CROSSTALK 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 matrices 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 temperature and time-aging time superposition techniques.

Experimental Studies
Materials
The materials used in this study were thermoplastic amorphous polyimides (LaRCTM-Si), lightly crosslinked with phenyl-ethyl vinyl end-groups (LaRCTM-PETI-Si), and were prepared by Uniphase Inc., Schenecady, 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-averaged molecular weights (M), the polydispersity indices (M/M) and the molecular weight between crosslinks (M) of the materials are shown in Table 1.

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Viscoelastic Properties: Tensile Creep Compliance Tests
Tensile creep tests were performed at three specific test temperatures below the glass transition temperature (AT = Tg - Tm = 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 monomeric 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. Aging times (tA) 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].

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

\[ S(t) = S_0 e^{(t^\beta)} \]

where \( S_0 \), \( \tau \), \( \alpha \) and \( \beta \) 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.

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 \( \alpha \), 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 creep compliance momentary curves at different aging times.

Equation 1 to sequenced short-lerm creep compliance data.

\[ \mu = \frac{d \log a}{d \log t} \]

where \( t_A \) is the aging time. Aging shifts (\( \mu \)) were calculated for all cases using the sets of master curves.

Isothermal momentary master curves (MMC) 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 \( \alpha(T) \). For this study, the collection of individual MMCs for each temperature per crosslink density and molecular weight were collapsed into single master curves using TTSP. The collapse was made using a single reference curve (AT=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_0 =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.

Aging Shift Factors versus Temperature. Figure 3 TTSP shift factors as a function of reduced temperature; and the temperature-sensitivity of the different crosslink density materials. The TTSP shift factors are the horizontal time shifts that are required to shift the MMC data to the reference temperature of AT=20°C. The slope of the TTSP shift factor with respect to temperature is given in Equation 3 as:

\[
\delta_t = -\frac{d\log a_t}{dT}
\]

These results are also plotted in Figure 3.

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.

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References