Chapter

2. Literature Review of Properties

2.1. Rheology

Having established the structural consequences of degradation as well as methods of measurement, we now turn to the properties of polycarbonate. It is well known that degradation leads to changes in molecular weight, which subsequently causes changes in material characteristics. One of the areas most sensitive to this is rheology.

Recently, a comprehensive review of polycarbonate rheology was published[1]. As such, no review will be attempted here, but a summary of the relevant points of the aforementioned article will be given.

One study[2] referred to in the review article examines linear PC with weight average molecular weights ranging from 16,600-35,000 g/mol. Polydispersities all fall in the range 2.4-2.6, and the temperatures of interest are those far above T_g (i.e., $T_g + 50°C$). Data have been generated for G', G'', and $|\eta*|$ versus frequency at temperatures ranging from 205°C ($T_g + 50°C$) to 324°C, which is the upper limit for processing. Time-temperature superposition has been applied to produce master curves with a reference temperature of 275°C. Reduced variables are

$$G'_p = G'(T_0\rho_0 / T\rho)$$
$$G''_p = G''(T_0\rho_0 / T\rho) \qquad \text{Equation 2.1-1}$$
$$|\eta*| = |\eta*|(T_0\rho_0 / T\rho)$$

[1] Jordan, T. C. and W. D. Richards in *Handbook of Polycarbonate Science and Technology*, D. G. LeGrand and J. T. Bendler, ed., Marcel Dekker, Inc., NY, p. 179, 2000.
[2] Yoshimura, D. K. and W. D. Richards, *ANTEC Proc.*, 1603-1606, 1990.

where T_0 is the reference temperature, T is the temperature where the data were generated, ρ_0 is the density at T_0, and ρ is that at T. An empirical relationship between density and temperature is also given for PC:

$$\rho = \frac{10^3}{\exp\left(-0.307 + 1.86 \times 10^{-5} T^{3/2}\right)}$$
Equation 2.1-2

where T is in absolute units and density is in kg/m^3. The original derivation[3] of this expression took no account of any dependence on molecular weight because it involved only a single sample. However, since other researchers[1] have used Equation 2.1-2 over a range of molecular weights, it will be applied here in the same manner.

Shift factors for the PC master curves exhibit nonlinearity, thus precluding the use of the Arrhenius fit. Instead, a WLF (Williams-Landel-Ferry) formalism with two empirical constants, C_1^0 and C_2^0, best fits the data:

$$\log a_T = \frac{-C_1^0 (T - T_0)}{C_2^0 + (T - T_0)}$$
Equation 2.1-3

An equivalent form of the WLF expression is

$$a_T = \exp\left(\frac{1}{\beta(T - T_\infty)} - \frac{1}{\beta(T_0 - T_\infty)}\right)$$
Equation 2.1-4

This equation is derived on the basis of free-volume arguments for the temperature-dependence of viscoelastic properties. Thus, β is related to the thermal expansion coefficient of the fractional free volume. The Vogel temperature, T_∞, is the temperature where free volume would go to zero in the absence of T_g. Fractional free volume can be shown to be proportional to $\beta(T - T_\infty)$. This expression offers the advantage that the parameters β and T_∞ are independent of T_0, which is not true for C_1^0 and C_2^0. β and T_∞ are related to the WLF constants by

$$C_1^0 = 1/\beta(T_0 - T_\infty)$$
$$C_2^0 = T_0 - T_\infty$$
Equation 2.1-5

[3] Zoller, P., *J. Polym. Sci.: Poly. Phys.*, **20**, 1453, 1982.

Values for β and T_∞ have been found by fitting to appropriate data. For PC, β exhibits no molecular weight dependence and is found to be 8.0×10^{-4} K^{-1}. T_∞ shows an inverse proportionality to a function of molecular weight, decreasing as molecular weight falls. Analogous to the Fox-Flory expression, which will be discussed in Section 2.2, for T_g, T_∞ is expected to depend on $M_n^{1/2}$. Since polydispersity does not change with molecular weight, both T_g and T_∞ can be taken as inverse functions of M_w:

$$T_g = 155 - 2.1 \times 10^5 / M_w$$
$$T_\infty = 108 - 2.8 \times 10^5 / M_w$$

Equation 2.1-6

Regarding the data presented in the review, two points should be made. First, one feature of the storage modulus, G′, curve, shown in Figure 2.1-1, is the so-called plateau modulus, G_N^0, present at high frequencies. This quantity is related to the molecular weight between entanglements, M_e, by

$$G_N^0 = \rho RT / M_e$$

Equation 2.1-7

(ignoring the 4/5 factor of Doi and Edwards). Therefore, a master curve including these high frequencies is one way to predict the value of M_e.
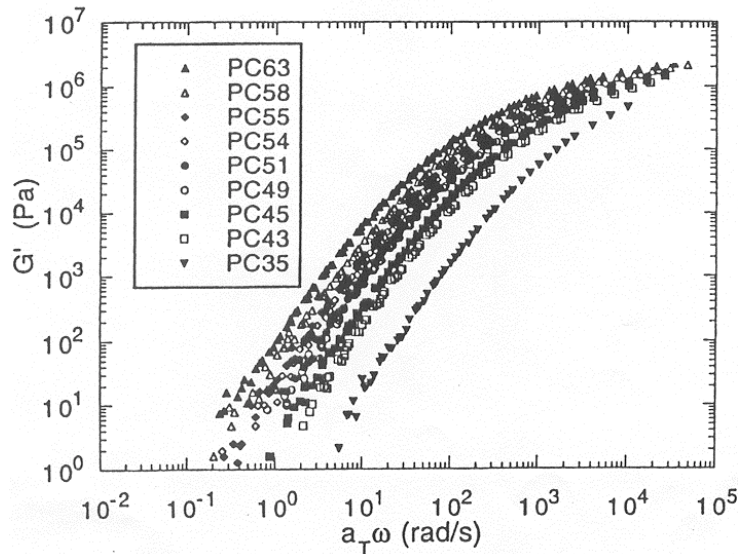

Figure 2.1-1 Storage master curve at a reference temperature of 275°C for various polycarbonate samples.[1]

Secondly, the empirical Cox-Merz rule can be applied to these data:

$$\eta(\dot{\gamma}) = \left| \eta * (\omega) \right|_{\dot{\gamma}=\omega}$$ Equation 2.1-8

This merely states that the frequency dependence of $\left| \eta * \right|$ is analogous to the shear rate dependence of $\eta(\dot{\gamma})$. Thus, this allows a value for η_0 (a steady shear quantity) to be extracted from dynamic data.

It should be noted here that literature values have been reported[4] for both M_e and M_c, the critical (entanglement) molecular weight of PC. M_e has been shown to be in the range $1.2\text{-}1.6 \times 10^3$ and M_c varies from $3.9\text{-}6 \times 10^3$. This agrees with the trend that $M_c \approx$ 2-3 M_e.[5]

Jordan and Richards also outline a viscosity model for linear PC. An important point to note for the polycarbonate studied here is that there is no significant variation in the molecular weight distribution. Consequently, there should be no changes in the shape of the viscosity-shear rate curves at different molecular weights. This allows one viscosity model with a single set of parameters to describe all molecular weights. For this purpose, a modified Cross model has been chosen:

$$\eta = \eta_0 \left[1 + (\lambda\dot{\gamma})^{0.8} \right]^{-1}$$ Equation 2.1-9

It should be noted that λ is a characteristic relaxation time which is a function of both molecular weight and temperature. At low shear rates ($\dot{\gamma} \to 0$), $\eta \to \eta_0$. At high shear rates, the Cross model reduces to a power law model where n = 0.2:

$$\eta = \eta_0 (\lambda\dot{\gamma})^{n-1}$$ Equation 2.1-10

Equation 2.1-9 shows excellent agreement with data (Figure 2.1-2) and allows determination of η_0 and λ.

[4] Fetters, L. J., D. J. Lohse, S. T. Milner, and W. W. Graessley, *Macro.*, **32**, 6847, 1999.
[5] Colby, R. H., L. J. Fetters, and W. W. Graessley, *Macro.*, **20**, 2226, 1987.
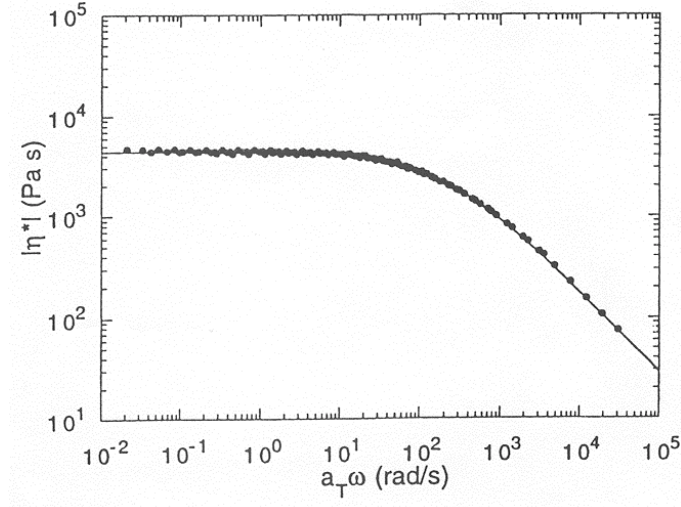
Figure 2.1-2 Experimental viscosity data and viscosity model for polycarbonate.[1]

It is possible to relate the zero shear rate viscosity η_0 to the characteristic relaxation time λ:

$$\eta_0 = k\rho T\lambda \qquad \text{Equation 2.1-11}$$

where k is a constant. Clearly, plotting η_0 versus $\rho T\lambda$ should be linear with slope k. For the linear PCs of this study, k was found to be 1.5. Then Equation 2.1-9 becomes

$$\eta(\dot{\gamma}) = \frac{1.5\rho T\lambda}{\left[1 + (\lambda\dot{\gamma})^{0.8}\right]} \qquad \text{Equation 2.1-12}$$

The characteristic relaxation time λ can be determined by fitting Equation 2.1-12 to the viscosity master curves.

From Equation 2.1-1 and Equation 2.1-11, one can relate the shift factor a_T to λ:

$$a_T = \frac{\lambda}{\lambda_0} \qquad \text{Equation 2.1-13}$$

In the usual manner, λ_0 is the characteristic relaxation time at the reference temperature. From Equation 2.1-4, the dependence of λ on molecular weight and temperature is described by

$$\lambda(T, \overline{M}_w) = \lambda_b \exp\left[\frac{1}{\beta(T - T_\infty)}\right] \qquad \text{Equation 2.1-14}$$

λ_b is a function of $\overline{M}_w$ as given by

$$\lambda_b = 1.4 \times 10^{-21} (\overline{M}_w)^{3.4} \qquad\qquad \text{Equation 2.1-15}$$

Equation 2.1-12 and Equation 2.1-14 fit both high and low molecular weight over the full temperature and shear rate range with an error of less than 15% as can be seen in Figure 2.1-3.
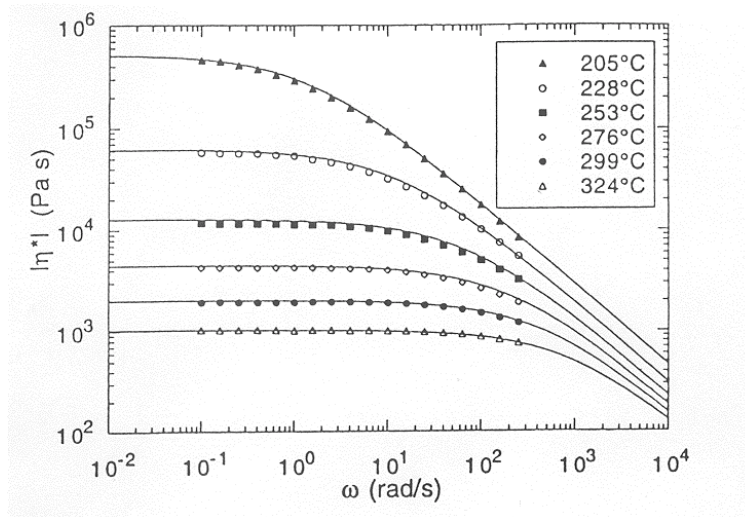

Figure 2.1-3 Comparison of the viscosity model predictions to the viscosity data of polycarbonate.[1]

This viscosity model can now be used to predict the viscosity behavior of PC with confidence. It should be pointed out that more drastic changes in polydispersity may lead to a broadening in the transition zone from Newtonian to power law behavior as seen in Figure 2.1-4 where PDI increases from 2.6 to 3.0.
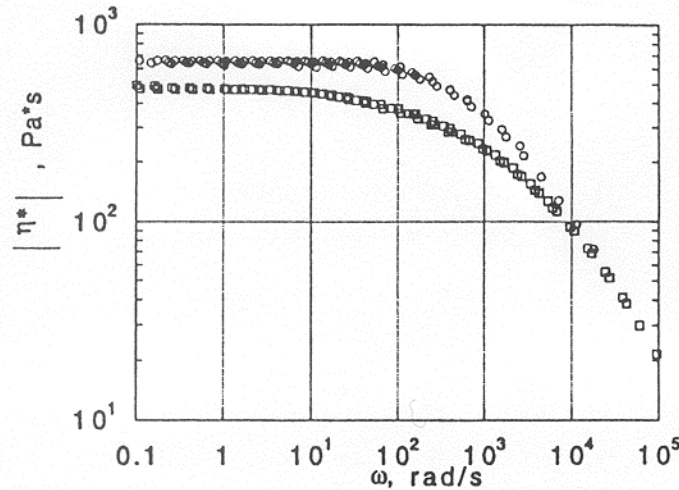
Figure 2.1-4 Influence of polydispersity on the shape of the viscosity curve. Squares represent a polydispersity of 3.0, circles are 2.6.[1]

The rheological model just outlined provides a relationship between molecular weight and viscosity specifically for polycarbonate. However, it does entail a certain level of complexity. Many simpler general expressions relating viscosity and molecular weight have been developed. Flory and Fox[6] were some of the first researchers to study this type of relationship. Fractions of polystyrene and polyisobutylene with a range of molecular weights were prepared. Molecular weight was measured by intrinsic viscosity, and, for these fractions, $\overline{M}_v$ was taken to be equivalent to $\overline{M}_w$. Melt viscosities in the range 1-100 poises were measured using a capillary viscometer. A coaxial viscometer was used to determine higher (10^5-10^{11} poises) viscosities. Viscosities for some mixtures of these fractions were also examined.

It was found that PS showed an increase in viscosity versus molecular weight up to a critical value, and then a plateau as shown in Figure 2.1-5. Fox and Flory also report that their empirical relationship,

$$\log \eta = A + C\overline{M}_w^{1/2} \qquad \text{Equation 2.1-16}$$

where A and C are constant at a given temperature, does not strictly hold for the polymers investigated. It is suggested that the relationship can perhaps be used as a

rough estimate over a narrow range of molecular weights, but cannot accurately predict values of viscosity in general.
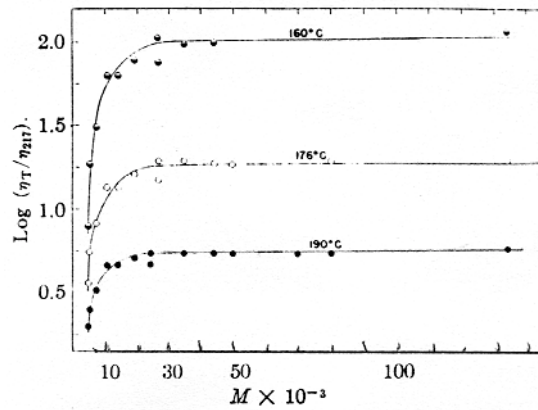

Figure 2.1-5 Viscosity versus molecular weight for polystyrene fractions.[6]

By examining fractions of polyisobutylene[7], it was also found that a linear relationship existed between log log (η / η_{ref}) and $1/M_n$, as well as between log log η and M_n for molecular weights above a critical value. Fitting data to both of these expressions can enable prediction and even limited extrapolation.

Fox and Loshaek[8] first advanced the theory of a universal viscosity law for polymers above a critical (entanglement) molecular weight. The linear relationship is as follows:

$$\log \eta = 3.4 \log Z_w + K \qquad \text{Equation 2.1-17}$$

where K is a function of temperature and Z_w is the weight average chain length,

$$Z_w = \sum w_i Z_i \qquad \text{Equation 2.1-18}$$

where w_i is the weight fraction of chains having a chain length Z_i. This expression showed good fit to data for various polymer systems.

Closmann and Seba[9] studied the physical properties of oils of various molecular weights. They found the following correlation between viscosity, density, and molecular weight:

[6] Fox, T. G. and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2384, 1948.
[7] Fox, T. G. and P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221, 1951.

$$\ln \eta = A + B\ln\rho + CM + D\ln M \qquad \text{Equation 2.1-19}$$

where viscosity is in units of cP (mPa·s), density is given by g/cm^3, and molecular weight, M, is in g/mol. The constants are determined by a least squares fitting technique.

Most rheological models, while taking into account non-Newtonian nature, do not include terms for polydispersity. Dobkowski[10,11] expands on previous work by adding a polydispersity term to some common equations. For example, melt viscosity is related to molecular weight by

$$\eta_0 = A\overline{M}_x^{3.4} q^{(a_2)_x} \qquad \text{Equation 2.1-20}$$

where $\overline{M}_x$ is either $\overline{M}_w$ or $\overline{M}_n$ (traditionally, $\overline{M}_w$), q is the polydispersity, $\overline{M}_w/\overline{M}_n$, and $(a_2)_x$ is the polydispersity exponent, reportedly –0.074 ± 0.004 for $\overline{M}_w$ or 0.741 ± 0.005 for $\overline{M}_n$ of commercial polycarbonate, and A is a constant in the range 0.0124-0.0132 for PC. It should be noted that taking q as 1 (monodisperse) results in the Bueche[12] expression commonly used for melt viscosity.

Lomellini[13] studied the rheology of PC with the aim of determining whether WLF or Arrhenius formalisms provided a better description of the data. Samples were tested in a parallel plate rheometer in an oscillatory strain mode at frequencies ranging from 0.1-100 rad/s at a maximum strain of 20% (within the linear viscoelastic region). Measurements were made at temperatures ranging from 200-330°C, and master curves were produced from these data.

It is generally accepted that the WLF methodology is best applied at temperatures close to T_g ($T_g < T < T_g + 100°C$), while the Arrhenius expression fits better at higher (T $> T_g + 100°C$) temperatures. This is due to the fact that the WLF equation takes into account that free volume is linearly dependent on temperature above T_g. However, at high enough temperatures, free volume is no longer the rate limiting factor. However, Lomellini's study concluded that the WLF expression actually provides a slightly better

[8] Fox, T. G. and S. Loshaek, *J. Appl. Phys.*, **26**, 1080, 1955.
[9] Closmann, P. J. and R. D. Seba, *J. Canad. Petroleum Tech.*, **29**, 115, 1990.
[10] Dobkowski, D., *Eur. Polym. J.*, **17**, 1131, 1981.
[11] Dobkowski, D., *Eur. Polym. J.*, **18**, 1051, 1982.
[12] Bueche, F., *J Chem. Phys.*, **40**, 484, 1964.
[13] Lomellini, P., *Makromol. Chem.*, **193**, 69, 1992.

fit over the entire range studied. Thus, for PC, either expression could theoretically be utilized for describing the master curves resulting from rheological testing.

Several groups[14,15,16] have investigated methods to obtain molecular weight distribution information from viscosity data. Some begin with the equation

$$Y(X) = \int_0^{1/X} mf(m)dm + \frac{1}{X} \int_{1/X}^{\infty} f(m)dm \qquad \text{Equation 2.1-21}$$

where

$$Y = \left(\frac{\eta}{\eta_0}\right)^{1/\alpha}$$

$$X = \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{\nu/\alpha} \qquad \text{Equation 2.1-22}$$

$$m = \frac{M}{M_w}$$

Here, $\dot{\gamma}_c$ is the characteristic shear rate for the viscosity function, η, α is usually taken as 3.4, M is the molecular weight, M_w is the weight average molecular weight, $\dot{\gamma}$ is the shear rate, η_0 is the zero-shear-rate viscosity, and $-\nu$ is the final slope of the power law region.

One method of analysis for Equation 2.1-21 is the differential approach adopted by a few groups.[14,16] They differentiate Equation 2.1-21 using Leibniz's rule and then apply the resulting equation to the viscosity data. An advantage here is that no assumption regarding the shape of the molecular weight distribution is necessary, but the method does incorporate an assumed shape for the viscosity function at both ends of the frequency range. However, too narrow a frequency range on the viscosity data can cause misleading results such as ghost peaks.

An alternative is to solve Equation 2.1-21 via an integral approach. The integrated form can be fitted to the experimental data using a constrained nonlinear least squares fitting procedure. It does become necessary, though, to assume a shape for the

[14] Tuminello, W. H. and N. Cudré-Mauroux, *Polym Eng. Sci.*, **31**, 1496, 1991.
[15] Liu, Y., M. T. Shaw, and W. H. Tuminello, *J. Rheol.*, **42**, 453, 1998.

molecular weight distribution. Hence this approach would be less favorable than the differential technique.

Liu et al.[15] utilized both of these methods on a given set of data to determine which approach gave better results. While the differential method is fast and fairly sensitive, the integral method appears more robust, particularly with incomplete viscosity data. At present, inconsistencies from both methods are significant.

Another group[17,18,19] has been working on a similar technique to obtain the molecular weight distribution of a linear, narrow molecular weight distribution polymer from viscoelastic data, specifically, $G'(\omega)$. While all the mathematical details will not be covered here, the main equation relies on the plateau modulus, G_N^0:

$$G'(\omega) = \frac{G_N^0(\omega\tau_0)^c}{1+(\omega\tau_0)^c} \qquad \text{Equation 2.1-23}$$

where τ_0 and c are numerical parameters. This equation can be linearized as

$$\log\left[\frac{G_N^0}{G'(\omega)}-1\right] = -c(\log\omega + \log\tau_0) \qquad \text{Equation 2.1-24}$$

such that plotting the left-hand-side versus $\log\omega$ gives a slope of –c and an intercept related to τ_0. The determination of these numerical parameters then allows calculation of a normalized relaxation spectrum, $H(\tau)$:

$$\begin{aligned}
H(\tau) &= DG + DG'/2 \quad \text{positive slope of } H(\tau) \text{ vs. } \ln\tau \\
H(\tau) &= DG - DG'/2 \quad \text{negative slope of } H(\tau) \text{ vs. } \ln\tau
\end{aligned} \qquad \text{Equation 2.1-25}$$

where

$$\begin{aligned}
DG &= \frac{c(\tau_0\omega)^c}{1+(\tau_0\omega)^c} - \frac{c(\tau_0^c\omega^c)^2}{(1+\tau_0^c\omega^c)^2} \\
DG' &= \frac{c^2\tau_0^c\omega^c}{1+\tau_0\omega^c} - 3\frac{c^2(\tau_0^c\omega^c)^2}{(1+\tau_0^c\omega^c)^2} + 2\frac{c^2(\tau_0^c\omega^c)^3}{(1+\tau_0^c\omega^c)^3}
\end{aligned} \qquad \text{Equation 2.1-26}$$

[16] Malkin, A. Y. and A. E. Teishev, *Polym. Eng. Sci.*, **31**, 1590, 1991.
[17] Yu, T. L., *J. Macromol. Sci.-Phys.*, **B31**, 175, 1992.
[18] Yu, T. L., S. C. Ma., and J. C. Chen, *J. Macromol. Sci.-Phys.*, **B32**, 229, 1993.
[19] Yu, T. L. and S. C. Ma, *Polym. J.*, **24**, 1321, 1992.

Once $H(\tau)$ is known, the next step is generating a weight fraction differential molecular weight distribution curve, $W(\tau)$. This is accomplished via a computer iteration procedure. It is known that

$$H(\tau_j) = 2h(\tau_j) \int\limits_{\ln \tau_j}^{\infty} h(\tau_k) d \ln \tau_k \qquad \text{Equation 2.1-27}$$

where $h(\tau) = W(\tau)\tau$. Plots of $H(\tau)$ versus $\ln \tau$ and $W(\tau)$ versus $\ln \tau$ are generated and the $\ln \tau$ axes divided into N intervals each equal to Δ. Then Equation 2.1-27 is integrated using the trapezoid rule. Next, τ can be converted to molecular weight by

$$\tau_i = kM_i^a \qquad \text{Equation 2.1-28}$$

where a = 3.4 for $1 < M_w/M_c < 50$ and

$$k = \frac{M_{w_r}}{M_w} a \qquad \text{Equation 2.1-29}$$

where M_{wr} is the relative weight average molecular weight and M_w is obtained from some other method like GPC or light scattering. To find M_{wr}, k=1 in Equation 2.1-28. Then M_w and M_n can be calculated. In fact, Yu successfully applied this method to PS and generated the molecular weight distribution from rheological data.

In order to account for polydispersity in the polymers, a shift factor must be introduced in the aforementioned method. This application is detailed in another study by Yu[18] where binary mixtures of monodisperse PS were prepared to yield a broad overall distribution. This shift factor is defined as

$$\tau_{i,m} = \tau_i A_{i,m} \qquad \text{Equation 2.1-30}$$

where $\tau_{i,m}$ is the relaxation time of chain i mixed with other chains, τ_i is the relaxation time of chain i without mixing with other chains, and $\log(A_{i,m})$ is the shift factor. Equation 2.1-30 then leads to

$$H(\tau_{i,m}) = H(\tau_i, A_{i,m}) \qquad \text{Equation 2.1-31}$$

The shift factor is related to the weight average molar mass of the mixture, $M_{w,m}$, by

$$A_{i,m} = (M_{w,m} / M_{i,m})^b \qquad\qquad \text{Equation 2.1-32}$$

where $b = 1.4$.

The same iterative procedure is then utilized with the only difference being the use of the shifted relaxation time spectrum, $H(\tau_{i,m})$. In a later work[19], it is also demonstrated that an analogous procedure can be applied to loss modulus data.

While these techniques present an interesting relationship between molecular weight distribution and rheology, their utility may not be so high considering the ease of measuring both quantities. The procedure to generate the molecular weight distribution is somewhat laborious, involving an iterative technique and some computer programming. Since gel permeation chromatography readily gives the same information, it is still the preferred method.

From this summary, it is evident that several relationships exist to relate rheology to molecular weight. These range from simple proportionalities to more complex equations taking into account other aspects of the polymer, such as polydispersity. Applying these equations can help link structurally-caused molecular weight changes to a downstream property such as viscosity.

2.2. Material Properties

Degradation is well-studied on a fundamental, structural level. To lend practical utility, it is necessary to relate it to measurable properties. Predicting polymer properties from degradation conditions requires accurate structure-property correlations. These expressions relate some known structural feature of the polymer, such as molecular weight, to a property of interest, like tensile strength, viscosity, glass transition temperature, or even specific volume. Some such applicable relations will be summarized here.

It is generally accepted that Flory[20] was the first to relate molecular weight and certain properties, such as tensile strength, T, in polymers. He began by proposing a series functionality:

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[20] Flory, P. J., *J. Am. Chem. Soc.*, **67**, 2048, 1945.

$$T = f\left(\frac{1}{M}\right) = a_0 + \frac{a_1}{M} + \frac{a_2}{M^2} + \dots \qquad \text{Equation 2.2-1}$$

It is known that, for homogeneous blends of two polymers, properties are additive and are functions of $<M_n>$:

$$T_{blend} = f\left(\frac{1}{\overline{M}_n}\right) \qquad \text{Equation 2.2-2}$$

If w_i and M_i are weight fractions and molecular weights of the ith component, respectively, then

$$\frac{1}{\overline{M}_n} = \sum_i (w_i / M_i) \qquad \text{Equation 2.2-3}$$

therefore,

$$T_{blend} = f\left(\sum_i w_i / M_i\right) \qquad \text{Equation 2.2-4}$$

Substituting Equation 2.2-4 into the series expansion of Equation 2.2-1 yields

$$T_{blend} = a_0 + a_1 \sum_i (w_i / M_i) + a_2 \left(\sum_i (w_i / M_i)\right)^2 + \dots \qquad \text{Equation 2.2-5}$$

Again, it is known that some blend properties are additive functions of weight fraction, $T_{blend} = \sum_i w_i T_i$. In order for this functionality to agree with Equation 2.2-5, terms a_2 and higher must be identically zero, leading to

$$T = a_0 + \frac{K}{\overline{M}_n} \qquad \text{Equation 2.2-6}$$

While this expression has been used for over 50 years, it does not lead to satisfactory results in some cases, most notably for broad molecular weight distribution polymers. However, it does serve as a good starting point for any structure-property relationship, and, in the absence of a better model, is still favored. It should be noted that when the property in question is the glass transition, Equation 2.2-6 is commonly referred to as the Fox-Flory expression.

A systematic study[21] to test the Fox-Flory equation was carried out on several samples of polystyrene with an assortment of both molecular weights and distributions. It was found that tensile strength and elongation were linearly dependent on $\overline{M}_n^{-1}$, but that narrow and broad molecular weight distribution samples showed varying linear fits. Another result of the study was the finding that the narrower the distribution, the poorer the property at a given $\overline{M}_n$, and the better the property at a given $\overline{M}_w$, suggesting a dependence on a molecular weight average somewhere between $\overline{M}_n$ and $\overline{M}_w$. By contrast, tensile impact strength was seen to follow quite well a relationship with weight average molecular weight.

A minor modification of the Fox-Flory relationship was proposed by Ogawa[22]. Instead of an inverse dependence on number average molecular weight, this author utilized the square root of the product of the weight average and number average values:

$$T = T_\infty - \frac{K}{\left(\overline{M}_n \overline{M}_w\right)^{1/2}} \qquad \text{Equation 2.2-7}$$

It was shown that this functional relationship also can be used to predict tensile strength and demonstrated good agreement for both elongation at yield and flexural modulus for polystyrene.

In addition to the Fox-Flory relationship, another functional relation has been proposed[23] to relate the glass transition temperature to molecular weight:

$$\frac{1}{T_g} = \frac{1}{T_{g,\infty}} + \frac{K}{T_{g,\infty}^2} \frac{1}{M} \qquad \text{Equation 2.2-8}$$

This expression was successfully applied to several polymers including polystyrene, polymethylmethacrylate, and polyisobutylene. It should be noted that the K constant in both the Fox-Flory relation and in Equation 2.2-8 appear to be the same. Recent research[24] has indicated that K can be given by

[21] McCormick, H. W., F. W. Brower and L. Kin, *J. Poly. Sci.*, **39**, 87, 1959.
[22] Ogawa, T., *J. Appl. Polym. Sci.*, **44**, 1869, 1992.
[23] Fox, T. G. and S. Loshaek, *J. Polym. Sci.*, **15**, 371, 1955.
[24] Bicerano, J., *Prediction of Polymer Properties*, 2nd ed., Marcel Dekker, NY, 1996.

$$K \approx 0.002715 T_{g,\infty}^3 \qquad \text{Equation 2.2-9}$$

Rheological properties were also examined. Narrower distribution samples behaved in a more Newtonian manner than broader ones, and decreasing molecular weight also led to more Newtonian character. Zero shear rate melt viscosity was determined to relate to $\overline{M}_w$. However, high shear melt viscosity measurements indicated a separate relationship for narrow and broad samples although both were also related to $\overline{M}_w$.

As a consequence of the rheological work covered in Section 2.1, Dobkowski[10,11] extended the Fox-Flory equation by including a term for polydispersity. The first step involved rewriting the equation for some property P as

$$(P_\infty - P) = KM^{-1} \qquad \text{Equation 2.2-10}$$

Adding a polydispersity term leads to

$$(P_\infty - P) = A\overline{M}_x^a q^{(a_2)_x} \qquad \text{Equation 2.2-11}$$

For T_g of polycarbonate, the above equation yields $T_{g\infty} = 436$ K, $A = 3.4 \times 10^5$, and $a = -1$. The value of $(a_2)_x$ as reported here is -0.63 and $(a_2)_w$ is 0.38. Note that the Fox-Flory expression was derived on the basis of number-average values, so those values would likely be utilized in Equation 2.2-11.

Other researchers who applied Flory's results included Golden and coworkers[25] who looked at the relationship between mechanical properties and molecular weight for polycarbonate. Different molecular weights, as measured by intrinsic viscosity, were attained by irradiating samples for various times. Samples were tested both in tension and flexure, but flexure was reported to be more reliable for brittle specimens. It was found that, in the region of brittle failure ($\overline{M}_v < 13,000$), the flexural strength σ_F could be calculated according to a linear relationship dependent on $\overline{M}_v$, the viscosity average molecular weight. Golden also presents a relationship between radiation dose R and $\overline{M}_v$, and expressions for the tensile yield strength, and flexural modulus and strength for the

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[25] Golden, J. H., B. L. Hammant, and E. A. Hazell, *J. Poly. Sci. Part A*, **2**, 4787, 1964.

ductile region in terms of R. Clearly, with the aforementioned R-$\overline{M}_v$ expression, one could easily develop equations relating tensile strength and flexural properties directly to molecular weights. It is unclear whether these equations have application beyond the particular system for which they were developed.

In an extension of this work[26], the authors looked at a range of testing rates for flexural tests. They found that for modulus, there is essentially no rate dependence but there does exist an increase in modulus with decreasing molecular weight except for the lowest molecular weights.

The authors then prepared master curves of stress versus molecular weight for various strain rates as in Figure 2.2-1. Once this procedure was shown to give acceptable results, it was also determined that a master curve of flexural strength versus the logarithm of the strain rate could be prepared by shifting the data both horizontally and vertically. The resulting master curve is shown in Figure 2.2-2. These master curves allow prediction of flexural strength-molecular weight or flexural strength-log (strain rate) curves at a specified molecular weight or strain rate. Golden concludes that rate and molecular weight act in equivalent ways on the stress properties of polycarbonate.
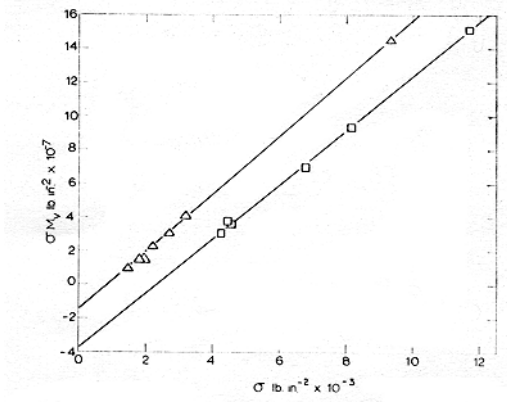

Figure 2.2-1 Stress versus molecular weight in the brittle region. Squares represent a strain rate of 1 min^{-1}, triangles a rate of 0.0001 min^{-1}.[26]

[26] Golden, J. H., B. L. Hammant, and E. A. Hazell, *J. Appl. Poly. Sci.*, 1**2**, 557, 1968.
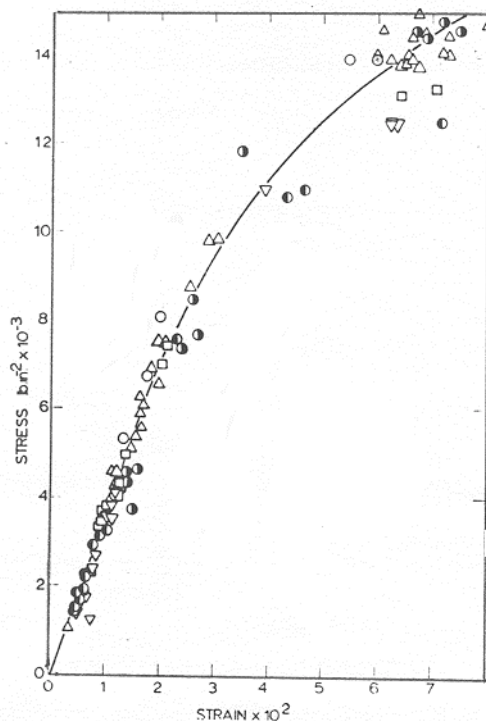
Figure 2.2-2 Stress versus strain for molecular weights ranging from 5300-21,900 and at various strain rates.[26]

Pezzin and coworkers[27] also looked at the relationship between the resulting properties and polymeric structure, specifically that between the glass transition temperature and molecular weight of PVC. Using the Fox-Flory relationship,

$$T_g = T_{g,\infty} - \frac{K}{\overline{M}_n}$$

Equation 2.2-12

yielded good results only for $\overline{M}_n > 3000$. In an effort to describe the T_g over a wider range of molecular weights, several other approaches were considered. A free volume treatment, for example, yields an identical relationship where K is given by $2\theta\rho N/\alpha_f$ where θ is excess free volume (from an end group), ρ is density, N is Avogadro's number, and α_f is the difference of expansion coefficients above and below T_g. Because the functional dependence is identical, this method was found to also be unsatisfactory.

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[27] Pezzin, G., F. Zilio-Grandi, and P. Sanmartin, *Eur. Polym. J.*, **6**, 1053, 1970.

The next approach tried was that of Somcynsky and Patterson which relies on the theory of corresponding states. This more complicated fit also yields the same relationship where K is now $bM_0T_{g,\infty}/a$ where b/a is a quantity which is inversely related to flexibility of the chain, M_0 is the molecular weight of a chain segment, and $T_{g,\infty}$ is the glass transition at infinite molecular weight.

As a last approach, the authors turned to Gibbs' and DiMarzio's statistical mechanical theory of supercooled liquids. Quite a complicated relationship results from this:

$$\frac{x}{x-3}\left\{\frac{\ln v_0}{1-v_0}+\frac{1+v_0}{1-v_0}\ln\left[\frac{(x+1)(1-v_0)}{2xv_0}+1\right]+\frac{\ln 3(x+1)}{x}\right\}=\frac{2\beta\exp\beta}{1+2\exp\beta}-\ln(1+2\exp\beta)$$

Equation 2.2-13

where $\beta=\varepsilon/kT_g$. Here, ε is the flex energy (energy difference between rotational conformers), k is Boltzmann's constant, x is the number of chain atoms in the polymer, and v_0 is the fraction of holes (free volume fraction at T_g). Pezzin reports that this expression quite well describes the T_g behavior over the entire range of molecular weights studied.

It was not mentioned in Pezzin's study what the entanglement molecular weight is for PVC. Quite likely, it is somewhere in the range where the Fox-Flory relationship ceases to hold (i.e., around 3000). If a researcher is only interested in behavior above entanglement, Fox-Flory is quite adequate and offers much greater simplicity than the Gibbs-DiMarzio approach, and is thus favored.

Adam et. al.[28] looked at the effect of degradation on the structure-property relationships for polycarbonate. Specifically, they studied how molecular weight affects thermal properties, such as thermal degradation and the glass transition. Molecular weights were measured using vapor pressure osmometry and intrinsic viscosity. Thermal degradation was examined via thermogravimetric analysis as well as infrared spectroscopy. The results from TGA indicate that degradation is greater for lower molecular weight samples, suggesting that endgroup effects are involved. However, it should be noted that more volatile fragments are expected with a lower molecular weight

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[28] Adam, G. A., J. N. Hay, I. W. Parsons, and R. N. Haward, *Polymer*, **7**, 517, 1976.

sample even with random scission. FTIR was employed to track changes in the endgroups which correspond to degradation rates. Finally, glass transition measurements were performed and the data fitted to the Fox-Flory equation (Equation 2.2-12) such that $T_{g,\infty} = 432$ K and K $= 1.45 \times 10^5$ mol·K.

While the Fox-Flory functional relationship has been shown to be inexact, many newer studies have still used it as their basis. Colby et al.[29]looked at the relationship between molecular weight and various properties for polybutadiene. They point out that density, thermal expansion coefficient, and glass transition temperature all exhibit linear inverse molecular weight dependences, the same relationship as in Equation 2.2-12.

Bicerano[24] presents a slight variation on the well-known expression by presenting an equation as follows:

$$T_g = T_{g,\infty} - \frac{K'}{(K'' + M_n)} \qquad \text{Equation 2.2-14}$$

Here, the mathematical interaction between K′ and K″ allow fitting over a broader range of number average molecular weight and with greater sensitivity as would be expected when another adjustable parameter is added. The values for the constants are found by simply fitting the data to the expression.

More recently, researchers have tried to refine the Flory's approach. Bersted and Anderson[30] examined the influence of molecular weight and molecular weight distribution on the tensile properties of numerous samples of PS. These samples exhibited a range of molecular weights and, in some cases, blends were prepared to produce varying distributions. All molecular weight values were measured via gel permeation chromatography. Specimens were then injection molded into tensile bars and subsequently annealed to relax orientation before mechanical testing.

Many authors still use Flory's relationship (Equation 2.2-6) between mechanical properties and molecular weight. However, this particular study shows that such an expression only fits narrow distributions well. Other researchers have attempted correlations with $\overline{M}_z$ which reflects the high molecular weight tail. This type of

[29] Colby, R. H., L. J. Fetters, and W. W. Graessley, *Macro*., **20**, 2226, 1987.
[30] Bersted, B. H. and T. G. Anderson, *J. Appl. Poly. Sci*., **39**, 499, 1990.

formalism again fails to describe the broad distributions. This study points out that the use of $\overline{M}_w$ better describes both narrow and polydisperse samples, but ascribes this to coincidence.

Bersted and Anderson's proposed new model takes tensile strength proportional to entanglement density. Any chain with molecular weight less than a threshold molecular weight, $M_T (\cong M_C^{1.5})$ does not contribute to the strength. So for a sample with any polydispersity,

$$\sigma \propto \sum n_i \cdot (\text{number of entanglements per molecule for molecules of molecular weight } M_i)$$

Equation 2.2-15

on a unit volume basis. Then,

$$\sigma \propto \sum_{i=1}^{\infty} (\rho N_0 / M_i) \cdot \left[(M_i - M_T) / M_e \right] w_i$$

Equation 2.2-16

with ρ being density, M_e the molecular weight between entanglements, and w_i the weight fraction of i. As mentioned above, chains of molecular weight less than M_T do not contribute to strength, so this species will be considered as a diluent with fraction $(1-\phi)$. The above equation then becomes

$$\sigma \propto (\rho N_0 / M_e) \sum_{i=T}^{\infty} (w_i - w_i M_T / M_i)$$

Equation 2.2-17

or

$$\sigma \propto \phi(\rho N_0 / M_e) \cdot \left(1 - \frac{M_T}{\overline{M}_n^*} \right)$$

Equation 2.2-18

where $\dfrac{1}{\overline{M}_n^*} \equiv \sum_{i=T}^{\infty} \dfrac{\overline{w}_i}{M_i} = \dfrac{1}{\phi} \sum_{i=T}^{\infty} \dfrac{w_i}{M_i}$ and $\overline{w}_i = \dfrac{w_i}{\phi}$ where $\overline{w}_i$ is the renormalized molecular weight distribution excluding weight fractions of $M_i \leq M_T$. Then,

$$\sum_{i=T}^{\infty} \overline{w}_i \equiv 1 \quad \text{and} \quad \sum_{i=T}^{\infty} w_i = \phi$$

Equation 2.2-19

This leads to

$$\sigma = \sigma_\infty \left(1 - \frac{M_T}{\overline{M}_n^*} \right) \phi \qquad \text{Equation 2.2-20}$$

where $\phi \left(1 - \dfrac{M_T}{\overline{M}_n^*} \right)$ is called the failure property parameter and σ_∞ is the tensile strength

at infinite molecular weight. Equation 2.2-20 is identical in form to Flory's equation. The exceptions are the ϕ term and the use of $\overline{M}_n^*$, both of which have been corrected for chains of molecular weight less than M_T.

The method to find M_T, as described by Bersted and Anderson, is essentially an exercise in fitting. One should calculate the failure property parameter for several values of M_T ($FP(M_T)$), then fit tensile strength versus $FP(M_T)$ to either a linear or logarithmic expression:

$$\sigma = A + K[FP(M_T)]$$
$$\log \sigma = \log K + B \log[FP(M_T)] \qquad \text{Equation 2.2-21}$$

The proper value of M_T is then the one that gives the best fit for both narrow and broad distributions. This means that for a linear fit, the intercept approaches zero and for the logarithmic equation, the slope approached 1.

For predictive purposes, this technique has a distinct disadvantage. A researcher would need to actually measure tensile properties for several different molecular weight samples in order to find M_T. However, having to perform the measurements negates the utility of being able to predict results without testing. If values of M_T were tabulated for numerous polymers, this procedure would then be much more attractive.

With computers becoming more commonplace and powerful, a more rigorous approach to structure-property relations has been tried recently. One research group[31,32], Katirzky et al., has been attempting to correlate T_gs of various polymers using a Quantitative Structure-Property Relationship (QSPR). The method looks at descriptions which are calculated strictly from structural information of a small (3 repeat unit)

[31] Katirzky, A. R., P. Rachwal, K. W. Law, M. Karelson, and V. S. Lobanov, *J. Chem. Inf. Comput. Sci.*, **36**, 879, 1996.
[32] Katirzky, A. R., P. Rachwal, K. W. Law, M. Karelson, and V. S. Lobanov, *J. Chem. Inf. Comput. Sci.*, **38**, 300, 1998.

fragment of the polymer. Descriptors include constitutional, geometrical, topological, electrostatic, quantum –chemical, and thermodynamic classes of data.

Katirzky reports success using a five-parameter correlation which takes into account shape and bulkiness of the polymer as well as intermolecular electrostatic interactions. However, the correlation is limited to linear polymers of relatively high (>50,000) molecular weight where T_g is essentially independent of chain length. At present, such a method is therefore not applicable to the proposed study.

To meet the proposed goal of relating properties to molecular weight changes, there are obviously several methods to choose from. This review provides an idea of some of these techniques as well as their advantages or drawbacks.