CROSSLINK DENSITY AND MOLECULAR WEIGHT EFFECTS ON THE VISCOELASTIC RESPONSE OF A GLASSY HIGH-PERFORMANCE POLYIMIDE

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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 [1-3]. Thus, the ability to predict material performance using intrinsic properties, such as crosslink density and molecular weight, would greatly enhance the efficiency of design and development of PMCs.

The objective of this paper is to discuss and present the results of an experimental study that considers the effects of crosslink density, molecular weight and temperature on the viscoelastic behavior including physical aging of an advanced polymer. Five distinct variations in crosslink density were used to evaluate the differences in mechanical performance of an advanced 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 physical aging-related parameters were evaluated as a function of temperature crosslink density and molecular weight using time-temperature and time-aging time superposition techniques.

Experimental Studies

Materials. The materials used in this study were thermoplastic amorphous polyimides (LaRC^{TM}-SI), lightly crosslinked with phenyl-ethynyl end-groups (LaRC^{TM}-PETI-SI), and were prepared by Imitec Inc., Schenectady, NY. Extended synthesis descriptions of this material have been published elsewhere [4, 5]. The molecular weights for the materials were determined on the as-received powders using gel permeation chromatography. The weight-average molecular weights ($\bar{M}_w$), the polydispersity indices ($\bar{M}_w/\bar{M}_n$) and the molecular weight between crosslinks (M_c) of the materials are shown in **Table 1**. The powder was dried under vacuum above T_g (for each crosslink density) for 24 hours to remove any residual solvents prior to compression molding in air. Neat resin plaques were formed isothermally for one hour under constant pressure and rectangular test coupons were machined from these plaques. Differential scanning calorimetry (DSC) was performed to determine the glass transition temperature of the molded material (contained in **Table 1**).

Table 1. Intrinsic Material Properties

%	$\bar{M}_w$	$\bar{M}_c$	$(\bar{M}_w/\bar{M}_n)$	T_g [°C]	T_{test} [°C]		
	[g/mol]	[g/mol]		(cured)	ΔT=15	20	25
	(LaRC^{TM}-SI)						
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
	(LaRC^{TM}-PETI-SI)						
4	31275	2980	3.03	258.7	234	239	244
5	24290	3662	2.75	261.5	237	242	247
7	15410	5440	2.45	256.6	231	236	241
9	10850	2242	2.27	264.8	239	244	249
11	8743	2606	2.04	262.7	237	242	247

Viscoelastic Properties: Tensile Creep Compliance Tests. Tensile creep tests were performed at three specific test temperatures below the glass transition temperature ($\Delta T = T_g - T_{test}$ = 25, 20, 15 °C). These test temperatures, listed in **Table 1**, were selected to ensure that measurable physical aging occurred within the test period. All tests were performed at stress levels within the linear viscoelastic strain range determined by checking the proportionality condition and Boltzmann's superposition [6].

Tensile load was applied through an axially symmetric dead-weight system. Strain was measured using high-temperature strain gages applied in a longitudinal direction, on each face of the specimen. To establish the effects of physical aging on the viscoelastic properties, a well-documented technique that measures the momentary creep compliance as described by Struik [7] was used for all tests. For these momentary tests, the duration of each creep segment was 1/10th the duration of the prior total aging time. The aging times (t_e) selected for starting each creep segment were 2, 4, 8, 24, 48, 72 and 96 hours, respectively. After each creep segment, the specimen was unloaded and allowed to recover until the start of the next creep segment, as depicted in **Figure 1**. To provide for the test condition that all specimens start the test sequence in the same unaged condition, the specimens were rejuvenated according to Struik's procedure [7].
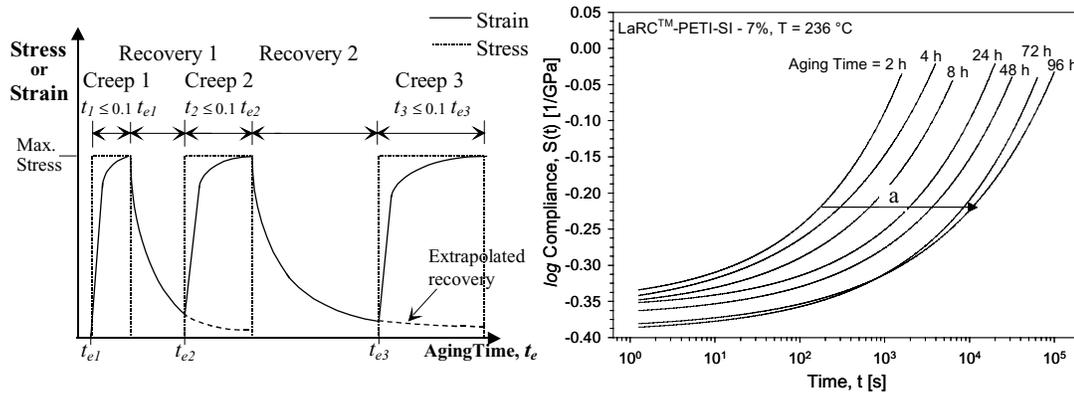
Figure 1. Sequenced short-term creep and recovery tests; and creep compliance momentary curves at different aging times.

Analysis of viscoelastic behavior and aging. The time-dependent linear creep compliance was modeled with a three-parameter expression given by,

$$S(t) = S_o e^{(t/\tau)^\beta} \qquad (1)$$

where S_o, t, τ, and β are the initial compliance, time, retardation time and shape parameter of the distribution of molecular relaxation times, respectively. The three material parameters were found from curve fits of Equation 1 to sequenced short-term creep compliance data.

Due to physical aging of the polymer, the momentary creep compliance curves are separated by time shifts related to the degree of aging. Therefore, time-aging time superposition of the 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 [7], physical aging can be characterized by the aging shift factor a, which 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. The longest aging time (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, is used to determine the aging shift rate, μ,

$$\mu = \frac{-d \log a}{d \log t_e} \qquad (2)$$

where t_e is the aging time. Aging shift rates (μ) were calculated for all cases using the sets of master curves.

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) [6], requires that creep compliance be a function of temperature (T) and time (t), such that the real time t is related by the temperature shift factor $a_T(T)$. For this study, the collection of individual MMCs for each temperature per crosslink density and molecular weight were collapsed into single material master curves using TTSP. The collapse was made using a single reference curve ($\Delta T = 20°C$) and horizontal (time) shifts only.

Results and Discussion

All results have been examined by comparing the viscoelastic creep compliance versus time as a function of temperature, crosslink density and molecular weight. In the following results, a comparison of properties will be given in terms of the lowest crosslink density material only, *viz.* 7% (M_c ~5440 g/mol). Common to all temperatures and materials studied 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 1** where the 2 h aging time curve attains the same log creep compliance of -0.05 GPa^{-1} after ~1000 s, as the 96 h aging time curve after nearly 100,000 s; notwithstanding the decrease in initial creep compliance in moving from the 2 h to 96 h aging time curve. Thus, the specimen stiffness increases with aging time.

Aging Shift Factors and Aging Shift Rates. Comparisons of aging shift factors at three reduced temperatures are shown in **Figure 2**. It can be seen that aging shift factor decreases as aging time increases in a monotonic fashion. There is no difference in this respect between high and low crosslink density, or even, high and low molecular weight materials.
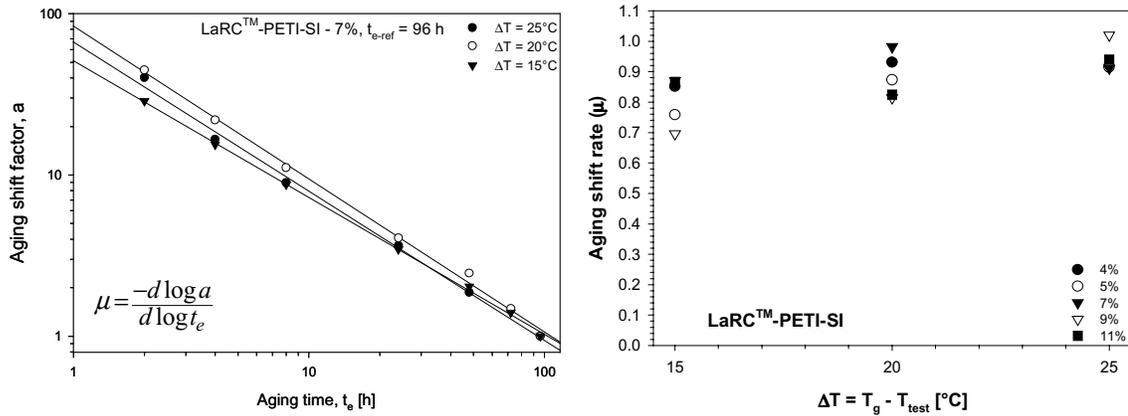
Figure 2. Aging shift factors and shift rates plotted as a function of aging time at three reduced temperatures for the crosslinked materials.

A linear fit of all the aging shift factors versus the logarithmic aging time (t_e) for each momentary creep compliance curve gives the aging shift rate, μ, where it can be plotted as a function of reduced temperature. In general, μ decreases as temperature is increased towards T_g. This is true for all crosslink densities and is most pronounced for the 9% material (highest crosslink density).

Time-Temperature Superposition. The three momentary master curve (MMC) parameters (S_o, τ and β) were found by fitting Equation 1 to the collapsed momentary data sets. Isothermal MMCs for each crosslink density material were collapsed to coincide with the $\Delta T = 20°C$ reference curve. The TTSP shift factors are the horizontal time shifts that are required to shift the MMC data, to the reference temperature of $\Delta T = 20°C$. In **Figure 3**, TTSP shift factors are plotted as a function of reduced temperature for all crosslink densities. It can be seen that the TTSP shift factors increase as temperature increases towards T_g, for all crosslink densities. Furthermore, at the highest test temperature ($\Delta T = 15°C$), there is a clear separation between high and low crosslink density TTSP shift factors. By plotting this data as a function of molecular weight between crosslinks (M_c), an indication of the temperature sensitivity of the creep compliance for each crosslink density will be obtained. The slope, or rate of change of TTSP shift factor with respect to temperature is given in Equation 3 as:

$$\delta_T = \frac{-d \log a_T}{dT} \tag{3}$$

These results are also plotted in **Figure 3.**
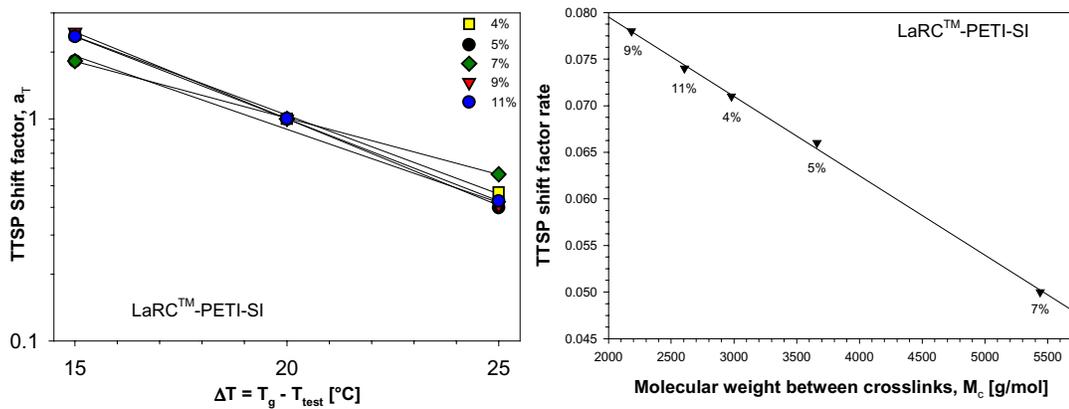
Figure 3 TTSP shift factors as a function of reduced temperature; and the temperature-sensitivity of the different crosslink density materials.

Long-term Creep Compliance. The effects of both test temperature and molecular weight on long-term test (>1100 hours) data are conveniently summarized in **Figure 4**. 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. An equivalent set of results were found for high crosslink density materials, showing increased creep and creep rate.
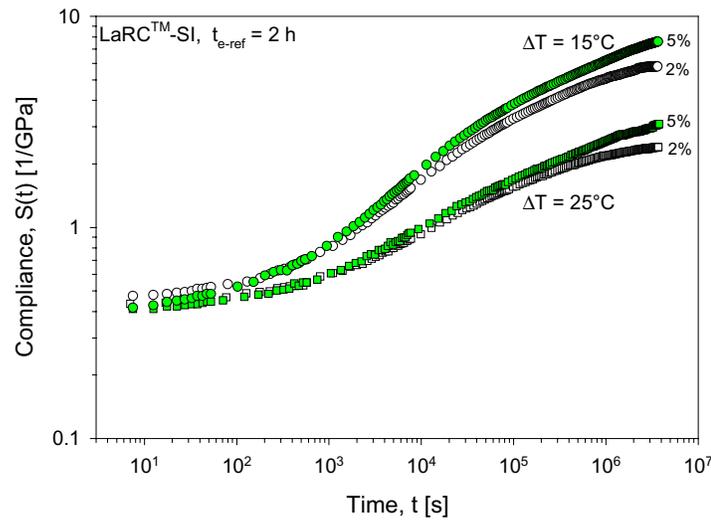
Figure 4 The effect of molecular weight and test temperature on the long-term viscoelastic response of one high and one low molecular weight material.

Conclusions

The effects of crosslink density and molecular weight on the viscoelastic performance of an advanced polymer matrix were investigated through 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 crosslink density and 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 crosslink density and molecular weight. Low molecular weight and high crosslink density materials have increased creep compliance and creep rate, and are more sensitive to increases in temperature. At timescales >1100 hours, physical aging serves to significantly decrease the creep compliance and creep rate of all the materials tested. It was found that the low molecular weight and high crosslink density materials were less influenced by the effects of physical aging, compared with the high molecular weight and low crosslink density materials.

Acknowledgements

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