Influence of the Level of Gelation on Physical Ageing Kinetics of uPVC Pipes

E. Drenth, T.C. Bor, H.A. Visser, M. Wolters

Faculty of Engineering Technology. University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands

The physical ageing kinetics of uPVC pipes with different levels of gelation were investigated. No significant influence of the level of gelation on both the deformation kinetics and the physical ageing kinetics were observed. As a consequence, installed uPVC pipes as employed for gas, water and sewer purposes age in a way that is independent of the level of gelation.

Introduction

The process of physical ageing of polymer products do not only depend on the conditions during service life, but also on the processing conditions during their production. Engels [1] showed that by taking into account physical ageing during the cooling phase after injection moulding, it is possible to relate the processing conditions quantitatively to the mechanical properties of injection moulded polymer glasses. His work focused on polycarbonate, but the underlying theory can, in principle, also be applied to other glassy polymers. Here it will be applied to extruded uPVC pipes.

The initial quality of uPVC pipes after production is, not only related to cooling conditions after extrusion, but also to the level of gelation of the polymer network. The level of gelation is a measure for the degree to which the particulate structure of uPVC powder, which is fed into the extruder, has been broken down and to which extent an entanglement network has been formed [2]. As the level of gelation of uPVC does not change after production, it can be seen as a measure of the initial quality of uPVC pipes [3].

Numerous experimental studies have shown that the yield properties of PVC are not influenced by the level of gelation [2,4,5,6,7]. It is suggested that molecular rearrangements during yielding are independent of the density of entanglements and secondary crystalline junctions [4,5]. Therefore, it is expected that the level of gelation will also not influence the physical ageing kinetics, though no experimental data is available to support this statement. For the practical implementation of a residual lifetime assessment method of uPVC gas, water or sewer pipes as proposed by Visser [8], which is based on the physical ageing kinetics of the material, it is imperative to study the influence of the level of gelation on physical ageing. In this paper the results of such a study with pipes of different levels of gelation are presented.

Modelling Deformation and Physical Ageing Kinetics

For modelling of the deformation kinetics and physical ageing kinetics the approach used by Visser is adopted [8,9]. The following pressure-modified Eyring relation is applied to model the deformation kinetics:

$$\dot{\bar{\gamma}}(T, p, \bar{\tau}) = \dot{\gamma}_0 \exp\left(\frac{-\Delta U}{RT}\right)\sinh\left(\frac{\bar{\tau} v^*}{RT}\right)\exp\left(\frac{-\mu p v^*}{RT}\right). \qquad (1)$$

The relation gives an equivalent plastic strain rate $\dot{\bar{\gamma}}$ from a given thermo-dynamical history $\dot{\gamma}_0$, temperature T, equivalent stress $\bar{\tau}$ and hydrostatic pressure p. The activation energy ΔU and activation volume v^* were determined by tensile test data at various temperatures and strain rates. The pressure dependence μ was determined using data of tensile tests conducted at superimposed hydrostatic pressures as measured by [12]. The universal gas constant is denoted by R. The term $\dot{\gamma}_0$ captures the physical ageing kinetics according to:

$$\dot{\gamma}_0\left(T,\bar{\tau},t\right)=b_0\left(\frac{t_{eff}\left(T,\bar{\tau},t\right)+t_{ini}}{t_0}\right)^{b_1}, \tag{2}$$

where b_0 and b_1 are constants, t_{ini} is the initial age of the material and t_0 = 1 s. The effective time t_{eff} accounts for the influence of temperature and stress on aging rate. In this study, the specimens were aged by annealing at elevated temperatures without a applying an (ageing) stress. For these conditions the effective reduces to:

$$t_{eff}\left(T_a,t_a\right)=\frac{t_a}{a_T\left(T_a\right)}, \tag{3}$$

where a_T is an Arrhenius time-temperature induced acceleration factor given by:

$$a_T\left(T_a\right)=\exp\left[\frac{\Delta U_a}{R}\left(\frac{1}{T_a}-\frac{1}{T_{ref}}\right)\right], \tag{4}$$

where t_a is the ageing time at temperature T_a and ΔU_a is the ageing activation energy. As $\bar{\tau}$ >> 0.5 MPa the term involving the equivalent stress $\bar{\tau}$ can be written as an exponential ($\sinh(x) \approx 1/2 \exp(x)$ for x >> 1). All mechanical tests in this study were carried out in uniaxial tension. Hence, the equivalent terms can be written according to the definitions: $\dot{\bar{\gamma}}=\sqrt{3}\dot{\varepsilon}$, $\bar{\tau}=\sigma/\sqrt{3}$, and $p=-\sigma/3$. Hence Eq. (1) can be written as:

$$\dot{\varepsilon}=\frac{1}{2\sqrt{3}}\dot{\gamma}_0\exp\left[\frac{\sigma v^*}{3RT}\left(\mu+\sqrt{3}\right)-\frac{\Delta U}{RT}\right], \tag{5}$$

where $\dot{\varepsilon}$ is the applied strain rate during tensile testing, and σ the engineering stress during testing.

Experimental

The uPVC specimens were taken from unused pipes (Ø 50 mm) having levels of gelation ranging from 33 % to 90 %. The levels of gelation were obtained from the manufacturer of the uPVC pipes who had used the Macklow-Smith rheology method [2]. Segments of the pipes were cut with a band saw and were rejuvenated in a hot press at 100 °C for 25 minutes. Tensile specimens of dimension 70x10x5 mm^3 with a gauge length of 30 mm were milled from the flattened segments. Tensile tests at 23 °C were performed with a Zwick Z5 with a 2.5 kN force cell. Tensile tests at temperatures 20 °C, 40 °C and 60 °C were performed on a Zwick Z1445 with a 5 kN force cell and equipped with a temperature controlled chamber. The engineering stress and strain rate are calculated from measured force and applied crosshead speed, respectively.

Deformation kinetics

The yield stress of uPVC samples with different levels of gelation at various temperatures and strain rates are shown in Figure 1. All sets of uPVC specimens, differing in level of gelation, show similar yield stress behaviour for the temperatures and strain rates considered. Therefore, only one set of parameters is sufficient to describe all uPVC sets.

The pressure dependence μ for uPVC can be determined from data of Yuan *et. al.* [12] as has been done by Visser [9] who found a value μ = 0.14; this value is also adopted here. Using Eq. (5), the parameters found here are ΔU = 266 kJ mol^{-1}, v^* = 2.06·10^{-3} m^3 mol^{-1} and $\dot{\gamma}_0$ = 2.50 · 10^{31} s^{-1}. The activation energy and activation volume are comparable to those found by Bauwens-Crowet *et. al.*[10], Havriliak [11] and Visser [9] (ΔU = 295, 316, 297 kJ mol^{-1}, v^* = 1.9·10^{-3}, 2.6·10^{-3}, 2.06·10^{-3} m^3 mol^{-1}, respectively).

Only the α-relaxation (main chain mobility) is present for the range of temperatures and strain rates considered. A significant influence of the level of gelation on the β-relaxation will not be expected as the conformational changes related to this relaxation process are more local than the conformational changes related to the α-relaxation.

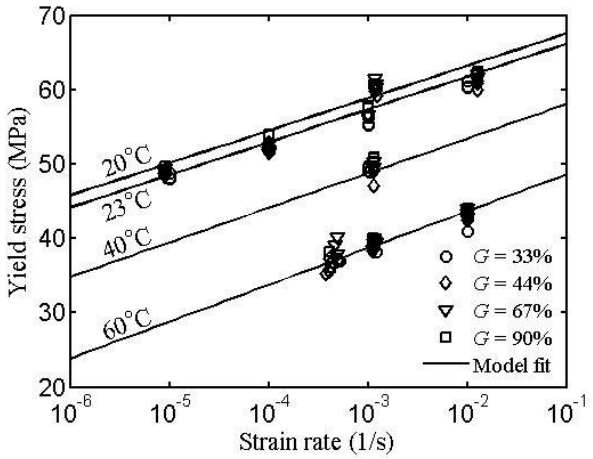

Figure 1: The yield stress determined in tension for various strain rates and temperatures for uPVC tensile bars of different levels of gelation. The solid lines are model fits employing Eq. 5 on all data simultaneously.

Physical Ageing kinetics

The yield stress values determined for each level of gelation and for various ageing times and ageing temperatures are shifted using Eq. (4) to a reference temperature of 10 °C. This is the typical average temperature of buried PVC pipes. Details about the fitting procedure of determining the ageing activation energy ΔU_a can be found in [8]. Each set of samples with a different level of gelation has a slightly different optimal activation energy ΔU_a, but the differences are relatively small (ΔU_a = 185, 171, 194, 187 kJ mol^{-1} which correspond to levels of gelation of 33, 44, 67, 90 %, respectively.). Therefore, the average of the separately determined activation energies of each level of gelation is calculated and used to shift all yield stress values. A value of $\langle \Delta U_a \rangle$ = 184 kJ mol^{-1} has been determined, which results in a good description of the experimental data. The so-obtained shifted yield stresses for each level of gelation are shown in Figure 2.

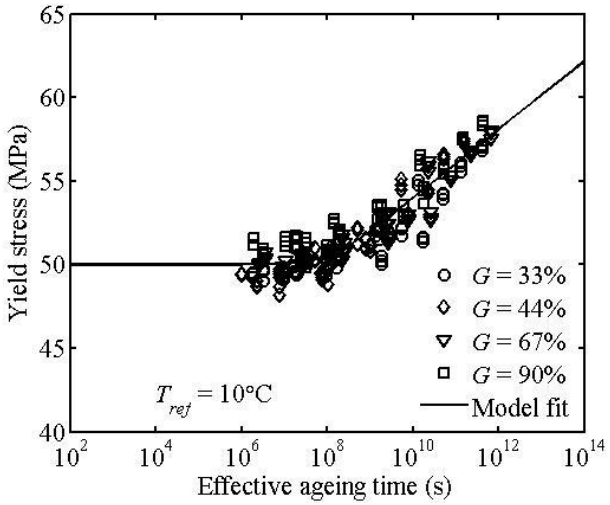

Figure 2: Markers: shifted uPVC yield stress as a function of the effective ageing time plotted for each level of gelation (G). The effective ageing time follows from the use of Eqs. 2 – 4. Solid line: a single least squares fit of the shifted yield stress for each level of gelation using Eq. 5.

No significant influence of the level of gelation on physical ageing can be observed as shown in Figure 2. Therefore, a single master curve can be constructed which describes the physical ageing kinetics of all samples with different levels of gelation employing Eq. (5). The obtained ageing parameters are $b_0 = 4.58 \cdot 10^{38}$ s^{-1}, b_1 = -0.49 and $t_{ini} = 1.21 \cdot 10^8$ s. All parameters used in this work are summarised in Table 1.

Table 1: the values of the parameters used in this work.

$\mu = 0.14$	- †	$b_0 = 4.58 \cdot 10^{38}$	s^{-1}
$v^* = 2.06 \cdot 10^{-3}$	$m^3\ mol^{-1}$	$b_1 = -0.49$	-
$\Delta U = 2.66 \cdot 10^5$	$J\ mol^{-1}$	$\langle \Delta U_a \rangle = 1.84 \cdot 10^5$	$J\ mol^{-1}$ ‡

† Value for μ determined by Visser [9] from the data of Yuan et.al. [12].
‡ The average value of the ageing activation energies of each level of gelation.

Discussion

It was observed that the level of gelation has no significant influence on the deformation kinetics within the range of temperatures and strain rates considered. This supports the theory that the level of gelation is related to the density of entanglements and secondary crystalline junctions, which will have no significant influence on the segmental mobility (yield stress) of the polymer chains.

As shown in Figure 2, the physical ageing kinetics of uPVC pipes are not influenced by the level of gelation. During physical ageing, the polymer is in a non-equilibrium state and the polymer chains undergo small conformational changes. It is suggested that the density of entanglements and secondary crystalline junctions do not influence the ability of the polymer chains to undergo conformational changes that take place during physical ageing. This can be explained by assuming that the distance between entanglements and secondary crystalline junctions is larger than the length of the chain part involved in conformational changes during physical ageing.

Conclusion

Experimental evidence of the insensitivity of the physical ageing kinetics to the level of gelation was obtained. It can therefore be concluded that installed uPVC gas, water or sewer pipes age in a way that is independent of the level of gelation.

Acknowledgements

The financial support of Cogas, Alliander, Enexis, Stedin, Bureauleiding, Vitens, Rendo Netwerken and Delta Netwerkbedrijf is gratefully acknowledged.

References

[1] Engels, T.A.P., *Predicting performance of glassy polymers*, Ph.D. thesis, Eindhoven University of Technology, The Netherlands, 2008.
[2] Benjamin, P., *Plastics and Rubber: Materials and Applications* **1980**, 5, 151–160.
[3] Hermkens, R.; Wolters, M.; Weller, J.; Visser, H.A., PVC pipes in gas distribution: still going strong! In *Plastics Pipes XIV*, Budapest, 2008.
[4] Covas, J.A.; Gilbert, M.; Marshall, D.E., *Plastics and Rubber Processing and Applications* **1988**, 9, 107–116.
[5] Terselius, B.; Jansson, J.F., *Plastics and Rubber Processing and Applications* **1984**, 4, 291–299.
[6] Kuriyama, T.; Narisawa, I.; Shina, R.; Kotaki, M., *Journal of Vinyl and Additive Technology* **1998**, 4, 164–168.
[7] Uitenham, L.C.; Geil, P.H., *Journal of Macromolecular Science, Part B* **1981**, 20, 593–622.
[8] Visser, H.A.; Bor, T.C.; Wolters, M.; Wismans, J.G.F.; Govaert, L.E., *Macromolecular Materials and Engineering* **2010**, 295, 1066-1081.
[9] Visser, H.A.; Bor, T.C.; Wolters, M.; Engels, T.A.P.; Govaert, L.E., *Macromolecular Materials and Engineering* **2010**, 295, 637-651.
[10] Bauwens-Crowet, C.; Bauwens, J. C.; Homes, G., *Journal of Polymer Science Part A-2: Polymer Physics* **1969**, 7, 735–742.
[11] Havriliak, S.; Shortridge, T.J., *Journal of Applied Polymer Science* **1989**, 37, 2827–2836.
[12] Yuan, J.; Hiltner, A.; Baer, E., *Journal of Materials Science* **1983**, 18, 3063–3071.