Correlation between viscoelastic behaviour and small angle X-ray scattering of thermo-reversible polyvinyl chloride gels

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During the thermo-reversible ageing process of 10% solutions of polyvinyl chloride in di(2-ethylhexyl)-phthalate (DOP) as well as in Reomol ATM, the small angle X-ray scattering and the storage modulus were measured. The ageing of polyvinyl chloride proceeds in Reomol much faster than in DOP. A clear correlation between the storage modulus and the crystalline structure in the gels during the ageing process is shown. The distance between the crystallites appears to be independent of the degree of ageing, in DOP as well as in Reomol. In both cases this distance is estimated to be ~300 Å.

INTRODUCTION

It is generally accepted that hard and plasticized polyvinyl chloride show a certain degree of crystallinity[1–8], assuming that this crystallinity persists above the softening point temperature of PVC. The work reported here carried on from an investigation made by Te Nijenhuis and Dijkstra[7] into the ageing of a moderately concentrated PVC/DOP system. Such a system, containing 10% (w/w) PVC, transforms into a gel at temperatures below 110°C. The ageing of the gel can be observed from the rise of the storage modulus, G', with time. The kinetics of ageing suggest that the crosslinks in the PVC network, in the gel, are formed by crystallites[7,8] (see *Figure 1*). Literature, however, does not provide evidence of the presence of crystallites in such highly dilute systems. In this work the presence of PVC crystallites in the gel is confirmed by means of the small angle X-ray scattering (SAXS) technique. A relationship is also established between the rise of the storage modulus and the increase in crystallinity during ageing. As well as DOP, a second plasticizer, Reomol, has been used in the investigations.

EXPERIMENTAL

Preparation of sample

The polyvinyl chloride used was Solvic 239, a suspension polymer made by Solvay. Its weight-average molecular weight, $\bar{M}_w$, was 240 000, determined by means of the light scattering technique. The plasticizers applied were di-(2-ethylhexyl)phthalate (DOP) by Fluka, and Reomol ATM by Ciba Geigy. Reomol is the trimellitic acid ester of alphanol 79, a mixture of branched alcohols. All samples had the same composition, expressed in weight percentages, viz 9.9% PVC, 89.9% plasticizer, and 0.2% stabilizer. The stabilizer consisted of 80% dibutyl tindilaurate and 20% zincstearate. The solutions were prepared by heating the thoroughly mixed slurry for 20 min at 160°C in a thick-walled glass tube. After filling, the tube was evacuated for several hours. To remove any trace of oxygen, the tube was occasionally flushed with nitrogen, after which it was sealed. During heating it was constantly turned end over end. In this way the PVC was dissolved in the plasticizer to form a clear solution.

The dynamic viscometer

For the measurement of the storage and loss moduli, G' and G'', use was made of a dynamic viscometer designed by one of the authors[8]. This apparatus is an improved version of Den Otter's dynamic viscometer[9,10], which is based on a principle developed by Morrison, Zapas and De Witt[11]. Accurate data can be obtained in the range of very low frequencies, and also in those cases where the phase angle differs slightly from either zero or ninety degrees.

The apparatus was filled with the solution at 150°C, and the temperature was maintained for 20 min, after which the viscometer was cooled quickly to the desired ageing temperature. The ageing temperature was varied from −20 to 110°C.

The Kratky camera

The SAXS measurements were made with a Kratky U-slit collimated camera[12] using CuKα radiation monochromated by a nickel filter in the primary beam. In this camera the sample is irradiated by an X-ray beam of line-shaped cross section, to give so-called smeared scattering patterns. The intensity of the scattered beam was measured by counting the number of pulses per unit time by means of a proportional counter and a pulse height discriminator, which improves the monochromatization. To eliminate the influence of variations in the intensity of the primary beam, the scattered intensity is presented

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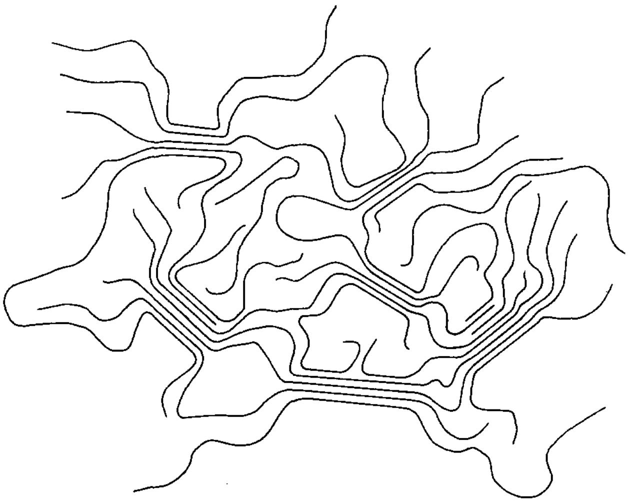

Figure 1 Schematic view of a gel network of PVC/plasticizer systems. The multifunctional crosslinks are formed by crystallites

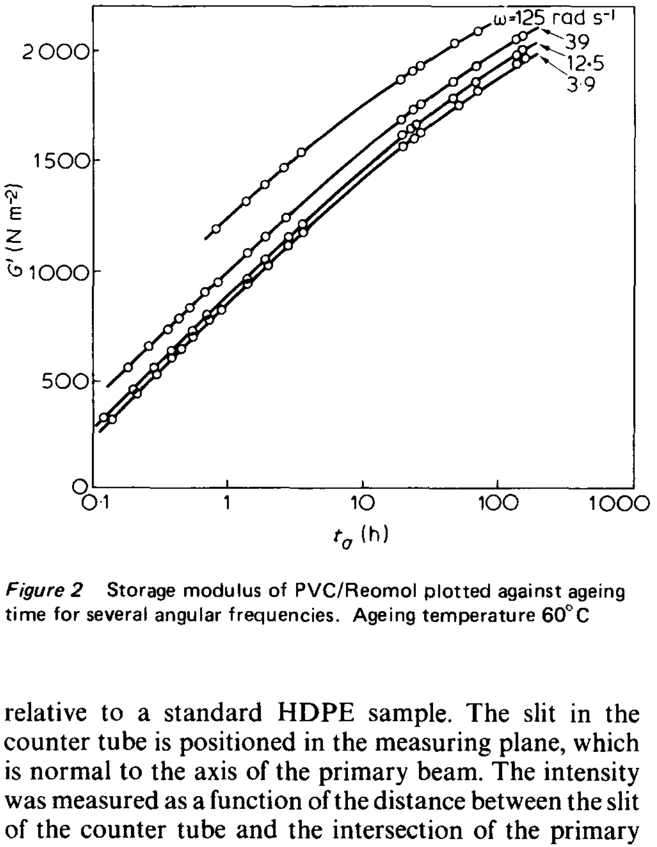

Figure 2 Storage modulus of PVC/Reomol plotted against ageing time for several angular frequencies. Ageing temperature 60°C

relative to a standard HDPE sample. The slit in the counter tube is positioned in the measuring plane, which is normal to the axis of the primary beam. The intensity was measured as a function of the distance between the slit of the counter tube and the intersection of the primary beam with the measuring plane. Between this distance and the scattering angle the following relation exists (providing the scattering angle is small):

$$2\theta = m/a, \qquad (1)$$

with 2θ being the scattering angle (rads), m the distance between the slit and the primary beam in the measuring plane (mm), and a the distance between the sample and the measuring plane (mm). The latter distance was 215 mm, so that, with $m = 1$ mm, we have $2\theta = 4.65 \times 10^{-3}$ rads. A glass capillary was filled with the solution and conditioned at 150°C. The sample was then cooled to the desired ageing temperature and introduced into the camera, which was thermostated at the same temperature.

The course of the scattering intensity with ageing time was measured for a limited number of scattering angles in a time span of 24 h. The gel was then rejuvenated at 150°C for 20 min and the procedure repeated at another scattering angle.

In this way the entire scattering pattern could be determined. It had been found already, from dynamic-mechanical measurements, that the ageing process is not affected by a repeated rejuvenation of the gel at 150°C[7,8] — the ageing process is thermo-reversible.

RESULTS

Dynamic mechanical measurements

Dynamic mechanical measurements have been described for the PVC/DOP system[7,8]. The change of the storage modulus with time is similar for PVC/Reomol and PVC/DOP. *Figure 2* shows, for various frequencies, the storage modulus of the PVC/Reomol system as a function of the logarithm of the ageing time, $\log t_a$, at an ageing temperature of 60°C. With short ageing times ($t_a < 3$ h), there is a linear relation between G' and $\log t_a$, with the slope being virtually independent of the angular frequency. When the ageing time increases, the curves flatten out the slope $\mathrm{d}G'/d \log t_a$ becomes smaller as the ageing time increases. *Figure 3*, showing the ageing curves for a temperature of 80°C, indicates that there is an initial period of non-linear behaviour before the curves begin to show linearity to run parallel to each other. *Figure 3* also shows the change of the storage modulus of the PVC/DOP system for virtually the same ageing temperature (79°C). It appears that the ageing curves are analogous in shape, however, the ageing process is considerably slower in PVC/DOP than in PVC/Reomol. At an ageing temperature of 80°C it takes over 100 h for the curves to begin flattening out.

Figure 4 gives a log–log representation of the storage modulus of PVC/Reomol as a function of the frequency at an ageing temperature of 110°C. This figure shows the gradual formation of a rubber plateau. When the ageing time is short (0.3 h), the system behaves like a liquid, the storage modulus being strongly dependent on the fre-

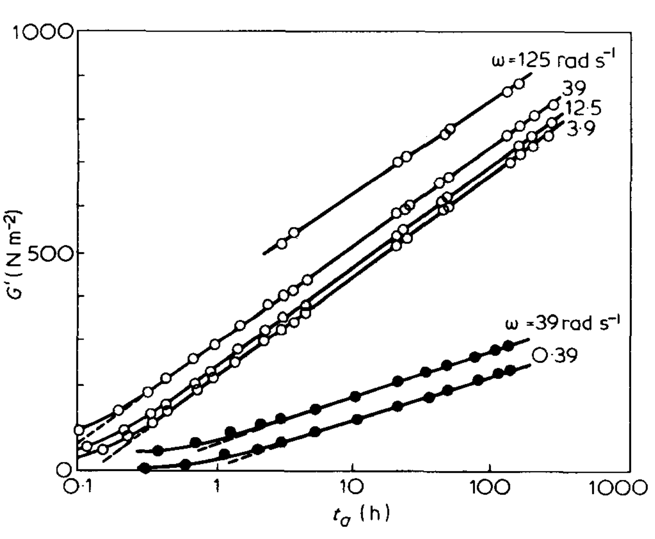

Figure 3 Storage modulus of PVC/Reomol (open symbols) and PVC/DOP (filled symbols) plotted against ageing time for several angular frequencies. Ageing temperatures 80 and 79°C respectively

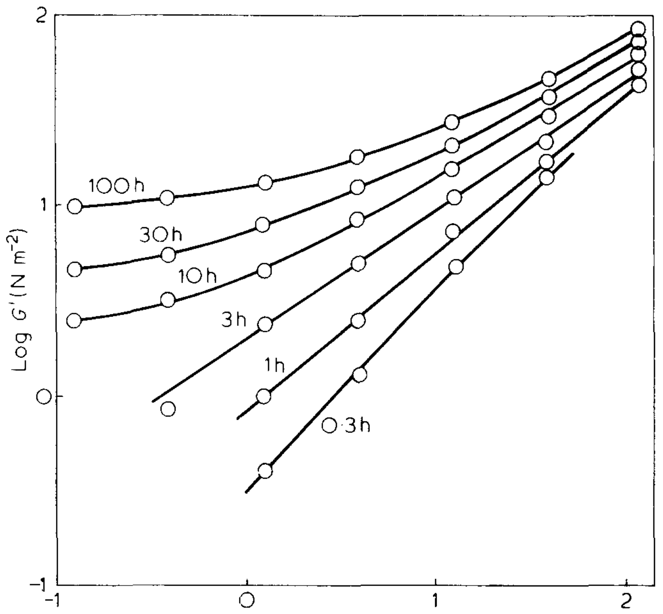

Figure 4 Storage modulus of PVC/Reomol plotted against angular frequency for several ageing times. Ageing temperature 110°C

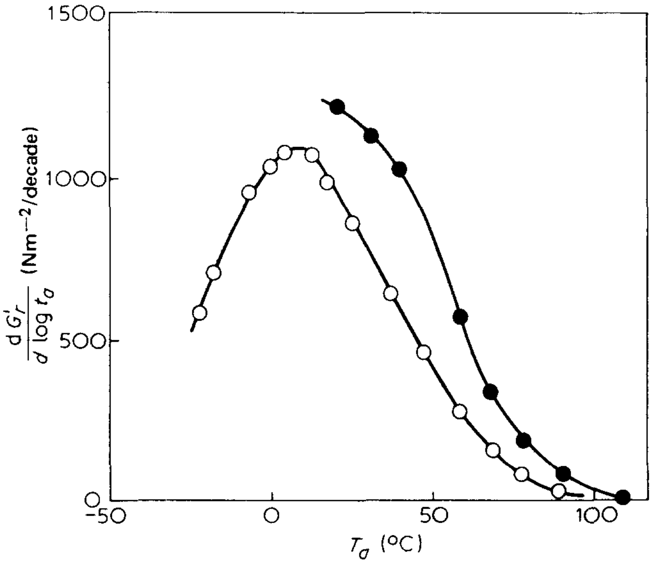

Figure 5 Reduced rate of ageing, dG'/d log t_a, of PVC/Reomol (●) and of PVC/DOP (○). Reference temperature 25.7°C

quency. However, as ageing proceeds, the (low-frequency) storage modulus becomes independent of the frequency, i.e. the system becomes rubberlike. The PVC/DOP system does not show development of such a rubber plateau even after 140 h ageing at 110°C[7,8].

The measure of the 'rate of ageing' used by the authors is the slope of the linear section of the ageing curve, dG'/dlogt_a. For the PVC/DOP system this slope is virtually independent of the frequency, and therefore equal to dG_e/dlogt_a, with G_e being the low-frequency limit of G'. Likewise for PVC/Reomol the slope at the lowest frequency is virtually independent of the frequency, but at higher frequencies it decreases. The measure of the rate of ageing used here is the slope at the low frequencies. The frequency dependence of the slope for the PVC/Reomol system is less distinct as the ageing temperature is higher; beyond 80°C this dependence no longer exists. A possible explanation of this phenomenon is that as the temperature decreases and the frequency increases, the (dynamic) glass–rubber transition is approached. At the glass–rubber transition the dependence of the storage modulus on the structure of PVC/plasticizer systems is weak, so that the increase of the storage modulus will be small in this temperature range of the ageing process.

Figure 5 shows the rate of ageing as a function of the ageing temperature for both PVC/plasticizer systems. Subscript r indicates that the moduli measured at the various ageing temperatures were reduced to a single reference temperature T_0 (25.7°C) for the purpose of comparison[13]:

$$G_r' = G'(T_0) = G'(T)c_0 T_0/(cT) \qquad (2)$$

where c and c_0 are the concentrations, in kg m^{-3}, at temperatures T and T_0, respectively.

Notably the curve indicating the change in the rate of ageing of the PVC/DOP system shows a clear resemblance to a crystallization curve (denoting the rate of crystallization as a function of temperature). For the rate of ageing of the PVC/Reomol system no maximum was found. At temperatures below 20°C the ageing process of this system is so fast that, as a consequence of the corresponding shrinkage, the gel is released from the walls

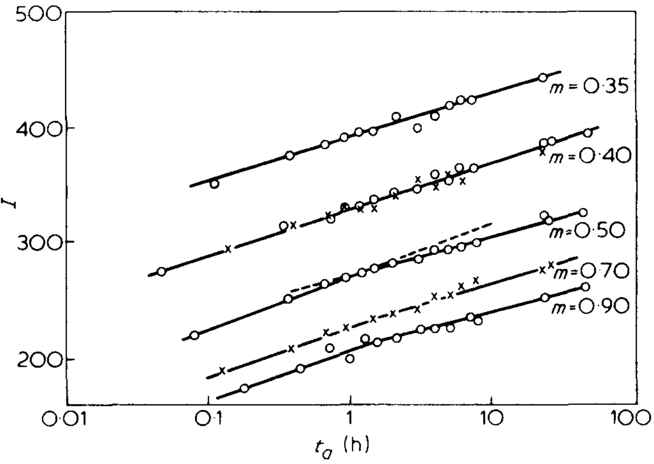

Figure 6 Scattering intensity of PVC/DOP plotted against ageing time for several scattering angles. Ageing temperature 28.5°C. The different symbols refer to different samples

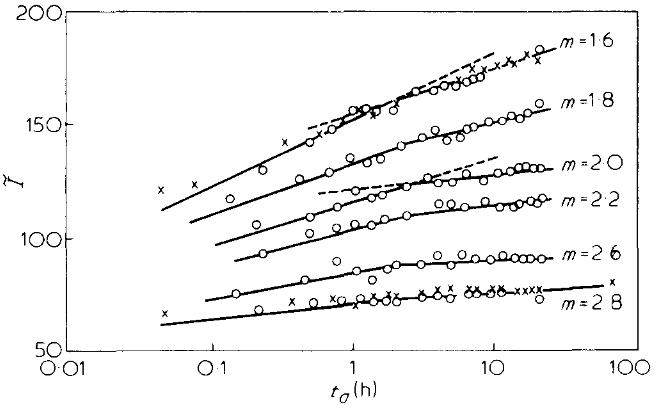

Figure 7 Scattering intensity of PVC/Reomol plotted against ageing time for several scattering angles. Ageing temperature 28.5°C. The different symbols refer to different samples

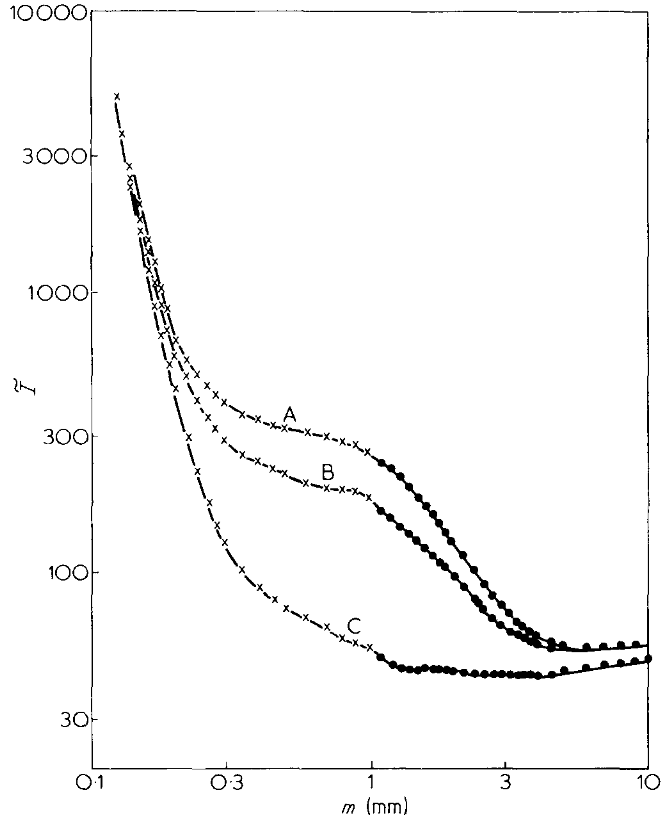

Figure 8 Scattering curves at 28.5°C. A and B PVC/Reomol after 10 and 0.1 h of ageing respectively; C Reomol. Slit width 60 μ (●) and 30 μ (x)

of the measuring cell. This makes measurements of the dynamic mechanical properties impossible.

Information on the change in the loss modulus, G'', is given by refs 7 and 8.

Small angle X-ray scattering

Intensity of the scattered radiation. The ageing process could also be studied by means of SAXS.

All measurements were performed at 28.5°C. *Figures 6* and *7* show, for the PVC/DOP and the PVC/Reomol system, respectively, the change of $\tilde{I}(m)$ — the intensity of the scattered radiation — as a function of the ageing time, with the scattering angle as parameter. Like the storage modulus, $\tilde{I}(m)$ bears a linear relation to $\log t_a$. As the scattering angle becomes larger, the dependence of $\tilde{I}(m)$ on the ageing time becomes less pronounced, until $\tilde{I}(m)$ remains constant at large scattering angles.

In a certain range of angles the $\tilde{I}(m)$ vs. $\log t_a$ curves show a change in slope. The slope continues at a smaller angle. For PVC/DOP this transition occurs ~1.5 h after the start of the ageing process (*Figure 6*), reaching from $m = 0.50$ mm to $m = 1.80$ mm.

In the case of PVC/Reomol the transition is distinct (*Figure 7*). It occurs after ~2.5 h and extends from $m = 1.00$ to those values of m at which the intensity no longer changes with time. With this system, another such transition occurs from the smallest angle to $m = 0.70$ mm after ~10 h.

The PVC/Reomol system was also subjected to measurements with a smaller camera slit (30 instead of 60 microns). This gives a more reliable value for $\tilde{I}(m)$ at the smallest angles. Like the dynamic mechanical measurements, the SAXS measurements can be reproduced after rejuvenation of the PVC/plasticizer system for a short time at 150°C.

Smeared scattering patterns. The $\tilde{I}(m)$ vs. $\log t_a$ curves were used to compose the smeared $\tilde{I}(m)$ vs. m scattering patterns for different ageing times. As an example, *Figure 8* gives the scattering patterns of the PVC/Reomol system after ageing for 0.1 and 10 h.

The patterns obtained in this way still contain contributions from the camera background and the plasticizer. In *Figure 9* the $\tilde{I}-\tilde{I}_{\mathrm{solv}}$ vs. , scattering patterns of the PVC/DOP system after ageing times of 0.1, 1.0 and 10 h have been corrected for these factors. *Figure 10* gives similar patterns for the PVC/Reomol system. The patterns for both systems show a shoulder, which is more distinct in the case of the PVC/Reomol system.

Smear-corrected scattering patterns. The 'smeared' scattering patterns determined by means of the Kratky camera were 'de-smeared'. By means of a computer program[14] the smeared patterns were processed to give scattering patterns such as would have been obtained with an X-ray beam of point-shaped instead of line-shaped section. In general, such patterns show more relief, and give more information on the size structure of the material investigated. *Figures 11* and *12* give the de-smeared patterns for the two PVC/plasticizer systems. These patterns show a secondary maximum corresponding to the shoulder in the original patterns. From the position of this maximum a 'long distance' can be derived by means of Bragg's law:

$$d = \frac{\lambda}{2\sin\theta} \approx \frac{\lambda}{2\theta} \approx \frac{a\lambda}{m} \tag{3}$$

with d = long distance (Å), and λ = wavelength of the X-rays (Å).

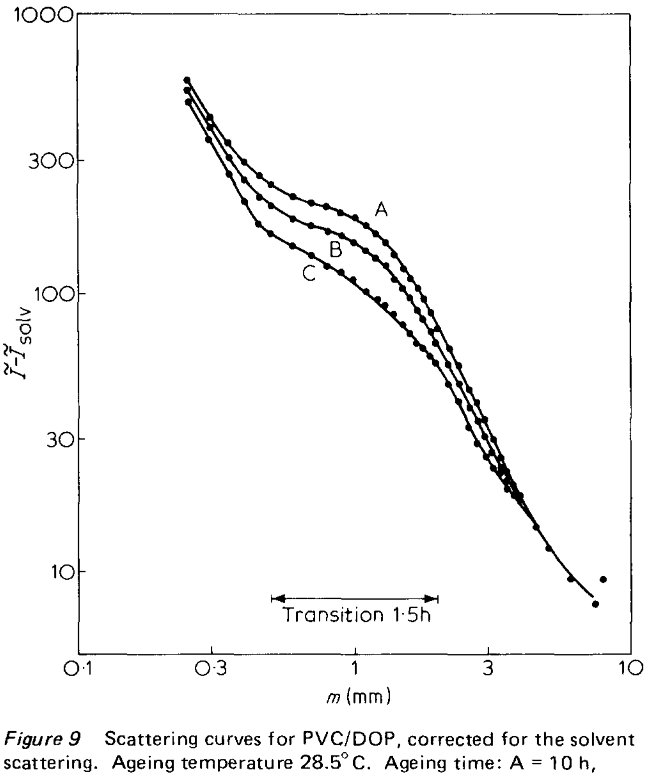

Figure 9 Scattering curves for PVC/DOP, corrected for the solvent scattering. Ageing temperature 28.5°C. Ageing time: A = 10 h, B = 1 h, C = 0.1 h

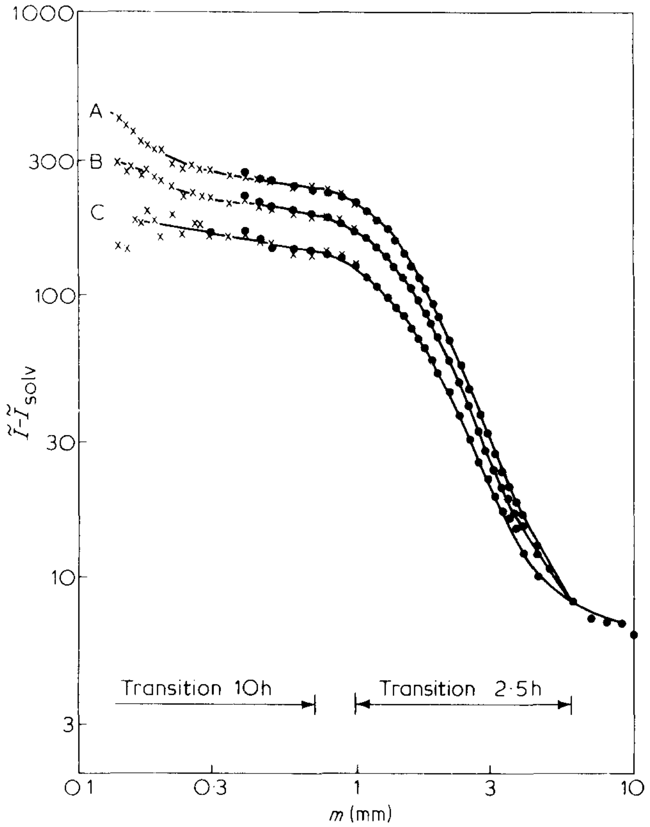

Figure 10 Scattering curves for PVC/Reomol, corrected for the solvent scattering. Ageing temperature 28.5°C. A, B and C 10, 1 and 0.1 h of ageing respectively. Slit width 60 μ (●) and 30 μ (x)

For both PVC/plasticizer systems, the maximum is at about $m = 1.0$ mm. This corresponds to a 'long distance' of 330 Å. The 'long distance' has the same value for both systems and does not vary with time.

The invariant. $\tilde{Q}$ is a measure of the volume fraction of the disperse phase. It is given by:

$$\tilde{Q} = \int_0^{\prime} \tilde{I}(m) m \, dm \tag{4}$$

The relation between the invariant and the volume fraction of the disperse phase is given by:

$$w_1 = C\tilde{Q} \tag{5}$$

w_1 is the volume fraction of the disperse phase. For the calculation of the constant C, refer to the appendix. To determine the invariant, the scattering, already corrected for the contributions of the plasticizer and the camera background, has been additionally corrected for contributions by the amorphous PVC scattering. It was assumed that the amorphous scattering, $\tilde{I}_a$, has the same value throughout the angular range[15]. The amorphous scattering was determined at large angles, where there are no other contributions to the scattering pattern.

Figures 13 and *14* show, for the two PVC/plasticizer systems, the change of $(\tilde{I} - \tilde{I}_s - \tilde{I}_a) \cdot m$ as a function of m, with the ageing time as parameter. Extrapolation towards $m = 0$ was carried out as indicated. As appears from *Figure 13*, the influence of the primary beam is smaller when the measurements are made with a narrower slit. This is the reason why the extrapolation shown in *Figure 13* was performed in the way indicated. The area under the curve equals the invariant. *Figure 15* shows the invariant plotted as a function of the ageing time. It is seen that the crystallinity increases linearly as a function of $\log t_a$ (see also the appendix). The increase is stronger for the

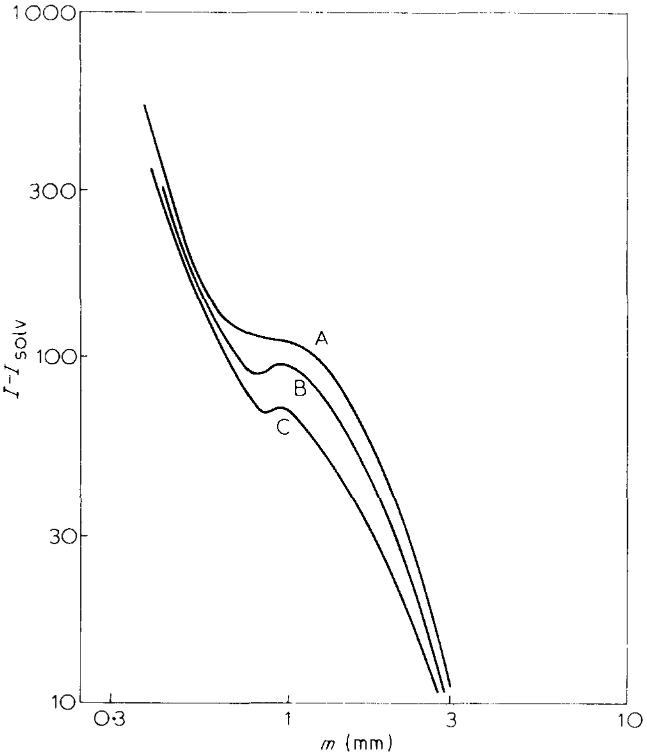

Figure 11 Desmeared scattering curves for PVC/DOP, corrected for the solvent-scattering. Ageing temperature 28.5°C. Ageing time: A = 10 h; B = 1 h; C = 0.1 h

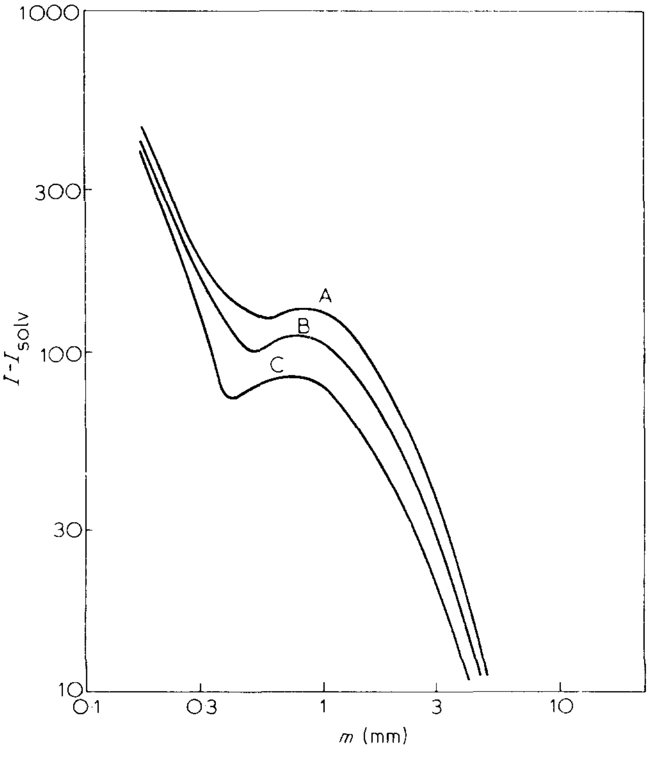

Figure 12 Desmeared scattering curves for PVC/Reomol, corrected for the solvent-scattering. Ageing temperature 28.5°C. Ageing time: A = 10 h, B = 1 h; C = 0.1 h

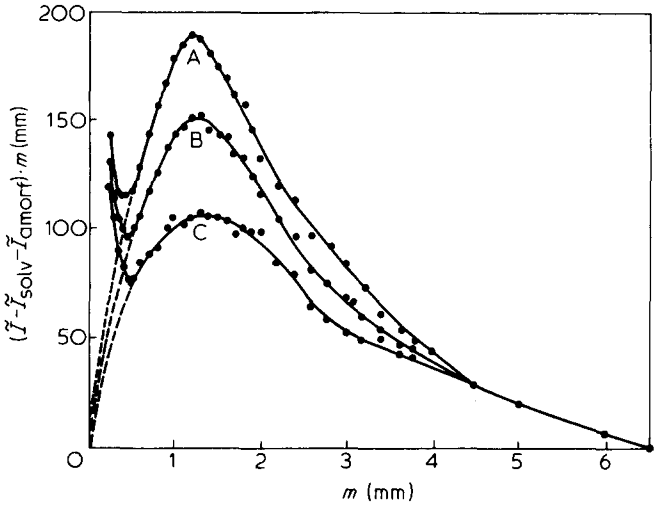

Figure 13 Scattering intensity, corrected for scattering of the solvent and the amorphous fraction, multiplied by the scattering angle, for PVC/DOP. Ageing temperature 28.5°C. Ageing time: A = 10 h, B = 1 h, C = 0.1 h

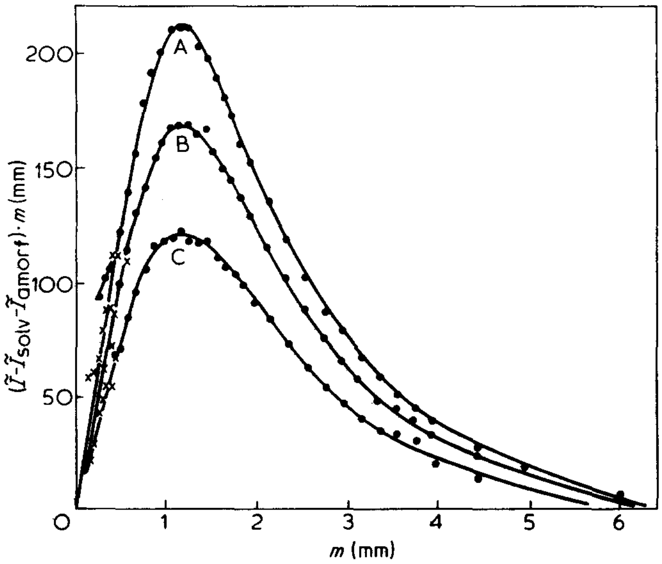

Figure 14 Scattering intensity, corrected for scattering of the solvent and the amorphous fraction, multiplied by the scattering angle, for PVC/Reomol. Ageing temperature 28.5°C. Slit width 60 μ (●) and 30 μ (x). Ageing time: A = 10 h, B = 1 h, C = 0.1 h

PVC/Reomol system. The maximum in the graph for the invariant corresponds to the shoulder in the de-smeared scattering patterns. For both PVC/plasticizer systems the maximum is situated at $\sim m = 1.25$ mm. This value does not change with time, indicating indeed, that the long distance does not change with time either. According to Bragg's law $m = 1.25$ mm corresponds to a long distance of ~270 Å.

DISCUSSION

Correlation between rigidity and crystallinity

The dynamic mechanical measurements show that the rigidity (G') of the PVC gels increases with ageing time. The SAXS measurements indicate an increase in structuring ($\tilde{Q}$) with ageing time. Both increases bear a linear relation to the logarithm of the ageing time and are thermoreversible. After 25 h of ageing at 28.5°C the $\tilde{I}$ vs. $\log t_a$ curves as well as the G' vs. $\log t_a$ curves of the PVC/Reomol gel develop a transition. From this one can conclude that the increase in structuring and the increase of the rigidity must be attributed to the same process. This could be the consequence of a crystallization process because:

(1) The curve indicating the change of the ageing rate as a function of temperature (*Figure 5*) shows strong resemblance to a crystallization curve.

(2) The process is thermo-reversible.

(3) During the process some of the material assumes a particulate structure.

The presence of crystalline PVC could not be proved by wide-angle X-ray diffraction.

A reasonable explanation for the very low (not detectable) intensity of the wide-angle X-ray diffraction (WAXD) could be: small degree of crystallinity, poor ordering within the crystallites and their small dimensions. It was not possible to prove the presence of crystallinity by differential scanning calorimetry (d.s.c.): no melting peak could be detected. However, the maximum crystallinity in our systems is only 1% by volume and in reality much lower.

The increase of the storage modulus is caused by an increase in the number of elastically effective chains

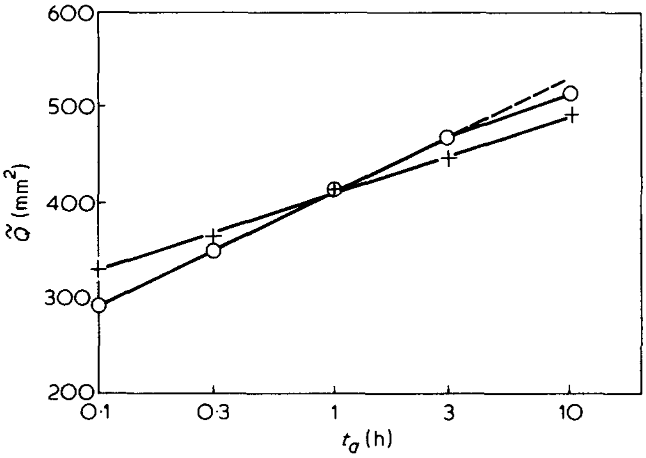

Figure 15 The invariant of PVC/DOP (○) and of PVC/Reomol (+) plotted against ageing time. Ageing temperature 28.5°C

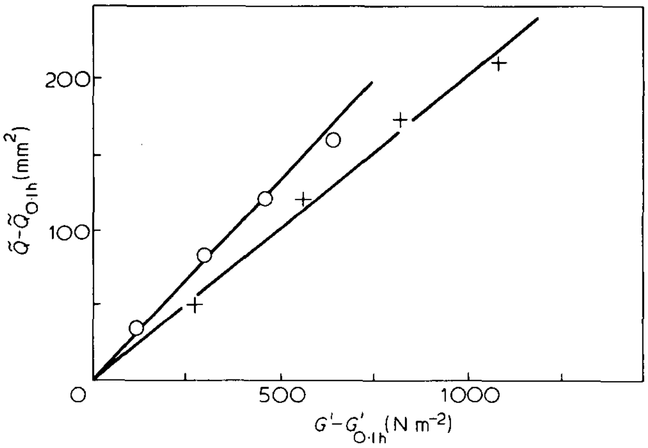

Figure 16 Increase of the invariant of PVC/DOP (○) and of PVC/Reomol (+) plotted against the increase of the storage modulus after 0.1 h of ageing. Ageing temperature 28.5°C

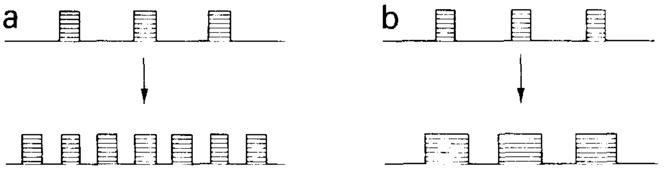

Figure 17 Schematic view of possible causes of the increase of scattering intensity during the ageing process: (a) the number of crystallites increases; (b) the size of the crystallites increases

between crosslinks. This latter increase can be the consequence of an increase in the number of multifunctional cross-links (increase of the number of crystallites) and/or an increase of the functionality of the crosslinks (growth of the crystallites).

Figure 16 shows the relation between the modulus G' and the volume fraction of crystalline PVC, of which $\tilde{Q}$ is a measure. Possible contributions by structures not changing with time are eliminated in a somewhat arbitrary way by subtracting their values after 0.1 h ageing.

It would be better to subtract the $\tilde{Q}$ value of a non-aged system. However, this would require measurements at 150°C, for which the apparatus is not yet suitable.

Figure 16 shows that a linear relationship exists between the volume fraction of the crystalline phase and the modulus. The PVC/DOP system has a lower modulus at a given value of the invariant, than the PVC/Reomol system. The following explanations could apply here:

(1) The number of elastically effective network chains is lower for a given volume fraction of the crystalline phase, which causes the modulus to be lower.

(2) The difference in density between the crystalline phase and the amorphous PVC/DOP phase is greater, so that for a given volume fraction of the crystalline phase the invariant has a higher value.

Structure

Figures 11 and *12* show an increasing intensity of the scattering when ageing proceeds. This is the consequence of increase of the number of crystallites (see *Figure 17a*) and/or increase of the size of the crystallites (see *Figure 17b*) or ordering within them. From the de-smeared scattering patterns (*Figures 11* and *12*) a 'long distance' of $\sim$330 Å could be derived for both PVC/plasticizer systems. The $\tilde{I}\cdot m$ vs. m curves (*Figures 13* and *14*) indicate a 'long distance' of $\sim$270 Å. A discrepancy exists between these values. Although the value of the 'long distance' calculated from the $\tilde{I}\cdot m$ vs. m is preferred, as a consequence of the lower accuracy of the maximum in the de-smeared scattering patterns, one can conclude that the 'long distance' has a value of 300 ± 30 Å. However, more important than the exact value of the 'long distance' is the fact that it does not change when ageing proceeds. The increase of the intensity of the scattering patterns is attended with a simultaneous increase of the storage modulus, indicating that the increase of ordered structure causes an increase of the number of elastically effective network chains between crosslinks.

The following three structural models for the ageing of PVC gels can now be developed:

(1) The crystalline phase is composed of clusters of more or less equidistant lamellae;

(a) as ageing proceeds the number of lamellae increases.

(b) as ageing proceeds the number of lamellae remains constant but the crystalline ordering within the lamellae increases.

(2) There is a uniform distribution (a more or less cubic lattice) of PVC crystallites throughout the system (see *Figure 18*) as ageing proceeds, the crystallites grow in size, but their number and location remain the same.

Model (1a) corresponds to an increasing intensity of the X-ray scattering with ageing time because the total amount of crystalline phase increases, and with an increasing distinction of the 'long distance'-maximum, because of the increasing expansion of the ordering.

Models (1b) and (2) correspond to an increasing intensity of the X-ray scattering only and no increase of the distinction of the maximum shall be detected because there is no increase of spatial ordering between the crystallites.

Model (2) corresponds to an increasing functionality of the crosslinks and hence with an increasing storage modulus whereas Model (1b) corresponds to a constant functionality and so to a constant storage modulus.

From these considerations one can conclude that the structure of the PVC gel fits in best with Model (2) because an increase of the storage modulus is observed but there is no increase of distinction of the maximum (see *Figures 11* and *12*). Also it is more probable that there is a structure of crystallites not increasing in number, if it is assumed that the structure of the gel is determined already before the ageing process starts. It is likely that during the treatment of the PVC/plasticizer systems at 150°C no molecular solution is formed, but that PVC agglomerates remain present which, after quenching, form crystallites. The existence of PVC agglomerates agrees with the structures found in PVC melts[16–18]. It is assumed that during the formation of the PVC melt the powder grains disintegrate to form particles which continue in existence in the melt at high temperature and under great shear stresses. These particles in the melt contain non-melted crystal structures. As in the formation of the PVC melt, the powder grains will also disintegrate when the PVC/plasticizer system is treated at 150°C. The powder particles would swell in the plasticizer, but the crystallites contained in the starting material would remain (partly melted or in the form of agglomerates) and appear again during ageing. The number of nuclei playing a role during ageing would depend on the ageing temperature, being higher as the temperature is lower. The nuclei would be formed at the

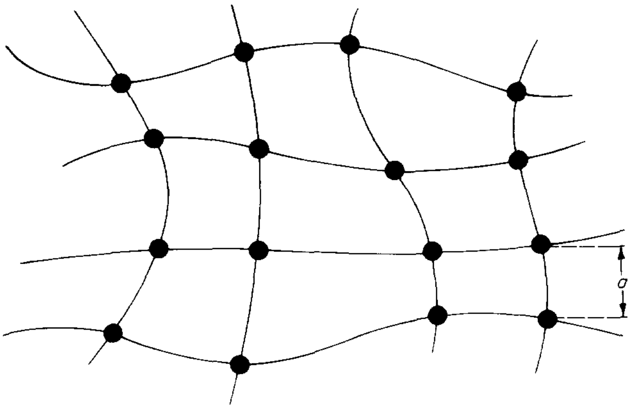

Figure 18 Schematic view of the paracrystalline lattice in gels. The mean value of *a* is the 'long distance'

Table 1 The invariant and the volume fraction of the crystalline phase as a function of the ageing time

t_a (h)	$\tilde{Q}$ (mm^2)	w_1
0.1	332	0.008
1	416	0.010
10	492	0.012

Table 2 Corrected values of the crystallinity of PVC as a function of the ageing time

Ageing time (h)	Crystallinity of PVC (%)
0.1	1.8
1	3.8
10	5.8

start of the ageing process, and then grow into crystallites. Therefore it is easy to understand that the 'long distance' does not change during ageing. Also Ohta and coworkers[19] arrive at the conclusion that the formation of nuclei occurs only at the start of the crystallization process. They conclude this from measurements of the crystallization kinetics of PVC melts carried out by means of d.s.c. Gezovich and Geil[4] found an increase in the long distance with increasing plasticizer content. This agrees with the model proposed here: as the plasticizer content rises, the swelling will become greater, as will the distance between the partly melted crystallites or agglomerates. The increase of the intensity of the scattering patterns is coupled with a simultaneous increase of the storage modulus, indicating that the increase of ordered structure causes an increase of the number of elastically effective network chains between crosslinks.

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APPENDIX

The relation between the invariant and the crystalline fraction is given by:

$$w_1 = \frac{1}{(\rho_{e1}-\rho_{e2})^2}\cdot\frac{2\pi}{i_e\cdot \mathrm{N}^2\lambda^3}\cdot\frac{1}{aD}\cdot\frac{0.0162}{a\cdot Tr}\cdot Q \qquad (6)$$

with: w_1 = volume fraction of the crystalline phase; $\rho_{e1}-\rho_{e2}$ = difference in electron density between crystalline phase and amorphous phase (about 0.2×10^{-3} mol·el/mm^3); i_e = Thompson scattering constant for a free electron (7.90×10^{-24} mm^2); N = Avogadro's number; λ = wavelength of X-rays (1.54×10^{-7} mm); a = distance between counter slit and sample (205 mm); D = thickness of sample; Tr = transmission by sample; and 0.0162 = calibration factor of standard HDPE sample.

The calculation of the difference in electron density was based on an ideal PVC crystal structure. *Table 1* shows the values of w_1 calculated for the PVC/DOP system for a number of ageing times.

If $w_1 = 0.012$ ($t_a = 10$ h), 12% of the total PVC is in the crystalline form. This is a rather high percentage as the maximum crystalline percentage in PVC is believed to be 10–15%[5].

Assuming that there is not yet any crystallinity at $G' = 0$, other values for the crystallinity can be calculated (*Table 2*), using $\tilde{Q}-\tilde{Q}_0$ instead of $\tilde{Q}$; $\tilde{Q}_0$ is the value of $\tilde{Q}$ at $G' = 0$, obtained by extrapolation of $\tilde{Q}$ vs. G'. This is reasonable because impurities in the commercially used PVC give a contribution to $\tilde{Q}$, independent of time. Although the crystallinity, calculated in this way, has still relatively high values, the results are more compatible with the 10–15% maximum crystallinity in PVC.