

# Effects of rubbery phase and absorbed water on impact-modified nylon 66

## Part 1 Fatigue crack propagation response

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The fatigue crack propagation (FCP) response of impact-modified nylon was investigated as a function of rubbery second phase content and absorbed water level. Particular attention was given to the influence of these material variables on the amount of hysteretic heating as measured with an infrared microscope. FCP resistance was raised when heating was localized near the crack tip, but lowered by more generalized specimen heating. Variations in FCP behaviour were found to depend strongly on changes in the dynamic storage and loss moduli resulting from hysteretic heating, with the heating-induced modulus changes being more important than the absolute temperature increase of the sample. The combination of rubbery phase and absorbed water produced greater specimen heating and, in general, produced poorer FCP resistance than with the presence of either factor alone.

### 1. Introduction

The growing use of polymeric materials in structural applications makes it increasingly important to evaluate their mechanical properties, both static and dynamic. The latter are especially important since fatigue failures can occur when the response of a material to dynamic loading is not properly known. An important aspect of fatigue behaviour is the rate of growth of a crack from a pre-existent flaw or cracking, i.e. the crack propagation (FCP) rate. In this type of test the crack growth rate,  $da/dN$  (where  $a$  is crack length and  $N$  is the number of cycles), is measured as a function of the stress intensity range,  $\Delta K$ , which is a function of flaw size and geometry as well as stress range. Such data are often found to follow the Paris relation, at least over a range of  $\Delta K$

$$\frac{da}{dN} = A(\Delta K)^m \quad (1)$$

where  $A$  and  $m$  are constants.

As a consequence of their viscoelastic nature, certain polymeric materials undergo appreciable hysteretic heating when subjected to cyclic strain. For the case of an uncracked specimen uniaxially stressed in tension, Ferry [1] has expressed the rate of heat production as

$$\dot{\mathcal{E}} = \frac{\pi(\Delta\sigma)^2 D'' f}{4} \quad (2)$$

where  $\dot{\mathcal{E}}$  is the volumetric rate of heat production ( $\text{MW m}^{-3}$ ),  $\Delta\sigma$  is the stress range ( $\text{MN m}^{-2}$ ),  $D''$  is the loss modulus ( $\text{m}^2 \text{MN}^{-1}$ ) and  $f$  is the test frequency (Hz).

For the case of a specimen containing a crack, Barenblatt *et al.* [2] derived the following equation

$$\Delta \dot{T} = \pi f (\Delta K)^2 D'' \Psi(\theta) / 4rh \quad (3)$$

where  $\Delta \dot{T}$  is the rate of temperature rise ( $\text{K sec}^{-1}$ ),  $\Delta K$  is the stress intensity rate ( $\text{MPa m}^{1/2}$ ),  $r, \theta$  are spherical coordinates with origin at crack tip,  $\Psi(\theta)$  is a function of  $\theta$  and  $h$  is the heat transfer coefficient ( $\text{MJ m}^{-3} \text{sec}^{-1}$ ).

The decrease in FCP rates with increasing test frequency observed in several polymeric materials has been explained in terms of localized heating which acts to blunt the crack tip [3, 4]. In agreement with this explanation, the FCP frequency sensitivity (defined as the decrease in FCP rate for a decade increase in frequency) was seen for a number of polymeric materials to be maximized in the region of the beta transition where  $D''$  and thus the heating would be expected to be maximized. More recently, Lang [5] concluded that FCP frequency sensitivity in certain polymers was related to the influence of frequency on the nature of cyclic deformation within the damage zone of the crack.

Although localized heating increases FCP resistance, large-scale heating can reduce FCP resistance. Hertzberg *et al.* [6] tested impact-modified nylon 66 and found that FCP rates increased with increasing frequency from 1 to 30 Hz. These investigators explained this negative frequency sensitivity in terms of a reduction of the effective modulus of the sample as a result of large-scale heating. This decreased modulus, in turn, led to increased strain per cycle and, consequently, greater cyclic damage.

In the earlier study of impact-modified nylon 66 [6], the dependence of crack growth rates at 10 Hz on the amount of toughening phase was found to be complex. At low values of  $\Delta K$ , the crack growth rates were lowest in the blends with large amounts of toughening phase. However, at high values of  $\Delta K$ , crack growth

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TABLE I Elevated-temperature equilibration of nylon 66

Relative humidity (%)	Wt % H <sub>2</sub> O in nylon	Treatment
50	2.6	Immersed in boiling saturated potassium acetate solution for 100 h
66	4.0	Immersed in boiling saturated sodium phosphate solution for 100 h
100	8.5	Immersed in boiling water for 138 h

rates were lowest in the blends with only small amounts of toughening phase. These results suggested the existence of beneficial, localized heating at low  $\Delta K$  levels, and detrimental, generalized heating at high  $\Delta K$  levels. In support of this hypothesis, the beneficial effect of the toughening phase persisted to higher levels of  $\Delta K$  with decreasing test frequency, thereby reflecting a shift in the balance between beneficial and detrimental specimen heating. It should be noted that the toughening phase also affects the fatigue resistance by decreasing the modulus of the blend. When the FCP data were normalized by dividing the applied stress intensity factor by the room-temperature modulus, the blend with the most impact-modifying phase exhibited the greatest FCP resistance.

In the absence of significant hysteretic heating, polymeric materials often exhibit zero FCP frequency sensitivity. However, zero frequency sensitivity may also occur in the presence of crack-tip heating, provided that the increased FCP resistance due to heating-induced crack blunting is balanced by a decrease in the storage modulus,  $E'$ . On this basis, Bretz and co-workers [7, 8] rationalized the lack of any appreciable FCP frequency sensitivity of room-temperature experiments involving nylon 66. Bretz [7] further demonstrated the competing effects of crack blunting and modulus degradation by conducting tests of nylon 66 at 10 Hz with various levels of absorbed water. The absorption of up to 8.5 wt % water serves to increase ductility while lowering yield strength, glassy modulus and glass transition temperature [9]. Bretz found that the maximum FCP resistance of nylon 66 at 10 Hz occurred when the polymer contained 2.2% water, and correlated this with a transient increase in the dynamic modulus of the nylon, associated with an antiplasticizing effect. Moreover, localized heating, which would enhance crack-tip blunting, was maximized in the nylon with 2.2% water.

Therefore, FCP resistance was maximized since both room-temperature modulus and damping properties were optimized in the nylon with 2.2% water.

The objective of this work was to examine how FCP of impact-modified nylon 66 is affected by the combined presence of rubber and water, particularly as

these additions influence creep and hysteretic heating. An evaluation was also made of the viscoelastic state of the material (as implicit in values of  $D''$  and  $E'$ ) and how these properties are influenced by temperature, the amount of imbibed water in the nylon, and the amount of modifying phase.

## 2. Experimental procedures

### 2.1. Material preparation

Injection-moulded plaques of the materials used in this study, 12.7 cm  $\times$  7.5 cm  $\times$  0.89 cm, were obtained in the dry as-moulded condition and stored in a dessicator prior to use. The compositions of the plaques included neat nylon 66 (N66) (Zytel 101), impact-modified nylon 66 (HI-N66) (Zytel ST-801), and blends of HI-N66 and N66 containing 25, 50 and 75% HI-N66. The blend HI-N66 consists of approximately 20 vol % of a rubbery polymer added to Zytel 101 for increased toughness [10]. The characterization of this material was reported on in a previous paper [11].

Specimens were fatigue-tested with moisture contents ranging from the dry as-moulded condition (< 0.2 wt %) to the fully-saturated state (8.5 wt %). Since the method of water equilibration may itself have an influence on FCP behaviour [7, 12, 13], specimens were equilibrated either at elevated temperature or at room temperature. To equilibrate at elevated temperature, plaques of nylon were immersed in boiling water or in various boiling salt solutions, thereby achieving the range of relative humidities and equilibrium water contents shown in Table I [14, 15]. The time required for equilibration was selected based on the thickness of the plaques [14].

For equilibration at room temperature, the plaques were stored in jars above water or saturated salt solutions at room temperature ( $24^\circ \pm 2^\circ \text{C}$ ) for approximately two years. The range of relative humidities and moisture contents obtained through this procedure is shown in Table II. The moisture contents given in Tables I and II represent essentially the amount of water absorbed in the nylon since the impact-modifying phase does not absorb a significant amount of water. After equilibration, all specimens were stored at the appropriate relative humidities until testing.

TABLE II Room-temperature equilibration of nylon 66

Relative humidity (%)	Wt % H <sub>2</sub> O in nylon	Treatment
0	0.2	Dry as-moulded
31	1.0	Suspended over saturated calcium chloride solution
43	2.0	Suspended over saturated potassium carbonate solution
66	4.0	Suspended over saturated sodium nitrite solution
100	8.5	Suspended over water

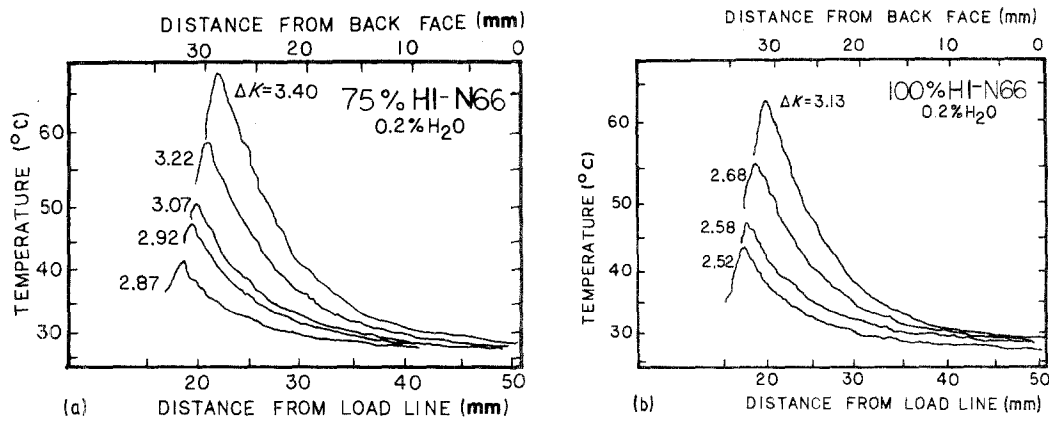


Figure 1 Temperature profiles recorded during FCP tests of (a) 75% and (b) 100% HI-N66 (0.2% water).

## 2.2. Fatigue crack propagation test procedures

Pin-loaded wedge-open loading (WOL) specimens ( $B = 8.9$  mm,  $W = 50.8$  mm,  $H = 24.7$  mm) were used for the FCP tests with the tensile axis oriented parallel to the moulding direction. Two WOL specimens were cut from each plaque; however, because a previous study of the modified nylons [6] had shown that FCP behaviour was isotropic, no effect of orientation was expected.

The  $K$ -calibration for the WOL specimen is given as [16]

$$K = PY\alpha/BW^{1/2} \quad (4)$$

where  $P$  is load (N),  $W$  is specimen width (m),  $B$  is specimen thickness (m) and  $a$  is crack length (m); also

$$Y = 0.8072 + 8.858 (a/W) - 30.23 (a/W)^2 \\ + 41.088 (a/W)^3 - 24.15 (a/W)^4 \\ + 4.951 (a/W)^5$$

and

$$\alpha = \frac{2 + (a/W)}{[1 - (a/W)]^{3/2}} \quad (6)$$

FCP tests were conducted at a cyclic frequency of 10 Hz using a closed-loop servohydraulic testing machine. The ratio of the minimum to the maximum load,  $R$ , was 0.1 for all tests. Tests were run at room temperature in laboratory air. The duration of the tests was not considered sufficient to alter the moisture level in the specimen bulk. Indeed, El-Hakeem and Culver [17] found only a slight change in FCP behaviour when specimens were tested when immersed in water. Machined notches were sharpened with a razor blade prior to crack initiation under cyclic loading at 50 to 100 Hz, with the loads and frequency being reduced until the test frequency was reached. Since crack initiation at high frequencies could cause significant specimen heating, specimens were allowed to cool for at least one hour prior to the collection of FCP data.

Crack growth was measured with a travelling microscope, typically at crack growth intervals of 0.2 to 0.3 mm. 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 to 20 sec. Crack growth rates,

$da/dN$ , were calculated according to the modified secant method

$$(da/dN)_i = (a_{i+1} - a_{i-1}) / (N_{i+1} - N_{i-1}) \quad (7)$$

and plotted as a function of the applied stress intensity factor range,  $\Delta K$ .

An infrared microscope was modified to allow for semi-automatic measurements of the surface temperature along the crack plane of the sample during the FCP tests. Experimental details are discussed elsewhere [18].

## 3. Experimental results

Specimen heating was observed in all tests of the nylon blends. Fig. 1 shows typical records of specimen temperature profiles during a fatigue test. The maximum temperature (approximately coincident with the crack tip) and temperatures remote from the crack tip both increased during a test, since the stress intensity factor increased with increasing crack length (see Equation 3). The greater net-section stress, acting on the decreased cross-sectional area of the unbroken ligament, also contributed to greater specimen heating (Equation 1) along with decreased heat transfer associated with the smaller unbroken ligament dimension. Fig. 1 also shows that, for most of the test, heating is localized near the crack tip; bulk heating of the specimen occurs only at higher  $\Delta K$  levels. In addition, note that the heating at a given  $\Delta K$  is higher for the material with the higher rubber content.

Figs. 2a to d show the crack growth rates,  $da/dN$ , as a function of the stress intensity range,  $\Delta K$ , for the four blends at four different water contents; also included for comparison are data for unmodified nylon 66 [7]. These results show that, for all water contents above 1%, FCP rates increased with increasing rubber content above that which occurs in the blend containing 25% HI-N66. It should be noted, however, that the overall fatigue resistance of the modified nylons was generally superior to that of unmodified nylon.

Fig. 3 shows the corresponding plots of maximum temperature rise,  $\Delta T$ , as a function of  $\Delta K$ . These data show that heating increased with increasing water content to 2.6%; little additional heating occurred at higher water levels. The maximum in heating with a water content of 2.6% is related to the peak in  $D''$ ,

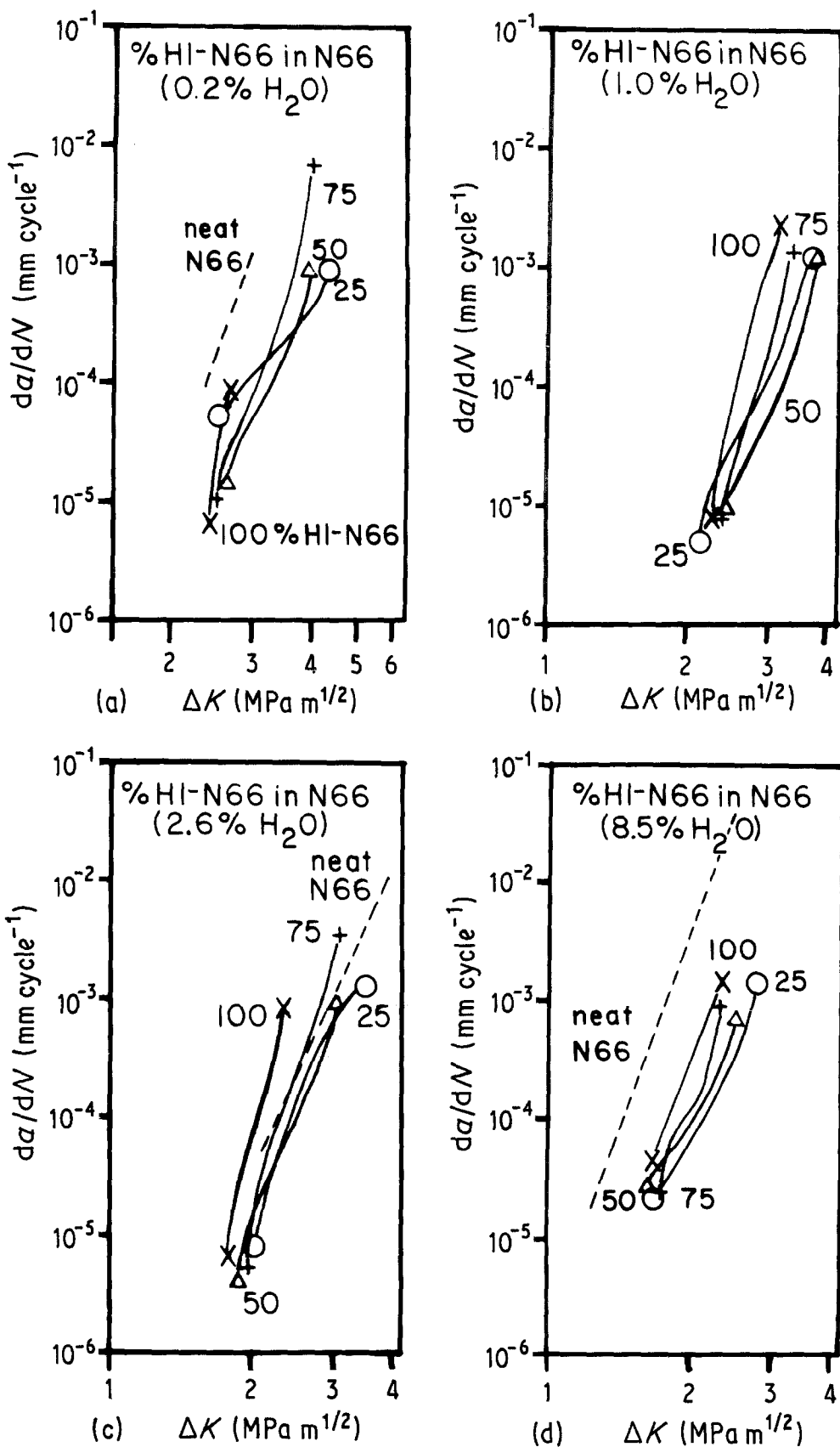


Figure 2 FCP response at 10 Hz of HI-N66 blends with (a) 0.2% water dry as-moulded; (b) 1.0% water, equilibrated at room-temperature; (c) 2.6% water; and (d) 8.5% equilibrated at elevated temperature. Nylon 66 data from Bretz *et al.* [7, 8, 12]. (Individual data points given in Hahn [19], but omitted here for clarity.)

which occurs near room temperature for that water content (see Fig. 7 in Section 4). The temperature plots show that  $\Delta T$  has a strong, linear dependence on  $\Delta K$  and not on  $(\Delta K)^2$ , as expected from Equation 3. The lack of agreement with Equation 3 is not surprising since conditions for the dependence on  $(\Delta K)^2$  are not met; specifically,  $D''$

varies with temperature, and the heated zone is not small compared to the size of the sample. Nonetheless, Equation 3 may be used qualitatively in discussing the data.

#### 4. Discussion

As noted above, the FCP response of nylon 66 and its

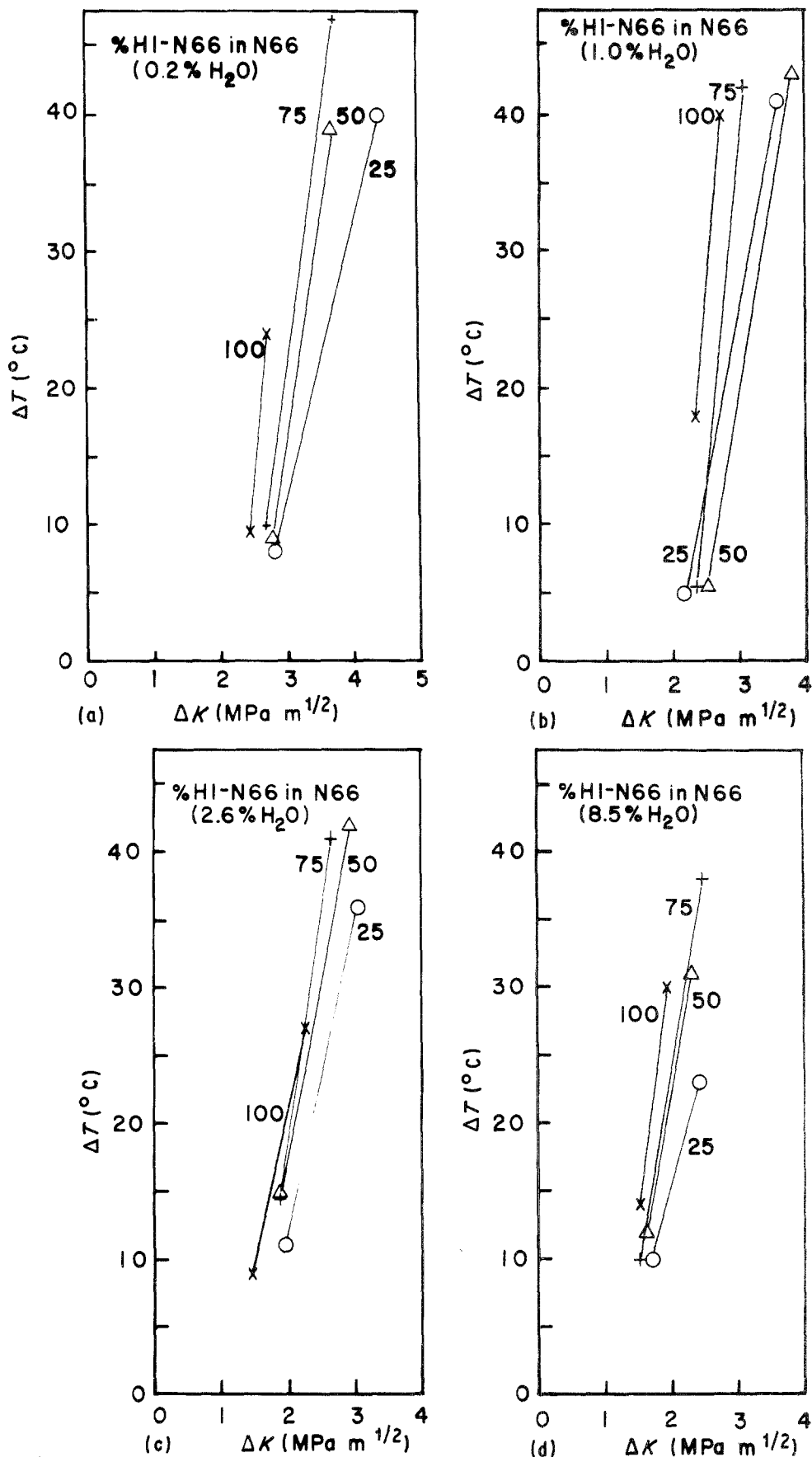


Figure 3 Temperature maxima recorded during FCP test at 10 Hz of HI-N66 blends. (a) 0.2%, (b) 1.0%, (c) 2.6% and (d) 8.5% water.

blends is strongly influenced by the amounts of rubbery phase and absorbed water. This arises from their associated influence on both the storage and loss components of the dynamic modulus [9, 11]; additions of  $> 2.2\%$  water and rubbery phase to nylon 66 both lead to a reduction in storage modulus at room temperature. At the same time, the associated increase in

the loss modulus causes more hysteretic heating, which leads to a further reduction in storage modulus. The amount by which the storage modulus decreases is determined both by the amount of heating and the rate of modulus change with temperature,  $dE'/dT$ . In turn, the amount of heating is related to the room temperature value of  $D''$ , which determines the initial

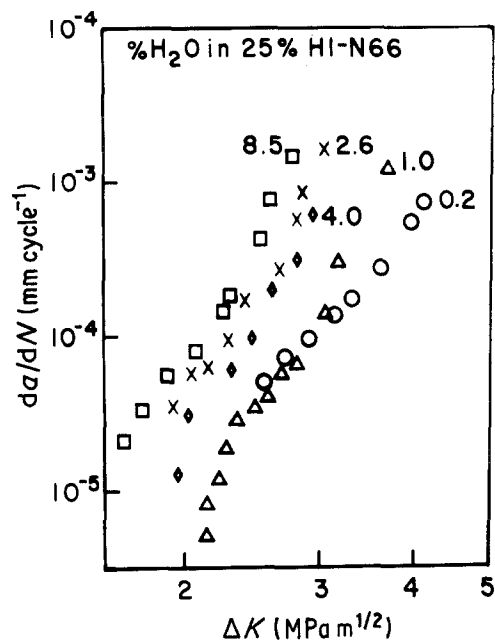


Figure 4 Effect of absorbed water on FCP response at 10 Hz for 25% HI-N66. (Some data points omitted for clarity.)

rate of heating (Equations 2 and 3), and to  $dD''/dT$ , which reflects how the heating rate changes with temperature.

Since water strongly affects the glass transition temperature  $T_g$ , the influence of water on FCP behaviour should be related to changes in the room-temperature modulus, as well as to hysteretic heating. Recall that Bretz [7, 8] found that for neat nylon 66, FCP rates at a given  $\Delta K$  are lowest for a water content of 2.2%. This growth rate minimum attributed to a combination of crack blunting induced by hysteretic heating and a slight increase in the room-temperature modulus, both increasing FCP resistance. In contrast, Figs. 4 and 5 show that FCP resistance in the nylon blends decreases monotonically with increasing water content. There is one exception to this trend: at low  $\Delta K$ , the material containing 25% HI-N66 in the dry

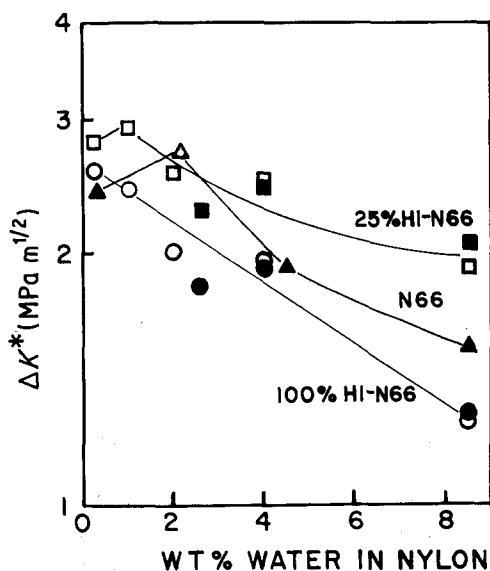


Figure 5 Dependence of  $\Delta K$  for  $da/dN = 10^{-4}$  mm cycle $^{-1}$  on water content for 0, 25 and 100% HI-N66. Filled symbols: equilibrated at elevated temperature. Open symbols: equilibrated at room-temperature.

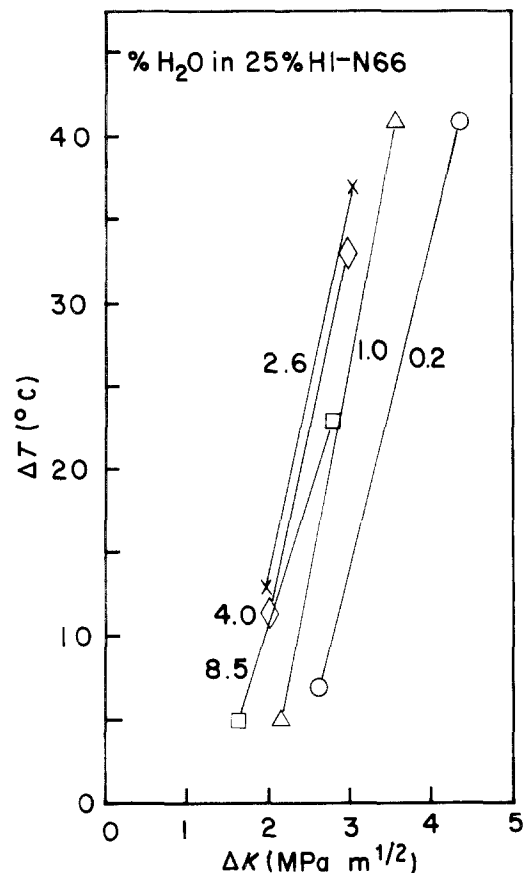


Figure 6 Temperature maxima recorded during FCP test at 10 Hz for 25% HI-N66.

condition exhibited higher FCP rates than when the material contained 1% water. However, at stress intensity ranges of  $\geq 3$  MPa m $^{1/2}$ , the crack growth rates for this material containing 1% water are greater than for the dry material. These differences are attributed to different levels of hysteretic heating generated in the two materials at different  $\Delta K$  levels.

The increase in the room-temperature storage modulus for water contents of up to 2.6% should, by itself, improve FCP resistance. However, hysteretic heating takes place to an increasing degree with the addition of up to 2.6% water (Fig. 6). The observed decrease in FCP resistance in this regime can, therefore, be attributed to a reduction in modulus induced by hysteretic heating. With water contents above 2.6%, FCP rates increase further, as seen in Fig. 4. However, this increase in FCP rates occurs without an increase in specimen heating above that associated with the presence of 2.6% water (Fig. 6). In this instance, the increasing crack growth rates are related to a drop in the dynamic modulus with increasing water content. For nylon with more than 2.6% water, decreased heating would be expected from viscoelastic data [13]. From Fig. 7, we see that for nylon with water contents greater than 2.6%, the loss compliance at room temperature large but  $dD''/dT$  is negative; thus,  $D''$  and the rate of heating should both decrease with increasing temperature.

Let us now consider the effects of this heating on the modulus. Fig. 7 shows that the room-temperature storage modulus decreases as the water content increases above 2.6%. A further drop in modulus

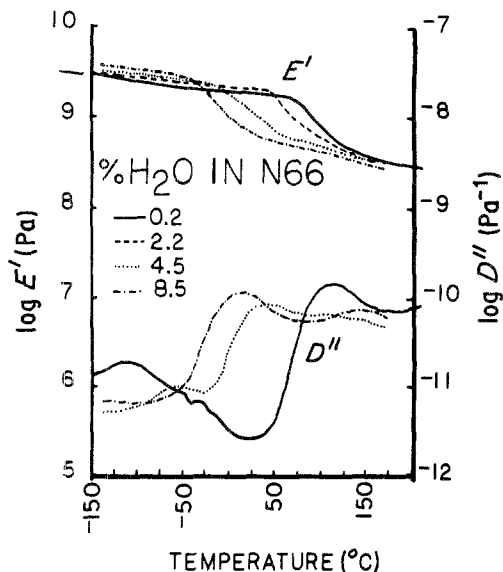


Figure 7 Dynamic spectra of Zytel 101 with < 0.2, 2.2, 4.0 and 8.5% water (equilibrated at elevated temperature).

takes place in conjunction with hysteretic heating. Thus, although less hysteretic heating takes place in the nylons with water contents of 4.0 and 8.5%, the consequences of this heating are greater. The higher FCP rates (as compared to the nylons with lower water contents) are a result of the heating-induced decrease in the modulus. For this reason, the effect of heating on the modulus, and not the *absolute* amount of heating, is the controlling factor with respect to FCP resistance.

Consider next the effect of water on the relative ranking of FCP rates in the 25, 50, 75 and 100% HI-N66 blends. Fig. 3a shows that increases in temperature are greater with increasing amounts of modifying phase. This is related to the viscoelastic data. It is seen from Fig. 8 [13] that an increase in the amount of the modifying phase does not shift the glass transition, but does lower the storage modulus and raise the loss compliance. Thus the enhanced heating is due to the increase in  $D''$  with greater amounts of HI-N66. Fig. 2a shows that, for the dry material, the richer blends have better FCP resistance at low  $\Delta K$  while the leaner blends show better FCP resistance at high values of  $\Delta K$ . Note that unmodified nylon has the highest FCP rates over the entire  $\Delta K$  range. The changes in the relative FCP resistance shown in Fig. 2a thus indicate that, for the richer blends, the amount of heating generated during the test improves FCP resistance at low  $\Delta K$ , but diminishes FCP resistance at high  $\Delta K$  levels where substantial lowering of the specimen stiffness occurs.

In the HI-N66 blends with 1% water (equilibrated at room temperature), Fig. 2b shows that the material containing 50% HI-N66 has the greatest FCP resistance over most of the  $\Delta K$  test range. The 25% material containing HI-N66 exhibited the highest FCP rates at low values of  $\Delta K$ , but has FCP rates equal to the 50% HI-N66 at high  $\Delta K$  values. Moreover, with a water content of 1% the superior fatigue resistance of the richer blends vanishes at lower  $\Delta K$  values than for the dry material. This is related to the greater amount of heating in the blends with 1%

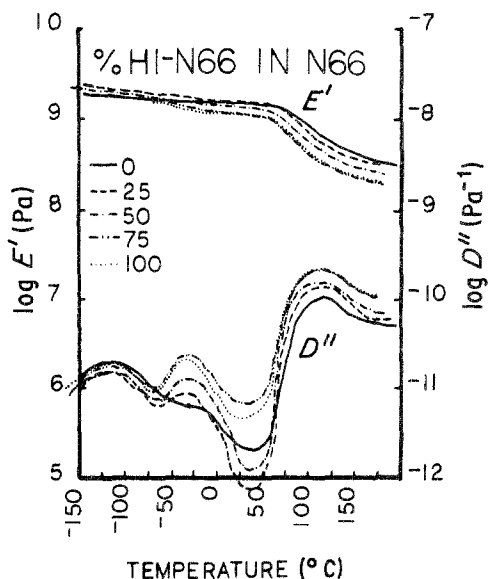


Figure 8 Dynamic spectra of dry as-moulded Zytel 101 and 25, 50, 75 and 100% HI-N66.

water, as shown in Fig. 3b. This greater level of heating causes the transition from beneficial to detrimental heating to occur at lower  $\Delta K$  levels.

The specimens with 2.6% water (equilibrated at elevated temperature) show still greater amounts of heating (Fig. 3c) which further compromised the beneficial effect of the rubbery phase. Fig. 2c shows that for a water content of 2.6%, the 100% HI-N66 had the highest FCP rates throughout the entire  $\Delta K$  range. Further, while the FCP rates of 75, 50 and 25% HI-N66 were similar at low values of  $\Delta K$ , the FCP rates increased with increasing rubber content at high values of  $\Delta K$ . Ultimately, the unmodified nylon (2.6% water) had nearly the best FCP resistance when tests were performed in the highest  $\Delta K$  regime (Fig. 2c). This lack of beneficial effect of rubber on FCP resistance at high  $\Delta K$  levels is related to the significant amount of heating generated in the HI-N66 blends.

A similar monotonic increase in FCP rates with rubber content is noted for the specimens with 8.5% water (Fig. 2d). Although less heating occurs at this water content (Fig. 3d), the heating still has a substantial effect because of the temperature shift of the storage modulus caused by the absorbed water (Fig. 7). Once again, the *absolute* amount of heating is not the controlling factor. No consistent variation in the FCP rates was noted as a function of the method of water equilibration (Fig. 5). The lack of an appreciable effect of the equilibration method on the FCP response suggests that moisture equilibration at elevated temperature will satisfactorily predict the effects of equilibration at room temperature.

In summary, the effect of water content on the relative ranking in FCP of the 25, 50, 75 and 100% HI-N66 blends is related to the specimen temperatures observed. At low water levels and low values of  $\Delta K$ , heating is beneficial, and blends with more rubber (or HI-N66) show the best FCP resistance. In this regime, heating is localized and contributes to crack-tip blunting which lowers the effective  $\Delta K$  level. Increases in the water content and/or the  $\Delta K$  level result in greater heating which appears to be

detrimental to fatigue resistance; consequently, at high  $\Delta K$  or high water content, blends with a higher rubber content have poorer FCP resistance. Since rubbery additions and extensive hysteretic heating bring about a substantial reduction in  $E'$  – the major cause for lowered FCP resistance in the rich blends containing water – it is interesting to note that when  $\Delta K$  is normalized with respect to the elastic modulus, the richer blends exhibited greater resistance to cyclic strain [19]. This finding is consistent with that reported by Hertzberg *et al.* [6] and by Bretz and co-workers [7, 8].

In a previous paper [11], it was noted that the spherulite size of the modified nylons ( $\sim 1 \mu\text{m}$ ) was much smaller than the unmodified nylons (10 to  $20 \mu\text{m}$ ). A finer spherulite size, by itself, has been demonstrated to result in superior FCP resistance [20, 21], although this is not always the case [22]. The question then arises as to whether the generally superior FCP response of the modified nylons is the result of the finer spherulite size or of the rubbery addition itself. Any possible beneficial effect of the finer spherulite morphology on FCP behaviour appears to be overwhelmed by the effect of the rubbery phase, since several mechanical properties do appear to be dominated by the rubbery phase. For example, the modulus and yield strength are lower at the higher HI-N66 contents, the reverse of the behaviour expected with a smaller spherulite size alone, as discussed by Kohan [9]. Further, the blends heat up considerably more than the unmodified nylon, although a finer spherulite size has been shown to decrease the level of hysteretic heating [20]. It would appear that rubber additions lead to improved FCP resistance at low  $\Delta K$  in spite of the fact that  $E'$  for the blend is lowered. Energy dissipation due to microvoid formation and subsequent coalescence in association with the rubbery particles contributes to attenuated FCP rates [23]. At high  $\Delta K$  levels, however, the level of heating is much greater and its impact on FCP resistance is decidedly deleterious.

## 5. Conclusions

The results show that changes in the viscoelastic state of nylon resulting from the addition of rubbery phase or absorbed water influence the FCP behaviour, not only by changing  $D''$  and  $dD''/dT$  and thus the rate of heating, but also by changing  $E'$ . The FCP response is sensitive to temperature changes with respect to  $T_g$  and not absolute temperature change. As a result, the FCP resistance of a given nylon blend generally decreases with increasing water content. The fatigue response of rubber-modified nylons appear to be independent of the method of water equilibration.

The amount of rubbery phase added in the commercial material, 20 vol %, is optimized for impact fracture resistance but not necessarily for fatigue resistance. The optimum rubber content for a given

application will depend on a number of factors, including stress or strain range, ambient humidity and temperature, and cyclic frequency.

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