

Physical Aging and Characterization of Engineering
Thermoplastics and Thermoplastic Modified Epoxies

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Dissertation Submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Chemistry

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May, 1998

Blacksburg, Virginia

Keywords: Polymers, Dilute Solution, Physical Aging, Relaxation Time Distributions

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(ABSTRACT)

In this work the relationship between physical properties, such as physical aging and relaxation time distributions, and chemical structure for a variety of polymeric systems were investigated. Although there is a vast amount of physical aging data for polymers, most of these studies do not attempt to correlate structure with physical aging. Therefore, a set of engineering thermoplastics was examined with the goal of relating certain of their characteristic molecular dimensions to their mechanical and volumetric physical aging attributes.

Another series of polymeric materials, based on a poly(ether sulfone) backbone, and having various endgroups differing in size, was also studied to determine physical aging rates and relaxation time distributions. Furthermore, it was concluded that the density of the poly(ether sulfones) increased while the glass transition temperature decreased as the endgroup became smaller.

Thermoplastic toughened epoxies were also examined to clarify the importance of covalent bonds between toughener and epoxy on physical aging, relaxation time distributions and fracture toughness. In these studies the covalently bonded tougheners differed from their non-reactive counterparts in the rates of volumetric physical aging at high temperatures for the difunctional epoxy. The solvent resistance of the reactive thermoplastic toughened tetrafunctional epoxy was higher than the non-reactive thermoplastic toughened system. The tetrafunctional epoxies with the reactive toughener also had higher toughener glass transition temperatures.

DEDICATION

to

my parents, Dr. William Muggli and Imelda Muggli

wife, Roswitha Muggli

and children, Florian, Janika, Seppi and Peter

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Thomas C. Ward for his guidance, patience and support during my stay at Virginia Tech. His enthusiasm for teaching and understanding polymer science is very enjoyable and refreshing. Furthermore, his understanding of the development of a research scientist has been a large aid in my growth in this field.

I would also like to show my appreciation to my committee, Dr Garth L. Wilkes and Dr. Herve Marand, for teaching important aspects of polymer science that were critical in my work, Dr. Harold M. McNair for introducing me to the world of chromatography and Dr. Harold C. Dorn for his assistance about comprehending physical phenomena.

The members of the Polypkem group have always been eager to give me assistance in research and with my family. Those members before me, Drs. Saikat Joardar, Taigyoo Park, Mark Vrana, Dan Hahn and Mr. Anthony Williams taught me how to survive and prosper in lab. Drs. Ojin Kwon and Kermit Kwan, along with Dave Porter, Robert Jensen, Jianli Wang, Jennifer Robertson, Emmett O'Brien, Sandra Case and Amy Eichstadt were not only great colleagues, but excellent friends, who all have a wonderful spirit.

I would like to thank those who helped me and my family get started in Blacksburg, Mr. Felix Gandara, Dr. Darrell Iller and the Muchai family. Furthermore, I am pleased to have worked with many outside of my laboratory, such as Chris Robertson, Chitra Subramanian, Dr. Dan Riley, Jeff Mecham, Rachel Giunta and Dr. Watson Srinivas.

Charles Tchatchoua has been most generous with his time and energy in helping me with both research and home life. His eagerness to help under any conditions demonstrates the kindness of his heart. His wisdom and comments have blessed me and my family since the start of our stay in Blacksburg.

The CASS and NSF office secretarial staffs have been very warm and gracious in working with me. They are always in good spirits and offer good advice. The physics

and electronics shop at Virginia Tech have helped me in many situations and have also been a good source of encouragement and humor.

I am thankful for my mother who first taught me chemistry and my father for his love of learning. My children, Florian, Janika, Seppi and Peter have been very considerate even when I could not spend much time with them. Finally, but most importantly, I would like to thank Roswitha, mein Schatzi, for her patience and love for me.

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Chapter 1. INTRODUCTION

Amorphous materials, including polymers, inorganic and organic glasses and metallic glasses, all exhibit a phenomenon known as physical aging. Physical aging is a non-equilibrium process in amorphous materials where properties change as they reside in a state below their glass transition temperature (T_g). Decreases in volume, enthalpy and entropy occur during this process in the glassy state. There are many problems associated with physical aging in amorphous polymeric systems; namely, alterations in the mechanical properties and density. Changes in mechanical properties are mainly detrimental, such as loss of ductility and fracture energy. The volume relaxation that is present in glassy systems causes the density to increase, which may be problematic when structures are designed with small tolerances and no consideration for physical aging is made. One desirable consequence of this physical aging phenomenon is a higher modulus, this modest improvement; however, comes at a large expense.

The deterioration in glasses' properties due to physical aging has resulted in much research to gain some understanding about the kinetics of this process. The studies conducted have rendered much empirical information and predictive methods for structural relaxation in the glassy state. Still, there is much room for achieving more comprehension. One related area that has had fewer endeavors is the study of the effect of various chemistries of polymeric materials on physical aging. Parameters such as backbone rigidity, endgroup size or nature, cross-link density and morphological attributes for phase separated systems have been less emphasized even though some studies have shown that these can play a large role. The present study includes some of these topics.

A way of understanding the polymer physics of the glass transition and its subsequent effects on the properties of the polymer in the glassy state is by examining relaxation time distributions. In simple systems there is a single relaxation time, a Debye relaxation time. However, polymeric materials are not simple relaxing systems and show a dispersion of relaxation times. The features of this dispersion can be described through

a stretched exponential function, or Kohlrausch-Williams-Watts (KWW) equation. Using the KWW function to express the relaxation time distribution, the influence of the aforementioned polymer parameters on this distribution will be investigated.

The various systems analyzed in this work include polyimides, polysulfones with different structure and endgroups and toughened epoxies. The first model that will be discussed concerns how backbone rigidity may modify the physical aging and relaxation time distributions. Second, when endgroups vary in size, the density and glass transition temperature change for some engineering thermoplastics. Therefore, the nature of the endgroup can play a significant role in the behavior of some polymer systems and perhaps contribute to physical aging and relaxation time distributions. Finally, the toughening of thermosets is important for maximizing their fracture toughness properties. Despite the improvement in some mechanical characteristics there are often other effects that are less desirable, such as a decrease in the flexural strength, softening temperature and a change in the physical aging properties. These aspects are studied and incorporated in this work.

This work is aimed at understanding the physical properties of amorphous polymeric materials, including their physical aging rates, relaxation time distributions and mechanical behavior. The results and conclusions that will be gained from this work will hopefully aid in understanding the non-equilibrium characteristics of glassy polymer systems and their glass to liquid transition. This understanding can be implemented to assist in designing materials for future applications or solving present problem.

Chapter 2. PHYSICAL AGING

2.1. INTRODUCTION

Physical aging is the occurrence of a change of thermodynamic properties with time of the amorphous fraction in polymeric systems, when the material is in the glassy state, as seen in Figure 2.1. Above the glass transition temperature a state of equilibrium can be regained, as represented by the equilibrium line. Therefore, as long as no chemical reactions have occurred, the material can be rejuvenated if raised to

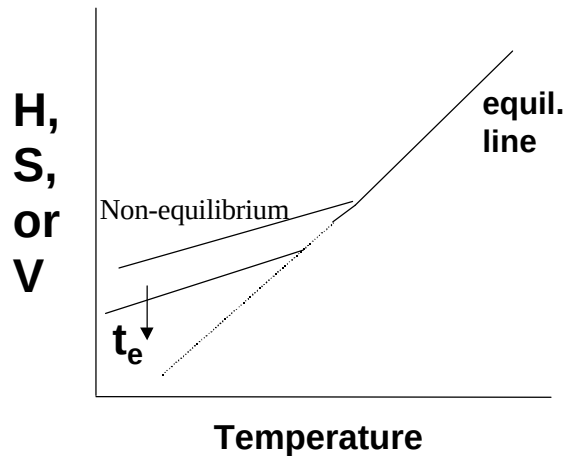


Figure 2.1. Physical aging plot with indication of enthalpy, entropy and volume changes with aging time (t_e)

temperatures higher than the T_g . This rejuvenation process is commonly used to deage the sample and show the reversibility of physical aging. The whole region from the glass transition temperature to lower temperatures is where physical aging may occur, but the rate of physical aging will vary. This region also corresponds to those temperatures where the materials studied in this work would be used in applications. Hence, the understanding of this process is paramount in assuring that materials do not unexpectedly fail. The physical aging literature large and hence only the aspects of physical aging pertinent to this study will be examined. Several thorough reviews of the literature on physical aging have served this interest area quite well.^{1,2,3} Nevertheless, three major areas of physical aging will be discussed because they support possible interpretations of

structure parameter effects on physical aging. These areas include transient mechanical experiments, such as creep recovery or stress relaxation. The other two areas are volume and enthalpy relaxation experiments. An emphasis on experimental results will underlie this examination of the literature.

2.2. CREEP RECOVERY AND STRESS RELAXATION

The majority of the transient mechanical experiments performed in the present work are creep recovery, therefore this area will be discussed more than stress relaxation. This standpoint is not to imply that creep tests are better, in fact, in many cases the results from both tests are similar from a physical aging rate perspective.

A creep recovery test involves the application of a constant stress to a sample. The strain, defined here as the change in length divided by the original length, is monitored as a function of time. A resultant quantity of interest is called the creep compliance:

$$D(t) = \frac{e(t)}{\sigma_0} \quad \text{Eq. 2.1}$$

where $D(t)$ is the creep compliance and σ_0 is the constant stress. The recovery part of the creep experiment takes place when the load is removed. In a low strain creep test there are two response regions, an instantaneous elastic and a time dependent viscoelastic response.^{4,5}

Physical aging creep tests as designed by Struik⁶ are similar to the above description of a creep test but with a few restrictions. These tests are performed mostly at a constant temperature. The sample is quenched from above the glass transition temperature to the starting temperature and equilibrated. After the equilibration step, aging time commences. After aging a period of time the initial creep test is run for the period of time denoted in Figure 2.2. Subsequently, the stress is removed from the sample, which then recovers to its pre-stressed state. The recovery time is sufficient to permit full relaxation of the structure to its original form; therefore, it is usually set at ten times the load time. This process assures that physical aging is not being reversed or altered by changing the constitutive parameters of the material under study. In regard to

this, the maximum strain level is usually kept below 0.2%, such that these creep tests are only slightly perturbing the system to probe the physical aging kinetics. After the initial creep – recovery cycle further creep – recovery cycles are implemented. With each subsequent creep test the creep and recovery time is tripled.

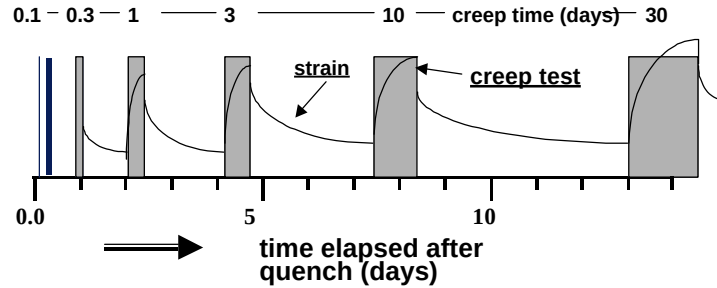


Figure 2.2. Load application for creep recovery test⁶

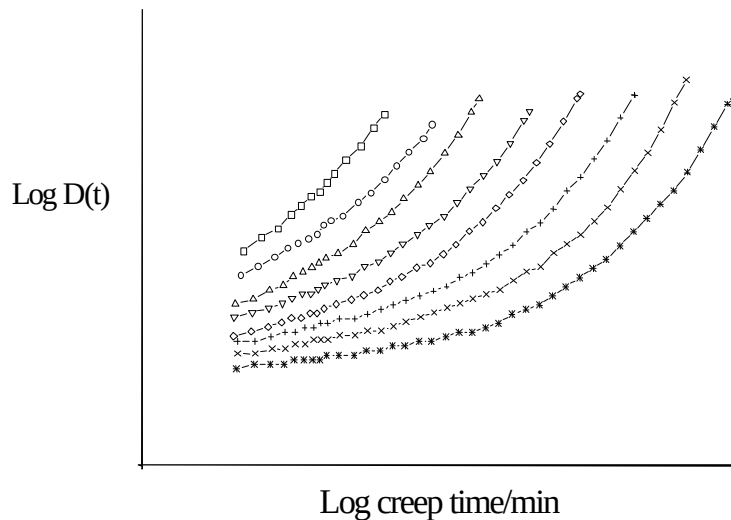


Figure 2.3. Schematic of creep curves from load tests outlined in Figure 2.2.

Typical creep curves are shown in Figure 2.3. It is evident from these curves that as the aging times (t_e) increase the creep compliance at identical creep times decreases. In other words, the material becomes stiffer as aging progresses when viewed at a common creep time. These creep curves also have the same shape and can be superimposed by shifting them horizontally on the creep time axis. If this is the case,

then the material is “thermorheologically simple”. A thermorheologically simple material can be defined as a material maintaining the same relaxation time distribution independent of any external perturbation, such as temperature, physical aging, humidity or pressure among others. Hence, time – aging time superpositioning, which is predicated on shifting all relaxation times by the same degree as will be demonstrated soon, can be invoked and the curves may be shifted or rescaled with time based on their varying aging times.⁶

Before showing the shifted creep data it will be helpful to examine the basis for superpositioning. Williams, Landel and Ferry⁷ proposed a shifting scheme that has its basis in free volume theory for liquids. Their scheme begins with an empirical equation, the Doolittle equation⁸ that relates the viscosity to free volume:

$$\eta(T) = A \exp\left(\frac{B}{f}\right) \quad \text{Eq. 2.2}$$

A and B are constants and f is the fractional free volume. The temperature dependence of the fractional free volume causes the viscosity to diverge near the glass transition temperature. Therefore, the ratio of the Doolittle equation at two different temperatures introduces the shift factor (a_T) through the relaxation time, τ :

$$a_T = \frac{\eta(T)}{\eta(T_g)} = \frac{\tau(T)}{\tau(T_g)} \quad \text{Eq. 2.3}$$

Note that a_T is defined for a shift due to temperature, the subscript recalls what type of perturbation the system underwent to have its behavior modified. The fractional free volume can also be described by

$$f(T) = f(T_g) + \Delta\alpha (T - T_g) \quad \text{Eq. 2.4}$$

in this case $\Delta\alpha$ refers to the difference in thermal expansion coefficients in the liquid (α_{liq}) and in the glassy (α_{gl}) state. Making the proper substitutions and taking logarithms one arrives at an expression for the log shift factor

$$\frac{\eta(T)}{\eta(T_g)} = \log(a_T) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad \text{Eq. 2.5}$$

where C_1 and C_2 are the WLF constants.

$$C_1 = -B / 2.303 f_g, C_2 = f_g / \Delta\alpha$$

All of the above discussion applies to materials in their liquid state. Nonetheless, these same analytical tools have been invoked for shifting curves in the glassy state, because there is a relationship between the viscosity or relaxation time and the fractional free volume of aged materials.

The general concepts from time rescaling will be used to evaluate the creep curves from the physical aging experiments. The idea is to shift the relaxation time distribution due to different aging times rather than different temperatures. Thus, the WLF equation is not applicable. Therefore, one defines a shift rate factor, μ :

$$m = \frac{d \log a_{te}}{d \log t_e} \quad \text{Eq. 2.6}$$

where $\log a_{te}$ is the log shift factor for aging time. In Figure 2.4 the master curve resulting from horizontal and vertical shifting of the isotherms in Figure 2.3 is shown.

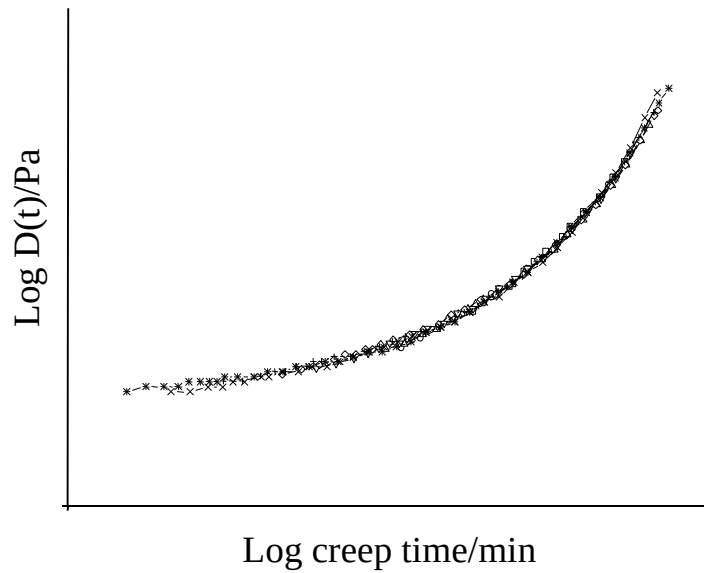


Figure 2.4. Schematic of master curve generated from superpositioning of creep curves in Figure 2.3

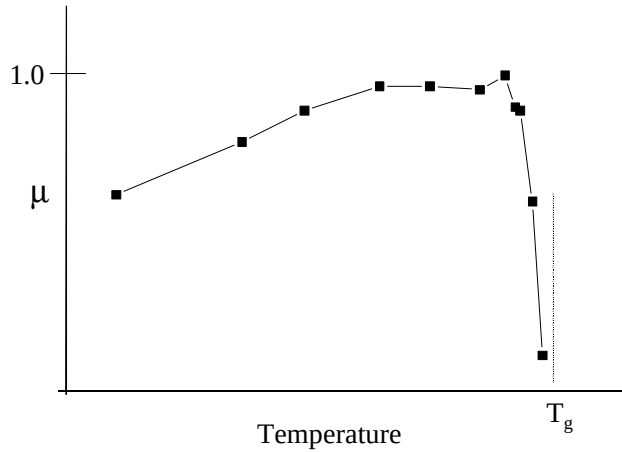


Figure 2.5. Physical aging rate (μ) spectrum, note sharp decrease as T_g is approached

A shift rate factor can also be calculated at various temperatures. Figure 2.5 summarizes the results for μ as a function of temperature for this material. Originally researchers speculated that μ would have a value of unity over a broad temperature range for most materials, polymeric or non-polymeric.⁶ However, it was witnessed that materials do not all age at the same rate. A temperature dependence on the shift rate factor for different materials; including polymers, existed. However, the effect of the polymer backbone flexibility on the physical aging rate has not been investigated explicitly. Some data in the literature indicates a trend in the shift rate factor,^{6,9} namely, the more rigid a polymer backbone the higher the temperature where the physical aging rate drops to lower values. In other words, the rate of change of the compliance or modulus due to physical aging is less for polymers with rigid backbones.

The creep curves from physical aging experiments often can be fit using a stretched exponential¹⁰ in a region close to the glass transition. The stretched exponential known as the Kohlrausch-Williams-Watts (KWW) form appears in the compliance equation:

$$D(t) = D_0 \left(1 + \exp \left(- \frac{t}{\tau} \right)^b \right) \quad \text{Eq. 2.7}$$

In this case β measures the breadth of the distribution of polymer relaxation times and τ is the primitive KWW relaxation time. This relaxation time can be used to calculate the

change in the configurational entropy, S_C , as a function of aging and temperature. Heat capacity data also allows direct evaluation of S_C due to the relationship between $\Delta C_p/T$ ^{11,12} and the configurational entropy, this discussion, however, will be completed later in this chapter.

2.3. ADAM-GIBBS FORMALISM

Instead of using a free volume approach like the Williams Landel and Ferry formalism to describe the glass transition and the temperature dependence of relaxation times, Gibbs and DiMarzio¹³ and later Adam and Gibbs¹¹ (AG) employ a configurational entropy model. Interestingly, Adam and Gibbs show that the WLF form and their form result in equivalent expressions when the constants of both equations are equated. The configurational entropy has a value in the melt that can be described by the number of ways that a system of constant number and volume can be rearranged. There is an obvious temperature dependence to this melt S_C . That is, as the temperature decreases, thermal energy is decreased causing certain configurations to become inaccessible. Furthermore, Adam and Gibbs use cooperativity arguments to describe the evolution of the configurational entropy as the temperature approaches a “thermodynamic equilibrium second order transition”, T_2 . They denote the commonly referred to glass transition temperature, hitherto defined as T_g , as the kinetic appearance of the glass transition, as generally seen by dielectric, enthalpy or mechanical experiments. The thermodynamic T_2 would manifest itself if experiments could be conducted on a long enough time scale.

The cooperative aspects of the AG approach arise through a division of the system into groups of particles, which conduct only cooperative interactions among other particles of its group. This means that there are no interactions between groups of particles. For polymeric systems this implies no intermolecular interactions, just interactions within a group, i.e. intragroup interactions. The term to describe the size of a cooperatively interacting group is z , defined as:

$$z = \frac{N}{n(T)} \quad \text{Eq. 2.8}$$

where n is the total number of cooperative subunits or groups and N is the total number of particles in the system. One can recognize that as the temperature is reduced the

particles move more cooperatively due to shorter interparticle distances and subsequently $n(T)$ decreases. When the thermodynamic second order transition has been transversed then z would be equal to N . The consequence of decreasing temperature on S_c is intuitive: if the number of possible configurations, W_c , is equal to unity then the configurational entropy tends toward zero because:

$$S_c = k \ln W_c \quad \text{Eq. 2.9}$$

According to AG theory S_c does not converge to zero until T_2 is reached, which those authors have shown to be nearly 100 C below T_g .

Adam and Gibbs develop their ideas further by showing that there exists a critical cooperatively interacting particle size, z^* , that is important in describing the temperature dependence of the relaxation times. First of all the probability of a transition occurring from one configuration to another is given by:

$$W(T) = A \exp\left(\frac{-z\Delta\mu}{kT}\right) \quad \text{Eq. 2.10}$$

$\Delta\mu$ is essentially the rotational potential energy barrier of a monomer segment, this term has also been shown to be relatively temperature and cooperative particle size (z) independent.¹⁴ The frequency factor, A , which represents the jump frequency of the cooperative unit in passing over the energy barrier is seen to also be temperature independent. The average transition probability in its final form can be given as

$$\bar{W}(T) = \bar{A} \exp\left(\frac{-z^*\Delta\mu}{kT}\right) \quad \text{Eq. 2.11}$$

This equation implies that the major portion of the transitions that occur at a given temperature are by cooperatively interacting particles that have the critical size z^* .

The configurational entropy for the macroscopic system is already given above. However, the definition for the configurational entropy of a cooperative subunit with z particles can be summarized as following:

$$s_c = S_c n / N \quad \text{Eq. 2.12}$$

Therefore s_c can be related to the number of configurations by

$$s_c = k \ln(W_c^{n/N}) \quad \text{Eq. 2.13}$$

For a mole of particles in a system the above equation becomes:

$$s_C = k \ln(W_C^{z/N_A}) \quad \text{Eq. 2.14}$$

in which N_A is Avogadro's number. There is a critical size, z^* , which still is large enough to allow for a transition from one configuration to another. The number of configurations with this critical size for a cooperative unit will be $W_C^{z^*/N_A}$. The critical configurational entropy for this minimum size of relaxing subunit is

$$s_C = k \ln(W_C^{z^*/N_A}) \quad \text{Eq. 2.15}$$

The critical size for a cooperatively interacting group of particles is then

$$z^* = N_A \frac{s_C^*}{S_C} \quad \text{Eq. 2.16}$$

Inserting this final expression into the average transition probability results in

$$\overline{W}(T) = \overline{A} \exp\left(\frac{-\Delta m N_A s_C^*}{k T S_C}\right) \quad \text{Eq. 2.17}$$

Since the transition probability is inversely proportional to the relaxation time, the above formula can be rewritten as

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta m N_A s_C^*}{k T S_C}\right) \quad \text{Eq. 2.18}$$

In this analysis τ_0 is related to the inverse of the attempt frequency for the cooperative unit to overcome the energy barrier separating two configurations. This term is also seen as being temperature independent.^{15,16,17} In their paper Adam and Gibbs also show that this expression can enter the WLF equation through the relaxation times and relate C_1 and C_2 to their constants of a_1 and a_2 . AG also show there is an universality to the WLF and AG constants if the reference temperatures are picked appropriately. Finally, they prove that an average value of 1.3 describes the ratio T_g/T_2 for many polymeric materials.

The derivation and conclusions of the Adam and Gibbs paper is important because their formalism has been widely adapted. Hence, in order to comprehend further developments a detailed foundation was provided. Matsuoka has employed AG theory to explain the distribution of relaxation times by assuming that the cooperative units are able to contain different number of particles, which means that z^* has different sizes.¹⁸ Ngai, on the other hand, invokes non-Debye character by allowing the cooperatively rearranging units to interact with other subunits.¹⁹ In essence this means that the

restriction that AG put on interactions outside of the cooperatively interacting particles is removed. These concepts will be encountered in later chapters.

The AG approach will be continued to promote the calculation, ultimately, of the configurational entropy as a function of aging time. To arrive at that point one needs an expression from equilibrium behavior for S_C , $\Delta\mu$ and a reasonable approximation for s_C^* . The equilibrium configurational entropy can be given as follows

$$S_C(T) = \int_{T_0}^T \frac{\Delta C_p}{T'} dT' \quad \text{Eq. 2.19}$$

The change in the heat capacity from the melt to the glass can be adjusted using Angell's approach²⁰, which states that ΔC_p decreases as the temperature increases, as is seen experimentally. Hence, using $\Delta C_p(T) = \Delta C_p(T_g) T_g/T$, the configurational entropy takes on this form

$$S_C(T) = T_g \Delta C_p(T_g) \frac{(T - T_0)}{TT_0} \quad \text{Eq. 2.20}$$

Substituting Eq. 2.20 into the equation that relates relaxation times with S_C (Eq. 2.18) results in:

$$t(T) = t_0 \exp \left(\frac{N_A \Delta \mu_{SC}^* T_0}{T_g \Delta C_p(T_g) k (T - T_0)} \right) \quad \text{Eq. 2.21}$$

There is a singularity when $T = T_0$, implying that the relaxation times would diverge at this temperature. This problem is resolved by stating that the configurational entropy goes to zero at T_0 . This final form looks similar to a Vogel-Fulcher (VF) equation

$$t(T) = t_0 \left(\frac{DT_0}{T - T_0} \right) \quad \text{Eq. 2.22}$$

when D is set equal to $N_A \Delta \mu_{SC}^* / T_g \Delta C_p(T_g) k$. In order to proceed further, it is necessary to see how D will be evaluated applying the VF equation. Dynamic mechanical or dielectric analysis for a material will result in τ as a function of temperature. Using the VF expression, values for τ_0 , D and T_0 can be determined. In this manner $\Delta \mu_{SC}^*$ is accessible from D after the change in heat capacity and glass transition temperature are calculated from differential scanning calorimetry. A complimentary approach is to perform time-temperature superpositioning of creep or stress relaxation data from aging

tests at specific aging times. Since the log shift factor is equal to $\log \tau(T)/\tau(T_{\text{ref}})$ from Eq. 2.3 it is apparent that this ratio will result in a value of the configurational entropy normalized to the reference curve since everything else is temperature independent and will cancel. This approach can be used readily to calculate the change in the configurational entropy as a function of temperature. This procedure will be used later; however, it will be beneficial to see the physical significance of the various other parameters used in this development.

The evaluation of s_c^* is based in part on bead theory^{3,16} or even virtual bonds if the polymer backbone structure is rigid. As mentioned earlier, the minimal number of configurations that can be assumed by a rearranging group of molecules is two. However, this may not be the critical configurational entropy. An accepted value of s_c^* for crankshaft type motions of bonded segments is $k \ln 3!$ ¹² Using this value along with the temperature and z^* independence of $\Delta\mu$, $\Delta\mu$ can be determined for a particular polymer system. After this value has been elucidated, the configurational entropy for the whole system can be determined via rearrangement of the Adam-Gibbs equation¹⁶

$$S_c = \frac{N_A s_c^* \Delta m}{kT \ln \frac{t}{t_0}} \quad \text{Eq. 2.23}$$

Therefore, using the calculated relaxation times from the aging creep curves by way of a KWW equation, Eq. 2.7, one can monitor the change in S_c due to aging by knowing $\Delta\mu$, τ_0 and s_c^* .

2.4. VOLUME RECOVERY AND PHYSICAL AGING

Some of the earliest physical aging tests on polymers were volume measurements as a function of aging time.²¹ It was known previously that inorganic glasses physically aged through work performed by Tool with inorganic silicates.^{22,23} However, it was not until these volume aging results were published that it was confirmed that physical aging occurred in polymer glasses.

The early temperature jump experiments using volume involved small temperature jumps from an equilibrated state, the information that can be extracted from

these experiments is interesting. One definition that evolved from this type of experiment is the departure from equilibrium:

$$d = \frac{v - v_{\infty}}{v_{\infty}} \quad \text{Eq. 2.24}$$

Where v is the instantaneous volume and v_{∞} is the equilibrium volume. This equation is specific for volume, but it can be generalized for any parameter

$$d = \frac{p - p_{\infty}}{p_{\infty}} \quad \text{Eq. 2.25}$$

In this formalism p is the property at any time after the system has been perturbed and p_{∞} is the equilibrium value for the property. Using either definition, in temperature jump experiments for volume recovery as for other experiments there is a difference if the jump is in a positive or negative direction.^{24,25} This indicates the nonlinear nature of the process. A positive jump, $\Delta T > 0$ results in negative displacement values, since the instantaneous volume will have a smaller value immediately after the jump than will the equilibrium volume. On the contraction side, $\Delta T < 0$, the displacement from equilibrium is positive because the initial volume is higher than the equilibrium value. The approach towards equilibrium ($\delta=0$) occurs in a gradual manner for the contraction experiment suggesting the non-exponential nature of the recovery. However, the expansion experiment shows almost a step function approach towards equilibrium. The reason for this discrepancy is that the change in the displacement with time depends on the relaxation time τ_i , which is a function of the structure of the glass.

$$\frac{dd_i}{dt} = \frac{d_i}{\tau_i} \quad \text{Eq. 2.26}$$

This differential equation, Eq. 2.26, shows that when the relaxation times are longer (expansion) that the recovery rate is slower than when relaxation times are shorter (contraction experiments).

When multiple temperature jumps are involved, the approach towards equilibrium changes character.²⁶ Instead of simple one directional approaches towards equilibrium, these multiple jump experiments demonstrate memory effects. Following a negative/positive jump sequence in temperature the sample initially expands from the temperature jump, but later it “recognizes” that its instantaneous volume is higher than

the equilibrium line and contraction commences. The exact time scale and magnitude for this temperature jump experiment depends on the degree of temperature jump and how long the initial state was held. When the temperature jump is large then the magnitude is high due to the large lag in response from the perturbation. In a down quench there is only contraction both from the contraction of the temperature drop and the equilibrium line lies below the quenched in state. Therefore, instead of demonstrating a peak there is only a decay in the graph of displacement versus log aging time. These experiments demonstrate both the non-exponentiality and non-linearity of the aging phenomena.

Although it is published that the simple downward quench experiments do not provide enough information,²⁷ these type of experiments were performed in the present study. The author feels that this information was very useful in ascertaining physical aging parameters. The rate of volumetric physical aging can be gained from these experiments. If the aging test temperature is very low where limited mobility occurs then one does have to be aware that the data may span two regions of behavior. This is because there is a larger lag time caused by the non-linearity of relaxation times at low temperatures which affects the volume recovery rate in contraction experiments.

The self-retarding nature of physical aging has been postulated for many years. In the self-retarding process equilibrium is approached in a non-exponential and non-linear fashion. The expressions showing these two characteristics are given in Eq. 2.27 through Eq. 2.29²²

$$f(t) = \int_0^{\infty} g(t) e^{-t/\tau} dt \quad \text{with} \quad \text{Eq. 2.27}$$

$$f(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad \text{empirical form of Eq. 2.27} \quad \text{Eq. 2.28}$$

$$t(d, T) = A \exp\left[-q(T - T_f) + (1 - x) \frac{dq}{\Delta a}\right] \quad \text{Eq. 2.29}$$

In these expressions β is related to the breadth of the distribution of relaxation times and τ is a primitive relaxation time. In Eq. 2.29 it also becomes apparent that the relaxation time is dependent on the structural state (δ) as mentioned earlier and also the “structural temperature” of the system (θ). A fictive temperature, T_f , is defined as the temperature that the system would be at if the glass had the equilibrium value of a property being

observed. The other terms in the above expressions, A and x, are constants, where x is the degree of non-linearity. From the present discussion and Eq. 2.26 the non-exponentiality and non-linearity are apparent. If x=1, one finds an Arrhenius expression in Eq. 2.29. Even though these expressions show the self-retarding nature of physical aging, a recent study on polycarbonate has shown that volume recovery follows the above model for about 6 months at room temperature, thereafter the volume decrease accelerates to about ten times the prior aging rate.²⁸ There was no evidence of any type of chemical aging or degradation caused by using a density gradient column in these experiments. The researchers took many precautions to insist that this behavior was not due to a non physical aging parameter. This behavior is very alarming since the aging rates are very high and mean that failure caused by physical aging could occur sooner than predicted by the self-retarding model. This behavior illustrates some of the difficulties in modeling physical aging phenomena.

2.5. ENTHALPY RECOVERY AND PHYSICAL AGING

On the surface, enthalpic recovery experiments are in some respects easier to perform than some of the other methods discussed here. Both for this reason plus cost issues, many enthalpic recovery experiments have been performed.³ The wealth of information derived from these experiments is also a cause for performing these experiments. Heat flow (dH/dt) is related to heat capacity through the heating rate and sample weight. Heat capacity is related to entropy:

$$dS = \frac{dq_{rev}}{T} = \frac{C_p(T)dT}{T} \quad \text{upon integrating both sides}$$

$$S(T) - S(T') = \int_{T'}^T \frac{C_p(T)dT}{T}$$

If $dq=dH_{transition}$ this leads to²⁹

$$S(T) - S(T') = \int_{T'}^T \frac{\Delta C_p(T)}{T} dT$$

If the transition is related to the glass transition then the entropic change is the configurational entropy change, where this value goes to zero at T' , i.e. $S_c(T')=0$ and:

$$S_c = \int_{T'}^T \frac{\Delta C_p(T)}{T} dT \quad \text{Eq. 2.30}$$

Angell uses an expression for $\Delta C_p(T)$ that is derived from experimental observations that this quantity decreases with increasing temperature,²⁰ therefore it can be written as $\Delta C_p(T) = \Delta C_p(T_g)T_g/T$. Upon substituting this expression in Eq. 2.30 and integrating the following equation is obtained:

$$S_c = T_g \Delta C_p(T_g) \frac{T - T'}{TT'} \quad \text{Eq. 2.31}$$

This expression is identical to Eq. 2.20 with the substitution of $T' = T_0$. The configurational entropy then can be used as discussed in the previous section.

The excess enthalpy (ΔH_a), the area between two successive differential calorimetry scans after isothermal aging, can be a useful parameter to examine structural effects on physical aging. The excess enthalpy can be calculated from experimental data:

$$\Delta H_a(t_e, T_a) = \int_{T'}^T (C_{p,1stscan} - C_{p,2ndscan}) dT \quad \text{Eq. 2.32}$$

This expression may also be represented by a time decay function when enough data is present^{30,31}

$$f(t) = \frac{\Delta H_\infty(T_a) - \Delta H(t_e, T_a)}{\Delta H_\infty(T_a)} \quad \text{Eq. 2.33}$$

where $\phi(t)$ has the same form as Eq. 2.28. Here it is obvious that a distribution of relaxation times exist as embodied in the $\phi(t)$ function and can be determined from Eq. 2.33. The calculated distribution of relaxation times does not necessarily correlate with other methods since the mechanism of relaxation could be different.

Finally, calorimetric measurements can result in the evaluation of an activation energy for the calorimetric glass transition process.^{1,3,32} Although these type of measurements are not directly related to physical aging since the system is cooled through the glass transition and then immediately heated at various heating rates, the activation energy for this process can be valuable. The activation energy, Δh^* , can be determined from the fictive temperature, T_f defined earlier, using Moynihan's method³³

$$\frac{d \ln Q}{d \left(\frac{1}{T_f} \right)} = - \frac{\Delta h^*}{R} \quad \text{Eq. 2.34}$$

Q is the cooling rate which generally ranges from 0.5 to 50⁰ C/min. It has been noted that there is a dependence on structure for the activation energy.^{3,32} As an example, as n increases in a series of polymethyl(α -n-alkyl) acrylates the activation energy decreases.³² The authors contribute this tendency to a reduction of the intermolecular interactions of the polar ester groups. The degree of packing will probably change across this series, although density values are not reported. Therefore, if one is examining chain rigidity effects on this activation energy then one has to take precautions that the other parameters are taken into account.

2.6. SUMMARY

The physical aging behavior in glasses can be investigated with many different techniques. The discussion here was limited to creep, volume and enthalpy recovery experiments. However, dielectric spectroscopy,^{34,35} positron annihilation spectroscopy,³⁶⁻³⁹ fluorescence spectroscopy,^{40,41,42} transient mechanical testing,⁴³ Fourier Infrared Spectroscopy⁴⁴ among other techniques have also been used to probe the kinetics of physical aging.

The rate at which physical aging occurs has also been summarized. However, there are not too many correlations of this rate with chemical structures. Some ongoing investigations show that at aging temperatures close to the T_g the cooperative rearranging domain size is related to the rate of physical aging.⁴⁵ Similar investigations, relating structure or fundamental chain parameters to physical aging processes should be forthcoming. Development of these type of relationships can aid in predicting behavior and designing systems that demonstrate little physical aging.

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Chapter 3. RELAXATION TIME DISTRIBUTION CALCULATIONS

The reason for performing relaxation time distributions is that polymeric materials have a broad relaxation time distribution compared to simple liquids and the breadth of relaxation times can afford some information about molecular dynamics in these systems. This broad relaxation time distribution gives rise to a dispersion of relaxation times from various experiments, such as dynamic mechanical, dielectric, differential scanning calorimetry, fluorescence spectroscopy among other types. A time decay function that mimics the experimental data well, the Kohlrausch, Williams and Watts expression (KWW), has been used extensively in describing relaxation phenomenon ranging from calorimetric aging experiments to the decay of fluorescing dyes in polymer glasses.¹⁻³

$$f(t) = \exp\left(-\left(\frac{t}{\tau}\right)^b\right) \quad \text{Eq. 3.1}$$

The distribution of relaxation times is related to β and the primitive relaxation time is τ . A physical meaning behind the fact that the KWW function agrees well with various types of relaxation data is still not known.

The purpose of this discussion is to demonstrate the application of a technique that is utilized in fitting dispersion data in the frequency domain with the KWW time decay function. This will later be used later to assess if polymer structure can influence the distribution of relaxation times. Furthermore, it will be desirable to demonstrate other models of dispersion data than the particular one used here. The development will follow a chronological and a complexity order, with the earlier models and equations being simpler and less general than the later models. The fitting programs used for calculating the relaxation time data are presented in appendices A-C.

It should be mentioned that much of the ensuing discussion can be found in work performed earlier in this research group,⁴ a good overview of relaxation phenomenon⁵ and books dedicated to dielectric relaxation.^{6,7} The simplest distribution of relaxation times is the Debye single relaxation time, which is an exponential relationship

$$f(t) = \exp\left(-\frac{t}{\tau}\right) \quad \text{Eq. 3.2}$$

The single relaxation time is given by τ . This expression has limited use in describing relaxation time distributions of polymeric systems, except at very high temperatures.

The Cole-Cole model⁸ is more complex than a Debye relaxation, in that their model is a superposition of relaxation times evenly distributed about the average relaxation time τ_0 . Although Park⁴ used a formalism based on dielectric experiments, the development is identical for dynamic mechanical data, employed in the current work. The expression for the dynamic mechanical data for a Cole-Cole model given in terms of the complex modulus (E^*) is:

$$\frac{E^* - E_\infty}{E_s - E_\infty} = \frac{1}{1 + (i\omega\tau_0)^{1-\alpha}} \quad \text{Eq. 3.3}$$

The limiting moduli at low and high frequencies are defined as E_s and E_∞ respectively. The average relaxation time is τ_0 . The fitting parameter α , which ranges from zero to unity, indicates how much the system deviates from a single relaxation time. The changes caused by different α values will become apparent shortly.

The expression that is used to fit experimental mechanical loss data is:

$$\frac{E''(\omega)}{E_s - E_\infty} = \frac{(\omega\tau_0)^{1-\alpha} \cos(\alpha\pi/2)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} \quad \text{Eq. 3.4}$$

When a complex plane plot, referred to as a Cole-Cole plot or Argand diagram is desired then the expression that fits the curve is:

$$\left[E' - \frac{E_s - E_\infty}{2} \right]^2 + \left[E'' + \frac{(E_s - E_\infty)}{2} \cot \alpha \frac{(1-\alpha)\pi}{2} \right]^2 = \left[\frac{(E_s - E_\infty)}{2} \operatorname{cosec} \frac{(1-\alpha)\pi}{2} \right]^2 \quad \text{Eq. 3.5}$$

Eq. 3.5 is an equation for a flattened hemisphere. If this expression is compared with that from a single relaxation time distribution, see Eq. 3.6 and subsequently graphed in a Cole-Cole diagram the differences are evident.

$$\left[E' - \frac{(E_s - E_\infty)}{2} \right]^2 + [E'']^2 = \left[\frac{(E_s - E_\infty)}{2} \right]^2 \quad \text{Eq. 3.6}$$

When $\alpha=0$ the single relaxation distribution is regained; however, as α tends towards 1 then the hemisphere is flattened, see Figure 3.1.

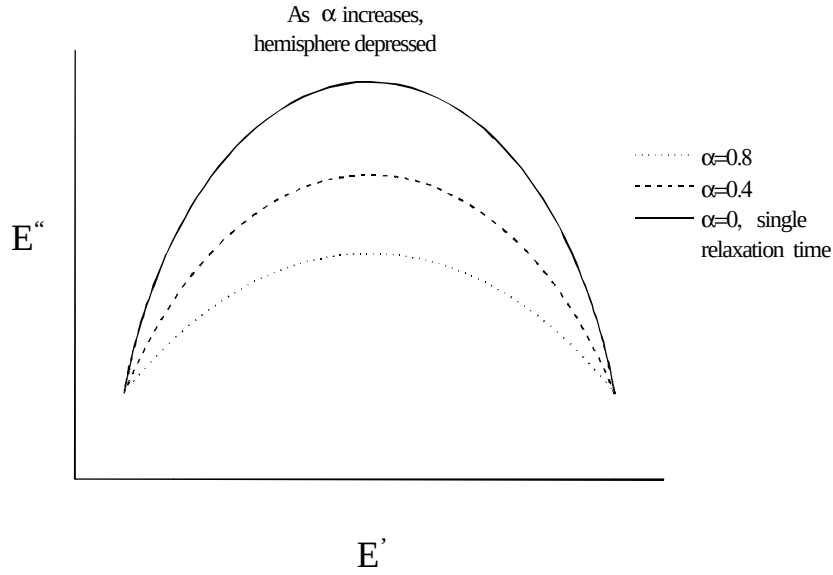


Figure 3.1. Schematic Cole-Cole plot with indicated deviations from single relaxation time distribution, $\alpha=0$ is Debye relaxation

The next model is the Davidson-Cole model,⁹ which was developed to deal with deviations from the Cole-Cole model of relaxation data at high frequencies. The Davidson-Cole model allows for skew in the relaxation dispersion. The complex modulus's frequency dependence is defined as:

$$\frac{E^* - E_\infty}{E_s - E_\infty} = \frac{1}{(1 + i\omega t_0)^\gamma} \quad \text{Eq. 3.7}$$

The adjustable parameter γ varies from 0 to 1, with 0 yielding a system with the most skewed behavior away from the hemisphere and 1 producing the system with a single relaxation time. Using this model to examine experimental data requires an operative expression:

$$\frac{E''(\omega)}{E_s - E_\infty} = (\cos(\arctan(\omega t_0)))^\gamma (\sin(\arctan(\omega t_0))) \quad \text{Eq. 3.8}$$

A complex plane plot for this model is shown in Figure 3.2.

Finally, the last model to describe experimental data in the frequency domain is the Havriliak-Negami (HN) equation.¹⁰ This is the most general expression and has the most adjustable parameters. This data has been used to fit dielectric^{11,12} and dynamic

mechanical^{13,14} data in the frequency domain. Evident from Eq. 3.9, the HN model has two parameters (α, γ) that can be varied:

$$\frac{E^* - E_\infty}{E_s - E_\infty} = \frac{1}{(1 + (i\omega t_0)^{1-\alpha})^\gamma} \quad \text{Eq. 3.9}$$

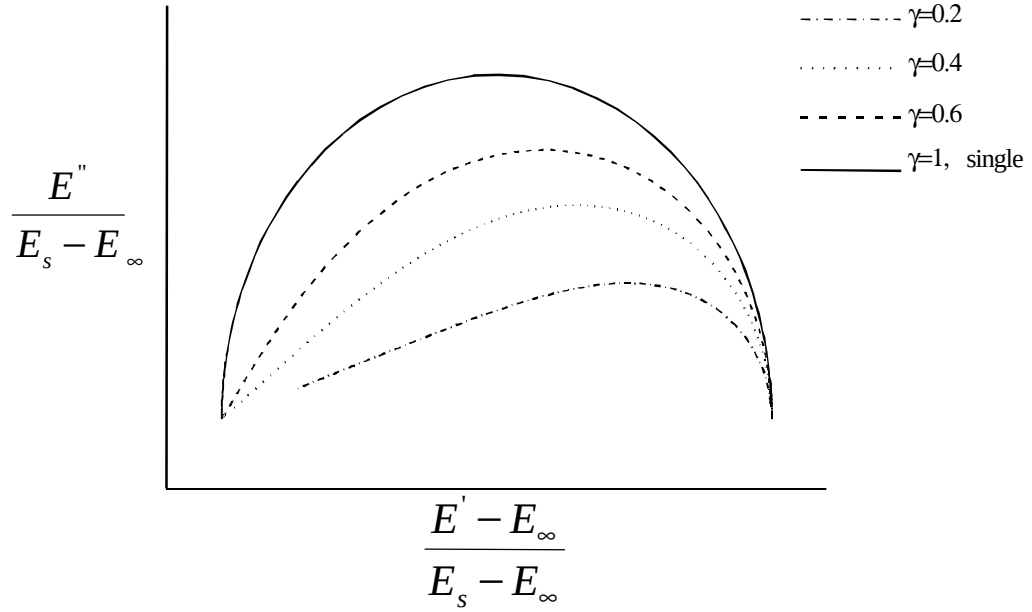


Figure 3.2. Schematic of a Davidson-Cole plot, showing more skew at smaller γ

The definitions of α, γ remain the same as above. The expression used to characterize data in the frequency domain is

$$E''(\omega) = \frac{(E_s - E_\infty) \sin(qg)}{r^{-g/2}} \quad \text{where} \quad \text{Eq. 3.10}$$

$$\left(\left(\frac{(\omega t_0)^{1-\alpha}}{1 + (\omega t_0)^{1-\alpha}} \right)^{\frac{1}{\gamma}} \right) \left(\frac{(\omega t_0)^{1-\alpha}}{1 + (\omega t_0)^{1-\alpha}} \right)^{\frac{1}{\gamma}} \text{ and}$$

$$= \arctan \left[\frac{(\omega t_0)^{1-\alpha} \sin(\alpha\pi/2)}{1 + (\omega t_0)^{1-\alpha} \cos(\alpha\pi/2)} \right]$$

The HN equation was used in this present study to describe relaxation data in the frequency domain. The complex plane plot for typical data is shown in Figure 3.3. A program to fit this data can be found in Appendix I. Since this expression plays a large

Fourier transform, to arrive at an expression for the time decay function, Eq. will be continued.

atically very difficult to express the HN equation in terms of a time

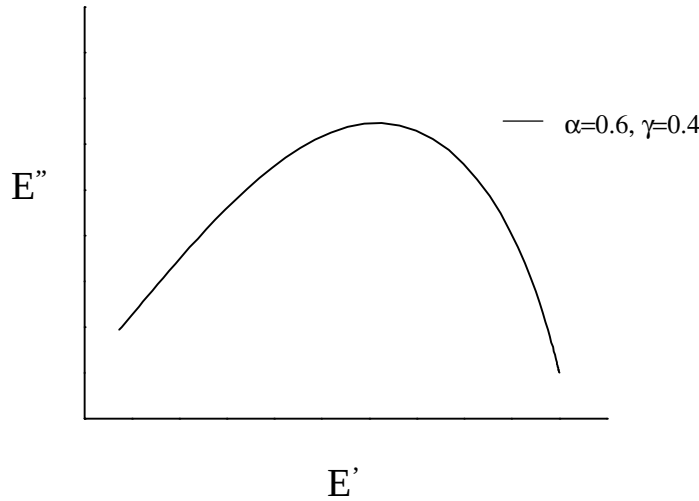


Figure 3.3: Schematic of Havriliak-Negami function in complex plane plot

decay function or relaxation distribution function. Therefore, the Fourier transform of the HN expression is generated to numerically calculate a time decay function.¹⁵ One first has to identify the frequency domain part, $g(\omega)$, of the Fourier pair and its corresponding time domain part, $f(t)$:

$$g(\omega) = \frac{E''(\omega)}{E_s - E_\infty} \quad \text{and} \quad \text{Eq. 3.11}$$

$$f(t) = -\frac{df(t)}{dt} \quad \text{Eq. 3.12}$$

Since $E''(\omega)$ is an odd function the odd part of $\exp(-i\omega t)$ which is $\sin \omega t$, is used in forming the Fourier transform:

$$-\frac{df(t)}{dt} = \frac{2}{\pi} \int_0^\infty \frac{E''(\omega)}{E_s - E_\infty} \sin(\omega t) d\omega \quad \text{Eq. 3.13}$$

Integrating both sides leaves one with

$$f(t) = \frac{2}{p} \int_0^{\infty} \frac{E''(w)}{E_s - E_{\infty}} \frac{\cos(wt)}{w} dw \quad \text{Eq. 3.14}$$

This expression was evaluated using loss modulus data and a computer program generated by Park,⁴ and is reproduced in Appendix II. The fitting parameters from the HN evaluation are used along with the increment size of the integration steps and integration limits in this program. A typical time decay function appears in Figure 3.4. From the time decay function, Eq. 3.1, τ and β are easily evaluated using a non-linear regression program, see Appendix C.

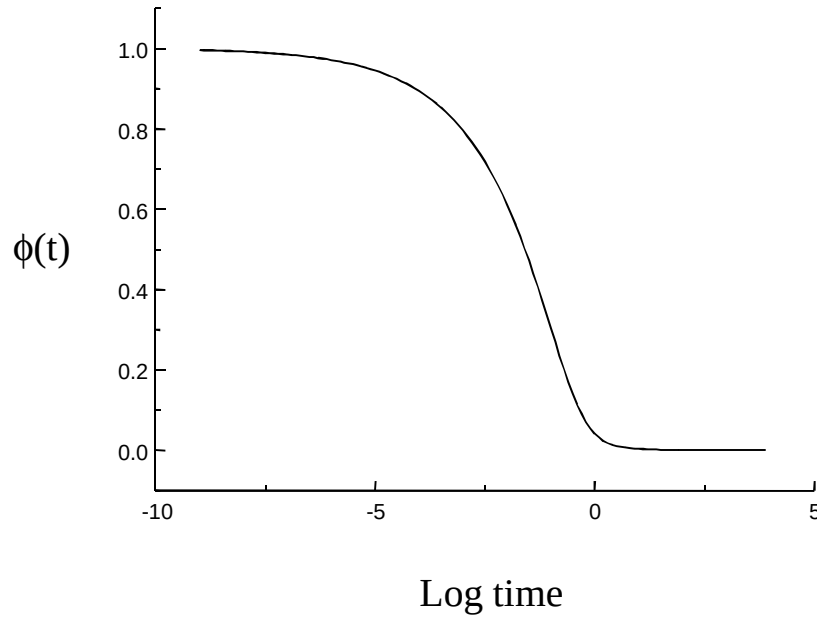


Figure 3.4: Schematic of time decay function

Besides generating values for τ and β it will also be interesting to note changes in the mean relaxation time, $\langle \tau \rangle$, as a function of temperature. Lindsey and Patterson¹⁶ have derived n-th moments of the average relaxation time:

$$\langle t^n \rangle = \frac{1}{\Gamma(n)} \int_0^{\infty} t^{n-1} f(t) dt \quad \text{Eq. 3.15}$$

where Γ represents a gamma function. For the KWW equation, examining the mean relaxation time, $n=1$, the expression reduces to

$$\langle t \rangle = \int_0^{\infty} \exp\left(-\left(\frac{t}{t_0}\right)^b\right) dt \quad \text{Eq. 3.16}$$

by changing variables ($x=(t/t_0)^b$) and putting Eq. 3.16 in the form of a gamma function one has

$$\langle t \rangle = \frac{t_0}{b} \int_0^{\infty} \exp(-x) x^{(1/b)-1} dx \quad \text{Eq. 3.17}$$

The result of this gamma function is

$$\langle t \rangle = \frac{t_0}{b} \Gamma\left(\frac{1}{b}\right) \quad \text{Eq. 3.18}$$

This completes the description of the process carried out in this study for calculating the distribution of relaxation times along with the mean relaxation time. The results of such analyses can be useful in interpreting structure's role on relaxation behavior, which ultimately governs many polymer properties. The present work will extend some of the previous analysis¹⁷⁻¹⁹ performed on relating chemical structure to the level of cooperative relaxation in polymers near their glass transition temperatures.

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Chapter 4. DILUTE SOLUTION CHARACTERIZATION

4.1. INTRODUCTION

The most expedient method of molecular weight determination of a polymer usually involves dilute solution characterization. Dilute solution techniques encompass liquid state nuclear magnetic resonance, vapor phase osmometry, size exclusion chromatography (SEC) among others. All of the techniques with the exception of SEC provide a single average molecular weight; however, size exclusion chromatography provides a molecular weight distribution. The discussion here will be focused on some of the theoretical aspects of dilute solution characterization, namely, unperturbed conditions of polymer chains, extrapolation methods from perturbed states back to unperturbed states and the use of SEC for determination of unperturbed or theta dimensions of polymer chains in solution.

4.2. UNPERTURBED CONDITIONS

Qualitatively the unperturbed state is the condition where a polymer chain is in a medium where the polymer chain interacts with itself as much as the surrounding medium. The medium could be either other chains of its same kind or a solvent. The unperturbed state is also referred to as a theta state and the conditions which allow the polymer to be in this condition are theta conditions. The advantage of finding a solvent and temperature that match the theta condition is that in this medium “unperturbed dimensions” exist, mimicking those the polymer would experience in an equilibrium melt state where the structural features are not obscured by external forces. Thus, much insight concerning molecular interpretations can take place in the theta condition in dilute solution.

There are some viscosity relationships for chains in the unperturbed state

$$[\eta]_{\theta} = K_{\theta} M^{1/2} \quad \text{Eq. 4.1}$$

The subscript θ refers to the unperturbed or theta state. The term on

the left is the intrinsic viscosity at the theta condition. The constant K_θ is developed below and is related to unperturbed dimensions. Finally, from Eq. 4.1 one recognizes that the intrinsic viscosity under these theta conditions will scale as the one-half power of molecular weight. Note that the intrinsic viscosity, which can be viewed as inverse density (units are volume/weight), scales to a larger power when the macromolecule is in a good solvent as reflected in the Mark-Houwink-Sakurada equation:

$$[\eta] = KM^a \quad \text{Eq. 4.2}$$

where $a > 0.5$ for good solvents and flexible chains.

The unperturbed dimensions of a polymer in dilute solution can be ascertained by finding the constant K_θ and with knowledge of the universal viscosity constant, Φ_0 ,

$$K_\theta = \Phi_0 \left(\frac{\langle R^2 \rangle_0}{M} \right)^{3/2} \quad \text{Eq. 4.3}$$

$\langle R^2 \rangle_0^{1/2}$ is the unperturbed mean square end-to-end distance, which is dependent on bond angles and bond rotational potential energies. The distance term has the following form if one views the chain as a random coil with a gaussian distribution of end-to-end lengths and with valence bond angles (θ) and hindered rotations about a rotational angle ϕ :

$$\langle R^2 \rangle_0 = nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} \right) \quad \text{Eq. 4.4}$$

The first term in this expression, nl^2 , comes directly from the freely jointed and rotating chain model when employing a gaussian distribution function. Here n is the number of statistical segments in the polymer chain ensemble and l is the length of the smallest statistical segment. For example, in vinyl polymers, n would be equivalent to the number of repeat units and l the length of the repeat unit.

In Eq. 4.5 $\langle R_g^2 \rangle_0$ is the unperturbed radius of gyration which describes the distribution of chain segments about the center of mass.¹ There exists a relationship between the two unperturbed dimensions for flexible linear chain polymers:

$$\frac{1}{6} \langle R^2 \rangle_0 = \langle R_g^2 \rangle_0 \quad \text{Eq. 4.5}$$

Another useful parameter that may be derived from determination of unperturbed dimensions is the characteristic ratio, C ,

$$C_{\infty} = \frac{\langle R^2 \rangle_0}{nl^2} \quad \text{Eq. 4.6}$$

Substitution of Eq. 4.4 into Eq. 4.6 shows how the characteristic ratio, which is defined here at infinite molecular weight, depends only on the bond angles and bond rotational potential energies

$$C_{\infty} = \left(\frac{1 - \cos \phi}{1 + \cos \phi} \right) \left(\frac{1 - \langle \cos f \rangle}{1 + \langle \cos f \rangle} \right) \quad \text{Eq. 4.7}$$

Essentially, the characteristic ratio indicates the degree of flexibility of a polymer chain. The larger the value of C , the more rigid is the macromolecule. A final unperturbed chain quantity that deserves mention is the temperature dependence of the characteristic ratio or the temperature coefficient of the unperturbed end-to-end distance

$$\frac{d \ln \langle R^2 \rangle_0}{dT} = \frac{d \left(\frac{1 - \langle \cos f \rangle}{1 + \langle \cos f \rangle} \right)}{dT} \quad \text{Eq. 4.8}$$

As can be seen in Eq. 4.4 the only parameter that will be temperature dependent is the average bond rotational angle. For example, in polyethylene, because trans (180°) is a more thermodynamically stable conformation than gauche (60°), the temperature coefficient of the unperturbed dimensions is negative.

4.3. EXTRAPOLATION TECHNIQUES

Although very useful polymer parameters can be determined from solution measurements at theta conditions, as shown above, there are many problems in performing experiments at theta conditions. Initially, if one is working with a new system, the theta conditions, (theta solvent and theta temperature) need to be determined. This is not always very straightforward. Moreover, at theta conditions the temperature control for an experiment must be very good, in order to prevent precipitation of the macromolecules. Frequently a cosolvent² is necessary to produce a theta solvent. Consequently, if one of the cosolvents has a higher vapor pressure, then the composition of the system will change, moving this system away from the theta condition. One

conclusion that can be drawn from the above observations is that performing experiments under theta conditions is difficult and time consuming. Accordingly, finding extrapolation techniques that permit one to extrapolate data from “good solvent” or “perturbed conditions” to the unperturbed limit will allow a more convenient determination of unperturbed dimensions.

Before investigating some of the theory here for extrapolations it will be helpful to examine the excluded volume effect and coil expansion factor, α , to ascertain what conditions may generate an unperturbed state. Excluded volume originates in macromolecular chain solutions because the number of segments is large and the chain is limited to a certain number of conformations due to some places being occupied by other segments in the chain. One may describe this as a self-avoiding walk or simply that two segments cannot occupy the same space at the same time. With some sites excluded, a further expansion of the polymer chain will be expected. In lower molecular weight systems this problem is not as acute because the number of segments per chain is small and the probability of self-exclusion is less likely.

In Flory’s model of the excluded volume effect a potential of mean force between polymer segments of the same chain was employed. Basically, the force balance was modeled between the osmotic force that wants to swell a polymer chain and an elastic restoring force. The elastic restoring force works against further expansion because it prefers to maximize entropy by maximizing the number of possible chain configurations. The potential of mean force, $V(R_g)$, or the interaction energy between segments on the same chain takes on the following form through use of a gaussian function and Flory-Huggins equation for the free energy of mixing^{3,4}

$$V(R_g)/kT = 2C_M\psi \left(1 - \frac{q}{T}\right) M^{1/2} x^{-3} \quad \text{Eq. 4.9}$$

The term ψ is the entropy part of the interaction parameter from Flory-Huggins theory. The theta temperature is represented by θ and x is

$$x = \frac{R_g}{\langle R_g^2 \rangle_0^{1/2}} = \alpha \quad \text{Eq. 4.10}$$

Finally, C_M can be summarized as

$$C_M = \left(\frac{27}{2^{5/2} \rho^{3/2}} \right) \left(\frac{\bar{v}^{-2}}{N_A V_0} \right) \left(\frac{\langle R^2 \rangle_0}{M} \right)^{-3/2} \quad \text{Eq. 4.11}$$

One can recognize the last term in brackets in Eq. 4.11 as the unperturbed end-to-end distance that was mentioned earlier. The middle term on the right combines $\bar{v}$, the polymer partial specific volume, Avogadro's number and V_0 , the molecular volume of the solvent. Finally, by substituting Eq. 4.11 in Eq. 4.9 and finding the maximum of this expression with respect to the radius of gyration (the point at which equilibrium has been established between the swelling and restoring forces) Flory arrived at an expression relating the coil expansion factor and C_M , θ , and molecular weight:

$$\alpha^5 - \alpha^3 = 2C_M \gamma \left(1 - \frac{\theta}{T} \right) M^{1/2} \quad \text{Eq. 4.12}$$

In this equation α approaches unity when $T=\theta$, $M^{1/2} \Rightarrow 0$, meaning there is no expansion at the theta temperature or when the molecules are small. Also, if C_M becomes zero then $\alpha = 1$ and the system is unperturbed. This latter scenario can take place when V_0 becomes quite large, as in the case when the polymer chain is being dissolved in polymer molecules of its own kind. In this case the molecular volume of the solvent is quite large and C_M will converge to zero. Therefore, the coil expansion factor is unity and the polymer chain would be in an unperturbed state when surrounded only by identical chains. Consequently, it is not surprising that values for unperturbed dimensions in the molten state studied by light scattering techniques compare well with those found from dilute solution measurements.⁵ When the coil expansion factor is unity, this means that there is a cancellation between the effects of the long range excluded volume (repulsion) and the short range van der Waals forces (attraction). One speaks of an ideal state in this case, much like the Boyle state for gases, where the second virial coefficient vanishes.

Extrapolation techniques for unperturbed conditions start by a modification of the intrinsic viscosity due to a good solvent as shown below:

$$[\eta] = [\eta]_i \alpha_\eta^3 \quad \text{Eq. 4.13}$$

where α_η^3 is the viscosity expansion factor, which is not necessarily equivalent to the expansion factor used above. Perturbation theory^{1,6} leads to an expression for the

viscosity expansion factor in terms of the perturbation that is generated by polymer interactions with good solvents

$$a_h^3 = 1 + 1.55z - \dots \quad \text{Eq. 4.14}$$

On the right hand side of Eq. 4.14 the first term, 1, describes the ideal state or unperturbed state that was covered previously, while the second term contains z , which is an index of the excluded volume. Eq. 4.14 holds for small values of perturbation, indicating that high molecular weight polymers in a good solvent may not be well described by this perturbation expression. The excluded volume parameter is described in Eq. 4.15

$$z = \left(\frac{3}{2p} \right)^{3/2} \left(\frac{B}{A^3} \right) M^{1/2} \quad \text{Eq. 4.15}$$

where

$$A^2 = \frac{\langle R^2 \rangle_0}{M} \quad \text{Eq. 4.16}$$

$$B = \frac{b}{M_s^2} \quad \text{Eq. 4.17}$$

The two parameters that are defined in Eq. 4.16 and Eq. 4.17 are used to explain the degree of perturbation. In Eq. 4.17 M_s is the molecular weight of the segment and β is the binary cluster integral. The cluster integral illustrates the pair correlation function of two segments ($g(\mathbf{R}_{ij})$) separated by a distance $\mathbf{R}$

$$b = \int [1 - g(\mathbf{R}_{ij})] d\mathbf{R}_{ij} \quad \text{with} \quad g(\mathbf{R}_{ij}) = \exp\left(\frac{-w(\mathbf{R}_{ij})}{kT}\right) \quad \text{Eq. 4.18}$$

with $w(\mathbf{R}_{ij})$ being the pair potential. In poor solvents $w(\mathbf{R}_{ij})$ is negative because the segments are in close proximity and the intramolecular interactions are attractive, resulting in a negative cluster integral. The binary cluster integral is usually assumed in the calculations, since a ternary cluster integral's contribution is assumed to be quite small, except in the situation of very high segmental density. In good solvents the pair potential is small because of the large separation between segments.

With all the parameters defined one can produce the expressions that are used to extrapolate from perturbed to unperturbed conditions. Substitution of Eq. 4.1 into Eq.

4.13 and subsequently Eq. 4.14 along with Eq. 4.15 into this expression provides a relationship between intrinsic viscosity and molecular weight that will permit one to find unperturbed dimensions:

$$\frac{[\eta]}{M^{1/2}} = K_q + 0.51\Phi_0 BM^{1/2} \quad \text{Eq. 4.19}$$

This is the Stockmayer-Fixman (SF) equation.⁷ A plot of the left side as a function of the square root of the molecular weight will obviously yield K_θ as the intercept from which the unperturbed dimensions can be calculated. The cluster integral can be inferred from the slope. There also exist modified Stockmayer-Fixman equations¹ that yield better results in some situations

$$\frac{[\eta]}{M^{1/2}} = K_q + 0.346\Phi_0 BM^{1/2} \quad \text{for } 0 < a_h^3 < 1.6 \quad \text{Eq. 4.20}$$

$$\frac{[\eta]}{M^{1/2}} = 1.05K_q + 0.287\Phi_0 BM^{1/2} \quad \text{for } 0 < a_h^3 < 2.5 \quad \text{Eq. 4.21}$$

These expressions become necessary when the solvent/polymer perturbation becomes larger. These deviations from the SF plot occur at high molecular weights in good solvents. In these cases z is larger and Eq. 4.13 must be modified due to the nonlinearity in the plot of α_η^3 as a function of z . In Eq. 4.20 and Eq. 4.21 the form of K_θ stays the same except for a small change in one case. Ultimately, these equations would serve the same purpose as Eq. 4.19 in the present study.

There are other equations for extrapolation techniques for random coil polymer chains - a few will be mentioned here. The first extrapolation expression in a chronological sense was the Fox-Flory-Schaeffgen equation:⁸

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_q^{2/3} + 0.858K_q^{2/3}\Phi_0 BM/[\eta] \quad \text{Eq. 4.22}$$

The problem with this form is that it leads to negative intercepts for experimental data.¹ It is also derived from the assumption that α_η is equivalent to α_{Rg} , which is not necessarily true.

Another extrapolation technique is the Kurata-Stockmayer equation⁹

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_q^{2/3} + 0.363\Phi_0 Bg(a_h)M^{2/3}/[\eta]^{1/3} \quad \text{(KS)} \quad \text{Eq. 4.23}$$

In the KS approach, graphing $[\eta]^{2/3}/M^{1/3}$ versus $M^{2/3}/[\eta]^{1/3}$ yields a first order approximation for K_θ . This first order approximation for K_θ can be substituted into the expression for $g(\alpha_\eta)$

$$g(a_h) = 8a_h^3 / (3a_h^2 + 1)^{3/2} \quad \text{Eq. 4.24}$$

by using Eq. 4.1 and Eq. 4.13. When these expressions are manipulated, $g(\alpha_\eta)$ can be rewritten in terms of intrinsic viscosity, molecular weight and K_θ (presently the first order approximation)

$$g(a_h) = 8 \frac{[\eta]}{K_q M^{1/2}} \left/ \left(3 \frac{[\eta]^{2/3}}{K_q^{2/3} M^{1/3}} + 1 \right)^{3/2} \right. \quad \text{Eq. 4.25}$$

Employing this expression for $g(\alpha_\eta)$, the data is further analyzed by plotting $[\eta]^{2/3}/M^{1/3}$ versus $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$ and a better value for K_θ is determined. This form has been shown to work well for vinyl polymers, except when high molecular weights and good solvents are used. As mentioned before, in this latter regime the perturbation is high due to the higher excluded volume effects and deviations occur because these extrapolation techniques are for lower levels of perturbation. Other extrapolation equations exist,^{10,11} but they are essentially similar to those given above and do not provide any further understanding for extrapolating to unperturbed dimensions. A way to correct for high molecular weights in good solvents has been proposed by Inagaki and Ptitsyn:

$$\frac{[\eta]^{4/5}}{M^{2/5}} = 0.786K_q^{4/5} + 0.454K_q^{2/15}\Phi_0^{2/3}B^{2/3}M^{1/3} \quad \text{Eq. 4.26}$$

This extrapolation technique works only for very expanded systems with much excluded volume, in other words where the SF or KS plots fail.

The above equations for chain dimensions work best for flexible polymer chains. However, for polymer systems where the exponent in Eq. 4.2 (Mark-Houwink-Sakurada equation) changes substantially, other expressions can take this behavior into account better. One of these is the Dondos-Benoit function,^{12,13} this function is derived from expressions that relate the intrinsic viscosity to density as mentioned at the onset of this chapter

$$\frac{1}{[\eta]} - \frac{1}{[\eta]_q} = \Delta r = \Delta r_\infty - \frac{A'}{M^{1/2}} = -A_2 - \frac{A'}{M^{1/2}} \quad \text{Eq. 4.27}$$

A' and A_2 (not the second virial coefficient) are constants and $\Delta\rho$ is the reduction in density of the polymer chain in solution when it goes from an unperturbed state ($[\eta]_0$) to a perturbed state ($[\eta]$). The term $\Delta\rho$ refers to the situation where the density of the perturbed state would tend towards zero. The next step is to rearrange and substitute Eq. 4.1 into Eq. 4.27

$$\frac{1}{[\eta]} = -A_2 + \frac{1}{K_q M^{1/2}} - \frac{A'}{M^{1/2}} \quad \text{Eq. 4.28}$$

Redefining some of the parameters one arrives at the final form of the Dondos-Benoit equation

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{M^{1/2}} \quad \text{Eq. 4.29}$$

where $A_1 = 1/K_0 - A'$. The slope of the plot of $1/[\eta]$ as a function of $1/M^{1/2}$ will produce K_0 if A' is negligible. This has been shown to be the case for a number of polymer systems.^{14,15} Therefore, in regions of lower molecular weight where the data may deviate from a Stockmayer-Fixman extrapolation one may apply the Dondos-Benoit equation. In conclusion, the Dondos-Benoit extrapolation can be shown to be equivalent to the SF equation when $A_2 M^{1/2} \ll A_1$, which is true at intermediate and lower molecular weights or rigid backbones.¹⁴ This inequality allows Eq. 4.29 to be evaluated by performing a series expansion and truncating after the second term to arrive at the following form

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_1} + \frac{A_2}{A_1^2} M^{1/2} \quad \text{Eq. 4.30}$$

Comparing this expression with Eq. 4.19, one readily sees that $1/A_1 = K_0$ and $A_2/A_1^2 = 0.51\Phi_0 B$ and the Stockmayer-Fixman equation is reproduced.

4.4. SIZE EXCLUSION CHROMATOGRAPHY

The next two sections will deal with the instrumentation and calculation of molecular weights from size exclusion chromatography (SEC). There will also be a discussion of how the extrapolation techniques described above can be used on the chromatograms generated by fractionating a polymer using gel permeation chromatography (GPC).

Size exclusion chromatography fractionates macromolecules by “size” in solution. The critical parameter is called the hydrodynamic volume. The larger the hydrodynamic volume or macromolecular size the less likely that the polymer chain will permeate the pores in the packing material of the GPC column. A view of the packing material is given in Figure 4.1. There are pores in this packing material that allow molecules of a small enough size to penetrate this area due to a chemical potential difference and reside there until Brownian motion brings them back out of the pores. Polymer chains that are too large will not permeate these void areas and hence remain in the mobile phase. This action translates into an earlier exit from the column and shorter elution time. Consequently, the larger molecules exit the column first and the smallest macromolecules elute last. All of these statements rest on the assumption that there are only steric effects¹⁶ and that there are no specific interactions of the polymers with the packing material.

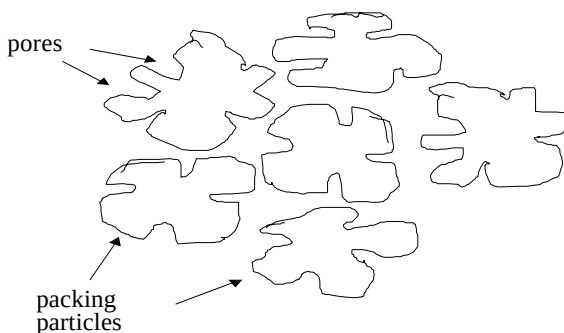


Figure 4.1. Packing material for GPC column

Since a detailed study of the chromatography aspects of SEC is beyond the scope of this work, only a few comments regarding this area will be made here. The columns used in GPC are typically packed with polystyrene-divinylbenzene beads. With the incorporation of divinylbenzene the material becomes an insoluble and intractable network. The beads are generally between 5 and 20 micrometers in diameter, with the smaller size allowing a better separation at the expense of higher backpressure. The nominal pore sizes that are reported on the columns refer to the contour length of the largest polymer molecule that can move into the pores. Detection is also necessary to

quantitate the eluent. Typically, a differential refractometer is used as a concentration detector. Figure 4.2 shows a typical concentration chromatogram. The detector signal, in

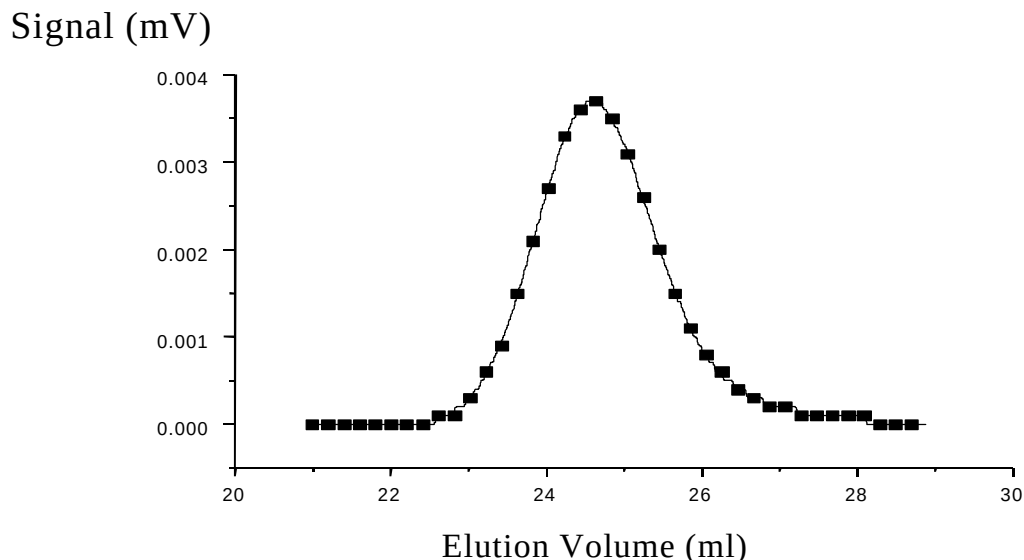


Figure 4.2. Raw data for isotactic polystyrene, received from Iller²⁹

this case mV, is integrated across the whole chromatogram. When this value is used along with the known weight of polymer that is injected on the column, a value for the weight of each slice can be calculated

$$w_i = W \frac{h_i}{\sum_i h_i} \quad \text{Eq. 4.31}$$

W is the known amount of material and h_i is the instantaneous signal height. An assumption in this calculation is that the refractive index increment is identical for all molecular species that are eluted from the column. This assumption may be incorrect when molecular weights are small and the endgroup can begin to play a significant role.¹⁷

Calibration in SEC generally is accomplished by running narrow molecular weight standards through the system. The molecular weight of these standards, typically atactic polystyrene, is determined separately, usually by light scattering, and therefore the elution volume at the signal peak value is recorded. Subsequently, a calibration graph of log molecular weight versus elution volume is created, see Figure 4.3, which is specific for the column set, solvent and operating temperature conditions.

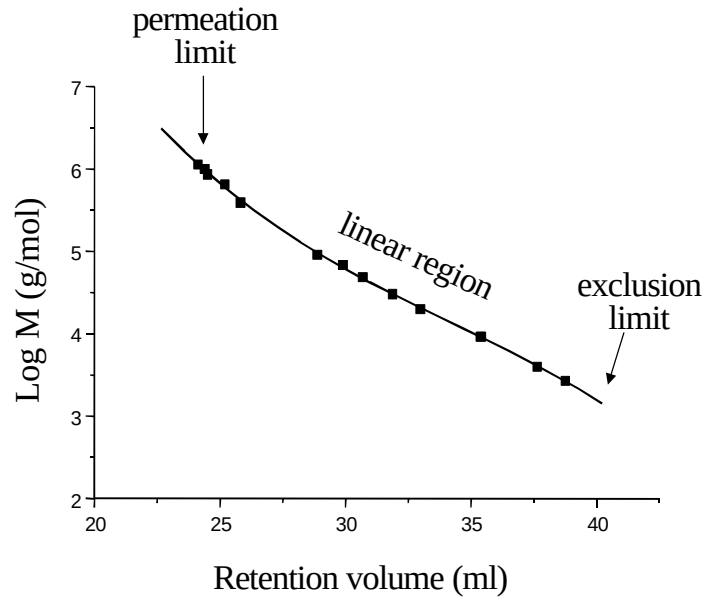


Figure 4.3: Calibration curve for polystyrene standards using 500 Å, 10³ Å, 10⁴ Å, 10⁵ Å Permangel[®] columns

In general one finds three distinct regions of the calibration curve as depicted in Figure 4.3. At the high molecular weight end the pores are too small for these species and therefore above a particular molecular size they all elute at the same volume. There is a linear middle region over which the system has its highest sensitivity for separating different size polymer molecules. Finally, at low molecular weights all of the chains can permeate all the pores and there is no discrimination among polymer chain sizes below a critical size. The best separation occurs in the linear region of the calibration curve.

Using a concentration detector it is possible to obtain absolute molecular weights only for polymer chains that are chemically identical to the standards. The reason for this is related to the nature of the fractionation mechanism in size exclusion chromatography, which is by hydrodynamic volume. The hydrodynamic volume can be written^{18,19}

$$V_{h,i} = [\eta]_i M_i \quad \text{Eq. 4.32}$$

The intrinsic viscosity can be replaced with Eq. 4.1 and Eq. 4.13 to show that the hydrodynamic volume depends on K_0 and the coil expansion factor

$$\text{Eq. 4.33}$$

$$V_{h,i} = K_q M_i^{3/2} a_h^3$$

K_θ and α_η^3 assume different values for different polymers and different temperatures in the same solvent. Therefore, it is unlikely that V_h would be identical for a polymer under investigation and for the standards used in calibrating the columns. Accordingly, only relative molecular weights can be determined when K_θ and α_η^3 differ between standard and the polymer being characterized. The discrepancy between relative and absolute molecular weights will result in incorrect evaluation of molecular weights, sometimes in very large error. A universal calibration procedure was developed to avoid such difficulties.

4.4.1. UNIVERSAL CALIBRATION

The development of universal calibration for SEC by Benoit and others¹⁸ eliminated the problem of being able to calculate only relative molecular weights. The starting point of universal calibration is Eq. 4.32. Hence, if the intrinsic viscosity can be measured for each eluting fraction then one may obtain absolute molecular weights. The original workers in this area^{20,21} collected the fractions that eluted from the GPC columns and performed intrinsic viscosity measurements on these fractions. This procedure is time-consuming and tedious, but was necessary for calculating absolute molecular weights. Others used the Mark-Houwink coefficients, Eq. 4.2, of the polymer under investigation to compute the intrinsic viscosity. However, these coefficients are not always known and can vary as a function of the molecular weight, solvent, temperature and other variables.^{22,23} Consequently, these corrections can only be applied for well known systems.

A big improvement for making size exclusion chromatography/universal calibration accessible as a common analytical tool was the differential viscometer.^{24,25} The differential viscometer, see Figure 4.4, is the fluid analog of a wheatstone bridge. In this device there are very narrow bore capillary columns that cause pressure drops. The advantage of the differential viscometer (described in detail below) is that it is a multiple

capillary bridge and eliminates some of the problems, such as geometry of the capillary or small flow fluctuations, caused by single capillary viscometers. The calculation of the

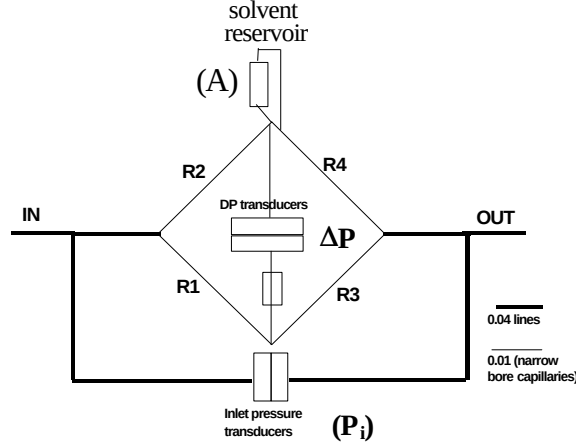


Figure 4.4: Viscotek Model 100 Differential Viscometer

intrinsic viscosity proceeds by first equating the two measured quantities, inlet pressure (P_i) and differential pressure (ΔP), with pressure drops across the bridge:²⁶

$$\frac{\Delta P}{P_i} = \frac{P_2 - P_1}{P_i} \quad \text{Eq. 4.34}$$

P_1 is the pressure drop across the capillary R_4 and P_2 across capillary R_3 . The GPC eluent flows through equal resistance capillaries R_1 and R_3 , therefore $P_i = 2P_2$ and Eq. 4.34 becomes

$$\frac{\Delta P}{P_i} = \frac{1}{2} \left(1 - \frac{P_1}{P_2} \right) \quad \text{Eq. 4.35}$$

Using Poiseuille's law for flow for R_3 and R_4 , the ratio of P_1/P_2 can be formed

$$\frac{P_1}{P_2} = \frac{\eta_0 Q_1}{\eta Q_2} \quad \text{Eq. 4.36}$$

where η_0 is the viscosity of the solvent that is contained in reservoir A. This solvent highly dilutes the incoming GPC eluent and thus practically pure solvent flows through R_4 . The solution viscosity is represented by η . The flow rates through each of these capillaries is given by Q , where Q_1 is the flow through R_2 and R_4 and Q_2 is the flow rate through R_1 and R_3 . The ratio of the flow rates is inversely proportional to the viscosities of the liquids that traverse these capillaries

$$\frac{Q_1}{Q_2} = \frac{h + h}{h + h_0} \quad \text{Eq. 4.37}$$

therefore $P_1/P_2 = 2\eta_0/\eta + \eta_0$. Substituting this expression into Eq. 4.35, the ratio of the differential pressure to the inlet pressure becomes

$$\frac{\Delta P}{P_i} = \frac{1}{2} \left(\frac{h - h_0}{h + h_0} \right) \quad \text{Eq. 4.38}$$

The specific viscosity, η_{sp} , is defined as $(\eta - \eta_0)/\eta_0$, substituting this ratio into the above equation

$$\frac{\Delta P}{P_i} = \frac{h_{sp}}{2h_{sp} + 4} \quad \text{Eq. 4.39}$$

Rearranging, one forms an expression for the specific viscosity in terms of the differential and inlet pressures

$$h_{sp} = \frac{4\Delta P}{P_i - 2\Delta P} \quad \text{Eq. 4.40}$$

The last step for ascertaining how the differential viscometer measures intrinsic viscosities is by applying one of the definitions of $[\eta]$

$$[\eta] = \lim_{c \rightarrow 0} \frac{h_{sp}}{C} \quad \text{Eq. 4.41}$$

After being fractionated by the SEC columns the concentration of the solute is very small, about 1/20 th of the original concentration. Therefore, this expression is valid when SEC columns are the fractionating mechanism. Nonetheless, the concentration has to be measured, this task is performed by the concentration detector. In most cases this detector will be a differential refractometer.

Similar to the relative molecular weight calibration described above, in the universal calibration case standards of known molecular weight are injected onto the columns. The signals from the concentration detector and differential viscometer are collected. The concentration of the standard injected on the column is known and the intrinsic viscosity of each standard can be evaluated by integrating the differential viscometer response. A typical universal calibration curve is depicted in Figure 4.5.

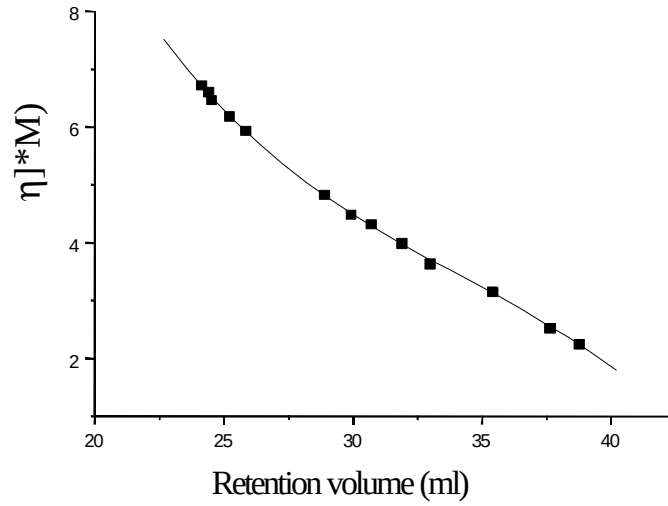


Figure 4.5: Universal calibration curve for PS standards

Molecular weight determination then continues by noting each retention volume and intrinsic viscosity. Then Eq. 4.32 can be utilized to ascertain the molecular weight of that particular slice. Each increment is assumed to be monodisperse and the following equations can be applied for generating the various average molecular weights

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum h_i}{\sum \frac{h_i}{M_i}} \quad \text{Eq. 4.42}$$

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum h_i M_i}{\sum h_i} \quad \text{Eq. 4.43}$$

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum h_i M_i^2}{\sum h_i M_i} \quad \text{Eq. 4.44}$$

h_i is the signal from the concentration detector. The subscripts on the molecular weights denote the number, weight and z average molecular weights, consequently

With the availability of a differential viscometer and the possibility of detecting instantaneous intrinsic viscosities at their corresponding molecular weights one can estimate unperturbed chain dimensions through some of the extrapolation techniques covered earlier.²⁷ In those extrapolation techniques, such as the Stockmayer-Fixman, Dondos-Benoit, Kurata-Stockmayer, etc., monodisperse fractions were assumed. The eluent from the GPC will have fractions with a narrow molecular weight distribution. A

Stockmayer-Fixman plot created in this manner using SEC is demonstrated by Figure 4.6, where the sample was atactic polystyrene and had a broad distribution of molecular weights. If samples with narrow molecular weight distributions are not present then there are other techniques that may be applied;²⁸ however, this is not a problem when using SEC, therefore these correction measures are not necessary.

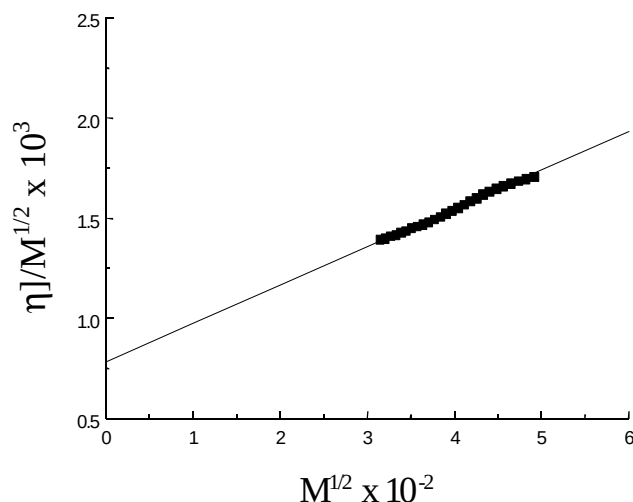


Figure 4.6: Stockmayer-Fixman plot of atactic PS

4.5. EXPERIMENTAL

The SEC system used was a Waters GPC/ALC 150C equipped with a differential refractometer as the concentration sensitive detector. A differential viscometer was connected in parallel with the differential refractometer. In the first set of samples, which were narrow molecular weight fractions of isotactic polystyrene, the injection, pump and column compartments were maintained at 30⁰ C. The columns used were 500 Å, 10³ Å, 10⁴ Å, 10⁵ Å Permagel[®] columns. The flow rate was set at 1.5 ml/min, injection volumes were typically 100 µl. For this first set of samples the standards along with most of the samples had concentrations of 1 mg/ml. Standards were purchased from Polysciences Inc.

For the remaining samples investigated in this work, the injection and column compartments were maintained at 60⁰ C, while the pump compartment was 50⁰ C. The columns used in separating the engineering thermoplastics were 10² Å, 10³ Å, 10⁴ Å HT[®]

columns from Waters Associates. This column set allowed better molecular weight determination for lower molecular weights than the first set of columns. The flow rate was set at 1 ml/min, injection volumes were typically 200 μ l. For this set of samples most of the samples had concentrations of 2-4 mg/ml. The columns employed for the atactic PS samples were 10^3 Å and 10^4 Å HT[®] columns. The other chromatographic conditions were the same as those for the engineering thermoplastics.

The chromatographs were analyzed with TriSEC GPC software from Viscotek Corp. The analyzed data was used for the extrapolations. Due to detection limits and their influence on the specific viscosity and concentration and subsequently on the intrinsic viscosity and molecular weight the whole data set was not used for extrapolation. In determining the data that was suitable for extrapolation two criterion were maintained. The first one was that if part of the data deviated abruptly from linearity in a direction not predicted by theory it was discarded. This stipulation was usually fairly obvious to determine and the larger deviations were a result of detection limits. The other criterion was that the concentration was above 0.0002 g/dl. This last criterion incorporated the whole chromatogram; however, as stated earlier if there were large deviations from linearity these data points were omitted. In all cases the main part of the chromatographic peak was incorporated in the data set.

4.6. STOCKMAYER-FIXMAN EXTRAPOLATION

The unperturbed dimensions for isotactic polystyrene (tacticity ranged from 92-97% isotactic triads²⁹) were determined employing a Stockmayer-Fixman extrapolation from a set of well fractionated samples,²⁹ shown in Figure 4.7. A few of these fractions were used for the Stockmayer-Fixman extrapolation involving the GPC and differential viscometer, see Figure 4.8. The resultant values of the intercept, which is equal to K_θ as seen from Eq. 4.19, are 0.159, 0.144 and 0.168 ml/g for the 10^6 , 5×10^5 and 6×10^5 Dalton fractions respectively. These results are all well within the literature values for K_θ , 0.10 to 0.17.^{30,31} This large range for the unperturbed dimensions for isotactic polystyrene could arise from different levels of isotacticity, where the larger values correspond to a

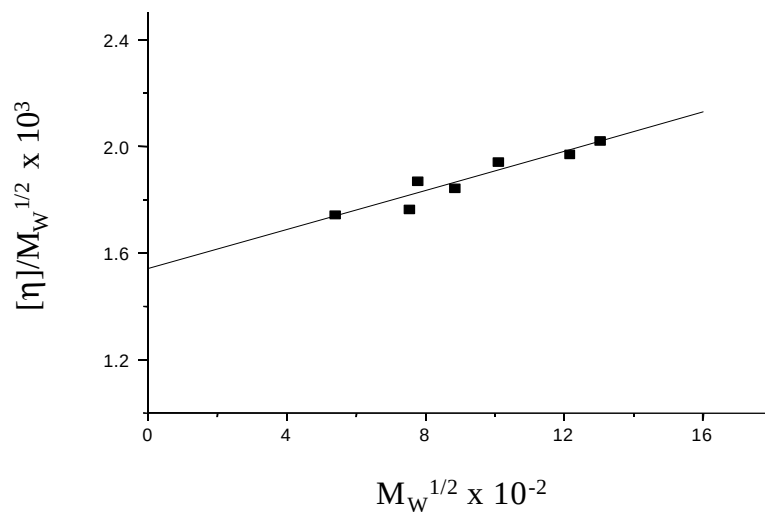


Figure 4.7: Stockmayer-Fixman extrapolation of iso-PS using narrow molecular weight fractions²⁹

higher degree of isotacticity. The intercepts of Figure 4.7 and Figure 4.8 should coincide since all of these fractions have roughly the same amount of isotactic nature. The intercepts are in good agreement.

The Stockmayer-Fixman plot using the GPC/DV method does demonstrate some deviation to expected linearity. As explained above this behavior arises when high

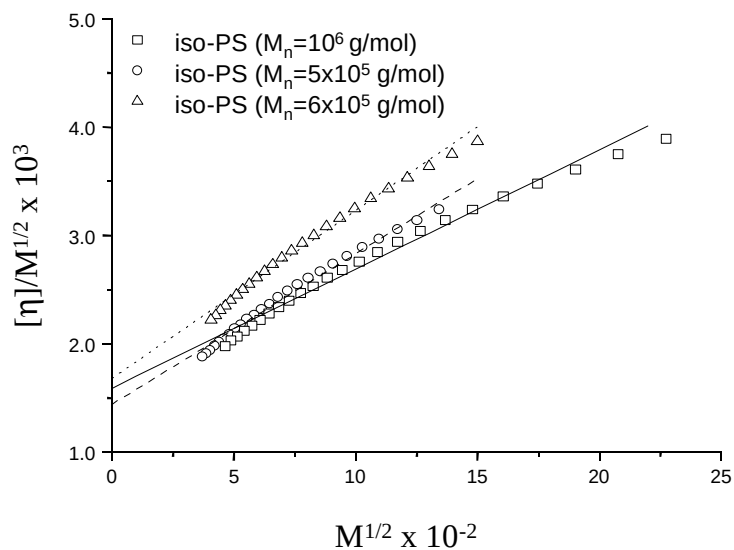


Figure 4.8. Stockmayer-Fixman plot of three polystyrene fractions using GPC/DV technique

molecular weight polymers are in good solvents and is due to the large level of perturbation. In this situation Eq. 4.14 does not account for the higher level of perturbation. In this occasion it is better to employ the Inagaki-Ptitsyn equation, see Eq. 4.26. In Figure 4.9 it is clear that the data do not deviate as much from the extrapolated

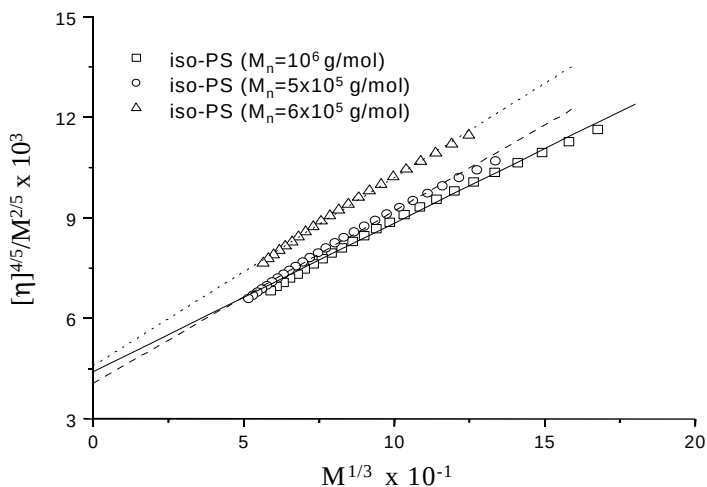


Figure 4.9. Inagaki-Ptitsyn plot for iso-PS fractions of indicated molecular weight

line as they do with the Stockmayer-Fixman plot. It should also be noted that the molecular weight range over which both extrapolations are performed are similar. The Inagaki-Ptitsyn equation's range is specifically confined to high molecular weight polymers in good solvents. Thus, if some lower molecular weight fractions are in the data set a deviation will also become evident. In order to calculate K_θ for an Inagaki-Ptitsyn plot recall that the intercept is equal to $0.786(K_\theta)^{4/5}$. Therefore, K_θ for these fractions are 0.153, 0.139 and 0.161 ml/g for the 10^6 , 5×10^5 and 6×10^5 fractions respectively. Once again these values demonstrate that the method works well, and that the uncertainty in the method is less than ten percent.

Another unperturbed dimension that was discussed earlier is the characteristic ratio. This quantity allows one to assess the rigidity or stiffness of a chain and to compare these values among a variety of polymer systems. The calculation for a vinylic polymer, such as polystyrene, is straightforward since there is no ambiguity concerning the length of a bond. In order to determine C , Eq. 4.3 and Eq. 4.6 will be applied. The

common value for the viscosity constant is 2.5×10^{23} (cgs) and $l = 1.54 \times 10^{-8}$ cm. Substituting in these quantities along with the average for K_θ (0.15 ± 0.01) from all extrapolations, C is 16 ± 1 for these polystyrene samples. As stated earlier this is within the boundaries of the literature values, 12-17 for iso-PS at 30° C.

The GPC/DV method gave results that match literature values for iso-PS high molecular weight fractions. To further gauge the validity of this method, atactic polystyrene samples with a broader distribution were investigated. The GPC instrumentation was the second one described in the experimental section, where the columns were heated to 60° C. In this study different concentrations and injection volumes were employed to note any concentration sensitivity to this technique.

Three different samples, with two different concentrations and injection volumes, were used. The parameter of concern is the total amount of material injected on the column, since the volume over which the sample eluted was identical, this distinction gave three different values for the total amount of material injected. The samples were differentiated by their concentrations and injection volumes. Figure 4.10 shows the results

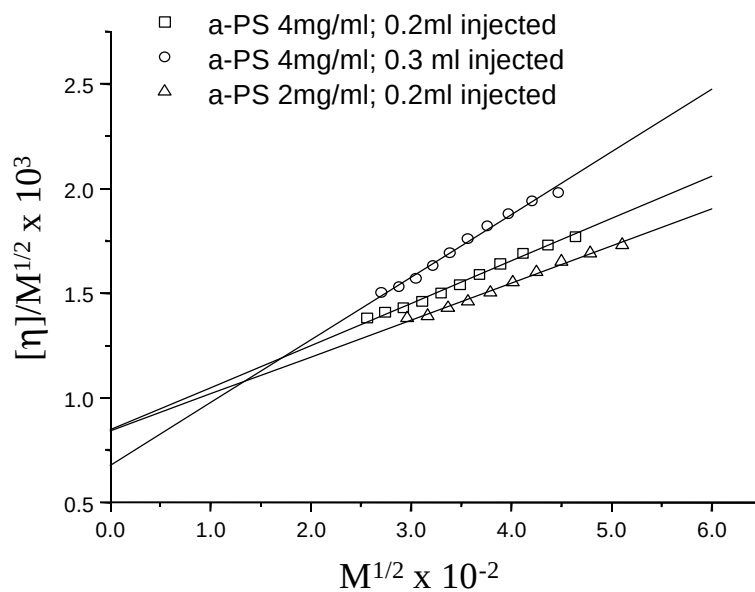


Figure 4.10. Stockmayer-Fixman plot for a-PS $M_n=10^5$

of the Stockmayer-Fixman extrapolation for atactic polystyrene. There existed some dependence of the extrapolation on the amount of material that was separated, this tendency was evident from the different slopes. This behavior indicated that the second term of the Stockmayer-Fixman equation, see Eq. 4.19, which depends on the binary cluster integral was not independent of concentration under these conditions. However, the typical range of material used for GPC analysis resided between these curves. The average value for K_θ is 0.079 ± 0.009 ml/g, resulting in C of 10 ± 1 , which is the same as an interpolated value for a-PS of 9.8 at 60°C .³²

Using an Inagaki-Ptitsyn extrapolation for this lower molecular weight polystyrene sample in n-methylpyrrolidone was not justified, because the molecular weight was not high enough. Furthermore, the SF extrapolation did not deviate for the molecular weight range investigated. Another analysis technique that was also investigated is the Dondos-Benoit extrapolation, see Eq. 4.29. This method works best for even lower molecular weight species (less than 10^5 g/mol) or rigid units. However it will be evaluated for its usefulness for higher molecular weight systems. The slopes in Figure 4.11 are similar in all cases with the less concentrated sample showing the largest slope (recall that for the DB method $K_\theta=1/\text{slope}$). Despite this, the K_θ values are all

Table 4.1. Results of extrapolation techniques for a-PS

	K_θ (mg/ml) from Stockmayer-Fixman extrapolation	K_θ (mg/ml) from Dondos- Benoit extrapolation
4 mg/ml with 0.3 ml injection	0.068	0.108
4 mg/ml with 0.2 ml injection	0.085	0.107
2 mg/ml with 0.2 ml injection	0.084	0.099

higher for the DB method, than in the Stockmayer-Fixman extrapolation, see Table 4.1. The reason for the discrepancy is that the DB technique fails when the intrinsic viscosity

becomes large. In this case there is only a small change in the left side of Eq. 4.27. Nonetheless, the DB technique works well with lower molecular weight species.

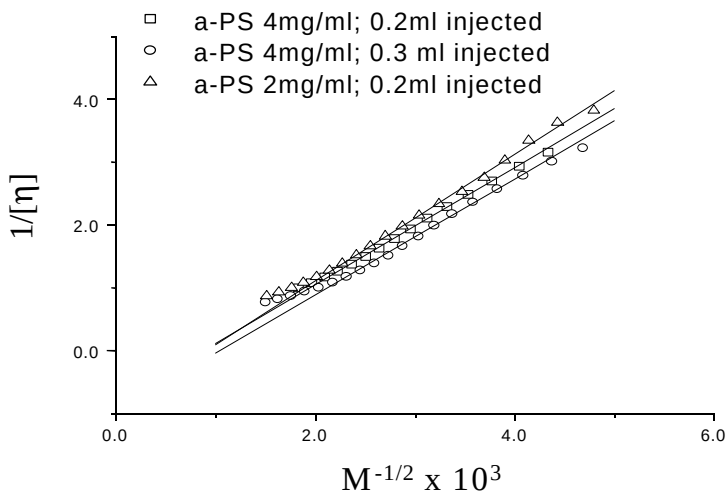


Figure 4.11. Dondos-Benoit plot for a-PS

Various engineering thermoplastics have also been investigated by this GPC/DV method. Most of these thermoplastics have a number average molecular weight in the neighborhood of 20000 daltons, although the exact value varies somewhat. This M_n allows these materials to be above a critical molecular weight for entanglements, but is not too high to inhibit processing conditions. Regardless of the exact value of these molecular weights, an analysis of their unperturbed conditions can be conducted. The only change in the calculation for the characteristic ratio will be in the calculation of the length of a “repeat unit”. In this vein the concept of virtual bonds is used. The structures of these engineering thermoplastics are shown in Figure 4.12. The results of BFPMPPO-SO₂ for the Stockmayer-Fixman plot and Dondos-Benoit extrapolation are shown as examples in Figure 4.13 and Figure 4.14 respectively. The calculated values for K_θ are 0.114 ml/g and 0.117 ml/g for the SF and DB methods, respectively. The other samples tested also confirmed that the extrapolation techniques used are valid because the K_θ values agree well among the different extrapolation methods.

The complete set of values for the remaining engineering thermoplastics are represented in Table 4.2. The manner in which the characteristic ratio is calculated will

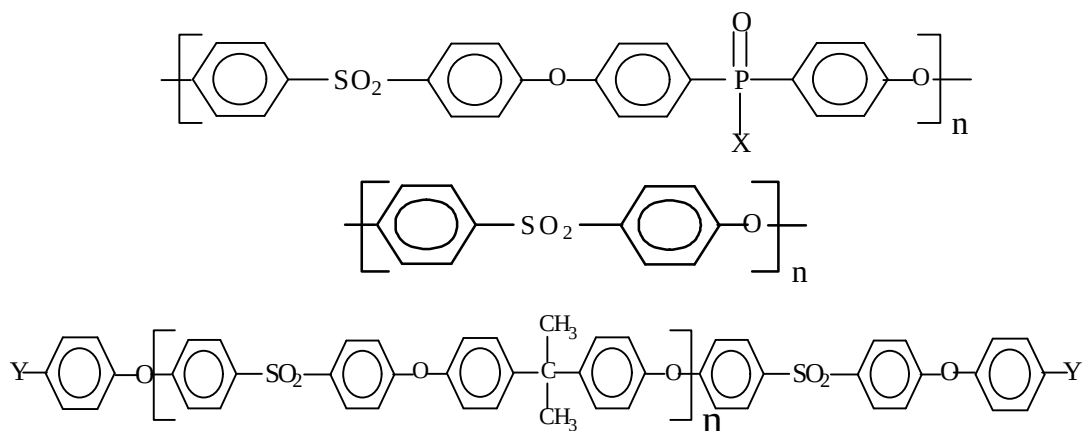


Figure 4.12. Engineering thermoplastics, where X= methyl (BFPMPPO- SO_2), x=phenyl (BFPPO- SO_2). Middle structure is Vitrex (ICI) and bottom polymer is PES- NH_2 , where Y= NH_2 .

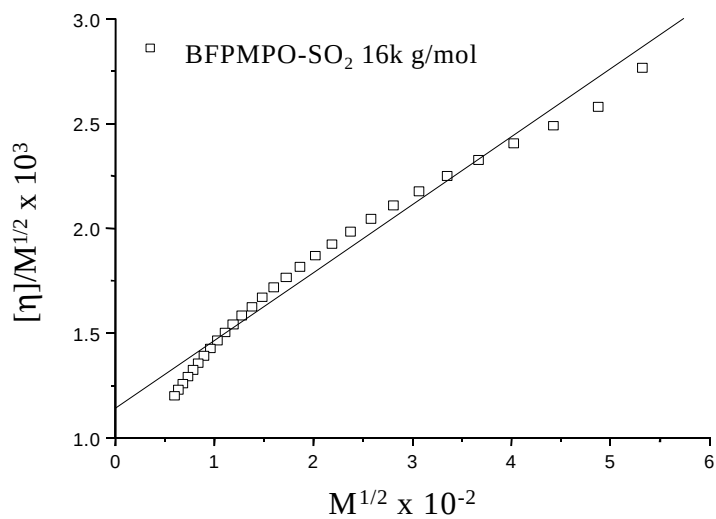


Figure 4.13. SF plot of BFPMPPO- SO_2

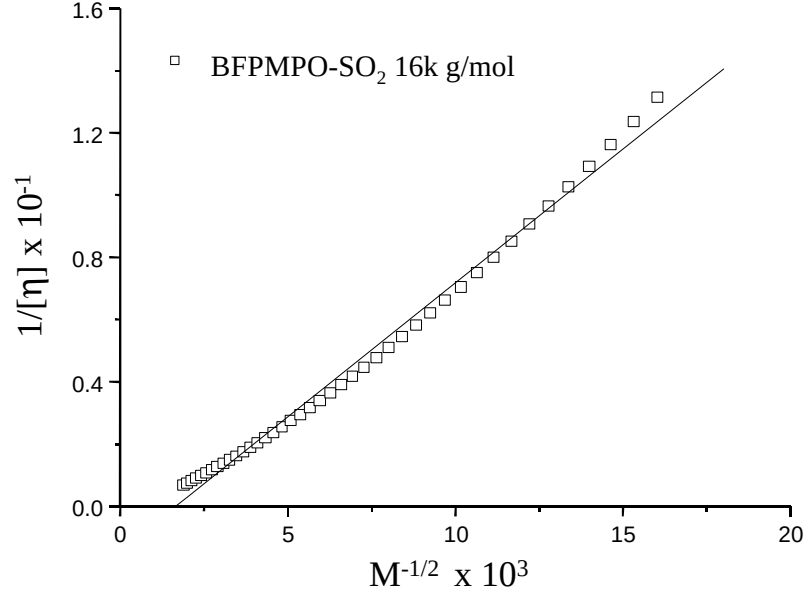


Figure 4.14. DB plot for BFPMPPO-SO₂

Table 4.2: Calculated values of unperturbed dimensions using GPC/DV method

	K_θ (ml/g)	l_{avg} (Å)	M_{seg} (g/mol)	C
BFPMPPO-SO ₂	0.116	5.85	116	2.0±0.2
BFPPO-SO ₂	0.123	5.85	131	2.4±0.2
PES-NH ₂	0.151	5.79	110	2.3±0.2
Victrax (ICI)	0.238	5.82	116	3.3±0.3
Ultem 1000(GE)	0.166			

be shown explicitly by the following:

$$C_\infty = \frac{\langle R^2 \rangle_0}{nl_0^2}$$

$$\text{with } \frac{\langle R^2 \rangle_0}{M} = \left(\frac{K_q}{\Phi_0} \right)^{2/3} \quad \text{and} \quad M = nM_{\text{seg}}$$

$$\frac{\langle R^2 \rangle_0}{n} = M_{seg} \left(\frac{K_q}{\Phi_0} \right)^{2/3} \quad \text{and finally}$$

$$\frac{\langle R^2 \rangle_0}{nl_0^2} = C_\infty = \frac{M_{seg} \left(\frac{K_q}{\Phi_0} \right)^{2/3}}{l_0^2}$$

Entering the values from Table 4.2 into these formulas, one can readily determine the characteristic ratio when a viscosity constant of 2.5×10^{23} (cgs) is used.¹ There is some debate as to what this viscosity constant should be.³³⁻³⁵ However, the value of 2.5×10^{23} is a common value employed when working with flexible polymers. The average lengths of the repeat units are ascertained from virtual bond lengths. The length of the O-C₆H₄-S virtual bond is 5.82 Å,³⁶ the length of the O-C₆H₄-P virtual bond is a little longer at 5.88 Å due to the difference in electronegativity between sulfur and phosphorus.

Table 4.2 illustrates the effect of structure on the flexibility of the polymer chains. Although the error in these values is between 5-10%, a trend is evident from the C values. Namely, that the phosphorus group causes the chain to become more flexible than does the sulfur group. Furthermore, the heavier phenyl group also creates a slightly more rigid chain than the methyl group. There could be two reasons for this latter phenomenon. The phenyl group is simply bulkier and forces the chain to be more expanded, along with the fact that the hydrogen atoms from the neighboring phenyl groups cause some steric repulsion forcing the phenyl group to assume out of the plane orientations and forcing the phosphorus – oxygen bond angle to be a little larger.

4.7. SUMMARY

Before concluding this chapter, it is important to point out the various aspects that have been discussed. Extrapolation techniques have been demonstrated for several thermoplastics that allow calculation of unperturbed chain dimensions from data obtained in the non-theta state. This was accomplished with SEC data. Many literature examples have previously shown that this perturbed state can be used for solution data extrapolation. This has rarely been performed with SEC experimental results. Stockmayer-Fixman, Inagaki-Ptitsyn or Dondos-Benoit plots do not operate over all ranges of perturbation, but rather they cover different regimes. But the discussed method

for creating extrapolation plots from gel permeation chromatography/differential viscometry data in this thesis has been successful. This method has been shown to work well compared to literature results for unperturbed dimensions for isotactic polystyrene and atactic polystyrene. In addition, K_0 and characteristic ratio values for a variety of engineering thermoplastics have been measured using this GPC/DV technique.

Finally, the importance of unperturbed dimensions in developing structure-property relationships should be noted in the context of later chapters. It has been explained earlier that if the polymer is dissolved in “itself” (i.e. a melt or glass) then the coil expansion factor becomes unity, see Eq. 4.11, and the polymer is in an unperturbed state. Therefore, unperturbed dimensions have been used to some extent as parameters in chain folding, adsorption and adhesion theories.²³ The work which follows is in part devoted to studying the effect of chain flexibility, which is inversely proportional to the characteristic ratio, on physical aging and molecular relaxation phenomenon. Hence, the elucidation of unperturbed dimensions was vital to ascertaining a correlation between these parameters.

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CHAPTER 5. PHYSICAL AGING IN ENGINEERING THERMOPLASTICS: ULTEM 1000, VICTREX, UDEL AND TWO NOVEL POLY(ARYLENE ETHER PHOSPHINE OXIDE SULFONES)

5.1. INTRODUCTION

Engineering thermoplastics have a wide range of applications, such as in the aerospace and electronics areas. In these systems these materials can be subjected to high temperatures and loads. High temperature stability is a necessity for these situations. Furthermore, due to the exposure to high temperatures that may approach the glass transition temperature of these materials, physical aging may be accelerated. The physical aging characteristics of bisphenol A polycarbonate, a common engineering thermoplastic, have been widely investigated in the literature.¹⁻⁷ Polycarbonate at ambient conditions can show signs of physical aging, which is more than 100⁰ C below its glass transition temperature. Other materials investigated herein and in the literature show signs of physical aging at temperatures far removed from the glass transition.⁸ An important practical question concerns the relation between physical aging and a coincident reduction in overall mechanical performance. Physical aging can cause a diminution of some of the mechanical properties of the material and ultimately might result in failure of the polymer system.⁹

Physical aging of many other glassy materials have been investigated, for example studies on polystyrene,^{10 -12} poly(methyl methacrylate),^{13 -15} etc. There have been some studies involving polyimides¹⁶ and polysulfones.¹⁷ These polymers are all totally amorphous glassy systems. Some physical aging investigations have examined semi-crystalline polymers,^{18 -25} thermosets,^{26 -29} composite structures^{30,31} and toughened thermosetting systems.^{32,33} The materials explored in the present chapter were used in their neat, unfilled totally amorphous state.

Earlier it was accepted that the rates of physical aging, be it either mechanical, volume or enthalpy, as expressed by Eq. 5.1- Eq. 5.3, were affected by transitions below

$$m = \frac{d \log a_{te}}{d \log t_e} \quad \text{Eq. 5.1}$$

$$b = -\frac{dV/V_0}{d \log t_e} \quad \text{Eq. 5.2}$$

$$d_H = \frac{d\Delta H_a}{d \log t_e} \quad \text{Eq. 5.3}$$

the T_g . This effect was manifested by a decrease in the physical aging rates as the sub-glass transition temperature was approached from higher temperatures.¹ This proposal that there is a decrease in the physical aging rate caused by the presence of secondary relaxations is not universally accepted.¹¹ Nonetheless, a better explanation of the decrease observed has not been forthcoming. This study examines this factual decrease as being a function of the rigidity of the backbone of the polymer chain. A rigid backbone will preclude many types of sub- T_g motions such as local crankshaft or bending motions that could result in higher rates of volume or mechanical aging. The characteristic ratio, C_∞ , is a good indicator of backbone rigidity, recall that a more rigid backbone produces a higher characteristic ratio.

$$C_\infty = \frac{\langle R^2 \rangle_0}{nl_0^2} = \left(\frac{1 - \cos \phi}{1 + \cos \phi} \right) \left(\frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} \right) \quad \text{Eq. 5.4}$$

The characteristic ratio and the background for its meaning are discussed in fuller length in the previous chapter. There it is also explained how the characteristic ratio can be determined using a common analytical tool, size exclusion chromatography. Ultimately, a higher characteristic ratio is related to the valence bond angles and rotational potential energies that exist in the backbone (expressed in the last two terms of Eq. 5.4). The only uncertainty in determining C_∞ for non-vinyl polymers is the calculation of l_0 .

Although the characteristic ratio may not be uniquely and explicitly incorporated in a relationship with the decrease in physical aging on lowering temperature, the purpose of this work is to assess if a correlation between the decrease in physical aging and the structure of engineering thermoplastics exists.

5.2. EXPERIMENTAL

5.2.1. CREEP RECOVERY

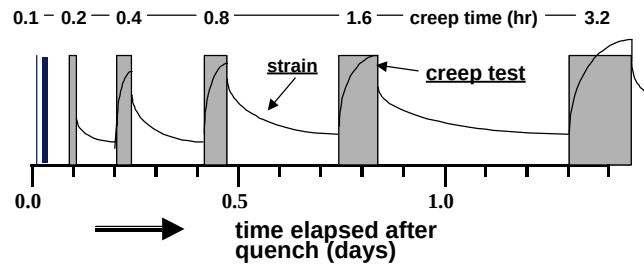
The samples for creep recovery and linear dilatometry were dried thoroughly before they were compression molded into plaques. The plaques were between 1.7-2.0 mm in thickness. Each sample's thermal history was erased before the experiment began by heating it in an oven to 15 - 18 °C above its glass transition for 5 minutes. Repeated trials under the same conditions demonstrated that this time was long enough to erase the thermal history of these samples.

The creep recovery experiments were conducted using a TA Instruments 983 DMA. These tests were conducted under isothermal conditions from 226°C to -60°C with a nitrogen purge of 30-40 ml/min. The isothermal control for these tests was ± 0.01 °C in a temperature range from the highest temperatures to near ambient conditions, sub-ambient control was ± 0.05 °C. Sample length was approximately 21 mm. The applied load was controlled such that the percent strain was below 0.1% in all but a few cases, but high enough for a strong signal.

The load program for this creep recovery test is illustrated in Figure 5.1. The initial load time was 0.05 hr (not shown), after application of this load the sample was allowed to recover for ten times longer. The second load step, as shown in Figure 5.1 (0.1 hr) was twice as long as the foregoing creep time with a corresponding recovery time that was 10 times the load time. This sequence was continued for 6-8 creep tests. The evaluation of the shift factors and master curves of the resultant creep compliance curves was performed using the TA superpositioning software. The recovery times were set for their length to insure that at the end of the recovery period the material had returned to its original state. This point was important to assure that physical aging was independent of the test. This was found to be the case for low stress levels.²⁹

5.2.2. VOLUME RECOVERY

Linear dilatometry was conducted using a Netzsch Dil 402, in which the isothermal length changes were monitored using a LVDT, see Figure 5.2. Rejuvenation of the samples was performed in an identical manner as the creep samples. The samples



- measure creep compliance
- age samples isothermally
- intermittently apply creep test

Figure 5.1. Load program for creep tests

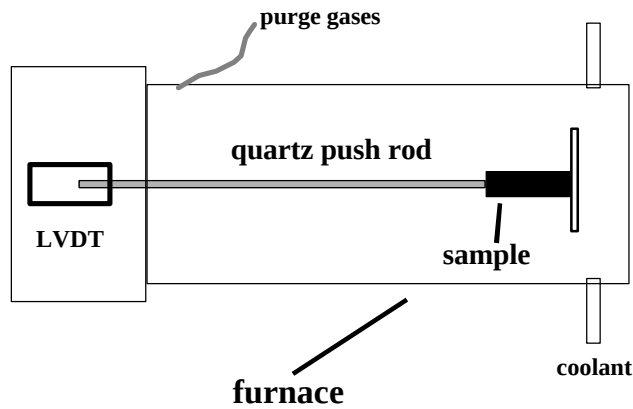


Figure 5.2. Diagram of the Dilatometer apparatus

were held under isothermal conditions with a control of $\pm 0.05^\circ\text{C}$ and a nitrogen purge of 25 ml/min. Sample dimensions varied from 18mm to 21mm in length. The volume relaxation rates were calculated using the expression given in Eq. 5.2, assuming that the materials were isotropic, and the length versus log time data. A simple proof of the correspondence between the length and volume relaxation rates is given in chapter 6.

This expression holds true only for isotropic materials. These samples were viewed as isotropic since the thickness of the samples used here are near 2 mm and any orientation is relieved during the rejuvenation step.

5.2.3. ENTHALPY RELAXATION

Differential scanning calorimetry experiments were done on a Perkin Elmer DSC-7. The DSC cell was calibrated with indium and zinc standards. A temperature profile for these tests was followed that would erase the thermal history, age and subsequently assess the aging of the sample. Initially the sample was heated to 30⁰C above its T_g and held for 10 minutes, then immediately quenched at 100⁰ C/min to the aging temperature. The sample was maintained at this temperature for the duration of the aging test and then quenched to 100⁰C. Following this point the sample was heated at 10⁰C/min until 50⁰ C above the glass transition temperature. The last steps involved quenching the sample to 100⁰C and running a second heat ramp under the same conditions as the first heat ramp. A visual description of the temperature program is afforded by Figure 5.3. The resultant data was converted to heat capacity for each experiment. The difference between the two runs was integrated and resulted in a heat of enthalpy due to aging for a given aging time and temperature. These values were used in Eq. 5.3 to assess the enthalpic aging displacement, δ_H .

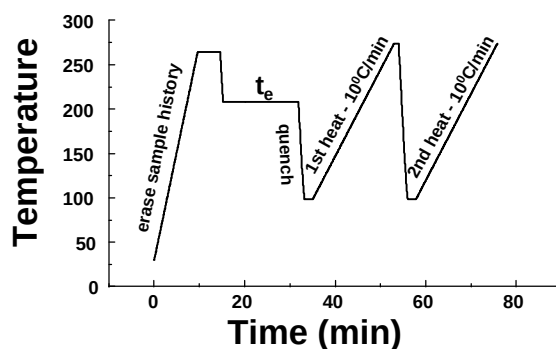


Figure 5.3. Temperature program for enthalpy recovery

5.3. RESULTS AND DISCUSSION

5.3.1. MATERIALS

The materials used in this work are either commercially available, Udel[®] (Amoco Chemicals), Victrex[®] (ICI) and Ultem[®] (G.E. Plastics) or have been synthesized in an earlier study, BFPPO-SO₂ and BFMPO-SO₂.³⁷ The structures of these polymers are

Table 5.1: Physical properties of investigated polymers

	M _n (g/mol)	T _g (° C)	C	β _{peak, 1Hz} (° C)
Udel	25000	186	2.1	-100
Victrex	20000	222	3.3	-100
Ultem	20000	217		90
BFPPO-SO ₂	18000	236	2.4	-100
BFPMPO-SO ₂	16000	232	2.0	-100

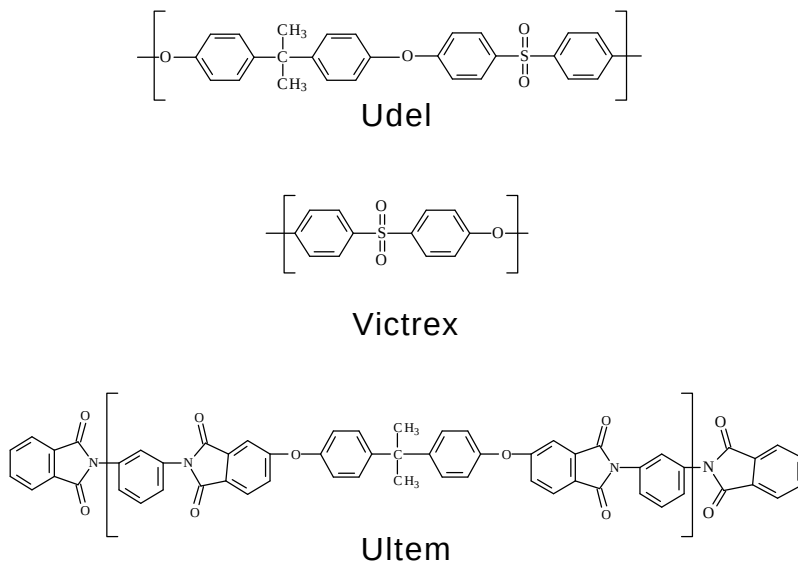
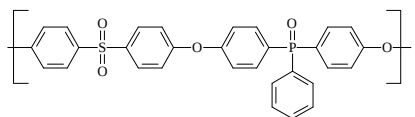
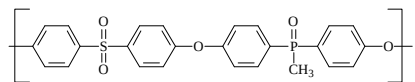


Figure 5.4. Three engineering thermoplastics used in this study



BFPPO-SO₂



BFPMPPO-SO₂

Figure 5.5. Phosphine oxide containing polymers, their synthesis is described elsewhere³⁷

given in Figure 5.4 and Figure 5.5. Some of the important physical parameters of these polymers are summarized in Table 5.1.

5.3.2. CREEP RECOVERY

Creep compliance curves from these aging tests are shown in Figure 5.6. The master curve generated from this set of creep curves is illustrated in Figure 5.7, the arrow indicates the relative magnitudes of horizontal and vertical shifting. The master curve illustrates that the curves overlay well. Therefore, the curvature of the creep compliance curves is consistent with aging rescaling of time. This is an indication that time-aging time superpositioning is justified. The other support for this procedure is that the log shift factor plot, note Figure 5.8, is continuous and smooth, which is a strong indication that superpositioning can be performed with this data. Determination of the shift rate factor from the creep compliance curves reveals a temperature dependence for all the materials, see Figure 5.9 and Figure 5.10. The major point of interest in this thesis was to examine the data for any structural relationship to the “onset” of the decrease in this shift rate factor

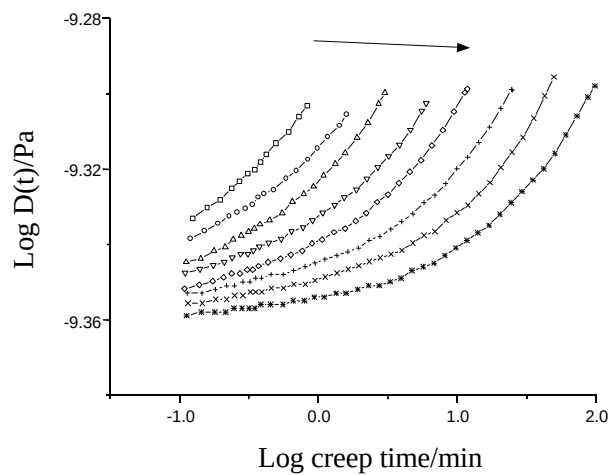


Figure 5.6. Creep curves from sequential creep test, Victrex[®] at 190⁰ C

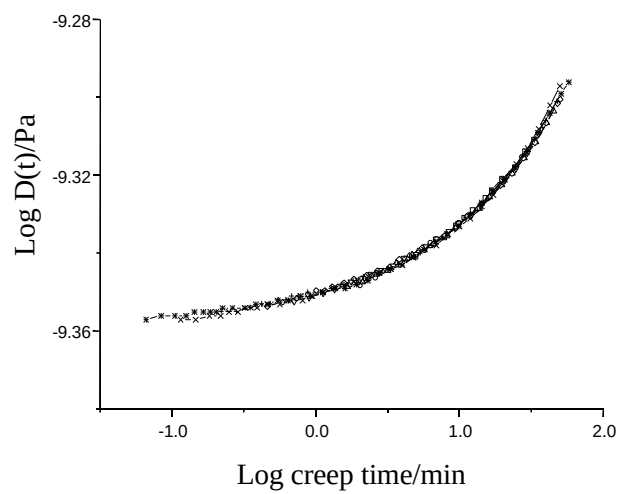


Figure 5.7. Master curve for Victrex[®] at 190⁰ C, $t_e=534$ min is reference

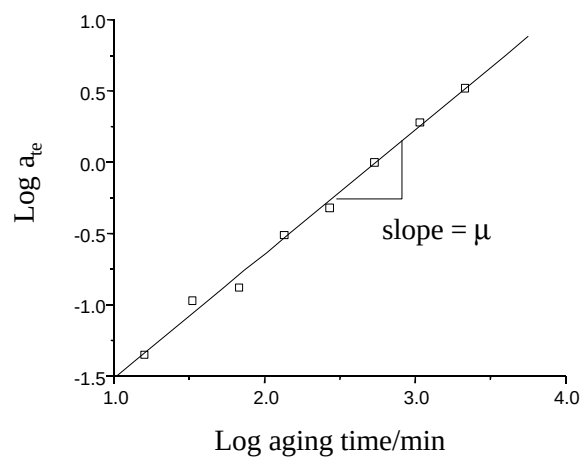


Figure 5.8. Log shift factor plot for Victrex[®] at 190⁰ C.

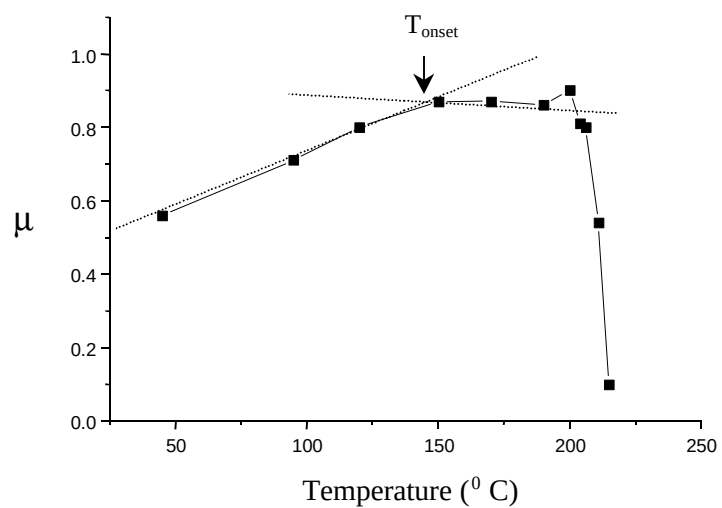


Figure 5.9. Temperature dependence of μ for Victrex[®]

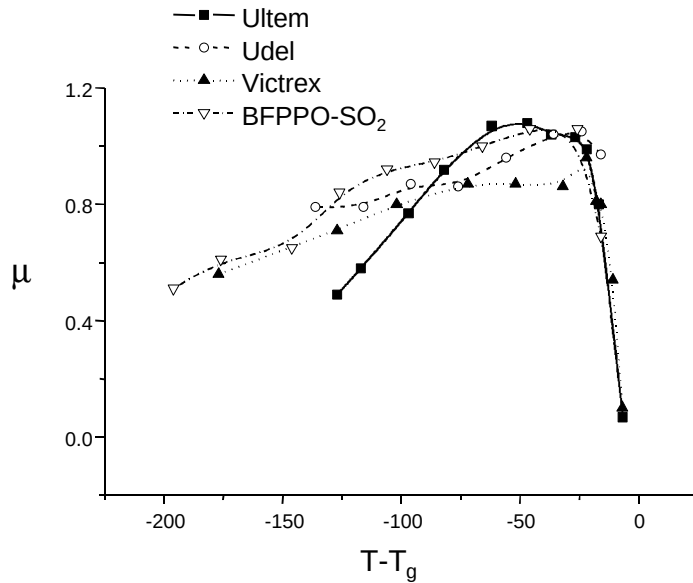


Figure 5.10. μ behavior for Victrex[®], Udel[®], BFPPO-SO₂ and Ultem[®]

with decreasing temperature. Taking the plateau region (low slope) at high temperatures as one reference line and the second as the initial decrease after this region, one can determine the onset point by the intersection of these two lines, see Figure 5.9.

Another scheme for calculating the temperature coefficient of the physical aging rate is by measuring the slopes for these four materials at temperatures below the maximum μ values. From this analysis it is apparent that Ultem[®] behaves quite differently than the other three materials. Ultem[®] has a secondary dispersion that extends higher than 100⁰ C depending upon the thermal history of the sample. The fall in Ultem's[®] physical aging rate on cooling could be related to the reduction of the secondary transition due to the decreased mobility caused by aging. This explanation would support Struik's early ideas about the nature of the drop in the physical aging rate.¹ The other three materials do not have a secondary dispersion until near -100⁰ C, which means that their physical aging rate may remain at a relatively high level until those temperatures. This behavior is not known since the experiments did not extend to these low temperatures. Nonetheless, there could remain other justifications for the physical aging tendencies.

Since creep data was collected at various temperatures for the same aging time, it is possible to perform time-temperature superposition. These results may lend some understanding to any structure-aging behavior properties. This analysis follows the usual time-temperature superpositioning procedure,^{34,35} except that the samples have been aged below their glass transition temperature for a specific time. The master curve is depicted in Figure 5.11. Extracting the shift factors, Figure 5.12, and converting these to a normalized configurational entropy through the relationships described in Chapter 2 and

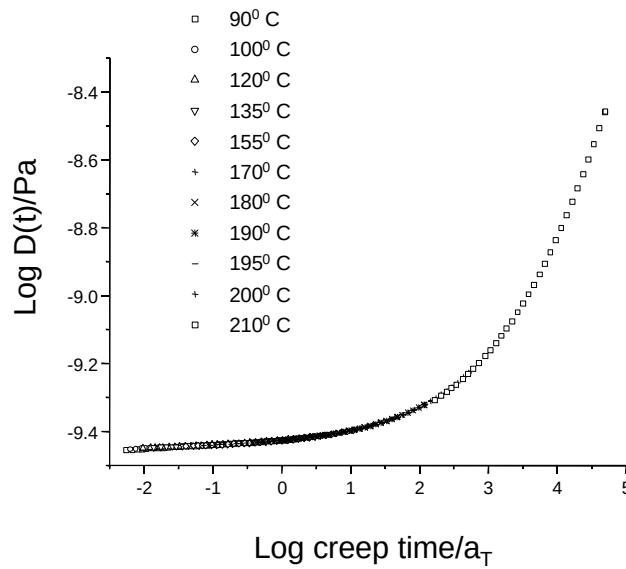


Figure 5.11. Master curve of Ultem[®] at $t_e=534$ min, 180^0 C= T_{ref}

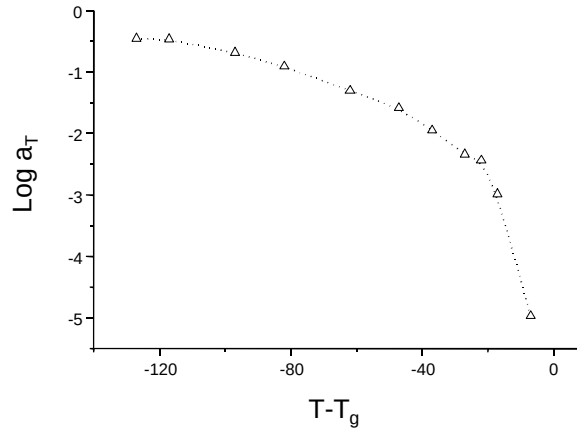


Figure 5.12. Log shift factor plot from master curve in Figure 5.11

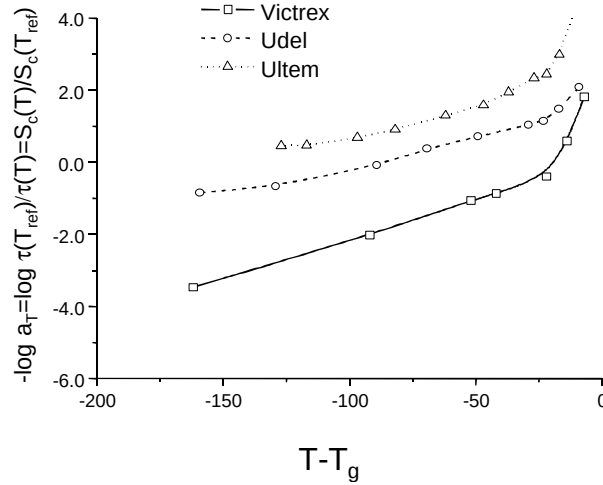


Figure 5.13. Normalized configurational entropy

$-\log a_T = \log [\tau(T_{ref})/\tau(T)]$, Figure 5.13 is produced. Two distinct regions in Figure 5.13 appear, as have been observed previously.³⁶ The high slope portion of the curves at higher temperatures is reminiscent of the equilibrium liquidus line for entropy, volume or enthalpy shown in Chapter 2. At lower temperatures the data deviates from the quasi-equilibrium line, and its slope is much smaller. This part may be described as a non-equilibrium region or the glassy state. The position, referenced to the glass transition, of

the transition zone between equilibrium and non-equilibrium behavior is suspected to be dependent on chain flexibility or rigidity according to results of Lee et al.³⁵ There may be some structural related basis for this transition zone since the slopes are different for the three materials shown in Figure 5.13. However, more data is needed to make a definitive conclusion about any such correlation.

5.3.3. VOLUME RECOVERY

The change in length of the phosphorus containing polymer is shown as a function of aging time in Figure 5.14. The original length of the sample in this plot was 18 mm, therefore the change of length as evident from Figure 5.14 is small. The linear dilatometry results were used to calculate the volumetric aging rates using Eq. 5.2. The volumetric physical aging rates are given in Figure 5.15 for BFPPO-SO₂. In this graph the technique for estimating the temperature where there is a large change in the volumetric physical aging rate is given by the dotted lines. The results for all the polymers studied are given in Figure 5.16. There are two regions of behavior for these materials. At higher temperatures the rate of volume relaxation is high, at the lower

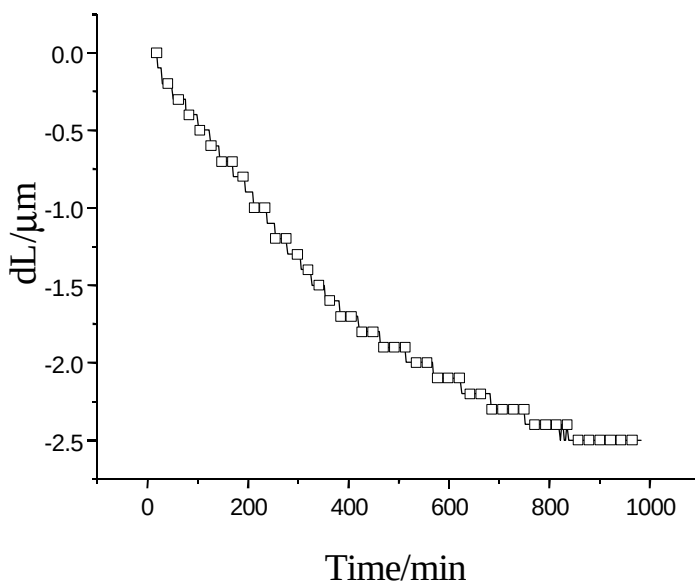


Figure 5.14. Length changes as function of time for BFPPO-SO₂ at 147⁰ C

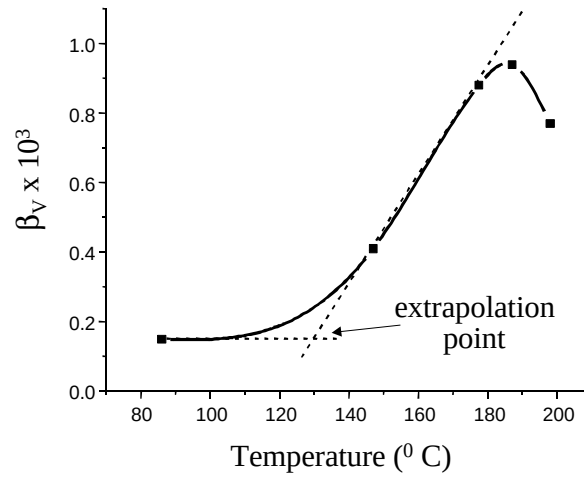


Figure 5.15. Volume relaxation rate for BFPPO-SO₂

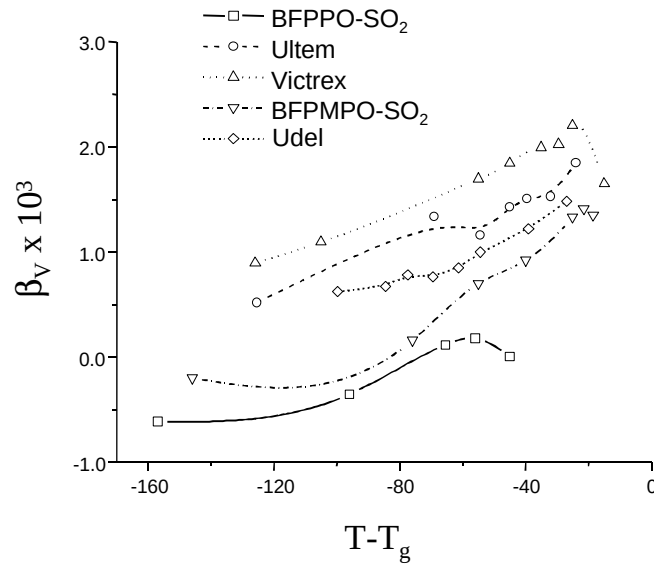


Figure 5.16. Volume relaxation rates for the indicated materials

temperatures the rates have diminished due to lower thermal energy. Any trend in the data which might indicate the influence of fundamental chain parameters is not obvious at the present time.

5.3.4. ENTHALPY RELAXATION

The schematic enthalpy path that a glassy sample would follow during its first thermal scan after being quenched and then aged is given by the short dashed line in

Figure 5.17. One notices that there is an overshoot of the glass transition before the material has acquired enough thermal energy to overcome the mobility constraints developed during the aging period. When an idealized heat flow or enthalpy is converted to the heat capacity using the heating rate and weight of the sample, Figure 5.18 is the result. If the material had a single relaxation time then a steeply rising function in the heat capacity would be witnessed. Generally, for polymers there is a broad distribution of relaxation times. Hence, the observed behavior will deviate from the ideal line. Due to the overshoot addressed previously, the aged sample does not follow the steeply

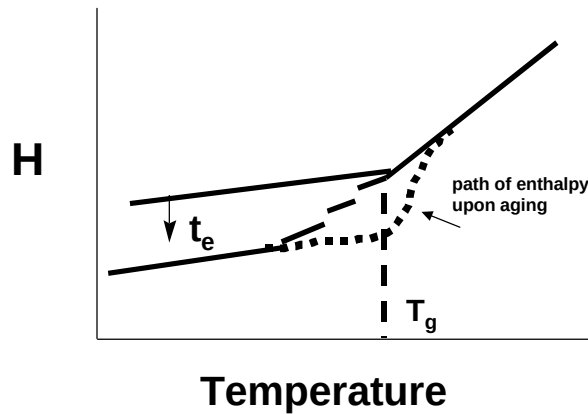


Figure 5.17. Schematic enthalpy path during 1st scan due to aging

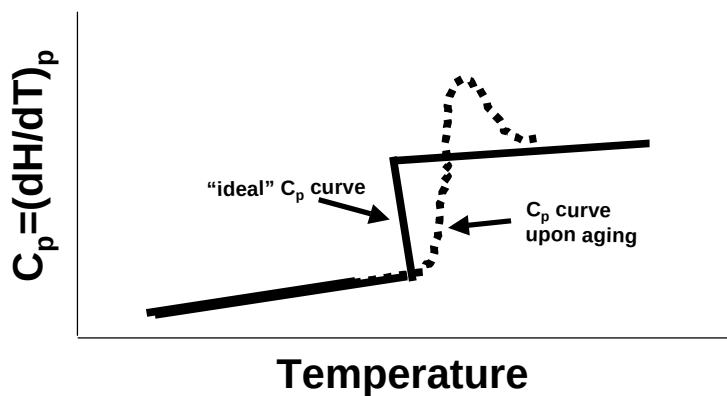


Figure 5.18. Schematic heat capacity changes due to aging

rising curve, but it exhibits a peak indicative of enthalpic recovery. The height and location of this peak depends on both the aging time (as seen in Figure 5.19) and aging temperature. As Figure 5.19 summarizes, at this particular aging temperature the longer the aging times the greater the peak magnitude and temperature.

One aging parameter that can be determined from these enthalpic aging studies is the excess enthalpy that is gained upon aging the sample at a constant temperature. This quantity is the area between the first and second heating scans after the sample has been aged. Figure 5.20 depicts such behavior. The lighter cross-hatched area subtracted from the darker cross-hatched area denotes the excess enthalpy recovered during the aging process. When the area is integrated for various aging times and temperatures a plot such as Figure 5.21 may be established. The various regions of Figure 5.21 can be described with the aid of the enthalpy – temperature plot, refer to Figure 5.17. The slope at the lower aging times and temperatures can be calculated and is equal to the enthalpic aging rate, Eq. 5.3. This rate denotes the rate at which enthalpy is attempting to relax to the equilibrium line in the glassy state. However, for some of the temperatures and aging times in Figure 5.21 there is zero slope, which indicates the attainment of equilibrium (or close to it in the case that there are some forbidden configurations in the glassy state). Equilibrium can be approached only at aging temperatures close to the glass transition temperature in finite times, because at these temperatures the quenched non-equilibrium structural state and equilibrium state are close to each other.

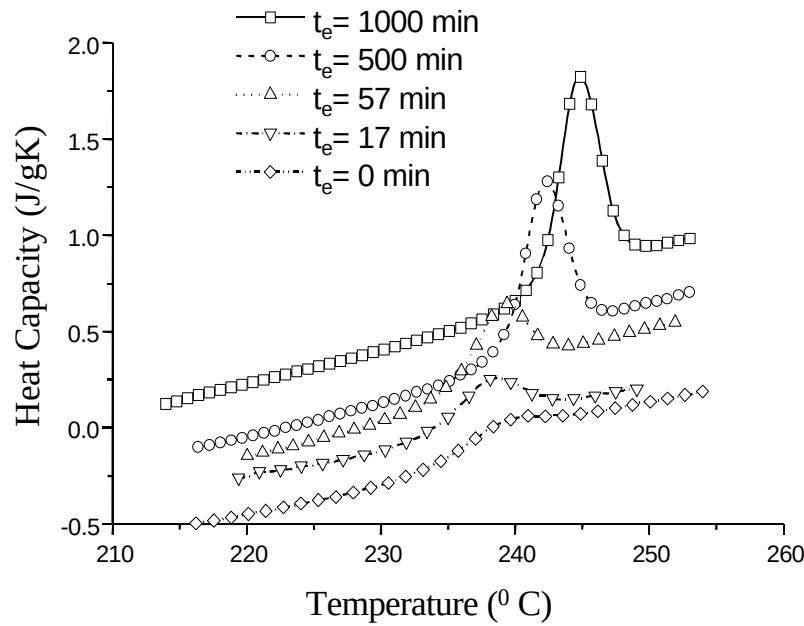


Figure 5.19. Enthalpy peaks as function of aging time for BFPPPO-SO₂ at 218.6° C

There is more mobility for possible recovery mechanisms at temperatures near the T_g . Moreover, the total recoverable excess enthalpy decreases as the glass transition temperature is approached. This can be symbolized by the decrease in the distance between the quenched state and equilibrium state in Figure 5.17. An explanation for such behavior originates in the relaxation time distribution, where at the higher temperatures some of the short relaxation times will not contribute to the physical aging processes. Figure 5.22 gives the plateau enthalpy as a function of temperature for the three materials

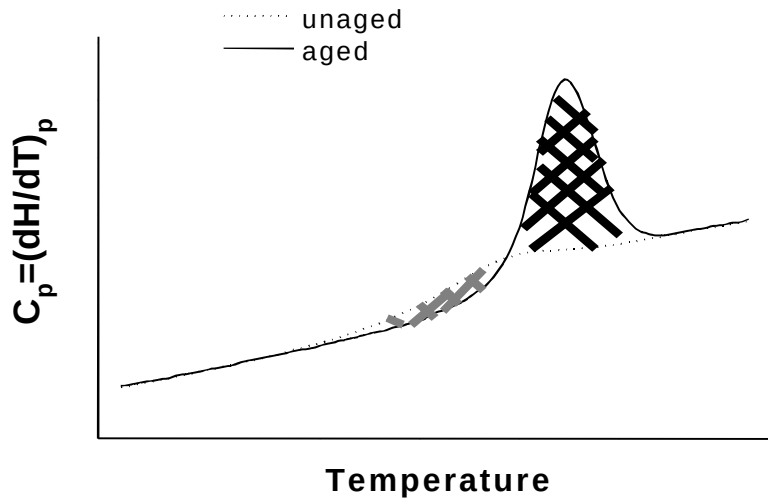


Figure 5.20. Calculation of ΔH_a for Victrex® at 217° C

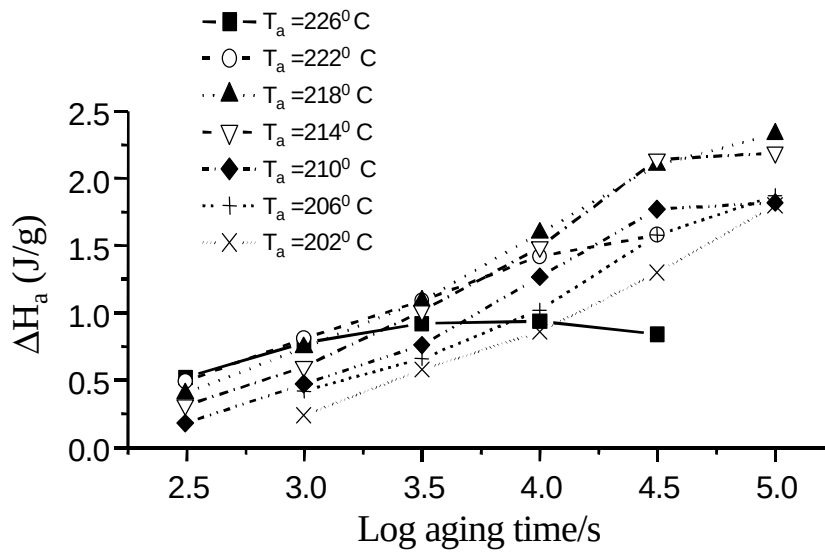


Figure 5.21. ΔH_a as a function of temperature and aging time for BFPPO-SO₂

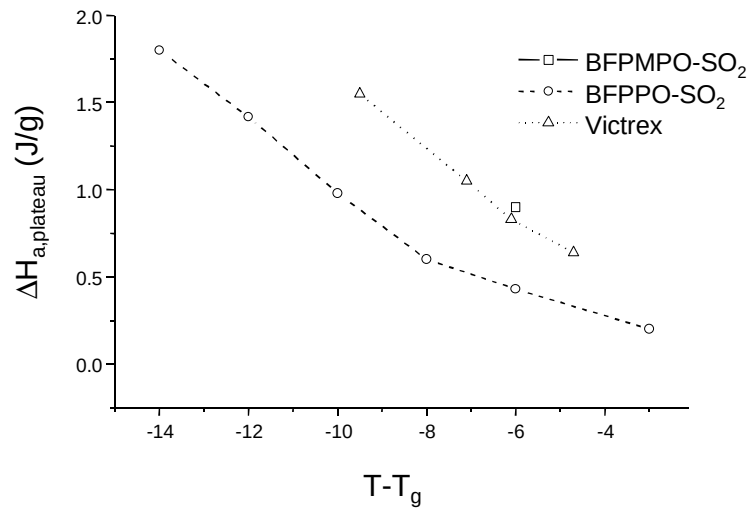


Figure 5.22. Plateau ΔH_a versus temperature for the indicated materials

studied here. In this data it is apparent that BFPPO-SO₂ has an equilibrium state closer to that of the quenched state than the other polymers because of the lower excess enthalpy values at any $T-T_g$ value compared to the other materials. It should be mentioned again that the molecular weights are similar for these materials and that they all exhibit behavior that indicates that entanglements are present.³⁷

The slopes of the lines in the first region of Figure 5.21 were determined and represented in Figure 5.23 for the materials. The behavior is similar at temperatures close to the T_g . However, below $T-T_g = -20^\circ\text{C}$ the curves differ. This trend is similar for this set of materials to its creep behavior where the curves close to the glass transition temperature all follow a similar curve, see Figure 5.10. This observation reiterates that close to their T_g these polymers age similarly. However, the volumetric recovery curves do not follow the same pattern, see Figure 5.16.

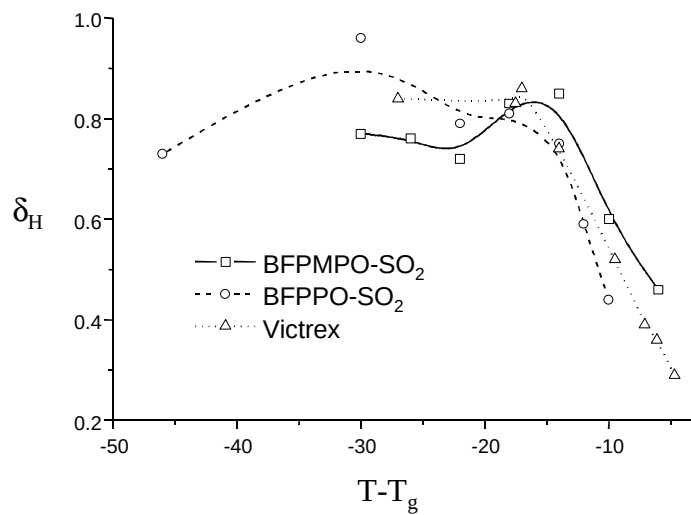


Figure 5.23. Summary of the enthalpy relaxation rate for these materials

5.4. SUMMARY

This study has shown that there are some significant differences in the mechanical physical aging behavior for the thermoplastics examined. Notably, Ultem[®]'s physical aging rate decreases rapidly on lowering the temperature near the point where the secondary dispersion has a maximum in a dynamic mechanical scan at 1 Hz and $1^\circ\text{C}/\text{min}$ heating rate. The other systems have relatively high physical aging rates at this temperature and correspondingly have secondary transitions far below this temperature range. The volume recovery data showed some differences, but a general conclusion could not be reached for this group of materials.

The materials examined in enthalpy relaxation experiments showed that at high temperatures the physical aging rate curves all follow the same trend, but deviated when

the temperature was lowered. Interestingly, BFPPO-SO₂ has lower excess enthalpy plateau values than the other two materials, even though all of the materials underwent an identical quench cycle. Although the other phosphine oxide containing polymer, BFPMPPO-SO₂, does not follow this behavior, it is noted that BFPPO-SO₂ has a pendant phenyl group on the phosphorus. This additional phenyl group may restrict the number of attainable conformations in the glassy state more so than the other two polymers, which have phenyl groups only in the backbone.

In examining this particular set of materials, no relationship between the aging behavior and fundamental chain parameters has been found. However, using data from the literature, where polymers with a broader range of C have been examined, there seems to be some dependence, at least from creep recovery results, of the decrease in the physical aging rate when lowering temperature on the characteristic ratio, see Figure 5.24.

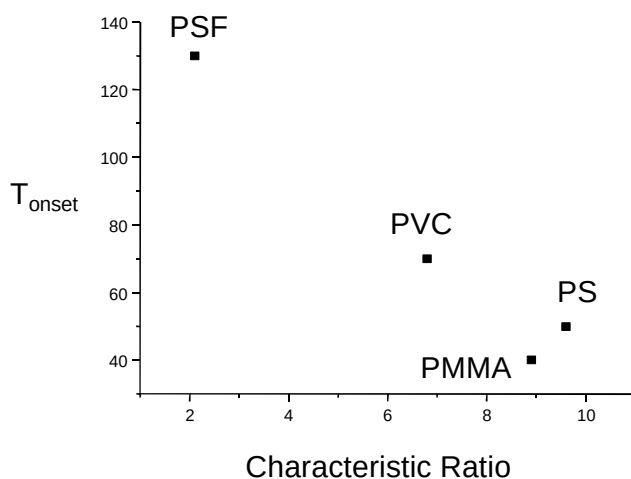


Figure 5.24. Relationship between various polymer's physical aging properties and fundamental chain parameters

(The onset temperature determination is described in the creep recovery section.) Figure 5.24 has C values that range from 2 to 10, while for the set of materials in this present

study the range was only 2.0 to 3.3. In light of this fact, there remains a possibility for a relationship between C and physical aging.

5.5. REFERENCES

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Chapter 6. ENDGROUP EFFECT ON PHYSICAL AGING AND RELAXATION PHENOMENON FOR POLY(ETHER SULFONES)

6.1. INTRODUCTION

"Endgroups" refer to the terminal substituents that exist at the end of a polymer chain and which may influence polymer properties. Some of these contributions may be related to functionality for curing or the ability to react into a network. Improved combustion resistance due to non-flammable endgroups can be a purpose for desiring certain endgroups. Endgroups can also affect the glass transition temperature and mechanical aging. Improved service lifetime because of a more thermally stable endgroup can also play a role in deciding if a particular endgroup will be added.¹ Many times the endgroup of a polymer may be quite different than the remainder of the chain, which could cause the endcap to be incompatible with the polymer resulting in the formation of a second phase. However, this behavior has not been detected in this series of poly(ether sulfones).

In this chapter it will be demonstrated that endgroups play a large role in some polymer properties and less so in others. For example, using different endgroups changes the density, surface tension and glass transition temperatures of polymers with identical backbone structures. This type of modification has been investigated before.²⁻³ The endgroup can play a special role, because its chemical structure may differ from the rest of the backbone. Furthermore, its degrees of freedom, or mobility, are usually quite different from those repeat units further inside the chain.^{6,7,8} However, when the molecular weight becomes large, the end effects will become negligible since their concentration is reduced. Nonetheless, for most engineering thermoplastics the desirable molecular weights are only slightly above a critical molecular weight for entanglements. In these cases, as will be elucidated in the present work, endgroups can provide an important contribution to physical and mechanical properties of polymers.

The size of the endgroup can affect polymer properties in a variety of ways. The larger the volume of the endgroup, which is generally viewed as a defect, the more

difficult it will be to arrange this endgroup into an average free volume. This process will result in a decrease in the density. Secondly, with increasing size of the endgroup the less mobile the endgroup should become, which further restricts the motion of neighboring segments on the chain. Effectively, the energy necessary to overcome this inhibition increases, which subsequently increases the glass transition temperature. This last effect is also entropic in nature - an increase in the size or rigidity of the endgroup decreases the number of ways that the chain can reconfigure itself. This reduces the entropy of the polymer chain. Since an increase in endgroup size can result in increased volume but decreased entropy, there may be competing effects in assessing various polymer properties. The increase in volume would result in lower densities and lower glass transition temperatures if one examines the physics from a free volume argument. However, if the configurational entropy decreases, then an increase in the glass transition temperature and melt viscosity would result.

The relationship of physical aging to the size of the endgroup has been assessed in an earlier study employing polycarbonate.³ In this study the researchers investigated the changes in the mechanical properties due to physical aging as a function of the endgroup size. The observed trend was that larger endgroups resulted in less mechanical property deterioration as a function of aging time. The glass transition temperatures along with the melt viscosities increased as the size of the endgroup increased; however, no density values were reported. In the present study, in addition to T_g evaluations and density determinations, creep and volume recovery properties as a function of endgroup size were ascertained.

6.2. SYNTHESIS

The commercial poly(ether sulfone) (PES) that was used as a control was Udel[®] (Amoco Chemicals). Udel[®] is a methoxy terminated poly(ether sulfone), therefore poly(ether sulfones) with varying endgroups were synthesized for this study. The monomers that were employed were bisphenol A and dichlorodiphenyl sulfone, both from Amoco Chemicals. Figure 6.1 shows the scheme for the synthesis of endcapped poly(ether sulfones), prepared via nucleophilic aromatic substitution.⁹⁻¹¹ Two different series of molecular weights were made, one set with a theoretical number average

molecular weight of 15000 g/mol and the other with a value of 25000 g/mol. These molecular weights were chosen because the lower value is below the critical molecular weight for entanglements, hence the absence of entanglements on physical aging and other polymer properties could be ascertained. The higher value is large enough for entanglements to develop, but not too high to cause processing difficulties or very low endgroup concentrations. Furthermore, this value is close to that of Udel[®], which near 28000 g/mol.

The theoretical molecular weights were obtained using the Carother's equation.¹² The controlled molecular weights were accomplished by adding a monofunctional endcap in addition to an excess of dichlorodiphenylsulfone. Once the monofunctional endcap has added to the chain, further addition reactions are not possible and the chain is effectively terminated with the monofunctional monomer. Controlled molecular weights are important when one is concerned with processing, such as extrusion, injection

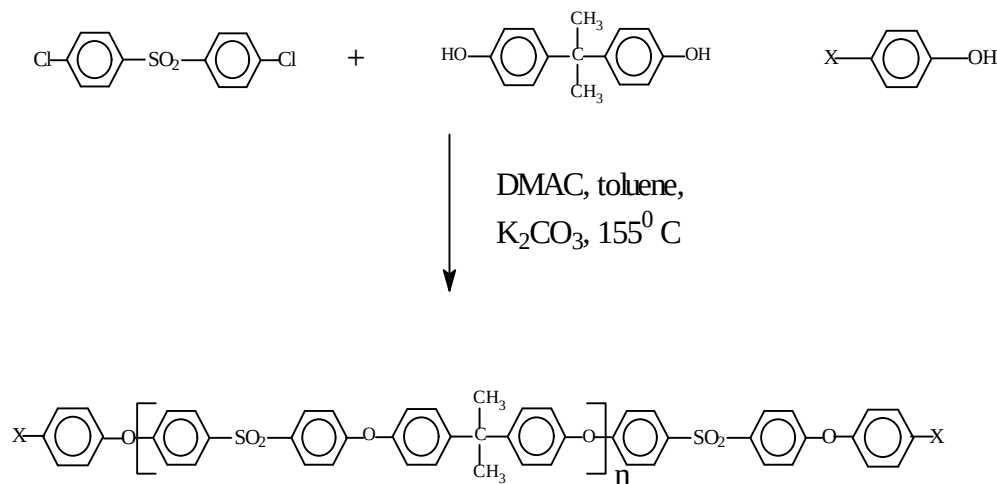


Figure 6.1. Synthesis of poly(ether sulfones) where x= H, iso-propyl phenol, NH₂, CH₃, n-propyl, t-butyl, and trityl (triphenyl methane)

molding or solvent casting. Once the entanglement molecular weight has been reached any additional molecular weight increase can cause processing difficulties without the concomitant increase in physical properties.

Some of the endgroups required purification in order to achieve monomer grade quality, which means a purity of 99.9% or better. Phenol, supplied from Aldrich, and meta-amino phenol were sublimed at 120⁰ C under vacuum. Tert-butyl phenol (Amoco),

along with p-cresol (Aldrich), n-propyl (Aldrich) and bisphenol A (Amoco) were used as received. Trityl alcohol was prepared via the Grignard reagent of bromobenzene and benzophenone. Trityl phenol was synthesized using a Friedel-Craft reaction of trityl alcohol under acidic conditions. Trityl phenol was recrystallized from ethanol and a small amount of toluene. Nuclear magnetic spectroscopy and melting point determination (275⁰ C) of trityl phenol confirmed that the product was the desired one.

The synthesis of poly(ether sulfone) followed Figure 6.1. The amount of endgroup necessary was calculated via Carother's equation for molecular weight control:

$$r = \frac{N_{A-A}}{(N_{B-B} + 2N_B)}, \quad r = \frac{(DP-1)}{(DP+1)} \quad \text{and} \quad DP = \left(\overline{M}_n / M_{monomer, avg} \right)$$

N_{A-A} =dichlorodiphenylsulfone (difunctional monomer in excess)

N_{B-B} =bisphenol A

N_B =monofunctional monomer (phenol derivative)

DP = degree of polymerization.

r = the molar excess of A-A monomer

M_n =number average molecular weight

Using this process the molecular weight can be controlled.

6.3. CHARACTERIZATION

6.3.1. MOLECULAR WEIGHT DETERMINATION

Gel permeation chromatography (GPC) (instrumentation described in Chapter 4) data indicated good reproducibility of the molecular weight. Figure 6.2 and Figure 6.3 show the GPC signals for the differential viscometer and concentration detectors, respectively. The molecular weight could also be determined in some cases from solution NMR because of the different chemical shifts of protons in the endgroups versus the chemical shift of protons in the repeat unit. All NMR tests on the poly(ether sulfone) have been performed on a Varian Unity 400 MHz nuclear magnetic spectrometer in deuterated chloroform.

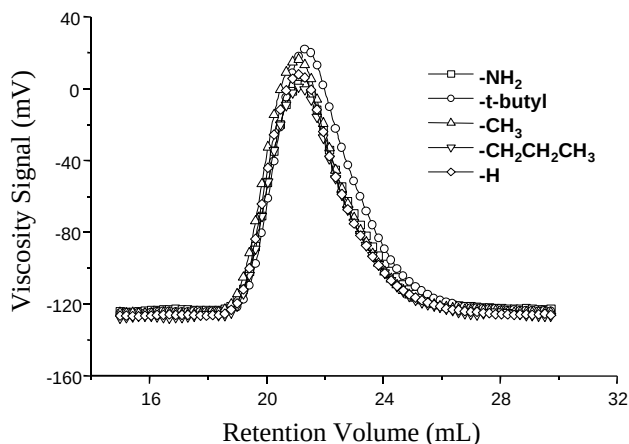


Figure 6.2. Viscosity profiles for low molecular weight PES

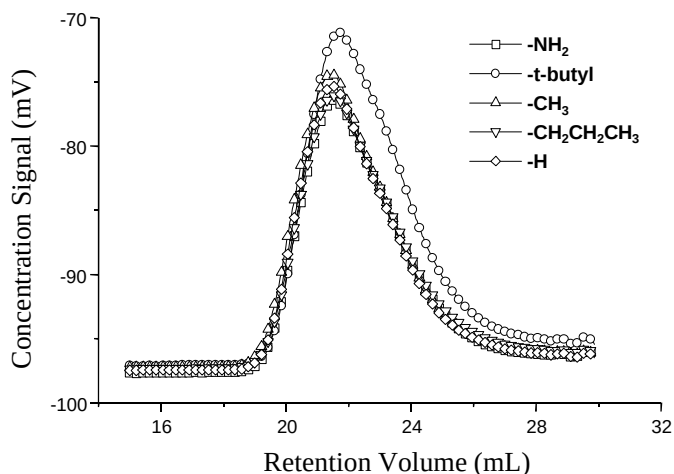


Figure 6.3. GPC curves for PES with indicated endgroups

Another technique for molecular weight determination was endgroup titration. The m-amino endgroup was titrated with a proton donor. The number average molecular weight was obtained explicitly using a hydrobromic/glacial acetic acid titrant (0.02-0.03 N). The titrant was standardized with potassium hydrogen phthalate (KHP) by dissolving 0.02 g KHP in 30 ml glacial acetic acid. This solution is then poured into chloroform and titrated. A polymer sample (0.5 gm for $M_n=15000$) was dissolved in chloroform. Upon dissolution of the polymer, 30 ml of glacial acetic acid was added and this solution was titrated. The endpoint of the titration was determined by a change in color of the indicator, crystal blue. The endpoint was also ascertained automatically by noting the

change in the potential from a MCI GT-05 automatic titrator. The $\langle M_n \rangle$ was calculated using the relationship of $\langle M_n \rangle = nW/NV$ where n represents the number of the endgroups, assuming $n=2$. Furthermore, W is the sample weight, N is the titrant normality and V is the titrant volume.

6.3.2. DIFFERENTIAL SCANNING CALORIMETRY

Glass transition temperatures were determined from differential scanning calorimetry. A Perkin-Elmer DSC 7 at a heating rate of $10^{\circ}\text{C}/\text{min}$ with indium and lead as calibrants was employed. Flat samples of approximately 10 mg were used in order to achieve a good signal without causing thermal lag problems. In the thermograms, Figure 6.9 and Figure 6.10, one can detect the glass transition via the increase in the heat flow between $170\text{--}190^{\circ}\text{C}$.

6.3.3. DENSITY MEASUREMENTS

The density of these materials was determined from an instrumented pycnometer setup, Accupyc (Micromeritics Inc). The uncertainty of the measurements given by the manufacturer of this instrument is listed at $\pm 0.0001\text{ g}/\text{cm}^3$. However, it has been shown by other users that the uncertainty is to $\pm 0.001\text{ g}/\text{cm}^3$.

6.3.4. DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis resolved secondary relaxations for the poly(ether sulfones) and aided in relaxation time distribution determinations. A TA instruments DMA 2980 was used at $3^{\circ}\text{C}/\text{min}$ from -140°C to 150°C . The experiment was performed in bending mode with a displacement of 25 microns and the cryogenic unit attached. Sample cross-sectional areas were kept constant at 0.2 cm^2 . To calculate the relaxation times, frequency sweeps at various isotherms were acquired. This task is realized by scanning 18 frequencies ranging from 0.25 Hz to 190 Hz between 160°C and 220°C at 3°C intervals in bending mode with a displacement of $25\text{ }\mu\text{m}$. These data were then fit to the Havriliak-Negami equation as previously discussed, whereupon the resulting adjustable parameters were applied in generating a time decay function for this material as a function of time. Subsequently, the breadth of relaxation times can be

ascertained from using a KWW equation to fit the time decay function. This protocol has already been outlined in chapter 3.

6.3.5. DIELECTRIC SPECTROSCOPY

Dielectric spectroscopy was also used in calculating relaxation time dispersions. Polymer Laboratories software was used in combination with a GENRAD 1689 RLC Digibridge. The voltage was set at 1000 mV and frequencies between 20 Hz and 100 kHz were scanned at a heating rate of $0.3^{\circ}\text{C}/\text{min}$. This heating rate assured that all frequencies could be collected within 1°C , which is sufficient to assume an isothermal experiment.

6.3.6. AGING TESTS

The experimental conditions for the endcapped poly(ether sulfones) for creep recovery and dilatometry experiments were similar to those for the engineering thermoplastics from Chapter 5. There are a few differences, which will be described in this section. The samples for creep recovery and linear dilatometry were thoroughly dried before they were compression molded into 2 mm thick plaques. Each sample's thermal history was erased before the experiment was performed by heating it in an oven to 18°C above its glass transition for 5 minutes. Repeated runs under the same conditions demonstrate that these conditions erase the thermal history of these samples without causing any deformation of the sample.

The creep recovery experiments were conducted using a TA Instruments 983 DMA. These tests are conducted under isothermal conditions from -20°C to 180°C . The isothermal control for these tests is 0.01°C in a temperature range from the highest temperatures to near ambient conditions, sub-ambient control is 0.05°C . Nitrogen was used as the purge gas in all of the experiments. Sample dimensions were 21.3 mm in length with a cross sectional area of 0.16 cm^2 . The load was controlled such that the percent strain was below 0.1% in most cases, which was high enough for a good signal. The evaluation of the shift factors and master curves was performed using the TA DMA SuprPos V4.1B superpositioning software.

Linear dilatometry was performed using a Netzsch Dil 402 instrument, in which the length changes are monitored using a LVDT. The samples were held under

isothermal conditions with a control of $\pm 0.05^\circ\text{C}$ and a nitrogen purge of 25 ml/min in an attached high temperature furnace. Sample dimensions varied from 20mm to 26mm in length. The length changes were typically monitored for over 1000 minutes.

6.4. RESULTS AND DISCUSSION

6.4.1. MOLECULAR WEIGHT DETERMINATION

Molecular weight characterization using solution NMR was performed for t-butyl and n-propyl endcapped PES. There is no chemical shift overlap of the methyl hydrogens from the bisphenol A moiety with any of the protons in these endgroups, except for the beta carbon's protons of n-propyl. In the latter case only non-overlapping proton peaks are utilized. Figure 6.4 shows the typical proton shifts for a t-butyl endcapped poly(ether sulfone).¹³ Table 6.1 summarizes the molecular weights using the various techniques for the lower molecular weight poly(ether sulfones). It should also be pointed out that the uncertainty in this technique is about 2000 g/mol. Furthermore, above 20000 g/mol the error becomes too large, therefore only the lower molecular weight species are calculated. The ^{13}C spectrum, Figure 6.5, also indicates that poly(ether sulfone) is the product.

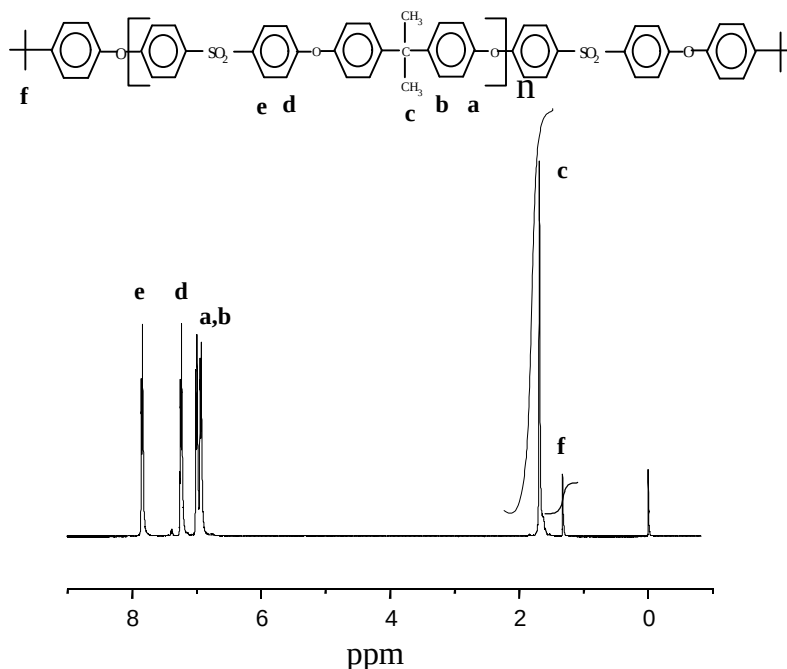


Figure 6.4: ^1H spectrum for lower molecular weight t-butyl terminated PES

Table 6.1: Summary of molecular weights for the lower molecular weight series

	GPC ($M_n \times 10^{-3}$ g/mol)	Solution NMR ($M_n \times 10^{-3}$ g/mol)	Endgroup titration ($M_n \times 10^{-3}$ g/mol)
PES-NH ₂	18		19
PES-t-butyl	14	17	
PES-CH ₃	18		
PES-n-propyl	17	18	
PES-H	17		
PES-trityl	17		

The differences between molecular weights measured via GPC and endgroup analysis of these systems is within the error of all the techniques. However, the t-butyl endgroup deviates the most. If one calculates the number of end groups that would be present using GPC and solution NMR results, the degree of endgroup substitution would remain around 80%. This value still is high enough to show an endgroup effect, as will be witnessed shortly.

It is also possible that some of the endgroups could degrade during the aging tests. Therefore, after aging was performed the t-butyl endcapped poly(ether sulfone) was

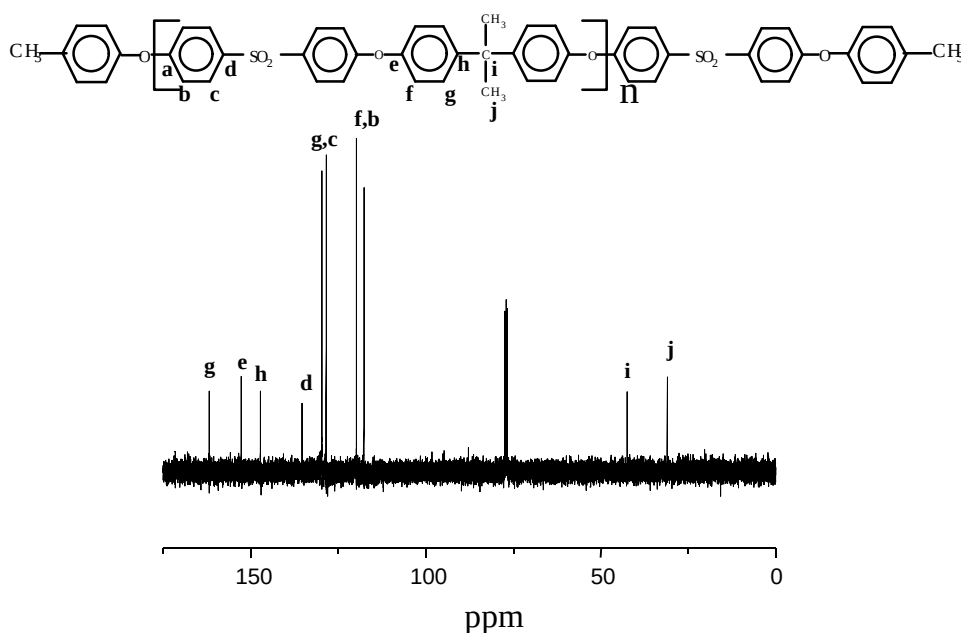


Figure 6.5. ¹³C spectrum for PES-CH₃

analyzed for any endgroup degradation. Comparison of Figure 6.4 and Figure 6.6 shows that the two NMR spectra look similar. After integration, the apparent number average molecular weight increased from 16.5×10^3 to 17.2×10^3 , which is within the error of this technique. Furthermore, the amine terminated poly(ether sulfone) demonstrated no change in its elution behavior using size exclusion chromatography, see Figure 6.7.

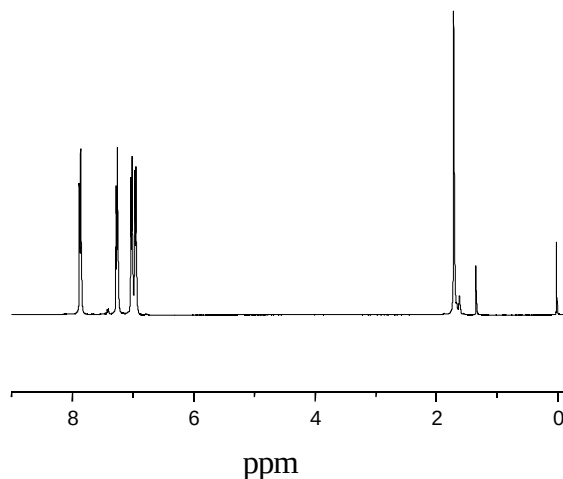


Figure 6.6. ^1H spectrum of PES-t-butyl after being subjected to all aging tests

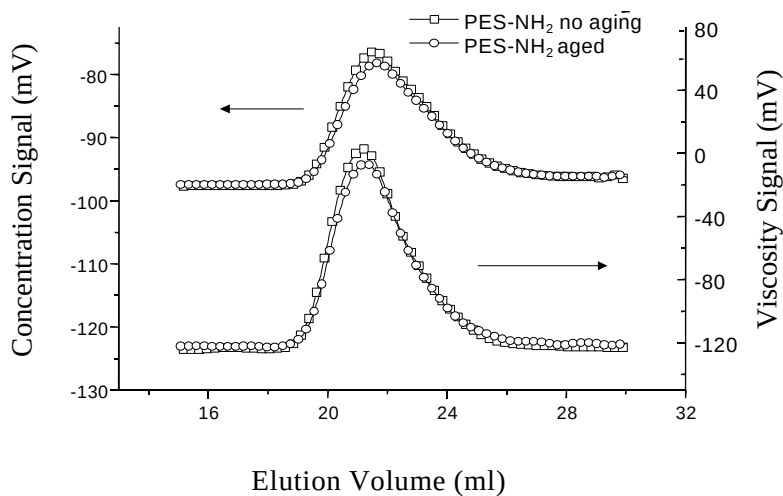


Figure 6.7. GPC chromatograms with aged and unaged samples of PES-NH₂
 These results, along with no changes in the glass transition temperature determined from the second scan from DSC, indicate strongly that no chemical aging has occurred in these

materials after being exposed to elevated temperatures for the particular aging times. Hence, any variation in the behavior should be from physical aging processes.

In synthesizing the PESs, cyclic species are formed. These molecules are generally low in molecular weight and could affect the material properties if present in a high concentration. Figure 6.8 represents two PESs, a 18000 g/mol CH_3 terminated PES and Udel[®], along with the calibration curve used in analyzing the GPC data. This figure demonstrates that the cyclic concentration is small and comparable for the two polymers. A small rise in the chromatograms near a retention volume of 30 ml denotes the presence of these cyclics. The calibration curve is linear at low molecular weights, indicating the ability to separate low molecular weight species, such as cyclics. Therefore, as a result of the chromatograms, Figure 6.3 and Figure 6.8, and calibration curve it can be assumed that the concentration of cyclics in the synthesized polymers is low.

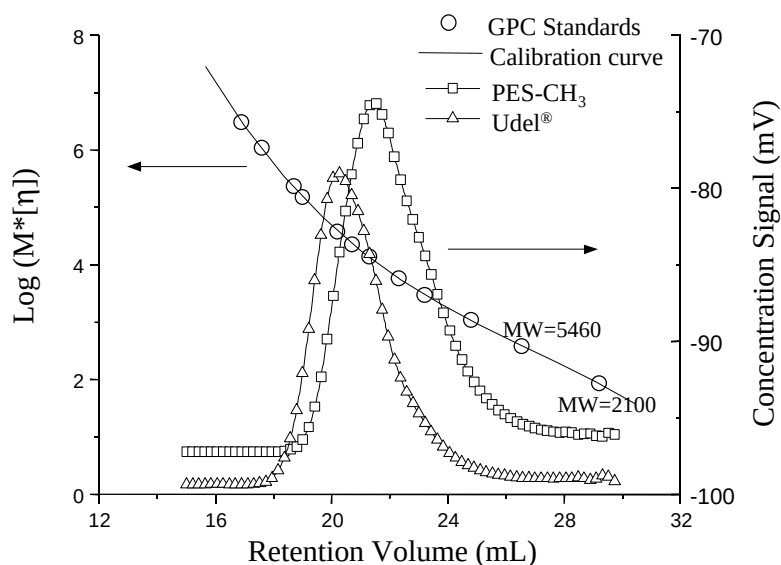


Figure 6.8. Chromatograms of PESs and calibration curve for GPC

6.4.2. DIFFERENTIAL SCANNING CALORIMETRY

From Figure 6.9 one sees that the endgroup plays a role in the glass transition temperature, with the larger endgroups in the series H, CH_3 , n-propyl, and t-butyl only having slightly higher T_g s. Trityl phenol, on the other hand, increases the glass transition substantially. The amine and bisphenol A endcaps have the possibility of undergoing specific intermolecular interactions, therefore they are not included in this comparison.

In the three samples of the higher molecular weight series there is a small correlation between endgroup size and T_g . For this series t-butyl has a slightly higher

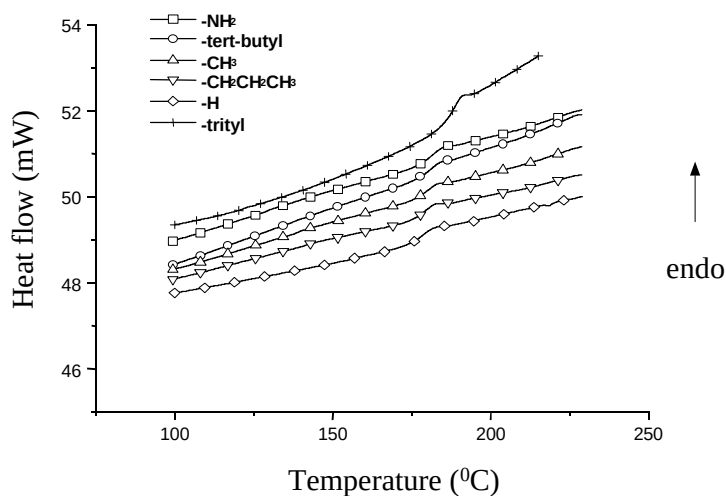


Figure 6.9. DSC thermogram of the lower molecular weight polymers

glass transition temperature than either hydrogen or methyl terminated PES as is demonstrated in Figure 6.10.

6.4.3. DENSITY

In addition to a T_g discrepancy, there are differences in the density of these systems. Table 6.2 reports the densities for the low and high molecular weight series. The densities are given at 25⁰ C. Since their T_g are different this density should be

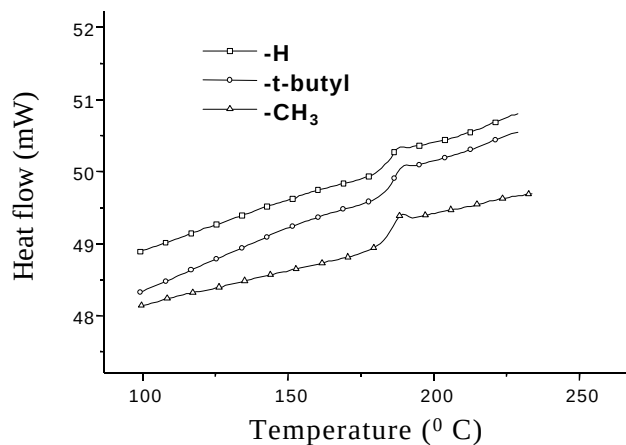


Figure 6.10. DSC of higher molecular weight poly(ether sulfones)

corrected to a common structural temperature state by using the coefficient of thermal expansion, α_v , as follows

$$r_{25} V_{25} = r_{T_g} V_{T_g} \quad \text{Eq. 6.1}$$

$$V_{T_g} = V_{25} + dV_{T_g-25} = V_{25} + a_v V_{25} (T_g - 25) \quad \text{Eq. 6.2}$$

rearranging and substituting Eq. 6.2 in Eq. 6.1 one has

$$r_{T_g} = \frac{r_{25} V_{25}}{V_{25} (1 + a_v (T_g - 25))} \quad \text{Eq. 6.3}$$

Densities calculated this way allow the values to be compared in a common structural state. These densities are also presented in the table below.

Table 6.2: Densities, thermal expansion coefficients and T_g for all the terminated PES

Low molecular weight series

Endgroup	$\rho_{25} \text{ (g/cm}^3\text{)}$	$\rho_{T_g} \text{ (using Eq. 6.3)}$	$\alpha_v \times 10^4 \text{ (K}^{-1}\text{)}$	$T_g \text{ } ^\circ\text{C (DSC)}$
H	1.2412	1.2096	1.71	177.8
CH ₃	1.2392	1.2068	1.74	179.2
n-propyl	1.2377	1.2046	1.79	178.5
t-butyl	1.2358	1.2033	1.74	180
trityl	1.2351			187.6
NH ₂	1.2429	1.2100	1.74	181.5

High molecular weight series

H	1.2389	1.2056	1.73	184.8
CH ₃	1.2385	1.2045	1.77	184.4
t-butyl	1.2385	1.2020	1.73	187

In this table the volume expansion coefficients are deduced from the linear expansion coefficients by the relationship between volume and linear expansion coefficients for isotropic materials: $3\alpha_l = \alpha_v$. This is a very good approximation for isotropic materials, since

$$a_v \propto \frac{dV}{V_0} = \frac{V_f - V_0}{V_0} \quad \text{and} \quad V_f = (dl_x + l_x)(dl_y + l_y)(dl_z + l_z)$$

When V_f is expanded four terms will be generated

$$V_f = l_{i,0}^3 + 3dl_i l_{i,0}^2 + 3dl_i^2 l_{i,0} + dl_i^3$$

and when this expression is divided by V_0 ($l_{i,0}^3$)

$$\frac{V_f}{V_0} = 1 + 3a_i + 3a_i^2 + a_i^3 = (1 + a_i)^3$$

Given that the material is isotropic, all α_i are equal, therefore the final relationship between the volume and linear expansion coefficients is

$$a_v = (1 + a_l)^3 - 1 \cong 3a_l$$

The last approximation is very good because $\alpha_l \gg \alpha_l^2$.

The length expansion results are shown in Figure 6.11. As can be witnessed through Figure 6.11 the expansion coefficients are similar. The same is true for

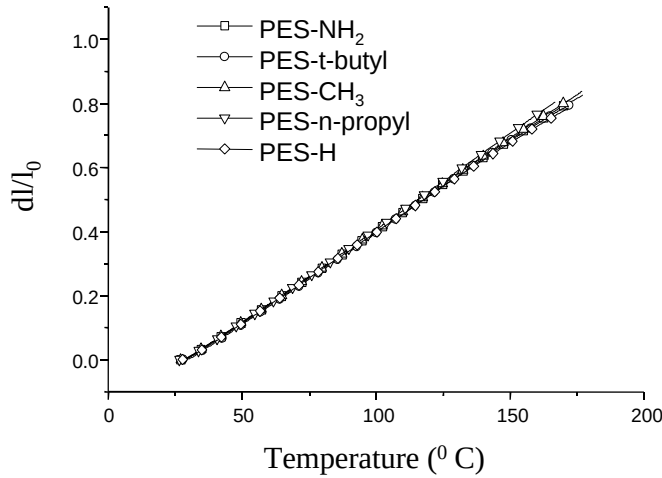


Figure 6.11. Normalized length changes as a function of temperature the higher molecular weights series. On the other hand, the density measurements show an interesting trend: as the size of the endgroup increases, there is a systematic depression of the normalized density within the hydrocarbon endgroup series.

The glass transition and density results suggest two opposing mechanisms. Figure 6.12 illustrates this effect, where the thick gray bars indicate trendlines. The two prevailing mechanisms are due to packing and configurational entropy reductions for these poly(ether sulfones) with different endgroups.

6.4.4. TRANSIENT AND DYNAMIC MECHANICAL ANALYSIS

Poly(ether sulfones) are known to have a substantial secondary or beta relaxation between -100°C and 0°C .¹⁴ This secondary relaxation mechanism generally translates into desirable mechanical properties, such as toughness and ductility. The increase in these mechanical properties occurs due to the availability of a dissipation mechanism

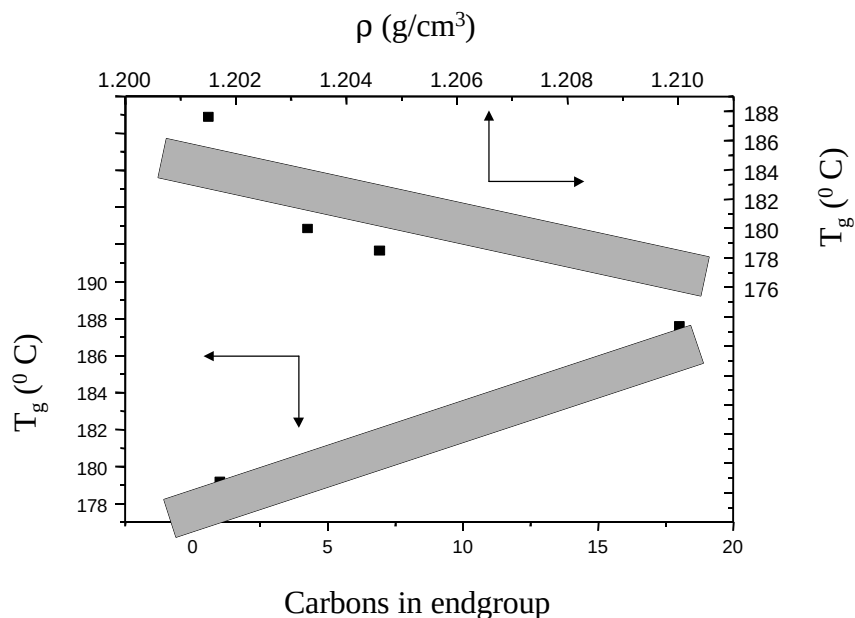


Figure 6.12: Dependence of T_g on size of endgroup and density of polymer when the material undergoes a mechanical perturbation. Changing the endgroup size should play little role in affecting this beta relaxation which is known to originate from the bisphenol A moiety in the structure. Figure 6.13 shows the magnitude and breadth of this secondary relaxation, whereas Figure 6.14 demonstrates a concomitant depression in storage modulus which accompanies the beta transition.

The mechanical properties of the lower and higher molecular weight poly(ether sulfones) characterized here differ significantly. The variance emanates from the molecular weight dependence on mechanical properties. If the molecular weight is below the critical molecular weight for entanglements, then the mechanical properties, such as yielding, ductility and toughness display a sharp decline. The lower molecular weight series is below this critical molecular weight, whereas the higher molecular weight

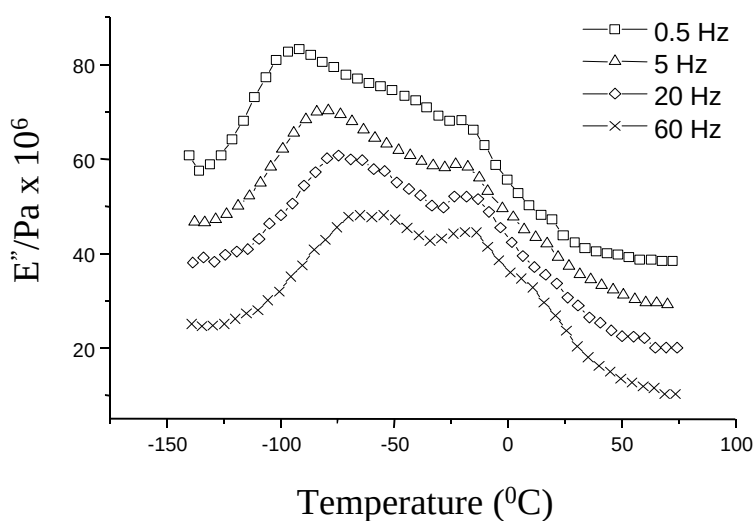


Figure 6.13. Frequency dependence of loss modulus for PES-trityl

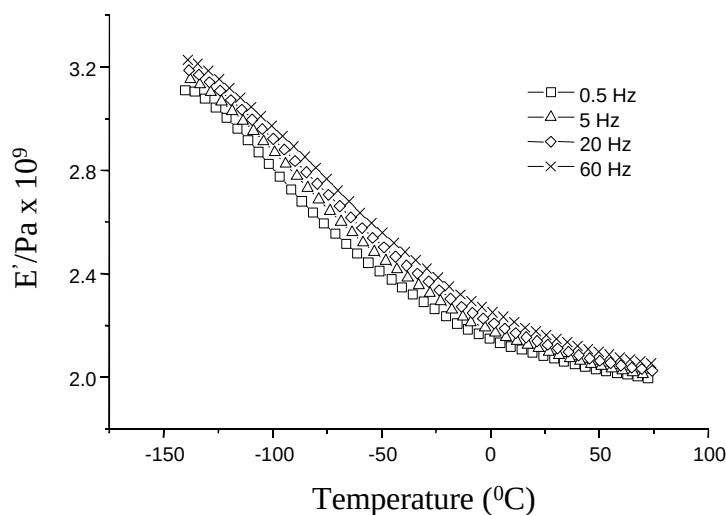


Figure 6.14. Low temperature storage modulus of PES-trityl

materials exceed this criterion. Failure occurs below the yield point for almost all of the lower molecular materials, as shown in Figure 6.15. Figure 6.16 demonstrates the trend when entanglements are present, the region near 7-10% extension is where the material yields. The initial slope of all the materials are similar, which shows the relative independence of Young's modulus on molecular weight.

The lower molecular weight group does have some endgroup dependence, perhaps attributable to differences in densities. Figure 6.17 represents the tensile strength

as a function of density, there is a slight trend towards higher tensile strength as the density increases. For a homologous series this trend seems intuitive. As segments in the chains begin to slip past each other in a shearing motion, which would happen near the yield point, the degree of packing (or open “hopping” sites) will dictate how much energy is needed to strain the sample. In the case of potential hydrogen bonding, excess energy is needed to break the hydrogen bonds between segments, thus increasing the tensile

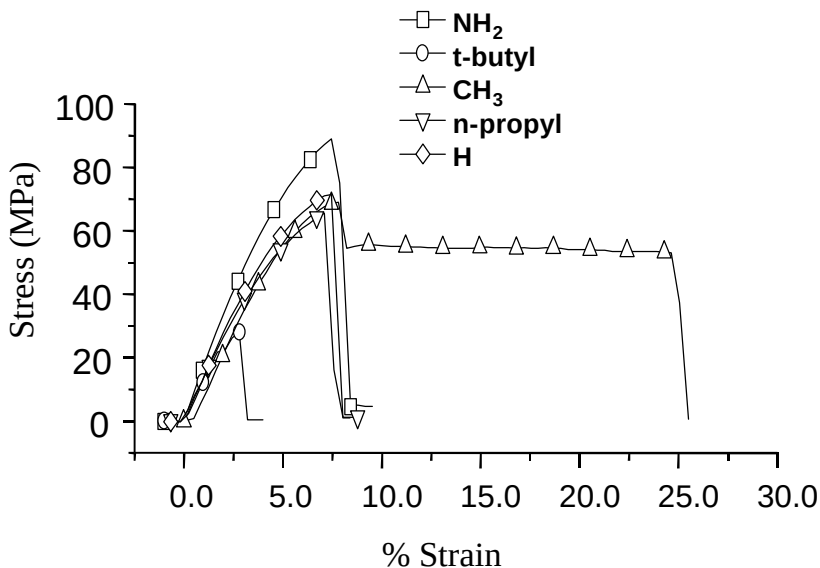


Figure 6.15. Stress-strain behavior for low molecular weight PES series

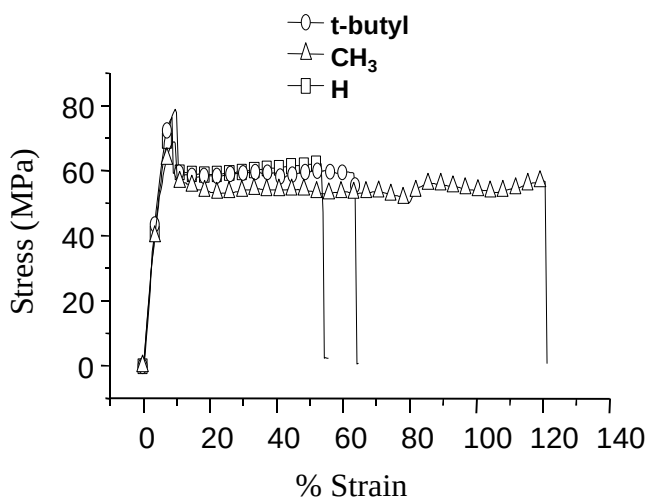


Figure 6.16. Stress-strain behavior for high molecular weight PES series strength, e.g. the amine terminated poly(ether sulfone). However, when the strain reaches high enough levels only entanglements are available to keep the material intact, hence in the lower molecular weight systems no yielding is possible and brittle fracture

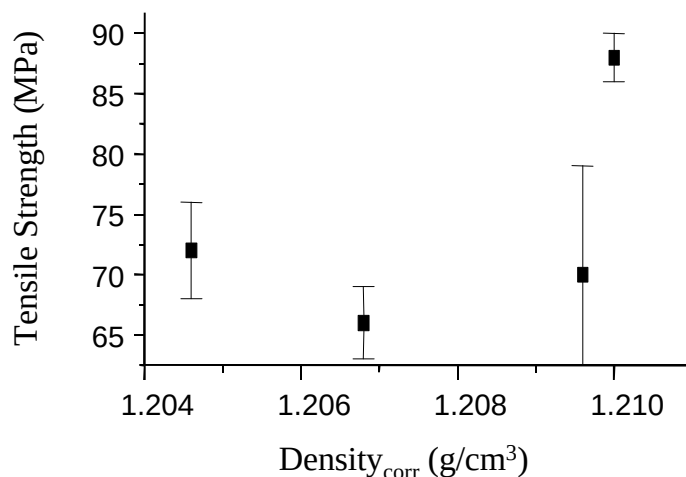


Figure 6.17. Tensile strength – density relationship low MW series results. The density dependence on Young's modulus relates back to the density of chains or the number of chains that will be stressed in a cross section normal to the load. Subsequently, as the density increases the number of chains present increases as packing improves and more stress is required to achieve the same extension. Figure 6.18 confirms

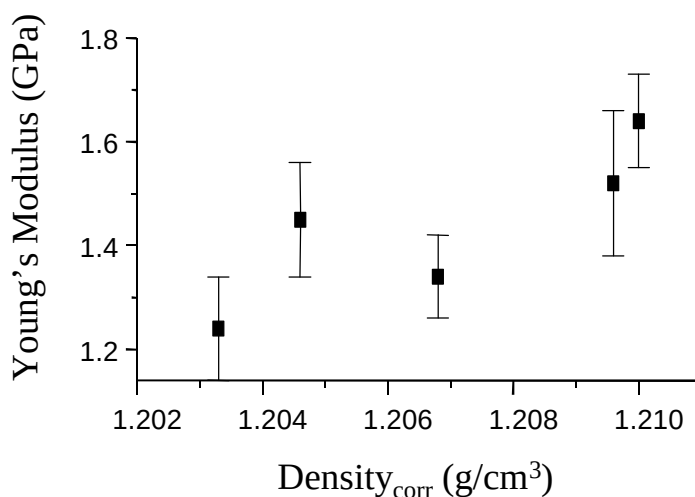


Figure 6.18. Young's modulus related to the corrected density this behavior. The nature of the endgroup does cause differences in the mechanical properties of the lower molecular weight series, however the biggest differences in ductility and toughness are seen through the molecular weight dependence. The anomaly in the strain at break for the low molecular weight methyl terminated polymer can be explained as a balance of two effects. The first effect is due to the molecular weight

being close to the critical molecular weight for entanglements and the second is related to the packing which determines local motion. The overlap of these two effects causes PES-methyl to act ductile and yield.

Typical data used for calculating the relaxation time dispersions appears in Figure 6.19. The relaxation time distribution results are shown in Figure 6.20 - Figure 6.22 for the 25000 molecular weight series. The dispersion of relaxation times is described via the beta parameter of a KWW expression that was examined in Chapter 3. There are a couple of aspects that warrant discussion concerning this parameter. First, all of the beta values, except for those at the last temperature, fall within 0.41 – 0.04. There is no discernable trend of the beta parameter with the endgroup character, although Udel® and

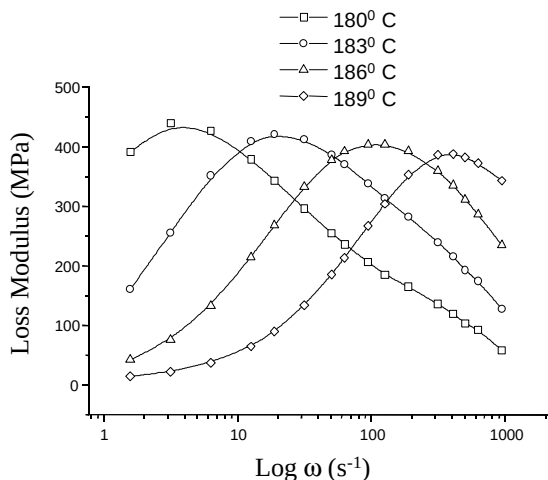


Figure 6.19. Experimental loss modulus for 23k PES-t-butyl

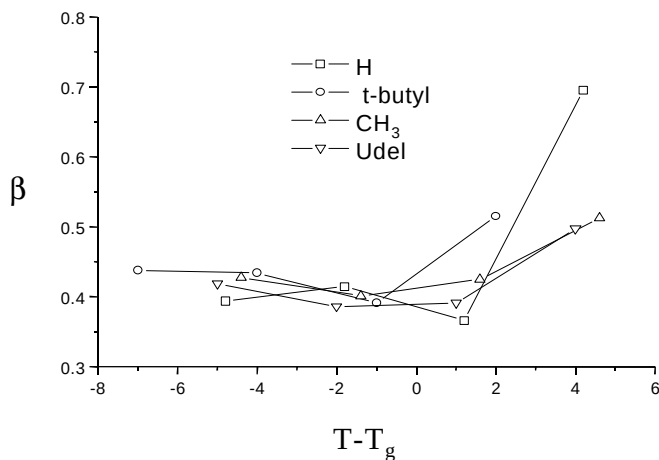


Figure 6.20. Temperature dependence on beta for high molecular weight series

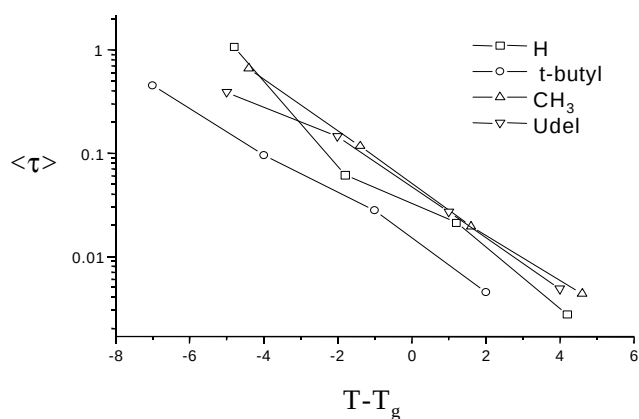


Figure 6.21. Mean relaxation time for the high MW series poly(ether sulfones) the methyl terminated poly(ether sulfone) follow the same behavior. Udel is methoxy endcapped, therefore the similarity in the shape of the curves between Udel and PES-CH₃ indicates that even though absolute values differ, the manner in which the relaxation times change is identical. At the three lower temperatures (normalized to the glass transition temperature) the relaxation time distribution appears to remain constant, indicating that thermorheological simplicity is maintained under these test conditions.

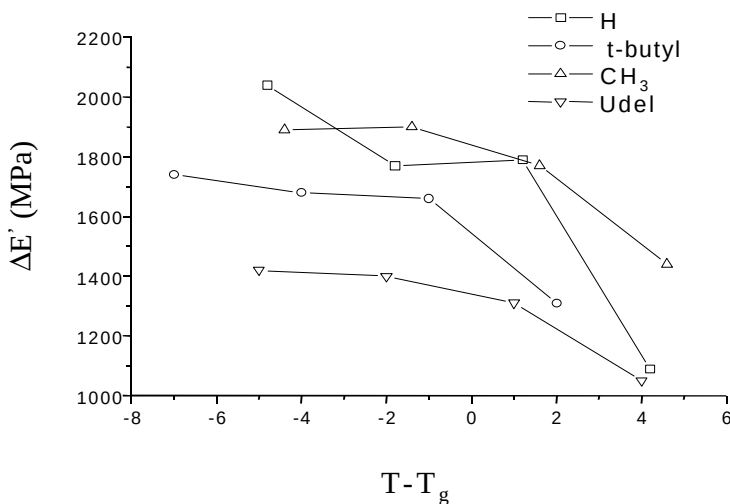


Figure 6.22. Change in the relaxed and unrelaxed storage moduli for the various systems. However, one notices that there is an increase in beta, which indicates a narrowing of the relaxation time distribution. In effect the complexity of the relaxation modes is reduced. A change in the relaxation time distribution would render time-temperature superpositioning invalid because there is not simply a shifting of the distribution on the

measuring time axis, but also a change in the nature of the relaxation motions. This statement applies to a strict assessment of superpositioning principles; however, due to the empirical nature of superpositioning, slight changes in relaxation time distributions do not affect the ability to superimpose to a first approximation. Later, it will be shown that the change in the relaxation time distribution at the higher temperatures is less dramatic for the higher molecular weights.

Another parameter that can be used to assess relaxation time dispersions is the average relaxation time, $\langle\tau\rangle$. Figure 6.21 demonstrates the nature of the change in τ as a function of temperature. The curves show that the average relaxation times decrease as temperature increases. The slopes are identical for all of the materials, consequently the activation energy for the relaxation is similar for all of the various endcapped polymers. Attention should be drawn to the fact that the Udel and CH₃ terminated PES fall on the same line. The last parameter generated from the data fitting routine is the oscillator strength, or the difference between the unrelaxed modulus (E'_u) and the relaxed modulus (E'_r). This value tends to fall as the temperature is raised. Once again, the correspondence in shape between Udel and CH₃ terminated PES is remarkable; this is attributed to the similarity in the endgroup.

The lower molecular weight poly(ether sulfones) show some similar trends to those from the higher molecular weight materials. Namely, relaxation strength and activation energies seem lightly dependent on the endgroup size. On the other hand, the distribution of relaxation times, β , appears to vary for different endgroups. Convolutioned

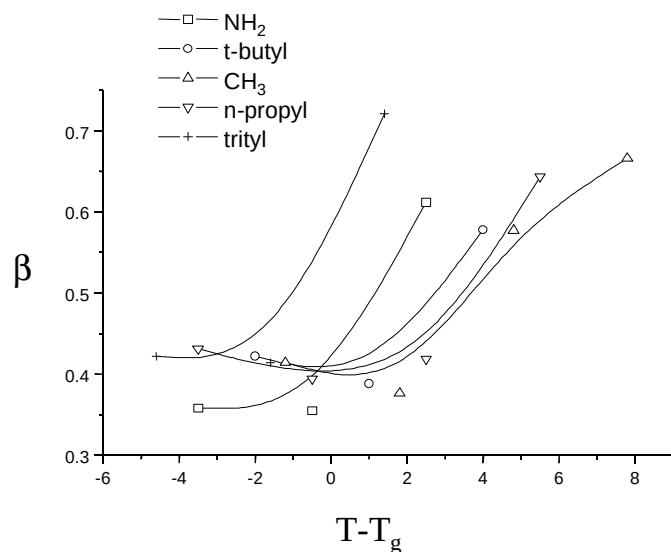


Figure 6.23. Relaxation time distribution parameter for the lower molecular weight PES with a possible endgroup dependence, β is also temperature dependent. Figure 6.23 indicates these characteristics. Two polymers are omitted to improve the clarity of the plot. A few trends are apparent in this series of terminated polymers. The endgroups that can participate in hydrogen bonding, NH_2 and bisphenol A (not shown) have lower β parameters than the other materials, with NH_2 having an especially low value (0.35), designating a broad distribution of relaxation times. It was originally thought that any contributions from hydrogen bonding would decrease at the high temperatures (180-190^o C) used in this test because of the weakness of these bonds at high temperatures. However, at the initial temperatures shown there appears to be a dependence of the relaxation motions on hydrogen bonding.

Another effect noted is a general relationship suggesting that larger endgroups are related to narrower relaxation time distributions. The effect initially appears to be minor, but when the β curves are superimposed some traits emerge, see Figure 6.24. The vertical shift, as demonstrated in Figure 6.25, will illustrate the difference in relaxation time distributions. The trend line in this figure indicates that as the endgroup increases in size, quantitated through the number of protons, the relaxation distribution narrows. This behavior could be a manifestation of the closer packing that occurs with smaller endgroups and the subsequent larger degree of intermolecular coupling.

One more point is that the change in the relaxation time distributions with temperature are similar except for the omitted endcaps (H and bisphenol A). This common behavior could indicate that the relaxation time dispersion varies in the same manner, regardless of the absolute breadth of the dispersion. This means that the differences in packing and mobility due to endgroup size can be normalized.

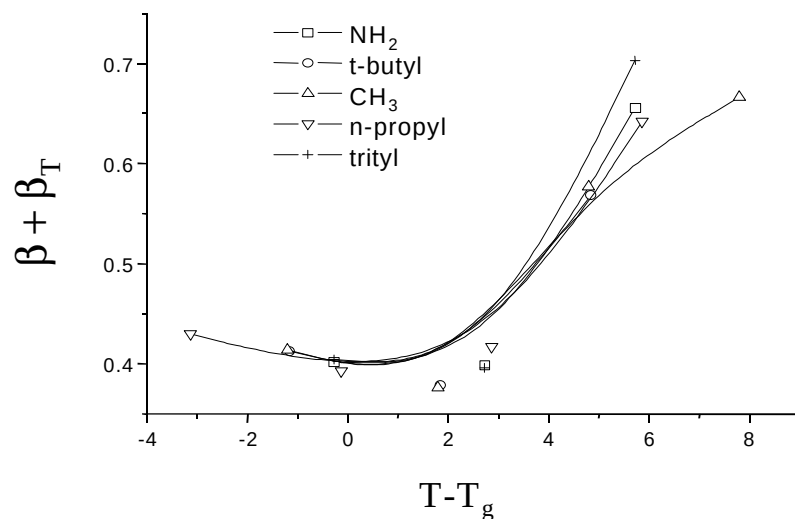


Figure 6.24. Shifted β parameters showing similar temperature behavior

6.4.5. DIELECTRIC ANALYSIS

Dielectric spectroscopy also permitted calculation of relaxation time distributions. The dielectric analyzer probes dipole moments and their relaxations, which can afford another method of investigating molecular motion on a smaller length scale than dynamic mechanical spectroscopy. Figure 6.26 shows the results of a step-isothermal experiment, which can also be represented in the frequency domain as isotherms, as in Figure 6.27.

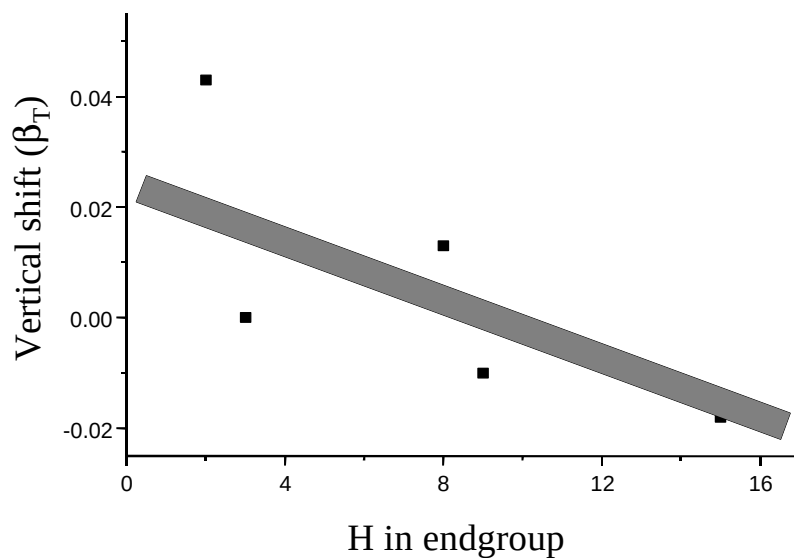


Figure 6.25. Vertical shift parameters for the relaxation time distributions correlated with the size of the endgroups

These dielectric loss curves are fit to the Havriliak-Negami equation and ultimately will allow an assessment of the relaxation time dispersion and its mean

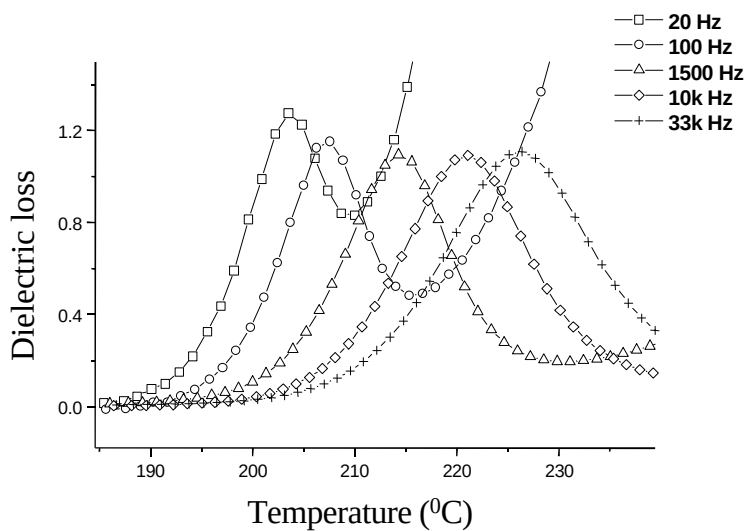


Figure 6.26. Experimental dielectric loss data for PES-bisphenol A

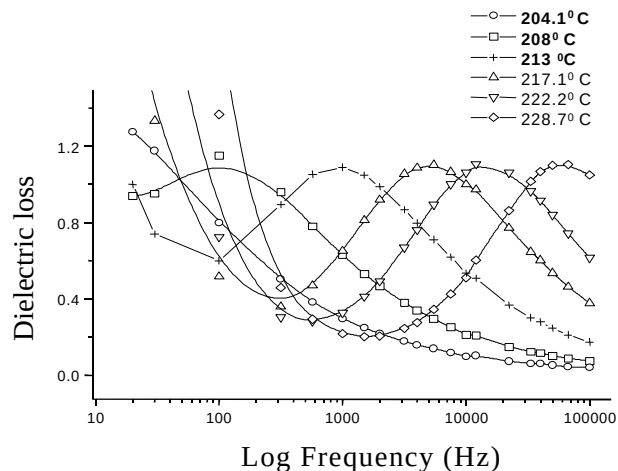


Figure 6.27. Dielectric loss data in the frequency domain

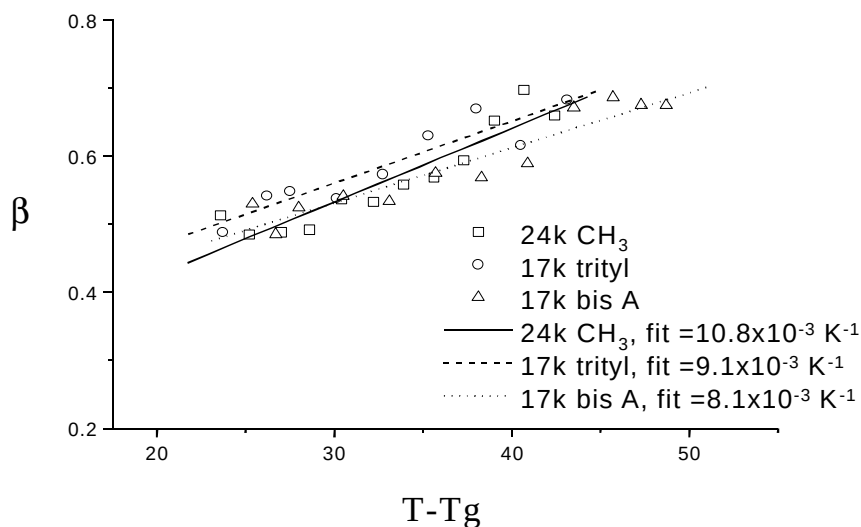


Figure 6.28. Relaxation time distribution's temperature dependence for indicated PES relaxation time. In Figure 6.28, β is graphed as a function of temperature. The temperature dependence of β is different in dielectric analysis than dynamic mechanical tests, compare Figure 6.28 with Figure 6.20 and Figure 6.23. The initial β value from dielectric experiments is higher than mechanical, but this value changes in a regular linear fashion, unlike the β from mechanical data. This behavior could arise because the relaxation mechanism of the dipoles remains constant across this temperature range. On the other hand, for mechanical experiments at higher temperatures there might be additional mechanisms to molecular diffusion and intermolecular cooperative motions.

Similar to the dynamic mechanical results, the trityl terminated poly(ether sulfone) had on average a higher beta value than the other two PESs over the temperature range investigated. This difference must arise from the packing frustration that the large trityl group causes. The larger resultant intermolecular distance subsequently causes less intermolecular cooperative motion to occur and the chains can relax more independently of their neighboring chains. These differences are small, but the trend is consistent. However, the activation energy and the pre-exponential factor for the relaxation process, quantitated through an Arrhenius calculation, indicate a higher activation energy but a lower attempt frequency (also calculated from a Vogel-Fulcher analysis) for the trityl endgroup. Therefore, it appears that the larger endgroup even affects the motions of segments further removed from the terminus. Hence, the relaxation time distributions are narrower than for the other materials, but the mean relaxation times of the distributions remain higher at certain temperatures equi-distant from the glass transition.

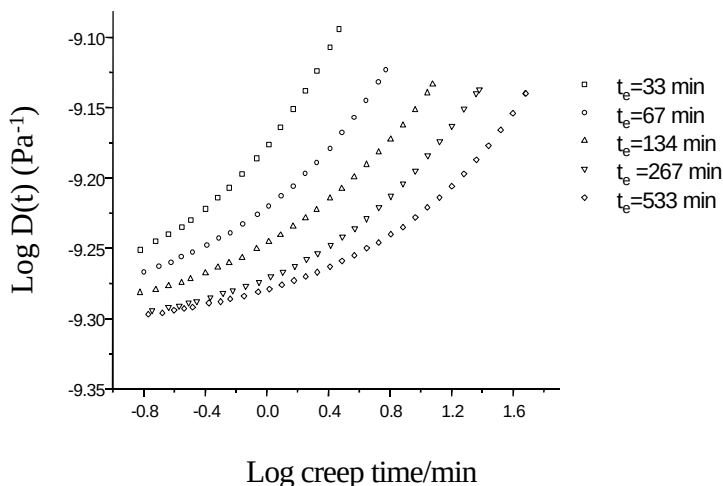


Figure 6.29. Creep curves from sequential creep aging tests for PES-NH₂ at 170⁰ C

6.4.6. PHYSICAL AGING TESTS

The physical aging characteristics of these poly(ether sulfones) with the various endgroups have been probed using creep recovery and length dilatometry. Typical results of the creep recovery from these tests appear in Figure 6.29. Using the ideas of superpositioning, in this case time-aging time superpositioning, one can create a master curve, see Figure 6.30, from the data in Figure 6.29 by employing horizontal and vertical shifts. The shift factors necessary to produce the master curve are subsequently applied

in a log shift factor plot, as in Figure 6.31. The slope of this curve is the rate of physical aging for this creep recovery test. This value indicates at what rate the relaxation times are being shifted along the time axis. If the material were at equilibrium, the various creep curves at different aging times would overlay without any shifting. In all the creep recovery experiments vertical shifting was necessary; however, the value of the largest vertical shifting rate is on the order of 2-3% of the horizontal shifting rate. The vertical shift rate generally follows the trend of the horizontal shift rate.

When the physical aging rates are plotted as a function of temperature, as in Figure 6.32, then some interesting behavior is evident. At the high temperatures, where

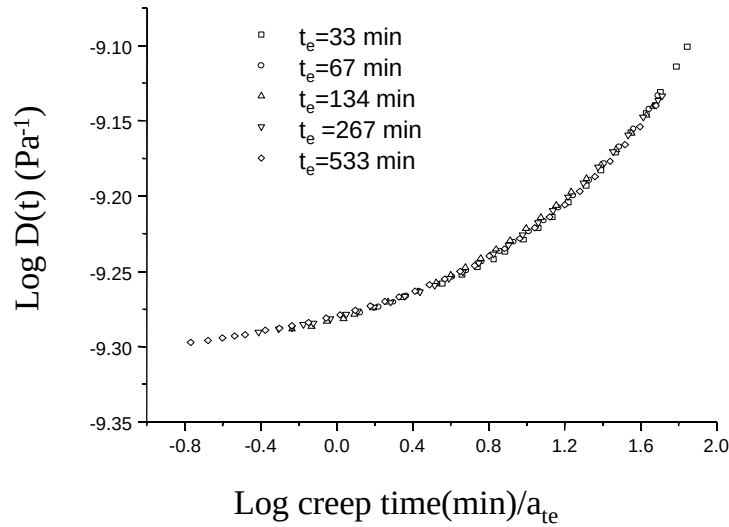


Figure 6.30. Master curve for the creep tests, $t_{e,\text{ref}}=533$ min

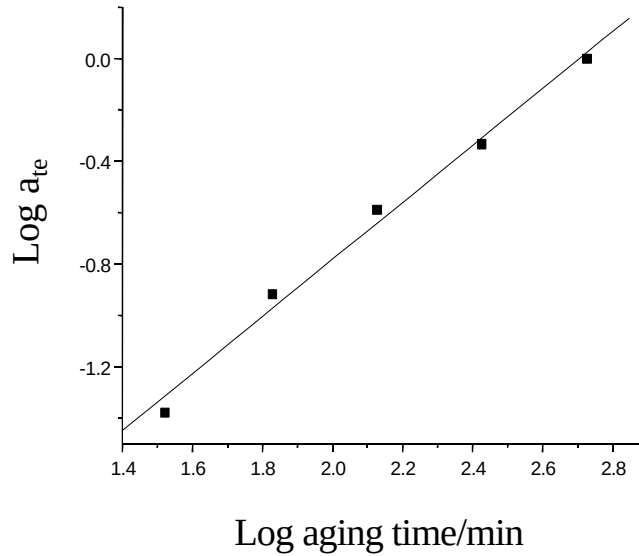


Figure 6.31. Log shift factor plot, the slope is the physical aging rate the material and its relaxation times are near or close to equilibrium the rate of physical aging is small, since only a portion of these relaxation times are contributing to the physical aging process. When the temperature is lowered the material exists farther from equilibrium and all the relaxation times in the distribution contribute to the physical aging process, causing a high rate of physical aging as seen in Figure 6.32. A further drop in the temperature causes one or both of the following phenomena to occur: either some of the relaxation times become too long to be activated during the creep process or the temperature is too low to overcome energy barriers for some molecular motion. Further decreasing the temperature accentuates this process and results in additional drops of the physical aging rate.

The effect of the endgroups on this physical aging rate for a particular polymer system may seem small at first, since endgroup effects seem secondary to

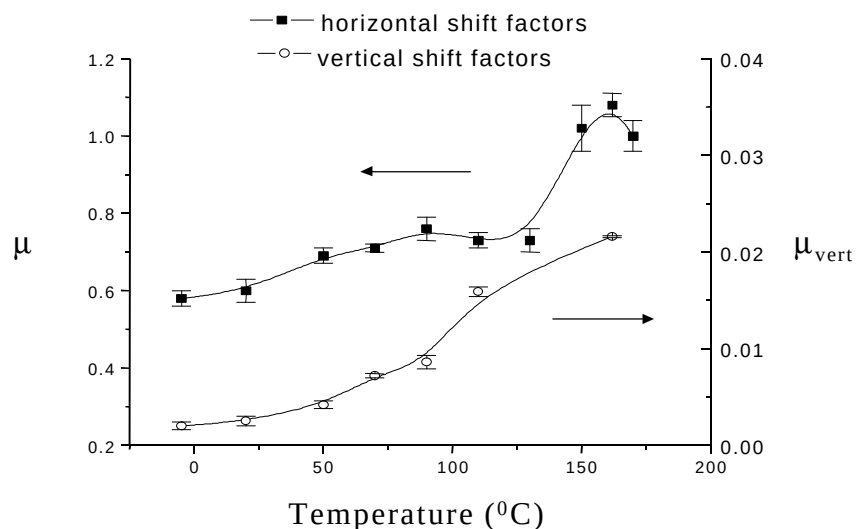


Figure 6.32. Evaluation of the physical aging rate as a function of temperature differences in polymer backbone, morphology or processing conditions on physical aging. Nonetheless, the different systems investigated show some differences in physical aging rates due to the size and nature of the endgroup. The two points made earlier that the endgroup can affect the density of a polymer by 0.01 g/cm^3 and the glass transition temperature by nearly 10°C , gives credence to the idea that endgroups may play a role in physical aging. Figure 6.33 demonstrates the physical aging rate tendencies for the lower molecular weight PES polymers. Their general shapes are similar due to the changing phenomena as outlined above. However, there are differences in the details of the shape. For example, the breadth of the high temperature side of the μ spectrum is different in going from the amine endcap to n-propyl and finally to the trityl terminated system. Another manner in which one could assess if there is any endgroup dependency would be to examine the onset temperature where μ goes from maximum to lower values on cooling. The evaluation for the “onset” temperature is given in Chapter 5. Quantitation of this parameter as a function of endgroup size produces Figure 6.34, which shows a trend towards higher onset temperatures (or lower $T_g - T_{\text{onset}}$ values) as the endgroup has fewer carbons or the density of the polymer is increased.

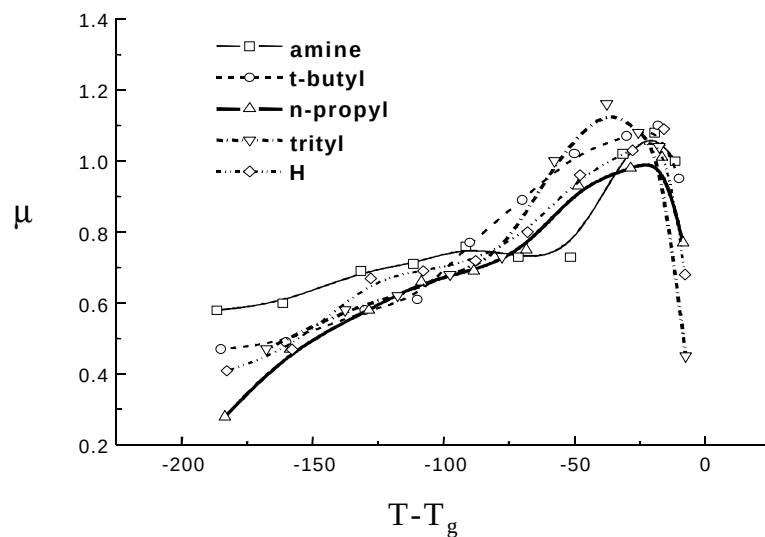


Figure 6.33. μ spectrum for all the lower molecular weight PES, reduced to their T_g

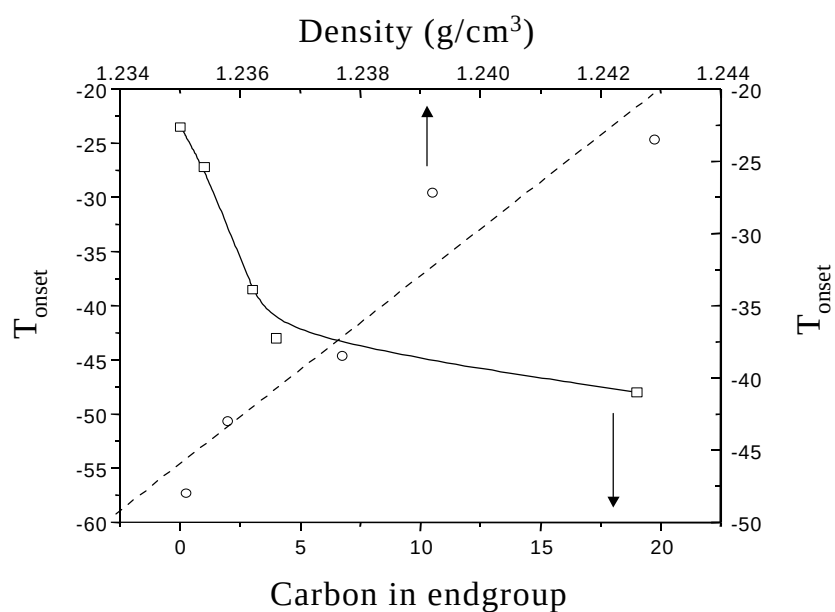


Figure 6.34. Correlation between onset of decrease of μ with cooling and the density or size of endgroup of the polymer

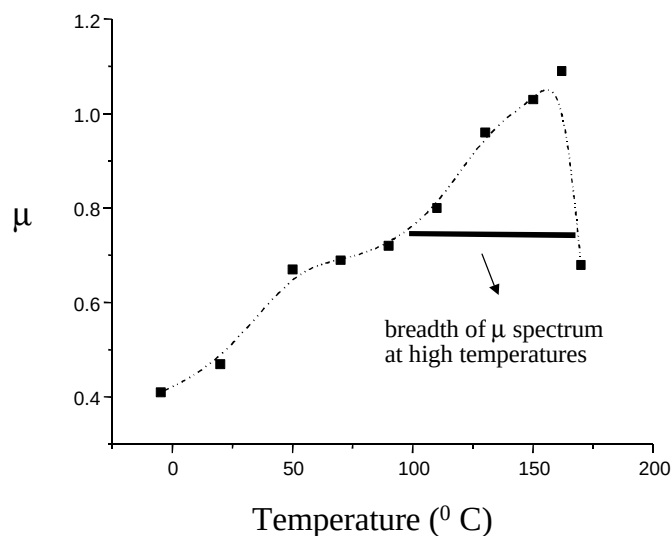


Figure 6.35. Calculation of the breadth of the μ spectrum at high temperatures

Another phenomena related to the size of the endgroup is the breadth of the μ spectrum at the high temperature side to the distribution of relaxation times. Figure 6.35 illustrates how this quantity is measured. When this temperature breadth is plotted as a function of beta, see Figure 6.36, a slight dependence is witnessed with larger beta values identified with a broader temperature range over which physical aging is high. The real physical meaning behind this dependence could be explained as a manifestation of hydrogen bonding in the amine terminated PES or as a result of intermolecular cooperative motion hindering physical aging at decreasing temperature. Near ambient temperatures there appears to be no dependence of the creep physical aging rate on endgroup size.

In the higher molecular weight series there is less variation in the physical aging behavior except perhaps in the middle portion of the curve. No significant dependence of physical aging on endgroup size is noted in these curves, see Figure 6.37. In general, the higher rates of physical aging persist to lower temperatures for the higher molecular weight PESs. The slope of the curves is lower than for the lower molecular weight poly(ether sulfones) between the temperatures of T_g-25 and T_g-150 . Although

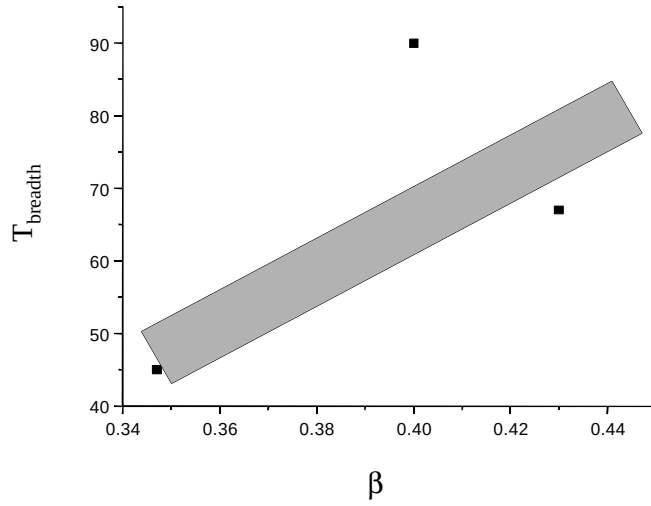


Figure 6.36. Breadth of physical aging rate spectrum versus the distribution of relaxation times

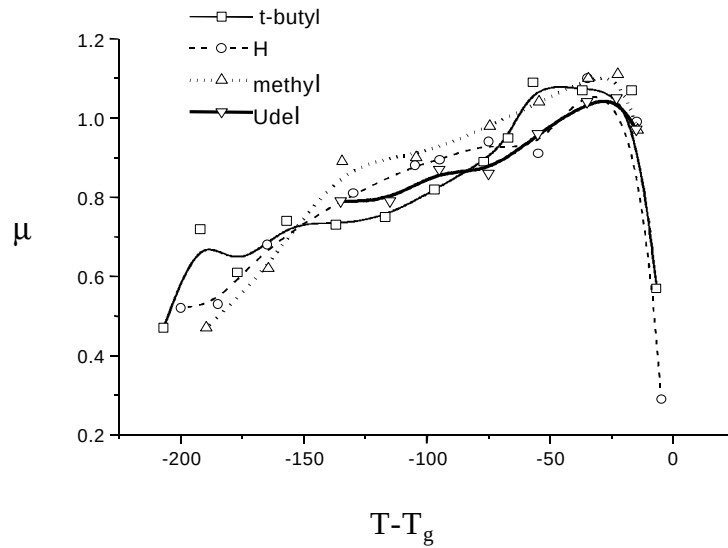


Figure 6.37. μ spectrum for the higher molecular weight series PES the magnitude and shape of the secondary relaxation remains constant at different molecular weights, there could be a molecular weight dependence on other relaxation mechanisms that could be operative at low strain levels. The mechanical data suggests the presence of entanglements for the higher molecular weight materials. These entanglements could restrict the chains from assuming an equilibrium conformation.

A final aspect concerning the mechanical physical aging behavior in these series is the correspondence between Udel, which is methoxy terminated, and the methyl terminated PES. A similar parity was maintained for the relaxation time distribution characteristics of these two polymers. In Figure 6.37, the shape is markedly similar, but the curves are offset by a vertical factor. There is a molecular weight difference of 3000 to 4000 g/mol, although they both are above the entanglement molecular weight. This parallelism may indicate some influence of the endgroups even on higher molecular weight poly(ether sulfones).

In assessing the physical aging behavior of the dilatometry studies, the lower molecular weight series will be introduced first. These results are depicted in Figure 6.38 and Figure 6.39. Two materials that show a big difference from the others are the t-

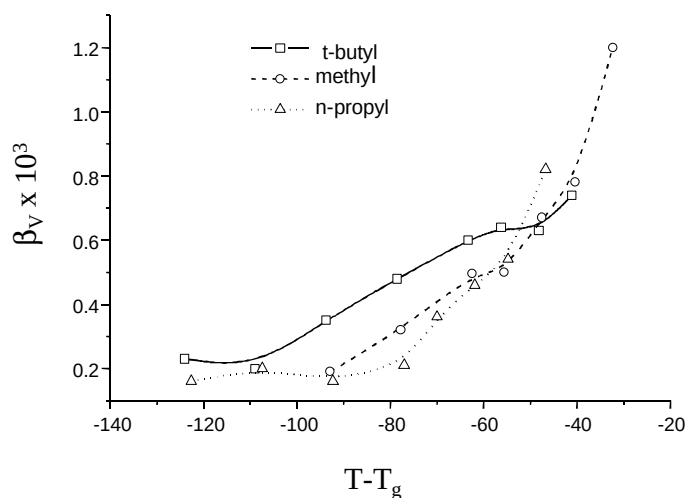


Figure 6.38. Volume recovery rates determined from length changes for the indicated low molecular weight PES

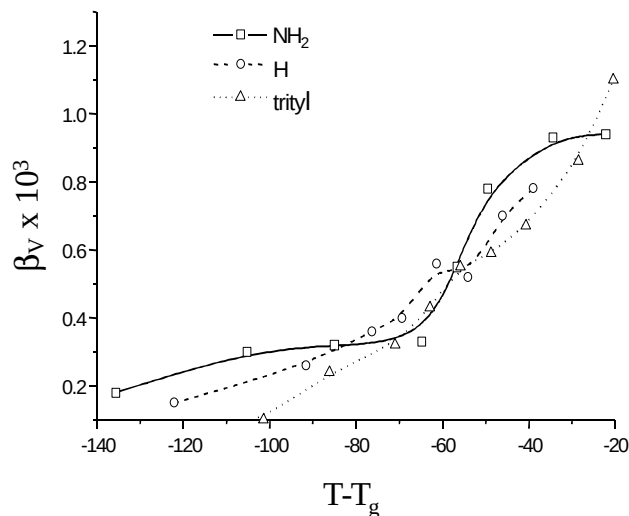


Figure 6.39. Same as in Figure 6.38, except for PES with these endgroups butyl and amine terminated PESs. The t-butyl system shows a very high level of volumetric physical aging spanning a broad temperature range. This characteristic cannot be explained solely on the basis of density, since trityl-PES has an even lower density, but is at the other extreme for its volumetric physical aging rate. A combination of effects probably arises in this system, such as molecular weight, density and endgroup size. The amine terminated polymer has no “knee” (marked slope shift) in its β_V versus temperature curve. All the other systems investigated here plus other polymers based on bisphenol A monomer demonstrate a similar knee in this curve between $T_g - 40$ and $T_g - 70^\circ \text{C}$.^{15,18} This knee is in the same temperature range where the mechanical physical aging rate decreases for the amine terminated material.

Other researchers have looked at systems that have endgroups that potentially hydrogen bond,^{16,17} and reported effects from this hydrogen bonding. Furthermore, the effect of hydrogen bonding increased as the concentration of endgroups augmented through a reduction of the polymer molecular weight. These results were obtained from calorimetry experiments and therefore no knee would be present. Unfortunately, the exact nature of the “knee” in these dilatometry experiments is not known and hence its absence for an amine endgroup is not completely understood.

An onset temperature for decreasing physical aging is measured as indicated in Figure 6.40. From this evaluation one can assess if there is any influence of density or endgroup size on this onset temperature. Such an evaluation is shown in Figure 6.41 and

a trendline is drawn to demonstrate the existence of a density dependence (endgroup size and density are interrelated as given in Table 2. This relationship implies that for poly(ether sulfones), the additional defects that exist in the packing maintain a higher rate of volumetric recovery to lower temperatures. It does not imply anything about the absolute rate of volumetric recovery, which appears to be independent of density. The higher molecular weight systems have some similarities to their lower molecular weight analogs.

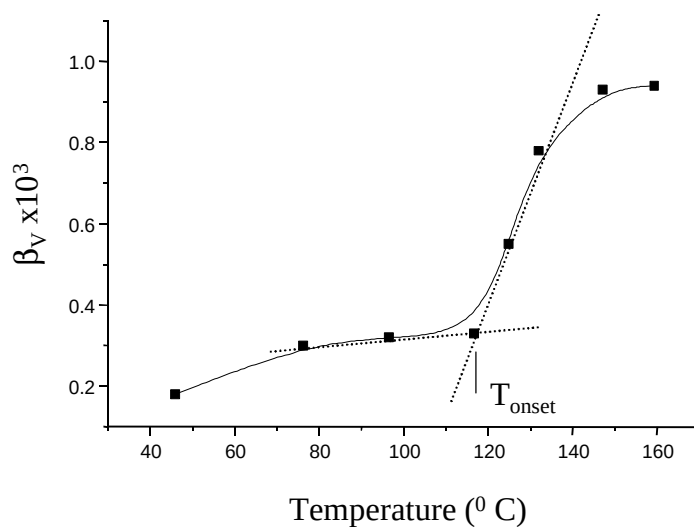


Figure 6.40. Assessment of the onset temperature for the decrease in physical aging rate

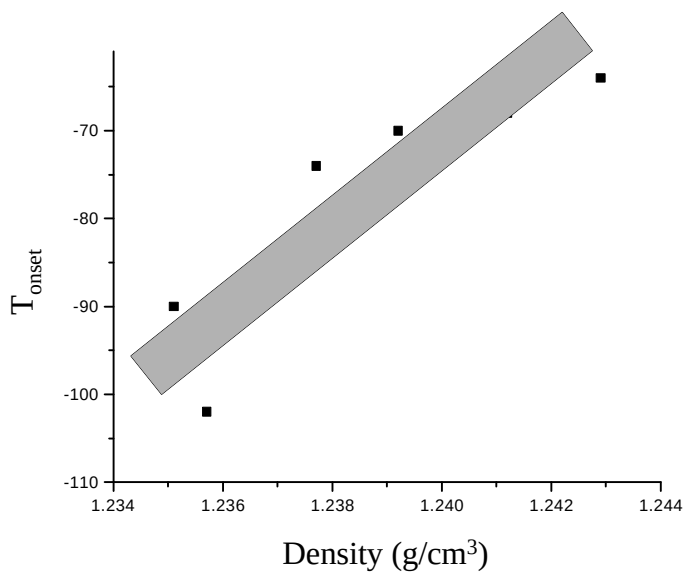


Figure 6.41. Correlation between T_{onset} for volumetric aging rate and density

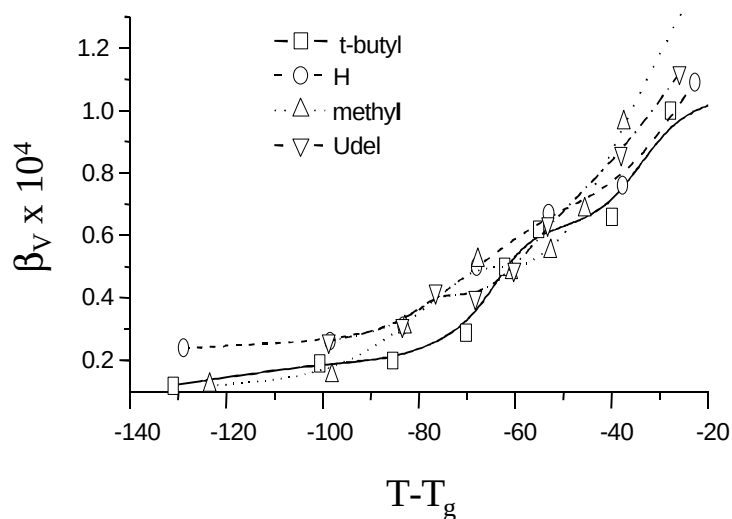


Figure 6.42. Volume recovery of high molecular weight PES

The general shape of the curves are the same along with the presence of a knee in the curve, note Figure 6.42. In this series one can recognize that the larger the endgroup, the lower the absolute value of the volume recovery across all temperatures except at the lowest measured ones. This means that the size of the endgroup could retard or even hinder some localized motion which allows for volume to recover towards its equilibrium condition in the glassy state.

Another approach to measuring physical aging processes is the sensitivity index that was introduced by Struik.¹⁸ The sensitivity index is simply the ratio of the mechanical to volumetric physical aging rates. It can give an indication if the same relative changes occur between mechanical and volumetric relaxation. It may also indicate if the same relative changes occur among the poly(ether sulfones). Figure 6.43 demonstrates that the higher molecular weight materials converge to the same point at high aging temperatures, the discrepancy at lower temperatures is due to the uncertainty

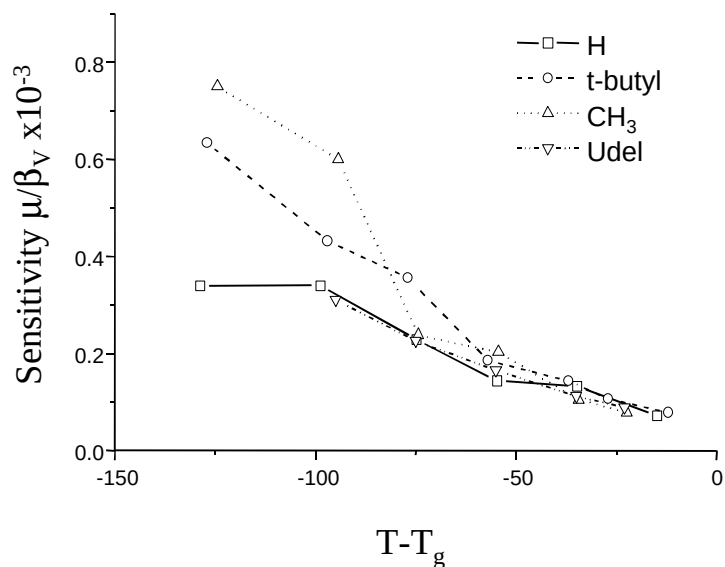


Figure 6.43. Sensitivity plot of the higher molecular weight series

in the volume recovery rate at low thermal energy levels. Figure 6.44 indicates that at higher temperatures the relative changes that are occurring are similar in all of these lower molecular weight systems. However, there are variations, but these could be due to the endgroups. The endgroups ranged from one that hydrogen bonds to one that was quite large in size. Finally, Figure 6.45 shows that the same endgroup but different molecular weights produces converging lines at the high temperatures. If the sensitivity is an accurate probe of mechanisms which cause physical aging, then these results imply that even though the mechanisms for physical aging may differ among this group of polymers, the temperature dependence of these changes for both mechanical and volumetric recovery remains constant.

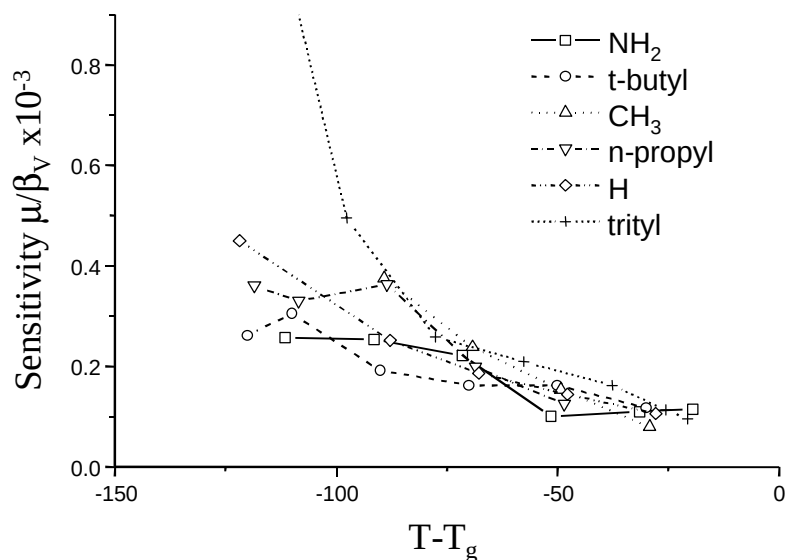


Figure 6.44. Sensitivity plot for lower molecular weight PES polymers

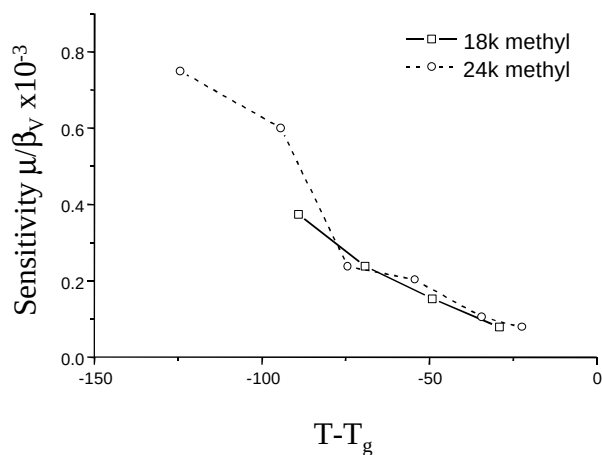


Figure 6.45. Sensitivity plot for high and low molecular weight PES-methyl

6.5. SUMMARY

The size and chemical nature of the endgroup play a large role in determining the physical characteristics of the polymer. For the low molecular weight series the densities decrease as the endgroup increases in size; however, the glass transition temperature witnesses a rise. The relaxation time distributions are also weakly endgroup dependent, with larger endgroups appearing to have a narrower relaxation time dispersion. In the case where hydrogen bonding is present, both in the amine and bisphenol A terminated

PES, the dispersion broadens. Physical aging shows some endcap dependence. As this terminus size increases (or density decreases), one tends to see the onset temperature where a decrease in physical aging rate occurs with lowering temperature moves further away from the glass transition temperature. This behavior is observed both in mechanical and volumetric recovery experiments for the lower molecular weight series. On the other hand, an increase in the endgroup size causes the absolute volumetric physical aging rate to decrease for higher molecular weight materials.

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CHAPTER 7. PHYSICAL AGING AND RELAXATION TIME DISTRIBUTIONS IN THERMOPLASTIC TOUGHENED EPOXY NETWORKS

7.1. INTRODUCTION

Many adhesive systems contain an amorphous polymer fraction, often in the form of a cross-linked thermoset. Some of these amorphous thermosets are epoxy resins. These epoxies, either as difunctional, trifunctional or even tetrafunctional resins have high heat deflection temperatures, flexural strength and modulus if they are cured with high performance diamines. One drawback of these highly cross-linked network systems is their low fracture toughness and energy. A solution to this problem that has been employed over the last couple of decades has been the incorporation of another phase into the epoxy system. Hence, the development of rubber toughened epoxies has become an area of high interest and commercial importance.^{1,2} The fracture toughness and energy at low and high strain rates dramatically increases with the addition of a small weight fraction of rubber.^{3,4} This improvement in fracture behavior is often accompanied by a concomitant decrease in the flexural strength and heat stability.

An effort has been made by various research groups to use tough thermoplastics as tougheners.⁵⁻⁷ An advantage of using thermoplastics as tougheners is their high glass transition temperature, hence the temperature stability and flexural strength do not diminish substantially.⁸⁻¹⁰ Until the temperature drops below the secondary relaxation temperature, usually in the range from -100°C to -50°C , the ductility and therefore the fracture toughness is not affected. Furthermore, these high performance thermoplastics are very tough polymers; most of them yield before breaking, allowing the brittle neat epoxies to be toughened. The manufacture of these systems can be more cumbersome than their rubber toughened counterparts due to higher viscosities. Therefore, it is necessary to maximize performance while minimizing the content of thermoplastic toughener.¹¹⁻¹³

With the incorporation of the thermoplastic toughener in the epoxy network both of the components will be in a non-equilibrium state at most use temperatures, namely at

temperatures below both glass transition temperatures. This situation implies that both components will be susceptible to physical aging. The prominence of physical aging can only lower the attributes of the polymer system. The slight gain from physical aging in modulus values due to densification is far overshadowed by the embrittlement and volume shrinkage that these systems will endure.

As a reminder, physical aging is the reduction of the thermodynamic properties of volume, enthalpy and entropy while the system is in the glassy or non-equilibrium state. Above the T_g the material can assume an equilibrium state again, which can also cause the material to be rejuvenated. However, upon lowering the system below the T_g into the glassy state, physical aging can commence again. The evolution of the material towards its equilibrium glassy state occurs in a non-linear and non-exponential manner. This evolution process is explained in Chapter 2.

7.2. MULTIPLE COMPONENT MATERIALS

In multiple component systems the interaction between the different components could affect physical aging behavior, especially in miscible or partially miscible cases.^{14,15} However, in phase separated structures the components should be uncorrelated with respect to each other, with only minor interplay between phases. This perspective is perhaps oversimplified since the role of the interface between the phases could demonstrate different aging dynamics than in either of the bulk materials. The nature of the continuous phase may also play a role depending on what experiment is performed. Furthermore, there is always the chance of having residual stress build up due to thermal expansion mismatches. This residual stress could increase the rate of physical aging. In any of these cases it is difficult to separate the contributions of physical aging to the whole unit from either of the components. Nonetheless, the same type of parameters, μ and β_v , can be calculated as was illustrated in the previous discussion.

One method of determining the role of thermoplastic tougheners in the physical aging of toughened epoxies is to examine the relaxation distribution of the toughener phase. If it is phase separated from the epoxy component, a change in the relaxation distribution from the bulk material might elucidate how this component interacts with the epoxy phase. The nature and degree of phase separation is also important. For example,

a system with toughener as the dispersed phase in the epoxy matrix may show physical aging behavior similar to the neat epoxy. The phase inverted case (epoxy dispersed in toughener matrix) may show aging behavior closer to the bulk toughener.

As developed in Chapter 3, the relaxation time distribution can be summarized with the Kohlrausch-Williams-Watts (KWW) equation, shown here again in Eq. 7.1. The role of intermolecular cooperativity, whose magnitude is signified by β in Eq. 7.1, and physical aging will be explored for the toughened systems encountered in this study. The shape of the physical aging rate plot for mechanical and volumetric relaxation may reflect

$$f(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad \text{Eq. 7.1}$$

the degree of intermolecular cooperativity. The additional attributes of morphology and interfacial adhesion between toughener and epoxy phases and their effect on cooperativity and physical aging properties will be investigated.

7.3. EXPERIMENTAL

Many of the experimental details have been elucidated in earlier chapters, namely creep recovery, volume dilatometry and dynamic mechanical analysis for relaxation time distribution studies.

7.4. SAMPLE PREPARATION

Sample preparation ranged from the synthesis of the toughener to the casting and curing of the epoxy-toughener blend. The synthesis of the poly(ethersulfone) involved the chain growth polymerization of dichlorodiphenylsulfone and bisphenol A, both received from Amoco Chemicals, in N,N-dimethylacetamide. The synthesis was described in the previous chapter. Figure 7.1 shows the details of the reaction scheme. As seen in Figure 7.1 the polymers were endcapped with selected monofunctional phenol derivatives. This design served two purposes, firstly to control molecular weight and secondly to create a reactive (m-aminophenol) and a non-reactive (p-cresol) endgroup. The amine group can react with an epoxy ring and hence be incorporated into the network. The poly(ethersulfone)s had number average molecular weights of 18×10^3 .

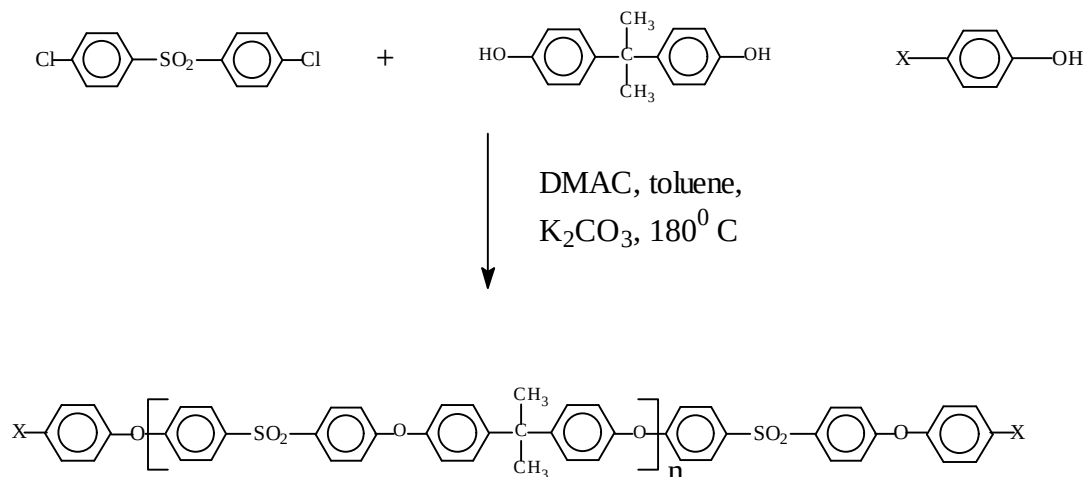


Figure 7.1: Reaction scheme for PES, X =CH₃ and NH₂.

These values were determined from gel permeation chromatography using the same experiments described in Chapter 4.

The toughener was dissolved in chloroform to make a 10% solution and subsequently precipitated in methanol to create a fine powder. The fine powder readily mixed with Epon 828,^{16,17} donated by Shell Chemicals, at 120⁰C. The toughener was loaded at 20% weight fraction of the total weight. The mixture was maintained under vacuum while continuously stirring until all of the polymer was dissolved. Lastly, the curing agent, DDS, from Acros, was added in a stoichiometric ratio. Stirring was continued until all of the DDS dissolved, the mixture was degassed in a vacuum oven and then poured into a pre-heated mold. The samples were cured for four hours at 130⁰ C and subsequently post-cured at 220⁰ C for two hours.

7.5. RESULTS AND DISCUSSION

7.5.1. STRUCTURE - PROPERTY RELATIONSHIPS

The glass transition temperatures of the epoxy and poly(ethersulfone) phases in their neat state differ by 30-40⁰ C. From the differential scanning calorimetry results one

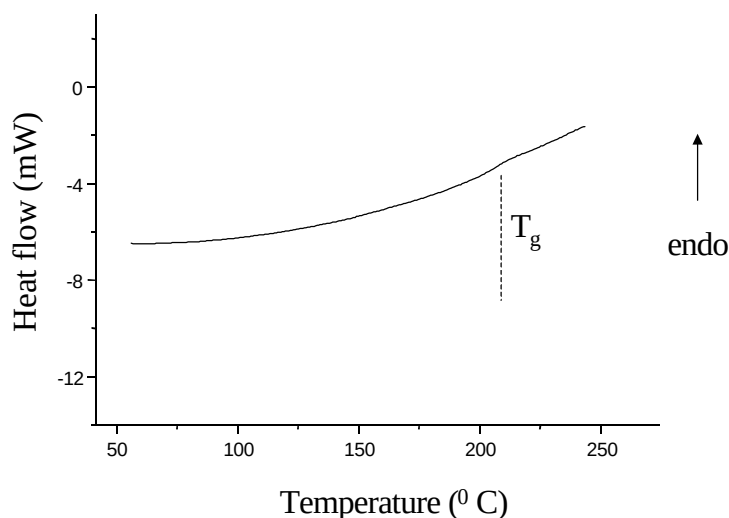


Figure 7.2: DSC of epoxy/PES-NH₂ 20%

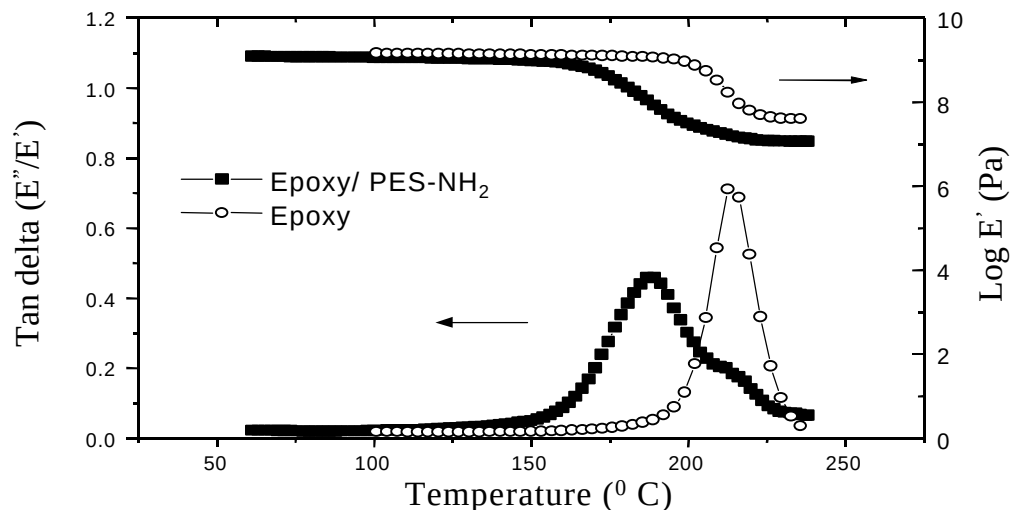


Figure 7.3: Dynamic Mechanical analysis of Epoxy/PES-NH₂

can only see a broad, diffuse transition, see Figure 7.2. However, the tan delta from dynamic mechanical analysis, see Figure 7.3, clearly shows the different phases present in the toughened system as opposed to one phase in the neat epoxy. Therefore, the epoxy and toughener are fairly well phase separated, since the glass transition temperature of the epoxy in the thermoplastic modified structure does not drop very much compared to the neat system. Morphological features as portrayed by Scanning Electron Microscopy (SEM), Figure 7.4 and Figure 7.5 show two distinct phases. These micrographs also indicate a rather complex morphology. In both toughened systems the two phases are co-continuous. This means that in some regions the epoxy is the matrix with dispersed toughener and in other regions the toughener is the matrix with dispersed epoxy particles.

This type of morphology is typical of spinodal decomposition which occurs in fast reacting systems at high enough volume fraction of the secondary phase.^{18,19} The fracture toughness, K_{IC} of the reactive and non-reactive systems is comparable in value and show nearly a doubling from the neat epoxy value of $0.7 \text{ MPa m}^{0.5}$.¹⁷

7.5.2. PHYSICAL AGING

Physical aging temperatures of 170°C , 162°C , 150°C , 130°C , 90°C , 70°C and 40°C were used for creep recovery for the toughened epoxy systems. For the neat epoxy the temperatures differed slightly because of the higher T_g of the epoxy phase, these experimental temperatures were 193°C , 180°C , 162°C , 150°C , 130°C , 90°C and 70°C . To complement the investigation, the thermoplastic tougheners were also characterized for their physical aging trends at 170°C , 162°C , 156°C , 150°C , 130°C , 110°C , 90°C , 70°C , 50°C , 20°C and -5°C .

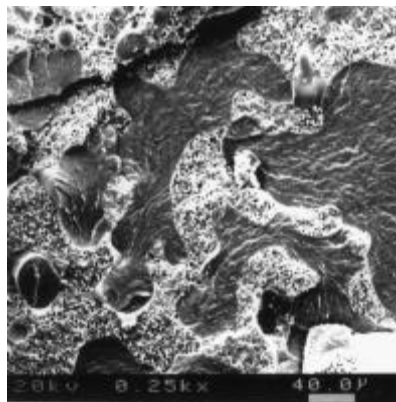


Figure 7.4: SEM of Epoxy/PES-CH₃ 20% fracture surface

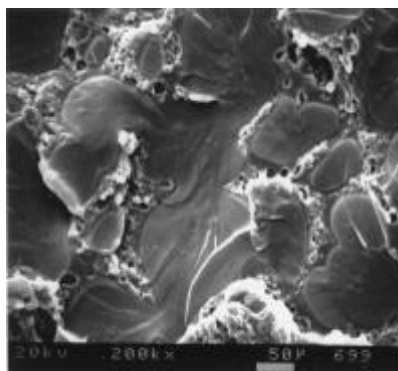


Figure 7.5: SEM of Epoxy/PES-NH₂ 20% fracture surface

In Figure 7.6 the master curve of Epon 828 toughened with the 18000 g/mol reactive poly(ethersulfone) is shown, the test was performed at 150⁰ C with a reference aging time of 534 minutes. The corresponding shift rate is included in Figure 7.7. Figure 7.8 summarizes the shift rate factors as a function of temperature for Epoxy/PES-NH₂. One detects a temperature dependence of the physical aging rate from this plot. At higher temperatures the distribution of relaxation times contains relaxation times that are shorter than or equivalent to the test time and hence do not contribute to physical aging in

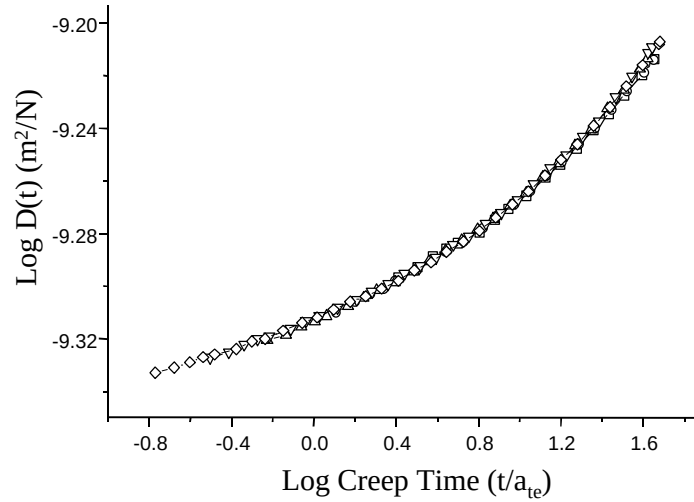


Figure 7.6: Master curve for Epoxy/PES-NH₂, $t_e=33, 67, 134, 267, 534$ (reference) minutes

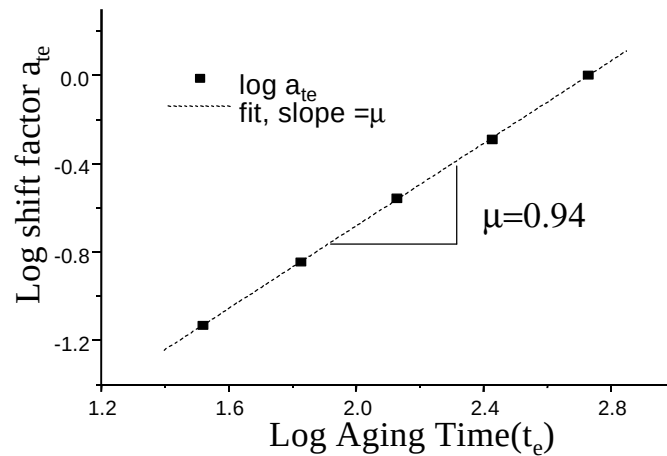


Figure 7.7: Shift factor plot for Epoxy/PES-NH₂ at 150⁰ C

the material. This trend produces a smaller shift rate factor. As temperatures move away from the glass transition, almost all the relaxation times are longer than the experimental time and may add to physical aging processes. While the available thermal energy is

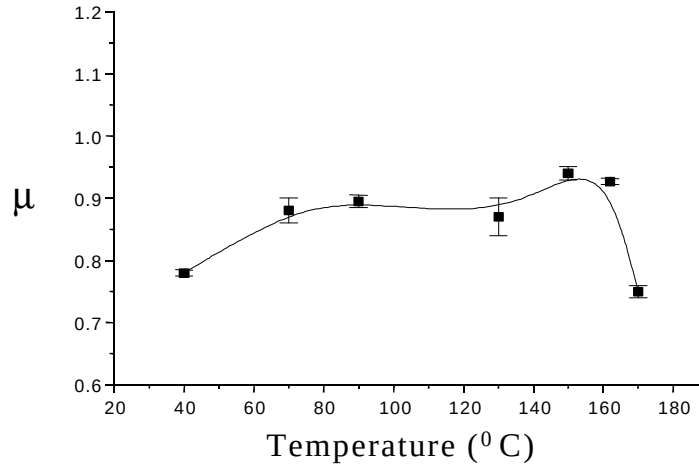


Figure 7.8: μ spectrum for Epoxy/PES-NH₂

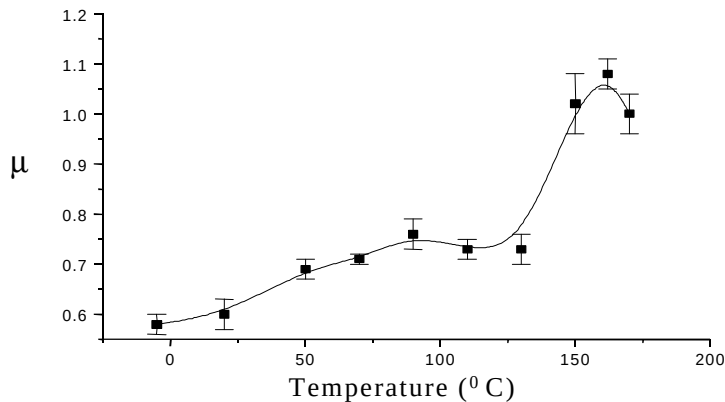


Figure 7.9: μ spectrum of neat PES-NH₂

higher at these temperatures the aging rate remains high; however, as the available thermal energy diminishes, there are fewer processes that can be thermally activated, causing fewer relaxation mechanisms to occur. Subsequently, physical aging decreases in rate.

The results for the two tougheners, PES-NH₂ and PES-CH₃ are summarized in Figure 7.9 and Figure 7.10. Figure 7.11 and Figure 7.12 show the behavior for the

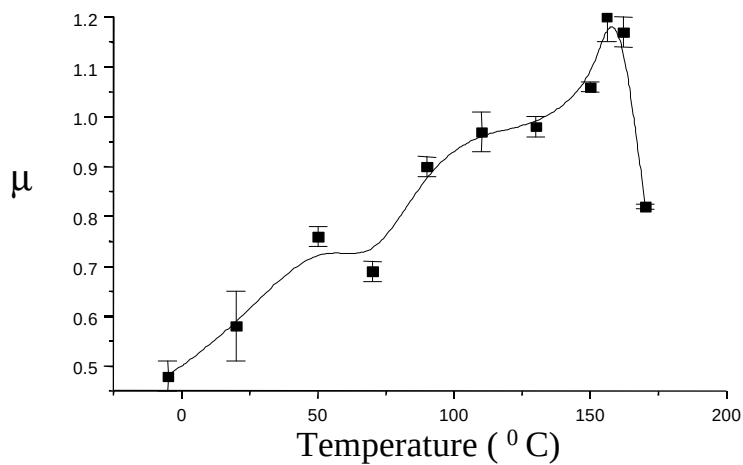


Figure 7.10: μ spectrum of PES-CH₃

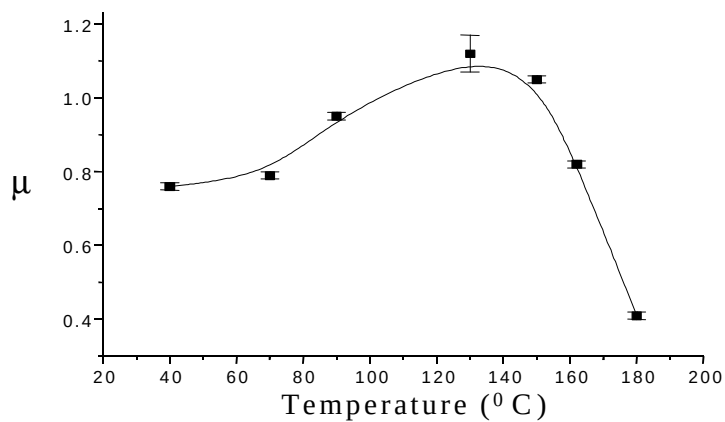


Figure 7.11: μ spectrum of epoxy/PES-CH₃

epoxy/PES-CH₃ system and the neat epoxy, respectively. A comparison of Figure 7.9 and Figure 7.10 verifies that there are differences in physical aging behavior due to endgroups. Although the backbones of the poly(ethersulfone)s are identical, there is a density disparity between the two polymers. The amine terminated polymer has a density

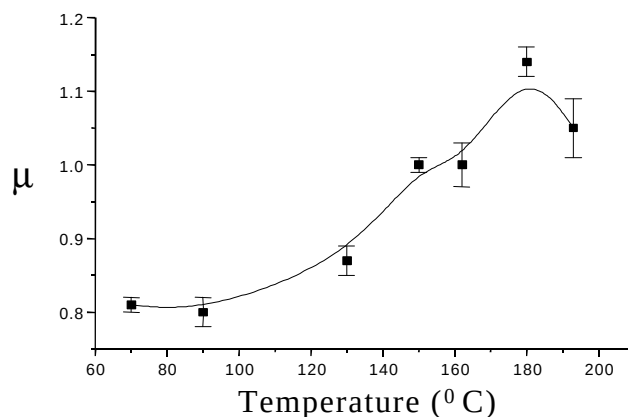


Figure 7.12: μ spectrum for neat epoxy

at 25⁰ C of $1.243 \pm 0.001 \text{ g/cm}^3$, whereas the methyl terminated system is $1.239 \pm 0.001 \text{ g/cm}^3$. One explanation for the density variance is that the amine group could be engaged in hydrogen bonding, while the methyl substituent cannot. The potential difference due to hydrogen bonding seems minor; however Jong and coworkers²⁰ postulated a similar phenomena in hydroxy terminated poly(ethersulfone)s. The T_g (from DSC) discrepancy is small, 181.5⁰ C and 179.2⁰ C for PES-NH₂ and PES-CH₃, respectively. This variance is small due to the similar molecular weights and that hydrogen bonds are weakened at higher temperatures. Even though this difference is modest, density, T_g and hydrogen bonding all have the same tendency for these two polymers.

The curves shown in Figure 7.8 and Figure 7.11, representing the toughened epoxy systems, vary from the behavior seen in the neat epoxy, Figure 7.12. If one were to apply an additivity relationship then the toughened materials would have physical aging behavior as in Figure 7.13. As is apparent, the physical aging behavior does not simply fall on an additivity line. Due to the co-continuous thermoplastic and epoxy phases, these low strain experiments may be reflecting a contribution to physical aging from both of the phases; however, not in proportion to their weight or volume fraction but perhaps to each phases effective surface area.

Another aspect of these physical aging rate curves is the sharp decrease of μ towards lower physical aging rates, values such as 0.7-0.8. In examining Figure 7.8

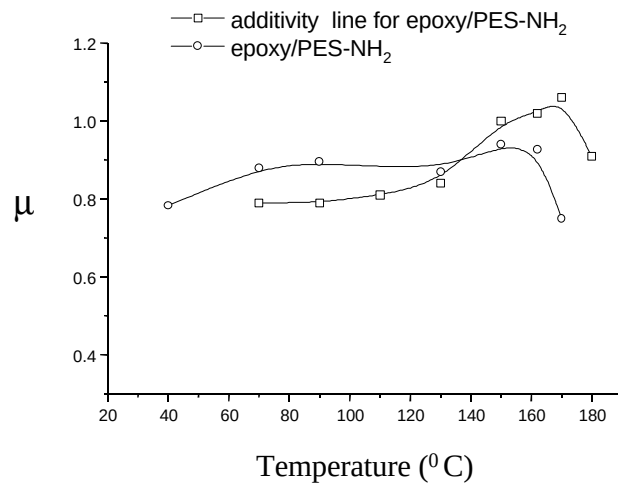


Figure 7.13: Additivity plot using weight fraction

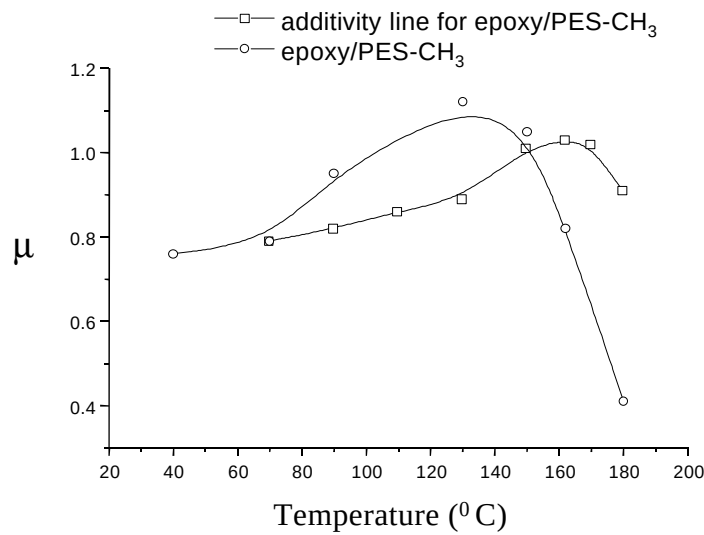


Figure 7.14: Data and additivity lines for toughened epoxy

through Figure 7.12, except Figure 7.11, the onset of decreasing μ values occurs at nearly the same temperature for the toughened epoxy as for the toughener. Moreover, if two lines are drawn to quantitate this onset temperature, as in Figure 7.15,

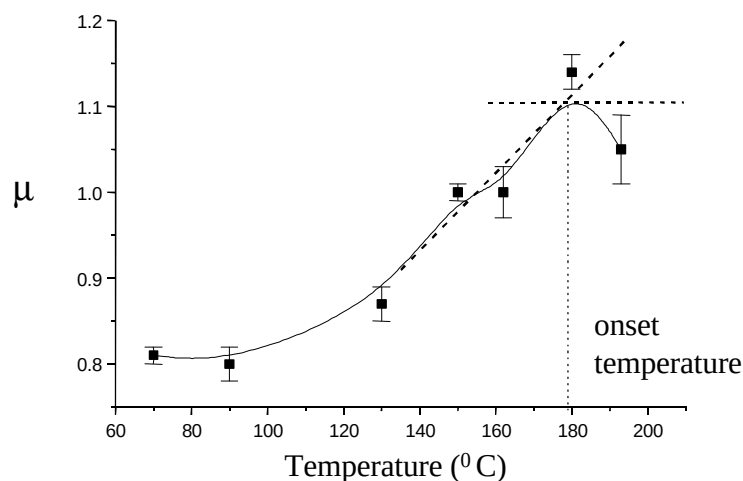


Figure 7.15: Calculation for T_{onset}

one notices that the onset temperatures subtracted from their T_g are in the order PES-NH₂ > neat EPON 828 > PES-CH₃. The physical significance of this onset in the decrease of the physical aging rate is the temperature or temperature range at which the aforementioned thermodynamic properties change at a slower rate. This fact implies that the material is then more stable during use. Although no direct correlation is known between these results and larger scale strain experiments, this implies that other mechanical properties would behave similarly, such as the loss of ductility, tensile strength or modulus.

Another feature of physical aging is volume relaxation, which will be used to evaluate physical aging in these systems. Typical linear dilatometry raw data are

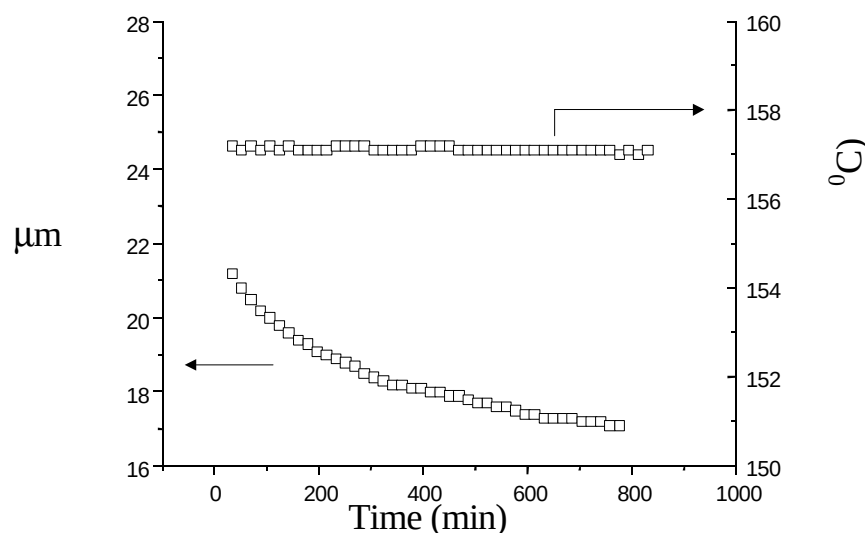


Figure 7.16: Length changes during aging for Epoxy/PES-NH₂ @ 100⁰ C represented in, Figure 7.16. The ordinate units are micrometers, this indicates that the size change is small, since original sample lengths are 20-25 mm. Nonetheless, these slight dimensional changes can have substantial effects on adhesive systems due to embrittlement and loss of ductility. These changes subsequently affect viscoelastic dissipation during crack growth and possibly render a lower fracture energy. With a normalized length change as a function of aging time, one can calculate the volumetric physical aging rate (β_v). The β_v temperature dependence is also determined and shown in Figure 7.17 through Figure 7.19 for the poly(ethersulfone)s, toughened epoxies and neat epoxy, respectively. It is evident from this data that the two tougheners

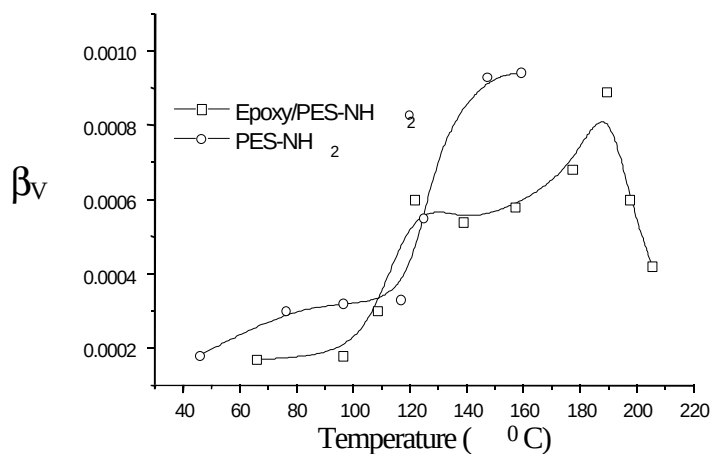


Figure 7.17: β spectrum for toughened epoxy

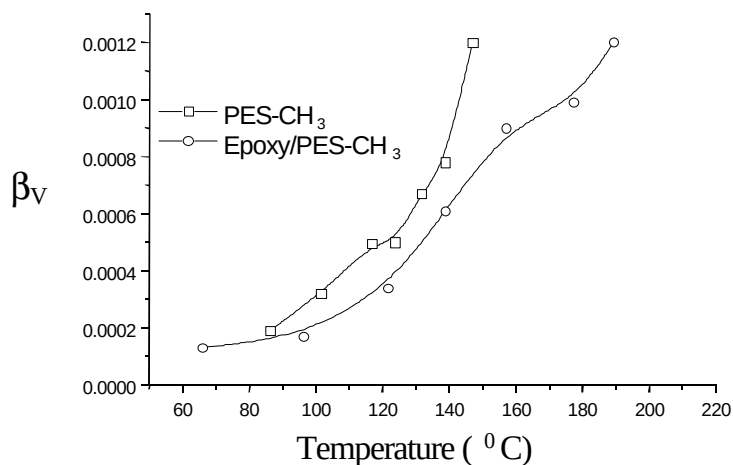


Figure 7.18: β spectrum for toughened epoxy

result in different trends. The PES-NH₂ toughened material mirrors the shape of the neat epoxy curve at higher temperatures although the magnitude is slightly higher. At lower temperatures the neat epoxy and neat toughener curves are closer and the toughened epoxy falls in between these curves. In contrast, when a non-reactive endgroup is attached to the poly(ethersulfone) the behavior changes markedly. As is evident in

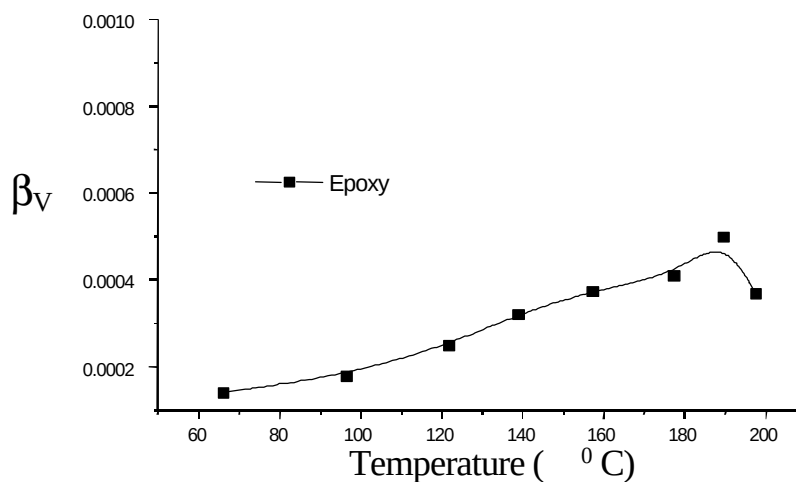


Figure 7.19: β spectrum of epoxy

Figure 7.18 the high temperature behavior of the PES-CH₃ toughened epoxy follows that of the toughener, the physical aging rate shows continuously increasing values. For the lower temperatures, β_V is similar for all three materials; it appears that all of the materials

age at the same rate in this region. In this area physical aging seems to be less dependent on the nature of the system.

The volume relaxation graphs bring out an interesting difference between the two toughened epoxies. At higher temperatures the epoxy with the non-reactive toughener densifies at a faster rate than its reactive analog. This distinction could originate from the manner in which the toughener interacts with the higher volume fraction epoxy phase. The two components are phase separated as described in Figure 7.3; however, there is a possible reason for the different physical aging behavior noted in Figure 7.17 and Figure 7.18. This reason deals with the possibility that PES-NH₂ is anchored better in the epoxy phase due to the reaction of its amine group with an epoxide ring. The reactive poly(ethersulfone)s generate toughened epoxies that are more solvent resistant than the non-reactive poly(ether sulfone)s,¹⁷ therefore there is evidence that the interaction between epoxy and toughener is stronger for the reactive case. Another method of examining the degree of interaction between epoxy and toughener is to calculate the relaxation time distribution and mean relaxation time. These results will be presented in the next section.

7.6. RELAXATION TIME DISTRIBUTION

Step-isothermal data for the dynamic mechanical loss modulus for an amine terminated poly(ethersulfone) is shown in Figure 7.20. These isotherms are fit using

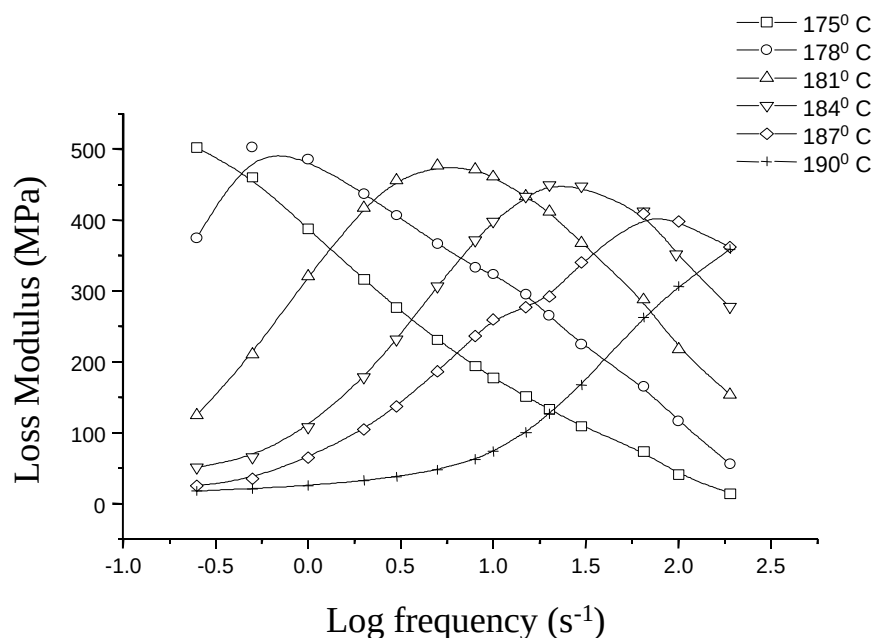


Figure 7.20: Isothermal data for PES-NH₂

the Havriliak-Negami equation; the resultant values for some of the fitting parameters at various temperatures are shown in Figure 7.21. One point to mention is that some of the fitting parameters appear to be temperature dependent. The time decay function in Chapter 3 is calculated using the fitting parameters from the Havriliak-Negami equation.

Using the KWW equation, one can obtain a quantitative indication of the changes in polymer relaxation time distributions. These calculations produce the values summarized in Figure 7.22. As stated previously, the range of β extends from zero to unity; however, values for polymers are usually between 0.2 to 0.8. The upper limit here denotes a case where the system has a narrower relaxation time distribution. The neat toughener has a large β value, 0.7, characterizing this material as being a simpler solid than the neat epoxy. This system has a much broader distribution than the neat toughener does. The toughener in the epoxy- poly(ethersulfone) material has a broader distribution of relaxation times than in its neat state, in fact, the toughener's relaxation time distribution in the toughened material approaches that of the epoxy. The most plausible explanation for this scenario is that some epoxy remains dissolved in the poly(ethersulfone) phase. This could also be the explanation for the slight decrease in the T_g of this phase.

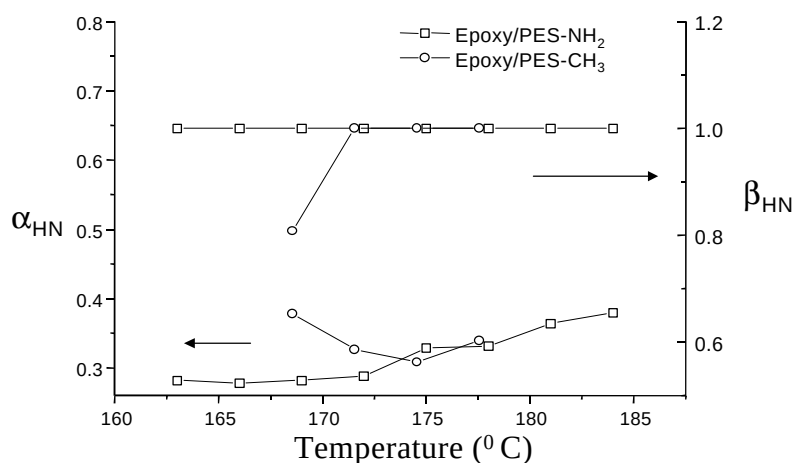


Figure 7.21: Havriliak-Negami fitting parameters for the various systems

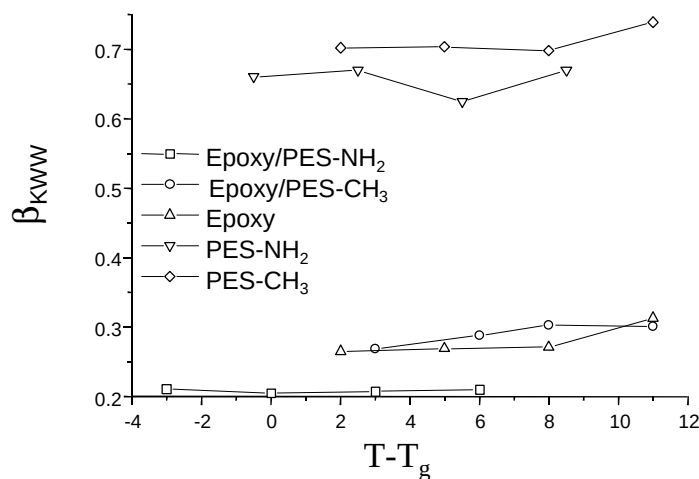


Figure 7.22: Relaxation time distributions for indicated materials

An important aspect to discuss at this point is the possibility of the poly(ethersulfone)'s loss modulus being modified due to contributions from the epoxy phase. The glass transitions of the two components vary by at least 30⁰ C, this generally is sufficient to experimentally resolve any possible contribution to the loss modulus from the second phase. Furthermore, the contributions would be seen in the lower frequencies, since the epoxy would be more likely to contribute to the loss modulus at these lower frequencies. Figure 7.20 shows no evidence at any temperature of a contribution to the loss modulus from the epoxy phase at low frequencies. There also exists no secondary

transition between 160⁰ C – 190⁰ C in the epoxy that could possibly add to the loss modulus.

7.7. SUMMARY

Quantitating physical aging phenomena is important when using amorphous polymeric materials. It becomes especially critical to understand physical aging rates when the systems are designed for high performance applications as is the case for the toughened epoxies researched in this work. This work indicates that the rate of physical aging, either through creep recovery or volume measurements, increases at higher temperatures. Even at moderate temperatures, i.e., temperatures near 100⁰ C, there is a change in the creep compliance at short aging times, which could result in larger changes in the creep compliance extrapolated to longer aging times. This aspect is one important point illustrated by this study. Another noteworthy item is that the toughened system has equal or higher μ values than the epoxy or toughener alone at certain temperatures. With eighty percent epoxy content, the expectation was that the toughened system would behave like the epoxy in its macroscopic aging. The neat epoxy actually has a higher value of mechanical physical aging than the neat toughener does at some temperatures, therefore reproducing the toughener's values for μ would be desirable. The trends in physical aging of the toughener and toughened epoxy are similar; however the absolute value is higher for the toughened material.

Unlike the creep recovery physical aging data, the volume relaxation results indicate an intermediate response for the thermoplastic modified epoxies. In the non-reactive thermoplastic case, the response is closer to the poly(ethersulfone) polymer than to the epoxy. Naturally, at low temperatures, the curves tend to converge, because of the low level of molecular motion in any of these polymeric materials. There is only the possibility of dispersive interactions between the non-reactive toughener and epoxy, therefore interfacial interactions are at a minimum. The level of interphase interactions may even be further reduced due to possible residual stresses that can develop when the coefficients of thermal expansion are different and the sample is quenched into its final state.

When an amine terminated poly(ethersulfone); which can open an epoxy ring just like the curing agent, acts as the toughener the volume recovery data alters. The lower temperature trends are similar to those of the toughener. At higher temperatures, instead of reaching relatively high β_V values, the conduct of the material changes and appears more like an epoxy. This shift in behavior from being toughener-like to epoxy-like causes one to propose that morphological features and possibly interfacial adhesion or interactions are playing a role. This shift in behavior is also an important one, because it means that the volume change slows down relative to the non-reactive analog at higher use temperatures. A final point that gives credence to better interfacial properties for the reactive toughener – epoxy interphase is the density data. The epoxy/PES-NH₂ network has a density that is on the additivity line of the two components. For the epoxy/PES-CH₃ composite there is a deviation from the additivity line for the density. The actual density lies lower than the calculated value from the neat components, meaning that additional volume is incorporated in the system. It is quite probable that the additional volume is added near the interphase, where the dissimilar materials have phase separated and do not contain any links across this boundary.

Ultimately, all the desirable mechanical properties are generated through phase separation. Both the dynamic mechanical analysis and scanning electron microscopy prove that the two components phase separate under the curing conditions used in this work. The change in the relaxation time distribution is large for the poly(ethersulfone) polymers and arises from the epoxy dissolved in the thermoplastic rich phase.

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CHAPTER 8. CHARACTERIZATION AND AGING BEHAVIOR OF TOUGHENED TETRAFUNCTIONAL EPOXIES

8.1. INTRODUCTION

High performance adhesive applications, such as in the aerospace or transportation industries, often necessitate materials that can endure extreme conditions. These extreme conditions include high and low temperatures, humidity, stress, and contact with solvents, etc. Many materials are precluded from high performance applications because they lack resistance to one or more of these type of conditions. The materials that have been developed for these applications are generally fairly costly, as they require extensive testing before they are qualified.

Epoxies and polyimides have found widespread use in high performance structures. This is partially due to their resistance to the above mentioned severe conditions. In the case of the epoxy systems, one is dealing with highly cross-linked materials, which imparts high temperature, solvent and humidity resistance.^{1,2} The drawback to achieving all of these attributes is that the epoxies become very susceptible to failure from high stresses, due to the brittle nature of the network structure. Less brittle networks can generally be produced by reducing the degree of cross-linking; however, the concomitant reduction in glass transition and solvent resistance is not desirable. Another alternative is to add a second phase that can increase the energy dissipation when a material is subjected to stresses.

Various schemes have been used to toughen epoxies via a second phase. One good method for toughening epoxies has been to add a rubber component.³⁻⁶ Upon phase separating, the rubber, typically based on acrylonitrile-butadiene, will increase the fracture toughness. The rise in fracture toughness appears because of possible shear yielding and crazing in the epoxy and/or bridging of the rubber particles across the crack tip. All of these mechanisms can be operative in the epoxy systems if a sufficient volume fraction of a second rubber phase is created in the epoxy matrix. The toughening effect is developed without a drop in the flexural modulus or strength if the level of rubber is held

near or below about 10%, this degree of loading will generally produce an epoxy matrix with dispersed rubber particles.

Although the rubber toughening route can generate a higher fracture energy epoxy system, a problem with this material is that the rubber will tend to degrade at higher temperatures. One solution to this dilemma is to employ an engineering thermoplastic as the second phase.^{7,8} If the neat engineering thermoplastic demonstrates ductile behavior and consequently is a tough polymer at the application temperature, then it may effectively increase the overall fracture toughness when added to epoxies. Another advantage resulting from this combination is that the flexural modulus should not diminish much because of the high modulus of the neat thermoplastic. Therefore, the concentration of the thermoplastic can be increased until the systems show macroscopic phase separation, which generally occurs in the region of 25-40 weight percent when the thermoplastic is above its critical molecular weight for entanglements.

Even though thermoplastic modified networks have improved fracture toughness, there are limitations to this technology. The loading levels of thermoplastics in the epoxies which result in a significant improvement in toughness values are generally near 15 weight percent. However, different morphologies may be created at different thermoplastic concentrations. For example, ten percent by weight thermoplastic generates a dispersed thermoplastic phase in an epoxy matrix. At 15 weight percent a co-continuous structure is formed. Further increases in toughener concentration to twenty percent and beyond generally create a phase inverted morphology, with the thermoplastic being the continuous phase. These conclusions depend on the particular epoxy system, the molecular weight and presence of specific interactions of the toughener, and cure temperature. These higher loading systems are believed to substantially increase toughness because of possible ductile yielding in the continuous thermoplastic phase. Such energy dissipation greatly enhances the fracture toughness. However, a strong rate dependence on the ductile yielding will then also exist, as is the case with the neat thermoplastic. Consequently, under impact conditions, where high strain rates are generated, there may be no toughening effect over the neat epoxy resin.

The toughening benefits of thermoplastic modified network materials are partially negated by other shortcomings. At the higher loadings that are necessary for substantial

toughening, the solvent resistance can drop. Since a continuous thermoplastic phase is present, the solvent can diffuse within the thermoplastic and cause plasticization, stress cracking or even dissolve the toughener. One remediation tactic for such a limitation is to use thermoplastics that have modified endgroups which can react into the network. This modification can serve a couple of purposes; namely, to improve the interfacial interactions or strength via covalent bonds^{9,10} and also to increase the solvent resistance. Furthermore, when a phase-inverted structure has been created the creep compliance is raised at temperatures near the T_g of the thermoplastic; however, the incorporation of a reactive toughener will limit the increase in the creep compliance.

A practical problem for thermoplastic modified epoxies arises in the manufacturing process. The process often requires the use of a solvent to allow mixing of the polymer and epoxy monomer. This solvent is drawn off with use of a vacuum; however, residual solvent can easily persist in the blended mixture. The residual solvent's effect on final properties could be damaging. If solvent is not used, then the viscosity of the mixture can become excessive and difficult to manage. Entrapped air becomes a problem in this case. Using a fine polymer powder permits facile dissolution of the polymer in the epoxy resin. On the other hand, this fine powder can have adsorbed water or cause entrapped air to be produced upon mixing with the epoxy. These limitations can be obviated in part by mixing under vacuum, a further complication in manufacturing.

A further potential change in the thermoplastic modified epoxy system is in their physical aging behavior. If the thermoplastic has a lower glass transition temperature than the epoxy, which is true in the present study, the overall physical aging processes may be accelerated at certain elevated application temperatures. Moreover, if the thermoplastic is the continuous phase, common at 20% by weight of thermoplastic and above, the material might creep to a larger extent. The type of morphology may influence the aging process, since dispersed polymer particles in the matrix will not influence macroscopic creep or diffusion properties. Nonetheless, due to the rigorous environments that these structures could be exposed to, a determination of their physical aging parameters is necessary to assess their durability in high performance applications.

Commercial difunctional, trifunctional and tetrafunctional epoxies are available. The higher the functionality, the higher the cross-link density, which translates into higher glass transition temperatures. For comparison, the highest T_g for a difunctional epoxy network based on bisphenol A and diaminodiphenyl sulfone (4, 4' DDS) curing agent is 215⁰ C.¹¹ Whereas, for a tetrafunctional monomer based on diaminodiphenyl methane and DDS curing agent glass transition temperatures above 260⁰ C can easily be attained without going to full conversion.¹² One disadvantage to the increased cross-link density produced by tetrafunctional epoxies is that the epoxies become even more brittle. For example a fracture toughness values of 0.7 MPa*m^{1/2} for the difunctional epoxy can be compared with 0.5 MPa*m^{1/2} for the tetrafunctional material.^{11,12} Even though toughening by glassy or ‘hard’ particles in brittle matrices was viewed in the early investigations as having little effect without good interfacial interactions,^{13,14} results have proven this hypothesis to be somewhat incorrect.^{12,15-17} Such hard particles, or materials not in the rubbery plateau region of their mechanical spectrum at the test temperature, may toughen a brittle matrix, but perhaps not as effectively as rubber particles. Again, note that a continuous rubber phase is detrimental to the flexural strength and modulus of the material, whereas a thermoplastic below its T_g (“hard” particles) will retain these good characteristics.

As discussed in the previous paragraph, tetrafunctional epoxies cured with DDS easily attain high glass transition temperatures. The tetrafunctional epoxy cures rapidly due to its high functionality; however, there are various cure schedules in the literature that indicate long curing conditions. Some of these cure schedules have long cycles above 250⁰ C, which could result in degradation of the epoxy system. The variation in cure schedules has lead the author to monitor curing of the tetrafunctional epoxy with DDS using dielectric spectroscopy.

8.2. CHEMISTRY OF TETRAFUNCTIONAL EPOXIES

The manufacture of tetraglycidyl diaminodiphenylmethane (TGDDM) proceeds from the reaction of one mole of diaminodiphenylmethane (DDM) with four moles of epichlorohydrin. The product of this reaction undergoes dechlorohydration in basic conditions to give TGDDM in the second step, see Figure 8.1. This process cannot be a

single pot reaction since DDM is a curing agent for epoxies. The epoxy would react with DDM to some extent to create higher molecular weight species. The reaction depicted in Figure 8.1 is not quantitative for the commercially available tetrafunctional epoxies, therefore the number of equivalents per molecule is less than four.

A generalized reaction scheme for the cross-linking reaction of an epoxide ring and an amine is represented in Figure 8.2. There are various possible side reactions to this generalized reaction when employing TGDDM.¹⁸⁻²⁰ These include some cyclic structures which result from intramolecular reactions of the epoxide rings with a secondary amine that has formed from the reaction of an epoxy and diamine. The side reactions occur at higher temperatures and in situations where the epoxy rings are in excess. The significance of the side reactions is that different mechanisms can be operative at different reactant concentrations or cure temperatures. Therefore, following the cure kinetics of these systems can be challenging.

To calculate the percent conversion at gelation, one employs the expression given in Eq. 8.1.

$$P_{gel} = \frac{1}{\{r[1 + P_A(f_A - 2)][1 + P_B(f_B - 2)]\}^{1/2}} \quad \text{Eq. 8.1}$$

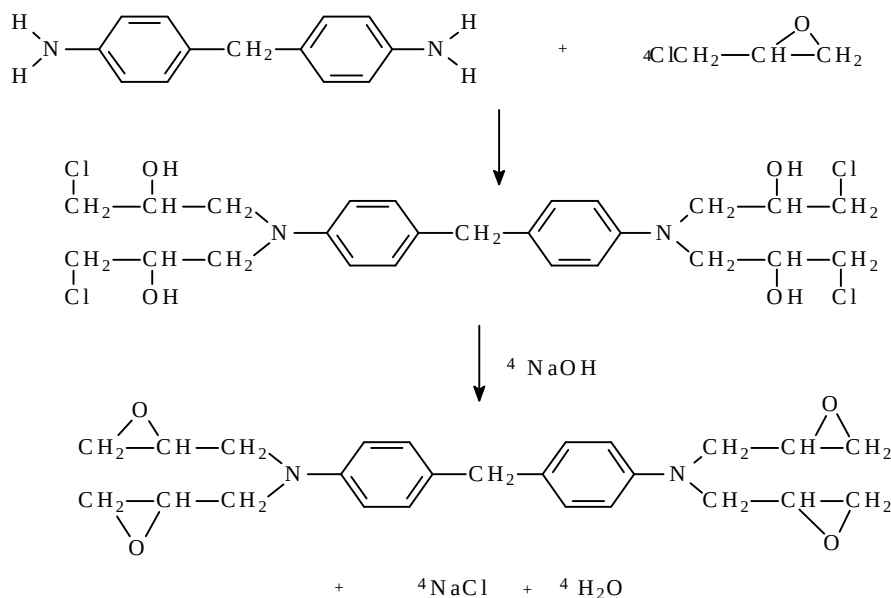


Figure 8.1: Dechlorohydration step in producing TGDDM

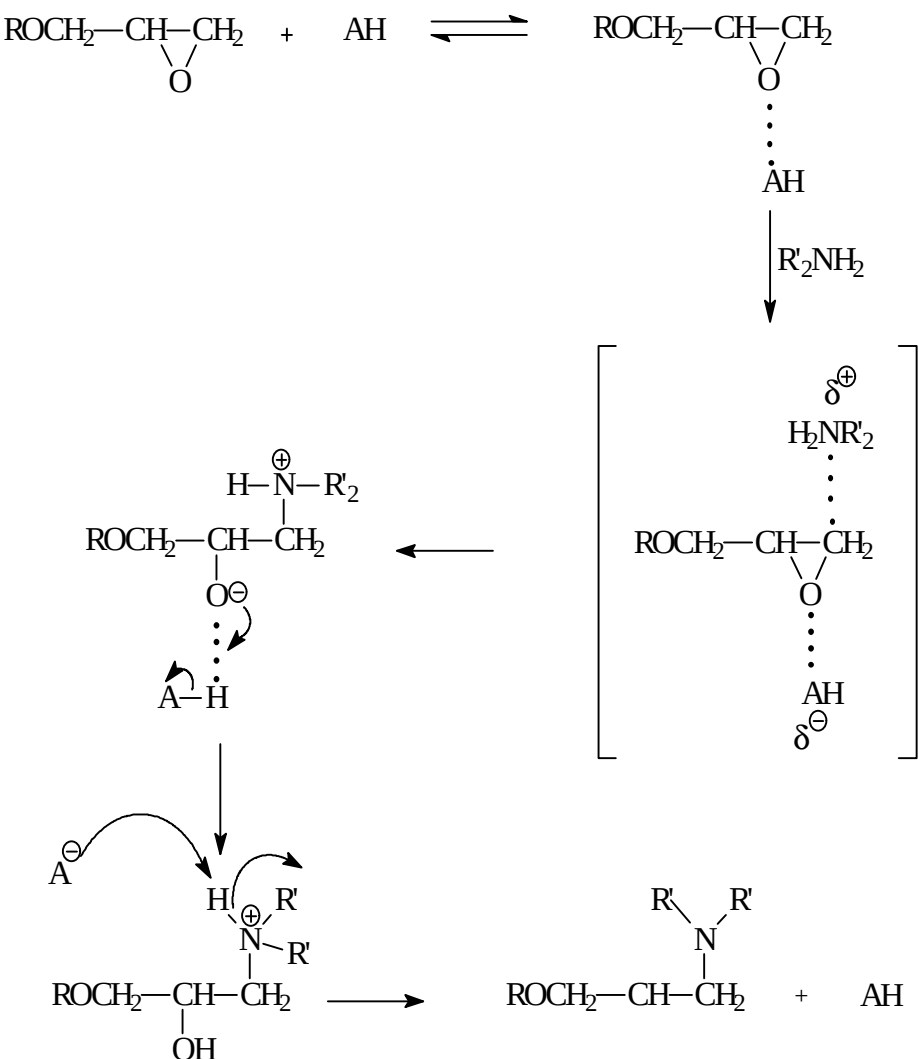


Figure 8.2: Generalized reaction of amine and epoxide group

The extent of conversion which results in gelation is P_{gel} , r is the ratio of total A groups to B groups, where A and B are the reactants. The average molar functionality of A and B, f_A and f_B , must both be at least two and one has to be greater than two to achieve a macroscopic three-dimensional system. P_A and P_B are the fraction of multifunctional A and B groups out of all A and B groups. Consequently, for a stoichiometric ratio ($r = 1$) of a tetrafunctional epoxy ($f_A = 4$, $P_A = 1$) with a tetrafunctional diamine ($f_B = 4$, $P_B = 1$) the theoretical gel point is $1/[3 \cdot 3]^{0.5}$ or 0.33. In actuality, the average functionality of the tetrafunctional epoxy is 3.7. By making the good assumption that all epoxy molecules have a functionality greater than 2, the gel point is predicted to be $P = 0.35$.

8.3. EXPERIMENTAL

8.3.1. SAMPLE PREPARATION

The commercially available tetrafunctional epoxy employed in this study was MY721, donated by Ciba-Geigy. The epoxy was titrated to ascertain the average functionality per molecule, the experimental setup for the titration is identical to that described previously concerning the poly(ether sulfones). The curing agent was 4,4'-diaminodiphenylsulfone. The tougheners used were Ultem[®], GE Plastics, a polyetherimide based on bisphenol A and three analogs to Ultem prepared by Dr. Hong Zhuang and Mr. Charles Tchatchoua, which were controlled for their molecular weight using m-phenylene diamine. The molecular weights and theoretical molecular weights (given in parentheses) of the synthesized tougheners were 11800 (10k), 14900 (15k) and 19300 (20k).²¹ The endgroup of each polyetherimide was an amine group, allowing these tougheners to react into the epoxy network. Although these molecular weights were not exactly the theoretical molecular weights, the values in parentheses will be used to describe the toughener. Percent loading of the toughener in the epoxy resin varied from 5 to 25 weight percent for Ultem[®] toughened materials and 5 to 20 % for the reactive tougheners.

To facilitate the dissolution of the polymer in the epoxy monomer, a 10% polymer solution in chloroform was precipitated into methanol to get a finely dispersed powder. The powder was thoroughly dried in a vacuum oven to remove all methanol and water. Before being charged into a round bottom flask with the epoxy, the polymer powder was sifted through a mesh with pores 25 μm in diameter. The epoxy-polymer mixture was stirred under vacuum until all of the polymer had dissolved at 150⁰ C. After adding and dissolving the curing agent, DDS, the mixture was poured into a pre-heated silicone rubber mold. The stoichiometric amount of DDS added was simply calculated by:

$$\text{grams}(\text{DDS}) = \frac{\text{grams}(\text{TGDDM})}{114} * 64$$

where 114 and 64 represent the equivalent molecular weight of TGDDM and DDS, respectively. The epoxy was degassed for 5-6 minutes at 150-160⁰ C. Finally, the tetrafunctional epoxy mixture was cured at 160⁰ C for 2 hours followed by a step at 220⁰

C for 1 hour and 15 minutes at 240⁰ C. The oven was programmed to cool at 4⁰ C/min to ambient temperature.

8.3.2. GEL FRACTION DETERMINATION

The soluble fraction was resolved by Soxhlet extraction. The samples to be extracted, approximately 0.5 grams, were placed in thimbles that had been soaked in chloroform for 12 hours and subsequently dried for 12 hrs to a stable weight. The samples were weighed in the thimbles and then extracted for 4 days using refluxing chloroform. Afterwards, the thimbles were removed and dried for 24 hours in a vacuum oven at 100⁰ C. Finally, the samples were weighed and the gel fraction was calculated.

8.3.3. DIELECTRIC MONITORING OF CURE

Monitoring of the cure process via dielectric analysis utilized remote sensing probes from Micromet. An external oven was operated to maintain isothermal control. The dielectric analyzer is a 1689 RLC Digibridge from GenRad, which is controlled through Polymer Laboratories software. The isothermal cure was monitored at various temperatures ranging from 100⁰ C to 190⁰ C. The capacitance and dielectric dissipation is measured at 4-5 frequencies between 100 Hz and 100 kHz. The data was then analyzed as a function of time. The analysis is presented in the results and discussion section.

8.3.4. DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis (DMA) was used to determine the glass transition temperature of the cured material. The tests were performed in single cantilever bending with a heating rate of 3⁰ C/min on a Polymer Laboratories Mark II DMTA. A single frequency scan at 1 Hz was obtained.

8.3.5. SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) aided in assessing the morphological features of the toughened epoxy systems. As suspected the materials phase separated into an epoxy rich and toughener rich phase. SEM of fractured surfaces helped determine the morphology, because the toughener tended to undergo some ductile fracture and create a

rough surface. An ISI-SX SEM with an accelerating energy for the electron beam of 20 kV and a working distance of 15 mm was operated. The samples were gold sputtered for three minutes to insure that the samples were conductive. To conclude if the amine terminated tougheners imparted more chemical resistance than the non-reactive tougheners, samples were etched in chloroform for 10 days. The etched samples were then dried in vacuum for two days and examined with the electron microscope.

8.3.6. PHYSICAL AGING MEASUREMENTS

The rate of physical aging was monitored by dilatometry tests. This test has been discussed at length in previous chapters, therefore much of the details are omitted here. The only difference in the dilatometry tests was that the samples were between 18-20 mm in length with a cross-sectional area of 0.2 mm^2 . In the length dilatometry experiments the samples were preheated to 240°C and held at that temperature for 5 minutes, followed by quenching to the start temperature. This temperature is not above the glass transition of the epoxy phase. However, the epoxy has a T_g in the range $260\text{-}270^\circ \text{C}$, which for these systems precludes erasing the thermal history, since degradation or further cure may continue if temperatures rise above the T_g of the tetrafunctional epoxy. The preliminary objective in this part of the study was to examine the effect of the toughener on the aging behavior. Therefore, increasing the temperature to 240°C (more than 20°C above the toughener T_g in all cases) should suffice for the present evaluation of aging effects.

8.3.7. MECHANICAL TESTING

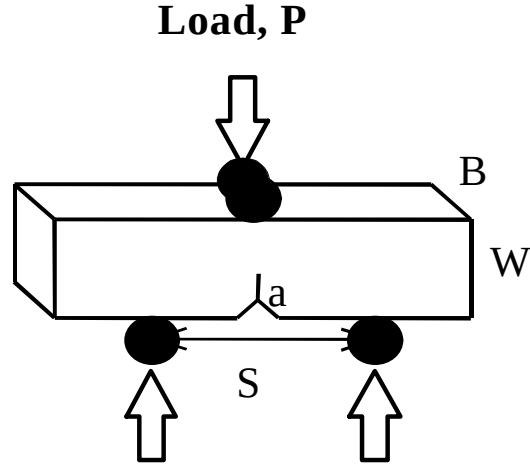


Figure 8.3: SENB geometry, the parameters are described below

The mechanical measurement geometry selected to assess the fracture toughness of the toughened tetrafunctional epoxies was a single edge notch beam (SENB) sample. The geometry of this sample is given in Figure 8.3 and follows ASTM D 5045 – 91. The samples were machined to achieve the dimensions specified in this standard. The jig used for testing the specimens was in compliance with the standard. An Instron 1143 was used at a crosshead speed of 1 mm/min at ambient conditions. For the calculation of the fracture toughness the maximum load was recorded, as well as the exact dimensions of the sample along with the initial crack length. The expression for the fracture toughness (K_{IC}) is shown below:

$$K_{IC} = \frac{PS}{BW^{3/2}} f(x) \quad \text{Eq. 8.2}$$

$$\text{where } f(x) = \frac{3x^{1/2} [1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{2(1+2x)(1-x)^{3/2}}$$

P=load at failure (N)

B=specimen thickness (mm)

S=span length (mm)

W=sample depth (mm)

x=a/W, a=precrack length (mm)

Flexural modulus was also determined from the initial slope of a stress-strain curve. The same instrument was used as for the SENB test with the same crosshead speed and environment. The bending jig was slightly modified from the previous test to accommodate ASTM D 5943 – 96. A small modification of the specimens was necessary because of the sample quantity limitations. The length to thickness ratio was smaller than specified, which makes the samples seem stiffer. However, for the purpose of this study, which was to compare among samples with a common geometry, this discrepancy was not viewed as critical for relative comparisons.

8.4. RESULTS AND DISCUSSION

8.4.1. DIELECTRIC CURE STUDIES

In monitoring the curing reaction by dielectric spectroscopy one can potentially acquire much data about the physical changes that the curing material is undergoing. The time to vitrification can be readily determined from the spectrum, as will be proven in the development below. The gel point is more difficult to determine, since no electrical event is associated with gelation.²² Nonetheless, researchers have proposed good methods to estimate the time to gel during isothermal and ramping cure schedules.^{23 - 26} This discussion will be limited to isothermal cures.

In the production of the tetrafunctional resin from DDM and epichlorohydrin, see Figure 8.1, a strong base is needed. Not all of this base will be used, therefore this must be neutralized. From both of these processes ions remain in the resin, these ions will be able to move in the medium towards the oppositely charged electrode. This is the origin of most dc conductivity in the system under investigation. The difunctional epoxy based on bisphenol A (DGEBA) also has a residual ion content on the order of 10 ppm, which is sufficient to produce a dc conductivity effect in the dielectric signal. These ion currents are a source of a useful probe in dielectric studies on curing resins. Figure 8.4 depicts the mechanism of dc conductivity in the presence of an electric field. As the system reacts and builds up viscosity, Figure 8.5 expresses the phenomena that are occurring with the

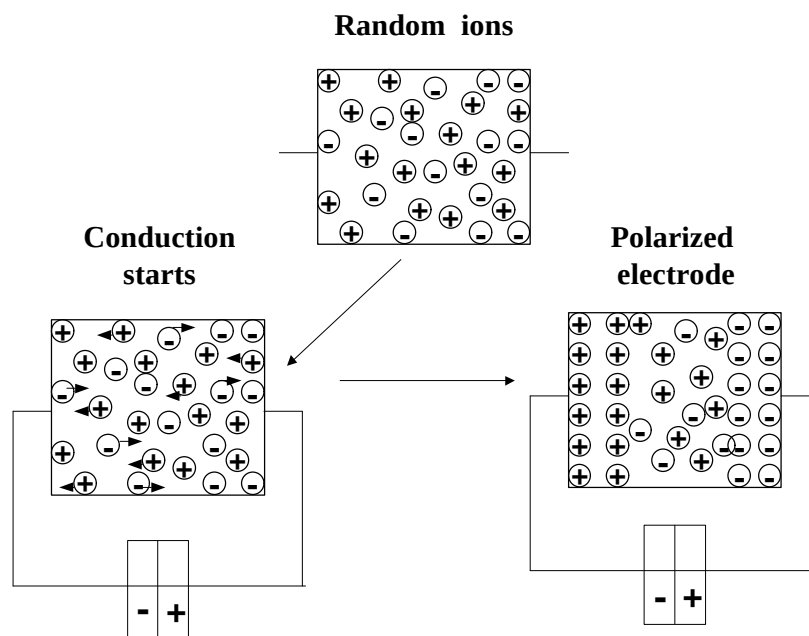


Figure 8.4: After the electric field has been applied conduction begins and a polarized electrode is formed

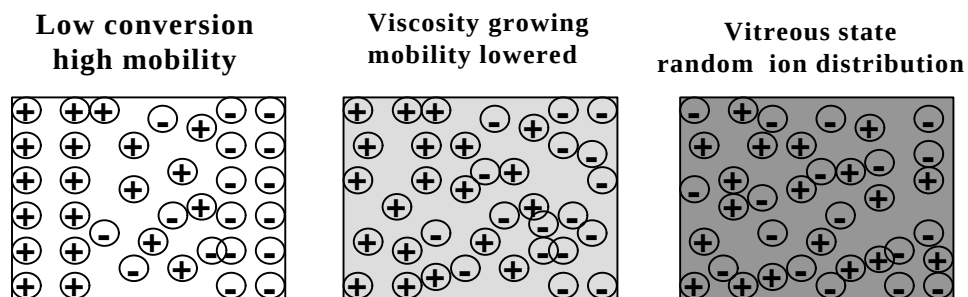


Figure 8.5: Loss of conductivity as function of viscosity during curing process

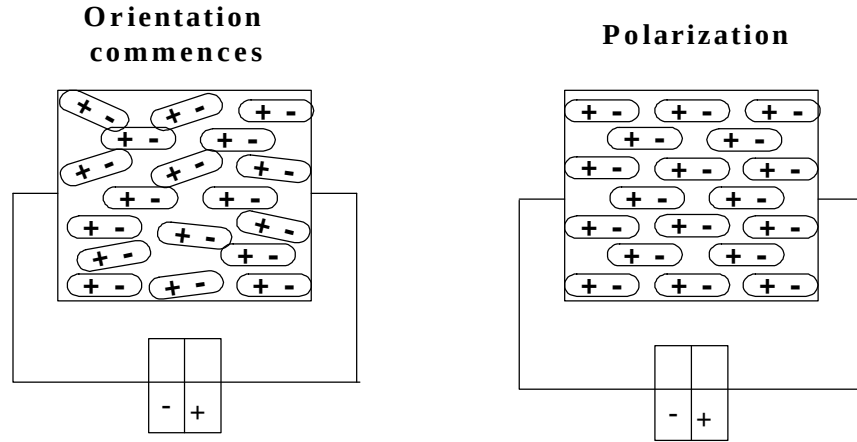


Figure 8.6: Changes in dipole orientation as electric field is applied:
relaxation time changes during cure process

ions. The dipoles also react to an applied electric stimulus as shown in Figure 8.6. When the system is going through its glass transition a process which is the reverse of that in Figure 8.6 occurs. Namely, the dipoles become very sluggish and cannot respond to an electric field oscillating at a particular frequency, therefore the dipoles become quasi-locked into a random orientation.

Resins containing ions have contributions to both the dielectric permittivity and dielectric loss in addition to those that arise from dipolar relaxations. These additional factors are detailed in Eq. 8.3 and Eq. 8.4:

$$\epsilon'(\omega, T, t_c) = \left(Z_0 \sin\left(\frac{a\omega}{2}\right) \omega^{-(1+a)} \right) G^2(\omega, T, t_c) / C_0 + \epsilon'_{dip}(\omega, T, t_c) \quad \text{Eq. 8.3}$$

$$\epsilon''(\omega, T, t_c) = (s_0(T, t_c) / \omega \epsilon_0) - \left(Z_0 \cos\left(\frac{a\omega}{2}\right) \omega^{-a} \right) G^2(\omega, T, t_c) / C_0 + \epsilon''_{dip}(\omega, T, t_c) \quad \text{Eq. 8.4}$$

The supplementary terms, besides the dipolar effects (ϵ'_{dip} and ϵ''_{dip}) are represented in the r.h.s. first term of Eq. 8.3 and the first and second r.h.s. terms of Eq. 8.4. The first term in Eq. 8.4 originates from dc conductivity (σ_0) and is dependent on the frequency. In all of the terms T is the temperature of cure and t_c is the time of cure. The contributions to the measured permittivity and loss that are common to both deal with space charge influences in the resin that could develop from high concentrations of ions. The components of these terms are Z_0 , the impedance of the electrode-insulator interface, G ,

the conductivity and C_0 , the capacitance of the sample. In most normal samples the ion concentration is not sufficient to cause space charges to develop, therefore this contribution can be neglected and Eq. 8.3 and Eq. 8.4 simplify to

$$e'(w, T, t_c) = e'_{dip}(w, T, t_c) \quad \text{Eq. 8.5}$$

$$e''(w, T, t_c) = e''_{ion}(T, t_c) + e''_{dip}(w, T, t_c) \quad \text{Eq. 8.6}$$

where $\epsilon''_{ion} = \sigma / \omega \epsilon_0$.

Although the ion concentration is usually not high enough to produce the space charge effect, the ionic or dc conductivity can be used in the analysis of curing resins. This effect is the first term on the r.h.s. of Eq. 8.4. The conductivity decreases as the curing process continues, because of the inverse relationship between viscosity (which rises as cure progresses) and conductivity. However, ionic mobility is still present after gelation has occurred, since the ions are not large diffusants, This ion mobility contributes to conductance even after gelation. This phenomenon causes uncertainty in extracting a gelation time from curing studies employing dielectric analysis. Methods for calculating a dielectric gelation time have been attempted with some success. One expression that works well is²

$$s_0(T, t_c) = s_0(T, t_c \rightarrow 0) \left[\frac{t_{gel}(T) - t_c(T)}{t_{gel}(T)} \right]^{x(T)} \quad \text{Eq. 8.7}$$

As is evident from Eq. 8.7, as $x(T)$ increases the drop in conductivity becomes sharper. This expression can be used in the determination of t_{gel} for difunctional epoxy resins. Another expression that relates changes in conductivity to physical events during the cure cycle is the following²

$$s(T, t_c) = A(T) \exp \left\{ \frac{-B(T)}{t_0(T) - t_c} \right\} \quad \text{Eq. 8.8}$$

$A(T)$, $B(T)$ and t_0 are empirical fitting parameters. This expression is the familiar Vogel-Fulcher (VF) equation with times replacing temperatures. It basically describes the change in viscosity (conductance) as a point of singularity ($t_0(T)$) is approached. This equation leads to a “ t_0 ” which is closer to a vitrification time than a gelation time, because the VF equation is usually applied to the glass transition phenomena. It is also

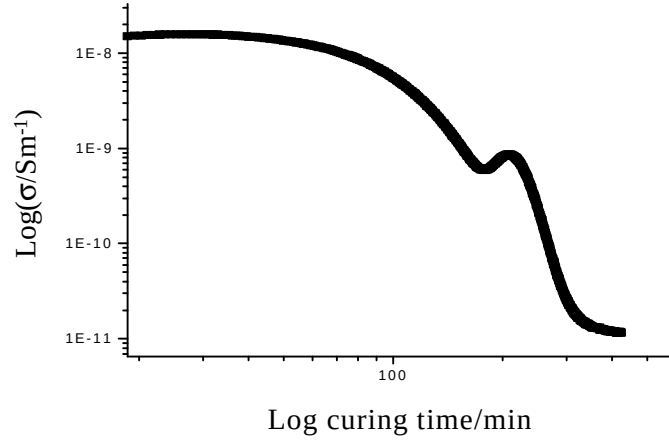


Figure 8.7: Conductivity changes as network is formed.

Peak on the right is the vitrification peak.

obvious from this formalism and experimental results that conductance persists at a relatively high level even after gelation, and even close to vitrification, see Figure 8.7. Due to the better match with gelation times of Eq. 8.7 this expression is employed in calculating gelation times in this study.

An isothermal curing process can be used to demonstrate dielectric behavior as a function of cure time that is analogous to the behavior of a static dielectric (no changes in chemical structure during measurement) in the frequency domain. Figure 8.8 reproduces this analogy. The reason for this analogy is developed in the following argument. Classical dielectric theory indicates that the complex permittivity of a dielectric material subjected to an alternating field can be written as a superposition of all the electrical displacements (Boltzmann superposition):

$$\epsilon^*(i\omega, T, t_c) = \epsilon_\infty(T, t_c) + [\epsilon_0(T, t_c) - \epsilon_\infty(T, t_c)] \int_0^\infty \exp(-i\omega t) * \left(-\frac{\partial \Phi(t)}{\partial t} \right) dt \quad \text{Eq. 8.9}$$

In this equation $\epsilon_0(T, t_c)$ and $\epsilon_\infty(T, t_c)$ represent the permittivity at low and high frequencies respectively. The symbol $\Phi(t)$ denotes a relaxation function whose form is shown in Eq. 3.1

$$[\Phi(t)]_{t_c} = \exp \left[- \left(\frac{t}{\tau} \right)^b \right] \quad \text{Eq. 8.10}$$

This relaxation function is the ubiquitous KWW expression and is constant for a specific time of curing. The values of t and τ in Eq. 8.9 and Eq. 3.1 have a strict interpretation: t

is the time for the observation of the decay of polarization from the electric field stimulus during which τ (in this case an average relaxation time) is invariant. Throughout the curing process τ is changing as the system forms covalent cross-links. However, during the decay process (for 1 kHz frequency ca. 1 ms) the structure can easily be viewed as invariant for a thermal cure where total cure time is on the order of hours. This approximation permits one to write Eq. 3.1 in the form of a time invariant expression

$$N^*(i\omega\tau) = \int_0^\infty \exp(-i\omega\tau) \left(-\frac{\partial\Phi}{\partial t} \right) dt \quad \text{with} \quad \text{Eq. 8.11}$$

$$N^*(i\omega\tau) = N'(\omega\tau) - iN''(\omega\tau)$$

N is a function of the product of ω and τ of the structural state of the epoxy at any t_c . By combining Eq. 8.9 and Eq. 8.11 and separating the permittivity and dielectric loss one has

$$\epsilon'(T, t_c) = \epsilon_\infty + \frac{A_p}{T} N'(\omega\tau(T, t_c)) \quad \text{and} \quad \text{Eq. 8.12}$$

$$\epsilon''(T, t_c) = \frac{A_p}{T} N''(\omega\tau(T, t_c)) \quad \text{Eq. 8.13}$$

The difference between the dielectric permittivity at low and high frequencies ($\epsilon_0 - \epsilon_\infty$), the oscillator strength, is given by A_p , which decreases as the temperature and t_c are increased. The value of ϵ_∞ remains constant throughout the cure since it should be measured at very high frequencies where only the infrared contributions are significant and dipolar or even dc conductivity contributions are negligible.²⁷⁻²⁹ The dipolar component of ϵ_0 is difficult to measure during the cure because of dc conduction occurring when viscosity is low and mobility is high. This term has been estimated in research with special resins where ions have been practically eliminated.²⁷⁻²⁹ The conclusion from these experiments is that ϵ_0 changes only by 10%. Hence, the notable changes in the complex permittivity are found due to τ varying from 10^{-9} to 10^4 seconds as the system reacts. With this in mind Eq. 8.9 can be simplified by showing that on the r.h.s. the relaxation function is dependent on the time of cure:

$$\epsilon^*(i\omega, T, t_c) = \epsilon_\infty(T) + [\epsilon_0(T) - \epsilon_\infty(T)] * N^*(i\omega\tau(T, t_c)) \quad \text{Eq. 8.14}$$

The important conclusion from this development is that Eq. 8.14 shows the same behavior regardless if ω or τ (variability arises from progression of cure) is taken as

the experimental variable. Hence, plots of dielectric loss as a function of cure time resemble those plots made of dielectric loss as a function of frequency or temperature, see Figure 8.7. Therefore, from plots of dielectric loss versus curing time the vitrification time can be readily identified and used in creating time-temperature transformation diagrams (TTT diagrams). Furthermore, complex plane plots can be produced, where the real and imaginary parts of the complex permittivity are extracted at different cure times, Figure 8.8. These type of Argand diagrams have similar trends to those using frequencies (Figure 8.9) to generate such diagrams, a comparison of Figure 8.8 with Figure 8.9 demonstrates this correspondence.

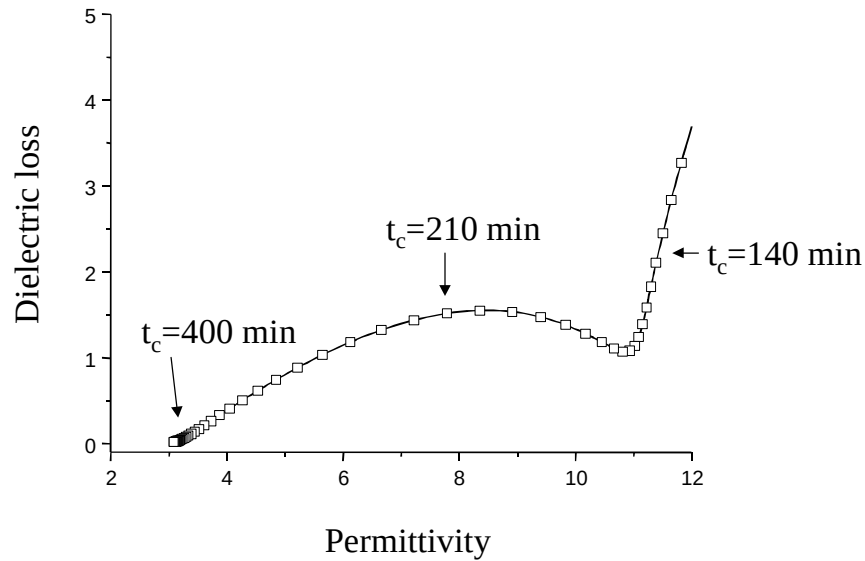


Figure 8.8: ϵ'' from TGDDM/DDS @ 1000 Hz, 120⁰ C

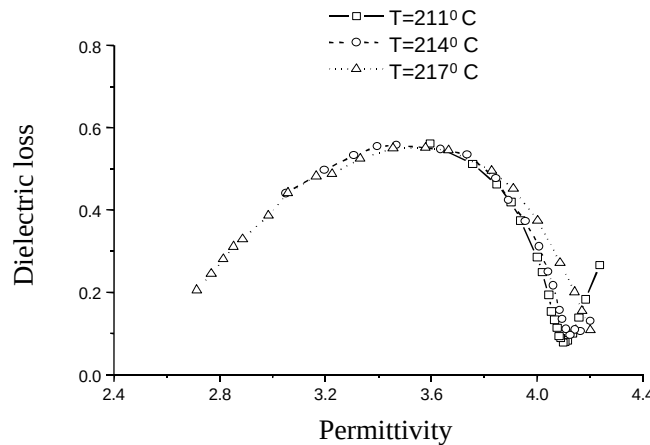


Figure 8.9: Argand diagram generated from variable frequency experiment

A TTT diagram was developed for the materials of this chapter using the above techniques and schemes. The gelation line is created by fitting the conductance data to Eq. 8.7 (omitting data from the Cole arc in Figure 8.8). When this time plus the time to reach vitrification are recorded as a function of cure temperature, Figure 8.10 is generated for a TGDDM/DDS system. Gelation is the line that appears at shorter times, since gelation precedes vitrification.

Other curing agents were utilized in this cure study, specifically, bis-(3,3' aminophenyl) phenyl phosphine oxide (BAPPO) and bis-(3,3' aminophenyl) methyl phosphine oxide (BAMPO). The structures of these monomers are given below in Figure 8.11. In comparing BAMPO and BAPPO to DDS, Figure 8.12, a clear difference is that BAMPO and BAPPO are meta substituted, whereas DDS is para substituted in this case.

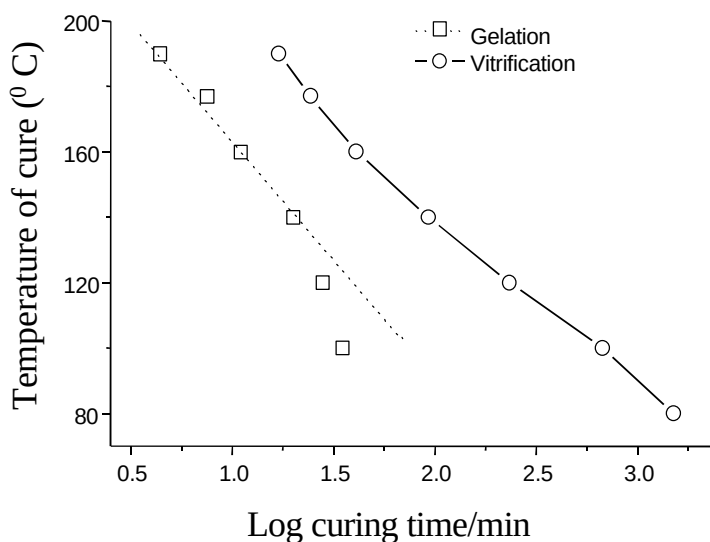
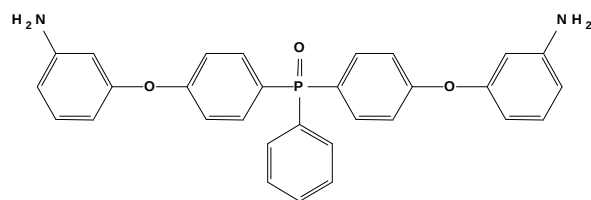
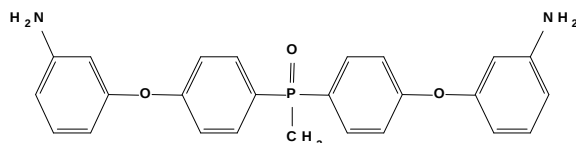


Figure 8.10: TTT diagram for TGDDM/DDS @ 1000 Hz



BAPPO



BAMPO

Figure 8.11: Two phosphine-oxide containing diamines

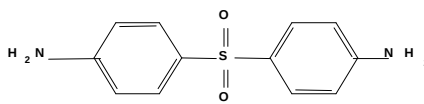


Figure 8.12: 4,4' DDS curing agent

The sulfonyl group acts as an electron withdrawing group because of the difference in the electronegativity between sulfur and oxygen. The phosphine oxide moiety also has an electron withdrawing effect, with the negative charge similarly residing on the oxygen atom. The free electrons on the nitrogen in the para position are shared by the phenyl ring in resonance structures, indicating that they are less available for donation or catalyzing the epoxide ring opening. Therefore, even though BAMPO and BAPPO are larger in size their reactivity is enhanced over that of 4,4' DDS. Using this rationale it is not surprising to see that the two curing systems containing the phosphine oxide moieties gel and vitrify quicker than those based on 4,4' DDS. Figure 8.13 and Figure 8.14 demonstrate this behavior explicitly. A more subtle difference between the reactivity of BAMPO and BAPPO could be explained by the fact that BAPPO's mobility is reduced by its large pendant phenyl group. This difference is a secondary effect in regards to the variation caused by meta or para substitution.

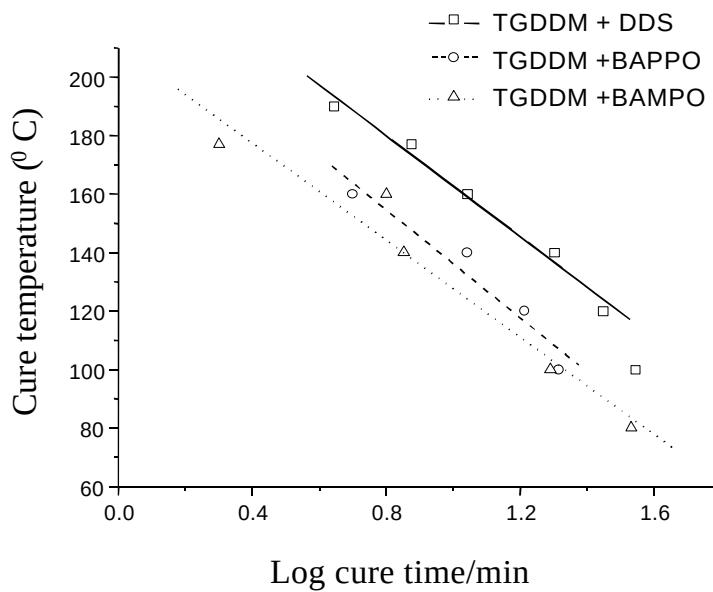


Figure 8.13: Gelation times measured by dielectric analysis for three curing agents

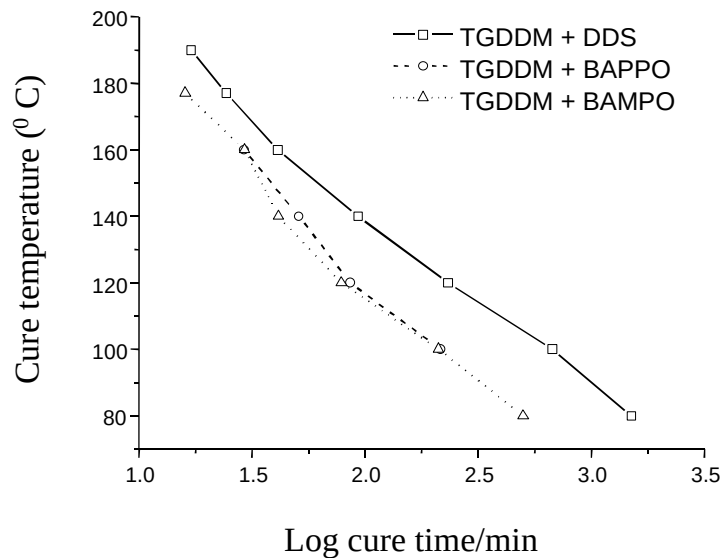


Figure 8.14: Vittrification curves from dielectric analysis for 3 curing agents

Some dielectric studies were conducted using a PEI-NH₂ 15k toughened TGDDM/DDS system. The results of these tests are shown in Figure 8.15 and Figure 8.16 for cure temperatures of 160⁰ C and 140⁰ C. The spectra are more complicated due

to the additional component and the two phase system that form. The toughener phase separates from the epoxy prior to gelation, where dc conductivity is still large. Besides the dc conductivity contributing to the dielectric loss signal, after phase separation there are interfacial effects due to differing conductivities of the two phases. These effects were studied and described by Maxwell,³⁰ Wagner³¹ and Sillars.³² Unfortunately, the dc conductivity obscures the exact detection of the phase separation process. Nonetheless, this method looks promising and should be examined more with similar systems in the future.

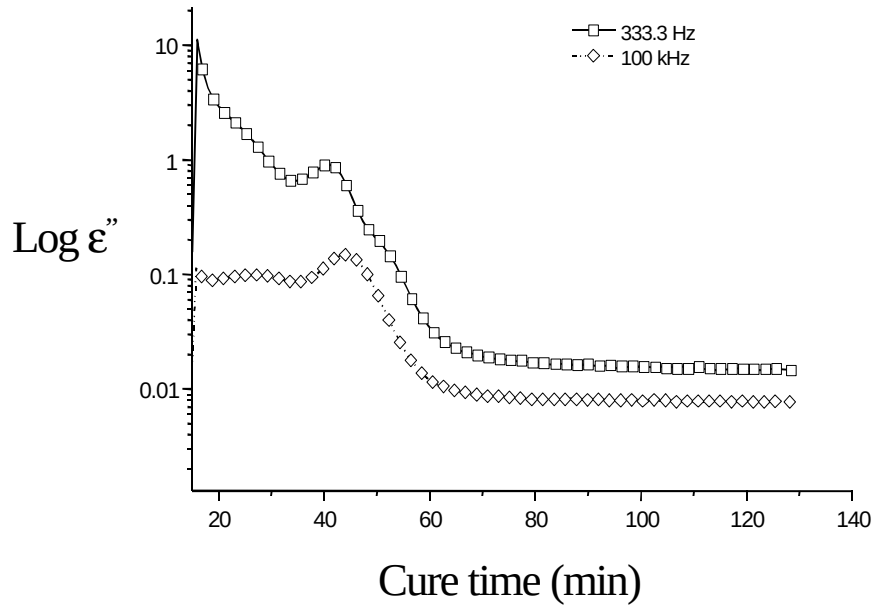


Figure 8.15: Dielectric monitoring of cure for toughened system at 160⁰ C

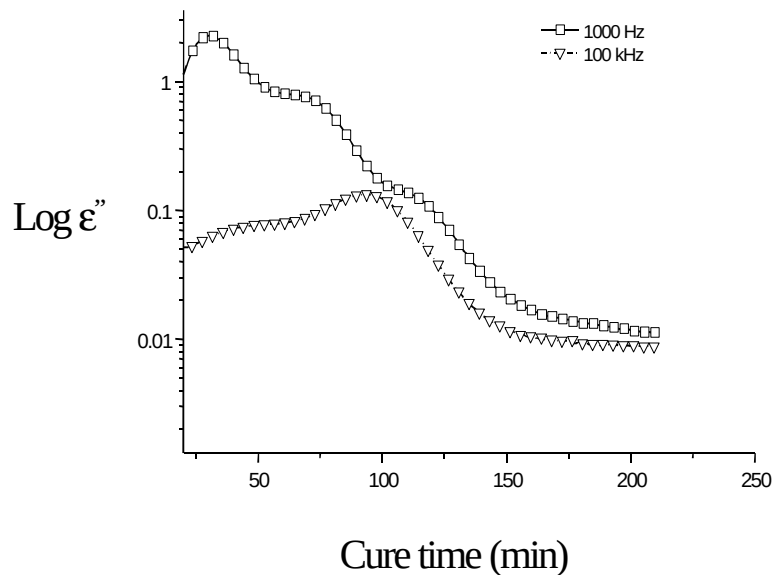


Figure 8.16: Cure of toughened system at 140⁰ C

8.4.2. DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis aided in determining if the toughened epoxies phase separated and to resolve the molecular relaxations associated with each phase. Samples without any thermal treatment after being removed from the silicone molds (as-cast samples) showed two transitions. One transition, whose peak ranged from

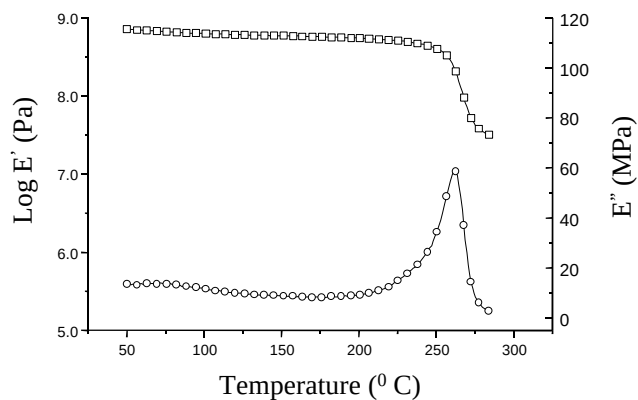


Figure 8.17: Storage and loss moduli for TGDDM/DDS

175-212⁰ C corresponded to the polyetherimide toughener, either reactive or non-reactive. The non-reactive polyetherimide always had a lower glass transition temperature than the reactive one at the same loading level.

The other thermal event which ranged from 260-270⁰ C was the epoxy T_g. The dynamic mechanical characteristics of these materials are illustrated in Figure 8.17- Figure 8.21. Figure 8.17 shows the behavior of the neat epoxy cured with DDS, note that the T_g of the epoxy phase is near 270⁰ C. In the next plots, Figure 8.18- Figure 8.21, one sees that first, as the composition moves to higher toughener concentrations that the glass transition temperature of this phase increases. This phenomenon can be explained with the aid of a phase diagram for a similar material, as will be summarized soon. Second, the epoxy phase composition does not change much as the overall composition is adjusted. Finally, the reactive polyetherimides all have higher transition temperatures for the toughener rich phase at the same composition. Figure 8.22 and Figure 8.23 condenses all

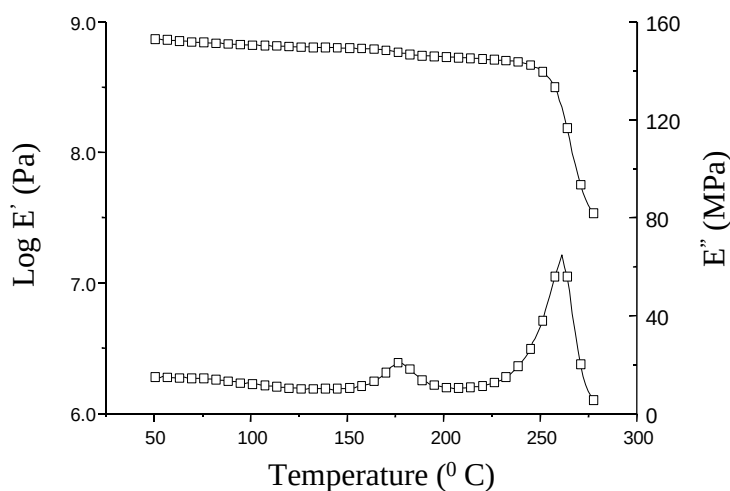


Figure 8.18: DMA results for TGDDM/Ultem 10%

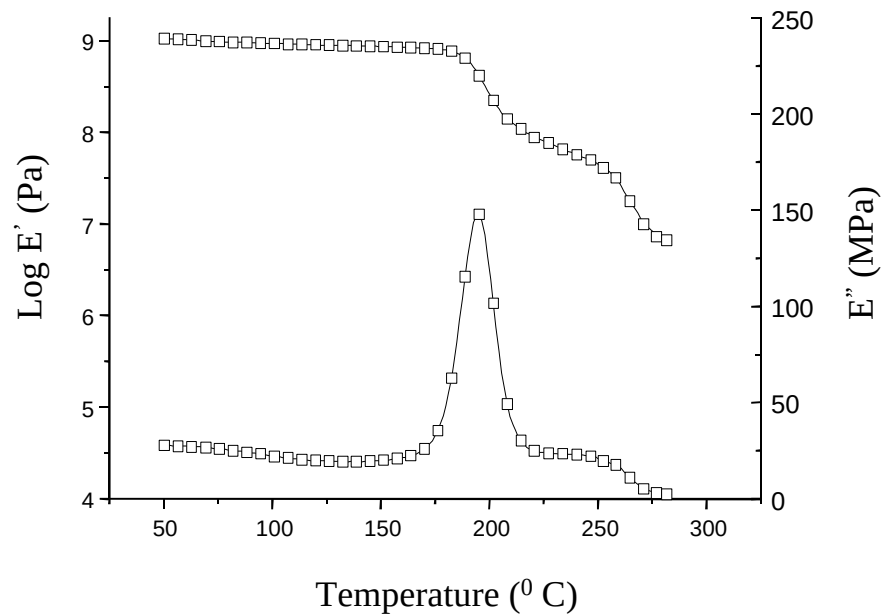


Figure 8.19: DMA of 25% Ultem modified epoxy

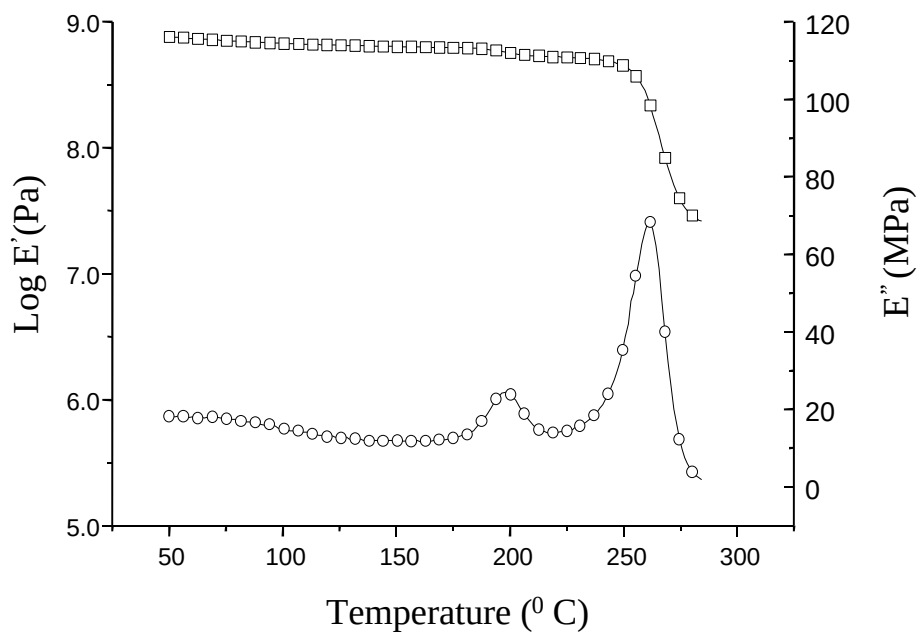


Figure 8.20: DMA of PEI-NH₂ 20k 10% toughened system

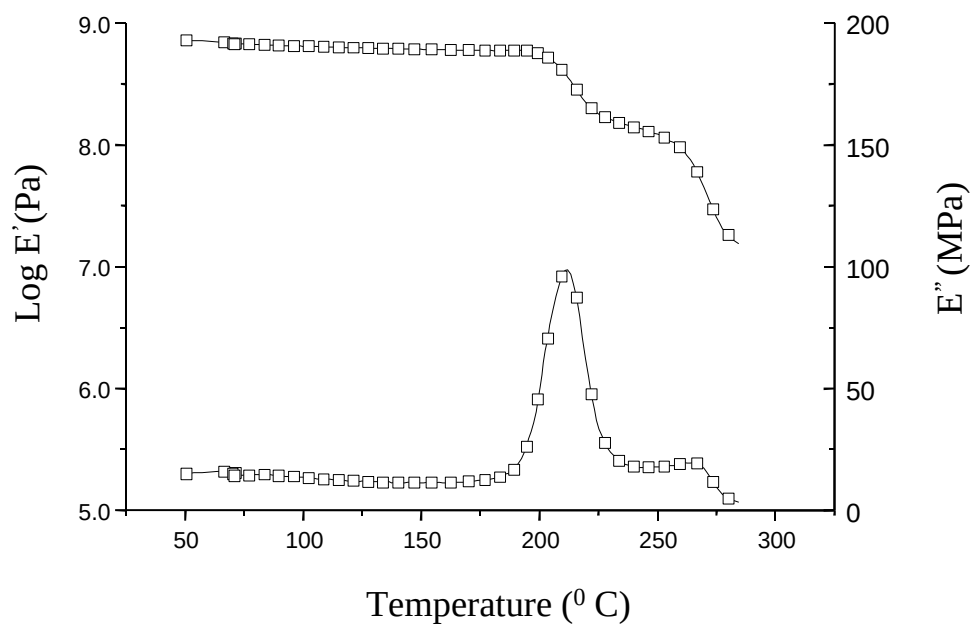


Figure 8.21: DMA of PEI-NH₂ 20k 20% modified TGDDM epoxy

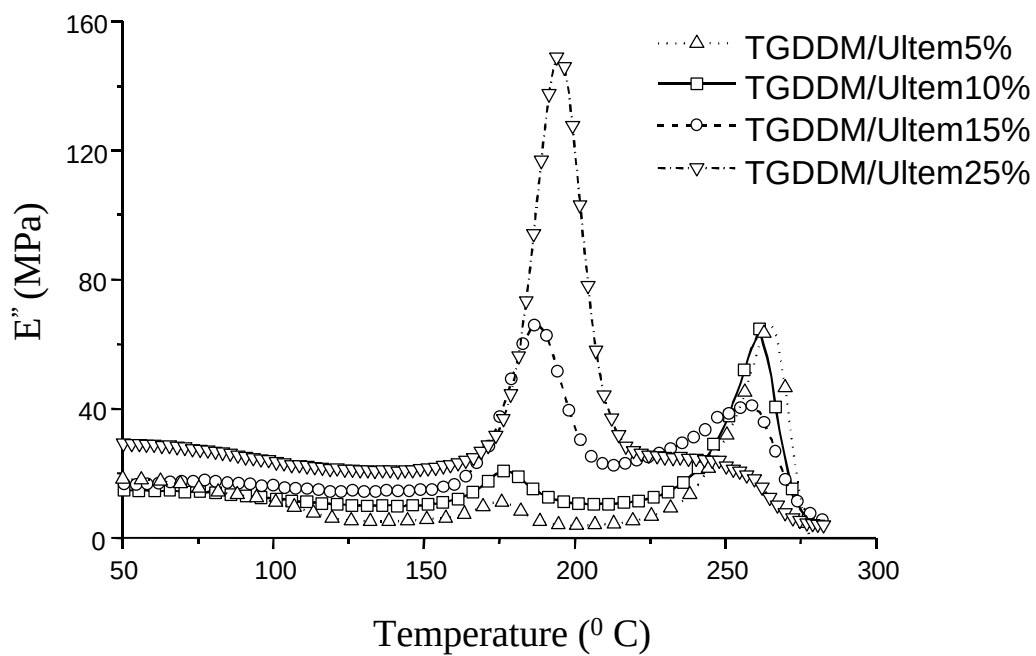


Figure 8.22: Summary of Ultem modified TGDDM

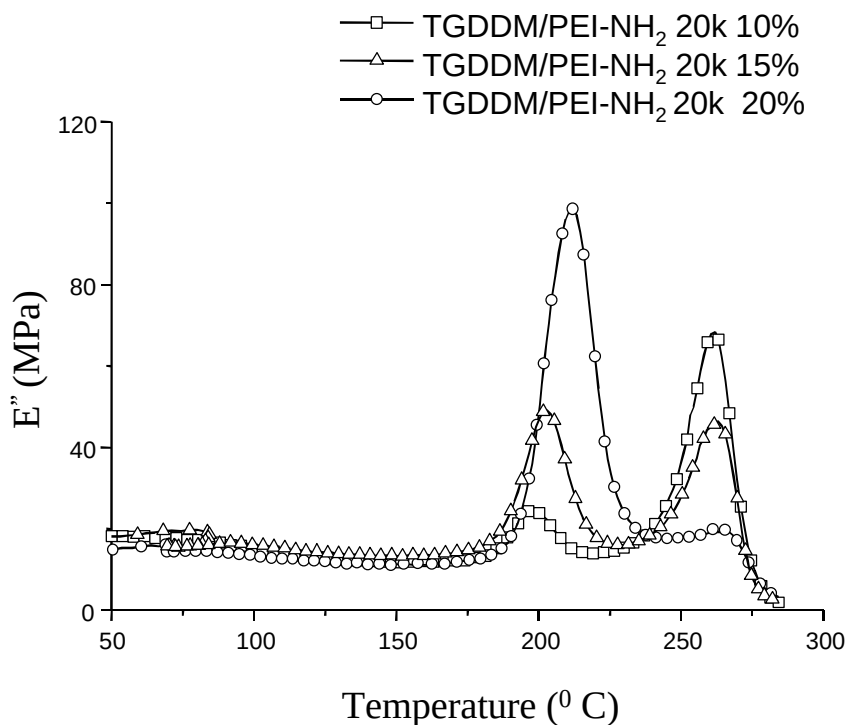


Figure 8.23: Summary of PEI-NH₂ 20k modified TGDDM

this information into one graph. As expected, the magnitude of the mechanical loss for the toughener also increases as the composition shifts to higher toughener concentrations. Ultimately, all of the tougheners are summarized together in a single plot, see Figure 8.24. The epoxy T_g , Figure 8.25, remains constant for all of the formulated systems. There is the same distinct trend for all of the tougheners as described above, namely that the $T_{g, \text{toughener}}$ increases for a higher toughener composition. The one toughener that deviates from this trend is the 10k reactive polyetherimide. The reason for this discrepancy is not clear; however, an explanation will be attempted.

The explanation for the previously described behavior will be given in this section. This discussion will revolve around Figure 8.26, which is a phase diagram showing binodal and spinodal lines for phase separation. This diagram is generated from Flory-Huggins theory, in which combinatorial and enthalpic terms yield a free energy of mixing expression. Instead of examining this graph in the usual way as a function of temperature, the conversion (P) is used since a polymerizing material is considered. Conversion refers to the ratio of reacted functional groups to total initial functional groups. The shape of the curves in Figure 8.26 depends on various parameters, the only

one that will essentially change in this study is the molecular weight. As the molecular weight is decreased, the critical volume fraction of polymer (the minimum of the curves) will shift to higher compositions and the curve will develop a more symmetrical shape. For the reactive 15k and 20k polyetherimides and Ultem this phase diagram will apply. For the 10k reactive toughener the minimum will move to higher ϕ_2 values. From this diagram one can see that when a 15, 20 or 25% composition phase separates (assuming the perturbation for each system will be equal when phase separation commences) the

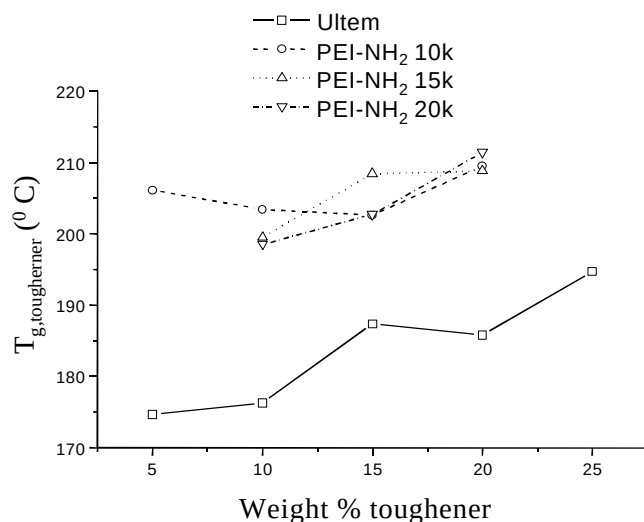


Figure 8.24: Summary of $T_{g, \text{toughener}}$ dependence on composition

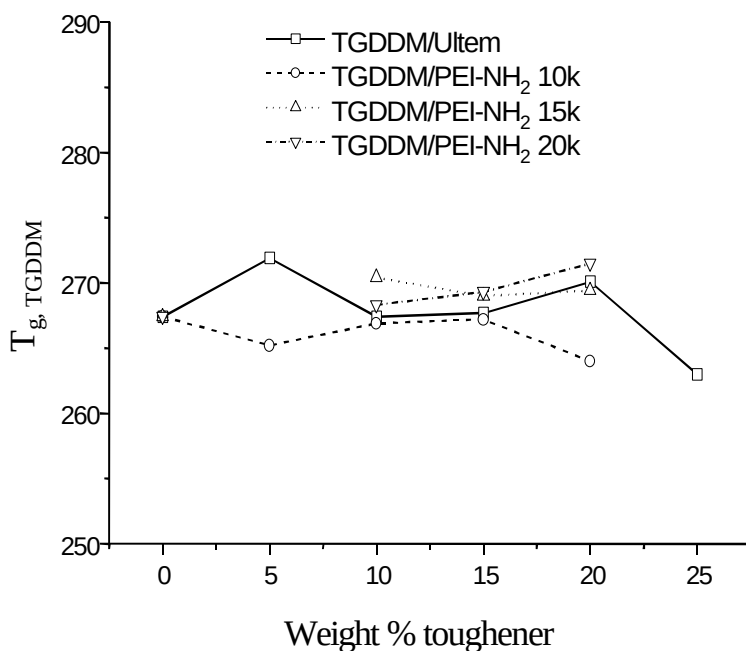


Figure 8.25: Epoxy T_g as function of composition

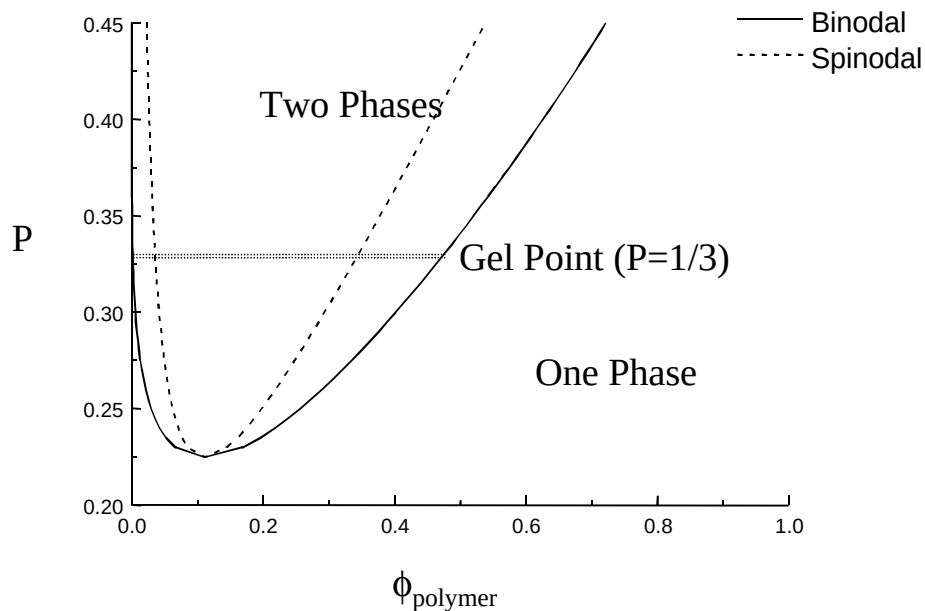


Figure 8.26: Phase diagram for toughened epoxy systems

system will be in the spinodal region (evident in the co-continuous nature of the microstructure for the systems containing 15% toughener and above).

For a system that spinodally decomposes, the two phases will move along a tie line into the meta-stable binodal region to the equilibrium line. Further phase separation will probably occur in the binodal region to produce dispersed secondary phases in the main primary phases. Unfortunately, the exact nature of the compositional variation of each phase as a function of conversion has not been calculated. When higher initial concentrations of toughener are used phase inversion proceeds. This behavior can be seen by drawing a vertical line up from 0.25 in Figure 8.26 and noting that anywhere before the gel point the tie line distance between 0.25 and the binodal line on the right is smaller than that on the left. Thus, from the lever rule the toughener phase will be the larger volume fraction phase and hence the continuous phase. After the initial phase separation step the toughener rich phase will change composition until gelation has occurred. The final composition of the toughener rich phase in systems with a higher initial composition of toughener usually produces a higher volume fraction of toughener at gelation, whereupon composition is fixed, than systems with an initial lower

composition of toughener. This procedure will cause a higher T_g of the toughener phase as the initial composition moves to higher volume fractions of toughener. Hence, the observations for three of the tougheners can be described in this manner. The 10k materials have to be explained by shifting the critical point of the phase diagram to higher ϕ_{polymer} values. With this in mind one could imagine that initial lower toughener compositions could result in a different scenario.

Thus far no mention has been made of the epoxy rich phase, the reason for this is because the phase diagram (Figure 8.26) is very steep on that side, especially near gelation. Therefore, variations in original composition do not have a large effect on the percent composition of the epoxy rich phase after phase separation. The development of a descriptive model for all of these toughened systems is limited by the fact that the degree of conversion of the epoxy in the toughener phase is unknown. Furthermore, after phase separation has occurred the systems undergo additional thermal treatments that may affect the final state of each phase in any of the toughened materials. Nonetheless, the toughener T_g is dependent on the initial composition. This knowledge can be paramount in designing a composition for a material for specific applications.

8.4.3. SCANNING ELECTRON MICROSCOPY

Besides giving information about the morphological features present in these fast reacting tetrafunctional epoxies, the scanning electron micrographs support the discussion about the dynamic mechanical behavior. The morphology is dependent on the molecular weight as was covered in the discussion about phase separation. Moreover, there are differences between the 20k reactive polyetherimide and the 20k Ultem toughened systems. As the molecular weight decreases there is a deviation from having the toughener as a continuous phase. Even at 20% loading the 10k PEI-NH₂ material has only small regions of continuous toughener, see (c) and (d) in Figure 8.27. At 10% (a) and 15% (b) loadings this toughener distinctly shows only dispersed toughener particles. This behavior can be contrasted with Figure 8.28 and Figure 8.29 that demonstrate the

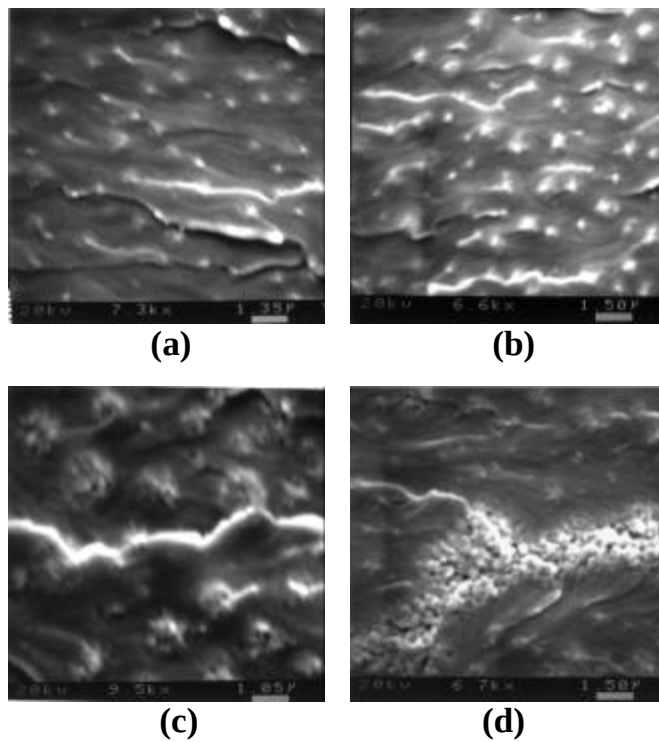


Figure 8.27: TGDDM/PEI-NH₂ 10k micrographs (a) 10%;
(b) 15%; (c),(d) 20% PEI-NH₂

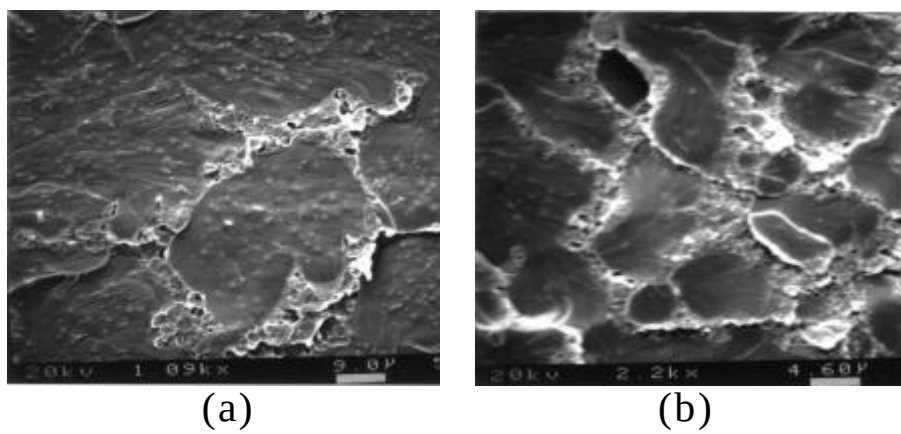


Figure 8.28: TGDDM/PEI-NH₂ 15k (a)15%; (b)20% toughener content

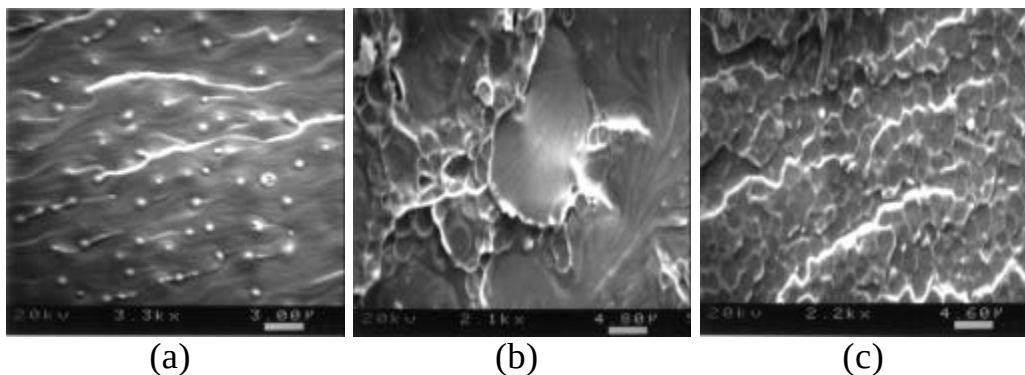


Figure 8.29: TGDDM/PEI-NH₂ 20k (a)10%; (b)15%; (c)20%

morphology of the 15k and 20k PEI-NH₂ toughened systems. Although the 15k modified system does not have a phase inverted morphology at 20%, it has an apparent large volume fraction of continuous toughener phase.

The 20k amine terminated PEI material roughly parallels the Ultem toughened system in its morphology, compare Figure 8.29 with (a) in Figure 8.30 - Figure 8.32. There is a dispersed morphology at 10% loading in both cases. At 15% both have co-continuous morphologies and finally at 20% there exists the phase inverted morphology. Ultem also shows a phase inverted morphology at 25% as expected, see Figure 8.33.

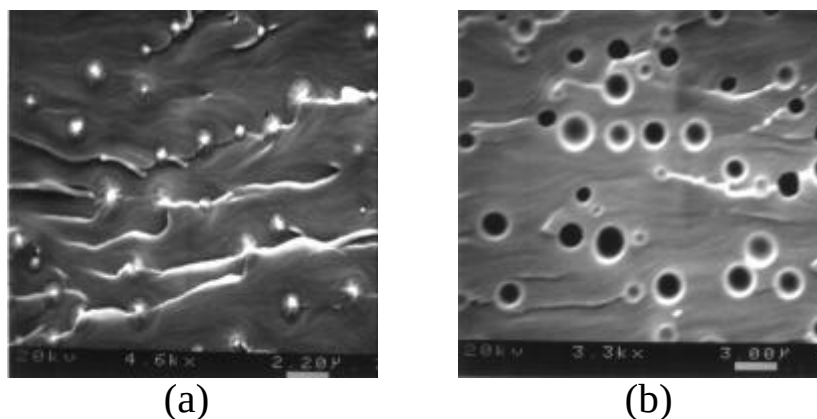
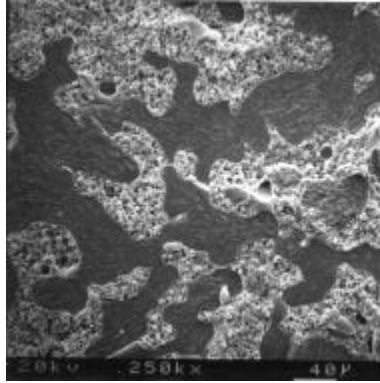
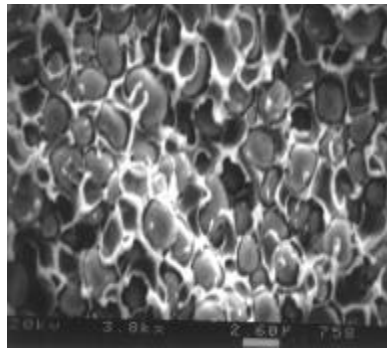


Figure 8.30: TGDDM/Ultem 10% (a)fracture surface (b)CHCl₃ etched

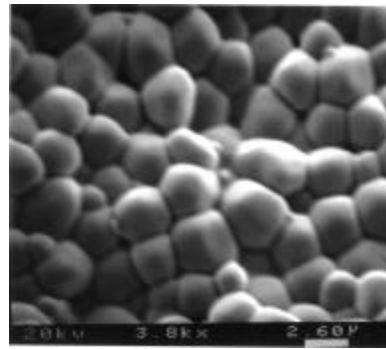


(a)

Figure 8.31: TGDDM/Ultem 15%

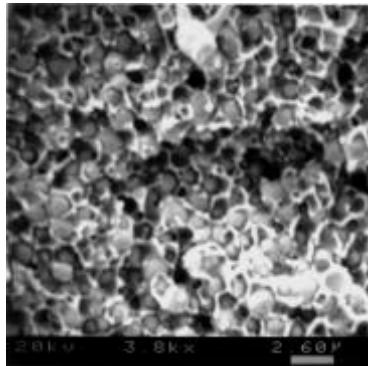


(a)

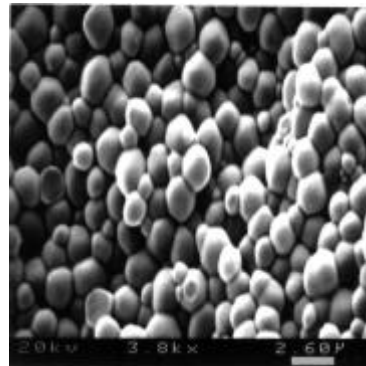


(b)

Figure 8.32: TGDDM/Ultem 20% (a)fracture surface (b)CHCl₃ etched



(a)



(b)

Figure 8.33: TGDDM/Ultem 25% (a)fracture surface (b)CHCl₃ etched

All of the samples were etched in chloroform for 10 days unless they fell apart before then. The only samples that decomposed were the 15, 20 and 25% Ultem[®] toughened samples, which were only etched for 7 hours. The samples were vacuum dried

and examined for dissolution of the toughener on the surface. The etched Ultem[®] samples are shown in (b) of Figure 8.30 - Figure 8.33. In all of these materials the Ultem[®] was removed from the surface to leave only epoxy on the surface. All of the reactive PEI modified systems remained identical to their unetched state, there was no evidence that the toughener was removed. This point gives credence to the idea that the amine terminal group does react with an epoxide group to achieve covalent interfacial interactions.

8.4.4. AGING BEHAVIOR

The dilatometric aging behavior is demonstrated in Figure 8.34. The TGDDM curve is shifted to lower temperatures relative to the other materials, because the glass transition

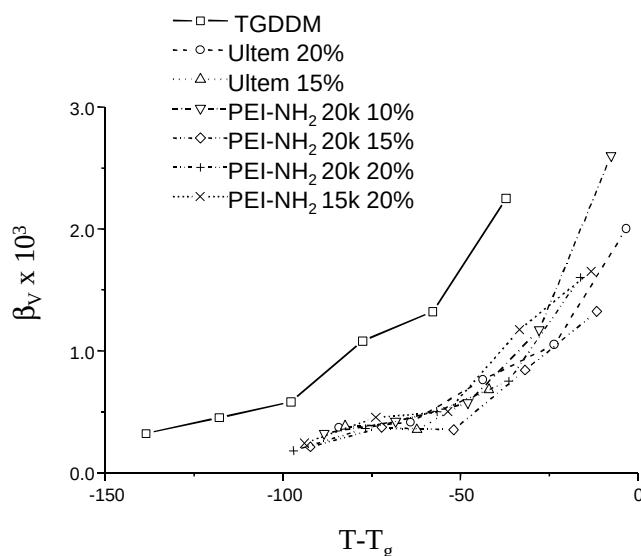


Figure 8.34: Volume aging behavior for epoxy materials

temperature of the epoxy is used in this case versus that of the toughener in the others. It seems that the aging behavior is governed to a large extent by the epoxy component, since all of the curves are similar. Even at lower temperatures this seems to hold. The behavior at high temperatures, with the unusually high volume relaxation rates, is indicative of another process besides reversible physical aging as seen in the other chapters in this work. This behavior is much more typical of residual cure that could occur when a system is not cured to 100% conversion. Residual cure is probably not

operative until above 160⁰ C for most of these systems since there is only local mobility below these temperatures for short aging times, refer to the loss modulus curves in Figure 8.18 to Figure 8.23.

The T_g of the epoxy phase is not affected by this aging process because any residual cure will only happen in the toughener phase since the mobility in the epoxy rich phase is even lower at the aging temperatures. The only temperature that showed an unusually high aging rate for the neat epoxy system is the highest aging temperature of 220⁰ C. This temperature is the point at which the loss modulus in Figure 8.17 begins to deviate from the baseline suggesting that there is some relaxation occurring and the possibility for an increased rate of diffusion controlled reactions to proceed.

At the aging temperatures surveyed in this study it is not evident that there is any degradation or oxidation. The aging times were short for much of these processes to take place. None of the phases had a drop in their glass transition temperatures. To gauge the physical aging parameters of these systems the materials might have to be more fully cured. However, the limitation here is that a practical cure schedule for the TGDDM resin to insure everything is reacted but that good toughness values are retained is difficult to produce. Nonetheless, at the lower aging temperatures only physical aging is present. These temperatures also represent common application temperatures as in the aerospace industry, therefore the aging behavior in this regime is of practical interest.

8.4.5. MECHANICAL TESTING

The mechanical testing results showed an improvement in the fracture toughness without sacrifices in the flexural modulus, see Figure 8.35 and Figure 8.36. The most

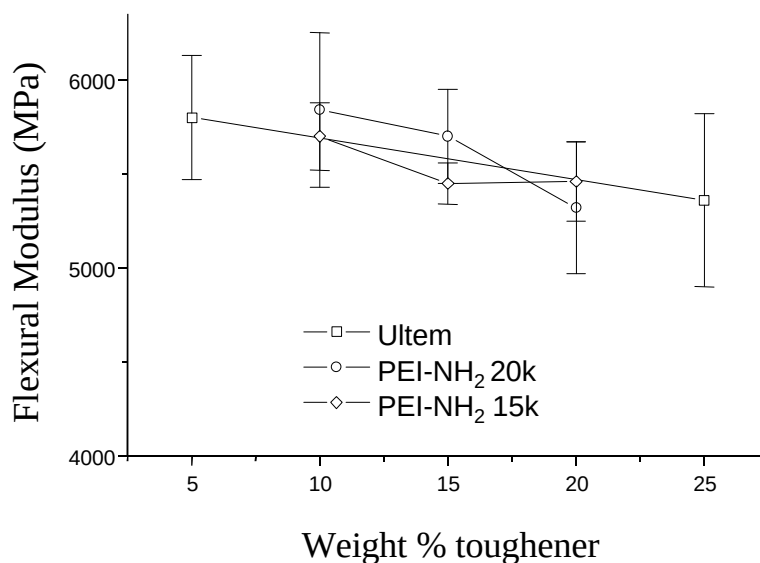


Figure 8.35: Flexural modulus for several materials

dramatic increase came at 15% Ultem addition to the TGDDM matrix and a large jump was also witnessed at 20% PEI-NH₂ loading in the epoxy material. These results and all the others are summarized in Figure 8.36. There is only a small enhancement of the fracture toughness at 10% loading for all of the thermoplastic modifiers. This result

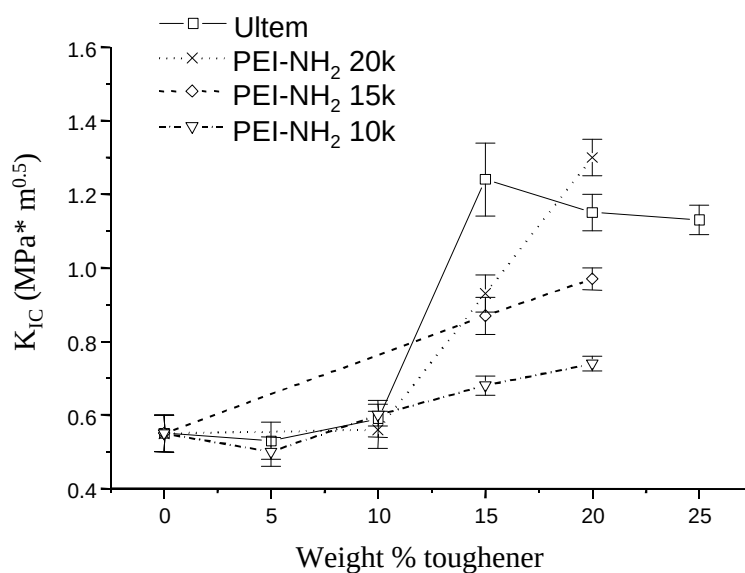


Figure 8.36: Fracture toughness values

supports earlier arguments concerning the ability of “hard” spheres to toughen brittle matrices. There are many toughening mechanisms that are operative in rubber toughened

systems, such as shear yielding, crazing in the epoxy near the rubber particles, crack bridging and others. These mechanisms allow rubber modifiers to improve toughness at low compositions, less than 15%. However, many of these mechanisms are not available to the thermoplastic toughener, because it is not elastic like a rubber at the test temperature. On the other hand, any deformation of the thermoplastic dissipates much energy, therefore some improvement is seen with dispersed toughener particles. The real improvement is when there are some continuous toughener regions as in the co-continuous or phase inverted morphology. These features create the opportunity for yielding in the continuous toughener phase, which is very energy intensive. Hence, to see the real improvements in fracture toughness a continuous toughener phase is necessitated.

8.4.6. SOXHLET EXTRACTION

The extractable fraction of the toughened epoxy materials increased as the weight fraction of Ultem in the epoxy increased. This trend is shown in Figure 8.37. In the case of 15 through 25% Ultem loadings, the continuous phase is the soluble thermoplastic. Subsequently, when the matrix is dissolved away there is no more structure holding up the epoxy particles. For the 15 through 25% loadings this is indeed what happened. It is easy to deduce that the thermoplastic is the extracted material, because the untoughened epoxy control had nothing extracted. This result sheds significant light on the possibility of using a high loading (15% to 25%) of a non-reactive polyetherimide as a toughener in these epoxy materials in an application where solvent resistance is paramount.

The solvent resistance of the amine terminated systems shows highly improved resistance to the extraction solvent. It appears in this case that no extractables are existent in the PEI-NH₂ toughened materials. Compared to the Ultem modified systems it also is apparent that none of the thermoplastic is being removed by the refluxing chloroform. This substantiates the chemical resistance of the amine terminated polyetherimides over Ultem.

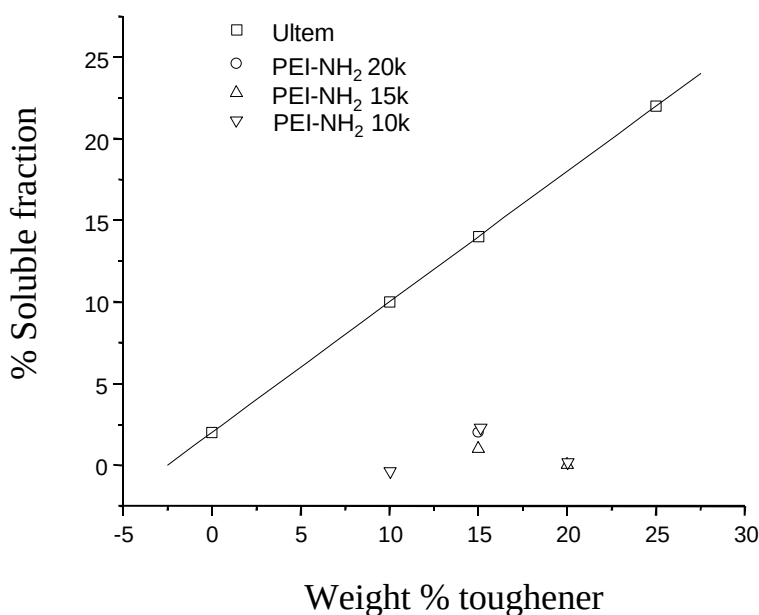


Figure 8.37: Soxhlet extractions of toughened tetrafunctional epoxies

8.5. SUMMARY

This study has shown improved fracture properties of thermoplastic modified tetrafunctional epoxies over the unmodified systems, without a concomitant decrease in the flexural modulus. The solvent resistance improves greatly when the thermoplastic can react into the network. This behavior is demonstrated by the micrographs of the etched samples and the soxhlet extraction results.

Dielectric spectroscopy was confirmed to be a useful technique to follow the reaction kinetics and to develop a TTT diagram provided correct interpretations of the data were made. The results of the acquired TTT diagram are used to develop a more practical cure schedule than what is commonly applied. This cure schedule allows the attainment of a high T_g epoxy phase, as witnessed by DMA, and a phase separated structure, which became evident through SEM. These properties lend the system higher heat and fracture resistance.

Incorporation of the toughener into the viscous TGDDM resin was achieved without the use of solvent. The absence of having solvent involved in the mixture insures

that no residual solvent will be present which could deteriorate the aging resistance of the formulated systems.

The aging behavior of the materials were investigated. It was determined that above 160-180⁰ C the presence of residual cure or other non-reversible processes become important and make the evaluation of physical aging contributions difficult to ascertain.

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Chapter 9. CONCLUSIONS

It was demonstrated that unperturbed dimensions of polymers in dilute solution could be readily calculated using gel permeation chromatography, when data were analyzed with known extrapolation techniques from the perturbed state. The calculated values for several model systems matched well with literature values. Unperturbed dimensions for novel poly(arylene ether phosphine oxide) were obtained. These molecular dimensions were used in attempting correlations between their magnitudes, e.g. the characteristic ratio, and physical aging rates in the glassy state.

The physical aging of some engineering thermoplastics were determined via dimensional and calorimetric experiments. The mechanical physical aging behavior for these systems showed very similar trends across the temperature spectrum, with the exception of a commercial polyetherimide. This latter system showed a sharp decrease in the rate of mechanical physical aging on cooling near its secondary transition. The volumetric physical aging rate demonstrated more differences; however, within the scope of this work no conclusions could be established with, e.g. the characteristic ratio.

The influence of polymer endgroups on physical properties was studied for a set of poly(ether sulfones), with M_n above and below critical entanglement values. The properties investigated were the glass transition temperature, density, relaxation time distribution and physical aging rates. Generally, as the size of the endgroup grows the T_g increases and density decreases. Furthermore, the relaxation time distribution had a weak dependence on endgroup size which appeared to decrease as the size expands. As the endgroup size increases, one tends to see a decline in the physical aging rate with cooling shift to temperatures further from the glass transition. In the systems where the endgroups had the potential to hydrogen bond, an increase in the relaxation time dispersion plus a lower rate of physical aging near the T_g was found.

Thermoplastic toughened epoxies were also examined for various structure-property relationships. In a comparison of two difunctional toughened epoxies, it was found that if a toughener is used that does not react into the epoxy network the volumetric

physical aging rate rises very quickly near the T_g of the toughener. On the other hand, if a reactive toughener, one which is incorporated chemically into the network, was used with a difunctional epoxy, the volumetric aging rate mimics the behavior of the epoxy. Most of the other properties were similar, except for some differences in the morphology which could explain the different volume aging rates and the densities.

A tetrafunctional epoxy, that was toughened with reactive and non-reactive tougheners was also investigated. The fracture toughness rose as toughener content increased. The reactive toughener/epoxy system only achieved higher toughness values than the non-reactive toughener/epoxy system at the highest loading level, 20% by weight. However, the solvent resistance is greatly improved with the reactive toughener. Aging was governed by the epoxy phase in these systems, because the cure schedule did not allow for total conversion of all the epoxide rings.

Chapter 10. APPENDIX A

10.1. HAVRILIAK-NEGAMI FITTING FUNCTION

```
Clear["Global`@"];
SetDirectory["c:\disperrelax\hn"];
data=Readlist["vicbend228.txt",{Number, Number}]
k=((1-a)Pi/2);
theta[w_]:= ArcTan[(w tau)^a Cos[k]/(1=(w tau)^a Sin[k])];
r[w_]:= (1+(w tau)^a Sin[k])^2 + ((w tau)^a Cos[k])^2;
loss[w_]:= d Sin[theta[w]g]/(r[w])^g/2;
<<Statistics`NonlinearFit[data, loss[w], w,
{{a, 0.6}, {g, 0.52}, {d, 1200}, {tau, 0.01}},
ShowProgress -> True,
AccuracyGoal-> 10,
PrecisionGoal-> 10,
MaxIterations->50,
Method->LevenbergMarquardt]
```

Chapter 11. APPENDIX B

11.1. TIME DECAY FUNCTION CALCULATION

```
Clear["Global`@"];
SetDirectory["c:\disperrelax\acf"];
a=Input["Input alpha of H-N model"];
Print["alpha ", a];
g=Input["Input gamma of H-N model"];
Print["gamma ", g];
tau=Input["Input tau of H-N model"];
Print["tau ", tau];
k=((1-a)Pi/2);
theta[w_]:= ArcTan[(w tau)a Cos[k]/(1-(w tau)a Sin[k])];
r[w_]:= (1+(w tau)a Sin[k])2 + ((w tau)a Cos[k])2;
amp[w_]:= 0.5Pi Sin[theta[w] g]/(r[w])g/2;
fname= InputString["Input the name of the data file to store ACF calc. results"]
OpenWrite[fname]
Do[t=10lt; hp=N[Pi/t];
Print["====="];
Print["half period", hp];s=0; l1=0, l2=l1+hp;
obj[w_]:=amp[w](Cos[wt]/w);
Print[" "];(Label[again]);
m=NIntegrate[obj[w], {w, l1, l2}, MaxRecursion ->40];
s=s+m; l1+=hp; l2 +=hp;
If[Abs[m]>10-6, Goto[again]]); Print["ACF at t=", t, " is ", s, " up to w=", l2];
Write[fname, lt, "=", s], {lt, -11, 5, 0.1}];
```

Chapter 12. APPENDIX C

12.1. KWW: RELAXATION TIME DISTRIBUTION FUNCTION

```
Clear["Global`@"];
SetDirectory["c:\disperrelax\hn"];
Off[General::spell, General::spell1];
k= InputString["Input name of the data file"]
l=ReadList[. {Number, Number}];
yt=0.367879;
Do[If[l[[I, 2]]>=yt, Continue[],
(k2=I;k1=k2-1; Break[])], {I, 1, Length[l]};
logtau= (yt-l[[k2,2]])*(l[[k2, 1]]-l[[k1, 1]])/(l[[k1, 2]]-l[[k2,2]])
taucent=N[10logtau];
m=Table[{ }, {I, 1, Length[l]}, {j, 1, 2}];
Do[(m[[I,1]]=N[Log[10]*(l[[I,1]]-logtau)]);
m[[I,2]]=N[Log[-Log[l[[I,2]]]]]),
{I, 1, Length[l]};
sl=Fit[m, {0, x}, x]
slopeg=Coefficients[sl,x]
Do[l[[I,1]]=10l[[I,1]], {I, 1, Length[l]}]
<<Statistics`NonlinearFit`;
ans=NonlinearFit[l, Exp[-(t/taucent)beta], t, {beta, slopeg},
ShowProgress->True,
AccuracyGoal->10,
PrecisionGoal->10,
MaxIterations ->50;
Method->LevenbergMarquardt]
```

VITA

The author, Mark W. Muggli, was born in November 1966 in St. Paul, Minnesota. After completing high school, he attended St. John's University in Minnesota. Before completing his degree, he studied in Styria, Austria where he met his wife Roswitha Strobl. The author finished his bachelor's degree in December 1992 and commenced graduate studies in chemistry under the direction of Professor Thomas C. Ward. The author defended his doctorate in May, 1998 and will be employed at 3M Company in St. Paul, Minnesota.