α Mechanical relaxation in poly(vinyl chloride): effect of ageing and crosslinking

R. Flores* and J. Perez
GEMPPM, u.a. CNRS 341, INSA, 69621 Villeurbanne, France

and P. Cassagnau and A. Michel
Laboratoire des Matériaux Organiques, CNRS, 69390 Vernaison, France

and J. Y. Cavaillé
CERMAV, CNRS, BP 53x, 38041 Grenoble, France
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Two types of poly(vinyl chloride) (PVC) samples are studied by mechanical spectroscopy, namely (i) a commercially available PVC that is submitted to different heat treatments and (ii) the same PVC but slightly crosslinked in order to compare the effect of this chemical crosslinking with the effect of the physical crosslinking obtained after ageing at $T > T_g$. The comparison is made by means of a theoretical approach for the non-elastic deformation of polymers.

(Keywords: poly(vinyl chloride); dynamic mechanical properties; ageing)

INTRODUCTION

It is generally accepted that hard and plasticized poly(vinyl chloride) (PVC) shows a certain degree of crystallinity. The existence of this crystallinity has been demonstrated by a number of techniques such as small- and wide-angle X-ray scattering (SAXS and WAXS)[1–3]. There is no direct evidence about the morphology of the crystallites; however, it has been assumed that they are of a fringed micelle type[4].

This crystallinity is found to increase fairly rapidly with syndiotacticity (which increases with decreasing polymerization temperature); it is around 5–10% for commercial PVC, which is polymerized at 50°C. This type of material has about 30% of syndiotactic triads.

It is well known that morphological changes can be induced on PVC by suitable thermal and mechanical treatments. These changes in local order have been inferred from d.s.c., scattering (SAXS and WAXS), density and dynamic mechanical measurements. Phillips *et al.*[5] have attributed changes in properties caused by heat treatment near and above the glass transition temperature (T_g) to changes in free volume. Michel *et al.*[6], Rybnikar[7] and Witenhafer[8] have treated PVC at high temperatures (> 180°C) and have attributed the observed changes to crystallization. Illers[9] suggested that heat treatments above T_g caused crystallization, while heat treatments below T_g caused decrease in free volume in amorphous regions. The same conclusion has been inferred by Gray and Gilbert[10]. Nakajima[11] and Picòn *et al.*[12] have observed that, at relatively low processing temperatures (< 200°C), the flow behaviour of PVC is highly irregular as compared with that of other thermoplastics. They attribute this behaviour to crystalline nucleation resulting in the appearance of sites for physical crosslinking. This conclusion has been discussed by Blundell[13] and Walsh[14], who have observed that the flow behaviour of fluidized PVC resembles that of a slightly crosslinked gel. Dorrestijn *et al.*[4] have found that the rigidity (G') of PVC gels increases with ageing time. They proposed that there is a uniform distribution (a more or less cubic lattice) of PVC crystallites throughout the system as ageing proceeds; the crystallites grow in size, but their number and location remain the same. This is also possible if we consider that the structure of a gel is determined before the beginning of the ageing process. Furthermore, they have found that the process is thermoreversible. Brown *et al.*[15] have made a comparison between rigid and plasticized PVC as a function of annealing temperature, annealing time and plasticizer concentration. They observed that the addition of plasticizer had surprisingly little effect on the crystallinity of 'commercial' PVC and in particular on the annealing and melting properties of these crystallites. Tsitsilianis *et al.*[16] have concluded that the influence of crystallinity on the physical ageing of PVC can mainly be attributed to the entire structure of the material, including the crystalline phase and the disturbed and undisturbed regions of the amorphous phase, and less to the percentage of induced crystallinity.

It is clear that the need to gain a fuller understanding of the influence of changes in local order on physical properties during thermal and mechanical treatments is very important to know the final properties of the polymer.

The purpose of this paper is to study the microstructural

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* To whom correspondence should be addressed

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changes in PVC during thermal and mechanical treatments by mechanical spectroscopy. Moreover, a crosslinked PVC will be studied and its mechanical behaviour will be compared with the behaviour of a linear PVC. The results will be analysed by means of a model describing the molecular basis of non-elastic deformation of amorphous polymers.

EXPERIMENTAL

The PVC used was a suspension polymer made by Marvylan. The average molecular weights of the polymer were determined by gel permeation chromatography (g.p.c.) in tetrahydrofuran (THF) at 298 K, using a standard Waters g.p.c. apparatus: $\bar{M}_n = 54\,100$ and $\bar{M}_w = 107\,100$ ($\bar{M}_w/\bar{M}_n = 2$). The following basic formulation was used for linear PVC (L-PVC): PVC, 100 phr; dialkyltin dioctylthioglycolate (Ciba-Geigy) as stabilizer, 2 phr; waxes of polyethylene, 0.7 phr, and stearic acid (Merck), 0.1 phr, as lubricants. For crosslinked PVC (C-PVC), 8 phr 1,2-ethanedioxydibutyltin ($Bu_2Sn(OCH_2)_2$) and 4 phr calcium ethylene glycolate ($Ca(OCH_2)_2$) were added. The $Bu_2Sn(OCH_2)_2$ causes crosslinking in PVC through nucleophilic substitution (SN_2 reaction) of chlorine atoms. After dry mixing in a Henschel mixer at high speed (1000 rev min^{-1}) for a few minutes at 378 K, the mixture was extruded in a Leistritz LSM 30–40 mm inter-meshing counter-rotating twin-screw extruder at 453 K, moulded at 473 K and cooled at room temperature. Crosslinking was performed after extrusion of the mixture at 463 K in a Lescuyer pressing machine for 10–15 min, as has been given elsewhere[17].

The mean molecular weight between crosslinks ($\bar{M}_c$) was determined from the swelling rate after immersion of the polymer in THF for 48 h[18]:

$$\bar{M}_c = \frac{V_1\rho_2(v_2/2 - v_2^{1/3})}{\ln(1-v_2)+v_2+\chi_1 v_2^2}$$

where $1/(2\bar{M}_c)$ is the molar number of crosslinks per gram of polymer, V_1 is the molar volume of THF (76.33 ml mol^{-1}), v_2 is the volume fraction of PVC in the gel (0.071), ρ_2 is the density of PVC (1.4 g ml^{-1}) and χ_1 is the interaction parameter of the PVC–THF system (0.14). C-PVC has at least one crosslink per polymer chain.

Mechanical behaviour was measured with the help of a mechanical spectrometer developed in our laboratory[19] and available from Metravib Instrument (Ecully, France); it consisted of a forced oscillation pendulum, working in the temperature range 100–700 K and frequency range 5×10^{-5} to 5 Hz. The mean strain was less than 10^{-4} and the viscoelastic behaviour of polymer materials appeared to be independent of the applied stress over the whole strain amplitude range in all the temperature range used for experiments. The temperature of the sample remained constant to within 0.2 K.

The storage (G') and loss (G'') moduli of the complex shear modulus (G^*) and the internal friction $\tan\phi$ ($=G''/G'$) were measured as a function of frequency (under isothermal conditions) or temperature (for one of several fixed frequencies). Resolution is better than $\tan\phi = 5\times10^{-4}$, with an accuracy that is about ±5%, while relative changes in G' lower than 10^{-3} can be easily detected.

RESULTS

G' and $\tan\phi$ ($=G''/G'$) at 1 Hz for linear PVC (L-PVC) measured over the temperature range of 100–450 K are shown in *Figures 1* and *2*. Two relaxations are distinguished: the principal or α relaxation (at 362 K) and, at lower temperature, the secondary or β relaxation (at 226 K). At temperatures higher than 400 K we can see the flow of polymer. In the same figures, the isochronal behaviour of crosslinked PVC (C-PVC) is also shown. As with L-PVC, it exhibits α and β relaxations ($T_\alpha = 355$ K, $T_\beta = 217$ K), but at high temperature (>400 K) the flow of chains is more difficult. The isothermal behaviours of G' and $\tan\phi$ in the temperature range of 362–340 K for L-PVC are shown in *Figures 3* and *4*. These results show that for the 362, 359, 357 and 356 K isotherms there is an anomalous behaviour at low frequencies. In fact, we can see that the G' modulus is higher for the 357 K isotherm than for the 356 K isotherm at frequencies $<10^{-2}$ Hz. This behaviour explains the variation of the peak in $\tan\phi$ (see *Figure 4*). In spite of this, the construction of master curves in G', G'' and $\tan\phi$ is satisfactory, as can be seen in *Figures 5* and *6*.

Similar results were obtained under isothermal conditions for C-PVC as shown in *Figures 7* and *8*, where a small variation of the peak height was registered.

DISCUSSION

In order to relate the macroscopic behaviour as measured by the spectrometer to molecular motions, the mechanical behaviour through the glass transition range (α relaxation)

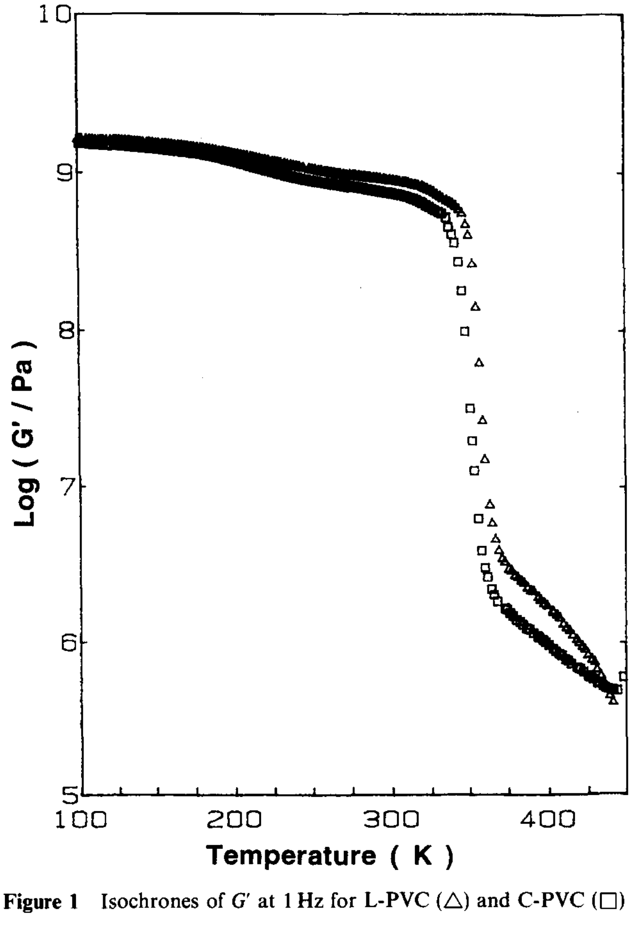

Figure 1 Isochrones of G' at 1 Hz for L-PVC (△) and C-PVC (□)

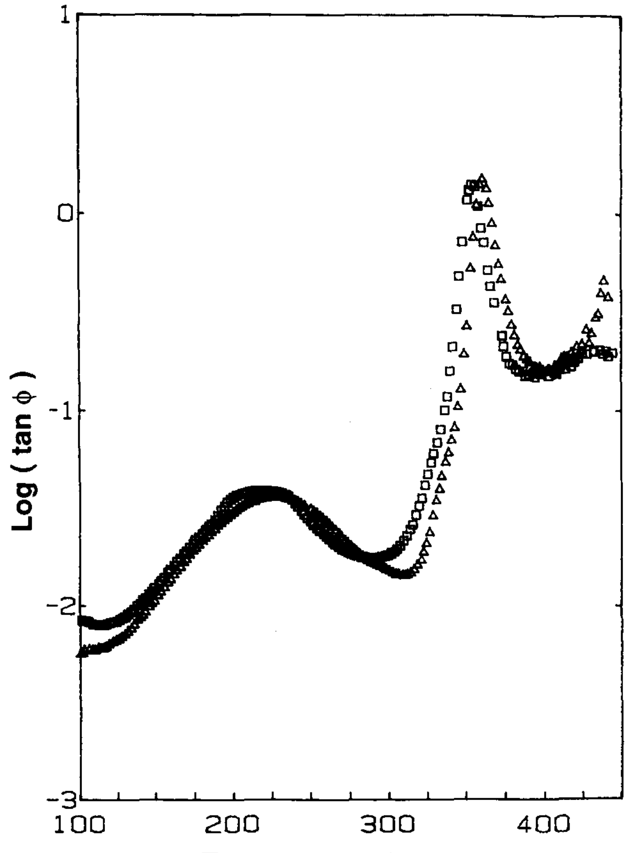

Figure 2 Isochrones of tan ϕ at 1 Hz for L-PVC (△) and C-PVC (□)

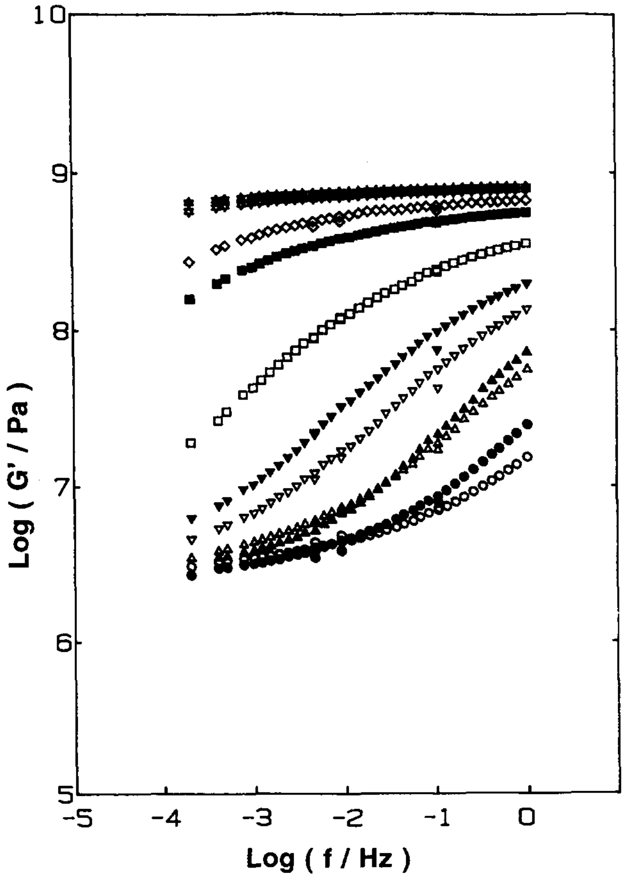

Figure 3 Isothermal plots of G' against frequency for the α relaxation process in L-PVC at several temperatures: (✱) 340 K; (✡) 342 K; (◇) 345 K; (■) 346 K; (□) 350 K; (▼) 353 K; (▽) 355 K; (▲) 356 K; (△) 357 K; (●) 359 K; (○) 362 K

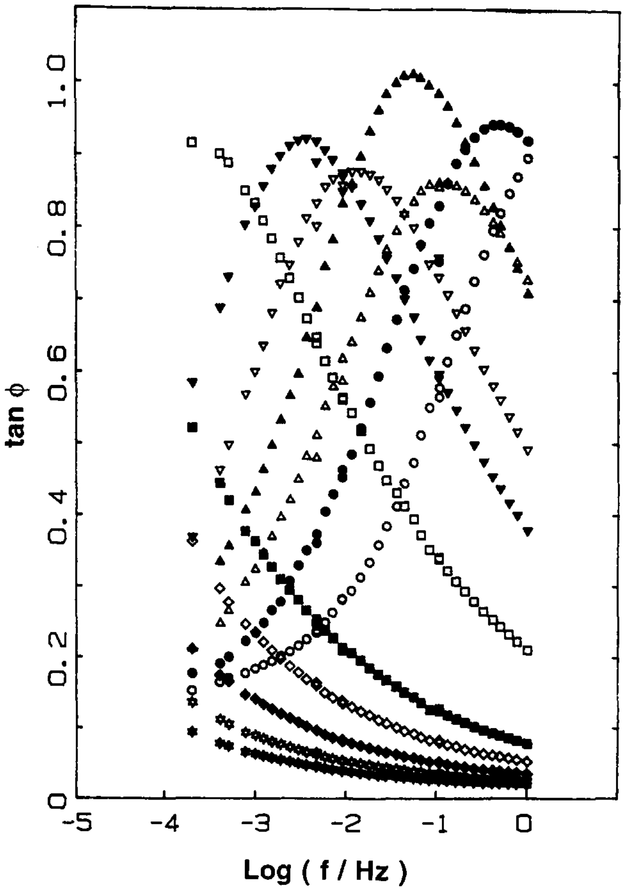

Figure 4 Isothermal plots of tan ϕ against frequency for the α relaxation process in L-PVC at several temperatures: symbols as for *Figure 3*

has been predicted by a model of molecular mobility developed by Perez *et al.*[20–24]. It is based on three main assumptions, briefly recalled here:

(i) The polymer is considered as a packing of repeat units linked together through intra- and intermolecular forces. The concept of a 'defect' is introduced in the case of repeat units that exhibit, with their first neighbours, an increment of enthalpy, entropy and specific volume or compactness, by comparison with a close-packed arrangement of the same units. Based on the usual thermodynamic arguments, it is possible to evaluate the defect concentration C_d when the system is in equilibrium, i.e. at $T > T_g$. At $T < T_g$, $C_d(T) = C_d(T_g)$, except if physical ageing has to be taken into account, leading to a change of C_d as a function of time, $C_d(T, t)$.

(ii) The non-elastic deformation results firstly from the thermomechanical activation of some of these defects; then defects, once activated, become sheared microdomains (s.m.d.).

(iii) If the applied stress remains, this elementary process could be followed by the expansion of s.m.d., owing to correlated movements of units (series process or hierarchical correlation). The characteristic time depends on time during this process, and the theory yields a value characterizing the whole process:

$$\tau_{\mathrm{mol}} = t_0\left(\frac{\tau_\beta}{t_0}\right)^{1/\chi} \qquad (1)$$

where $0 < \chi < 1$ is the correlation parameter (χ increases with C_d); τ_β is the time characteristic of local motions

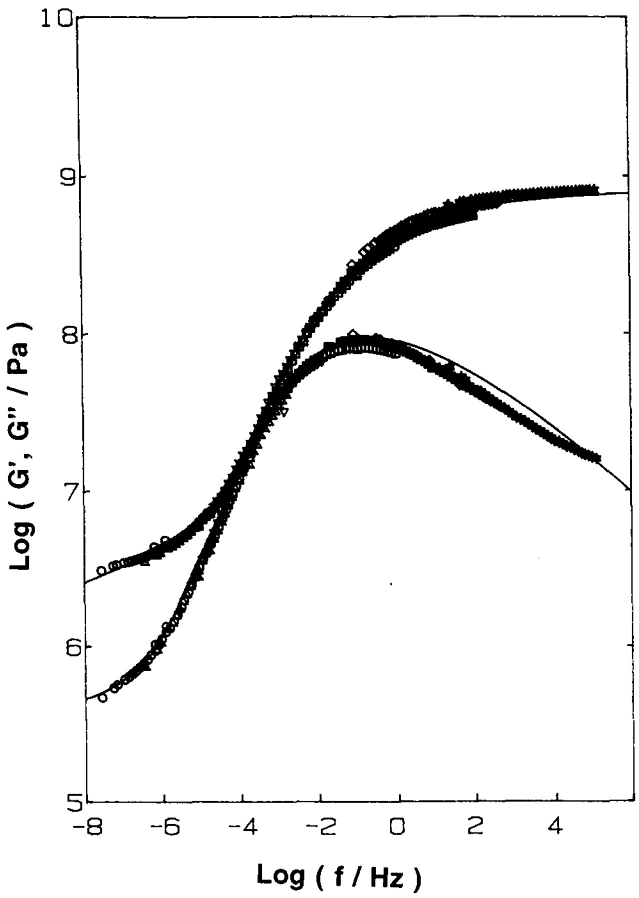

Figure 5 Master curves of G' and G'' for L-PVC: experimental data (symbols) and calculated curves (solid lines) (see *Table 1* for parameters)

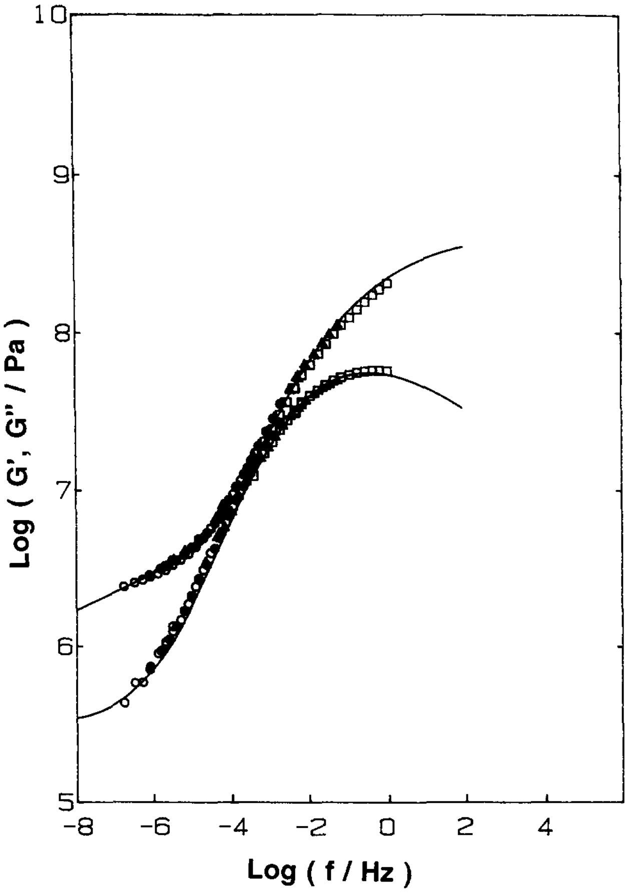

Figure 7 Master curves of G' and G'' for C-PVC: experimental data (symbols) and calculated curves (solid lines) (see *Table 1* for parameters)

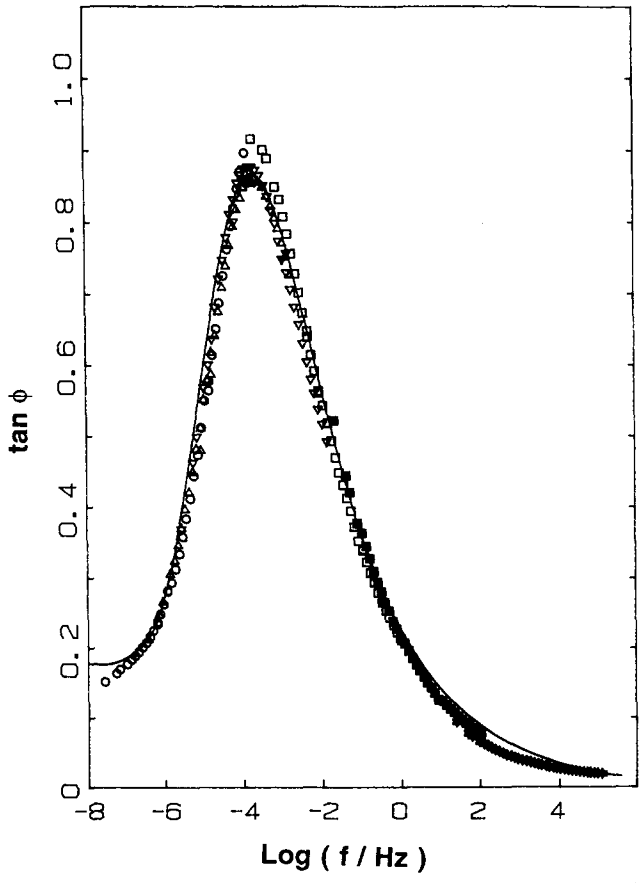

Figure 6 Master curve of tan ϕ for L-PVC: experimental data (symbols) and calculated curves (solid line) (see *Table 1* for parameters)

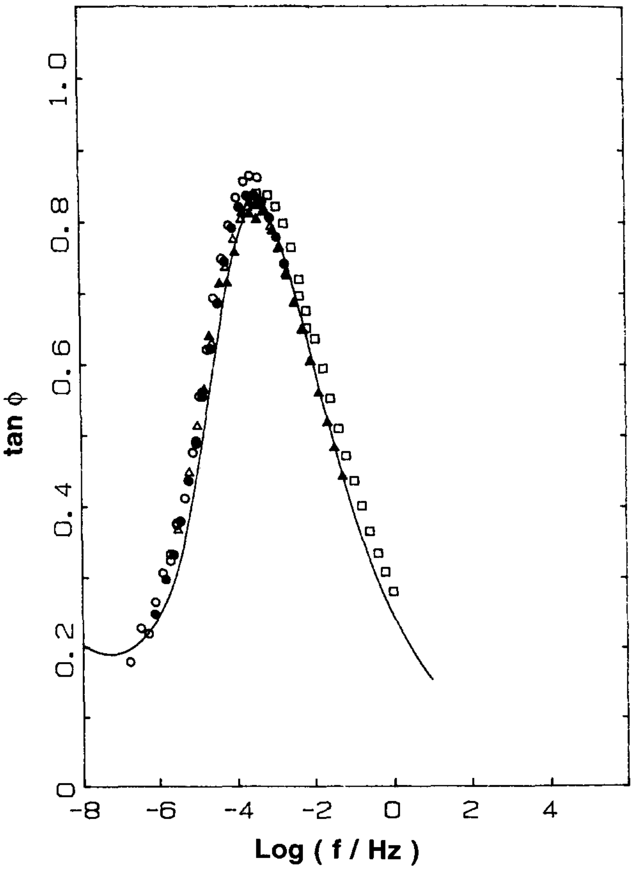

Figure 8 Master curve of tan ϕ for C-PVC: experimental data (symbols) and calculated curves (solid line) (see *Table 1* for parameters)

identified with molecular movements responsible for the so-called β relaxation; and t_0 is a scaling time parameter. For experimental times lower than τ_{mol}, the deformation is mainly anelastic (the system recovers its previous configuration), whereas for a longer time, internal stresses all along the lines bordering s.m.d. are suppressed owing to the annihilation of these lines (viscoplasticity).

These main ideas lead to an expression of the compliance $J(t)$ $(=\varepsilon(t)/\sigma)$ in which three terms appear, namely the elastic, the anelastic and the viscoplastic components[20–24]:

$$J(t)=\frac{1}{G_{\mathrm{U}}}+A\left\{1-\exp\left[-\left(\frac{t}{\tau_{\mathrm{mol}}}\right)^{\chi}\right]\right\}+A'\left(\frac{t}{\tau_{\mathrm{mol}}}\right)^{\chi'} \quad (2)$$

where G_{U} is the unrelaxed (or elastic) modulus, and A and A' are parameters corresponding to the relaxation strength and are proportional to C_{d}. Parameter χ' $(0<\chi<\chi'<1)$ relates the change of χ with strain ($\chi'=1$ for molecular glasses). It is noteworthy that χ' is very sensitive to the presence of crosslink nodes or crystallites[25].

In order to compare theoretical calculations with experimental data, it is convenient to derive $J(t)$ into the complex shear modulus (as a function of frequency ω), using the Fourier transform[20–23]:

$$G^*=G_{\mathrm{R}}+\frac{G_{\mathrm{U}}-G_{\mathrm{R}}}{1+(\mathrm{i}\omega\tau_{\mathrm{mol}})^{-\chi}+Q(\mathrm{i}\omega\tau_{\mathrm{mol}})^{-\chi'}} \quad (3)$$

where G_{R} is the rubber plateau modulus and Q, a function of A and A', is about unity.

With the purpose of describing the terminal zone and since the effect of the flow of chains remains weak in the temperature range corresponding to our data, it is assumed that the modulus $G^*_{\mathrm{R}}(\mathrm{i}\omega)$ corresponding to this zone can be written as[26,27]:

$$G^*_{\mathrm{R}}(\mathrm{i}\omega)=G_{\mathrm{R}}\sum_{j=1}^{n}\frac{\mathrm{i}\omega\tau_{\mathrm{e},j}}{1+\mathrm{i}\omega\tau_{\mathrm{e},j}} \quad (4)$$

where $\tau_{\mathrm{e},j}$ is the time characteristic of the flow of chains, with $\tau_{\mathrm{e},j}=\tau_{\mathrm{mol}}f_{\mathrm{e}}2^j$ (f_{e} is a factor depending on molecular weight or polymerization degree). The distribution of $\tau_{\mathrm{e},j}$ is approximated by a box (width = 20).

This approach has been used extensively to interpret experimental data, obtained with a mechanical spectrometer, with success[28].

The comparison of the theory with experimental data requires the determination of G_{U}, G_{R}, χ, χ', Q, τ_{mol} and f_{e}. Each of these can be determined independently of the others. The presentation of data in a complex-plane plot of G'' *versus* G' (Cole–Cole plot) leads to information about the α relaxation[23]: the maximum value of G'' is related to Q; G_{U} and G_{R} are given by the high- and low-frequency limits, respectively; $\chi=2\theta/\pi$ and $\chi'=2\theta'/\pi$, where θ and θ' are the angles made by the plot at the low- and high-frequency intercepts, respectively (a more accurate determination of χ' is obtained by fitting the linear plot of $\tan\phi$ *versus* $\log f$); f_{e} can be determined by fitting experimental data in the high-temperature range.

Figures 5 and *6* exhibit calculated master curves for L-PVC, and *Figures 7* and *8* exhibit those for C-PVC. There is good agreement between experimental points and calculated curves in both cases. The parameters used in the simulations are shown in *Table 1*.

Table 1 Results for L-PVC, C-PVC, aged PVC and L-PVC with different thermal treatments. $G_{\mathrm{U}}=0.45$ to 1.1 GPa, $\chi=0.23$ to 0.31 and $Q=0.20$

Sample	Curve type	G_{R} (MPa)	χ'	f_{e} (10^4)
L-PVC	Master curves	3.5	0.6	80
	Isochronal	2.0	0.76	3
C-PVC	Master curves	2.8	0.61	20
	Isochronal	1.5	0.76	7
L-PVC	Before ageing	2.6	0.7	5
	After ageing	3.0	0.6	80
PVC M428	Master curves	3.0	0.5	1000
PVC M473	Master curves	3.2	0.5	500
PVC M503	Master curves	5.0	0.5	700

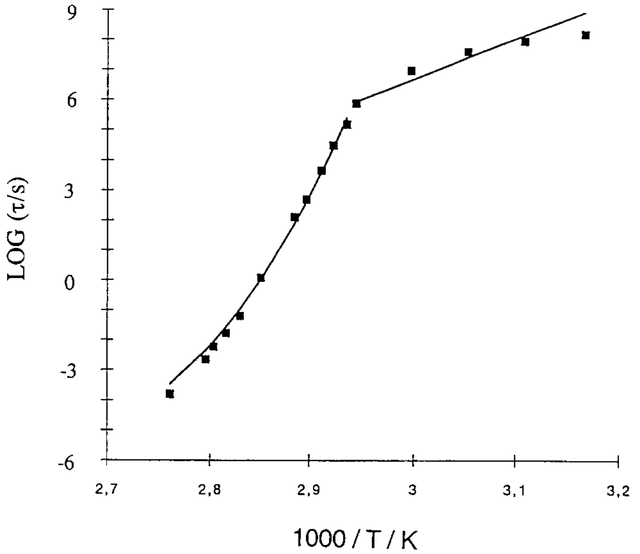

Figure 9 The relaxation time of the α relaxation process for PVC plotted against the reciprocal temperature: experimental data (■) obtained under isothermal conditions and calculated curves (solid lines) with $C=0.05$ and $\chi(T_{\mathrm{g}})=0.25$

The temperature dependence of χ (or τ_{mol}) can be determined by sets of measurements at the metastable equilibrium and under isoconfigurational conditions. We have verified that two parts can be distinguished corresponding to the Arrhenius law ($T<T_{\mathrm{g}}$) and the so-called Vogel–Fulcher–Tammann (VFT) law ($T>T_{\mathrm{g}}$) (*Figure 9*). In the former case χ has been considered constant; equation (1) indicates that the origin of the VFT law in the latter case could be the temperature dependence of χ. This dependence has been taken as[29]:

$$\chi(T)=\frac{1}{1+\{[\chi(T_{\mathrm{g}})]^{-1}-1\}\exp[-C(T-T_{\mathrm{g}})]} \quad (5)$$

where $\chi(T_{\mathrm{g}})$ is the value of χ for isoconfigurational conditions (Arrhenius range) and C is a constant determined by fitting experimental data to a calculated curve in the VFT range. It is worth noting that, having obtained the relation between χ and temperature (or τ_{mol} and temperature, see equation (1)), it is easy to calculate the isochronal thermograms. Results for L-PVC and C-PVC simulation are presented in *Figures 10* and *11*. The calculated curves correspond reasonably well to the experimental ones. The values used in the simulation are shown in *Table 1*. Results of f_{e} under isothermal conditions are not exact because the temperature range is not high enough to see the flow of chains.

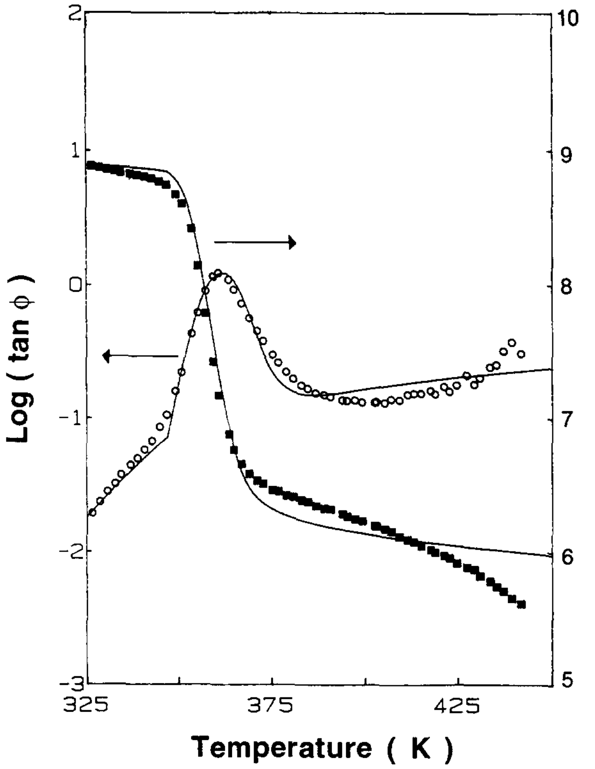

Figure 10 Isochrones of G' (■) and $\tan\phi$ (○) for L-PVC at 1 Hz in the α relaxation range. Also shown are the calculated curves (solid lines)

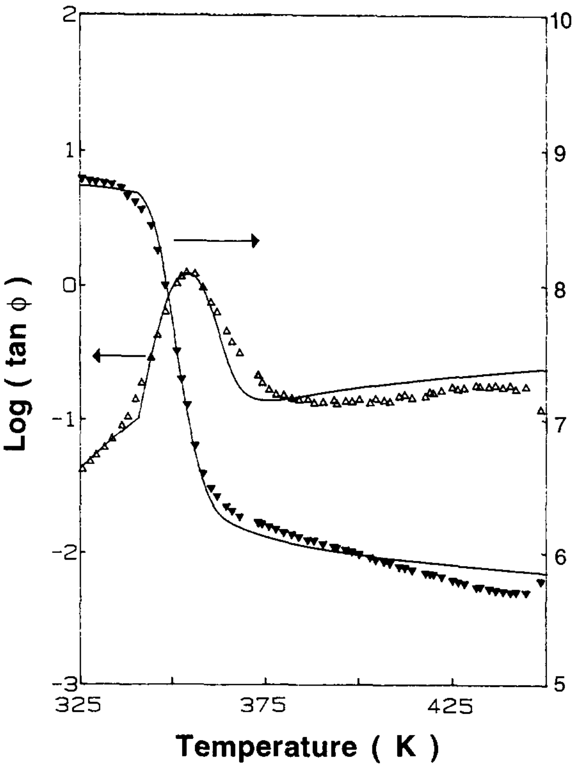

Figure 11 Isochrones of G' (▼) and $\tan\phi$ (△) for C-PVC at 1 Hz in the α relaxation range. Also shown are the calculated curves (solid lines)

As can be seen in *Table 1*, under isothermal conditions (master curves) C-PVC shows a rubber plateau lower than for L-PVC. It is possible that the crosslinking agent behaves like a plasticizer system or that the substitution of chlorine atoms during crosslinking decreases local chain-to-chain interactions. The increase of f_e for C-PVC is the most important difference between the two polymers in isochronal conditions. It means that the time τ_e is higher for the crosslinked polymer, leading to a flow of polymer chains at higher temperatures.

Comparison between the isochronal and isothermal parameters used in the calculated curves for L-PVC gives different values. In fact, it seems that L-PVC shows the behaviour of a crosslinked polymer under isothermal conditions by comparison with the isochronal behaviour because: (i) G_R is higher and (ii) χ' decreases. This means that the polymer is ordered and that the length of free segmental chains is lowered. It is obvious that differences registered during isothermal measurements are responsible for this behaviour. Reasonably, it can be assumed that, during isothermal measurement, a change in structural order happens and this change brings out a decrease in $\tan\phi$ (increase of G_R) (see *Figures 3* and *4*).

In order to verify this idea, isothermal experiments at 356 K ($T > T_g$) over 5 days were made, and G', G'' and $\tan\phi$ were measured each day. Results for G' and $\tan\phi$ are given in *Figures 12* and *13*. As can be seen, there is an evolution of L-PVC as ageing proceeds. In addition, the ageing process is thermoreversible because the polymer was rejuvenated at 423 K for 30 min and the initial state was found again. *Figure 14* shows these results.

The theoretical model was applied to isotherms of L-PVC before and after 5 days of ageing at 356 K in order to explain this process. Results of the simulation are given in *Figures 12* and *13*, and the parameters used

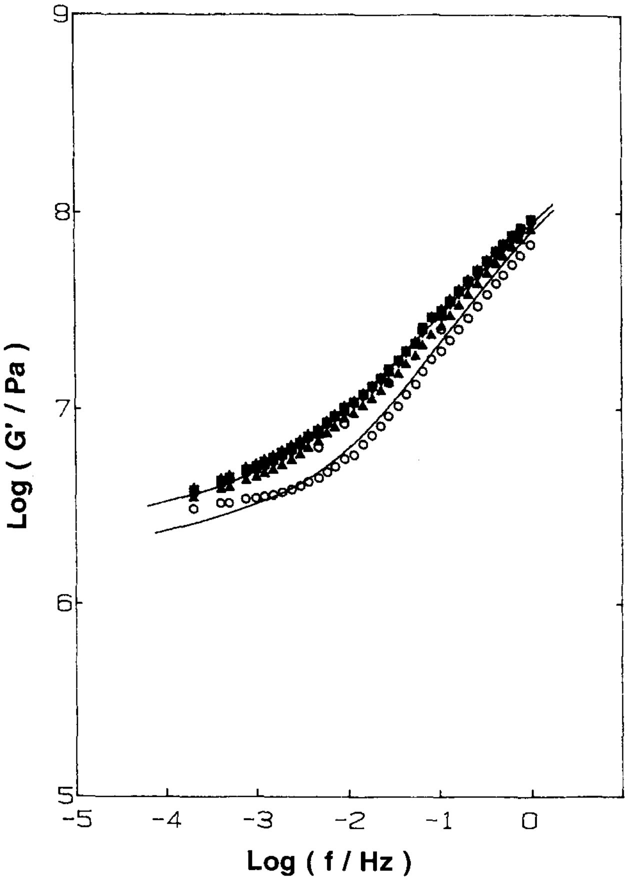

Figure 12 Isothermal plots of G' against frequency for L-PVC at 356 K as a function of time: (○) day 1; (▲) day 2; (△) day 3; (■) day 4; (✱) day 5. Also shown are the calculated curves (solid lines)

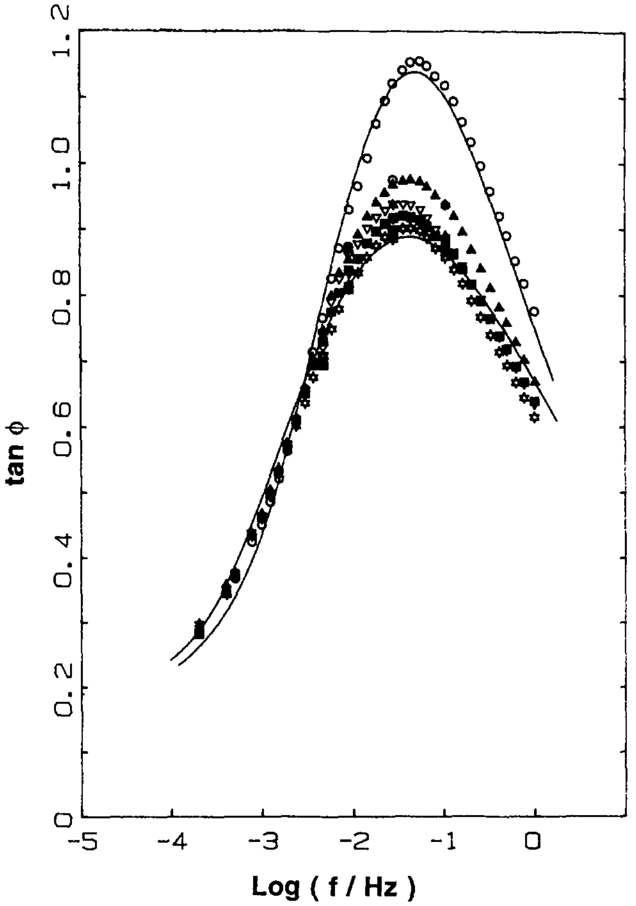

Figure 13 Isothermal plots of tan ϕ against frequency for L-PVC at 356 K as a function of time: symbols as for *Figure 12*. Also shown are the calculated curves (solid lines)

are shown in *Table 1*. The same observations can be seen: (i) increase of G_R and f_e and (ii) decrease of χ'. It is clear that in both cases structural reorganization has taken place when ageing proceeds in L-PVC. This change is most probably the result of an increase of local order, sometimes discussed in terms of 'paracrystallinity' or 'mesomorphic state', which can be induced by above-T_g annealing procedures, and the existence of such an ordered state acts as a network with physical crosslinks. The levelling of the modulus at lower frequencies and the decrease of tan ϕ intensity may be attributed to the formation of this physical network. In addition, destruction of this network can be made by heating the sample for a few minutes at higher temperature than the ageing temperature. It is worth while to note that this temperature is only 20°C higher than the temperature of the ageing process[10]. All these features are in agreement with the theoretical model: after ageing L-PVC presents a higher relaxed modulus as can be expected from the formation of the physical network; the χ' parameter decreases; the mean distance between physical nodes is lower; in fact the formation of ordered domains makes the motion of chains more difficult.

This effect is not visible in isochronal measurements because the heating rate ($1\,\mathrm{K\,min^{-1}}$) does not allow organization of domains. In isochronal curves at high temperatures we can see the flow of chains because the effect of the physical network decreases with increasing temperature due to 'melting' of it. However in C-PVC chemical bonds subsist even at high temperatures, and as a result the flow of chains is more difficult. This effect is predicted by the model through f_e. In fact, the variation of f_e (in other words τ_e) for C-PVC suggests that this PVC will flow at higher temperatures (and times) than L-PVC, in agreement with experimental observations. We must note that, although a description of the general features of isochronal behaviour for L-PVC and C-PVC has been made with success, simulation is not good after α relaxation. We can explain this by the fact that the theoretical model is developed for amorphous or highly crosslinked polymers. L-PVC has an amorphous and a crystalline phase. The model does not take account of the crystalline phase for calculations. In the case of C-PVC, there are two types of crosslinks, physical and chemical, and consequently this PVC can be considered as a two-interpenetrating-network polymer: the first one is a physical network, which is reversible with temperature, and the second one is permanent at any temperature. Maybe, we have to fix a range for the contributions of each type of crosslinking.

Three samples of L-PVC were prepared at 428, 473 and 503 K (M428, M473 and M503) in a Haake Plasticorder internal mixer in order to determine the effect of thermal treatments on PVC. The isothermal study and modelling of these polymers were carried out as has been mentioned earlier in this paper. The results are given in *Table 1*. As can be seen, there is no change of χ' at any heat treatment temperature. This means that mobility (and local order) is the same, after isothermal study at any temperature of PVC processing. As results

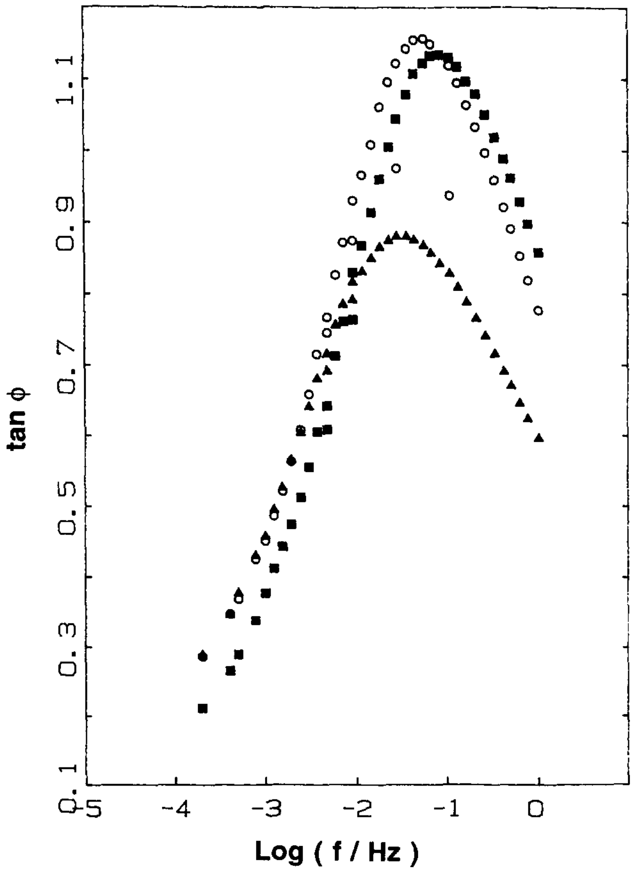

Figure 14 Isothermal plots of tan ϕ against frequency for L-PVC: (○) at 356 K as received; (▲) after ageing at 356 K for 5 days; (■) after ageing at 356 K for 5 days and then 'rejuvenated' by heating at 423 K for 30 min

correspond to isothermal conditions, we cannot compare f_e for all PVC because, as pointed out earlier, the experimental temperature is not high enough to see the flow of chains. As has been reported by Sahraoui[30], thermal destruction of initial local order can bring about the formation of another new order that he calls 'mesophase'. So beyond entanglements, we can think of a physical network with a density of crosslinks formed by (i) crystallites and (ii) local order, determined by the microstructure. In the case of chemical crosslinking by means of covalent bonds, the density of crosslinks must take into account the contribution of this network in addition to the physical network. Only the contribution of (i) and (ii) varies with thermomechanical treatments.

CONCLUSIONS

It has been shown that the data for the rheological behaviour of L-PVC and C-PVC through the glass transition can be described by theoretical relationships implying parameters that have a precise physical meaning. The theoretical model can explain the behaviour of PVC when ageing proceeds or when it has been modified by chemical crosslinking. Analysis of the parameters used in simulations gives information about the microstructure and mechanical properties of the polymer.

When L-PVC is subjected to ageing at $T > T_g$, local ordering occurs, resulting in a modification of the physical network. This process is thermoreversible.

At high temperatures ($\gg T_g$) the contribution of the physical network decreases strongly and the flow of chains appears, but if there is a chemical network this will offer more resistance to heating.

Finally, the global network formed in PVC by crystallites and ordered structures remains constant at all processing temperatures. The effect of thermal ageing at temperatures higher than T_g is to densify until a limiting amount of the physical network which is formed by crystallites and all other ordered structures.

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