

MOLECULAR WEIGHT EFFECTS ON THE VISCOELASTIC RESPONSE OF A POLYIMIDE*

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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 each material with 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 increased creep compliance and creep compliance 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.

KEY WORDS: polyimides, ageing, mechanical properties.

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, hence affecting its long-term durability.

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 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.

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Failure or degradation of performance in PMCs is usually 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 and therefore interpretations of mechanical behavior have been focused on analysis of elastic solids. The physics of glassy polymers is a mature subject [1-2] and closely associated is the abundant interest in physical aging mechanisms that occur in glassy polymers [3]. Physical aging is the process describing 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 [4], and is essentially thermoreversible. An accepted methodology for evaluating the extent of physical aging in glassy polymers is the use of creep compliance tests [3-6]. In these studies, investigations were made into the concepts of effective time theory and relationships between aging and free volume evolution. The combination of tension creep tests, concepts of linear viscoelasticity, and mechanics of composite materials have been done more recently [7] utilizing high performance PMCs tested below the glass transition (T_g) temperature. Studies by Gates and others [8-9] 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 provided the material properties required to make long-term predictions.

Despite a wealth of literature on the molecular weight effects on the mechanical properties of glassy polymers [10-12], there is surprisingly little information addressing the role of molecular weight on the viscoelastic response of glassy polymers. Odani and others [13-14] 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 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 [15-16]. Other workers have been trying to establish the effects of molecular weight on the unit cell free volume as a means for understanding physical aging. Yu and others [17], and Singh and Eftekhari [18] have used positron annihilation lifetime spectroscopy to evaluate the free volume size and found that a decrease in molecular weight increases the cell's free volume. Recently, Matsuoka and Hale [19] 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 of and discuss an experimental study that considers the effects of molecular weight on the viscoelastic behavior and physical aging of an advanced polymer. Five distinct variations in molecular weight were used to evaluate the differences in mechanical performance of an advanced glassy thermoplastic polyimide. The physical aging behavior was isolated by conducting sequenced, short-term isothermal creep compliance tests in tension. These tests were performed over a range of sub-glass transition temperatures. The material constants, material master curves and 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. LaRCTM-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 [20], were prepared by reacting an excess of the diamine with an appropriately reduced quantity of the dianhydrides in *N*-methyl-2-pyrrolidinone (NMP). Extended synthesis descriptions of this material have been published elsewhere [21]. These molecular weights and intrinsic viscosities for LaRC™-SI were determined on the as-received powders using gel permeation chromatography [20]. The weight-average molecular weights (\overline{M}_w) and the polydispersity indices of the materials are shown in Table 1. The differences in the molecular weight (M_w) distribution per sample are more easily discerned when weight averages are compared.

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.

2.3 Test Instrumentation and Procedures Tensile 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 aging occurred within the test period. 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_g s are indicated in Table 1. To place equal emphasis on the results, due to the different T_g s of the materials, the test temperature is referenced to the glass transition temperature. The *reduced temperature* is defined as:

$$\Delta T = T_g - T_{test} \quad (1)$$

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 each face of the specimen. Proper selection of the gage type and adhesive bond gave a coefficient of thermal expansion (CTE) match and stability at elevated temperatures. Apparent thermal strain was corrected for by using the compensating gage technique ([22]), which allows for the separation of the load-induced strain from the thermal strain. 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. Change in the T_g from the unaged condition over extended aging times was measured by Allen [23] and found to remain within 3 K for 10,000 hours of isothermal aging at 180°C on a similar thermoplastic polyimide. It was therefore 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. Due to limited amounts of material only one test coupon was tested at each temperature within each molecular weight offset, and these samples were not retested.

% Offset	\overline{M}_w (g/mol)	$\frac{\overline{M}_w}{\overline{M}_n}$	T_g (°C) (cured)	$\Delta T=15$ K (°C)	$\Delta T=20$ K (°C)	$\Delta T=25$ K (°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 (\overline{M}_w) and polydispersity indices 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 by differential scanning calorimetry (DSC), after [20]. Creep test temperatures (°C) are presented as a reduced temperature ($\Delta T = T_g - \text{test temperature}$).

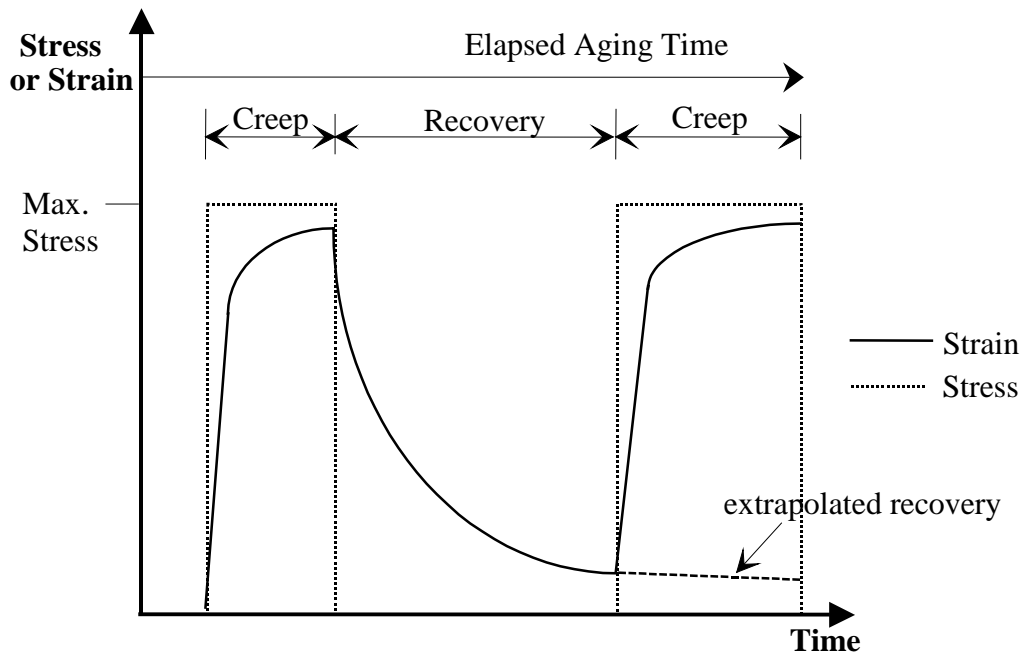


Figure 1 Sequenced short-term creep and recovery tests.

2.3.1 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 [3]. 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 .

To explore the effects of physical aging on the creep properties, a well-documented technique that measures the creep compliance as described in [3] 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 Fig. 1. The recovery stage distinguishes between reversible and irreversible creep strains; that is, between viscoelastic and plastic deformations.

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 Fig. 1.

2.3.2 Analysis of viscoelastic behavior For a polymer loaded with constant uniaxial tension under isothermal conditions, the time-dependent linear creep compliance was modeled with a three parameter expression given by

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

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 sequenced short-term creep and recovery tests, as depicted in Fig. 1. 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 [3], horizontal separation of the sequenced creep compliance curves is due to physical aging and can be characterized by the aging shift factor ($-\log a$). This shift factor is simply defined as the horizontal distance required to shift a compliance curve to coincide with a reference compliance curve. The reference compliance curve could be any of the sequenced curves, but for convenience of data manipulation, the longest (96 hour) compliance curve was selected as the reference during formation of the MMC. A linear fit of all the shift factors ($\log a$) versus the logarithmic aging time ($\log t_e$) for each MMC, gave the aging shift rate:

$$\mu = \frac{-d \log a}{d \log t_e} \quad (3)$$

where t_e is the aging 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 4:

$$\tau_e = \tau_{ref} \left(\frac{t_e}{t_{eref}} \right)^\mu \quad (4)$$

where t_{eref} is the reference aging time [24].

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 [25]. 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.

The use of time-temperature superposition (TTSP) ([26, 27]) requires that creep compliance be a function of temperature (T) and time (t) such that

$$S = S(T, t) \quad (5)$$

and that

$$S(T, t) = S(T_o, \zeta) \quad (6)$$

$$\zeta = t/a_T(T) \quad (7)$$

where ζ 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.

The collection of individual MMCs for each temperature per molecular weight can be collapsed into single material master curves using TTSP. The collapse is 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 $\Delta T=20$ K. Characterizing these master curves with an expression like 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 2. Aging shift rates (μ) were calculated for all cases using the sets of master curves. These calculated values are also given in Table 2.

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 LaRCTM-SI [28], 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 (51070 - 24290 g/mol) and the low molecular weight materials are the 4-5% offsets (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.

3.1 Momentary Creep Compliance Curves The momentary creep compliance curves are plotted as a function of time: for a high molecular weight material (1%) at three temperatures below the T_g in Fig.2, and a low molecular weight material (4%) at equivalent reduced temperatures in Fig. 3. Common to all temperatures and all molecular weights is the fact that an increase in aging time generally decreases the creep compliance and also the creep rate.

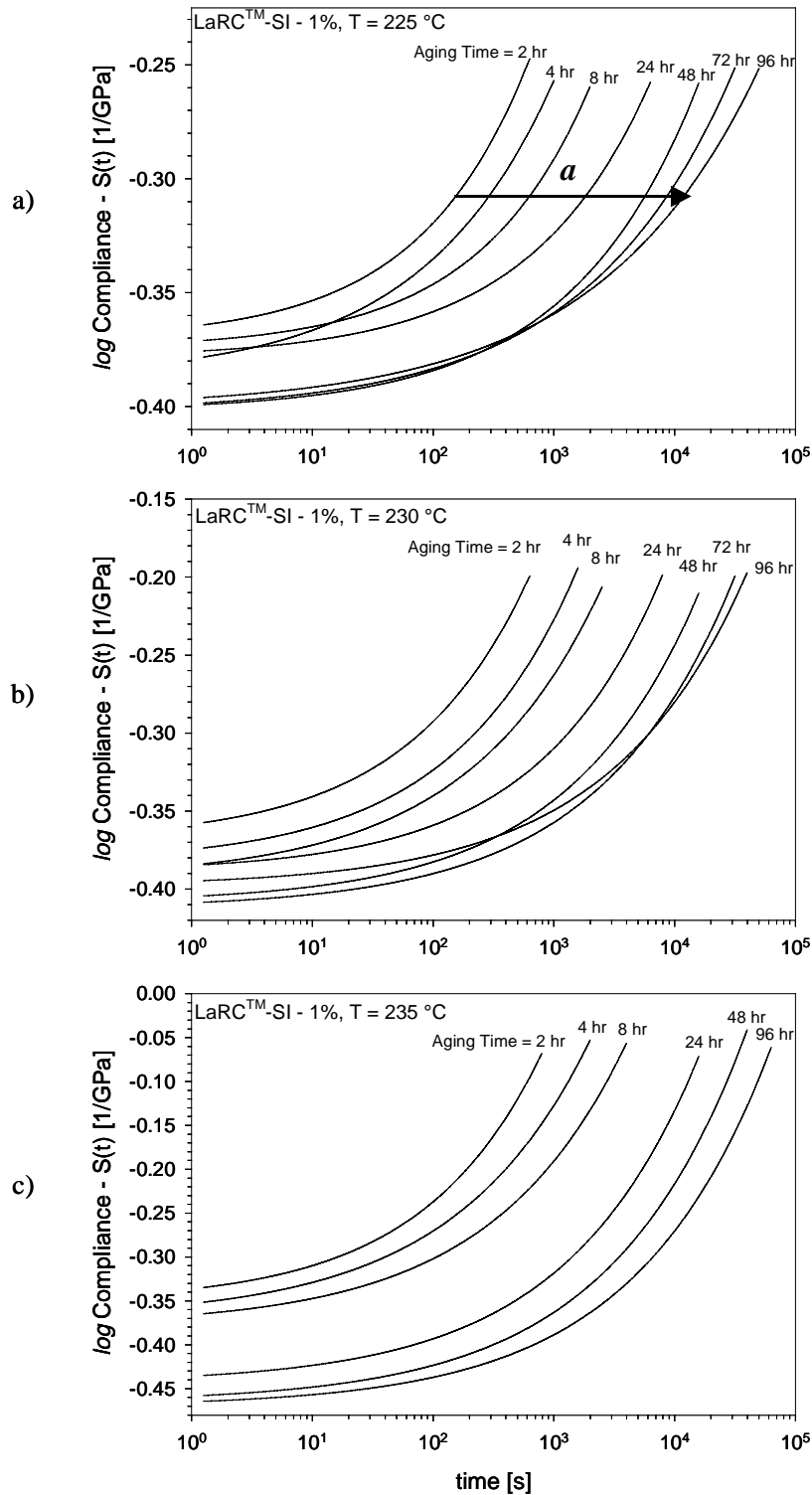


Figure 2 Creep compliance momentary curves plotted as a function of time for the three test temperatures at 1% molecular weight offset. The creep compliance momentary curves are shifted to coincide with the 96 h aging time reference curve.

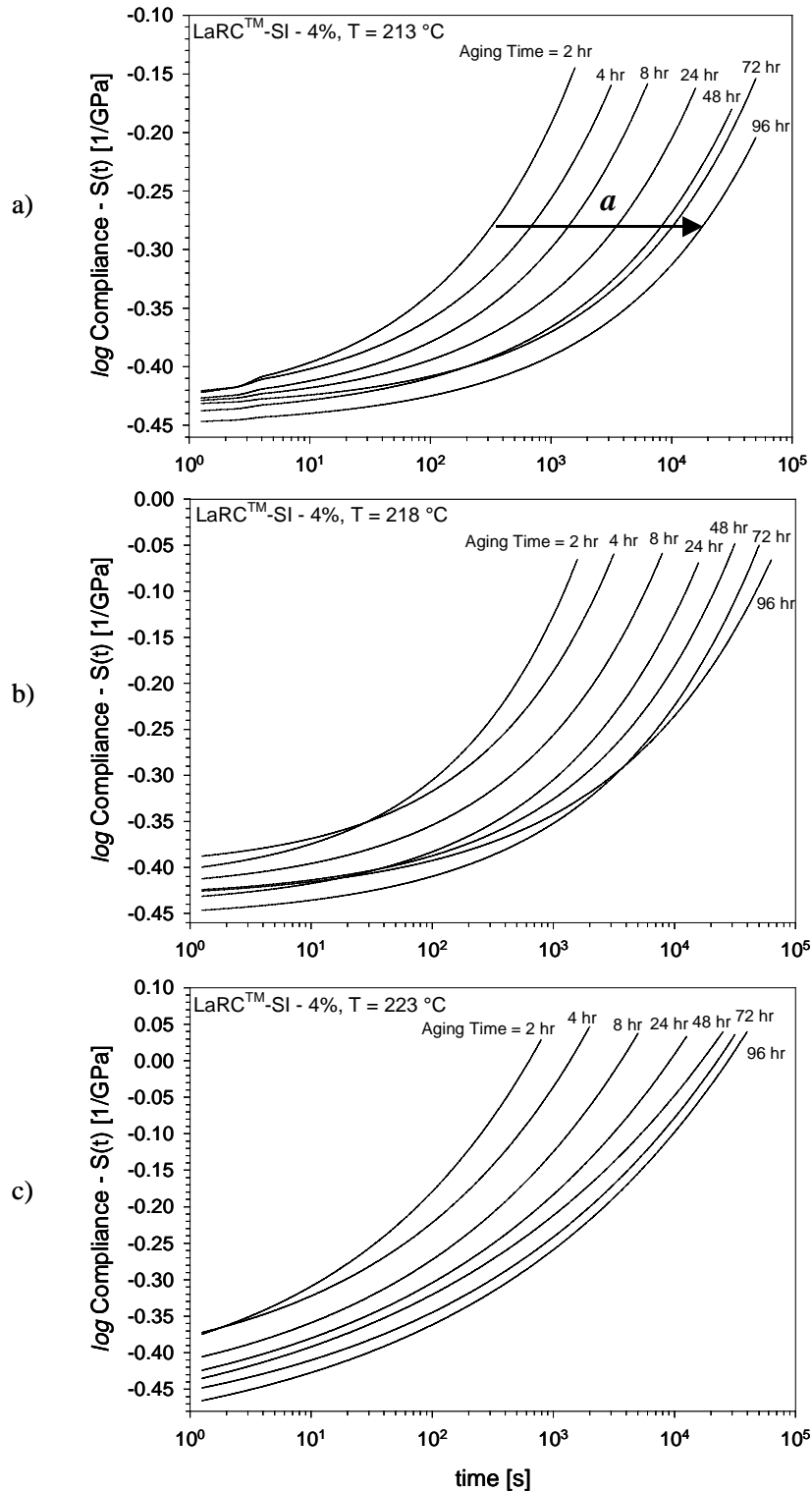


Figure 3 Creep compliance momentary curves plotted as a function of time for the three test temperatures at 4% molecular weight offset. The creep compliance momentary curves are shifted to coincide with the 96 h aging time reference curve.

This is exemplified in Fig. 2c where the 2 h aging time curve has the same creep compliance after 1000 s, as the 96 h aging time curve after nearly 100,000 s. 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 Fig. 2a with Fig. 2c and Fig. 3a with Fig. 3c. There is also a clear difference in the creep rates when comparing the low and high molecular weight materials; in general, the lower molecular weight material has a larger creep rate over the higher molecular weight. This decrease in creep compliance rate with increase in molecular weight has also been seen in other glassy thermoplastic materials [13, 29]. There are some creep curves that cross over each other (in both Figs. 2-3) 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 creep compliance curve will have an increased creep rate as compared with a higher aging time curve; 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 are attributable to scatter in the specimen's data.

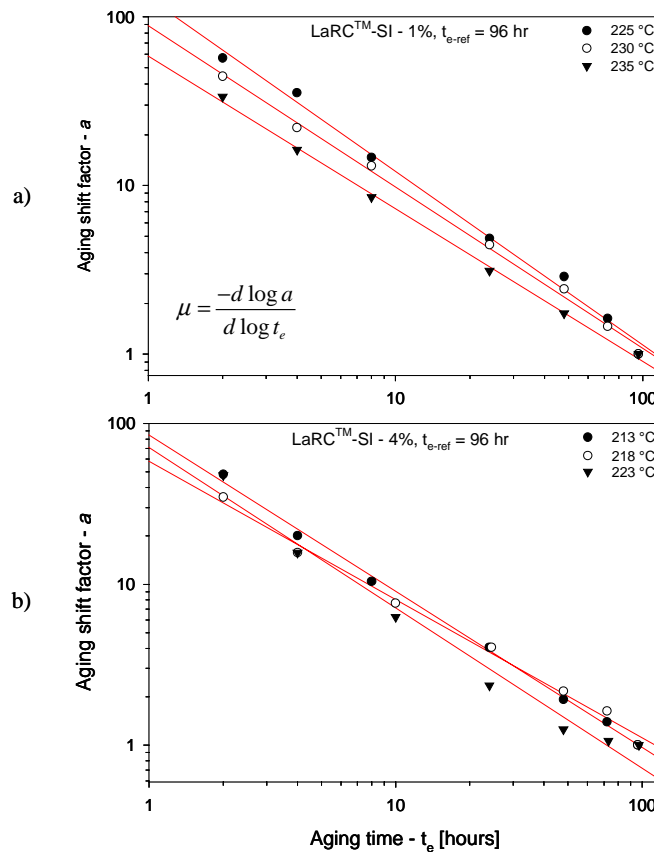


Figure 4 Aging shift factors plotted as a function of aging time for LaRC™-SI 1% (a) and 4% (b), respectively. The creep compliance curves of Figs. 2-3 are shifted horizontally to the 96 h aging time reference curve to obtain the shift factors.

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 Fig. 4. It can be seen that aging shift factor decreases as aging time increases in a monotonic fashion. There appears to be no difference in this respect between high and low molecular weight materials. Thus, there is no change in the shift rate and the shift factors are constant for all molecular weights. When data of different molecular weights are compared, the values for μ in Table 2 are close to each other, for each reduced temperature – this value is unity. 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 Fig. 5. 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. Therefore, the aging shifts required from low-aged to high-aged creep compliance curves are greater at lower temperatures for an equivalent aging time. Thus, more physical aging is occurring in the specimen at the lower test temperatures. This would seem logical when argued on the grounds of molecular mobility and degree of supercooling from equilibrium. An increase in temperature towards the T_g increases the molecular mobility of the polymer chains, and as a consequence the rate of physical aging is increased.

\overline{M}_w (g/mol)	T (°C)	ΔT (K)	S_o (GPa ⁻¹)	τ (s)	β	μ	a_T
51070 (1%)	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
41100 (2%)	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
24290 (3%)	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
21180 (4%)	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
15880 (5%)	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 2. Momentary master curve parameters and TTSP shift factors for all molecular weight LaRCTM-SI materials and test temperatures (°C) ($\Delta T=25, 20, 15$ K).

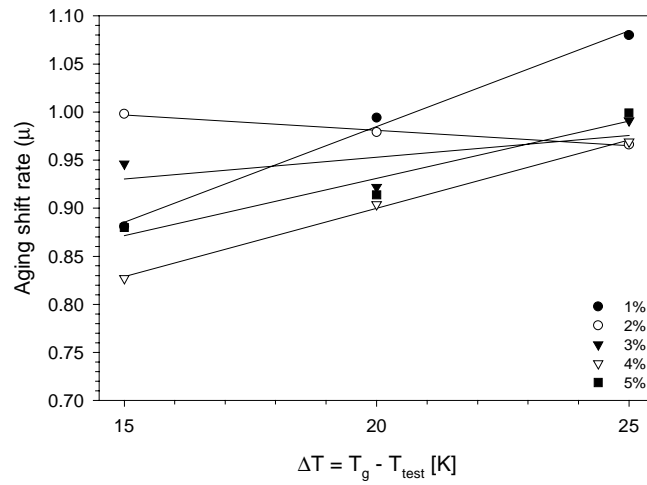


Figure 5 Aging shift rates plotted as a function of reduced temperature for all molecular weights. The aging shift factors of Fig. 4 were differentiated with respect to aging time.

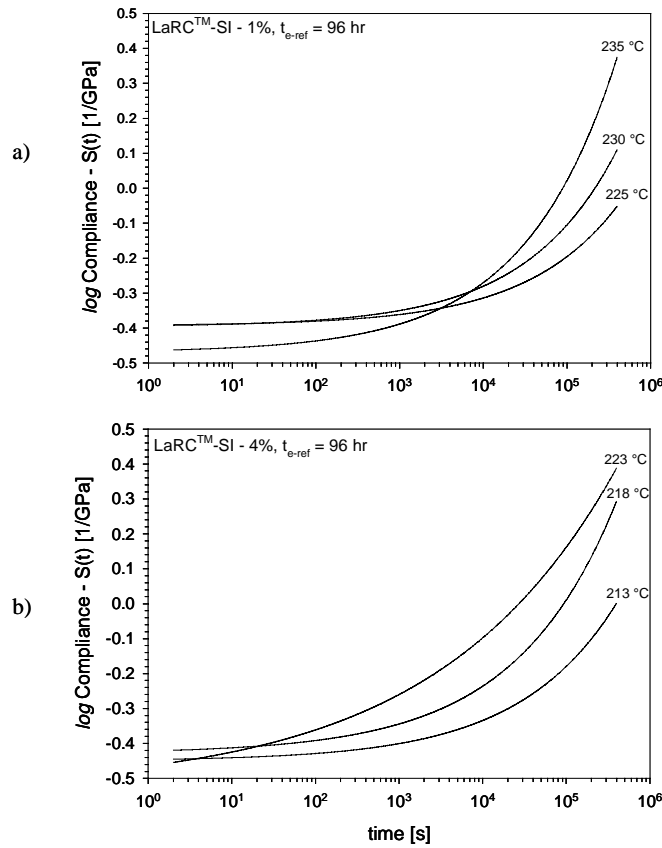


Figure 6 Creep compliance momentary master curves (MMCs) plotted as a function of time for the three test temperatures at molecular weights of: a) 1% and b) 4%. The creep compliance momentary curves of Figs. 2-3 are shifted to coincide with the 96 h aging time reference curve.

3.3 Creep Compliance Momentary Master Curves (MMCs) A comparison of the creep compliance MMCs for the high and low molecular weight materials are plotted as a function of time at the three equivalent reduced temperatures in Fig. 6. The three MMC parameters (S_0 , τ and β), given in Table 2, were found by fitting Equation 2 to the collapsed momentary data sets. Common to both Fig.6a and Fig. 6b is the relationship of increased compliance with increase in temperature, and also increase in creep rate with increase in temperature. Fig. 6 also exhibits a crossing over of curves. This occurs in the highest test temperature and is due to lower initial creep compliance than in the other temperatures. This decrease in initial creep compliance with increase in temperature comes from the curves in Figs. 2-3. Since creep compliance curves are shifted to the 96 h aging time curve, used as the reference, clearly the initial compliance of the 96 h aging time curve of Fig. 2c is much less than its counterparts in Figs. 2a and Fig. 2b. Furthermore, the shapes of the curves are different between the two sets of molecular weights (Fig. 6a-b), and this stems from the fact that the creep compliance momentary curves (Figs. 2-3) show this difference too. These differences in material response with temperature could also be attributed to sample variability. However, since only one specimen was used at each temperature, the sample error cannot be evaluated.

3.4. Time-Temperature Superposition Master Curves Each set of isothermal MMCs (Fig. 6) for each molecular weight was collapsed to coincide with the $\Delta T=20$ K reference curve using horizontal (time) shifts only to form a TTSP master curve shown in Fig. 7. The three temperatures from each molecular weight's MMC data were combined into a single data set and a least squares fit was performed to obtain parameters (S_0 , 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 a lower initial compliance but a similar creep rate to the other high molecular weight (1-2%) materials. The crossing over of the curves is a manifestation that is carried through from the MMCs, where each molecular weight has different initial compliances.

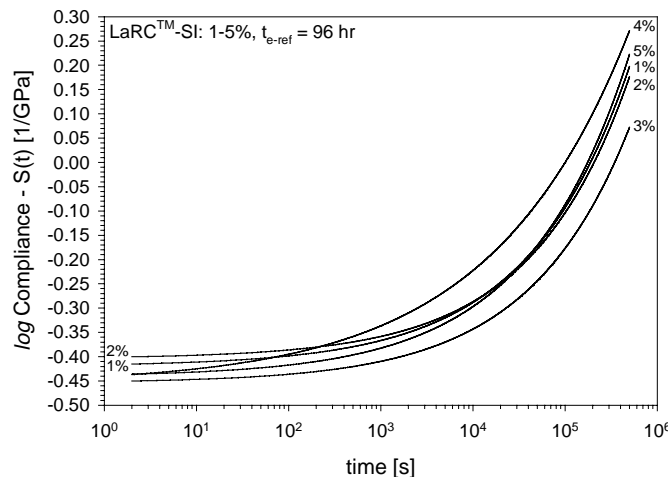


Figure 7 Creep compliance Master curves plotted as a function of time for all molecular weights. The creep compliance MMCs of Fig. 6 are shifted horizontally to the $\Delta T=20$ K reference temperature for each molecular weight.

3.5 Time-temperature superposition shift factors The TTSP shift factors are the horizontal time shifts that are required to shift the MMC data, plotted in Fig. 6, to the reference temperature of $\Delta T=20$ K. In Fig. 8, 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 creep compliance 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. Thus, it is conjectured that 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 ($\Delta T=15$ K), there is a clear separation between high and low molecular weight TTSP shift factors. By plotting this data (Fig. 8) as a function of molecular weight, an indication of the different materials' creep compliance sensitivity to temperature will be obtained. The slope, or rate of change of TTSP shift factor with respect to temperature is given in Equation 8 as:

$$\delta_T = \frac{-d \log a_T}{dT} \quad (8)$$

Fig. 9 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 their viscoelastic responses.

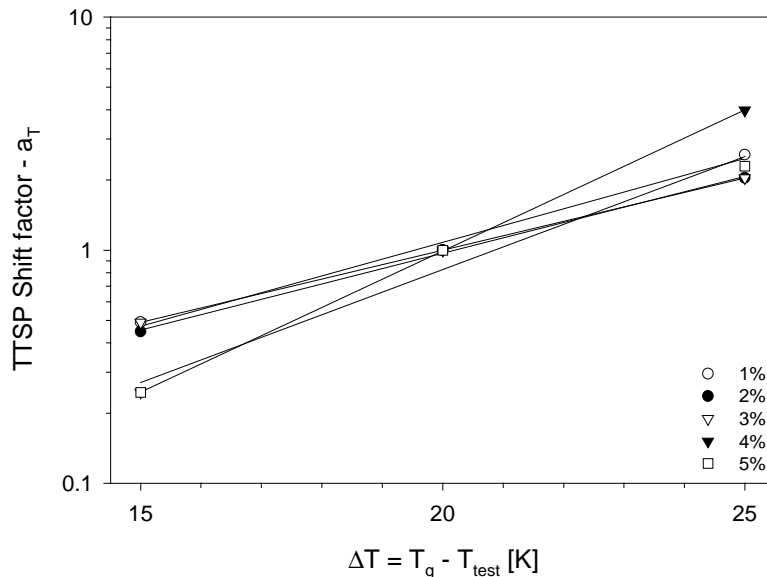


Figure 8 TTSP shift factors plotted as a function of reduced temperature for all molecular weights. The MMCs, for all molecular weights, were shifted horizontally to a reference temperature of $\Delta T=20$ K.

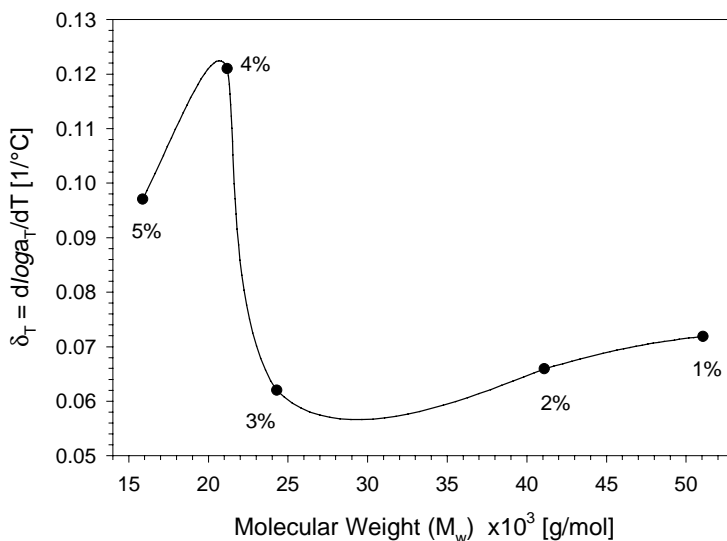


Figure 9 The reduced temperature derivative of TTSP shift factors (Fig. 8) plotted as a function of molecular weight to indicate the temperature sensitivity of each molecular weight.

5. CONCLUSIONS

Experiments were performed to determine the effects of molecular weight, elevated temperature and physical aging on the creep compliance of LaRCTM-SI loaded in tension. The short term (96 hour) 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 an increased creep magnitude and increased creep rate, than 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 $\overline{M}_w \sim 25$ kg/mol. It is therefore conjectured that an increase in molecular mobility occurs with an increase in temperature and, consequently, will increase the rate of physical aging. It is likely, then, that the low molecular weight materials would exhibit greater molecular mobility than that apparent in the high molecular weight materials, due to fewer physical entanglements. Thus, the effect of molecular weight on the creep compliance is more influential at low molecular weights and at higher temperatures near the T_g , and this would suggest that the rate of physical aging is increased as a result.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. R. N. Haward, The Physics of Glassy Polymers, (John Wiley & Sons, New York, 1973).

2. G. B. McKenna, in Comprehensive Polymer Science, C. Booth, C. Price, Eds. (Pergamon, Oxford, 1989), vol. 2, pp. 311-362.
3. L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, (Elsevier Scientific Publishing Company, New York, 1978).
4. J. Zhou, Polymer, 34, 4252-4257 (1993).
5. B. E. Read, P. E. Tomlins, G. D. Dean, Polymer, 31, 1204-1215 (1990).
6. A. Lee, G. B. McKenna, Polym. Eng. Sci., 31, 431-435 (1990).
7. J. Z. Wang, et al., Composites Sci. Tech., 54, 405-415 (1995).
8. T. S. Gates, in High Temperature and Environmental Effects on Polymeric Composites, vol. ASTM STP 1174, C. E. Harris, T. S. Gates, Eds. (American Society for Testing and Materials, Philadelphia, 1993) pp. 201-221.
9. T. S. Gates, D. R. Veazie, L. C. Brinson, J. Composite Mater., 31, 2478-2505 (1997).
10. P. I. Vincent, Polymer, 13, 558-560 (1972).
11. R. P. Kusy, D. T. Turner, Polymer, 18, 391 (1977).
12. P. Prentice, J. Mater. Sci., 20, 1445-54 (1985).
13. N. Nemoto, M. Moriwaki, H. Odani, M. Kurata, Macromolecules, 4, 215 (1971).
14. H. Odani, N. Nemoto, M. Kurata, Bull. Inst. Chem. Res., Kyoto Univ., 50, 117-33 (1972).
15. K. L. Ngai, D. J. Plazek, C. A. Bero, Macromolecules, 26, 1065-1071 (1993).
16. D. J. Plazek, et al., Colloid and Polym. Sci., 272, 1430-1438 (1994).
17. Z. Yu, U. Yashi, J. D. McGervey, A. M. Jamieson, R. Simha, J. Polym. Sci. Polym. Phys., 32, 2637-2644 (1994).
18. J. J. Singh, A. Eftekhari, Nucl. Instrum. & Methods Phys. Res., B63, 477-483 (1992).
19. S. Matsuoka, A. Hale, J. Appl. Polym. Sci., 64, 77-93 (1997).
20. E. J. Siochi, P. R. Young, R. G. Bryant, in Materials Challenge - Diversification and the Future, (SAMPE, Los Angeles, California, 1995), vol. 40(1), pp. 11-18.
21. R. G. Bryant, High Perform. Polym., 8, 607-615 (1996).
22. W. M. Murry, and Miller, W. R., The Bonded Electrical Resistance Strain Gage, (Oxford University Press, New York, 1992).
23. H. Allen, "Boeing Materials Technology Report", BZ56B-CSC-21, (Boeing Commercial Airplane Group, 1993).
24. L. C. Brinson, T. S. Gates, Int. J. Solids Struct., 32, 827-846 (1995).
25. R. L. Hastie, D. H. Morris, in High Temperature and Environmental Effects in Polymer Matrix Composites, C. Harris, T. Gates, Eds. (American Society for Testing and Materials, Philadelphia, 1992), vol. ASTM STP 1174, pp. 163-185.
26. H. Leaderman, Elastic and creep properties of filamentous materials and other high polymers, (Textile Foundation, Washington, D.C., 1943).
27. W. N. Findley, J. S. Lai, K. Onaran, Creep and Relaxation of Nonlinear Viscoelastic Materials, (North-Holland Publishing Company, Toronto, 1976).
28. L. M. Nicholson, K. S. Whitley, T. S. Gates, J. A. Hinkley, SAMPE International Symposium, 40(1), 794-808 (1999).
29. T. Fujimoto, M. Ozaki, M. Nagasawa, J. Polym. Sci., A2, 6, 129 (1968).

A Short Biography of Lee M. Nicholson, Ph.D.

Lee graduated in December 1997 with a Ph.D. from the Department of Materials Science and Metallurgy, University of Cambridge. His doctoral thesis presented the 3D simulation of stress-induced crystallization in the sequential-biaxial drawing process of films, and was sponsored by ICI Films Plc. Since gaining a National Research Council fellowship, Lee has been working, for the last two years, with Dr Thomas Gates at NASA Langley Research Center. His time has been spent performing experiments to evaluate the role of molecular variables on both the elastic and viscoelastic properties of aerospace polymers and composites. He's just commenced his final year and hopes to find suitable employment in the US thereafter.