blends and the component properties are summarized in Table 5.1. The components of the reactor made blends were separated by solvent extraction of the polypropylene matrix with boiling xylene as the solvent. The EP phase has a small xylene soluble fraction that is extracted with the PP in this process.

5.2.2. Injection-molding

A standard tensile bar mold cavity (16 cm x 1.8 cm x 0.3 cm) was used with a mold wall temperature of 24°C, a melt injection temperature of 202°C and an 8 second fill time. In addition to making full tensile bars for comparing the extent of tiger striping with the two blends, short shots of roughly half the mold volume were also made with an injection time of 4 s. Stroke lengths of 1.32 cm and 1.35 cm respectively were used with blends B1 and B2 (a stroke length of 2.3 cm corresponds to a full shot). Short shots allow us to evaluate the two-phase morphology near the advancing melt front and interpret the dispersed phase deformation observed in the flow mark and out-of-flow-mark surfaces.

5.2.3. Morphological characterization

Scanning electron microscopy (SEM) specimens were prepared by etching with methyl-cyclohexane to dissolve the EP elastomer phase which leaves voids that appear dark in the micrographs. Sections were microtomed from the two different surface

regions (x-y plane), two near wall regions (x-z plane) and the core region near the flow front (x-z plane) of the short shot, as shown in Figure 5.2. The SEM images were analyzed with the help of image analysis software packages from Sigma Scan (Jandel Scientific, Sigma Scan Pro 3.0) and Scion Image (Scion Corporation, Scion Image Version 3b).

5.2.4. Rheological characterization

Test specimens for rheological characterizations were made by compression molding powder or pellets into disks with a 10 ton force over 5 minutes at 200°C. The blends and the component materials were subjected to oscillatory shear on a Rheometrics Mechanical Spectrometer RMS-800 at 200°C using a 50 mm parallel plate configuration. Frequencies ranging from 0.02 – 200 rad/s were employed. A strain sweep was conducted at several frequencies to identify the maximum strain for testing in the linear viscoelastic range. The blends were also characterized in steady shear at shear rates ranging from 0.1 – 200 s⁻¹. The linear viscoelastic transient viscosity growth η_0^+ was measured for these materials at a shear rate of 0.005 s⁻¹ in a TA Instruments AR 2000 rheometer with 25 mm parallel plates.

Shear creep and recovery curves were recorded by operating the TA Instruments AR 2000 rheometer in the controlled stress mode with 25 mm parallel plates. The zero-shear viscosity η_0 and the characteristic relaxation time λ_0 of the blend components at

200°C were obtained from linear shear creep measurements at low stresses (ranging from 5 – 50 Pa). Other nonlinear viscoelastic tests were conducted at 180°C where creep was recorded up to a strain of 10 at shear stresses ranging from 100-3000 Pa; these curves were shifted by time-temperature superposition to 200°C. The lower temperature was used to minimize degradation at the long times involved. Upon attainment of the desired strain, γ_{max} (at time $t = t_I$), the stress was set to 0 and the strain recovery was recorded at subsequent times ($t' = t - t_I$.) The instantaneous strain during recovery $\gamma(t')$ is subtracted from γ_{max} to obtain the recoverable strain $\gamma_r(t')$.

$$\gamma_r(t') = \gamma_{max} - \gamma(t') \quad (5.1)$$

5.2.4a. Extensional viscosity

The melt extensional viscosity (η_E) was measured with lubricated skin-core flow through a semi-hyperboloidal die [Cogswell (1978), Everage and Ballman (1978), Pendse and Collier (1996)] fitted in a Dynisco capillary rheometer. The die profile is given by $r^2(z + z_0) = \text{constant}$, as shown in Figure 5.3. The die chosen here offers a fixed Hencky strain of 4.9 based on the entrance and exit cross sectional areas as defined below.

$$\epsilon_H = \ln\left(\frac{A_{entrance}}{A_{exit}}\right) \quad (5.2)$$

The inlet diameter of the die is same as that of the rheometer barrel. The die profile is designed to provide a uniform extensional strain rate ($\dot{\epsilon}$), for a given piston velocity (V_p).

$$\dot{\epsilon} = \frac{V_P}{L} \exp \epsilon_H \quad (5.3)$$

where L is the length of the die. The flow of the test polymer was lubricated with an immiscible, low-viscosity LLDPE “skin” (made from Dowlex LLDPE 2503, MFR = 105). Prefabricated skin-core billets, with core/skin ratio of 70/30 by volume to ensure proper lubrication, were used for measurements. With adequate lubrication, the pressure drop ΔP over the die length can be used to evaluate a “strain averaged” extensional viscosity η_E as follows [Everage and Ballman (1978), Pendse and Collier (1996)].

$$\eta_E (\dot{\epsilon}, \epsilon_H) = \Delta P / \dot{\epsilon} \epsilon_H \quad (5.4)$$

Extensional viscosities of the blend components were thus measured at strain rates ranging from 0.5 - 25 s⁻¹. The pressure transient in each run was carefully monitored for stable flow before recording the pressure drop. A strain hardening parameter (χ) in extension was evaluated with respect to three times the linear viscoelastic startup shear viscosity growth function as shown below [Kurzbeck et al.(1999)].

$$\chi(\epsilon_H, \dot{\epsilon}) = \eta_E^+(\dot{\epsilon}, \epsilon_H) / 3\eta_0^+(t = \epsilon_H / \dot{\epsilon}) \quad (5.5)$$

The linear viscoelastic shear viscosity transient in the denominator was evaluated at a time equal to the residence time of the melt in the semi-hyperboloidal die for a chosen strain rate.

5.3. RESULTS AND DISCUSSION

5.3.1. Flow mark frequency and blend rheology

Flow marks are observed in tensile bars molded from both blends; the difference between the flow mark patterns obtained with blends B1 and B2 is illustrated in Figure 5.4. The flow marks are spaced closer together in the bars from B1; the flow-mark spacing (distance between the centers of two neighboring flow-marks) is 15 mm in the B1 tensile bars and 20 mm in the B2 tensile bars. It is clear from the greater number of flow-marks on bars molded from B1 that the instability is more pronounced in blend B1. The flow front must oscillate with greater frequency during injection molding of blend B1 to produce the observed surface patterns. It is worth noting here that the melt injection rate was not varied in this work.

Of several rheological tests conducted on the two blends -- steady shear viscosity curves, nonlinear extensional viscosity in flow through a semi-hyperboloidal die, linear viscoelastic shear creep recovery and linear transient viscosity growth -- the latter two

tests showed the most difference between the two. The two blends have very similar steady shear viscosity curves as shown in Figure 5.5. The linear shear creep recovery curves plotted in Figure 5.6 show clearly that the recovery is faster in B1 than in B2. The linear viscoelastic limit of extensional viscosity growth is 3 times the linear viscoelastic shear viscosity growth obtained at very low strain rates and is plotted in Figure 5.7 for the two blends. These curves are noticeably different for the two blends, with B1 having the faster response. The nonlinear strain averaged extensional viscosity η_E^+ at a total Hencky strain of 4.9 is also plotted in Figure 5.7 as a function of the residence time $t=4.9/\dot{\epsilon}$ for several strain rates. Relative to the magnitude of $3\eta_0^+(t)$ at comparable times ($t=4.9/\dot{\epsilon}$), the nonlinear extensional viscosities of both blends are higher at all the strain rates. Thus both blends exhibit extensional strain hardening. Although the extensional viscosity curves are close for the two blends, the strain hardening relative to the linear viscosity growth is lower in B1, especially at high strain rates, as shown in Figure 5.8. From Figure 5.8, it is also clear that the strain hardening parameter (χ , cf. equation 5.5,) shows a steeper decline with increasing strain rate for blend B1 than for blend B2. The higher frequency of flow marks in blend B1 goes with the lower extent of strain hardening in this blend. Hence trends in the degree of strain hardening of the blends and the frequency of flow marks appear to be consistent with the predictions of Bogaerds et al.(2004).

5.3.2. Surface morphology of injection molded short shots [Papworth (2001)]

The contrast or difference in gloss between the out-of-flow-mark and flow-mark regions is also more striking in the bars molded from B1 than in the bars from B2. Representative SEM micrographs of these regions and of the core near the flow front in short shots are presented in Figures 5.9-5.11 for blend B1 and in Figures 5.12-5.14 for blend B2. Two orthogonal views were obtained for the flow mark and out-of-flow mark regions; the core region of the flow front was viewed only in the x-z plane. The surface morphology in the x-y plane is presented in a zoom view as well in Figures 5.10 and 5.13. These figures show that for the TPO blends of this study, the disperse phase is present in both regions, in contrast to observations of Hamada and Tsunasawa (1996) with PC/ABS blends. The following analysis will also show that the particle concentration is the same in these regions. The near wall micrographs in the x-z plane (Figures 5.11 and 5.14) reveal that the surface morphology extends to a depth of 20-30 μm . It is apparent from combining the surface micrographs with the near-wall micrographs that in the case of B1, the elastomer particles in the out-of-flow mark region are cylindrical with axes oriented along the flow direction while the particles in the flow mark region are elliptical disks with the disk thickness aligned with the z-coordinate along the mold gap. In the case of B2, the elastomer particles are uniformly cylindrical in the out-of-flow mark region but in the flow mark region, the strands are shorter and thicker on one end. In both blends, the particles are much more stretched and oriented in the out-of-flow mark regions than in the flow mark regions; the difference in particle shapes between regions is very prominent in the case of B1.

The change of particle shape between the surface regions could be caused by a combination of retraction, breakup and coalescence of the dispersed phase. In order to identify the dominant mechanism among these, a quantitative comparison of particle sizes and aspect ratios in the two types of surface regions was carried out with several micrographs for each case. The total micrograph area analyzed was the same for both out-of-flow-mark and flow mark regions and the results are listed in Table 5.2. The particle size distributions in the various regions including the core are presented in Figures 5.15 (a) for B1 and in Fig 5.15 (b) for B2. In both cases, the particle sizes are more nearly uniform in the core region than in the surface regions; and the particle size distributions in both types of surface regions are broad and bimodal. For B1, the first peak of these distributions for smaller particles is at the same size for the two surface regions and also matches that for the core. The area under this peak is also the smallest for the flow mark region. These trends indicate that there was no drop breakup in the transition between the two surface regions. For B2, the first peak for both surface regions is again at the same size and this size is bigger than the corresponding size for the core; the area under the first peak is also smallest for the flow mark region. These trends eliminate drop breakup as a cause of the change between the two surface regions.

The mean particle projected area in different regions is listed, along with mean dimensions in Table 5.2. It is worth noting that the mean x and y dimensions for the surface regions were based on a large number of particles but the z-dimension was not; the number of particles in the near-wall x-z micrographs was much less than in the x-y

surface micrographs. The mean particle area and the characteristic z-dimension have been put together to evaluate a representative particle volume for each region, with a specified shape; this is also tabulated in Table 5.2. Comparison of the mean particle volume appears to indicate some coalescence, especially in the case of B1. The total particle volumes associated with different regions were very close, demonstrating that the volume fraction of particles was the same in both types of surface regions.

The differences in degree of stretch between the surface regions may be examined first by evaluating the particle aspect ratios in the x-y plane. The aspect ratio distributions for the dispersed phase in various regions are presented in Figure 5.16 (a) for B1 and in Fig 5.16 (b) for B2. The aspect ratio recorded in the x-y projection is a true aspect ratio because a high degree of particle alignment is observed in both orthogonal planes (x-y and x-z) for all particle projections near the wall. The aspect ratio distribution is very broad for the out-of-flow mark region in both cases. Compared to the aspect ratio distribution for the core region which is narrow with a mean of about 2 in both cases, this signifies a broad range of stretch for the particles in the out-of-flow mark regions. The two blends are quite different in the aspect ratio distributions of the flow mark regions. The aspect ratio distribution is quite narrow for the flow mark region in the case of B1 with a mean of 2.1. Compared to the mean aspect ratio of 11.5 for particles in the out-of-flow mark region in B1, this would indicate that the particles are retracting to a more isotropic shape. The aspect ratio distribution in the flow mark region for B2 is broader than for B1 and has a mean of 8.1. Compared to the mean aspect ratio of 12.5 in the out-of-flow mark region for B2, this would indicate incomplete retraction

as is evident from the images themselves. As noted earlier, the retraction is evident in the strands with one of the ends becoming thicker. A further indication of the extent of retraction may be obtained by comparing stretch ratios for the two regions. A stretch ratio may be defined as $\bar{x} / 2R_{eq}$, the ratio of the particle dimension along the flow (x-) direction to the diameter of the equivalent sphere ($2R_{eq}$). As seen in Table 5.2, for B1, the stretch ratio declines from 4 for the out-of-flow mark region to 1.6 for the flow mark region. For B2, The stretch ratio declines from 5.1 for the out-of-flow mark region to 3.4 for the flow mark region. This establishes retraction of stretched elastomer particles as a dominant mechanism for the change of shape. Hence the contrast between flow marks and other regions on the surface is governed by the extent of recovery from stretching of the elastomer phase.

5.3.3. Rapid retraction and elastomer rheology

It remains to relate the rheology of components in the blends to observed differences in the extent of recovery of the dispersed phase in the two blends. It is important to note that the timescales available during injection molding operations for the observed recovery are of the order of seconds. Over such times, the elastomer recovery must be driven by elastic stresses rather than interfacial tension. Interfacial tension driven recovery is much slower than injection rates and is usually completed over several thousand seconds particularly under quiescent no-flow conditions as reported by Cohen and Carriere (1989.a and 1989.b, 1997), Rundqvist et al. (1996), and Gramespacher and

Meissner (1995, 1997). The matrix viscosity and relaxation time will affect this rate as well (Hooper et al. (2001), Tretheway and Leal (2001)). The shear viscosity curves presented in Figure 5.17 as well as the extensional viscosity curves presented in Figure 5.18, of the dispersed EP elastomers in B1 and B2 are much higher than the corresponding curves of the matrix polypropylenes (PP) which have very similar viscosity curves in both shear and extension. The characteristic relaxation times of the EP elastomers (see Table 5.1) are also higher than those of the matrix polypropylenes so that flow induced stresses would decay faster in the matrix PP phase than in the dispersed EP phase. Hence it is appropriate to examine the recovery of the elastomer phase in the two blends at short times. This was done with nonlinear shear creep and recovery tests.

The nonlinear creep curves $\gamma(t)$ have been recorded up to a shear strain of 10 at 200°C and stresses ranging from 100 Pa to 3000 Pa; the stress is then released and the creep recovery transients $\gamma_r(t')$ are recorded. These curves have been plotted together for the highest tested shear stress $\tau = 3000$ Pa in Figures 5.19 (a) and (b) for the dispersed EP elastomers in B1 and B2 respectively. As shown by Munstedt and coworkers (1979, 1998), each point $\gamma_r(t')$ on the recovery curve also represents the recoverable strain in the elastomer melts when deformed to a total strain $\gamma(t)$ that is less than the maximum strain of 10 under the imposed stress. Figure 5.19 shows that the transient recoverable strain is higher in the EP phase of B1 than in B2. The ratio of recovered strain relative to the imposed strain at times of 1 to 2 s is relevant because these are the timescales of interest in rapid processing operations such as injection molding. At times of the order of 1-2 s,

the recoverable strain for the elastomer in B1 closely follows the total strain, while the recoverable strain of the elastomer in B2 is significantly lower than the imposed strain.

The transient recoverable strain at 1 s from the nonlinear creep recovery experiments conducted at 200°C is plotted against the creep stress (τ) for the elastomers in B1 and B2, in Figure 5.20. In this figure, the recoverable strains at $t' = 1$ s during recovery have been scaled by the linear equilibrium recoverable strain ($J_e^0 \tau$) corresponding to that stress. This figure shows that the short time recovery of the elastomer in B1 is consistently higher in the entire range of stress. The trends in shear creep recovery are consistent with the extents of recovery observed in the dispersed EP phases in flow mark regions of the injection molded articles. Similar trends are to be expected in recovery following extensional flow at the advancing flow front. Experiments for investigating rapid recovery of suspended elastomer drops following controlled extensional flow are underway in our laboratory.

5.4. CONCLUSIONS

Asynchronous flow marks on the surface of tensile bars injection molded from different reactor-made blends of polypropylene and ethylene-propylene copolymer elastomers in the same proportions have been found to appear with a greater frequency for the blend B1 which also exhibited a greater contrast between the surface regions. The linear shear creep recovery and the linear viscoelastic shear viscosity growth of B1 were

faster than for B2. The major difference between surface regions was found to be in the degree of stretching and orientation of the dispersed elastomer phase. The dispersed phase was highly stretched to cylindrical strands with a mean aspect ratio of about 12 in the glossy surface regions of both blends while it was retracted in the dull regions to different extents in the two cases. The retracted shape in the dull surface region was that of a disk for blend B1 and the contrast between the regions was most striking. In the other blend B2, the partially retracted shape was that of shorter strands with a mean aspect ratio of 8 which were thicker at one end, and the contrast between the regions was less severe. A comparison of the particle size distributions in different regions established that rapid retraction of the suspended elastomer phase was the dominant cause of changes in particle shape between surface regions. The two matrix polymers in B1 and B2 had very similar shear viscosity curves as well as extensional viscosity curves but the elastomers in the two blends showed large differences in these curves. Testing of the two elastomer components in nonlinear shear creep and creep recovery showed that at a time of 1 s, the fractional strain recovery of the elastomer in B1 was much higher than that of the elastomer in B2. Hence the nonlinear elastic recovery of the elastomer phase at short times is an important factor in flow mark formation with blends of polypropylene and olefinic elastomers.

Table 5.1 Composition of the reactor made blends and component properties at 200°C

Blend	B1	B2
Matrix specifications		
Composition	Polypropylene copolymer with 3wt. % ethylene	Polypropylene homopolymer
MFR [dg/min]	31	25
η_0 [Pa-s]	920	1010
$\lambda_0 = \eta_0 J_e^0$ [s]	48	7
Dispersed phase specifications		
Composition	Ethylene-propylene random copolymer (EP)	Ethylene-propylene random copolymer (EP)
MFR	6.4	8.0
Ethylene / propylene wt. ratio	65 / 35	55 / 45
η_0 [Pa-s]	69400	15750
J_e^0 [Pa ⁻¹]	0.39×10^{-2}	1.15×10^{-2}
λ_0 [s]	273	181
Wt. % EP in blend	32	35

Table 5.2. Results of morphology analysis on injection molded TPO short-shots (see Fig. 2 for coordinate labels)

Property	Blend B1			Blend B2		
	Core	Out-of-flow-mark	Flow-mark	Core	Out-of-flow-mark	Flow-mark
Total micrograph area [μm^2]	8245	8229	8280	8244	8229	8280
# of particles in micrograph	1373	493	228	2068	433	350
Mean projected particle area [μm^2]	1.25	2.8	4.2	0.9	3.8	3.0
Mean x –dim [μm]	1.4	5.6	2.9	1.4	7.2	5.4
Mean y –dim [μm]	*	0.6	1.5	*	0.6	0.7
Characteristic z –dim [μm]	0.8	0.6	0.7	0.5	0.6	0.9
Mean aspect ratio	1.8	11.5	2.1	2.6	12.5	8.2
Mean particle volume [μm^3]	*	1.3	2.9	*	1.7	2.0
Equivalent sphere radius R_{eq} [μm]	*	0.7	0.9	*	0.7	0.8
Stretch ratio= $x/(2R_{\text{eq}})$	*	4	1.6	*	5.1	3.4

* Only x-z plane micrographs were available for the core region.

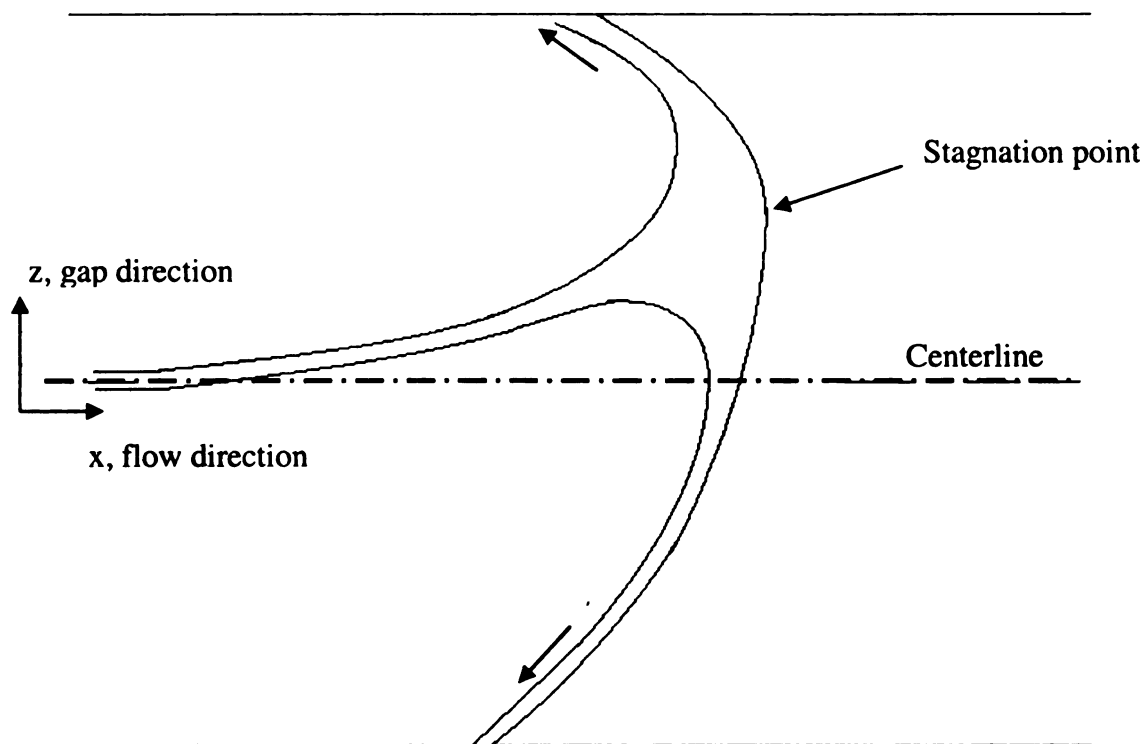


Figure 5.1. An unstable, advancing melt front during injection molding with flow marks, showing asymmetric path lines and an offset stagnation point.

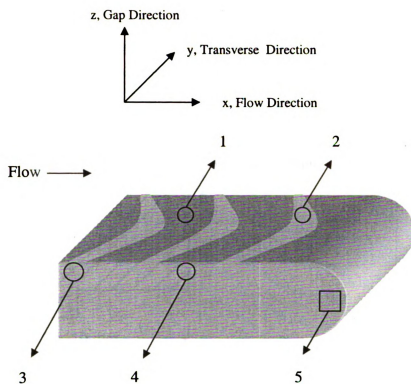


Figure 5.2. Various regions marked on a short shot for SEM image analysis

1. Out-of-flow-mark (glossy) surface, x-y plane
2. Flow-mark (dull) surface, x-y plane
3. Near-wall cross section beneath flow-mark region, x-z plane
4. Near-wall cross section beneath out-of-flow-mark region, x-z plane
5. Cross section of core upstream of flow front, x-z plane

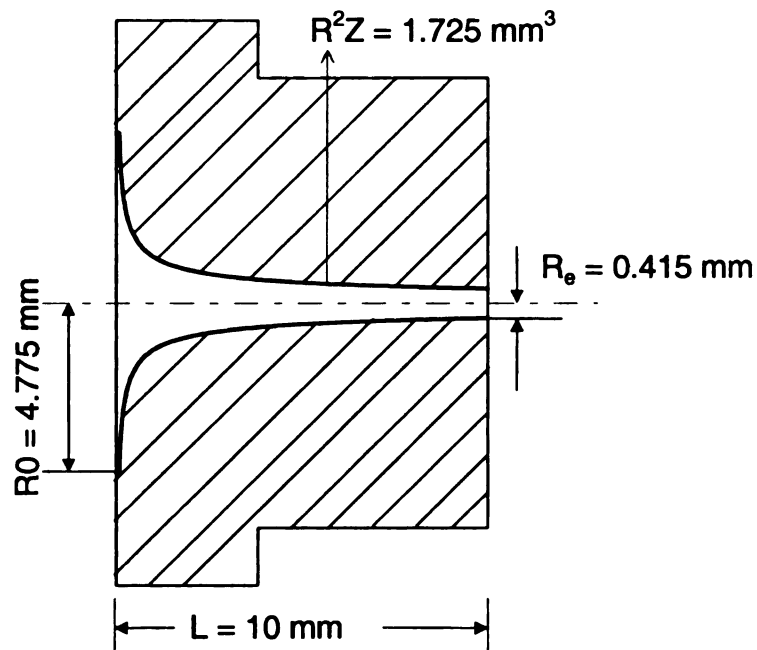


Figure 5.3. Profile of the semi-hyperboloidal converging die, designed to provide a uniform extensional strain rate and a Hencky strain of 4.9

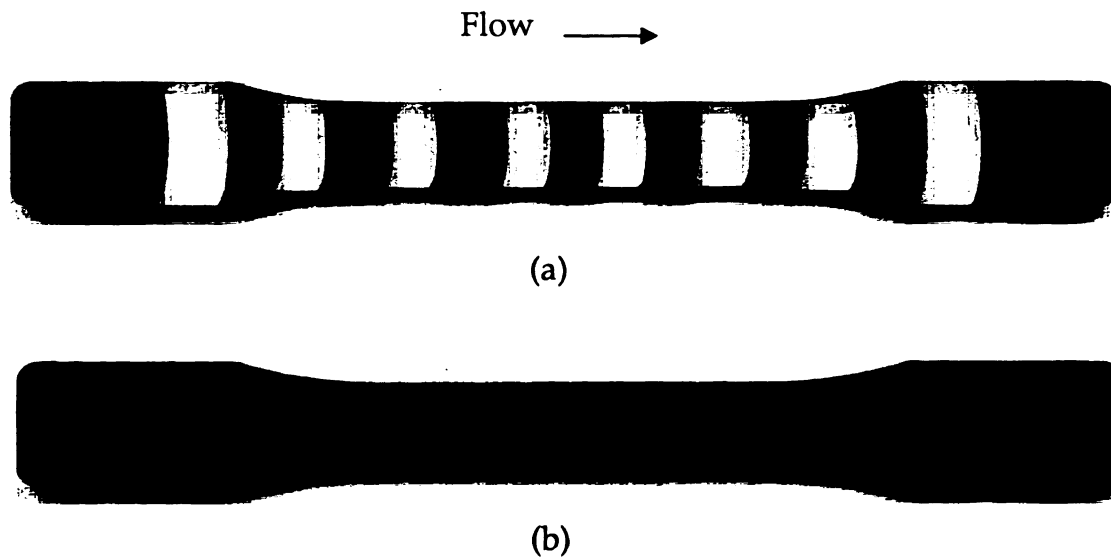


Figure 5.4. Comparison of tiger stripes or flow marks on tensile bars of two different blends. (a) Blend B1: high surface contrast between glossy (out-of-flow mark) and dull (flow mark) regions; (b) Blend B2: lower surface contrast. Gray portions represent dull regions.

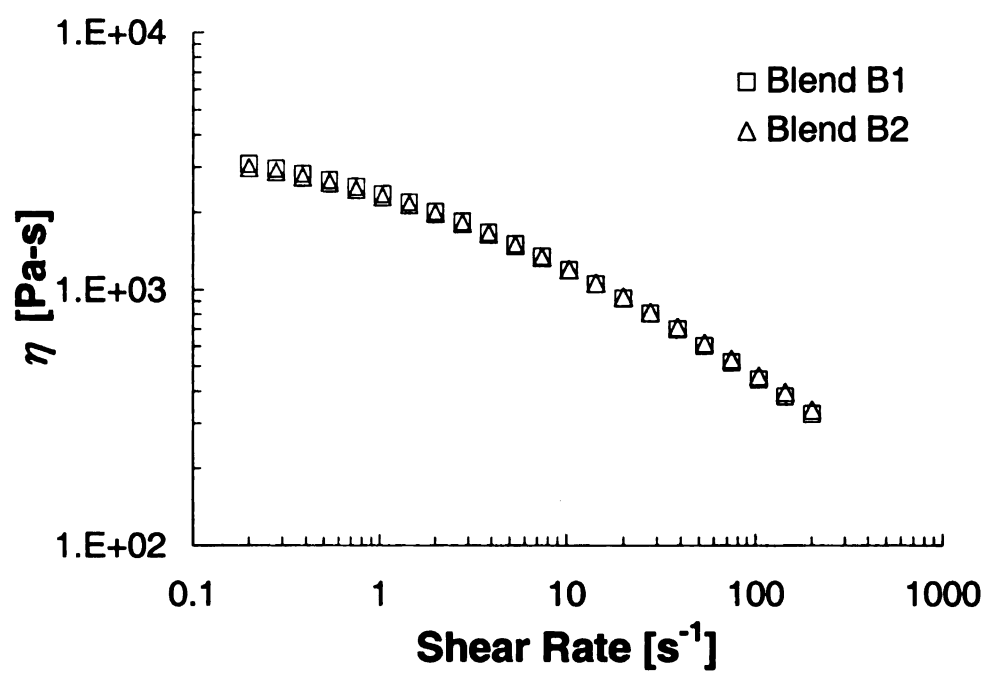


Figure 5.5. Shear viscosity curves of the reactor-made blends B1 and B2 measured at 200°C

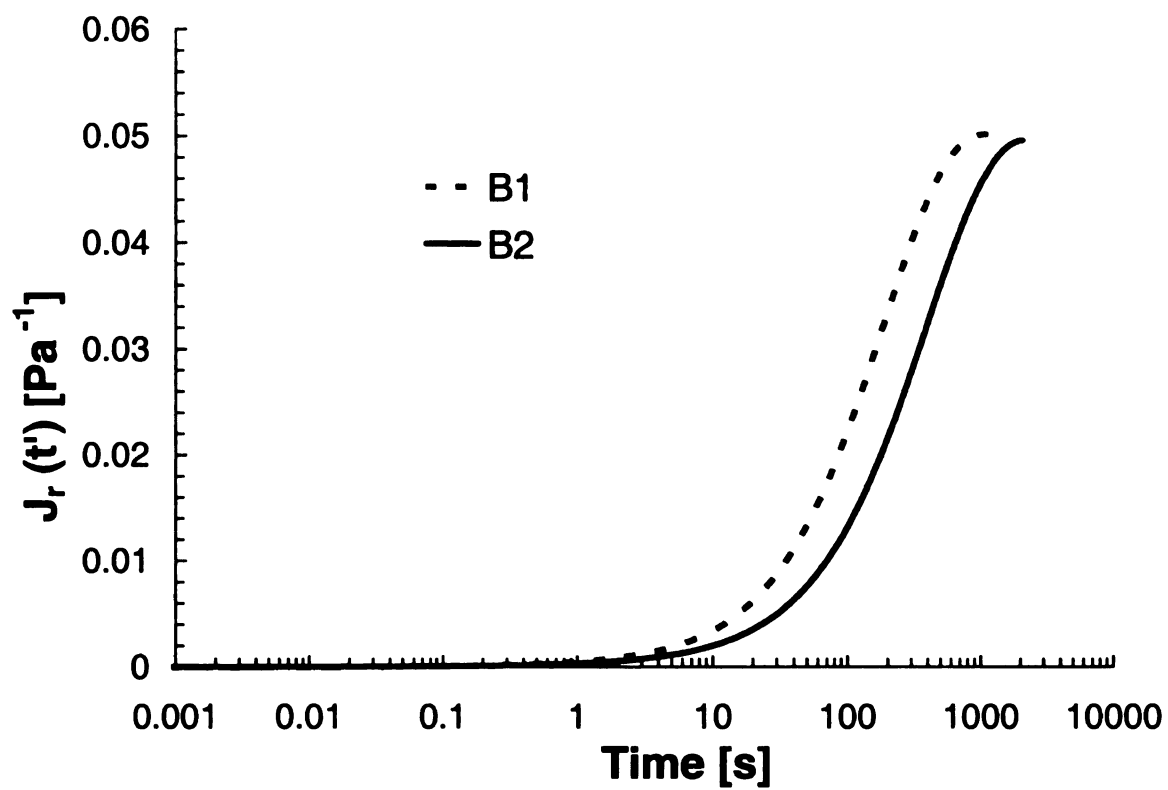


Figure 5.6. Linear shear creep recovery curves for the two blends at 200°C

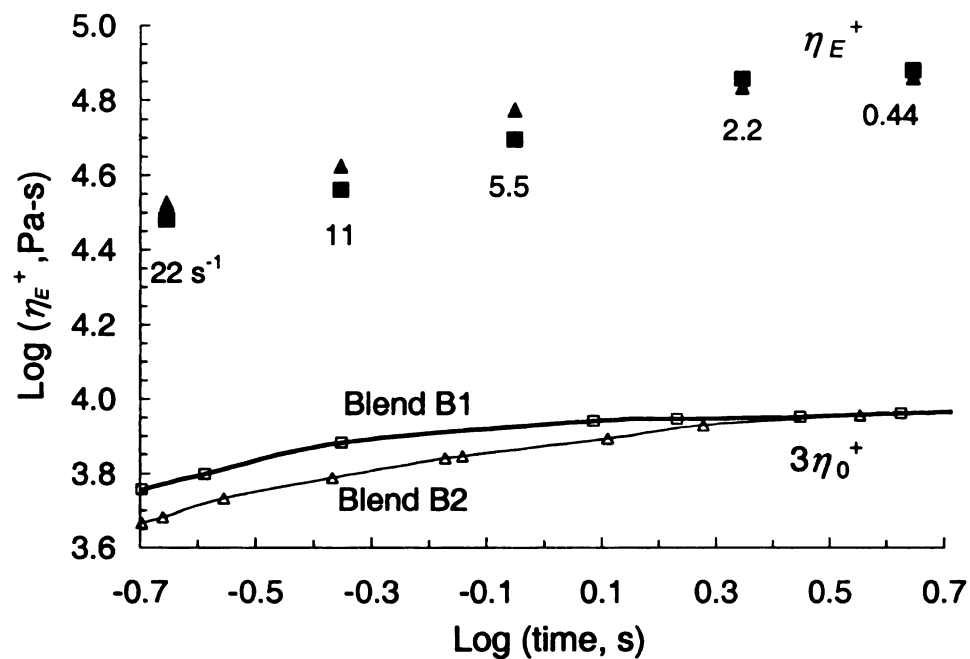


Figure 5.7. Three times the linear shear viscosity growth as a function of time at low strain rate (0.005 s^{-1}) for the two blends; and nonlinear strain averaged extensional viscosity of blends B1 (■) and B2 (▲) at Hencky strain $\epsilon_H = 4.9$ and 200°C , plotted as a function of the residence time in the semi-hyperboloidal die.

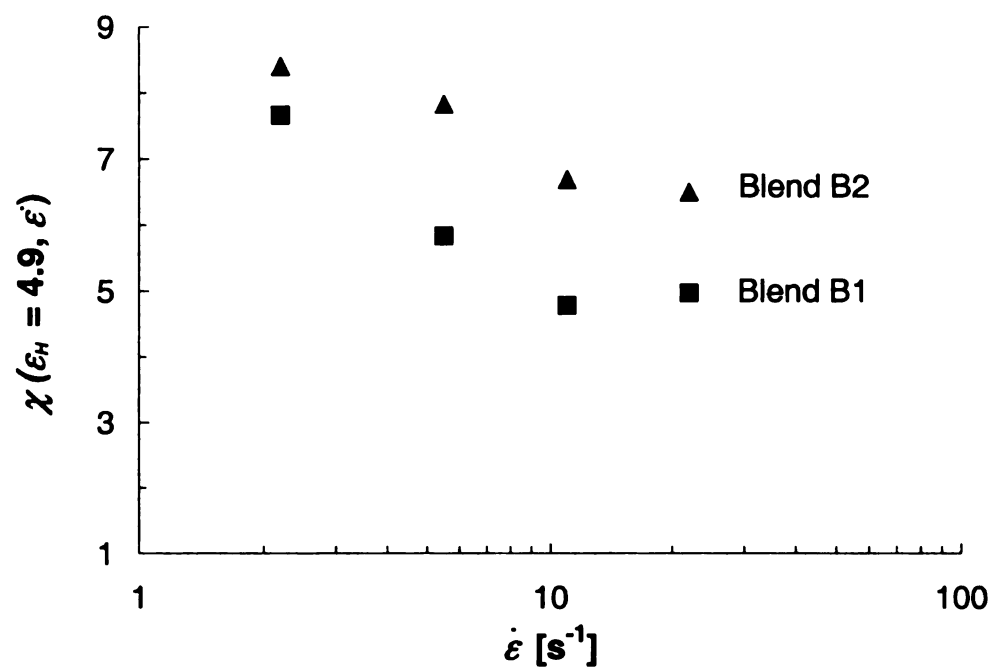


Figure 5.8. Extensional strain hardening parameter χ for the TPO blends evaluated at a Hencky strain $\epsilon_H = 4.9$ and 200°C

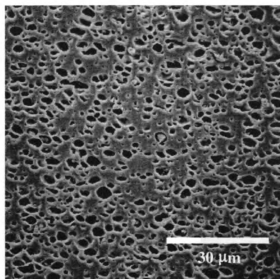


Figure 5.9. x-z plane section near the flow-front in the core region of blend B1

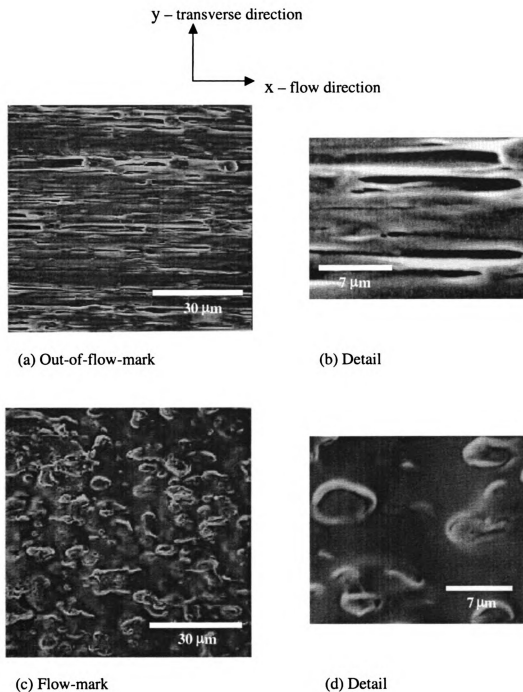


Figure 5.10. x-y plane sections from out-of-flow mark and flow mark surfaces in blend B1

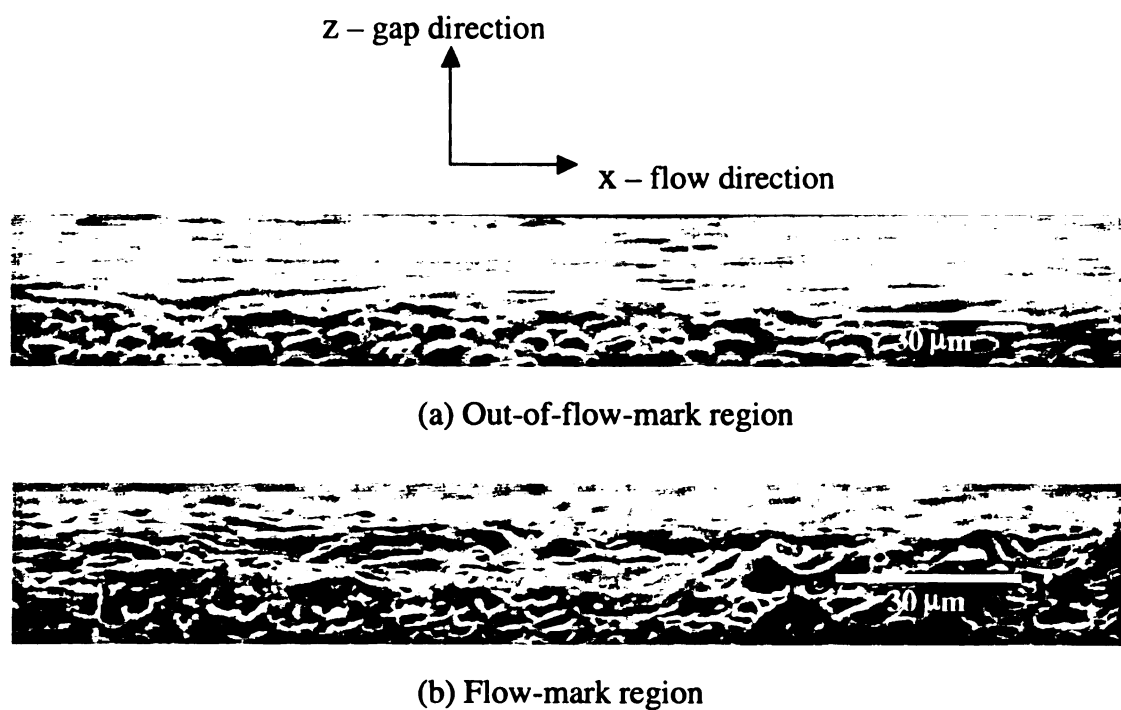


Figure 5.11. Near-wall sections in the x-z plane beneath the out-of-flow mark and flow mark surfaces of blend B1

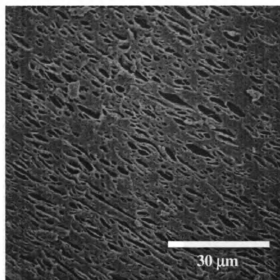


Figure 5.12. x-z plane section near the flow-front in the core region of blend B2

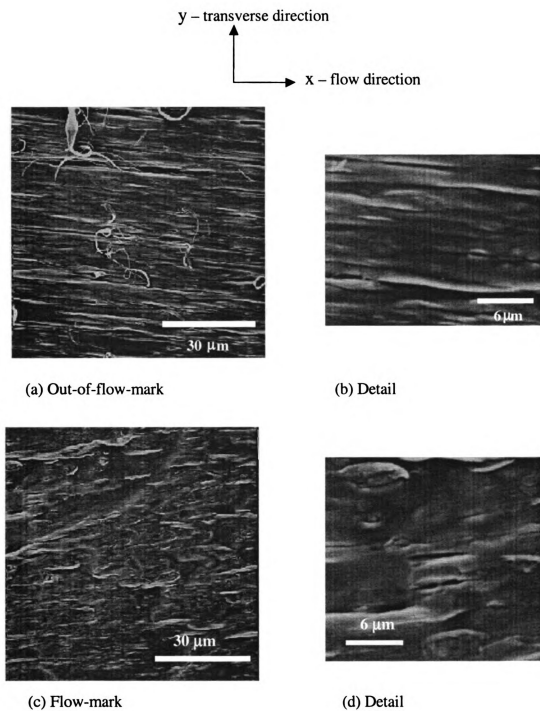


Figure 5.13. x-y plane sections from out-of-flow mark and flow mark surfaces in blend B2

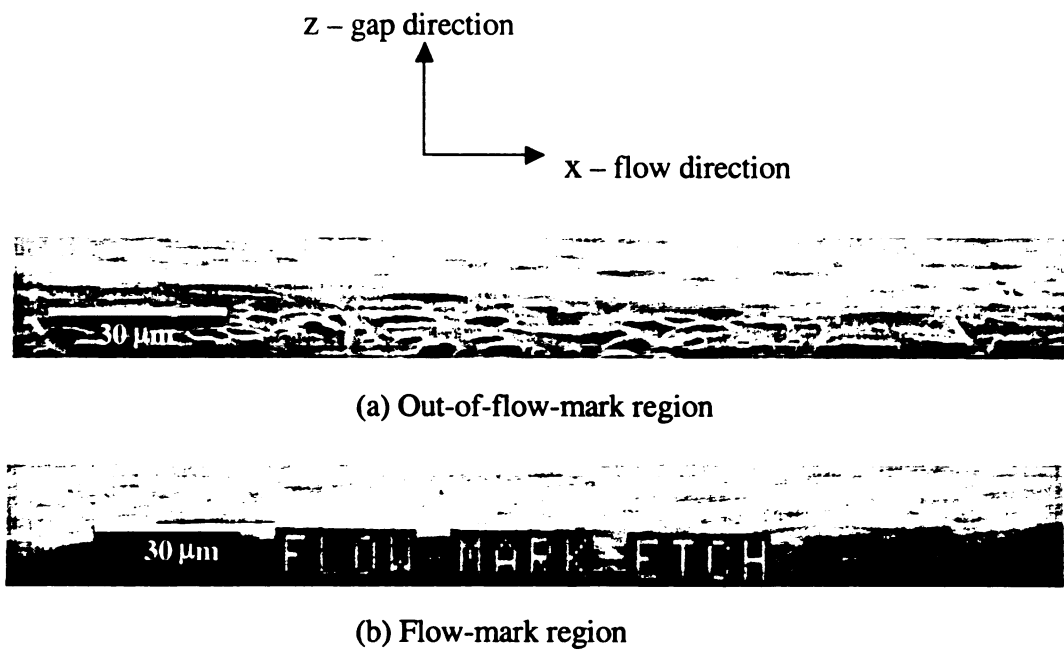
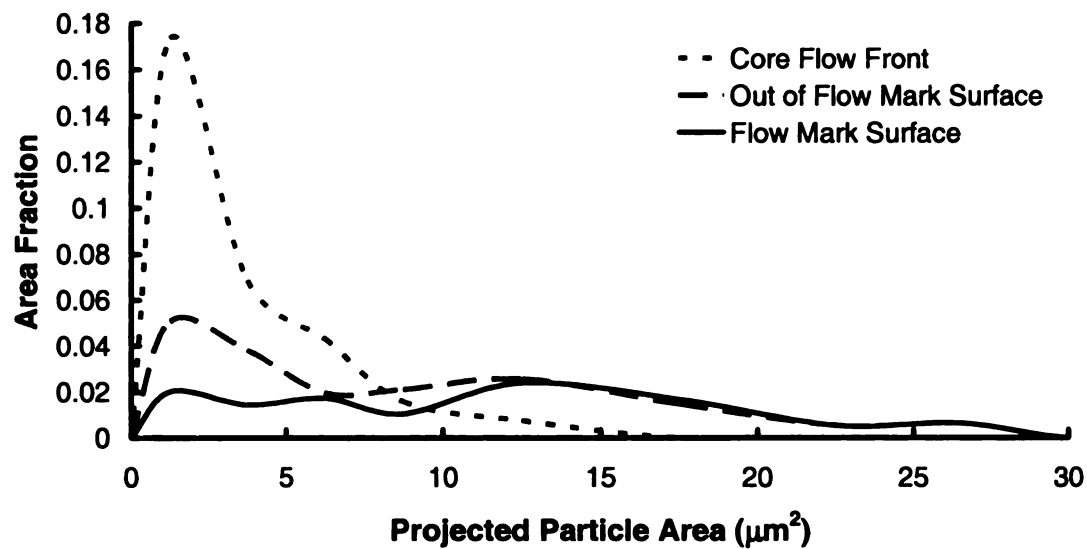
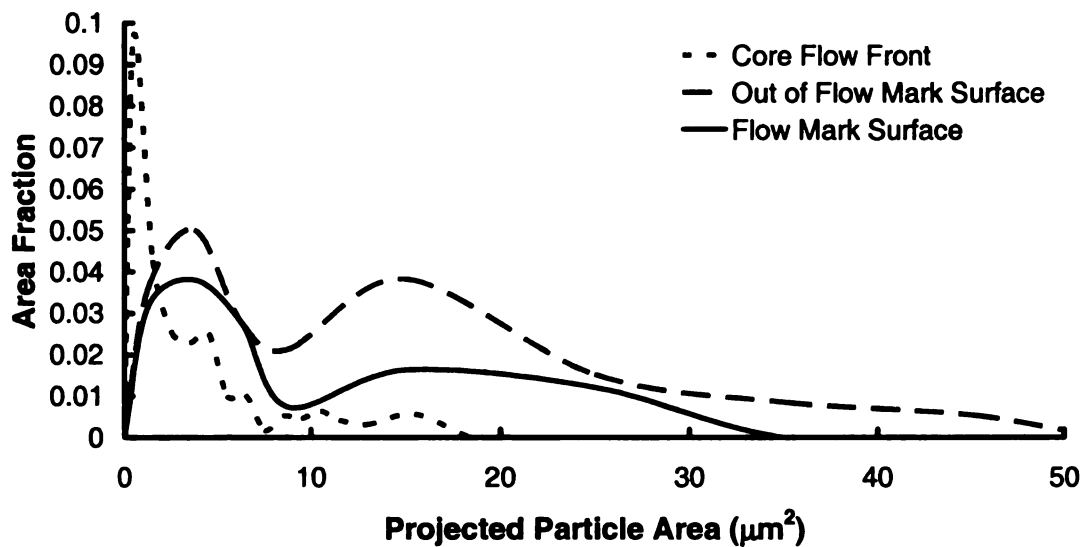


Figure 5.14. Near-wall sections in the x-z plane beneath the out-of-flow-mark and flow-mark surfaces of blend B2

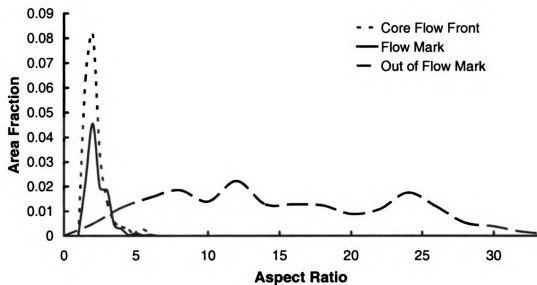


(a) Blend B1

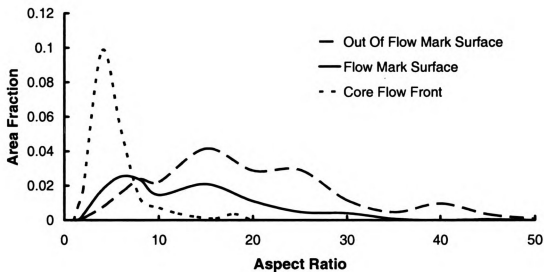


(b) Blend B2

Figure 5.15. Projected area distributions for the dispersed elastomer particles in various regions (a) for B1 and (b) for B2 [Papworth (2001)]



(a) Blend B1



(b) Blend B2

Figure 5.16. Aspect ratio distributions for the dispersed elastomer particles in various regions (a) for B1 and (b) for B2 [Papworth (2001)]

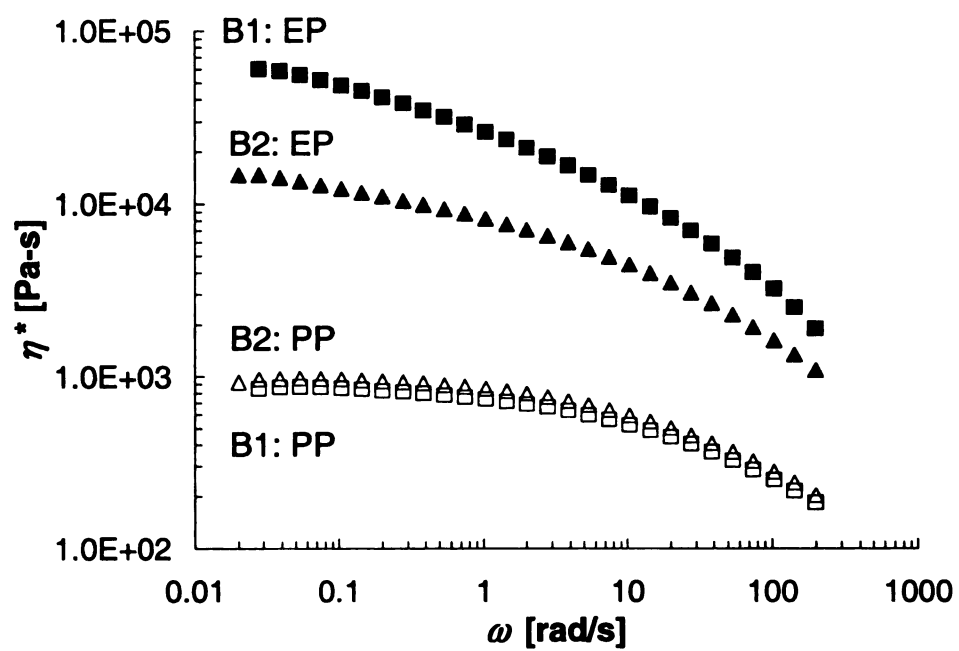


Figure 5.17. Dynamic shear viscosities of the PP matrices and EP dispersed phases of the blends at 200°C.

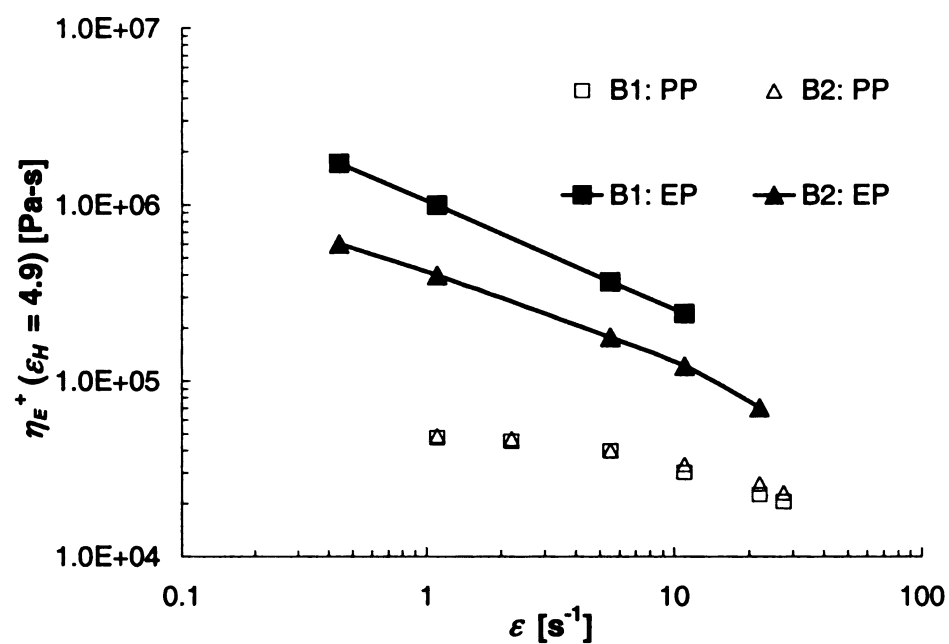


Figure 5.18. Strain averaged extensional viscosity of the matrix PP (open symbols) and dispersed EP elastomer phases (filled symbols) in blends B1 and B2, evaluated at Hencky strain $\epsilon_H = 4.9$ at 200°C

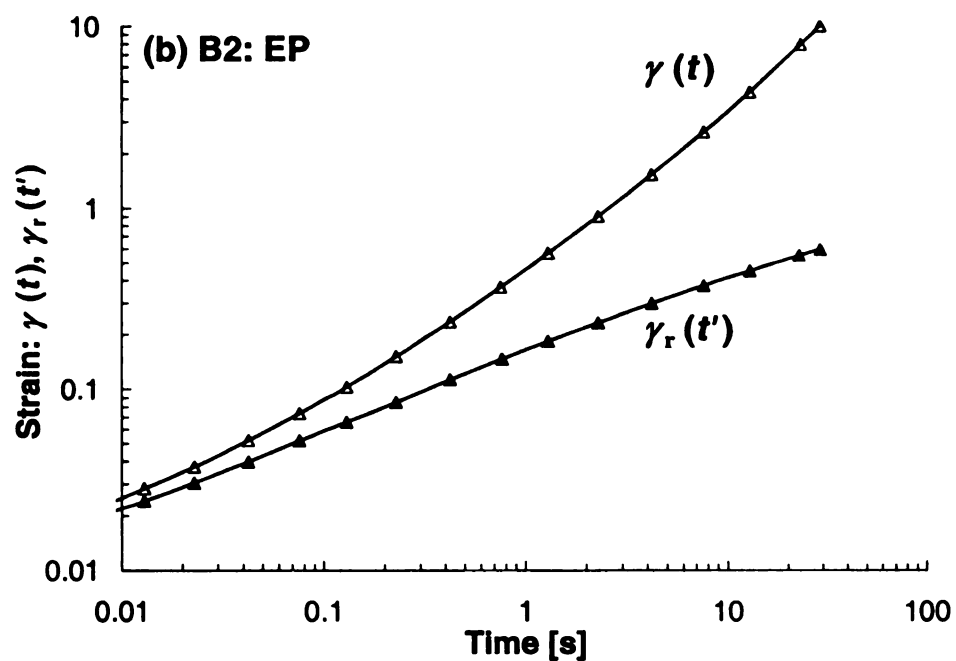
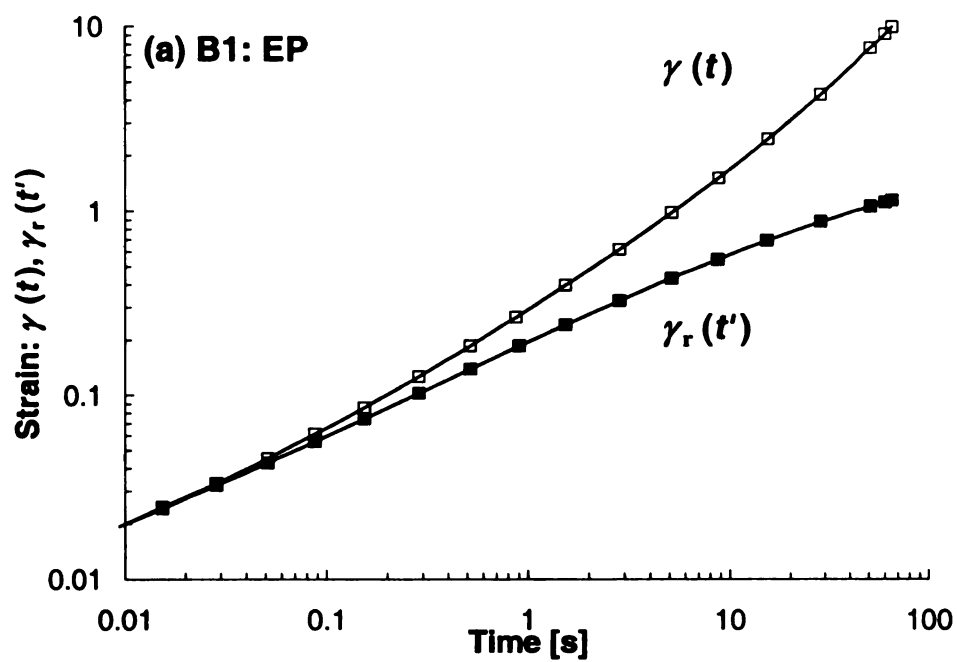


Figure 5.19. Total strain and recoverable strain during shear creep at 3000 Pa followed by constrained recovery for the EP elastomer phases of the blends at 200°C.

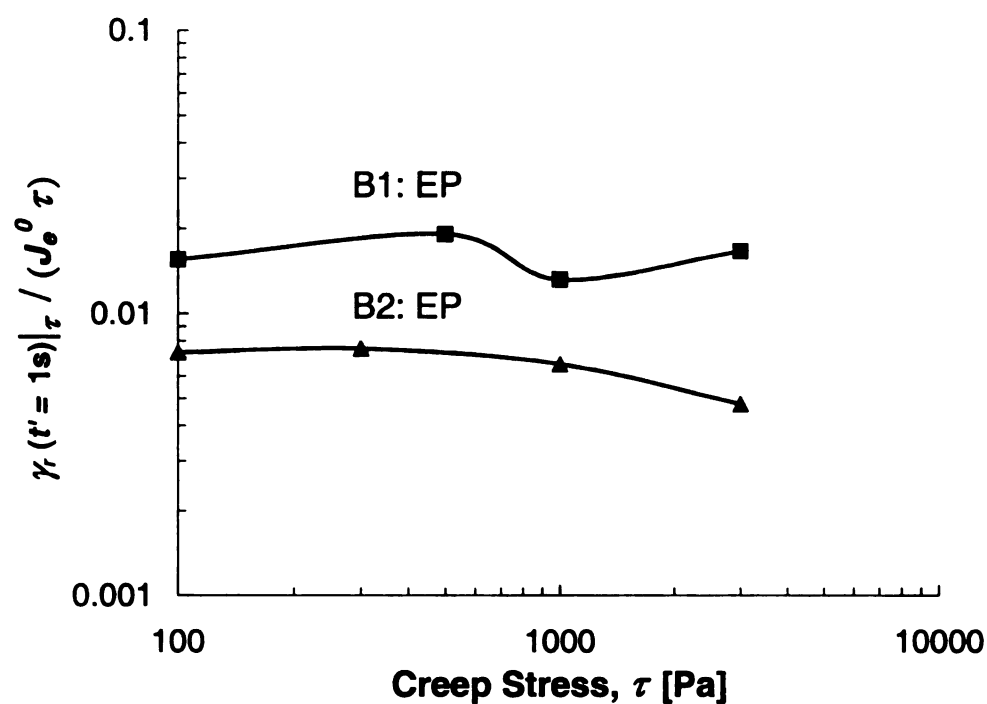


Figure 5.20. Recovered strain $\gamma(t' = 1 \text{ s})$ relative to the linear equilibrium recoverable strain corresponding to the creep stress during constrained recovery following shear creep at several stresses for the EP elastomer phases of the two blends, and at 200°C

Chapter 6.

RECOVERY OF ELASTOMERIC DROPS IN SUSPENSION FOLLOWING HIGH-RATE EXTENSIONAL FLOWS

SUMMARY

A new experimental apparatus has been assembled to study strain recovery after elongation of a model elastomer suspended in a less viscoelastic medium at room temperature. The rheological parameters and the flow conditions, which would result in a greater role of elastic forces in driving the dispersed phase recovery, have been investigated in this model flow setup designed for single drops. Small drops of well-characterized elastomers suspended in a matrix fluid of lower viscosity and elasticity, are stretched rapidly without wall effects in this setup; the stretch ratio of the drops is then recorded over time. Preliminary results confirm significant recovery over a few seconds. The times over which such initial recovery is observed are significantly shorter than the interfacial timescales for the fluid system investigated. Exploration of the full range of parameters with this setup is left for future work.

6.1. INTRODUCTION

Recovery of stretched drops can be brought about by interfacial tension between the drops and the matrix as well as elastic stresses within the drop. Interfacial tension is the only restoring force when both the drop as well as the matrix are Newtonian [see, for example, Tucker and Moldenaers (2002), Doi and Ohta (1991), Vinckier et al. (1997a, 1997b, 1999a, 1999b),]. On the other hand, strain recovery in many viscoelastic systems can also be modeled as solely driven by interfacial tension [see, for example, Paliarne (1990), Gramespacher and Meissner (1997), Okamoto et al. (1999)]. The apparent insignificance of elastic effects during drop recovery in these viscoelastic systems is the result of several factors – summed up into the four scenarios described below - which may prevent the manifestation of nonlinear elastic effects

1. Recovery following very small deformations [Paliarne (1990), Gramespacher and Meissner (1992), Graebing et al. (1993)]
2. Recovery in the absence of prior flow history – quiescent recovery of “imbedded” fibers and disks [Carriere et al. (1989), Cohen and Carriere. (1989a and 1989b), Rundqvist et al. (1996), Carriere and Silvis (1997)]
3. Recovery following very slow deformations [Gramespacher and Meissner (1997)]

4. Recovery of a drop in a matrix of comparable viscosity and elasticity [Gramespacher and Meissner (1997)] or in a matrix of substantially higher viscosity and elasticity [Yamane et al. (1998), Okamoto et al. (1999)]

In all the above four scenarios, elastic stresses within the drop would either not be substantial (due to low strains and low strain rates) or would not be very effective in driving the recovery (due to high matrix viscosity or strong matrix elastic effects which keep the drop deformed [Hooper et al. (2001), Tretheway and Leal (2001)]).

In contrast, as seen in Chapter 5, elastic effects within the dispersed phase, as assessed by nonlinear shear creep recovery, were key in driving the recovery of the blend. The rheology of the matrix and dispersed phases of these blends is summarized in Figure 6.1, and the key fluid and flow parameters are listed in Table 6.1. It is clear that the dispersed phase is more viscous and possesses greater elasticity than the matrix. Also, the blends are subjected to significant strain rates and high deformations during processing. This scenario presents the need to understand in a systematic fashion the various factors that enhance or hinder the role of elastic stresses in driving the recovery. In other words, the problem being addressed in this chapter, and in greater body of work in progress is - what are the conditions which are conducive to the manifestation of elastic effects during recovery. The obvious spectrum of parameters would include the elastomer and matrix rheology, the rate of deformation, $\dot{\epsilon}$, the maximum strain imposed during the deformation, prior to start of the recovery, ϵ_0 , the drop / matrix viscosity ratio, k , and the drop / matrix elasticity ratio, K .

To investigate these aspects in a controlled fashion, an experimental apparatus has been assembled to record recovery behavior in elastic drops suspended in a less viscous and elastic fluid, immediately following rapidly imposed high-strain flow-induced extensional deformations.

6.2. EXPERIMENTAL

6.2.1. Experimental Setup

The important flow features of the current experiment are summarized in the schematic shown in Figure 6.2. This experimental setup offers the following features

1. Imposition of *calibrated rapid high-strain extensional deformations via flow* on a viscoelastic drop suspended in a matrix of lower viscosity and elasticity
2. *Control of the rate of deformation, and the extent of deformation*
3. *Instantaneous removal of the extensional flow field* upon attaining a finite deformation

4. Setup to *observe and record the recovery of the drop immediately following deformation*

As shown in Figure 6.2, the extensional flow field is established by flow of the suspending fluid through a semi-hyperboloidal converging fixture with a profile $r^2(z+z_0)=C$, and offering a Hencky strain $\epsilon_H = 2$. The fixture, by virtue of its profile offers a constant extensional flow rate throughout its length. The drop is transported in a separate stream of the suspending fluid through the center and is introduced in this well-established extensional flow field just upstream of the convergence. Extensional strains are imposed on the drop as it flows through the convergence – it is ensured that the drop is small as compared to the exit of the converging fixture in order to avoid wall effects and any additional uncontrolled deformation. Once the stretched drop exits the fixture, the flow is stopped instantaneously by activating solenoid valves. Recovery of the drop is recorded from this point onwards using a high-speed camera (KODAK camera with CCD connected to an EKTAPRO high speed processor) capable of grabbing 50 frames per second.

The bulk flow of the matrix is served from a reservoir. The matrix fluid is conveyed using a screw pump which can operate up to pressure drops of about 250 Pa. The screw conveying mechanism of the pump offers high rate transport of fluids while ensuring minimal shear degradation. The feed from the pump is sent to a high pressure manifold, where the flow is distributed into five streams. Four streams feed the bulk flow of the suspending fluid through the flow cell, while the fifth stream is used exclusively

for conveying the drop. The four streams feeding the bulk flow enable faster equilibration of flow and quick establishment of the extensional flow field. The fifth stream is connected to the flow cell via a T-fitting, which can be opened to introduce the drop and then re-closed. The flow cell is essentially an axisymmetric cylinder made of pyrex high clarity glass. One glass tube is placed upstream of the semi-hyperboloidal converging fixture for introducing the fluid streams, and one tube is fixed downstream of the convergence and serves as the observation port to record recovery. The semi-hyperboloidal converging fixture is made stainless steel, and was machined to 0.001 mm tolerance at the Physics and Astronomy Workshop at Michigan State University using an automated milling machine.

The entire flow cell is submerged in a transparent rectangular trough made of clear polycarbonate walls filled with the same matrix fluid as that flowing inside the flow cell. This arrangement leads to obscuring of the glass tube surface, and therefore eliminates undesired optical effects arising from the curvature of the glass tube.

The screw pump is controlled by a regulator which allows adjustment of the screw rpm thus offering precise control of flow rates, and consequently extensional strain rates. The flow through the screw pump can be stopped instantaneously using a solenoid valve. The flow downstream of the flow cell also passes through the solenoid valve which can be instantaneously closed when activated.

6.2.1a. Flow kinematics

The parameters that may be precisely controlled in any experimental run in this setup are: (1) the initial size of the spherical drop, R_0 , (2) the macroscopic extensional strain imposed on the sample, which is fixed by the strain offered by the semi-hyperboloidal converging fixture, $\varepsilon_{H,\max} = 2.0$, and (3) the global extensional strain rate, which is fixed by the bulk flow rate through the semi-hyperboloidal fixture:

$$\dot{\varepsilon}_m = \frac{Q}{\pi C} \quad (6.1)$$

where C is the geometrical constant which governs the die profile ($r^2(z+z_0) = C = 0.3913 \text{ cm}^3$). $\dot{\varepsilon}_m$ remains constant throughout the length of the semi-hyperboloidal convergence. With this pump, flow rates of up to 40 ml / s can be obtained for a fluid of viscosity 1 Pa-s. This means that $\dot{\varepsilon}_m$ up to 35 s^{-1} may be achieved in the current experimental setup. With these parameters fixed, the capillary number of the flow is also known at the beginning of each run

$$Ca = \frac{\eta_m R_0 \dot{\varepsilon}}{\Gamma} \quad (6.2)$$

The matrix fluid experiences the $\varepsilon_{H,\max}$ and the $\dot{\varepsilon}_m$ imposed during the experiment.

The global stretch ratio in the matrix is the same as that imposed by the geometry

$$\lambda_{m,\max} = \exp(\varepsilon_{H,\max}) \quad (6.3)$$

The drop however does not experience the same strain rate or the macroscopic deformation imposed. The global stretch ratio in the drop is evaluated by comparing the longest drop dimension (which turns out to be aligned in the flow direction for strong flows such as the one imposed in this experiment) $L_{\max}$, immediately after the drop exits the semi-hyperboloidal fixture to that of the diameter of the initial spherical drop

$$\lambda_d, \max = \frac{L_{\max}}{2R_0} < \lambda_{m,\max} \quad (6.4)$$

It should also be noted that by virtue of the current setup, the strain rate and Hencky strain imposed on the drop cannot be independently controlled. This is because, as the strain rate increases, so does the capillary number - and since the macroscopic deformation does not vary because of the constant Hencky strain offered by the semi-hyperboloidal die - the deformation of the drop increases with increasing strain rate.

6.2.2. Materials

The selection of materials was primarily governed by the need to have two immiscible fluids which have similar densities, have different refractive indices to offer

proper contrast between the drop and the matrix phase, and which can be easily tailored to obtain a range of properties from viscous Newtonian to highly viscoelastic –especially for the drop phase.

The drop phase was chosen to be polydimethylsiloxane (PDMS). PDMS is available in a range of molecular weights, starting from low viscosity Newtonian fluids to high molecular weight elastomers. This makes it possible to blend PDMS of different molecular weights – this way obtaining deformable gels with a broad molecular weight distribution. One such gel was prepared for the current set of experiments by mixing four PDMS of widely different molecular weights. The matrix phase was chosen to be a mixture of polybutene and a chlorinated paraffin oil – formulated primarily to match the density with the PDMS drop fluid.

The mixture of polybutene and chlorinated paraffin oil is a Newtonian fluid, with a constant shear viscosity of 780 mPa-s at 25°C.

The drop fluid has a zero-shear viscosity of 20 Pa-s at 25°C. The viscoelasticity of the drop fluid is not as pronounced as some of the elastomers or even thermoplastics characterized in Chapters 4 and 5. The drop phase appears to be weakly elastic as seen in the startup shear viscosity curve plotted in Figure 6.3. As seen in the figure, the startup viscosity does not instantaneously reach the steady value of 20 Pa-s, indicating the non-Newtonian behavior of the drop phase. However, the transient is not very long and steady viscosity is reached within 1 s.

Dynamic data for the drop phase PDMS are presented in Figure 6.4 and 6.5. The storage moduli for the drop phase are measurable and have finite positive values at the lowest frequencies measured indicating the viscoelastic nature of the drop fluid. Over the first decade of the tested frequencies, terminal region may be seen based on the slopes of the storage and loss moduli curves with respect to frequency. The complex viscosity plotted in Figure 6.5 also remains constant at the zero-shear viscosity of 20 Pa-s in the first decade of frequency tested. At higher frequencies however, weak shear thinning is obvious.

The strongest evidence of viscoelasticity of the drop phase is obtained from stress relaxation and shear creep recovery experiments. The stress relaxation curves measured at strains of 0.05 and 1.0 are shown in Figure 6.6. Strong nonlinear damping can be observed at a strain of 1.0 with respect to the curve at 0.05. The curves at the two strains are parallel, indicating time-strain separability. The duration over which the stress relaxes is striking. In contrast to the startup shear viscosity and dynamic data which indicate small relaxation times for the PDMS, the stress relaxation experiments point to the presence of long relaxation times. The tube disengagement or “reptation” time assessed from a plot of $\ln \{ G(t) \}$ vs t plots [Takahashi (1995), Tobolski (1959), also see Section 4.4.3b], turns out to be 9.8 s, which is indicative of strong viscoelastic character. This long relaxation time may be the consequence of the presence of small amounts of the high molecular weight (2,000,000 CSt) silicone elastomer in the PDMS gel.

Strong elastic effects are also evident in shear creep recovery experiments. As seen in Figure 6.7, following nonlinear shear creep at 10 Pa up to a strain of about 45, the PDMS shows substantial recoverable compliance, and a long retardation time.

6.2.3. Determination of Interfacial Tension

The interfacial tension between the two fluids was measured by adopting the “imbedded fiber retraction” method used by Cohen et al. (1989) [Carriere and Silvis (1997)] to determine interfacial tension between polymer melts. To measure the interfacial tension, a short thread of the matrix fluid was vertically formed within a reservoir of PDMS using a thin syringe. While forming the thread, the fluid was released very slowly and without application of too much pressure to ensure absence of any flow induced stresses. During recovery, the thread first recovered at one end showing some fore-aft asymmetry forming a tear shaped drop as shown in Figure 6.8. But soon the fore-aft symmetry was restored and the thread evolved into a short ellipsoid and ultimately into a sphere. The evolution of drop shapes was recorded at regular intervals using a digital camera, and some of the pictures are shown in the collage in Figure 6.8. The evolution of the drop size during the later stages of its recovery starting from the ellipsoidal shape was modeled using a balance between interfacial tension forces and drag forces following Cohen et al. (1989)

$$6\pi\chi\eta_{eff}R\frac{dL}{dt} + \Gamma\frac{dA}{dL} = 0 \quad (6.5)$$

In the above equation, R and L are the instantaneous radius and length of the drop respectively, and A is the interfacial area. χ is a hydrodynamic interaction parameter between the drop and the matrix and is a function of the instantaneous drop shape, and η_{eff} is an effective viscosity given by

$$\eta_{eff} = \frac{\eta_m + 1.7\eta_d}{2.7} \quad (6.6)$$

Along with the drop sizes, the viscosities of the two fluids were also known, leaving only the interfacial tension as the fitting parameter. Carriere and Cohen (1989, 1997) modeled the drop shape as a cylinder with hemispherical end caps, and fixed the shape factor in Equation 6.5, as 1.0. Then the solution of the differential equation yields the following analytical expression for the evolution of drop size.

$$f(r) = 3 \ln \left[\frac{(1+r+r^2)^{1/2}}{1-r} \right] + 3^{3/2} \arctan \left[\frac{3^{1/2}r}{2+r} \right] - r - 8r^{-2} \quad (6.7)$$

In the above equation, r is the instantaneous radius of the thread normalized by the radius of the equivalent sphere

$$r = \frac{R}{R_0} \quad (6.8)$$

The parameter r is evaluated at regular intervals throughout the retraction process. The value of $f(r)$ is related to t through the equation below

$$f(r) = \lambda_{\Gamma}^{-1} t + f(r_e) \quad (6.9)$$

In the above equation, λ_{Γ} is an interfacial timescale, and r_e is the normalized fiber radius at the commencement of recovery

$$\lambda_{\Gamma} = \frac{\eta_{eff} R_0}{\Gamma} \quad (6.10)$$

$$r_e = \frac{R_e}{R_0} \quad (6.11)$$

The best fit to the experimental data with this analytical expression was obtained for an interfacial tension of 1.8 mN /m. The fit of expression to experimental data is good as seen in Figure 6.9. The experimental transient is smooth and monotonic, just like the theoretical curve, and without any abrupt transitions in slope - this encourages us to believe that the recovery observed is truly interfacial tension driven and any surfactant or stress effects are absent in this measurement. Thus, 1.7 mN/m was taken to be the interfacial tension between the two fluids. The value is slightly lower than the magnitude

of 2.0 mN / m reported between polybutene and PDMS, and this difference must be due to the presence of chlorparaffin oil in the polybutene.

6.2.4. Typical Parameter Ranges in the Experiment

The parameters that may end up affecting the fraction of recovery brought about by elasticity, will also affect the deformation of the drop. For example, high Deborah number deformations will also be associated with high capillary numbers, because both parameters are proportional to the strain rate of deformation $\dot{\epsilon}$. Thus a drop deformed at high rates will also be deformed to higher strains. Alternatively, when deformed at the same strain rate, a smaller drop will be deformed to a lesser extent than a larger drop. All these factors will come into play in governing the recovery.

In this experiment viscosity ratio between the drop and matrix fluids was chosen so as to simulate the actual blend setups. The typical ranges for the various parameters are given in Table 6.2. As shown in the table, the magnitudes of viscosity ratios, strain rates, capillary numbers, Reynolds numbers and the interfacial time constants for the current experimental setup and fluids are in the same range as those observed for actual TPO blend systems, as laid out in Table 6.1.

6.2.4a. Drop breakup Considerations

In addition to the absence of inertial effects (as evident by the low Reynolds numbers), the choice of the fluids as flow parameters has been made so as to ensure the absence of breakup of the stretched drops. Our operating ranges involve viscosity ratios ranging from 5-50. For simple shear flows with viscous drops, Grace has shown that drop breakup is ruled out if the viscosity ratios are greater than 1.0. Extensional flow on the other hand is a stronger flow, and drop breakup may occur at any magnitude of viscosity ratio.

Breakup of stretched filaments may occur via two mechanisms – “end pinching” or through capillary instabilities. The typical end pinch time constants for the current experimental fluids are around 200 s (refer to Equation 2.30). Elastic recovery on the other hand, if detectable, is expected to occur over timescales of 5-10 s. Breakup via end-pinching is therefore ruled out within timescales at which elastic recovery occurs. Stone et al. pointed out that when the viscosity ratio is greater than 1.0, drop breakup via Rayleigh instabilities is not seen up to an aspect ratio of 15. The macroscopic stretch ratios offered by the semi-hyperboloidal convergence are not greater than 8 (the drop phase was always stretched to lesser values, given the higher drop viscosity and elasticity as compared to the matrix). Based on above considerations, Rayleigh instabilities are also ruled out. Breakup is further ruled out because of the elasticity of the drops. Indeed, in these experiments, we did not observe any drop breakup with the experimental range of parameters.

6.3. RESULTS AND DISCUSSION

In Figure 6.10, the retraction of drop stretch ratio has been plotted during recovery driven solely by interfacial tension and in the absence of any elastic effects. This figure is an alternative way of representing Figure 6.9. The ordinate is the instantaneous drop length normalized by the drop length at maximum stretch (at the commencement of recovery). This method of presenting recovery data is suitable when recovery transients starting from different initial stretch ratios are to be compared. The figure also shows the results of the Carriere-Cohen drag and interfacial tension force balance described earlier. The experimental data and the predictions agree reasonably well. This transient for purely interfacial tension driven recovery is the base case with which elastic effects, if present, shall be compared. The smooth and monotonic recovery transient and the absence of any abrupt slope changes are indications that only one mechanism of restoration of drop shape and size is at work.

In Figure 6.12, the photo sequence shows some of the key length transitions during recovery of the PDMS drop following extension to a stretch ratio of 2.8, brought about at a macroscopic stretch rate of 12 s^{-1} . As can be seen the drop is ellipsoidal to begin with and remains ellipsoidal at all times until it finally reaches a shape close to a sphere. Care was taken to make sure that the drop emerging from the semi-hyperboloidal convergence was always ellipsoidal. There are two reasons for this. First of all, ellipsoidal drop shapes are considered ideal for phenomenological modeling of drop

deformation and recovery phenomena. Secondly, shapes other than ellipsoidal are indications of non-homogeneous deformation of the drop. For example, flattening of the drop along one of the minor axes would indicate high shear gradients. Loss of fore-aft symmetry would indicate non-homogeneous extension of the drop. With these additional features, it would be difficult to unambiguously relate the recovery behavior to the extension rate or other parameters. For example, when drops were chosen to be bigger than 10 microL, the drop size was such that wall effects came into play, resulting in the loss of fore-aft symmetry as shown in Figure 6.11. Such "space-shuttle" type shapes for drops has been reported in the finite element simulations by Singh, in the presence of wall effects. While it is clear from Figure 6.11 that even in the absence of fore-aft symmetry, the drop recovery behavior is quantifiable - but because of modeling considerations and in order to avoid accounting for spurious experimental effects and uncontrolled deformation, only spheroidal shapes were considered for evaluation of recovery.

Considering once again, the photo sequence for the recovery of spheroidal drop in Figure 6.12, there is clearly visible recovery in the first 1 s, the extent of which is similar to that observed over the next 9 s. Obviously, there seems to be a faster mechanism at work in the first few seconds. This is clearer when the drop stretch ratios are plotted at several times during recovery as shown in Figure 6.13. The transient clearly shows two steps, indicating the presence of two mechanisms of recovery. In the first stage, the aspect ratio shows a precipitous drop within 5 s, followed by a slower relaxation to sphere over the next 75 s.

In Figure 6.14, the same recovery transient, in terms of normalized instantaneous length, is compared to the prediction of drag - interfacial tension force balance with the same matrix and drop viscosities and drop size as the experiment. Clearly the initial recovery is much faster than interfacial tension driven recovery at comparable times. This recovery must be brought about by elastic effects.

Another test was conducted at a lower extension rate. The initial recovery transient for the two runs are compared along with purely interfacial tension driven recovery in Figure 6.15. This Figure clearly establishes the role of deformation rate in bringing about elastic effects during recovery. Compared to the drop deformed at 12 s^{-1} , the drop deformed at 10 s^{-1} shows lesser extent of initial recovery via elastic effects. Clearly, higher Deborah number gives rise to greater nonlinear effects resulting in faster initial recovery via elastic effects.

6.4 CONCLUSIONS

The new experimental setup allows the study of recovery of viscoelastic drops suspended in a less viscous and elastic matrix, immediately following rapid flow induced deformations. Creep recovery tests on the drop fluid reveal substantial elasticity in the drop phase. Following high rate extensional deformations to stretch ratios of about 2, a substantial portion of the imposed strain are recovered within 2-5 s, times much shorter

than the interfacial timescale. The recovery transient thus shows two stages, an initial rapid recovery followed by a slower relaxation to sphere. The extent of recovery in the initial stage relative to the total deformation is higher following deformation at a higher rate – confirming the elastic origins of the phenomenon. An investigation of the full range of parameters including viscosity ratios, initial strains and fluid rheological parameters will be continued in future.

Table 6.1. Typical material and flow parameters involved in rapid processing flows of TPO blends comprising an elastomeric dispersed phase in a thermoplastic matrix

Shear rates	$\dot{\gamma}$	50 100 s ⁻¹
Extension rates	$\dot{\epsilon}$	5 10 s ⁻¹
Shear viscosity ratios	$k = \frac{\eta_d}{\eta_m}$	10 - 50
Extensional viscosity ratios	$k_E = \frac{\eta_{E,d}}{\eta_{E,m}}$	5 - 20
Elasticity ratios	$K = \frac{G'_d}{G'_m} \Big _{\omega = 10s^{-1}}$	5 - 40
Reynolds numbers	$Re = \frac{R_0^2 \dot{\epsilon} \rho}{\eta_m}$	0
Capillary numbers	$Ca = \frac{\eta_m R_0 \dot{\epsilon}}{\Gamma}$	10 - 100
Interfacial time constant	$\lambda_\Gamma = \frac{\eta_m R_0}{4 \Gamma} \frac{(19k+16)(2k+3-2\phi(k-1))}{10(k+1)-2\phi(5k+2)}$	~ 2 - 25 s

Table 6.2. Materials and properties for room temperature drop studies

Property	Flow Parameter
Viscosity ratio	$k = 26$
Interfacial tension [N/m]	1.7×10^{-3}
Drop size [m]	0.0025
Extensional Strain Rate	$5 - 20 \text{ s}^{-1}$
Drop Reynolds Number	0.04 – 0.15
Capillary Numbers	5 - 20
Interfacial Time Constant	$\sim 100 \text{ s}$

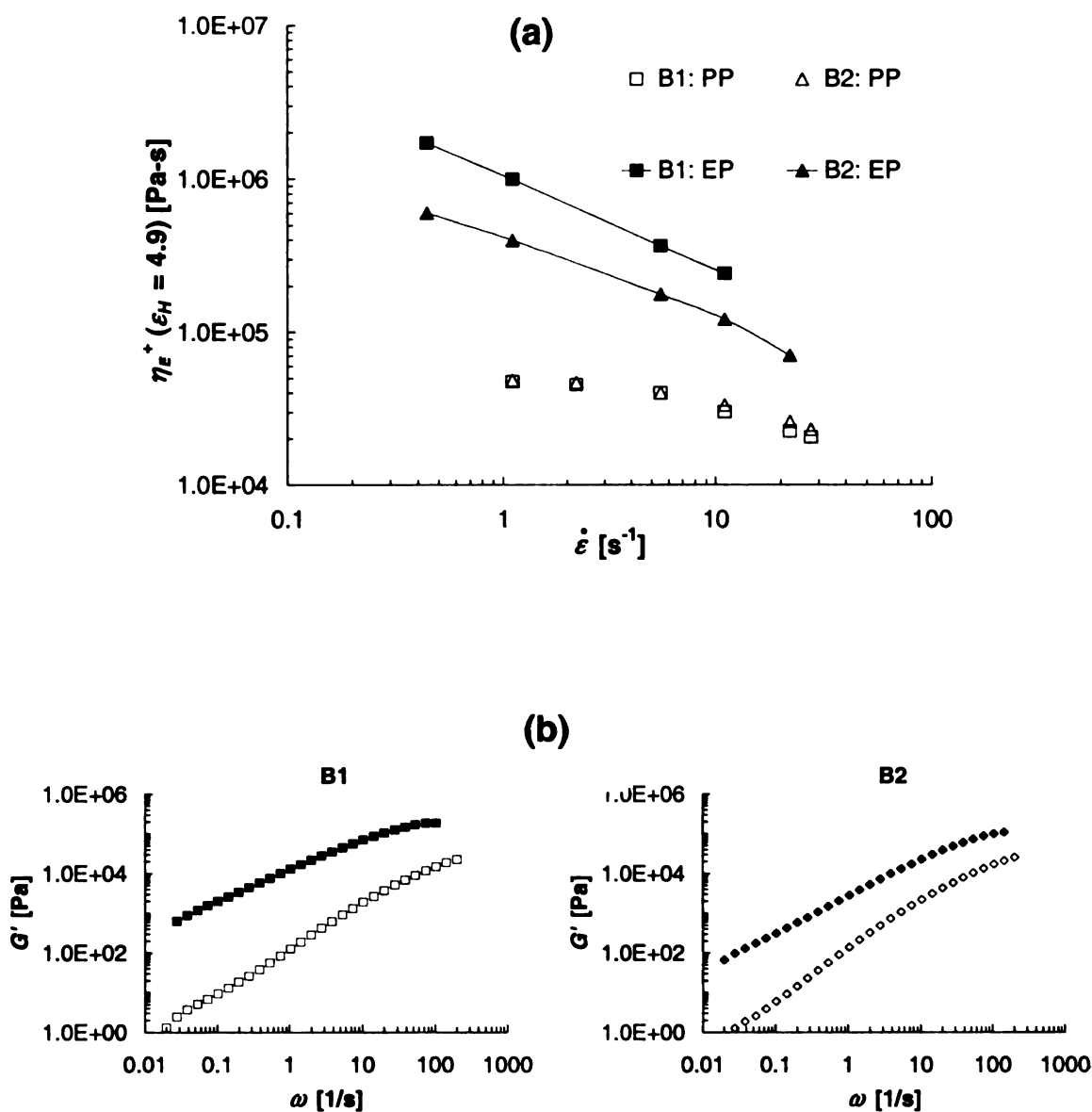


Figure 6.1. Typical matrix and dispersed phase properties of TPO blends. Blends B1 and B2 are same as those studied in Chapter 5. (a) Extensional viscosities of of PP matrices (open symbols) and EP elastomer dispersed phases (filled symbols) evaluated at Hencky strain $\epsilon_H = 4.9$ at 200°C (b) Dynamic storage moduli of the PP matrices (open symbols) and EP elastomer dispersed phases (filled symbols) of blends B1 and B2 at 200°C.

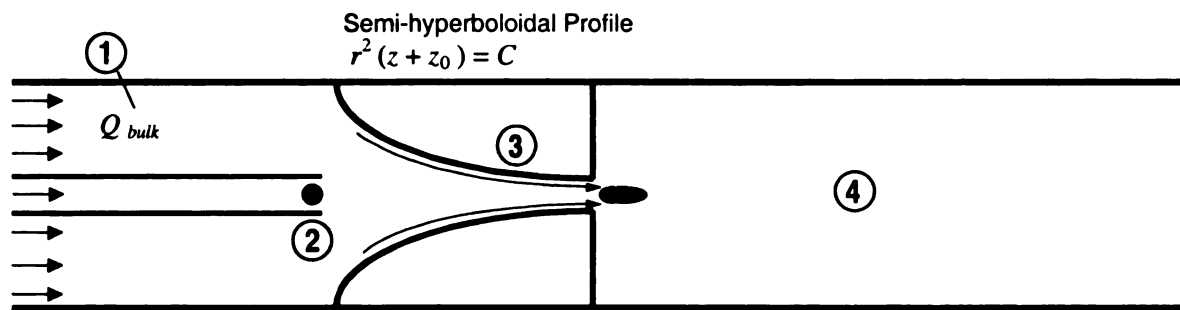


Figure 6.2. Mechanism for imposing rapid finite extensional strains on a viscoelastic drop suspended in a matrix of lower viscosity and elasticity, and observing the recovery behavior after stoppage of flow.

1. Flow of the viscous suspending fluid through the semi-hyperboloidal fixture establishes the high rate extensional flow field
2. The elastomer drop, transported separately in an inner stream of the suspending fluid is introduced to the extensional flow field established by the bulk flow just upstream of the convergence
3. Semi-hyperboloidal converging profile fixture offers a constant extensional strain rate over its entire length; the Hencky strain of the fixture is the upper limit of the strain attained by the drop. The current setup offers a Hencky strain of 2.0. The inlet diameter of the fixture is 20.00 mm, and the exit diameter is 7.38 mm. The length of the converging fixture is 25 mm.
4. Flow is instantaneously stopped once the elastomer drop exits the semi-hyperboloidal fixture and this removes the extensional flow field; the subsequent recovery of the stretched drop is recorded in the downstream portion with a high-speed camera

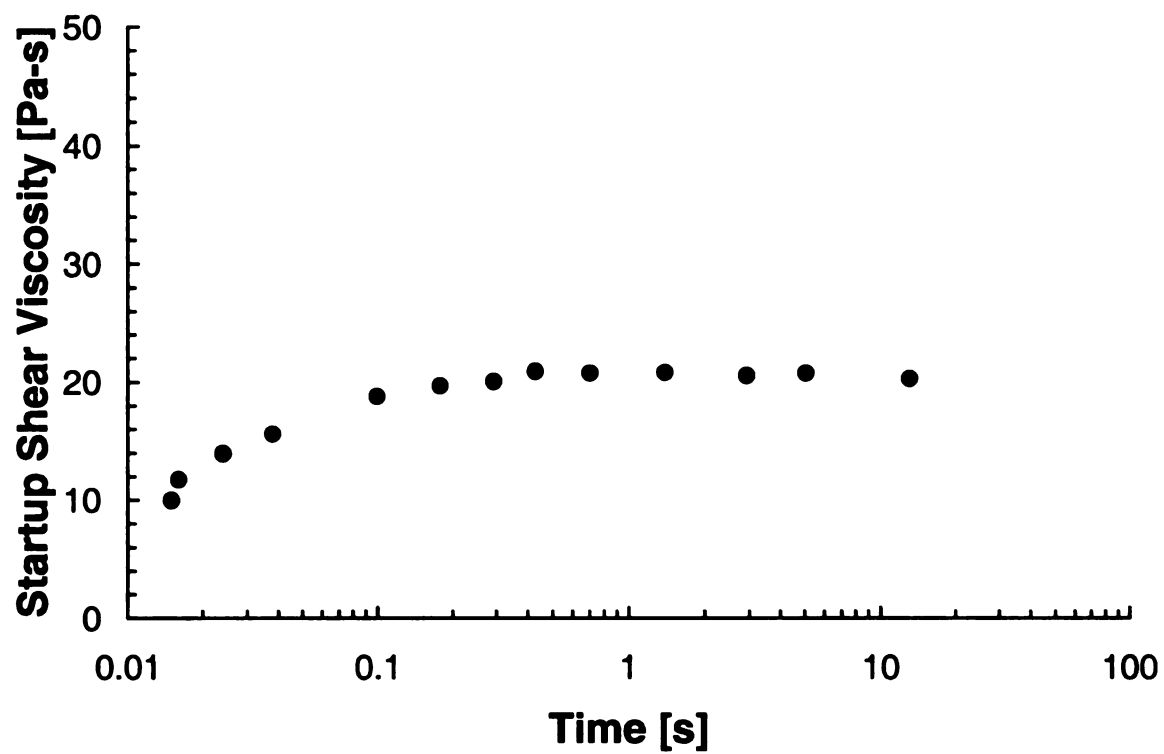


Figure 6.3. Growth of shear viscosity for the drop phase PDMS during step shear conducted at 0.05 s^{-1} , at 25°C

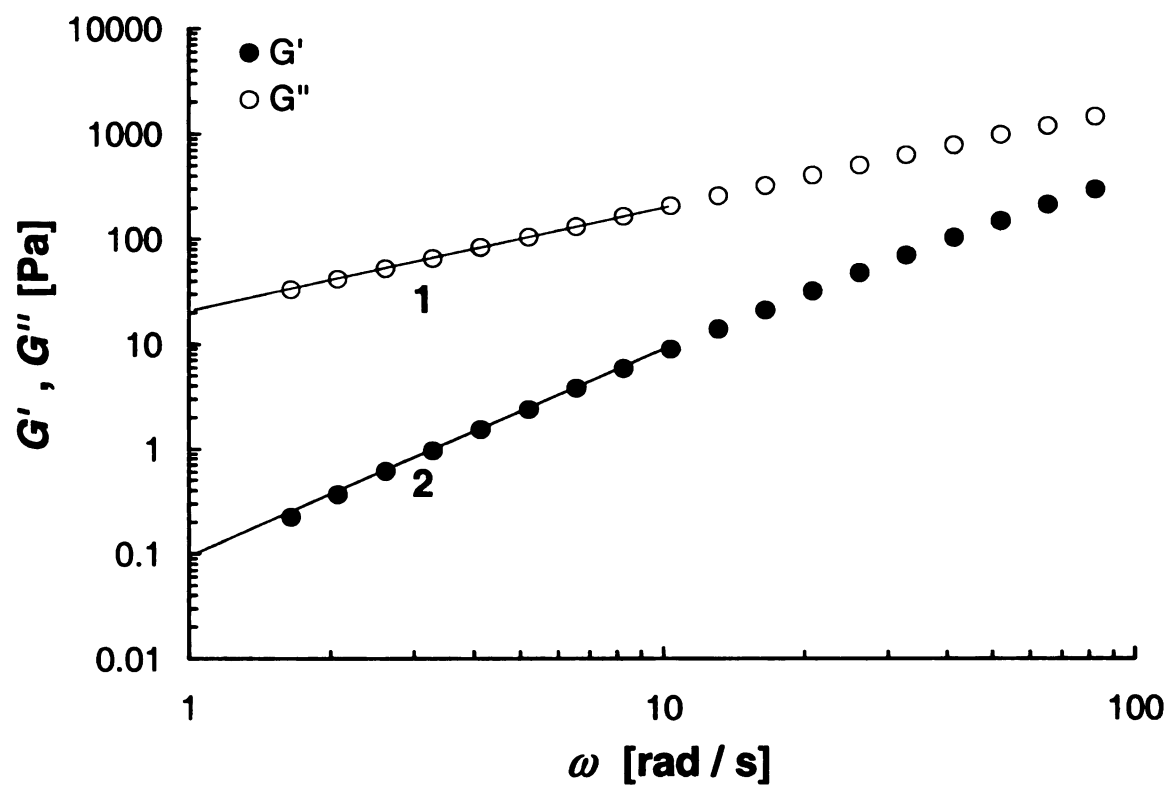


Figure 6.4 Dynamic moduli for the drop phase PDMS at 25°C

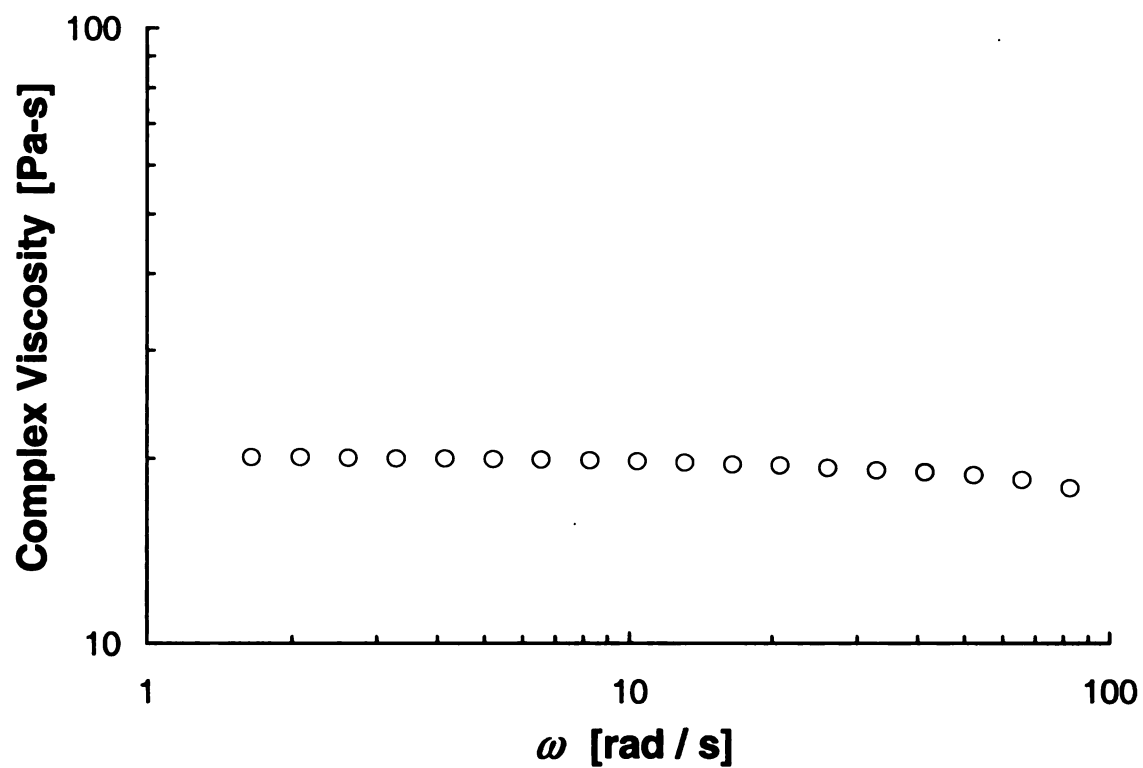


Figure 6.5. Frequency dependent complex viscosity of the drop phase PDMS at 25°C

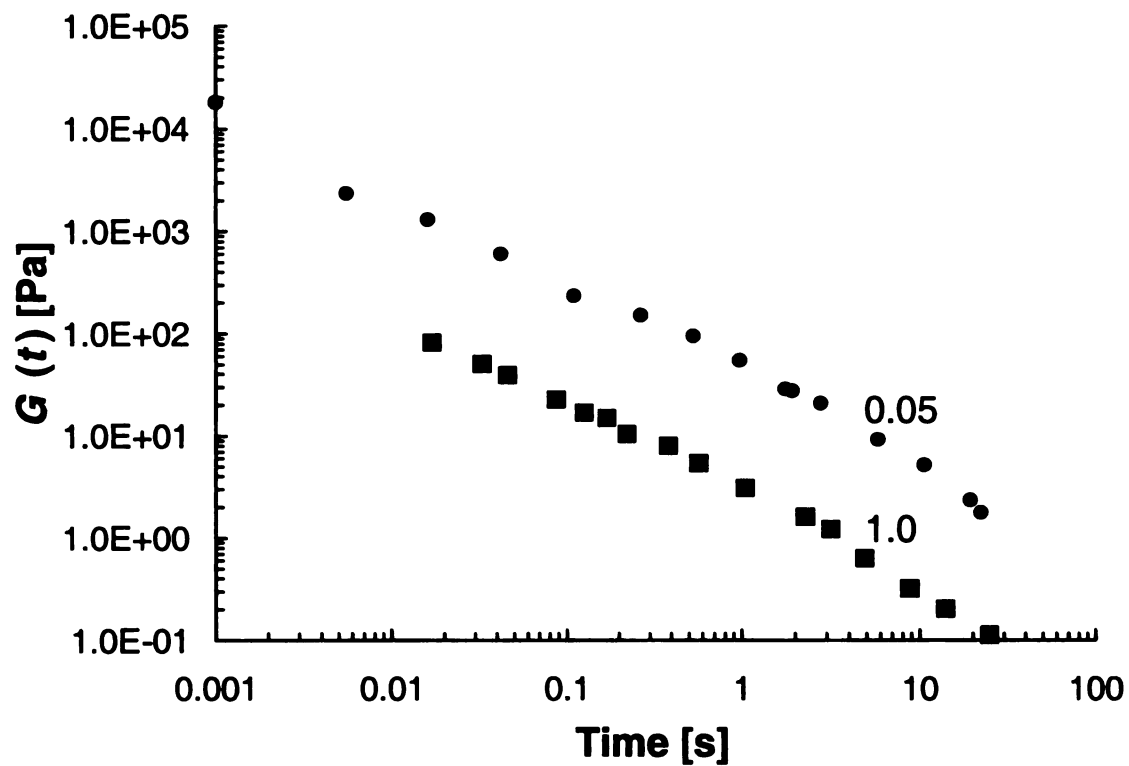


Figure 6.6. Shear stress relaxation curves for the drop phase PDMS at 25°C and two different strains as indicated within the figure.

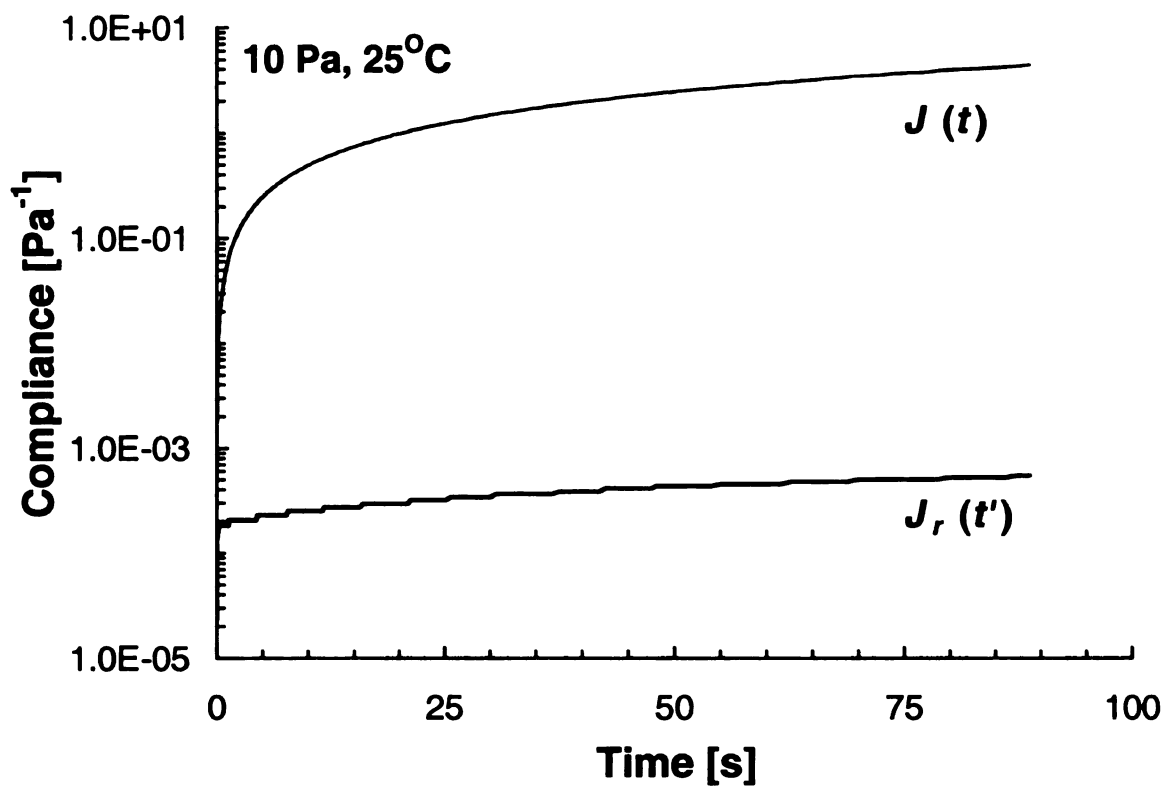


Figure 6.7. Shear creep at 10 Pa, and subsequent recovery for the drop phase PDMS measured at 25°C

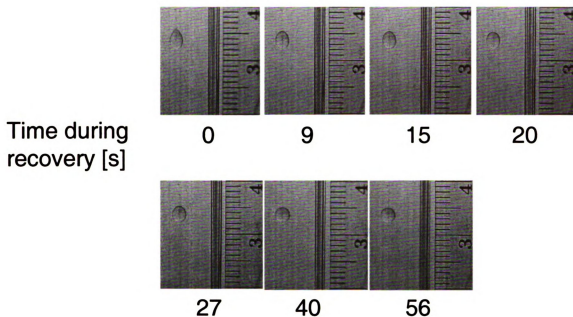


Figure 6.8. A photo sequence following quiescent recovery of a short filament made with the polybutene - chlorparaffin oil mixture imbedded in the high-viscosity PDMS reservoir

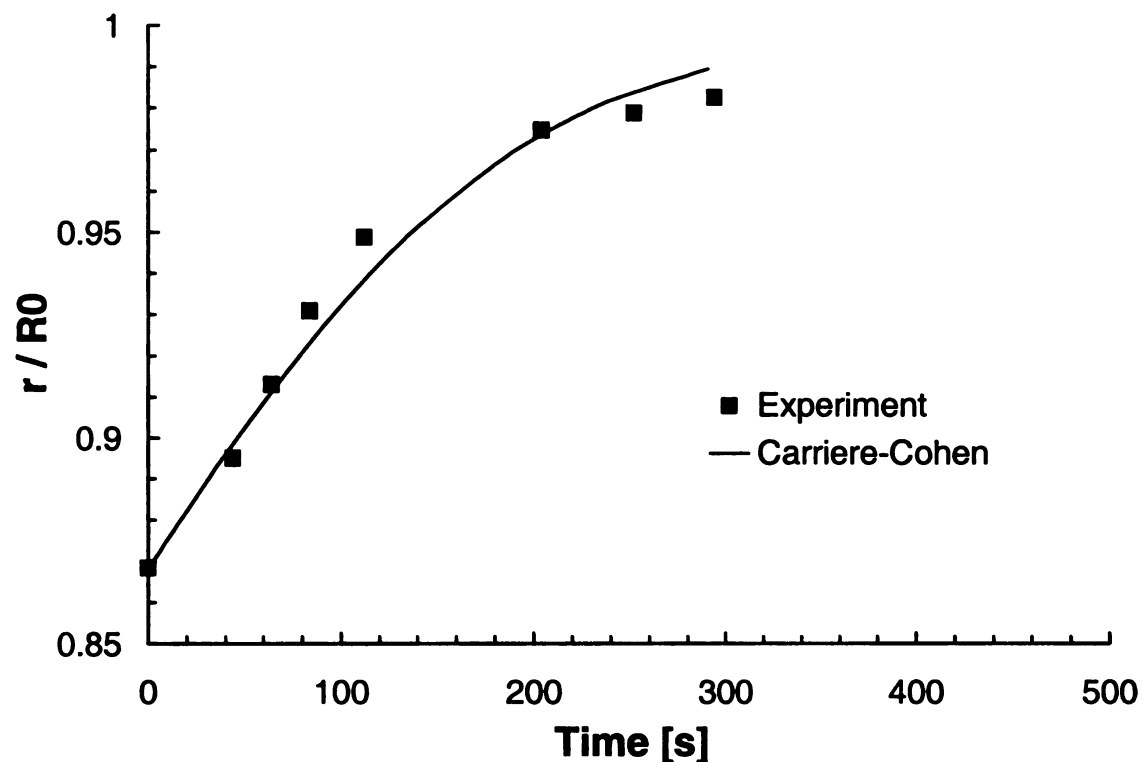


Figure 6.9. Estimation of interfacial tension from quiescent recovery of a short filament of polybutene – chlorparaffin oil mixture imbedded in a high viscosity PDMS reservoir. The points (■) are obtained from measurements of the photographs of the recovering drop at regular time intervals (Figure 6.8). The line is obtained from the shape evolution equation laid out in Section 6.2.3 for the force balance between interfacial tension forces and drag forces – interfacial tension is the fitting parameter to obtain the best fit over experimental data, while the drag force is calculated from known viscosities of the two fluids.

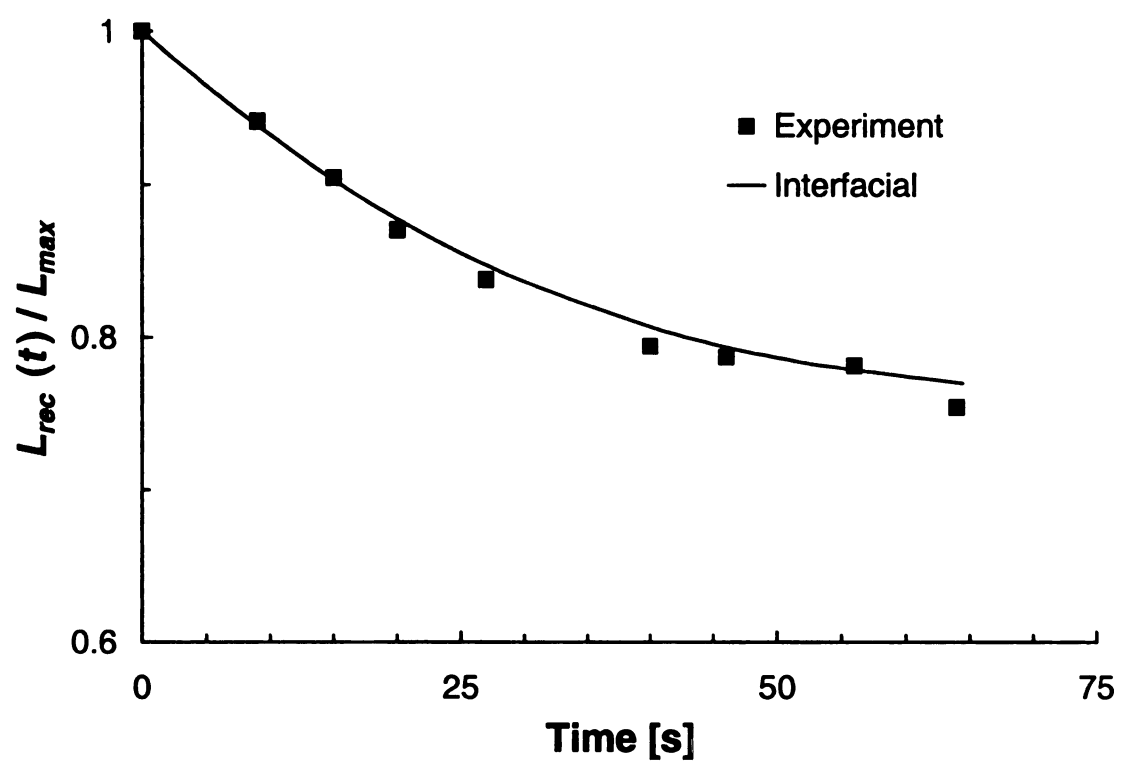


Figure 6.10. Typical drop shape recovery transient following low-rate deformation. Comparison of the experimentally observed transient and the predictions of interfacial tension –drag force balance proposed by Cohen et al. (1989) for quiescent interfacial tension driven recovery

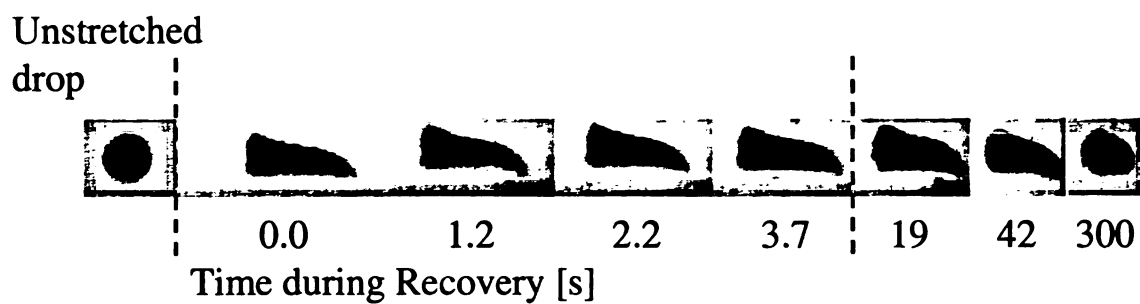


Figure 6.11. Drop shapes obtained with a 29 microL drop with $R_0/R_e = 0.55$, deformed at 10 s^{-1} . Wall effects are apparent from the fore-aft asymmetry of the drop.

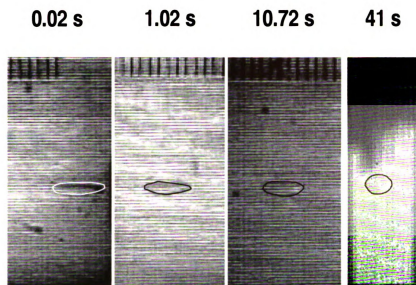


Figure 6.12. A typical photo sequence for drop shape recovery transient following high-rate deformation through the extension flow cell.

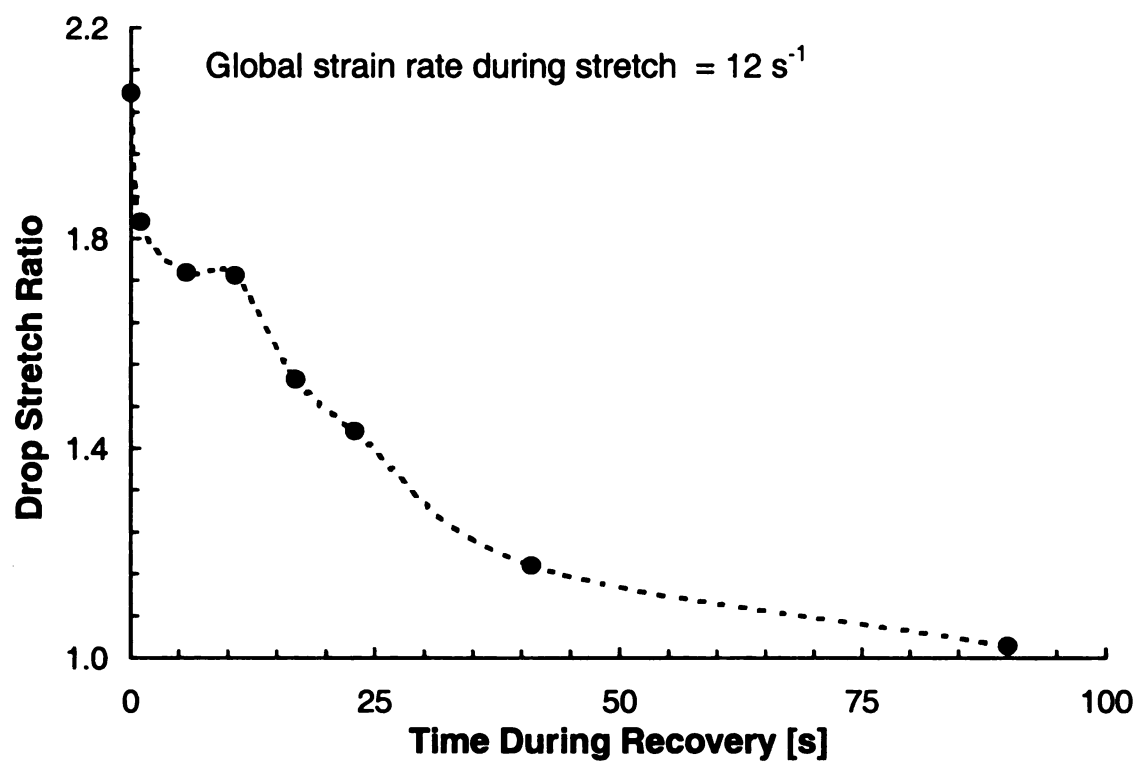


Figure 6.13. Evolution of aspect ratio during recovery following high-rate deformation through the extension flow cell

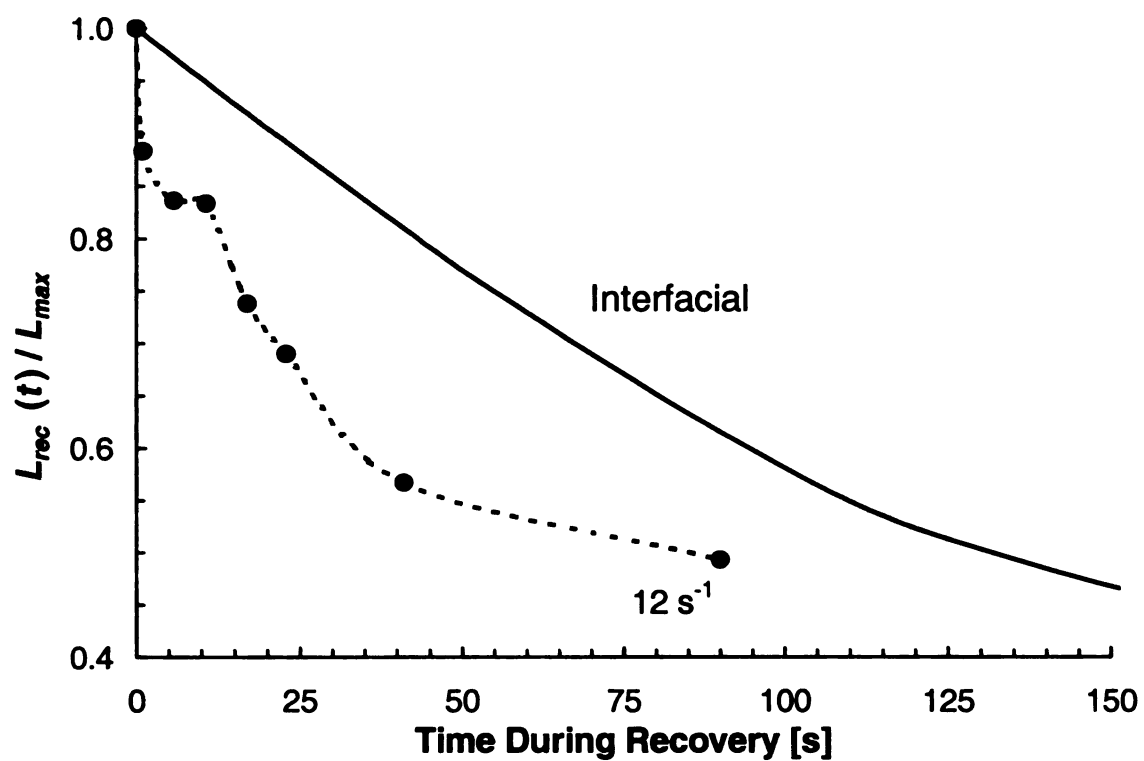


Figure 6.14. Comparison of the experimentally observed recovery transient following high-rate deformation and the predictions of interfacial tension –drag force balance proposed by Cohen et al. (1989) for quiescent interfacial tension driven recovery

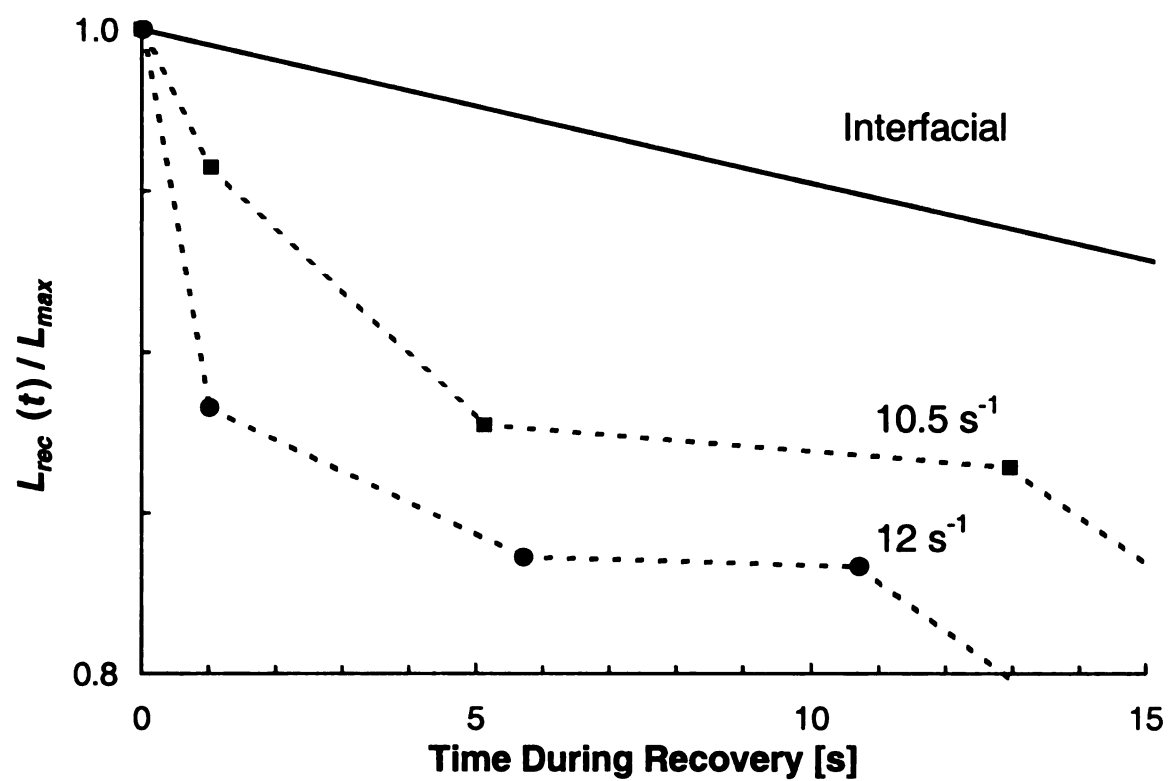


Figure 6.15. Recovery transients following high-rate deformations: effect of extensional strain rate on the extent of elastic recovery in the initial stage

Chapter 7.

CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSIONS

In this thesis, the nonlinear melt rheology of polyolefin random copolymer elastomers and thermoplastic olefin blends has been investigated. The relevance of component and blend rheology in strain recovery following nonlinear deformations in such systems has been analyzed. Three primary research problems were defined in this context. The principal conclusions are as shown below.

RESEARCH PROBLEM 1.

To investigate the interrelationship between of short-chain branching density in ethylene- α -olefin elastomers and their nonlinear melt rheology

Three random ethylene-octene copolymers with degrees of short-chain branching (SCB) ranging from 25 to 50 per 10 carbons and with similar molecular weights display a strong dependence of non linear shear creep recovery and elongational strain hardening

on SCB. The absence of even sparse long-chain branching was confirmed with several linear viscoelastic tests. The similarity of J_e^0 for the three copolymers rules out differences in any high molecular weight fractions among them.

Zero-shear viscosity of these copolymers follows the trends in backbone molecular weight closely. Although the steady recoverable shear compliance values are close for strains < 0.5 , they decrease progressively with increasing SCB density at higher strains of 25 to 100. This trend must be a consequence of the different degrees of primitive chain relaxation in the rapid equilibration stage obtained at large strains with different SCB.

Extensional viscosity of the elastomer melts was measured at several strain rates and at a Hencky strain of 4.9 using lubricated skin-core flow through semi-hyperboloidal dies. The range of extensional strain rates was broad enough to cover rates which are higher as well as lower than the rate of equilibration of the primitive polymer chain, given by the inverse of the Rouse timescales of the melts, τ_R^{-1} .

Extensional strain hardening, which decreases with increasing strain rate, is observed in all the three elastomer-melts, at all the rates tested. At low extension rates, below τ_R^{-1} , extensional strain hardening progressively increases with increasing SCB density. At higher rates, upon onset of primitive chain stretch, the strain hardening behavior for the three melts merges.

RESEARCH PROBLEM 2.

To study the effect of polyolefin elastomer and TPO blend rheology on the evolution of blend morphology in high-rate processing operations.

The flow mark problem associated with high-speed injection molding was studied in two thermoplastic olefin (TPO) blends. The blends had polypropylene (PP) matrices and ethylene-propylene (EP) elastomer dispersed phases. The composition of the blends was the same – the PP phases were very similar, but the EP dispersed phases differed in terms of SCB density. When injection molded under same conditions, blend B1 displayed greater frequency of flow marks and greater contrast between glossy and dull regions.

Melt rheology of the blends revealed that blend B1, which was more unstable during injection molding was also less strain hardening in extension as compared to blend B2. The trends in strain hardening in the blends followed those in strain hardening of the corresponding EP elastomers by themselves. The differences in degree of contrast between glossy and dull regions were traced to different degrees of strain recovery in the dispersed phases of the two blends. This recovery occurred over injection molding timescales of the order of a few seconds. Strain recovery after shear creep was higher in blend B1, that displayed more severe flow marks in injection molding; the corresponding elastomer by itself also showed a greater extent of creep recovery.

Thus the quick strain recovery observed in the elastomeric dispersed phases must be associated with elastic stresses rather than interfacial tension. In both blends, the dispersed elastomer phase was substantially more viscous and elastic as compared to the PP matrix. Thus the enhanced significance of elastic stresses in driving recovery must also be a consequence of the absence of any significant resistance to such recovery from the matrix.

RESEARCH PROBLEM 3

To evaluate the fluid and flow parameters governing elastic effects during recovery of elastomeric drops in suspension

An experimental apparatus was assembled to study strain recovery after elongation of a model elastomer suspended in a less viscoelastic medium at room temperature. In this apparatus, small drops of well-characterized elastomers suspended in a matrix fluid of lower viscosity and elasticity, are stretched rapidly without wall effects; the stretch ratio of the drops is then recorded over time. Preliminary studies were performed with a viscoelastic silicone elastomer drop suspended in a viscous Newtonian liquid. Creep recovery tests on the drop fluid revealed substantial elasticity in the drop phase.

Following high rate extensional deformations to stretch ratios of about 2, a substantial portion of the imposed strain were recovered within 2-5 s, times much shorter than the interfacial timescale. The recovery transient thus showed two stages, an initial rapid recovery followed by a slower relaxation to sphere. The extent of recovery in the initial stage relative to the total deformation was higher following deformation at a higher rate – confirming the elastic origins of the phenomenon.

7.2. FUTURE DIRECTIONS

THE DROP RECOVERY EXPERIMENT

It is clear that the experimental drop deformation-recovery setup is promising in that recovery immediately following controlled high-rate flow-induced deformations may be recorded for well controlled drop – matrix systems. In the preliminary results reported in Chapter 6, deformation rate was chosen as a means to tailor the elastic effects. Indeed, the rate of deformation had significant a significant effect on the extent of initial recovery brought about by elastic effects.

As pointed out earlier, this experiment offers a very flexible setup, where the drop properties as well as the matrix properties can be easily varied to investigate the entire spectrum of materials – Newtonian to elastomeric. Therefore with carefully chosen variables, there is a wealth of knowledge to be gained from this setup regarding the factors which bring about or hinder elastic recovery of the deformed drop. The variables that may be conveniently tailored are

- ♦ *Extent of initial deformation imposed on the drop:* as pointed out earlier, with the global Hencky strain offered by the semi-hyperboloidal convergence fixed, the extent of deformation imposed on the drop can be controlled by varying the capillary number or the extensional strain rate. On the other hand, another fixture offering a greater Hencky strain may be employed.

- ◆ *Viscosity ratio*

- ◆ *Elasticity ratio*: The suspending fluid in the current study reported in Chapter 6 was a Newtonian fluid. It would be interesting to increase the elasticity of the matrix phase – during the deformation stage, this would result in imposition of greater strains on the drop phase resulting in enhanced elastic effects, but at the same time the deformed drop would also face greater hindrance during recovery from the elastic matrix.

- ◆ *Molecular architecture*: Studies should be carried out in this setup with polymers having different molecular features – linear, sparse long-chain branched and profusely long-chain branched. For example, polyisobutylene elastomers with widely varying architecture are readily available and are suitable for room temperature drop studies

- ◆ *Deborah numbers De_R* : Another interesting aspect that should be pursued is to understand the significance of the magnitude of the deformation rate relative to the Rouse timescale of the material in governing the recovery. For example, it is known from reptation considerations that even as the deformation is being imposed, the primitive polymer chain tends to retract within the Rouse timescales thus relaxing the flow induced elastic stresses. However, if deformations are imposed at rates much higher than the retraction

rate of the primitive chain, un-relaxed elastic stresses would be substantially higher at the commencement of recovery leading to greater significance of elastic effects.

- ◆ *Blends and Melts*: Once these aspects are investigated in some detail, it may be worthwhile to study the behavior of semi-concentrated blends in the melt state.

MODELING OF DROP RECOVERY WITH ELASTIC EFFECTS

Another encouraging outcome of the current experiment is the possibility of obtaining ellipsoidal drop shapes. There exists a class of semi-empirical drop models known as ellipsoidal models [Maffettone and Minale (1998), Maffettone and Greco (2004)], which assume ellipsoidal drop shapes at all times. These semi-empirical phenomenological models are very easy to navigate and modify to include experimental variables. The only constraint is the drop shape which should remain ellipsoidal at all times. With the possibility of obtaining ellipsoidal drops confirmed with the current setup, the ellipsoidal models of Maffettone and Greco (2004) may be modified to incorporate stronger nonlinear rheological effects such as extensional strain hardening and the utility of these models may be extended to studying rapid elasticity driven recovery of elastomers.

APPENDIX

FORTRAN code for solution of the integral equation for prediction of strain during shear creep and recovery using K-BKZ constitutive equation

program ode

```
C-----
C WSCCRStGD_SPL_MOD.f

C Wagner Shear Creep Creep Recovery Strain Growth Decay . f
C SPLiced damping function
C MODified relaxation spectrum
C Growth of shear strain during shear creep followed by recovery
C Use of K-BKZ Model (Wagner)

C Wagner, JNNFM, 3(4), 39 (1978)
C -----
C Stress assumed constant
C Gives rise to a nonlinear Volterra integral equation of the second
C kind in shear strain (t0)
C Upon use of quadratures, this equation can be reduced to a non-
C linear algebraic equation which can be solved by iteration

C Wagner, Laun, Rheol Acta, 17(2), 138 (1978)
C-----

C -----
C Definition of variables
C -----

C n : Number of steps
C mode : number of relaxation mode
C Dt : time step [s]
C t_n : Current Time [s]
C k_step : global step counter
C ipause : local step counter
C Stress : Shear stress (tau_12) [Pa]
C g[i] : Weighting factor for relaxation spectrum [Pa/s]
C Lambda [i] : Relaxation spectrum time constants [s]
C Rel_Mod : Relaxation modulus [Pa]
C i,j : local step counters
C F : Shear strain at any time t (F(t))
C W_j : Quadrature weights
C t_j : time for network building, past time, t' [s]
C Mem_Func : Memory function [Pa]

C -----

      Implicit Double Precision (a-h,o-z)
      Double Precision Lambda(12),g(12),F(1000000)
      Double Precision a,m1,m2,Stress,Dt,t_n

C -----
C Variables common between the main program and the subroutine Func_t_0
C -----

      common / DampF / a,m1,m2,p1,p2,c1,c2
      common / Func1 / Stress,Dt,t_n
      common / Func2 / mode,Lambda,g,F
      common / Func3 / ipause
```

```

c-----
c constants
c-----

      null = 0

c-----
c Stress [Pa] is held constant
c -----

      Stress = 3.0D+04

c-----
c Discrete Relaxation Spectrum
c-----

c *****
c Relaxation Spectrum: TPO EPs
c *****

c-----
c B1: CA45 EP
c-----

c      Lambda(1) = 1.167D-02
c      Lambda(2) = 3.246D-02
c      Lambda(3) = 9.032D-02
c      Lambda(4) = 2.513D-01
c      Lambda(5) = 6.992D-01
c      Lambda(6) = 1.945D+00
c      Lambda(7) = 5.412D+00
c      Lambda(8) = 1.506D+01
c      Lambda(9) = 4.190D+01
c      Lambda(10) = 1.166D+02
c      Lambda(11) = 3.243D+02

c      g(1) = 2.682D+07
c      g(2) = 3.723D+06
c      g(3) = 7.667D+05
c      g(4) = 1.441D+05
c      g(5) = 2.853D+04
c      g(6) = 4.187D+03
c      g(7) = 7.042D+02
c      g(8) = 1.062D+02
c      g(9) = 1.392D+01
c      g(10) = 1.139D+00
c      g(11) = 2.898D-02

c      mode = 11

c-----
c B2: CA53 EP
c-----

c      Lambda(1) = 7.884D-03
c      Lambda(2) = 2.194D-02
c      Lambda(3) = 6.103D-02

```

```

c      Lambda(4) = 1.698D-01
c      Lambda(5) = 4.725D-01
c      Lambda(6) = 1.314D+00
c      Lambda(7) = 3.657D+00
c      Lambda(8) = 1.018D+01
c      Lambda(9) = 2.831D+01
c      Lambda(10) = 7.877D+01
c      Lambda(11) = 2.192D+02

```

```

c      g(1) = 2.304D+07
c      g(2) = 9.828D+05
c      g(3) = 6.734D+05
c      g(4) = 7.101D+04
c      g(5) = 1.270D+04
c      g(6) = 1.359D+03
c      g(7) = 2.051D+02
c      g(8) = 2.402D+01
c      g(9) = 4.396D+00
c      g(10) = 2.603D-01
c      g(11) = 3.547D-03

```

```

c      mode = 11

```

```

c *****
c Relaxation Spectrum: EPs
c *****

```

```

c      Lambda(1) = 9.9983D1
c      Lambda(2) = 3.7270D1
c      Lambda(3) = 1.3893D1
c      Lambda(4) = 5.1788D0
c      Lambda(5) = 1.9305D0
c      Lambda(6) = 7.1961D-1
c      Lambda(7) = 2.6824D-1
c      Lambda(8) = 9.9992D-2
c      Lambda(9) = 3.7273D-2
c      Lambda(10) = 1.3894D-2

```

```

c *****
c Weights: DUTRAL-CO034
c *****

```

```

c      g(1) = 1.3714D-01
c      g(2) = 2.9821D+00
c      g(3) = 2.8170D+01
c      g(4) = 1.7070D+02
c      g(5) = 1.0437D+03
c      g(6) = 7.5208D+03
c      g(7) = 5.6163D+04
c      g(8) = 4.9957D+05
c      g(9) = 1.8195D+06
c      g(10) = 2.5797D+07

```

```

c      mode = 10

```

```

c *****
c Weights: EPR 306 Polysar

```

```

C *****

C      g(1)  = 1.0670D0
C      g(2)  = 7.2800D0
C      g(3)  = 5.6766D1
C      g(4)  = 2.9225D2
C      g(5)  = 1.9044D3
C      g(6)  = 6.9214D3
C      g(7)  = 5.5146D4
C      g(8)  = 3.4576D5
C      g(9)  = 1.3807D6
C      g(10) = 2.8612D7

C      mode = 10

C *****
C Relaxation Spectrum: EOs
C *****

C -----
C EO1: ENGAGE 8480
C -----

      Lambda(1) = 1.064D-03
      Lambda(2) = 3.342D-03
      Lambda(3) = 1.050D-02
      Lambda(4) = 3.299D-02
      Lambda(5) = 1.037D-01
      Lambda(6) = 3.257D-01
      Lambda(7) = 1.023D+00
      Lambda(8) = 3.216D+00
      Lambda(9) = 1.010D+01
      Lambda(10) = 3.175D+01
      Lambda(11) = 1.500D+02

      g(1)  = 2.910D+08
      g(2)  = 6.272D+07
      g(3)  = 1.112D+07
      g(4)  = 2.026D+06
      g(5)  = 2.873D+05
      g(6)  = 3.974D+04
      g(7)  = 5.634D+03
      g(8)  = 6.210D+02
      g(9)  = 7.368D+01
      g(10) = 4.583D+00
      g(11) = 5.701D-01

      mode = 11

C -----
C EO2: ENGAGE-8003
C -----

C      Lambda(1) = 1.064D-03
C      Lambda(2) = 3.342D-03
C      Lambda(3) = 1.050D-02
C      Lambda(4) = 3.299D-02

```

```

c      Lambda(5)  = 1.037D-01
c      Lambda(6)  = 3.257D-01
c      Lambda(7)  = 1.023D+00
c      Lambda(8)  = 3.216D+00
c      Lambda(9)  = 1.010D+01
c      Lambda(10) = 3.175D+01
c      Lambda(11) = 9.976D+01

```

```

c      g(1)  = 2.3598D+08
c      g(2)  = 6.5469D+07
c      g(3)  = 1.5614D+07
c      g(4)  = 2.8348D+06
c      g(5)  = 3.6222D+05
c      g(6)  = 4.2188D+04
c      g(7)  = 4.8640D+03
c      g(8)  = 4.8092D+02
c      g(9)  = 5.2253D+01
c      g(10) = 3.4604D+00
c      g(11) = 1.8281D-01

```

```

c      mode = 11

```

```

c -----
c EO3: ENGAGE-8100
c -----

```

```

c      Lambda (1)  = 1.0636D-03
c      Lambda (2)  = 3.3418D-03
c      Lambda (3)  = 1.0500D-02
c      Lambda (4)  = 3.2992D-02
c      Lambda (5)  = 1.0366D-01
c      Lambda (6)  = 3.2572D-01
c      Lambda (7)  = 1.0234D+00
c      Lambda (8)  = 3.2158D+00
c      Lambda (9)  = 1.0104D+01
c      Lambda (10) = 3.1748D+01
c      Lambda (11) = 9.9755D+01

```

```

c      g(1)  = 1.8037D+08
c      g(2)  = 5.2380D+07
c      g(3)  = 1.2850D+07
c      g(4)  = 2.8451D+06
c      g(5)  = 4.2568D+05
c      g(6)  = 5.8966D+04
c      g(7)  = 4.9478D+03
c      g(8)  = 5.0999D+02
c      g(9)  = 3.9597D+01
c      g(10) = 2.7538D+00
c      g(11) = 1.5290D-01

```

```

c      mode = 11

```

```

c *****
c Damping Function Fitting Parameters
c *****

```

```

c *****

```

```

c CA45 EP Phase
c *****

c      a = 1.75

c      m = 0.1

c *****
c CA53 EP Phase
c *****

c      a = 0.6
c      m = 1.0

c *****
c EO1: ENGAGE 8480
c *****

      a = 0.045
      m1 = 2.25
      m2 = 1.0
      p1 = 1.0
      p2 = 0.0
      c1 = 1.0
      c2 = 0.0

c *****
c EO2: ENGAGE 8003
c *****

c      a = 0.2
c      m1 = 1.4
c      m2 = 1.0
c      p1 = 1.0
c      p2 = 0.0
c      c1 = 1.0
c      c2 = 0.0

c *****
c EO3: ENGAGE 8100
c *****

c      a = 0.525
c      m1 = 1.0
c      m2 = 1.0
c      p1 = 1.0
c      p2 = 0.0
c      c1 = 1.0
c      c2 = 0.0

c-----
c Inquiries
c-----

c *****
c Time Steps
c *****

```



```

Dt = 0.01                !time step

n = 7212                  !total # of steps

n_str_rem = 3606          !# of timesteps after which stress
                           !is removed

c-----
c prepare
c-----

      open (1,file="PLOTDAT")

      t_n = 0.0            ! initial time

      kstep  = 0           ! global step counter

      ipause = 0.0         ! batch step counter

c *****
c -----
c Calculation of initial shear strain F[1]
c Use of iterative algorithm to solve nonlinear algebraic
c equation developed in the function Func_t_0 below
c -----

c -----
c Initial guess for shear strain
c -----

      F(1) = 0.0001

      eps = 0.001

c -----
c Newton iterative method
c to solve above nonlinear algebraic equation
c defined in Func_t_0 defined below
c -----

      call newton_1_3_t0 (1000,F(1),eps)

c -----
c Output initial values
c -----

      write (6,100) kstep,t_n,F(1)
      write (1,100) kstep,t_n,F(1)

c -----
c *****

97  Continue              !Starting point for each new
                           !time or strain

c -----

```

```

c Increments
c -----

      kstep = kstep + 1
      ipause = ipause + 1
      t_n = ipause*Dt

c -----
c Setting up the value of stress
c Stress field is changed, particularly, stress is set to zero
c at a definite time; in this program, at exactly half the
c simulation time (n_str_rem)
c -----

      IF (ipause.ge.n_str_rem) THEN
        Stress = 0.0
      END IF

c -----
c Initial guess for instantaneous strain
c -----

      F(ipause+1) = F(ipause)
      eps = 0.0001

c -----
c Newton iterative method
c to solve the nonlinear algebraic equation
c defined in Func_t_n_creep or Func_t_n_recovery
c -----

      call newton_1_3_tn (ipause,n_str_rem,10000,F(ipause+1),eps)

c -----
c Output instantaneous stretch ratio values
c -----

      write (6,100) kstep,t_n,F(ipause+1)
      write (1,100) kstep,t_n,F(ipause+1)

c -----
c Checking for achievement of desired time
c -----

      IF (ipause.ne.n) GO TO 97

c-----
c all done
c-----

99  Continue

      write (1,100) null
      close (1)

100  Format (1x,i6,1x,f10.5,1x,f15.10)

```

```

        Stop

        End

c -----
c -----
c Subroutine to calculate the initial strain
c main program calls the nonlinear algebraic equation solver newton1.f
c newton1.f, in turn calls the subroutine defined below to get the
c nonlinear equation that needs to be solved
c -----
c -----

        subroutine Func_t_0 (x,Eqn)

c -----

        Implicit Double Precision (a-h,o-z)
        Double Precision Lambda(12),g(12),F(1000000)
        Double Precision a,m1,m2,Stress,Dt,t_n

c -----
c Variables common between the main program and the subroutine Func_t_0
c -----

        common / DampF / a,m1,m2,p1,p2,c1,c2
        common / Func1 / Stress,Dt,t_n
        common / Func2 / mode,Lambda,g,F
        common / Func3 / ipause

c -----
c Evaluation of relaxation modulus
c and the nonlinear equation expression
c -----

        Rel_Mod = 0.0D0

        DO i = 1,mode
            Rel_Mod = Rel_Mod + g(i)*Lambda(i)*EXP(-1*t_n/Lambda(i))
        END DO

        DF1 = c1/(((a*((ABS(x))**m1))+1)**p1)
        DF2 = c2/(((a*((ABS(x))**m2))+1)**p2)
        Damp_Func = DF1 + DF2

        Eqn = Stress - (Rel_Mod*Damp_Func*x)

        Return

        End

c -----
c -----
c Subroutine to calculate the instantaneous strain during creep
c main program calls the nonlinear algebraic equation solver newton1.f
c newton1.f, in turn calls the subroutine defined below to get the
c nonlinear equation that needs to be solved

```

```

C -----
C -----

      subroutine Func_t_n_creep (x,Eqn)

C -----

      Implicit Double Precision (a-h,o-z)
      Double Precision Lambda(12),g(12),F(1000000)
      Double Precision a,m1,m2,Mem_Func,Stress,Dt,t_n
      Double Precision A2,Inc_Strain,h_tn_tj,h_tn,A3

C -----
C Variables common between the main program and the subroutine Func_t_n
C -----

      common / DampF / a,m1,m2,p1,p2,c1,c2
      common / Func1 / Stress,Dt,t_n
      common / Func2 / mode,Lambda,g,F
      common / Func3 / ipause

C -----
C Relaxation modulus
C -----

      Rel_Mod = 0.0D0

      DO i = 1,mode
        Rel_Mod = Rel_Mod + g(i)*Lambda(i)*EXP(-t_n/Lambda(i))
      END DO

C -----
C Application of quadrature rule to evaluate the integral
C in order to calculate the instantaneous stretch ratio
C -----

      A2 = 0.0D0

      DO j = 0,ipause

C -----
C Setting up quadrature weights
C -----

        Remainder = j - (INT(j/2))*2

        IF (j.eq.0 .OR. j.eq.ipause) THEN
          W_j = 0.333333333333333
        ELSE IF (Remainder.eq.0) THEN
          W_j = 0.666666666666667
        ELSE
          W_j = 1.333333333333333
        END IF

C -----
C Past Time, time for network building, t'
C -----

```

```

      t_j = j*Dt

c -----
c Memory function
c -----

      Mem_Func = 0.0D0

      DO i = 1,mode
        Mem_Func = Mem_Func + g(i)*EXP(-(t_n - t_j)/Lambda(i))
      END DO

c -----
c Evaluation of other expressions
c -----

      Inc_Strain = x - F(j+1)                                !Incremental
                                                             !strain

      DF1 = c1/(((a*((ABS(x - F(j+1))))**m1))+1)**p1
      DF2 = c2/(((a*((ABS(x - F(j+1))))**m2))+1)**p2
      h_tn_tj = DF1 + DF2  !h(t,t')

      A2 = A2 + Dt*W_j*Mem_Func*h_tn_tj*Inc_Strain           !Term
                                                             !within
                                                             !integral

      END DO

      DF1 = c1/(((a*((ABS(x))**m1))+1)**p1)
      DF2 = c2/(((a*((ABS(x))**m2))+1)**p2)
      h_tn = DF1 + DF2                                         !h(t)

      A3 = Rel_Mod*h_tn*x                                       !Term
                                                             !Outside
                                                             !integral

      Eqn = Stress - A2 - A3

      Return

      End

c -----
c -----
c Subroutine to calculate the instantaneous strain during recovery
c main program calls the nonlinear algebraic equation solver newton1.f
c newton1.f, in turn calls the subroutine defined below to get the
c nonlinear equation that needs to be solved
c -----
c -----

      subroutine Func_t_n_recovery (x,Eqn)

c -----

```

```

      Implicit Double Precision (a-h,o-z)
      Double Precision Lambda(12),g(12),F(1000000)
      Double Precision a,m1,m2,Mem_Func,Stress,Dt,t_n
      Double Precision A2,h_tn_tj,Inc_Strain,h_tn,A3

c -----
c Variables common between the main program and the subroutine Func_t_n
c -----

      common / DampF / a,m1,m2,p1,p2,c1,c2
      common / Func1 / Stress,Dt,t_n
      common / Func2 / mode,Lambda,g,F
      common / Func3 / ipause

c -----
c Relaxation modulus
c -----

      Rel_Mod = 0.0D0

      DO i = 1,mode
         Rel_Mod = Rel_Mod + g(i)*Lambda(i)*EXP(-t_n/Lambda(i))
      END DO

c -----
c Application of quadrature rule to evaluate the integral
c in order to calculate the instantaneous stretch ratio
c -----

      A2 = 0.0D0

c *****
c -----
c Calculation of damping function
c The strain damping function h(t,t') is set to the minimum
c value attained by h(t,t') between times t'(t_j) and t(t_n)
c -----

c      Damp_Func = 1/((a*((ABS(x))**m1))+1)

c      Do j = 1,ipause
c         h_tn_tj = 1/((a*((ABS(x - F(j+1)))**m1))+1)
c         IF (h_tn_tj.lt.Damp_Func) THEN
c            Damp_Func = h_tn_tj
c         END IF
c      END DO

c -----
c *****

      DO j = 0,ipause

c -----
c Setting up quadrature weights
c -----

      Remainder = j - (INT(j/2))*2

```

```

      IF (j.eq.0 .OR. j.eq.ipause) THEN
        W_j = 0.333333333333333
      ELSE IF (Remainder.eq.0) THEN
        W_j = 0.666666666666667
      ELSE
        W_j = 1.333333333333333
      END IF

c -----
c Past Time, time for network building, t'
c -----

      t_j = j*Dt

c -----
c Memory function
c -----

      Mem_Func = 0.0D0

      DO i = 1,mode
        Mem_Func = Mem_Func + g(i)*EXP(-(t_n - t_j)/Lambda(i))
      END DO

c -----
c Evaluation of other expressions
c -----

      Inc_Strain = x - F(j+1)                                !Incremental
                                                             !(or decremental)
                                                             !strain

c -----
c Damping Function - for reversible damping
c -----

      DF1 = c1/(((a*((ABS(x - F(j+1)))**m1))+1)**p1)
      DF2 = c2/(((a*((ABS(x - F(j+1)))**m2))+1)**p2)
      Damp_Func = DF1 + DF2

      A2 = A2 + Dt*W_j*Mem_Func*Damp_Func*Inc_Strain        !Term
                                                             !within
                                                             !integral

      END DO

      DF1 = c1/(((a*((ABS(x))**m1))+1)**p1)
      DF2 = c2/(((a*((ABS(x))**m2))+1)**p2)
      h_tn = DF1 + DF2                                     !h(t)

      A3 = Rel_Mod*h_tn*x                                    !Term
                                                             !outside
                                                             !integral

      Eqn = Stress - A2 -A3

```

Return

End

```
C -----  
C Inclusion of relevant files  
C -----
```

Include 'Newton-t0-1202.f'

Include 'Newton-tn-1202.f'

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