

Environmental Stress Cracking of Poly(butylene succinate)/Cellulose Triacetate Blend Films

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ABSTRACT: Blend films of poly(butylene succinate) (PBS) with cellulose triacetate (CTA) were prepared using a solvent-cast technique. The environmental stress cracking (ESC) behavior of commercial PBS films and that of as-prepared PBS/CTA blend films were investigated in an aqueous NaOH solution. It was found that the fracture behavior of PBS films can be analyzed by linear fracture mechanics, that is, the stress-intensity factor, K , is found to control the crack-growth rate, da/dt , in PBS films. The enhancement of da/dt induced by increasing the normality of NaOH(aq) is more marked at a high value of K rather than

at a low value of K . Furthermore, the ESC behavior of the PBS/CTA blends was studied in NaOH(aq). It was found that the behavior cannot be analyzed by linear fracture mechanics and that the addition of CTA into PBS increases the ESC resistance of the blends. Large-scale yielding of the material around the crack tip seems to be responsible for the high ESC resistance of the blends. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 510–515, 2003

Key words: biodegradable; blends; fracture; stress; toughness

INTRODUCTION

In recent years, the increase in plastic rubbish has become a serious social problem. Biodegradable polymers should be used in many household and industrial applications to solve this problem. However, the polymers have not yet been widely used in these applications for the following reasons: (i) These polymers are more expensive than are other conventional polyolefin polymers, (ii) biodegradable polymers having many different kinds of physical properties are not produced, that is, the number of the polymers is not so large that all the applicable fields of the polymers have been covered, and (iii) the physical properties of the biodegradable polymers have not been fully investigated because the polymers have only been industrially produced in recent years.

Polymer blending is a convenient method to develop a new material. Many authors have produced new biodegradable materials by using this method and reported the physical properties of the blends.^{1–4} There are also reports on the applications for biodegradable polymers.^{5–7} The biodegradable polymers are used as structural elements in biodegradable environments such as in soil, seawater, and the human body. For the estimation of the reliability of the polymers in these environments, the hydrolysis mechanism of the polymers should be known. There are many reports on the hydrolysis mechanism of biode-

gradable polymers under no stress conditions.^{8,9} Taking account of the fact that stress is more or less applied to the structural elements in real situations, we should study the hydrolysis mechanism of biodegradable polymers subjected to applied stresses.

It is known that crack and crazes grow in polymers by the presence of an environment and a stress; this phenomenon is called environmental stress cracking (ESC).^{10–12} In most cases, there is no chemical interaction between the environment and the polymer. Since ESC is a characteristic phenomenon of polymers, many works on the ESC behavior of polymers have been reported. For example, we described the ESC behavior of a low-density polyethylene (LDPE) analyzed using linear fracture mechanics.^{13,14}

Poly(butylene succinate) (PBS) is an aliphatic polyester. The polymer has biodegradability and flexibility. In the previous work, we reported that homogeneous films are obtained from the blend of PBS with cellulose triacetate (CTA) and that the new materials having various thermal/mechanical properties can be produced by change of the blend ratio.¹⁵

The purpose of this article was to investigate the ESC behavior of PBS film and PBS/CTA blend film in a NaOH(aq) environment. In this discussion, we take account of the chemical reaction, namely, the hydrolysis of the polymer.

EXPERIMENTAL

Materials

PBS films having 60- μm thickness and pellets of PBS were supplied by the Showa High-Polymer Co., Ltd.

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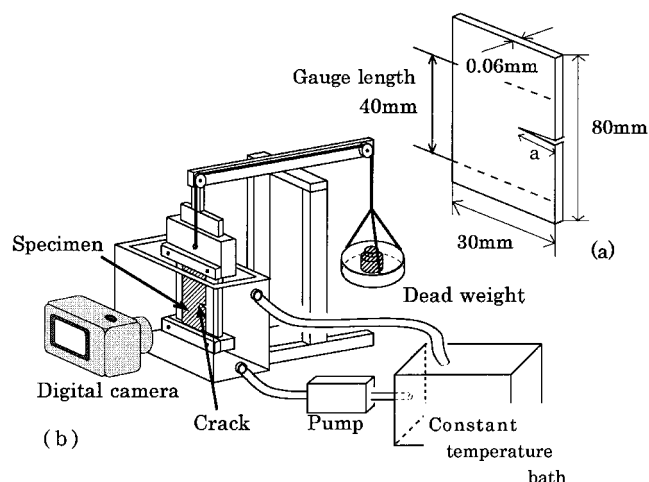


Figure 1 (a) Dimensions of the test specimen and (b) the apparatus used for observing ESC.

(Tokyo, Japan; commercial name, Bionolle B1001). The pellets were used for the preparation of the PSB blend films. CTA was supplied by the Mitsubishi Rayon Co., Ltd. (Toyama, Japan). Reagent-grade chloroform (Nacalai Tesque, Tokyo, Japan) was used as a cosolvent of PBS and CTA without further purification. Furthermore, reagent-grade NaOH was used for the hydrolysis experiment.

Preparation of blends

Specified amounts of PBS pellets and CTA were placed in a beaker; the total amount of these materials was 0.5 g. Chloroform (20–30 mL) was added to the beaker. After being stirred vigorously for about 2 h, the mixture became a homogeneous solution. The solution was cast onto a glass Petri dish. After chloroform was vaporized at 50°C, homogeneous films of about 50–80 μm in thickness were obtained. The blend film containing a given amount of CTA will be referred to as $\phi_{\text{CTA}} = X$, where X represents the weight percentage of CTA in the blend.

Method of ESC measurement

Figure 1 shows the dimensions of the test specimen and the apparatus used for observing the ESC. Since thin PBS films were used in the ESC experiments, the fracture seemed to occur under plane-stress conditions. In the center of a long edge of the each specimen, a sharp notch was introduced with a razor blade; an initial crack length in the range of 4–5 mm was arbitrarily chosen. For observation of the ESC behavior, we designed the apparatus to permit application of a constant load to the specimen in the environmental agent; NaOH(aq), having a given normality, was used as the environment. We controlled the temperature of the agent by circulating it in a constant tem-

perature bath. We can apply a given stress to the specimen by changing the dead weight. For the measurement conditions, the stress range 1.1–3.4 MPa, the temperature range 20–40°C, and the normality range 0.05–0.3N were chosen. The fracture behavior of PBS film was also observed under air and water environments. Photographs of the crack tip were recorded with a digital camera within specified time intervals. From the photographs, the crack length was estimated.

Observation of fracture surface

We observed the fracture surfaces with a scanning electron microscope (SEM, HITACHI S-2400) to investigate the effect of environments on the fracture surface and to characterize the mode of fracture. The specimens were removed from the liquid after being fractured, washed by water for about 1 h, and then dried at 50°C. The specimens were gold-coated prior to SEM observation.

Data analysis

The stress-intensity factor, K , of the specimen having a single-edge notch was calculated by using the Brown and Srawly relation¹⁶:

$$K = \sigma_{\infty}(a\pi)^{1/2}Y \quad (1)$$

where σ_{∞} is the applied stress; a , the crack length; and Y , a geometrical correction factor. The value of Y is given by

$$Y = 1.12 - 0.231(a/W) + 10.55(a/W)^2 - 21.72(a/W)^3 + 30.39(a/W)^4 \quad (2)$$

where W is the width of the specimen.

We calculated the value of K by substituting values of the applied stress and the instantaneous crack in eqs. (1) and (2). The crack-growth rate da/dt was also calculated from data on the crack length versus time.

RESULTS AND DISCUSSION

Fracture behavior of PBS films

Figure 2 shows the effect of the environment on the crack propagation in PBS films under a given loading condition. It can be seen that the crack propagates in the PBS films soaked only in a NaOH aqueous solution. This means that the crack propagation is enhanced not only by the applied stress but also by the kind of environment used.

Owing to the plastic constraint, dilatational stresses are created ahead of the crack tip by the application of stress. The dilatational stresses are thought to produce

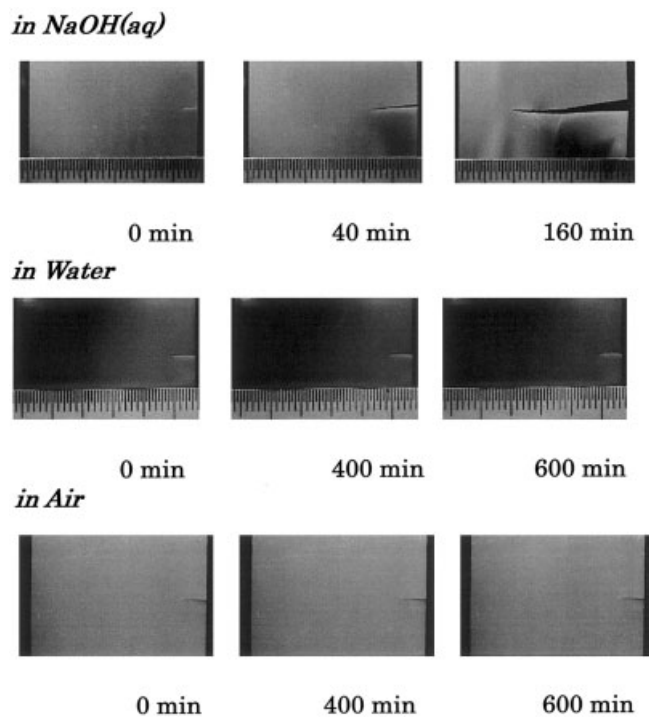


Figure 2 Effect of environments on the crack propagation in PBS films under a given loading condition; $\sigma_{\infty} = 3.4$ MPa.

microvoids and to promote the flow of environmental agents. By the flow of NaOH(aq), the PBS molecules are locally plasticized and then hydrolyzed. Consequently, the crack seems to propagate in the PBS films. We will discuss the following experimental results on the assumption that the crack-growth rate is controlled not only by the flow rate of the liquid but also by the rate of hydrolysis of the bulk material ahead of the crack tip; the hydrolysis rate of the bulk material increases with increasing normality of NaOH(aq).

Figure 3 shows the effect of the loading conditions on the relation between da/dt and K . As seen in Figure 3(a), da/dt appears to increase with increasing K . Since the increase in da/dt is particularly marked at low values of K , it seems that there is a threshold value of K for crack propagation. It should be noted that the crack-growth rates measured under three different loading conditions can be plotted on a single master curve. This means that da/dt is not controlled by the applied stress but controlled by K . This also implies that the ESC behavior of PBS films can be analyzed by using linear fracture mechanics. In other words, the experimental results suggest that the fracture of PBS in NaOH(aq) occurs under small-scale yielding conditions. As seen in Figure 3(b), the same conclusion is obtained when 0.3N NaOH(aq) is used as the environment. From these results, we conclude that the crack-growth rate of PBS films in NaOH(aq) is controlled only by K , regardless of the normality of the solution used.

The effects of temperature of NaOH(aq) on the da/dt versus K plots were investigated using two normalities of NaOH(aq). The results are shown in Figure 4. There is no clear temperature dependence of the da/dt versus K curves. In our previous works on the ESC behavior of LDPE in alcohols, we reported that the crack-growth rate is strongly influenced by the alcohol temperature,^{13,14} that is, it was found that the crack-growth rate increases with increasing temperature. We proposed that the increase in the crack-growth rate is attributed to the decrease in viscosity of the environmental agent. However, the temperature dependence of the viscosity of NaOH(aq) is not larger than that of alcohol in the temperature range used. Therefore, the da/dt versus K curves observed in NaOH(aq) seem to show no temperature dependence. Figure 5 shows the effect of the normality of

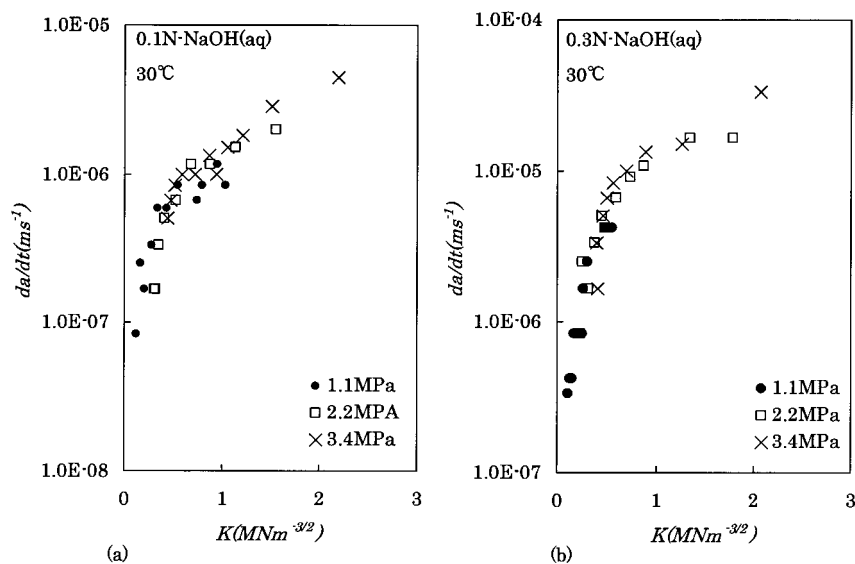


Figure 3 Effect of loading conditions on the relation between da/dt and K : (a) 0.1N NaOH(aq); (b) 0.3N NaOH(aq).

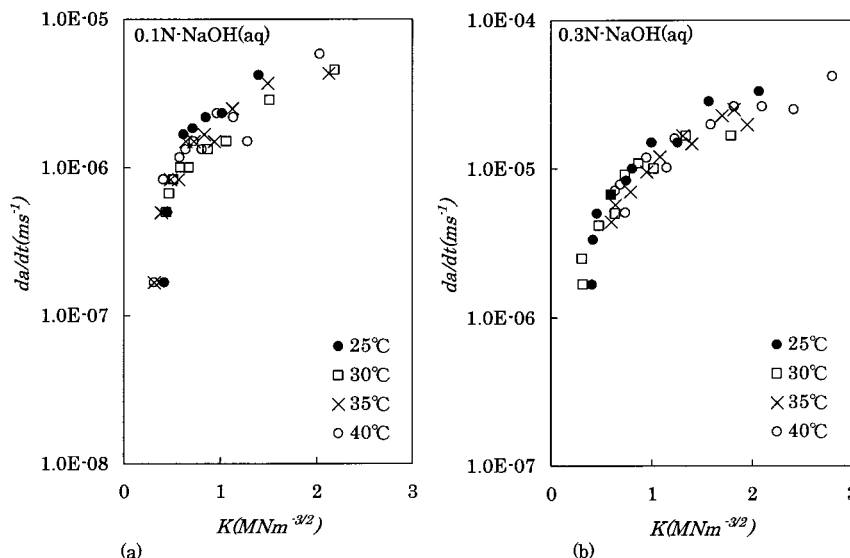


Figure 4 Effects of temperature of NaOH(aq) on the relation between da/dt and K : (a) 0.1N NaOH(aq); (b) 0.3N NaOH(aq).

NaOH(aq) on the relation between da/dt and K . It seems that there is a single threshold value of K for crack growth irrespective of the normality of NaOH(aq). Since the threshold value is independent of the normality, the flow rate of the liquid into the material around the crack tip seems to dominate the crack-growth rate. On the

other hand, it is noted that the crack-growth rate at a high value of K is relatively influenced by the normality. This result may suggest that the rate of hydrolysis of the bulk material around the crack tip controls the crack-growth rate when K is high. Although the fracture mechanism described above is disputable, our experimental data showing that the increase in the normality enhances the crack-growth rate particularly at a high value of K should be noted.

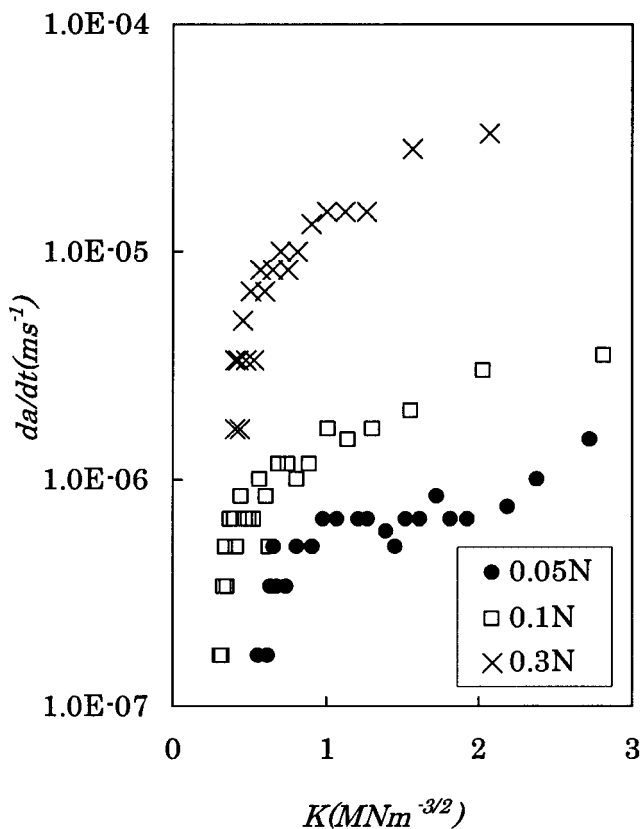


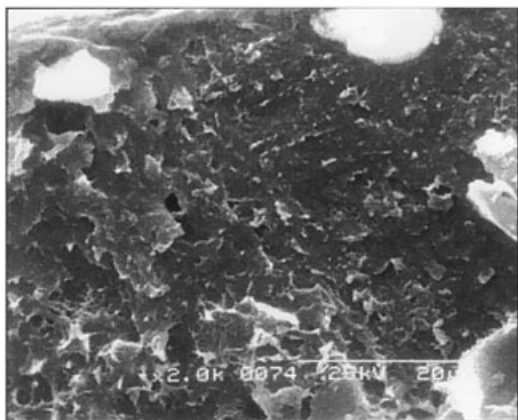
Figure 5 Effect of the normality of NaOH(aq) on the relation between da/dt and K .

Figure 6 shows the fracture surfaces of PBS films. Smooth surfaces are observed at the early stage of the crack growth. On the other hand, rough surfaces can be seen at the final stage of the crack growth. Therefore, the fractures in the initial stage and that in the final stage seem to occur under a brittle mode and under a ductile mode, respectively. As discussed previously, the crack-growth rate at a low value of K is dominated mainly by the flow rate of the liquid, while that at a high value of K is dominated by the rate of hydrolysis of the bulk material. This difference of the fracture mechanisms may be reflected in the morphology of the fracture surfaces.

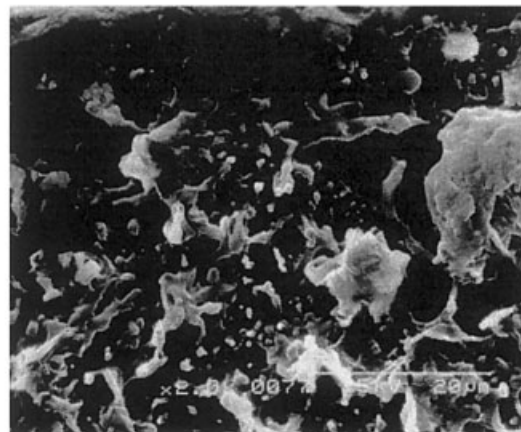
Fracture of PBS/CTA blends

The effects of ϕ_{CTA} on the relation between da/dt and K were investigated. The results are shown in Figure 7. It can be seen that the ESC resistance increases with increasing ϕ_{CTA} . This means that CTA molecules in the blends do not act as a stress concentrator, but, rather, act as an inhibitor of the crack growth. The effect of the applied stress on the relation between da/dt and K of the blend film was investigated. The results are shown in Figure 8. The da/dt versus K curves appear to be strongly dependent on the applied stress, namely, the crack-growth rate measured under the applied stress of 1.6

0.05N-NaOH(aq)

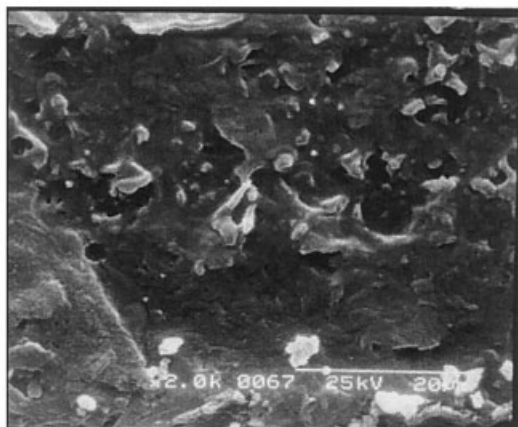


(a)

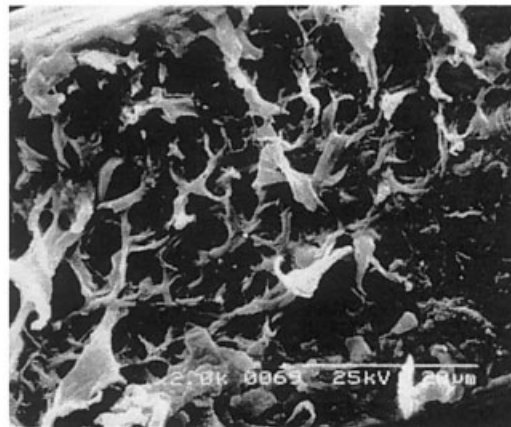


(b)

0.3N-NaOH(aq)



(c)



(d)

$20 \mu m$

→
Crack growth direction

Figure 6 SEM micrographs of fracture surface of PBS film: (a, c) early stage of the crack growth; (b, d) final stage of the crack growth.

MPa is markedly slower than that measured under the applied stress of 3.4 MPa. Since the da/dt versus K curve is strongly influenced by the applied stress, the fracture behavior cannot be analyzed by linear fracture mechanics, that is, the fracture of the blends occurs not under small-scale yielding but under large-scale yielding con-

ditions. The creation of the large-scale yielding would be responsible for the blends showing high ESC resistance. In the previous work, we reported that the PBS molecules are compatible with CTA molecules.¹⁵ In PBS-rich blends, the CTA molecules would be present in the amorphous PBS regions. Since the main chains of the

CTA molecules are scarcely hydrolyzed, the chains form ligaments to bind the crack surface. The presence of the chains would reduce the stress concentration at the crack tip and behave as obstacles for crack growth. Although this proposed mechanism seems to be plausible, there is no direct evidence to support the above explanations.

CONCLUSIONS

The ESC behavior of PBS films and that of PBS/CTA blend films were investigated in NaOH(aq). The following conclusions are deduced from the observed result: First, the crack-growth rate in PBS film depends only on the stress-intensity factor. This means that the fracture behavior of PBS films can be analyzed using linear fracture mechanics. Second, the crack-growth rate in PBS film is independent of the temperature of the NaOH(aq) used. Third, the crack-growth rate observed at a high value of K is markedly increased with increasing normality of NaOH(aq). Finally, the addition of the CTA improves the ESC resistance. Large-scale yielding is found to take place around the crack tip of the blends. This yielding seems to be responsible for the blends showing high ESC resistance.

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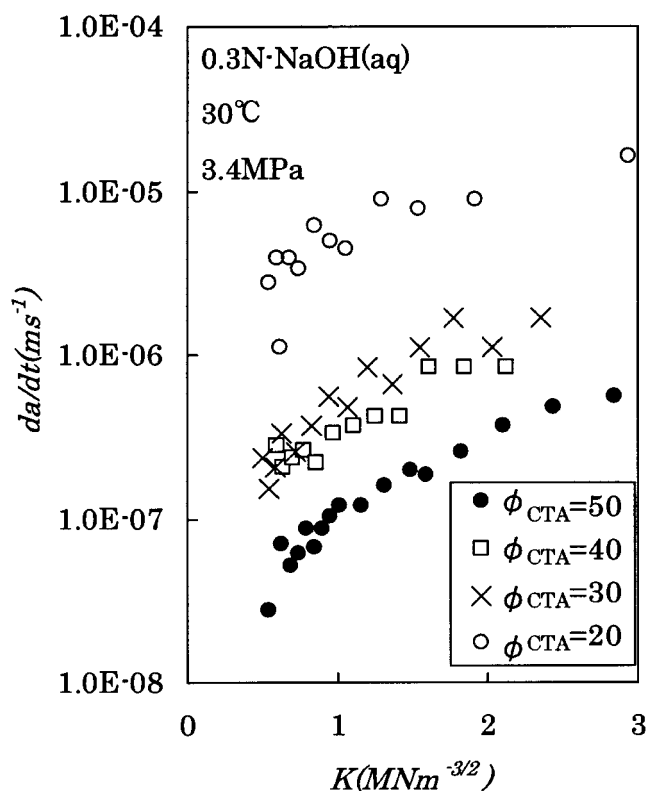


Figure 7 Effect of ϕ_{CTA} on the relation between da/dt and K ; $\sigma_{\infty} = 3.4$ MPa.

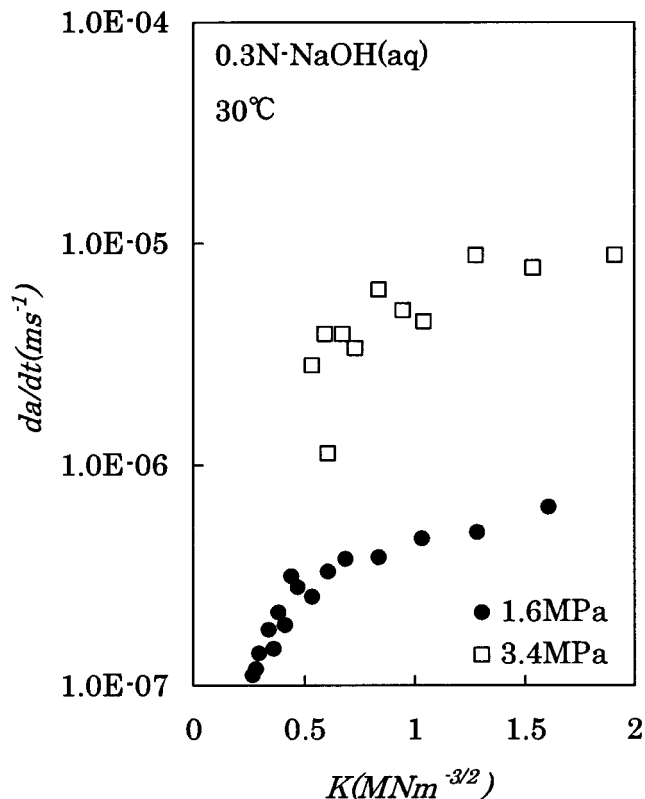


Figure 8 Effect of the applied stress on the relation between da/dt and K of the blend film.

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