Environmental stress cracking of PVC and PVC–CPE

Part I *Crazing*

J. BREEN
TNO Plastics and Rubber Research Institute, PO Box 6031, 2600 JA Delft, The Netherlands

The craze initiation of PVC and PVC–CPE in a number of vapour and liquid environments was studied. The observed decrease in the craze-initiation stress could be ascribed to the absorption of components by the PVC and the PVC–CPE matrix. The magnitude of the absorption depends on the activity of the components and on their interaction with the PVC matrix. The activity of the components was defined according to thermodynamics. The interaction of the components can be obtained from measurements of the angle of contact, though it is preferred to quantify this interaction by absorption experiments. A simple model is presented to predict the long-term craze-initiation stress of PVC in environments.

1. Introduction

In a previous paper, the failure mechanism of PVC (polyvinylchloride) and PVC–CPE (chlorinated polyethylene-modified PVC) materials in benzene-enriched natural-gas environments was studied under constant loading conditions [1]. It appeared that on increasing the benzene saturation of the environment, the critical stress level for crazing decreased. A qualitative interpretation in terms of sorption and plastification has been presented. The research programme was continued to obtain more insight in the environmental stress cracking of natural gas on PVC and PVC–CPE gaspipes of the low-pressure gas distribution system in the Netherlands. The objectives of the programme were (1) to find the origin of the environmental stress cracking in natural-gas environments, and (2) to predict the long-term failure process. In this paper the first objective will be treated. In forthcoming papers attention will be directed towards the second objective.

The research on environmental stress cracking of amorphous polymers by organic liquids has a long history (see, for instance, [2–4] and references therein). The more important studies present an explanation of environmental stress cracking in terms of physical or chemical phenomena occurring at the interface of a stressed or a strained polymer in a certain environment. Environmental stress cracking by physical actions is considered to be responsible for the failure process of PVC and PVC–CPE in gas environments. Therefore, this paper only deals with the physical phenomena related to environmental stress cracking.

In one of the first comprehensive studies on environmental stress cracking by physical actions, the accelerated craze initiation, craze growth and failure were interpreted by the wetting of the polymer surface by the liquid, its diffusion into the polymer and

swelling due to its sorption by the polymer [5, 6]. Other interpretations of the environmental stress cracking were based on solubility parameters and plasticization [7–9]. The relations between the sorption of liquid or vapour by the polymer, the swelling and plasticization of the polymer by this sorption, the reduction of the surface energies and the solubility parameters mean that several explanations are possible and that the fundamental origin of environmental stress cracking is obscured.

Complicating factors which have to be considered in studying environmental stress cracking are the origin of the crazing and the homogeneity of the materials under study. Accelerated crazing is directly associated with the environmental stress-cracking capacity of the environmental agent. It has been shown that surface crazes start at inhomogeneities, scratches or other stress raisers at the surface layer [10, 11]. However, the criterion of craze initiation does not seem obvious (see, for instance, the numerous criteria in [12]). In this paper, a simplified craze criterion, in which the influence of the stress raisers is incorporated, will be used.

The environmental stress-cracking capacity of stress-cracking agents was studied by sorption, surface tension and craze initiation. The experimental results are presented and explained in terms of these physical actions. The sorption experiments were performed on PVC and PVC–CPE specimens in benzene/n-hexane mixtures. The surface-tension experiments were performed only on PVC–CPE specimens with various liquids. The craze-initiation results were obtained in vapour and liquid environments.

2. Theory

If a polymer product is brought into a liquid or

vapour, it will adsorb this environment until equilibrium is reached. The equilibrium adsorption will be reached almost instantaneously. Besides this adsorption on the polymer surface, in vapours, capillary condensation can occur in small pores at the polymer interface. The condition for capillary condensation in cylindrical pores is given by [13]

$$\ln \frac{p}{p_0} \geqq - \frac{\Gamma V}{RTr} \qquad (1)$$

in which p/p_0 is the degree of vapour saturation (p = actual vapour pressure; p_0 = vapour pressure at saturation), Γ the surface tension of the condensed vapour, V the molar volume of the condensed vapour, R the gas constant, T the temperature (K), and r the radius of the cylindrical pore. Notwithstanding the capillary condensation, the activity of the (vapour) molecules in the pores and in the environment is identical. Thus an enhanced absorption due to capillary condensation will not occur.

For components like benzene and n-hexane, the right-hand part of Equation 1 is about $- 10^{-9} r^{-1}$ at ambient temperature. This means that the capillary condensation of vapour ($p/p_0 < 0.9$) will only occur in small pores with radii less than 10 nm. The size of a craze exceeds the pore size needed for capillary condensation by at least two orders of magnitude. Furthermore, the time-scale for the long-term craze initiation contradicts an adsorption process. Therefore, it is concluded that capillary condensation and adsorption do not determine the long-term craze-initiation process.

The equilibrium absorption will not be reached instantaneously. The penetration of liquid and vapour molecules into the polymer matrix takes time. If the absorption process is described by a Fickian behaviour, the penetration (absorption) scales with [14] $(D\,t)^{1/2}$, where D is the diffusion coefficient and t the period of exposure. At a low degree of vapour saturation, the diffusion coefficient of benzene in PVC is $2 \times 10^{-18}\,\mathrm{m^2\,s^{-1}}$ at 30 °C [15]. From this value it can be concluded that it takes about 10^6 s to saturate a 1 µm thick PVC layer. However, this value of the diffusion coefficient does not hold for the relatively highly saturated vapours and liquids under study and for stressed PVC products. If the (local) stress equals the drawing stress, the material will locally be in a kind of rubbery state. In the rubbery state the value of the diffusion coefficients of small molecules can be six orders of magnitude larger compared to the value corresponding to the glassy state. This can be verified by comparing the diffusion coefficient of alkanes in PVC and PE at room temperature [14, 15].

A high degree of vapour saturation or exposure to a liquid state can result in a non-Fickian absorption behaviour. This occurs when the equilibrium sorption of the environment by the polymer matrix is considerably large. In this case the penetration does not scale with $t^{1/2}$ but with [14] $t^n, n > 1/2$. When the penetration rate of a sharp penetration front is dominated by the stress-relaxation process at this front, the power n equals 1 [16].

Environmental stress cracking is often assumed to be determined by the equilibrium absorption [5–9]. The equilibrium absorption depends on the activity of the component that is absorbed and on the interaction between this component and the polymer. The equilibrium volume fraction of a liquid or a vapour in an amorphous polymer can be obtained in first approximation from [17]

$$\ln a = \ln v + (1 - v) + \varkappa(1 - v)^2 \qquad (2)$$

where a is the activity of the component in the environment, v the equilibrium volume fraction of this component in the polymer matrix and $\varkappa$ the interaction constant. The activity of a vapour is given by [17]

$$a = \frac{p}{p_0} \qquad (3)$$

where p is the actual vapour pressure and p_0 the vapour pressure at saturation.

Equation 2 is based on the Flory–Huggins lattice theory [18], in which the influence of the entanglement network is neglected. This is permitted at low equilibrium absorptions. However, at higher absorption values, the neglect of this influence results in wrong values of v. Instead of Equation 2, then, a modified equation, derived by Kramer [4], has to be applied. The interaction constant $\varkappa$ can be calculated from the cohesion energy density by solubility parameters [9]. The solubility parameters can be obtained from Barton [19] or by measurements of the angle of contact.

In the surface-tension experiments, a droplet of liquid is put on the polymer surface and the angle of contact is measured. This angle depends on the surface tension of the liquid used and on the interaction between the polymer surface and the liquid. From the equilibrium condition of a droplet on a polymer surface it follows [13]

$$\gamma_1 \cos \theta = \gamma_p - \gamma_{pl} \qquad (4)$$

where γ_1 is the surface tension of the liquid in air, θ the angle of contact, γ_p the surface tension of the polymer in air and γ_{pl} the surface tension of the liquid at the polymer interface. The surface tension can be divided in a polar and a dispersive part [13]

$$\gamma = \gamma^p + \gamma^d \qquad (5)$$

where the superscripts p and d stand for the polar and the dispersive interactions, respectively. The surface tension associated with the interaction between the liquid and the polymer can then be written as

$$\gamma_{pl} = \gamma_p + \gamma_1 - 2(\gamma_1^p \gamma_p^p)^{1/2} - 2(\gamma_1^d \gamma_p^d)^{1/2} \qquad (6)$$

Substitution of Equation 6 into Equation 4 leads to

$$\frac{\gamma_1}{(\gamma_1^d)^{1/2}}\left(\frac{1 + \cos \theta}{2}\right) = (\gamma_p^d)^{1/2} + \left(\frac{\gamma_1^p}{\gamma_1^d}\right)^{1/2} (\gamma_p^p)^{1/2} \qquad (7)$$

Thus by measuring the angle of contact of several liquids (with known values of γ_1, γ_1^p and γ_1^d) at the polymer surface, a polar and dispersive surface tension can be found for the polymer surface. Measuring the

angles of contact of several liquids at a polymer surface and calculating the surface tension of the polymer is a way to quantify the interaction between the polymer and the environment. The values of the surface tension are related to the interaction constant, $\varkappa$, of Equation 2.

The surface tension can be written in terms of the solubility parameter, δ, [19]

$$\gamma = kV^{1/3}\delta^2 \tag{8}$$

where γ is the surface tension, k a constant ($k \approx 1.8 \times 10^{-9}$ mol$^{1/3}$) and V the molar volume. The interaction constant $\varkappa$ consists of an enthalpic term, $\varkappa_H$, and an entropic term, $\varkappa_S$ [9]. The entropic term is approximated by a constant (0.3–0.4) [9]. The enthalpic term can in first approximation be given by [9]

$$\varkappa_H = \frac{V}{RT}(\delta_p - \delta_l)^2 \tag{9}$$

p and l represent polymer and liquid, respectively. Substitution of Equation 8 into Equation 9 results in a relation for $\varkappa_H$ in terms of values for the surface tension. Equation 9 becomes more accurate if the different contributions (polar, dispersive and hydrogen bonding) to the solubility parameters, defined in a way similar to Equation 5, are introduced [9, 19].

Nevertheless, a number of assumptions remains in calculating the interaction constant, $\varkappa$, from the angle of contact measurements. If $\varkappa$ is known, the equilibrium volume fraction absorbed by the polymer can be obtained from Equation 2. For a limited number of liquids, the equilibrium absorption can be obtained directly from sorption experiments. Then measurements to obtain $\varkappa$ can be omitted. The absorption of small components by the polymer matrix will decrease the glass–rubber transition temperature of the amorphous polymer [17]. The glass–rubber transition temperature of an amorphous polymer, in which the volume fraction of small components amounts to v, is approximated by [17, 20]

$$T_g(v) = 0.63vT_m + (1 - v) T_g(0) \tag{10}$$

where T_m is the melting temperature of the absorbed component and $T_g(0)$ the glass–rubber transition temperature of the pure amorphous polymer ($v = 0$).

Although the exact criterion for crazing is not obvious, there seems to be a direct relation between the drawing stress and the long-term craze-initiation stress for PVC materials studied in tension. According to the results obtained for PMMA by Ward [21] a simple relationship between the drawing stress and the glass-transition temperature can be assumed

$$\sigma_d(v, T) = \sigma_d(0, T)\frac{T_g(v) - T}{T_g(0) - T} \tag{11}$$

in which $T_g(0)$ and $T_g(v)$ are defined as in Equation 10. T is the actual temperature and $\sigma_d(0, T)$ represents the drawing stress of the pure amorphous polymer at this temperature. The drawing stress is defined as the stress value which leads to cold drawing.

With the relationship between the drawing stress and the craze-initiation stress, the latter can be inter-

preted in terms of absorption (diffusion), plasticization and drawing stress. The discussion of this interpretation will be presented later.

3. Experimental procedure
The PVC and the PVC–CPE materials are described earlier [1]. The chemicals used for the sorption, the angle of contact and the craze initiation were of analytical grade.

The sorption experiments were performed at 23 °C. Rectangular samples of about 1 g were put into the n-hexane/benzene mixtures for several months. The increase in weight of those samples as a function of the time of exposure was measured. Before each measurement, the reductant fluid droplets were wiped off. The surface-tension experiments were performed at room temperature. The samples were cleaned by n-hexane extraction for 7 h and a subsequent drying period for 14 h under vacuum. The surface tension of the liquids was measured with a Krüss K-8600 tensiometer. The angle of contact was determined from the shape of the droplet (advancing method).

The craze initiation measurements were described in the previous paper [1].

4. Results
The increase in weight of the PVC samples in the n-hexane/benzene mixtures as a function of the period of exposure are shown in Fig. 1. It is apparent from this figure that the equilibrium sorption decreases as
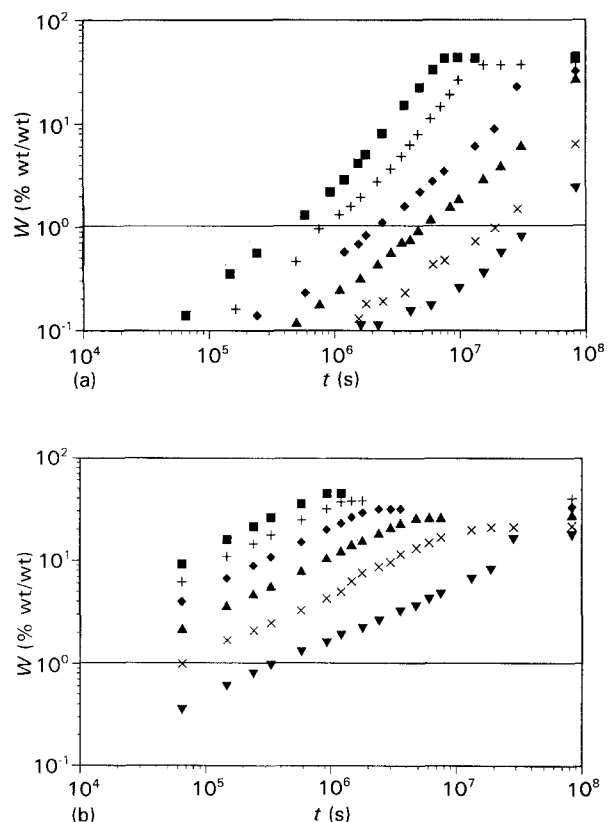

Figure 1 Relative increase in weight of PVC samples in benzene/ n-hexane mixtures as a function of the time of exposure. (a) Heat-treated PVC samples; (b) untreated PVC samples. (■) 90%, (+) 80%, (◆) 70%, (▲) 60%, (×) 50%, (▼) 40% benzene (vol.).

the concentration of n-hexane in the mixture increases. From this observation it is concluded that the interaction between benzene and PVC is more favourable than the interaction between n-hexane and PVC. The interaction can be quantified in terms of the interaction constant, $\varkappa$, presented in Equation 2. For PVC it is found that $\varkappa$ (benzene) = 0.8 and $\varkappa$ (n-hexane) = 2.1. Further it is observed that the absorption rate also decreases with increasing n-hexane concentration. Although the diffusion coefficient of benzene in PVC exceeds that of n-hexane in PVC by an order of magnitude, this only partly explains the lower absorption rate with increasing n-hexane volume fraction. According to a Fickian diffusion behaviour and the diffusion coefficients found by Berens and Hopfenberg [15] it should take more than 100 years to saturate the PVC samples with benzene and even longer to saturate PVC with n-hexane. From this argument it is clear that the observed diffusion behaviour is non-Fickian. The deviation of the initial slope of the absorption curve from 0.5 also suggests a non-Fickian behaviour.

The initial slope depends on whether the samples were exposed to a heat treatment. Without heat treatment the samples showed an initial slope of about 0.6, whereas with a heat treatment the samples showed an initial slope of 1.2. The heat treatment consisted of 0.5 h at 125 °C under slight compression and 3 h at 95 °C followed by a slow cooling to 23 °C. The dependence of the diffusion rate on the annealing procedure was observed earlier by Gilbert and Mulla and was ascribed to recrystallization and ageing [22].

The observed diffusion behaviour can be explained by a diffusion coefficient which increases with the concentration of absorbed liquid and by stress relaxation at a sharp penetration front in the polymer matrix during the absorption process. The latter phenomenon will probably dominate in the heat-treated PVC.

The absorption results for the PVC–CPE material are very similar to those for the PVC material and are, therefore, omitted.

The surface tension experiments are presented in Fig. 2 and in Table I. From the values for the dispersive part of the surface tension, γ_l^d, the $\gamma_{PVC-CPE}^d$ and $\gamma_{PVC-CPE}^p$ are calculated according to Equation 7.
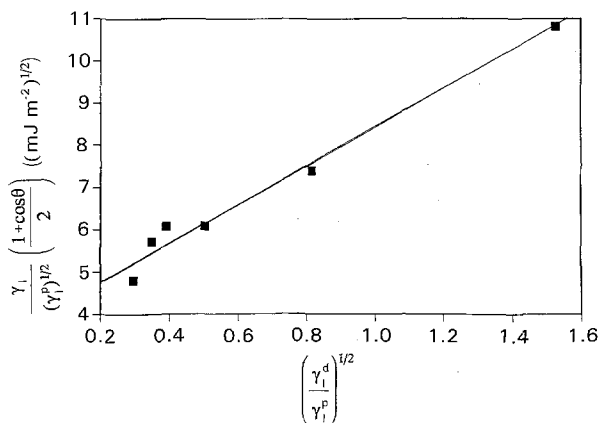
The results are $\gamma_{PVC-CPE}^d = 15.4 \, \text{mJ} \, \text{m}^{-2}$; $\gamma_{PVC-CPE}^p = 19.9 \, \text{mJ} \, \text{m}^{-2}$; $\gamma_{PVC-CPE} = 35.3 \, \text{mJ} \, \text{m}^{-2}$. The large $\gamma_{PVC-CPE}^p$ value is probably due to the additives (CPE, stabilizers, etc.) used in PVC–CPE. No surface-tension experiments were performed on the PVC material.

The interaction between the liquid and the PVC or PVC–CPE will be more favourable the smaller the difference in the values of the corresponding surface tensions. The smallest difference is obtained for cyclohexanone, which is known as a solvent for PVC. The next one is toluene, known as a swelling agent for PVC. The other liquids do not lead to significant changes in a PVC matrix, which does not experience a stress. However, in stressed PVC test strips, all liquids lead more or less to a decrease in the craze-initiation stress as can be observed in Fig. 3.

The craze-initiation curves (stress versus loading/exposure time) in saturated vapour of water, glycol, ethanol, n-hexane, toluene and cyclohexanone at 23 °C are shown in Fig. 3. The water vapour hardly influences the craze-initiation process. The glycol vapour lowers the craze-initiation stress slightly, whereas a moderate decrease is observed for the n-hexane and the ethanol vapour. In toluene and cyclohexanone vapour, a drastic decrease in craze-initiation stress is observed. Notice that the magnitude of the decrease in the craze-initiation stress correlates with the difference in the values of the surface tension of PVC–CPE and the corresponding liquid (see Table I). Notwithstanding this correlation, to relate the craze-initiation stress
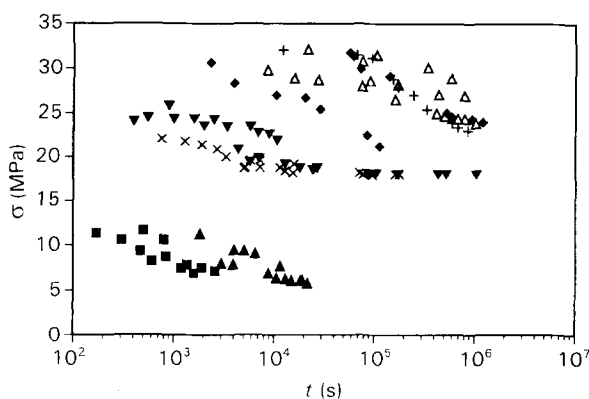

Figure 3 Loading stress versus time to crazing in air and in saturated vapours at 23 °C. (+) Air, (△) water, (▼) ethanol, (■) toluene, (◆) glycol, (×) n-hexane, (▲) cyclohexane.

TABLE I Angle of contact at the PVC–CPE surface for a number of liquids; experimental surface tension and dispersive part of the surface tension for these liquids

Liquid	θ (°)	γ_l (mJ m^{-2})	γ_l^d (mJ m^{-2}) [23–25]
Water	67 ± 2	72.6 ± 1.0	21.8
Glycol	50 ± 3	48.8	29.3
Cyclohexanone	36 ± 2	35.6	–
Ethanol	10 ± 2	23.3	–
Toluene	4 ± 2	29.3	26.1
n-hexane	0	21.2	19.5
Ethoxyethanol	0	21.6	23.6
Methylene iodine	60 ± 3	57.1	49.5

Figure 2 Representation of the surface-tension data according to Equation 9.

to the surface tension requires a number of assumptions (see Section 2). If possible, an approach using absorption data is preferred. With this approach the relative saturation of the vapour is simply taken into account. Furthermore the effect of mixtures on the craze initiation stress can also be investigated relatively easily.

The influence of the relative saturation of benzene in natural gas at 23 °C on the craze initiation stress of PVC and PVC–CPE was presented in a previous paper [1]. Here the influence of the relative saturation of n-decane in natural gas at 23 °C is shown in Fig. 4. Despite the scatter in the data points and the less pronounced effect of the relative saturation of n-decane compared to the effect of benzene vapour, the trend is clear. The higher the relative saturation, the lower is the craze-initiation stress.

Apart from experiments in vapour environments, craze-initiation experiments were performed in pure liquids and mixtures. The n-octane/benzene mixture was chosen to model the environmental stress cracking of natural-gas condensate. The results for PVC–CPE in air, n-octane and two n-octane/benzene mixtures are shown in Fig. 5. It is seen that a small amount of benzene lowers the craze-initiation stress dramatically.

The initial slope in the craze-initiation curves is due to a dynamic process, the absorption of vapour or liquid by the highly stressed zones around the stress
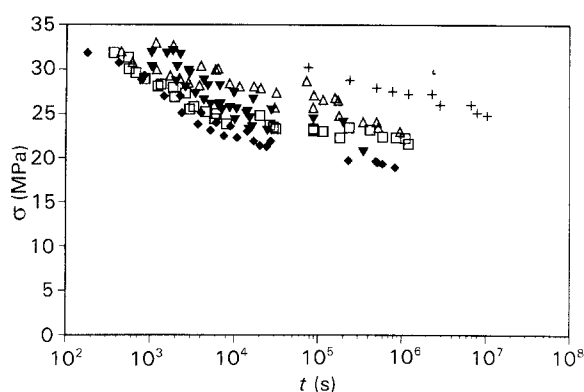
concentrators at the polymer surface. The subsequent decrease in curvature is related to the creation of a pseudo equilibrium situation in which the highly stressed zones at the surface are saturated with components from the environment, whereas the nominal stressed zones have hardly absorbed any component from the environment. The long-term craze-initiation stress as a function of the composition of the environment will be interpreted in the next section.

5. Discussion

The calculation of the long-term craze-initiation stress as a function of the relative vapour pressure of n-octane or benzene can be performed starting from Equation 2, where the activity is given by the relative vapour pressure (Equation 3) and $\varkappa$(benzene) = 0.8 and $\varkappa$(n-octane) $\approx \varkappa$(n-hexane) = 2.1. From Equation 2, the equilibrium volume fraction of benzene or n-octane as a function of the relative saturation can be obtained. The results are shown in Fig. 6. Owing to the large amount of absorption, the PVC matrix will become rubbery in the highly saturated benzene vapours. On the contrary, the absorption of n-octane by the PVC matrix remains low, even in the highly saturated n-octane vapours.

The equilibrium sorption of a one-component liquid by PVC can be obtained from Equation 2 by substituting $a = 1$. To calculate the equilibrium sorption of a mixture, Equation 2 has to be modified. The following equation can be derived from the Flory–Huggins lattice model for a two-component liquid [18]

$$\ln v_1 + \varkappa_{12}(v_2)^2 = \ln v_1' + (1 - v_1' - v_2') +$$

$$\varkappa_1(1 - v_1')^2 + \varkappa_2(v_2')^2 + (\varkappa_{12} - \varkappa_1 - \varkappa_2)v_2'(1 - v_1')$$

$$(12)$$

where $\varkappa_{12}$ quantifies the interaction between the two components of the mixture, $\varkappa_1$ is the interaction between component 1 and PVC, $\varkappa_2$ the interaction between component 2 and PVC, v_1 and v_2 the volume fraction of, respectively, components 1 and 2 in the polymer matrix and v_1' and v_2' the volume fraction of, respectively, components 1 and 2 in the mixture. It is assumed that the individual molecules of components

Figure 4 Loading stress versus time to crazing in air and n-decane-enriched natural gas at 23 °C. (+) Air, (△) 12.5%, (▼) 25%, (□) 50%, (◆) 80% n-decane vapour saturation.

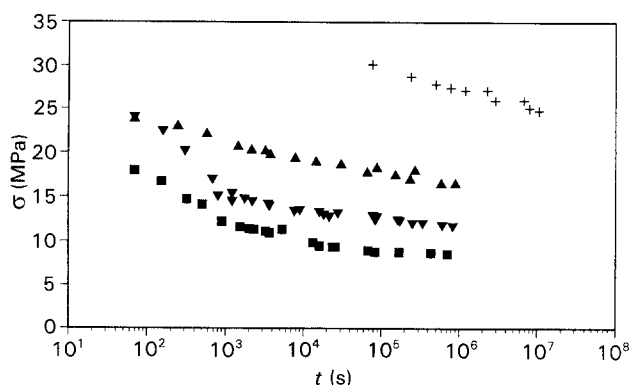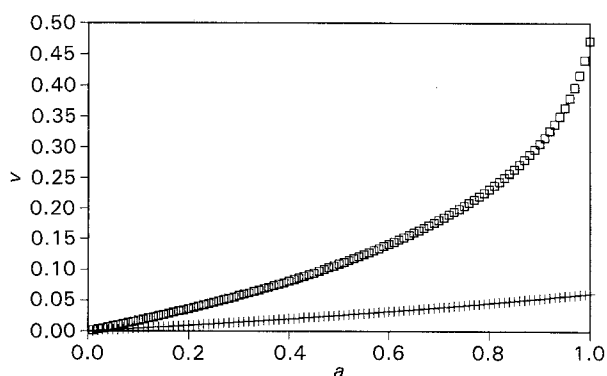*Figure 5* Loading stress versus time to failure for air, n-octane and n-octane/benzene mixtures. (+) Air, (▲) 100 vol %, (▼) 90 vol %, (■) 80 vol % n-octane.

Figure 6 Calculated equilibrium volume fraction, v, of (□) benzene and (+) n-octane vapour by PVC as a function of activity (relative saturation) of the vapours.

1 and 2 occupy the same volume in the lattice. Using $\varkappa_{12} = 1.1$ (this value follows from curve fitting of the sorption results presented in Fig. 1) and the earlier mentioned values of the interaction constants for benzene and n-octane, the equilibrium volume fraction $v_1 + v_2$ in the polymer matrix can be calculated. The results of this calculation are shown in Fig. 7.

The next step in modelling the long-term craze-initiation stress of PVC and PVC–CPE in vapours and liquids is to calculate the glass–rubber transition temperature of the saturated PVC matrix. For the one-component environment, the procedure is straightforward. Substitution of T_m, v and $T_g(0)$ = 358 K into Equation 10 leads to the required value. However, for the multicomponent systems there will be a number of T_m values involved. For a two-component system the following approximation is used

$$vT_m = v_1 T_{m1} + v_2 T_{m2} \qquad (13)$$

where the 1 and 2 represent the two components. A long-term craze-initiation stress of about 25 MPa was obtained in an inert environment for the PVC and the PVC–CPE material under study (air, 23 °C, 50% humidity). Thus, if the drawing stress, σ_d, is replaced by the craze-initiation stress, σ_c, and a value of 25 MPa is introduced into Equation 11 for $\sigma_c(0)$, the long-term craze-initiation stress of PVC and PVC–CPE can be calculated from the reduction of the glass–rubber transition temperature. In Fig. 8 the calculated craze-initiation stress in one-component vapour environments is shown as a function of the degree of saturation. For the n-octane vapour there is a good agreement between the predicted and the experimental values of the long-term craze-initiation stress. For the benzene vapour environment, this agreement is less satisfactory. The deviation for the highest benzene vapour pressure is probably caused by swelling of the surface. The deviations for the intermediate benzene vapour pressures could be caused by additional stresses which arise as a result of the fast and relatively large absorption of benzene in the vicinity of the stress raisers at the surface.

In Fig. 9 the experimental and the calculated results are shown for the n-octane/benzene mixtures. Here,
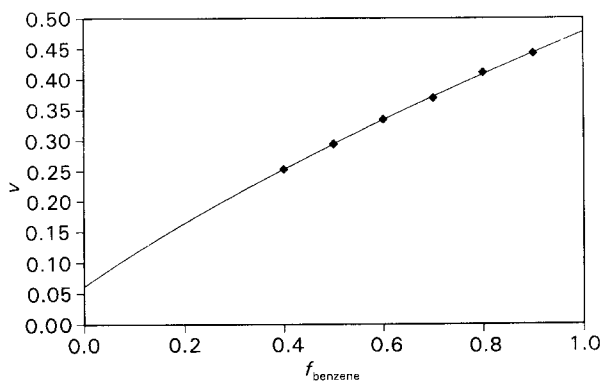
also, a reasonable agreement between the experimental and the predicted craze-initiation stresses is observed.

It is not always possible to obtain the equilibrium sorption directly from experiments. If the equilibrium sorption is reached very slowly or is very low, this sorption can be calculated from Equation 2 for a liquid and from Equation 12 for a two-component mixture. In order to perform this calculation, the interaction constant, $\varkappa$, must be known. The entropic contribution to this interaction constant is considered to be 0.4. The enthalpic contribution can be obtained from surface-tension data and solubility parameters using Equations 8 and 9. The results are summarized in Table II.

The solubility parameter of PVC–CPE (δ_{surf}) was obtained using $\gamma_{PVC-CPE} = 35\ mJ\ m^{-2}$ and $V(PVC-CPE) = 5 \times 10^{-5}\ m^3\ kg^{-1}$. The solubility parameters calculated from the surface-tension data are not in agreement with the data given by Barton [19] for liquids which show hydrogen bonding (water, glycol and ethanol). On the other hand, the values of the solubility parameters of the organic liquids n-hexane, toluene and cyclohexanone calculated from the surface-tension data compare well with the data from [19].
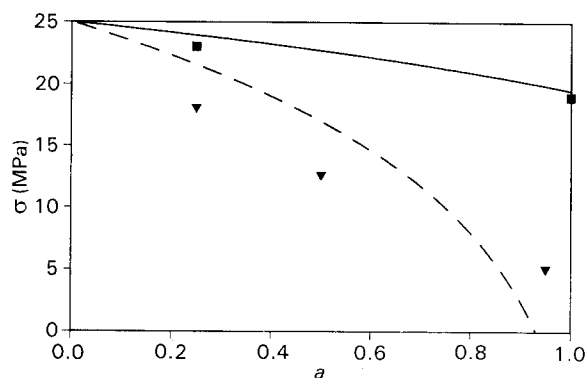

Figure 8 Experimental and calculated long-term craze-initiation stress as a function of activity of n-octane and benzene vapour. (▼) Benzene (experimental), (■) n-octane (experimental), (– – –) benzene (calculated), (———) n-octane (calculated).

Figure 7 Experimental equilibrium volume fraction, v, of (◆) n-hexane/benzene and the calculated equilibrium sorption versus benzene fraction in benzene/n-octane mixtures.
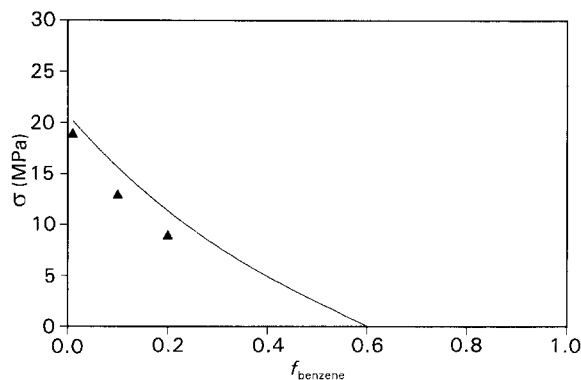

Figure 9 (▲) Experimental and (———) calculated long-term craze-initiation stress as a function of volume fraction of benzene in n-octane/benzene mixtures.

TABLE II Solubility parameters from surface-tension data according to Equation 8, δ_{surf}; solubility parameters from [19], δ_{lit}; enthalpic interaction constant, $\varkappa_H$, calculated from these solubility parameters according to Equation 9; volume fraction, v, calculated using $\varkappa = \varkappa_H$ + 0.4 and Equation 2; relative drawing stress, $\sigma_d(v)/\sigma(0)$, according to Equations 4 and 5

Component	δ_{surf} (MPa$^{1/2}$)	δ_{lit} (MPa$^{1/2}$)	$\varkappa_{H,surf}$	$\varkappa_{H,lit}$	v	$\sigma_d(v)/\sigma_d(0)$
Water	39	47.8	1.9	5.1	0.002	0.99
Glycol	27	34.9	0.4	4.1	0.004	0.99
Cyclohexanone	21	19.6	0.2	0.1	1	0
Ethanol	18	26.5	0.6	0.6	0.32	0
Toluene	20	18.2	0.4	0.4	0.46	0
n-hexane	15	14.9	3.4	2.2	0.034	0.86
PVC–CPE	23	21.4				

If the solubility parameters are divided into a polar, a dispersive and a hydrogen-bonding part, the enthalpic contribution to the interaction constant $\varkappa$ can be calculated analogously to Equation 9. Instead of the square of the difference of solubility parameters between liquid and polymer, the sum of the squares of the differences in the polar, the dispersive and the hydrogen-bonding part of the solubility parameters has to be used. Although this division leads to a more detailed treatment of the interaction, the value for the interaction constant, $\varkappa$, obtained in this way is not realistic (too high). Therefore those results are not presented in Table II.

The decrease in drawing stress due to the calculated sorption (the $\varkappa_{H,lit}$ data are used) compares reasonably with the experimentally observed decrease in the craze-initiation stress for the water, glycol and n-hexane vapour environments (see Fig. 3). The disagreement between the decrease in experimental craze-initiation stress and predicted drawing stress for the toluene and cyclohexanone vapours can be explained by a phase transition. At high sorption, PVC–CPE becomes rubbery and initiation of crazes becomes impossible.

A real discrepancy between the decrease in drawing stress and craze-initiation stress is observed for the ethanol vapour. In order to describe the decrease in craze-initiation stress, $\varkappa_H \approx 2$ should be used. This discrepancy means that one has to be careful when using solubility parameters to predict the craze-initiation stress.

6. Conclusion
The long-term craze-initiation stress of PVC and PVC–CPE in vapours and mixtures is a function of the activity of the different components and the interaction between these components and the polymer matrix. More precisely, there seems to be a direct relation between the reduction of the glass–rubber transition temperature due to the absorption of the environment and the reduction of the long-term craze-initiation stress.

Although surface-tension experiments give information about the interaction between the polymer matrix and a liquid, the relation between the surface stress and the environmental stress-cracking capacity is not straightforward. It appears that the Flory–Huggins interaction constant can be used for a prediction of the

long-term craze-initiation stress if no sorption data are available. This interaction constant is best approximated using the solubility parameters from Barton [19]. The solubility parameters calculated from the experimental surface-tension data are less satisfactory.

Adsorption and capillary condensation are not expected to affect the craze initiation process significantly.

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