Polymer Vol. 38 No. 24, pp. 5969-5975, 1997

0032-3861/97/$17.00+0.00
PII: S0032-3861(97)00153-5

Growth and healing of a surface crack in poly(methyl methacrylate) under case II diffusion of methanol

M. Kawagoe*, M. Nakanishi†, J. Qiu and M. Morita
Department of Mechanical Systems Engineering, Faculty of Engineering, Toyama Prefectural University, 5180 Kurokawa, Kosugi, Toyama 939-03, Japan
(Received 18 December 1996)

The behaviour of a pre-crack inserted in a surface swollen layer formed by case II diffusion of methanol in poly(methyl methacrylate) (PMMA) was investigated with reference to the distribution of internal compressive stress induced under constraint by the inner glassy core. The elastic analyses of internal stress were conducted by a finite element method using the data for the mechanical properties and the swelling strains preliminarily obtained for the sheet specimen overall swollen in methanol. The growth of the inserted crack in the surface swollen layer under static tension in methanol at 20°C was almost arrested for a long period at a position where the internal compressive stress in the tensile direction took the maximum magnitude near the boundary between the swollen layer and the glassy core. After being released from the internal compressive stress, the crack rapidly progressed to lead to a general fracture going across the boundary. A relatively long crack inserted in the thinner surface swollen layer completely disappeared in methanol at 40°C during 3 min under no external load. Crack healing, however, was not observed either in methanol at the lower temperature of 20°C or in the entirely swollen specimen, even at 40°C. These results suggest that both high temperature above the glass transition temperature of swollen PMMA and the significant internal compressive stress are required for crack healing. © 1997 Elsevier Science Ltd.

(Keywords: PMMA; case II diffusion; crack)

INTRODUCTION

Case II diffusion, of which a typical example is observed for a material system of poly(methyl methacrylate) (PMMA) and methanol at room temperature, is well characterized by the formation of a surface swollen layer clearly bounded by an inner glassy core[1]. In this layer the swollen polymer is almost in equilibrium and is highly softened so as to show lower elastic modulus and shear yield stress, i.e. softening or plasticization effects. For case II diffusion, in addition, it should be noted that the internal compressive stress is induced near the boundary in the surface swollen layer under constraint by the inner glassy core. Both the softening effects and the generation of internal compressive stress in the surface layer are expected to exert considerable influences on the strength of polymer.

Kawagoe and co-workers[2,3] have investigated the effect of case II diffusion on crazing and fatigue fracture of PMMA in a methanol environment, and revealed that a relatively thin surface swollen layer brings about dramatic increases both in the critical torsional moment for crazing and in the fatigue lifetime under cyclic tension, while a thicker swollen layer has less contribution to increasing the crazing resistance and the fatigue lifetime. Although they gave an interpretation to these results both from the softening effects and from the generation of compressive stress in the surface swollen layer mentioned above, it remained as only qualitative, because there was no quantitative evaluation of induced compressive stress.

The internal stresses caused by case II diffusion have been evaluated by several investigators. Alfrey *et al.*[4] have roughly estimated them on a cylindrical specimen in the aspect of continuum elastic mechanics, and obtained the simple distribution of internal stresses. For instance, the compressive and the tensile stresses in the longitudinal direction of a cylinder are uniformly distributed in the surface layer and the inner core, respectively, and are completely discontinuous at the boundary. It was also pointed out that, as the swelling front advances inward with time, the internal stress in the core increases, and brittle fracture or shear flow takes place when it reaches the tensile strength or the shear yield stress of the dry polymer in the core. Cohn and Marom have measured the swelling strains in three orthogonal directions for the systems of PMMA–methanol[5] and epoxy resin–methylene chloride[6]. For the latter case, in addition, they calculated the shear stress at the boundary and the tensile stress in the core, as functions of the distance from the core edge along the longitudinal axis, also using the continuum elastic theory, and related these to the formation of boundary and core cracks. However, the internal compressive stress in the surface swollen layer, in which we are now interested, was not evaluated in their study. Klier and Peppas[7] have calculated the

* To whom correspondence should be addressed
† Present address: Toshiba Engineering Co. Ltd, Saiwai-ku, Kawasaki 210, Japan

internal stresses induced by case II diffusion in another way based on an elasticity theory of swollen rubber. Their calculation shows that for a cylinder the magnitude of longitudinal compressive stress in the surface swollen layer monotonically increases with the distance from the surface and is greatest at the boundary, differing from the simple stress distribution given by Alfrey *et al.*[4]. Several investigations mentioned above have the merit of giving a quantitative evaluation for the distribution of internal stresses due to case II diffusion, but their results seem to be somewhat too simple. The theories developed by Thomas and Windle[8,9] and subsequently by Kramer's group[10-14], which well describe the substantial behaviour of case II diffusion from viewpoints of the network structure of swollen rubber and the physicochemistry of the osmotic pressure, do not provide the distribution of internal stress evolved in each layer, although the internal pressure (osmotic pressure) acting on the penetrant near the boundary may be exactly calculated.

Eventually, the methods of stress analysis developed by the previous investigations mentioned above can provide only a rough examination of the distribution of internal compressive stress, which may greatly affect the fracture behaviour in the surface swollen layer followed by case II diffusion. Thus, in this study we conduct the stress analysis by means of a finite element method (FEM) using the experimental data for mechanical properties and swelling strains in the rectangular PMMA specimen swollen in methanol, as Cohn and Marom have examined[6]. The FEM analysis in this study, however, is restricted to estimating the elastic stress components as the first approximation, although visco-elastic response should properly be considered for describing the behaviour of a swollen polymer. The calculated results of internal stress distribution are related to the observed growth process of a surface crack which is preliminarily introduced into the surface swollen layer before tensile loading. In addition, a possibility of crack healing in the swollen layer is also examined with reference both to the internal compressive stress and to the mobility of macromolecules, evaluated by differential scanning calorimetry (d.s.c), promoted by the plasticization effect of penetrant.

EXPERIMENTAL

Materials and sample preparation

The material used is a commercially available PMMA sheet of 2 mm thickness (purchased from Mitsubishi Rayon Co.). The rectangular specimens were prepared to the dimensions of $60 \times 12 \times 2\,mm^3$ for the measurements of the elastic modulus and the swelling strains. Other rectangular specimens with size of $21 \times 10 \times 3\,mm^3$ were prepared for measuring Poisson's ratio. The dumbbell-shaped specimens with gauge length of 15 mm and width of 6 mm, used for testing the tensile property and observing the behaviour of a surface crack, were machined from the sheet. The cut surfaces of the specimens were polished with an abrasive paper of No. 1000 and washed with soap and water. All the specimens were annealed at 90°C for 2 h in a forced-air oven and then kept in a desiccator at 20% relative humidity.

Measurements of basic mechanical properties

The basic mechanical properties, i.e. the elastic modulus, Poisson's ratio and the tensile strength, were measured on the virgin and the swollen specimens. The swollen specimens were prepared by immersing in methanol at 20°C to the equilibrium state of swelling, showing a saturated weight gain. The elastic modulus was evaluated by the storage modulus, E', measured by using a dynamic viscoelastic analyser, Fatigueron, VFA-1KNA (Orientec Co.), under a sinusoidal strain oscillating at 0.1 Hz. Poisson's ratios were obtained from the deformation of smaller rectangular specimens under compression by means of a hydraulic servo-controlled testing machine, Servopulser, FHF-FB10KN-10LA (Shimadzu Co.). The changes in width were measured using a micrometer at upper, medium and lower sites of the specimen, and the mean value was used for calculating Poisson's ratio. Teflon films were inserted between the anvil and the contact face of the specimen for reducing the friction between them. The quasi-static tensile properties were measured by means of the same testing machine as that for Poisson's ratio at an elongation speed of $5\,mm\,min^{-1}$.

All the tests mentioned above were conducted in air at 20 ± 1°C under application of methanol to the specimen surfaces for preventing them from drying, except for the virgin specimen.

Measurements of swelling strain

The rectangular specimen was immersed in methanol at 20°C until equilibrium swelling, and the changes in width and thickness and in length were measured by the micrometer and a vernier caliper, respectively. The swelling strain was given by the increment per unit length in each direction.

Observation of crack advance in the surface swollen layer

Figure 1 shows a schema of equipment for observing the behaviour of a crack inserted into the surface swollen layer. This equipment of our own making mainly consists of a loading system with a lever and a vessel with windows for observation, filled with methanol, the temperature of which is controlled by transporting methanol from and to a beaker placed in a thermo-controlled bath using water and ethylene glycol. The loading speed was adjusted by controlling a flow of sand used as a weight. The behaviour of the inserted crack was monitored by a stereo microscope, SZ6045TR (Olympas, Co.), with a video camera under polarized light, the

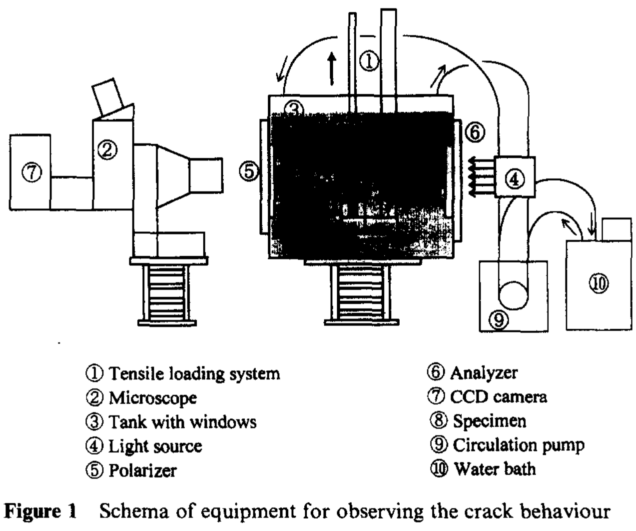

Figure 1 Schema of equipment for observing the crack behaviour

source of which is white, through the windows of the vessel. The image was recorded on a floppy disk by a still-video recorder, SR-300 (Olympas).

The specimen was immersed in methanol at 20°C until the surface swollen layer had grown to 0.5 mm. A pre-crack of about 0.05 mm length was immediately inserted into it by a razor mounted on a specially prepared device, perpendicular to the longitudinal direction of the specimen. The static tensile load (374 N) was slowly applied to the specimen immersed in methanol at 20°C by means of the above apparatus. The crack advancing behaviour was observed by the monitoring system mentioned above. For comparison, an overall swollen specimen was also tested in the same way under much lower load (28 N). This load was about a quarter of that obtained from the simple calculation based on the continuum elastic mechanics, because the calculated load was sufficiently large for the overall swollen specimen as to cause very rapid fracture just after loading.

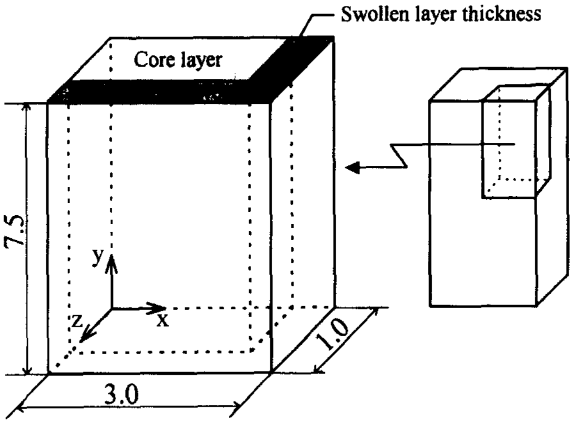

Figure 2 Orthogonal coordinates for the finite element analysis of internal stress

Examination of crack healing in the swollen layer

In the same way as that for the observation of crack advance, a pre-crack 0.05 mm long was inserted into the surface swollen layer grown to 0.5 mm in methanol at 20°C and tensed under the static load of 374 N until the crack length reached about 0.25 mm. After the tensile load was removed, the behaviour of the crack was observed by the monitoring system. A possibility of crack healing was also examined in methanol at 40°C. The preliminary experiments demonstrated that case II diffusion took place in methanol at 40°C by confirming both a proportionality of the weight gain with soaking time and a clear boundary separating the surface swollen layer from the core region in the specimen. At this temperature, however, the tensile load could not be applied to the specimen, because the squeezing force between the specimen and the chuck faces was relaxed due to great softening of the swollen surface. Thus, the behaviour of pre-cracks of about 0.2–0.25 mm length inserted into the surface swollen layer grown to several thicknesses in methanol at 40°C was observed in the same environment without external load.

Evaluation of the glass transition temperature

The glass transition temperatures, T_g, of the samples swollen in methanol at 20 and 40°C were measured by using a differential scanning calorimeter, DSC 3100 (MAC Science Co.), for evaluating the molecular mobility in relation to the possibility of crack healing in the surface swollen layer. Thin film samples of about 2 mg in weight cut from the PMMA sheet were immersed in methanol at 20 and 40°C to reach the equilibrium solubility and immediately enclosed in the aluminium

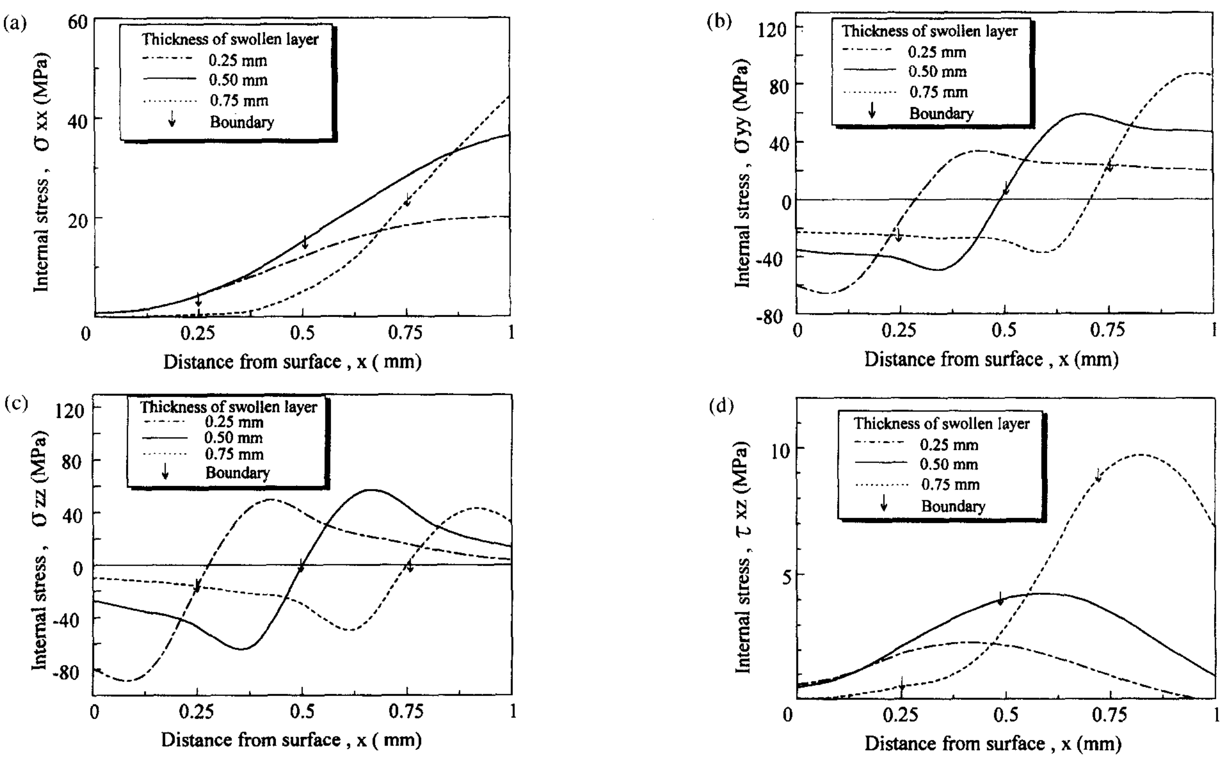

Figure 3 Distribution of internal stress on the x axis calculated by the FEM: (a) normal stress in the direction of specimen width, σ_{xx}; (b) normal stress in the longitudinal direction, σ_{yy}; (c) normal stress in the direction of specimen thickness, σ_{zz}; (d) shear stress component, τ_{zx}

sample pans with covers. These samples were cooled once to $-20^{\circ}C$ by liquid nitrogen and heated up to $110^{\circ}C$ at a rate of $10^{\circ}C\,min^{-1}$. A similar measurement was also conducted for the untreated PMMA, for comparison, from room temperature to $200^{\circ}C$ at $10^{\circ}C\,min^{-1}$.

Analysis of internal stresses

Three-dimensional analyses of the induced stresses in the surface swollen layer and the inner glassy core were performed by a FEM. A program for thermal stress analysis, ANSYS 5.0A (Swanson Analysis Systems), was applied by replacing the thermal expansion coefficient with the swelling strain in each direction, measured in methanol at 20°C. Considering the symmetrical geometry of the specimen, the stress calculation was performed for 1/8 part of the gauge region, which was divided into about 8000 small elements of a rectangular prism, in orthogonal coordinates, as shown in *Figure 2*. The thicknesses of the surface swollen layer supposed in the calculation were 0.25, 0.5 and 0.75 mm. In this study only the elastic stresses were estimated, ignoring the visoelastic responses of the polymer, because of no adequate constitutive equation for dry and swollen PMMAs and also because of the capacity of our personal computer, PC 9821 Xs (NEC Co.), requiring more than 48 h for the present calculation. The calculated values of the induced stresses thus seem to be overestimated, as a whole, particularly in the surface swollen layer. However, their distribution necessary for interpreting the surface crack behaviour may well be represented by the present analysis.

RESULTS AND DISCUSSION

Variations in the mechanical properties by swelling

The storage modulus, E', measured at 0.1 Hz was lowered to a greater extent from an initial value of 2512 to 508 MPa by the equilibrium swelling. Poisson's ratio, which was a mean value of the data obtained for nine specimens, was raised from 0.33 to 0.41, indicating that glassy PMMA approached the rubbery state by swelling. These values of the storage moduli and Poisson's ratios were used for the calculation of internal stresses by the FEM. The tensile behaviour also was so changed as to show a much lower strength of 4.3 MPa and greater elongation above 20%, from the initial state showing 73.3 MPa and 8%, respectively. Thus, PMMA swollen at the equilibrium state by absorbing methanol of about 20 wt% is highly softened or plasticized.

Swelling strains

The swelling strains in the directions of width (x axis), length (y axis) and thickness (z axis) of the specimen, measured at the equilibrium state of swelling, were 0.06, 0.06 and 0.15, respectively. Such anisotropic behaviour as that greater swelling strain obtained in the thickness direction has already been observed in the experiment of Cohn and Marom, also in the PMMA–methanol system[5]. They explained this behaviour by a model of the composite material including a single fibre with higher stiffness, although it is not referred to here. The above swelling strains obtained for the overall swollen specimen are directly applied to those in the surface swollen layer for the calculation of internal stresses by the FEM.

Distribution of internal stresses

Figures 3a, *3b* and *3c* show the distribution of the normal stress components existing on the x axis in *Figure 2* induced by case II diffusion, calculated for different thicknesses of the surface swollen layer. The arrows in the figures denote the location of the boundary between the surface swollen layer and the glassy core. The normal stresses in the direction of the specimen width, σ_{xx}, are always in tension and monotonically increase with increasing distance from the surface for all thicknesses of the swollen layer (*Figure 3a*). On the other hand, the normal stress in the longitudinal direction, σ_{yy}, indicates quite different distribution (*Figure 3b*). As is expected, σ_{yy} is in compression in the surface swollen layer and inversely in tension in the inner glassy core, but does not indicate discontinuity at the boundary, which was shown in the simple calculation of Alfrey *et al.*[4]. The magnitude of compressive stress is greater in the thinner surface layer, and its maximum value is not obtained just at the boundary, but near it in the surface layer, opposing the calculation of Klier and Peppas[7], which indicates monotonic increase in the magnitude of compressive stress towards the boundary. The normal stress in the direction of the specimen thickness, σ_{zz}, distributes in a similar manner to that of σ_{yy}, although it rapidly decreases in the inner core region (*Figure 3c*). It is noted from the above results that the stress states of biaxial compression and triaxial tension (dilatation) are generated in the surface and the core layers, respectively, particularly near the boundary. The biaxial compression is expected

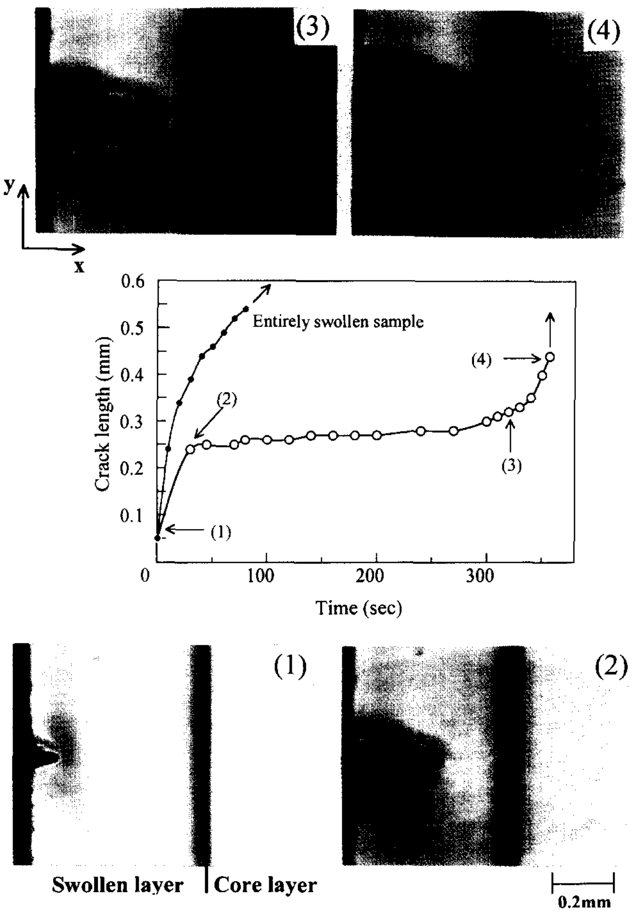

Figure 4 Growth behaviour of a pre-crack in the surface swollen layer under static tension in methanol at 20°C

to suppress the crack growth in the surface layer. If the tensile stress generated in the core region is at a higher level, it may cause craze nucleation and cracking, leading to fracture of this region, as Cohn and Marom have pointed out[5,6].

The shear stress components, τ_{xy} and τ_{yz}, on the x axis in *Figure 2* were calculated to show very small values, 0.01 and 0.001 MPa, respectively, even at the maximum, which may exert little influence on the deformation of the surface and core layers. The other shear component, τ_{zx}, however, indicates a relatively high value, as shown in *Figure 3d*. A higher value of about 10 MPa is obtained near the boundary for the case of a thicker swollen layer (0.75 mm). The progress of case II diffusion thus may bring about shear-dominated cracking or flow in the surface swollen layer near the boundary, as has also been pointed out by Cohn and Marom[5,6]. This shear-dominated deformation may also impede the crack growth in the surface layer, which is affected by the applied tensile stress acting normally to a crack plane.

The results of stress analysis mentioned above seem to support our interpretation of the previous experiments on crazing and fatigue under case II diffusion in the PMMA–methanol system[2,3], although it should be noted that the overestimated stresses are obtained in the present analysis by disregarding the viscoelastic response in the swollen polymer.

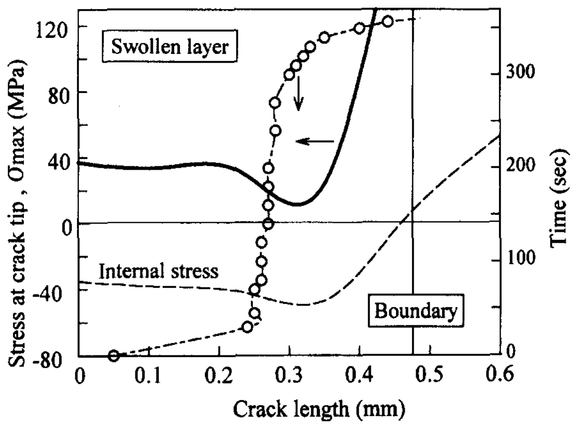

Figure 5 Correlation between the longitudinal component of internal stress, σ_{yy}, the concentrated stress at the crack tip, and the crack length varying with time under static tension

Behaviour of crack growth

A graph and four pictures in *Figure 4* represent the growth behaviour of a pre-crack inserted into the surface swollen layer under static tension in the environment of

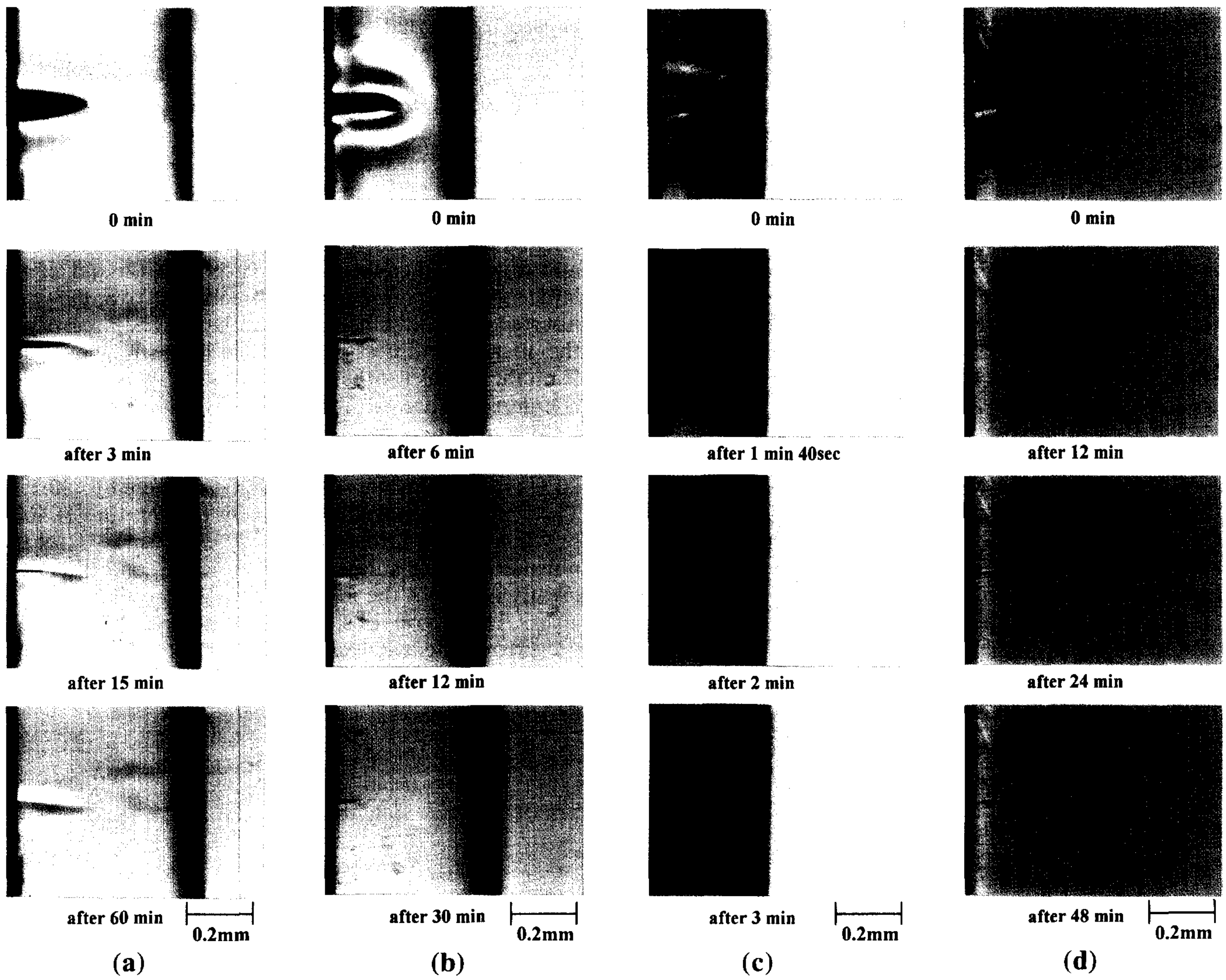

Figure 6 Crack healing in the surface swollen layer in methanol environment: (a) at 20°C; (b) at 40°C (thicker layer); (c) at 40°C (thinner layer); (d) at 40°C (entirely swollen sample)

methanol at 20°C. The pictures were taken by focusing on the crack front in the middle of the crack plane, which advanced more slowly, probably being affected by the fact that the normal stress component in the longitudinal direction, σ_{yy}, has greatest magnitude of compression at the site. Just after loading, the pre-crack with initial length of 0.05 mm (picture 1) rapidly advances to about 0.25 mm (picture 2). After that, however, the crack growth is almost arrested for a long loading period following an increase in crack opening displacement (picture 3) due to large creep deformation of the swollen polymer. Subsequently, the crack gradually progresses with the formation of a small sharp crack at the blunted crack front (picture 4) and finally reaches and passes through the boundary to cause general fracture of the glassy core.

Such interesting behaviour of crack growth in the surface swollen layer may be correlated with the distribution of internal stresses discussed above. *Figure 5* shows the correlation between the longitudinal component of induced stress (*Figure 3b*), σ_{yy}, the concentrated stress at the crack tip under tension, estimated by a simple calculation, and the variation of crack length with time (*Figure 4*). The stress concentration factor at the crack tip was simply assumed to hold a constant of 7, supposing an arrested crack with shape approximated by a half-ellipse (picture 3 in *Figure 4*). The external stress given by static tension also was simply calculated by the FEM for the surface and the inner layers, neglecting the swelling deformation of the surface layer. Superposing the external stress, increased seven times at the crack tip to the internal stress field induced by surface swelling (a dotted line in the figure), may be used to estimate the stress level at the crack tip for a certain crack length, as shown by a solid line in the figure. The stress at the entire surface will be much higher than obtained by this calculation, because of the much sharper tip of the initial crack. It is clear that a position in the surface swollen layer where the crack growth is arrested for a long time almost coincides with that where the tensile stress at the crack tip takes the minimum influenced by the distribution of the induced compressive stress. In conclusion, the crack advance is obviously controlled by the internal stress caused by the surface swelling following case II diffusion.

Examination of crack healing

The results of observations on crack healing are summarized in *Table 1* and partially shown in *Figure 6*. A crack grown to 0.22 mm in length in the surface swollen layer of 0.5 mm thickness at 20°C is gradually closed after unloading. The crack surfaces are almost in contact with each other after 30 min, but still remain, as shown in *Figure 6a*. This crack closure is not proved to result from either the internal compressive stress or the elastic recovery in the surface layer. The behaviour of inserted cracks at 40°C indicates some interesting features. The cracks, which are shorter than the thickness of the surface swollen layer [cases (b) and (c) in the table], do not completely disappear by immersion for a long time (30 min) (*Figure 6b*), while the cracks in the thinner swollen layer reaching near the boundary [cases (d) and (e)] readily disappear after only a few minutes (*Figure 6c*). In the overall swollen specimen [cases (f) and (g)], on the contrary, the crack still remains for a longer time, preserving its initial length, although it is entirely closed (*Figure 6d*). *Figure 7* shows the quasi-static tensile behaviour of the as-received specimen without a crack, the crack-healed specimen and the entirely swollen specimen without a crack, which were evaluated in air by using the same apparatus as that for measuring the basic mechanical factors for the FEM. Two latter specimens were tested after vacuum-drying at room temperature for 24 h. It is noted that the tensile strength of the crack-healed specimen is clearly recovered to that of the entirely swollen specimen. Compared with the as-received specimen, they are commonly at lower levels of the elastic modulus and the fracture stress and strain. The lower modulus is probably due to the plasticizing effect of residual methanol (about 1 wt% for the case of entire swelling), and the reduction of strength may be caused by internal tensile stress induced in the surface layer by desorption of methanol during vacuum-drying.

As discussed in the Experimental section (*Figure 2*), the FEM analyses indicate that the internal compressive stress in the longitudinal direction, σ_{yy}, takes the maximum magnitude in the surface swollen layer near the boundary, and also that the greater magnitude in σ_{yy} is obtained for the thinner surface swollen layer. The phenomenon of crack healing observed in the cases (d) and (e) may, therefore, take place with the aid of the large internal compressive stress acting all over the crack inserted into the thinner swollen layer. The necessity of the internal compression may also be easily understood from the results for the entirely swollen specimen, which is completely free of internal stresses. In addition, the results of d.s.c. measurement revealed that the glass transition temperature, T_g, of the specimen swollen at 20°C is 43.5°C, while that at 40°C is lowered to 30.3°C. This result means that the ambient temperature of 40°C providing crack healing obviously exceeds the T_g of the polymer in the surface swollen layer, and therefore greatly enhances the mobility of polymer chains in this layer. The above observations thus suggest that the occurrence of crack healing requires both moderate high

Table 1 Experimental results for crack healing in the surface swollen layer with several thicknesses in methanol at 20 and 40°C

Sample	Temperature of methanol (°C)	Swollen layer thickness (mm)	Initial crack length (mm)	Healing
a	20	0.50	0.22	No
b	40	0.53	0.20	Partially yes
c	40	0.45	0.18	Partially yes
d	40	0.30	0.25	Yes
e	40	0.30	0.20	Yes
f	40	6.0	0.25	No
g	40	(entirely swollen)	0.17	No

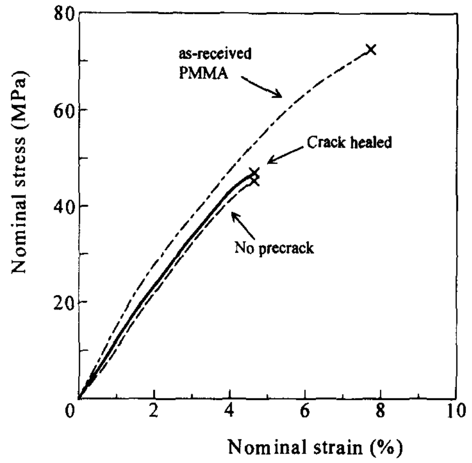

Figure 7 Tensile behaviour of the as-received specimen without crack, the crack-healed specimen, and the entirely swollen specimen without crack, in air at room temperature. Two latter specimens were tested after vacuum-drying at room temperature for 24 h

temperature for promoting the thermal motion of polymer chains and sufficient pressure to bring the crack surfaces into contact with each other.

The healing phenomena of craze and crack in solid polymers have already been studied by many researchers. It is well known that crazes readily disappear at temperatures above T_g[15,16]. Several experiments[17–19] on fracture toughness have demonstrated that, in order to heal a crack, besides high temperature above T_g, some pressure is also required to keep the crack surfaces in contact with each other for some period. It has been interpreted for these observations that the self-diffusion of polymer chains across an interface formed by the contact of crack surfaces under pressure brings about an interpenetration of chains and subsequent formation of physical links between chains migrating from each side of the interface. A more precise theory of crack healing has subsequently been developed by Kim and Wool[20]. All the above studies, however, treat the healing phenomena in dry conditions. Lin *et al.*[21] have also examined crack healing in PMMA in a methanol environment at 40–60°C. However their experiments are quite different from ours in that a crack is introduced on the specimen surface under dry conditions (in air) before exposure to methanol. They confirmed that crack healing took place at these temperatures, which were always higher than the T_g of PMMA swollen in methanol at each temperature, as in our experiments. It was also demonstrated that the rate of crack closure obeys Arrhenius's relation and is dominated by case I (Fickian) transport of methanol. In their interpretation, at the first stage of crack healing, wetting the crack surfaces by case I methanol transport, contributing to the recession of the crack surfaces, precedes the diffusion of polymer chains across the interface. This wetting process may play a similar role to the induced compressive stress in our experiment for making the interface.

Eventually, crack healing observed in our experiment may be brought about by the combined effects of two different mechanisms: the formation of an interface by the contact of crack surfaces under internal compression induced by surface swelling, and the self-diffusion of polymer chains across the interface forming the physical links between polymer chains coming from different sides of the interface.

CONCLUSIONS

The effects of case II diffusion on the growing behaviour of a surface pre-crack were investigated in a system of PMMA and methanol in relation to the distribution of internal stress induced by surface swelling. The stress components were calculated by a FEM, using the data for mechanical properties of the as-received and the entirely swollen specimens. The calculation reveals that the normal stress in the longitudinal direction is compressive in the surface swollen layer and inversely tensile in the inner glassy core, and that the compressive stress takes the maximum magnitude near the boundary between two layers. The growth of the pre-crack under static tension is clearly suppressed by this maximum compressive stress in the surface swollen layer. At higher ambient temperature above the glass transition temperature of the swollen polymer, where the case II feature still remains, a relatively long crack in the thinner surface swollen layer completely disappears in the absence of external load. This phenomenon of crack healing may be brought about by the formation of an interface by contact of crack surfaces under internal compression and the self-diffusion of polymer chains across the interface to make the physical links of chains with the aid of thermal energy. Since the material system examined in this study inherently possesses two requisites for crack healing, i.e. sufficient contact pressure and promoted thermal motion of polymer chains, it will be developed in the future as a 'smart' material with a self-healing function.

ACKNOWLEDGEMENTS

K. Nakamura and E. Okabana are thanked for their assistance in performing the experiments.

REFERENCES

1. Windle, A. H., in *Polymer Permeability*, ed. J. Comyn. Elsevier Applied Science, London, 1985, p.75.
2. Kawagoe, M. and Nunomoto, S., *Polymer*, 1991, **32**, 3130.
3. Kawagoe, M., Morita, M. and Nunomoto, S., *Kobunshi Ronbunshu*, 1992, **49**, 999.
4. Alfrey, T., Gurnee, E. F. and Lloyd, W. G., *J. Polym. Sci. (C)*, 1966, **12**, 249.
5. Cohn, D. and Marom, G., *Polym. Eng. Sci.*, 1982, **22**, 870.
6. Cohn, D. and Marom, G., *J. Appl. Polym. Sci.*, 1983, **28**, 1981.
7. Klier, J. and Peppas, N. A., *Polymer*, 1987, **28**, 1851.
8. Thomas, N. L. and Windle, A. H., *Polymer*, 1982, **23**, 529.
9. Thomas, N. L. and Windle, A. H., *Polymer*, 1981, **22**, 627.
10. Lasky, R. C., Kramer, E. J. and Hui, C.-Y., *Polymer*, 1988, **29**, 673.
11. Lasky, R. C., Kramer, E. J. and Hui, C.-Y., *Polymer*, 1988, **29**, 1131.
12. Hui, C.-Y., Wu, K.-C., Lasky, R. C. and Kramer, E. J., *J. Appl. Phys.*, 1987, **61**, 5129.
13. Hui, C.-Y., Wu, K.-C., Lasky, R. C. and Kramer, E. J., *J. Appl. Phys.*, 1987, **61**, 5137.
14. Mills, P. and Kramer, E. J., *J. Mater. Sci.*, 1986, **21**, 4151.
15. Spurr, O. K., Jr, and Niegisch, W. D., *J. Appl. Polym. Sci.*, 1962, **6**, 585.
16. Plummer, C. J. G. and Donald, A. M., *J. Mater. Sci.*, 1989, **24**, 1399.
17. Jud, K. and Kausch, H. H., *Polym. Bull.*, 1979, **1**, 697.
18. Jud, K., Kausch, H. H. and Williams, J. G., *J. Mater. Sci.*, 1981, **16**, 204.
19. Nguyen, T. Q., Kausch, H. H., Jud, K. and Dettenmaier, M., *Polymer*, 1982, **23**, 1305.
20. Kim, Y. H. and Wool, R. P., *Macromolecules*, 1983, **16**, 1115.
21. Lin, C. B., Lee, S. and Liu, K. S., *Polym. Eng. Sci.*, 1990, **30**, 1399.