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Mechanical Properties at the Gel Point of a Crystallizing Poly(vinyl chloride) Solution

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ABSTRACT: PVC plastisols during gelation are found to have the same evolution of mechanical behavior as chemically cross-linking systems. From the analogy between the physical and chemical gelation, we conclude that the PVC plastisol is at its gel point when it exhibits power law relaxation. This makes it possible to measure the gel point directly by using a simple rheological test. The "gel equation" for the stress can be used to model the flow of PVC plastisol gels for processing.

Introduction

Physical gelation is much less understood than chemical gelation. The transient nature of the physical network junctions makes it difficult to study physical gels near their gel point. It is even difficult to give a clear definition of the gel point. In comparison, the gel point of chemically cross-linking systems (1) is clearly defined as the instant at which the weight-average molecular weight diverges to infinity and (2) can be experimentally verified: the system can be dissolved before the gel point, and it does not dissolve beyond the gel point. Chemically cross-linking systems at the gel point were found to follow a limiting behavior, the gel equation of Winter and Chambon[1,2]

$$\tau(t) = S\int_{-\infty}^{t}(t - t')^{-n}\dot{\gamma}(t')\,\mathrm{d}t'; \quad 0 < n < 1 \qquad (1)$$

which describes the stress in a critical gel that is deformed at a rate $\dot{\gamma}(t')$, $-\infty < t' < t$. The front factor, S (Pa s^n), and the relaxation exponent, n, are network characteristic properties. As a consequence, the dynamic mechanical behavior at the gel point is given by dynamic moduli

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (2)$$

and a loss tangent

$$\tan \delta_c = \tan (n\pi/2) \qquad (3)$$

which is independent of frequency.

This knowledge of chemical gelation will, in this study, be applied to poly(vinyl chloride) (PVC) plastisols. The question to answer is whether a physical gel, such as PVC plastisol, transits through an intermediate state at a critical gelation time, t_c, at which it exhibits power law relaxation. This critical time can then be assumed to be the gel point.

Already moderately concentrated solutions of PVC in plasticizers show a strong tendency to form physical, thermoreversible gels. Te Nijenhuis and co-workers followed the aging process of 10% solutions of PVC in various plasticizers by means of dynamic mechanical spectroscopy[3-5] as well as SAXS.[5] It appeared that gels were obtained at temperatures below 110 °C. The modulus increased with increased aging time and decreased aging temperature. The increase of stiffness was accompanied by an increase of crystallinity (see Figure 18 in ref 5).

The mechanism of PVC gelation and the structure of the gel have still not been fully elucidated. However, it is generally accepted that small crystals serve as mechanical cross-links. The exact type of crystalline structure has been the subject of continued investigation[6,7] and will not be discussed here in detail. The crystallization seems to originate from the fact that the tacticity of commercial PVC is not completely random; the molecule prefers a more syndiotactic structure (e.g., 55% syndiotactic and 45% isotactic diads). Increase of the syndiotacticity is attended by an increase in crystallinity in the solid material as well as in solution. A crystallinity of about 0.1% can be calculated if one assumes that only the syndiotacticity is responsible for the crystallinity of PVC. However, model investigations of Juijn et al. showed that crystallinity is also possible if an even number of isotactic sequences is situated between syndiotactic sequences.[8,9] They arrived at a crystallinity of 8.5% for commercial PVC by assuming that at least 12 regular sequences are needed for crystallinity. An improved calculation[3] leads to a crystallinity of 28%, whereas values of 1.5% and 8% were obtained assuming that at least 20 regular sequences are needed. This rather strong tendency to form crystallites can provide a sufficient number of physical cross-links in PVC/plasticizer systems and, thus, explains their extremely rubberlike behavior.

Experimental Section

Materials. The poly(vinyl chloride) (PVC) used was Solvic 239, a suspension polymer of Solvay (M_w = 240 000) with different plasticizers: bis(2-ethylhexyl) phthalate (DOP) from Fluka, dibutyl phthalate (DBP) from Merck, and Reomol ATM from Ciba Geigy. Reomol is the trimellitic acid ester of alphanol 79, a mixture of branched alcohols. All samples had the same composition being expressed in weight percent, i.e., 9.9% PVC, 89.9% plasticizer, and 0.2% stabilizer (consisting of 80% dibutyltin dilaurate and 20% zinc stearate). For this composition the concentration of polymer at 25 °C was 0.10 g/cm^3. The solutions were prepared by heating the thoroughly mixed slurry for 20 min at 160 °C. The tube with the sample was evacuated during several hours. In order to remove oxygen it was flushed with nitrogen occasionally. It was constantly turned end-over-end during the heating.

Apparatus. The PVC solution was transferred into a dynamic rheometer as developed by Te Nijenhuis and Van Donselaar.[10] This apparatus is of the coaxial cylinder type, the inner cylinder being suspended between two torsion wires. To the top of the upper wire a sinusoidal movement is applied. The phase difference between this movement and the resulting movement of the inner cylinder is measured as well as the amplitudes of both angular displacements. Varying the shear amplitude up to γ = 1.2 allowed the linearity of the viscoelastic sample response to be checked. In fact, the calculated moduli were not affected by this variation in strain.

Experimental Results. After the solution was brought into a measuring cell of the dynamic rheometer, a temperature of 150

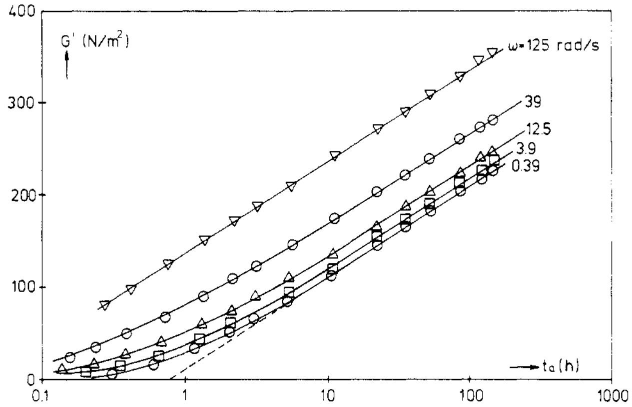

Figure 1. Storage modulus of PVC/DOP plotted against aging time for several angular frequencies. Aging temperature T_a = 79 °C.

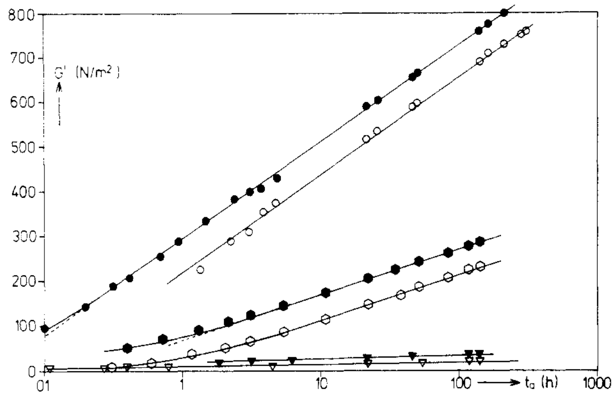

Figure 2. Storage modulus of PVC in different plasticizers plotted against aging time for two angular frequencies: open symbols ω = 0.39 rad/s, solid symbols ω = 39 rad/s. (○, ●) PVC/Reomol; (○, ●) PVC/DOP; (▽, ▼) PVC/DBP; aging temperature T_a = 80 °C.

°C was maintained during 20 min in order to remove traces of crystalline regions as completely as possible. Then the sample was cooled very quickly to the desired aging temperature, T_a, and measurements were started immediately ($t_a = 0$). At a small number of frequencies the moduli were measured as functions of the aging time t_a. As an example, in Figure 1 the storage moduli are shown as a function of the aging time at an aging temperature of 79 °C for the PVC/DOP system. It appears that, after some induction period, the storage moduli become linear functions of the logarithm of the aging time with slopes independent of the frequency. In Figure 2 the storage moduli are shown as a function of the aging times at an aging temperature of 80 °C for the three PVC/plasticizer systems. Again, the storage moduli became linear functions of log t_a with corresponding slopes independent of angular frequency. The aging process of PVC/Reomol is the quickest one, that of PVC/DBP the slowest one. By intersection of these kind of curves, shown in Figures 1 and 2, at certain aging times the moduli can be obtained as a function of the frequency, with the aging time as a parameter. The resulting modulus curves are shown in Figure 3 for PVC/DOP at 90 °C. At short aging times, $t_a < 0.2$ h, the behavior of the system is liquidlike, the storage modulus being strongly dependent on the frequency, whereas in the course of time a gradual formation of a rubber plateau is shown. Apparently, the gel point of this system at this temperature lies in between 0.2 and 1 h. Analogous plots are given in Figures 4 and 5 for the loss modulus and the loss tangent, tan $\delta = G''/G'$. The loss modulus increases gradually and goes through a slight maximum at an aging time somewhere between 20 and 100 h, depending on the frequency of the mechanical spectroscopy.[3,4] As a result, the loss tangent steadily decreases as the aging process proceeds.

By use of a special extrapolation method, the time–temperature–superposition principle could be applied to these thermoreversible systems.[3,4] In this way the frequency window could be extended. An example is given in Figure 6 for PVC/DOP which has been aged for 144 h at 90 and 110 °C, respectively. Apparently, at 110 °C even after 144 h the gel point has not yet been reached.

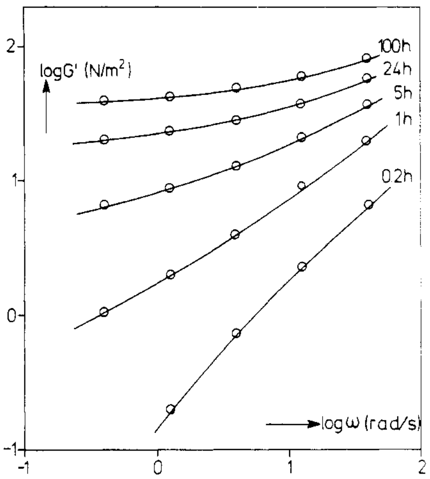

Figure 3. Storage modulus of PVC/DOP plotted against aging time for several angular frequencies. Aging temperature T_a = 90 °C.

Discussion

The dynamic mechanical behavior of gelling PVC solutions follows the same evolution as chemical gels. At short aging times t_a, the limiting behavior in the liquid state is observed as

$$G'(\omega) \simeq \omega^2 \quad G''(\omega) \simeq \omega \quad (\text{at } \omega \to 0) \tag{4}$$

while the solid state after sufficiently long aging results in a storage modulus

$$G'(\omega) = \text{const} \quad (\text{at } \omega \to 0) \tag{5}$$

The question now to be addressed is whether the data suggest an intermediate state of the PVC which is governed by the power law relaxation behavior of eq 1–3. This intermediate state could then be called the critical gel. The existence of such an intermediate state is not obvious since none of the data was taken directly at the gel point, and we actually do not yet know the location of the gel point, t_c. For finding this critical aging time, we plot $G''(\omega_i)/G'(\omega_i)$ as a function of aging time, with the frequency ω_i as a parameter, in the same way as we would to find the gel point of a chemical gel.[11] Such curves are shown in Figures 7–9. When these curves intersect in a single point, then there exists an intermediate power law relaxation state; i.e., the crossover of the curves marks the gel point. The PVC/DOP system at 90 °C reaches its gel point after about t_c = 0.7 h (see Figure 7) while it does not even come close to gelation when crystallized at 110 °C (Figure 8). The PVC/Reomol system at 110 °C reaches its gel point after about t_c = 2 h (Figure 9). The relaxation exponent, n, of both gels was about 0.8, as calculated from eq 3:

$$n = (2/\pi) \tan^{-1} (\tan \delta_c) \tag{6}$$

It is interesting to note that this method allowed determination of the gel point without taking data directly at the gel point. The converging lines in the tan δ plot even gave a projetion of the gel point much before the polymer had actually reached the gel point.

Conclusions

We conclude that crystallizing PVC solutions, exactly like chemically cross-linking systems, exhibit power law relaxation at an intermediate state. We assume that this intermediate state is identical with the gel point, $t = t_c$,

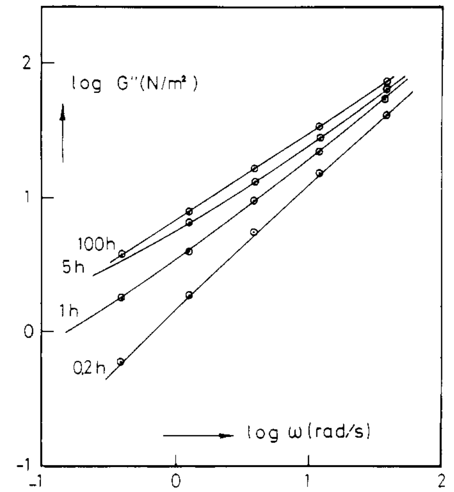

Figure 4. Loss modulus of PVC/DOP plotted against angular frequency for several aging times. Aging temperature T_a = 90 °C.

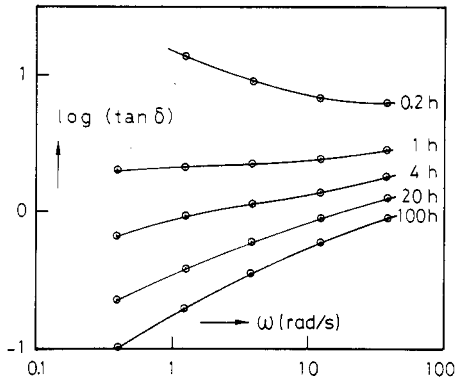

Figure 5. Loss tangent of PVC/DOP plotted against angular frequency for several aging times. Aging temperature T_a = 90 °C.

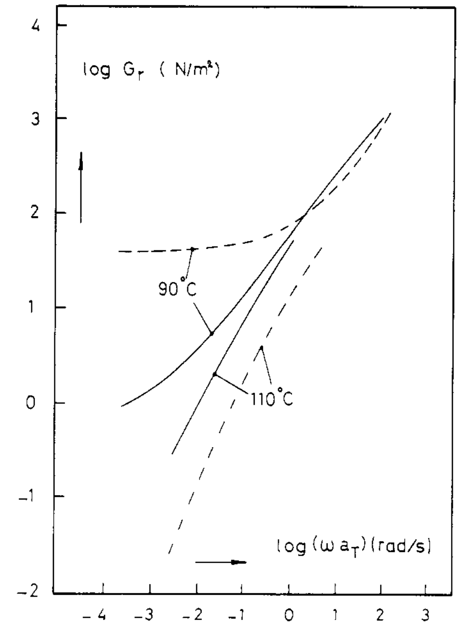

Figure 6. Master curves for storage and loss moduli of PVC/DOP for several aging temperatures T_a. Aging time is 144 h. Solid lines, loss modulus; dashed lines, storage modulus. Reference temperature is 25.7 °C.

since power law relaxation marks the gel point of chemical gels. The gel point can then be directly measured by following the loss tangent, tan δ(ω), during gelation, with the frequency ω as a parameter. The different tan δ curves intersect at the gel point, $t = t_c$. This is a novel way of defining the gel point of physical gels, and the universality of such a definition remains to be shown.

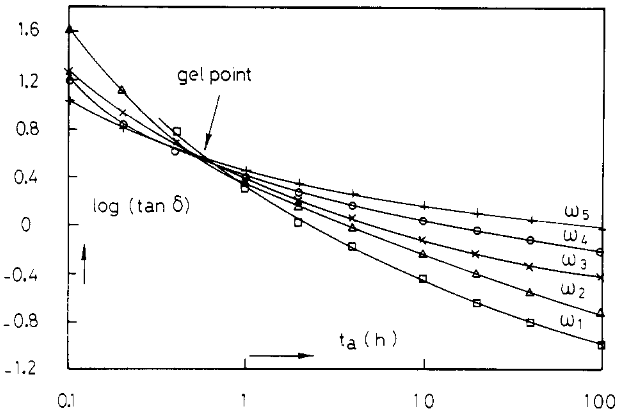

Figure 7. Loss tangent of PVC/DOP plotted against aging time for angular frequencies $ω_i$ = 0.39, 1.26, 3.9, 12.6, 31.6 rad/s. Aging temperature is T_a = 90 °C.

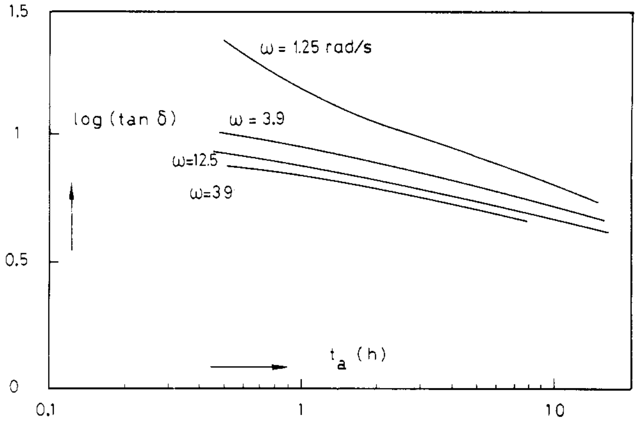

Figure 8. Loss tangent of PVC/DOP plotted against aging time for several angular frequencies. Aging temperature is 110 °C.

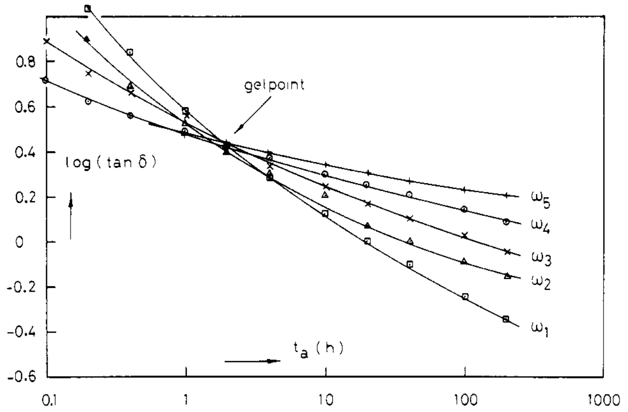

Figure 9. Loss tangent of PVC/Reomol plotted against aging time for angular frequencies $ω_i$ = 1.26, 3.9, 12.6, 39, 126 rad/s. Aging temperature is T_a = 110 °C.

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Registry No. DOP, 117-81-7; DBP, 84-74-2; Solvic 239, 9002-86-2; Reomol ATM, 52441-32-4.

References and Notes

(1) Winter, H. H.; Chambon, F. *J. Rheol.* (*N.Y.*) **1986**, *30*, 367.
(2) Chambon, F.; Winter, H. H. *J. Rheol.* (*N.Y.*) **1987**, *31*, 683.
(3) Te Nijenhuis, K. Doctoral Thesis, University of Delft, 1979.

(4) Te Nijenhuis, K.; Dijkstra, H. *Rheol. Acta* **1975**, *14*, 71.
(5) Dorrestijn, A.; Keijzers, A. E. M.; Te Nijenhuis, K. *Polymer* **1981**, *22*, 305.
(6) Yang, Y. S.; Geil, P. H. *J. Macromol. Sci., Phys.* **1983**, *B22*, 463.
(7) Mutin, P. H.; Guenet, J. M. *Polymer* **1988**, *29*, 30.
(8) Juijn, J. A. Doctoral Thesis, University of Delft, 1972.
(9) Juijn, J. A.; Gisolf, J. H.; De Jong, W. A. *Kolloid Z. Z. Polym.* **1973**, *251*, 456.
(10) Te Nijenhuis, K.; Van Donselaar, R. *Rheol. Acta* **1985**, *24*, 47.
(11) Holly, E. E.; Venkataraman, S. K.; Chambon, F.; Winter, H. H. *J. Non-Newtonian Fluid Mech.* **1988**, *27*, 17.

Equilibration in Glassy Polymer Blends: Effects on Interaction Parameters Measured by Small-Angle Neutron Scattering

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ABSTRACT: Small-angle neutron scattering (SANS) measurements of the Flory–Huggins interaction parameter χ in glassy polymer blends are shown to be subject to large systematic errors due to the fact that the composition fluctuations in the melt may fall out of equilibrium at widely differing temperatures T_e depending on cooling rate and molecular weight. As a concrete example we compute T_e for the system dilute deuteriated polystyrene (d-PS) in polyxylenyl ether (PXE) using measured diffusion coefficients of d-PS and show that, even at slow cooling rates, the resulting increase in T_e with d-PS molecular weight leads to decreasing negative values of χ that are in quantitative agreement with those measured in the same system by Jelenic et al.[1]

Introduction

One of the most promising applications of small-angle neutron scattering (SANS) in polymer research is its use for determining the Flory–Huggins segment–segment interaction parameter χ for miscible polymer blends.[1-14] While some of the measurements have been made as a function of temperature by using special specimen holders that permit the sample to be held at a given temperature during the SANS measurement, many of the measurements on blends that are glasses at room temperature have been made by the following method: The sample is homogenized by heating to temperatures well above the glass transition temperature T_g and then cooled to room temperature where the SANS measurements are made. Because the cooling is usually reasonably slow, it is assumed that the sample falls out of equilibrium at T_g so that the χ thus determined corresponds to χ at this temperature. While this method is popular because it simplifies the SANS measurements, the results on some systems are rather disappointing. For example in the system deuteriated polystyrene (d-PS)–poly(2,6-dimethyl-1,4-phenylene oxide) [or polyxylenyl ether (PXE)] the results from different investigators using SANS to determine the χ for blends of dilute d-PS in PXE vary from almost −0.04 to 0.00, well outside what should be the experimental error of the technique.[1-5] Even more disturbing are the careful measurements of Jelenic et al.[1] which appear to show that the magnitude of χ depends strongly on the molecular weight M of d-PS, decreasing monotonically from −0.0124 for $M = 24\,000$ to −0.0006 for $M = 465\,000$. The entire concept of a segment–segment interaction parameter seems meaningless if it depends this strongly on M.

In a following paper we examine the crucial assumption of this procedure, i.e. that the sample falls out of equilibrium only at T_g, and show that because of the very slow mutual diffusion in the molten state of many polymer blends, this assumption is not even approximately correct. Depending on the magnitude of the mutual diffusion coefficient D and the cooling rate, the sample can fall out of equilibrium at a temperature as much as 60 K above T_g. If the Flory–Huggins parameter depends strongly on temperature, the χ's measured by investigators using different cooling rates during sample preparation certainly will not be the same. Moreover if the molecular weight of the component polymers are changed as in the Jelenic et al. experiment,[1] that must change the temperature at which the sample falls our of equilibrium and hence the measured χ, since D decreases with increasing molecular weight.

While one might imagine special cases where this problem in achieving equilibrium would produce negligible error in the measured χ, it seems worthwhile to check whether it might be the reason for the scatter in the data for d-PS:PXE expecially since independent determinations of both D and $\chi(T)$ have been possible recently from measurements of tracer diffusion and mutual diffusion in this system. Using these values of D and $\chi(T)$ we show that the equilibration temperatures in d-PS:PXE do in fact lie well above T_g for reasonable cooling rates and moreover that the dependence of D on molecular weight M of d-PS can account for some of the apparent M dependence of χ measured by Jelenic et al.

Equilibration in Polymer Blends

The Flory–Huggins parameter can be determined by small-angle neutron scattering from blends of deuteriated and hydrogenated polymers because such scattering is sensitive to composition fluctuations in the blend, composition fluctuations which increase as χ becomes less negative and the spinodal is approached. The scattering at a wave vectors $\mathbf{q}$ ($q = (4\pi/\lambda)\sin(\theta/2)$ where θ and λ are the scattering angle and the wave length of the neutrons, respectively), corresponding to composition fluctuations with wave lengths $\sim q^{-1}$, is proportional to the

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