Fatigue crack growth of PMMA in organic agents

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Crack growth tests under cyclic loading were executed at 295 K in various organic agents using compact tension and pure bending specimens of polymethylmethacrylate (PMMA). The cyclic frequencies f for the two kinds of test were 0.4 to 1 and 33 Hz, respectively. Two interesting features are pointed out: (i) transitional behaviour is observed on a crack growth rate against stress intensity factor range ΔK diagram, and (ii) the fatigue fracture surfaces tested in highly viscous agents are covered with a new type of striation named "wavy striation", as reported previously. The crack growth rate at the transition was analysed based on fluid flow through the pores within the craze forming at the crack tip. The wavy striation was also investigated by use of the theory of meniscus instability. It is found that both the phenomena may be well described by a parameter $P = T(\Delta K)^2/\eta f$ where T and η are the surface tension and viscosity of the organic agents, respectively.

1. Introduction

The crack growth behaviour of polymers may be different under the action of a crazing agent from that in air because of its environmental attack on the crack front. Environmental crack growth under monotonic or static loading has been discussed qualitatively by Williams and Marshall [1]. According to them, the rate of crack growth (V) is well correlated with fracture mechanics parameters (FMP) such as stress intensity factor and energy release rate. The V against FMP diagram has three different regions: the slow-growth Region I where the viscoelastic property of the material subjected to the effect of the environment is dominant; Region II, where the penetration of the liquid into the crack or the craze zone ahead of it is important; and the fast-growth Region III where the growth mechanism is similar to that in air with no environmental attack. This qualitative explanation seems to describe the experimental results. However, the details of environmental crack growth under cyclic loading remain unclear, and are therefore investigated here.

A previous paper [2], which described the relationship between stress intensity factor range ΔK and crack growth rate dc/dN tested using polymethylmethacrylate (PMMA) sheets in some organic agents, revealed that (i) a transition on a log (ΔK) against log (dc/dN) diagram exists similarly to the case of static crack growth mentioned above, and (ii) the fatigue fracture surfaces of the samples are covered with a new type of striation.

As shown in Fig. 1, the fatigue fracture surface of PMMA tested in a highly viscous agent consists of three distinctive regions marked as W, B and L. A sudden change from W to B corresponds to the transition point stated above. The enlargement of Region W (Fig. 1b) indicates that the fatigue striations are regularly wavy. Because of their shape, they were named as "wavy striation" in the previous paper. The formation mechanism of the wavy striation was analysed on the basis of Taylor's meniscus instability, which occurs when a viscous liquid flows through a narrow gap between solid plates. The theoretical prediction, that the wavelength is strongly influenced by liquid properties such as surface tension and viscosity and other factors such as the elastic modulus of test material and the loading frequency, was in good agreement with the experimental trend. However, the transition behaviour of crack growth was not treated.

In this paper, therefore, the transition behaviour and the details of the wavy striation are discussed.

2. Experimental procedure

The material used was PMMA plate (Kanase Co., Japan) 10 mm thick, while the previous thickness was 5 mm. Compact tension (CT) specimens, the dimensions of which were geometrically similar to the ASTM standard ones except for the thickness, were machined from it. The dimensions of the rectangular samples, 100 mm × 96 mm, were slightly larger than the previous ones.

Fatigue tests were performed at zero-tension loading in a chamber filled with organic agent. The maximum load, which was held constant during one test, was chosen within the range 300 to 400 N. The loading frequency was mainly in the ranges 0.4 to 1 Hz and the test temperature was 295 K. The details of the experimental procedure were reported in the previous paper [2].

To investigate the effect of loading frequency on the formation of the wavy striation, a pure bending test was also carried out at a cyclic frequency of 33 Hz. The organic agent is directly dripped on to a shallow artificial notch cut along a direction perpendicular to

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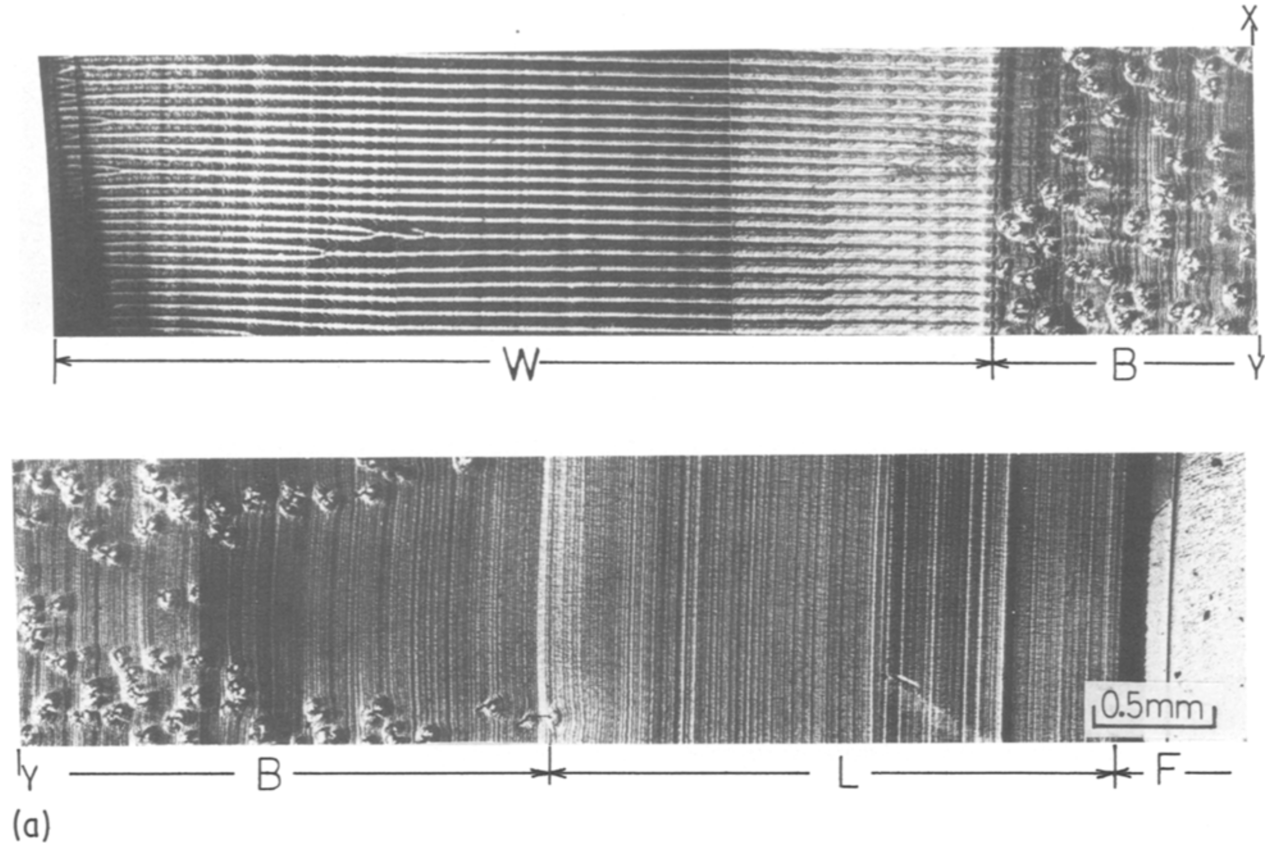

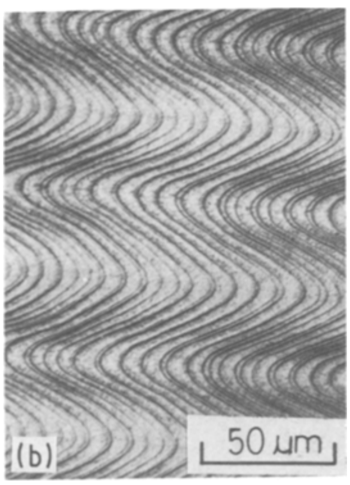

Figure 1 Fatigue fracture surfaces observed through an optical microscope. Crack propagates from left to right. (a) General view of the surface tested in propylene glycol. (b) Enlargement of region W.

TABLE I Properties of organic agents used in the present experiments*

Name of agent	Viscosity η (10^3 Pa sec)	Surface tension T (10^3 N m^{-1})
Alkanes		
Hexane	0.31	17
Octane	0.52	22
Dodecane	1.44	24
Mono-alcohols		
1-propanol	2.26	24
1-nonanol	14.3	26
Poly-alcohols		
Ethylene glycol	19.6	44
Triethylene glycol	47.0	42
Propylene glycol	48.0	72
Tetramethylene glycol	84.5	45
Pentamethylene glycol	112.0	43
Glycerol	950	57

*Values measured at 295 K by means of a viscometer and a surface tension meter.

the long axis of the specimen. In this test, a fatigue crack with a semielliptical shape develops from the notch root. The ratio k of the short to the long axes of the ellipse is about 0.3. For the calculation of stress intensity factor K, the following equation is used:

$$K = Y\sigma_B(\pi c)^{1/2}$$

where $\sigma_B = 6M/Wt^2$ and M is the bending moment, W the specimen width, t the specimen thickness, c the crack length and Y a correction factor. The computational result obtained by Ishida and Noguchi [3], which takes the ratio k into account, is used for the correction factor Y.

Both the tests were performed at 295 K. The organic agents used are listed in Table I, which includes the values of their viscosity and surface tension.

3. Results and discussion

3.1. General features

Typical examples of crack growth curves tested in hexane with relatively low viscosity and tetramethylene glycol (TMG) with high viscosity are shown in Fig. 2, where the results in air are also plotted for reference. Fig. 3 shows variations of the fracture marking with the length of crack. In Fig. 4, fatigue crack growth rates dc/dN obtained from the crack-growth curves are plotted as a function of stress intensity factor range ΔK. These figures are obtained from CT tests performed at a frequency of 0.5 to 0.8 Hz.

It is seen from Fig. 2 that the curve in TMG is slightly different from those in air and hexane. The

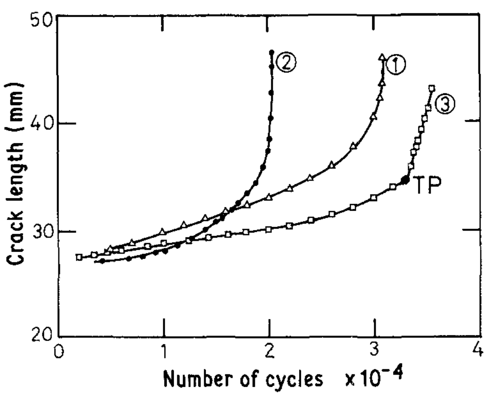

Figure 2 Examples of crack growth curves in some organic agents. 1 : in air, maximum load 400 kN; 2 : in hexane, maximum load 300 kN; 3 : in tetramethylene glycol, maximum load 400 N.

curve in TMG seems to have a break point at the place marked TP. Beyond the point TP, the crack length tends to increase linearly with an increase in the number of load cycles. In this region, therefore, the growth rate of fatigue crack is nearly insensitive to ΔK. This tendency was common to the tests executed in all agents with relatively high viscosity. This is clearly observed on the fractographs of Fig. 3. On the fracture surface tested in TMG, a drastic change in the fracture marking occurs at the crack length which corresponds to the point TP in Fig. 2. At that point, regularly wavy striations are abruptly replaced by bivalve shell-like markings. The details of the wavy striation referred to previously are described later. On the other hand, the fracture surface in hexane is covered from the beginning to the end of the test with long, straight striations crossing the entire specimen thickness and these are featureless, although the spacing between them increases with increasing crack length. For the test in air, a change is also observed in the fracture marking from a shell-like pattern (including irregular striations) to long, straight striations similar to those in hexane, but this transition is not so clearly recognized on a crack length–load cycles diagram.

These transitional behaviours are also indicated in Fig. 4. As shown in the figure, the ΔK–$\mathrm{d}c/\mathrm{d}N$ curves may consist of two regions, i.e. Region I at relatively low values of ΔK and Region II at high values of ΔK. In both regions, the usually used power-law relationship between $\mathrm{d}c/\mathrm{d}N$ and ΔK, i.e. $\mathrm{d}c/\mathrm{d}N = A(\Delta K)^m$ where A and m are constants, may be applied. In the highly viscous organic agents used here the exponents m, which are nearly insensitive to the kind of agent

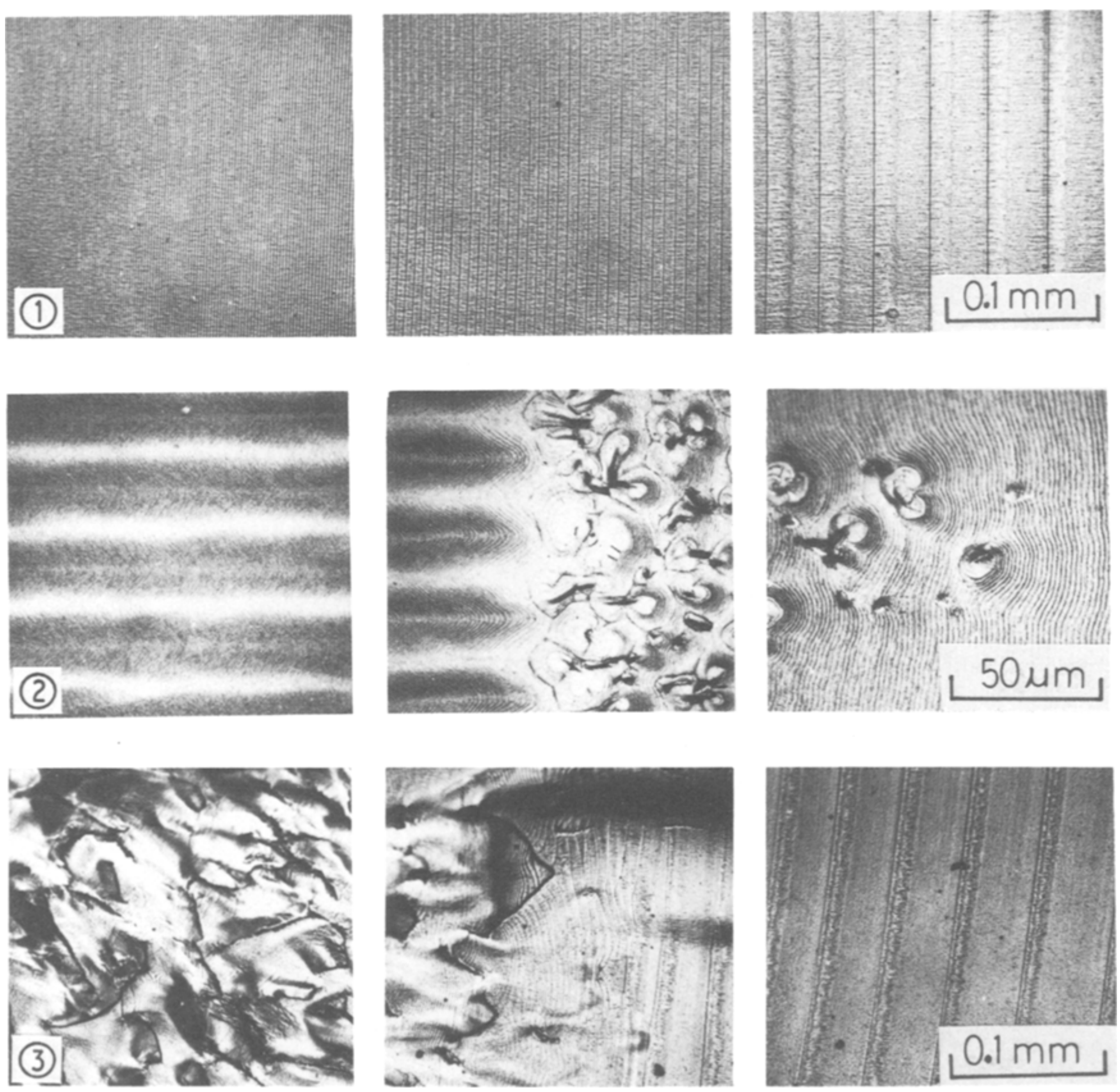

Figure 3 Variation of fracture markings with crack length. The numbers in circles correspond to those in Fig. 2. Crack grows from left to right.

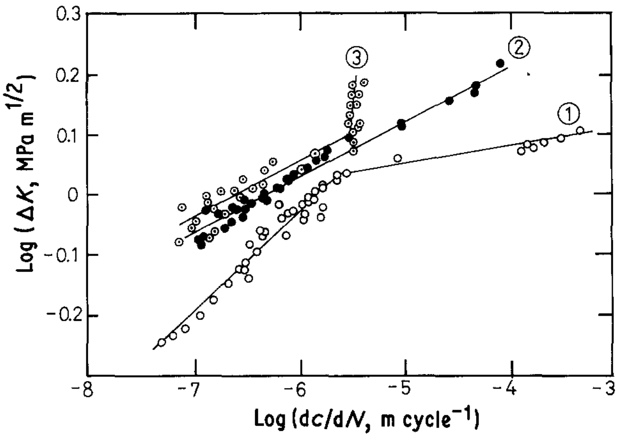

Figure 4 Fatigue crack growth rate dc/dN as a function of stress intensity factor range ΔK. The numbers in the circle correspond to those in Fig. 2.

used, are about 10 in Region I and 0.5 in Region II. The exponent m is smaller in Region II than in Region I. In air, however, the reverse is true: the values are about 4 in Region I and 30 in Region II. In hexane, the transition did not appear in the range of ΔK tested here. It is thought that in hexane, since the specimen breaks before the transition from Regions I to II occurs, such a transition is not observed on a ΔK–dc/dN curve.

3.2. Wavy striation

For the fatigue testing of PMMA plates immersed in highly viscous organic agents, the most striking feature is that regularly wavy striations form on the fracture surface. In the previous paper, this type of striation has been called "wavy striation" because of its shape. A schematic illustration of wavy striation is shown in Fig. 5. The fracture surface is slightly convex and concave and is periodically winding along the direction of specimen thickness. The shape of the striation is sinusoidal. The length from A to B is defined as the wavelength. As indicated in the previous paper [2], the wavy striations form during each load excursion. In this sense they are not different from the usually observed ones for various kinds of polymers.

In the previous paper, the initiation mechanism of wavy striation was discussed on the basis of the meniscus instability phenomenon that when viscous fluid flows through a narrow gap between solid plates, the fluid head becomes unstable to a small perturbation. This may be demonstrated by a simple test described in Fig. 6. The grease is thinly packed in place of viscous fluid between an adhesive tape and a glass

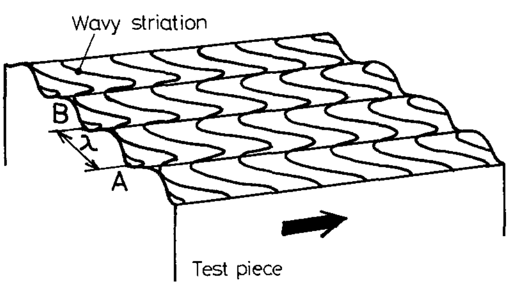

Figure 5 Schematic illustration of wavy striations.

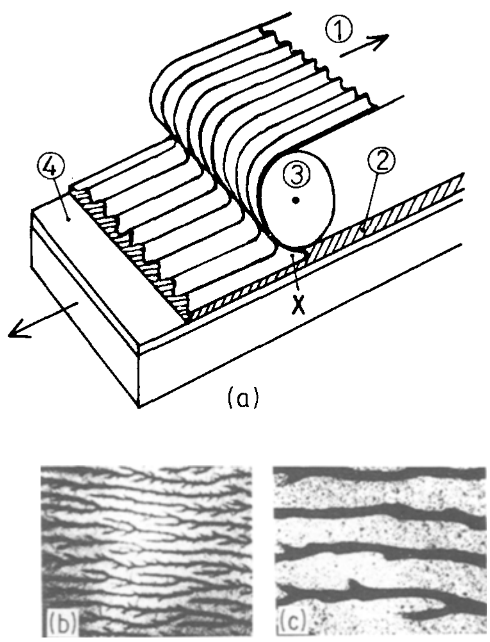

Figure 6 Simple test for obtaining striped patterns similar to the wavy mark. (a) Schematic illustration of test method. 1 : thin tape, 2 : grease, 3 : solid roller and 4 : glass plate. (b, c) Striped patterns left on the tape. The grease thickness of (c) is thicker than that of (b).

plate. When the tape is continuously torn from the glass plate by a solid cylinder, a striped pattern as shown in Fig. 6b is left on the grease attached to the tape and the glass plate. The striped patterns are very similar to the markings at Region W in Fig. 1, except for the existence of striations peculiar to cyclic loading. This pattern may be attributed to the meniscus instability which occurs at the air–grease interface denoted by Point X of Fig. 1. According to Taylor's theory, the wavelength λ is strongly influenced by the grease thickness, the tearing speed of the tape or the fluid velocity, and properties of the grease such as viscosity and surface tension. As is evident from the photographs of Fig. 6, the spacing λ between the stripes becomes wide as the grease thickness increases.

It may be supposed that this effect will occur within a narrow crevice between the crack planes. The interface of the viscous organic agent with the air stored within the crevice may become unstable due to cyclic loading, and it has a sinusoidal shape. The crests of the sinusoidal interface collide with the crack tip, weaken the polymer fibrils due to environmental attack, and are then traced on the fracture surface to form the wavy striation. If this mechanism is true, the wavelength λ may be expressed as a function of the viscosity η and surface tension T of the agent, the liquid velocity V and the gap h between the crack planes.

An analysis based on the method of Pearson [4] and others [5, 6] may be shown to lead to

$$\lambda = 2\pi(Th^2/\eta V)^{1/2} \quad (1)$$

Since the gap height h and the fluid velocity V will be proportional to the crack opening displacement and loading frequency f, respectively, Equation 1 may be rewritten as

$$\lambda \propto [T(\Delta K)^2/\eta f]^{1/2} \equiv P^{1/2} \quad (2)$$

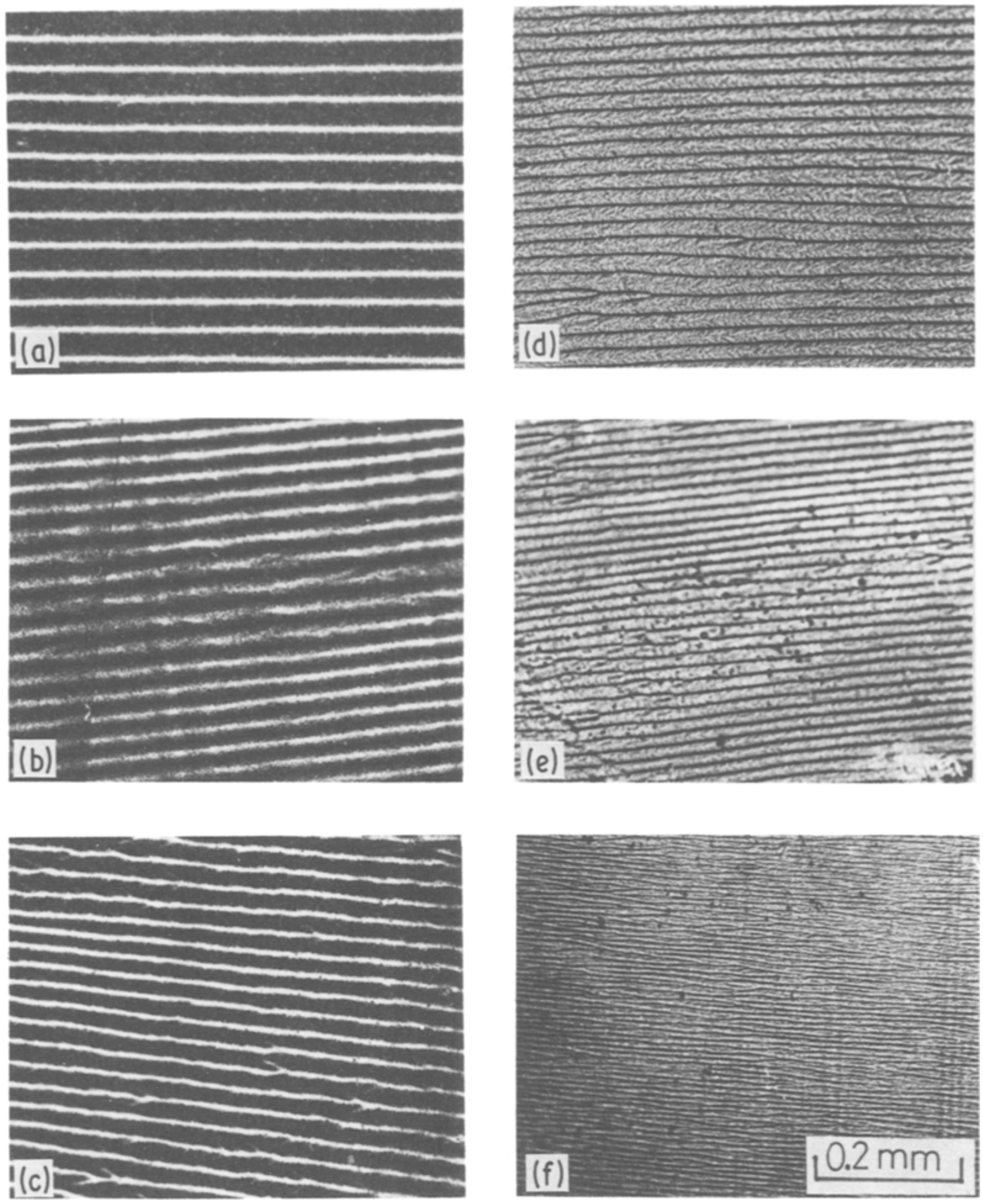

Figure 7 Wavy striations tested in (a, e) propylene glycol, (b) tetramethylene glycol, (c, f) pentamethylene glycol and (d) ethylene glycol. (a, b, c) CT tests at $f = 0.7\,\text{Hz}$; (d, e, f) bending tests at $f = 33\,\text{Hz}$.

where h is replaced by ΔK using the theory of linear fracture mechanics. It is found that the wavelength λ is determined by a parameter $P = T(\Delta K)^2/\eta f$. Comparison of Equation 2 with the experimental data is described below.

Fig. 7 shows examples of the fracture surfaces in some agents. The CT samples in the figure are tested at nearly the same values of ΔK and f. In the photographs, the wavy striations themselves are not so clearly observed, but the striped marks showing their wavelengths are distinctive. It may be found in the light of Table I that the wavelength λ tends to increase as the viscosity of the test agent decreases. In the agents from hexane to 1-propanol in Table I, wavy striations were not observed in both CT ($f = 0.4$ to 1 Hz) and bending ($f = 33\,\text{Hz}$) tests. Conversely, in both the tests in highly viscous agents they appeared on the fracture surface. In 1-nonanol and ethylene glycol, however, wavy striations did not form in the CT test but were observed in the bending test. A critical condition for the nucleation of the wavy striation, which may depend on η, T, V and h, has not been understood and will be left for future study.

The wavelengths λ measured from photographs such as those shown in Fig. 7 are plotted on the basis of Equation 2 in Fig. 8, where the previous data are also included. The present data, which are considerably scattered, somewhat depart from what is expected from the previous results. The reason for this departure remains unclear. In spite of this difference, the data have the same trend as the previous ones and nearly fall on the curve expected from Equation 2 except for the results in glycerol. The solid line in the figure is drawn with a slope 1/2 in a double logarithmic plot based on Equation 2. The good agreement between the experimental tendency and the theoretical prediction may provide evidence that wavy striation initiates due to the meniscus instability which occurs at the air–organic fluid interface when the fluid flows through a narrow gap between the crack planes.

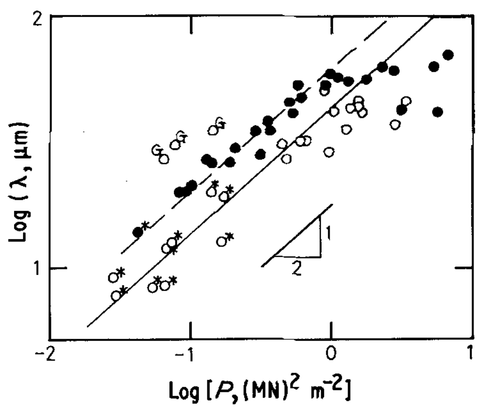

Figure 8 Wavelength of wavy striation as a function of a proposed parameter $P = T(\Delta K)^2/\eta f$. (○) Present results, (●) previous results.

3.3. Transition point

The trends of all the data obtained from CT tests are summarized in Fig. 9. In octane and dodecane, the viscosities of which are slightly higher than for hexane, the transitional behaviour mentioned in Section 3.1 seems to exist, although the fracture surfaces are similar to that in hexane and are not associated with an abrupt change in the fracture marking. In the highly viscous agents, on the other hand, the fracture mark suddenly changes from wavy striation to bivalve shell-like marking at the transition point. (In ethylene glycol, the fracture mark changes from long, straight striation to bivalve shell-like marking at the transition point.) In Region I, for all the agents used, the exponent m of the power-law relationship between dc/dN and ΔK is nearly independent of the type of agent. But in Region II, the value of m is about 2 to 4 in agents with low viscosity, while it is about 0.5 in the highly viscous ones. This difference may indicate that the mechanism of this transition is dependent on the type of agent. Besides the transition mechanism, the crack growth rate $(dc/dN)_T$ at the transition point is found to be sensitive to the environmental agent. The more viscous the fluid is, the faster is the velocity $(dc/dN)_T$.

According to the theory of Williams and Marshall [1, 7], there exist three different mechanisms of environmental crack growth under static loading as

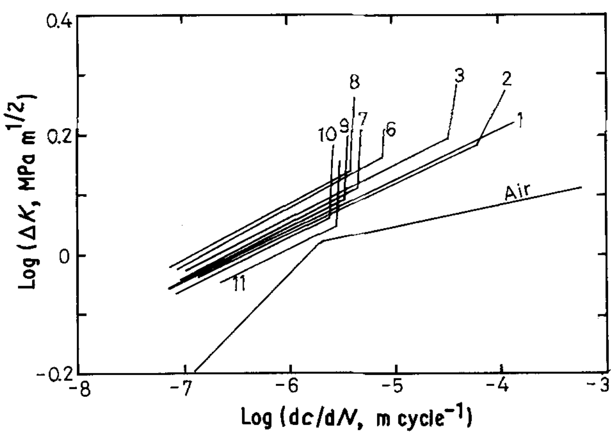

Figure 9 ΔK against dc/dN for various organic agents: (1) hexane, (2) octane, (3) dodecane, (4) 1-propanol, (5) 1-nonanol, (6) ethylene glycol, (7) triethylene glycol, (8) propylene glycol, (9) tetramethylene glycol, (10) pentamethylene glycol and (11) glycerol.

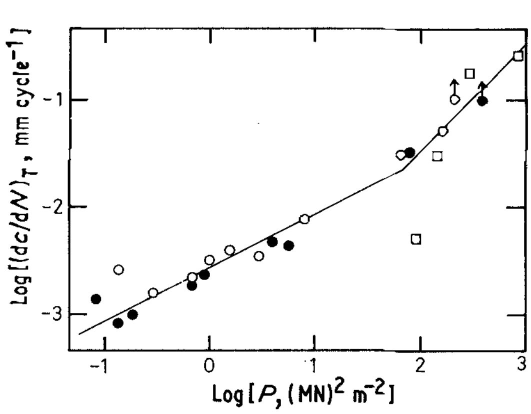

Figure 10 Crack growth rates $(dc/dN)_T$ at the transition as a function of the parameter P. (●) Previous results [2], (○) present results, (□) from Mai [9].

described in Section 1. Among them, the mechanism defined as flow-controlled crack growth may be applied to that of Region II denoted above. The growth rate $\dot{c}$ will be determined by the equation

$$\dot{c} = BK^2p/\eta \tag{3}$$

where K is the stress intensity factor, p the driving pressure of the fluid and B a constant related to the structure of the craze at the crack tip. Equation 3 assumes that $\dot{c}$ is equal to the fluid velocity V within the craze region which is calculated from Darsy's law. On the other hand, in Equation 1 a flow of fluid through a gap between the crack planes is assumed. Equation 3, therefore, is based on a viewpoint very different from that of Equation 1. In this sense the two equations may not be compatible, especially for computing the fluid velocity.

Replacing $\dot{c}$ and K in Equation 3 by dc/dN and ΔK, respectively, we can obtain the transition speed $(dc/dN)_T$ for environmental fatigue

$$\left(\frac{dc}{dN}\right)_T = \frac{B(\Delta K_T)^2p}{\eta f} \tag{4}$$

where ΔK_T is ΔK at the transition point. The right-hand side of Equation 4 denotes the distance over which the fluid moves during one cycle. In general, the driving pressure p is expressed as the sum of atmospheric pressure p_a and capillary pressure p_c. For a circular pore of radius r within the craze structure, p_c is approximately given by $p_c = 2T\cos\theta/r$ where θ is the contact angle at the fluid–solid interface. When $p_c \gg p_a$, Equation 4 is rewritten as

$$(dc/dN)_T \propto P \tag{5}$$

where $\cos\theta$ is set equal to unity for simplicity and P is the same parameter as used in Equation 2. In place of Equation 3, another equation which does not include the effect of K has been proposed by Kambour and Yee [8]. This K-independent equation rather than Equation 3 may fit the crack-growth behaviour of Region II in a highly viscous agent. As shown in Fig. 9, however, ΔK_T is not so affected by the type of agent. The parameter P will then be appropriate for describing the transition behaviour also in the K-independent equation.

The experimental relation between $(dc/dN)_T$ and P is plotted in Fig. 10. The previous results (denoted by solid circles) were measured from the transition points of the fracture marking, while the present data (open circles) were obtained by use of ΔK–dc/dN diagrams. In the figure, the results of Mai [9] are also included. Since his results are indicated in a dc/dN–R diagram where R is the energy release rate, ΔK_T is calculated from the relation $R = K^2/E$ with $E = 330\,\text{kgf}\,\text{mm}^{-2}$ (3.23 GPa). It may be pointed out from the figure that in agents with relatively low viscosity, Equation 5 is valid, but in highly viscous agents $(dc/dN)_T$ varies linearly with the square root of P rather than P. In other words, it may be concluded that the transitional behaviour is greatly influenced by the marking traced on the fracture surface. The reason for this aspect is not understood here, and should therefore be investigated in the future. Irrespective of this uncertainty, the parameter P is found to be useful for describing some features of environmental cracking.

4. Conclusions

Fatigue crack growth tests were performed using PMMA plates in organic agents with different viscosities. The results are summarized as follows:

1. A new type of striation, named "wavy striation" in the previous paper [2], was confirmed to form in organic agents with relatively high viscosity. Its wavelength was explained in terms of a parameter P derived from the theory of meniscus instability.

2. There exist two regions at least on a dc/dN–ΔK diagram. For transitional behaviour from one region to the other, the case where the fracture marking changes abruptly and the one where a special change in the fracture marking does not occur were observed. The former and the latter occurred in agents with high and low viscosities, respectively. The crack growth rate at the transition point is well described by the same parameter P as used for explaining the new type of striation.

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