Surface crazing in PVC and other polymers

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Initiation and growth of surface crazes in rigid PVC, subjected to tensile creep loads, has been studied experimentally for a wide variety of conditions. The tests were carried out at room temperature, at stress levels ranging from 10 to 50 MPa, in air or in the vapour of natural gas condensate (a crazing agent). PVCs with different molecular weights (K-values) and degrees of gelation were tested. Physical aging of the sample was considered by comparing quenched and aged samples. The behaviour under continuous loading was compared with that under cyclic loading. In cyclic loading, crazing behaviour differs markedly from that observed in continuous loading. The defects grow linearly with the number of load periods, i.e. linearly with the loading time, and they appear to be associated with cracks. In continuous loading, the craze length grows linearly with the logarithm of the loading time, after some initiation time has been passed. This logarithmic growth in constant loading is bounded by two processes of growth cessation. The first, at high stresses, coincides with gross yielding of the sample; the second, at low stress levels, is less well understood. The effects of stress level, crazing agent, K value, degree of gelation and physical aging on the processes of initiation and cessation of crazing under constant stress are discussed. The growth rate was shown to depend only on the stress; the crazing agent, molecular weight and degree of gelation have little influence. For other polymers, such as PS, PMMA and PC, the growth kinetics are essentially the same as for PVC. For these materials, the growth rate for crazing sharply decreases with increasing stress, according to the inverse second to inverse third power of the stress.

INTRODUCTION

This paper is part of a continuing study into crazing in PVC and the long-term strength of PVC. The study was instigated by the finding that parts of the gas network in Holland have become crazed[1,2], although there has not, as yet, been any indication that these crazes endanger safe operation. Much about the nature of crazing and the basic phenomenology of initiation and growth is already known, particularly for polystyrene (PS), polycarbonate (PC), and for poly(methyl methacrylate) (PMMA), and a number of review articles have appeared[3,4]. Particular attention has been paid to aspects of fracture mechanics in craze formation and growth[5-7]. In such studies, measurements are made of crazes at the tips of already existing cracks. The results are therefore particularly relevant to the question of crack propagation. In the present study, we have looked at the complementary phenomenon of surface craze initiation and growth in samples which were not deliberately pre-cracked. The resulting surface crazes were studied under creep conditions (constant loading). Knowledge of these surface crazing phenomena will eventually lead to a clearer understanding of crack formation.

The growth of surface crazes under creep conditions has been studied by a few authors. Kambour[4] has reviewed the general features of the kinetics. Surface crazes grow either linearly with the logarithm of the loading time; or, after such a period of growth, linearly with the loading time. These two types of kinetic behaviour may represent two extremes of craze growth kinetics in a creep experiment: (i) stable growth in which crazes grow linearly with the logarithm of the loading time or even cease to grow; (ii) unstable growth where the crazes grow linearly with the loading time and are possibly accompanied by crack formation or by crack

growth. In (ii), with a growing crack, failure will eventually follow. There is circumstantial evidence to support this viewpoint (e.g. ref. 4 and the data in refs. 5, 6 and 8). Here we have restricted ourselves to a study of surface growth for a number of PVCs. The material variables were the molecular weight (K value); and the quality of processing which was varied by changing the conditions of sample preparation. Both tough and brittle PVC was examined. Particular attention has been paid to the phenomenology of initiation and growth for constant loading and, to a lesser extent, for intermittent loading conditions. The experiments were carried out in air and a natural gas condensate. For simplicity, we have not carried out any experiments in liquid contact, because it has been shown that the kinetics of growth of such crazes depend on a number of complicating factors, e.g. the viscosity of the agent[7,9], the capillary pressure developed in the craze and the solubility of the craze ligaments in the agent[10].

EXPERIMENTAL

Apparatus

An outline of the measurement system is shown in *Figure 1*. A dumbbell shaped test strip of dimensions according to ISO R 527 was held in a frame. The tensile load was achieved by an oil driven piston working on one end of the test strip. The displacement of the piston and the creep deformation of the specimen was determined digitally to 1 μm by a Moiré fringe counter (Dr. J. Heidenhain, Metro 1030, Traunreut, W. Germany). The test frame was enclosed by glass windows for tests in an environment other than air. For experiments in natural gas condensate, a small oblong dish filled with
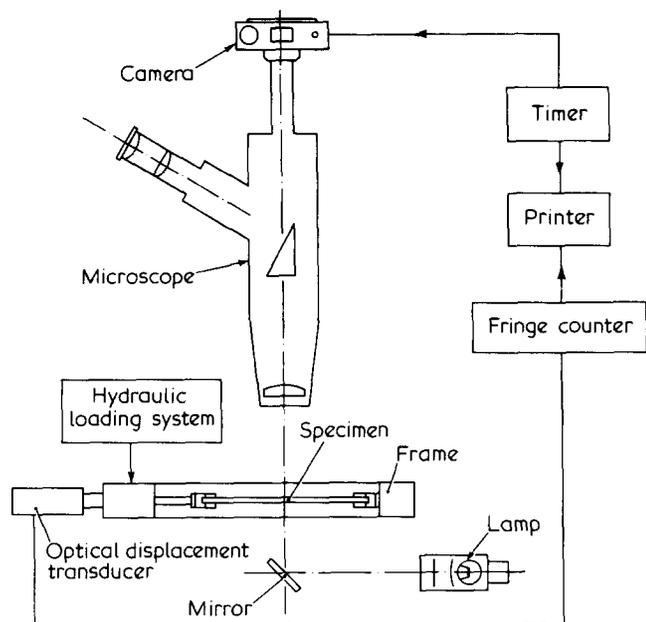
Figure 1 Schematic view of measurements system. At present the test frame can be thermostatically controlled for measurements up to 60°C. For tests under environmental conditions a receptacle, e.g. containing natural gas condensate, is place in the test frame. The system can be viewed obliquely also

condensate was placed in the chamber. Facilities existed to examine crazing in a continuous stream of condensate vapour, at temperatures up to 60°C.

Observation of surface crazes formed in the test strips was aided by the use of a mirror placed underneath (*Figure 1*). The surface lengths of crazes were determined from photographs taken with an automatic camera. The depth of penetration of surface crazes into the samples was not registered continuously. By viewing the specimen obliquely and correcting for refraction, or by measuring the apparent depths of penetration directly, it was found that the ratio of penetration depth: surface length was in the range 0.3 to 0.5 and did not seem to depend on the system under examination.

The apparatus was run automatically by a logarithmic timer, which relayed a pulse after 1, 2, 4, 8, 16 . . . etc. s to a printer to record the displacement; and another pulse to the automatic camera which photographed a selected region of crazing. Because of the specimen's creep, the selected craze moves from the field of view, but it was seldom necessary to move the test to correct for this. The whole system was placed in a room with 50% r.h. and temperature of 21°C.

Materials

PVCs examined are given in *Table 1* with the relevant *K* value, estimated molecular weight and source.

All resins were compounded at 100°C into dry blends in a tin stabilized formulation, containing 2% Advastab 17M, 1% Loxiol G12 and 0.5% Irgawax 366. The dry blends were used to make crystal-clear sheets, either by direct pressing or indirectly, by first making granulate to a low degree of gelation and pressing it. The average degree of gelation of the material formed in this way is a function of the pressing conditions. To restrict the number of conditions, we pressed at 190°C to obtain a tough material having a medium degree of gelation according to the characterization method of Gonze[11]. We pressed at 160°C to obtain a brittle material. Some measurements were also carried out on polystyrene (Styron

678 and Hostyron 4000Z) in order to generalize the comparison between brittle and tough materials.

The gas condensate was obtained from the VEG-Gas institute; its constituents are given in ref. 2.

RESULTS AND DISCUSSION

Effect of sample preparation

The method of sample preparation had a strong influence on the quality of the results. The shapes of crazes in dry blend samples pressed at 190°C, or in granulate pressed at any temperature, were normal and similar to the results illustrated in the literature, e.g. in ref. 4. However, we found very irregular craze shapes in dry blend samples pressed at 160°C. These shapes were similar to the wavy type illustrated in ref. 8. In addition, pressing of dry blends, rather than granules, always led to a less regular growth behaviour even for pressings at 190°C. On several occasions with dry blend pressings, crazes which had been initiated at an early stage were subsequently overtaken by crazes that had been initiated at a later stage. This irregular behaviour is explainable in terms of the relatively poor homogenization in the gelation level of the pressed dry blends. However, the dry blend studies brought out one interesting facet; *viz* that crazes were preferentially initiated at the grain boundaries of the original powder particles even for high temperature pressings. *Figure 2* illustrates this. crazes do not grow at random but mark out domains which are about the same size as pressed powder particles.

Initiation and cessation of craze growth: outline of results

As shown in *Figure 3*, the visible growth of crazes in PVC is bounded by a series of time-dependent stress levels:

Table 1 Materials

	K value	M_v	Type	Source	Code
Breon M110/50	65	1.4×10^5	Mass	BP Chemicals	IIIA
Solvic 223	56	0.8×10^5	Suspension	Solvay	IVA
Solvic 229	64	1.3×10^5	Suspension	Solvay	IA
Diamond 450	70	1.9×10^5	Suspension	Diamond Shamrock	VA
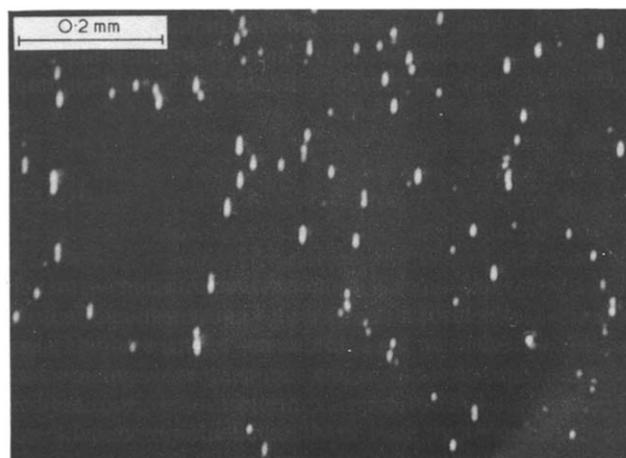
Figure 2 Photomicrograph showing preferred initiation of crazing at the boundries of the original grains. The sample was pressed at 190°C and no boundaries were visible before stressing close to the yield stress
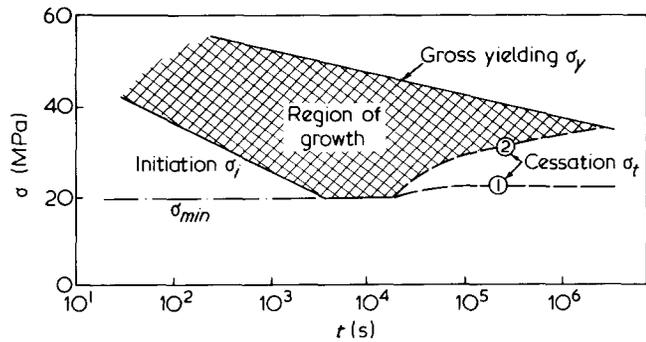
Figure 3 Schematic representation of the time—stress domain in which craze growth occurs in PVC IIIA. After initiation, craze growth can cease just before gross yielding (necking) occurs. Crazes can also cease to grow by a second process at lower stresses, which depends on the environment and the PVC gelation. Experiments suggest that growth may be bounded or unbounded as indicated by the lines 1 and 2 for σ_f
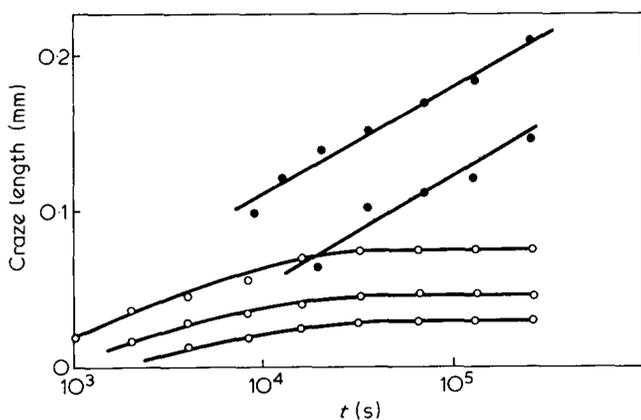
Figure 4 Craze lengths as a function of loading time, t, in air for medium gelled IIIA at two levels of stress. At 42 MPa necking occurred after about 3×10^5 s. In this figure and in the following figures the different lines pertain to different crazes. ●, $\sigma_{32.3}$; ○, σ_{42}

(a) There is a delay time for initiation of visible crazes. The delay time decreases with increasing stress as is shown by the σ_i line for condensate vapour in *Figure 3*. In air, it was found that the initiation times were increased by a factor of about ten for all stress levels. With PS, where craze initiation in air was delayed by a factor of about 10^4 with respect to that in condensate vapour, the regression line between stress and initiation time was noticeably steeper for air than for vapour;

(b) There is a certain threshold level σ_{min}, of stress below which crazes will not be initiated;

(c) At high stresses, craze growth ceases prior to delayed necking and yielding of the sample (σ_y line in *Figure 3*). Presumably, this is because of the formation of shear bands at the craze tips as has been seen for PVC[12]; shear bands are well known to hinder craze growth[4];

(d) We have also found evidence for a process of craze growth cessation at low stress levels, where gross yielding will not occur (σ_f lines in *Figure 3*). This further process of craze growth cessation is sensitive to the quality of the PVC under study i.e. its degree of gelation; and the environmental conditions. In *Figure 3*, cessation line 1 corresponds schematically to poorly gelled PVC in air or to medium gelled PVC in a crazing agent. Cessation line 2 corresponds to medium gelled PVC in air. An analogous phenemenon of craze growth cessation is known to occur in crack tip crazes[5]. However,

the investigations of Marshall *et al.* were of relatively short duration and cessation might have been due to craze growth beyond the influence of the stress concentration, at the crack tip.

The results shown schematically in *Figure 3* are illustrated by experimental data in *Figures 4—8*, which give the length of single crazes as a function of time. *Figures 4* and *5* deal with craze growth in air at stress levels of 42, 32.3 and
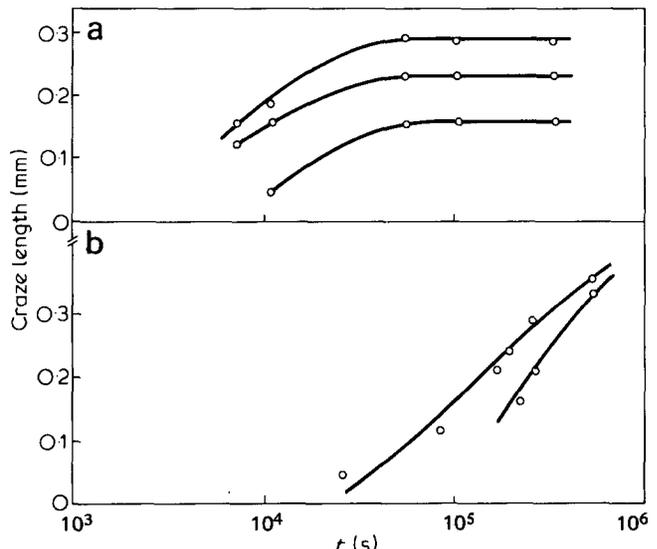
Figure 5 Craze growth in air for IIIA at a constant stress of 27.8 MPa and for two levels of gelation. a, medium gelled; b, poorly gelled. $\sigma_{27.8}$
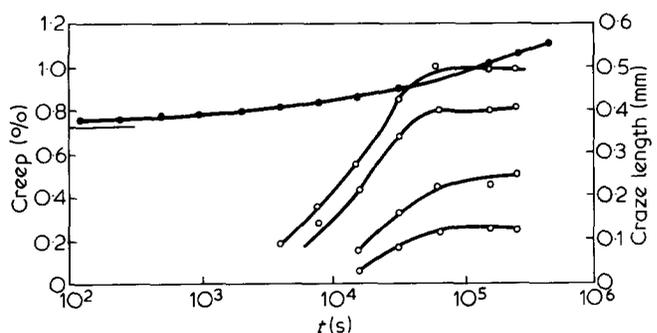
Figure 6 Craze length (○) and testpiece creep (●) for medium gelled IIIA as a function of loading time, t. The stress is 20.6 MPa, the temperature 21°C. The test was carried out in the presence of condensate vapour on strips moulded 39 days previously
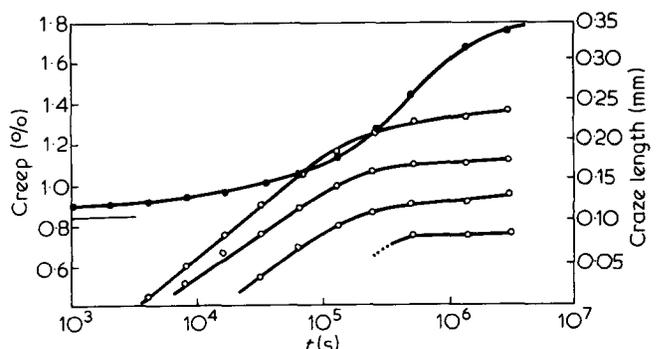
Figure 7 Craze length (○) and testpiece creep (●) for medium gelled IIIA in condensate vapour as a function of loading time, t. The stress is 22 MPa. Temperature, 21°C; strip moulded 60 days previously
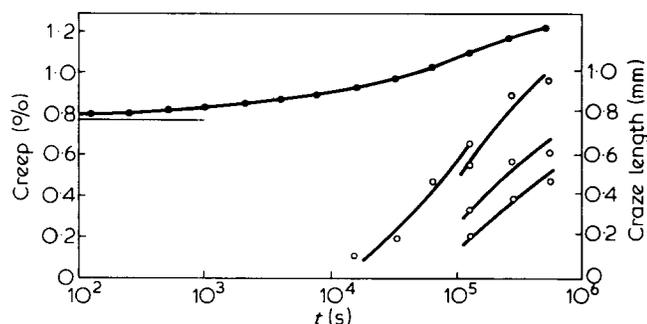
Figure 8 Craze (O) and creep (●) for poorly gelled IIIA as a function of loading time, t, in condensate vapour. The stress is 20 MPa and the temperature 21°C

27.8 MPa. At the highest tensile stress (*Figure 4*), craze growth ceases some time before visible necking of the sample takes place. At the intermediate level of stress (*Figure 4*), growth is continuous for the duration of the experiment. At the lowest stress level, craze growth ceases after a relatively short period, but only for the better gelled material (*Figure 5*). In the poorly gelled material, craze growth continues for the duration of the experiment.

Effect of crazing agent (vapour of natural gas condensate)

The presence of condensate vapour modifies the behaviour just described.

Figure 6 shows that, for medium gelled IIA at 20.6 MPa, i.e. close to the initiation threshold level (see *Figure 3*), craze growth ceases within one day. At 22 MPa, growth on the logarithmic scale is constant for about three days before it decreases to a much lower rate or ceases (*Figure 7*). Thus, it appears that the delay time for this second process of craze growth cessation increases with increasing stress.

In *Figures 6* and *7* we have shown simultaneously measured creep. The horizontal line on the left hand axis gives the creep deformation at 10 s. It is noticeable in *Figure 7* that, after about 10^6 s (about 11 days), the rate of creep decreases. This particular change may be due to loss of the more active condensate components from the reservoir*. We do not believe that this loss caused the much earlier decrease in the rate of craze growth. At still lower stresses, the growth period was completed within a few hours (cf. *Figure 6*) and this cannot be explained by loss of active components.

Figure 8 shows the results of a test in condensate vapour at a stress level of 20 MPa for poorly gelled IIIA. These measurements were carried out under conditions almost identical (the stress being marginally lower) to those of the measurements on medium gelled IIIA, so *Figure 8* may be compared to *Figure 6*. We observe that, in poorly gelled material, the initiation times are a factor of about 3 longer; whilst the growth continues over a time interval that is at least a factor of 10 longer.

The delay in cessation with the poorly gelled samples could be significant in that the process of craze growth cessation at low stress levels is determined by the ability of the material to form cavities. It could also be due to a lesser rate of relaxation of the stress concentration at the craze tip, because of a lower stability of craze fibrils in the poorly

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* As explained (EXPERIMENTAL, *Apparatus*) the condensate was placed in a small receptacle inside the chamber enclosing the test-piece. Visual checks showed that the receptacle did not dry out. Some later experiments have shown that the size of the receptacle could influence the craze growth result

processed material. This should imply, however, that the rate of growth in the poorly processed material would be higher than in the well processed material. We have no evidence for this (see *Growth kinetics* below).

Craze growth cessation in crack tip crazes in solvent media has been discussed previously[13]. It was found that, on cessation, the stress concentration moves from the craze tip to behind the craze tip. This was linked with the inability of solvent to plasticize the tip fully. The results of our kinetic studies would seem to agree with the notion that the craze tip is not fully plasticized, but, in view of the similarities we have found between surface craze cessation in air and in condensate vapour, it would seem likely that craze growth cessation has a more general basis. Currently, we are trying to determine whether cessation of surface craze growth could be the result of the existence of a threshold level for yielding and necking. This would explain a number of observed features of the process.

The influence of molecular weight

The effects of molecular weight on initiation and growth are indicated briefly in *Figure 9* for the materials with the lowest and the highest molecular weights of *Table 1*. Crazes were initiated earlier in the higher molecular weight material, but the differences were not large considering the normal wide range in initiation times. The initial logarithmic rates of growth are also the same essentially for the materials. However, it is seen that, for longer times, the rate of craze growth markedly diminishes for the higher K value material. Whether this is related to the process of craze growth cessation at low stress levels, as discussed earlier, or to a greater hardening of the fibrils, has yet to be determined.

Our results seem to indicate that molecular weight plays a role in craze initiation only through its influence on the localized moulding stresses present during sample preparation. Thus, material of higher molecular weight, having a higher viscosity, tends to have an earlier craze initiation. This would also explain the higher craze densities for the higher molecular weights in PS in refs. 14 and 15. The contrary results of Gotham[16], whereby an injection moulded grade of a low molecular weight PMMA crazed earlier and more profusely than a higher molecular weight grade which had been cast, are consistent with our hypothesis.

Other factors

Other factors are relevant to craze initiation and craze growth cessation. In the Netherlands during the 1960s, there was a changeover from coal gas to natural gas, which was alledgedly less corrosive. This change undoubtedly influenced the growth of any existing crazes in the gas network. We tried to model this alteration by measuring the

Figure 9 Craze length of the loading time, t, for IVA, K value 56, ●; VA, K value 70, O, in condensate vapour. Conditions: σ = MPa, temperature, 21°C; strip moulded about 8 months previously

Figure 10 Craze length, ○; creep, ●, as functions of loading time, *t*, for medium gelled VA in the vapour gas condensate. After 8 000 s the condensate was removed. Conditions: σ = 25 MPa, temperature, 21°C; strip moulded 8 months previously

Figure 11 An example of the initial growth of surface crazes at room temperature in a polystyrene (Hostyron 4000 Z). The environment was gas condensate vapour, the stress 12.8 MPa. After 10 min the experiment was discontinued because the craze density was too high

influence of the removal of the crazing agent, once crazing had been initiated. We conducted one experiment with medium gelled VA at a stress of 25 MPa: crazes would not usually be formed in air. The results given in *Figure 10* show that craze growth ceases almost instantaneously upon removal of the source of craze activity. Creep rate appears to decrease simultaneously. The presence of the vapour was somehow essential for continuing craze growth. The data in this Figure are consistent with the data of *Figure 5* (upper line) in that craze growth does not continue indefinitely for a material which has been well processed.

We have conducted a number of additional experiments on the influence of aging on subsequent crazing. Freshly moulded material had a lower degree of crazing; a few crazes always seemed to be initiated. For these, it was not possible to decide whether their initiation was influenced by the age of the sample or not. Rather similar conclusions have been made for polycarbonate[17].

Growth kinetics

A general, simple relation between craze surface length in PVC and time between initiation and cessation is of the form:

$$l_c = \beta \ln(t/t_i) \qquad (1)$$

where l_c is the surface length of craze; t is the loading time; t_i is the (extrapolated) initiation time of craze; and β is the constant (the logarithmic growth rate).

We have also found, at least for the initial stages of craze growth, that polystyrene behaves in a very similar way. *Figure 11* shows some results for PS in gas condensate vapour. On account of the very profuse crazing in PS, it was not possible to follow quantitative craze growth over a long period. A number of observations suggested that growth later ceased rather suddenly because of the surface interactions of closely ovelapping crazes, but that thickness growth continued. For very long times approaching fracture it is known that the kinetics of growth in PS do not follow equation (1)[4].

In PVC there are a number of departures from the general rule given by equation (1). Firstly, we have noted that longer crazes will nearly always tend to grow somewhat faster than shorter crazes, i.e. β depends on the initiation time. Secondly, it has been found that crazes sometimes grow faster than proportional to the logarithm of the loading time. Both of these effects can be seen in *Figure 12* where data for PVC of relatively low molecular weight are shown. The second effect has only been found with test-pieces exposed to condensate vapour and could be an indication of impending fracture. Poorly gelled material sometimes fractured in a brittle fashion during the constant loading experiments. In these cases, we often observed a sudden increase in the slope of the craze length against log time plot prior to fracture.

When all the above refinements to growth kinetics are ignored, and an average initial value of β from several crazes is used for a given stress level, it is found that, to a first approximation, β depends only on the stress, other factors being unimportant. This major result is illustrated in *Figure 13*, in which β has been plotted for a number of PVC types processed and measured under a variety of conditions. The Figure also includes literature data on other polymers, such as PMMA[18,19] and PC[17,20] and a few of our data on PS. *A review of all data reveals that surface craze growth has a very general and simple form that does not seem to be related to any structural differences between materials.* It
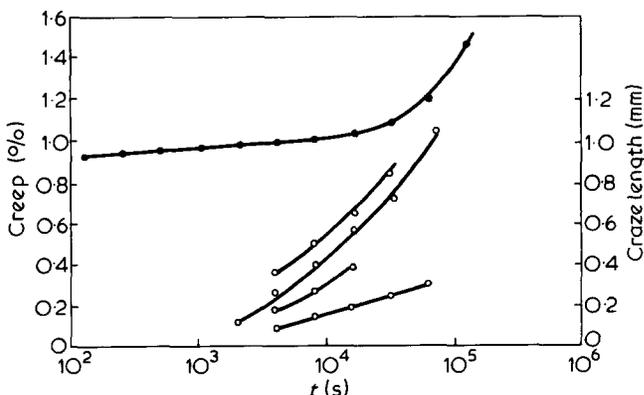
Figure 12 Craze length, ○; creep, ●, as function of loading time, *t*, for IVA in condensate vapour. Conditions: σ = MPa; temperature, 21°C; strip about 8 months old
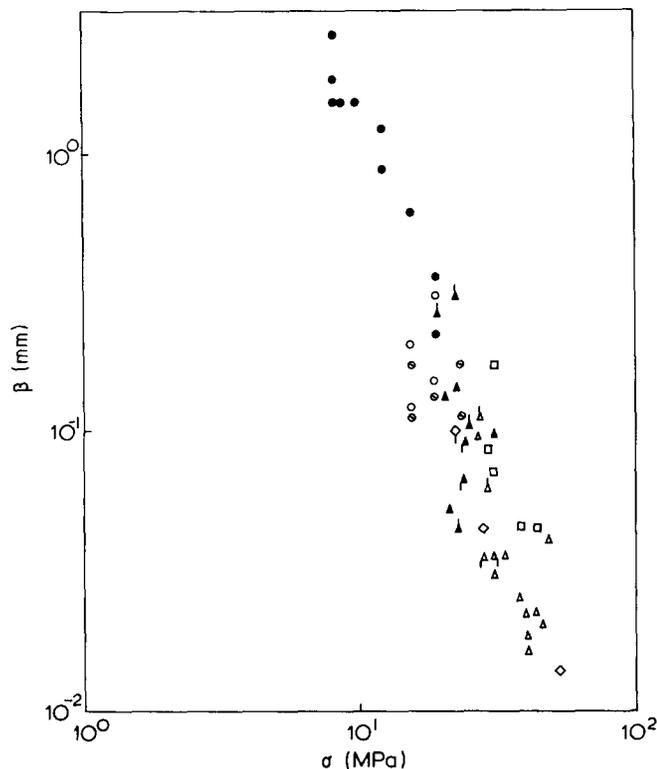
Figure 13 The parameter of growth β as a function of stress at room temperature for a number of PVCs processed under a variety of conditions. Our data on polystyrene (PS) and literature data on PMMA[18,19] and PC[17,20] are included. Open symbols, in air; filled symbols, in condensate vapour. △, ▲, PCV medium gelled IIIA; △, ▲, PVC poorly gelled IIIA; ◁, ◀, PVC VA; ◀, PVC IVA; ○, ◎, ●, polystyrene (Styron 678 and Hostyren 4000 Z); □, polycarbonate; ◇, poly(methyl methacrylate)
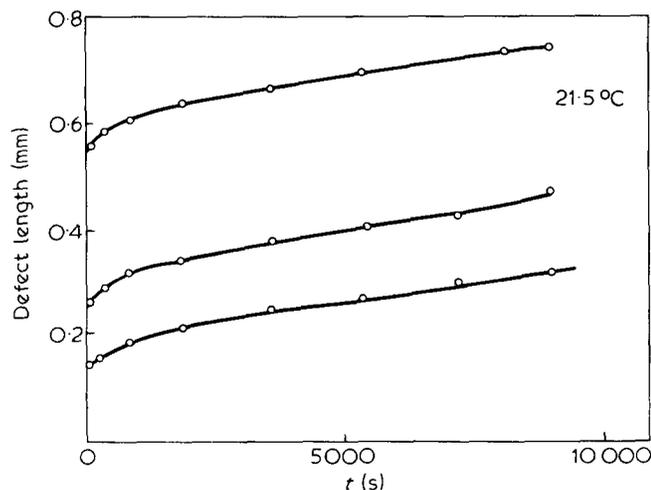
Figure 14 Growth of surface defects over the period up to fracture for medium gelled IIIA at a maximum stress of 39.6 MPa and a cyclic frequency of 0.1 Hz

appears that the craze growth parameter β is not influenced by the molecular weight (K value), the level of gelation in PVC, the presence of condensate vapour nor by the type of polymer. This suggests that a general and simple description can be found for the reported growth kinetics.

It is sometimes assumed that craze growth rate, like crack growth rate, will be accelerated by an increase in stress. *Figure 13* shows that, in our experiments, craze growth rate is strongly decelerated by an increase in stress. At a low stress, there are only a few crazes and these grow rapidly,

proportional to the inverse second or third power of the applied stress.

In view of the large influence which condensate vapour had on initiation, and on the density of crazing, it was very surprising to see that the growth kinetics under continuous loading remain largely unaffected by the presence of condensate vapour. This is more surprising since the experiment of *Figure 10* showed that condensate vapour was sometimes necessary for craze growth. We suggest that the reason for this is that the rate determining factor is not the yield stress, modified by the environment, but rather the yield stress at the very tip of the craze where the environmental agent has less access. In the limiting case, the rates will be determined by the yielding of the dry material — which was possibly the case in our investigation. Kramer *et al.*[13] have also suggested, on the basis of different kinds of experiments, that the very tip of a craze is not changed by the environmental agent.

Results for cyclic loading

The apparatus briefly described here was also designed to load the test samples cyclically instead of continuously. The hydraulic feed line connecting the air/oil pressure reservoir to the piston pulling the sample is interrupted by an electronically controlled valve system to admit or release pressure from the piston without losing pressure in the reservoir. By this means the samples are stressed in a square wave mode. The 'on' and 'off' periods are adjustable separately, with a highest frequency of about 0.5 Hz. The hydraulic feed line has been fitted with an adjustable throttle to dampen out excessively fast movements.

Measurements were made on medium gelled IIIA in air and the observed optical effect always appeared to consist of both a craze and a crack. The growth of the craze and crack combination is described. The presence of a crack was concluded on the basis of the optical appearance of the defect when viewed at various angles. In constant loading experiments, cracks were never seen with the medium gelled PVC, except at stresses close to the necking instability. The results of exploratory measurements, carried out at room temperature, are (see *Figures 14* and *15*):

(i) the defect grows intermittently with the on—off periods, the craze/crack length increases linearly with the number of loadings instead of linearly with log t;

(ii) brittle fracture occurs after some period in which the defect grows linearly with time.

An example of a set of measurements is given in *Figure 14*, in which defect lengths are plotted against the total experimental time. After about 10^4 seconds, the sample broke due to a defect which had grown from the thin edge of the rectangular cross section.
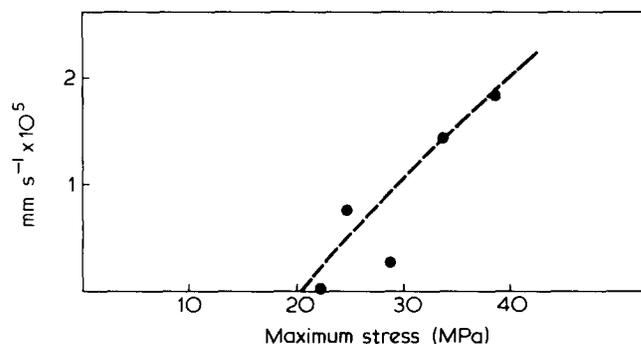
Figure 15 Linear rate of growth of defects during the period up to fracture for medium gelled IIIA as a function of the maximum stress

We have plotted the growth rates of defects against the applied stress in *Figure 15*.

Three points can be made from this Figure. Firstly, the rate of defect growth increases with increasing stress level, in contrast to the experiments in constant loading, where the rate of craze growth decreases. Secondly, the rate of defect growth at low stresses becomes negligible but fracture still ensues. Thirdly, the threshold stress of fracture in dynamic loading seems to be the same as the threshold stress for craze initiation in constant loading. This result is apparently not valid generally[21] but it has been suggested as a useful starting point for a design procedure[22].

With regard to the site of craze and fracture initiation, in most of the fatigue tests a small piece of degraded PVC was the source of the original craze. However, not all the degraded particles which were present close to the surface formed crazing sites; nor did there seem to be any correlation between the size of the degraded material and craze initiation. Clearly, some of the degraded particles are better bonded to the PVC matrix than others.

CONCLUSIONS

(1)   Under a constant stress, crazes in rigid PVC grow linearly with the logarithm of the loading time t, after some initiation time, t_i, has been passed.

(2)   The initiation time, t_i, decreases markedly with increasing stress, although not as fast as the delay time for gross yielding of the sample. Moreover, t_i can be reduced strongly by a crazing agent such as natural gas condensate, whilst molecular weight and degree of gelation have little influence.

(3)   Growth rate $\beta = dl_c/d\ln t (l_c$ = length of a craze) is approximately the same for all crazes observed in a particular sample, although there are indications that longer crazes grow somewhat faster than shorter crazes. Furthermore, deviations from the logarithmic growth law are sometimes observed in poorly gelled samples of PVC or in PVC subject to a crazing agent.

(4)   To a first approximation β depends on the stress level only; actually, it decreases with the second to third power of σ. Factors such as molecular weight, degree of gelation and the nature of the environment have little influence. Moreover, for other polymers, such as PS, PMMA and PC, the β versus σ relation is the same as for PVC.

(5)   Growth according to the log t law is bounded by two processes of cessation. The first coincides roughly with gross yielding of the sample; therefore this process of cessation is delayed with decreasing stress. For the second process of cessation, which applied at low stress levels, the reverse is true, i.e. cessation is delayed by increasing stress. The

second cessation process appears to be influenced by factors such as molecular weight, degree of gelation and environment.

(6)   Physical ageing appears to promote crazing; only a small amount of crazing was observed in quenched samples.

(7)   In cyclic loading, crazing strongly differs from that in continuous loading. Crazes grow linearly with the total time under load, the growth rate increases with stress and crazes appear to be associated with cracks. Above a certain threshold level, the test always leads to fracture of the sample.

ACKNOWLEDGEMENTS

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