Effects of Moisture Absorption on Fracture Behaviors of Acrylonitrile-Butadiene-Styrene Resin

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ABSTRACT: The effect of moisture absorption on fracture behaviors of acrylonitrile-butadiene-styrene (ABS) resin has been studied. For comparison, polystyrene (PS) and styrene-acrylonitrile (SAN) resin have been tested. The fracture toughness of PS and SAN resins is determined by the ASTM standard test method for brittle polymers. The fracture toughness of ABS resin is obtained on the basis of the multiple specimens method. The fracture toughness of PS and SAN resin decreases with the increase in moisture absorption. On the other hand, the fracture toughness of ABS resin slightly decreases despite enormous moisture absorption. On the specimens absorbing moisture, a bright whitening region and a milky coloring region are distinguished in the stress-whitening region, and the milky coloring region expands around the bright whitening region at the crack tip. From the transmission electron microscopic observation, the precraze formation can be recognized in this region. The crack-tip shielding effect induced by this formation compensates the fracture toughness decrease due to moisture absorption. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 435–442, 1999

Key words: ABS resin; fracture toughness; moisture absorption; SAN resin; polystyrene; TEM observation; craze; stress-whitening

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) resin is a family of thermoplastics that contains three monomeric units: acrylonitrile, butadiene, and styrene. Namely, a styrene/acrylonitrile (SAN) copolymer matrix contains discrete butadiene-based elastomer particles. Elastomer particles are grafted with SAN resin to achieve necessary interaction with the matrix polymer. As a result, SAN resin can be substantially toughened by the incorporation of rubber particles. Recently, Goto and co-researchers[1–3] have systematically researched that three parameters of the rubber phase (i.e., rubber particle size, rubber content, and rubber chemical structure) affect the Izot Impact strength.

The fracture behavior of ABS resin has been the subject of considerable research. Truss and Chadwick[4] investigated the craze and whitening process at a crack tip using a transparent ABS resin and observed the initial crack growth in the craze bundle. This result showed that the crazing affects the fracture behaviors. From transmission electron microscopic (TEM) observation using

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Table I Contents of Chemical Components

Sample	Components	Weight %
PS	PS	100
SAN resin	Styrene	77
	Acrylonitrile	23
ABS resin	Styrene	64
	Acrylonitrile	23
	Butadiene	13

thin films, Donald and Kramer[5] suggested that the crazing, the void nucleated by the larger rubber particles, and the shear deformation encouraged by the cavitation of smaller rubber particles are the important contributions to the toughness. Ni and colleagues[6] indicated that the whitening zone at crack tip consists of the cardioid zone that is associated with cavitation in the larger rubber particles and the finger-like zone radiating from the crack tip. Consequently, two kinds of stress-whitening state seem to exist at a crack tip of this ABS resin.

Most rubber-modified thermoplastics become brittle after a few months, or even weeks, out of doors. This tendency is one of the most serious limitations of these materials, because it excludes them from a wide range of applications for which they are otherwise suitable. Several papers have been published on the environmental effect (e.g., weathering[7,8]) or degradation of γ-irradiation[9]; but, nevertheless, very little attention has been paid to the moisture absorption affecting fracture toughness.

In this article, the effect of the moisture absorption on the fracture behaviors of ABS resin is investigated. For comparison the matrix material (SAN) resin and one of its components (polystyrene; PS) is tested at the same exposure conditions. Stress-whitening regions of ABS resin at a crack tip are observed for investigating the change of fracture toughness mechanism by transmission electron microscopy.

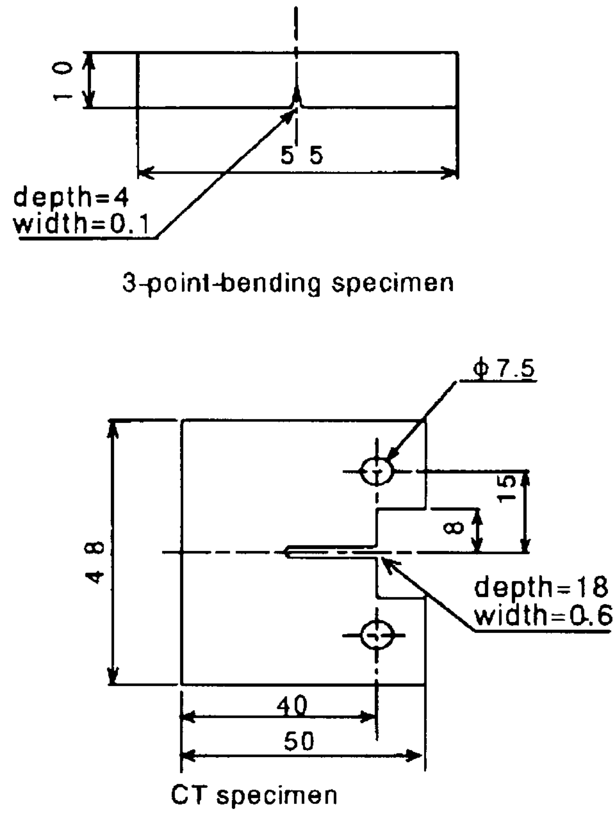

Figure 1 The dimensions of specimens.

EXPERIMENTAL

Procedures

The chemical components of PS, SAN resin, and ABS resin are shown in Table I. These materials were supplied by Daicel Chemical Industries, Ltd. Single-edge notch bend specimens of PS and SAN resin, and compact tension (CT) specimens of ABS resin were cut from injection-molded sheets of dimensions 150 mm × 223 mm × 3.2 mm. The shape of the specimens is shown in Figure 1. The notch to give an appropriate length was machined by a diamond blade. The tapping and sliding methods were used to introduce a precrack for single-edge notch bend and CT specimens, respectively. Specimens were exposed in a chamber with the condition given in Table II. After the exposure, the specimens were cooled down in air for several hours to room temperature. To estimate moisture absorption, the weight of the specimen was measured using an electronic balance before

Table II Conditions of Exposure Test

Specimen	Temperature (°C)	Humidity (%)	Days
As received (original)	—	—	—
1	85	85	4
2	40	85	4

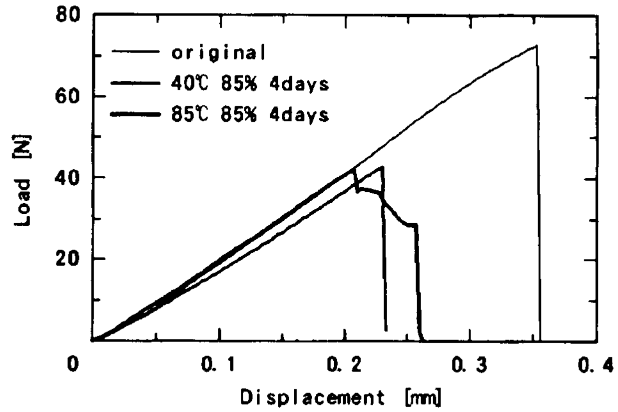

Figure 2 Typical load-displacement curves of PS specimens.

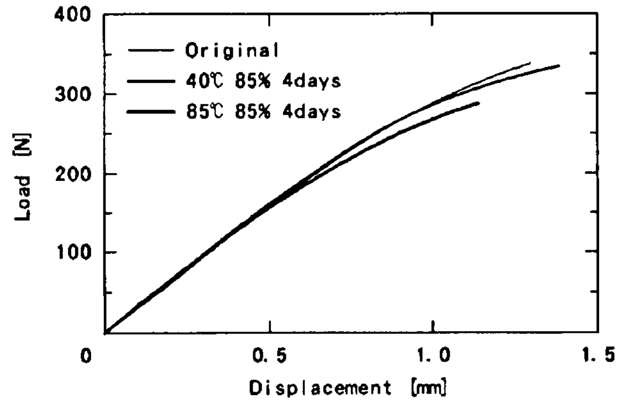

Figure 4 Typical load-displacement curves of ABS resin specimens.

and after exposure. The three-point-bend and CT tests were conducted using an Instron-type testing machine with a cross-head speed of 1 and 5 mm min^{-1}, respectively, at a temperature of 23 ± 1°C. The crack tip regions of some ABS resin specimens were also photographed during loading.

The damage regions of ABS resin were observed by transmission electron microscopy (JEM-100CX, produced by JEOL). Suitable grid squares were cut from the specimens and strained in OsO_4 for 48 h and RuO_4 for 2 h. Thin sections were cut perpendicular to the fracture surface.

Determination of Fracture Toughness of PS and SAN Resin

Figures 2 and 3 show load *vs.* displacement curves of PS and SAN resin, respectively, for the original (specimens as received), weakly wet (40°C, 85%, 4 days), and strongly wet (85°C, 85%, 4 days) conditions. The fracture toughnesses, K_{IC} of PS and SAN resins that fractured in a brittle manner were determined by the ASTM standard D5045-91a. As shown in Figure 2, "pop-in" fracture occurred in some exposed PS specimens so that the K_{IC} was obtained from the load value at the "pop-in" initiation. K_{IC} of the original SAN resin specimen was determined from the maximum load when the crack starts to propagate.

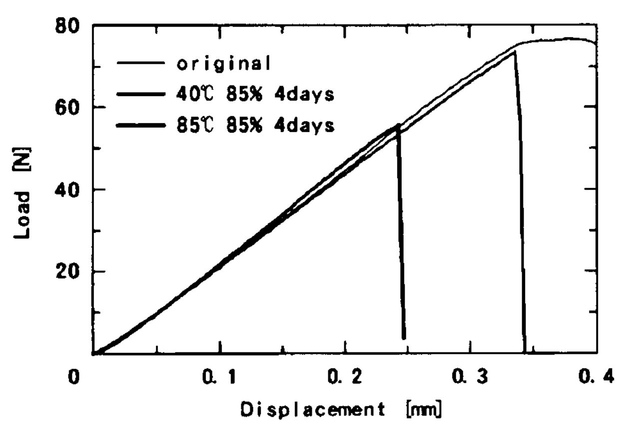

Figure 3 Typical load-displacement curves of SAN resin specimens.

Multiple Specimens Method in ABS Resin

Figure 4 shows load *vs.* displacement curves of ABS resin for the original, light wet, and hard wet conditions. For ABS resin specimens, it is noted that the maximum values of the load in Figure 4 do not correspond to the fracture initiation, but to the unloading point in the experiment. Because the crack propagation occurred in a stable manner for ABS resin, the multiple specimens method was applied to obtain fracture toughness. In the test, the specimens were loaded to different subcritical displacements to obtain different levels of crack growth. After unloading, the specimens were divided into two pieces after they were cooled down in liquid nitrogen. The initial crack length (a_0) and the crack growth length (Δa) were measured by using the optical microscope equipped with a x-y stage and a dial gage. This optical microscope has a CCD camera at the focus point and an image can be seen on a video monitor. Moreover, optical fibers are attached to the tip of the microscope and a hydrogen lamp is set at the opposite end of these fibers. Because high-intensity light through fibers is irradiated onto an

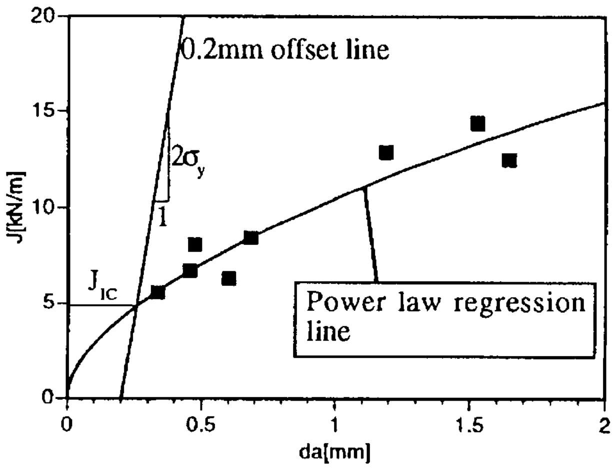

Figure 5 J-integral *versus* crack extension length curve of the original ABS resin specimens.

observed surface, the depth of focus is higher than a normal microscope.

The measurement of Δa seems to be difficult in the fracture test of ABS resin. Narisawa and Takemori[10] studied the fracture toughness of rubber-modified polymers. They suggested that the use of crack blunting lines might be misleading the determination of the fracture toughness because of the ambiguity of the blunting measurement (i.e. Δa). To measure a precise Δa, red ink was penetrated into the fracture surface for marking the crack tip before dividing the specimens and the microscope with optical fibers described previously were used. Consequently, we can accurately and exactly measure Δa, since it is easy to identify the position of crack tip.

Determination of Fracture Toughness of ABS Resin

Several papers[10,11] have been published in which the blunting line approach was used to determine experimentally J_{IC}. We examined the blunting line approach from the comparison between the fracture toughness determined from K_I with K_{IC} calculated from J_{IC} according to ASTM E813-89.

The relationship between Δa and the J-integral of original specimens was shown in Figure 5. If the stress field at the crack tip satisfies the small-scale yielding condition, consequently, the relationship between J_I and K_I is

$$J_I = G = (1 - \nu^2)K_I^2/E \qquad (1)$$

where G is the strain energy release rate, E is the Young's modulus, and ν is Poisson's ratio. K_{IC} was converted using eq. (1) and shown in Table III.

Table III Comparison of K_{IC} Calculated from J_{IC} According to ASTM E813-89, with K_{in} Determined from K_I

	Original	40°C 85% RH	85°C 85% RH
K_{IC} (from J_{IC})	3.47	2.90	2.97
K_{in}	3.64	3.13	3.15

RH, relative humidity.

The relationship between Δa and the stress intensity factor K_I of original specimens was shown in Figure 6. The solid line in this figure fitted the data by the least-squares method. This figure shows that the slope of this line until $\Delta a = 1.5$ mm is not so large. We decided K_{in} as the extrapolation of K_I to $\Delta a = 0$ and show the values in Table III with the other conditions. In all conditions, the differences of both values are <8%.

RESULTS

K_{IC} against Moisture Absorption

Figure 7 shows the variation of K_{IC} against the moisture absorption. K_{IC} of PS and SAN resin significantly decreases with the increase of moisture absorption. On the other hand, K_{IC} of the ABS resin slightly changes, even if the amount of moisture absorption of ABS resin is larger than that of PS and SAN resin. In the following sections, we discuss the reason by means of microscopic observations.

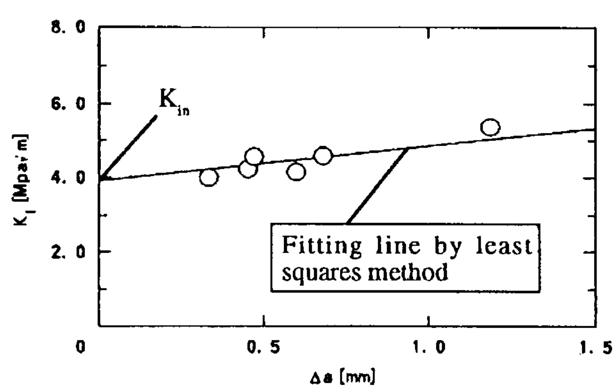

Figure 6 K_I *versus* crack extension length curve of the original ABS resin specimens.

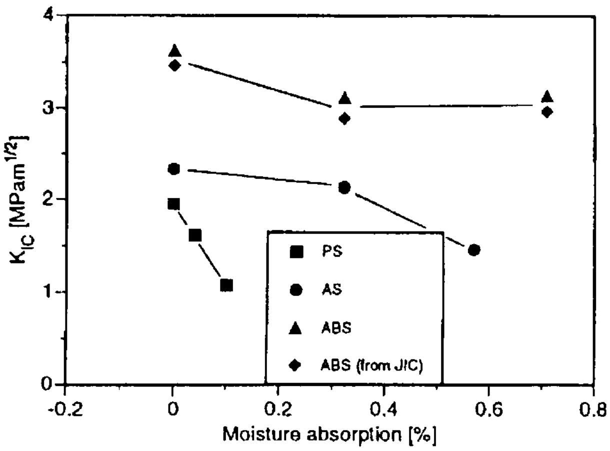

Figure 7 K_{IC} variation due to moisture absorption.

Whitening Region of ABS Resin

The photographs in Figure 8 show the side surfaces of original and 85°C 85% exposed ABS resin specimens during the tests. Although the applied load is almost same level (~ 350 N), the shapes and color of the stress-whitening region are different from each other. Figure 9 shows a schematic drawing of the whitening regions in Figure 8. Although the original specimens have only one whitening region at the crack tip, the 85°C 85% exposed specimen has two regions: the bright whitening region near the crack tip and the milky coloring region around the bright whitening region. To investigate the microdeformation, we performed TEM observation to the points indicated by A to C in Figure 9.

TEM Photograph of ABS Resin

Figure 10 shows the photograph at point A. Voids in some rubber particles and narrow bands around some rubber particles can be seen. Such voids and bands cannot be observed in the specimens before fracture testing. From the magnified photograph [Figure 10(b)], this band is identified with alignment of a small cavity that is regarded as the precraze proposed by Lu and colleagues.[12] The void nucleation and the precraze formation play the role of toughening mechanisms (i.e., the crack-tip shielding effect).[13]

The TEM photograph at point B is shown in Figure 11. By comparing it with Figure 10, the morphology at point B is similar to that at point A. Figure 12, which is the TEM photograph at point C (i.e., the morphology of the milky coloring region in 85°C 85% exposed specimen) shows the appearance of only the precraze formation, not the void nucleation. Because the milky coloring region exists surrounding the bright whitening region, the sequence of the stress-whitening process can be considered as follows (Figure 13): step 1—precraze formation in the SAN matrix around rubber particles by the triaxial tension stress; step 2—void nucleation in occluded rubber particles by the triaxial tension stress; and step 3—shear deformation between rubber particles by the release of triaxial constraint.

DISCUSSION

On PS and SAN Resin

As previously described, fracture toughness of PS and SAN resin significantly decrease with the

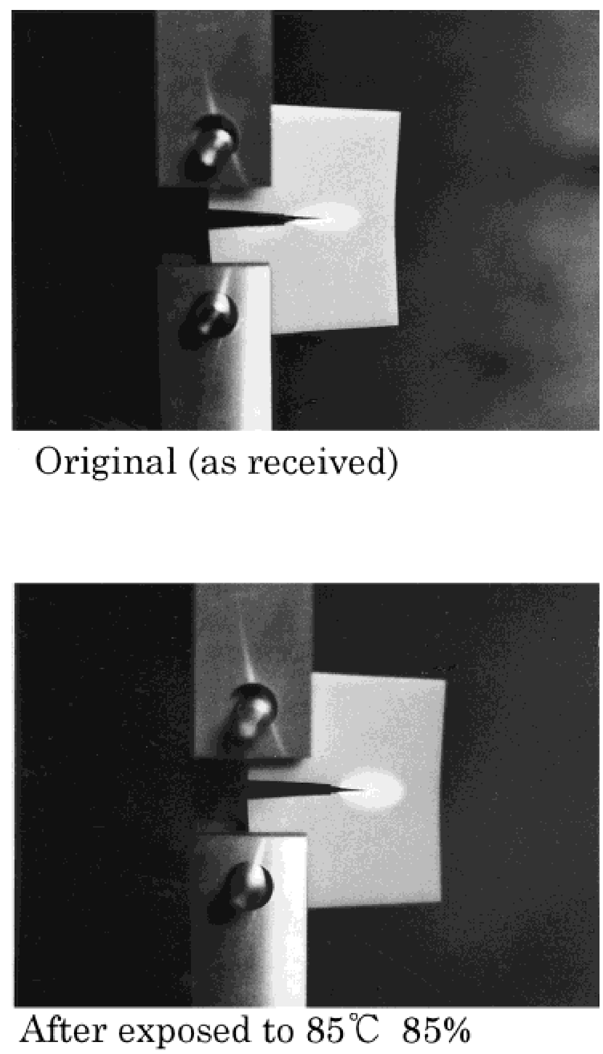

Figure 8 The whitening region at the crack tip of ABS resin.

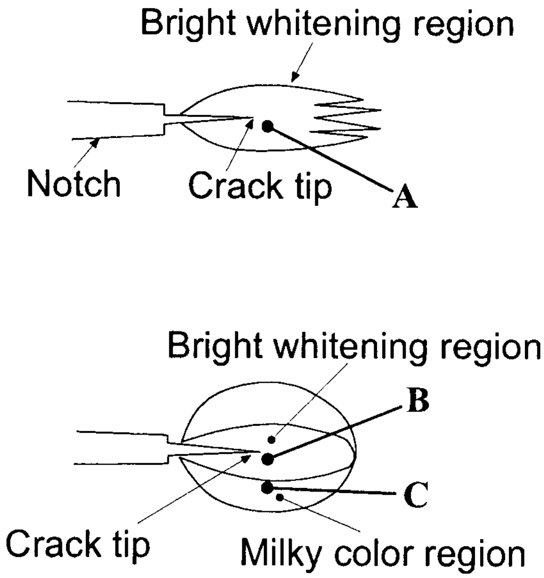

Figure 9 Schematic drawing of the whitening regions of ABS resin.

slight increase of moisture absorption. It has been reported that water accelerates the craze formation of PS.[14] This suggests that moisture causes the decline in the critical stress for craze formation. Because the craze formation is a dominant mechanism of initiating a crack, the fracture toughness decreases with absorbing moisture. On SAN resin, the decrease of the fracture toughness could be explained by a similar mechanism of PS.

On ABS Resin

As previously shown in Figure 7, the fracture toughness of ABS resin slightly decreases, despite a lot of moisture absorption. Figure 14 schematically shows the morphology at crack tip. Because the crack propagates to the matrix, SAN resin, the fracture toughness of ABS resin absorbing moisture, may be reduced according to the decrease of the matrix's fracture toughness. However, the stress-whitening region, which includes the milky coloring region, expands more than that of the original specimen despite applying the same stress. This mechanism compensates for the reduction of fracture toughness due to moisture absorption.

The milky coloring region may appear only if the precraze formation occurs at the lower stress level than that of internal void nucleation. On the original ABS resin, since precraze formation (step 1) and internal void nucleation (Step 2) might occur at the same time, the bright whitening region merely exists at crack tip.

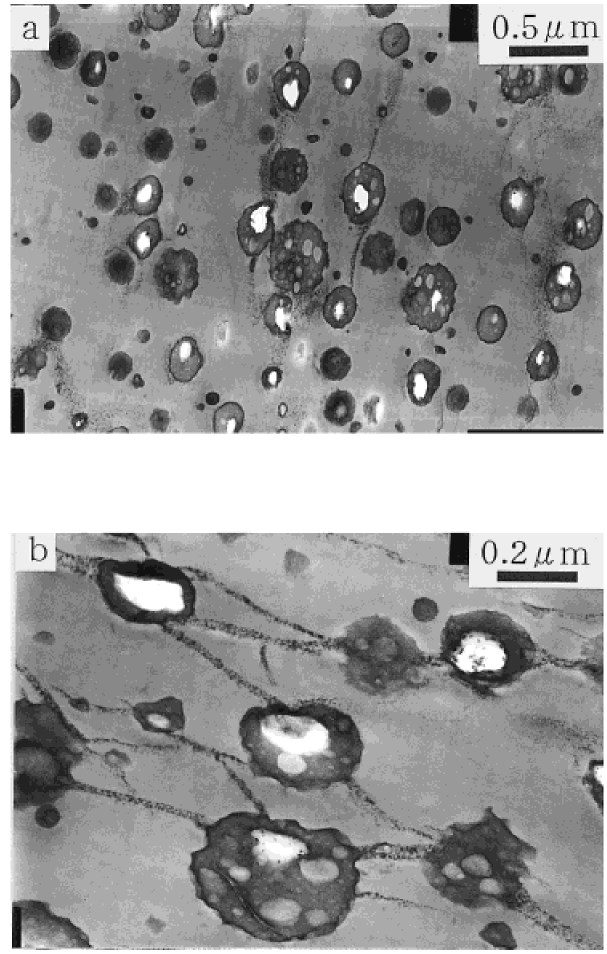

Figure 10 TEM photograph of original ABS resin at point A in Figure 9.

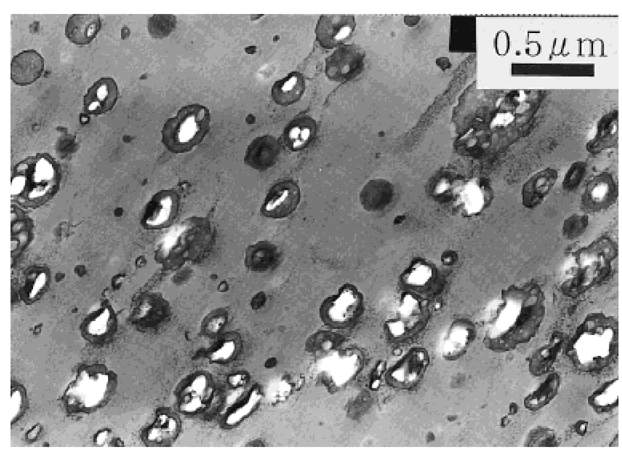

Figure 11 TEM photograph of 85°C 85% exposed ABS resin at point B in Figure 9.

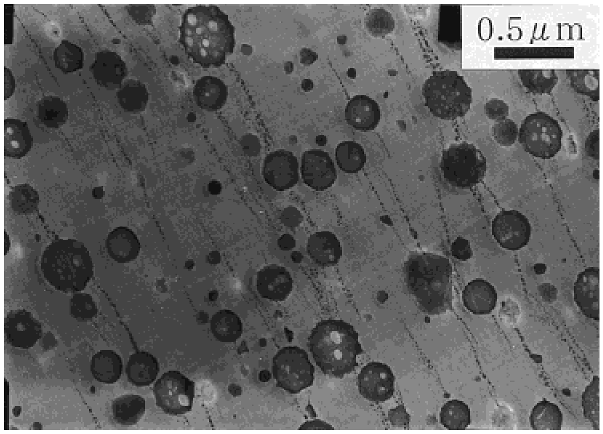

Figure 12 TEM photograph of 85°C 85% exposed ABS resin at point C in Figure 9.

CONCLUSIONS

Although fracture toughness of PS and SAN resin, which are matrixes of ABS resin, decrease with the increase of moisture absorption, that of ABS resin slightly decreases despite moisture absorption. On the specimen of ABS resin absorbing moisture, the milky coloring region appears around the normal bright whitening region and precraze formation, which plays the role of toughening as the crack-tip shielding effect is observed in this region by using transmission electron microscopy. The reason for little decrease of fracture

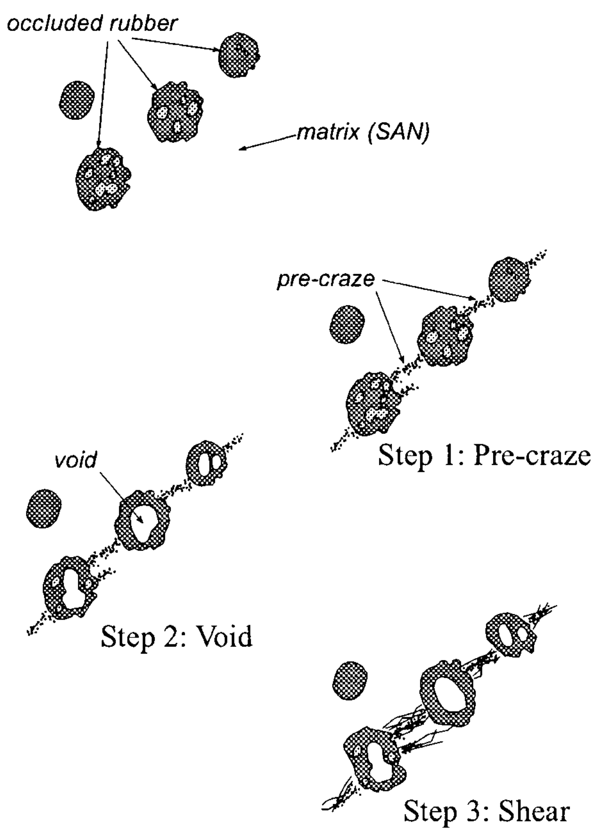

Figure 13 Stress-whitening process of ABS resin absorbing moisture.

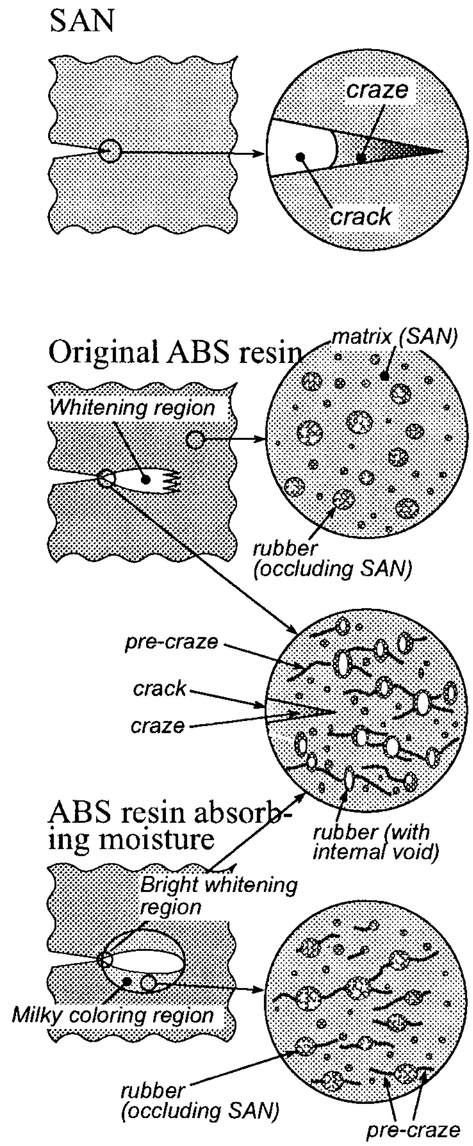

Figure 14 Schematic figure of the stress-whitening region of the original ABS resin and the ABS resin absorbing moisture. Figures on the left show the difference of stress-whitening on both specimens. Figures in the right show the microstructures of the nondamage zone, bright whitening region, and milky coloring region.

toughness of ABS resin absorbing moisture is that this stress-whitening region expands more, and this phenomenon prevents the reduction of toughness due to the brittleness of its matrix.

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