

Fatigue Mechanism of Fiber-Reinforced Polypropylene Swollen by Oil

K. IISAKA and Y. NAMAI, *Materials and Electronic Devices Laboratory, Mitsubishi Electric Corporation, Tsukaguchi-Honmachi, Amagasaki, Hyogo 661, Japan*

Synopsis

Fatigue mechanism was investigated for the fiber-reinforced polypropylene (FRPP) swollen by a small amount of oil. The curves of applied cyclic stress (S) vs. logarithm of cycles to failure (N) shifted into smaller values of S and N , respectively, by adding oil into the polymer and with increasing a test temperature. The endurance limiting stress (σ_e) for the swollen FRPP, defined as the stress at a long lifetime, became much the same as the one for the swollen unfilled polypropylene, though the former was considerably larger than the latter for the breaking strength measured in standard bending test. The activation energy and the activated volume, which have been determined by the Eyring's model from the S - N curves at higher stress levels, suggest that the introduction of a small amount of oil into the polymer lowers a motional unit associated with a fatigue process from 30 to several repeat units. The major decrease in σ_e by swelling can be explained in terms of the crack-nucleation theory. It is indicated that this decrease yields from the change in the stress-concentration factor.

INTRODUCTION

Fiber-reinforced polymers are more applicable as structural members under more severe environmental conditions. There are more uses of composite under cyclic loading at various atmosphere. The endurance limiting stress, defined as the stress at which the composite survives at a given number of cycles (e.g., 10^7) to failure, is required for engineering design. The static breaking strength measured in usual mechanical testing such as tensile or bending is often used as a standard for the endurance limiting stress, since a fatigue test is a tedious, time-consuming one. However, a material which is superior to the others at a static strength may sometimes give a poorer endurance limiting stress. Understanding of fatigue mechanism is important for designing of the most suitable composite.

The two major hypotheses have been proposed as the mechanism of fatigue failure of a polymer, that is, the ductile failure due to dissipative heating and the brittle one due to crack growth during cyclic loading. The mechanism of fatigue failure depends on various factors, such as loss energy per cycle in a sample, test frequency, heat transfer to the surroundings, and the shape of a specimen. The criterion whether a material occurs in the manner of thermal or brittle failure has been proposed as the functions of the above factors by Crawford and Benham.¹ In the previous studies, the fatigue rupture of polymer fibers was reported to occur by the mechanism of viscous flow, as in the case of the creep.² Also, Regel and Leksovski³

found later a correspondence between the respective results of long-term static and dynamic fatigue testing for a number of fibers and foils. For both types of testing, dependence of fatigue lifetime on stress can be expressed by a single exponential relation. These facts suggest that fatigue lifetime may be related to Eyring's equation for the description of viscous or plastic flow. However, Eyring's equation cannot explain fatigue behaviors at lower stress levels or longer lifetimes. On the other hand, it has been reported by Prevorsek and Kwon⁴ that the $S-N$ curves for fiber filaments can be explained over the broad range of lifetime, in terms of Prevorsek and Lyon's theory.⁵ Their theory, which is based on crack-nucleation, is applicable only for polymeric fibers in the glassy state. However, under the experimental condition where the temperature rise of a specimen is negligible during cyclic loading, the fatigue lifetime may be controlled by both times required to form and propagate a craze or crack. Hence, the fatigue process will be expected to be describable also for a bulk material by crack-nucleation theory, if the formation of a craze or crack is a rate-determining process.

Reinforcement of polymers with filler brings about the decrease in loss energy per cycle and the formation of inhomogeneous stress field or the change of stress concentration. These factors seem to be modified by addition of a low molecular-weight organic compound to a composite. Though the fatigue failure of fiber-reinforced thermoplastics has been investigated for various polymers,⁶⁻⁹ the mechanism has been not necessarily made clear.

The purpose of this study is to understand the fatigue mechanism for a fiber-reinforced polypropylene swollen by a small amount of oil, as a low molecular-weight material.

EXPERIMENTAL

The polymers used for this study were unfilled and glass-fiber-filled (30 wt %) polypropylenes, manufactured by the Mitsui Petrochemical Co. They were fabricated in a plate of 3 mm thickness by injection molding under the standard molding conditions. The specimens for fatigue testing were machined from the plates and had a cross section of 20×3 mm, broadened at both ends to 34 mm. This shape was designed so that failure would occur in a well-defined region from the clamping and loading points of the specimen. Preparation of swollen samples was done by immersing the samples into Spindle oil (viscosity, 12 cSt, at 30°C) controlled at the temperature of 60°C until the degree of swelling approached the equilibrium value. The degrees of swelling were about 4 and 2%, respectively, for the PP and the FRPP.

Flexural fatigue testing was done under the condition of constant amplitude of cyclic stress by the apparatus of Baldwin SF-01. Fatigue tests were performed in the circulated air chamber of 25, 60, and 80°C at a frequency of 1800 cpm. Flexural strength was measured at the crosshead speed of 500 mm/min by an Instron testing machine. The dynamic modulus and logarithmic decrement were measured over the temperature range of -20 and 180°C with a torsion pendulum.

RESULTS

In the fatigue experiment of the unfilled polypropylene, done for comparison, major deflection of a specimen occurred abruptly without fracture under a condition of a constant cyclic stress. The time for a major deflection to occur increased with decreasing an applied stress and became considerably long at lower stress levels. For the PP, the fatigue lifetime was defined as the time when the value of modulus became the 40% of that for a virgin sample. In the case of the FRPP, all of the specimens had fractured under cyclic loading. Figure 1 shows the $S-N$ curves at the environmental temperature of 25°C for the unswollen and swollen samples, respectively, of the PP and the FRPP. The experimental data for a flexural strength were also plotted in the same figure by regarding as the case where the number of cycle to failure equals to be one. The $S-N$ curves were generally similar to those previously reported.⁶ They can be approximately divided into two regions: namely, region I, a lifetime increased slowly as the stress decreased until $N = \text{about } 10^5$; region II, a lifetime increased largely above $N = \text{about } 10^5$. As the characteristic behaviors, the fatigue strength for the swollen FRPP lowered to the nearly same degree as well as that of the swollen PP, at region II, though the static flexural strength was considerably larger for the former than the latter. Figure 2 shows dependence of $S-N$ curves on test temperature for the unswollen and swollen FRPP. For both samples, the $S-N$ curves shifted to shorter lifetimes and to lower stresses with increasing temperature. In the case of the swollen sample, the temperature shift in the $S-N$ curves was small, compared with that of the unswollen sample.

Figure 3 shows dependence of dynamic mechanical damping on temperature for each sample. The fatigued specimens were cut off from the materials just before the fatigue failure at higher stress levels. The two mechanical dispersions were observed over the temperature range studied

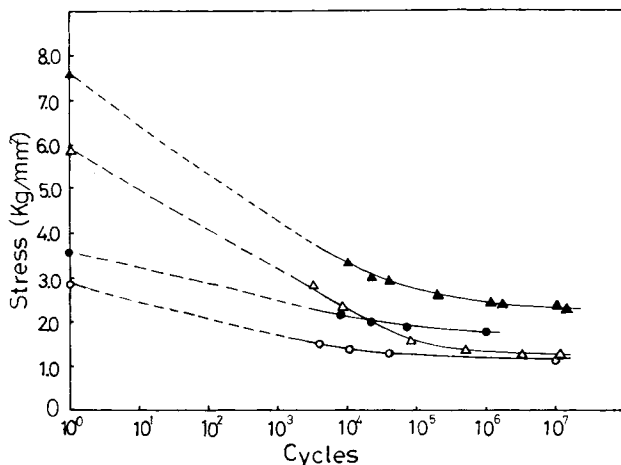


Fig. 1. $S-N$ curves, at the environmental temperature of 25°C: (▲) FRPP (30%), unswollen; (△) FRPP (30%) Swollen; (●) PP, unswollen; (○) PP, swollen.

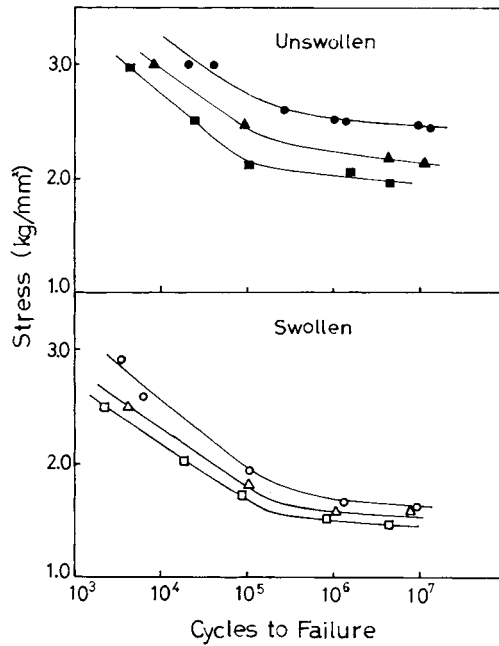


Fig. 2. Dependence of $S-N$ curves on environmental temperature (K) for FRPP: (●,○) 293; (▲,△) 333; (■,□) 353.

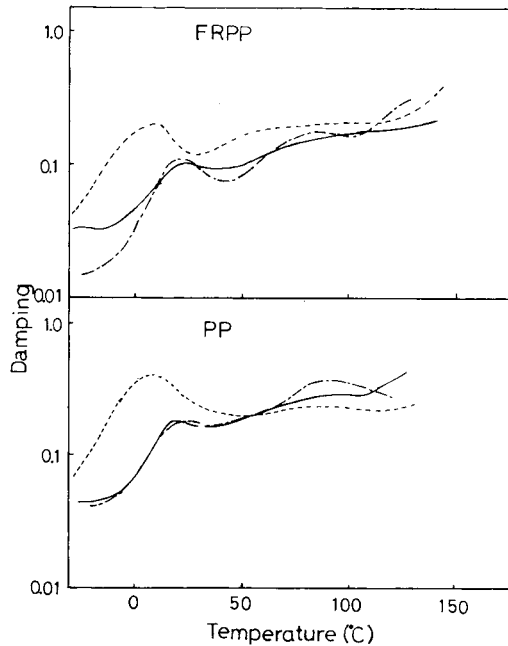


Fig. 3. Dependence of dynamic mechanical damping on temperature for original (—), swollen (- - -), and fatigued (---) samples. Fatigued samples (for unswollen): (FRPP) $\sigma = 2.51 \text{ kg/mm}^2$, $N = 2.16 \times 10^5$; $\sigma = 1.50 \text{ kg/mm}^2$, $N = 1.06 \times 10^7$.

here for all samples. The β -peak, appearing at about 80°C, is related to imperfect crystalline structure.¹⁰ The γ -peak, appearing at about 20°C, is ascribed to the glass to rubber transition in the amorphous region. The major difference between the fatigued and virgin samples was not observed in the dynamic mechanical properties. However, the β -peak for the fatigued sample became slightly clear, compared with the virgin one. By swelling, the γ -peak shifted to the lower temperature and the peak height became large. The damping over the temperature range between the γ -dispersion and the α -dispersion associated with melting became small for the swollen PP, but large for the swollen FRPP, compared with the unswollen samples.

DISCUSSION

Examination of the Thermal Aspect during Fatigue Process

In the case of polymer fatigue, the thermal aspect of failure should be considered because a polymer has a low thermal conductivity and high damping properties which result in a temperature rise in a specimen during cyclic loading. It is difficult to detect the intrinsic temperature of a specimen during a fatigue experiment. Therefore, at first, the thermal aspect has been examined for the present samples.

The rate of temperature rise of a specimen can be given by the following equation¹:

$$\frac{d\theta}{dt} = R - S\theta \quad (1)$$

$$R = \frac{\pi f \sigma_a^2}{C_p} \cdot \frac{\sin \delta}{E}, \quad S = \frac{\beta h}{\rho C_p}$$

where θ is the temperature rise of the specimen, f is the cyclic frequency, σ_a is the amplitude of stress, ρ is the density of the material, C_p is the specific heat, δ is the angle of the strain lags behind the stress, E is the modulus, β is the surface area to volume ratio, and h is the heat transfer coefficient.

To compute eq. (1), the value of h must be determined. Here, as a first approximation, it has been estimated from the experimental condition, corresponding to $d\theta/dt = 0$, in the fatigue test of the PP. The flexurel deflection of the specimen continues to increase gradually and then makes a rapid progress at higher stress levels. However, under a certain stress level it increases little by little at first until it becomes constant, as shown in Figure 4. The situation that the deflection becomes constant can be considered to correspond to the condition where the modulus, that is, the internal temperature for the specimen, does not vary with time. The average value of h , thus derived, is to be 0.0372 cal/cm s °C. Figure 5 shows the dependence of R and $S\theta$ on temperature rise, θ for each sample fatigued at the environmental temperature of 25°C. In the case of the PP, the rate of temperature rise, $d\theta/dt$, is always larger than zero at $\sigma \geq 1.9$ kg/mm² over the whole values of θ , but it becomes smaller than zero at $\sigma \leq 1.8$ kg/mm² after the temperature rise of about 10°C. This is consistent with the results of

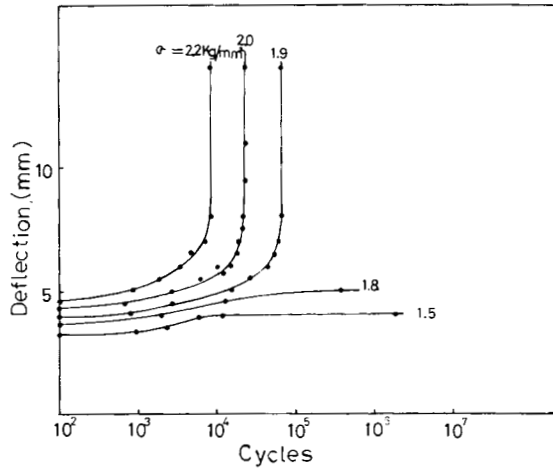


Fig. 4. Change of deflection during fatigue testing for PP specimen.

Figure 4. In the case of the FRPP, $d\theta/dt$ is always smaller than zero over the whole values of θ , at $\sigma \leq 6.0 \text{ kg/mm}^2$ for the unswollen sample and $\sigma \leq 3.7 \text{ kg/mm}^2$ for the swollen sample, respectively. Every stress levels studied here at any environmental temperature have been chosen to be less than the ones where the specimens soften to failure, owing to the rise of temperature.

Fatigue Behaviors at Higher Stress Levels (Region I)

Fatigue process can be classified into two steps: (a) the formation of a craze or crack via growth of a preexisting flaw (nucleation) and (b) the propagation of this craze or crack (propagation). Fatigue lifetime consists of both times of the t_N and t_p where t_N is the time required to form a craze or crack and t_p is the time required to propagate the craze or crack. It depends on the extent of an applied stress whether either t_N or t_p is more controllable in fatigue process. In region I, both t_N and t_p seem to be controllable, as suggested by Weaver and Beatty.¹¹

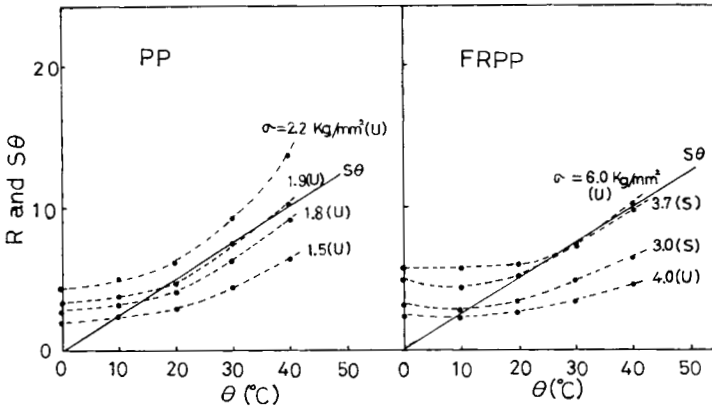


Fig. 5. R and $S\theta$ vs. θ in eq. (1).

To examine the underlying molecular mechanism, the activation energy has been determined from the dependence of lifetime on reciprocal temperature for each stress by Eyring's model:

$$t = t_0 \exp \frac{\Delta U_0 - \alpha \sigma}{RT} \quad (2)$$

where t_0 is the material constant, ΔU_0 is the activation energy, α is the activation volume multiplied by a stress concentration factor necessary to convert applied load to stress at the microscopic level, T is the temperature, and R is the universal gas constant. The values of the apparent activation energies, $\Delta U_a = \Delta U_0 - \alpha \sigma$, obtained for each stress were plotted vs. stress σ , as shown in Figure 6.

The values of ΔU_0 , which were obtained by extrapolation of ΔU_a to zero of σ , were 32 and 12 kcal/mol for the unswollen and the swollen FRPP, respectively. The activation energy for the unswollen FRPP is comparable with the one which corresponds to the segmental motion in the amorphous region of polypropylene.¹²

The values of α , which have been determined from the slope of lines in Figure 6, are 6300 and 1800 Å³, respectively, for the unswollen and the swollen samples. If the volume of the repeat unit is taken to be that of the repeat unit in the crystalline state of PP, it amounts to be about 75 Å³.¹³ Since the number of the repeat units that participate in the glass transition appears to be between 20 and 30,¹⁴ the activation volume lies between 1500 and 2250 Å³, and consequently the stress concentration factor q is computed to be about 3.5 in the case of the unswollen FRPP. The value of the activation volume is consistent with the one reported by Weaver and Beatty¹¹ and also the value of q is not unreasonable one.

By swelling, both values of ΔU_0 and α decrease considerably. The value

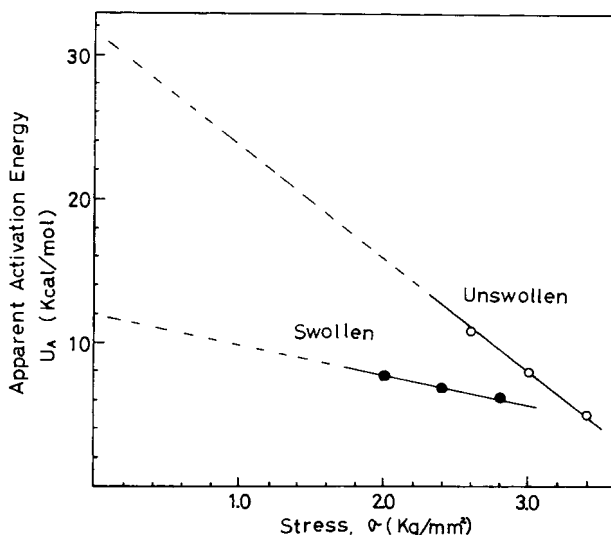


Fig. 6. Apparent activation energy vs. stress.

of ΔU_0 is approximately the same as that associated with the glass-II transition,¹² where several repeat units appear to participate in motion.¹⁵ Accordingly, the activation volume is estimated to be about 250 \AA^3 , and the value of q can be derived to be 7.

As observed from the dynamic mechanical measurements, the β -dispersion increases largely, while the α -dispersion scarcely varies, by swelling. The FRPP absorbs only several % of a Spindle oil and, consequently, does not diminish the modulus to large extent. From the above results, the FRPP seems to absorb preferentially the oil molecules at the amorphous region of the matrix. The molecular chains are more strained at the boundary between the amorphous and the crystalline parts, where a craze or crack nucleates.

The activation volume was reported to be several hundreds \AA^3 for poly(vinyl chloride)¹⁶ and high-density polyethylene¹⁷ when the rearrangement of chain segments occurred during the creep-rupture experiments. The rearrangement of chain segments or flow process is made easier by plasticization at the amorphous region. As a result, the activation energy and the activation volume are thought to have decreased.

In general, if the plasticization occurs by introducing a low molecular-weight material into polymers, q would decrease since flaws or cracks within a specimen cause to heal. The increase in q can be explained as follows. The oil molecules are preferentially absorbed at the amorphous region of the matrix and at the interface between the glass fiber and the matrix. They permeate from one amorphous part into the neighboring amorphous part through a crystalline region, or from one interface into the neighboring interface through the matrix. It is proposed as the permeation mechanism that the oil molecule diffuses through the matrix by the wedge action, as if alcohol molecules as nonsolvents diffuse through polystyrene.¹⁸ As the results of crazing or debonding between the fiber and the matrix, q will increase. The increase in q may be larger for the FRPP than for the PP, because the former contains more flaws within the sample which are feasible to absorb the low-molecular-weight material. This is supported by the fact that the damping over the temperature range between the α - and the γ -dispersions increases for the swollen FRPP, as indicated that the increase in damping is due to the slippage between the fiber and the matrix,¹⁹ or the deformation of a crazed material.²⁰

Fatigue Behaviors at Lower Stress Levels (Region II)

The $S-N$ curves for polymeric materials are not generally characterized by a clear endurance limiting stress, compared with the case of metal. The fatigue behaviors at longer lifetimes are important for practical usages, but there is little understanding of this up to now. It is difficult to determine the ΔU_0 and α at region II on account of the smaller slopes of the $S-N$ curves. As the fatigue mechanism of region II, craze or crack initiation appears to be more controllable.

According to the crack-nucleation theory, the growth of cracks may be regarded as a thermally activated process in which polymer segments are

transferred from the state in which all segments are completely surrounded by like segments (α -phase), to the surface of cracks (β -phase). Cracks are stable and stress-sustaining when the size of them is smaller than critical, but, as soon as this size is exceeded, the cracks become unstable and the polymer fractures catastrophically. The time to failure, t_f , can be approximated to be a time required to form an unstable crack. Under cyclic stress σ , N_f is represented by Prevorsek and Lyon's, since $N_f = (\text{frequency} \times t_f)$:

$$\log N_f = A - B\sigma^2 + C\sigma^{-4}$$

$$A = \log \frac{h}{kTZ} + \frac{\Delta F}{2.3kT} \quad (3)$$

$$B = \frac{Vq^2}{4.6kTE}$$

$$C = \frac{\pi\gamma^3 E^2}{13.8kT(1-\mu^2)q^4}$$

where k and h are Boltzman and Planck constants, T is the temperature, Z is the concentration of nucleation sites, ΔF is the free energy of activation associated with crack growth, v is the effective volume of the vacancy created by the breakage of a certain segment, E is the Young's modulus, q is the stress-concentration factor, γ is the fracture surface energy, and μ is the Poisson ratio.

However, the above equation is based on a linear elastic fracture mechanics. A usual polymeric material deforms plastically at a tip of a crack. A fracture phenomenon must be treated according to a nonlinear elastic fracture mechanics, when the extent of plastic deformation is comparable to a crack length. Therefore, application of eq. (3) is limited in the case of lower stress levels, where t_N is a rate-determining process. Here, we have tried to interpret the fatigue behaviors of region II by using eq. (3).

In eq. (3) the contribution of the second term on the right-hand side to N_f is small at a longer lifetime. Therefore, eq. (3) can be rewritten by

$$\log N_f \simeq A + C\sigma^{-4} \quad (4)$$

$$\sigma_e \simeq \frac{1}{q} \times \left(\frac{C'}{\log N_f - A} \right)^{1/4} \quad (5)$$

where

$$C' = \frac{\pi^3\gamma^3 E^2}{13.8kT(1-\mu^2)}$$

On the other hand, since the fracture strength σ_f corresponds to the case where the number of cycle to failure equals 1,

$$0 = A - B\sigma_f^2 + C\sigma_f^{-4} \quad (6)$$

TABLE I
Change in σ_f and σ_e ($N_f = 10^7$) by Swelling for the FRPP

		σ_f	σ_e
Unswollen (kg/mm ²)		7.65	2.4
Swollen (kg/mm ²)		6.0	1.3
% Decrease by swelling	Obs	21%	46%
	Calcd	—	50–55%

Since

$$B\sigma_f^2 > C\sigma_f^{-4} \quad (7)$$

Accordingly,

$$A \simeq B\sigma_f^2 \quad (8)$$

As well as eq. (5),

$$\sigma_e \simeq \frac{1}{q} \times \left(\frac{C'}{\log N_f - B\sigma_f^2} \right)^{1/4} \quad (9)$$

where σ_e is the endurance limiting stress at a longer lifetime or region II.

Equations (5) and (9) imply that σ_e is most dependent on q . It is difficult to compute the exact value of σ_e since eqs. (5) and (9) are approximate ones. Here, the effect of swelling on σ_e has been examined for the FRPP, according to these equations. The parameters which vary by swelling are E , γ , Z , q , ΔV , ΔF , and σ_f . Among these parameters, E and σ_f decrease by about 20%, and γ and Z may decrease and increase, respectively, though the percentages are unknown. In eqs. (5) and (9), the numerator in the parenthesis decreases, while the denominator increases, by swelling. However, the contribution of the parenthesis to σ_e is small, on account of the proportionality of the fourth root. The change in σ_e can be estimated mainly by taking into consideration of q . The estimated value is consistent with the observed one, as shown in Table 1.

Even though the static fracture strength σ_f is considerably larger for the swollen FRPP than for the swollen PP, the fatigue strength for both samples is nearly the same at a longer lifetime (for example, at $N_f = 10^7$). This is due to the facts that the structural change is large in the case of the FRPP and the fatigue endurance limit is largely dependent on q . If the static strength is used as a standard for the endurance limit, the erroneous engineering design would be done.

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