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On the properties of organic liquids affecting the crazing behaviour in glassy polymers

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The properties of organic liquids affecting the environmental stress crazing in glassy poly(methyl methacrylate), polycarbonate and polyvinyl chloride were examined with reference to the diffusivity into the polymers. The isochronal bending tests for the sheet specimens were conducted by a traditional method using the elliptical bending device in environments of five alcohols, four *n*-alkanes and three good solvents at 30°C. The diffusivity of these liquids exclusive of *n*-pentane and the solvents was evaluated by measuring the weight gain of specimen under the accelerated soaking at 52°C. The absorption rate of each liquid, given by an initial weight gain per unit time, was shown to be correlated with a new factor consisting of the viscosity and molar volume of environmental liquid and of a ratio of dielectric constant of liquid to that of polymer. The critical crazing strains in alcohols and *n*-alkanes were also demonstrated to relate to this factor. In good solvents no crazing but dissolution of polymer surface was observed. It thus may be concluded that the crazing is strongly correlated with the diffusivity of environmental liquid, and in addition that the liquid with the above factor of greater value clearly tends to cause the environmental crazing in glassy polymers.

1. Introduction

Crazing in glassy polymers, as well known, is generally facilitated in the environments of organic liquid [1, 2]. Most studies have so far examined the relationship between the critical strain or stress for crazing and the solubility of environmental liquid in the polymer [3–8]. Kambour *et al.* [3, 4] have revealed that the crazing strain measured by an elliptical bending device, the original form of which was devised by Bergen [9], is lowered with decreasing the difference between the solubility parameters of the polymer and the liquid. Other investigators [6, 7], in addition, have indicated that the crazing strain is well correlated with the equilibrium solubility of liquid in the polymer. In this manner it has been widely recognized that the mechanical resistance for crazing in glassy polymers is lowered in the environmental liquids with higher solubility in the polymers.

It should be noted, however, that crazing is a dynamic phenomenon with strong time-dependence, while the solubility parameter and the equilibrium solubility of liquid are properly the quantities related to the equilibrium state independent of time. It thus seems curious that the non-equilibrium process of crazing is primarily affected by the equilibrium quantity on the solubility. Kawagoe *et al.* [10, 11] have demonstrated that the critical crazing stress in poly(methyl methacrylate) (PMMA) exposed to alcohols and *n*-alkanes is not correlated with the solubility parameter, nor with the equilibrium solubility, and suggested that crazing is due to the localized plasticization facilitated by the diffusion of environmental reagent, which is the time-dependent dynamic process of mass transport. They have pointed out, however, only a rough relationship between the crazing resistance and the diffusivity of environmental liquid into the polymer. In addition, it is ambiguous whether their suggestion derived from the results for the crazing stress in PMMA is also applicable to those for the crazing strain not only in PMMA but in other glassy polymers.

In view of the above, we conducted the isochronal bending tests to examine the crazing strain in the sheet specimens of PMMA, polycarbonate (PC) and polyvinyl chloride (PVC), following a traditional way using the elliptical bending device in the environments of five alcohols, four *n*-alkanes and three good solvents at 30°C. The diffusivity of each reagent, excluding *n*-pentane and the good solvents, was evaluated by a change of weight gain of specimen during a beginning short period of accelerated soaking process at 52°C, and was discussed in relation to the physical properties of reagent. Based on these experimental results the relationship between the crazing strain and the diffusivity of environmental reagent was also discussed.

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2. Experimental

2.1. Materials and sample preparation

The materials used were commercially available sheets of PMMA (Mitsubishi Rayon Co., Ltd.), PC (Asahi Kasei Corporation) and PVC (Mitsubishi Plastics, Inc.) of 1mm thickness. The rectangular specimens were machined from the sheets to the dimensions of 40 × 5 × 1 mm for the measurements of weight gain in the reagents. Other rectangular specimens with size of 130 × 10 × 1 mm were prepared for measuring the critical crazing strain. Their cut surfaces were polished with an abrasive paper of No. 1000, and washed with soap and water. The PMMA, PC and PVC specimens were annealed at 90, 140 and 65°C, respectively, for 6 h in a forced-air oven, and then kept in a desiccator at 20% relative humidity. In case of the crazing strain measurements a silicon adhesive was thinly applied to the side edges of specimen to prevent the environmental liquids from penetrating.

2.2. Organic liquids as the environmental reagents

Five kinds of alcohols, i.e., methanol, ethanol, 1-butanol, 2-ethyl-1-butanol and 1-octanol, four *n*-alkanes, i.e., *n*-pentane, *n*-hexane, *n*-nonane and *n*-dodecane, and three good solvents, i.e., acetone, benzene and toluene, were used as the environmental reagents. The good solvents, however, were excluded for the absorption experiments mentioned below for dissolving the above polymers. Their basic properties at 20°C (partially at 25°C) are given in Table I [12, 13]. The viscosity, η, is generally increased with increasing the molar volume, and is higher in alcohols than in *n*-alkanes. The dielectric constant, e, reflecting the electrical interaction is much greater in polar solvents of alcohols than in non-polar *n*-alkanes. The values of solubility parameter, δ, of three good solvents are very near those of the above polymers [14], although 1-octanol and *n*-dodecane also have similar values of δ.

2.3. Measurements of weight gain in the reagents

The variations in weight gain of the specimens in the above alcohols and *n*-alkanes were measured at an enhanced temperature of 52°C for acceleration (*n*-pentane was excluded for lower boiling temperature of 36.1°C). In this connection, the preliminary experiments at 30°C, which was the temperature set for the crazing strain measurements described below, showed almost no significant variation in weight gain except for a PMMA-methanol system. The specimens were soaked in the sealed test tubes of reagent kept in a water bath, Model 461 (Shibata Kagaku Co., Ltd.), and periodically pulled out for weighing with an electronic balance, AE240 (Mettler-Toledo AG). After the weight measurements, the specimens were immediately returned to the former state. The initial rate of weight gain of specimen was obtained for evaluating the diffusivity of each reagent into the polymer.

2.4. Measurements of critical crazing strain

The critical strain for crazing was measured for all the combinations of polymer and reagent shown in Table I by means of an elliptical bending device, which was made from a stainless steel (SUS 304) plate of 20 mm thickness by wire-cutting to have the semi-major and the semi-minor axes of 100 and 50 mm, respectively, by making reference to the literatures [9, 15]. Corresponding to the curvature of ellipse, the outer surface of above-mentioned rectangular specimen with 130 × 10 × 1 mm bent on this elliptical device is subjected to the bending strain in tension of 0.25 to 1.5%, according to the equation [15]

$$\varepsilon = (b/2a^2)[1 - (1/a^2 - b^2/a^4)x^2]^{-3/2}t \qquad (1)$$

where ε is the strain at a distance x from the semi-minor axis along the major one, a and b the semi-major

TABLE I The basic properties of organic liquids used as the environmental reagents at 20°C, and the solubility parameter and the dielectric constant of polymers

	Molar volume (10^{-6}m^3/mol)	Solubility parameter ((MJ/m^3)$^{1/2}$)	Viscosity (mPa sec)	Surface tension (mN /m)	Dielectric constant (F/m)
Methanol	40.7	29.7	0.59	22.55	33.1(25°C)
Ethanol	58.5	26.0	1.17	22.27	23.8(25°C)
1-butanol	91.5	23.3	2.95	24.60	17.1(25°C)
2-ethyl-1-butanol	123.2	21.5	5.63	28.00	13.3(25°C)[a]
1-Octanol	157.7	21.1	8.93	26.06	10.3
n-pentane	116.2	14.4	0.23	15.50	1.84
n-hexane	131.6	14.9	0.31	17.90	1.89
n-nonane	178.6	15.6	0.72	22.92	1.97
n-dodecane	228.6	16.2	1.51	25.44	2.02
Acetone	73.3	20.3	0.30	26.26	20.7
Benzene	89.4	18.8	0.60	28.18	2.28
Toluene	106.8	18.2	0.59	28.53	2.24
PMMA	–	19.4	–	–	3.15
PC	–	19.4	–	–	2.94
PVC	–	19.6	–	–	3.05

[a] The value of 1-hexanol is given in place of indistinct value of 2-ethyl-1-butanol.

and semi-minor axes of ellipse, respectively, and t the sample thickness.

The specimen equipped on the device was soaked in a sealed vessel of test liquid kept in a constant low-temperature chamber, Model IN61 (Yamato Scientific Co., Ltd.), the temperature in which was maintained at 30°C. After the soaking for a fixed time of 15 min, the specimen was brought out to determine the boundary between the crazed and the sound (non-crazed) regions on the outer surface of specimen by using an optical microscope, Axioplan (Carl Zeiss, Inc.), at a magnification of ×100. Substituting the numerical value of distance from the boundary position to the semi-minor axis into x in the above equation gives the isochronal critical strain for crazing on each combination of polymer and reagent.

3. Results and discussion

3.1. Absorption behaviour of organic liquids

Fig 1a and b present the results of weight-gain measurements for PVC in five alcohols and three n-alkanes, respectively, as the examples of absorption behaviour of reagent by glassy polymer. In the time range to 100 h of soaking in these liquids the weight gain gradually increases with time, and is always greater in the liquid with smaller molar volume, although it in alcohol is about ten times as great as that in n-alkane. Thus the absorption rate, defined here as an inclination of tangent line at the origin of each curve, also increases with decreasing molar volume of reagent. The similar trends were observed both for PMMA and PC immersed in these liquids, although the absorption by PMMA was much greater and faster than that by PC and PVC in general. The trend of present study on absorption rate of alcohol by PMMA is in accordance with the observations of our previous study [11] and of Andrews *et al.* [16]. Incidentally, according to them, the equilibrium solubility of alcohol in PMMA observed at 45°C for very long time of immersion (~5000 h) increases with decreasing the difference of solubility parameters of PMMA and alcohol. However, the equilibrium solubility can not be discussed here, because the present measurements were conducted for restricted short times, mainly aiming to evaluate the absorption rate.

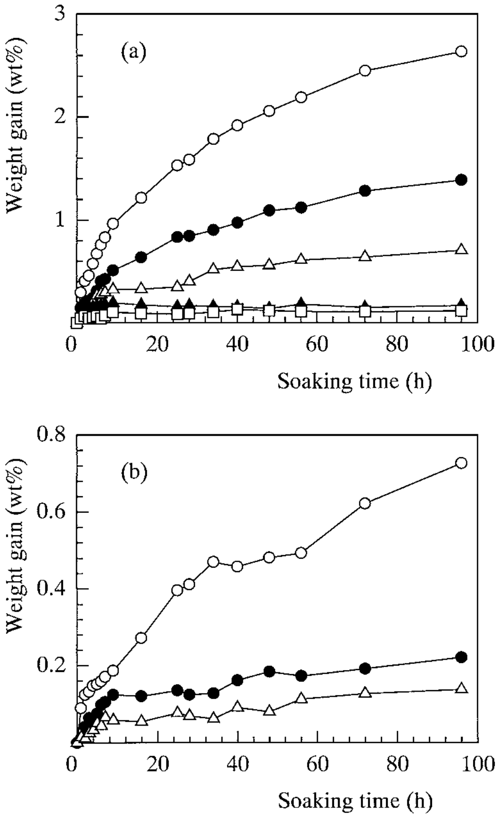

Figure 1 Weight gain of a PVC sheet, 1 mm thick, at 52°C in: (a) alcohols of (○) methanol, (●) ethanol, (△) 1-butanol, (▲) 2-ethyl-1-butanol, (□) 1-octanol; and (b) n-alkanes of (○) n-hexane, (●) n-nonane, (△) n-dodecane.

TABLE II Absorption rate of reagent by polymers given in the unit of wt%/sec

	PMMA	PC	PVC
Methanol	2.69×10^{-3}	6.61×10^{-5}	8.15×10^{-5}
Ethanol	7.40×10^{-4}	1.55×10^{-5}	3.98×10^{-5}
1-butanol	3.71×10^{-5}	9.70×10^{-6}	1.86×10^{-5}
2-ethyl-1-butanol	2.75×10^{-5}	5.99×10^{-6}	2.03×10^{-5}
1-octanol	1.44×10^{-5}	2.24×10^{-6}	8.90×10^{-6}
n-pentane	–	–	–
n-hexane	5.22×10^{-6}	9.60×10^{-6}	1.73×10^{-5}
n-nonane	3.56×10^{-6}	6.11×10^{-6}	5.92×10^{-6}
n-dodecane	1.54×10^{-6}	2.48×10^{-6}	3.52×10^{-6}

The absorption rate, as mentioned above, was determined by an inclination of tangent line drawn at the origin (starting point) of the curve of weight-gain against soaking time like Fig. 1. The value of absorption rate, D, obtained in such a way for all the combinations of polymers and reagents (exclusive of n-pentane and good solvents) are given in the unit of wt%/sec in Table II. The table shows that the absorption rate is decreased with increasing the molar volume. This feature becomes more evident by plotting the logarithm of D against the molar volume of reagent, V, as shown in Fig. 2. The trend in the figure may not be contrary to a relation of

$$\log D \propto -V \tag{2}$$

This expression is fundamentally the same as that presented by Ogawa and Masuichi [17] for describing the diffusion behaviour of organic vapors into PC films (D is given as a Fickian diffusion coefficient in their study). The relation given by Equation 2, however, is separately applied to the respective results in alcohols and n-alkanes, except for PVC. That is, the absorption rate of alcohol by PMMA is always greater than that of n-alkane with the same molar volume, but the reversed relation is obtained for PC. Thus two distinguished curves corresponding to the different groups of reagent are shown in parallel for PMMA and PC.

Asmussen and Ueberreiter [18] have examined the diffusion of several organic liquids into polystyrene (PS), and suggested the diffusion coefficient to well be correlated with a factor of $1/(\eta r)$, where η is the viscosity of liquid, and r is the mean radius of liquid molecule. This relation is similar to the Einstein-Stokes law for the movement of sphere in the viscous fluid. But it should be emphasized that the similarity is only formal,

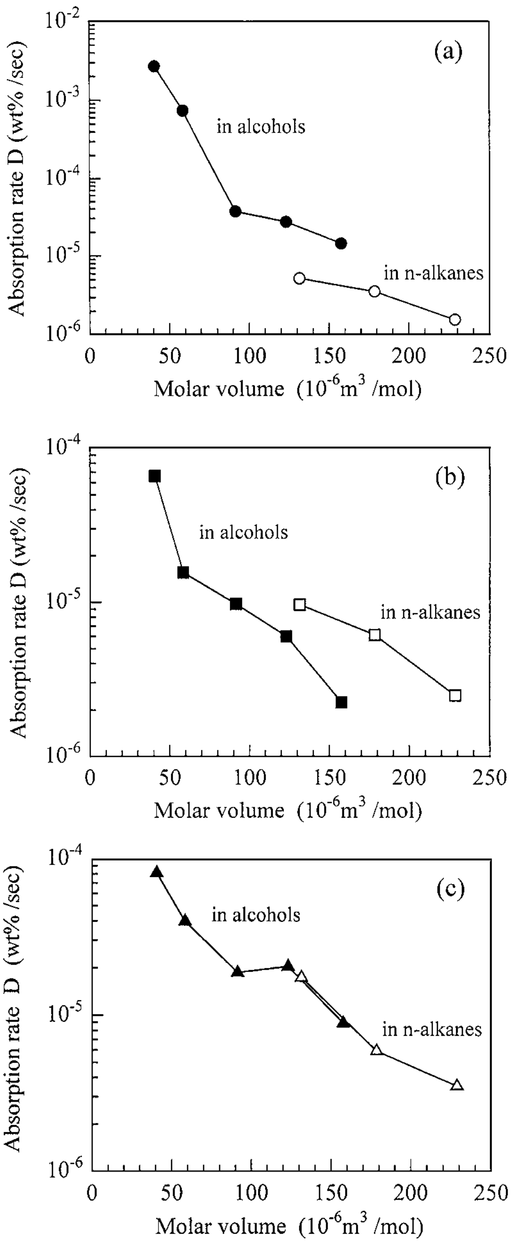

Figure 2 Absorption rate, D, as a function of the molar volume of reagent, V, for (a) PMMA, (b) PC, and (c) PVC.

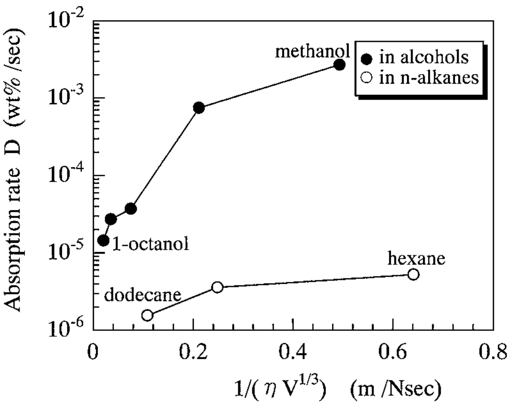

Figure 3 Relation of the logarithmic absorption rate of reagent, log D, to $1/(\eta V^{1/3})$ for PMMA.

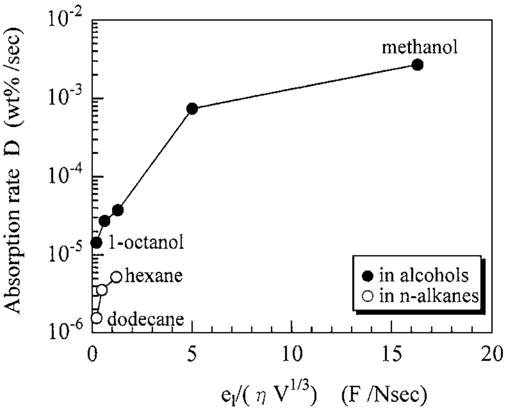

Figure 4 Dependence of the logarithmic absorption rate of reagent, log D, on $e_l/(\eta V^{1/3})$ for PMMA.

because in case of Einstein-Stokes law r is not the radius of liquid molecule but of sphere moving into the surrounding liquid with viscosity, η. Since the molecular radius, r, is proportional to $V^{1/3}$, the above factor may be rewritten as $1/(\eta V^{1/3})$. Fig. 3 shows the relationship between the logarithm of D and $1/(\eta V^{1/3})$ for PMMA, where D is again the absorption rate of reagent shown in Table II. It seems reasonable that the absorption rate increases with increasing this factor. But two different curves corresponding to alcohol and n-alkane are separately drawn, as well as in Fig. 2. In other words, the figure does not explain why such a large difference in the absorption rates between alcohol and n-alkane is produced.

Recently Yamamizu *et al.* [19] has modified the above factor of Asmussen and Ueberreiter by introducing the dielectric constant of liquid, e_l, to consider a chemical interaction with the polymer. Their modified factor is given by $e_l/(\eta V^{1/3})$. They demonstrated that this factor is effective to account for the swelling behaviour of cross-linked PS in a wide variety of solvents, and suggested that the greater diffusion rate of polar solvents into PS may arise from the chemical adsorption of penetrant molecules onto the polymer chains. Plotting the logarithm of D against this factor of $e_l/(\eta V^{1/3})$ for PMMA provides the relation in Fig. 4. Compared with Fig. 2 and 3, the absorption behaviour of different reagents may be expressed by the unified curve, although a respectable difference still remains.

In the study of Yamamizu *et al.* only the dielectric constant of liquid is introduced. For examining the effects of chemical interaction on the absorption behaviour of liquid, the dielectric constant of polymer should also be taken into account. Then a new factor of $(e_l/e_p)^m/(\eta V^{1/3})$ is proposed, where e_p is the dielectric constant of polymer, and m is a constant. This factor is derived empirically by further modifying the above factor of Yamamizu *et al.* Since the physical basis of term of $(e_l/e_p)^m$ remains to be constructed, a rational way to determine the value of m is not established. Accordingly the relation of D to the new factor of $(e_l/e_p)^m/(\eta V^{1/3})$ was examined by putting various values into m. As a result it was found that in case of $m = 2$ a linear relationship holds between the logarithms of both D and $(e_l/e_p)^2/(\eta V^{1/3})$ for the absorption behaviour of reagents by PMMA. Fig. 5 shows a straight line relationship, given by the least-squares method, on which all the data of absorption rate by PMMA in both alcohol and n-alkane are assembled. Fig. 6a and b present the similar diagrams for

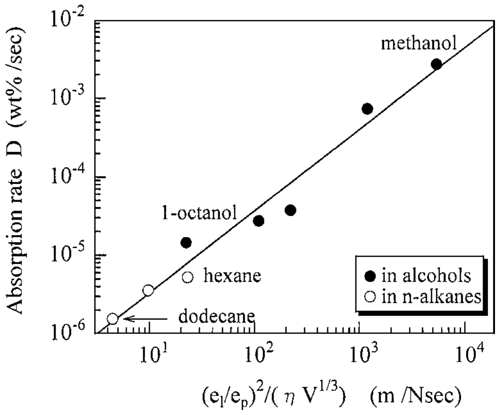

Figure 5 Relationship between both the logarithms of absorption rate of reagent, D, and a new factor of $(e_1/e_p)^2/(\eta V^{1/3})$ for PMMA.

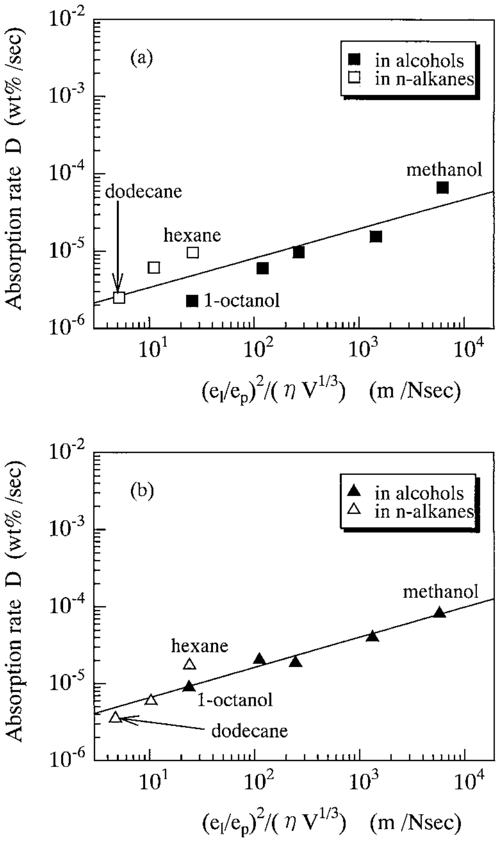

Figure 6 Relation of log D to log $[(e_1/e_p)^2/(\eta V^{1/3})]$ for (a) PC and (b) PVC.

PC and PVC, respectively. The linear relations of log D to log $(e_1/e_p)^2/(\eta V^{1/3})$ are also identified, although their inclinations are relatively small compared with that for PMMA (Fig. 5). Consequently it may be concluded that a linear relationship between log D and log $(e_1/e_p)^2/(\eta V^{1/3})$ holds in the absorption behaviour of alcohols and n-alkanes by PMMA, PC and PVC.

3.2. Crazing strain affected by the diffusivity or solubility of reagent

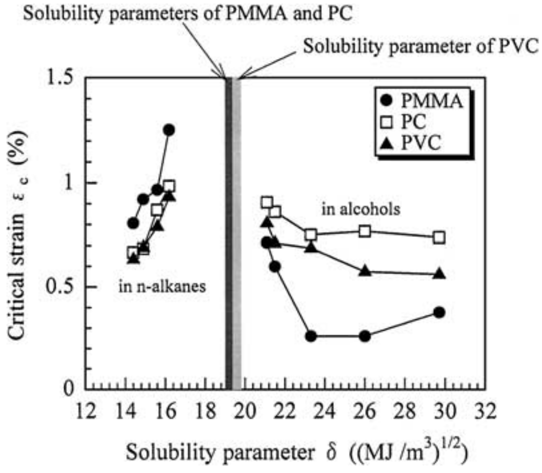

Figure 7 Relation of critical crazing strains for PMMA, PC and PVC to the solubility parameter of environmental reagent.

Fig. 7 shows the experimental data of critical crazing strain, ε_c, obtained for the combinations of polymer and reagent, excluding three good solvents, in conjunction with the solubility parameter of reagent, δ. The solubility parameters of polymers are in the range represented by the thick lines. The reason why the data in the good solvents are eliminated in the figure is described later. The crazing strains in alcohols and n-alkanes commonly tend to increase with decreasing the difference between the solubility parameters of polymer and reagent. This trend is the same as that of crazing stress observed in our previous study [11], and consequently is wholly opposite to those of the crazing strain reported by many investigators [3, 4, 8]. For the combinations of polymer and good solvents of acetone, benzene and toluene a great number of fissures appearing to be crazes with the naked eye were formed on all over the specimen surface. Regarding these fissures as crazes may lead to the very low values of ε_c of about zero, being consistent with the above current results [3–8]. However, a micrograph in Fig. 8, taken by a scanning electron microscopy, S-4000 (Hitachi Co., Ltd.), of one of the fissures on the surface of PMMA specimen tested in acetone does not show the well-known microstructure of craze with fine elongated fibrils and voids [1], but only a groove with elliptical holes. (The fine tortoise-shell marks were probably formed by the tensile stress generated by surface shrinkage after pulling out the specimen from the solvent.) In addition, according to the preliminary experiments, fine grooves were clearly observed to run, probably along the pre-existing scratches, on the surface of specimen immersed in acetone for 15 min even under no strain. Therefore, these fissures seem to be neither crazes nor cracks, but to be mainly formed by dissolution of polymer surface by the solvent. It thus may be pertinent that the results obtained in three good solvents are eliminated in Fig. 7 and also from the discussions hereafter.

In Fig. 9 the crazing strain, ε_c, measured on PMMA in alcohols and n-alkanes are plotted against the molar volume of environmental reagent. ε_c generally increases with increasing molar volume of reagent, although ε_c in alcohols is always lower than in n-alkanes. With regard to that the lowest value of ε_c is not observed in methanol with the smallest molecular volume but in ethanol, the large amount of methanol diffusing rapidly into PMMA may relieve the stress concentration at the tip of surface flaw, which is a potential site for craze

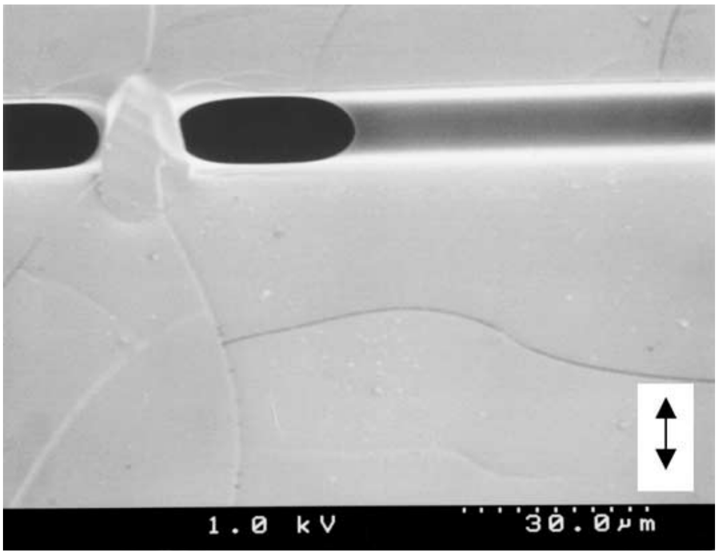

Figure 8 Scanning electron micrograph of specimen surface of PMMA strained in acetone. An arrow denotes the tensile direction.

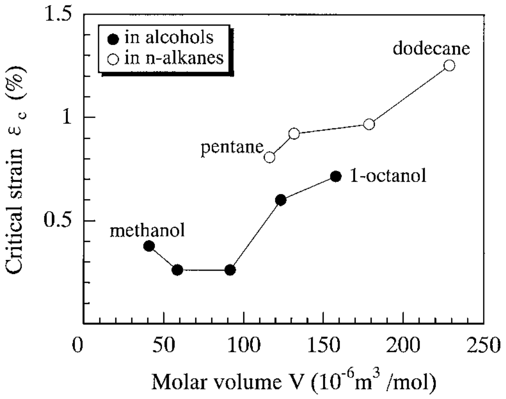

Figure 9 Crazing strain, ε_c, for PMMA plotted against the molar volume of reagent, V.

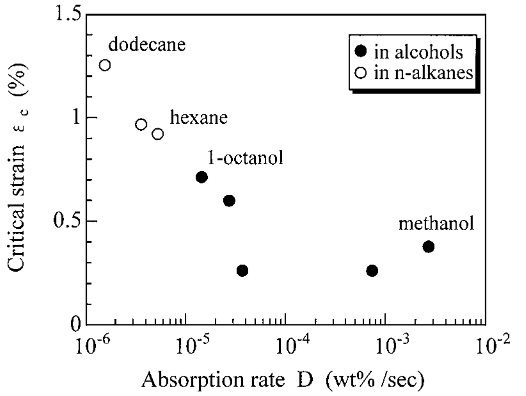

Figure 10 Relation of crazing strain, ε_c, for PMMA to the logarithmic absorption rate of reagent, log D.

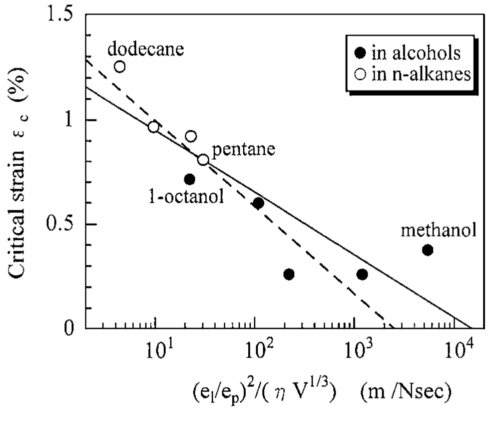

Figure 11 Relation of crazing strain, ε_c, for PMMA to the logarithm of $(e_l/e_p)^2/(\eta V^{1/3})$. The broken line denotes the trend except methanol.

nucleation [20, 21], by a plasticization effect. Such features of the crazing strain shown in the figure are almost the same as those of the crazing stress observed in our previous study [11]. Therefore the same dependency of mechanical resistance for crazing on the molar volume of environmental reagent, at least on PMMA, may hold, irrespective of loading type. This result supposes that crazing is closely related to the diffusivity of environmental reagent, as also has been previously pointed out [11, 21].

Then plotting the values of ε_c for PMMA against the logarithm of D gives a relation in Fig. 10, although the testing temperatures for measuring ε_c and D are different (30 and 52°C). The figure shows that the crazing strain is lowered as the absorption rate increases (with the exception of methanol), therefore, and also suggests that the crazing strain is correlated with the newly proposed factor affecting the diffusivity of reagent into the polymers. From a practical viewpoint it may be much more useful to obtain a relationship between ε_c and this new factor, instead of D, because the physical quantities consisting of this factor are easily found in the materials like the references [12–14].

Assuming the features of absorption behaviour observed at 52°C to hold at 30°C, the factor of $(e_l/e_p)^2/(\eta V^{1/3})$ also may be applied to examine the relation with ε_c at this temperature. Fig. 11 shows ε_c for PMMA plotted against the logarithm of $(e_l/e_p)^2/(\eta V^{1/3})$, where the basic properties of liquids and polymers at 20°C (partially at 25°C) in Table I are again adopted. The data in both alcohols and n-alkanes are generally placed on or near a straight solid line, which is again drawn by the least squares method. Ignoring the data in methanol, which may induce great stress relaxation due to large amount of absorption, we

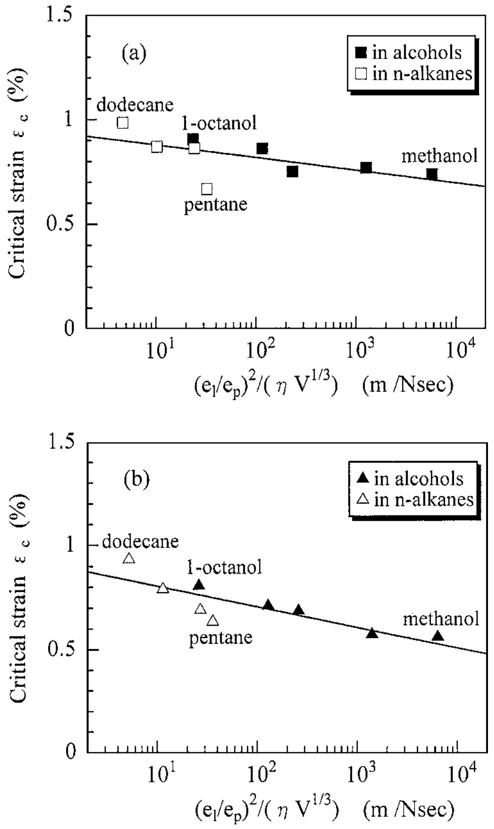

Figure 12 Relationship between ε_c and $\log[(e_1/e_p)^2/(\eta V^{1/3})]$ for (a) PC and (b) PVC.

obtain a broken line, which further agrees well with the data. The figure clearly indicates that ε_c is decreased as the factor of $(e_1/e_p)^2/(\eta V^{1/3})$ controlling the absorption rate of reagent by the polymer is increased.

Considering the temperature-dependence of properties of environmental reagents and polymers may more properly explain the trend. Fig. 12a and b present the similar diagrams for PC and PVC, respectively. Also for both the polymers ε_c is well correlated with the above factor on the absorption rate. The level of ε_c for each polymer will be generally lowered with an increase in the soaking time in the reagent, maintaining the trend, because the plasticization proceeds with increasing quantity of penetrant.

As is demonstrated by the above examinations, the crazing strains in PMMA, PC and PVC exposed to alcohols and n-alkanes commonly are not dominated by the solubility parameter but by the absorption rate of reagent, which may be adequately evaluated by the factor of $(e_1/e_p)^2/(\eta V^{1/3})$. The physical content of this empirical factor is required to elucidate in future. In addition, its applicability to other combinations of polymer and reagent also has to be widely examined.

4. Conclusions

The isochronal bending tests were conducted for the sheet specimens of PMMA, PC and PVC in the environments of alcohols, n-alkanes and good solvents at 30°C by following a traditional way using the elliptical bending device. Eliminating the results obtained in good solvents, which did not give rise to crazing but to dissolution of polymers, the crazing strains are not correlated with the solubility parameter, opposing a number of current studies. The crazing behaviour is much more strongly affected by the absorption rate of reagent by the polymer. That is, the crazing strains are generally lowered with increasing absorption rate, which may be controlled by a factor consisting of the viscosity and molar volume of reagent and of a ratio of dielectric constant reflecting a chemical interaction between polymer and reagent.

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