Fatigue crack propagation in crystalline polymers: effect of moisture in nylon 66

P. E. BRETZ, R.W. HERTZBERG, J.A. MANSON *Materials Research Center, Lehigh University, Bethlehem, PA 18015, USA*

As part of a study of the effects of crystallinity on fatigue crack propagation (FCP) behaviour in crystalline polymers, the FCP response of nylon 66 was examined as a function of both stress intensity factor range (ΔK) and water content. It was found that FCP rates were exponential functions of ΔK , as expected. However, the FCP rates at constant ΔK decreased as the water content was increased to about 3%; at saturation (8% water), the FCP rates were higher than that observed in dry specimens. Results were interpreted in terms of the incorporation of tightly bound water up to a maximum of one water molecule per two amide groups (at \sim 2% water), followed by the incorporation of loosely bound water (at saturation). The tightly bound water evidently toughens the polymer, while the loosely bound water has a predominantly weakening effect. Examination of fracture surfaces revealed a transition from terminal unstable crack growth (at water contents up to 3%) to tearing (at saturation). Classical fatigue striations were observed only in the specimens containing 2% water $-$ the first time such striations have been unequivocally identified for any crystalline polymer.

1. **Introduction**

Fatigue crack propagation (FCP) in polymers is of increasing concern to both scientists and engineers. Since many service conditions involve cyclic or repetitive loads (which are inherently more damaging than equal static ones), an understanding of fatigue behaviour is important in the selection of materials and in the design of parts. The crack propagation phenomenon is especially important for all real materials containing pre-existent flaws that may, under appropriate loading conditions, develop into catastrophic cracks [1, 2]. At the same time, the relationship between polymer structure, composition, and morphology and the kinetics and energetics of failure is of fundamental physico-chemical interest,

For these reasons, an extensive programme was developed in this laboratory to discover the role of polymer chemistry in fatigue, and to identify the molecular micromechanisms involved [3-9]. As the investigation proceeded, it was noted that as a group, crystalline polymers [in particular, nylon 66, polyacetal, and poly(vinylidene fluoride)] exhibited both higher fracture toughness values and lower FCP rates (at a given cyclic load range) than amorphous or poorly crystalline polymers. However, since only a few FCP studies of limited scope had been reported on crystalline polymers here and elsewhere [3,9, 10], a more detailed exploration of the effects of structural and morphological parameters was begun, with emphasis on the effects of molecular weight, crystallinity, and crystalline texture on FCP *per se* and on the mechanisms of failure. Because of their especially high resistance to FCP, nylon 66 and poly(vinylidene fluoride) were selected for preliminary investigation; this paper is concerned with nylon *66.*

The selection of a polyamide such as nylon 66 necessarily brings in an additional question: interaction with sorbed moisture. Effects of moisture on the mechanical behaviour of polyamides have long been known, and have been reviewed by McCrum *et al.* [11], Papir *et al.* [12], and Kohan [13]; effects on the ultimate behaviour of nylon 66 are also summarized in the trade literature [14]. Thus in general, Young's modulus and yield strength tend to decrease, while impact toughness tends to increase, with increasing water content.

0022-2461/79/102482-11 \$03.10/0 © 1979 Chapman and Hall Ltd.

Dynamic mechanical spectroscopy and other studies provide evidence that water exists in both tightly bound and weakly bound states [12], and it has been shown that many properties exhibit a transition when water content exceeds the ratio of one water molecule per two amide groups (corresponding to tightly bound water).

Less is known about the effects on fatigue. Fatigue tests on unnotched specimens [14] are reported to indicate that the fatigue strength (the stress corresponding to failure at a given number of cycles) can be reduced by as much as 30% when nylon 66 is equilibrated at 50% relative humidity (r.h.). Also, preliminary fatigue crack propagation (FCP) tests by Manson and Hertzberg [3] showed that "wet" nylon 66 samples that had been soaked in water for six weeks exhibited higher crack growth rates at a given stress intensity factor range than samples of the same polymer which had been vacuum dried. Since the exact moisture levels in these specimens were not measured and the tests were conducted at different cyclic frequencies, a quantitative relationship between water content and FCP behaviour was not established.

The objective of the research described in this paper was to establish base-line data for subsequent studies of FCP in nylon 66, and determine in detail the specific effect of moisture content on the fatigue crack propagation behaviour. In addition, fractographic analyses were made to identify fatigue micromechanisms in such a crystalline polymer for comparison with mechanisms reported in amorphous plastics. In addition, attention was given to noting any differences that might appear in the micromechanisms of fatigue fracture as a function of moisture content.

2. Experimental procedure

Injection-moulded plaques of nylon 66 [8.55mm (0.333in.) thick] were obtained in the dry, as-moulded condition through the courtesy of Dr E. Flexman, E. I. duPont de Nemours and Co. The grade concerned, Zytel 101, has a molecular weight of 17 000; the per cent crystallinity was about 50. These plaques had been sealed in plastic bags immediately after moulding to prevent moisture pick-up and were stored in a desiccator following the opening of the bags. Equilibration at higher moisture contents was performed according to the standard methods [14] outlined in Table I.

Fatigue crack propagation tests were performed on 73 mm \times 73 mm (2.9 in \times 2.9 in) tension speci-

TABLE I Moisture conditioning procedure for nylon 66

r.h. $(\%)$	wt% H_2O^*	Method
0	< 0.2	As-received
23	$0.8 - 0.9$	Suspended for 24 h above a boiling, saturated NaBr solution
50	2.6	Boiled for 48 h in a saturated KC ₂ H ₂ O ₂ solution
100	8.5	Boiled for 138 h in water
*See [14].		

mens that had been machined from the plaques. An electrohydraulic closed-loop test machine was used to produce a constant-amplitude, 10Hz sinusoidal load. All tests were performed in duplicate at room temperature in laboratory air at an average ambient relative humidity of 40%. In view of the slow rate of moisture equilibration in air at room temperature [14], the difference between the ambient r.h. and that of the nylon being tested was presumed to be unimportant within the time period of the test $(3 \text{ to } 5 \text{ h})$.

Crack growth rate data were analysed to compare the incremental crack growth rate per cycle, da/dN, with the applied stress intensity factor range at the crack tip, ΔK . The value of ΔK is given by

$$
\Delta K = Y \Delta \sigma \sqrt{a} (\text{MPa m}^{1/2}), \quad (1)
$$

where $\Delta \sigma$ = applied remote stress range (MPa)

 $a =$ crack length (m) $Y =$ geometric correction factor

Test results revealed that da/dN depended on ΔK with a relationship of the form

$$
\frac{\mathrm{d}a}{\mathrm{d}N} = A(\Delta K)^m. \tag{2}
$$

Crack-length readings were recorded with the aid of a calibrated travelling optical microscope equipped with a $50 \times$ eyepiece. Since the nylon 66 samples were opaque, each crack length reading corresponded to the intersection of the crack front with the free surface of the specimen. This allows for an accurate measurement of crack length when the crack profile is uniform across the sample thickness, as was the case in samples equilibrated at zero and 23 per cent relative humidity. Specimens equilibrated at 50 and 100 per cent relative humidity, however, developed parabolic-shaped

cracks with the crack length at mid-thickness extending as much as several millimetres further than the corresponding crack position at the two free surfaces. Furthermore, the crack profile was seen to become more parabolic at higher ΔK levels, associated with a greater tendency towards a plane-stress condition. For this reason, it was desirable to redetermine the ΔK and $d\alpha/dN$ values originally computed in order to account for the *average* crack lengths being greater than the value inferred from the surface measurement alone. To accomplish this, the effective crack length associated with a particular surface crack length measurement was determined by averaging five separate crack-length readings at locations roughly 5, 30, 50, 70 and 95 per cent of the distance across the specimen thickness. It was possible to carry out this procedure only in the 50% r.h. sample since this specimen alone showed clear crack front profiles corresponding to instances where the test machine was stopped to allow time for a crack tip reading.

Fractographic studies were conducted on an ETEC Autoscan scanning electron microscope (SEM) at an accelerating potential of 20 kV. Each fracture surface was coated with vacuum deposited layers of gold and carbon prior to examination to prevent specimen charging and minimize the degradation of the fracture surface under the electron beam.

3. Results and discussion

3.1. Effect of moisture on FCP rates

The crack growth rate responses of the nylon 66 samples containing different moisture contents are shown in Fig. 1. The data shown by a dotted line for the 50% r.h. sample correspond to ΔK and da/dN values determined from effective cracklength measurements based on an average of five separate crack length readings (see Section 2). Apparently both ΔK and da/dN values are increased by the redefinition of crack length and result in an extension of the actual data base.

The fatigue data indicate that nylon 66 conditioned to 23% r.h. (0.8 wt\% H_2O) exhibited essentially the same behaviour as the dry specimens (within limits of resolution involving test scatter), while the addition of further moisture to reach the 50% r.h. level reduced crack growth rates at a given ΔK value by a factor of about 2.5. Interestingly, the saturated nylon $(100\%$ r.h.) showed significantly higher growth rates than those

Figure 1 Fatigue crack growth rates in nylon 66 as a function of per cent relative humidity.

observed at any other moisture level and 9 to 10 times higher than growth rates in the 50% r.h. samples. These latter results are consistent with the preliminary observations reported previously [3] and discussed above.

A simple rationalization of the observed effects of water content can be proposed by considering the hydrogen-bonding and plasticizing nature of water in polyamides $[11-13]$. It has long been known that both the α and β transitions are shifted to increasingly lower temperatures by the sorption of increasing proportions of water [11]. However, the rate of decrease of T_{α} is greatest below about 2% water by weight [12, 16, 17]. For a sample of 60% crystallinity, 2% water corresponds to about one water molecule per 1.4 amide groups; 3% water corresponds to about one water molecule per 2 amide groups. The decrease in T_{α} in this range of water content has been attributed to the breaking of hydrogen bonds between amide groups and the formation of water bridges between them [11, 12]. Paradoxically, at the same time that the hydrogen bonds between the polymer molecules are being disrupted, the molecular packing is improved, as shown by a decrease in specific volume of the tightly bound water [18]. At higher concentrations, the water is presumed to be more loosely bound, and presumably serves essentially as a diluent. Thus, the increased mobility of the polyamides at water contents of about 2% to 3% may well lead to enough localized

deformation at the crack tip to permit blunting of the crack, thus decreasing the proportion of strain energy available for crack propagation, and lowering the FCP rate at a given ΔK . On saturation, however, gross plasticization undoubtedly occurs, as is evident in a 2.5-fold reduction in Young's modulus, $E[13]$, in comparison with the values for samples equilibrated at up to 50% r.h. (\sim 2.6%) water overall). Such dilution and reduced intermolecular attraction between polymer molecules may be expected to result in a decrease in the constraint (lower E) exerted on the crack tip by the bulk material ahead of it, and hence an *increase* in the FCP rate at a given value of ΔK . In other words, the strain per loading cycle, $\Delta \epsilon$, must then increase, since $\Delta \epsilon = \Delta \sigma / E$. The saturated nylon must then accumulate more damage per loading cycle than would be the case with the drier specimens; a higher FCP rate will then be expected at a given value of $\Delta \sigma$ (and hence ΔK).

With our specimens, the inversion point (at which the beneficial effect of the localized viscoelastic flow is offset) appears to correspond to the case of equilibration at 50% r.h. to offset.

In any case, even though dynamic mechanical spectra to determine values of storage and loss moduli have not yet been obtained, results are at least consistent with the observations of gross heating, and with observations of the decrease in E in saturated nylon 66 ([13], p. 318). (Further discussion of hysteretic heating and modulus follows below). Since, however, there is an inconsistency with observations $[12, 16]$ that the drop in E with increasing water content levels off (in nylon 6) at water concentrations greater than about 2%, a more rigorous argument will require the obtaining of dynamic spectra at the frequency concerned.

Additional evidence for enhanced chain mobility in the 50% and 100% r.h. tests was observed by noting a rise in temperature at the crack tip during the fatigue test. Whereas the dry specimen and the one equilibrated at 23% r.h. experienced no noticeable temperature rise during testing, the crack tip temperature of the higher moisture content specimens rose an estimated 15 to 20° C. Such a temperature change is indicative of an irreversible deformation process such as large-scale chain motion at the crack tip. Thus if crack-tip heating is localized, permitting localized deformation and crack blunting, FCP rates may be decreased; however, if the heating involves more than a small volume element at the crack tip, the consequent softening is believed to result in enhanced specimen compliance and higher crack growth rates. The latter condition has been encountered in the case of impact modified nylon 66 [19].

The relationship of these results to the question of fatigue strength and endurance must now be considered. Clearly, with these tests the longest fatigue life may be expected for specimens containing 2.6% water (corresponding to equilibration at 50% r.h.). However, an apparent contradiction between the present findings and the previously mentioned results by Kohan [13] requires resolution. The latter results were based on S-N plots (i.e., maximum stress versus number of cycles to failure). It is known that nylon 66 experiences a significant temperature elevation during S-N tests because of its relatively large loss tangent. This temperature elevation is amplified if the polymer contains moisture (note observations above); therefore, it would be expected that nylon 66 equilibrated at 50% r.h. would experience a greater temperature rise during a fatigue test than a dry sample. This temperature elevation, in turn, would result in a decrease in the modulus of nylon, the decrease being greater for the 50% r.h. sample than for the sample in the as-moulded condition. Since the specimens were fatigued between fixed load limits, the 50% r.h. sample would experience greater cyclic strains and, therefore, more damage per cycle than the dry specimens. For this reason, the nylon 66 samples equilibrated at 50% r.h. would be expected to exhibit inferior fatigue properties in the S-N test. In the present FCP tests, on the other hand, hysteretic heating is not sufficient to cause a drop in modulus at this level of water content, because the cyclic deformation is confined to the crack tip region with the bulk of the specimen acting as a heat sink, whereas in the $S-N$ tests, the whole specimen experiences the load. As discussed previously, the effect of moisture in this test is to allow for increased plastic deformation and crack tip blunting, thereby lowering crack growth rates. Hence, these FCP tests, conducted on *notched* rather than unnotched specimens, lead to the conclusion that nylon 66 equilibrated at 50% r.h. is the superior material under cyclic loading conditions. By comparison, the inferior FCP response of the fully saturated nylon 66 samples can be rationalized in terms of the much lower elastic modulus throughout the specimen, thus allowing for large amounts of cyclic damage within the fixed load limits of the crack growth

Figure 2 Macroscopic fatigue fracture surface appearance associated with different moisture levels, (a) 0% r.h.; (b) 23% r.h.; (c) 50% r,h.; (d) 100% r.h,

experiment. Therefore, the relative fatigue resistance of a nylon 66 component as a function of moisture content is found to vary with the test procedure $-$ in this case whether one uses notched or unnotched specimens. This fact must be clearly recognized when making component design decisions.

3.2. Fractography: macroscopic fracture surface details

Low-magnification $(10 \times)$ examination of the fracture surfaces of the nylon 66 fatigue specimens revealed a number of different morphological features associated with samples containing various moisture levels. It was observed that specimens equilibrated at 50% and 100% r.h. exhibited stresswhitening in the stable fatigue cracking zone, while specimens with lower moisture contents (equilibrated at 0% and 23% r.h.) revealed no stress whitening. The occurrence of stress whitening in the 50% and 100% r.h. samples further reflects the ability of these moisture-laden samples to undergo significant plastic deformation at the crack tip, while the 0% and 23% r.h. test specimens did not exhibit the same degree of plastic deformation.

The overall fracture surface texture of the specimens changed dramatically with moisture content. In the region of stable fatigue crack growth, the 0% and 23% r.h. specimens developed relatively flat, featureless surfaces; alternatively, the 50% and 100% r.h. samples revealed a very rugged fracture surface topography (see Fig. 2). In addition, the 50% r.h. samples showed large arrest lines at high stress intensity levels ($\Delta K > 3.7$ MPa m^{1/2}) as shown in Fig. 3. These arrest lines were associated with the periodic interruption of the FCP test to read the crack tip position and imply the occurrence of creep. The significance of the finer lines in Fig. 3 will be considered in the following section.

During the actual fatigue tests, it was noted that the 0%, 23% and 50% r.h. nylon 66 specimens failed by rapid, unstable crack propagation in the final load cycle, whereas the saturated specimens (100% r.h.) failed by stable but very high growth rate $($ 1 mm per cycle) fatigue fracture at large ΔK levels (>4 MPa m^{1/2}). Fig. 4a represents the typical appearance of the fast fracture region found in nylon samples equilibrated at 0%, 23% and 50% r.h. These surfaces were characterized by a grouping of crisp, curved lines which emanated

from some central point along the boundary of the crack front just prior to instability. It should also be noted that this fast fracture region exhibited no evidence of stress-whitening; this was the case, regardless of the moisture level in any specimen. The distinguishing feature noted on the terminal fracture surfaces in the 100% r.h. nylon samples was the widely separated arrest lines corresponding to the extent of tearing in each load cycle (Fig. 4b). Further comments on these arrest lines will be deferred to the following section.

Two other fracture surface features were associated only with the unstable fracture regions in the 0 to 50% r.h. specimens. When the fatigue crack began to grow unstably, it tended to branch, with several secondary cracks appearing in clusters above and below the main crack path (Fig. 5). Secondly, a series of bands parallel to the crack front were observed near the back surface of the fast fracture zone (Fig. 6). These bands, reminiscent of clamshell markings found on fracture

Figure 3 Coarse and fine arrest lines found on fatigue fracture surface in nylon 66 equilibrated to 50% r.h.

Figure 4 Fast fracture surface appearance. (a) 50% r.h. Note curved lines radiating from central point. (b) 100% r.h. Note arrest lines believed to be striations.

surfaces resulting from non-uniform fatigue crack growth, were clearly located, however, in the fast fracture region only, and cannot reflect events occurring during stable crack extension. Instead, these lines are believed to be associated with the interaction of the advancing crack front with the elastic stress wave reflected from the back surface.

3.3. Fractography: microscopic fracture markings

As was the case with macroscopic observations,

major differences were noted in the microscopic $(380 \times)$ fracture surface micromorphology of specimens equilibrated to different moisture levels. The dry specimens revealed very crisp, facet-like markings over the entire fatigue fracture surface, as shown in Fig. 7a. Such faceting suggests that limited crack tip plastic deformation had occurred. The average size of these small facets is approximately $10~\mu$ m, which, interestingly, compares favourably with the spherulite size of $6.5 \text{ }\mu\text{m}$ as determined by solvent etching in xylene. Whether

Figure 5 Branching occurs at point where unstable crack growth begins.

Figure 6 Fracture bands near back surface due to stress wave-crack front interactions.

these facets reflect interaction of the crack front with individual nylon spherulites, however, must await further study.

In contrast to the case of the 0% and 23% r.h. specimens, the nylon samples equilibrated at 50% and 100% r.h. revealed severely perturbed fracture surfaces indicative of extensive plastic deformation and drawing at the crack tip. The fractographs shown in Figs. 7b and c (50% and 100% r.h., respectively) were taken at the same applied ΔK level as Fig. 7a; the distorted nature of these fracture surfaces relative to those of the dry specimen is clearly evident.

Recent studies [5, 20] regarding the fractography of polymers have identified two types of linear fracture markings oriented parallel to the advancing crack front: discontinuous growth bands (DGB) and fatigue striations. The DGB markings are found generally at low ΔK levels and represent discrete crack growth increments corresponding to the crack tip plastic zone dimension. Crack advance in this region is discontinuous with the crack remaining dormant periodically for as many as $10⁵$ cycles. Fatigue striations are found at higher ΔK levels, and reflect the amount of crack advance in a single load cycle.

Within the ΔK regime investigated in the present study, no discontinuous growth bands were seen in nylon 66 regardless of moisture content. By con-

trast, discontinuous fatigue crack growth has been reported in semicrystalline polyacetal [20, 21] and in low density polyethylene [22], as well as in several amorphous polymers. Since the discontinuous growth process in semi-crystalline polymers is not as well understood as in amorphous polymers, the reason for the absence of DGB formation in nylon 66 is not clear at this time. For example, DGB formation has been shown to depend on ΔK level [5] and test frequency [5, 21,23].

Fatigue striations were found on the fracture surfaces of 50% r.h. samples (Fig. 8). Since these markings were observed on that part of the fracture surface which contained parabolically-shaped crack fronts, it was again necessary to redefine the ΔK values corresponding to the locations where striation measurements were taken. Since all striation measurements were confined to the central section of the specimen thickness, the effective crack length was computed to be the average of three separate crack length readings taken 30, 50 and 70 per cent of the distance across the specimen thickness. A comparison between the measured striation spacings and the macroscopic growth rate data clearly identify these lines as fatigue striations (see Fig. 9). Other investigators $[22, 24-28]$ have observed fatigue fracture lines in semi-crystalline polymers and concluded that they represented fatigue striations. Since no supporting macroscopic growth rate data were available to establish this point with certainty, and since similar lines could correspond to a different crack growth process (i.e. DGB formation), these earlier findings must be considered to be inconchisive. Therefore, the present data appear to represent the first unequivocal evidence of striation formation in a semi-crystalline polymer and clearly show the close relationship between macroscopic and microscopic crack growth rates.

Some fracture markings which looked very like fatigue striations were observed at very large crack lengths in the 100% r.h. samples. Since no macroscopic FCP data were obtained from this region of the fracture, there is no unequivocal proof that these markings were striations. However, judging from their morphology, and the behaviour of the specimen during the fatigue test, they do appear to represent crack arrest positions after each loading cycle.

The reason why striations were not seen in nylon 66 samples equilibrated at 0% and 23% r.h. is not clear at this time. While it is tempting to speculate

that the deformation mechanisms in the 50% r.h. samples may have been more ideally suited for striation formation, it should be noted that striations were seen in this material only at ΔK levels above 3.2 MPa $m^{1/2}$. By contrast, the 0% and 23% r.h. samples had fractured prior to that ΔK level.

4. Conclusions

(1) Fatigue crack growth rates in nylon 66 equilibrated at 50% r.h. were as much as 2.5 times lower than those found in specimens equilibrated at 0% r.h. or 23% r.h. Crack growth rates for saturated (100% r.h.) nylon 66 were 2 times higher than for any other moisture level, and about 3 2490

Figure 7 Fracture surface appearance associated with different moisture levels. (a) 0% r.h.; (b) 50% r.h.; (c) 100% r.h. $\Delta K = 2.1$ MPa m^{1/2}.

times those for the dry (0% r.h.) specimen. It is tentatively concluded that the FCP resistance as a function of water content reflects first an improvement as tightly bound water is incorporated up to a level of about 2% (at 50% r.h.). A degradation in behaviour at higher water contents is attributed to dilution with loosely bound water and weakening due to consequent loss of stiffness.

(2) Terminal fracture in nylon 66 occurred by unstable crack propagation for all moisture levels except the fully saturated condition. In fully saturated specimens, fatigue growth accelerated to extremely high rates $($ >1 mm per cycle), but unstable crack propagation did not occur. This change in mode is attributed to gross plasticization by loosely bound water.

(3) Stress whitening was observed only on the. fatigue fracture surfaces of those nylon 66 specimens equilibratedat 50% and 100% r.h. In addition, the fracture surfaces of these specimens were much rougher than those of samples equilibrated at 0% and 23% r.h.

(4) Fatigue striations were dearly identified only in the 50% r.h. samples in a size range corresponding to FCP rates of from 2×10^{-2} to 1×10^{-1} mm per cycle, and agreed closely with macroscopically determined growth rates at comparable ΔK levels. Striation-like markings were observed also at higher growth rates in saturated nylon 66 samples but no such fracture surface

Figure 8 Fatigue striations in nylon 66 equilibrated at 50% r.h.

markings were observed on the fatigue fracture surfaces of the 0% r.h. and 23% r.h. samples. In any case, the confirmation of fatigue striations in one type of specimen provides the first unequivocal evidence for such markings in any crystalline polymer.

(5) It has been found that the relative fatigue resistance of nylon 66 as a function of moisture

Figure 9 Correlation between macroscopic growth increments per loading cycle and striation spacings as a function of ΔK in nylon 66 equilibrated at 50% r.h.

content will vary with experimental test procedure, and specifically whether notched or unnotched specimens are used. This fact must be clearly recogized when making component design decisions.

Acknowledgements

This work was supported in part by the Office of Naval Research.

References

- 1. E.H. ANDREWS, "Fracture in Polymers" (Elsevier, New York, 1968).
- 2. R. W. HERTZBERG, " Deformation and Fracture Mechanics of Engineering Materials" (Wiley, New York, 1976).
- 3. J.A. MANSON and R. W. HERTZBERG, *CriL Rev. Macro. Sci.* 1 (1973) 433.
- 4. R. W. HERTZBERG, J. A. MANSON and M. D. SKIBO, *Polymer. Eng. Sci.* 15 (1975) 252.
- 5. M. D. SKIBO, R. W. HERTZBERG, J. A. MANSON and S. L. KIM, *J. Mater. Sci.* 12 (1977) 531.
- 6. S. L. KIM, M. SKIBO, J. A. MANSON and R. W. *HERTZBERG, Polymer. Eng. Sci.* 17 (1977) 194.
- 7. M. D. SKIBO, R. W. HERTZBERG, J. A. MANSON and S. L. KIM, J. *Mater. Sci.* 12 (1977) 551.
- 8. M. D. SKIBO, J. JANISZEWSKI, R. HERTZBERG and J. A. MANSON, Proceedings of the International Conference on Toughening of Plastics, 1978 (Plastics and Rubber Institute, London) paper 25.
- 9. M. D. SKIBO, J. A. MANSON, R. W. HERTZBERG and E. A. COLLINS, *J. MacromoL ScL-Phys.* B14 (1977) 525.
- 10. E.H. ANDREWS and B. J. *WALKER, Proc. R. Soc. London A* 325 (1971) 57.
- 11. N. G. McCRUM, B. F. READ and G. WILLIAMS, "Anelastic and Dielectric Effects in Polymeric Solids" (Wiley, New York, 1967).
- 12. Y. S. PAPIR, S. KAPUR, C. E. ROGERS and E. BAER, J. *Polymer. Sci.* 10 (1972) 1305.
- 13. M. I. KOHAN, "Nylon Plastics" (John Wiley & Sons, Inc., New York, 1973).
- 14. "Zytel" Design Handbook, E. I. duPont de Nemours and Company, 1972.
- 15. R. PUFFR and J. SEBENDA, in "Macromolecular Chemistry, Prague, 1965", edited by O. Wichferle and B. Sedlvacek (Interscience, New York, 1967) p. 79.
- 16. D. C. PREVORSEK, R. H. BUTLER and H. REIMSCHUSSEL, Jr. *Polymer. Sci. A2* 9 (1971) 867.
- 17. K.H. *ILLERS, Makromol. Chem.* 38 (1960) 168.
- 18. H. W. STARKWEATHER, J.. *Macromol. Sci.* B3 (1969) 727.
- 19. M. D. SKIBO, R. W. HERTZBERG, and J. A. MANSON, unpublished work on toughened nylon, Lehigh University (1978).
- 20. R. W. HERTZBERG, M. D. SKIBO, and J. A. MANSON, ASTM Symposium on Fatigue Mechanisms, Kansas City, 1978 (to be published).
- 21. R, W. HERTZBERG, M. D. SKIBO and J. A. MANSON, *J. Mater. Sci.* 13 (1978) 1038.
- 22. A. F. LAGHOUATI, Thesis, 3rd Cycle, Universite de Technologie de Compiegne (1977).
- 23. M. D. SKIBO, R. W. HERTZBERG and J. A. MANSON, 3 r. *Mater. Sei.* 11 (1976) 479.
- 24. B. TOMKINS and W. D. BIGGS, *ibid..* 4 (1969) 544.
- 25. L. J. BROUTMAN and S. K, GAGGAR, *Int. J. Polymer. Mater.* 1 (1972) 295.
- 26. W. J. PLUMBRIDGE, J. Mater. Sci. 7 (1972) 939.
- 27. K. YAMADA and M. SUZUKI, *Kobunshi Kagaku* 30 (1973) 206.
- 28. A. J. McEVILY Jr, R. C. BOETTNER and T. L. JOHNSTON, in "Fatigue - An Interdisciplinary Approach" (Syracuse University Press, Syracuse, NY, 1964).

Received 31 January and accepted 21 February 1979.