

Ageing in wet PVC gels studied by gel-sol transition temperature and Raman spectroscopy

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The ageing of PVC gels made with cyclohexanone has been studied for times up to two weeks by measurement of gel-sol transition temperature and for times up to two years by Raman spectroscopy. The results suggest that the major factor in the ageing of gels of concentration between about 20 and 35% by weight of PVC in cyclohexanone after they are about one day old is that the gels become more homogeneous, with no significant changes in the overall crystallinity or conformational distribution of the PVC taking place. The measurement of gel-sol transition temperature suggests that this process is probably essentially completed within a period of about two weeks but the Raman spectra suggest that there may be some changes in the nature of the PVC-cyclohexanone interaction still taking place for times up to about 150 days and this may be associated with hydrogen bonding.

(Keywords: ageing; gels; PVC; gel-sol transition temperature; Raman spectroscopy)

INTRODUCTION

We have recently shown¹ that Raman spectroscopy can provide useful information about the structure of wet gels of poly(vinyl chloride) (PVC) made with cyclohexanone, i.e. gels with the solvent still present. In this paper we report studies of the ageing of such gels as indicated by changes in the gel-sol transition temperature and in the Raman spectrum.

Upon cooling a solution of PVC in cyclohexanone, a gel will form if the concentration of PVC is $\geq 20\%$. Such gelation is termed thermoreversible because if the gel is heated it will return to the sol state, and this cycle can be repeated indefinitely. The temperature at which the gel turns into the sol is called the gel-sol transition temperature, T_{gs} , but the transition between the two states often exhibits hysteresis², the magnitude of which depends on the polymer and the solvent. The gel-sol transition temperature, T_{gs} , is therefore not necessarily the same as the sol-gel transition temperature, T_{sg} . We have measured T_{gs} , since this can be done by simpler methods. Furthermore, even at low temperature the process of gelation may take a considerable time, and therefore the measurement of T_{sg} requires the gel to be held at each temperature for prolonged periods^{2,3}.

PREPARATION OF GELS

The PVC used was M110/50, a mass polymer of a commercial grade made by the British Petroleum Com-

pany, with $M_n = 68\,000$. The gels were made and their concentrations determined as explained in Reference 1. Gels of concentrations 21.4, 25.9, 26.5 and 34.0% by weight were used.

MEASUREMENT OF THE GEL-SOL TRANSITION TEMPERATURE

Most of the techniques used for finding T_{gs} employ a method for determining the temperature at which the gel yields under a small stress. In the method developed by Paul³ the height of a mercury drop was measured as the temperature of the gel was slowly raised. When the yield stress of the gel is approximately equal to the stress exerted by the mercury drop, the drop will begin to fall. Measurements were taken for drop weights between 1 and 5 g, and the true value of T_{gs} was then found by extrapolation to zero weight. This extrapolation, however, never amounted to more than 2 or 3°C, and Takahashi *et al.*⁴ demonstrated, using steel balls, that if the weight was < 100 mg the correction was negligible. In this study 2 mm steel balls of 32 mg weight were therefore used.

The gel was heated in a glass-walled water bath, the temperature of which was controlled by a heater and stirrer. The scale on the heater was calibrated using a precision thermometer. The gel was immersed in the bath at a temperature roughly 10–15°C below T_{gs} and left for approximately 1 h to reach equilibrium. After this the temperature was increased by 0.5°C every 6 min. After the temperature was adjusted the gel was allowed 5 min to reach equilibrium and then the height of the steel ball was measured using a travelling microscope.

A typical plot of height against temperature is shown in *Figure 1*. As the temperature is increased there is an initial linear decrease in the height of the ball. Each time

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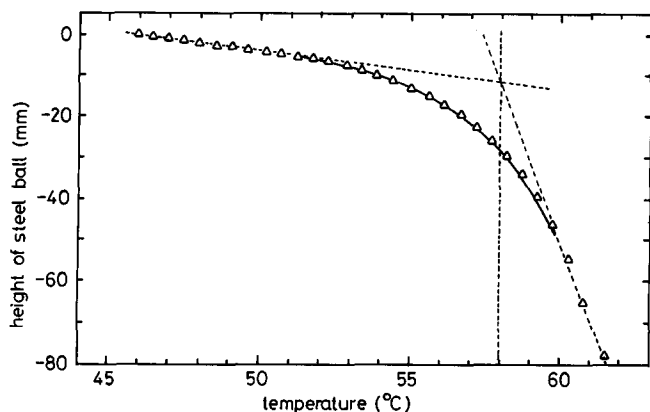


Figure 1 Method for measuring the gel-sol transition temperature

the temperature was raised, however, the ball moved downwards for only the first 2 or 3 min, and then reached an equilibrium position. This initial linear drop is therefore attributed to a decrease in the gel modulus as the temperature is raised. About 2–3°C above T_{gs} the graph is again approximately linear, but with a much steeper gradient. Here the ball does not reach an equilibrium position, and the sample is therefore a viscous solution. At intermediate temperatures close to T_{gs} the height of the ball does not have a simple relationship with temperature. This can probably be attributed to two effects. Just below T_{gs} the weight of the ball is greater than the yield stress of the gel and shearing begins to occur. At temperatures slightly above T_{gs} the infinite gel network no longer exists, but the aggregates of molecules are still very large. As the temperature is increased these aggregates break up fairly quickly, and consequently there is a rapid change in the viscosity of the solution. A reasonably accurate measure of the temperature at which the gel turns into a solution can, however, be obtained by extrapolation of the two linear portions of the graph. Such an extrapolation may not give the true value of T_{gs} , but the inaccuracies are unlikely to be greater than $\pm 1^\circ\text{C}$. The errors in relative measurements of T_{gs} are estimated to be less than $\pm 0.5^\circ\text{C}$.

A gel of $(25.9 \pm 0.5)\%$ concentration was made in a test tube of 24 mm diameter to a depth of approximately 115 mm. The tube was sealed with a polyethylene coated stopper to prevent solvent evaporation. The diameter of the tube was chosen to reduce the thermal lag between the water bath and the centre of the gel, thus allowing the ball to reach an equilibrium position before its height was measured, while minimizing the drag effects from the sides. The sample was left overnight to cool and gel, and a steel ball was then placed approximately 5 mm below the surface using a pair of tweezers. The following day T_{gs} was measured using the method described above and found to be 58°C . The maximum temperature reached was 61.5°C , after which the sample was removed from the water bath and allowed to cool. The following day a second steel ball was inserted in the gel. After again leaving the gel overnight T_{gs} was measured and was found to have increased to 62.7°C . The maximum temperature reached on this run was 65.7°C . Since T_{gs} had increased, the cycle above was repeated until a total of six values of T_{gs} had been obtained. These are shown in Table 1, along with the maximum temperature attained on each run.

The values of T_{gs} are plotted against run number in

Figure 2. The points appear to follow an exponential rise and were therefore fitted with a function of the form

$$T_{gs} = a(1 - e^{-bn}) + c$$

where a , b and c are constants and n is the run number. The fitted curve is also shown in Figure 2. The fit is very good, implying that T_{gs} rises towards a maximum at which a stable equilibrium is reached. The constants were found to have the values $a = 19.2$, $b = 0.704$ and $c = 48.3$. The maximum value of T_{gs} is given by $a + c = 67.5^\circ\text{C}$.

After the six runs shown in Table 1 the sample was heated to 140°C in an oven for approximately 30 min. After the gel had been left overnight to cool, a steel ball was inserted into it and the following day T_{gs} was again measured. It was found to be 57.5°C , a value that is the same, to within experimental error, as that found in run 1. Clearly, whatever effect occurred in runs 1–6, it was reversed by heating, presumably because complete molecular dispersion of the PVC was achieved. Note that in the original preparation of the gels all PVC solutions were held at 140°C for a short time before being allowed to cool and gel.

To determine whether an increase in T_{gs} occurs with time at room temperature the gel was again heated to 140°C for 30 min and then left to age for 12 d (the ball being inserted on the eleventh day). This is the time over which the runs shown in Table 1 were taken, and the value of T_{gs} obtained should therefore be directly comparable with that found in run 6. The value of T_{gs} was found to be 66.1°C , which is shown in Table 1 for comparison. Although this value of T_{gs} is not as high as that found in run 6, it is clear that ageing has taken place.

The increase in T_{gs} described above implies a stabilization of the network structure in the gel. This stabilization appears to be faster at higher temperatures, presumably because of the increased mobility of the PVC molecules.

Table 1 Gel-sol transition temperatures found on different runs

Run number	T_{gs} ($^\circ\text{C}$) ($\pm 0.5^\circ\text{C}$)	Maximum temperature ($^\circ\text{C}$)
1	58.0	61.5
2	62.7	65.7
3	65.3	67.7
4	66.2	68.7
5	66.9	69.2
6	67.2	70.3
Aged	66.1	68.7
Annealed	67.5	69.7

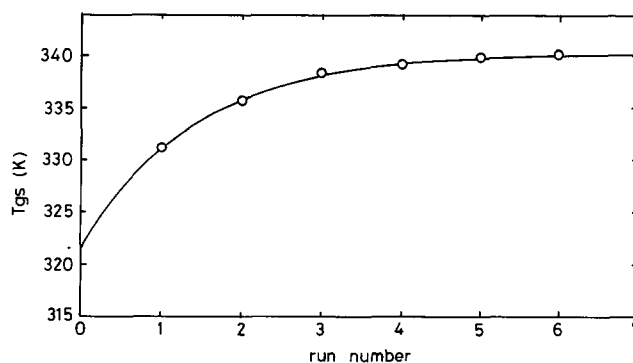


Figure 2 Gel-sol transition temperature, T_{gs} , as a function of run number (days from original preparation of gel = $2 \times$ run no.). \circ , Experimental data; —, fitted exponential

To try to obtain the highest value of T_{gs} , and therefore the most stable network, the gel was annealed in the following way. After heating to 140°C for approximately 30 min to destroy any aggregates, the gel was placed in a silicone oil bath for 16 h at 66°C, which is just below the maximum observed value of T_{gs} . The temperature was then reduced by 2°C every 20 min, finishing at 22°C after a further 7 h. After leaving the gel overnight a steel ball was inserted into it. The following day T_{gs} was measured and was found to be 67.5°C, the asymptotic value in Figure 2. This value is also included in Table 1 for comparison.

Finally, the gel was heated to 140°C for approximately 30 min and T_{gs} measured as for run 1. As before, it was found to have returned, to within experimental error, to its initial value of 58°C. Although no quantitative measurements were taken here, note that the gel became appreciably stiffer as the value of T_{gs} increased.

EFFECT OF AGEING OF GELS ON THE RAMAN SPECTRUM

Several authors^{5,6} have reported ageing effects over periods up to two years, particularly an increase in modulus. To look for any evidence of this ageing in the Raman spectrum, spectra of the 21.4% gel were taken 1, 39, 72 and 739 d after the sample was prepared. Spectra of the 26.5% gel were taken 1, 8, 43, 78 and 438 d after preparation, and spectra of the 34.0% gel were taken after 1, 8, 43, 78 and 761 d. All spectra were obtained in the C-Cl stretching region (540–780 cm^{-1}) using parallel polarizer and analyser polarization directions in the way described in Reference 1. The spectrum of the solvent, which has two strong peaks in this region, was removed by the method also described in Reference 1.

Two major peaks are directly observable in the C-Cl stretching region of PVC, at 635 and 695 cm^{-1} , and the ratio of the heights of these peaks has been shown by the work described in Reference 1 and other work referred to there to be strongly sensitive to changes in molecular conformation and/or crystal structures. This ratio was therefore measured for the gel spectra but was not found

to change significantly with age for any of the three samples, as can be seen in Table 2. To look more closely for any changes in the spectrum due to ageing, for each concentration the spectrum of the 1 d old gel was subtracted from the spectra of the gel after longer ageing times. The spectra were normalized to have the same area before subtraction. This gave four difference spectra for the gel of 26.5% concentration, four for the gel of 34.0% concentration and three for the gel of 21.4% concentration.

The four difference spectra for the 26.5% gel are shown in Figure 3 as an example. Two obvious features show systematic trends, a positive peak at $\approx 646 \text{ cm}^{-1}$ and a negative peak at $\approx 662 \text{ cm}^{-1}$. The heights of these two peaks are shown in Table 3 for the 26.5 and 34.0% gels. These were determined by simple measurements from the plotted spectra. The peak at 646 cm^{-1} was too small to give meaningful measurements for the 21.4% gel, and is therefore not included in the table. In Figure 4 these heights are shown plotted against the difference in ageing times when the spectra were taken.

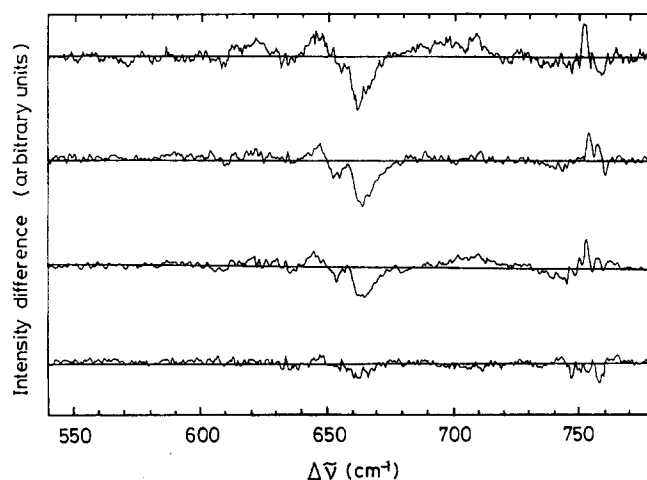


Figure 3 Difference spectra for 26.5% PVC gel at different times after preparation. From bottom to top: 8 d–1 d; 43 d–1 d; 78 d–1 d; 438 d–1 d. The negative peak in the top spectrum is approximately $0.15 \times$ the largest intensity in the original spectra

Table 2 Ratio of the heights of the peaks at 635 and 695 cm^{-1} for spectra taken after various ageing times

Sample concentration (%)	Days after preparation								
	1	8	39	43	72	78	438	739	761
21.4	0.92	–	0.92	–	0.92	–	–	0.92	–
26.5	0.92	0.91	–	0.93	–	0.91	0.93	–	–
34.0	0.94	0.94	–	0.95	–	0.94	–	–	0.95

Table 3 Heights (arbitrary units) of peaks in difference spectra for aged gels^a

Sample concentration (%)	Wavenumber (cm^{-1})	Difference between times when spectra were taken (d)							
		7	38	42	71	77	437	738	760
21.4	662	–	9.0	–	11.5	–	–	16.0	–
26.5	646	1.0	–	5.0	–	7.5	9.5	–	–
	662	6.0	–	15.0	–	21.5	26.0	–	–
34.0	646	1.5	–	3.5	–	4.0	–	–	6.5
	662	1.5	–	12.5	–	12.5	–	–	16.5

^a Errors: for 21.4% gel, ± 3 ; 26.5% and 34.0% gels, ± 2

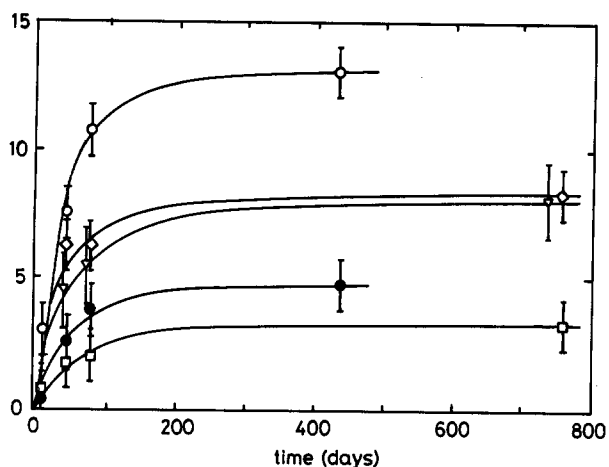


Figure 4 Peak height as a function of ageing time for difference spectra: ∇ , 21.4% gel, 662 cm^{-1} ; \bullet , 26.5% gel, 646 cm^{-1} ; \circ , 26.5% gel, 662 cm^{-1} ; \square , 34.0% gel, 646 cm^{-1} ; \diamond , 34.0% gel, 662 cm^{-1}

DISCUSSION

For ageing times between 1 d and approximately 760 d, it appears to be only small changes in the Raman spectrum. The fact that ageing of PVC–cyclohexanone takes place over at least a two week period is, however, shown clearly by the measurements of the solvent transition temperature. The trend observed in T_{gs} is qualitatively similar to that seen by other authors^{5,6} for the change in gel modulus with ageing time. This suggests that the mechanisms giving rise to both effects are similar. It is worth noting, however, that although an increase in modulus with ageing time is characteristic of all PVC–gel systems, this is not the case for T_{gs} . Yang *et al.*⁷ found that for gels made with dioxane, dimethylthalate, bromobenzene and dichloroethane the values of T_{gs} were independent of ageing, while Harrison *et al.*⁸ reported only a small increase for PVC–dioxane gels. Yang *et al.*⁷ and Dorrestijn *et al.*⁶ found an increase in crystallinity of gels for times up to 24 and 10 h, respectively, but the Raman spectra show that the long term ageing of the present gels does not involve an increase in crystallinity. This is demonstrated clearly by the difference spectra in Figure 3, in which there is no evidence of any change in the intensities at 608 and 653.5 cm^{-1} , where the peaks due to crystalline material were found¹. In fact, the most significant change that occurs in the spectrum is the appearance of two peaks at approximately 646 and 662 cm^{-1} , one of which is positive and the other negative. Figure 4 shows that the heights of these peaks exhibit similar trends with time for each gel. This appears to be an exponential rise which approaches a maximum value after approximately 150 d, which is similar to the variation of gel modulus with ageing time found by Walter⁵. It may be significant, however, that the changes that occur in the spectrum with time are all located around one of the solvent peaks. A positive and a negative peak of this sort are characteristic of the interaction of two peaks which are displaced with respect to each other. It is thus possible that in the gel the peak that occurs at 653.5 cm^{-1} in the pure solvent has shifted with respect to the solvent peak at 750.5 cm^{-1} (which is known to remain in the same position), and that this shift changes with time. The fact that the changes in the spectrum may be associated with the solvent rather than

the PVC is also indicated by the fact that no peak has previously been found in the spectrum of PVC at 662 cm^{-1} . Furthermore, if these changes in the spectrum are associated with conformational changes in the PVC, it is surprising that there is no significant effect on the ratio of the peak heights given in Table 2. There is no obvious reason why the solvent itself should age, and the changes in the spectrum are therefore probably connected with the ageing of the gel network via a change in the polymer solvent interaction.

If the changes observed are associated solely with the solvent spectrum, as they appear to be, then the implication is that any long term ageing that takes place does not alter the concentrations of the various conformations present. Considering the large change in the gel–solvent transition temperature over a two week period, and the increase in gel modulus observed by Walter⁵ over a similar or greater time scale depending on the concentration, this is difficult to explain. A tentative proposal is that ageing in the medium term is connected with inhomogeneities in the gel. If these occur on a significantly smaller scale than the volume of the gel from which Raman scattering is sampled by the spectrophotometer, then the observed spectrum will represent the average conformational and structural state. Presumably, as ageing proceeds the gel becomes more homogeneous. This could produce a change in T_{gs} and the physical properties without there necessarily being any significant change in the Raman spectrum of the PVC.

The changes observed in the Raman spectrum of the solvent could be associated with development of hydrogen bonding between the C=O group of the cyclohexanone and the H atoms of the PVC, since the peak at 653.5 cm^{-1} has been assigned by Rey-Lafon *et al.*⁹ to the $\gamma(\text{C}=\text{O})$ out of plane bending mode. If the frequency of this mode were lowered by hydrogen bonding the effects seen in the spectrum would occur if the degree of hydrogen bonding increased with time. Such changes could be taking place alongside any homogenization and even after this was essentially complete.

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