The influence of temperature and absorbed water on the fatigue crack propagation in nylon-6,6

M. T. Hahn,* R. W. Hertzberg,** J. A. Manson† and L. H. Sperling‡

Polymer Science and Engineering Program, Materials Research Center, Coxe Lab 32, Lehigh University, Bethlehem, Pennsylvania 18015, USA

The effect of absorbed water on the fatigue crack propagation (FCP) of nylon-6,6 was investigated over a range of test temperatures and is correlated with dynamic mechanical properties. Both the storage modulus, a measure of specimen stiffness, and the loss compliance, a measure of energy dissipation and hysteretic heating, influence FCP response. At a given temperature, fatigue resistance is greatest for a given water content corresponding to an optimum combination of storage modulus, E', and loss compliance, D''. The use of an empirical shift parameter to normalize the temperature dependence of the FCP behaviour of nylon with various water contents is discussed.

(Keywords: fatigue; crack propagation; nylon-6,6)

INTRODUCTION

The growth of a fatigue crack through a polymeric solid is governed by the material's viscoelastic properties as represented by the complex dynamic modulus, $E^* = E' + iE''$, where E' is the storage modulus and E'' the loss modulus. Both components affect the fatigue crack growth process. The storage modulus represents energy stored elastically with increasing values of E' leading to lower levels of cyclic deformation and associated fatigue damage. The loss modulus is a measure of energy dissipated within the solid and is often manifested by hysteretic heating of the specimen. The volumetric rate of heating, $\dot{\varepsilon}$, in a viscoelastic medium subjected to an alternating stress range, $\Delta\sigma$, at a cyclic frequency f is given as[1]

$$\dot{\varepsilon} = \pi f \frac{E''}{(E'^2 + E''^2)} \frac{(\Delta\sigma)^2}{4} = \pi f D'' \frac{(\Delta\sigma)^2}{4} \qquad (1)$$

where D'' is the loss compliance.

Such hysteretic heating can affect fatigue crack growth in different ways. When such heating is localized near the crack tip, it has been argued[2,3] that enhanced molecular motions near the crack tip often results in crack tip blunting and increased resistance to fatigue crack propagation (FCP). In such cases, an increase in the test frequency increases the amount of beneficial blunting and reduces FCP rates; the material's FCP resistance is said to be frequency-sensitive. Similarly, localized heating has been observed to affect the fast-fracture behaviour of poly(methyl methacrylate) (PMMA). Clutton and Williams[4] found that localized heating caused by fast fracture accounts for the increased fracture toughness observed with increasing crack speed in PMMA. They

were able to simulate such localized heating effects by externally heating the sample in the vicinity of the crack tip. Fatigue frequency sensitivity has also been attributed to frequency-induced changes in fracture toughness, K_c, storage modulus, E',[5] and yield strength, σ_{ys},[6] even though the crack tip experiences little, if any, temperature rise. While such frequency-induced changes in mechanical properties may influence behaviour in some cases, frequency-sensitive FCP response is observed in materials in which K_c and E' do not change to any great degree[7]. Such frequency effects may then be attributed to temperature increases.

In the absence of hysteretic heating, polymeric materials may exhibit zero FCP frequency sensitivity. Moreover, zero frequency sensitivity may occur even in the presence of crack-tip heating, provided the increased FCP resistance due to crack blunting is balanced by decreases in specimen modulus, E', which tend to lower FCP resistance. Using this argument, Bretz[8] explained why nylon-6,6 tested at room temperature showed little FCP frequency sensitivity despite measurable heating. Bretz further demonstrated the competing effects of crack blunting and modulus degradation by conducting tests of nylon-6,6 at 10 Hz with various levels of absorbed water. Nylon-6,6 absorbs up to 8.5 wt % water, which increases ductility and lowers yield strength. Imbibed water also raises the value of the glassy modulus initially and lowers the glass transition temperature[9]. Bretz found that the maximum in FCP resistance at 10 Hz occurred at 2.2 % water, and correlated this maximum for that water content with optimization of the complex modulus of the nylon; i.e. localized heating (governed by E'' or D'') was maximized in the nylon with 2.2 % water, and resulted in beneficial crack-tip blunting. Simultaneously, E' of nylon was also maximized at this water content. Therefore, an optimum combination of stiffness (E') and localized heating (E'' or D'') in the nylon with 2.2 % water contributed to a maximization in room temperature FCP resistance.

* Presently, General Research Corporation, 5383 Hollister Avenue, PO Box 6770, Santa Barbara, CA 93160-6770, USA.
** Also, Department of Metallurgy and Materials Engineering.
† Also, Department of Chemistry.
‡ Also, Department of Chemical Engineering.

The relative ranking of fatigue resistance as a function of absorbed water is expected to change with temperature, in parallel with the changes in the complex modulus. For example, the superior fatigue resistance at 23°C for nylon-6,6 with 2.2% water as compared with dry nylon-6,6 is lost when the material is tested at 52°C. In this instance, the temperature-induced decrease in E' for the nylon containing water is greater than that recorded in the dry nylon. Thus, the balance between localized heating and stiffness change is important in determining fatigue response. To study further the role of these two factors in determining FCP resistance, nylon-6,6 with a range of moisture contents was studied both above and below room temperature. The results are then compared with the associated changes in E' and D''.

EXPERIMENTAL

Materials

Injection-moulded plaques of nylon-6,6 (Zytel 101) $M_n = 17\,800$ [8,10] ($12.7 \times 7.5 \times 0.89$ cm), were obtained in the dry as-moulded (<0.2 wt% water) condition and stored in a dessicator prior to moisture conditioning or testing. Moisture conditioning procedures to obtain 2.6, 4.5 and 8.5 ± 0.1 wt% water absorption are described elsewhere[11,12]. After equilibration, all specimens were stored at the appropriate relative humidities until tested.

Constant-load fatigue crack propagation tests were conducted on pin-loaded wedge-open loading (WOL) specimens ($B = 8.9$ mm, $W = 50.8$ mm, $H = 24.7$ mm) using a closed-loop servohydraulic testing machine. The ratio of the minimum load to the maximum load, R, was 0.1 for all tests. Machined notches were sharpened with a razor blade prior to crack initiation at 50–100 Hz, with the loads and frequency being reduced until the test conditions were reached. Since crack initiation at high frequencies could cause significant specimen heating, specimens were allowed to cool for at least one hour before testing. For the low-temperature tests, special care was taken to reduce the loads as much as possible during precracking at room temperature. This was important since the yield strength increases with decreasing temperature, thereby making the plastic zone much smaller at low temperature. If the loads were not reduced sufficiently, a significant delay resulted in the continuation of crack propagation. The duration of the tests was not considered sufficient to alter the moisture level in the specimen bulk. Indeed, El-Hakeem and Culver[13] found only a slight difference in FCP behaviour from that in air when specimens were tested in water.

Crack growth measurements were typically made at crack growth intervals of 0.2–0.3 ± 0.01 mm, using a Gaertner travelling microscope. Load cycling was interrupted to make these measurements; since the specimen could cool during such hold periods, test interruptions were kept as brief as possible, usually 15–20 s.

Crack growth rates, da/dN, were calculated according to the modified secant method:

$$(da/dN)_i = (a_{i+1} - a_{i-1})/(N_{i+1} - N_{i-1}) \qquad (2)$$

where a_{i+1} and a_{i-1} are crack lengths in mm and N_{i+1} and N_{i-1} are the number of loading cycles at the $i+1$ th and $i-1$ th interval, respectively. Crack growth rate

values were then plotted as a function of the associated applied stress intensity factor range, ΔK. Tests were conducted at $-70°C$, $-33°C$, $0°C$, $23°C$ and $52°C \pm 2°C$ with non-ambient temperature tests being performed in an environmental chamber. The 52°C temperature was achieved by means of a rheostat-controlled electrical heating tape placed inside the chamber. For the low-temperature tests, a cylinder of nitrogen gas was used to pressurize a 20-litre Dewar bottle of liquid nitrogen. The temperature was regulated by controlling the resulting flow of cold nitrogen gas from the Dewar. Temperature was monitored using a copper–constantan thermocouple which was taped to the specimen. A double window in the front of the chamber, filled with dry nitrogen gas, prevented fogging and allowed optical measurement of the crack. Dynamic mechanical spectra were obtained at 110 Hz using an Autovibron elastoviscosimeter, model DDV-III C.

RESULTS AND DISCUSSION

The fatigue crack growth rates in nylon-6,6 at $\Delta K = 2.5$ MPa m$^{1/2}$ are shown in *Figure 1* as a function of water content and test temperature. Tests were conducted at 50–100 Hz except at 22°C and 52°C where the frequency was set at 10 Hz. (The higher test frequency at the lower temperatures did not have a significant influence on crack growth rates.) It is clear that the relative ranking in FCP response of nylon-6,6 with the various moisture contents changes with temperature.

As summarized above, Bretz[8,10] showed that the influence of water on the FCP response of nylon-6,6 at room temperature was the result of the competing effects of crack blunting, which tends to retard FCP, and modulus degradation which tends to increase FCP rates. Owing to these competing factors, FCP rates at room temperature were a minimum at a water content of 2.6%, as shown in *Figure 1*. The dynamic mechanical data given in *Figure 2* are in agreement with this observation since, at room temperature, nylon with 2.6% water exhibits the highest storage modulus, and possesses a high value of loss compliance. The higher FCP rates in the nylon specimens with 4.0% and 8.5% water are due to their
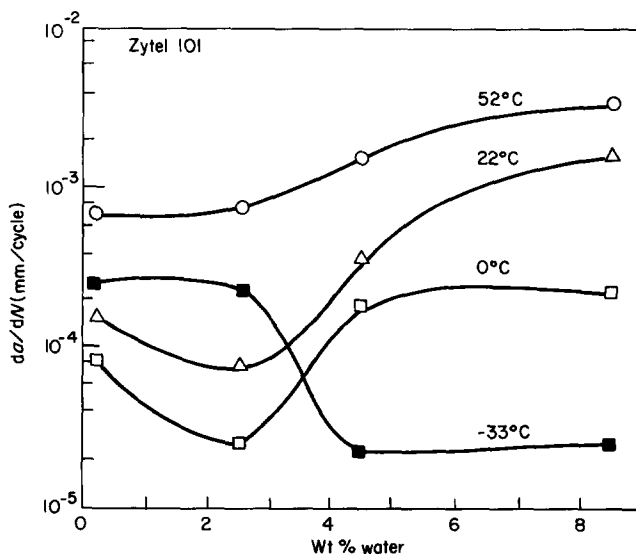

Figure 1 FCP rates at $\Delta K = 2.5$ MPa m$^{1/2}$ vs. water content for nylon-6,6 tested at (■) $-33°C$, (□) 0°C, (△) 22°C and (○) 52°C
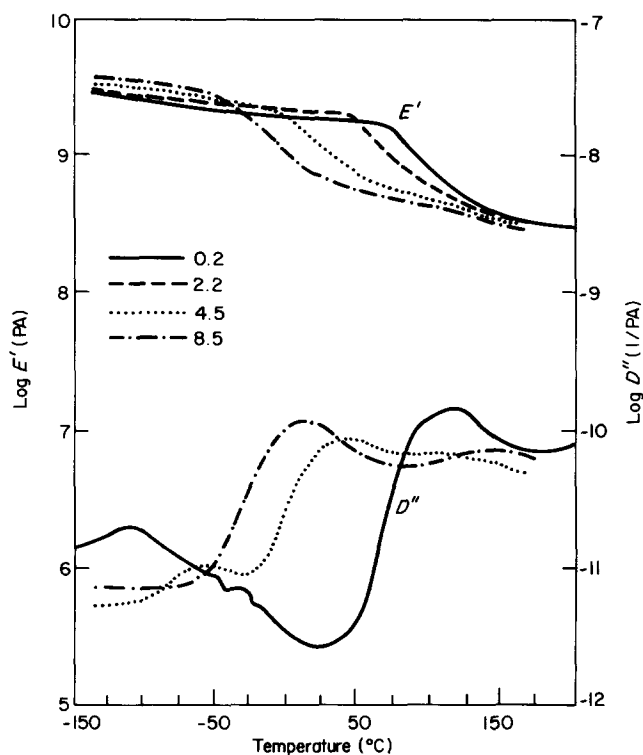
Figure 2 Effect of water on the modulus–temperature behaviour of nylon-6,6 $(M_n = 17\,000)$; (———) 0.2% H_2O; (———) 2.2% H_2O; (·····) 4.5% H_2O; (—·—·—) 8.5% H_2O in nylon-6,6

lower E', since the associated values of D'' do not differ substantially from D'' of nylon with 2.6% water*. Similar arguments are used to explain the observed FCP behaviour at 0°C. At 0°C, the persistent low FCP resistance of the nylon with 4.0 and 8.5% water is due to its relatively low modulus at this temperature.

Bretz[8,10] found that the superior FCP resistance at room temperature of the nylon with 2.6% water was eliminated when the test temperature was increased to 52°C, because the storage modulus of the nylon with 2.6% water decreased while the storage modulus of dry nylon remained essentially constant. *Figure 1* shows these FCP data along with fatigue data associated with water contents of 4.0 and 8.5%. The monotonic increase in FCP rates with increasing water content greater than 2% parallels the decrease in storage modulus with increasing water content.

At −33°C, a dramatic inversion in FCP rates occurs: FCP rates decrease monotonically with increasing water content. Since for any water content, the storage modulus of nylon is on the glassy plateau at this temperature, it is doubtful that E' controls the differences in FCP response. More likely, the decrease in FCP rates with increasing water content reflects the impact of increasing D'' with increasing water content. The greater D'' levels in the nylons with higher water contents would be expected to induce more crack blunting and result in reduced FCP rates. Thus, the changes in FCP behaviour of nylon as a function of water content and temperature are related to the values of E' and D''. The influence of E' is greatest at high temperatures while the influence of D'' is most important at low temperatures. Maximum FCP

---

*The higher crack growth rates at room temperature in the dry nylon samples (0.2% water) relative to that of nylon containing 2.6% water are attributed to the lower value of D'' in the dry sample.

resistance, therefore, occurs with an optimum combination of a high loss compliance so as to maximize crack blunting, and a high value of the storage modulus, which minimizes crack-tip strains.

An alternative method of data analysis is now considered. *Figure 3* shows FCP rates at $\Delta K = 2.5\,MPa\,m^{\frac{1}{2}}$ as a function of $1/T$ for the several water contents examined. If a single activated process had controlled fatigue response over this temperature range, then the plot of crack growth rate *versus* reciprocal temperature would have yielded a straight line with a slope proportional to the activation energy for the rate-controlling step. *Figure 3* shows that this is not the case. Although FCP rates decline steadily with temperature for the 4.0 and 8.5% water contents, the FCP rates of the nylon with 0.2 and 2.6% water reach a minimum at 0°C. These findings are consistent with fracture mechanism transitions noted as a function of test temperature for nylon containing water levels up to 2.6% whereas the same fracture mechanism was observed at all test temperatures with nylon samples containing 4.0 and 8.5% water[14]. Clearly there is no simple Arrhenius-type relationship to describe the FCP behaviour of nylon-6,6 samples with different water levels.

For water contents of 0.2 and 2.6%, the minima in growth rates observed at 0°C represent the optimum set of viscoelastic properties with respect to FCP resistance. Below 0°C, D'' decreases, while E' does not increase. For nylon with water contents of 4.0 and 8.5%, the decrease in growth rates as the test temperature decreases from 52°C to −33°C suggests that increases in D'' or E' or both are improving FCP resistance. This also suggests that if the temperature were decreased further, FCP rates would eventually increase, if decreases in D'' were no longer compensated for by increases in E'. This was indeed found to be the case: At −70°C, FCP rates in water-saturated nylon were greater than those recorded at −33°C. This decrease in FCP resistance is related to a decrease in D'' with E' remaining essentially constant.
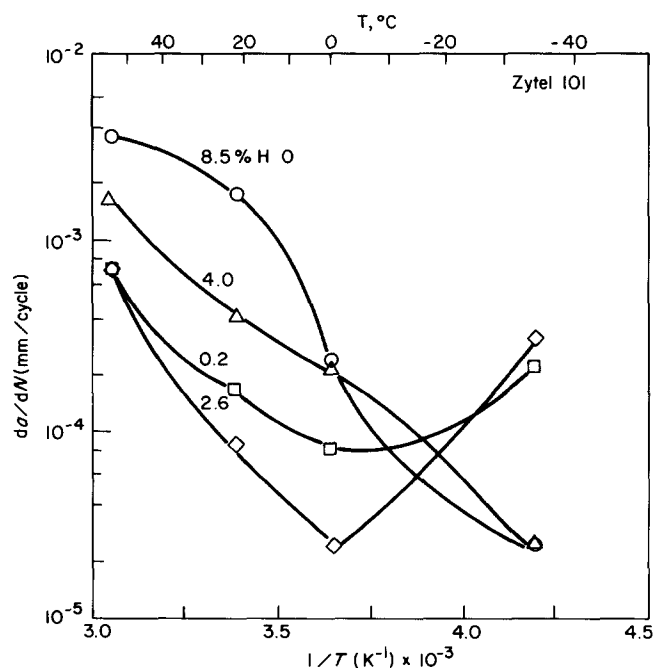

Figure 3 FCP rates at $\Delta K = 2.5\,MPa\,m^{1/2}$ vs. $1/T$ for nylon-6,6 with 0.2, 2.6, 4.0 and 8.5% water
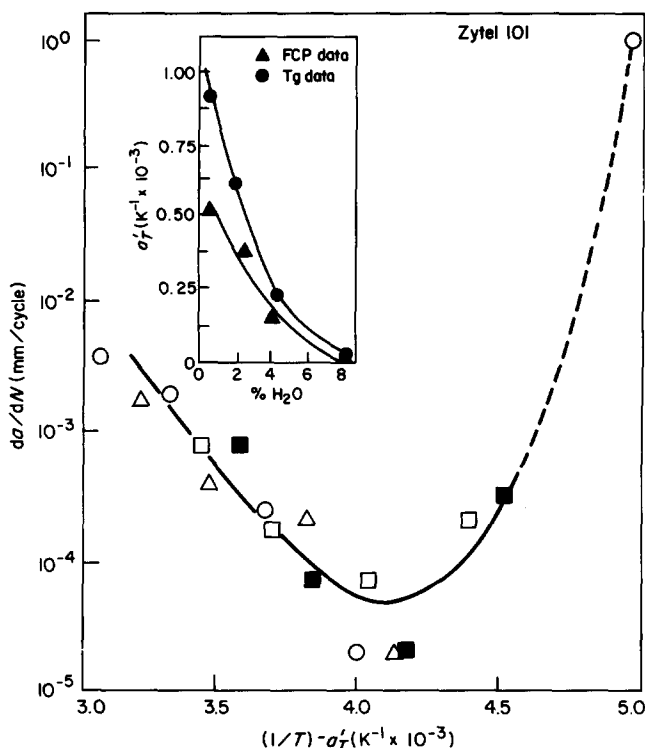
Figure 4 Master curve of da/dN vs. $1/T$, showing crack propagation approaches a minimum value at about 50 K below T_g, taking into account frequency, temperature and the quantity of absorbed water: ■, 0.2% H_2O; □, 2.6% H_2O; △, 4.0% H_2O; ○, 8.5% H_2O in nylon-6,6. Inset: comparison of shift factors a'_T (from FCP data) with a_T calculated from dynamic mechanical data: ●, T_g data; ▲, FCP data

The shapes of the individual curves in *Figure 3* suggested that the data might be segments of the same master curve. Accordingly, each curve was shifted by an arbitrary amount, a'_T, so as to give a best fit with the Da/dN vs. $1/T$ curve for nylon containing 8.5% water. The factors a'_T differ from the more commonly used shift factor a_T in that a_T has units of time divided by time, whereas a'_T has units of reciprocal temperature. Of course, time and temperature are related in this case through the time–temperature superposition principle[1]. The resulting master curve is shown in *Figure 4*; the shift factors, a'_T, are shown in the inset and compared to the shift in T_g as a function of water content. (The data point at the right in this Figure, which is connected to the rest of the data by the dashed line, represents a single test result at $-70°C$.) The shift in a'_T parallels the shift in T_g although the shift factors are not identical. (T_g as used here denotes the temperature at which a maximum in D'' and an inflection in E' is observed in viscoelastic tests at 110 Hz.) Since the data fall along a single curve and the associated shift factors, a'_T, vary in a manner consistent with the viscoelastic data, criteria for the use of the superposition principle[1] appear to be met, despite the unusual choice of

axes. It is concluded that for all water contents, maximum FCP resistance is realized when the test temperature is such that E' is still at or near the glassy value, but D'' is high enough to provide significant energy dissipation to retard crack growth.

As noted previously, a parallel change in fracture surface appearance from a brittle to ductile mode is also seen with temperature change and imbibed water level as these variables impact the viscoelastic behaviour[14].

CONCLUSIONS

The normalization of the fatigue crack propagation data shows that the effects of test temperature and absorbed water on FCP behaviour of nylon are both due to the influence of these variables on the viscoelastic state of nylon. In all cases, fatigue resistance is maximized by an optimum combination of E' so as to minimize fatigue damage and D'' values that maximize energy dissipation. The trend of empirical FCP shift factors a'_T parallels the trend in shift factors that normalize the viscoelastic data (i.e. T_g vs. % water), thereby supporting the validity of such an approach.

REFERENCES

1 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980
2 Skibo, M. D., Hertzberg, R. W. and Manson, J. A. 'Fracture 1977', 3 ICF 4, Waterloo, Canada, p. 1127, 1977
3 Hertzberg, R. W., Manson, J. A. and Skibo, M. D. *Polymer* 1978, **19**, 358
4 Clutton, E. O. and Williams, J. G. *J. Mater. Sci.* 1981, **16**, 2583
5 Williams, J. G. *J. Mater. Sci.* 1977, **12**, 2525
6 Lang, R. W., Manson, J. A., Hertzberg, R. W. and Schimer, R. *Polym. Eng. Sci.* 1984, **24**, 833
7 Hertzberg, R. W., Skibo, M. D., Manson, J. A. and Donald, J. K. *J. Mater. Sci.* 1979, **14**, 1754
8 Bretz, P. E., 'Fatigue Crack Propagation of Semicrystalline Polymers', *Ph.D. Dissertation*, Lehigh University, 1980
9 Kohan, M. I. 'Nylon Plastics', Wiley–Interscience, New York, 1973
10 Bretz, P. E., Hertzberg, R. W., Manson, J. A. and Ramirez, A. *ACS Symposium Series No.* 127, 531, 1980
11 Hahn, M. T. 'The Effect of Test and Material Variables on Fatigue Crack Propagation in Nylon-6,6 Blends', *Ph.D. Dissertation*, Lehigh University, 1983
12 Hahn, M. T., Hertzberg, R. W. and Manson, J. A. *J. Mater. Sci.* 1986, **21**, 31
13 El-Hakeem, H. A. and Culver, L. E. *Int. J. Fatigue* 1979, **1**, 133
14 Hahn, M. T., Hertzberg, R. W. and Manson, J. A. *J. Mater. Sci.* 1986, **21**, 39