Effects of Prior Aging at 288°C in Argon Environment on Time-Dependent Deformation Behavior of a Thermoset Polymer at Elevated Temperature, Part 1: Experiments

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ABSTRACT: The inelastic deformation behavior of PMR-15 neat resin, a high-temperature thermoset polymer, aged at 288°C in argon environment for up to 2000 h was investigated. The experimental program was designed to explore the influence of prior isothermal aging on monotonic loading and unloading at various strain rates. In addition, the relaxation response and the creep behavior of specimens subjected to prior aging of various durations were evaluated. All tests were performed at 288°C. The time-dependent mechanical behavior of the PMR-15 polymer is strongly influenced by prior isothermal aging. The elastic modulus increased and the departure from quasi-linear behavior was delayed with prior aging time. Stress levels in the region of inelastic flow increased with prior aging time. Furthermore, prior aging significantly decreased the polymer's capacity for inelastic straining, including the material's capacity to accumulate creep strain. Conversely, the relaxation response was not affected by the prior aging. © 2009 Wiley Periodicals, Inc.† J Appl Polym Sci 114: 2956–2962, 2009

Key words: ageing; creep; high-temperature materials; viscoelastic properties; polyimides

INTRODUCTION

Polymer matrix composites (PMCs) are excellent candidates for use in high-temperature applications, such as aircraft turbine engines and engine exhaust washed structures, as well as high-speed aircraft skins.[1–6] These applications require extended exposures to temperatures approaching the glass transition temperature (T_g) of the polymer matrix and to oxidizing environments, which cause chemical changes as well as thermal degradation of the matrix material.[2,3,7] The chemical changes occurring in the polymer matrix result in changes in its mechanical response and properties. To assure long-term durability and structural integrity of the PMC components, a thorough understanding of the effects of the exposure to elevated temperature and to oxidizing environment on the mechanical behavior of the polymer matrix is essential.

Among the thermosetting polyimide resins, PMR-15 is of particular interest because of its superior high-temperature properties and ease of processing.[8–10] Designed for use at temperatures near its T_g, the PMR-15 resin is extensively used as a matrix material in high-temperature structural composites for aerospace applications. Significant progress has been made in understanding the effects of isothermal aging on the thermo oxidative stability of PMR-15 neat resin and PMR-15 based composites.[2–5,7,11,12] Bowles et al[2–4] aged PMR-15 specimens in air at 288, 316, and 343°C for up to 4000 h. It was found that while thermal degradation occurred throughout the material, the oxidative degradation occurred mainly within a thin surface layer where oxygen diffused into the material. It was observed that the oxidized surface layer, which had different properties than the unoxidized interior material, developed and grew during thermal aging. However, at all aging temperatures the thickness of the oxidized layer asymptotically approached a constant value of about 170 μm as the aging time increased. Recent studies[13–18] document the growth of the thermo-oxidative layer and the changes in elastic moduli and chemical composition resulting from isothermal aging. Ripberger et al[15] reported that the thickness of the oxidation layer was ~ 55 μm after 50 h of aging at 343°C and varied between 107 and 129 μm after 342 h at 343°C. Furthermore, the aforementioned studies revealed that the interior core of the PMR-15 specimens was protected from oxidative

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degradation by the surface layer and remained relatively unchanged during thermal aging.

Most published research is focused on thermal oxidation of neat polymer systems. There are limited studies that consider the effects of thermal aging on the mechanical performance of high temperature polymers. Several research efforts evaluated the effects of aging on the tensile and compressive properties of PMR-15 based composites.[4,5,12,18] Recently Ruggles-Wrenn and Broeckert[19] investigated the effects of thermal aging at a temperature near the T_g on creep and recovery behavior of the PMR-15 neat resin at elevated temperature. Creep tests at stress levels of 10 and 20 MPa were conducted at 288°C on specimens subjected to prior thermal aging at 288°C in air or in argon environment. Results revealed that prior aging had a noticeable effect on T_g, as well as on high-temperature tensile properties and tensile creep performance of the PMR-15 polyimide. Other studies[20,21] explored the rate (time)-dependent mechanical behavior of the PMR-15 polymer at 288°C. It was found that the material exhibited positive, nonlinear strain rate sensitivity during monotonic loading and unloading. Moreover creep, recovery, and relaxation behaviors were also strongly influenced by prior loading rate. The experimental results suggested that the inelastic behavior of the PMR-15 polymer at 288°C could be represented using the viscoplasticity theory based on overstress (VBO)—a unified constitutive model with an overstress dependence of the inelastic rate of deformation. McClung and Ruggles-Wrenn[22] developed a systematic experimentally based procedure for determining parameters and functions of the VBO model, then employed the VBO to predict the response of the PMR-15 polymer under various test histories at 288°C. The predictions of the material response were in good agreement with the experimental data.

The objective of this study is to investigate the influence of thermal aging at a temperature near the T_g on rate (time)–dependent mechanical behavior of the PMR-15 neat resin at elevated temperature. The experimental results presented here not only give insight into the changes in the inelastic behavior of the PMR-15 polyimide with prior aging time, but also provide a foundation for extending the VBO to capture the effects of prior aging on the deformation behavior of this polymer.

MATERIAL AND EXPERIMENTAL ARRANGEMENTS

The material studied was PMR-15 neat resin, a thermosetting polyimide used as a matrix material for high-temperature polymer-matrix composites. The PMR-15 polymer has a glass transition temperature of 347°C and a long-term use temperature of 288°C. The PMR-15 neat resin panels were manufactured and postcured by HyComp Inc. (Cleveland, OH). The details of the PMR-15 chemistry and processing, as well as the schematic of the free standing postcure cycle are given elsewhere.[19,20] Dogbone shaped test specimens of 150-mm total length with a 7.6-mm wide gage section were machined from the 3.18-mm thick panels using diamond-grinding. All specimens were washed with a common household soap and thoroughly rinsed with distilled water to remove contaminants from the machining process. The specimens were then dried in a vacuum oven at 105°C for at least 24 h, and subsequently stored in a dry-air-purged desiccator until aging and/or testing.

Specimens were aged in an argon environment at 288°C, which is the design maximum sustained service temperature of PMR-15 based composites in aerospace applications. The aging times were 50, 100, 250, 500, 1000, and 2000 h. The isothermal aging was accomplished in a Blue M model 7780 air-circulating oven that provided continuous replenishment of argon by convection through the oven inlet. Ultra high purity argon gas (99.999% pure) was supplied to the Blue M oven from a liquid argon tank. When specimens were taken out for periodic inspection and/or testing, the oven was opened without cooling and closed immediately. Then the oven automatically entered the 18-min purge cycle to flush out any ambient atmosphere that had entered the chamber. The flow rate of argon was $\sim$ 30 SCFH during the steady state operation and $\sim$ 150 SCFH during the purge cycle.

A servo-hydraulic MTS machine equipped with water-cooled hydraulic wedge grips, a compact resistance-heated furnace, and a temperature controller were used in all tests. A TestStar II digital controller was used for input signal generation and data acquisition. An MTS low contact force, high-temperature uniaxial extensometer of 12.5-mm gage length was used for measurement of strain. All tests, with the exception of creep tests, were performed under strain control mode with strain rates ranging from 10^{-6} to 10^{-3} s^{-1} and, of course, with $\dot{\varepsilon} = 0$ s^{-1} for any relaxation intervals. The immediate control mode switch capability of the system afforded the ability to load a specimen at a constant strain rate under strain control and to seamlessly switch to load control upon reaching a target value of strain or stress to conduct a creep test.

For elevated temperature testing, thermocouples were attached to the specimens using Kapton tape to calibrate the furnace on a periodic basis. The furnace controller (using a noncontacting thermocouple exposed to the ambient environment near the test specimen) was adjusted to determine the power setting needed to achieve the desired temperature of the test specimen. Thermocouples were not attached to the test specimens after the furnace was calibrated.

All tests were carried out at 288°C in a laboratory air environment. In all tests, the specimen was heated to 288°C at the rate of 2°C/min, and held at 288°C for an additional 45 min before testing.

EXPERIMENTAL OBSERVATIONS

This study aims to investigate the influence of prior isothermal aging on the rate (time)-dependent mechanical behavior of the PMR-15 neat resin at 288°C. Strain-controlled tests of monotonic loading with periods of relaxation were conducted on specimens aged at 288°C for various durations in argon. Effects of prior aging on creep behavior following strain-controlled loading were also explored. Specimens aged for 50, 100, 250, 500, 1000, and 2000 h were used in this study.

Strain rate sensitivity—influence of prior aging

A previous study[20] revealed that the unaged PMR-15 polymer exhibited positive, nonlinear strain rate sensitivity at 288°C. To explore the effects of prior aging on strain rate sensitivity of the PMR-15 polymer, each group of specimens isothermally aged for a given duration was subjected to tensile tests at constant strain rates of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} s^{-1}. Results are typified in Figure 1, where stress–strain curves obtained for specimens aged for 250 h are presented. Data for the unaged PMR-15 resin from prior work[20] are shown in Figure 1 for comparison. It is seen that the stress–strain behavior of the aged specimens is also strongly influenced by the strain rate. The stress–strain curves obtained for the aged specimens do not show a distinct linear range. However, the stress–strain curves obtained at different strain rates for the specimens subjected to prior aging of a given duration exhibit the same quasi-elastic slope upon leaving the origin. After the transition from the initial quasi-elastic behavior to the inelastic regime, the aged material exhibits positive strain rate sensitivity. The flow stress level increases with increasing strain rate. The shape of the stress–strain curve also undergoes a gradual change as the strain rate increases. Transition from the quasi-linear elastic behavior to inelastic flow becomes much more pronounced with increasing strain rate. The stress–strain curves produced at faster strain rates depart from near-linearity at considerably higher stress levels than those obtained at slower strain rates. Note that the trends observed for the specimens subjected to 250 h of prior aging were seen for all aged specimens in this study.

While prior aging time has little qualitative influence on the strain rate sensitivity, it has significant quantitative effects on the stress–strain behavior of the PMR-15 polymer. Figure 2 presents the tensile

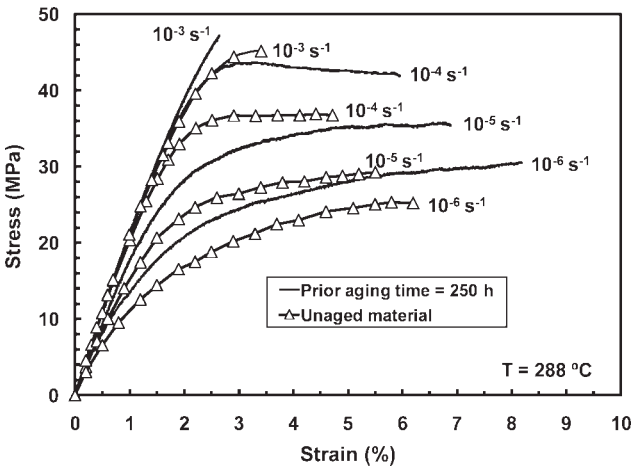

Figure 1 Stress–strain curves for PMR-15 specimens aged for 250 h at 288°C in argon obtained in tensile tests to failure conducted at constant strain rates of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} s^{-1} at 288°C. Data for the unaged PMR-15 from McClung et al.[20] The dependence of the stress–strain behavior on the strain rate is evident.

stress–strain curves obtained at strain rates of 10^{-6} and 10^{-4} s^{-1} for the unaged material and for specimens aged for 100, 250, and 1000 h. It is seen that the elastic modulus increases with prior aging time. The effect of prior aging on the elastic modulus, which is further illustrated in Figure 3, is consistent with the observations reported earlier.[19] Furthermore, stress–strain curves in Figure 2 show that for a given strain rate the departure from quasi-linear behavior occurs at higher stress levels for specimens subjected to longer prior aging times. To quantify the departure from near-linearity proportional limit stress was measured using the 0.2% offset method in accordance with the procedure in ASTM standard D 638. The increase in proportional limit stress with prior aging time is clearly seen in Figure 4. It is noteworthy that for a given prior aging time, similar increase in proportional limit stress was observed for all strain rates. For specimens subjected to 1000 h of prior aging an average increase in proportional limit stress was $\sim$ 6 MPa.

In addition to the increases in elastic modulus and in proportional limit stress, the stress–strain curves in Figure 2 also exhibit an increase in the tangent modulus with prior aging time. In this study, the tangent modulus is defined as the slope of the stress–strain curve at the largest strain obtained at the strain rate of 10^{-6} s^{-1}. The continuous increase in tangent modulus with prior aging time is apparent in Figure 5. Finally, it is seen that prior aging causes an increase in flow stress. The change in flow stress measured at the strain of 3% and 4.5% is plotted vs prior aging time for each strain rate in Figure 6. It is noteworthy that the increase in flow stress appears to be relatively independent of the strain

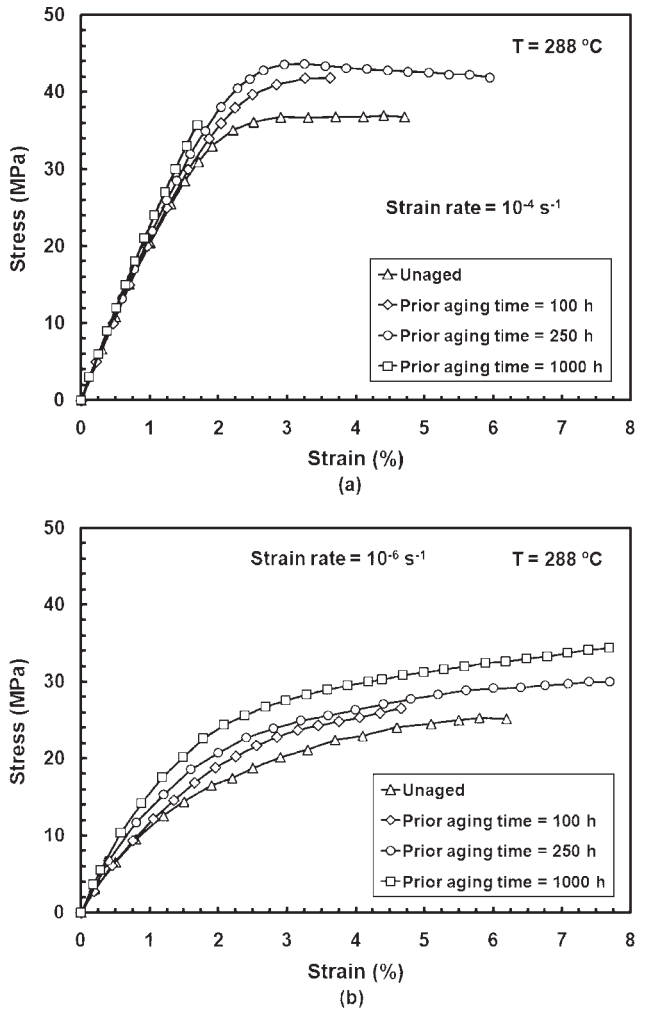

Figure 2 Stress–strain curves for PMR-15 specimens aged at 288°C in argon obtained in tensile tests to failure conducted at constant strain rates of (a) 10^{-4} s^{-1} and (b) 10^{-6} s^{-1}. Quantitative effects of prior aging on stress–strain behavior are evident.

rate. The average increase in flow stress was ~ 6 MPa for specimens subjected to 1000 h of prior aging.

Lastly, it was observed that prior aging for 2000 h severely decreased the polymer's capacity for inelastic straining at all strain rates in the 10^{-6} to 10^{-3} s^{-1} range. The stress–strain curves obtained for specimens aged for 2000 h (Fig. 7) show that failures occur either within or just outside the quasi-elastic region. Consistent with these early failures, specimens aged for 2000 h exhibited considerably lower values of tensile strength. For example, at 10^{-4} s^{-1} the average tensile strength was 36 MPa for the material aged for 1000 h, but only 28 MPa for the specimens aged for 2000 h.

Relaxation behavior—influence of prior aging

To evaluate the effects of prior aging on relaxation behavior, monotonic tests with intermittent periods

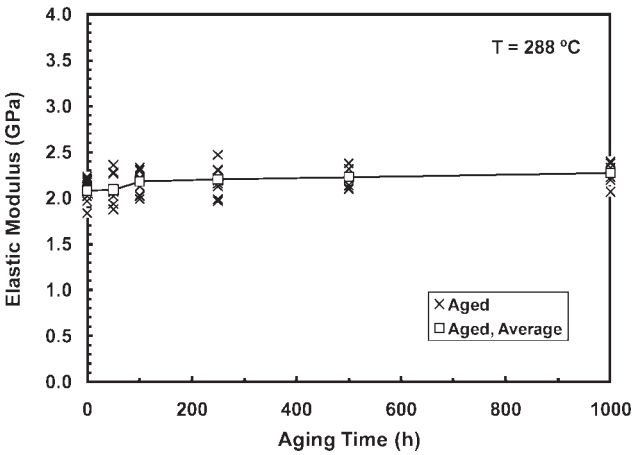

Figure 3 Elastic modulus at 288°C vs. prior aging time for the PMR-15 neat resin aged at 288°C in argon. Elastic modulus increases with prior aging time.

of relaxation of fixed duration were conducted on specimens subjected to prior aging for 50, 100, 250, 500, and 1000 h. In these strain-controlled tests, a specimen is loaded at a constant strain rate to a specific strain in the region of fully established inelastic flow, where a 12-h relaxation period is performed. After completion of the relaxation period, straining is resumed at a given strain rate and continues to specimen failure. The tests were carried out in strain control using the strain rates of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} s^{-1} during loading. Two tests were conducted at each strain rate incorporating a relaxation period at (1) the strain of 3% and (2) the strain of 4.5%. Results of the relaxation tests are typified in Figure 8 (a,b), where the stress decrease is presented as a function of relaxation time for prior strain rates of 10^{-5} and at 10^{-6} s^{-1}, respectively. Figure 8 (a,b) each present results obtained for the PMR-15 specimens

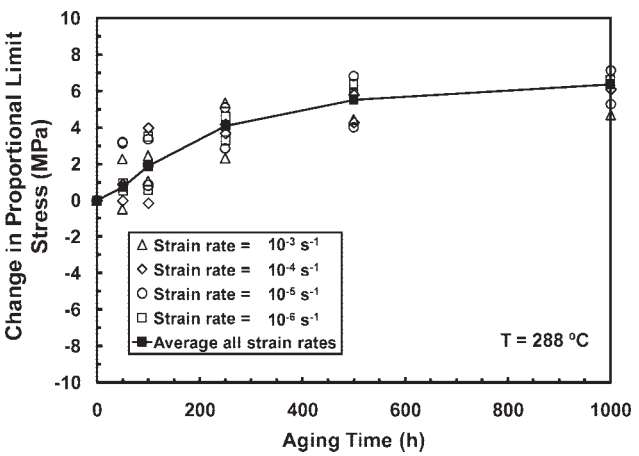

Figure 4 Change in proportional limit stress at 288°C vs. prior aging time for the PMR-15 neat resin aged at 288°C in argon. For all strain rates proportional limit increases with prior aging time.

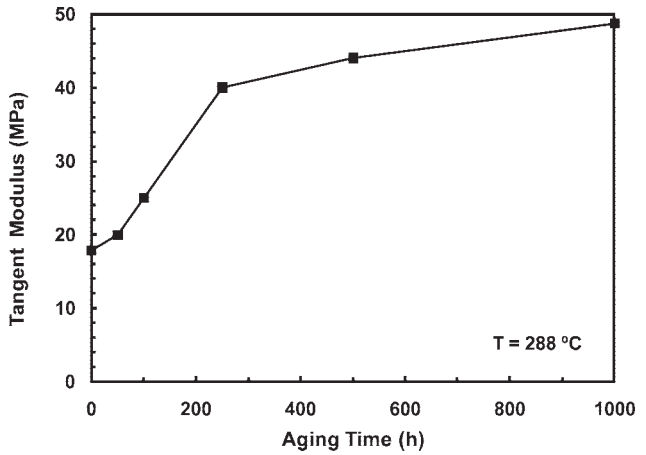

Figure 5 Tangent modulus at 288°C vs. prior aging time for the PMR-15 neat resin aged at 288°C in argon. Tangent modulus increases with prior aging time.

subjected to prior aging of various durations in relaxation tests at $\varepsilon = 3\%$ and at $\varepsilon = 4.5\%$.

Previous work[20] has shown that the relaxation behavior of the unaged PMR-15 at 288°C is profoundly influenced by prior strain rate. Similar observation can be made for the PMR-15 polymer subjected to prior aging at 288°C in argon. Strong influence of prior strain rate on relaxation behavior of the aged PMR-15 specimens is apparent in Figure 8. A larger stress drop is seen in relaxation following loading at 10^{-5} s^{-1} than in relaxation preceded by loading at 10^{-6} s^{-1}. Furthermore, it is seen that the decrease in stress during relaxation is essentially independent of the stress and strain at the beginning of the relaxation period. For a given prior strain rate and a given prior aging time, the relaxation curves produced at $\varepsilon = 3\%$ and at $\varepsilon = 4.5\%$ are nearly the same. Most importantly, results in Figure 8 reveal that the relaxation behavior is independent of prior

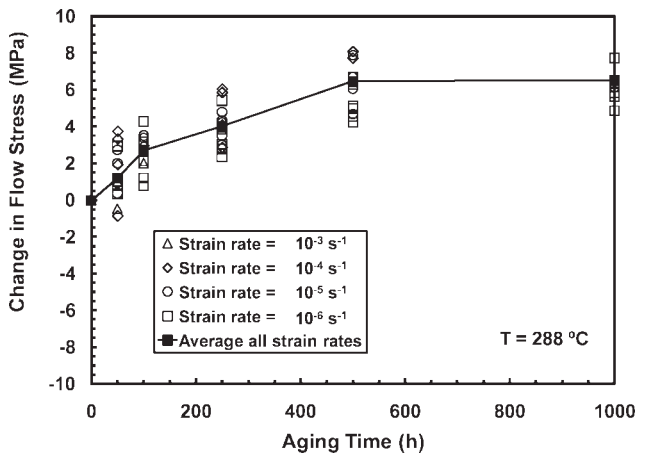

Figure 6 Change in flow stress at 288°C vs. prior aging time for the PMR-15 aged at 288°C in argon. Change in flow stress is measured at 3% and at 4.5% strain.

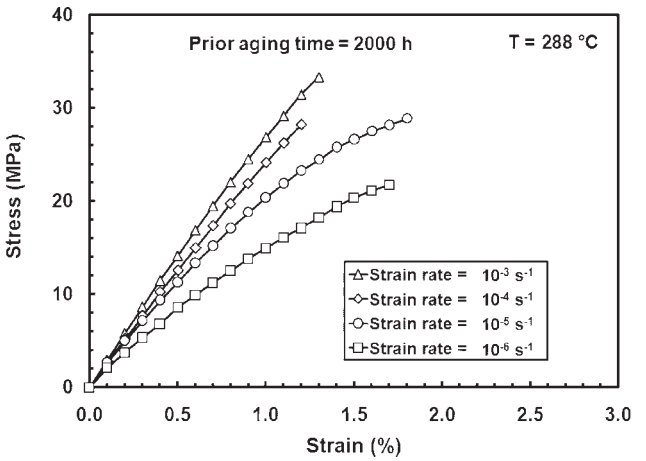

Figure 7 Stress–strain curves for the PMR-15 neat resin aged for 2000 h at 288°C in argon obtained in tensile tests to failure conducted at constant strain rates of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} s^{-1} at 288°C. The loss of the material's capacity for inelastic straining is evident.

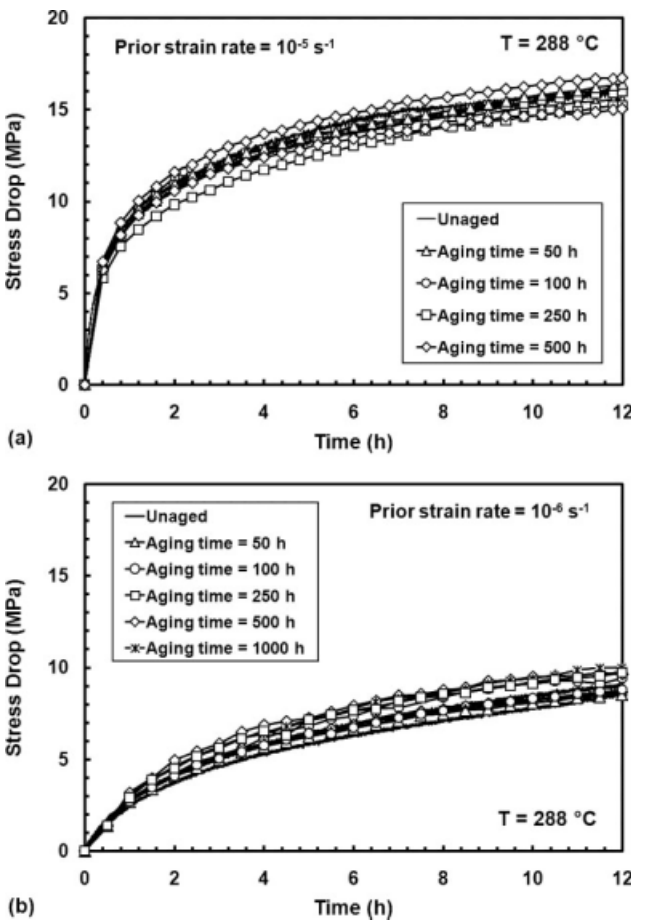

Figure 8 Stress decrease vs relaxation time for PMR-15 specimens aged at 288°C in argon, relaxation at $\varepsilon = 3\%$ and 4.5%: (a) prior strain rate is 10^{-5} s^{-1} and (b) prior strain rate is 10^{-6} s^{-1}. Stress drop during relaxation of a fixed duration is independent of the prior aging time.

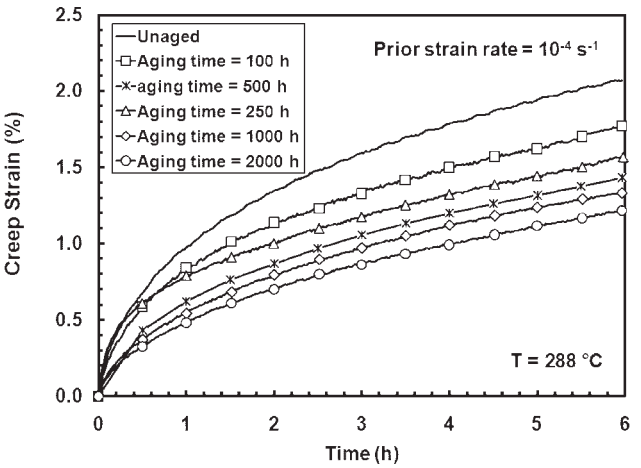

Figure 9 Creep strain vs time at 21 MPa and 288°C for the PMR-15 polymer aged at 288°C in argon. Effect of prior aging time on creep strain is apparent. Creep strain decreases nonlinearly with prior aging time.

aging time. For each of the prior strain rates, the relaxation curves measured for specimens subjected to various prior aging times are randomly distributed within a narrow scatter band. In some cases, the difference between the relaxation curves produced by specimens with different prior aging times is less than the difference between the curves obtained for specimens with the same prior aging time. It is evident that within a given strain rate the stress drop during relaxation is not affected by prior aging time.

Creep behavior—influence of prior aging

The effect of prior aging on the creep response was explored in 6-h creep tests conducted at 21 MPa on specimens subjected to prior aging of varying durations. In these tests the specimens were loaded to the creep stress in strain control at a constant strain rate of 10^{-4} s^{-1}. The capability of the testing system to instantaneously switch control mode made it possible to load a specimen to a target creep stress at a constant strain rate under strain control, then switch mode to load control to perform a creep test. Results presented in Figure 9 show that primary and secondary creep regimes were observed in all tests regardless of the prior aging time. While prior aging appears to have little influence on the appearance of the creep curves, it has a noticeable effect on the strain accumulated during 6 h of creep. The largest creep strain was accumulated by the unaged polymer. The creep strain decreased as the prior aging time increased. Prior aging noticeably decreased the polymer's capacity to accumulate creep strain. This result is consistent with observations reported earlier.[19]

CONCLUDING REMARKS

The effects of prior aging at 288°C in argon on the inelastic deformation behavior of the PMR-15 polymer at 288°C were evaluated. The PMR-15 neat resin subjected to prior aging exhibits positive, nonlinear strain rate sensitivity during monotonic loading. For a given prior aging time, a unique stress–strain curve is produced for each strain rate in the inelastic flow region. For a given strain rate, prior aging has significant quantitative effects on the stress–strain behavior of the PMR-15 polymer. The elastic modulus increases with prior aging time. Departure from the quasi-linear behavior is delayed as the prior aging time increases. The tangent modulus (slope of the stress–strain curve obtained at the largest strain) increases continuously with prior aging time. The stress level in the region of fully established inelastic flow also increases with prior aging time. The change in flow stress due to prior aging is independent of the strain rate. Prior aging has negligible effect on relaxation behavior. The stress change during relaxation is independent of prior aging time or of the stress and strain at the beginning of relaxation and depends only on time and prior strain rate. Creep behavior is noticeably affected by prior aging. Creep strain accumulation decreases with increasing prior aging time.

The results presented here served as a basis for extending the VBO to capture the effects of prior aging on time-dependent deformation behavior of PMR-15 polymer at elevated temperature. A companion article will introduce the VBO and its capability to model the observed behaviors.

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References

1. Marais, C.; Villoutreix, G. J Appl Polym Sci 1998, 69, 1983.
2. Bowles, K. J.; Layne, D.; Leonhardt, T. A. Isothermal aging effects on PMR-15 resin, NASA Tech Memo 105648, 1992.
3. Tsuji, L. C.; McManus, H. L.; Bowles, K. J. Mechanical properties of degraded PMR-15 resin, NASA/TM-1998–208487, 1998.
4. Bowles, K. J.; Tsuji, L. C.; Kamvouris, J. E.; Roberts, G. D. Long-term isothermal aging effects on weight loss, compression properties, and dimensions of T650–35 fabric-reinforced PMR-15 composites—data, NASA/TM-2003–211870, 2003.
5. Schoeppner, G. A.; Tandon, G. P.; Ripberger, E. R. Comp A 2007, 38, 890.
6. Kamvouris, J. E.; Roberts, G. D.; Pereira, J. M.; Rabzak, C. Physical and chemical aging effects in PMR-15 neat resin, ASTM STP 1302, 1997, 243.
7. Bowles, K. J.; Meyers, A. Specimen geometry effects on graphite/PMR-15 composites during thermo-oxidative aging, NASA/TM-87204, 1986.
8. Chuang, K. DMBZ Polyimides Provide an Alternative to PMR-15 for High-Temperature Applications; Research and Technology, 2003; NASA/TM-2004–212729; NASA/Glenn Research Center: Cleveland, OH, 2004, p 27.

9. Bowles, K. J.; Papadopoulos, D. S.; Inghram, L. L.; McCorkle, L. S.; Klan, O. V. Longtime durability of PMR-15 matrix polymer at 204, 260, 288, and 316°C, NASA/TM-1998–208487, 2001.
10. Odegard, G.; Kumosa, M. Comp Sci Technol 2000, 60, 2979.
11. Bowles, K. J.; Roberts, G. D.; Kamvouris, J. E. Long-term isothermal aging effects on carbon fabric-reinforced PMR-15 composites: compression strength, NASA/TM-107129, 1995.
12. Bowles, K. J. Thermal and mechanical durability of graphite-fiber-reinforced PMR-15 composites, NASA TM 113116/REV1, 1998.
13. Colin, X.; Verdu, J. Comp Sci Technol 2005, 65, 411.
14. Meadors, M. A.; Lowell, C. E.; Cavano, P. J.; Herrera-Fierro, P. High Perform Polym 1996, 8, 363.
15. Ripberger, E.; Tandon, G. P.; Schoeppner, G. A. Characterizing Oxidative Degradation of PMR-15 Resin. In Proceedings of the Spring SAMPE 2004 Symposium/Exhibition, Long Beach, CA, 2004.
16. Schoeppner, G. A.; Tandon G. P. Aging and Durability of PMR-15 High Temperature Polyimide. In Proceedings of the 35th International SAMPE Technical Conference, Dayton, OH, 2003.
17. Wang, S. S.; Chen, X. J Eng Mat Technol 2006, 128, 81.
18. Rupnowski, P.; Gentz, M.; Armentrout, D.; Sutter, J. K.; Kumosa, M. Acta Mater 2005, 53, 4555.
19. Ruggles-Wrenn, M. B.; Broeckert, J. L. J Appl Polym Sci 2008, 107, 1378.
20. McClung, A; Ruggles-Wrenn, M. B. Polym Test 2008, 27, 908.
21. Falcone, C. M.; Ruggles-Wrenn, M. B. J Press Vessel Technol Trans ASME 2009, 131, 011403–1.
22. McClung, A.; Ruggles-Wrenn, M. B. J Press Vessel Technol Trans ASME 2009, 131, 031405–1.