

CHAPTER II

LITERATURE SURVEY

Wu (1985) measured the dynamic rheological functions of four tetrafluoroethylene and hexafluoropropylene melts, having the same monomer content but different molecular weights. They converted their rheological data to obtain the corresponding molecular weight distributions curves by the deconvolution of the moduli in the terminal and plateau zones. The zero shear viscosity η_0 for $M > M_c$ was found to obey the following relation: $\eta_0 = \eta_0(M_c) (M/M_c)^3 \exp \{2.26(1-(M_c/M)^{0.5})\}$ where $\eta_0(M_c)$ is the zero shear viscosity, and M_c is the critical entanglement molecular weight.

Wu (1985) developed a method by which polymer molecular weight and its distribution curve can be accurately determined from dynamic melt viscoelasticity in the terminal and plateau zones. The method was illustrated with a series of monodisperse and polydisperse polystyrenes. The average molecular weight values obtained deviated less than 5-10 percent from the values determined by light scattering, osmometry and gel permeation chromatography.

Tuminello (1986) demonstrated a method for determining the molecular weight distribution of a polymer melt using the dynamic storage modulus (G'), the plateau modulus (G_N^0), and the zero shear complex viscosity (η^*_0). The cumulative molecular weight distribution was found to be inversely proportional to $(MW)^{3.4}$. The zero shear viscosity was assumed to depend on the weight-average molecular weight (M_w) as $\eta^*_0 \propto (M_w)^{3.4}$. M_w , M_n (number-average molecular weight) and M_w/M_n were calculated and found to agree with the data obtained from the size exclusion chromatography with 10 percent errors, for broad and bimodal distribution samples. M_w/M_n values were predicted to be approximately 20 percent higher than the true values for narrow distribution samples. This resulted from not accounting for

the finite distribution of relaxation times for the monodisperse samples. For the bimodal distribution samples, the method cannot account for the plasticizing effect of short chains mixed with long chains.

Grassley *et al.* (1986) studied the thermorheological effects of long chain branching in entangled polymer melts by measuring the dynamic modulus of entangled melts of star branched polymers over wide ranges of frequency and temperature. Polyisoprene, polybutadiene of several vinyl contents, and their hydrogenation products were examined for the evidence of thermorheological complexity, and the temperature dependence of viscosity for linear and branched polymers with the same microstructure. The temperature coefficients were found to be larger for branched polymers of some species. The excess temperature dependence appeared to depend on a thermally activated process rather than the free volume process that governs viscosity for linear polymers. The activation energies were used to estimate activation coefficients for the various species. A rough connection was established between these values and their temperature coefficient of chain dimensions for the species. For the saturated polymers, corresponding in microstructure to copolymers of ethylene, it appeared to be a systematic relationship with the mole fraction of counit. The results were in general agreed with expectations based on the difference in relaxation mechanisms available to entangled linear and branched polymers.

Cloizeaux (1988) introduced the double reptation model to predict the stress relaxation function $G(t)$ of polymer melts from the simple reptation (or the tube model). The results showed a better agreement with the experimental data more than the simple reptation did. The improvement was obtained without introducing additional parameters. In polymer melt, the concept of double reptation involves a stress point P at which two polymers, A and B, are entangled. The stress at P will disappear if one end point of a polymer chain

reptates through the motionless point P . The stress relaxation function is determined by

$$G(t) = G_N^0 m_d(t) = G_N^0 \left(\sum_{A,B} \varphi_A \varphi_B p_A(t) p_B(t) \right) \quad (2.1)$$

$$p_A(t) = \exp[-t / \tau_A] \quad (2.2)$$

where G_N^0 is the plateau modulus of polymer, m_d is a fraction of unrelaxed stress at time t , φ_A is a volume fraction of polymer chain A , $p_A(t)$ is the tube survival probability of chain A at time t and τ_A is a relaxation time of polymer chain A .

Tuminello *et al.* (1988) determined the molecular weight distribution of poly(tetrafluoroethylene), PTFE, by using dynamic rheological and creep measurements. The results indicated that the molecular weight distributions for PTFE were bimodal whose shape was dependent on the concentration of surfactant relative to that of PTFE. From the value of G_N^0 , they found that, in terms of the number of chain atoms between entanglements (N_e), the flexibilities of PTFE, hexafluoropropylene-tetrafluoroethylene (FEP) copolymer, and polyethylene (PE) are very similar. They illustrated that the inherent chain stiffness of PTFE is very similar to that of polyethylene.

Wu (1988) developed a method to determine molecular weight distribution by using the relationship between the relaxation time spectrum $H(\tau)$ in the terminal zone and the volume-fraction differential molecular weight distribution function $P(M)$ by considering binary chain contacts for stress transmission,

$$P(M) = \left[\frac{(1/2)H(\tau)}{\left[\int_{\ln \tau}^{\infty} H(\tau) d \ln \tau \right]^{1/2}} \right]_{\tau = \lambda M} \quad (2.3)$$

where β and λ are constants for a given chemical type. This formula was used to determine the molecular weight distribution curves from the stress relaxation modulus spectrum at 370°C. It was found that poly(tetrafluoroethylene) typically had a bimodal molecular weight distribution. The entanglement molecular weight (M_e) was 5490, and the number of main-chain atoms between entanglement points was 110, consistent with a flexible chain. The zero shear melt viscosity was $\eta_0 = 1.79 \times 10^{-13} M_w^{2.94 \pm 0.13}$, where η_0 was in Pa.s and M_w/M_e was between 2000 to 12000.

Ball and McLeish (1989) introduced dynamic dilution for the constraint release in the dynamics of branched polymers to an outstanding problem in the viscosity of star polymer melts. In the approximation of complete separation of time scales along a star arm, it was shown that cooperative effects dilute the effective entanglement by a factor of 3, giving much improved quantitative agreement with rheological experiments. Polydispersity was found to affect the terminal time and viscosity only by the weight of an average molecular weight.

Cloizeaux (1990) reported a method to calculate the stress relaxation function, $G(t)$, of a melt made of long entangled polymers of monodisperse polymers of molecular mass M by applying a modified reptation theory. The shape of relaxation changed when M was varied. This effect depends on a relaxation time τ which is proportional to M^3 and internal time i which is proportional to M^2 . The new parameter is $H = \tau/i$, which is the number of entanglements per polymer chain. For blends made of polydisperse polymers belonging to the same species, $G(t)$ was calculated by using directly the double reptation principle. The theory, which is combined with the double reptation principle, is rather successful. The theory predicts $G''(\omega)$ rather accurately for monodisperse and polydisperse melts. In addition it can explain the viscosity anomaly that was observed in monodisperse melts.

Tsenoglou (1991) developed a molecular model to explain the viscoelastic behavior of entangled homopolymer blends of arbitrary molecular weight distribution in the terminal relaxation regime. The model calculates the population densities, the hierarchy of dissolution, and renewal of the various types of entanglements in a composite network formed by linear chains of similar or dissimilar lengths. The results are utilized in the derivation of simple blending rules for the time dependent relaxation modulus, the dynamic moduli, the viscosity, and the recoverable compliance of the dense homopolymer mixtures.

Viovy *et al.* (1991) considered concepts of reptation and constraint release to model the dynamics of polydisperse linear polymers. The mechanisms of constraint release in concentrated polymer solutions can be divided into two categories. Tube dilution occurred when constraint release caused a widening of the effective tube confining the chain. Tube reorganization referred to relaxation of the tube due to motion of the surrounding chains without changing the effective tube diameter. By comparing the motion of the chain with the motion of the tube, the determination of the effective tube diameter was done and concluded that the tube only dilates when some of the constraints were below the entanglement molecular weight.

Tuminello *et al.* (1993) predicted the molecular weight distributions of ethylene tetrafluoroethylene copolymer (PETFE) by using dynamic mechanical analysis of their melts. The results from the rheological technique indicated much broader distributions than those determined by dynamic light scattering. The rheological technique would predict a broader distribution if long-chain branchings were present. The presence of broadening was observed when plotting the zero shear viscosity versus the weight-average molecular weight. The well-known 3.4 power law would have been obtained if these were linear chains. The long-chain branching was considered to be the cause

of the discrepancies between the molecular weight distribution prediction from the light scattering and the rheological techniques.

Mead (1994) developed numerical and analytical methods to invert the double reptation mixing rule to determine the molecular weight distribution (MWD). The analytic method involved *Mellin* transforms which was developed for the case of a single exponential monodisperse relaxation function. Numerical methods were developed for general multiple time constant monodisperse relaxation functions. The power-law relaxation modulus associated with broad molecular weight distribution commercial polymer was analytically inverted to generate the corresponding molecular weight distribution. The molecular weight distribution calculated from rheological data (storage modulus, loss modulus, viscosity, and plateau modulus) for polybutadiene and polypropylene were in close agreement with the gel permeation chromatography (GPC) data. This method is very sensitive to small amounts of high molecular weight material present.

Llorens *et al.* (2000) developed a method to calculate the molecular weight distribution (MWD) of polymeric material from rheological data. This technique was developed for linear commercial polymers by assuming a log-normal molecular weight distribution. The rheological data include the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, ranging from the terminal zone to the rubberlike zone. The method was tested with 5 different polymers: two polydimethylsiloxane, polyisoprene, random copolymer of ethylene and propylene, and polystyrene. The storage modulus and loss modulus master curve from terminal to rubbery plateau region data was used to adjust the polydispersity index. The calculated number, weight, and z molecular weight average were in good agreement with experimental data. The calculated polydispersity index was slightly higher than experimental data.

Pattamaprom *et al.* (2000) extended the “dual constraint” model developed by Mead, Van Dyke *et al.* by including early-time contour length

fluctuations and constraint release Rouse relaxation. Then compared the predictions with literature data for several monodisperse polymer melts, including polybutadiene, polyisoprene, and polystyrene, for both linear and star architectures. The predictions were extended to the rheological behavior of bidisperse and polydisperse polymers. The model parameters τ_e (the relaxation time for a segment of a chain, $\tau_e = \zeta a^2 M_e / 3\pi^2 N_{en,i} k_B T M_0$) and G_N^0 , which are independent of polymer molecular weight and architecture, were obtained from the literature for polymer with the same chemical composition and at the same temperature. The model appeared to predict the monodisperse, bidisperse, and polydisperse literature data well without adjustable parameters, except for polystyrene at low temperature. The prediction showed a few weakness points in both star and linear polymers. For star polymers, the model failed at low N_{en} (the number of entanglements per polymer chain) which may be affected from the number of arms that might affect the terminal relaxation time. For a best fit data of linear polymers, the model seems to need a different value of τ_e when the number of entanglements is either too low or too high. The problem may arise either from some inaccuracy of the “tube” concept at low numbers of entanglements or from the form of the prefactor (τ_R) used in the model. For binary blends, the dual constraint model works almost perfectly for both linear-linear blends and star-star blends at all concentrations. The outstanding point of the model was that it could be universally applied to the linear and star polymers, whether monodisperse, bidisperse, or polydisperse, without introducing additional parameters other than the ones required for the original Doi –Edwards model.