JOURNAL OF MATERIALS SCIENCE 26 (1991) 5212–5220

Environmental stress cracking of PVC: effects of natural gas with different amounts of benzene

J. BREEN, D. J. VAN DIJK*
TNO Centre for Polymeric Materials, Physics Department, P.O. Box 71, 2600 AB Delft, The Netherlands.

Craze initiation, craze growth and ultimate fracture were studied in PVC (polyvinylchloride) and PVC–CPE (PVC blend with 10% chlorinated polyethylene) under a constant load in air and in natural gas enriched with benzene. The craze initiation results are similar for PVC and PVC–CPE. The craze initiation stress is decreased dramatically at high benzene concentrations ($\geqslant$ 25000 p.p.m.). Preferential and enhanced sorption of benzene molecules near surface inhomogeneities, the craze initiators, are held responsible for this phenomenon. Initial craze-growth rates in natural gas enriched with benzene increase compared to those in air. However, in all the environments studied, a limited logarithmic craze growth is observed, and growth seems limited to this constant logarithmic interval. The logarithmic craze growth and the termination of craze growth are attributed to a reduction of the stress at the craze tip. The failure mode of PVC and PVC–CPE in air and in gas with 5000–6000 p.p.m. benzene is yielding. A brittle branch appears in the failure curve (failure stress against loading time) in the more concentrated benzene vapours. This branch is attributed to a reduction in the stability of the crazes.

1. Introduction

Rigid poly(vinylchloride) (PVC) and chlorinated polyethylene (CPE)-modified PVC are used as gas pipes in the low-pressure part (< 0.2 bar) of the Dutch natural gas distribution network. Natural gas consists mainly of methane, a compound which is known to be non-aggressive towards PVC or PVC–CPE at atmospheric pressures and at temperatures between 5 and 25 °C [1]. However, natural gas also contains small amounts of components which are potentially harmful, such as benzene and toluene [1]. The long-term behaviour of PVC and PVC–CPE as a function of the concentration of suspected natural gas components has been studied extensively at TNO.

The present article describes craze initiation, craze growth and time to failure under constant load in natural gas environments in which the benzene vapour concentration was varied extensively. The influence of benzene on the failure process of PVC and PVC–CPE was studied for two reasons. Firstly, an increase in the benzene concentration of the distributed natural gas will occur if gas fields other than the Groningen one are explored [1]. Secondly, benzene has been chosen as it is known to be a swelling agent for PVC [2]. Therefore benzene is thought to be an environmental stress cracking (ESC) agent for PVC and PVC–CPE.

The ESC phenomenon can be caused by a physical and/or chemical interaction between the environment and the polymer [3, 4]. A well-known chemical interaction is the degradation of polyethylene by photo-oxidation [5]. By contrast, a physical interaction does not result in degradation but is due to sorption [6]. The sorption of liquid or vapour modifies the polymeric matrix, and the modulus and yield stress decrease [6]. Notwithstanding the different origin of the interaction, the polymer fails at lower stress levels and/or shorter times in an ESC environment. Moreover, the polymer generally becomes more brittle.

The ESC of PVC due to benzene vapour is of a physical origin. The penetration of the benzene molecules into the PVC matrix causes a reduction in mechanical properties and an acceleration of the failure process. The diffusion of small molecules in PVC has been studied by Berens and co-workers [7, 8]. The equilibrium sorption of small molecules can be described fairly well by the Flory–Huggins theory [8]. However, the rate of sorption is more complicated as it depends on the activity of the molecules, their size, the free volume of the polymer and the local segmental mobility of the polymer chains [7–9]. Brown has shown that even gas molecules like N_2, O_2 and Ar induce ESC at very low temperatures [10]. The increased activity of the gas molecules near the boiling point of the agents is responsible for this ESC. The activity of vapour molecules scales with the relative

---

[*] *Present address*: Fasson Nederland BV, Leiden, The Netherlands.

saturation of the vapour. For this reason hardly any ESC is expected in environments containing less than 1 mol % of benzene.

The sorption of small molecules by a stressed or strained polymer leads to enhanced craze initiation and craze growth [3, 11]: hence the enhanced brittle fracture of polymers in an ESC environment is associated with these processes. Adequate models for craze initiation and craze growth of unnotched PVC and PVC–CPE materials under a constant load are not available, despite the fact that craze morphology and craze growth have been studied extensively [12–15]. In this article a qualitative interpretation of the observed craze initiation and craze growth will be presented. Moreover, the brittle branch of the failure curves is interpreted in terms of a weakening of the craze fibrils.

2. Experimental procedure

2.1. Polymers

The PVC materials studied are obtained from 110 mm diameter pipes: PVC–CPE, Polva-Hostalit Z-G41; and PVC, Polva-PVC-W41. The first is of gas-pipe quality, whereas the latter is of water-pipe quality. The materials are comparable in *K*-value and degree of gelation. The addition of about 10% CPE in the PVC–CPE blend is responsible for most of the differences in tensile strength, Young's modulus and impact strength between PVC and PVC–CPE.

The 110 mm diameter pipes were cut into pieces about 200 mm long. Next these pieces were divided into four equal arc segments, which were straightened by compression moulding at 125 °C. Afterwards, a heat treatment was performed at 95 °C for 3 h to reduce internal stresses.

2.2. Equipment

A tapered test strip (thickness, 2.7 mm; width varying from 10 to 20 mm; length, 120 mm) was used for the craze initiation and craze growth experiments. The strip was subjected to a constant load in a frame, which could be enclosed by glass windows for measurements in environments other than air [15]. The constant load was realized by an oil-driven piston which acted on one end of the strip. The stress gradient (the stress decreases by a factor of two along 90 mm of the strip) was used to determine the craze initiation stress as a function of the loading time.

Surface crazes were observed with a light microscope (magnification × 50–100) in oblique light. In order to increase the contrast between a craze and the background, the yellow PVC materials were treated with hydrogen sulphide. Hydrogen sulphide reacts chemically with the lead (II) ions of the stabilizer used in the PVC materials. The test strips were exposed to hydrogen sulphide gas for 24 h. This treatment results in a black surface layer of about 10 μm.

A dumbbell-shaped test strip, of which the dimensions of the smallest part are thickness, 2.7; width, 4.0; length, 20.0 mm, was used for the failure experiments under constant load. The top clamp on the strip was attached to the top of the frame. The frame was fixed to a table in which a bearing was positioned for a rod attached to the bottom clamp (see Fig. 1). In order to prevent gas leakage through the bearing, Teflon bellows were used. The strip could be loaded by attaching dead weights to the rod. The frame was enclosed by a glass cover for measurements in environments other than air.

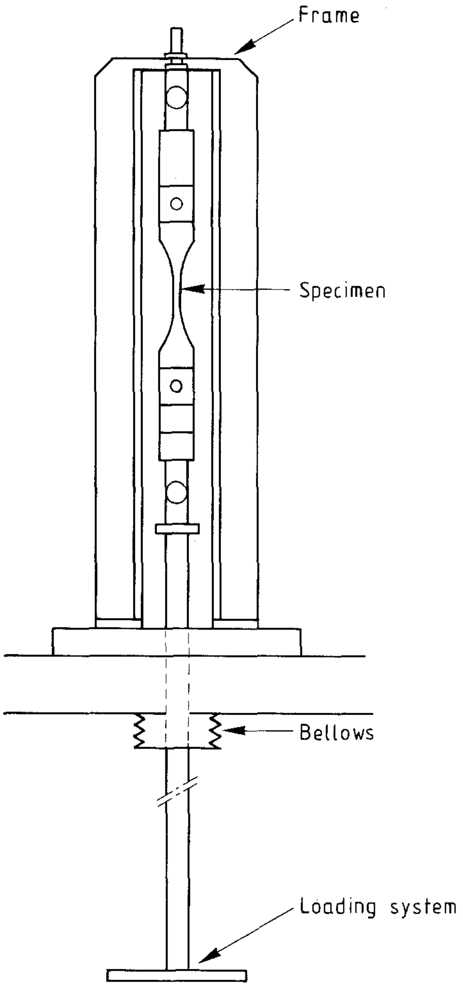

Figure 1 Schematic view of the constant load measurement system.

All experiments were performed under constant load, because this is the most severe situation for gas pipes. In practice, the loading conditions of gas pipes are mainly determined by the ground load. The low gas pressure (< 0.2 bar) is of minor importance. The soil characteristics therefore virtually determine the actual loading conditions of the gas pipe. In the worst case this means a constant stress.

2.3. Environments

The benzene environments were obtained by a continuous injection of liquid benzene in a natural gas flow, and benzene concentration was monitored by a gas chromatograph. During the experiments, a fluctuation in concentration of less than 10% was observed. Natural gas was used as the carrier gas, because the principal aim of this study was to investigate environmental stress cracking of PVC materials in benzene-enriched gas environments.

The composition of the benzene-enriched environments is presented in Table I; benzene concentrations are given in p.p.m. and in relative saturations at 23 °C. Although the temperature of a PVC and PVC–CPE gas pipe in service varies between 5 and 10 °C, the measurements have been performed at ambient temperature for practical reasons. The same reason applies for the choice of the high concentrations of benzene, which will be much lower in service.

3. Results

3.1. Craze initiation

The craze initiation curves in air and in natural gas–benzene vapour mixtures are shown for PVC and PVC–CPE under constant load in Figs 2 and 3, respectively. The natural gas environment, which mainly consists of methane, did not show additional stress corrosion compared to air in our experiments. Therefore the decrease in the craze initiation stress in the natural gas–benzene vapour mixtures has to be attributed to the presence of benzene.

Obviously, the decrease in craze initiation stress becomes significant in the 25 000 p.p.m. benzene environment. By contrast, the low benzene concentration of 5000 p.p.m. induces no significant decrease in the craze initiation stress relative to air.

TABLE I Benzene vapour concentrations used (in p.p.m. and in relative saturations at 23 °C)

c (p.p.m.)	c (% r.s.)
5000/6000	5
25 000/30 000	25
60 000	50
110 000	95

Another aspect, which can be observed from Figs 2 and 3, is the fact that the craze initiation stress for PVC almost equals that for PVC–CPE in the concentrated benzene ($\geqslant$ 25 000 p.p.m.) environments. This suggests that in these environments, the presence of a rubber phase like CPE hardly results in a delay of craze initiation. However, in air and in natural gas with 5000 p.p.m. benzene, differences are seen in craze initiation stresses of PVC and PVC–CPE, particularly at short times.

The PVC–CPE results show that the curvature of craze initiation stress against loading time decreases at longer times. This aspect, together with the decrease in craze initiation stress as a function of benzene concentration, will be discussed in section 4 below.

3.2. Craze growth

The length of the surface crazes measured on the surface was studied in air and in the natural gas–benzene mixtures. Some of the results are shown in Fig. 4. As observed earlier by Wales in air and in gas condensate vapour [15], we found that the surface-craze growth in PVC and PVC–CPE also ceases in the benzene vapours.

A number of mechanisms may contribute to this cessation of the craze growth, such as shear bands and swelling of the surface layer. This makes craze growth complex and results in an enormous scatter in the ultimate craze lengths observed: these ultimate craze lengths for PVC in natural gas with 60 000 p.p.m.

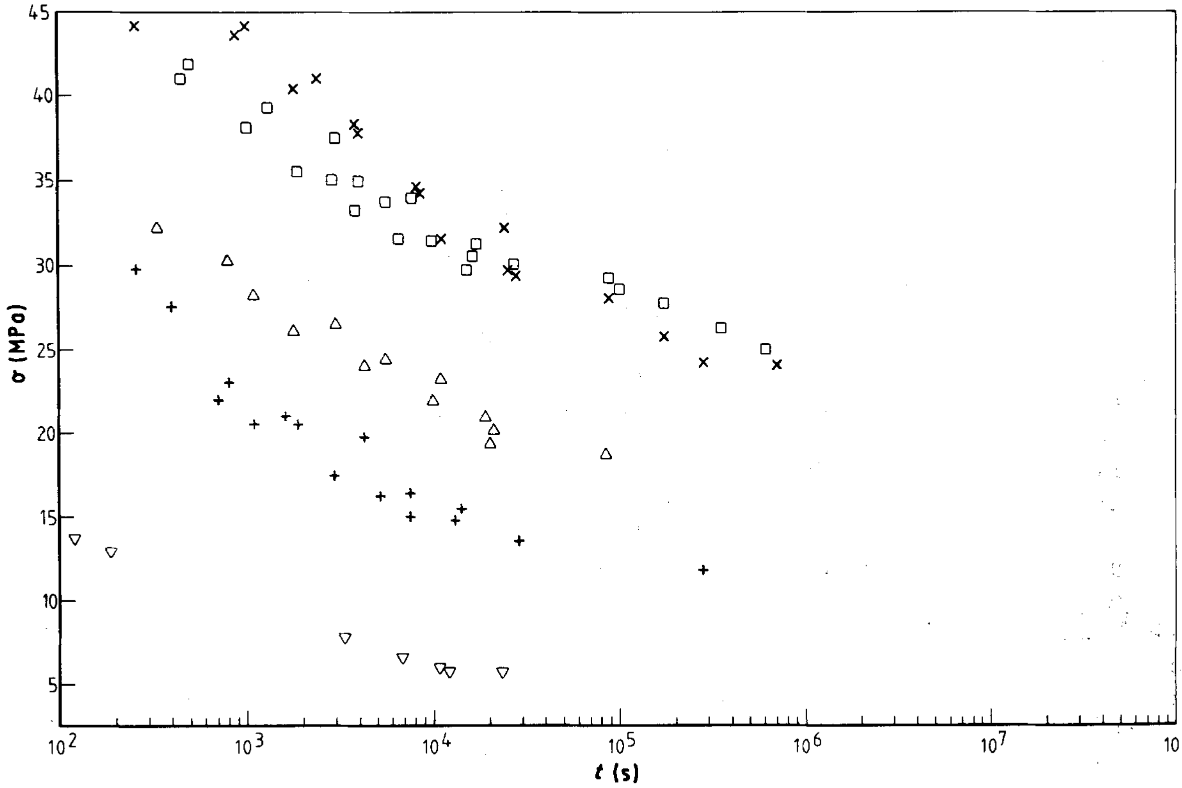

Figure 2 PVC craze-initiation results, applied stress against craze initiation time, for four benzene vapour concentrations: gas with □, 5000; △, 25 000; +, 60 000; ▽, 110 000 p.p.m. benzene; ×, air. Temperature, 23 °C.

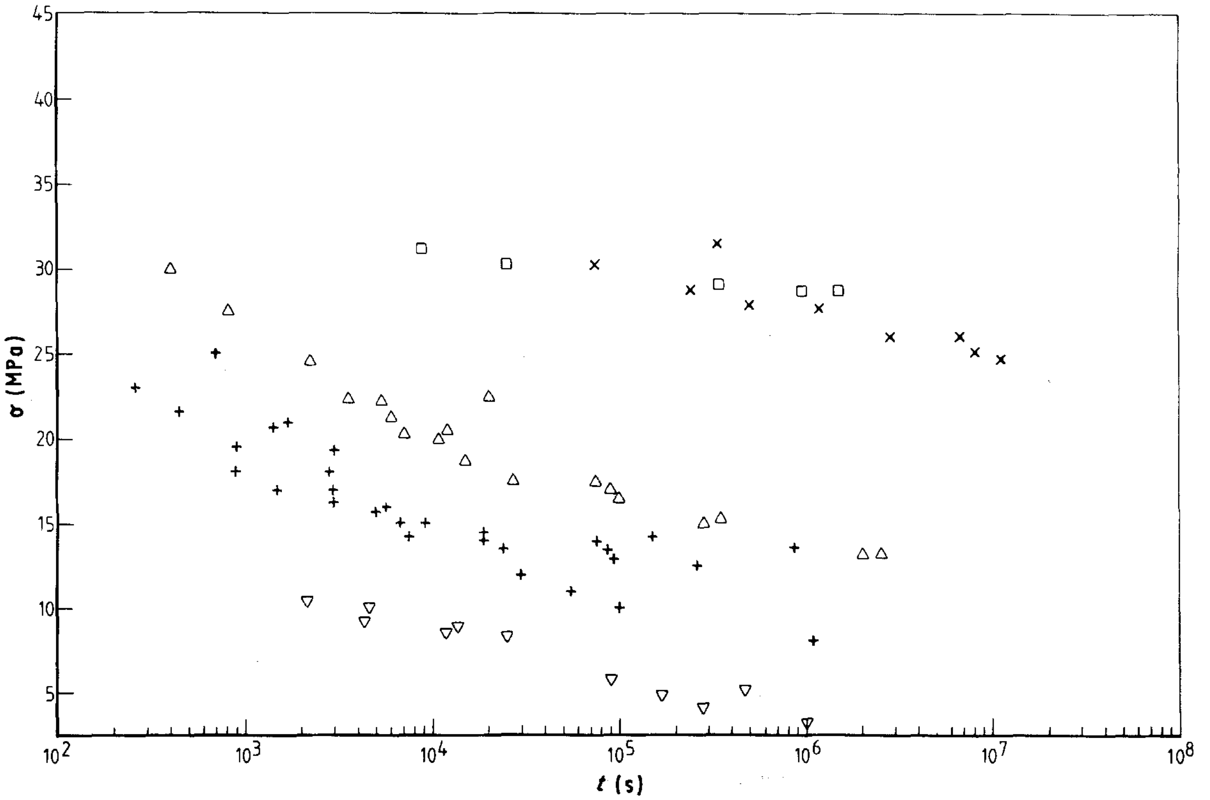

Figure 3 PVC–CPE craze-initiation results, applied stress against craze initiation time, for four benzene vapour concentrations: gas with □, 5000; △, 25 000; + 60 000; ▽, 110 000 p.p.m. benzene; ×, air; Temperature, 23 °C.

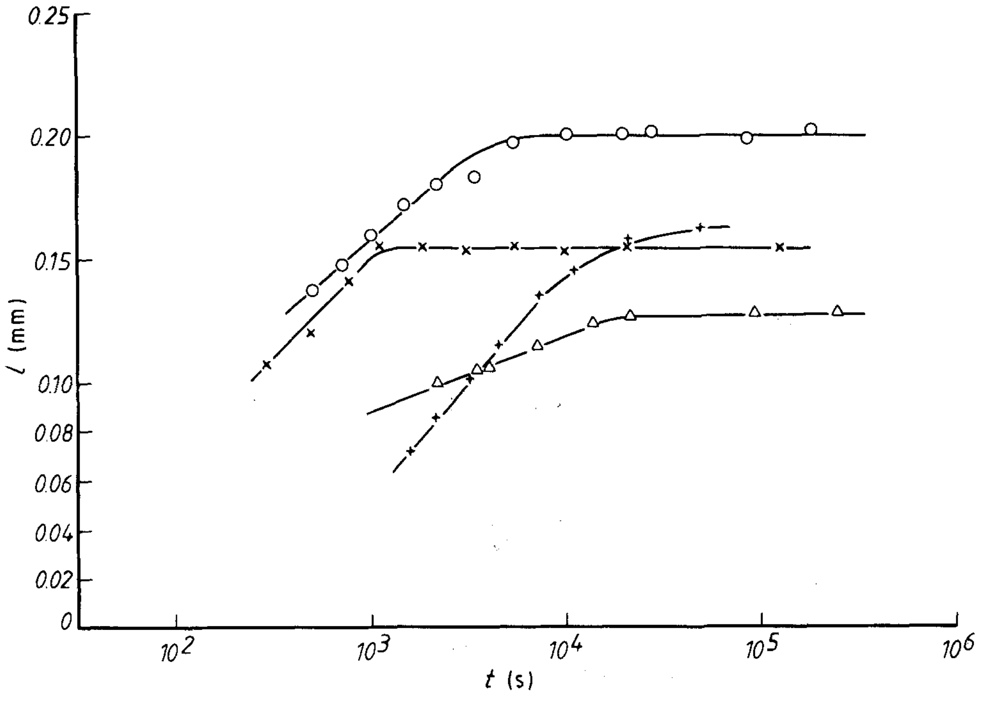

Figure 4 Craze lengths as a function of loading time. △, PVC in natural gas with 25 000 p.p.m. benzene, $\sigma = 29.4$ MPa; ○, PVC, 60 000 p.p.m. benzene, $\sigma = 24.0$ MPa; +, PVC–CPE, 25 000 p.p.m. benzene, $\sigma = 26.8$ MPa; × PVC–CPE, 60 000 p.p.m. benzene, $\sigma = 24.0$ MPa. Temperature, 23 °C.

benzene are shown in Fig. 5. It is concluded that the crazes formed in gas with 60 000 p.p.m. benzene are rather short in length. This observation almost excludes a failure process in PVC by craze growth.

In order to confirm this statement, the in-depth profile of a few selected, relatively large and no longer growing crazes was examined by slicing the material with a microtome perpendicular to the surface, and perpendicular to the craze length. The craze depth of subsequent slices was measured and is shown in Fig. 6 for four crazes. The craze profiles show the length of the craze as a function of its depth. The length of the selected crazes was about 300 μm. It is noticed that the depth of the craze is of the same magnitude as the

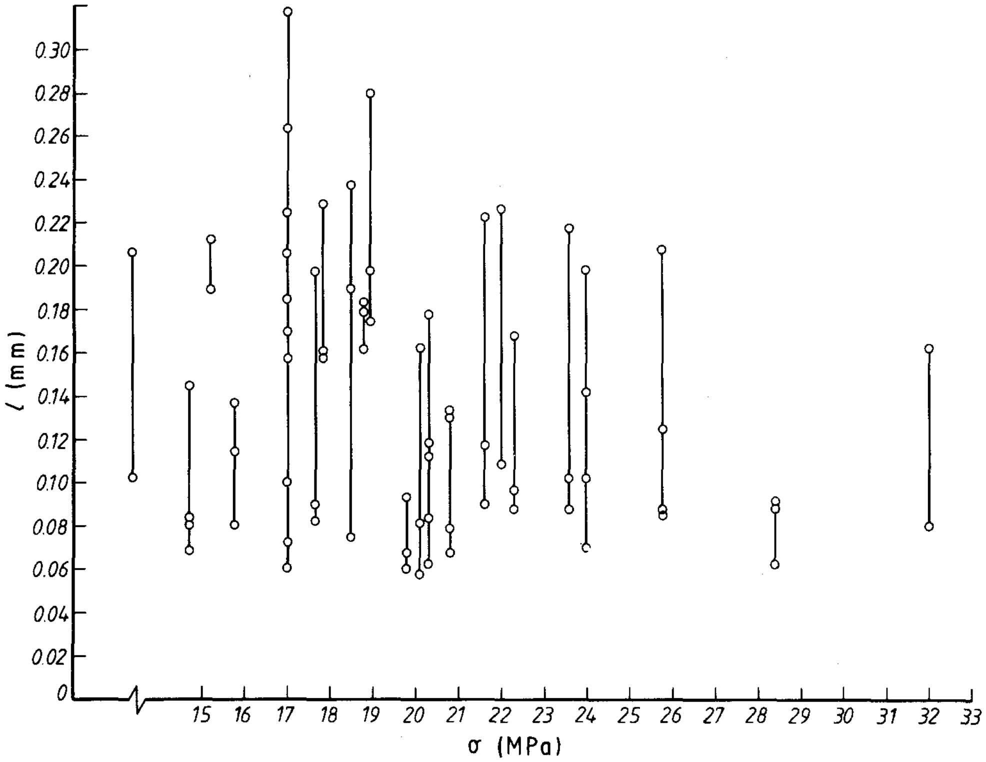

Figure 5 Final craze length as a function of applied stress for PVC in natural gas with 60 000 p.p.m. benzene at 23 °C.

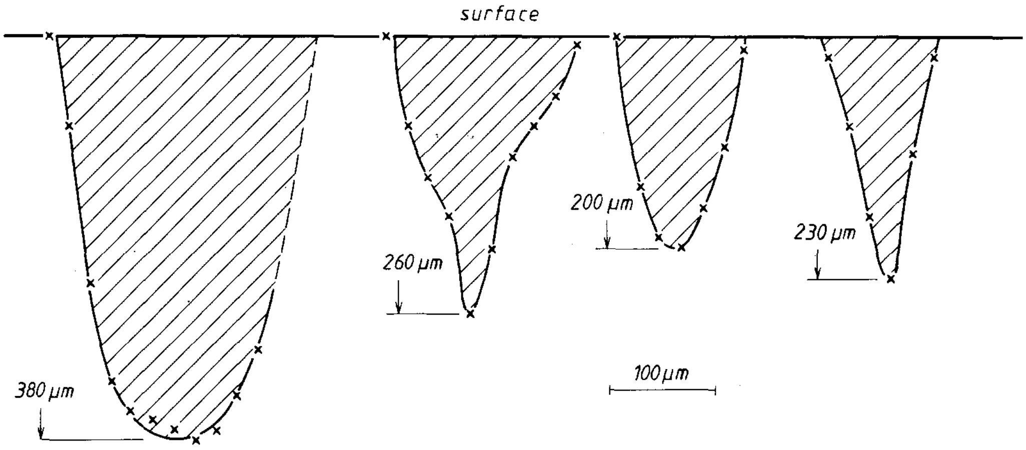

Figure 6 Craze profiles for PVC after 6.1×10^5 s in natural gas with 25 000 p.p.m. benzene under a constant load of 27 MPa. Temperature, 23 °C.

length of the craze. A limited craze length on the surface seems to correlate to a limited craze depth, although the craze depth in general seems to be larger than the craze length at the surface.

Another remarkable feature of craze growth in PVC and in PVC–CPE can be observed in Fig. 4. The craze length increases with the logarithm of the loading time in the first part of the curve. The logarithmic growth rate, $dl/d \ln t$, was determined for the different environments studied. Again an enormous scatter in the logarithmic growth rates was observed. The highest logarithmic growth rate for PVC in the natural gas with 60 000 p.p.m. benzene was 0.25 mm per decade.

3.3. Failure

The failure behaviour of the PVC and PVC–CPE materials was studied by constant load experiments on dumbbell-shaped strips. The time to failure, as a function of the applied stress, is presented in Fig. 7 for PVC and in Fig. 8 for PVC–CPE.

The stress which corresponds to a certain time to failure is almost identical in air and in the gas with 6000 p.p.m. benzene. However, the more concentrated benzene vapours cause a distinct decrease in the stress at a given time to failure when compared to air. Especially, the failure stress of PVC in 60 000 p.p.m. benzene decreases considerably.

Although this fall seems more dramatic for PVC than for PVC–CPE, the long-term failure stress of PVC in gas with 60 000 p.p.m. benzene is not inferior to that of PVC–CPE. The smaller drop in the failure stress for PVC–CPE in the 60 000 p.p.m. benzene environment is caused by the lower failure stress in air of PVC–CPE compared to that of PVC.

The failure of PVC materials in the concentrated

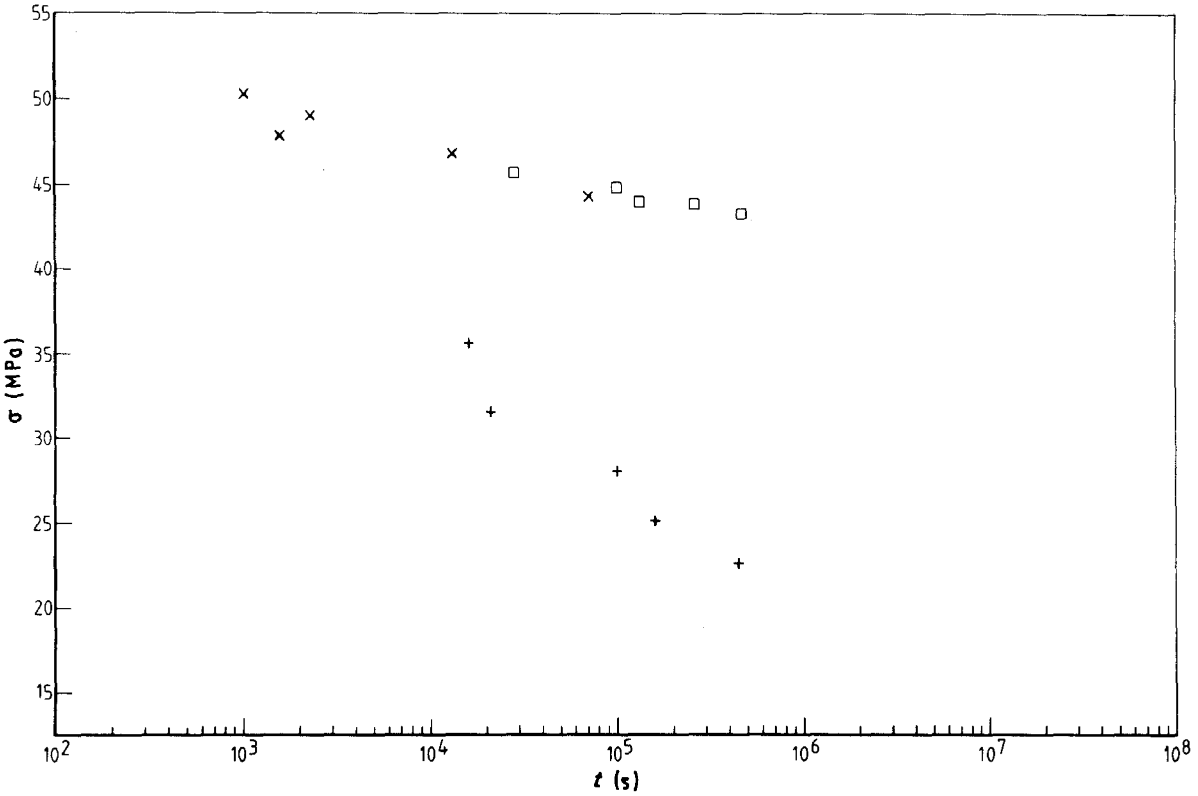

Figure 7 Applied stress against time to failure for PVC in gas with □, 6000 and +, 60 000 p.p.m. benzene; ×, in air. Temperature, 23 °C.

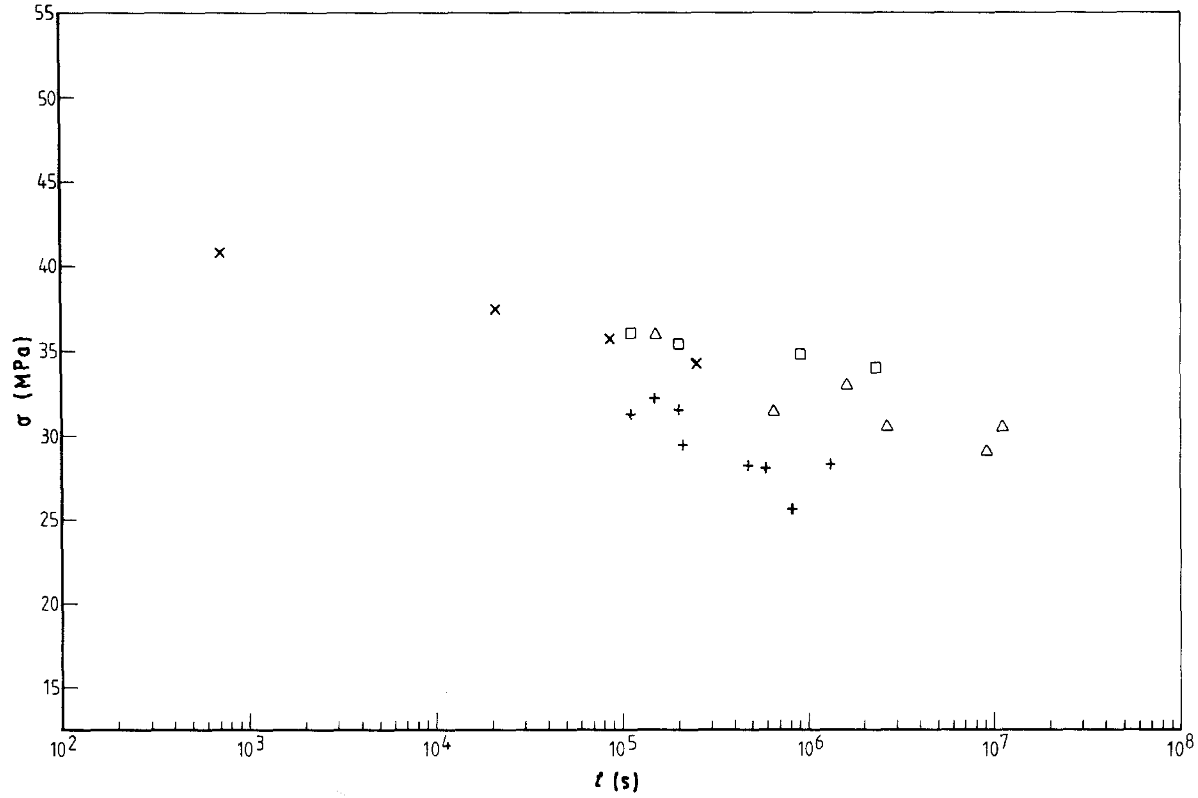

Figure 8 Applied stress against time to failure for PVC–CPE in gas with □, 6000; △, 25 000 and +, 60 000 p.p.m. benzene; ×, in air. Temperature 23 °C.

benzene environments are also studied with the SEM: a micrograph of a fracture surface of PVC–CPE in natural gas with 25 000 p.p.m. benzene is shown in Fig. 9. The limited craze size is clearly visible on the left of the fracture surface.

4. Discussion

4.1. Craze initiation

The model of Argon [16] is used to explain the observed craze-initiation curves. In this model, craze initiation is preceeded by cavitation. The cavitation

Figure 9 SEM micrograph of a fractured surface for PVC–CPE in gas with 25 000 p.p.m. benzene under a constant load of 30 MPa. Time to fracture: 1.1×10^7 s. Temperature, 23 °C.

process is produced by the stress field in the vicinity of inhomogeneities. The surfaces of the PVC and PVC–CPE test strips studied contain inhomogeneities due to scratches and particles (dust, additives and/or crystallites).

The cavitation is supposed to be thermally activated and is stress dependent. A pore will develop when enough energy is built up in the neighbourhood to overcome the surface energy. A concentration of stored elastic energy is built up by the stress concentration in the vicinity of inhomogeneities. The formation of pores will thus take place near inhomogeneities.

When under a tensile stress a critical porosity is exceeded, the micropores will transform into a craze. The porosity will be less extended around the smaller inhomogeneities, and therefore the smaller inhomogeneities can only act as a craze initiator at higher stress levels. This also explains the larger craze density at higher stress levels.

According to Argon's model, the curvature in the craze initiation curves (see Figs 2 and 3) is due to the decreasing probability of pore formation at lower stresses. An aspect which is not implemented in Argon's model, but which contributes to the decrease in curvature, is the viscoelastic behaviour (creep) of stressed polymers. Creep will inhibit the formation of crazes.

It is observed that craze initiation on the surface is more favoured than that in the interior of the strip. The enhanced dilatation in the surface layer, which is held responsible for this phenomenon, seems to be related to the difference in the stress field near surface and bulk inhomogeneities [16]. It is also possible that this preference of craze initiation for the surface indicates that the pore formation is preceded by local yielding, a process which can take place only at the surface. The cavitation process then apparently occurs in the oriented yielded zone, and is enhanced by the lateral stresses provoked by the local plastic yield. In case of an ESC environment, the penetration of small molecules into the polymer leads to an additional acceleration.

Brown showed that the equilibrium sorption is a function of the interaction between the small penetrating molecules and the polymer chains, but also of the local stress [17]. The higher tensile stress in the vicinity of inhomogeneities results in a higher sorption. The craze initiation is related to the equilibrium sorption, but will mainly depend on the sorption rate. Apart from the affinity between the penetrating molecules and the polymer chains, the sorption rate depends on the size of the penetrating molecules and on the segmental mobility [7]. The highest sorption will be realized in case of small molecules, a strong affinity and a high polymer mobility. The mobility of the polymer chains is enhanced by stress concentrations (near inhomogeneities) and high temperatures.

The preferential sorption of benzene molecules near surface inhomogeneities in PVC and PVC–CPE decreases the local yield stress and the local modulus, and leads to a reduction of the craze-initiation stress. A theory which relates the sorption (rate) with the drop in the local yield stress and with the local modulus is not available. In spite of this lack of knowledge, the large drop in craze initiation stress for the 25 000 against the 5000 p.p.m. benzene environment (see Figs 2 and 3) probably results from a change in sorption behaviour (case I → case II diffusion) [8].

In air and in natural gas enriched with 5000 p.p.m. benzene, PVC–CPE hardly shows craze initiation in our experiments, because the craze-initiation stress almost equals the yield stress. The yield stress of PVC exceeds that of PVC–CPE by about 10 MPa, whereas the long-term craze initiation stress of PVC almost equals that of PVC–CPE. Therefore crazing is observed for PVC in the stress interval between the yield stress and the long-term craze initiation stress. In the more concentrated benzene environments, the difference between the overall yield stress and the craze initiation stress increases for both PVC and PVC–CPE. In these environments, both materials showed similar craze initiation behaviour.

4.2. Craze growth

The craze growth data for PVC and PVC–CPE in air and in the natural gas–benzene environments are difficult to quantify. The observed growth is not linear and thus not consistent with the models postulated by Argon [18]. These models interpret craze growth by pore formation at higher stresses and by a repeated interface convolution (meniscus instability) at lower stresses. The reason why these models are not consistent with our results (logarithmic craze growth and the termination of the craze growth) are obvious: both models assume a constant loading and neglect any time dependence of the molecular processes (the viscoelastic behaviour). Although models have been proposed which predict a decrease in craze growth rate as a function of loading time, they do not predict an abrupt termination of craze growth [19, 20]. A logarithmic craze growth is obtained if creep determines the craze growth [19]. However, craze growth is also affected by the population of crazes and by the viscoelastic behaviour of the bulk material [20].

An aspect which has received little attention, but may be important for ductile polymers, is necking. Necking will orientate the polymer chains in the direction of the tensile stress and hence will blunt the craze. This will strongly reduce the craze growth.

The craze growth at the tip requires a flow process, which depends on the local yield stress. Thus the initial craze growth rate will approximately scale with the reciprocal of the craze-initiation time. The logarithmic craze-growth rates which we found confirm this conclusion. The penetration of benzene molecules at the craze tip reduces the yield stress and enhances the initial craze-growth rate.

Craze growth stops as soon as the stress at the craze tip drops below the yield stress. This can be a result of neighbouring crazes, viscoelastic behaviour and/or blunting. Blunting may occur if the craze growth in the width (creep of craze fibrils) exceeds that in the length (meniscus instability). The dependence of these phenomena on the distribution of surface inhomogeneities and on the local stress leads to scatter in the ultimate craze length (see Fig. 5). In the benzene-enriched environments, another termination mechanism is possible — swelling. If the surface layer swells due to the sorption of benzene molecules, the tensile stress in the surface layer is reduced.

The larger craze growth on the surface and in depth (Fig. 6) can be interpreted in terms of the previous arguments for the cessation of craze growth. The stress field at the craze tip in the depth direction will be less influenced by neighbouring crazes, because the density of neighbouring crazes in the inner layers is lower (at least for the larger and deeper crazes); by viscoelastic processes, because the flow of material is reduced due to a transition from a plane stress to a plane strain situation for the inner layers; and by sorption, because the transport of benzene molecules will decrease in the craze–bulk interface for the inner layers.

4.3. Failure

The results of the constant load experiments up to failure are presented in Figs 7 and 8. The small slope of the failure curves in air and in gas enriched with 6000 p.p.m. benzene suggests a ductile failure behaviour, which is governed by yielding. This conclusion is supported by the observation that failure in air and in the 6000 p.p.m. benzene environment occurs by necking. Although crazes are formed in these environments, they hardly seem to determine the failure in PVC. Figs 7 and 8 show that PVC fails at a higher stress than PVC–CPE in air and in the 6000 p.p.m. benzene vapour. According to the previous argument, this can be explained by the higher yield stress of PVC relative to that of PVC–CPE.

In the more concentrated benzene environments ($\geqslant$ 25 000 p.p.m.) a drop in the failure stress relative to the yield line in air is observed. This steep line is sometimes called the brittle branch. For PVC and PVC–CPE, this brittle branch can be related to craze growth and craze stability. It is known that craze fibrils fail at a critical size in inert environments [14]. The failure of craze fibrils leads to a reduction of the load carrying capacity of the craze and in general to an acceleration of the failure process. However, in the gas–benzene environments a termination of craze growth is observed and it is questionable whether a critical size will be reached. In the concentrated benzene environments, the craze fibril stability seems to affect the time to failure to a larger extent than the craze growth. From a number of studies it follows that the craze is able to carry a stress which almost equals the applied stress [21]. Due to the smaller polymeric volume fraction of a craze relative to the bulk polymer, the stress in an individual craze fibril will exceed the applied stress. The higher stress in the craze fibrils and at the craze–bulk interface subject the craze fibrils to additional creep, especially in environments which cause weakening [19]. This fibril creep causes a reduction of the craze stability and thereby a drop in failure stress.

The following interpretation of the failure curves of PVC and PVC–CPE in concentrated benzene vapours is proposed. Yielding occurs at high stresses and short times, because at short times the sorption of benzene by PVC and PVC–CPE is very low. At intermediate stresses, craze initiation and craze growth occur. The failure follows from a reduction of the load-carrying capacity of crazes (failure or weakening of fibrils). This seems to be in agreement with the SEM micrograph of a fracture surface of PVC–CPE shown in Fig. 9. At low stresses, no failure occurs because the craze growth has stopped and the stress in the remaining virgin part of the load-carrying cross-section of the test strip does not exceed the yield stress.

5. Conclusions

1. At surface inhomogeneities the conditions for pore formation and crazing can be fulfilled for PVC in all environments studied and for PVC–CPE in the benzene-enriched natural gas environments. These conditions can hardly be fulfilled for PVC–CPE in air, because in air the tensile stress necessary for craze initiation almost equals the yield stress of PVC–CPE.

2. The craze-initiation stress is strongly reduced in the concentrated ($\geqslant$ 25 000 p.p.m.) benzene environ-

ments due to preferential sorption of benzene molecules in the vicinity of the inhomogeneities.

3. The craze-initiation conditions are similar for PVC and PVC–CPE in the environments studied.

4. The logarithmic craze growth and the termination of craze growth point to a decrease in the stress at the craze tip. This reduction is caused by neighbouring crazes, creep of the craze fibrils and/or bulk polymer, and blunting of the craze tip.

5. The craze growth is accelerated in the benzene-enriched environments. However, in these environments termination of craze growth is also observed. In the concentrated benzene–natural gas vapours, swelling of the PVC and the PVC–CPE surface layer can contribute to the termination of growth.

6. Although the craze growth at the surface is measured, whereas that in depth cannot be measured, it is concluded from craze profiles that the growth in depth is also limited.

7. Homogeneous yielding is observed in air and in natural gas with 5000–6000 p.p.m. benzene for both PVC and PVC–CPE. The higher yield stress of PVC compared to that of PVC–CPE follows directly from the failure curves.

8. In the more concentrated benzene–natural gas vapours, a brittle branch is observed due to reduction of the stability of the crazes formed. Destabilization of the crazes by sorption of benzene may explain the drop in the failure stress in these environments.

6. Acknowledgements

This work was sponsored by VEG–Gasinstituut, Nederlandse Gasunie and Ministerie van Economische Zaken. The authors thank Professor Dr Ir L. C. E. Struik (DSM), Professor Dr Ir J. van Turnhout (TNO), Dr Ir M. Wolters (VEG-Gasinstituut) and Ir L. Oranje (Nederlandse Gasunie) for valuable discussions, Mr R. H. J. W. A. Drent for the development of the equipment, and Mr A. M. Ringenaldus and Miss C. Zoeteweij for performing the experiments.

References

1. M. WOLTERS, *Plast. Rubber Process. Appl.* **3** (1983) 323.
2. P. I. VINCENT and S. RAHA, *Polymer* **3** (1972) 283.
3. R. P. KAMBOUR, *J. Polym. Sci. Macromol. Rev.* **7** (1973) 1.
4. H. H. KAUSCH, "Polymer Fracture" 2nd Edn (Springer, Berlin, 1987) p. 279.
5. P. VINK, in "Degradation and Stabilisation of Polyolefins", edited by N. S. Allen (Applied Science, London, 1983) p. 213.
6. R. R. KAMBOUR, in "Mechanisms of Environmental-Sensitive Cracking of Materials" Surrey, UK, 1977, edited by P. R. Swaun, F. P. Ford and A. R. C. Westwood (The Metal Society, London) p. 213.
7. A. A. BERENS and H. B. HOPFENBERG, *J. Membrane Sci.* **10** (1980) 283.
8. A. R. BERENS, *J. Appl. Polym. Sci.* **37** (1989) 901.
9. H. FUJITA, *Fortschr. Hochpolym.-Forsch.* **3** (1961) 1.
10. N. BROWN, in "Failure of Plastics", edited by W. Brostow and R. D. Corneliussen (Hanser, Munich, 1986) p. 287.
11. E. J. KRAMER, in "Developments in Polymer Fracture—1", edited by E. H. Andrews (Applied Science, London, 1979) p. 55.
12. G. H. MICHLER, *Plaste u. Kautschuk* **35** (1988) 423.
13. *Idem, ibid.* **36** (1989) 18.
14. W. DÖLL, *Adv. Polym. Sci.* **52/53** (1983) 105.
15. J. L. S. WALES, *Polymer* **21** (1980) 684.
16. A. S. ARGON, *Pure & Appl. Chem.* **43** (1975) 247.
17. H. R. BROWN, *J. Polym. Sci. Polym. Phys.* **27** (1989) 1273.
18. A. S. ARGON and M. M. SALAMA, *Phil. Mag.* **36** (1977) 1217.
18. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, *J. Mater. Sci.* **11** (1976) 7.
19. Z. D. ZHANG, S. S. CHERN and C. C. HSIAO, *J. Appl. Phys.* **54** (1983) 5568.
20. E. J. KRAMER, *Adv. Polym. Sci.* **52/53** (1983) 1.

Received 26 March
and accepted 20 December 1990