Peculiar Dynamic Viscoelastic Behavior of Thermoreversible PVC Gels

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ABSTRACT: Dynamic viscoelastic measurements of PVC-based aged gels reveal the existence of two pseudoequilibrium moduli independent of temperature, frequency, and strain amplitude: G_{e1} at low temperatures and G_{e2} at intermediate temperatures ($G_{e1} > G_{e2}$). A maximum in tan δ spectra is observed at intermediate temperatures. From these results and DSC results (which reveal the existence of a low-temperature endotherm, besides the gel-melting endotherm) a transition, T_s, fixed in the range 45–65 °C, is defined. The results of thermal analysis are coincident with those reported in recent literature for PVC gels in several solvents. Diffusion coefficient versus temperature data seems to confirm the existence of the transition only in the case of PVC/Reofos gels. Clark and Ross-Murphy's cascade model is applied to the concentration dependence of G_{e1} and G_{e2}, using functionalities of $f = 3$–5. These values of "f" are obtained assuming that crystals of an average of 40-Å length produce the connectedness required for gelation. In order to analyze the hypothesis of liquid–liquid phase separation as responsible of the relatively high values of the modulus G_{e2}, the effect of an increment of concentration in G_{e2} is evaluated. The fact that the values of G_{e1} are higher than those that can be obtained from a simple increment of concentration of polymer (polymer-rich phase) lead us to think that the participation of another type of link, besides crystallites, in the formation of the structure of aged gels is an open hypothesis.

Introduction

Thermoreversible gels obtained by cooling solutions of polymers are systems formed by linkages constituted by association of separated loci. In the majority of the cases the nature of the linkages or physical cross-links remains a matter of debate, and it can be said that physical gelation has been less studied and understood than the chemical gelation caused by covalent cross-linking. However, there is presently an increasing interest in the formation and properties of biopolymer and synthetic polymer thermoreversible gels. Because of the commercial importance of poly(vinyl chloride) (PVC) and the facility of this polymer to form gels with different types of plasticizers, much of the work on gels refers to these systems.

Several techniques, including differential scanning calorimetry (DSC), simple rheological measurements (ball-drop test), and microscopy, have been used to study the properties of gels and the origin of the gel network, but in spite of the importance of dynamic viscoelastic measurements in polymer science, this technique has been scarcely used. Some of the published works have been devoted to the study of the physical gelation of PVC- and PS-based gels by means of frequency scan measurements at different gelation times and/or temperatures,[1–6] but the majority of the papers deal with the influence of concentration and temperature on storage shear modulus, G', or Young modulus, E'. Studies on biopolymers like agar–agar and agarose gels,[7–10] amylose,[11] various disordered biopolymers including gelatin,[12] rigid rodlike liquid-crystalline polypeptides gels,[13,14] and nonfilamentous actin protein gels[15] have been reported in the literature.

For synthetic polymer based gels, measurements on ultrahigh molecular polyethylene gels,[16] thermotropic copolyesters[17,18] gels, and PVC-based gels[19,20] have been reported.

In general, we can assert that research on rheology of gels has been focused to the variation of the modulus (obtained by compression, shear, or elongation in steady or dynamic conditions) with concentration and gel fusion temperature studies, which involve ball-drop test and DSC measurements. In this sense, the main contribution of dynamic viscoelastic measurements has been to determine accurately a temperature- and frequency-independent modulus in order to relate it with the nature of tie points, which give rise to the gel.

In the present paper we report and discuss dynamic viscoelastic measurements of PVC-based gels in an attempt to interpret the existence of the transition, which takes place at temperatures close to 50 °C.

Experimental Section

Materials. Two commercial-grade suspension-polymerized PVC samples (Industrias Químicas Asua, Bilbao, Basque Country), MS 2209 and MS 2212, with molecular weights (obtained in a Waters 150C ALC/GPC) $M_w = 55\,300$, $M_w/M_n = 2.42$, and $M_w = 88\,100$, $M_w/M_n = 3.12$, respectively, were used. The average molecular weights obtained from intrinsic viscosity measurements in cyclohexanone at 30 °C are $M_v = 40\,600$ for MS2209 and $M_v = 62\,500$ for MS2212. The tacticity of the samples were determined by ^{13}C NMR in a deuteriated pyridine solution, giving the following results for the triads: MS2212, i = 17.92%, s = 31.94%, h = 50.14%; MS2209, i = 18.80%, s = 30.10%, h = 51.10%.

Gels of concentration 118–360 g/L (grams of polymer per liter of solution) were obtained by cooling from homogeneous solutions at temperatures ranging from 140 to 180 °C. Two solvents were used: bis(2-ethylhexyl) phthalate (Induflex DOP, $\rho = 0.986$ g/cm^3, $\eta = 55$ cSt at 25 °C, from CEPSA, Spain) and an isopropylated phenyl phosphate (Ciba-Geigy's Reofos 50, $\rho = 1.174$ g/cm^3, $\eta = 50$ cSt at 25 °C).

Viscoelastic Measurements. Dynamic viscoelastic measurements were performed in a Polymer Laboratories DMTA apparatus, using the parallel plate shear mode to measure the storage modulus, G', the loss modulus, G'', and the loss tangent, tan δ. Good adhesion to the standard plates of the DMTA was obtained by using gel disks of 2-mm thickness and 12-mm diameter.

Experiments were carried out with maximum strains of 0.5%, 2%, and 8%, frequency 1 Hz, and temperature scan 2 °C/min.

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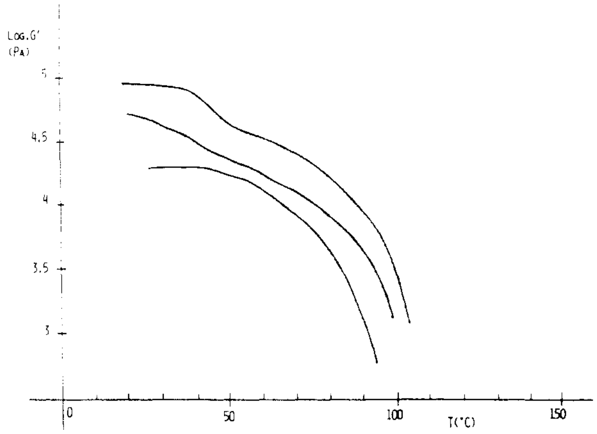

Figure 1. Logarithm of storage modulus as a function of temperature for fresh and aged gels of MS2212/Reofos (c = 187 g/L). The upper curve corresponds to a gel aged 7 days and the intermediate and lower curves correspond to gels aged 4 h and 15 min, respectively (see text).

Isothermal tests with a maximum strain of 0.5% at frequencies ranging from 0.03 to 30 Hz were also performed.

The effect of the gel preparation and aging on the dynamic viscoelasticity was analyzed. Gels prepared from solutions at 140, 150, 160, 170, and 180 °C were studied.

To study the aging effect, the sample was subjected to a temperature scan in the DMTA up to the temperature at which tan δ = 1 (this corresponds to the beginning of the melting of the sample) and kept at this temperature for 15 min; then the sample was allowed to cool to room temperature, and a new scan was carried out after a certain aging time.

Differential Scanning Calorimetry. A Perkin-Elmer DSC-2C calorimeter, equipped with a 3700 Data Station, was used at heating rates of 20 °C/min to analyze gels of c = 160 g/L and c = 187 g/L in DOP and Reofos at temperatures from 25 to 140 °C.

Solvent Sorption Measurements. Sorption measurements were performed to determine the average diffusion coefficient, D, of the solvent at temperatures ranging from 20 to 80 °C. Disks of diameter 12 mm and height 1 mm were prepared and weighed. They were then immersed in an excess of their preparation solvent at a constant temperature. Solvent uptake was followed gravimetrically at various intervals.

Results and Discussion

Dynamic Viscoelasticity of Fresh and Aged Gels. In Figure 1 we present the storage modulus, G', as a function of temperature for three MS2212/Reofos gels (c = 187 g/L), which differ in their thermal histories. The upper curve corresponds to a gel prepared from a solution at 160 °C and kept at room temperature for 7 days; the intermediate curve corresponds to a 160 °C and 7 days gel, but the measurement was carried out after the gel was fused; then the temperature was decreased to room temperature and kept 4 h (recovery time 4 h), and the lowest curve corresponds to a fused gel with a recovering time of 15 min. The results obtained for the rest of the concentrations show the same behavior, which can be described by the following features.

(i) After fusion and subsequent cooling at room temperature, gels tend to recover their structure as can be seen from the lowest curve, which shows a temperature-independent modulus at low temperatures.

(ii) After 24 h, for PVC/DOP gels, and 72 h, for PVC/Reofos gels, the moduli reach the same values as the gels kept at room temperature for 7 days.

(iii) The aged and fresh gels differ by the presence of a plateau zone at intermediate temperatures, which is characteristic only of the aged gels. For aged gels the following characteristic parameters can be defined from Figure 2: G_{e1}, value of the storage modulus at the first plateau (low temperature); G_{e2}, value of the modulus at the second plateau (intermediate temperature); T_s, temperature at which transition from the first plateau to the second plateau takes place (maximum peak in tan δ).

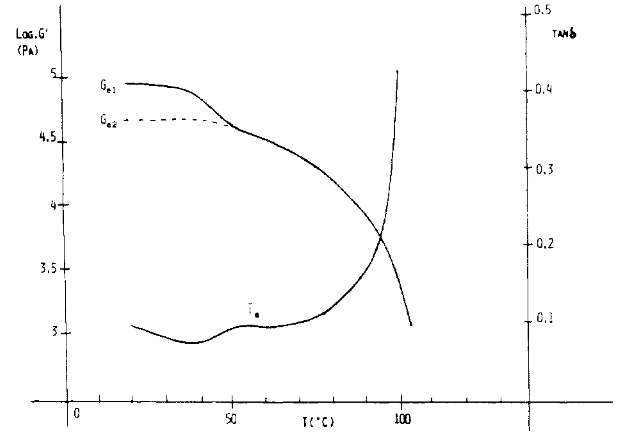

Figure 2. Logarithm of storage modulus and loss tangent as a function of temperature for an aged gel of MS2212/Reofos (c = 187 g/L). The values of G_{e1}, G_{e2}, and T_s are presented in Table I.

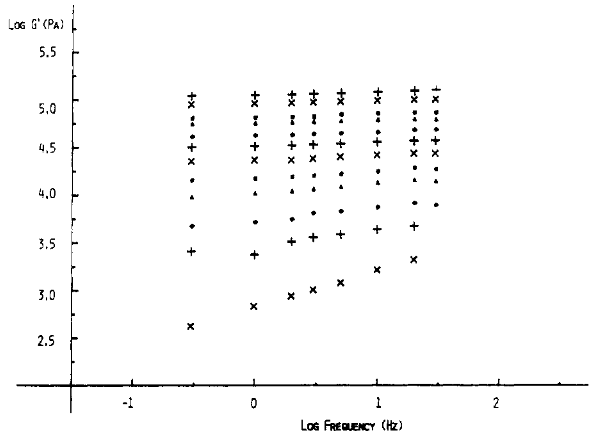

Figure 3. Logarithm of storage modulus as a function of frequency at different temperatures for an aged gel of MS2212/Reofos (c = 240 g/L). From top to bottom: 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, and 140 °C.

(iv) Aged gels obtained from solutions at 160, 170, and 180 °C give rise to the same G_{e1}, G_{e2}, and T_s values. The temperature at which the solution is prepared, before the subsequent formation of the gel, does not affect the value of the storage modulus, G', at least in the range 160–180 °C. However, gels obtained from solutions at 140 and 150 °C give significantly lower moduli.

(v) The characteristic parameters G_{e1}, G_{e2}, and T_s (obtained from temperature scans at 1 Hz) are independent of the maximum strains, in the range of the values considered in this work. At low temperatures the frequency dependence of the storage modulus, G', is very weak, but as the temperature is increased the dependence becomes stronger (Figure 3).

In Figure 2, we can also observe that the beginning of the fusion of the gel gives rise to a sharp increase in tan δ and a sharp decrease in G'. The rest of PVC/Reofos and PVC/DOP aged gels present the same type of spectra, and the values of G_{e1}, G_{e2}, and T_s (defined in Figure 2) are summarized in Table I.

The existence of the T_s temperature, called by us the sub(gel–sol) transition temperature, signifies an original behavior because, although the fusion or gel–sol transition

Table I
Values of the Parameters T_s, G_{e1}, and G_{e2} Characteristic of Aged Gels (See Figure 2)

C, g/L	T_s, °C	G_{e1}, Pa	G_{e2}, Pa
		2209/DOP	
360	59	132 000	76 000
306	52	100 000	64 500
255	50	70 800	50 000
207	59	35 500	14 500
160	53	14 000	10 000
		2209/Reofos	
350	58	141 000	74 000
290	55	132 000	64 500
240	45	66 000	38 000
187	50	29 000	14 000
138		9 300	
		2212/DOP	
360	64	158 000	100 000
306	65	158 000	85 000
255	62	102 000	67 500
207	65	61 600	36 300
160	62	32 000	20 500
118	62	10 000	5 400
		2212/Reofos	
350	58.5	158 500	89 000
290	55	162 000	93 000
240	59	100 000	58 900
187	57	85 000	46 800
138	60	35 500	26 300
90		6 200	

temperature has been determined in many gels, a transition at low temperatures is exclusive of PVC-based gels. In 1988 we reported the observation of the sub(gel–sol) transition temperature, T_s, in PVC/DOP gels[20] by dynamic viscoelastic measurements, but we could not detect it by DSC. Recently, Mutin and Guenet[21] have presented a careful study (which included the use of a different type of pan, without noticing any difference in the results) of the thermal properties of PVC gels in various solvents, pointing out the appearance of two endotherms: (a) an endotherm corresponding to the gel melting, which disappears on second heating, and (b) an endotherm fixed at 50 °C (independent of concentration) exclusive of aged gels and that does not disappear after second heating.

Taking into account these interesting results, we carried out thermal analysis measurements, repeating accurately the experimental conditions described by Mutin and Guenet. In Figure 4 we present the first heating scan and second heating scan (after melting) of aged MS2209/Reofos (c = 187 g/L) gel. A great similitude is observed between our Figure 4 and Figure 1 of ref 21 (which refers to 17.5% PVC/diethyl malonate gels), especially in what the endotherm at lower temperature concerns: in both cases the endotherm begins at 50 °C and the maximum takes place at ≈62 °C for PVC/diethyl malonate and 66 °C for PVC/Reofos. The enthalpy is in our case 0.08 cal/g, which is of the same order of the value ≈0.1 cal/g quoted by the referred authors as general for their gels. We have to point out that our second heating scans do not give endotherms at all, probably due to the fact that the second scan was performed immediately after reaching room temperature (in the work of Mutin and Guenet the gels were aged 24 h at 20 °C).

We summarize our first scan data of c = 160 g/L and c = 187 g/L in Table II. T_{11} and T_{12} are defined as the beginning and the maximum, respectively, of the lower temperature endotherm, and T_{21} and T_{22} indicate the beginning and the maximum, respectively, of the gel melting endotherm. For high molecular weight PVC gels, fusion takes place at higher temperatures than the range covered in our scans.

Table II
First Scan Data of PVC/DOP (c = 160 g/L) and PVC/Reofos (c = 187 g/L) Gels

sample	T_{11}, °C	T_{12}, °C	ΔH_1, cal/g	T_{21}, °C	T_{22}, °C	ΔH_2, cal/g
2209/DOP	60	74	0.08	113	122	0.51
2209/Reofos	50	66	0.09	110	125	0.25
2212/DOP	62	74	0.17			
2212/Reofos	54	66	0.08			

[a] T_{11} and T_{12} represent the beginning and the maximum, respectively, of the lower temperature endotherm (ΔH_1). T_{21} and T_{22} indicate the beginning and the maximum, respectively, of the gel-melting endotherm (ΔH_2) (see Figure 4).

The coincidence of the values of T_{11} with values of T_s obtained by viscoelastic measurements (Table I) is remarkable and confirms the existence of a sub(gel–sol) transition temperature.

Some outstanding points can be extracted from the comparison of dynamic viscoelasticity and DSC results. Although some scatter is observed in the values presented in Table I, we can assert that T_s is independent of concentration, a result that is in agreement with the fact pointed out by Mutin and Guenet[21] that the temperature location of the lower temperature endotherm does not vary with concentration. However, it is worth mentioning that, according to our dynamic viscoelastic results, T_s is slightly higher for high molecular weight PVC gels. Concerning the influence of the solvent, we can deduce from Tables I and II that Reofos (which possesses similar viscosity as DOP but higher polarity and aromaticity and can be considered a better solvent) give rise to gels of lower T_s (or T_{11}) but higher values of G_{e1} and G_{e2}. In order to propose an explanation on how and why the polarity and aromaticity affects these parameters, experimental results with other solvents are needed.

In an attempt to understand the nature of the transition observed by DSC and dynamic viscoelasticity, some hypothesis, based on the origin of the mechanism of formation of the gel, can be presented. It has been suggested[22-25] that in certain cases gelation can be induced by phase separation into polymer-rich and polymer-poor regions. This hypothesis is based in phase diagrams that separate a zone of gelation accompanied by liquid–liquid phase separation from a zone of gelation without liquid–liquid phase separation.

Following Kawanishi et al.,[25] we consider it possible that the formation of aged gels takes place in two steps: the system is initially gelled by crystallites forming a network, and posteriorly an interconnected structure of polymer-rich and polymer-poor regions is formed. We think that the two plateau zones observed in the storage modulus during heating (Figure 2) are related to both processes. The lower plateau G_{e2} corresponds to the system gelled by crystallization and the plateau G_{e1} to the gelation in the polymer-rich region, which is produced as well by crystallization although the existence of another type of link is not neglected (see next section). During cooling of the solution, crystallization takes palce, and due to the relatively high viscosity of the system, a certain time is necessary to phase separate.[26] This can be the reason why fresh gels only show the G_{e2} plateau at low temperatures and the subsequent melting at high temperatures; however, when an aged gel is heated, a transition from a two-phase gel to a homogeneous gel can be detected at temperatures lower than those corresponding to the melting.

Table III
Optimized Values for the Parameters c_0, a, and k Used in Equation 2 (See Text)

	G_{e1}					G_{e2}				
sample	f	c_0, g/L	K, L/mol	a	$\sum\Delta^2$	f	c_0, g/L	K, L/mol	a	$\sum\Delta^2$
2209/DOP	3	86.7	312	21	8.27×10^{-3}	3	74.1	365	9.5	4.84×10^{-2}
2209/Reofos	3	75.4	359	19.7	1.18×10^{-2}	3	79.5	340.4	11.3	1.14×10^{-2}
2212/DOP	4	58.9	199	17	1.11×10^{-2}	4	60.2	194.6	10.5	1.15×10^{-2}
	5	59.7	93	13.4	1.11×10^{-2}	5	62	89.6	8.6	1.15×10^{-2}
2212/Reofos	4	44.7	262	14.9	4.58×10^{-2}	4	21.3	551	5.4	9.72×10^{-3}
	5	44.9	123.6	11.7	4.46×10^{-2}	5	21.9	254	4.3	9.42×10^{-3}

Nevertheless, the analysis of the effect of concentration on both moduli G_{e1} and G_{e2} leads us to suggest that phase separation is not the sole mechanism underlying the sub(gel–sol) T_s transition.

Concentration Dependence of G_{e1} and G_{e2}. The fact that the statistical theory of rubber elasticity explains the mechanical properties of rubbers without the necessity for introducing any peculiar special properties related to the chemical structure of the molecule has led some authors to apply it to gels with permanent (irreversible) chemical tetrafunctional cross-links.[27] The same theory has also been applied[28] to the calculation of an approximate value for the molecular weights between entanglements M_e from the pseudoequilibrium shear modulus at the inflection in the stress relaxation curve or from the curve for the shear storage modulus, G', as a function of frequency.

More recently the case of thermoreversible gels has been analyzed in terms of the classical theory of rubber elasticity, in order to obtain additional information concerning the structure of the gel. In this sense it is worthy pointing out the works on atactic polystyrene gel in CS_2;[29,30] a molecular weight between associations of 2700 was obtained, applying the theory of rubber elasticity to the shear moduli of gels of $c = 200$ g/L. On the other hand, Clark et al.,[1] working with gels of 9.5% solutions of PS ($M_w = 900\,000$) in CS_2, calculated approximately 2–3 trifunctional cross-links for each molecule. The moduli of thermoreversible polyethylene gels have also been related to the effective molecular weight between lamellar crystallites acting as cross-links.[31]

An alternative to the statistical theory of rubber elasticity has been given by Clark and Ross-Murphy[8-12] for the concentration dependence of gel shear modulus. In their cascade theory the number of elastically active network chains per primary chain is given by

$$N_e(f,\alpha) = f\alpha(1 - \nu)^2(1 - \beta)/2 \qquad (1)$$

where f is the functionality (number of sites per polymer molecule potentially available for bonding to others), α is the proportion of functionalities that have reacted, ν is the extinction probability (obtained as the lowest positive root of the equation $\nu = (1 - \alpha + \alpha\nu)^{f-1}$), and

$$\beta = \frac{(f-1)\alpha\nu}{1 - \alpha + \alpha\nu}$$

The equation describing the G (in Pascals) versus c (in grams per liters) relationship is

$$G = \frac{aRT(f-1)\alpha(1-\nu)^2(1-\beta)}{2K(f-2)^2}\left(\frac{c}{c_0}\right)(1000) \qquad (2)$$

where "a" is a nonideality factor measuring the deviation from ideal rubber elasticity and K is an equilibrium constant determined by assuming a second-order forward reaction and first-order back-reaction for the association of reactive sites

$$K = \frac{\alpha}{Nf(1-\alpha)^2} \qquad (3)$$

where N is the number of moles of polymer per liter. The quantity c_0 is the critical concentration given by

$$c_0 = \frac{M(f-1)}{Kf(f-2)^2} \qquad (4)$$

As pointed out by Clark and Ross-Murphy, experimental G versus c data can easily be fitted by using eq 2 if f, "a", and K are systematically varied until a best least-squares fit is achieved.

In order to apply the cascade theory to our experimental frequency and strain-independent G_{e1} and G_{e2} moduli, we have fixed the functionality f and optimized the values of "a" and K. We can evaluate the functionality of PVC-based gels from the argumentation explained in the next paragraph.

The tacticity of both samples (see the Experimental Section) is very similar and typical of commercial PVC samples, for which a crystallinity of about 8% can be assumed.[2] On the other hand, it has been proposed[32-33] that, in commercial PVC-s, crystals of an average of 40-Å length produce the connectedness required for gelation. Taking 2.31 Å as the average length of the chain bonds and provided that for the MS2209 sample the molecular weight is 40 600, which corresponds to 650 repeating units (of molecular weight 62.5), assuming a crystallinity of 8%, we deduce that there are three crystallites of 40 Å for each MS2209 polymer chain. For MS2212 (molecular weight 62 500) the same calculation leads to an average of 4.6 crystallites for each chain.

As we suppose that gelation occurs via small crystals serving as physical cross-links, we apply the cascade theory fixing the functionality "f" as the number of crystallites of 40 Å for each polymer chain. Therefore, in the case of MS2209-based gels, we fix $f = 3$ in eq 2 and "a" and K are varied to achieve the best fit. For gels based in the MS2212 sample we adjust "a" and K, taking $f = 4$ and $f = 5$.

Guenet et al.[21,34,35] have stated that, besides the links that are formed between syndiosegments of PVC, additional links must exist to justify the relatively high values of the mechanical modulus and the physical aging of these gels. However, since the origin of this second type of link is uncertain (although some hypotheses have been advanced), we have supposed the same functionality "f" to adjust G_{e1} and G_{e2}.

The results of the application of the cascade theory (eq 2) are presented in Table III. In Figure 5 the case of MS2212/DOP is shown. The values of the critical concentration c_0 obtained from eq 4 are reasonable, taking into account that solutions of less than 10% of PVC do not gel at the temperatures considered in this work. When the values of the adjustable parameters for the best fits of G_{e1} and G_{e2} are compared, it is seen that the difference concerns mainly the values of the parameter "a", which

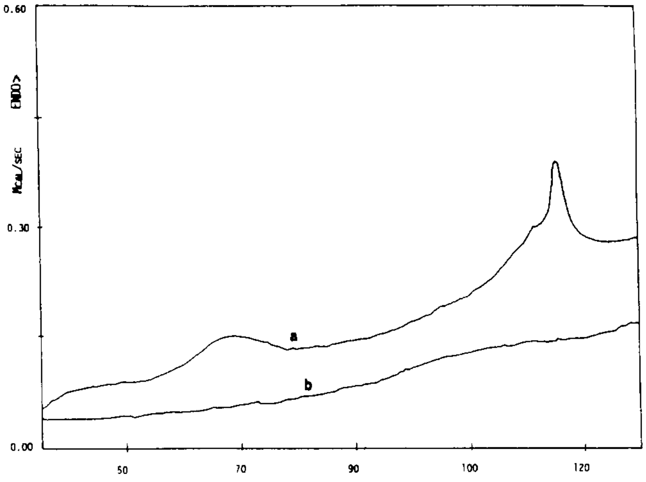

Figure 4. DSC thermograms on a MS2209/Reofos (c = 187 g/L) aged gel at 20 °C/min: (a) first heating scan; (b) second heating scan after melting.

are always greater than unity. Following Clark and Ross-Murphy,[12] $a > 1$ signifies that the elastically active chains are stiffer than those envisaged by statistical theory of rubber elasticity: excess of unity in the parameter "a" would reflect enthalpic contributions to the modulus per network chain. On the other hand, the fact that "a" values in Table III are higher for G_{e1} could be interpreted as due to some lateral aggregation, which could suggest that "f" should be increased, so "a" would then remain constant.

The hypothesis of the liquid–liquid phase separation can be discussed on the basis of the cascade theory. As this process implies the formation of a polymer-rich phase, we assume that an increment in concentration in eq 2 (with the parameters "a", f, and K corresponding to the best fit for G_{e2}) should give the values of G_{e1}. However, the maximum value that can be obtained with eq 2 by using $f = 5$, $a = 8.6$, and $K = 89.6$ is G_{e2} = 132 000 Pa for a concentration of c = 400 g/L, and at concentrations of c = 450 g/L and c = 500 g/L the theoretical values decrease to 128 000 and 117 000 Pa, respectively. Since these values are lower than the experimental value G_{e1} = 158 000 Pa for concentrations of 360 and 306 g/L (see Table I), we deduce that an increment in concentration in the polymer-rich phase does not justify the experimental values of G_{e1}.

We therefore conclude that liquid–liquid phase separation cannot justify by itself the difference between the values of G_{e1} and G_{e2} and that the hypothesis of the weak links (i.e., formation of complexes between PVC and the solvent) proposed by Guenet et al. has to be taken into account.

Diffusion of Solvents in the Gels. Experimental results of the weight gain M_t of disks of MS2212/DOP (c = 160 g/L) immersed in DOP are presented in Figure 6. Similar results are obtained for the rest of the samples.

The generalized diffusion equation proposed by Kwei et al.[36]

$$M_t = c_0(D/v + \nu t) \qquad (5)$$

where D is the average diffusion coefficient and ν represents the velocity of solvent penetration, is applied to the linear region of M_t data. In Figure 7 we present the variation of the diffusion coefficient with temperature for MS2209/DOP and MS2209/Reofos gels.

Some authors have used solvent sorption measurements as a technique to investigate second-order transitions and structural changes in polymers. In this sense Duda and Vrentas[37] considered that the sharp change in the activation energy of diffusion, near 150 °C, is evidence of the so-called liquid–liquid transition.[38] However, crystallinity changes in PVC (produced during extrusion at different temperatures and shear) do not affect diffusion parameter.[39] In the case of PVC-based gels,[21] the swelling ratio plotted as a function of temperature deviates from linearity at $T > 40$ °C: this deviation is associated with the low-melting endotherm observed by DSC. However,

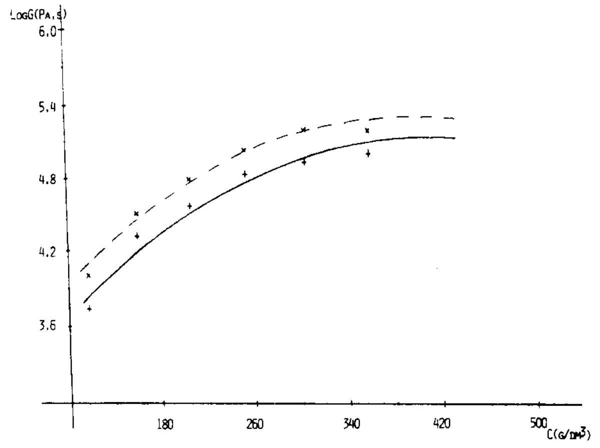

Figure 5. Concentration dependence of G_{e1} (×) and G_{e2} (+) of MS2212/DOP gels. The curves are calculated by using eq 2: (- - -) $f = 5$, c_0 = 59.7 (g/L), k = 93 (L/mol), a = 13.4; (—) $f = 5$, c_0 = 62 (g/L), k = 89.6 (L/mol), a = 8.6.

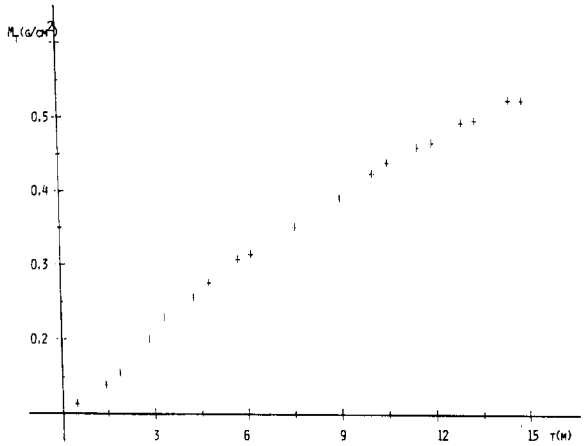

Figure 6. Weight gain as a function of time for MS2209/DOP (c = 161 g/L) gel at T = 35 °C.

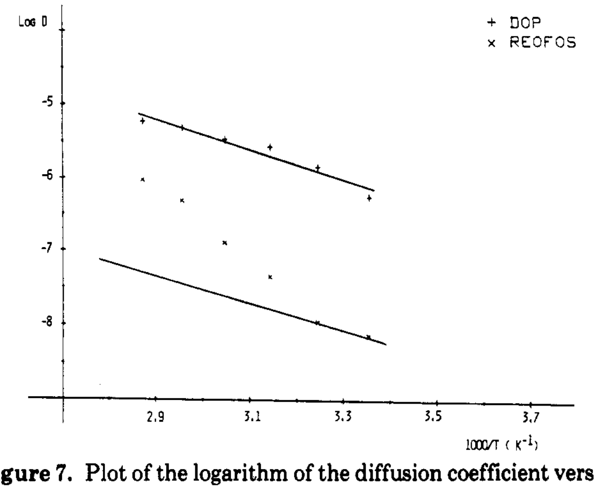

Figure 7. Plot of the logarithm of the diffusion coefficient versus the reciprocal of the absolute temperature for MS2209/DOP (c = 207 g/L) (+) and MS2209/Reofos (c = 187 g/L) (×) gels. The lines are drawn by using the activation energies of flow of DOP and Reofos, respectively (see text).

when bis(2-ethylhexyl) phthalate is used as solvent, the swelling does not exhibit any deviation, although for this type of gel the low-melting endotherm is always present.

Our results, presented in Figure 7, reveal that in the case of PVC/DOP gels the diffusion coefficient changes with temperature following an Arrhenius behavior $D = D_0 \exp(-E/RT)$ with an activation energy of $E = 9.2$ kcal/mol, which agrees with the activation energy corresponding to the variation of the viscosity of DOP with temperature. This confirms previous results[40,41] on the relation between the diffusion coefficient and the viscosity of the solvent. For PVC/Reofos gels the results are different since the data cannot be fitted to an Arrhenius type equation. As can be seen in Figure 7 at $T > 55$ °C the dependence of D with respect to temperature becomes stronger than the dependence of the solvent (Reofos) viscosity with temperature.

This fact could indicate that some kind of change in the structure or morphology of the gel happens above this temperature, which coincides with the aforedefined T_s transition.

Conclusions

1. Dynamic viscoelastic measurements carried out with fresh gels show the existence of a plateau zone for G' at low temperatures and an increment in tan δ as the gel-melting process begins. For aged gels, however, two plateau zones are observed, defining two storage moduli: G_{e1} at low temperatures and G_{e2} at intermediate temperatures.

2. A transition temperature, T_s, is defined as the temperature for which the transition from the first plateau modulus to the second plateau modulus occurs. This corresponds to a maximum in the tan δ spectrum and to the beginning (T_{11}) of a low-temperature endotherm as observed by DSC. Thermal analysis results are coincident with those reported by Mutin and Guenet for PVC gels in various solvents.

3. The sub(gel–sol) transition T_s, ranges from 45 to 65 °C. Slightly higher values of T_s are observed for high molecular weight PVC resin (MS2212), but the concentration of polymer does not influence it. The isopropylated phenyl phosphate (Reofos) solvent gives rise to gels with a lower T_s (or T_{11}) than the bis(2-ethylhexyl) phthalate (DOP).

4. From the application of Clark and Ross-Murphy's cascade model to the concentration dependence of G_{e1} and G_{e2}, it is concluded that the formation of a polymer-rich phase in aged gels does not justify by itself the high values of the G_{e1} modulus.

The variation of the diffusion coefficient of the solvent with temperature follows a simple Arrhenius type equation for PVC/DOP gels, whereas the PVC/Reofos gels the diffusion coefficient increases more rapidly with temperature at $T > 55$ °C.

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