

Oxidative Aging of Thermoplastic Polyimide Films

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SYNOPSIS

Two linear polyimides were subjected to accelerated isothermal aging at temperatures between 300 and 400°C. Losses in toughness correlated well with changes in glass transition temperature (T_g) of the films, but not with weight loss. Both materials have extrapolated lifetimes of 100,000 h near their T_g 's. © 1995 John Wiley & Sons, Inc.†

INTRODUCTION

Polyimides exhibit outstanding thermooxidative stability with respect to weight loss and retention of adhesive properties.¹ Because of their consideration for long-term (e.g., 100,000 h) use in aerospace structural applications, it is desirable to have meaningful accelerated tests to evaluate the expected lifetimes of new materials. Too often, reliance is placed on weight loss data alone. This could easily be misleading, because the relationship between small degrees of weight loss and mechanical property retention is *a priori* unknown; many materials even undergo an initial weight gain. In addition, weight changes of composite and bulk resin samples are often accompanied by cracking. The resulting increases in surface area and other surface effects complicate the task of extracting meaningful kinetic data.²

Residual strength measurements relate more clearly to the end use, but depending on the choice of test, even these mechanical measurements may fail to reflect the extent of surface damage on aged specimens.³

The present work was undertaken to avoid some of these problems. Aging was monitored by changes in toughness, which should be related to the useful lifetime as a structural material. The specimens were thin films, so damage should be reflected in rapid property changes, without the complication of

lengthy diffusion of oxygen into and reaction products out of a bulk specimen.

EXPERIMENTAL

The materials studied were high molecular weight thermoplastic polyimides developed at NASA Langley. LaRC™-TPI is a polyimide from 3,3'-diaminobenzophenone and benzophenone tetracarboxylic dianhydride.⁴ LaRC™-IA is a polyimide from 3,4'-oxydianiline (ODA) and oxydiphthalic anhydride (ODPA).⁵ Films of polyamic acid were cast on soda-lime glass plates from ca. 20% solutions in dimethylacetamide/diglyme or in *N*-methyl pyrrolidone. They were dried until tack free in a low-humidity enclosure, imidized for 1 h each at 100, 200, and 300°C, then cooled and released from the plates by soaking in warm water.

Aging took place in air-circulating ovens on steel plates that had been coated with a silicone mold release agent. Small weights were used to keep the edges of the films from curling; thus shrinkage in the plane of the film was not appreciably constrained.

Room temperature fracture toughness was determined on edge-notched tensile strips by a procedure described earlier.⁶ Briefly, 1.3 × 7 cm strips of film were notched on one edge with a razor blade and stretched at about 0.2 cm/min in a motorized tensile frame. The onset of crack growth was observed with a 200× microscope, and the corresponding critical load was used to calculate a critical stress intensity factor K_c via standard expressions.⁷ For each aging condition, results from 5 to 10 specimens with var-

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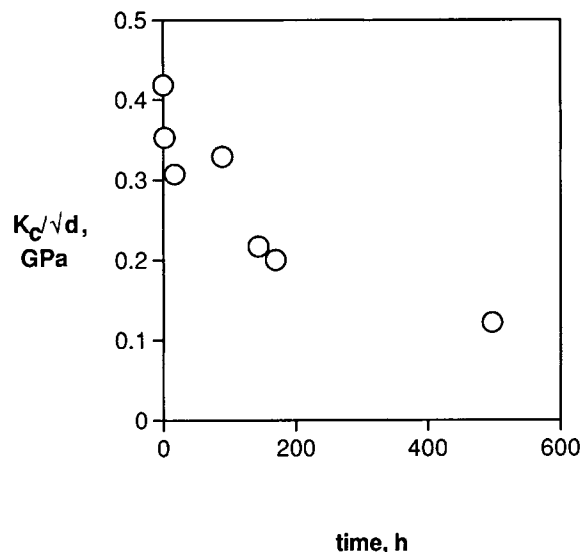


Figure 1 Normalized toughness vs. time at 340°C in air for LaRC™-TPI.

ious crack lengths were averaged. Because it is not always possible to control the thickness of solvent-cast films, measured toughnesses K_c were normalized to 25- μm thickness by dividing by the square root of thickness.⁶

Isothermal weight loss of virgin (previously unaged) films was determined using a Seiko Thermogravimetric Analyzer under 40 mL/min flowing air. Films were dried at 100°C for 30 min in the instrument before being raised to the aging temperature at 50°C/min. Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC operated at 20°C/min.

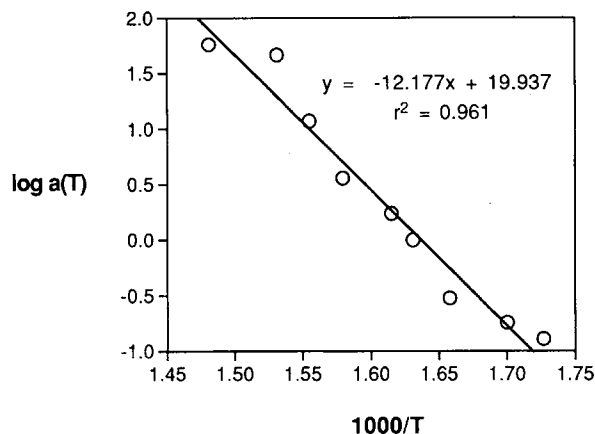


Figure 3 Shift factors from Figure 2.

RESULTS AND DISCUSSION

With increased aging, both materials darkened from bright yellow to brownish and eventually to dark brown. The starting films were flexible and cut cleanly; films that had undergone extensive oxidation tended to chip when cut and could be broken by bending. During the fracture toughness test, embrittled films broke abruptly, without much slow stable crack growth, and microscopic observation indicated a reduced critical crack tip opening angle compared to the initial unaged material. Figure 1 shows the decrease in toughness with time for LaRC-TPI at 340°C. The toughness falls by about half in 200 h at this temperature. By way of comparison, Traeger and Salazar's data for elongation at break of 5-mil Kapton imply a similar half-life of about 144 h at this temperature.⁸

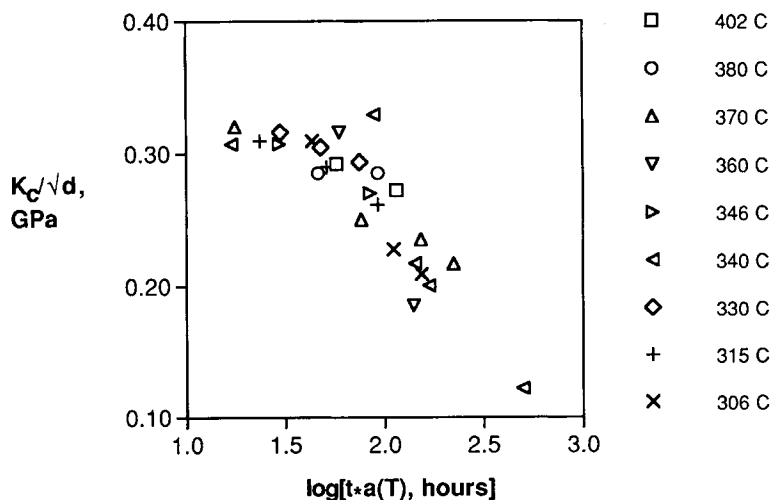


Figure 2 Master curve showing superposition of toughness data for LaRC™-TPI at various temperatures. Reference temperature $T_{ref} = 613$ K (340°C).

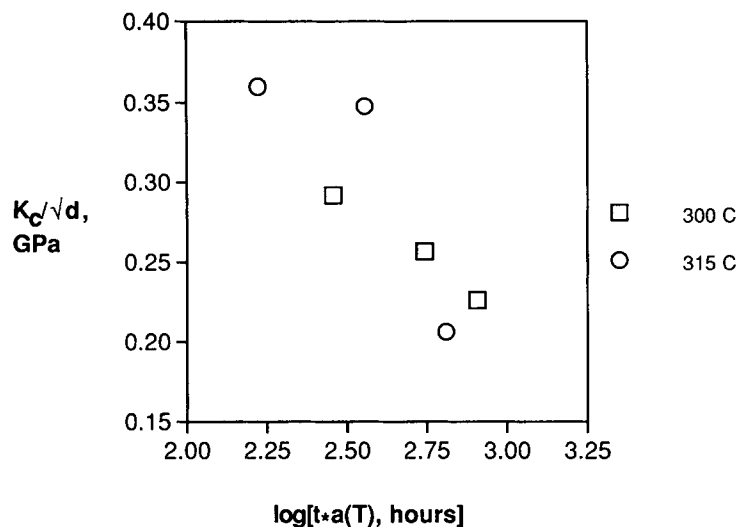


Figure 4 Normalized shifted toughness of aged LaRC™-IA films. $T_{\text{ref}} = 603 \text{ K}$ (330°C).

The usual approach to describe the temperature dependence of this rate would be an Arrhenius-type plot. Because of the large number of specimens needed to produce a single point, however, the data at most temperatures are rather sparse in the present experiments. It is difficult to derive meaningful rate constants. Consequently, we adopt the method of Gillen and coworkers.⁹ Their procedure uses all the data, requires no assumptions about the form of the rate law, and is equivalent to an Arrhenius description. In this procedure, time is plotted on a log scale, and individual property-loss curves are shifted horizontally to bring them into coincidence. The shift factors $a(T)$ used in the superposition are related to the Arrhenius activation energy E by:

$$\ln[a(T)] = (E/R)(1/T_{\text{ref}} - 1/T), \quad (1)$$

where R is the gas constant and T_{ref} is the chosen reference temperature.

Figure 2 shows this procedure applied to the toughness data on LaRC-TPI and demonstrates that the superposition is quite good. Furthermore, as shown in Figure 3, the shift factors required to align the data obey eq. (1) satisfactorily. The least-squares slope in Figure 3 implies an activation energy of 233 kJ/mol. A similar procedure, when applied to the less extensive data set on LaRC-IA, gives reasonable superposition (Fig. 4) with an activation energy of 204 kJ/mol.

It is of interest to compare these data with isothermal weight loss rates in LaRC™-TPI (Fig. 5). Using a procedure analogous to that employed with the toughness data, weight losses in air at 385 and 404°C were superposed via a logarithmic shift of

0.37 ± 0.02 , which corresponds to an activation energy of $167 \pm 9 \text{ kJ/mol}$, quite a bit less than the values derived from the toughness changes above. It does agree well with values of $40 \pm 10 \text{ kcal}$ ($167 \pm 42 \text{ kJ}$) quoted for weight loss in a variety of ODP- containing imides.¹⁰ More recently, Crossland et al.¹¹ found activation energies of 110–170 kJ/mol for the initial stages of weight loss in air of an assortment of addition and condensation polyimides. It appears, therefore, that toughness loss has a substantially higher activation energy than weight loss and by implication, a different mechanism. To see how this works out in the present case, consider the following example. At 404°C , according to the data in Figures 2 and 5, a 50% toughness loss occurs in about 2 h with a concomitant 2.2% weight loss. At 350°C , a

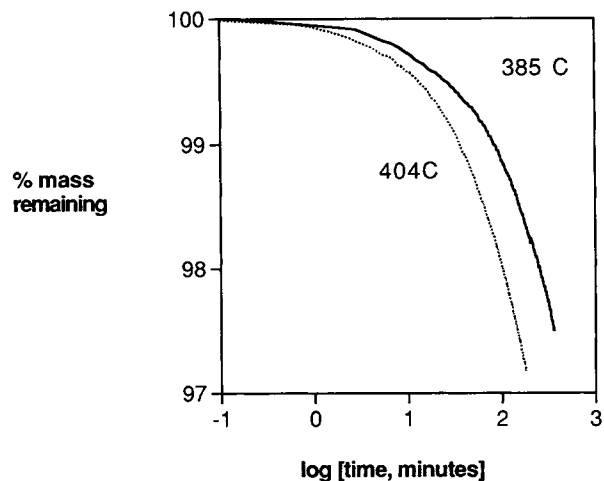


Figure 5 Isothermal weight loss in air of LaRC™-TPI at two temperatures.

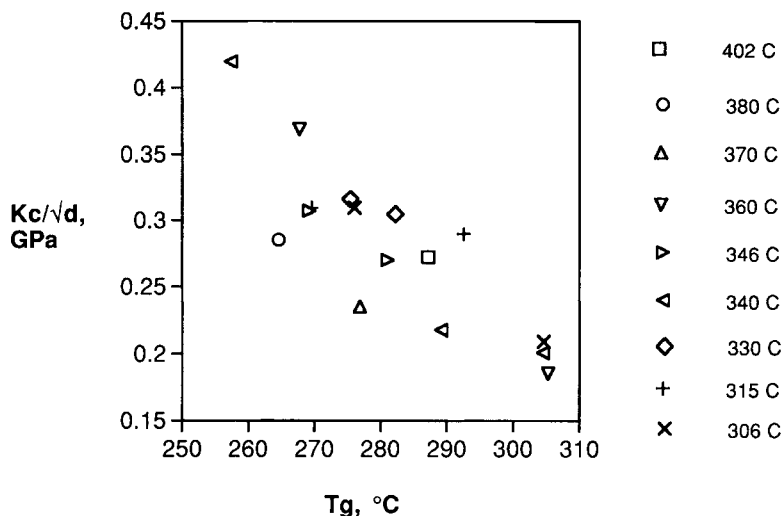


Figure 6 Normalized toughness of LaRC™-TPI vs. T_g of aged film.

50% toughness loss occurs in about 4100 h with a predicted weight loss of not 2.2%, but rather well over 3%, out of the range of Figure 5. At still lower temperatures, the discrepancy would increase. Of course, as mentioned in the Introduction, there is no reason why there should necessarily be a one-to-one correspondence between weight loss and loss of mechanical properties. Dine-Hart et al.¹² years ago described the rapid chemical changes in a polyimide resin at elevated temperature. By the time a polypyromellitimide film had lost 2–3% of its mass at 400°C, fully half of the diamine moieties in the chain had undergone chemical reactions.

Chemical analysis of polyimides is difficult, so we do not yet have analogous results on our thermo-

plastic imides. We do have DSC results on selected films, however, and they seem to reflect a similar effect. All of our tested aged films exhibited rises in T_g ; in one case the change was as much as 47°C. Evidently considerable crosslinking and/or change in backbone chemistry accompanies the first few percent of mass loss. In fact, as seen in Figure 6, toughness can be predicted from a knowledge of T_g of the aged film (linear correlation coefficient 0.84). With Dine-Hart et al., then, we conclude that a structure very different from the starting polymer forms rather early. It also follows that kinetic analyses performed in the later stages of weight loss could be quite misleading, because almost none of the starting polymer remains.

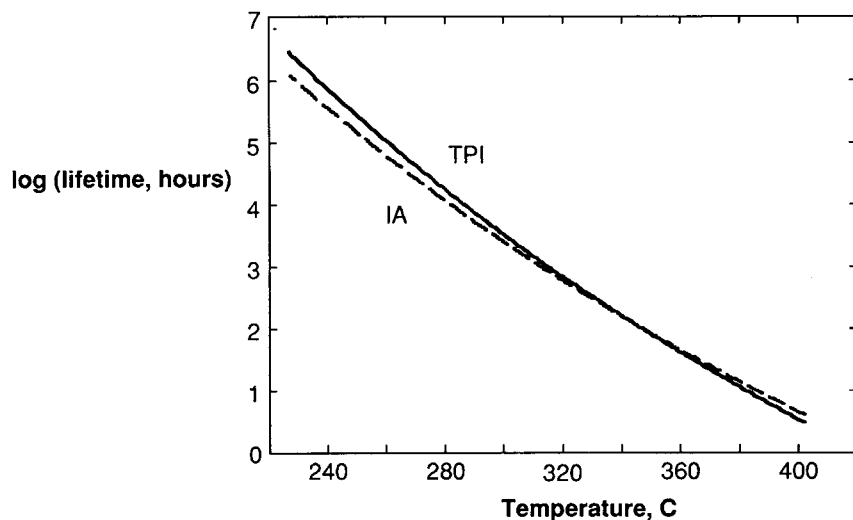


Figure 7 Extrapolated time for 50% toughness loss in two polyimide film materials.

From the data in Figures 2 and 4 and the activation energies, toughness half-lives can be extrapolated to lower temperatures. We note in passing that although half-life is often used to characterize a first-order decay process, the shifting procedure does not require any particular form for the rate law. In our case, in fact, a first-order plot does not give a very good fit. Another criterion (e.g., 90% retention of toughness) could have been chosen just as easily, although 50% is convenient to read from the master curve. As shown in Figure 7, the two materials behave almost identically. It is interesting and somewhat unexpected that with respect to retention of mechanical properties, polyimides containing ether or ketone linkages are equivalent. Based on these data, the lifetimes (defined as the time for toughness to drop to one-half its initial value) extrapolate to 100,000 h at about 260°C, which is close to the glass transition temperature. It is probably not a good idea to try to extrapolate through T_g , because the degradation pathways might change. In fact, Laius et al.,¹³ using Arrhenius-type plots, claim to have observed a change in activation energy at T_g in some materials.

We therefore conclude that the useful life of these materials is very long at any realistic use temperature. This would seem to be consistent with adhesive strength data for LaRC-TPI¹⁴ that show no significant decrease after 50,000 h at 232°C.

CONCLUSIONS

Plane-stress fracture toughness can be used to quantify the effects of oxidative aging in high-performance polymers. The loss in toughness appears to follow an Arrhenius form, allowing extrapolation of accelerated aging data to lower temperatures. A

logarithmic shifting procedure is a convenient way to obtain the Arrhenius activation energy.

At least in this case, it was shown that weight loss is not a good predictor of mechanical performance when comparing data obtained over a range of temperatures.

REFERENCES

1. P. M. Hergenrother, in *Encyclopedia of Polymer Science and Engineering*, Vol. 7, 2nd ed., Wiley, New York, 1987, p. 639.
2. K. J. Bowles, D. Jayne, and T. A. Leonhardt, *SAMPE Q.*, **January**, 3 (1993).
3. J. A. Hinkley and J. B. Nelson, *J. Adv. Mater.*, **25**(3), 45 (1994).
4. V. L. Bell, *J. Polym. Sci.-Chem.*, **14**, 2275 (1976).
5. D. J. Progar and T. L. St Clair, *J. Adhes. Sci. Technol.*, **4**(7), 527 (1990).
6. J. A. Hinkley and S. L. Mings, *Polymer*, **31**, 75 (1990).
7. W. F. Brown and J. Srawley in *ASTM STP 410*, American Society for Testing and Materials, Philadelphia, 1966.
8. R. K. Traeger and E. A. Salazar, *Polym. Prepr.*, **12**(2), 292 (1971).
9. K. T. Gillen, J. Wise, and R. L. Clough, *Proc. 39th International SAMPE Symposium*, 2196 (1994).
10. M. M. Koton and Yu. N. Sazanov, *Polym. Sci. USSR*, **17**, 1688 (1975).
11. B. Crossland, G. J. Knight, and W. W. Wright, *Br. Polym. J.*, **19**, 291 (1987).
12. R. A. Dine-Hart, D. B. V. Parker, and W. W. Wright, *Br. Polym. J.*, **3**, 235 (1971).
13. L. A. Laius, Ye. N. Dergacheva, T. I. Zhukova, and M. I. Bessonov, *Polym. Sci. USSR*, **28**(11), 2674 (1986).
14. C. L. Hendricks and J. N. Hale, in *Welding, Bonding and Fastening 1984*, J. D. Buckley and B. A. Stein, Eds., NASA Conference Publication 2387, 1985.

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