

Chapter

5. Property Results

5.1. Introduction

From an engineering perspective, prediction of polymer end-use properties from structural features, such as molecular weight, chemical composition, and morphology, is very attractive. This is particularly true for harsh service environments where degradation of the material can occur, leading to potential failure of the part in question. Advance knowledge of material properties in such an environment is advantageous for safety and financial reasons not only by preventing failures, but also by keeping the polymeric device in service for the entire length of its useful life.

In the present study, it has already been shown that molecular weight can be predicted from thermal history, in the form of τ , the degree of degradation, as detailed in Chapter 4. Structure-property expressions, which are common in the literature, relate a structural feature, usually molecular weight, to some engineering property such as tensile strength, melt viscosity, or T_g . The goal of this part of the present study is to develop a direct connection, analogous to the appropriate structure-property relationship, between thermal history, τ , and the property of interest. Such an expression would allow prediction of engineering parameters of a class of polymers based only upon the knowledge of the environmental history and the original parameters.

In order to develop these relationships, properties, including T_g , tensile strength, and melt viscosity, were measured for PC samples having a spectrum of molecular weights which resulted from differing levels of thermal degradation. Various structure-property relationships from the literature which relate the property of interest to molecular weight were applied to the resulting data. In Chapter 4, expressions were derived correlating τ to the molecular weight. This relationship can be utilized in conjunction with the new structure-property relationships, or τ can be directly linked to the parameter of interest. In either case, a predictive model based solely on knowledge of the environmental history of the sample can be developed for various parameters.

5.2. Differential Scanning Calorimetry Measurements

5.2.1. T_g Measurements

One of the most salient polymer properties which changes concurrently with variations in molecular weight is the glass transition temperature. This feature was analyzed via differential scanning calorimetry using a DuPont Dual Sample DSC. Circular samples (approximately 6 mm diameter) were punched from the compression molded films (thickness approximately 0.2 mm) and stacked in the DSC pans such that the total sample weight was on the order of 10 mg. Specimens were then scanned at a rate of 10°C/min to a temperature above T_g , held for a few minutes to erase any thermal history and aging, and then quenched and rescanned. The second scan was taken in each case in order to equalize the thermal history of each sample. The results for PC(Lab), with the endotherm in the -y direction, are shown in Figure 5.2.1-1-Figure 5.2.1-4. Although some of the thermograms exhibited noise, clear T_g 's were evident for each sample. These graphs demonstrate the expected trends of decreasing T_g 's with increasing amounts of degradation. The T_g values, taken as the temperature corresponding to the mid-point of the transition, are summarized in Table 5.2.1-1.

Also shown in Table 5.2.1-1 are the results for PC(Lex), and the associated thermograms are illustrated in Figure 5.2.1-5. These data do not follow a well-defined trend as the T_g apparently begins to increase at the highest degradation levels. This could be due to crosslinking at this extreme condition, which would be consistent with the difficulty encountered in dissolving the material in methylene chloride. However, this sample appeared fully dissolved in other solvents (NMP and chloroform), which would tend to indicate that gelation is not occurring. In either case, it is evident that further study of the effect of the stabilizer is warranted based on the results so far. Thus, any results obtained for this highly degraded material should be utilized only with caution.

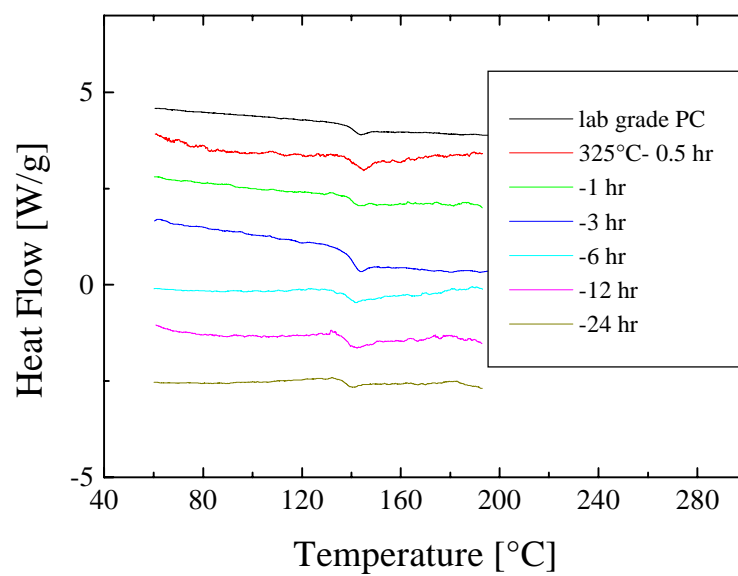


Figure 5.2.1-1DSC thermograms for PC(Lab) degraded at 325°C.

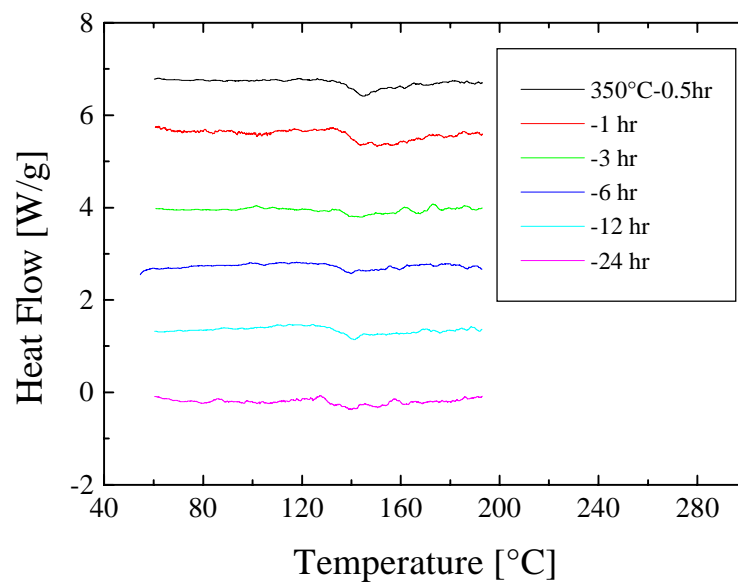


Figure 5.2.1-2 DSC thermograms for PC(Lab) degraded at 350°C.

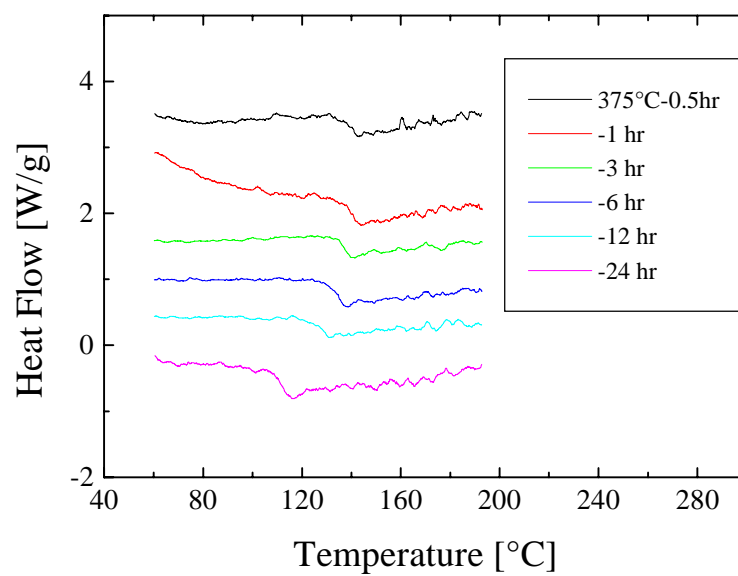


Figure 5.2.1-3 DSC thermograms for PC(Lab) degraded at 375°C.

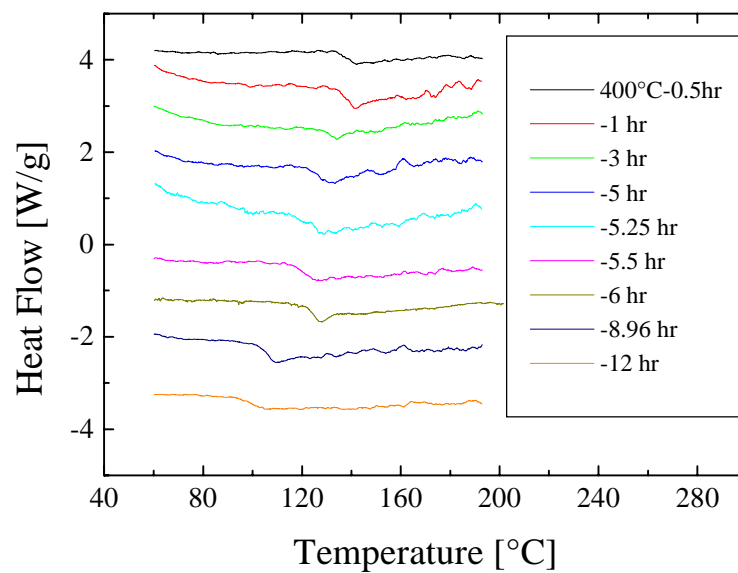


Figure 5.2.1-4 DSC thermograms for PC(Lab) degraded at 400°C.

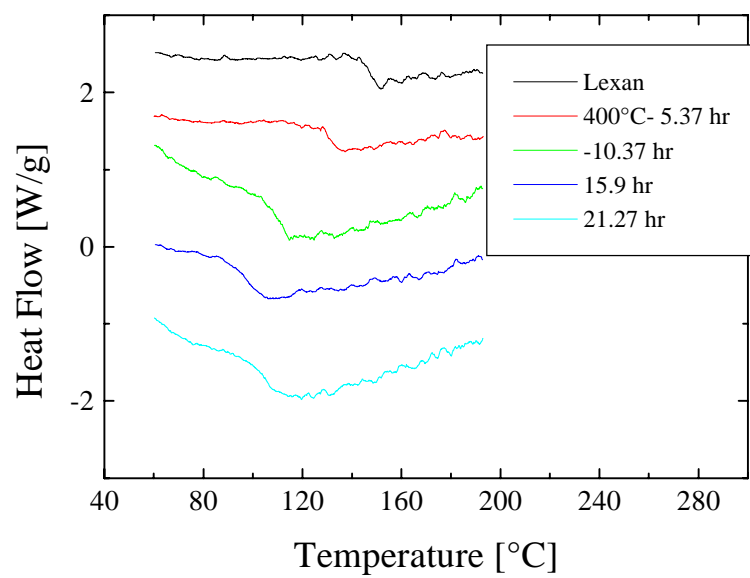


Figure 5.2.1-5 DSC thermograms for PC(Lex).

Table 5.2.1-1
Summary of DSC Results

Material	T _g [°C]
PC(Lab)	141.3
325°C-0.5 hr	141.3
-1 hr	141.2
-3 hr	140.3
-6 hr	138.8
-12 hr	138.0
-24 hr	137.4
350°C-0.5 hr	140.6
-1 hr	138.9
-3 hr	137.1
-6 hr	137.1
-12 hr	136.7
-24 hr	129.2
375°C-0.5 hr	140.5
-1 hr	140
-3 hr	137.3
-6 hr	135.0
-12 hr	129.8
-24 hr	111.6
400°C-0.5 hr	139.3
-1 hr	139.1
-3 hr	131.4
-5 hr	129.0
-5.25 hr	125.3
-5.5 hr	121.9
-6 hr	124.9
-8.96 hr	106.2
-12 hr	101.1
PC(Lex)	147.8
400°C-5.37 hr	131.3
-10.37 hr	111.2
-15.9 hr	98.2
-21.27 hr	103.8

5.2.2. T_g Prediction

In order to provide a predictive model for the glass transition temperature, it is necessary to relate this quantity to the degree of degradation, τ . It has previously been shown by Flory¹ that T_g can be related to the reciprocal of the number average molecular weight. In Chapter 4, it was concluded that \overline{M}_n could also be inversely related to τ . Therefore, it is a natural extension of these relationships to presume that T_g may be analogously related to τ in a linear fashion. Such a relationship is shown in Figure 5.2.2-1 and leads to the expression

$$\tau = 20.7 - 0.05T_g \quad \text{Equation 5.2.2-1}$$

Likewise, such an equation can be deduced for the commercial polymer. However, it should be noted that for generating a predictive model for the data, the point at the highest level of degradation was disregarded even though it is shown in Figure 5.2.2-2. Because this point does not seem to follow the trend exhibited by the rest of the data, and due to the difficulties already discussed regarding this sample, it was excluded from the modeling expressions. The remaining data can be described by the expression

$$\tau = 12.4 - 0.03T_g \quad \text{Equation 5.2.2-2}$$

¹ Flory, P. J., *J. Amer. Chem. Soc.*, **67**, 2048, 1945.

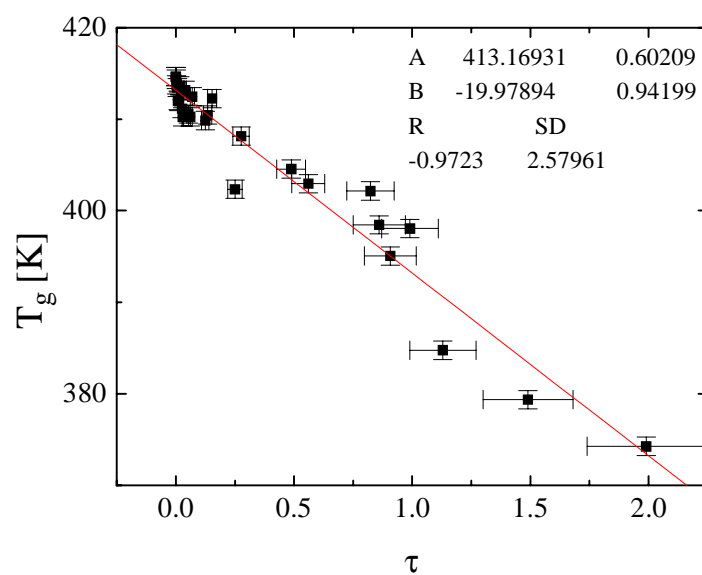


Figure 5.2.2-1 Relationship between T_g and τ for PC(Lab).

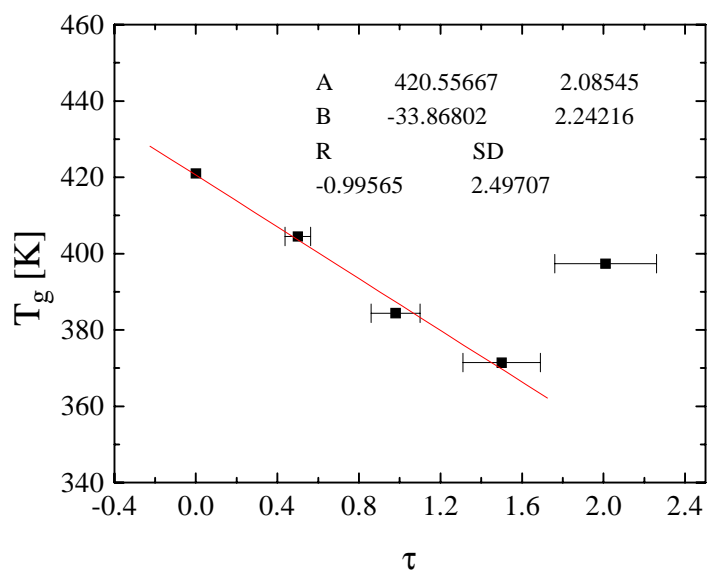


Figure 5.2.2-2 Relationship between T_g and τ for PC(Lex).

Several general expressions relating properties such as T_g or tensile strength to the molecular weight have been proposed over the years. The most basic is that of Flory¹ which can also be derived from free volume arguments:

$$P = P_{\infty} - \frac{K}{\overline{M}_n} \quad \text{Equation 5.2.2-3}$$

where P is a property (such as T_g), P_{∞} is the property at infinite molecular weight, and K is a constant. The data obtained from DSC can be modeled using Equation 5.2.2-3 as shown in Figure 5.2.2-3 and Figure 5.2.2-4 for both grades of PC. For PC(Lab), this relationship results in a $T_{g\infty}$ of 160°C and $K = 2.7 \times 10^5$ g K/mol which are comparable to those reported by Adam et al² ($T_{g\infty} = 159^\circ\text{C}$ and $K = 1.5 \times 10^5$ g K/mol). Similarly, for PC(Lex), $T_{g\infty} = 166^\circ\text{C}$ and $K = 4.2 \times 10^5$ g K/mol. However, the resulting values for PC(Lex) disregard the data point representing the greatest degree of degradation, so the constant values should be used only with extreme caution.

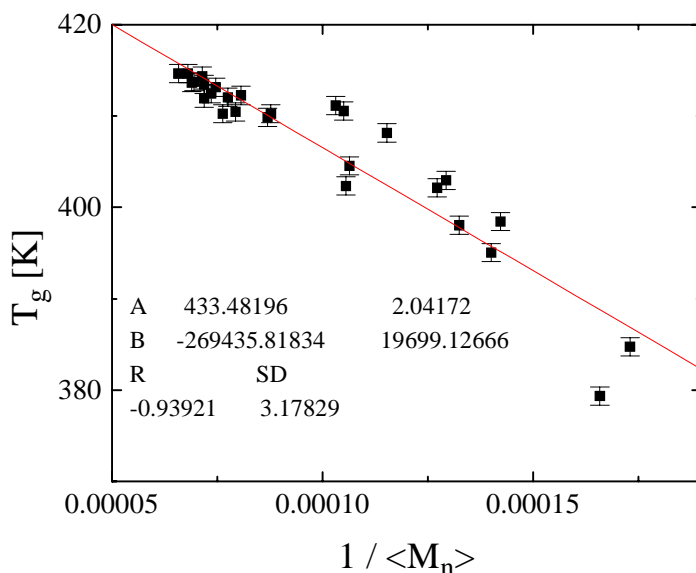


Figure 5.2.2-3 Relationship between T_g and reciprocal molecular weight for PC(Lab).

² Adam, G. A., J. N. Hay, I. W. Parsons, R. N. Haward, *Polymer*, **7**, 517, 1976.

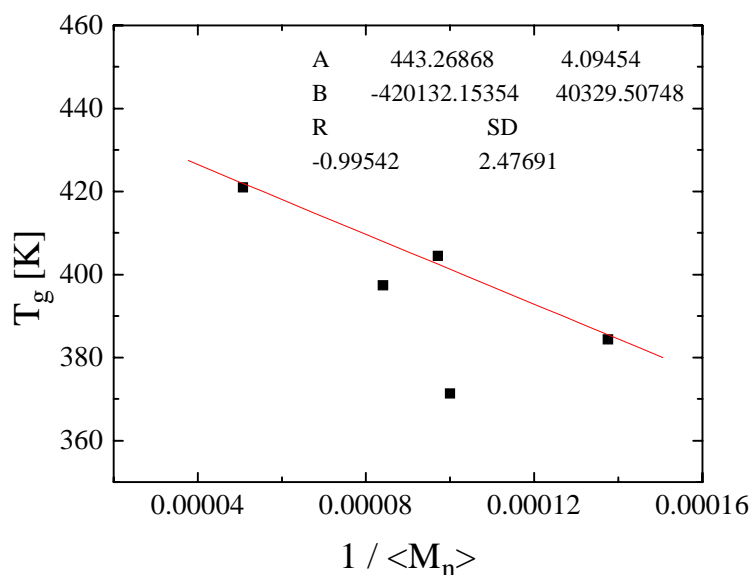


Figure 5.2.2-4 Relationship between T_g and reciprocal molecular weight for PC(Lex).

In another attempt to model the glass transition temperature, Ogawa³ proposed a slight modification to Flory's method. Instead of relating T_g to the number average molecular weight, Ogawa relates the properties to the square root of the product of the weight average and number average molecular weights in an attempt to account for the polydispersity of the system:

$$P = P_{\infty} - \frac{K}{(\overline{M}_n \overline{M}_w)^{0.5}} \quad \text{Equation 5.2.2-4}$$

Modeling the DSC data of the present study using Equation 5.2.2-4, as shown in Figure 5.2.2-5 for PC(Lab), resulted in a slightly better fit than that found from Flory's model, as indicated by the lower value for the statistical r value. Based on Ogawa's model, it was found that $T_{g\infty} = 169^{\circ}\text{C}$ and $K = 4.7 \times 10^5 \text{ g K/mol}$ for PC(Lab). Due to the high level of uncertainty in the PC(Lex) data, it was not treated by Ogawa's method since any results would likely have little accuracy.

³ Ogawa, T., *J. Appl. Polym. Sci.*, **44**, 1896, 1992.

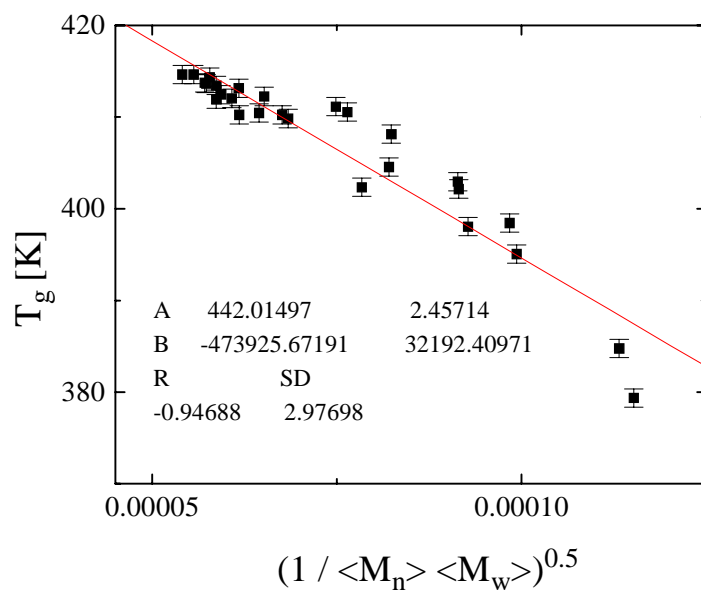


Figure 5.2.2-5 Ogawa's relationship applied to PC(Lab).

A more sophisticated T_g model was proposed by Fox and Loshaek⁴:

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{K}{T_{g\infty}^2} \frac{1}{\overline{M}_n} \quad \text{Equation 5.2.2-5}$$

When the data of the present study were plotted according to this expression, as seen in Figure 5.2.2-6, results were once again obtained for both K and $T_{g\infty}$. PC(Lab) exhibited a $T_{g\infty}$ of 164°C and a K of 3.2×10^5 g K/mol.

⁴ Fox, T. G. and S. Loshaek, *J. Polym. Sci.*, **15**, 371, 1955.

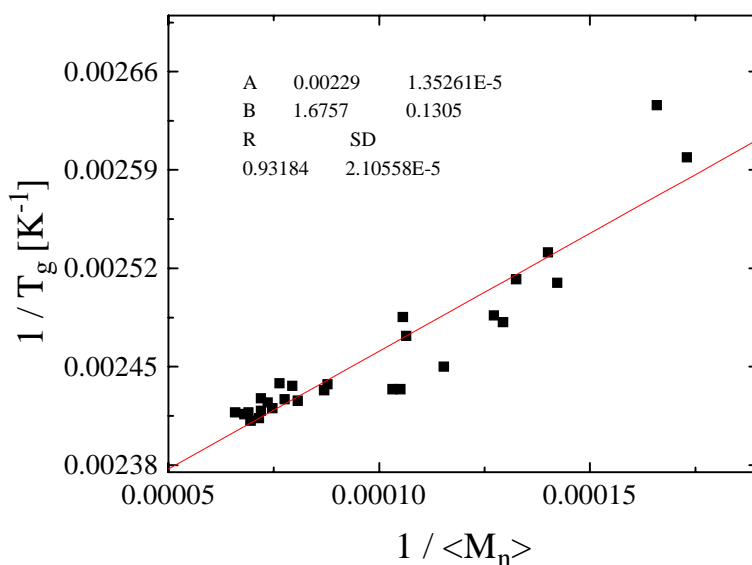


Figure 5.2.2-6 Fox-Loshak fit of DSC data for PC(Lab).

The T_g – molecular weight relationships discussed thus far have not addressed the issue of the breadth of the molecular weight distribution; but, instead assumed a monodisperse system. Dobkowski⁵ includes the polydispersity as an additional term, $q = M_w/M_n$, in the expression

$$(P_\infty - P) = A \bar{M}_x^a q^{(a_2)_x} g_v^{a_3} \quad \text{Equation 5.2.2-6}$$

where g_v is a branching factor which is unity for the present study, and A , a , a_2 , and a_3 are constants. Dobkowski found that for PC: $a = -1$, $(a_2)_n$ (when number average molecular weight is utilized) = -0.63, and $(a_2)_w$ (weight average molecular weight) = 0.38. Utilizing number average molecular weight and the constants just described, application of this model to the data of the present study, as shown in Figure 5.2.2-7, yielded $T_{g\infty} = 172^\circ\text{C}$ and $A = 5.5 \times 10^5 \text{ g K/mol}$. The use of the weight average molecular weight, along with the appropriate constants noted above, resulted in the relationship shown graphically in Figure 5.2.2-8 with values for $T_{g\infty}$ (172°C) and A ($5.5 \times 10^5 \text{ g K/mol}$). These numbers are identical to those calculated based on the number average molecular weight. It

should be noted that this model, while slightly more sophisticated, seems to provide a better representation of the data as evidenced by the value of the statistical $r = 0.95$ which is slightly higher than those achieved by the aforementioned models.

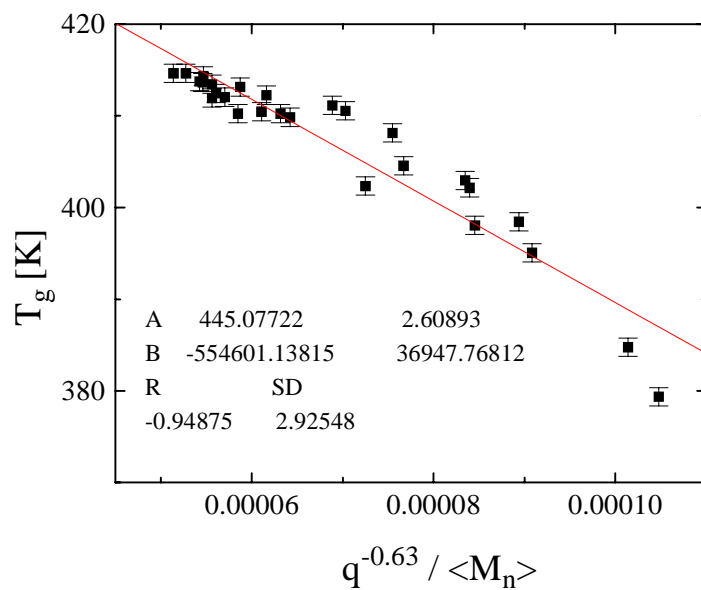


Figure 5.2.2-7 Dobkowski's model, utilizing number average molecular weight, applied to DSC data from PC(Lab).

⁵ Dobkowski, Z., *Eur. Polym. J.*, **17**, 1131, 1981.

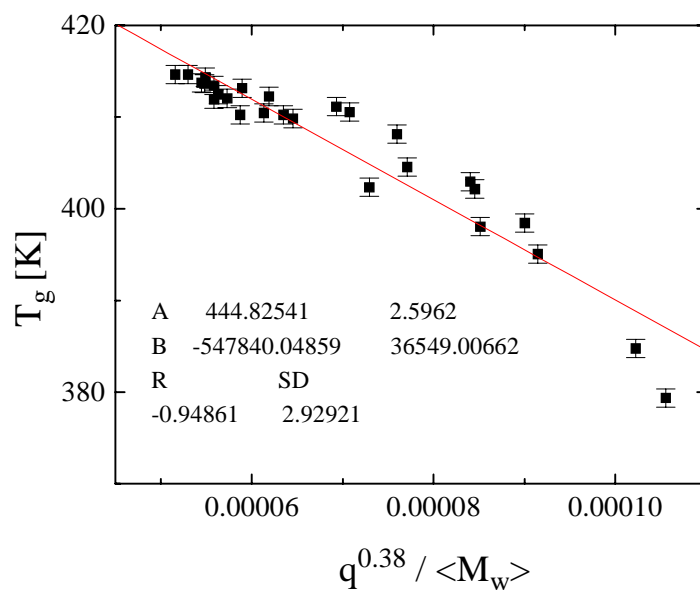


Figure 5.2.2-8 Dobkowski's model, utilizing weight average molecular weight, applied to DSC data from PC(Lab).

One further modification to Flory's original model was made by Bicerano⁶, who added another constant:

$$T_g = T_{g\infty} - \frac{K'}{(K'' + M_n)} \quad \text{Equation 5.2.2-7}$$

Application of this expression to the data of this study yielded the relationship seen in Figure 5.2.2-9 with $T_{g\infty} = 148^\circ\text{C}$, $K' = 7.9 \times 10^4 \text{ g K/mol}$, and $K'' = 3.8 \times 10^3 \text{ g/mol}$. This model seems to follow the trend of the data quite well. However, with an additional adjustable constant a better fit would certainly be expected and any physical meaning of the constants is now uncertain. This is highlighted by the fact that $T_{g\infty}$ value obtained by this method which is lower than some measured T_g values for polycarbonate which is clearly a nonphysical interpretation of the parameter.

⁶ Bicerano, J., *Prediction of Polymer Properties*, 2nd ed., Marcel Dekker, NY, 1996.

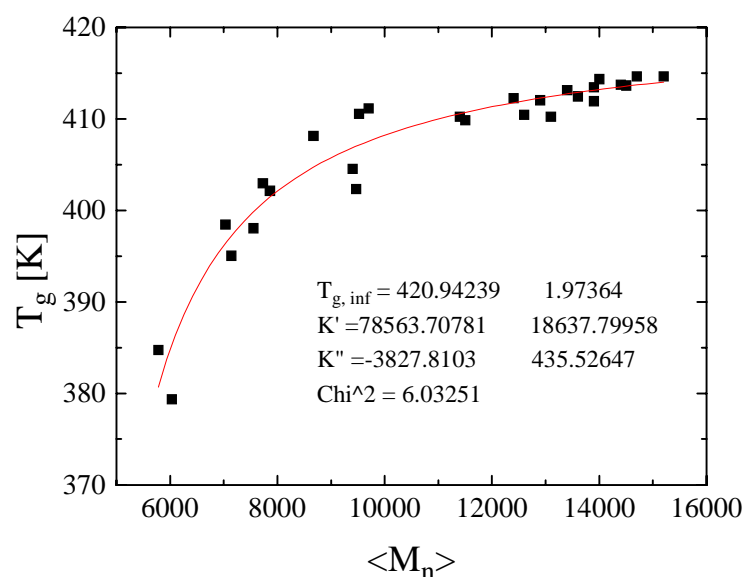


Figure 5.2.2-9 Bicerano's model applied to the DSC data for PC(Lab).

In summary, it has been shown that there is a direct linear relationship between τ and T_g . From the preceding examples, it is also clear that several different models can be utilized to relate the glass transition temperature to the molecular weight of a given sample. These expressions predict T_g *a priori* from knowledge of the environmental history of the sample and its original properties, as described by the methodology of this thesis.

5.3. Mechanical Testing

5.3.1. Stress-Strain Measurements

Mechanical properties are also important engineering parameters which exhibit marked dependence on molecular weight. In order to study how this feature of the PC polymer changes with environmental exposure, tensile tests were performed with an Instron 1123 on miniature dogbone samples cut using a die (ASTM D3368). Stress-strain tests were run on specimens from several of the thermally degraded materials at crosshead speed of 1 mm/min. Samples of PC(Lex) analyzed in this manner demonstrated significant yielding associated with the characteristic toughness of PC. However, it should be noted that PC(Lab) did not evidence this feature to the same

extent, most likely due to the fact that PC(Lab) has a lower molecular weight than PC(Lex). The critical entanglement molecular weight for PC has been reported to be approximately 4800 g/mol⁷. The number average molecular weight for PC(Lab) was found, by GPC, to be around 15,000 g/mol, while that for PC(Lex) was around 20,000 g/mol. PC(Lab) being closer to the entanglement value would thus be expected to exhibit poorer mechanical values. Raw stress-strain data can be seen in Figure 5.3.1-1 for PC(Lex) and PC(Lab), as well as for samples with two levels of thermal degradation, illustrating the change in mechanical response with environmental exposure.

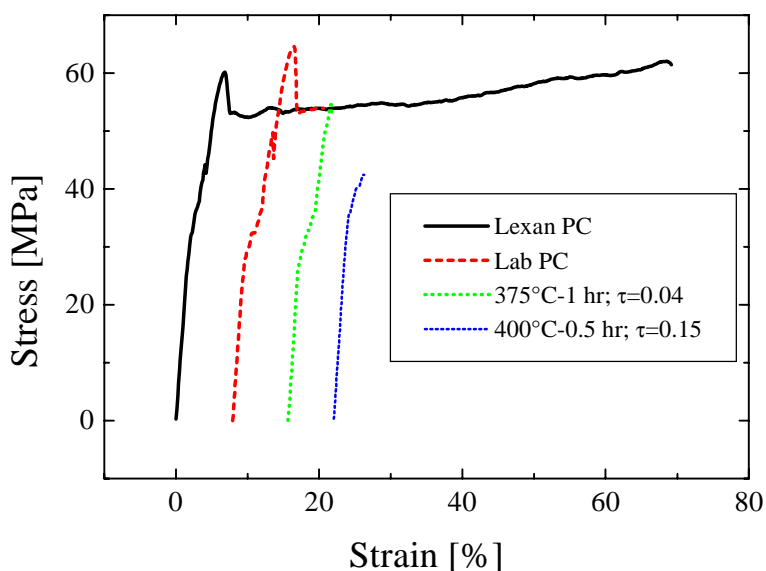


Figure 5.3.1-1 Comparison of stress-strain results for the PC samples indicated. Curves are displaced from 0% strain for clarity.

From the stress-strain curves of the present study, three separate quantities were extracted. The modulus was calculated from the initial slope of the curve, and the peak value of the curve was taken as the tensile strength. The area under the curve is proportional to the strain energy absorption of the sample per unit volume and provides a measure of the toughness of the polymer. These three quantities were calculated for each sample and are summarized in Table 5.3.1-1. It should be noted that whenever ultimate

⁷ Wool, Richard P., *Polymer Interfaces: Structure and Strength*, Hanser, Munich, 1995.

mechanical properties are measured it is expected that scatter will be present. This is due to the fact that, when materials are tested to failure as with ultimate properties, any flaws in the sample act as stress concentrators and produce misleading results. Since flaws are generally not uniformly distributed among samples, a range of results is seen. The relatively high amount of scatter seen in the data of this study is likely due to the fact that the samples were rather close to entanglement values and thus exhibited brittle behavior, which tends to increase observed error. In addition, with thin films, any small (i.e., not visible to the naked eye) flaw in the sample represents a greater relative volume than would be the case for a thicker sample. Thus, the results of microscopic flaws were magnified and contributed to increased scatter of the data.

Figure 5.3.1-2 presents the relationship between tensile strength and the degree of degradation, τ , for PC(Lab) samples tested. No testing could be performed for samples with higher degradation levels since the specimens were so brittle that dogbones could not be cut. For the samples that could be tested, the strength showed a marked decrease with increasing τ in a roughly linear fashion, as seen by the line in the graph, and resulted in the expression

$$TS = 54.5 - 197.1\tau \quad \text{Equation 5.3.1-1}$$

Although this relationship does not fully represent the physical situation, it seems to capture the overall trend and suggests a connection between τ and tensile strength which would facilitate prediction based only on knowledge of the thermal history.

Just as for the tensile strength data, a relationship between modulus and the thermal history is desired. As seen in Figure 5.3.1-3 the data, within the error of the experiment, showed essentially no change indicating that modulus is essentially independent of τ . Such a trend is not unexpected since modulus is not strongly dependent on the molecular weight of the sample when well below the T_g . Finally, Figure 5.3.1-4 shows the analogous graph for toughness where it is observed that a near-instantaneous drop is seen for even the lowest degree of degradation with subsequent values being equivalent.

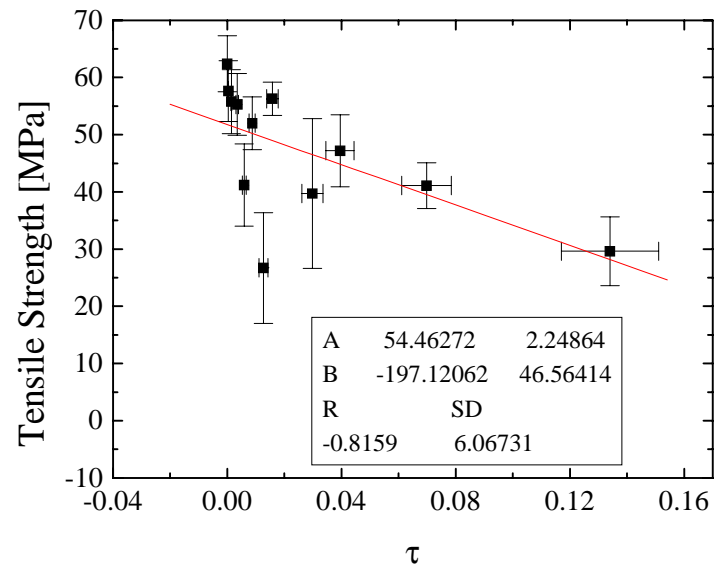


Figure 5.3.1-2 Effect of thermal history on tensile strength for PC(Lab).

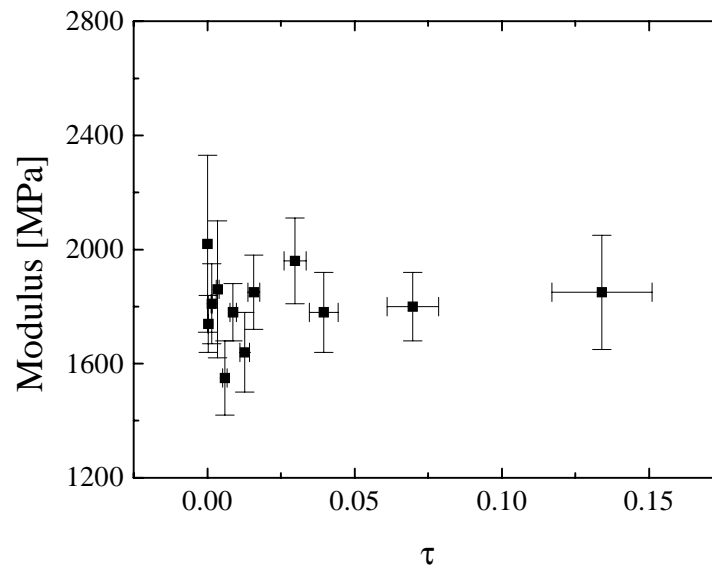


Figure 5.3.1-3 Effect of thermal history on modulus for PC(Lab).

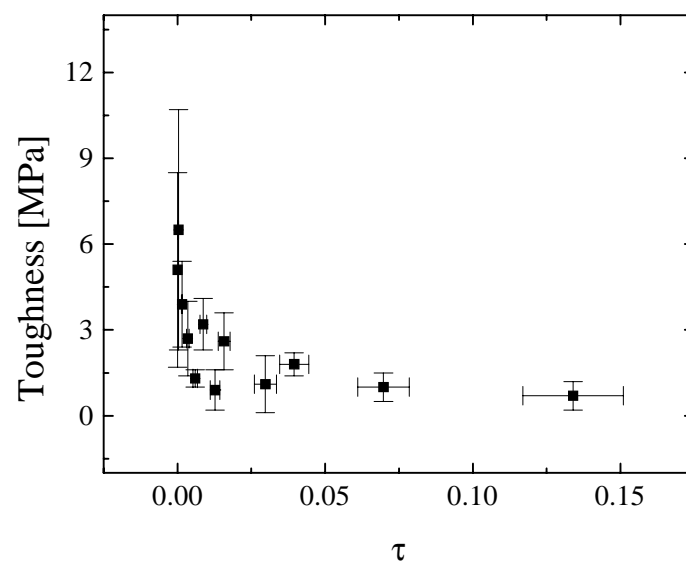


Figure 5.3.1-4 Effect of thermal history on toughness for PC(Lab).

Table 5.3.1-1

Summary of Mechanical Results

Material	TS [MPa]	Modulus [MPa]	Toughness [MPa]
PC(Lex)	61.1 (2.7)	1800 (150)	35.2 (9.1)
PC(Lab)	62.4 (4.9)	2020 (310)	5.1 (3.4)
325°C-0.5 hr	57.6 (5.3)	1740 (100)	6.5 (4.2)
-1 hr	55.8 (5.6)	1810 (140)	3.9 (1.5)
-3 hr	41.2 (7.2)	1550 (130)	1.3 (0.3)
-6 hr	26.7 (9.7)	1640 (140)	0.9 (0.7)
350°C-0.5 hr	55.3 (5.4)	1860 (240)	2.7 (1.3)
-1 hr	52.0 (4.6)	1780 (100)	3.2 (1.0)
-3 hr	39.7 (13.1)	1960 (150)	1.1 (1.0)
375°C-0.5 hr	56.3 (2.9)	1850 (130)	2.6 (1.0)
-1 hr	47.2 (6.3)	1780 (140)	1.8 (0.4)
-3 hr	29.6 (6.0)	1850 (200)	0.7 (0.5)
400°C-0.5 hr	41.1 (4.0)	1800 (120)	1.0 (0.5)

5.3.2. Tensile Strength Predictions

As illustrated in Figure 5.3.1-2 for the present study, tensile strength is a strong function of molecular weight for polymers. In order to more accurately model this relationship, structure-property expressions have been developed, analogous to those previously discussed for glass transition temperature, correlating these two properties. The most basic, as seen in the previous section, is that proposed by Flory¹ where tensile strength is inversely related to molecular weight (see Equation 5.2.2-3). Application of this model to the data of the present study, shown in Figure 5.3.2-1, seemed to encompass the majority of the data within the experimental error of the mechanical tests and yielded $TS_{\infty} = 186.0$ MPa and $K = 1.89 \times 10^6$ g MPa/mol. In Chapter 4 a correlation between molecular weight and environmental history was developed which, in conjunction with

the relationship between tensile strength and molecular weight just established, allows prediction of TS based only on knowledge of τ .

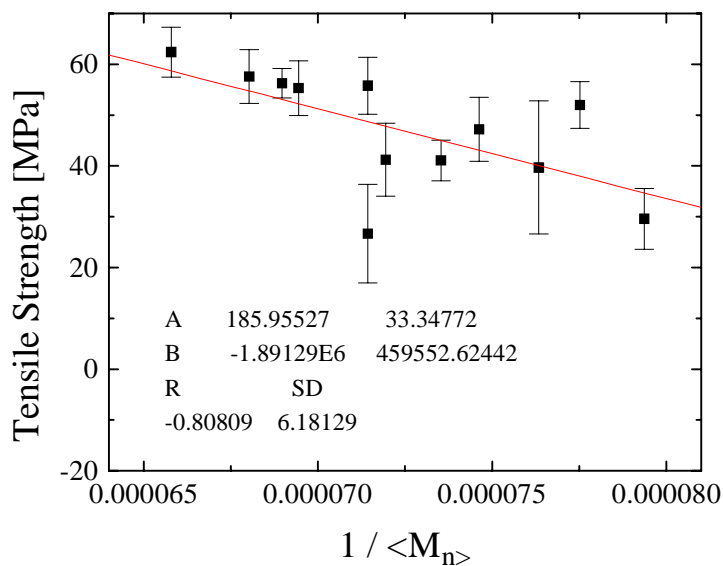


Figure 5.3.2-1 Flory's model (Equation 5.2.2-3) applied to tensile strength data for PC(Lab).

As demonstrated in Section 5.2.2, slight modifications of Flory's expression lead to minor variations in the representations of the data being modeled. Ogawa's³ relationship, which utilizes both weight average and number average molecular weights, resulted in a somewhat more accurate description of the data as seen in Figure 5.3.2-2. This model resulted in $TS_{\infty} = 215.2$ MPa and $K = 2.82 \times 10^6$ g MPa/mol.

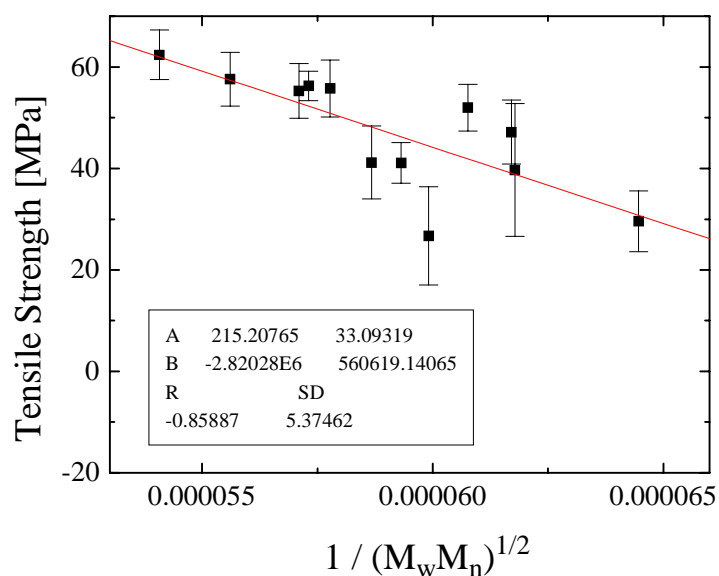


Figure 5.3.2-2 Ogawa's model applied to tensile strength data for PC(Lab).

As also discussed earlier, a further refinement of Flory's basic relationship was proposed by Dobkowski⁵ (Equation 5.2.2-6) who included terms to incorporate the effects of polydispersity in the system. This equation also allows for the use of either the number average or weight average molecular weight. Applying Dobkowski's model to the PC(Lab) data of this study produces the graphs shown in Figure 5.3.2-3 and Figure 5.3.2-4, respectively. Based on the constants calculated from this model, it is clear that utilization of either molecular weight yielded nearly identical results, with a slightly more accurate description of the data than those obtained from Flory's or Ogawa's models. Application of Dobkowski's relationships resulted in $TS_{\infty} = 219.9$ MPa and $K = 3.06 \times 10^6$ g MPa/mol using number average molecular weight and $TS_{\infty} = 219.6$ MPa and $K = 3.04 \times 10^6$ g MPa/mol from weight average molecular weight.

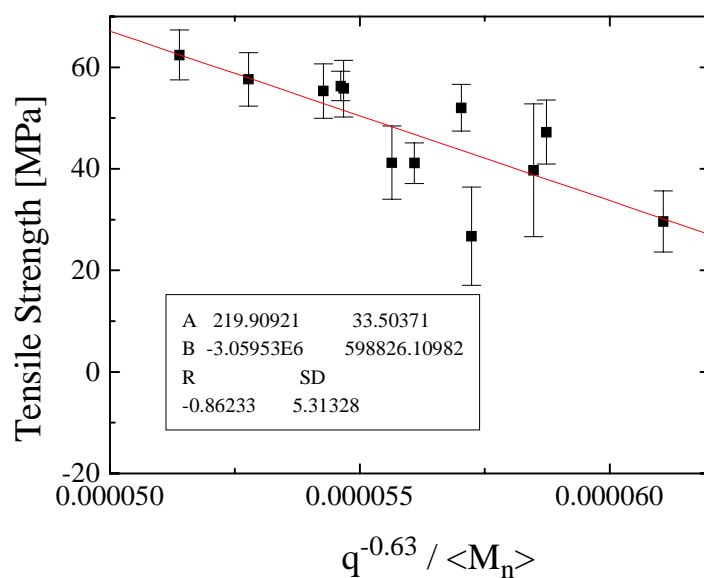


Figure 5.3.2-3 Dobkowski's model, utilizing number average molecular weight, applied to tensile strength data for PC(Lab).

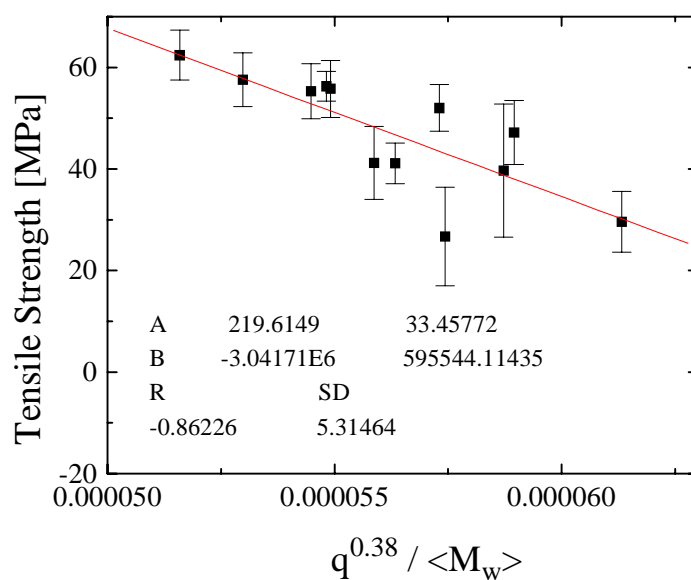


Figure 5.3.2-4 Dobkowski's method, utilizing weight average molecular weight, applied to tensile strength data for PC(Lab).

From the aforementioned examples, it is clear that a relationship between the tensile strength and environmental history, τ , can be quantified. Just as in the case of the

glass transition temperature, several researchers have sought to develop more accurate structure-property expressions to model tensile strength-molecular weight behavior. Based on the results from application of the models discussed in this section, it appears that the data is best described by Dobkowski's model which relates TS to \overline{M}_w or \overline{M}_n . This structure-property relationships seem to better predict the behavior of the tensile strength as a function of molecular weight than does a direct correlation between TS and τ . The correlation between molecular weight and τ has already been described in Chapter 4 and can be combined with Dobkowski's model to directly relate TS to τ . None of the models discussed exactly predict the TS-molecular weight behavior, but they do seem to capture the basic trends quite well, affirming that tensile strength can be calculated based solely on thermal history.

5.4. Rheology

5.4.1. Viscosity Measurements

In terms of processing, one of the most important features of a polymer is its rheological behavior. Recalling that

$$\eta^* \propto \overline{M}_w^{3.4} \quad \text{Equation 5.4.1-1}$$

it is apparent that slight variations in the molecular weight are translated into more dramatic changes in the flow behavior. This can, in turn, drastically affect the characteristics of any part subsequently manufactured from that material. Therefore, prediction of the melt viscosity as a function of environmental history can help alleviate processing problems posed by these viscosity changes. Since both melt processing and recycling of scrap involve higher temperature histories for PC, the rheology data are of special interest for this thesis.

In the present study, frequency sweeps in a parallel plate mode were carried out on samples of each of the degraded materials as well as both undegraded PC(Lab) and PC(Lex) in a TA Instruments AR1000 rheometer equipped with an ETC (environmental test chamber) in a nitrogen environment. Frequencies ranged from 1 to 100 rad/s with a 2% strain, and temperature steps were taken every 10°C from approximately 60°C to

110°C above T_g (closer steps were taken for the PC(Lab), undegraded material). Samples, which were stored in a dessicator prior to testing to prevent moisture absorption, consisted of stacked pieces cut or broken from the compression molded films, or small fragments of these films when brittleness precluded cutting. In either case, the test gap between the parallel plates was kept constant at 500 μm . Enough extra sample was inserted to ensure that, once the desired gap was reached, the sample was consolidated and did not contain any air bubbles. Excess material was then simply scraped off the edges of the plates.

After the frequency sweeps were performed, it was noted that the raw data exhibited a slight upward “tail” where there is an increase in complex viscosity at the lower frequencies. This can be seen in the master curve of Figure 5.4.1-1 for PC(Lab). Since it is well-known that polymeric materials in general, and polycarbonate specifically, show a horizontal plateau in this region, this behavior seemed curious. Upon consultation with technical experts at TA Instruments, it was found that this phenomenon was an artifact of the instrumentation caused by the thermal expansion of the plates when the temperature was ramped. This expansion created more force on the sample which in turn caused an apparent increase in the viscosity. Since it was determined that this effect did not truly represent the characteristics of the polymer, the data were simply shifted downward so that a zero-shear-plateau region was evident. It was felt that such a curve more closely resembled the true behavior of the polycarbonate.

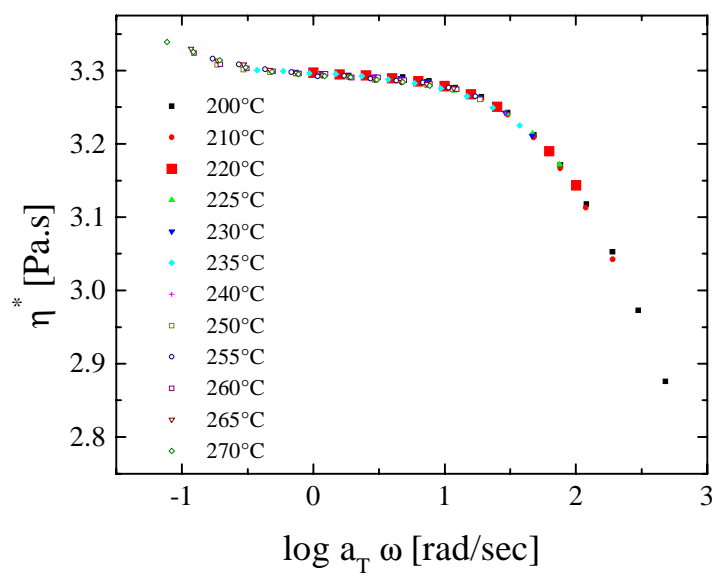


Figure 5.4.1-1 Master curve for PC(Lab) showing increase in η^* at low frequencies. This sample has $\tau = 0$ (no degradation).

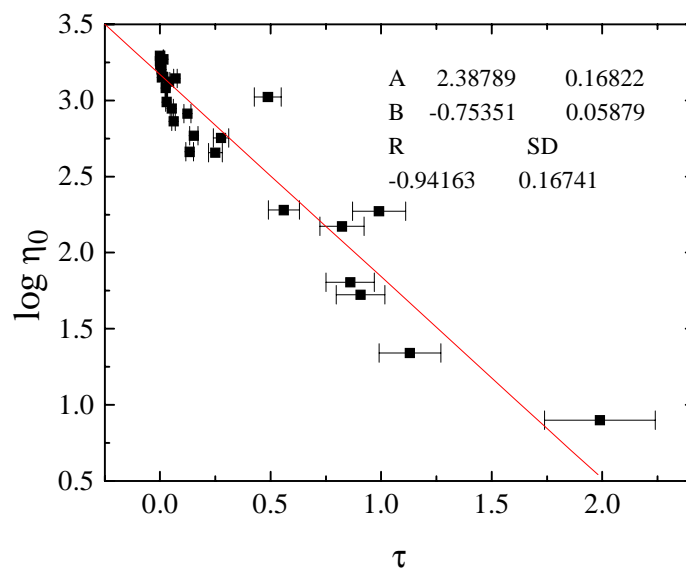


Figure 5.4.1-2 Effect of thermal history on zero shear rate viscosity for PC(Lab).

From the step isothermal frequency sweeps, master curves and the associated shift factor plots were prepared for each sample at a reference temperature of 220°C. Since

viscosity exhibits a marked temperature dependence, vertical shifting, in addition to the usual horizontal shifting, is expected and necessary in this case.⁸ Typically, this vertical shifting is described by scaling the zero shear rate viscosity for a particular temperature by the η_0 for the reference temperature. The resultant data for PC(Lab) degraded at various temperatures are shown in Figure 5.4.1-3-Figure 5.4.1-5 (325°C), Figure 5.4.1-6-Figure 5.4.1-8 (350°C), Figure 5.4.1-9-Figure 5.4.1-11 (375°C), and Figure 5.4.1-12-Figure 5.4.1-14 (400°C). These figures illustrate that all shift factors from a single isotherm agreed rather well. The shift factor plots can be represented by smooth functions without discontinuities, supporting the superposition methodology. Furthermore, when either the horizontal or vertical shift factors for all the samples were combined in the same graph, one notes that they are consistent, as can be seen in Figure 5.4.1-15 and Figure 5.4.1-16. For either the vertical or horizontal shift factors, the line resulting from superposition of all the PC(Lab) samples can be modeled with a simple polynomial:

$$\log a_T = A_1(T - T_{\text{ref}}) + A_2(T - T_{\text{ref}})^2 \quad \text{Equation 5.4.1-2}$$

and values for the constants, A_1 and A_2 , were obtained. For the horizontal shift, A_1 was found to be -0.02 ± 0.0004 and A_2 was $1.6 \times 10^{-4} \pm 1 \times 10^{-5}$. The same expression can be applied to the vertical shift factors, yielding $A_1 = -0.03 \pm 0.0002$ and $A_2 = 1 \times 10^{-4} \pm 5.8 \times 10^{-6}$, and has therefore been utilized in this study. Prediction of the shift factor would be a simple exercise achieved by utilizing the polynomial equation along with the constants just obtained.

The viscosity plateau region at low frequency in polymers corresponds to the zero shear rate viscosity, η_0 , of the material⁸. The relationship of $\log \eta_0$ to τ , the degree of degradation, for PC(Lab), appears to be roughly linear, as illustrated in Figure 5.4.1-2. This correlation,

$$\tau = 2.4 - 0.75 \log \eta_0 \quad \text{Equation 5.4.1-3}$$

allows prediction of η_0 based solely on knowledge of τ .

⁸ Bird, R. B., R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, v.1, Wiley, NY, 1987.

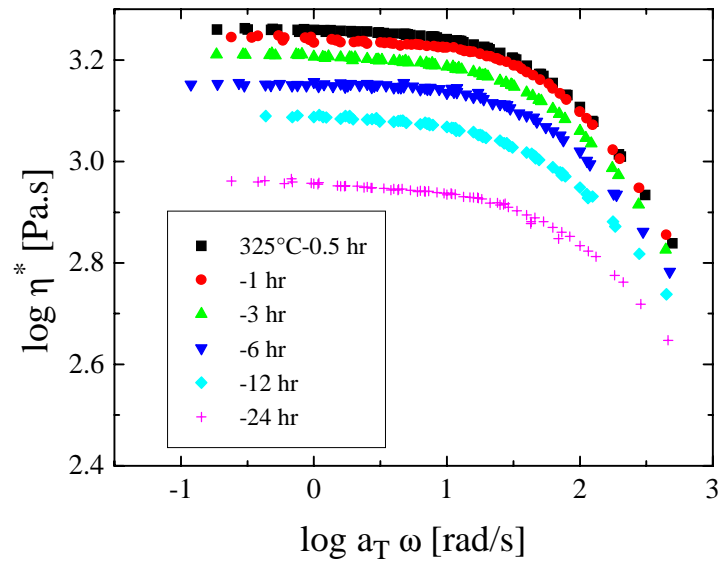


Figure 5.4.1-3 Master curves for PC(Lab) degraded at 325°C.

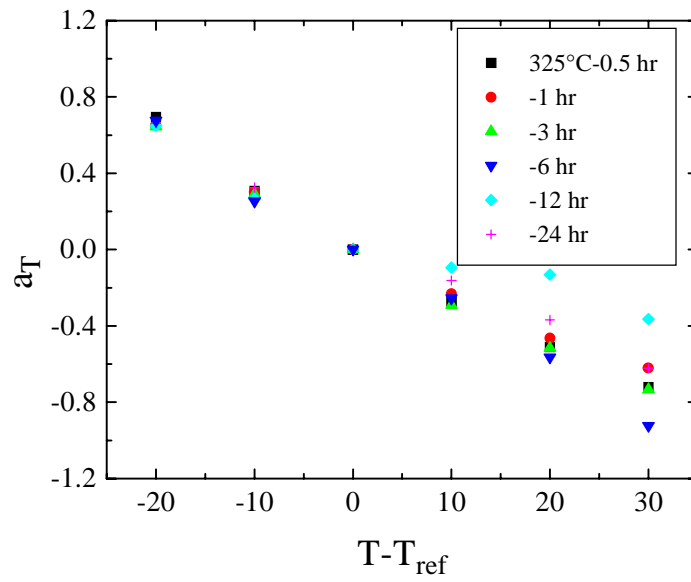


Figure 5.4.1-4 Horizontal shift factors for PC(Lab) degraded at 325°C.

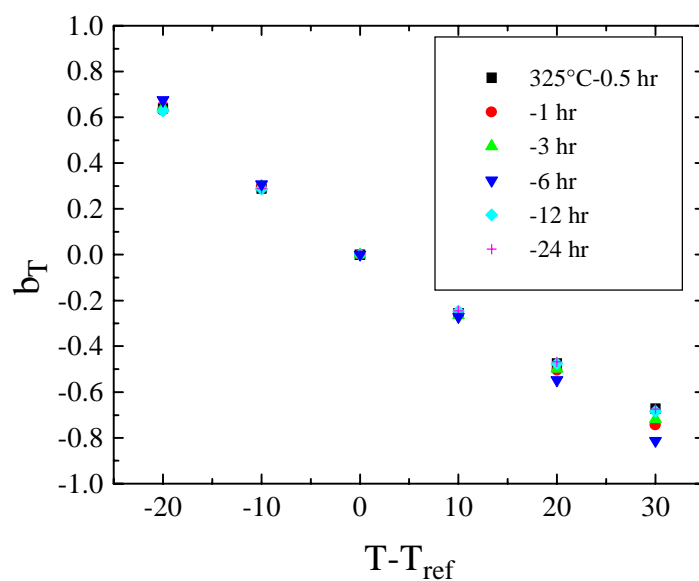


Figure 5.4.1-5 Vertical shift factors for PC(Lab) degraded at 325°C.

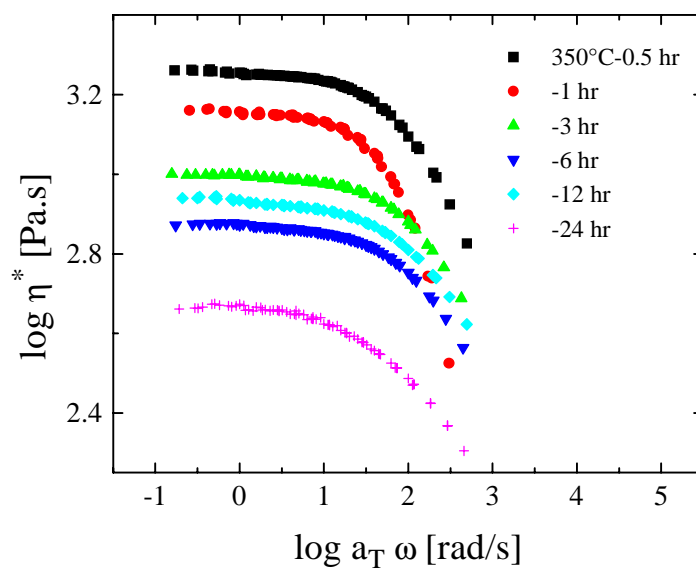


Figure 5.4.1-6 Master curves for PC(Lab) degraded at 350°C.

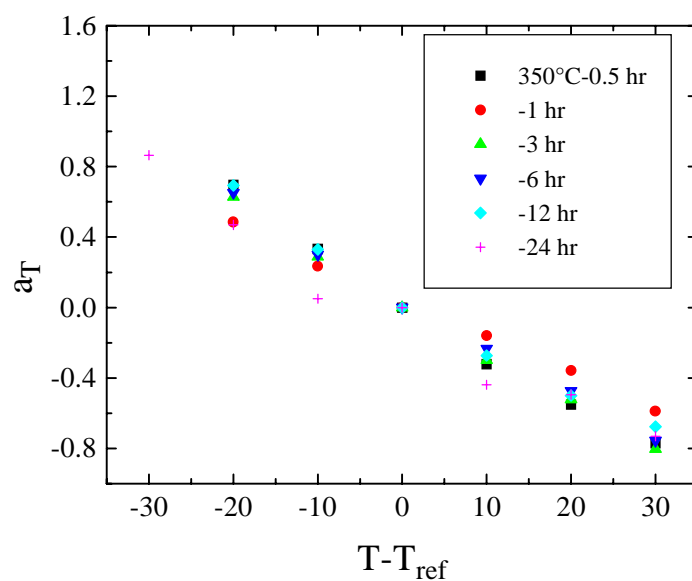


Figure 5.4.1-7 Horizontal shift factors for PC(Lab) degraded at 350°C.

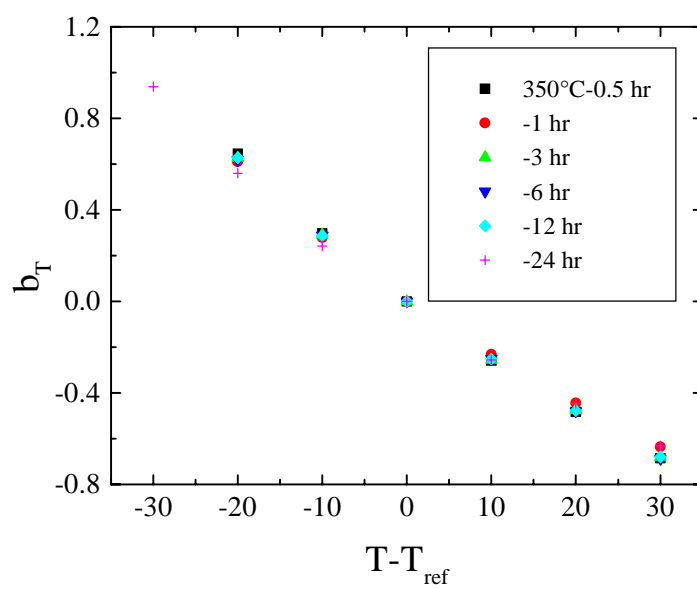


Figure 5.4.1-8 Vertical shift factors for PC(Lab) degraded at 350°C.

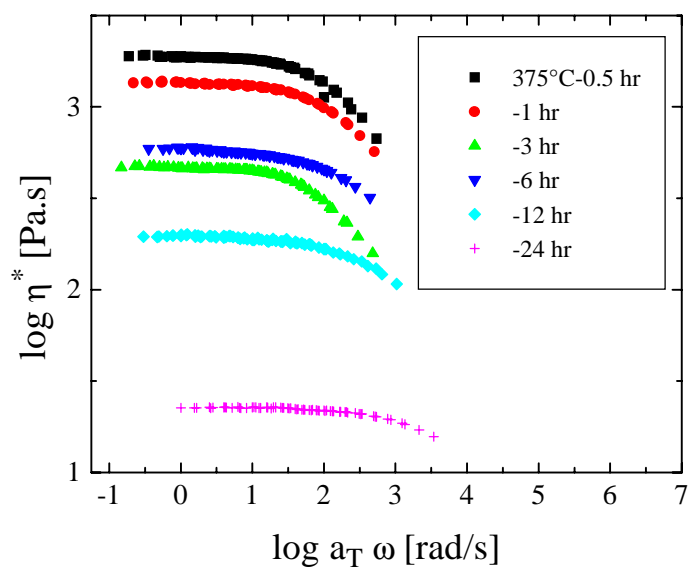


Figure 5.4.1-9 Master curves for PC(Lab) degraded at 375°C.

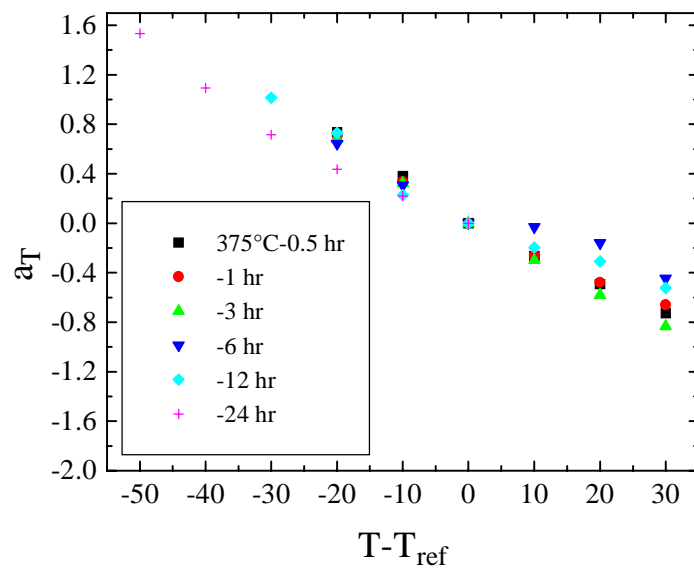


Figure 5.4.1-10 Horizontal shift factors for PC(Lab) degraded at 375°C.

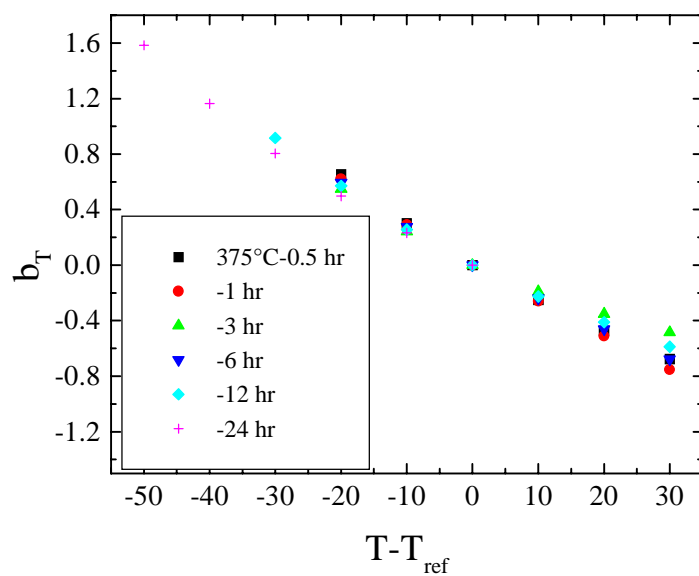


Figure 5.4.1-11 Vertical shift factors for PC(Lab) degraded at 375°C.

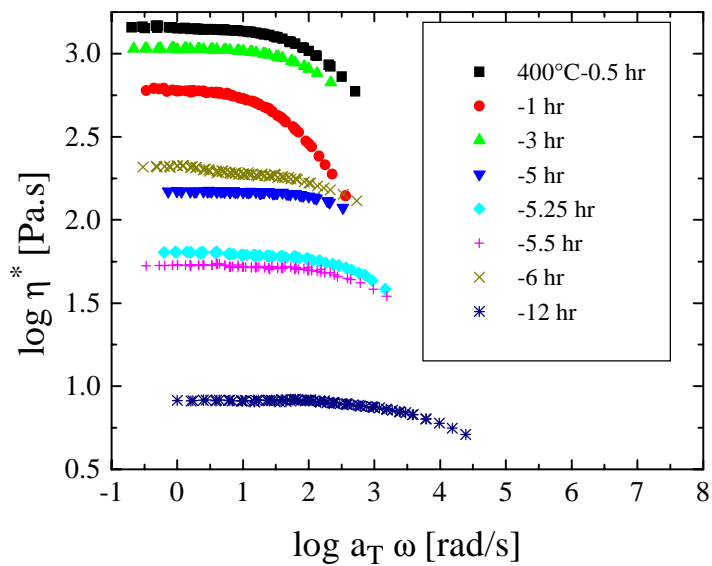


Figure 5.4.1-12 Master curves for PC(Lab) degraded at 400°C.

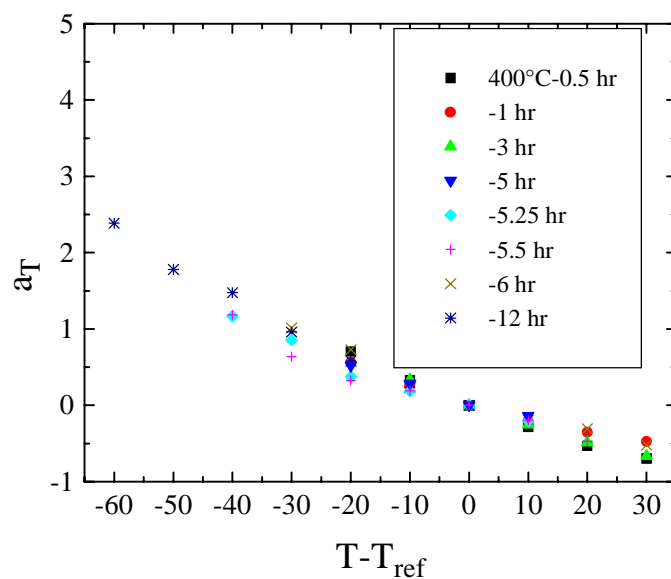


Figure 5.4.1-13 Horizontal shift factors for PC(Lab) degraded at 400°C.

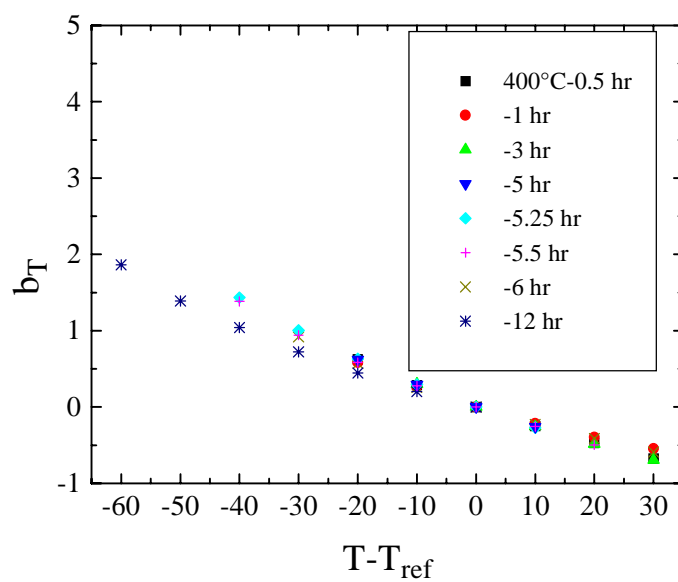


Figure 5.4.1-14 Vertical shift factors for PC(Lab) degraded at 400°C.

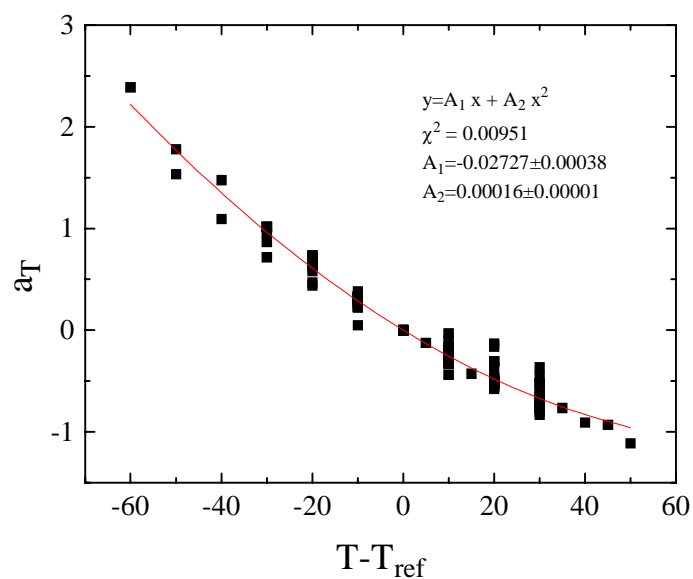


Figure 5.4.1-15 Horizontal shift factors from all PC(Lab) samples modeled by the WLF expression.

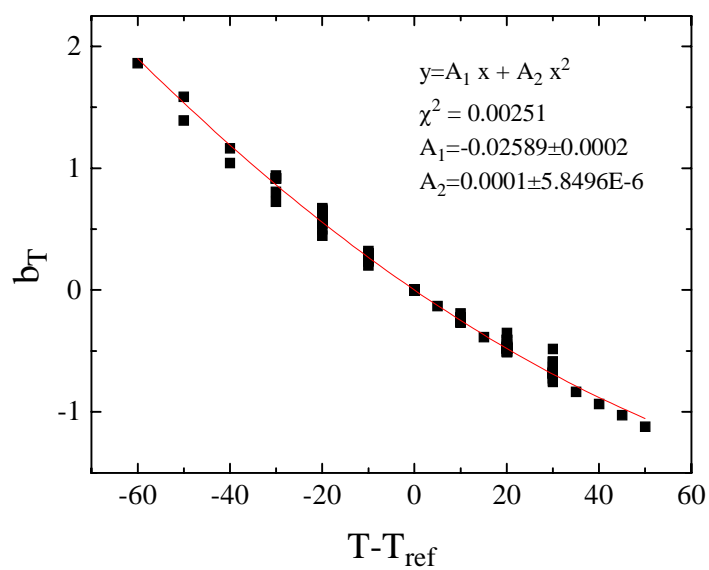


Figure 5.4.1-16 Vertical shift factors from all PC(Lab) samples modeled by the WLF expression.

5.4.2. Viscosity Predictions

In an effort to facilitate prediction of polycarbonate melt viscosity, Jordan and Richards⁹ developed a model which yielded the following equations:

$$\eta(\dot{\gamma}) = \left[\frac{1.5\rho T\lambda}{1 + (\lambda\dot{\gamma})^{0.8}} \right] \quad \text{Equation 5.4.2-1}$$

where

$$\rho = \frac{10^3}{\exp(-0.307 + 1.86 \times 10^{-5} T^{3/2})} \quad \text{Equation 5.4.2-2}$$

Using the Cox-Merz rule, the shear rate, $\dot{\gamma}$ can be related to the frequency, ω , allowing direct application of this model to the data for each of the degraded PC samples of the present study, as well as the undegraded materials. This will yield values for a characteristic relaxation time, λ for each sample. The Jordan-Richards model applied to one such sample is seen in Figure 5.4.2-1. While the agreement is not as precise as could be desired, it should be noted that Jordan and Richards were fitting Equation 5.4.2-1 to a single isotherm, whereas in this study an entire master curve is being described. The increased breadth of the data of this study compared to that of the study which established Equation 5.4.2-1 contributes to the lack of agreement. The relationship between the relaxation times calculated from the model and the thermal history, τ , as in Figure 5.4.2-2, can be described by an exponential function:

$$\lambda = 2.02 \times 10^{-3} e^{\tau/0.21} \quad \text{Equation 5.4.2-3}$$

Equation 5.4.2-3 allows calculation of λ based on knowledge of τ , the thermal history. The characteristic relaxation time, λ , in conjunction with the model just discussed, allows prediction of the viscosity curve for PC.

⁹ 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.

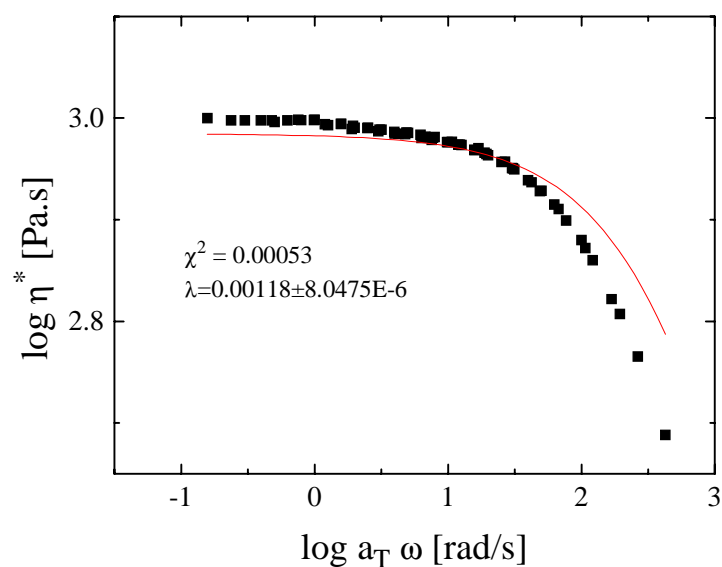


Figure 5.4.2-1 Richards and Jordan's model applied to PC(Lab) degraded at 350°C, 3 hr.

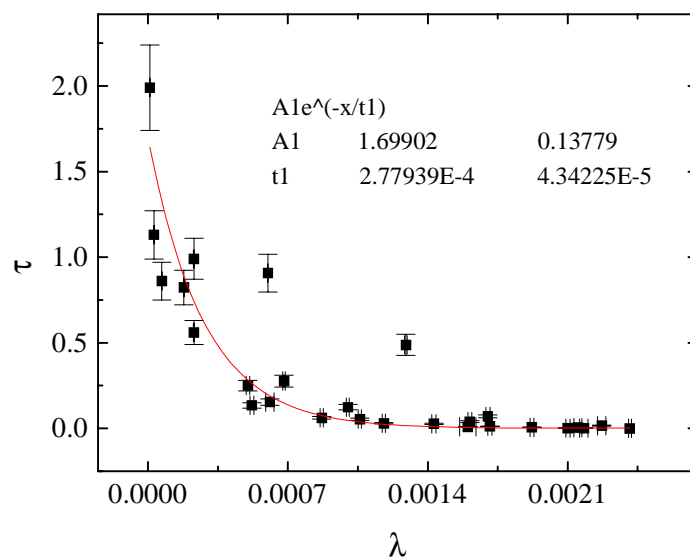


Figure 5.4.2-2 Relationship between relaxation times and degree of degradation for PC(Lab) samples.

While the Jordan and Richards' model provides an adequate description of the PC rheological data of the present study, deviations from the data were apparent. Therefore, another method of predicting the viscosity-shear rate behavior as a function of thermal

history was necessary. To that end, a doubly-reduced or “overall” master curve, composed of master curves prepared for samples which had undergone various levels of degradation, was developed.

Master curves for selected isotherms, with τ ranging from 0 (undegraded PC(Lab)) to 2 (400°C, 12 hr) are shown in Figure 5.4.2-3. Next, these curves were simply shifted, just like any isotherm, such that a new, overall master curve, Figure 5.4.2-4, was formed. The validity of this technique was confirmed when the shift factor plots, Figure 5.4.2-5 and Figure 5.4.2-6 were examined. The trends of these plots appear quite regular with no discontinuities which would indicate that the superpositions were invalid. Furthermore, both the vertical and horizontal shifts can be described quite well by a polynomial expression in the form

$$\log a_T \text{ or } \log b_T = A_1\tau + A_2\tau^2 \quad \text{Equation 5.4.2-4}$$

Equation 5.4.2-4 allows calculation of a shift factor based only on knowledge of τ . It is then a simple matter to shift the overall master curve accordingly. Because of the significant errors associated with the constants A_1 and A_2 obtained from the present data, caution should be taken when applying the shifting. Repeating these tests in order to lessen this error is recommended to more accurately predict any trends. Clearly, this methodology allows prediction of melt viscosities and entire flow curves for a polymer *a priori* based solely on knowledge of environmental history.

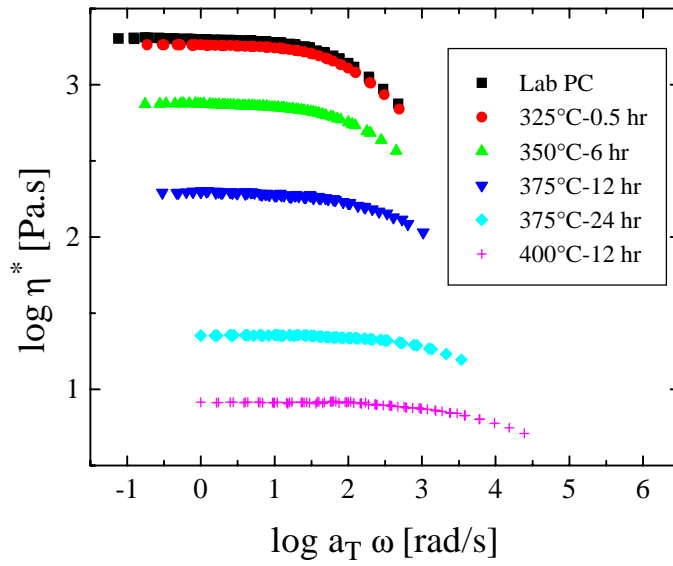


Figure 5.4.2-3 Master curves for the indicated samples of PC(Lab).

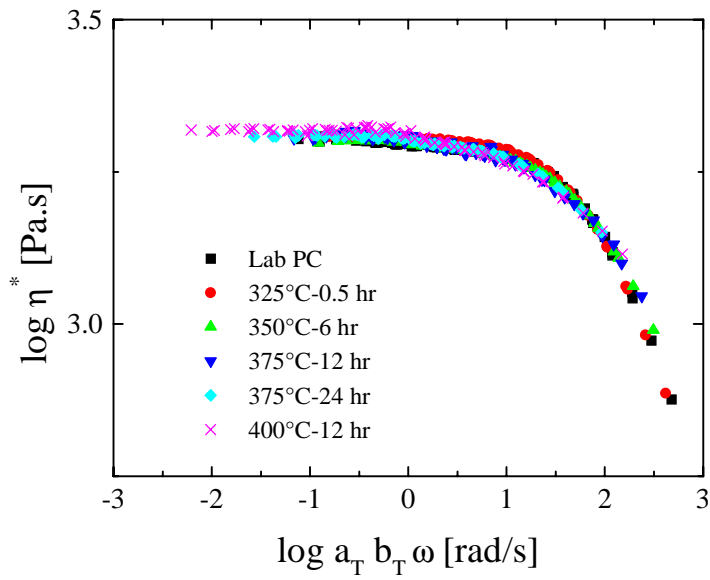


Figure 5.4.2-4 Overall master curve for PC(Lab).

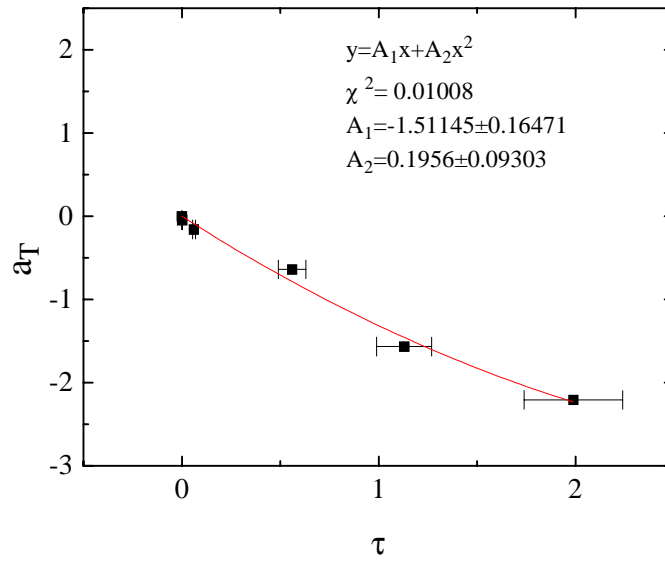


Figure 5.4.2-5 Horizontal shift factors, modeled by the WLF equation, for the overall master curve.

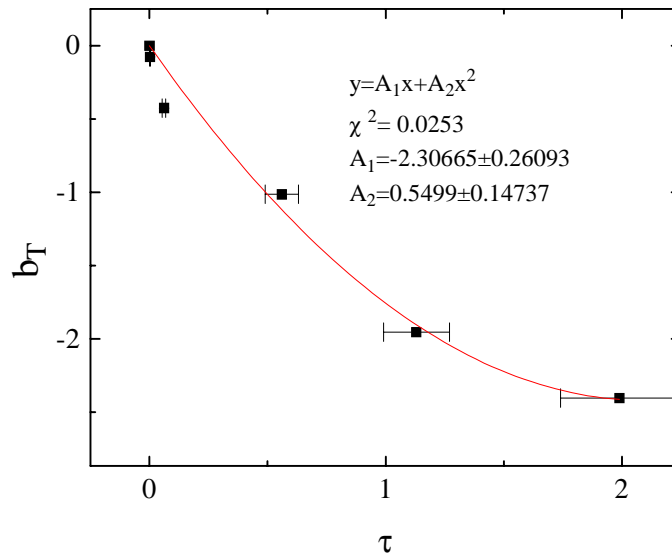


Figure 5.4.2-6 Vertical shift factors, modeled by the WLF equation, for the overall master curve.

5.5. Summary

From the preceding examples, it is clear that knowledge of the environmental history, τ , can be utilized to predict many engineering properties of a polymer, such as tensile strength, T_g , and melt viscosity. This tool bridges the gap between the fundamental changes associated with environmental exposure, such as variations in molecular weight, and the resultant property changes, the understanding of which are crucial to any application of the material. Thus, a methodology has effectively been established to elucidate engineering properties solely from a material's environmental history and its original properties.