NASA/TM-2000-210312

The Combined Influence of Molecular Weight and Temperature on the Aging and Viscoelastic Response of a Glassy Thermoplastic Polyimide

Lee M. Nicholson
Institute for Computer Applications in Science and Engineering
Langley Research Center, Hampton, Virginia

Karen S. Whitley and Thomas S. Gates
Langley Research Center, Hampton, Virginia

September 2000

The NASA STI Program Office ... in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers, but having less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results ... even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA STI Help Desk at (301) 621-0134

- Phone the NASA STI Help Desk at (301) 621-0390

- Write to:
  NASA STI Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076-1320

NASA/TM-2000-210312

The Combined Influence of Molecular Weight and Temperature on the Aging and Viscoelastic Response of a Glassy Thermoplastic Polyimide

Lee M. Nicholson
Institute for Computer Applications in Science and Engineering
Langley Research Center, Hampton, Virginia

Karen S. Whitley and Thomas S. Gates
Langley Research Center, Hampton, Virginia

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23681-2199

September 2000

Available from:

NASA Center for AeroSpace Information (CASI)
7121 Standard Drive
Hanover, MD 21076-1320
(301) 621-0390

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161-2171
(703) 605-6000

The Combined Influence of Molecular Weight and Temperature on the Aging and Viscoelastic Response of A Glassy Thermoplastic Polyimide

Lee M. Nicholson[†], Karen S. Whitley, and Thomas S. Gates[*]

NASA Langley Research Center,
Mechanics & Durability Branch, Structures & Materials Competency
MS 188E, 2 West Reid Street, Hampton, VA 23681-2199

Abstract

The effect of molecular weight on the viscoelastic performance of an advanced polymer (LaRC™-SI) was investigated through the use of creep compliance tests. Testing consisted of short-term isothermal creep and recovery with the creep segments performed under constant load. The tests were conducted at three temperatures below the glass transition temperature of five materials of different molecular weight. Through the use of time-aging-time superposition procedures, the material constants, material master curves and aging-related parameters were evaluated at each temperature for a given molecular weight. The time-temperature superposition technique helped to describe the effect of temperature on the timescale of the viscoelastic response of each molecular weight. It was shown that the low molecular weight materials have higher creep compliance and creep rate, and are more sensitive to temperature than the high molecular weight materials. Furthermore, a critical molecular weight transition was observed to occur at a weight-average molecular weight of $\bar{M}_w$~25,000 g/mol below which, the temperature sensitivity of the time-temperature superposition shift factor increases significantly. The short-term creep compliance data were used in association with Struik's effective time theory to predict the long-term creep compliance behavior for the different molecular weights. At long timescales, physical aging serves to significantly decrease the creep compliance and creep rate of all the materials tested. Long-term test data verified the predictive creep behavior. Materials with higher temperature and lower molecular weights had greater creep compliance and higher creep rates.

KEY WORDS: molecular weight, temperature, physical aging, creep compliance, polyimide.

1. Introduction

Durability and long-term performance are among the primary concerns for the use of advanced polymer matrix composites (PMCs) in modern aerospace structural applications. For a PMC subjected to long-term exposure at elevated temperatures, the viscoelastic nature of the polymer matrix will contribute to macroscopic changes in composite stiffness, strength and fatigue life. Over time, changes in the polymer due to *physical aging* will have profound effects on the viscoelastic compliance of the material, and hence will affect its long-term durability [1].

The ability to predict material performance using intrinsic properties, such as molecular weight, would greatly enhance the efficiency of design and development of PMCs. It would be advantageous, therefore, if structural analysts and material developers could accurately account

[†] Institute for Computer Applications in Science & Engineering (ICASE), NASA Langley Research Center
[*] Author to whom correspondence should be addressed

for the effects of molecular weight and elicit a desired macroscopic mechanical response from the material by optimizing specific parameters at the microscopic level. Currently, there is no unified understanding of exactly how the intrinsic chemical and physical properties (like molecular weight, cross-link density, free volume) of the polymer affect the resultant mechanical performance. In the following paper, experimental data is presented that can serve as a basis for developing a predictive model to provide material properties.

Failure or degradation of performance in PMCs is predominantly associated with loss in mechanical load carrying capability of the polymer matrix. It is the glass transition temperature of the polymer matrix that bounds the upper useful service temperature of the polymer composite system. Therefore, interpretations of mechanical behavior have been focused on analysis of elastic solids. The physics of glassy polymers is a mature subject [2, 3]. Closely associated is the abundant interest in physical aging mechanisms that occur in glassy polymers [4]. Physical aging is the contraction of a supercooled glass to its equilibrium state and results in the embrittlement of the solid. Physical aging is distinct from chemical aging in that it is not driven by degradation or oxidation mechanisms [5], and is essentially thermoreversible. An accepted methodology for evaluating the extent of physical aging in glassy polymers is the use of creep compliance tests [4, 6, 7]. In these latter studies, investigations were made into the concepts of effective time theory and relationships between physical aging and free volume evolution. Tension creep tests, concepts of linear viscoelasticity, and mechanics of composite materials have been combined more recently [8] in tests of high performance PMCs below the glass transition (T_g) temperature. Studies by Gates and others [9, 10] showed that the sequence creep testing procedures produced repeatable test data for thermoplastic composite systems, and the time-temperature and time-aging-time superposition techniques could be used to make long-term predictions.

Despite a wealth of literature on the molecular weight effects on the mechanical properties of glassy polymers [11-13], there is surprisingly little information addressing the role of molecular weight in the viscoelastic response of glassy polymers. Odani and others [14, 15] considered the effect of molecular weight distribution on the viscoelastic parameters of polystyrene and poly(*cis*-isoprene), derived from creep and relaxation measurements, along with viscosity data. More recently Plazek and others [16, 17] made creep and recoverable creep measurements on low molecular weight amorphous polystyrene and poly(methyl-phenyl-siloxane) and found that the steady state recoverable compliance decreased markedly with temperature as T_g was approached from above. Other workers have been trying to establish the effects of molecular weight on the free volume as a means for understanding physical aging. Yu and others [18], and Singh and Eftekhari [19] have used positron annihilation lifetime spectroscopy to evaluate the free volume size and found that a decrease in molecular weight increases the free volume. Recently, Matsuoka and Hale [20] have considered the relaxation modes dominated by conformers to explain the dynamics of physical aging. They used the molecular weight of a conformer as a ratio of its density, as the parameter for predicting the viscoelastic behavior.

The objective of this paper is to present the results (and discuss an experimental study that considers the effects) of molecular weight and temperature on the viscoelastic behavior and physical aging of an advanced polymer. Five distinct variations in molecular weight were used to reveal differences in mechanical performance of an advanced glassy thermoplastic polyimide. Conducting sequenced, short-term isothermal creep compliance tests in tension isolated the physical aging behavior. These tests were performed over a range of sub-glass transition temperatures. The material constants, material master curves and physical aging-related

parameters were evaluated as a function of temperature and molecular weight using time-temperature and time-aging-time superposition techniques.

2. Experimental Method

2.1 Materials

The materials used in this study were prepared by Imitec Inc., Schenectady, NY, and received in powder form. LaRC™-SI (NASA Langley Research Center-Soluble Imide) was synthesized from 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,4'-oxydianiline (3,4'-ODA). The different molecular weights, designated by their percent offsets [21], were prepared by reacting an excess of the diamine with an appropriately reduced quantity of the dianhydrides in *N*-methyl-2-pyrrolidinone (NMP) and endcapped with phthalic anhydride (PA). Extended synthesis descriptions of this material have been published elsewhere [22]. These molecular weights and intrinsic viscosities for LaRC™-SI were determined on the as-received powders using gel permeation chromatography [21]. The weight-average molecular weights ($\bar{M}_w$) and the polydispersity indices $\left(\bar{M}_w/\bar{M}_n\right)$ of the materials are shown in Table 1. The differences in the molecular weight distribution per sample are more easily discerned when weight-averages are compared. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 7™ to determine the glass transition temperature of the molded material. Polymer sample weights of 2-5 mg were used under a nitrogenous atmosphere at a heating rate of 10°C/min. The glass transition temperature was taken at the inflection point in the heat flow versus temperature curve; the T_gs are indicated in Table 1. The elastic properties of the different molecular weight materials, were obtained by monotonic tensile tests, as described in detail by Nicholson *et al.* [23]; these are presented in Table 2.

2.2 Test-Coupon Manufacture

The powder was dried under vacuum at 215°C for 48 hours to remove any residual solvents prior to being compression molded in air. The powder was placed in a 152 x 152 mm stainless steel mold lined with Kapton™ film and spray-coated with Frekote 33-NC™ release agent. Neat resin plaques were formed at 340°C for one hour under 3.1 MPa of pressure. Rectangular test coupons (with rectangular cross-section) measuring approximately 150 x 17.5 x 5.8 mm were machined from the plaques; see Figure 1. One test coupon per molecular weight variation was evaluated repeatedly for all three of the test temperatures as indicated in Table 1.

2.3 Test Instrumentation and Procedures

Tensile creep tests were performed at three specific test temperatures below the glass transition temperature. Listed in Table 1, these test temperatures were selected to ensure that measurable physical aging occurred within the test period. To place equal emphasis on the results, due to the different T_gs of the materials, the test temperature is referenced to the glass transition temperature. The *reduced temperature* is defined as:

$$\Delta T = T_g - T_{test} \tag{1}$$

The creep tests were performed in a convection oven equipped with a digital controller. Thermocouples monitoring the test temperature and providing feedback for the oven controller were placed near the coupon's test section. Tensile load was applied through a uniaxially symmetric dead-weight system during the creep segments. Strain in the coupon's test section

was measured with high-temperature strain gages applied in a longitudinal direction, on the back and front faces of the specimen. Proper selection of the gage type and adhesive bond is important to ensure equivalent thermal expansion rates with those of the specimen for stability in measurement at elevated temperatures. The specimen and gage were dried at 110°C for 120 hours and the gage-bonding agent was post-cured at 210°C for 2 hours. Apparent thermal strain was corrected for by using the compensating gage technique [24], which allowed for the separation of the load-induced strain from the thermal strain. The strain-gage voltages were then passed through a signal conditioner and collected by a digital data acquisition system, along with time and temperature variables; see Figure 1.

It was assumed that there would be negligible chemical aging effects in the material and the T_g would remain constant over the duration of the test period. The lifetime of a similar thermoplastic polyimide (LaRC™-TPI), was measured over extended oxidative-aging times by Hinkley *et al.* [25]. The change in the fracture toughness to drop to one half of its initial value, yielded an extrapolated lifetime of 100,000 hours when isothermally aged at 260°C, which is close to its T_g. This is a lifetime of more than two orders of magnitude longer than the long-term-test time presented here.

2.3.1 Conditions for linearity

Determination of the stress level necessary to stay within the linear viscoelastic strain range was made by checking that the proportionality condition and Boltzmann's superposition (Findley *et al.* [26]) would be satisfied. Creep and creep-recovery tests provided data for verifying superposition. Proportionality checks were performed by plotting isothermal creep compliance versus test time for a specimen that was repeatedly rejuvenated (described below), quenched and loaded at various stress levels. The supposed transition from a linear to nonlinear behavior would be evident by the vertical separation of the creep compliance curves with increasing stress. These linearity checks were made at the lowest and highest test temperatures thereby bracketing the extreme effects of temperature and applied stress. The applied stress level was chosen to be $\sim 6.5\times10^{-4}$ GPa.

2.3.2 Short-term Creep Compliance Tests

To provide for the test condition that all specimens start the test sequence in the same unaged condition, specimen rejuvenation was followed according to Struik [4]. Struik showed that physical aging is thermoreversible by isothermal heating above T_g prior to quenching and this effectively "rejuvenates" the material. Rejuvenation attempts to render the material microstructure to a metastable isotropic state. In the current tests, the gauged specimen was heated to 10°C above the T_g (for each material offset) and held isothermally for 15 minutes, immediately before the start of any physical aging test sequence. High-pressure cool air was used to quench the specimen to below the T_g. Upon reaching the desired test temperature, the material aging starts and the time is recorded.

To explore the effects of physical aging on the creep properties, a well-documented technique that measures the creep compliance, as described in [4], was used for all tests. This procedure consisted of a periodic sequence of creep, under constant load, and recovery tests while the specimen isothermally ages; depicted in Figure 2.

For this study, the duration of each creep segment was 1/10th the duration of the prior total aging time. The aging times (time after quench) selected for starting each creep segment were 2, 4, 8, 24, 48, 72 and 96 hours. After each creep segment, the specimen was unloaded and allowed to recover until the start of the next creep segment. To account for any remaining residual strain due to a lack of complete recovery, the strain measured in the creep segment was corrected by subtracting the extrapolated recovery strain from the prior creep curve as illustrated in Figure 2.

2.3.3 Long-term Creep Compliance Tests

The long-term tests were performed using a 2 hours aging time as a reference. The applied load provided the same stress condition as used in the short-term sequenced creep compliance tests. The load on the specimen was maintained for just over 1100 hours (~4×10^6 s).

2.4 Analysis of viscoelastic behavior and aging

For a polymer loaded with constant uniaxial tension under isothermal conditions, the time-dependent linear creep compliance was modeled with a three-parameter Kolrausch-Williams-Watts (KWW) [27, 28] expression given by

$$S(t) = S_o e^{(t/\tau)^{\beta}} \tag{2}$$

where S_o, t, τ, and β are the initial compliance, time, retardation time and shape parameter, respectively. The three material parameters are found from curve fits of Equation 2 to sequenced short-term creep and recovery tests, as depicted in Figure 2.

Due to physical aging of the polymer during testing, the short-term sequenced creep compliance curves are separated by time shifts related to the degree of aging. Therefore, time-aging-time superposition of the short term creep compliance test data provided the means for the sequenced, short-term data to be collapsed into a single momentary master curve (MMC) at each test temperature. As demonstrated by Struik [4], physical aging can be characterized by the aging shift factor a. This shift factor is simply defined as the horizontal distance required to shift a creep compliance curve along the time axis to coincide with a reference creep compliance curve (*n.b.* creep-test time, t, is not the same as aging time t_e). Each momentary creep curve is associated with a particular aging time. The reference creep compliance curve could be any of the sequenced curves, but for convenience of data manipulation, the longest (96 hours) creep compliance curve was selected as the reference during formation of the MMC. A linear fit of the logarithm of all the shift factors (*log a*) versus the logarithmic aging time (*log* t_e) for each MMC, gave the aging shift rate:

$$\mu = \frac{-d \log a}{d \log t_e} \tag{3}$$

where t_e is the aging time. For any aging time (t_e) the aging time shift factor $\left(a_{t_e}\right)$ can be written as

$$a_{t_e} = \left(\frac{t_{eref}}{t_e} \right)^{\mu} \tag{4}$$

where t_{eref} is the reference aging time [29].

Any creep compliance curve can be translated to a new reference time. For a horizontal (log *time*) translation of a compliance curve, only the retardation time parameter needs to be recalculated. Given the aging shift rate and reference curve parameters, the translation from one aging time to another was accomplished through the use of Equation 5:

$$\tau_e = \tau_{ref}\left(\frac{t_e}{t_{eref}}\right)^{\mu} \tag{5}$$

To facilitate the collapse of the shifted data for the momentary master curve (MMC), vertical (compliance) shifts were also utilized. This use of small vertical shifts in reduction of PMC tensile creep compliance/aging data was also reported [30, 31]. The vertical shifts for all data sets were small in comparison to the magnitude of the corresponding horizontal (time) shifts. No clear trends existed in these vertical shifts and analysis of vertical shift factors versus aging time did not lend itself to developing a constant vertical shift rate. A computer code, written by Bradshaw [32], was used to help collapse the short-term creep compliance curves into a master curve and generate the associated master curve and physical aging parameters using both horizontal and vertical shifting.

2.4.1 Long-term Creep Compliance and Physical Aging

If the loading time of a material is not short in comparison to the previous aging time, then aging proceeds even as the test progresses. This set of circumstances will be generally referred to as a long-term test. If the initial aging time is t_e^o, at some later time during the test the aging time is $t + t_e^o$, where t is the test time. When the test time approaches and exceeds the value of the initial aging time, the long-term creep response deviates from the momentary. Taking the initial aging time t_e^o to be the reference aging time ($t_{eref} = t_e^o$), the shift factor at any instant in time can be defined based on the shift rate μ:

$$a_{t_e^o}(t) = \left(\frac{t_e^o}{t_e^o + t}\right)^{\mu} \tag{6}$$

During aging, the mechanical relaxation times increase with aging time. To account for the cumulative effects of aging, the effective time increment was defined by Struik [4] as:

$$d\lambda = a_{t_e^o}(t)dt \tag{7}$$

and the total test time can be reduced to the effective time λ,

$$\lambda = \int_o^t a_{t_e^o}(\xi)d\xi \tag{8}$$

Integration of Equation 8 using Equation 6 leads to two distinct expressions for effective time

$$\mu = 1 \ldots \lambda = t_e^o \ln\left({}^{t}\!/_{t_e^o} + 1 \right);$$
$$\mu \neq 1 \ldots \lambda = \frac{t_e^o}{1-\mu} \ln\left[\left({}^{t}\!/_{t_e^o} + 1 \right)^{1-\mu} - 1 \right] \tag{9}$$

Substituting the effective time for real time in Equation 2 gives

$$S(t) = S_o e^{(\lambda/\tau(t_e^o))^\beta} \tag{10}$$

which provides the expression to predict long-term creep compliance that accounts for physical aging based only on the parameters derived from the short-term test (S_o, τ, β) and the aging shift rate μ. For further discussion of the use of effective time in long-term predictions the reader is referred to Brinson and Gates [29].

Isothermal momentary master curves (MMCs) can be further reduced to a single master curve through the use of time-temperature superposition. The use of time-temperature superposition (TTSP) ([26, 33]) requires that creep compliance be a function of temperature (T) and time (t) such that

$$S = S(T, t) \tag{11}$$

and that

$$S(T, t) = S(T_o, \varsigma) \tag{12}$$

$$\varsigma = {}^{t}\!/_{a_T(T)} \tag{13}$$

where ς is the reduced time that is related to the real time t by the temperature shift factor $a_T(T)$ and T_o is the reference temperature.

For this study, the collection of individual MMCs for various temperatures per molecular weight were collapsed into single material master curves using TTSP. The collapse was made using a single reference curve and horizontal (time) shifts only. The TTSP master curves for each molecular weight offset were consolidated using a reduced reference temperature of $\Delta T = 20^oC$. Characterizing these master curves with Equation 2 along with the reference aging time and reference temperature allows the investigator to calculate, in principle, the individual creep compliance curve for any test condition. The three curve fit parameters used to characterize each of the MMCs are given in Table 3. Aging shift rates (μ) were calculated for all cases using the sets of master curves. These calculated values are also given in Table 3.

2.4.2 Error Analysis

Comparisons of model predictions to long-term experimental data indicate that some of the tests versus prediction curves are not always in perfect agreement. An assessment of errors associated with these curves must include errors due to both the experimental methods and the analytical model. Considering the experimental aspects first, potential sources of error include material variability, instrumentation accuracy, fluctuations in test environments, and data analysis techniques. Performing repeat tests, ensuring accurate and frequent calibration of test equipment, and careful experimental procedures minimized these sources of error.

The largest sources of potential error associated with the predictive model may be due to the selection of the KWW function to represent creep compliance and the reliance on creep data alone to capture the aging related behavior. Although the KWW function has many desirable characteristics including simplicity and an established history of use, O'Connell and McKenna [34] indicate the KWW function can fit the data well over short (4 decades) times but may have reduced accuracy for long-term (7 decade) predictions. Alternatives include the use of the nonlinear Schapery model [35] as given by Skrypnyk [36] and the incorporation of a Prony series in the hereditary integral as given by Bradshaw and Brinson [37]. Additional work by Bradshaw and Brinson [38] has also shown the increased accuracy available when using the complete set of sequenced creep and recovery data to construct the aging related parameters. The use of alternative functions and data reduction techniques may in fact reduce the error but it also increases the complexity of the model and the associated number of material parameters. This presents difficulties documenting the data in a format that others may easily use for their own subsequent investigations. Simplicity and ease of use have been the deciding factors in the authors' selection of the current approach.

3. Results And Discussion

All results have been examined by comparing the viscoelastic creep compliance versus time as a function of temperature and molecular weight. In a previous work that evaluated the effects of molecular weight on the elastic (time-independent) properties of LaRC™-SI [39], a clear distinction in the mechanical properties between high and low molecular weights was discovered. Therefore, the same classification will be adopted in this study: the high molecular weight materials are considered to be the 1-3% offsets ($\bar{M}_w$ = 51070 - 24290 g/mol) and the low molecular weight materials are the 4-5% offsets ($\bar{M}_w$ = 21180 - 15880 g/mol). In the following results, a comparison of properties will be given in terms of one high and one low molecular weight material, *viz.* 2% ($\bar{M}_w$ = 41100 g/mol) and 5% ($\bar{M}_w$ = 15880 g/mol).

3.1 Momentary Creep Compliance Curves

The momentary creep compliance curves are plotted as a function of time: for a high molecular weight material (2%) at three temperatures below the T_g in Figure 3, and a low molecular weight material (5%) at equivalent reduced temperatures in Figure 4. Common to all temperatures and all molecular weights is the fact that an increase in aging time generally decreases the overall creep compliance and also the creep rate. This is exemplified in Figure 3a where the 2 hours (h) aging time curve attains the same log creep compliance of –0.25 GPa^{-1} after 800 seconds (s), as the 96 h aging time curve after nearly 50,000 s. The initial creep compliance also decreases in moving from the 2 h to 96 h aging time curve. Thus, the specimen stiffness increases with aging time.

It can also be seen that there is an increase in creep rate with increase in temperature by comparing Figure 3a with Figure 3c and similarly, in Figure 4a with Figure 4c. For example, in Figure 3a, it takes the 96 h aging time curve ~50,000 s to attain a log creep compliance of –0.25 GPa^{-1}, whereas in Figure 3b and Figure 3c, it takes ~20,000 s and ~9,000 s, respectively, to reach this value. There are some creep curves that cross over each other (in both Figs. 3-4) and this occurs when a lower aging time curve has a lower initial compliance than a higher aging time curve.

Although one would expect the initial compliance to decrease with aging time, it is still expected that a lower aging time (2 h) creep compliance curve will have an increased creep rate as compared with a higher aging time (4 h) curve; indeed, this is observed in all cross over cases. Since the shifting procedure uses an objective least squares fit to the data and there is no change in the rate of aging, these changes in the initial creep compliance may be attributable to scatter in the specimen's data.

3.2 Aging Shift Factors and Aging Shift Rates

A linear fit of all the shift factors versus the logarithmic aging time (t_e) for each momentary creep compliance curve gives the aging shift rate, μ. Comparisons of aging shift factors for high and low molecular weights at three equivalent reduced temperatures are shown in Figure 5. It can be seen that aging shift factor decreases linearly with increase in aging time. This means that the creep decelerates with increase in aging time. There appears to be no difference in this respect between high and low molecular weight materials, when comparing Figure 5a with Figure 5b. Thus, there is no change in the shift rate as a function of molecular weight and the shift factors are consistently similar for all molecular weights.

When data of different molecular weights are compared in Table 3, the values for μ are approximately equivalent and close to unity, for each reduced temperature. However, when temperature is the chosen variable, the slope of the linear fits to the aging shift factors, reveals a temperature dependency, as seen in Figure 6. It is seen that, in general, aging shift rate decreases as temperature is increased towards T_g. This is true for all molecular weights, except for the 2% material. This would be in accord with Struik's proposal that μ decreases on approach to the thermodynamic equilibrium state.

3.3 Creep Compliance Momentary Master Curves (MMCs)

A comparison of the creep compliance MMCs for the high and low molecular weight materials is plotted as a function of time at the three equivalent reduced temperatures in Figure 7. The three MMC parameters (S_o, τ and β), given in Table 3, were found by fitting Equation 2 to the collapsed momentary data sets. Common to both Figure 7a and Figure 7b is the relationship of increased compliance with increase in temperature, and also increase in creep rate with increase in temperature.

There is a clear difference in the creep rates when comparing the low and high molecular weight material at the highest temperature. Aside from the slightly lower initial creep compliance of the lower molecular weight material, the lower molecular weight material has a larger creep rate than the higher molecular weight material. In Figure 7b (low molecular weight), the high temperature curve reaches a log creep compliance of 0.44 GPa^{-1}, but the high temperature curve in Figure 7a (high molecular weight) reaches only 0.26 GPa^{-1}. This increase in the rate of creep with decrease in molecular weight has also been seen in other glassy thermoplastic materials [14, 40].

3.4. Time-Temperature Superposition Master Curves

Isothermal MMCs (Figure 7) for each molecular weight were collapsed to coincide with the $\Delta T=20^oC$ reference curve using only horizontal (time) shifts to form a TTSP master curve, as shown in Figure 8. The three temperatures from the MMC data of each molecular weight were combined into a single data set and a least squares fit was performed to obtain parameters (S_o, τ

and β). These parameters were then inserted into Equation 2 to create the master curve for each molecular weight.

Noticeably, the low molecular weight materials (4-5%) exhibit greater creep compliance and creep rate. The 3% material has the lowest initial creep compliance but a similar creep rate to the other high molecular weight (1-2%) materials. The crossing over effect of the curves is readily apparent, as seen before, but is attributable to a molecular weight effect. For example, the descending order of initial creep compliances is 2, 1, 5, 4, and 3 %. The final descending order of creep compliance at t = 500,000 s is 4, 5, 1, 2, and 3 %. This implies that the low molecular weight (5%) material has a lower initial compliance than the high molecular weight (2%) material but a greater creep rate than the 2% material. The same is also true of the 4% and 1% materials.

3.5 Time-temperature superposition shift factors

At higher temperatures, the polymer chains have increased mobility and the time it takes the material to creep is therefore decreased. Furthermore, at the highest test temperature ($\Delta T=15^{o}C$), there is a clear separation between high and low molecular weight TTSP shift factors.

The TTSP shift factors are the horizontal time shifts that are required to shift the MMC data, plotted in Figure 7, to the reference temperature of $\Delta T=20^{o}C$. In Figure 9, these TTSP shift factors are plotted as a function of reduced temperature for all molecular weights. It can be seen that the TTSP shift factors decrease as temperature increases towards T_g for all molecular weights. Therefore, the time shift required to collapse a momentary master curve to the reference temperature curve decreases with increase in temperature as it approaches T_g. In this instance, the high temperature creep compliance curve requires less horizontal time shift than the low temperature creep compliance curve.

By plotting these data from Figure 9 as a function of molecular weight, an indication of the temperature sensitivity of the creep compliance for each molecular weight will be obtained. The slope, or rate of change of TTSP shift factor with respect to temperature is given in Equation 8 as:

$$\delta_T = \frac{-d \log a_T}{dT} \tag{14}$$

Figure 10 summarizes the different materials' behavior. Thus, the high molecular weight materials are seen to be less sensitive to temperature as compared with the low molecular weight materials. There appears to be a distinct molecular weight transition that occurs below 25 kg/mol, so materials that have a molecular weight less than this value will show increased sensitivity to temperature in the timescale of their viscoelastic responses.

3.6 Long-term Creep Compliance

The long-term creep compliance of the material was investigated using a 2 h aging time prior to the application of constant load for the duration of ~1100 hours (~4×10^6 s). The data can be compared with a predicted KWW expression (Equation 10) using Struik's effective time theory (Equation 9) such that short-term test data are extrapolated to predict long-term viscoelastic behavior. Presented in Figure 11 are the long-term test data taken from a high molecular weight material (2%) at the lowest test temperature. The predicted curve is remarkably good at capturing the overall trend in material behavior. As a comparison, the momentary master curve is

included for predicting the response of the material for the same aging time reference of 2 h. Clearly physical aging serves to dramatically decrease the creep compliance of the material. In this example, the aging effect is seen to commence at approximately 10,000 s.

3.6.1 Comparison of Long term Creep Compliance with Prediction for molecular weight variations

For a more rigorous test of the predicted long-term behavior, Figure 12 presents long-term test data for high (2%) and low (5%) molecular weights for two test temperatures, $\Delta T = 15, 25^{o}C$. The predicted curve appears to match the lower test temperature data better than the high temperature. The predicted curve for the high temperature does not account for sufficient aging at long timescales. In comparing Figure 12a with Figure 12b, it is noticeable that the high molecular weight material has a better match with the predicted curves than those of low molecular weight.

The effects of both test temperature and molecular weight on long-term test data are conveniently summarized in Figure 13. A 2 h aging time was established prior to loading and was used as the reference aging time. The effect of increased temperature is to increase the creep compliance and creep rate, as has been shown previously. In the long-term viscoelastic response, the low molecular weight materials show increased creep compliance and creep rate over the high molecular weight material. Upon closer examination of the two different data sets, it can be seen that the incipient separation between the high and low molecular weight materials happens approximately three times faster for the high temperature (~600 s) versus the low test temperature (~2,000 s).

3.7 Long term Creep Compliance Predictions

The predicted creep compliance behavior for long-term testing is extended to the timescale of the acquired long-term test data. Displayed in Figure 14 is the predicted behavior for the high (2%) and low (5%) molecular weight materials, at the three reduced temperatures as indicated. The 2 h aging time was used as the reference. The consistent effect of temperature is apparent; the higher the test temperature (lower ΔT), the higher the creep compliance and creep rate. There are no inconsistencies in the data when comparing the molecular weights, Figure 14a with Figure 14b, but it is clear that the high temperature curve in Figure 14b has the largest creep compliance and creep rate of any curve in these two data sets. The different initial compliances arise because of the effects of temperature.

The predicted long-term creep compliance for each molecular weight at a test temperature of $\Delta T = 20^{o}C$ is presented in Figure 15. The final order of the creep compliance as a function of molecular weight is as indicated. The curve for the 3% material has a low creep compliance and creep rate, whereas the 4% material has high creep compliance and creep rate. There is little difference in the order between the other molecular weights.

4. Conclusions

Experiments were performed to determine the effects of molecular weight, elevated temperature and physical aging on the creep compliance of LaRC^{TM}-SI loaded in tension. The short term (96 hours) creep compliance tests, run over a range of sub-T_g temperatures, provided material constants, material master curves and aging related parameters.

The results from the short-term aging behavior indicated that the monotonic decrease in aging shift factor with increase in aging time proved to be independent of molecular weight. However, the time-temperature superposition analysis of the creep compliance showed that low molecular weight materials have increased creep compliance and increased creep rate, over that seen in the high molecular weight materials. Furthermore, the temperature sensitivity of the TTSP shift factor is dramatically increased for molecular weights less than $\bar{M}_w$ ~ 25 kg/mol.

The effects of creep loading for long timescales (>1100 hours) provided a means for evaluating the predictive model, and the long-term effects of molecular weight and temperature. The model predictions compared favorably with the long-term test data. It was shown that a decrease in the molecular weight and an increase in the temperature both serve to increase the creep compliance and creep rate.

Thus, for any given temperature, the effect of reducing the molecular weight is somewhat akin to raising the test temperature: the creep compliance and creep rate are increased. It is likely, then, that the polymer segmental mobility is higher in a low molecular weight material since it is not hindered as much by the presence of physical entanglements. This increase in segmental mobility is associated with more available free volume in which to move. Therefore, for a constant temperature over long timescales, the low molecular weight materials are less influenced by physical aging than their high molecular weight counterparts.

5. Acknowledgements

The authors are grateful for the technical assistance of Mr. C. E. Townsley. This work was performed while Dr. Nicholson held a National Research Council Research Associateship at NASA Langley Research Center.

6. References

[1] McKenna, G. B.: On the physics required for prediction of long term performance of polymers and their composites, *Journal of Research of the National Institute of Standards and Technology*. Vol. 99, 1994, pp. 169-189.

[2] Haward, R. N.: *The Physics of Glassy Polymers*. New York: John Wiley & Sons, 1973.

[3] McKenna, G. B.: Glass Formation and Glassy Behavior, *Comprehensive Polymer Science, 2*, C. Booth and C. Price, Eds. Oxford: Pergamon, 1989, pp. 311-362.

[4] Struik, L. C. E.: *Physical Aging in Amorphous Polymers and Other Materials*. New York: Elsevier Scientific Publishing Company, 1978.

[5] Zhou, J.: Constitutive model of polymer materials including chemical ageing and mechanical damage and its experimental verification, *Polymer*. Vol. 34, 1993, pp. 4252-4257.

[6] Read, B. E.; Tomlins, P. E., and Dean, G. D.: Physical ageing and short-term creep in amorphous and semicrystalline polymers, *Polymer*. Vol. 31, 1990, pp. 1204-1215.

[7] Lee, A. and McKenna, G. B.: Viscoelastic response of epoxy glasses subjected to different thermal treatments, *Polymer Engineering and Science*. Vol. 31, 1990, pp. 431-435.

[8] Wang, J. Z.; Parvatareddy, H.; Chang, T.; Iyengar, N.; Dillard, D. A., and Reifsnider, K. L.: Physical Aging Behavior of High-Performance Composites, *Composites Science and Technology*. Vol. 54, 1995, pp. 405-415.

[9] Gates, T. S.: Effects of Elevated Temperature on the Viscoplastic Modeling of Graphite/Polymeric Composites, *High Temperature and Environmental Effects on Polymeric Composites, ASTM STP 1174*, C. E. Harris and T. S. Gates, Eds. Philadelphia: American Society for Testing and Materials, 1993, pp. 201-221.

[10] Gates, T. S.; Veazie, D. R., and Brinson, L. C.: Creep and Physical Aging in a Polymeric Composite: Comparison of Tension and Compression, *Journal of Composite Materials*. Vol. 31, 1997, pp. 2478-2505.
[11] Vincent, P. I.: A correlation between critical tensile strength and polymer cross-sectional area, *Polymer*. Vol. 13, 1972, pp. 558-560.
[12] Kusy, R. P. and Turner, D. T.: Influence of molecular-weight of poly(methyl methacrylate) on fracture morphology in notched tension, *Polymer*. Vol. 18, 1977, pp. 391-402.
[13] Prentice, P.: The influence of molecular weight on the fracture of thermoplastic glassy polymers, *Journal of Materials Science*. Vol. 20, 1985, pp. 1445-54.
[14] Nemoto, N.; Moriwaki, M.; Odani, H., and Kurata, M.: Viscoelastic properties of narrow-distribution polymers. 3. Shear creep studies of narrow-distribution poly (*cis*-isoprene), *Macromolecules*. Vol. 4, 1971, pp. 215.
[15] Odani, H.; Nemoto, N., and Kurata, M.: The viscoelastic properties of undiluted linear polymers of narrow molecular weight distribution in the terminal zone, *Bulletin of the Institute for Chemical Research, Kyoto University*. Vol. 50, 1972, pp. 117-33.
[16] Ngai, K. L.; Plazek, D. J., and Bero, C. A.: Viscoelastic properties of amorphous polymers 2: Anomalous temperature dependence of the steady-state recoverable compliance in low molecular weight polymers, *Macromolecules*. Vol. 26, 1993, pp. 1065-1071.
[17] Plazek, D. J.; Bero, C. A.; Neumeister, S.; Floudas, G.; Fytas, G., and Ngai, K. L.: Viscoelastic properties of amorphous polymers 3: Low molecular weight poly(methylphenylsiloxane), *Colloid and Polymer Science*. Vol. 272, 1994, pp. 1430-1438.
[18] Yu, Z.; Yashi, U.; McGervey, J. D.; Jamieson, A. M., and Simha, R.: Molecular weight-dependence of free volume in polystyrene studied by positron annihilation measurements, *Journal of Polymer Science, Part B: Polymer Physics*. Vol. 32, 1994, pp. 2637-2644.
[19] Singh, J. J. and Eftekhari, A.: Free volume model for molecular weights of polymers, *Nuclear Instruments & Methods in Physics Research*. Vol. B63, 1992, pp. 477-483.
[20] Matsuoka, S. and Hale, A.: Cooperative relaxation processes in polymers, *Journal of Applied Polymer Science*. Vol. 64, 1997, pp. 77-93.
[21] Siochi, E. J.; Young, P. R., and Bryant, R. G.: Effect of molecular weight on the properties of a soluble polyimide, *Materials Challenge - Diversification and the Future, 40(1)*. Los Angeles, California: SAMPE, 1995, pp. 11-18.
[22] Bryant, R. G.: LARC-SI: a soluble aromatic polyimide, *High Performance Polymers*. Vol. 8, 1996, pp. 607-615.
[23] Nicholson, L. M.; Whitley, K. S.; Gates, T. S., and Hinkley, J. A.: *Influence of molecular weight on the mechanical performance of a thermoplastic glassy polyimide*, NASA TM 1999-209720, 1999.
[24] Murry, W. M., and Miller, W. R.: *The Bonded Electrical Resistance Strain Gage*. New York: Oxford University Press, 1992.
[25] Hinkley, J. A. and Yue, J. J.: Oxidative Aging of Thermoplastic Polyimide Films, *Journal of Applied Polymer Science*. Vol. 57, 1995, pp. 1539-1543.
[26] Findley, W. N.; Lai, J. S., and Onaran, K.: *Creep and Relaxation of Nonlinear Viscoelastic Materials*. Toronto: North-Holland Publishing Company, 1976.
[27] Kohlrausch, R.: Theorie des Elektrischen Rückstandes in der Leidener Flasche (Theory of residual charge in a Leyden Jar), *Annalen der Physik und Chemie, 91*, J. C. Poggendorf, Ed., 1854, pp. 179-214.
[28] Williams, G. and Watts, D. C.: Nonsymmetrical dielectric relaxation behavior arising from a simple empirical decay function, *Transactions of the Faraday Society*. Vol. 66, 1970, pp. 80-85.
[29] Brinson, L. C. and Gates, T. S.: Effects of physical aging on long term creep of polymers and polymer matrix composites, *International Journal of Solids and Structures*. Vol. 32, 1995, pp. 827-846.

[30] McKenna, G. B.; Leterrier, Y., and Schultheisz, C. R.: The Evolution of Material Properties During Physical Aging, *Use of Plastics and Plastic Composites: Materials and Mechanics Issues, MD -46*, Y. K. Stokes, Ed.: The American Society of Mechanical Engineers, 1993.

[31] Hastie, R. L. and Morris, D. H.: The Effect of Physical Aging on the Creep Response of a Thermoplastic Composite, *High Temperature and Environmental Effects in Polymer Matrix Composites, ASTM STP 1174*, C. Harris and T. Gates, Eds. Philadelphia: American Society for Testing and Materials, 1992, pp. 163-185.

[32] Bradshaw, R. D. and Brinson, L. C.: Physical Aging in Polymers and Polymer Composites: An Analysis and Method for Time-Aging Time Superposition, *Polymer Engineering and Science*. Vol. 37, 1997, pp. 31-44.

[33] Leaderman, H.: *Elastic and creep properties of filamentous materials and other high polymers*. Washington, D.C.: Textile Foundation, 1943.

[34] O'Connell, P. A. and McKenna, G. B.: Large Deformation Response of Polycarbonate: Time-Temperature, Time-Aging Time and Time-Strain Superposition, *Polymer Engineering and Science*. Vol. 37, 1997, pp. 1485-1495.

[35] Schapery, R. A.: Inelastic Behavior of Composite Materials, *ASME Winter Annual Meeting, AMD-13*, C. T. Herakovich, Ed. Houston: ASME, 1975, pp. 122-150.

[36] Skrypnyk, I. D.; Spoormaker, J. L., and Kandachar, P.: A constitutive model for long-term behavior of polymers, *Time dependent and nonlinear effects in polymers and composites, STP 1357*, R. A. Schapery and C. T. Sun, Eds. West Conshohocken, PA: American Society for Testing and Materials, 2000, pp. 70-82.

[37] Bradshaw, R. D. and Brinson, L. C.: A Sign Control Method for Fitting and Interconverting Material Functions for Linearly Viscoelastic Solids, *Mechanics of Time-Dependent Materials*. Vol. 1, 1997, pp. 85-108.

[38] Bradshaw, R. D. and Brinson, L. C.: Recovering Nonisothermal Physical Aging Shift Factors via Continuous Test Data: Theory and Experimental Results, *Journal of Engineering Materials and Technology*. Vol. 119, 1997, pp. 233-241.

[39] Nicholson, L. M.; Whitley, K. S.; Gates, T. S., and Hinkley, J. A.: How molecular structure affects mechanical properties of an advanced polymer, *Proceedings of SAMPE*. Vol. 44(2), 1999, pp. 794-808.

[40] Fujimoto, T.; Ozaki, N., and Nagasawa, M.: Stress relaxation of monodisperse poly(α-methylstyrene), *Journal of Polymer Science A2*. Vol. 6, 1968, pp. 129.

% Offset	$\bar{M}_w$ [g/mol]	$(\bar{M}_w/\bar{M}_n)$	T_g [°C] (cured)	T_{test} [°C]	[°C]	[°C]
1	51070	4.57	250	235	230	225
2	41100	2.98	246	231	226	221
3	24290	2.30	238	223	218	213
4	21180	2.04	238	223	218	213
5	15880	1.79	234	219	214	209

Table 1. Weight-average molecular weight ($\bar{M}_w$) and polydispersity indices $(\bar{M}_w/\bar{M}_n)$ of various LaRC™-SI materials are designated by their percent offsets. Glass transition (T_g) temperatures were measured on the cured LaRC™-SI resin specimens [21].

% Offset	$\bar{M}_w$ [g/mol]	T_{test} [°C]	ΔT [°C]	Av. E [GPa]	Av. ν	Av. G [GPa]
1	51070	225	25	2.150	0.355	0.793
		235	15	1.777	0.359	0.654
2	41100	221	25	2.293	0.376	0.833
		231	15	1.830	0.350	0.678
3	24290	213	25	2.303	0.369	0.841
		223	15	2.191	0.389	0.789
4	21180	213	25	2.369	0.416	0.836
		223	15	1.898	0.368	0.694
5	15880	209	25	2.434	0.377	0.884
		219	15	2.056	0.351	0.761

Table 2. Mechanical properties for LaRC™-SI. Mechanical test temperatures (T_{test}) and the indicated property: averaged Young's Modulus (E); averaged Poisson's ratio (ν); and averaged Shear Modulus (G) [23].

% Offset	$\bar{M}_w$ [g/mol]	T_{test} [°C]	ΔT [°C]	S_o [GPa^{-1}]	τ (s)	β	μ	$\mathbf{a}_T$
1	51070	225	25	0.404	7.30E+05	0.397	1.080	0.410
		230	20	0.402	2.72E+05	0.401	0.994	0.000
		235	15	0.339	7.30E+04	0.392	0.881	0.309
2	41100	221	25	0.385	4.71E+05	0.419	0.966	0.310
		226	20	0.401	2.85E+05	0.407	0.979	0.000
		231	15	0.398	1.31E+05	0.406	0.998	0.350
3	24290	213	25	0.375	8.51E+05	0.375	0.991	0.310
		218	20	0.371	3.21E+05	0.411	0.922	0.000
		223	15	0.313	1.52E+05	0.403	0.946	0.310
4	21180	213	25	0.355	3.61E+05	0.369	0.969	0.600
		218	20	0.373	9.68E+04	0.358	0.904	0.000
		223	15	0.295	1.03E+04	0.204	0.827	0.610
5	15880	209	25	0.361	4.91E+05	0.392	0.999	0.360
		214	20	0.353	2.13E+05	0.395	0.914	0.000
		219	15	0.373	6.67E+04	0.386	0.880	0.610

Table 3. Momentary master curve parameters, test temperatures (°C) and TTSP shift factors for all molecular weight LaRC™-SI materials.

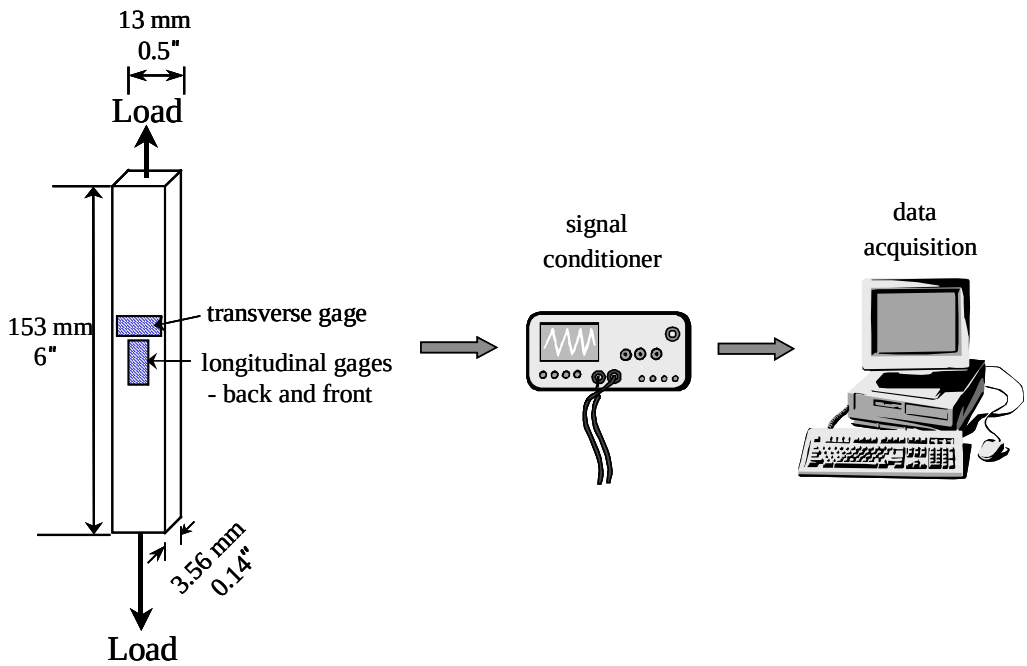

Figure 1. Test specimen geometry and data acquisition system.

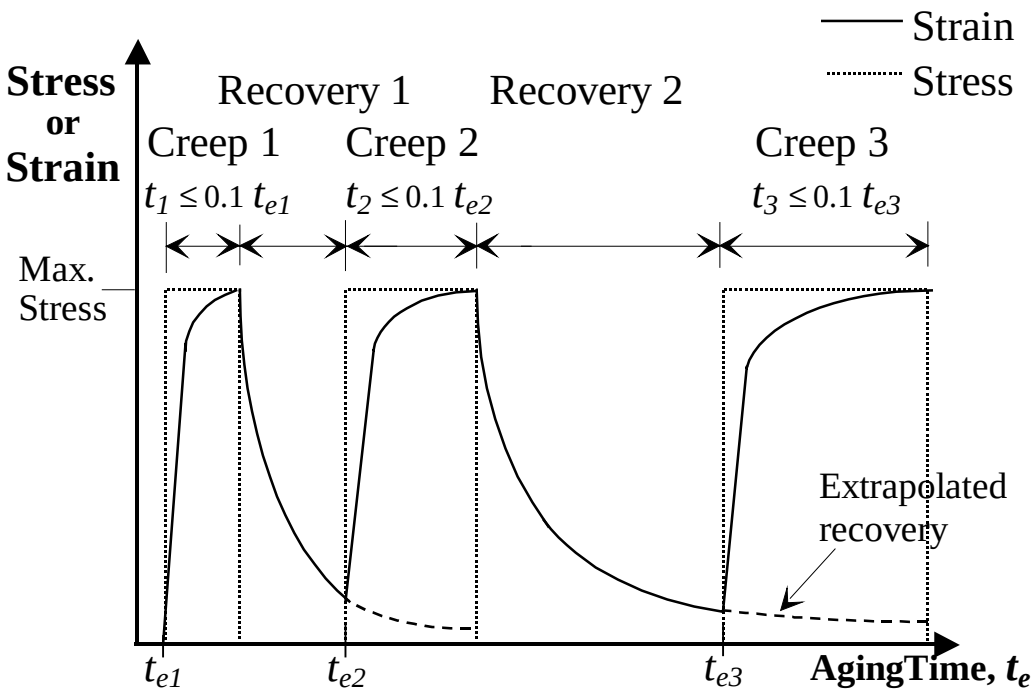

Figure 2. Sequenced short-term creep and recovery tests.

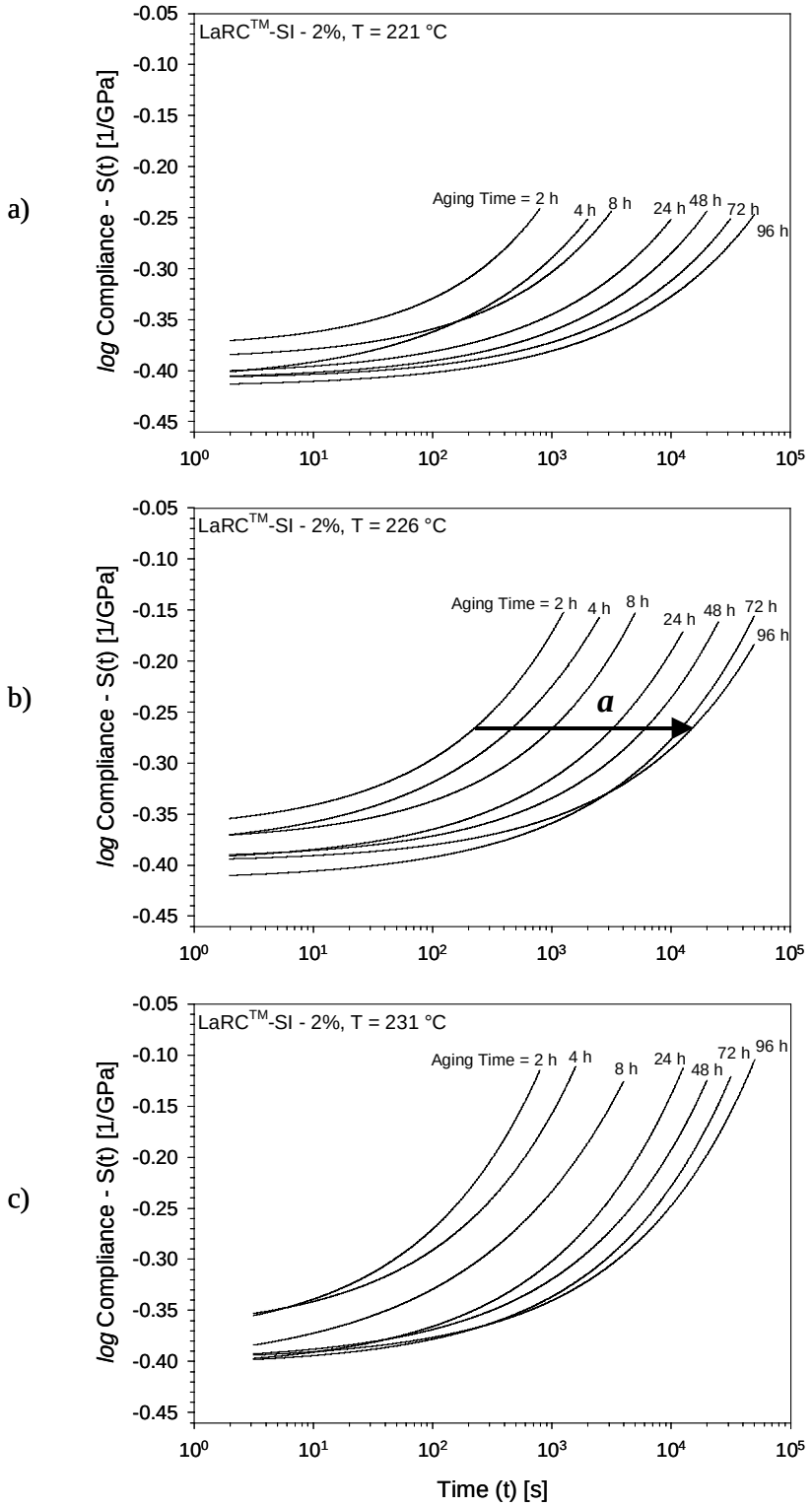

Figure 3. Creep compliance momentary curves plotted as a function of time for the three test temperatures at 2% molecular weight offset. The creep compliance momentary curves are shifted to coincide with the 96 hours aging time reference curve.

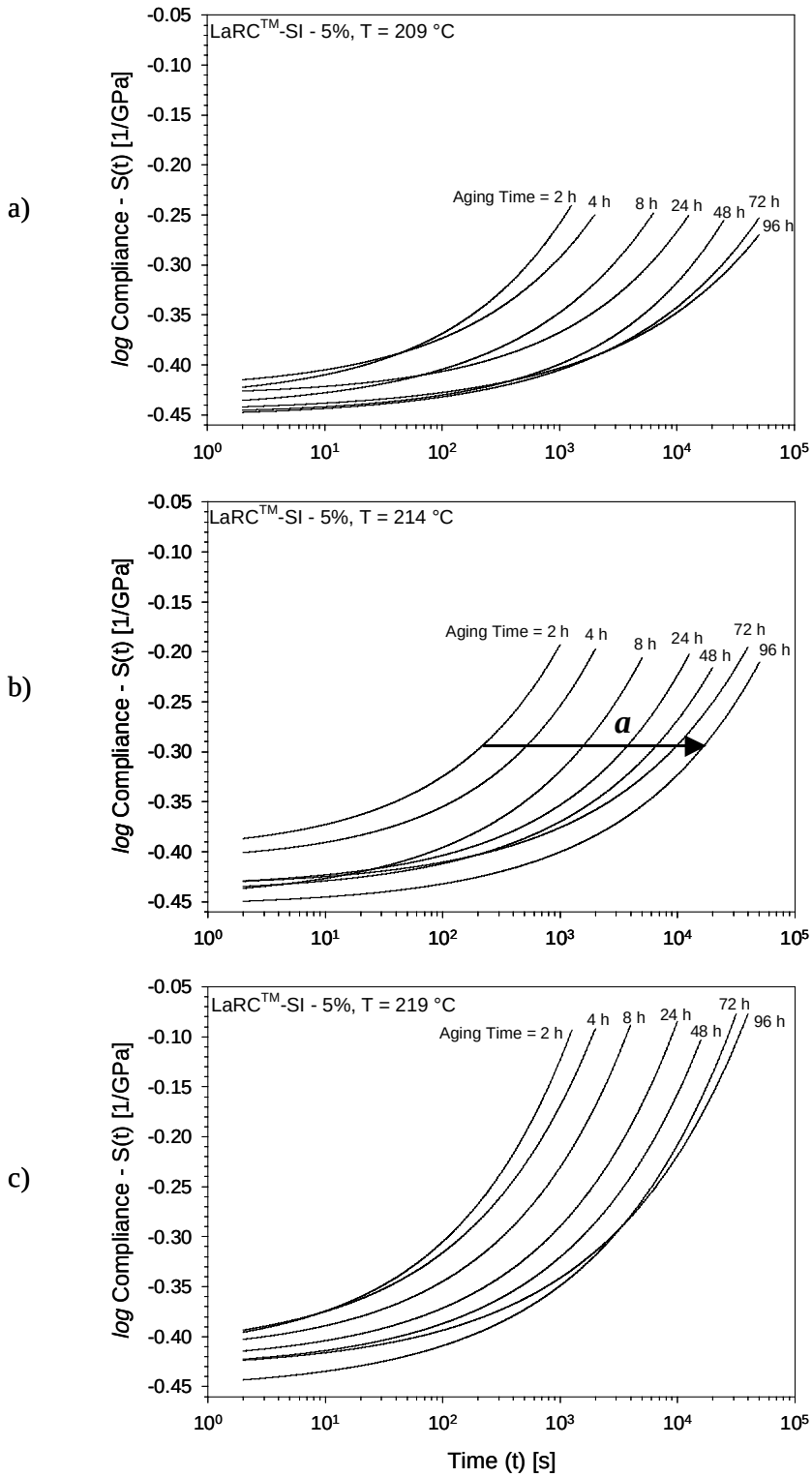

Figure 4. Creep compliance momentary curves plotted as a function of time for the three test temperatures at 5% molecular weight offset. The creep compliance momentary curves are shifted to coincide with the 96 hours aging time reference curve.

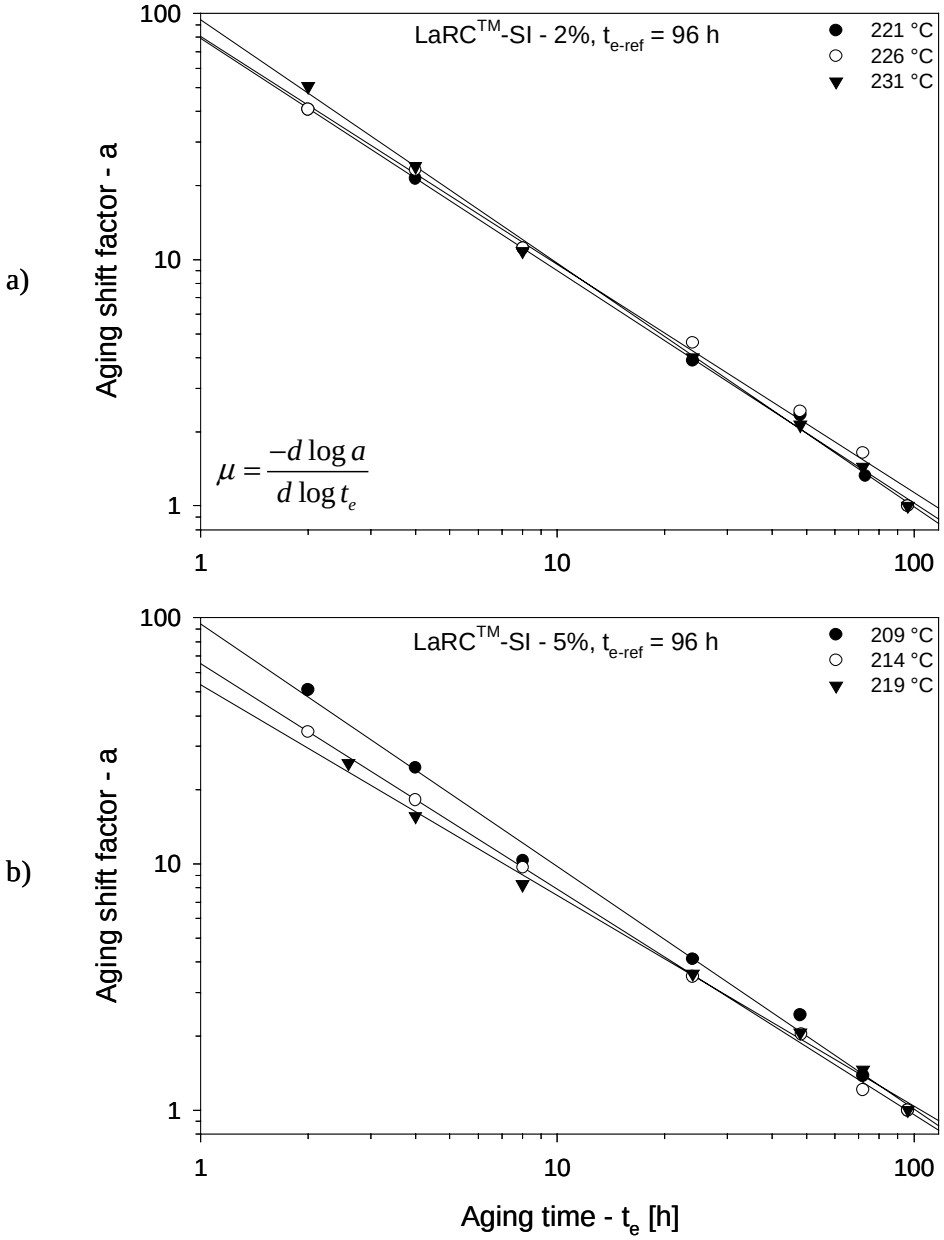

Figure 5. Aging shift factors plotted as a function of aging time for LaRC™-SI 2% (a) and 5% (b), respectively. The creep compliance curves of Figs. 3-4 are shifted horizontally to the 96 hours aging time reference curve to obtain the shift factors.

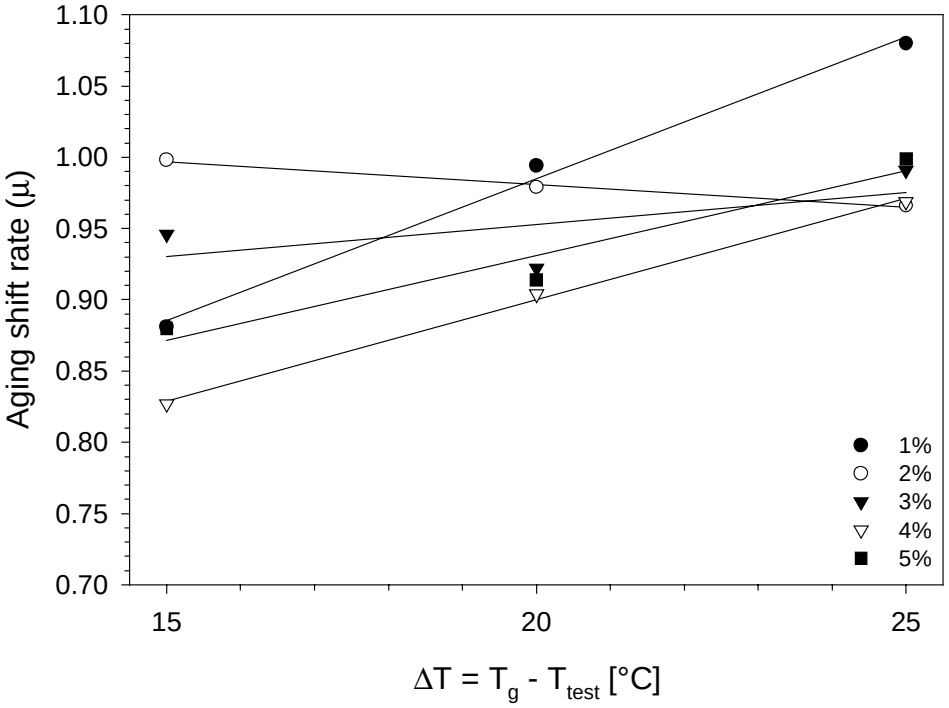

Figure 6. Aging shift rates plotted as a function of reduced temperature for all molecular weights. The aging shift factors of Figure 5 were differentiated with respect to aging time, t_e.

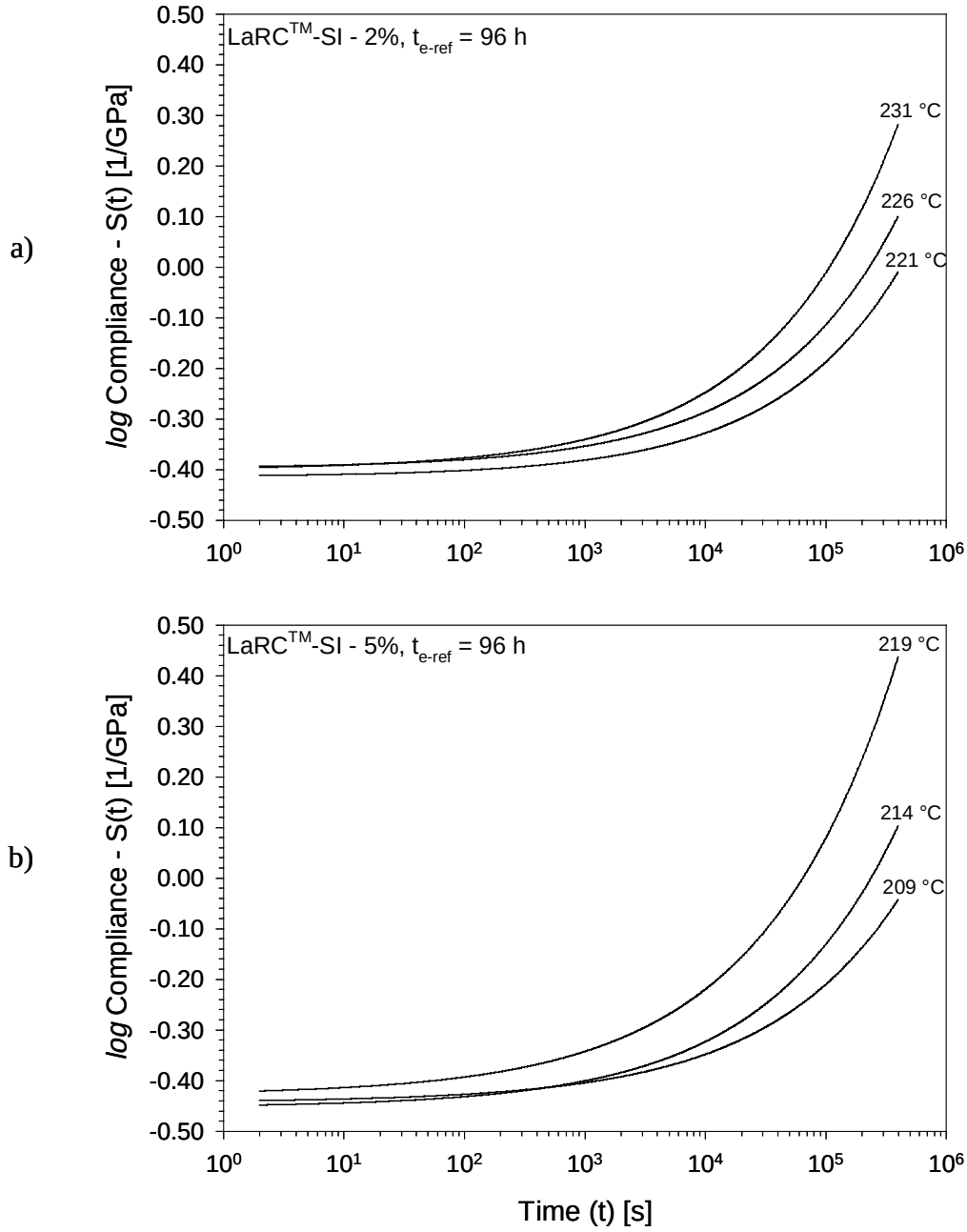

Figure 7. Creep compliance momentary master curves (MMCs) plotted as a function of time for the three test temperatures at molecular weights of: a) 2% and b) 5%. The creep compliance momentary curves of Figs. 3-4 are shifted to coincide with the 96 hours aging time reference curve.

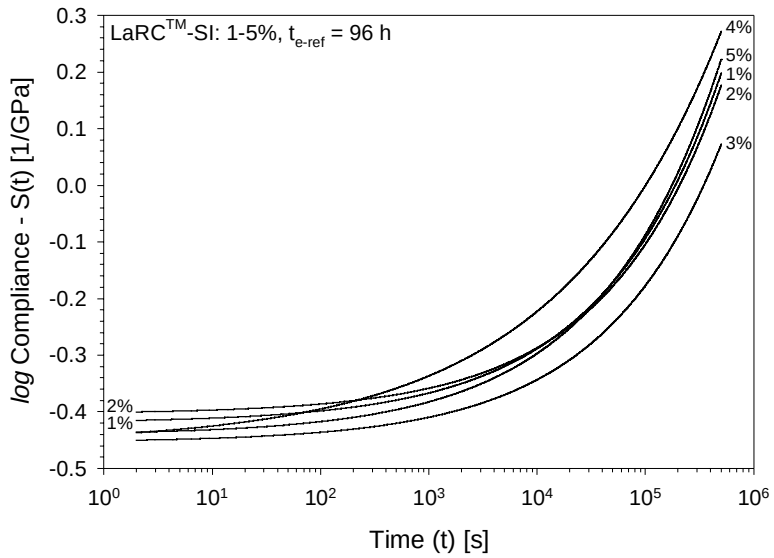

Figure 8. Creep compliance master curves plotted as a function of time for all molecular weights. The creep compliance MMCs of Figure 7 are shifted horizontally to the $\Delta T=20^{o}C$ reference temperature for each molecular weight.

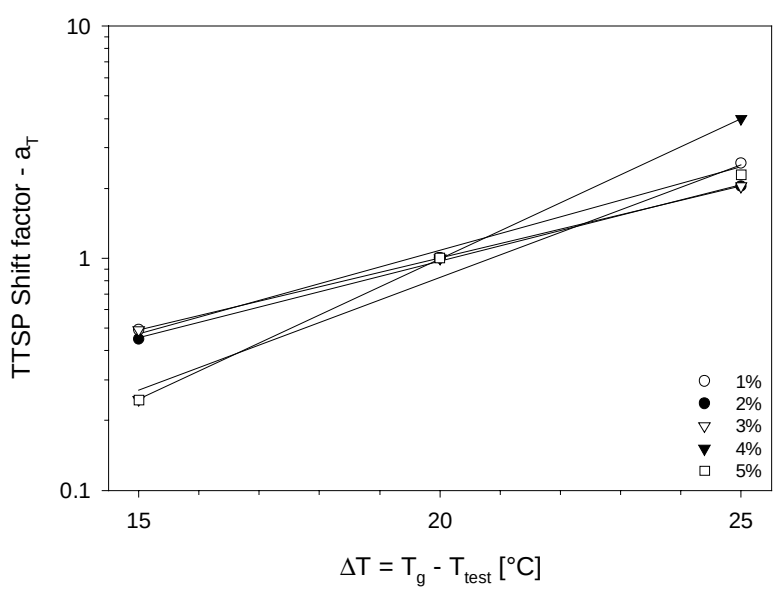

Figure 9. TTSP shift factors plotted as a function of reduced temperature for all molecular weights. The MMCs, for all molecular weights, were shifted horizontally to a reference temperature of $\Delta T=20^{o}C$.

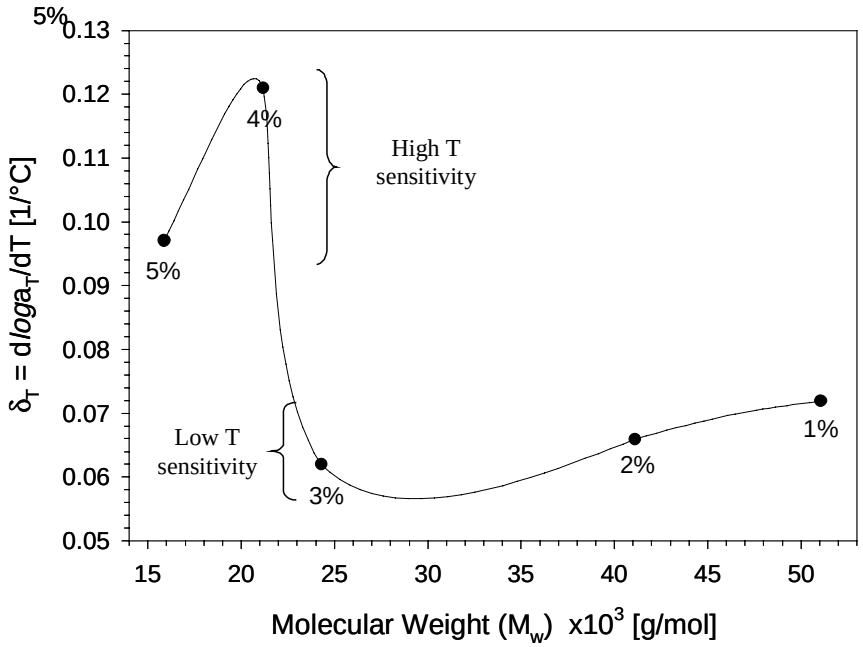

Figure 10. The reduced temperature derivative of TTSP shift factors (Figure 9) plotted as a function of molecular weight to indicate the temperature sensitivity of each molecular weight.

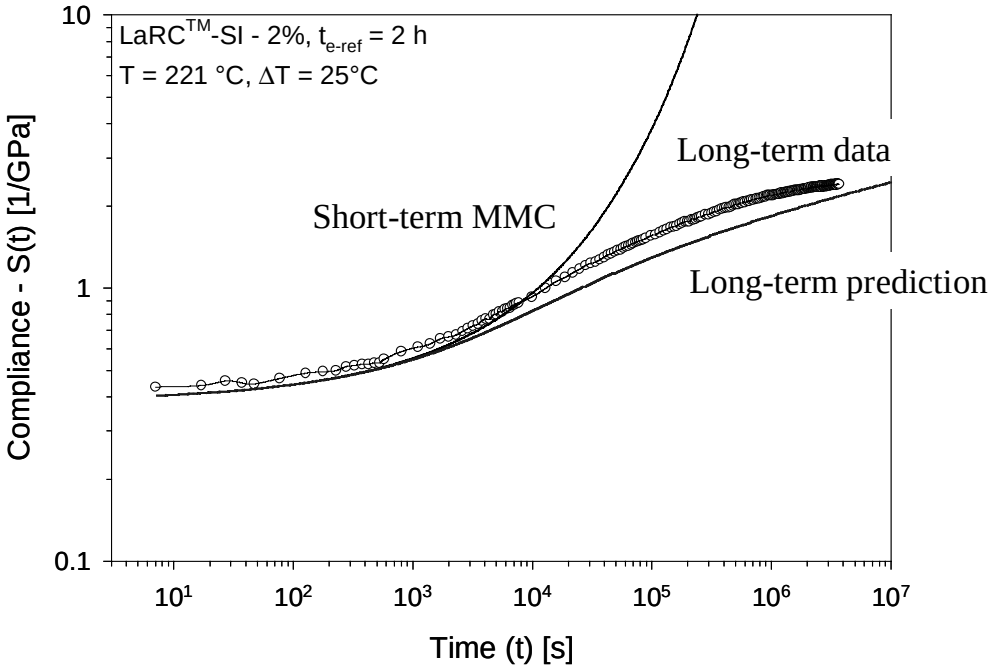

Figure 11. Long-term creep compliance test data with predicted curves and the unaged prediction (taken from the short-term momentary master curve data) at a reduced temperature for the high molecular weight material, with an aging time of 2 hours.

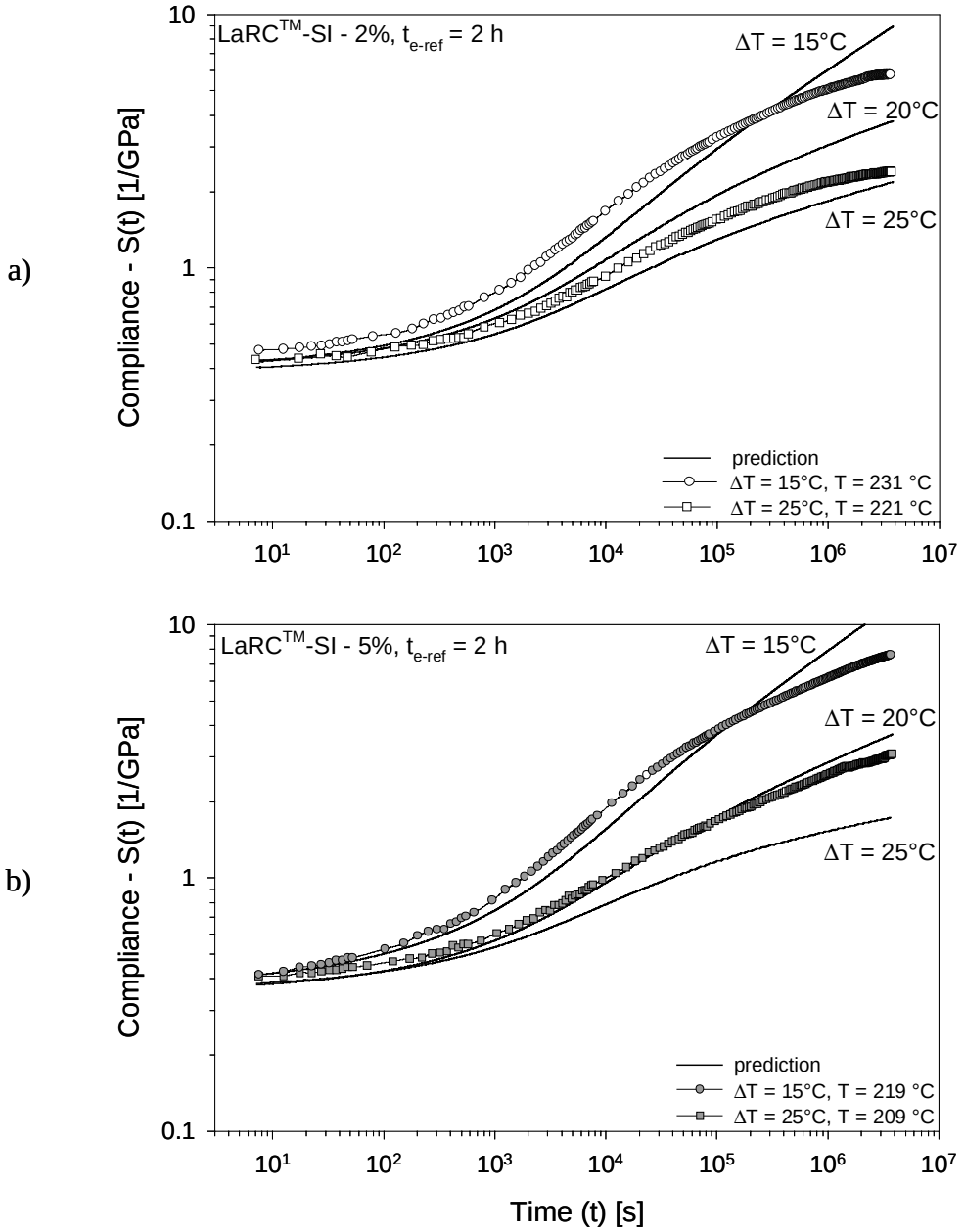

Figure 12. Comparison of long-term predictions with long-term test data for high (a) and low (b) molecular weights at two test temperatures.

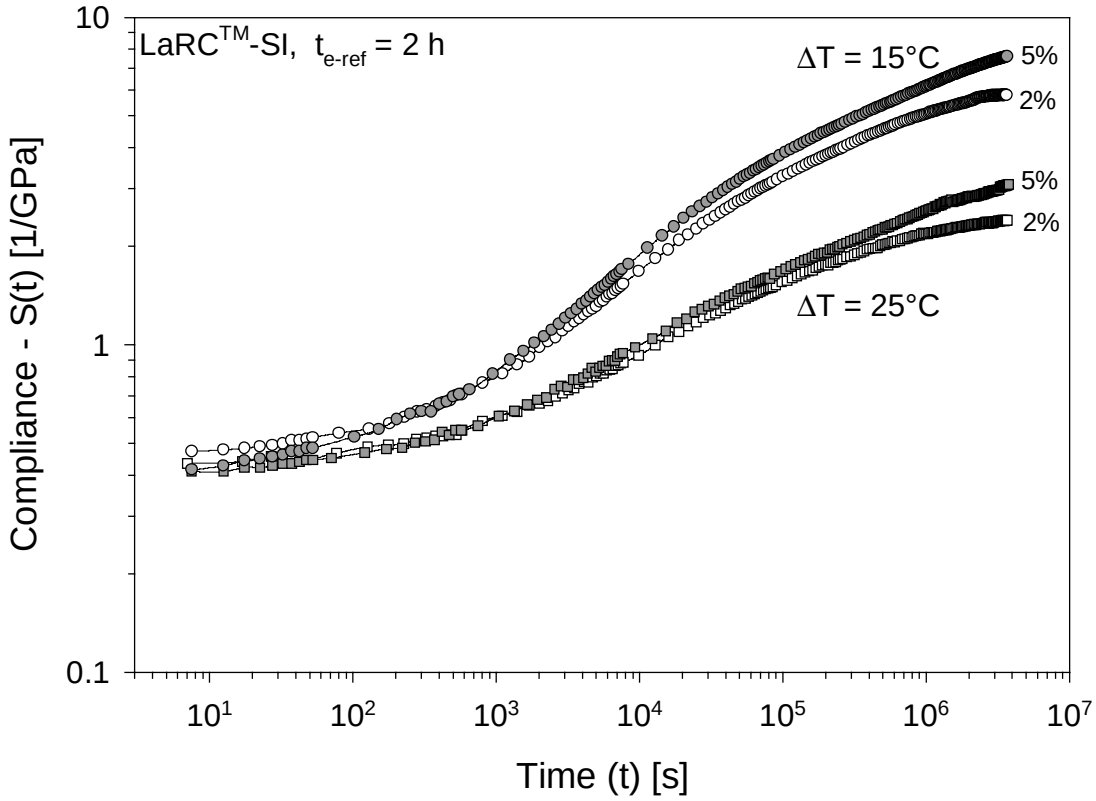

Figure 13. The effect of molecular weight and test temperature on the long-term viscoelastic response.

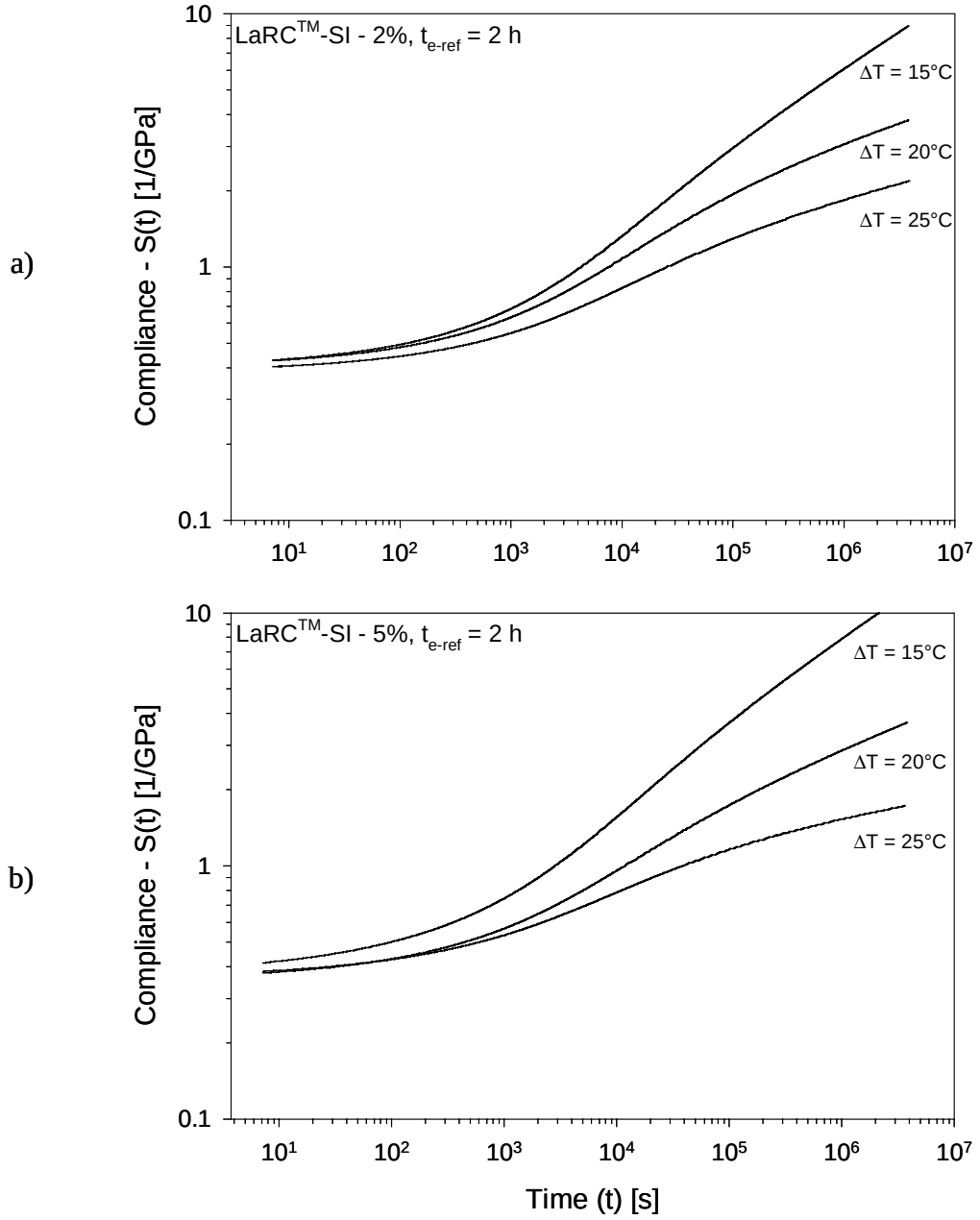

Figure 14. Long-term creep compliance predictions at reduced test temperatures for the high (a) and low (b) molecular weight materials, using a reference aging time of 2 hours.

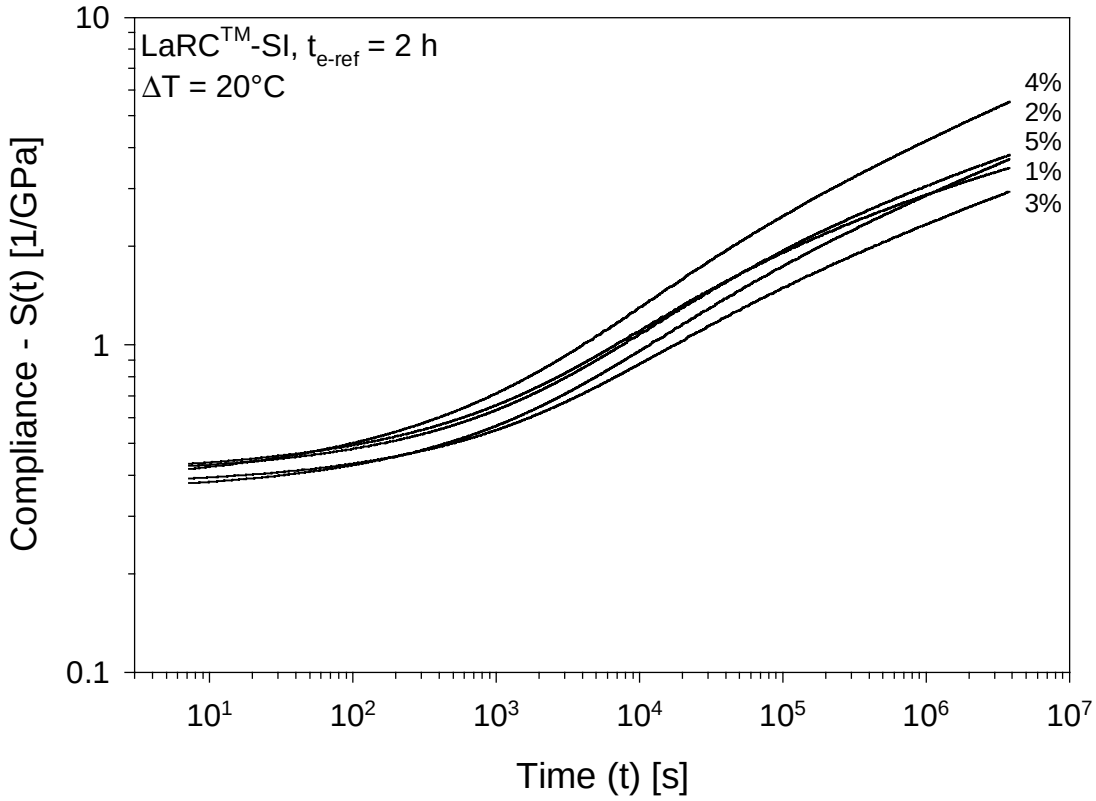

Figure 15. Predicted long-term creep compliance as a function of molecular weight at a reduced test temperature of $\Delta T = 20^{o}C$. The aging time reference used for the prediction was 2 hours.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
September 2000

3. REPORT TYPE AND DATES COVERED
Technical Memorandum

4. TITLE AND SUBTITLE
The Combined Influence of Molecular Weight and Temperature on the Aging and Viscoelastic Response of a Glassy Thermoplastic Polyimide

5. FUNDING NUMBERS
WU 706-13-31-02

6. AUTHOR(S)
Lee M. Nicholson, Karen S. Whitley, and Thomas S. Gates

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NASA Langley Research Center
Hampton, VA 23681-2199

8. PERFORMING ORGANIZATION REPORT NUMBER
L-18005

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NASA/TM-2000-210312

11. SUPPLEMENTARY NOTES
Nicholson: Institute for Computer Applications in Science and Engineering, Langley Research Center, Hampton, VA; Whitley and Gates: Langley Research Center, Hampton, VA

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified-Unlimited
Subject Category 27 Distribution: Standard
Availability: NASA CASI (301) 621-0390

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
The effect of molecular weight on the viscoelastic performance of an advanced polymer (LaRC™-SI) was investigated through the use of creep compliance tests. Testing consisted of short-term isothermal creep and recovery with the creep segments performed under constant load. The tests were conducted at three temperatures below the glass transition temperature of five materials of different molecular weight. Through the use of time-aging-time superposition procedures, the material constants, material master curves and aging-related parameters were evaluated at each temperature for a given molecular weight. The time-temperature superposition technique helped to describe the effect of temperature on the timescale of the viscoelastic response of each molecular weight. It was shown that the low molecular weight materials have higher creep compliance and creep rate, and are more sensitive to temperature than the high molecular weight materials. Furthermore, a critical molecular weight transition was observed to occur at a weight-average molecular weight of ~25000 g/mol below which, the temperature sensitivity of the time-temperature superposition shift factor increases rapidly. The short-term creep compliance data were used in association with Struik's effective time theory to predict the long-term creep compliance behavior for the different molecular weights. At long timescales, physical aging serves to significantly decrease the creep compliance and creep rate of all the materials tested.

14. SUBJECT TERMS
Polyimides, thermoplastic, glassy, molecular weight, high-temperature, creep compliance, physical aging, viscoelastic, durability

15. NUMBER OF PAGES
33

16. PRICE CODE
A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL