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DSC INVESTIGATIONS OF PVC AND PVC/CPE GAS PIPES

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ABSTRACT

The DSC method of Gilbert and Vyvoda(1) to measure the degree of gelation of PVC may be used for PVC/CPE as well, but the method was found to be only empirical. The "crystallinity" of PVCs may be determined by measuring the peak height of the exotherm crystallisation peak ($\Delta cp_1 - \Delta cp_2$). The area of the CPE melting peak as measured from the second heating-curve may probably be used to determine the CPE content of PVC/CPE, if the same type of CPE is present.

INTRODUCTION

In the Netherlands PVC and PVC/CPE (Chlorinated Polyethylene-impact modifier) are used as pipe materials for low pressure gas distribution grids. The quality of these pipes is assessed by mechanical tests and DSC.

Some important properties investigated with DSC are the degree of gelation(1), the crystallinity(2) and the amount of CPE in PVC/CPE.

EXPERIMENTAL METHODS

The investigations were carried out with a Perkin Elmer DSC-2 instrument connected through a Hewlett Packard 3421A Data Acquisition Unit to a Hewlett Packard HP 86 microcomputer. All the measurements were done in nitrogen at a heating rate of 10 °C/min. Calibration was carried out with indium and tin. The samples were kindly supplied by Polva Nederland B.V. and Wavin KLS B.V. (uPVC and Hostalit Z).

RESULTS AND DISCUSSION

1. Degree of gelation

For PVC/CPE a correlation was found (Figure 1) between the degree of gelation as measured using the Macklow/Smith rheological method(3) and the DSC method of Gilbert and Vyvoda(1). The standard deviation of the DSC method for PVC/CPE at 70%

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gelation (which is near the optimum[4] value) is 5.9%. However, at this moment it is unknown whether this uncertainty is due to the experimental noise or reflects normal inhomogeneities in the pipes. It is believed, that the latter effect also plays a role, because systematic differences have been found between inside and outside surface of the pipes.

To study the significance of the DSC method further, the following sequence of temperature programs was given to one sample with 70% gelation:

1. Heating at 10 °C/min to 200 °C during which the DSC curve was measured.
2. Cooling at 10 °C/min to 20 °C.
3. Heating at 10 °C/min to T_l °C and maintaining this temperature for 3 minutes.
4. Quickly removing the sample from the DSC and immediately quenching it in water of 22 °C and restarting at (1).

Initially T_l was 190 °C; T_l was lowered with an extra 10 °C every time stage 3 was reached. The sequence was stopped when T_l = 120 °C.

The results are presented in Figure 2. T_l is indicated with an arrow; the upper curve is of the first heating. Although the area of peak A[1] decreases monotonically with T_l, it is very unlikely that the degree of gelation also decreases. This means, that the area of peak A correlates merely by coincidence with the degree of gelation. The changing area of peak A reflects in fact the different temperatures just before quenching. In the practice of extruded PVCs (that are also quenched) this means that the end temperature of peak A correlates closely with the extrusion temperature[1].

Crystallinity of PVC and PVC/CPE

The condition of low crystallinity of extruded PVC and PVC/CPE samples changes into a better ordered state above T_g, as evidenced by the exotherm between 90 and 105 °C[2]. This crystallisation is not measured by peak integration because of overlapping with the melting peak of CPE between 100 and 120 °C, but by determining the peak height. The maximum and minimum distance from the curve to the from lower temperatures extended baseline is called Δcp_1 and Δcp_2 respectively (Figure 3). Because slightly incorrect drawing of the baseline causes scatter in Δcp_1 (Figure 4), this scatter is also present in Δcp_2. In the difference $\Delta cp_1 - \Delta cp_2$ this scatter is almost leveled out. It is proposed to use $\Delta cp_1 - \Delta cp_2$ as a measure of the crystallisation effect and the crystallinity of PVCs. The crystallinity may be very important for gas pipes, because the rate of absorption of craze inducing aromatics from the natural gas is probably very much dependent on crystallinity(5) (Figure 5). Similar curves were found for PVC, although the rate of absorption was generally lower than for PVC/CPE.

3. The CPE content of PVC/CPE

When a PVC/CPE sample is heated for the second time in the DSC, crystallisation effects have almost disappeared and the double melting endotherm of CPE has merged into a single one. The area of this peak is probably a measure of the CPE content, if the same kind of CPE is present, as in our case. ΔH of two different PVC/CPEs was 0.33 and 1.19 Joule/g respectively. The first sample has an E modulus twice as high as the second sample probably due to a lower CPE content. Quantitative values of the CPE contents are not yet available.

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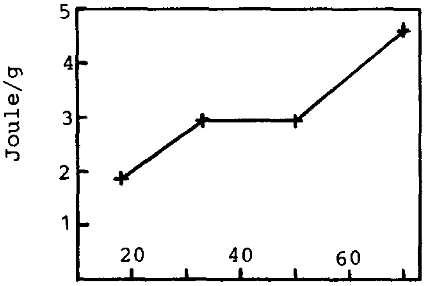


Figure 1. Peak A vs. degree of gelation (PVC/CPE)

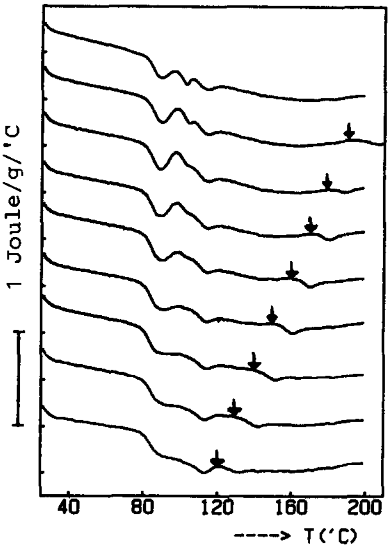


Figure 2. Influence of temperature T_1 on DSC curve (PVC/CPE)

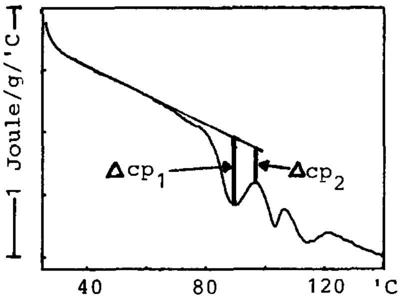


Figure 3. Definition of Δcp_1 and Δcp_2 (PVC/CPE)

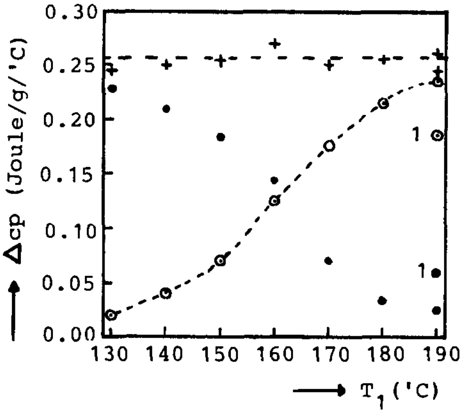
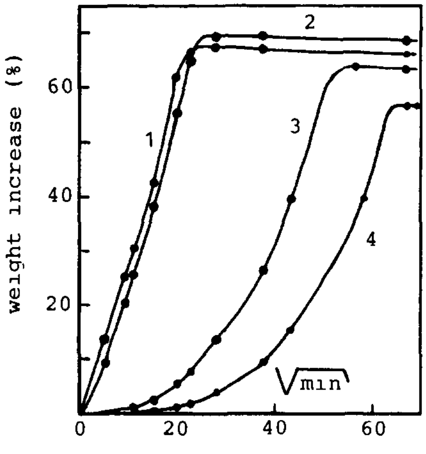


Figure 4. Influence of T_1 on Δcp_1 and Δcp_2 (PVC/CPE)

+= Δcp_1, ●=Δcp_2, ⊙=$\Delta cp_1 - \Delta cp_2$

1 : not immediately quenched



1: Outside surface 2: Quenched from 165 'C. 3: Cooling 10 'C/min. 4: 17 h at 120 'C. m=37 mg

Figure 5. Absorption of liquid toluene in PVC/CPE