Impression Creep of PMR-15 Resin at Elevated Temperatures

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The polyimides formed from the polymerization of monomeric-reactants (PMR) approach have been increasingly used as matrix materials in fiber-reinforced composites on aerospace and space structures for high temperature applications. The performance of PMR-based structures depends on the mechanical durability of PMR resins at elevated temperatures, including creep and stress relaxation. In this work, the creep behavior of PMR-15 resin was studied using the impression technique in the temperature range of 563–613 K and the punching stress range of 76–381 MPa. It was found that there existed a steady state creep for the creep tests performed at temperatures of 563 K and higher, from which a constant impression velocity was calculated. The steady state impression velocity increased with temperature and punching stress with the stress exponent in the range of 1.5–2.2. The average of the apparent activation energy of the PMR-15 was calculated as 122.7 ± 6.1 kJ/mol. POLYM. ENG. SCI., 50:209–213, 2010. © 2009 Society of Plastics Engineers

INTRODUCTION

Thermosetting polymers have been increasingly used as matrix materials in fiber-reinforced composites for aerospace and space structures, whose operating temperature could be 573 K or higher [1–4]. Among the thermosetting polyimide resins, polymerization of monomeric-reactants 15 (PMR-15) is of practical interest due to its superior high-temperature properties and good formability. The mechanical behavior of the PMR-based resins has been extensively studied at room temperature. However, there are only a few studies on the creep behavior of PMR-15 resin at elevated temperatures. To assure structural integrity of polyimide-based composite structures, a thorough understanding of the time-dependent plastic deformation (creep) of PMR-15 resin at elevated temperatures is essential.

Marais and Villoutreix [5] were among the first to study the creep behavior of PMR-15-type resin at elevated temperatures. They used a tensile test to examine the creep behavior and an extensometer to monitor the creep displacement. The testing temperatures ranged from 523 to 573 K and the stress levels were varied from 30% to 70% of the ultimate tensile strength of 47 MPa. They fitted the long-term creep strain as a simple power function of time. McClung and Ruggles-Wrenn [6] and Falcone and Ruggles-Wrenn [7] have recently studied the rate-dependent creep deformation of PMR-15 resins. The effect of loading history on creep was studied in stepwise creep tests. The strain-time response was found to depend upon the prior deformation history. Ruggles-Wrenn and Broeckert [8] had performed tensile-creep experiments on isothermally aged PMR-15 resin. The dog-bone-shaped PMR-15 specimens, previously aged at 561 K for ~1000 h, were tested on a servo-controlled MTS machine at a constant temperature of 561 K for a creep time of 25 h followed by a recovery period of 50 h. The isothermal aging caused the increase in the glass transition temperature of the polymer and the reduction in the creep strain.

Recently, the creep behavior of PMR-15 resin was studied at a temperature 550 K by the researchers at the Air Force Research Laboratory's Materials and Manufacturing Directorate. Similar to the published results, the creep deformation of the PMR-15 resin started with a short transient stage, which was followed by a steady

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state stage. The steady-state creep rate, $\dot{\varepsilon}$, could be related to tensile stress (σ) and temperature (T) by the Norton power law:

$$\dot{\varepsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right), \quad (1)$$

where A is a constant, n is the stress exponent, Q is the activation energy, and R is the gas constant. The stress exponent was obtained as $n = 2.0$ [9].

Different techniques have been used to study the creep deformation of materials, including tensile creep, compressive creep, and impression creep. In the impression creep as introduced by Li and coworkers [10–12], a flat-ended cylindrical punch is pushed onto a material under a constant load. During the test, the contact area between the punch and the sample remains the same and a constant punching stress (the normal load divided by the cross-sectional area of the punch) is obtained. The impression technique has been used to study the creep behavior of metallic materials [10, 12–21], polymers [22, 23], and amorphous material [24] and to measure the viscosity of polymers [25]. The advantage of using the impression technique includes that multiple impression tests can be made on one sample of small size, which reduces microstructural variation and offers a simple and inexpensive way for the preparation of samples.

The purpose of this work is to study the creep deformation of a PMR-15 resin, using the impression technique. The impression test is performed in the temperature range of 563 $\sim$ 613 K under the punching stresses of 76 $\sim$ 381 MPa. The dependence of the steady state impression velocity on the punching stress is analyzed, using the power law relation. The dependence of the impression velocity on temperature is also discussed.

EXPERIMENTAL

Rectangular plaques of PMR-15 resin were compression-molded by HyComp Inc. (Cleveland, OH) and subsequently post-cured at the Air Force Research Laboratory's Materials and Manufacturing Directorate (Wright-Patterson Air Force Base, OH). The post-curing temperature was 589 K, and the post-curing time was 16 h. Small specimens of 15 mm $\times$10 mm $\times$4 mm in dimensions were cut from the plaques, using a diamond saw with distilled water as a cooling liquid. The specimens were washed using common-household soap and then rinsed with distilled water for a minimum of 5 min. The specimens were then dried with standard paper towel and placed in a vacuum oven at 378 K for a minimum of 48 h to remove any moisture in the specimens. The specimens were stored in a nitrogen-purged desiccator until performing the impression test.

The glass transition temperature (T_g) of the PMR-15 specimens was measured by a dynamic mechanical analyzer (Rheometric Scientific ARES 3A1, Rheometric Scientific, Piscataway, NJ). The heating rate was 1 K/min and the oscillation frequency was 1 Hz. The T_g was determined as the peak of the tan δ curve: $T_g = 628$ K.

The RSA III (Rheometric Solids Analyzer, Rheometric Scientific, Piscataway, NJ) was modified to perform the impression creep test. The flat-ended cylindrical punch of 0.3 mm in diameter was made of stainless steel. The surface of the specimens was ground and polished mechanically to obtain flat surface for the tests. The impression creep tests were performed over a temperature range of 563–613 K. The control of temperature was within $\pm$0.2 K. Before performing the impression test on the specimen, the temperature of the chamber in the RSA III was raised to the desired temperature and stabilized for at least 30 min. Then the sample stage was lifted slowly to be in touch with the punch until the prescribed load was applied to the indenter. The controlled stress (punching stress: σ_{imp}) applied to the punch varied from 76 to 381 MPa. During the test, the impression depth was measured continuously by an LVDT with a resolution of 0.5 μm.

RESULTS AND DISCUSSION

Impression Creep Curves

During the impression creep test, the load applied to the punch was maintained as a constant. For a constant cross-sectional area of the punch, the punching stress remained as a constant. Figure 1 shows the variation of the impression depth with the impression time for temperature of 573 K and under several punching stresses. Figure 2 shows the variation of the impression depth with the impression time at several temperatures under the same punching stress of 208 MPa. Similar to the compression creep, the creep deformation can be divided into two stages: (1) transient and (2) steady state. The transient

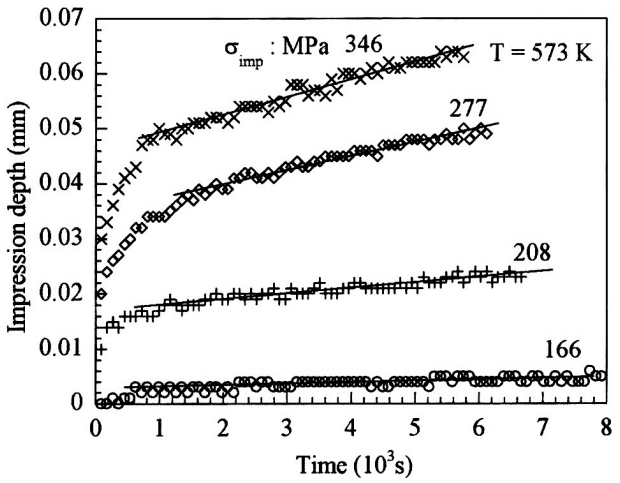

FIG. 1. Variation of the impression depth with time for several punching stresses at temperature of 573 K (punch diameter: 0.3 mm).

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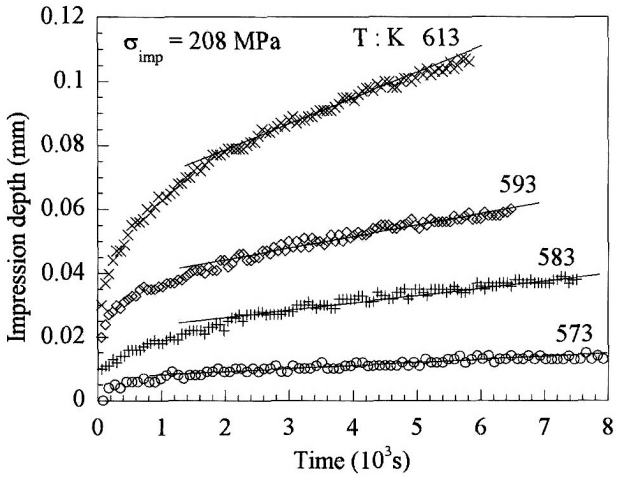

FIG. 2. Variation of the impression depth with time for several temperatures at a punching stress of 208 MPa (punch diameter: 0.3 mm).

stage is controlled by the system compliance and elasto-plastic behavior of the material, which depend on the load and temperature as shown in Figs. 1 and 2. In the steady state, the elastic deformation has no effect on the creep behavior, and the impression depth is a linear function of the impression time. Using the slope of the impression depth-time curves, one can calculate the impression velocity for the steady state creep. Obviously, the impression velocity increases with the increase in the punching stress at the same temperature and with increasing temperature for the same punching stress.

Stress Dependence of the Impression Velocity

It is known that the impression test is a localized test, which is associated with the evolution of the local plastic zone underneath the punch. In contrast to the indentation test using spherical or pyramidal indenters, the size of the plastic zone underneath the punch remains the same during penetration and the impression velocity represents the propagation speed of the plastic zone. From the finite element simulation of power-law materials [26] and the approach suggested by Chu and Li [10], the relation between tensile-strain rate and impression velocity and the relation between tensile stress and punching stress can be expressed as

$$\dot{\varepsilon} = V/2a \quad \text{and} \quad \sigma_{\text{imp}} = F/\pi a^2 = c\sigma, \tag{2}$$

where V is the impression velocity in the steady state creep, a is the punch radius, F is the normal force applied to the punch, and c is a constant depending on primarily the ratio of elastic modulus to yield strength (E/σ_y), the stress exponent, the indenter geometry, and the friction at the indenter-sample interface [10, 26, 27]. However, it should be noted that the exact value of the constant c has no influence on the calculation of stress exponent (n) and thermal activation parameters such as activation energy (Q). Substitution of *Eq. 2* into *Eq. 1* gives

$$V = 2aA\left(\frac{\sigma_{\text{imp}}}{c}\right)^n \exp\left(\frac{-Q}{RT}\right). \tag{3}$$

The impression velocity is proportional to the punch diameter and to the n-power of the punching stress, as verified by the impression creep of metallic materials [10, 12–21] and polymers [22, 23].

The dependence of the impression velocity on the punching stress is depicted in Fig. 3 by using log-log scale, from which one can calculate the stress exponent as

$$n = \left.\frac{\Delta \ln V}{\Delta \ln(\sigma_{\text{imp}})}\right|_T. \tag{4}$$

The stress exponent ranges from 1.5 to 1.6 for temperatures of 583 K and higher; and the stress exponent is 2.2 for temperatures of 563 and 573 K comparable to the result of 2 reported by Lu et al. [9]. The difference in the stress exponent in two temperature ranges is likely due to the effect of the free volume in the PMR-15 resin. In general, the specific free volume (free volume per atomic volume) increases with the increase in temperature, which reduces the resistance to the polymeric flow; and the flow behavior of polymers becomes Newtonian when temperature approaches to the glass transition temperature. This results in the decrease in the stress exponent with increasing temperature.

Temperature Dependence of the Impression Velocity

As given in *Eq. 3*, the impression velocity is a function of temperature, dependent on the activation energy. The dependence of the impression velocity on temperature is shown in Fig. 4 for different temperatures. Using *Eq. 3* to

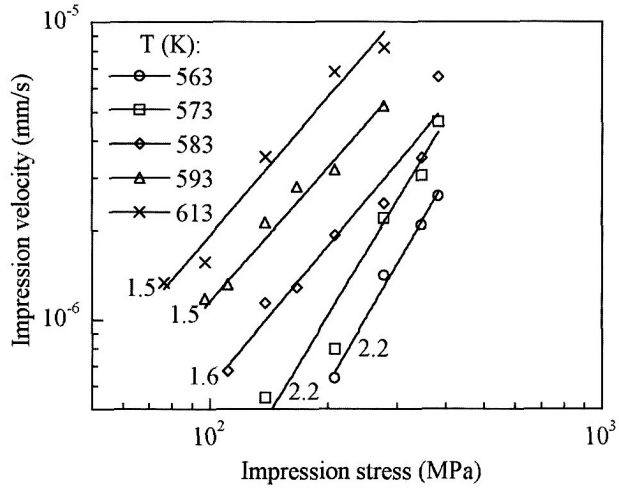

FIG. 3. Stress dependence of the impression velocity for the PMR-15 resin at different temperatures (punch diameter: 0.3 mm).

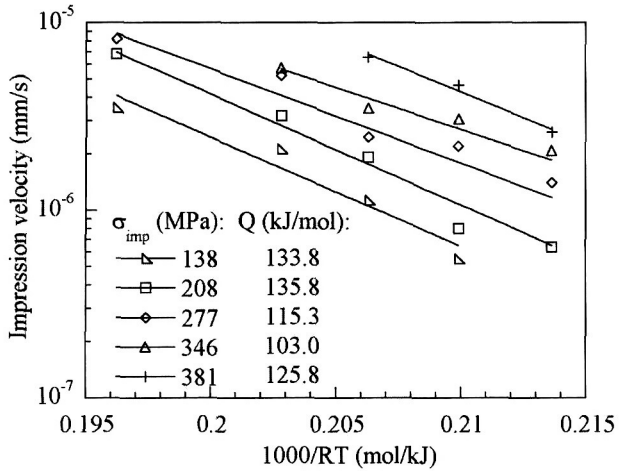

FIG. 4. Temperature dependence of the impression velocity for the PMR-15 resin at different punching stresses (punch diameter: 0.3 mm).

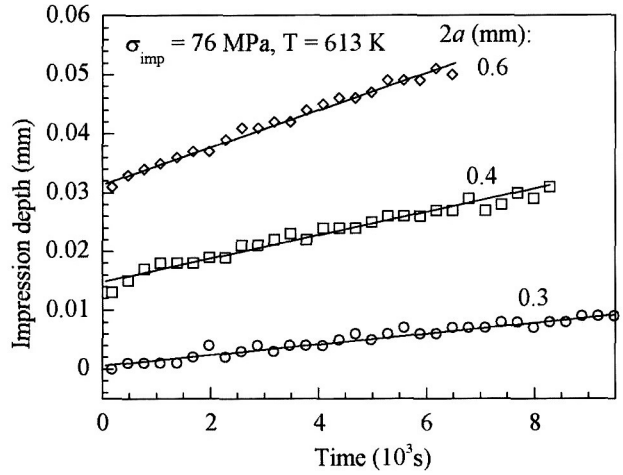

FIG. 6. Impression curves for different punch sizes under a punching stress of 76 MPa and at temperature of 613 K.

fit the impression velocity vs. temperature curves, one obtains the apparent activation energy in the range of 103–135.8 kJ/mol.

It is known that the thermal activation energy represents the energy barrier that molecules/polymer-chains need to overcome for the material flow. In general, the apparent activation energy decreases with the increase in applied stress due to the stress-assisted activation process. Figure 5 shows the variation of the apparent activation energy with the punching stress. The apparent activation energy slightly decreases with the increase in the punching stress in accord with the stress-assisted activation process. The average of the apparent activation energy is 122.7 ± 6.1 kJ/mol.

Size effect on the Impression Velocity

According to *Eq. 3*, the impression velocity is proportional to the diameter of the punch. To verify this relation, punches of three different diameters of 0.3, 0.4, and 0.6 mm were used to measure the creep behavior of the PMR-15 resin at a punching stress of 76 MPa. Figure 6 shows the impression depth vs. time curves for the impression creep of PMR-15 resin. Similar to Figs. 1 and 2, the PMR-15 resin experienced a short-transient stage and then reached the steady state creep. The PMR-15 resin had a higher creep rate when a punch of larger size was used. This result suggests that the localized creep behavior of the PMR-15 is a function of the punch size.

Figure 7 shows the dependence of the impression velocity on the punch size. A linear relation between the impression velocity and the punch size is observed in accord with *Eq. 3*. This suggests that the impression velocity is proportional to the strain rate and the punch size, verifying the relation given in *Eq. 2*. The creep deformation of the PMR-15 resin can be described by *Eq. 3*, which correlated the localized creep deformation to the tensile/compression creep through *Eq. 2*.

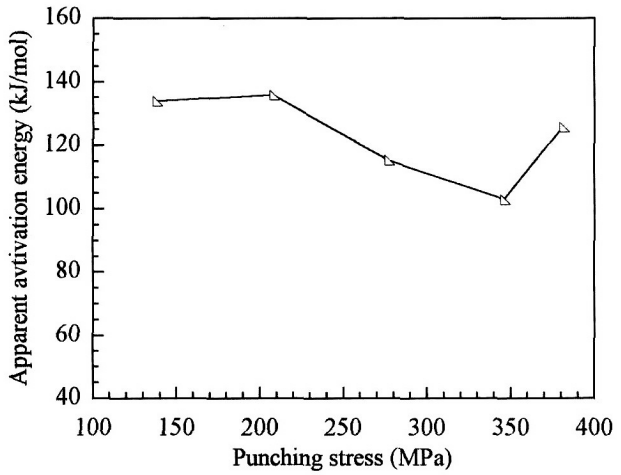

FIG. 5. Variation of the apparent activation energy with the punching stress.

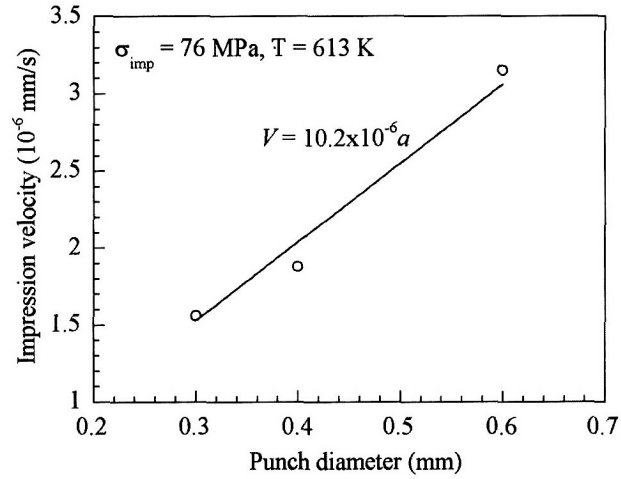

FIG. 7. Dependence of the impression velocity on the punch size.

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SUMMARY

Using the impression technique, the creep deformation of the PMR-15 resin was studied in the temperature range of 563–613 K and the punching stresses of 76–381 MPa. It was found that the impression creep consisted of two stages: (1) a short transient stage and (2) a steady state stage, similar to the compression creep. The steady state creep of the PMR-15 resin can be described by a power-law relation between the impression velocity and the punching stress. The stress exponent for the power-law relation is in the range of 1.5–2.2, consistent with the tensile results. The average of the apparent activation energy for the PMR-15 near the glass transition temperature is 122.7 ± 6.1 kJ/mol. The apparent activation energy slightly decreases with the increase in the punching stress due to the stress-assisted activation process.

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