

The Effect of Molecular Weight on Fatigue Crack Propagation in Nylon 66 and Polyacetal

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Synopsis

The influence of molecular weight on fatigue and fracture behavior in nylon 66 (N66) and polyacetal (PA) is examined. Fatigue crack propagation (FCP) resistance and apparent fracture toughness (K_{IC}) in these two semicrystalline polymers increase with increasing molecular weight in a manner consistent with that reported for another semicrystalline polymer (HDPE) as well as for several amorphous polymers. The improved FCP resistance with increasing molecular weight is attributed to the development of a molecular entanglement network that more effectively resists cyclic-load-induced breakdown. A type of discontinuous crack growth is identified in PA at 100 Hz and in N66 (2.6% H₂O) at 50 Hz and compared with that observed in amorphous polymers.

INTRODUCTION

The beneficial effect of increased molecular weight (MW) on the fatigue behavior of amorphous polymers has been well documented in the literature. Constant-stress-amplitude tests on unnotched polystyrene (PS) specimens showed a significant increase in fatigue life as MW was raised from 1.6×10^5 to 8.6×10^5 .^{1,2} In poly(methyl methacrylate) (PMMA), crack growth rates decreased by nearly two orders of magnitude (at constant stress intensity factor, ΔK) when MW was increased from 1.1×10^5 to 4.8×10^5 .³ Similarly, a change in MW from 6×10^4 to 2×10^5 in poly(vinyl chloride) (PVC) resulted in a 1000-fold decrease in crack velocity^{3,4-6} and a concurrent increase in toughness. Recently, it has been shown that the inclusion of very small amounts of high-MW species to a PMMA matrix can dramatically decrease crack growth rates, while the addition of a low-MW tail will accelerate crack propagation.^{7,8} Such findings parallel closely the report that otherwise weak crazes in low-MW polystyrene thin films are stabilized containing limited high-MW additions.⁹ These studies demonstrate the sensitivity of FCP behavior to molecular weight distribution (MWD) as well as to MW itself.

Thus, at least in amorphous polymers, the effects of MW and MWD on fatigue response have been rationalized in terms of a cyclic load-induced disentanglement model. Prior to actual crack advance, the crack tip region deforms plastically by cyclic-induced unraveling of the polymer chains. Increasing the MW of the polymer is believed to retard such disentanglement, thereby reducing crack

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growth rates. Such an effect is consistent with proposals to explain the effects of MW on viscoelastic response¹⁰⁻¹³ at long times. Indeed, a quantitative theory has been developed that interprets the FCP rates in terms of the fraction of molecules whose size is greater than the minimum molecular weight required for the development of an entanglement network.¹³ The theory also relates FCP rates to the characteristic relaxation time, which is an inverse measure of the relative ease of disentanglement. In any case, the relaxation behavior of a polymer is bound to be sensitive to the presence of high or low-molecular weight tails.¹²

The influence of MW on the fatigue properties of semicrystalline polymers, by contrast, has received little attention, with most investigations focused on relationships between tensile mechanical properties and MW. For example, it is known that both the impact strength and elongation at fracture¹⁴⁻¹⁶ increase with increasing MW in nylon 66 (N66) and polyacetal (PA). An increase from 13% to 75% in the room-temperature fracture strain of PA, associated with an increase in number-average MW (\bar{M}_n) from 3×10^4 to 7×10^4 , probably constitutes further evidence of increasingly effective chain entanglement networks (presumably in the chain sequences linking crystallites) at higher molecular weights, though effects of crystallinity per se may also be involved. The improvement of these mechanical properties with increasing MW suggests a similar improvement in fatigue behavior.

Recently, Laghouati and co-workers^{17,18} reported that fatigue crack growth rates in high-density polyethylene (HDPE) decreased by several orders of magnitude as MW was increased from 4.5×10^4 to 2.0×10^5 . (For a given thermal history, the spherulite diameter changed by a factor of 3 and the crystalline fraction varied between 43% and 69% over the MW range examined.) These data represent the first direct evidence for an influence of MW on FCP rates in semicrystalline polymers, analogous to its effect on crack growth in amorphous polymers.

As reviewed by Hertzberg and co-workers,^{19,20} the fatigue fracture surfaces of engineering plastics often reveal two fundamentally different sets of fracture bands which represent crack front locations during the progress of the crack across the specimen width. One set of bands—called fatigue striations—represent the location of the crack front after each loading cycle. Hence, the width of each band corresponds to the amount of incremental crack extension resulting from that loading excursion. Bretz et al.^{21,22} have reported on fatigue striations in N66 containing various amounts of imbibed water. The other major set of fracture bands—referred to as discontinuous growth bands (DGB)—reflects the changing dimension of the crack tip plastic zone. In this instance, the crack tip remains stationary, though load cycling contributes toward growth of the associated plastic zone. At some critical point, the crack suddenly strikes through the entire damage zone before arresting at the elastic-plastic boundary. Recent studies of amorphous PMMA²³ and PVC²⁴ have shown that changes in MW and MWD can influence the resulting fatigue fracture surface micromorphology.

The generality of the dependency of FCP on MW is tested further in the present report by examining fatigue crack growth behavior in specimens of N66 and PA polymerized to varying molecular weights. In addition, fatigue fracture surface markings are identified and correlated with FCP behavior.

EXPERIMENTAL PROCEDURE

Materials

The polymers tested in this program are commercial grades of N66 and PA supplied by the E. I. duPont de Nemours and Co., through the courtesy of Mr. E. Flexman. Typical values of MW are listed in Table I, along with the thickness of the test panels. The N66 was supplied in a dry, as-molded condition (<0.2 wt % H₂O); other levels of moisture content in test specimens were achieved prior to fatigue testing by equilibrating panels in boiling salt solutions, according to procedures outlined elsewhere.^{21,25}

Fatigue Test Procedures

Compact tension (CT) specimens were prepared with a mechanical notch introduced by a jeweler's saw. The notch root was subsequently sharpened with a razor blade to accelerate crack initiation. Fatigue tests were performed on an electrohydraulic closed-loop testing machine, using a sinusoidal waveform of constant load amplitude and a minimum-to-maximum load ratio (*R*) of 0.1. Duplicate tests were conducted for all PA and most N66 test conditions, with all tests being performed in laboratory air at 22°C and in an average ambient relative humidity of 40%. Fatigue testing of PA was conducted at 100 Hz to shorten the time span of the test, since stable crack growth in this polymer occurs only at very low growth rates.²⁶ With the exception of several specimens tested at 50 Hz, all N66 panels were cycled at 10 Hz.

Before any fatigue data were obtained, each specimen was precracked to create a sharp fatigue crack beyond the mechanical notch. The precracking procedure varied for each polymer, but generally was conducted at 50 or 100 Hz. On occasion, precracking loads were set higher than the load range used during actual testing so as to accelerate initiation of the fatigue crack. However, no crack growth data were obtained until the fatigue crack had growth several millimeters past the precracked zone at the subsequent test load range.²⁷ When crack tip heating occurred as a result of the high-frequency-precracking procedure, data collection was delayed for at least 30 min to allow the crack tip region to cool to ambient temperature.

TABLE I
MW and Specimen Thicknesses of Specimens used for FCP Studies

Polymer	Number Average	Weight Average	Nominal thickness (mm)
	MW, ^a <i>M_n</i>	MW, ^a <i>M_w</i>	
N66 (Zytel 101)	17,000	34,000	6.4 and 8.6
(Zytel 42)	34,000	68,000	
PA (Delrin 900)	30,000	60,000	3.4 and 6.6
(Delrin 500)	40,000	80,000	
(Delrin 100)	70,000	140,000	

^a Typical values reported by the supplier.

Crack growth was measured optically using a Gaertner traveling microscope with 50× capability. The FCP test was interrupted periodically for 5–10 s to record the crack tip position and the associated number of cycles; these interruptions occurred typically after crack growth increments of 0.25–0.50 mm. Incremental crack growth rates were calculated as follows:

$$\left(\frac{da}{dN}\right)_i = \frac{a_{i+1} - a_{i-1}}{N_{i+1} - N_{i-1}} \quad (1)$$

where a = crack length and N = number of cycles. Crack growth rate data were plotted vs. the stress intensity factor range at the crack tip, ΔK , given by

$$K = Y \frac{\Delta P}{BW} \sqrt{a} \quad (\text{MPa} \sqrt{\text{m}}) \quad (2)$$

where ΔP = applied load range (N); B = thickness (m); W = width (m); and Y is a geometric correction factor given by $Y = 29.6 - 185.5(a/w) + 655.7(a/w)^2 - 1017.0(a/w)^3 + 638.9(a/w)^4$.

Fracture Surface Examination

Fracture surfaces were studied using an optical microscope and an ETEC Autoscan scanning electron microscope (SEM); for the latter instrument, a 20-kV accelerating voltage was used. Prior to SEM examination, specimens were coated either by a vacuum evaporated layer of gold and carbon or a sputter-coated film from a gold-palladium target.

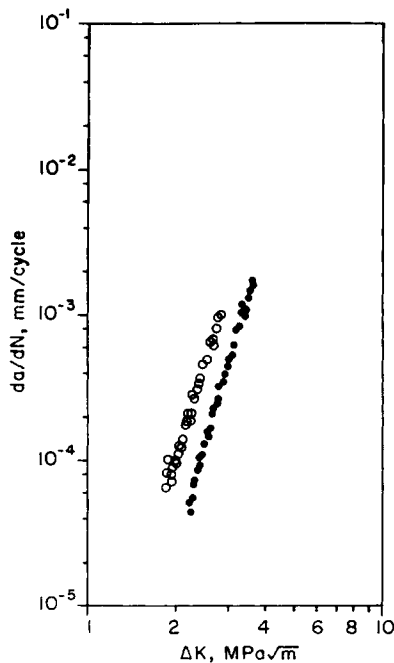


Fig. 1. Effect of M_n on fatigue crack growth rates in dry N66. MW: (○) 17,000; (●) 34,000.

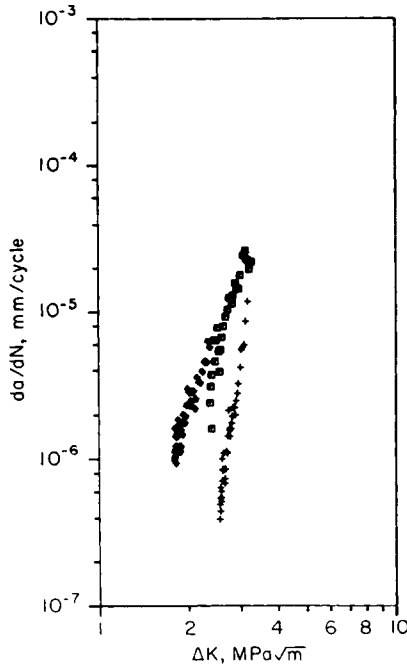


Fig. 2. Effect of M_n on fatigue crack growth rates in PA. MW: (\diamond) 30,000; (\square) 40,000; (+) 70,000.

EXPERIMENTAL RESULTS AND DISCUSSION

Macroscopic Crack Growth Rates

Fatigue crack growth rates for dry, as-molded (~ 0 wt % H_2O) N66 having number-average molecular weights (M_n) of 17,000 and 34,000 are shown in Figure 1. It is seen that when the M_n was doubled, the crack growth rates decreased uniformly by a factor of 3.5 at all ΔK levels examined. Similar results are shown in Figure 2 for the case of polyacetal, although the improvement in FCP resistance with increasing MW was seen to be relatively greater at lower ΔK levels. By estimating the apparent fracture toughness from the maximum stress intensity value prior to catastrophic fracture (K_{cf}), it is evident that increasing MW also increased material toughness (Table II).

FCP data for N66 equilibrated to various moisture levels up to saturation (8.5 wt % H_2O) have recently been reported elsewhere.^{21,25} These results showed that FCP rates in both nylon 66 materials decreased with a 2–3 wt % addition

TABLE II
Apparent Fracture Toughness (K_{cf}) vs. MW for N66 and PA

Material	M_n	K_{cf}^a ($MPa\sqrt{m}$)
N66	17,000	3.2
N66	34,000	4.2
PA	30,000	2.8
PA	40,000	3.5
PA	70,000	3.6

^a Estimated from the maximum value of ΔK attained just prior to fracture.

of water. Furthermore, the superior fatigue resistance of high-MW N66 relative to that of the low-MW N66 persisted over this range of imbibed water, with crack growth rates remaining about three times *lower* in the material with the *higher* MW. However, further increases in moisture content are found to degrade FCP resistance of both nylons with relatively greater reductions being exhibited by the high-MW material. As a result, there is no difference in FCP behavior at saturation. The decrease of modulus that occurs upon absorption of large amounts of water into N66^{14,15,25} is apparently sufficient to negate the beneficial effect of increased MW on FCP behavior. (No evidence was found for hydrolytic instability, which would cause a decrease in MW.) We conclude from these data for N66 and PA along with those of Laghouati et al.^{17,18} that semicrystalline polymers exhibit a strong sensitivity of FCP to MW, similar to that reported for amorphous polymers.³⁻⁸

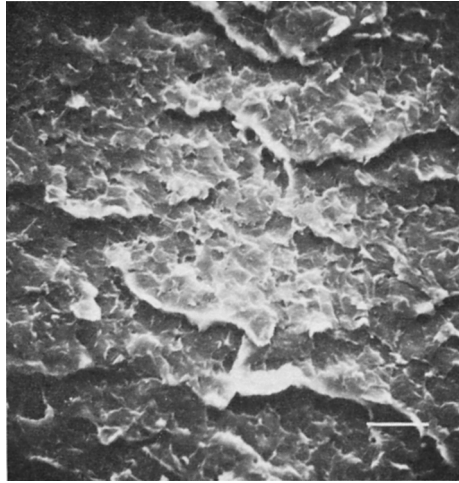
Fracture Surface Morphology

An examination of the surfaces of fatigue fractures in dry nylon 66 revealed no differences in macroscopic appearance as a function of MW. No fracture surface whitening is visible in the fatigue or the fast fracture region (the zone of catastrophic fracture at the end of stable FCP). The surface texture in the fatigue zone is very smooth, and the crack bifurcates at the beginning of the fast fracture region. The fracture surface morphology of PA is summarized in Table III. For this material, stress whitening and a rough fracture surface texture are noted on the fatigue fracture surfaces. Again it is apparent that MW has no effect on the macroscopic fracture appearance of the PA samples.

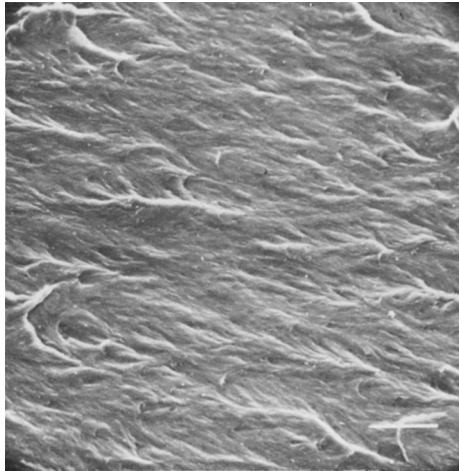
Unlike the case of dry N66, in which the *macroscopic* fracture appearance does not vary with MW, a distinct difference does exist in overall *microscopic* texture. Low-MW N66 has a patchy morphology, as shown in Figure 3(a). (Crack propagation direction in all micrographs is from left to right.) Closer inspection reveals crisp, facetlike markings over the entire fatigue fracture surface. The average size of these small facets is approximately 10 μm , which is close to the diameter of the average spherulite in the material (5–6 μm as determined by etching). In fact, a recent study²⁸ of deformation and fracture processes in semicrystalline polymers confirmed that dry, low-MW N66 fractures in a trans-spherulitic manner. This observation is consistent with the macroscopically flat fracture surface mentioned earlier, itself an indication of limited crack

TABLE III
Fractographic Observations for Polyacetals

	$M_n = 30,000$	40,000	70,000
Surface whitening	yes	yes	yes
Texture	rough, patchy	rough, patchy	rough, patchy
Terminal fracture	brittle	brittle	brittle
Trans-spherulitic fracture	yes	yes	yes
Striations	no	no	no
DG bands	yes	yes	yes



(a)



(b)

Fig. 3. (a) Patchy fracture surface morphology in dry N66 ($M_n = 17,000$). $\Delta K = 2.1 \text{ MPa}\sqrt{\text{m}}$. Scale bar = $30 \mu\text{m}$. (b) Fracture surface appearance of dry N66 ($M_n = 34,000$). Note evidence of drawing. $\Delta K = 2.2 \text{ MPa}\sqrt{\text{m}}$. Scale bar = $20 \mu\text{m}$.

tip plasticity. As Figure 3(b) shows, however, the fracture surface of *high*-MW N66 (at approximately the same ΔK level) does *not* exhibit a patchy morphology; instead, the surface appears to be drawn out in the direction of crack growth. As a result, no correlation between the fracture surface details and the measured spherulite size of $5 \mu\text{m}$ is evident at the higher MW.

Since the macroscopic appearance of dry N66 does not vary with MW, this change in the micromechanism of crack propagation with MW is somewhat surprising. Recall, however, that crack growth rates in dry N66 decreased with increasing MW. This implies that a greater fraction of the applied mechanical energy is dissipated by cyclic damage mechanisms in the high-MW polymer; consequently, the driving force available to drive the crack must have been re-

duced. The greater cyclic damage which occurs in high-MW N66 apparently is sufficient to perturb the spherulite structure so that no evidence of trans-spherulitic fracture is seen.

An examination of the fracture surface micromorphology associated with FCP in PA confirmed the earlier work of Hertzberg et al.²⁶; the crack was found to follow a predominantly trans-spherulitic path at all molecular weights. Figure 4 shows the radial pattern on the fracture surface of an intermediate-MW sample. Also in agreement with the earlier study is the observation of occasional nodules on the fracture surface; these are presumed to be particles of an additive such as a stabilizer or processing aid.

Fracture Surface Lineage

Two significant types of fatigue fracture lineage have been identified in polymers. Classical fatigue striations constitute one type of fracture band and reflect the crack growth increment during consecutive load excursions. By contrast, discontinuous growth bands (DGB) are formed when the fatigue crack remains motionless for some period of cyclic loading before striking forward abruptly during the last cycle of the period. The material through which the crack advances is surely damaged during the prior cyclic loading period by some deformation process. In a number of instances, craze formation takes place.^{3,19,29} The DG band spacing in several amorphous polymers^{3,19,29} and in PA²⁶ has been equated to the Dugdale plastic zone dimension, R , defined below³⁰:

$$R = \frac{\pi}{8} \left(\frac{K_{\max}}{\sigma_{ys}} \right)^2 \quad (3)$$

The distinction between these two fatigue fracture mechanisms—striations and DG bands—is important, since they represent fundamentally different fracture processes. Moreover, post-fracture examinations of failed components can lead to erroneous conclusions with regard to service lives unless the relationship between the number of fracture bands observed and the number of loading cycles is known.

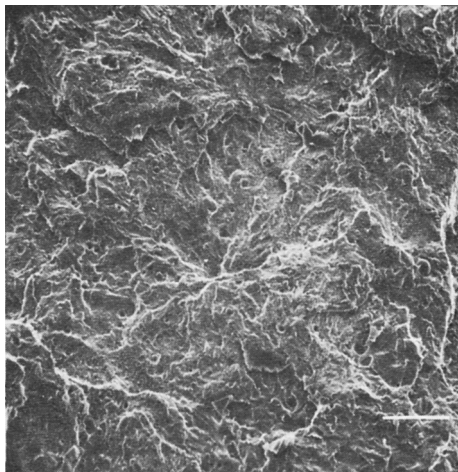


Fig. 4. Fracture surface of PA showing trans-spherulitic fracture. Scale bar = 20 μm .



Fig. 5. DG bands in PA. Note ragged appearance. Scale bar = 1 mm.

No fracture lineage of any kind was observed in the dry N66 specimens at either molecular weight. However, this was not the case for test panels containing 1.7–5.7% H_2O when tested at 10 Hz. Within this moisture content range, N66 specimens of both MW contained fatigue striations. Observations with regard to striation formation in nylons have been discussed elsewhere.^{21,22}

Fatigue striations were not observed on the fracture surface of PA at any value of MW. However, all specimens did exhibit a very patchy surface with a superimposed array of rough bands. Figure 5 shows this band structure in the lowest-MW PA (in which the lineage is most easily seen). Similar markings were found in low- and high-MW N66 samples containing 2.6% H_2O which were tested at 50 Hz. In these specimens, ragged bands covered a limited region of the fracture surface at the lowest ΔK levels tested (Fig. 6). This coarse lineage in both PA and N66 is believed to be evidence for a discontinuous growth mechanism. Unlike earlier studies^{19,26,29} of DG bands, however, the lineage spacing does not agree with the Dugdale model; i.e., when $\log(\text{band spacing})$ is plotted against $\log(\Delta K)$, the slope is much greater than 2. For example, Figure 7 shows the band size data for N66; in addition to extremely high slopes (8–10), these data indicate a dependence of band size on MW. This MW dependence, which was

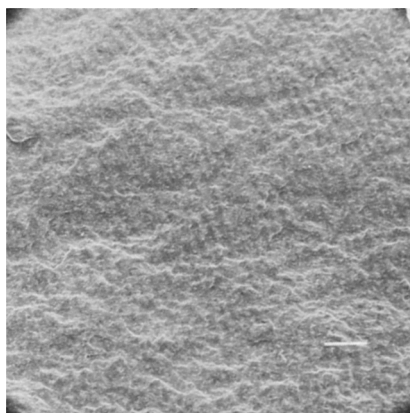


Fig. 6. Ragged lineage in N66 ($M_n = 34,000$, 2.6% H_2O) tested at 50 Hz. These lines are believed to be DG bands. Scale bar = 0.3 mm.

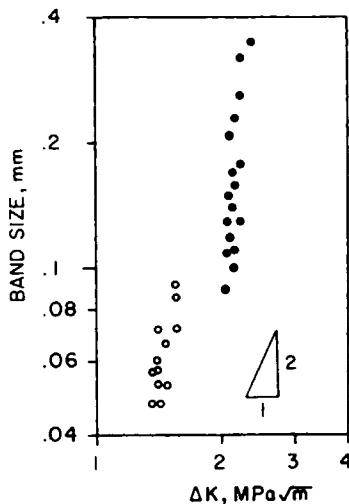


Fig. 7. Dependence of band size on ΔK for N66 (2.6% H_2O ; MW is number average) tested at 50 Hz. MW: (○) 17,000; (●) 34,000.

also noted in the PA specimens, is unexpected, since yield strength is not believed to be a strong function of MW in this range.¹⁶ (Recall that the Dugdale plastic zone size is related to the inverse square of σ_{ys} .)

We are tempted to speculate that these bands are evidence of a different DG mechanism unique to semicrystalline polymers. However, since the kinetics of discontinuous crack growth in semicrystalline materials are not well understood, no firm conclusions with regard to the nature of these DG bands seem appropriate at this time. Clearly, more work in this area is required.

CONCLUSIONS

1. Fatigue crack growth rates decreased and the apparent toughness (K_{cf}) increased with increasing MW in N66 and PA. This behavior is consistent with that reported for another semicrystalline polymer (HDPE) and for several amorphous polymers.

2. The effect of MW on FCP behavior may be rationalized in terms of a model in which progressive disentanglement of the chain sequence linking crystallites takes place. While the actual mechanism of crack tip plastic deformation in semicrystalline polymers is not yet clear, an increase in MW should make chain disentanglement more difficult, thereby reducing crack growth rates.

3. A discontinuous crack growth mechanism was identified in PA tested at 100 Hz and in N66 (2.6% H_2O) tested at 50 Hz. This DG mechanism appears to be distinct from that observed in amorphous polymers in that band spacings decreased with increasing MW, and the slope of \log (band size) vs. \log (ΔK) was very high (8–10).

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