ENVIRONMENTAL STRESS CRACKING OF PVC PIPE MATERIALS

Mannes Wolters, GASTEC NV, Apeldoorn, The Netherlands

ABSTRACT

In the Netherlands, rigid PVC and impact-modified PVC pipes have been used in gas distribution systems for dozens of years. In general, these pipes have performed excellently. Some years ago, however, questions were raised about the resistance of these materials to certain gas constituents. An extensive research programme was then started to investigate these problems.The results of this research programme are reported in this paper and are of value to other pipe applications as well.

Crazing and cracking in various gaseous environments and in natural gas condensate have been examined in many long-term studies. Long-term failure in PVC pipe systems is always preceded by crazing. Crazing and cracking are strongly affected by the various gaseous environments. However, below certain concentrations, which are representative of the commonly distributed natural gases, higher hydrocarbons have no detrimental effect on PVC pipe materials. Natural gas condensate only affects PVC under extreme conditions which hardly ever occur. It was proven once again that (impact-modified) PVC is an excellent pipe material for low-pressure gas distribution systems.

Introduction

At present, about 50 per cent of the Dutch gas distribution grid consist of rigid and impact-modified PVC pipes with a maximum operating pressure of 100 mbar. In total, about 20,000 km of rigid PVC and about 35,000 km of impact-modified PVC pipes are in use. Rigid PVC pipes have been laid since about 1955 and impact-modified PVC was introduced as pipe material at the end of the sixties. At the moment, impact-modified PVC is the predominant gas distribution pipe material in the Netherlands. Specially constructed rubber ring joints facilitate pipe jointing and cut costs. The experiences with these PVC pipe systems are generally excellent. In other countries, PVC is hardly used for gas distribution, but extensively in other areas like water distribution.

In the eighties, questions were raised about the environmental stress cracking behaviour of PVC pipes. Changes in the composition of the gas distributed in the Netherlands might lead to a deterioration of PVC pipe materials due to the presence of certain gas components such as aromatics. Consequently, Gasunie, the main Dutch gas transmission company, and GASTEC, on behalf of the Dutch gas distribution companies, jointly started to investigate these problems and completed their study in 1994.

This paper describes the main results of this study. Most attention is paid to the effects of gas components and gas condensate. However, the study also resulted in a general understanding of the failure mechanisms in PVC pipe material, and is therefore of interest to other applications as well.

Failure behaviour in non-agressive environments

Crazing plays an important role in failure mechanisms of PVC materials. Years ago, it was generally accepted that the presence of crazes in plastics was due to the combination of a mechanical stress or strain and an agressive environment. In the seventies and eighties, however, it was found that craze initiation can also occur in non-agressive environments. In addition, crazes do not always lead to failure, but they often stop growing. However, if failure occurs, cracking is almost always preceded by craze initiation and growth.

To predict the long-term behaviour of PVC pipe materials under real conditions, it is therefore incorrect to only consider the occurrence of crazing. Instead, the crazing and cracking behaviour as a function of stress and the environment should be considered. To this end, many long-term experiments on PVC pipe materials have been performed. Dumbbells taken from pipes were exposed to various gaseous environments at different constant stress levels. Optical microscopy was used to measure craze initiation time and craze growth [Ref. 1]. Time to failure was also recorded.

The crazing and failure behaviour of PVC materials is schematically represented in Figure 1. This stress vs. time diagram shows craze initiation, craze growth, brittle fracture and yield [Ref. 2].
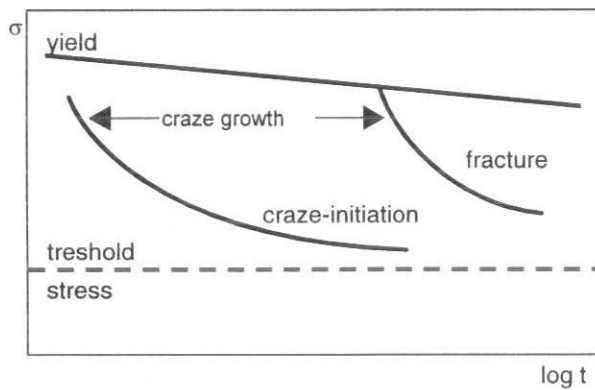

Figure 1. Craze initiation, craze growth, yield and fracture in PVC

There is a linear relation between yield stress and the logarithm of time. Yielding precedes ductile fracture, as is often found in internal water pressure tests. Yielding of PVC is hardly influenced by material quality.

In unnotched samples crazes always initiate at the surface on small imperfections. This suggests that crazes initiate because of local stress concentrations. Viscoelasticity also plays a role in craze initiation. There is no fixed craze initiation stress, this stress being time-dependent. In constant load experiments high stress will result in short craze initiation times, while lower stresses will produce much longer craze initiation times. Probably, a threshold stress can be defined below which no crazes will initiate, even after very long loading times. After initiation at moment t_i, the craze will grow - under constant mechanical loading - at a constant logarithmic rate.

Craze growth behaviour will probably be determined by the viscoelastic properties of the material. The stress concentration at the craze tip is the driving force behind craze growth; the 'logarithmic' craze growth may be caused by stress relaxation at the craze tip. In many cases, craze growth stops some time near the yield curve.

When the fibrils within a craze fail, a crack is formed. At the tip of this crack a craze will grow again. If the crack formed exceeds a certain critical stress intensity, rapid unstable failure of the sample will occur. If the crack has not yet reached a critical stress intensity, craze growth at the crack tip will stabilize crack growth. Crack and craze will then grow simultaneously into the material. New fibrils will be formed at the craze tip, while at the same time craze fibrils will break. This way, crack and craze will grow together until the crack exceeds the critical stress intensity and final fracture of the sample occurs. So, slow stable crack growth is strongly connected with crazing at the crack tip.

The effects of gaseous environments.

Stress corrosion in various solvents has been studied extensively, but less research has been conducted into the effects of gases and vapours [Ref. 4].
A qualitative representation of the effects of a stress corrosion environment on crazing and fracture is given in Figure 2. Craze initiation can be strongly affected by an environment. It both accelerates craze initiation and lowers the threshold stress for crazing. The brittle fracture curve is also affected by the environment and shifts more or less proportionally to the craze initiation curve on a logarirthmic scale! The distance in time between the craze initiation curve and the brittle fracture curve primarily depends on material quality, though the environment may also affect this distance.
Stress corrosion seems to be mainly caused by absorption of the medium by the polymer. Diffusion of this medium into the polymers is also important. If diffusion occurs quickly, the absorption and weakening effects will take place over larger areas and homogeneous yielding may arrest possible craze growth processes.
It may be concluded that an environment which strongly interacts with the specific polymer, but diffuses rather slowly into the polymer will have a stronger stress corrosion effect.
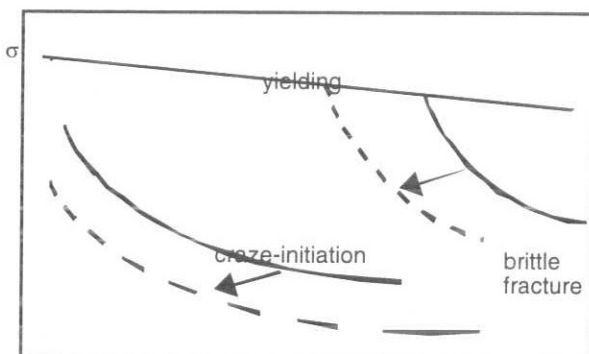

Figure 2: The effects of a stress crazing agent on craze initiation and brittle fracture (schematically)
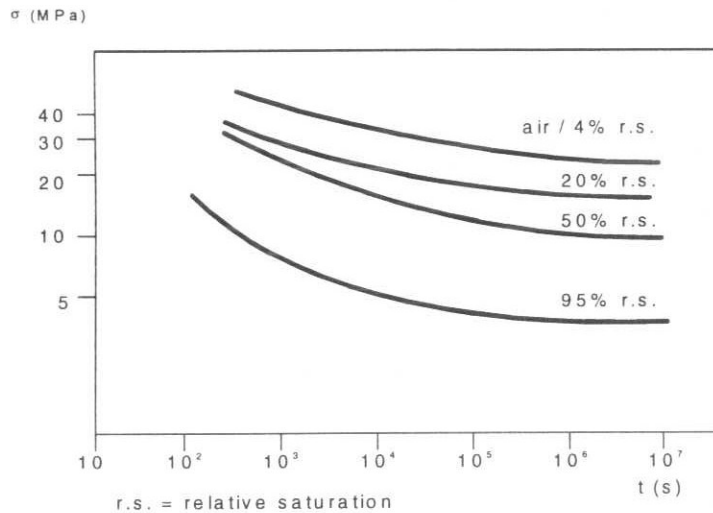
207

The effects of aromatics

Figure 3: Craze initiation in PVC under constant loading in various environments of natural gas with aromatic vapour.

Aromatics in gas have a considerable impact on craze initiation behaviour. Figure 3 shows the relation between mechanical stress and craze initiation time in various aromatically enriched natural gas environments. Craze initiation is considerably accelerated at high aromatic concentrations. However, at low aromatic concentrations, for instance here at a 4% relative degree of saturation of aromatics in natural gas, i.e. about 5,000 ppm, no effects on craze initiation were found.

Figure 3 shows the results of limited tests which were carried out during a period of about 3 months. Of course, the possible impact in 50 years time is of more importance. That's why the results have been extrapolated to 50 years. In other words, the results of these short-term tests were used to calculate the stress at which after 50 years craze initiation will occur. This 50-year craze initiation stress is shown in Figure 4.
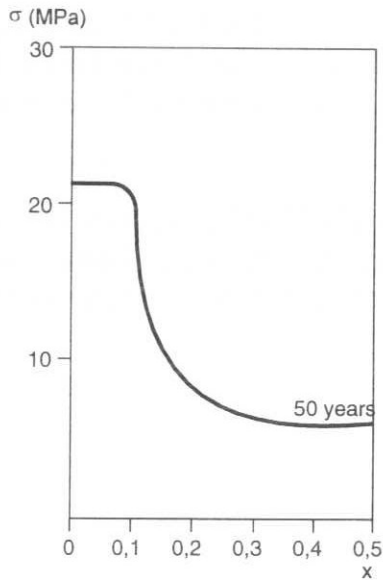
Figure 4: 50-year craze initiation stress as
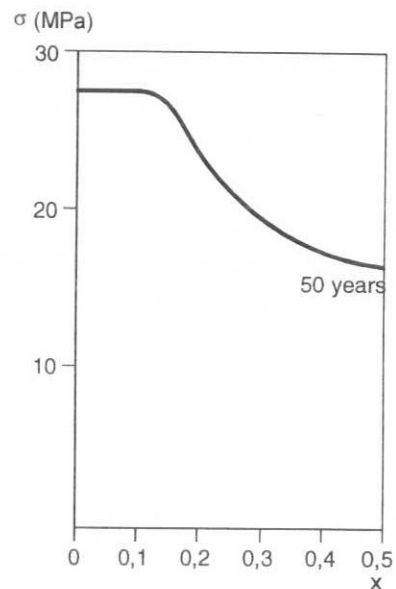a function of relative aromatic
concentration

Figure 6: (50- year) failure stress as a
function of relative aromatic
concentration

Figure 4 shows that the 50-year craze initiation stress does not change significantly up to a relative aromatic concentration of about 0.1, i.e. about 10,000 ppm. So, during the entire 50-year life there will be no acceleration of craze initiation in gases with a maximum aromatic concentration of 10,000 ppm. However, there is a considerable impact at higher aromatic concentrations, and craze initiation already occurs at much lower stresses.

In addition to the possible effects of gaseous environments on craze initiation, the possible effects on the final failure behaviour have to be determined. To this end, test bars were subjected to a constant mechanical load until failure occurred. Figure 5 shows some results of these tests in two gaseous environments. At higher aromatic concentrations, here a 50% relative degree of saturation, failure will already occur at much lower stresses and after shorter periods than in air or in gaseous environments with low aromatic concentrations.
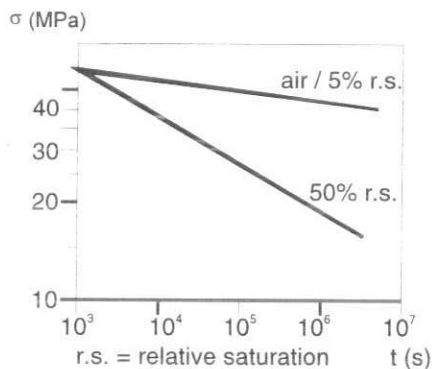

Figure 5: Failure behaviour of rigid PVC in various aromatic environments

The results of these relatively short-time tests have also been extrapolated to 50 years. Figure 6 shows the 50-year failure stress in various aromatic environments. The 50-year failure stress is the stress at which after 50 years material failure will occur, and is considerably lower at higher aromatic concentrations.

At higher aromatic concentrations, i.e. exceeding approximately 10,000 ppm, craze initiation and failure are accelerated almost simultaneously on a logarithmic time scale. Figure 7 shows the impact of high concentrations of aromatic vapour in natural gas on craze initiation and failure behaviour of PVC (50,000 ppm aromatics).
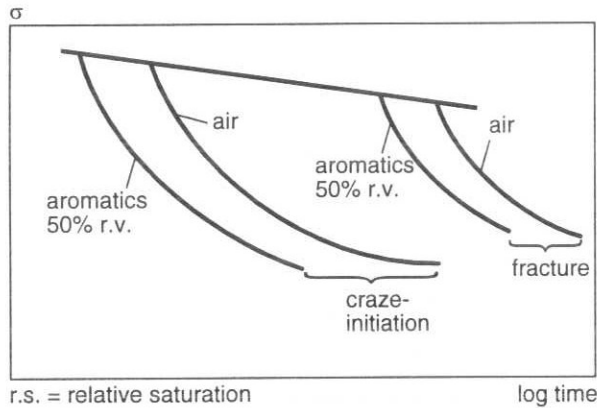

Figure 7: Impact of aromatics on PVC

Because of the presence of aromatic vapour, the craze initiation and failure curves move to the left over an identical distance. Besides, the failure process is accelerated much more than the craze initiation process on a linear time scale.
And finally, the threshold stress, above which craze initiation and failure occur, is decreased due to the presence of high aromatic concentrations.

The effects of aliphatics

Natural gas not only contains aromatics, but other higher hydrocarbons as well, which could adversely affect plastic pipe materials. A limited research project has been carried out into a number of these components, a group of aliphatic hydrocarbons such as hexane, decane etc. For the purposes of this test natural gas was enriched with certain aliphatics.
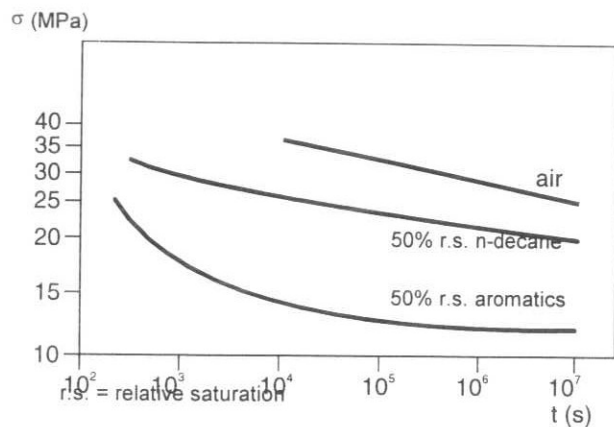
σ (MPa)

Figure 8: Craze initiation in varous gaseous environments

Figure 8 shows the effects of various gaseous environments on craze initiation. High concentrations of aliphatics turn out to also significantly accelerate craze initiation in PVC, shown here for a natural gas enriched with n-decane vapour (50% relative degree of saturation). However, the impact of aliphatics proves to be much lower than that of aromatics at the same relative degree of saturation. High concentrations of aliphatics in natural gas also have a considerable impact on failure behaviour (Figure 9).
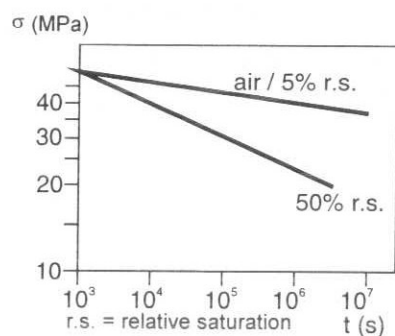
σ (MPa)

Figure 9: Failure behaviour of rigid PVC in various n-decane environments

At a 50% relative degree of saturation of n-decane in natural gas brittle fracturee in natural gas already occurs at much lower stresses. No effects on failure behaviour were found at low relative aliphatic concentrations. The results of these relatively short-term experiments were also extrapolated to 50 years. Figure 10 shows the 50-year failure stress as a function of the relative n-decane concentration.
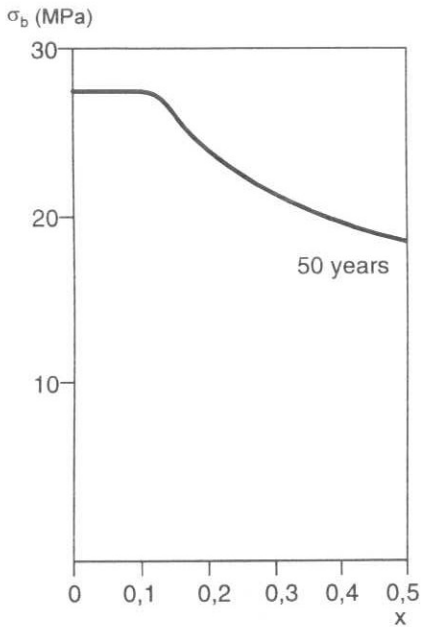
Figure 10: (50-year) failure stress as a function of relative n-decane concentration

No impact on failure behaviour was found up to a relative concentration of about 0.1, above which a decrease was found compared to the failure stress in non-agressive environments. The impact of n-decane on crazing and failure behaviour can also be presented in a stress log time diagram (Figure 11).
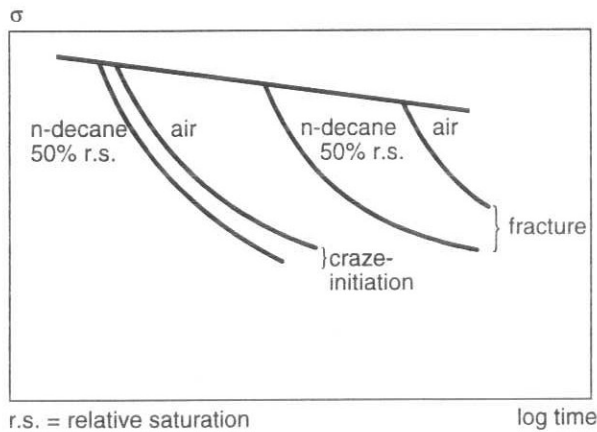

Figure 11: Impact of n-decane on PVC

In aliphatically rich environments craze initiation is slightly accelerated compared to craze initiation in air. However, aliphatics have a much lower impact on craze initiation than aromatics, although failure behaviour is strongly affected by aliphatics. The presence of these aliphatics reduces time to failure considerably and the fracture becomes more brittle.
To summarize, the presence of aliphatics results in a reduction of the distance between the craze initiation and failure curves. In other words, craze and crack growth are apparently strongly affected by the aliphatic environment. Aromatic environments have a much lower impact on these parameters; on a logarithmic scale the distance between the craze initiation and failure curves remains the same.

The effects of natural gas condensate

Gas condensate can be present in the gas distribution system under certain conditions. Gas condensate is a mixture of higher aliphatic and aromatic hydrocarbons. The possible deterioration of PVC due to gas condensate was examined in a laboratory. This laboratory research project was divided into two parts:

- materials testing where small test specimens from pipe materials were used to study craze initiation and growth and failure behaviour due to gas condensate;
- pipe testing where real conditions were simulated as much as possible in the laboratory by exposing small sections of pipe during a specified period to condensate and - simultaneously - to a mechanical load. After these tests it was assessed to what extent the sections of pipe had been deteriorated. It was examined in particular how and to what extent the impact resistance of a PVC pipe decreases due to the presence of crazes. These crazes are formed under circumstances which in practice can indeed occur. Changes in impact resistance were determined using so-called brittle-ductile transition temperatures, T_{b-t}.

The effects of gas condensate were determined by comparing the results in condensate environments with those in inert environments. In addition, environments were used in which the concentrations of larger hydrocarbon molecules were still not so high as to result in a liquid phase (condensate). The difference between such an environment and a really liquid condensate environment is referred to as the degree of saturation.

The laboratory tests show that the saturated vapour over the condensate has the same effect on craze initiation and failure behaviour as condensate liquid. However, the stress corrosion impact of condensate vapour sharply diminishes as the degree of saturation decreases.

Due to the simultaneous exposure to condensate and mechanical loading the brittle-ductile transition temperature, T_{b-t}, of rigid PVC changed only marginally even when high loads were applied. For impact-modified PVC, only the test specimens that were exposed to condensate at the highest stresses showed a clear T_{b-t} increase up to values that are comparable to rigid PVC. On the inside of these test specimens craze initiation was so intensive that dark coloured bands were visible.

This research project shows that the presence of natural gas condensate can result in an undesired situation only if extreme conditions occur simultaneously. These conditions are:

- the condensate has been present in the gas pipe for quite some time;
- a very high stress is present locally due to a point or line load; this kind of load is caused by hard sharp objects pressing against the pipe, such as rocks.

However, the stresses that occur in a pipe hardly ever reach such a high level that the brittle fracture described above can occur due to the presence of condensate.

The impact resistance of PVC pipe materials can decrease due to the presence of condensate in places where very high material stresses exist. The impact resistance of rigid PVC will diminish only slightly. The impact resistance of impact-modified PVC can strongly decrease to values that are comparable to those of rigid PVC. This decrease means that damage will occur sooner during work on or around the gas pipes.

Conclusions

First, some conclusions concerning craze initiation:

- In rigid and impact-modified PVC craze initiation can occur above a certain threshold stress, independent of the gas environment;
- Only at high concentrations of certain gas constituents, for instance aromatics oder higher aliphatics, craze initiation is accelerated and the stress at which it can occur - the threshold stress - is decreased;

- However, at the current concentrations of gas constituents as well as the concentrations to be expected in the future these effects are unlikely;

The occurrence or absence of crazes is an insufficient criterium for determining the effects of gaseous environments. Attention should be paid in particular to failure behaviour. As far as failure behaviour is concerned, the following conclusions can be drawn:

- Crazes generally do not continue to grow and do not cause brittle fracture or embrittlement. Consequently, the occurrence or absence of crazes in itself is not a good measure of the susceptibility to stress corrosion;
- Brittle fracture can occur relatively quickly in PVC only at high enough stresses and poor material quality, independent of the environment, i.e. both in agressive and non-agressive environments;
- Long-term failure mechanisms are accelerated only at high concentrations of certain gas constituents. For instance, up to 10,000 ppm of aromatics in natural gas no accelerated deterioration of mechanical behaviour is expected within 50 years;
- Gases with aromatic concentrations of up to 1,000 ppm, which is expected to be the maximum feasible concentration in natural gas, have no detrimental effect on the current Dutch PVC gas distribution systems.

The conclusions concerning type of material and material quality are:

- Under constant mechanical loading craze initiation is identical in rigid and impact-modified PVC. In other words, if the same mechanical load is applied, crazes occur in both rigid and impact-modified PVC pipe material after the same period of time;
- However, if deformation is constant, which is more in line with real conditions, impact-modified PVC is more advantageous than rigid PVC. In that case, crazes will occur sooner at the same strain in rigid PVC than in impact-modified PVC.

Concerning the impact of gas condensate it can be concluded that crazing and embrittlement occur only if condensate has been present for quite some time in a highly externally loaded PVC pipe. However, this situation is highly unlikely.

The general conclusion is that (impact-modified) PVC remains an excellent pipe material for low-pressure gas distribution systems.

Acknowledgements

References

1. Breen and D.J. van Dijk,
   J. Mater, Sci 26 (1991) 5212
2. J.L.S. Wales, Polymer 21 (1980) 684.
3. Williams, "Linear Fracture Mechanics", Adv. Polym. Sci. 27 (1978)
4. N. Brown, "Mechanical Behaviour in Gaseous Environments" in "Failure of Plastics", eds. W. Brostow and R.D. Corneliussen, Hanser Publ., München (1986)