Polyolefins

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Processing, Structure Development, and Properties

Leseprobe 1

7.3   Rheological Properties of Polymer Melts

The fundamental flow properties of polyolefin melts and how they depend on polymer structure will now be the focus of our attention.

The shear viscosity (η) of polymer fluids represents their resistance to flow. Consider a fixed Cartesian coordinate with 1-, 2- and 3-axes. A shear flow described by $v_1(x_2)$ moves past this axis (Fig. 7.7). This flow has a velocity gradient dv_1/dx_2 associated with it. A shear stress σ_{12} develops, which is proportional to this velocity gradient and the shear viscosity of the material,

$$\sigma_{12} = \eta \, \frac{\partial v_1}{\partial x_2} \tag{7.1}$$

The shear viscosity has the units $(F/A)/(V/L)$, where F is the units of force, A of area, V is velocity, and L is length. This is equivalent to $F\,t/L$. In metric units, this is $N \cdot s/m$ or $Pa \cdot s$. The value of the viscosity of water in these units is 0.001 $Pa \cdot s$, and for oils the viscosity ranges from 0.1 to 1.0 $Pa \cdot s$.
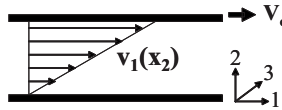

Figure 7.7 Shear flow

The shear viscosity of Newtonian fluids was studied extensively in the 19th century. For polymer solutions, it has been investigated since the 1920s. The first shear viscosity measurements of a polymer melt were those for natural rubber by Mooney [12] in 1936. Further measurements were published by various investigators in the 1940s continuing to the present [13–21]. It was found that the shear viscosity was a constant (η_o) at low shear rates and subsequently decreases with increasing shear rate. Figure 7.8 shows typical examples of shear viscosity-shear rate curves for isotactic polypropylene melts of varying molecular weight and molecular weight distribution [8].

The dependence of the zero shear viscosity (η_o) on molecular weight of linear polymers was investigated by Flory [13] and Fox and Flory [15–17]. They concluded that for low molecular weights, η_o varies with the first power of the molecular weight. For high molecular weights, η_o increased with the 3.4 power of the molecular weight (weight average molecular weight).
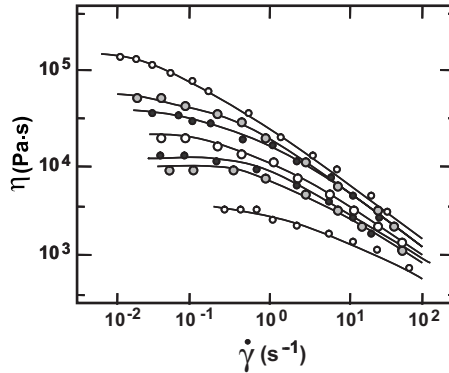
$$\eta_o \sim M_w^{3.4} \tag{7.2}$$

Figure 7.8 Shear viscosity-shear rate curves for isotactic polypropylene melts which have varying molecular weight and molecular weight distribution (Yamane and White [8])

Figure 7.9 shows a plot of η_o as a function of molecular weight M_w for isotactic polypropylene melts. For high molecular weight long chain branched polymer melts, η_o increases even more rapidly with molecular weight [22]. With polystyrene that has high molecular weight structural units and shorter chain lengths, this behavior has not been found [23].

Molecular weight distribution as well as long chain branching influences the dependence of shear viscosity on molecular weight in polyolefins. In the 1960s, Vinogradov and Malkin [18] found that for various polymers, the plots of η / η_o vs. $\eta_o \dot{\gamma}$ were independent of temperature. Subsequent investigations by Onogi et al. [24] and others [8, 21] showed that for linear polymers, these plots were dependent on molecular weight distribution. Specially, η / η_o decreased more rapidly with increasing $\eta_o \dot{\gamma}$ for broad
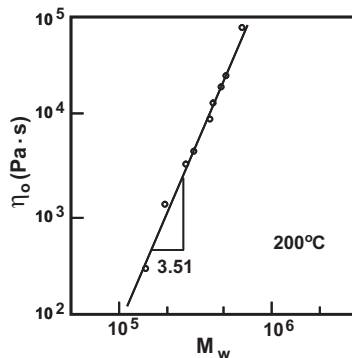

Figure 7.9 Zero shear viscosity (η_o) as a function of molecular weight (M_w) for isotactic polypropylene (Yamane and White [8])
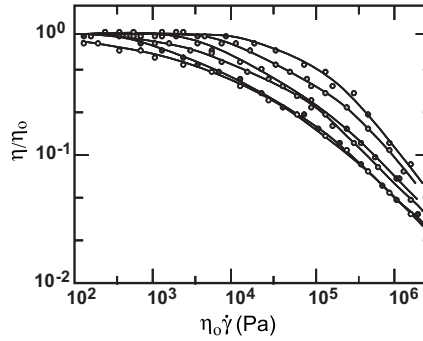
Figure 7.10 Reduced shear viscosity η / η_o as a function of $\eta_o \, \dot{\gamma}$ (Yamane and White [8])

molecular weight distribution polymer melts. Plots of η / η_o versus $\eta_o \, \dot{\gamma}$ for isotactic polypropylenes were published by Minoshima et al. [21]. This effort was continued by Yamane and White [8] (see Fig. 7.10).

Table 7.1 summarizes η / η_o at various $\eta_o \, \dot{\gamma}$ for flexible polymer melts of varying M_w/M_n. These data can be used to estimate the breadth of the molecular weight distribution for linear polymers rather than resorting high temperature chromatography.

In steady shear flow, there are also normal stresses σ_{11}, σ_{22}, and σ_{33}. For Newtonian fluids, these stresses are equal to one another and to the hydrodynamic pressure. As noted by Weissenberg [25], for fluids with elastic memory such as polymer solutions and melts, tensile normal stresses σ_{11} develop along streamlines, and compressive normal stresses σ_{22} develop perpendicular to the flow. This causes a rod-climbing in curvilinear flows known as the Weissenberg effect (Fig. 7.11).

Table 7.1 Molecular Weight Distribution from η / η_o vs. $\eta_o \, \dot{\gamma}$ plot (from Yamane and White [8])

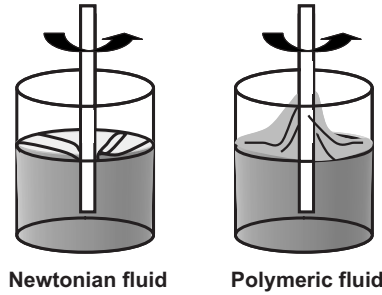| $\eta / \eta_o \cdot 0.1$ (at $\eta_o \, \dot{\gamma} = 10^5$ Pa)	Sample M_w/M_n
5.15	1.1
3.80	3.5
3.15	3.5–4.0
2.85	4.0–4.5
2.70	4.5–5.0
2.60	4.5–6.5
2.55	6.7
2.20	7.0–8.0
1.90	8.0–9.0
1.80	9.0
1.73	17.0

Figure 7.11 Rod-climbing in curvilinear flows for polymeric fluids (Weissenberg effect)

The normal stress differences (N_1 and N_2) are even functions of shear rate unlike the shear stress σ_{12} which is an odd function. We may write the normal stress differences as

$$N_1 = \sigma_{11} - \sigma_{22} = \Psi_1\, \dot{\gamma}^2 \tag{7.3a}$$

$$N_2 = \sigma_{22} - \sigma_{33} = \Psi_2\, \dot{\gamma}^2 \tag{7.3b}$$

where Ψ_1 and Ψ_2 are known as the first and second normal stress coefficients. It is found for polymer melts that [20, 21, 26, 27]

$$N_1 > 0 \tag{7.4a}$$

$$N_2 < 0 \tag{7.4b}$$

For Newtonian fluids, N_1 and N_2 are zero.

White and Kondo [28] suggested that the theory of non-linear viscoelasticity implies that

$$\lim_{\dot{\gamma} \to 0} \Psi_1 = \Psi_{1,o} \sim M^{6.8} \tag{7.5}$$

They analyzed molten atactic polystyrene data and found $\Psi_{1,o}$ to vary with the 6th power of molecular weight at low shear rates.

The first normal stress coefficient Ψ_1 is strongly dependent on the breadth of the molecular weight distribution, being strongly favored by higher molecular weight fractions. Oda et al. [29] developed a correlation for atactic polystyrene melts of form

$$N_1 = A\, \sigma_{12}^a \tag{7.6}$$

where A increased with the breadth of the distribution. The value a ranged between 1.6 and 2.0. Similar behavior was found by Minoshima et al. [21] for isotactic polypropylenes. They showed that N_1 / σ_{12}^2 increased with the 2.1 power of M_z / M_w (see Eqs. 2.8 and 2.9).

There have been many investigations of uniaxial extension of polyolefin melts. For these flows, $v_1 = \dot{\varepsilon}\, x_1$, $v_2 = -\dfrac{\dot{\varepsilon}}{2}\, x_2$, and $v_3 = -\dfrac{\dot{\varepsilon}}{2}\, x_3$ (Fig. 7.12). An elongational viscosity (η_{el}) may be defined as

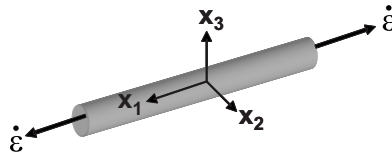$$\sigma_{11} = \eta_{el}\, \frac{dv_1}{dx_1} \tag{7.7}$$

Figure 7.12 Uniaxial extension

In 1906, Trouton [30] had shown theoretically and experimentally that for Newtonian fluids, η_{el} was equal to $3\eta_o$. The first measurements of elongational viscosity for polymer melts were made by Ballman [31] for atactic polystyrene in 1965. For polymer melts, at low stretch rates, η_{el} behaves as a Newtonian fluid and is equal to $3\eta_o$. Depending on molecular weight distribution and the occurrence of long chain branching, η_{el} may vary considerably with stretch rate. For long chain-branched polyethylene, η_{el} rises rapidly with stretch rate [21, 32–34]. For linear polymer melts, η_{el} is roughly constant for narrower molecular weight distributions. However, increasing the breadth of the molecular weight distribution causes η_{el} to decrease with stretch ratio [21, 34].

The rheological properties of polymer melts strongly depend on temperature. The shear and elongational viscosity as well as the normal stress differences increase with decreasing temperature. Generally, the dependence varies with T_g, being larger for greater $T - T_g$. An important correlation of small strain viscoelastic behavior with $T - T_g$ was given by Williams, Landel and Ferry (WLF) [35].

When the temperature approaches the crystalline melting temperature for crystallizing polymer melts, crystallization may occur. The rate of crystallization is enhanced by the application of stresses because they induce polymer chain orientation (see Sections 7.5 to 7.8). This is best known for *cis*-1,4-polyisoprene (natural rubber) in uniaxial extension [36, 37].

7.4   Effects of Additives

It has been found that small amounts of additives may induce slippage of polyolefin melts flowing on steel and other metal surfaces. The simplest of these additives are amphiphilic fatty molecules such as carboxylic acids, stearates, and amides [38]. The effects of additives on other thermoplastics including polystyrene and polyamides are much smaller.

In experiments with thin layers it is known [39–41] that fatty acids are much more effective lubricants for metals than are hydrocarbon oils. It is only for thick lubricant layers that Reynolds hydrodynamic lubrication theory [42] is valid. There are experimental proofs [41] that there are chemical reactions between carboxylic acids and the metal surfaces, which tie the carboxylic acid to the surface.

Small amounts of fluoroelastomers are also known to induce slippage between polyolefins and metal surfaces [43–46]. This is used commercially in the extrusion of linear low density polyethylene. Most effective are fluoroelastomers with carboxylic end groups. These end groups survive from the free radical polymerization initiator and exist in certain commercial fluoroelastomers. Here again, we may have the reaction of a carboxylic acid with a metal.

7.5   Early Observations of Flow Birefringence

Early investigators such as Bartolinus and Brewster observed birefringence in single crystals. In 1815, Brewster [47] found that certain substances such as glass and natural rubber became birefringent when stresses were applied.

Birefringence (double refraction) was first observed in flowing liquids by Maxwell [48] in 1873 using Canada balsam. There were relatively few subsequent observations in the following years. These studies were mainly conducted with dilute solutions of anisotropic protein molecules [49–51]. Measurements of flow birefringence on flexible chain polymers only became common in the late 1950s with measurements by Philippoff and his coworkers [52–55]. Their first efforts were with polymer solutions [52–54]. In 1961, Dexter, Miller, and Philippoff [55] published the first investigation for a flowing polyolefin melt (polyethylene). Subsequent studies by Janeschitz-Kriegl and Wales [19, 56] found similar flow birefringence developed in isotactic polypropylene and atactic polystyrene melts.

7.6   **Flow Birefringence and Stress**

Maxwell [57], following up on Brewster's observations [47] on stressed glass and rubber, suggested that the birefringence developed in transparent isotropic elastic solids could be used to experimentally determine stress fields. Maxwell basically hypothesized that the refractive index tensor $\underline{\mathbf{n}}$ varies linearly and coaxially with the deviatoric stress tensor $\underline{\mathbf{P}}$ as

$$\underline{\mathbf{n}} = \frac{1}{3} \cdot (t \, r \, \underline{\mathbf{n}}) \cdot \underline{\mathbf{I}} + C \cdot \underline{\mathbf{P}} \qquad (7.8)$$

where C became known as the stress-optical coefficient. This proposal of Maxwell was developed into the area of photoelastic stress analysis by the end of the century [58, 59], which was widely used for a century to experimentally solve complex stress analysis problems.

Maxwell [60] subsequently developed an electromagnetic theory of optical phenomena for both isotropic and anisotropic media. He associated birefringence with the dielectric constant and refractive index tensor characteristics of anisotropic dielectrics. Maxwell's theory is developed in more familiar notations by authors such as Born [61, 62] and Sommerfeld [63]

Lorentz [64, 65] criticized Maxwell's electromagnetic theory for being phenomenological and not considering the molecular level. Lorentz [64, 65] and Lorenz [66] associated the dielectric and refractive index characteristics of isotropic media with the molecular polarizability, which controls the shifting of electron clouds by imposed electric fields. They related the molecular polarizability, α, to the dielectric constant of an isotropic condensed material, κ, and the refractive index, n, by:

$$\frac{\kappa - 1}{\kappa + 2} = \frac{n^2 - 1}{n^2 + 2} = \frac{N \, \alpha}{3} \qquad (7.9)$$

Debye [67] later noted that this equation requires a correction for molecules with permanent dipoles.

Subsequently it was realized that in optically anisotropic media, one had to consider anisotropic polarizabilities or a polarizability tensor (α_{ij}). This was described in general by Born [61] in his 1932 treatise 'Optik' and specifically for polymers in 1941–1942 by F. H. Muller [68] and Kuhn and Grun [69]. The latter authors modeled the deformation of a network of flexible polymer chains and predicted the development of birefringence.

The level of birefringence was found to be proportional to the applied stress, that is

$$\Delta n = C\,\sigma \tag{7.10a}$$

or

$$(n_1 - n_2) = C\,(\sigma_1 - \sigma_2) \tag{7.10b}$$

where σ_1 and σ_2 are principal stresses. This is the same as Eq. (7.8). C was predicted to be

$$C = \frac{2}{90\,k\,T} \cdot \frac{(\bar{n}^2 + 2)}{\bar{n}} \cdot (\alpha_{//} - \alpha_{\perp}) \tag{7.11}$$

where $\bar{n}$ is the mean refractive index, and $\alpha_{//}$ and $\alpha_{\perp}$ are the polarizabilities along and perpendicular to the polymer chain, respectively. The Kuhn-Grun theory was verified experimentally by Treloar [36, 37] for vulcanized natural rubber (when it does not crystallize).

Lodge [70] in a 1956 paper argued that the theory of Kuhn and Grun [69] should be valid for flowing systems of flexible polymer chains such as solutions. Philippoff [52, 53] quickly developed experimental tools for shear flow measurements and made extensive experimental measurements with his coworkers [52–55], including the first data for polymer melts [55]. During the next 20 years, notably Janeschitz-Kriegl, Wales and their coworkers [19, 56, 71–74] extensively studied the flow birefringence of polymer melts and the stress-optical equation Eqs. (7.8) and (7.10). Both steady state and transient flows were investigated.

It must be realized that the linear stress-optical equation Eq. (7.10) is only valid up to modest stresses and not valid near transition temperatures. Matsumoto and Bogue [75] working with polystyrene found an upper stress limit for linearity of 10^5 Pa. At higher stresses, the birefringence increases more slowly.