EFFECTS OF MOLECULAR STRUCTURE ON MACROSCOPIC MECHANICAL PROPERTIES OF AN ADVANCED POLYMER (LARC™-SI)

Lee M. Nicholson[†], Jeffrey A. Hinkley, Karen S. Whitley and Thomas S. Gates
[†]National Research Council Resident Associate
NASA Langley Research Center, Hampton, VA 23681-2199

Abstract

Mechanical testing of an advanced polymer resin with known variations in molecular weight was performed over a range of temperatures below the glass transition temperature. The elastic properties, inelastic elongation behavior, and notched tensile strength all as a function of molecular weight and test temperature were determined. It was shown that notched tensile strength is a strong function of both temperature and molecular weight, whereas stiffness is only a strong function of temperature.

Introduction

Modern tendencies in the design and production of advanced structural materials strive for optimal mechanical properties with a minimum of weight. State-of-the-art polyimides in conjunction with reinforcing components such as graphite fibers create novel polymer matrix composites (PMC's). In airframe structure, these PMC's can give up to 40% weight savings, along with a reduction in the number of parts (1).

Failure or degradation of performance in PMC's is usually associated with loss in mechanical load carrying capability of the polymer matrix. Early experiments by Nielsen (2) on atactic polystyrene have shown that below the glass transition temperature (T_g) the relative effect of molecular weight on mechanical properties increases as the experimental regimen moves from elastic to viscoelastic to large strain and finally fracture testing. Matsuoka (3) noted that in the glassy state, the molecular weight affects the toughness and impact strength of the polymer; impact strength increases with molecular weight. The dependence of fracture toughness on molecular weight and test temperature was studied by Walsh and Termonia (4) for poly(methyl methacrylate). They found that changes in fracture toughness were strongly dependent on the temperature and on the molecular weight distribution.

Despite the relevance of this afore-cited literature, there is still no unified understanding of exactly how the intrinsic chemical and physical properties of the polymer affect the resultant mechanical performance. The ability to predict performance using intrinsic properties as inputs would greatly enhance the efficiency of design and development of PMC's. Data from experiments can serve as a basis for model construction and provide material properties required by the selected model. One of the first steps in the construction of a model is the careful experimental correlation of thermal-mechanical behavior of a well-characterized polymer to known changes in intrinsic properties.

The objective of this paper is to detail and summarize the testing of an advanced polymer (LaRC™-SI). Using five known variations in molecular weight, static tests were performed over a range of temperatures below the glass transition. Results from these tests will be presented along with descriptions of the material and test methods.

Experimental

The materials used in this study were prepared by Imitec Inc., Schenectady, NY, and received in powder form. LaRC™-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). Extended synthesis descriptions of this material have been published elsewhere (5, 6). Molecular weights were determined on the as-received powders using gel permeation chromatography (7) The weight-average molecular weight ($\overline{M_w}$) and the polydispersity index of the samples are shown in Table 1. The differences in the molecular weight distribution per sample, are more easily discerned when weight averages are compared.

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 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. Mechanical test coupons measuring approximately 150 x 17.5 x 5.8 mm were machined from the plaques. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 7 to determine the glass transition temperature (Tg) of the cured material. Polymer sample weights of 2-5 mg were used under a nitrogenous atmosphere at a heating rate of 10°C/min.

Static Test Instrumentation and Procedures

The goal of the static tests was to determine the elastic properties, inelastic elongation behavior, and notched tensile strength as a function of molecular weight, test

temperature and cross-link density. Due to space limitations, only the molecular weight data are reported here. Static tensile tests were performed at six specific test temperatures below the glass transition temperature (Tg). The Tg's for each molecular weight are shown in Table 1. To place equal emphasis on the results, the temperature is referenced to the difference between glass transition and test temperature, as defined below:

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

Uniaxial tensile tests were performed using a 22.2 kN servo-hydraulic test system equipped with a heated test chamber. The specimens were enclosed in the chamber and mounted in mechanical wedge type grips. During the course of a test, temperature was monitored with several thermocouples placed near the specimen. The test temperature was stabilized first and then a tensile load was applied at a constant ramp rate of 22.2 N/s. The tests were terminated when failure occurred or the desired elongation was achieved.

A high-temperature strain gage was applied to each specimen in a direction transverse to the length on the face of the specimen. The specimen and gage were subsequently dried at 110°C for 120 hours and post-cured at 210°C for 2 hours. Longitudinal strain was measured using an extensometer mounted on the thin edge of the specimen. The output voltages from the strain gages were filtered and amplified by a strain gage conditioner before the conditioned output was collected by the digital data acquisition system.

The engineering stress on the specimen was determined from the load measured by the servo-hydraulic system's load cell divided by the average cross-sectional area measured prior to the test. Each recorded measurement is an average of at least three replicates of each molecular weight at each test temperature.

Notched Tensile Strength

For a given molecular weight, at least two tests at each temperature were made using the notched specimen geometry. To facilitate a controlled failure, an edge notch was cut in the specimen using a jeweler's blade (0.38 mm width) mounted on a handsaw. The notch was placed on one side only, at 44 mm from the bottom grip and extended approximately 2 mm in from the free edge. Tensile strength was calculated from the maximum load achieved during the tensile test divided by the original, unnotched cross sectional area. Photomicrographs were taken of the notched surface after failure to determine the morphology of the failure surface (shown in fig. 6).

Elastic Properties

Young's Modulus, (E) was calculated using equation (2) from the least squares fit to the slope of the linear portion of the stress, (σ), versus the longitudinal strain, (ε_x), curve. Similarly, Poisson's Ratio, (ν) equation (3), was calculated as the slope of the transverse strain, (ε_y), versus the longitudinal strain in the same linear region. Shear Modulus, (G) equation (4), was calculated in terms of E and ν.

$$E = \frac{\sigma}{\varepsilon_x} \qquad (2)$$

$$\nu = -\frac{\varepsilon_y}{\varepsilon_x} \qquad (3)$$

$$G = \frac{E}{2(1 + \nu)} \qquad (4)$$

Results and Discussion

The experimental results are presented for all the measured static behavior. All results have been examined by comparing the property of interest to variations in test temperature and molecular weight.

Elastic Properties

Young's Modulus (E) and Shear Modulus (G) versus temperature are given in figure 1. As expected, both E and G decrease as temperature is raised. The rate of change of E with temperature is fairly uniform up to 200°C. From 200°C to the highest temperature (~235°C) there was a sharp decrease in modulus because the temperature was in the vicinity of the softening point of the material. In accord with Young's Modulus, G decreases in a uniform manner as the temperature is raised, but with a shallower gradient. The start of the sharp decrease in modulus occurs at a higher temperature of ~220°C. Common to both data sets is the fact that the low molecular weight materials lose their mechanical properties at a slower rate initially than the high molecular weight material.

The variations of E and G with molecular weight are shown in figures 2 and 3, respectively. It can be seen that there is not a strong dependence of the Young's Modulus or Shear Modulus on molecular weight. However, there is some sensitivity in the modulus occurring between 22000 and 25000 g/mol molecular weight in both the Shear and Young's Moduli. In addition, both figures illustrate the temperature dependence on each modulus.

Strength

Notched tensile strength (NTS) versus temperature and molecular weight are shown in figures 4 and 5, respectively. Figure 4 illustrates the strong dependence of NTS on temperature. In general, NTS decreases as temperature increases. Over the range from room temperature to 150°C, the two highest molecular weight materials show a much lower rate of change in NTS

compared to the lower molecular weight materials. However, in the range from 150°C to 230°C the converse is true with the lower molecular weight materials showing a lower dependency of NTS on temperature than the high molecular weight materials. Furthermore, the NTS of the high molecular weight materials declines rapidly in this high temperature region.

The data on NTS versus molecular weight, as shown in figure 5, indicate a sharp change in NTS occurring about 22000 g/mol molecular weight. At this transition the higher temperature data series exhibit a larger change in the NTS, as much as 300%, compared with 150% change at room temperature. At molecular weights higher than this "critical molecular weight", the NTS is increased and conversely, at lower molecular weights the NTS is reduced. There is a marginal drop in NTS at the highest molecular weight.

Fractography

Additional evidence on the effects of temperature and molecular weight was obtained by examination of the failure surface. The photomicrographs of the notched surface after failure are provided in figure 6 for selected materials and temperatures. A failure surface was classified as ductile if the photomicrograph showed evidence of material elongation and smooth, glassy looking surfaces. A brittle failure can be defined by the evidence of sharp edges and multiple crack sites. Figure 6 displays nine microstructural images characterizing the failure surfaces at various labeled points on the NTS versus molecular weight curve for three selected temperature intervals. Regarding the low molecular weight material (images: a, d, g) and the high molecular weight material (images: c, f, i), it can be seen that there is a marked transition from a brittle failure mode to a ductile failure mode. Upon examination of the images tracing a temperature series of NTS, it can be seen that there are distinct differences in the failure surfaces for different molecular weight materials. This is more clearly expressed in the interpolated surface plot of figure 7. Here, the dominant mechanical property of NTS is conveniently summarized in one diagram expressed as functions of molecular weight and temperature.

Conclusions

The physical characterization and the mechanical response of an advanced polymer has been determined. The observed microstructures have helped to characterize further the brittle to ductile transition as a function of molecular weight. Evidence from the experimental validation suggests that the notched tensile strength is a strong function of both temperature and molecular weight. The Young's modulus and Shear modulus are strong functions of temperature, but weak functions of molecular weight.

For optimal material selection and part design, the results suggest the following choices of materials. When designing for stiffness (E, G): i) as a f(T): low molecular weight (15880, 21180 g/mol) material up to 170°C. ii) as a f(Mw): high molecular weight (>25000 g/mol) material for all temperatures. When designing for strength (NTS): i) as a f(T): high molecular weight (51070, 41100 g/mol) material up to 140°C. ii) as a f(Mw): high molecular weight (>25000 g/mol) material for all temperatures.

Acknowledgements

References

1. A. K. Noor, S. M. Spearing, W. W. Adams, S. L. Venneri, in *Aerospace America* . (1998) pp. 24-31.
2. L. E. Nielsen, *Mechanical properties of polymers and composites* (Marcel Dekker, New York, 1974), vol. 1.
3. S. Matsuoka, *Relaxation phenomena in polymers* (Hanser, Munich, 1992).
4. D. J. Walsh, Y. Termonia, *Polymer communications* **29**, 90-92 (1988).
5. R. G. Bryant, *High Performance Polymers* **8**, 607-615 (1996).
6. T. H. Hou, R. G. Bryant, *High Performance Polymers* **9**, 437-448 (1997).
7. E. J. Siochi, P. R. Young, R. G. Bryant, *Effect of molecular weight on the properties of a soluble polyimide*, vol. 40(1) (SAMPE, Los Angeles, California, 1995).
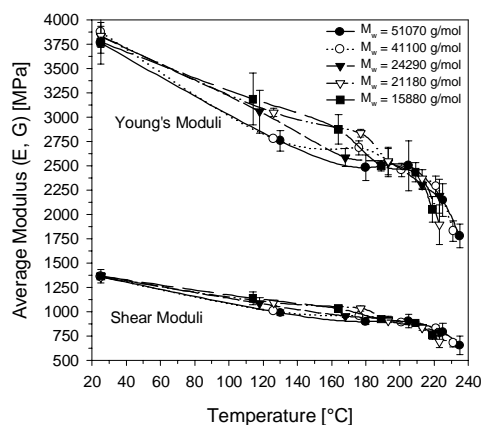
Figure 1. Averaged Young's and Shear moduli plotted as a function of temperature for various molecular weights.
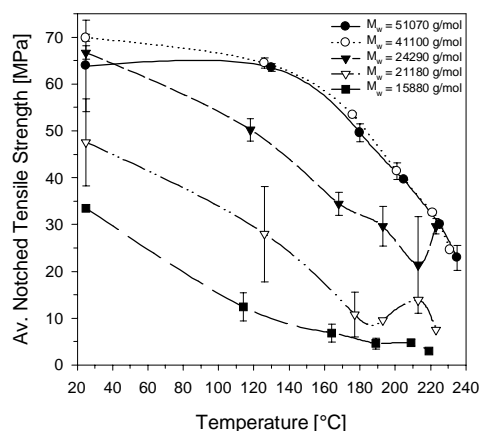

Figure 4. Averaged Notched Tensile Strength plotted as a function of temperature for various molecular weights.
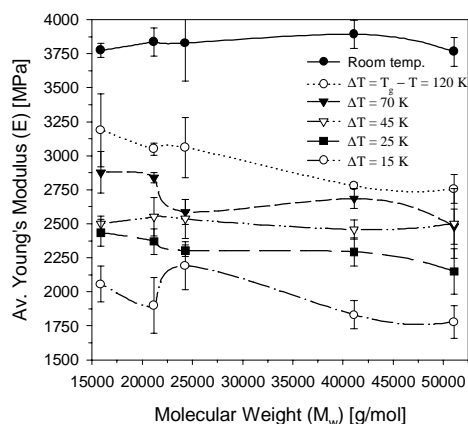

Figure 2. Averaged Young's moduli plotted as a function of molecular weight at various temperature intervals.
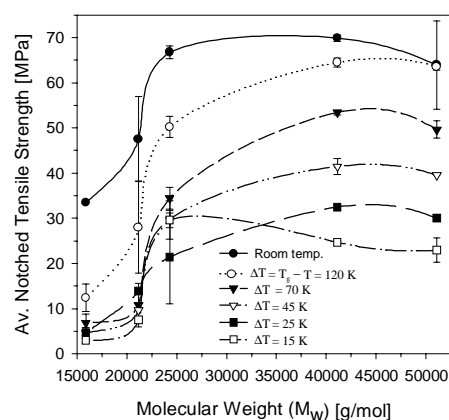

Figure 5. Averaged Notched Tensile Strength plotted as a function of molecular weight at various temperature intervals.
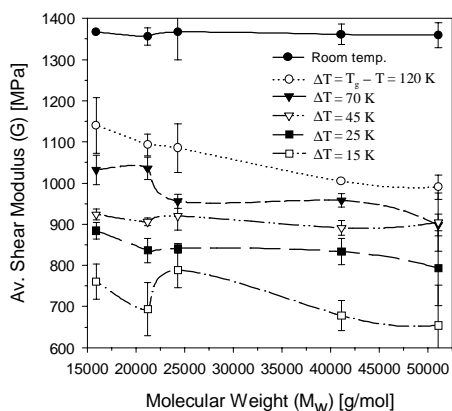

Figure 3. Averaged Shear moduli plotted as a function of molecular weight at various temperature intervals.

$\overline{M_w}$ (g/mol)	$\dfrac{\overline{M_w}}{\overline{M_n}}$	Tg (°C)	ΔT 15 K	ΔT 25 K	ΔT 45 K	ΔT 70 K	ΔT 120 K
51070	4.57	250	235	225	205	180	130
41100	2.98	246	231	221	201	176	126
24290	2.30	238	223	213	193	168	118
21180	2.04	238	223	213	193	177*	126*
15880	1.79	234	219	209	189	164	114

Table 1. Static Test Temperatures (°C) and molecular weights. (ΔT = Tg − Test Temperature); * The actual test temperatures deviated from ΔT.
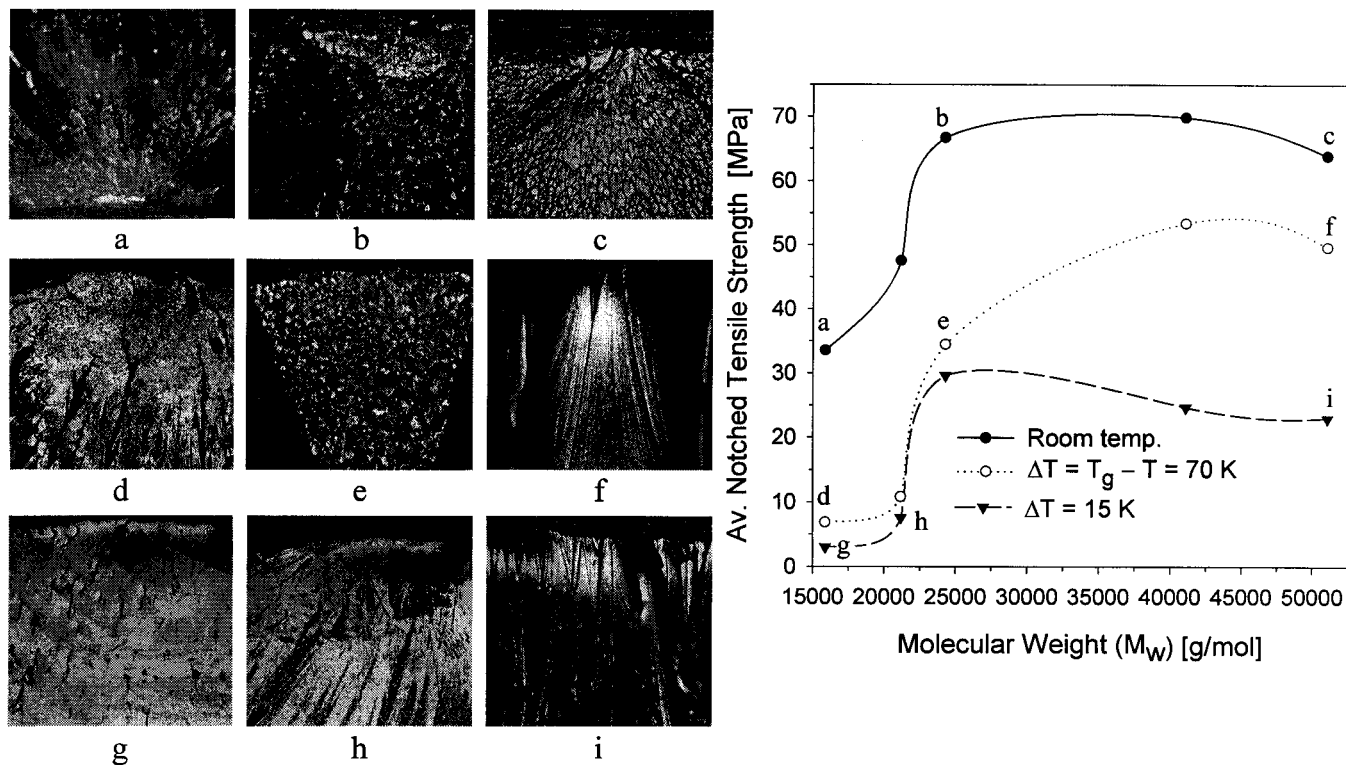
Figure 6. Microstructural images taken of the fracture surface corresponding to the appropriately indicated regions on the NTS versus molecular weight curves for selected temperature intervals.
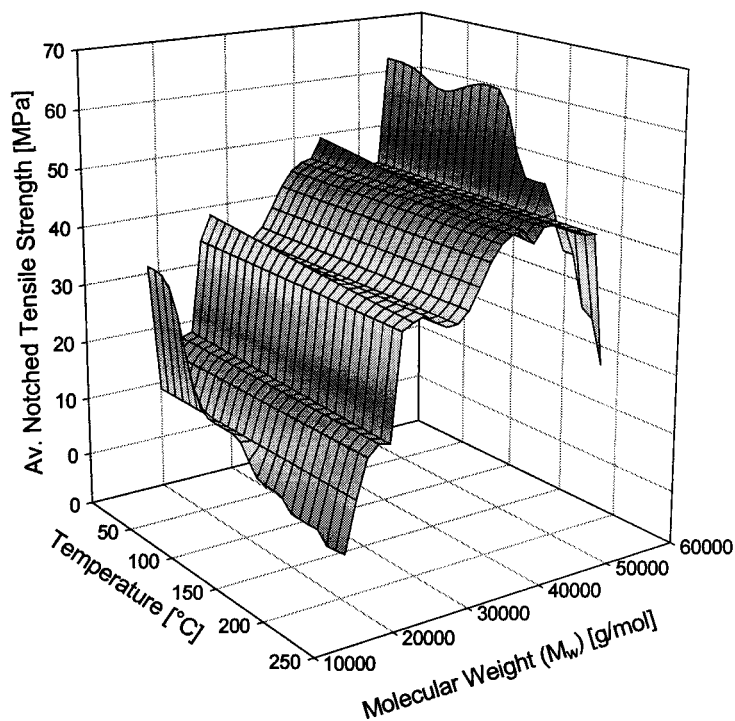

Figure 7. An interpolated 3D surface mesh interrelating temperature and molecular weight with NTS.

Keyword/Phrase Index

Molecular weight, elastic properties, Tg, advanced polymer.