

A study of plasticization effects in poly(vinyl chloride)

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Internally and externally plasticized poly(vinyl chloride) (PVC) samples have been investigated by means of different techniques concerning volumetric, elastic and dynamic properties and the results have been compared to those obtained from pure PVC. In all the cases, the glass transition temperature of PVC is markedly lowered. However, this decrease is more important for the external plasticization. This is confirmed by the position of the dielectric loss peaks of the α relaxation. Independently from the changes in temperature, the shape of the relaxation function is modified only in the case of internally plasticized PVC. We suggest that this change in the relaxation function could be related to the small variations produced in the wide angle diffraction patterns of the samples. We can observe that the plasticization effect is linked to a decreasing of the intensity of the dielectric β relaxation process but no important changes are produced in the activation energy of this process. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(vinyl chloride); plasticization; α and β relaxations)

INTRODUCTION

It has been often observed that any modification of the composition or structure leading to a decrease of the glass transition temperature (T_g) (e.g. external or internal plasticization) can also lead to an increase of the quasi static (relaxed) elastic modulus in the glassy state, just below T_g . Many examples of this somewhat surprising behaviour have been published in the case of linear polymers such as poly(vinyl chloride)^{1,2}, aromatic backbone polymers³ as well as networks such as epoxies^{4–6}. It was first tentatively interpreted in terms of variations of the packing density or free volume fraction but it is now clear that it is linked to an unpredicted effect of plasticization on local (β) relaxation processes. As a matter of fact, it can be observed in all the above-mentioned cases that plasticization leads to a decrease of the β dissipation band and to the concomitant decrease of the modulus gap associated to the β relaxation process. In some cases, for instance epoxies⁴, it has been checked that the unrelaxed (ultrasonic) modulus is not affected by this phenomenon. Thus, we are in an apparently paradoxical situation where a given structural change favours the cooperative mobility (effect on T_g and on the α relaxation process), but disfavours the local mobility (effect on the β relaxation process). Concerning this latter effect, all the studied systems seem to display a common feature: the high temperature tail of the β relaxation process is more affected by antiplasticization than the low temperature one. In other

words, plasticization/antiplasticization inhibits mainly the local motions having presumably the highest degree of cooperativity.

Poly(vinyl chloride) (PVC) appears to be a very interesting basis for a study of the antiplasticization effect: its characteristic temperatures corresponding to the glass transition and to the β relaxation are not very far from room temperature but they are well separated: $T_g \approx 80^\circ\text{C}$; $T_\beta(1\text{ Hz}) \approx -40^\circ\text{C}$. A large choice of external plasticizers is available. Furthermore, the presence of labile chlorine atoms allows us to envisage internal plasticization through controlled substitution reactions^{7–9}. It seemed to us interesting to make a detailed study of plasticization and antiplasticization effects in two PVC systems internally and externally plasticized by 2-ethyl hexyl thioglycolate, respectively.

Dielectric measurements, which were proved during many years to be a very useful tool in the study of the molecular mobility in polymeric materials^{10,11}, will be used to study the effects of these structural modifications on the molecular motions corresponding to α and β relaxation processes.

EXPERIMENTAL

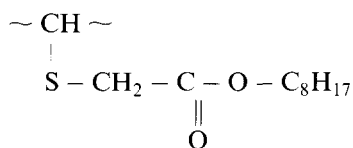
Samples

PVC was obtained by bulk polymerization at 70°C which was stopped at a conversion ratio of 62%. The average number molecular weight ($M_n \approx 44\,000$) was determined at 34°C in cyclohexanone using a Knauer membrane osmometer.

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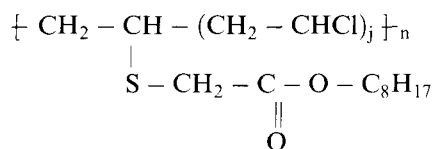
Three kinds of samples were studied in this work:

- (1) pure unplasticized PVC (sample A);
- (2) internally plasticized PVC (samples B₁, B₂, B₃) obtained by nucleophilic substitution of chlorine atoms by the ethyl hexyl thioglycolate (EHTG) group by means of reaction of PVC with potassium 2-ethyl hexyl thioglycolate as reactive (in molar concentration of 1/1):



The degree of substitution, determined from a previously published method⁷⁻⁹ is 7.3%, 6.7% and 5.2% for samples B₁, B₂ and B₃ respectively.

Two definitions of the plasticizer weight fraction w can be proposed. Both are based on the above structure, representative of the average composition of the material



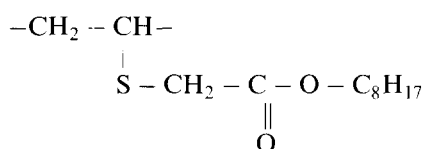
The degree of substitution $x = (1 + j)^{-1}$ has been experimentally determined. From this value we can deduce:

- (a) the weight fraction of the EHTG moiety

$$w = \frac{203}{62.5j + 27 + 203}$$

which can be compared with the weight fraction of the external plasticizer

- (b) the weight fraction of the vinyl comonomer containing the EHTG moiety

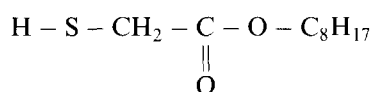


$$w' = \frac{230}{62.5j + 27 + 203}$$

In this case, we consider the internally plasticized polymer as a copolymer. The values of w and w' are listed in Table 1. PVC and the plasticizer are miscible in the concentration range under study. Thus, assuming that the volumes are additive, we can calculate the volume fraction of the plasticizing species $v = w(\rho/\rho_s)$ where ρ and ρ_s are, respectively, the volumic mass of the plasticized PVC and the thiol ($\rho_s = 1200 \text{ kg m}^{-3}$). The values are listed in Table 1.

- (3) externally plasticized PVC (samples C₁, C₂, C₃ and C₄) obtained by a physical mixture of the polymer

and the thiol corresponding to the grafted thioglycolate in series B.



The nominal weight fractions were 19%, 10%, 5% and 2% for samples C₁, C₂, C₃ and C₄ respectively. The compound was prepared by mixing the polymer with EHTG for 10 min at room temperature, then moulded in pellets for 5 min at $T_g + 50^\circ\text{C}$ at a pressure of 25 MPa. The mould temperature is rather low to ensure that the plasticizer does not diffuse out of the sample during the processing. However, we can assess that the product is properly fused because the mechanical properties of unplasticized PVC are in good agreement with the values of the literature¹².

Characterization of samples

The concentration of EHTG in PVC pellets is measured by i.r. spectrometry at 1734 cm^{-1} using a Perkin-Elmer FT i.r. apparatus. The molar absorptivity is $410 \text{ kg mol}^{-1} \text{ cm}^{-1}$.

The T_g value for each sample was determined by differential scanning calorimetry (d.s.c.) by means of a Perkin-Elmer DSC4 apparatus. The sensitivity and the scanning rate were 2 mcal s^{-1} and 10 K min^{-1} , respectively.

The density was determined by pycnometry at 20°C using a laboratory balance with a relative precision of 10^{-4} .

The linear expansion coefficient (α) was determined with an Adamel Dilatometer DI21 at 10 K min^{-1} heating rate.

Ultrasonic measurements were made at 5 MHz using pulsar receiver SOFRANEL 5055 and two probes SOFRANEL M110 and V156. The precision and reproducibility essentially depend on how parallel the sample surfaces are. They were less than 2% in the cases under study. The moduli were calculated using the relations

$$v_L^2 = \frac{B3(1-\nu)}{\rho(1+\nu)} \quad v_T^2 = \frac{G}{\rho} \quad (1)$$

$$E = 3B(1-2\nu) = 2G(1+\nu) \quad (2)$$

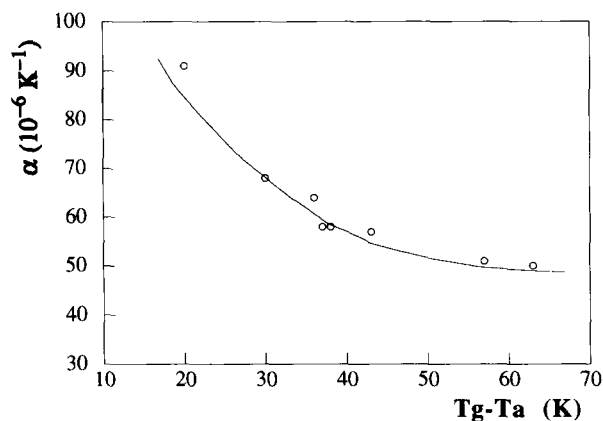
where v_L and v_T are respectively the longitudinal and transversal wave propagation rates, E , B and G are the Young's, bulk and shear moduli, respectively, ρ is the density and ν the Poisson's ratio.

Wide angle X-ray scattering (WAXS)

In order to have a structural characterization of the samples, WAXS measurements were performed in a powder diffractometer (X-ray generator Philips PW1729, vertical goniometer Philips PW1820 and graphite monochromator) equipped with a sample holder HETTK (from ANTON PAAR) that allows us to record the X-ray intensity scattered by the specimen whose temperature can be varied between 20 K and 700 K. In all the cases, the patterns were obtained at temperatures 50 K below the respective T_g of each sample; in this framework the diffractograms are representative of each sample at the same isostructural state owing to the

Table 1 Volumetric and elastic characteristics of the samples used in this work. The column $w_{i,r}$ shows the experimental values for w obtained by i.r. measurements

Sample	$w (\times 100)$	$w_{i,r} (\times 100)$	$w' (\times 100)$	$\rho (\text{kg m}^{-3})$	$\nu (\times 100)$	$\alpha (10^{-6} \text{K}^{-1})$	ν	$E_u (\text{GPa})$	$T_g (\text{K})$
A	0.0	0.0	0.0	1400	0.0	50	0.364	4.4	356
B ₁	19.8		22.5	1350	25.3	64	0.366	4.5	329
B ₂	18.5		20.9	1350	23.5	58	0.366	4.6	330
B ₃	14.8		16.8	1370	19.2	57	0.369	4.3	336
C ₁	19.0	14.0		1310	20.7	91	0.413	2.5	313
C ₂	10.0	8.7		1364	11.4	68	0.365	3.9	323
C ₃	5.0	5.5		1395	5.9	58	0.360	4.5	331
C ₄	2.0	2.0		1394	2.3	51	0.364	4.5	350


Figure 1 Dilatation coefficients of the samples plotted vs the difference between their glass transition temperature T_g and room temperature T_a

fact (which will be discussed below) that the T_g of PVC is lowered when the polymer is plasticized. $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was used in all the cases.

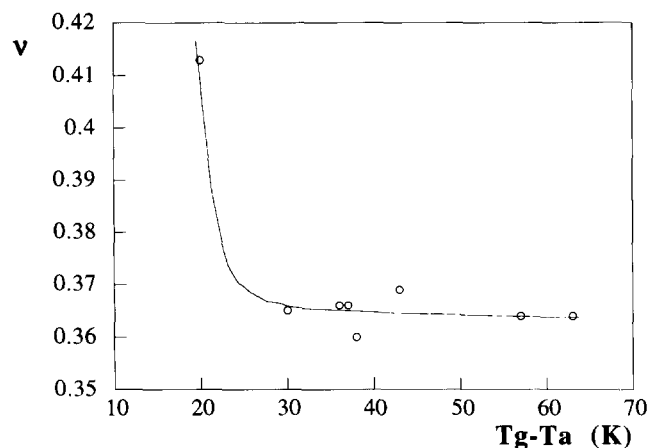
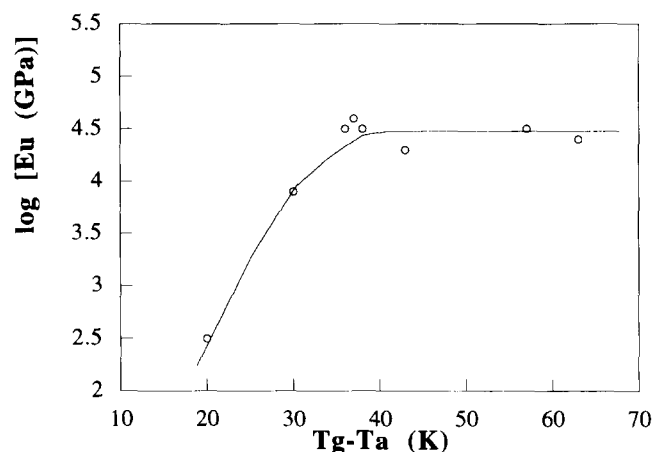
Dynamic electric thermal analysis (DETA)

The experimental DETA system has already been described in different studies¹³⁻¹⁶. The set-up, consisting of an EG&G PAR 5208 two phase Lock-in analyser fully controlled by a computer, allows us to measure simultaneously the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$) of a given material (whose temperature is controlled within 0.1 K) under a controlled atmosphere of helium in a frequency range between 1 Hz and 10^5 Hz and a temperature range between 100 K and 600 K.

RESULTS AND DISCUSSION

Volumetric properties

The expansivity coefficient (Table 1) appears as a decreasing function of T_g . It is plotted in Figure 1 against $T_g - T_a$, where T_a is the room temperature (20°C). All the points are close to a unique curve which can be considered as a master curve. As a matter of fact, the variation of α with the temperature for a given sample exhibits a pseudo parabolic shape in the domain just below T_g . The curves $\alpha = f(T)$ of two samples showing glass transition temperatures of respectively T_{g1} and T_{g2} must be superimposed by translation of amplitude ($T_{g1} - T_{g2}$) along the temperature axis.


Figure 2 Poisson's ratios of the samples plotted vs the difference between their glass transition temperature T_g and room temperature T_a

Figure 3 Young's moduli of the samples plotted vs the difference between their glass transition temperature T_g and room temperature T_a

Elastic properties

The values of Young's modulus E_u and Poisson's ratio ν determined by ultrasonic measurements are listed in Table 1. They display the same trend as the coefficient of dilatation; in other words, their temperature behaviour can be represented by a single master curve by plotting E_u and ν against $(T_g - T_a)$ (see Figures 2 and 3). It can be observed that, for low plasticization extends, typically for T_g depressions lower than 30°C , there is apparently no significant effect. From previously published values of

the activation energy for the β relaxation process in PVC^{10,11}, it can be deduced that this relaxation process is located around T_a for a frequency of 5 MHz. Thus, the reported value of E_u is close to the unrelaxed modulus one. Since this latter is essentially linked to the cohesive energy density, we can conclude that the cohesivity is not seriously modified in the range of plasticizer concentrations under consideration, which is of little surprise for miscible systems. For higher extents of plasticization (T_g depression above 30°C), e.g. when T_g is in the immediate vicinity of room temperature, we expect an increase of ν towards 0.5 and a decrease of the stiffness, which is effectively observed. No significant difference between the results corresponding to internally and externally plasticized samples is noticed.

Glass transition temperature

Values of T_g determined by d.s.c. are listed in Table 2. Many semi-empirical or theoretical relationships linking T_g to the structure and composition are tested:

(a) Fox relationship¹⁷

$$\frac{1}{T_g} = \frac{1-w}{T_{g_p}} + \frac{w}{T_{g_s}} \quad (3)$$

where T_{g_p} and T_{g_s} denote respectively the T_g value for the polymer and the one of the plasticizing species. From this relation we can determine the latter by

$$\frac{1}{T_{g_s}} = \frac{1}{w} \left(\frac{1}{T_g} - \frac{1}{T_{g_p}} \right) + \frac{1}{T_{g_p}} \quad (4)$$

The results are listed in Table 2.

(b) Kelley-Bueche relationship¹⁸

$$T_g = \frac{\alpha_p(1-v)T_{g_p} + \alpha_s v T_{g_s}}{\alpha_p(1-v) + \alpha_s v} \quad (5)$$

where α_p and α_s are the coefficients of free volume expansion for the polymer and for the plasticizing species respectively. This relationship can be arranged as

$$f(w) = \frac{T_{g_p} - T_g}{w T_{g_p}} = b \frac{T_g}{T_{g_p}} - a \quad (6)$$

where $a = (\alpha_p T_{g_s} / \alpha_p T_{g_p}) - 1$ and $b = (\alpha_s / \alpha_p) - 1$. By plotting $f(w)$ vs T_g / T_{g_p} , we expect a straight line of slope b . The values of $f(w)$ are given in Table 2.

(c) Couchman's relationship¹⁹

$$\ln T_g = \frac{(1-w)\Delta C_{p_p} \ln T_{g_p} + w\Delta C_{p_s} \ln T_{g_s}}{(1-w)\Delta C_{p_p} + w\Delta C_{p_s}} \quad (7)$$

where ΔC_{p_p} and ΔC_{p_s} denote the gap of heat capacity at T_g for the polymer and for the plasticizing species respectively. As in the precedent case, we can define $g(w)$ as

$$g(w) = \frac{\ln T_{g_p} - \ln T_g}{w \ln T_{g_p}} = b' \frac{\ln T_g}{\ln T_{g_p}} - a' \quad (8)$$

where $a' = (\Delta C_{p_s} \ln T_{g_s} / \Delta C_{p_p} \ln T_{g_p}) - 1$ and $b' = (\Delta C_{p_s} / \Delta C_{p_p}) - 1$. The values of $g(w)$ are shown in Table 2.

The results call for the following comments:

- The plasticizing efficiency can be assessed by T_{g_s} , $f(w)$ or $g(w)$ depending on the chosen theory. Globally, they display the expected trends, e.g. internal plasticization is less efficient than external plasticization.
- Whatever the chosen theory, the quantity related to the plasticizer efficiency shows an extreme at $w = 5.5\%$ whereas all the theories predict a monotonic variation. It can be observed that other physical properties such as density or Poisson's ratio also display a singularity at the same concentration, which confirms that the corresponding effect of T_g is significant. It is interesting to note that this concentration corresponds to an average intermolecular distance of 1.64 nm, e.g. a value higher but in the same order of magnitude as the size of the plasticizer species. Thus, it could be tentatively suggested that the plasticizer efficiency begins to increase when the probability of the molecular interactions between plasticizer molecules becomes high. This hypothesis could find some support in Di Benedetto's theory²⁰ in which T_g depends on three types of interactions: P-P, P-S and S-S (P = polymer, S = plasticizer). S-S interactions would become important only above a critical concentration.
- Concerning internal plasticization, the chosen concentrations are too close to one another to establish the validity of the theories under consideration or to choose between one theory or another. If, as it has been previously shown⁷⁻⁹, the substitution of chlorine atoms is strongly influenced by the stereostructure of the polymer, a prediction of T_g must take into account the copolymer effect of the thioglycolate containing structural units, but also the suppression of the copolymer effect of the reacted vinylchloride units. We observe experimentally the balance of these two effects but we lack data to distinguish between them.

Dynamic electric thermal analysis (DETA)

In this section and in the following one the analysis will be restricted to samples A, B₁ and C₁ in order to compare the results from DETA and from WAXS corresponding to pure PVC and to samples representative of series B and C (with the same amount of EHTG plasticizer).

α relaxation of PVC. Figure 4 shows the raw experimental loss dielectric curves obtained for the three samples in the range of temperatures corresponding to their

Table 2 Thermal characteristics of the samples used in this work

Sample	w (×100)	T_g (K)	T_g/T_{g_p}	T_{g_s} (K)	f(w)	g(w)
A	0.0	356				
B ₁	19.8	329	0.924	258	0.384	0.0679
B ₂	18.5	330	0.927	255	0.395	0.0697
B ₃	14.8	336	0.944	260	0.378	0.0663
C ₁	19.0	313	0.879	225	0.637	0.1155
C ₂	10.0	323	0.907	164	0.930	0.1661
C ₃	5.0	331	0.930	150	1.400	0.2471
C ₄	2.0	350	0.983	192	0.850	0.1459

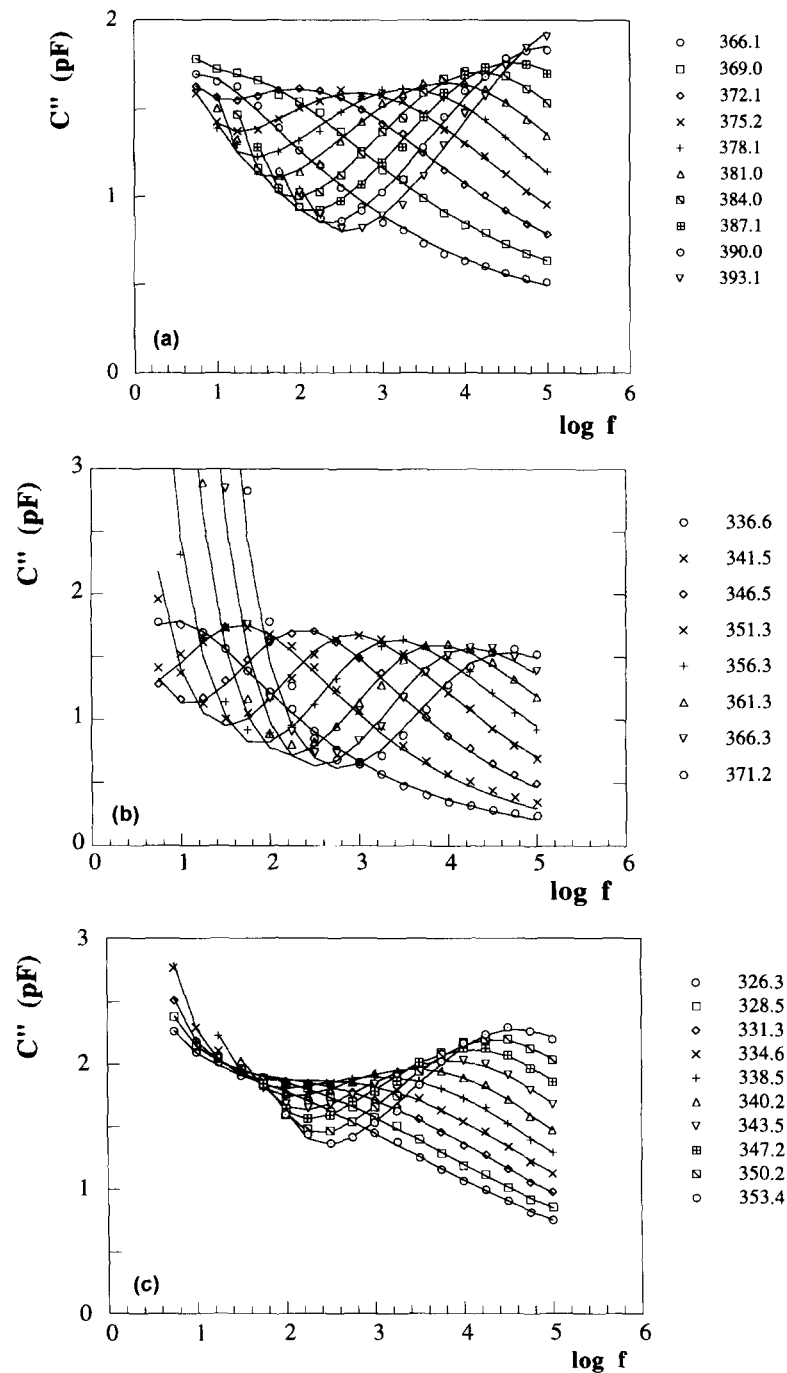


Figure 4 Experimental loss capacity data C'' (proportional to the imaginary part of the dielectric constant ϵ'') plotted against the frequency ($f = \omega_m/2\pi$) in the α relaxation for samples A (a), B₁ (b) and C₁ (c). Solid lines show the fitting of the experimental points to an addition of the HN function and the contributions of the conductivity and β relaxation in this region (see the text). In the legend the numbers mean the temperature of the isotherm in K

glass transition. It can be observed that the plasticization of PVC changes appreciably the shape of the loss curves: in the low frequency side the conductivity for the samples C₁ and B₁ is much higher than that of sample A in relation to the maximum of the curves and, on the other hand, the curves obtained for samples A and B₁ are larger than the ones of sample C₁. Nevertheless, this last effect is not very clear at this plot. Prior to a quantitative study, it is necessary to correct these data due, first, to the losses of the β relaxation process that overlap with the α one in the high-frequency region, and, second, to the presence of an important conductivity tail in the low-frequency

side of the relaxation peaks. The correction method has been previously used^{16,21} in recent studies.

The temperature dependence of the frequency of the loss maxima (ω_m , or $f_m = \omega_m/2\pi$, or the relaxation times τ_{HN}) obeys the Vogel-Fulcher (VF)^{22,23} relationship (see Figure 5) as

$$f_m = f_0 \exp[-DT_0/(T - T_0)] \quad (9)$$

It must be recalled that VF law is equivalent to the well known Williams, Landel and Ferry (WLF) equation²⁴ where $T_0 = T_g - C_2$, C_2 being one of the WLF

Table 3 VF parameters corresponding to each sample in the α relaxation of PVC

Sample	$\log f_0$	D (K)	T_0 (K)
A	9.6	1.8	337
B ₁	11.2	4.9	279
C ₁	10.4	4.4	270

Table 4 Values for the shape parameters of the HN function, α and γ , and for the coupling parameter β of the Ngai's coupling model obtained in each sample

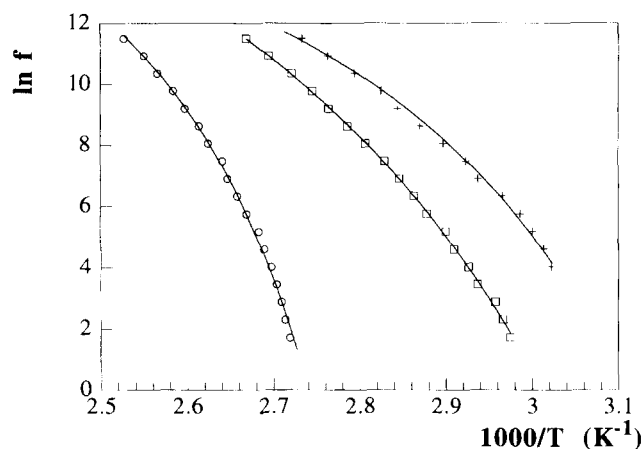
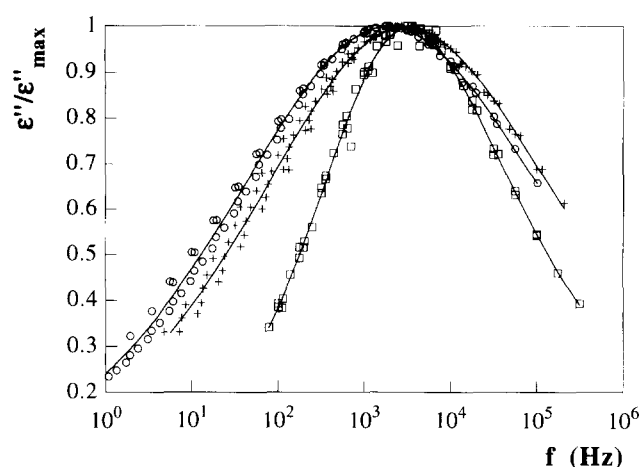
Sample	α	γ	β
A	0.37	0.82	0.24
B ₁	0.61	0.53	0.35
C ₁	0.37	0.83	0.25

constants. D is a parameter related to the fragility concept introduced by Angell²⁵ and f_0 is a pre-exponential factor. Table 3 shows the parameters obtained in each case from the fittings to the VF law. As expected, T_0 decreases in the case of the plasticized sample and is lower for the external (C₁) than for the internal (B₁) plasticized sample. At this point, it is interesting to point out that the plasticization effect, in addition to the temperature lowering of the α relaxation process, results in drastic changes in the time scale of the relaxation in the two plasticized PVC samples: both f_0 and D parameters change significantly in the two cases. The time scale (shown by f_0) of the relaxation process is almost changed in one order of magnitude and the fragility (shown by D) is also seriously transformed meaning that internally and externally plasticized PVC samples are stronger than pure PVC, this polymer being very peculiar because of its high fragility values^{16,21}.

The complex dielectric permittivity data are well described in the three samples by the Havriliak–Negami (HN) empirical function²⁶ expressed by

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau_{\text{HN}})^\alpha]^\gamma} \quad (10)$$

where ϵ_s and ϵ_∞ are the asymptotic values of the real part of the dielectric constant at low and high temperatures respectively, τ_{HN} is an average relaxation time characteristic of the material at a given temperature and α and γ are the shape parameters of the relaxation function (both of them ranging between 0 and 1). Owing to the fact that, within the experimental dispersion, the values of the shape parameters of the HN function, α and γ , do not change appreciably with the temperatures of the DETA experiment, master curves have been built for all the samples (see Figure 6) with the loss data already corrected from the conductivity and from the overlapping of β relaxation. The three master curves have been drawn by using the temperature of the loss maximum at 1000 Hz in each case (379 K, 357 K and 340 K for samples A, B₁ and C₁ respectively) as temperature of reference in order to study the relaxation functions of the three samples at the same isostructural state. A fitting of these curves to the HN function allows us to know the shape parameters in each case (see Table 4). We observe differences between the three samples that can be summarized as follows:


Figure 5 Relaxation map obtained for the three samples A (circles), B₁ (squares) and C₁ (crosses). Continuous lines represent the fitting to a VF law in each case. Note that $f = \omega/2\pi$

Figure 6 Master curves built for the three samples A (circles), B₁ (squares) and C₁ (crosses). Continuous lines represent the fitting to the HN function in each case. Note that $f = \omega/2\pi$

- The frequency of the maximum is shifted towards higher values when PVC is modified. This fact is in straight correlation with the changes in the time scale of the α relaxation (or in the lowering of its characteristic temperature) that have been observed in Figure 5.
- Concerning the shape parameters of the relaxation function obtained in each case, the differences are very important in the case of sample B₁. We can see in Figure 6 that, even if the master curves of samples A and C₁ are shifted in the frequency domain, their shapes do not vary appreciably and these two curves can be superposed in a graphic representation normalized to the frequency of the maximum, excepting the lowest frequency side where sample C₁ shows a slightly higher slope than sample A. Nevertheless, it is evident that the relaxation function is drastically narrowed in the case of sample B₁. This is the greatest difference that is found between the dielectric response in the three samples and it will be an important subject of discussion below.

The shape parameters used to describe the relaxation function for the material in the frequency domain make

it difficult, because of the empirical character of the HN function, to relate these parameters to the structural characteristics of the material. In the last years, Ngai's coupling model of relaxation processes, assuming that a correlation of motions exists among the microscopic units (i.e. chain segments) responsible for the observed macroscopic behaviour, has been widely used to interpret relaxation results in very different types of glassy materials concerning miscellaneous problems²⁷⁻²⁹. In a complex correlated system, a relaxing unit tends to relax at short times with an uncoupled or independent (called 'primitive' in this framework) rate $W_0 = 1/\tau_m$ (where τ_m is the so-called primitive relaxation time associated to the uncoupled or primitive motion) until a characteristic time $t_c = 1/\omega_c$ is reached, after which the effects of correlations modify the dynamics. It is considered that beyond t_c the rate W_0 is slowed down by a self similar function of time

$$W(t) = W_0(\omega_c t)^{-(1-\beta)} \quad (11)$$

The exponent $(1 - \beta)$ is known as the coupling parameter n . The normalized correlation function, $g(t)$, obeys the equation

$$\frac{dg(t)}{dt} = -W(t)g(t) \quad (12)$$

which leads to

$$g(t) = \exp[-t/\tau_m], \quad \omega_c t \ll 1 \quad (13)$$

$$g(t) = \exp[-(t/\tau_{WW})^\beta], \quad \omega_c t > 1 \quad (14)$$

Expression (17) is the well known Kohlrausch-Williams-Watts (KWW) stretched exponential function^{30,31} where τ_{WW} is a characteristic relaxation time at a given temperature and the parameter β (ranging between 0 and 1) describes the non-exponentiality or the non-Debye character of the relaxation process where τ_{WW} is related to the primitive time τ_m given by

$$\tau_{WW} = [\beta\omega_c^{(1-\beta)}\tau_m]^{1/\beta} \quad (15)$$

Recent results^{32,33} from quasielastic neutron scattering on a PVC sample very similar structurally (molecular weight, tacticity distribution, etc.) to the one used in this work suggesting that t_c should be of the order of 10^{-11} - 10^{-12} s providing an experimental support to Ngai's coupling scheme.

At this point, the problem is how to analyse the relaxation data in the frequency domain in terms of the coupling model formulated in the time domain, that is, how to obtain the Ngai's coupling parameter β corresponding to the stretched exponential KWW relaxation function in the time domain from the parameters characterizing the HN relaxation function in the frequency domain. This problem has been recently solved³⁴ establishing the KWW and HN functions are straightforwardly related by a non-analytical form; the KWW function can be considered to be well described by a Fourier transformation of the HN function within small imprecisions if the shape parameters α and γ show simultaneously values in the intervals

$$0.40 \leq \alpha \leq 1 \quad (16)$$

$$0.25 \leq \gamma \leq 1 \quad (17)$$

Reference 35 provides a non-analytical correspondence

between pairs of α and γ values [that are in the range indicated by conditions (16) and (17)] and the β parameter of the KWW function that fits with good accuracy the Fourier transformation of the HN function characterized by the given α and γ parameters. In these conditions, we can obtain a measure of the complexity of the relaxation process by means of the parameter β (which is the coupling strength of a fundamental relaxation mode to a complex system) and the relaxation time τ_{WW} for the process in the time domain. In this framework, we have calculated the value of the β parameter for each sample. Results for samples A and C₁ (in α parameter) are just in the limit imposed by condition (16), and we observe the very low value obtained for the coupling β parameter, around 0.25 (see Table 4), in these two samples. This fact indicates the strong coupling strength characteristic of PVC and the mixing with EHTG does not alter the value of β and, hence, the molecular coupling. On the contrary, sample B₁ shows an appreciably higher value of β (around 0.35) indicating that the strong coupling characteristic of PVC has been seriously diminished. Within the framework of Ngai's coupling model, we have evaluated the apparent activation energy for the α process at the macroscopic level E_a from the parameters D and T_0 that are shown in Table 1 for each sample as

$$E_a = K \frac{d(\log f_m)}{d(1/T)} = KDT_0 \frac{T^2}{(T - T_0)^2} \quad (18)$$

where K is Boltzmann's constant. The coupling model predicts that the activation energy for the relaxation process in its earlier stages (at a microscopic level) is

$$E_m = \beta E_a \quad (19)$$

In Figure 7 we observe the values of E_m and E_a plotted against $T - T_g$. This plot calls for the following comments:

- (a) Concerning E_a values, the plasticized samples show lower values than unplasticized PVC, so that the plasticization carries not only the lowering of the characteristic temperature of the α relaxation but also a decreasing of the characteristic energy of the process.

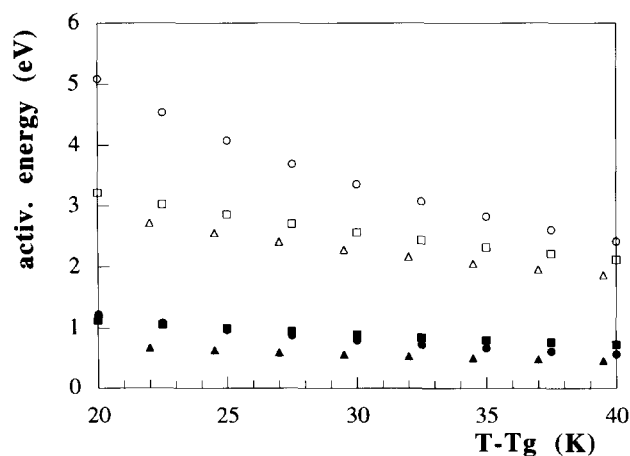


Figure 7 Plot of the macroscopic apparent activation energy E_a (empty symbols) and of the microscopic activation energy (full symbols) for samples A (circles), B₁ (squares) and C₁ (triangles)

(b) On the other hand, E_m values for the three samples are not constant with the temperature because of the VF origin of E_a and the constant character for β . It appears that E_m values do not differ significantly from A to B₁. In contrast, externally plasticized PVC shows, in all the temperature range where the experimental results are obtained, E_m values systematically lower than the ones of the two other samples.

β relaxation of PVC

In opposition to the segmental molecular motions performed in the α relaxation process, the molecular mobility in the β process is performed by smaller units and thus assumed to be more localized through the material^{10,11}. In the case of PVC, this relaxation process is usually found to be located some decennials of degrees below room temperature when one makes the experiment at low frequencies. Concerning the shape of this relaxation function, it is currently assumed that β relaxation does not follow the time-temperature superposition principle³⁵ and the data in this region are not capable to fit a HN function with fixed shape parameters as is the case in the α relaxation. Because of this fact, we

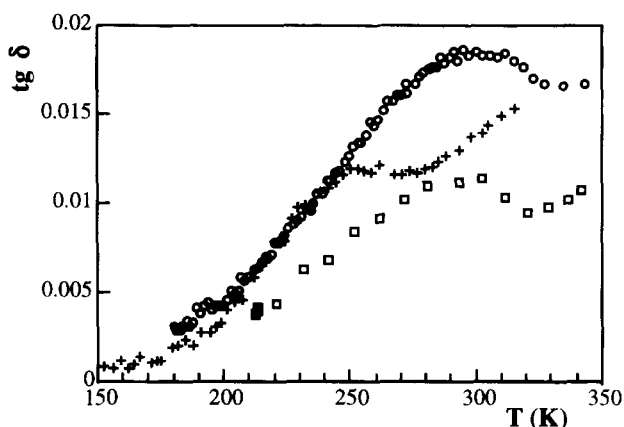


Figure 8 Isochronal (100 Hz) loss curves obtained for samples A (circles), B₁ (squares) and C₁ (crosses) in the β relaxation region

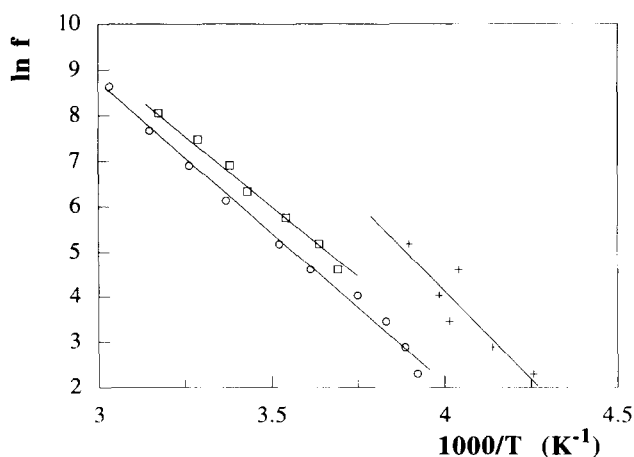


Figure 9 Arrhenius plot of the frequencies of the loss maxima obtained for the three samples A (circles), B₁ (squares) and C₁ (crosses). Continuous lines represent the fitting to the Arrhenius law in each case. Note that $f = \omega/2\pi$

will work with the isochronal curves to compare the results of the three samples.

Figure 8 shows, for the three samples, the loss tangent ($\text{tg } \delta = \epsilon''/\epsilon'$) values obtained below room temperature at a frequency of 100 Hz. We can observe there that the process is very wide in temperature and, in the high temperature side, the strong overlapping between α and β processes means that the loss signal does not decrease after the maximum; this effect is more pronounced when one studies β losses at higher frequencies and the maxima corresponding to the β relaxation are not observed because this process, owing to its very low activation energy, is drastically shifted towards higher temperatures and then masked by the α loss signal. This effect is emphasized in the case of the two plasticized samples, especially in the case of the external plasticization, where the α relaxation process appears at lower temperatures and, in consequence, a greater overlapping between α and β processes is produced. In this context one can observe β maxima only in the loss curves corresponding to low frequencies. The plasticization of PVC results in two different effects in the β relaxation:

- the temperature of the loss maxima is lightly shifted towards lower values;
- the maximum amplitude of the loss band is noticeably decreased, especially for the internally plasticized sample.

The temperature dependence of the frequency of the loss maxima f_m is found to be Arrhenius type^{10,11}, showing the thermally activated character of this process

$$f_m = f_0 \exp(-E/KT) \quad (20)$$

where E is the activation energy for the relaxation process. Figure 9 shows an Arrhenius plot of the frequencies of the loss maxima for the three samples. The points corresponding to the plasticized PVC samples are shifted towards lower temperatures in comparison to the points from pure PVC. This fact results in a small change in the time scale of the relaxation process that is reflected in the higher values found for the pre-exponential factor of the fitting to the Arrhenius law (see Table 5). We can observe that the activation energy E for the β relaxation process of PVC is not altered, within the experimental dispersion, by the plasticization.

These experimental facts, especially case (b), reminds us of the antiplasticization effect observed in slightly plasticized PVC^{11,36}, whose two main consequences on the mechanical β relaxation process are an increase of the elastic modulus and a disappearance of the β loss peak. Thus, it seems that antiplasticization is observed in the dielectric local molecular motions in external as well as in internal plasticization confirming its very general character since it has been reported, for PVC, in the case of low molecular weight additives^{11,36} as well as macromolecular^{10,11,37,38} ones. Further work concerning the dielectric and mechanical β relaxation process of

Table 5 Arrhenius parameters corresponding to each sample in the β relaxation of PVC

Sample	$\log f_0$	E (eV)
A	12.4	0.59
B ₁	12.7	0.57
C ₁	14.8	0.64

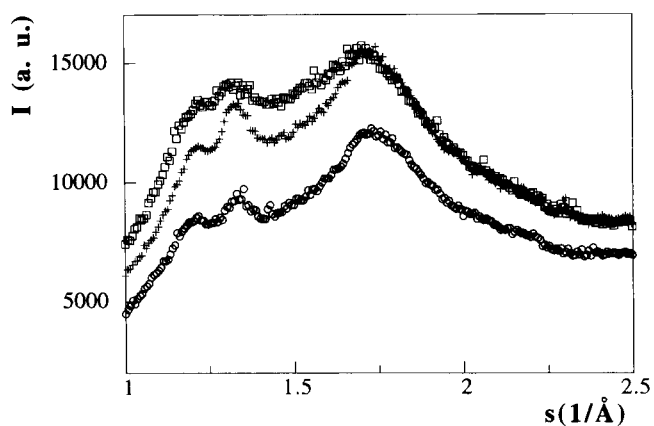


Figure 10 WAXS patterns obtained for the three samples A (circles), B₁ (squares) and C₁ (crosses)

plasticized PVC, not only with EHTG but with other additives, is now in progress in order to study in depth this effect whose molecular mechanism is not still clear.

Wide angle X-ray scattering (WAXS)

Raw WAXS patterns for the three samples are shown in *Figure 10* in the medium angle region (that means for values of the scattering vector s lower than 2.5 \AA^{-1}). s is related to the scattering angle, 2θ , by means of Bragg's law

$$s = 4\pi(\sin \theta)/\lambda \quad (21)$$

In glassy polymers intensity maxima found in this region are interpreted as arising from interchain structural correlations³⁹.

First, we will focus our attention on the diffraction pattern of pure PVC. Some controversy about the interpretation of the WAXS patterns of PVC is found in the literature. Certain authors currently assume the existence of a certain small amount (less than 10% for highly isotactic PVC samples similar to that studied in this work) of a crystalline phase consisting of an orthorhombic cell formed by syndiotactic chains in the planar zig-zag configuration^{40,41}. In this framework the scattering pattern of PVC is considered as crystalline with an underlying signal provoked by the amorphous phase. Nevertheless, recently several authors⁴² began to realize that the non-crystalline phase was very important in the explanation of the properties of PVC; analysis⁴³ of the scattering pattern of isotactic chemically modified PVC lead us to conclude that a wide variety of size and perfection of the ordered entities as well as a lack of order in the chain direction that allow us to conclude that the term crystallinity in the case of non-syndiotactic PVC has to be used with some prudence. Moreover, Yoon and coworkers⁴⁴ have made, by means of molecular dynamics and subsequent fitting of the experimental data, an interpretation of the scattering pattern of atactic PVC in terms of a non-crystalline order based on interchain orientational correlations with highly parallel segments tending to occur in small localized clusters rather than being homogeneously distributed. Some WAXS peak at around 0.5 \AA^{-1} has been signalled^{16,21} as possible experimental evidence for this model. In this scheme, the main peak obtained between 1.5 \AA^{-1} and 2 \AA^{-1} has been signalled to correspond to interchain correlations between chlorine atoms (Cl-Cl). On the

other hand, the small peaks obtained between 1 \AA^{-1} and 1.5 \AA^{-1} can be associated with interchain correlations between carbon atoms (C-C) and between chlorine and hydrogen atoms (Cl-H, methylene), assuming an absence of a crystalline phase in the polymer, but this fact would show the existence of certain specific interchain interactions. In order to reinforce this idea, we must point out here that the main peak (between 1.5 \AA^{-1} and 2 \AA^{-1}) shows an evolution of its angular position against the temperature that is sensitive to the glass transition⁴⁵ indicating that interchain structural correlation distances behave in different ways in the glassy and liquid states (at temperatures below and above T_g respectively) as it has been found for a wide variety of glassy polymers⁴⁶. Our experience in WAXS with other PVC samples of different characteristics (from strongly syndiotactic to strongly isotactic) indicates that these two peaks can be found separately or strongly overlapped⁴⁵ (in this case only one diffraction peak can be detected in this region). Moreover, when PVC is modified by stereospecific substitution of chlorine atoms by functional molecular groups, the intensity of these peaks is drastically changed and even they disappear^{43,45}. The reasons for these variations in different kinds of PVC are not clear at the moment and some complementary research is necessary to elucidate the structural origin of the diffraction peaks found in this region.

Nevertheless, in our case we can observe very small structural variations between the three samples. First, we observe in *Figure 10* that the WAXS patterns of the two plasticized PVC samples show an intensity higher than that obtained for pure PVC. This fact can be explained by the existence of a sulfur atom in the EHTG group and the higher scattering power of this group. Plasticized samples show the same intensity in the main peak because the concentration of the EHTG group is the same in the two cases. If one looks at the angular position of the main peak, it is found at lower angular position for the plasticized samples (around 1.71 \AA^{-1}) in comparison to the position obtained for pure PVC (around 1.74 \AA^{-1}). This difference in the position of the maximum of the peak (s_m) implies differences in the characteristic length of the structural interchain correlations (d) through the expression

$$d = 2\pi/s_m \quad (22)$$

The values obtained for d are around 3.6 \AA and 3.7 \AA , in the case of pure PVC and the plasticized samples, respectively. At this point, we think that these changes could be related to the appreciable lowering of T_g (or the position of the loss peaks) that has been shown and commented on above. It has been seen in other samples of PVC modified with other functional groups, like benzenethiolate, that the shape of the scattering pattern of PVC is drastically changed and the structural order of PVC is rapidly annihilated⁴³. Those structural changes imply variations in T_g (of some 30 K) that present good correlation with a decrease in the angular position of the main diffraction peak⁴⁵ (of some 25% in the characteristic correlation distance). This correlation can be explained by the fact that larger spatial amplitude between polymeric chains induced by the modification with EHTG leads to a larger facility for the molecular mobility and hence segmental molecular motions will be easier.

On the other hand, we can observe in *Figure 10* that WAXS patterns from the three samples are different in the angular region below the maximum of the main peak. The difference between patterns of samples A and C₁ is constant over all the angular positions. This is easily observed when one normalizes these two patterns (e.g. to the intensity of the main peak) and the consequent curves coincide with very good precision; it allows us to conclude that no structural changes are produced when PVC is externally plasticized. Nevertheless, we observe that, in the case of the internally plasticized sample, the intensity obtained below the main peak and above 1.2 \AA^{-1} is much higher than the one from the externally plasticized sample and, moreover, the two small diffraction peaks are less defined while the diffracted intensity between these two small peaks and the main peak is higher in the case of the internally plasticized sample. This fact could be interpreted, as it occurs in ref. 43 with PVC internally plasticized by the benzenethiolate group, in terms of a spatial broadening of the structural correlations characteristic of PVC when the polymer is substituted by the EHTG group leading to a delocalization of the main structural interactions characteristic of PVC.

At this point, we think that the change of the intermolecular coupling induced by the internal plasticization of PVC could be related, at least qualitatively, to the results from WAXS exposed above indicating that some relative loss of the interchain correlations around 1.25 \AA^{-1} , although some structural interaction is still present in this region. In any case, the internally plasticized sample still shows a low value for the coupling parameter in comparison to the values that are obtained in other glassy polymers like polycarbonate, poly(vinyl acetate), phenoxy, poly(vinyl methyl ether), etc.^{15,47}. These facts lead us to think that it is important to investigate the plasticization of polymers not only in the decreasing of the α relaxation characteristic temperature (or the decreasing of T_g) but also the parameters characterizing molecular motions taking part in the glass transition region.

CONCLUSIONS

Among all the results reported in this work, different conclusions are drawn. Plasticization of PVC leads to changes in parameters characterizing the volumetric and elastic properties of the material such as expansion coefficient, Young's modulus and Poisson's ratio. It is observed that these variations do not depend on the method of the plasticization, i.e. internal or external, because, in the three cases, the values obtained for all the samples can be fitted by the same behaviour in some kind of master curve. On the contrary, the glass transition temperature of the plasticized samples acts in a different manner depending on the method of plasticization: externally plasticized samples show lower T_g values in comparison to the internally plasticized ones and one concludes that external plasticization is more efficient than internal plasticization if the efficiency of the plasticization is represented by the lowering of T_g . The positions of the loss peaks from dielectric α relaxation measurements investigated in two samples of PVC with very similar amounts of plasticizer, one internally and the other externally plasticized, confirm the higher efficiency of the external plasticization.

Nevertheless, the shape of the dielectric α relaxation

function is not altered in the case of the external plasticization although the one obtained for the internally plasticized sample is narrowed in comparison to the one obtained for pure PVC. The loss of the non-exponential character of the α relaxation process can be interpreted in terms of an extinction of intermolecular coupling in the level of segmental molecular motions. In order to see if there is a structural origin for these changes, the interchain structural correlations have been studied by means of wide angle X-ray diffraction. Recently, the shape of the scattering pattern of externally plasticized PVC is not changed in comparison to the one obtained for pure PVC, while the diffraction signal is slightly different for the internally plasticized PVC. This fact can be interpreted in terms of a spatial broadening of interchain structural correlations in the case of the last sample. It seems that, at least qualitatively, the results corresponding to the shape of the relaxation function can be related to the ones corresponding to the static structure factor. However, an effective correlation between these two subjects must be confirmed and developed with further work concerning plasticization of PVC with other low molecular weight plasticizers and with other substituting groups different from ethyl hexyl thioglycolate, and also at different concentrations. This is now in progress.

The results corresponding to dielectric β relaxation process show that the plasticization effect is attached to a corresponding decrease of the intensity of this process, the well known antiplasticization effect, whatever the way of plasticizing PVC. It is also shown that the temperature of the maxima of the loss peaks is markedly decreased in comparison to the pure PVC, but no drastic changes are appreciated in the activation energy for this relaxation process.

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REFERENCES

- 1 Bohn, L. *Kunststoffe* 1963, **53**, 826
- 2 Pezzin, G., Ajiroldi, G. and Garbuglio, C. *J. Appl. Polym. Sci.* 1967, **1**, 25
- 3 Robeson, L. M. and Faucher, J. A. *Polym. Lett.* 1969, **7**, 35
- 4 Bellenger, V., Boye, J., Dhaoui, W., Lacabanne, C. and Verdu, J. *Polym. Eng. Sci.* 1990, **6**, 321
- 5 Ochi, M., Shimbo, M., Saga, M. and Takashima, N. *J. Polym. Sci. Polym. Phys. Ed.* 1986, **B24**, 2185
- 6 Williams, J. G. *J. Appl. Polym. Sci.* 1979, **23**, 3433
- 7 Millán, J., Martínez, G. and Mijangos, C. *J. Polym. Sci. Polym. Chem. Ed.* 1985, **27**, 483
- 8 Millán, J., Martínez, G. and Mijangos, C. *Makromol. Chem. Macromol. Symp.* 1989, **29**, 185
- 9 Guarrotxena, N., Martínez, G., Gómez-Elvira, J. M. and Millán, J. *Eur. Polym. J.* 1993, **29**, 685
- 10 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', 2nd edn, Dover, New York, 1991

- 11 Hedvig, P. 'Dielectric Spectroscopy of Polymers', Adam Hilger, Bristol, 1977
- 12 Van Krevelen, D. W. 'Properties of Polymers', 3rd edn, Elsevier, Amsterdam, 1990, p. 445
- 13 Alegria, A., Colmenero, J., del Val, J. J. and Barandiaran, J. M. *Polymer* 1985, **26**, 913
- 14 del Val, J. J., Colmenero, J., Mijangos, C., Martinez, G. and Millan, J. *Macromol. Chem.* 1989, **190**, 3257
- 15 Alegria, A., Guerrica-Echevarria, E., Telleria, I. and Colmenero, J. *Phys. Rev. B* 1993, **47**, 14857
- 16 Elicegui, A., del Val, J. J., Colmenero, J., Martinez, G., Millan, J., Bellenger, V. and Verdu, J. *Macromol. Chem. Phys.* 1996, **197**, 991
- 17 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
- 18 Kelley, F. N. and Bueche, F. J. *J. Polym. Sci.* 1961, **50**, 549
- 19 Couchman, P. R. *Polym. Eng. Sci.* 1984, **24**, 135
- 20 Di Benedetto, A. J. *J. Polym. Sci. Polym. Phys. Ed.* 1987, **B25**, 1949
- 21 Elicegui, A., del Val, J. J., Colmenero, J., Martínez, G. and Millán, J. *J. Non-Cryst. Solids* 1994, **172-174**, 955
- 22 Vogel, H. *Phys. Z* 1921, **22**, 645
- 23 Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **8**, 3339
- 24 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
- 25 Angell, C. A. *J. Non-Cryst. Solids* 1991, **131-133**, 13
- 26 Havriliak, S. and Negami, S. *Polymer* 1967, **8**, 161
- 27 Ngai, K. L. and White, T. *Phys. Rev. B* 1979, **20**, 2475
- 28 Ngai, K. L. and Wright, G. B. (Eds) 'Relaxations in Complex Systems', U.S. Government Printing Office, Washington, 1985
- 29 Ngai, K. L. *J. Non-Cryst. Solids* 1991, **131-133**, 80
- 30 Kohlrausch, F. *Pogg. Ann. Phys.* 1863, **29**, 337
- 31 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **8**, 161
- 32 Colmenero, J., Arbe, A. and Alegria, A. *Phys. Rev. Lett.* 1993, **71**, 2603
- 33 Colmenero, J., Arbe, A. and Alegria, A. *Physica A* 1993, **201**, 38
- 34 Alvarez, F., Alegria, A. and Colmenero, J. *Phys. Rev. B* 1993, **47**, 125
- 35 Colmenero, J., Arbe, A. and Alegria, A. *Physica A* 1993, **202**, 447
- 36 Kinjo, N. and Nakagawa, T. *Polymer J.* 1973, **4**, 143 (see references cited therein)
- 37 Vrentas, J. S., Duda, J. L. and Ling, H.-C. *Macromolecules* 1988, **21**, 1470
- 38 Sundgren, N., Bergman, G. and Shur, Y. *J. Appl. Polym. Sci.* 1978, **22**, 1255
- 39 Mitchell, G. R. in 'Comprehensive Polymer Science' (Eds G. Allen, J. C. Bevington, L. Both and C. Price), Vol. 1, Pergamon Press, Oxford, 1989, p. 687
- 40 Guerrero, S. J., Veleso, H. and Randon, E. *Polymer* 1990, **31**, 1615
- 41 Gilbert, M. J. *Macromol. Sci. Rev. Macromol. Chem. Phys.* 1994, **C34**, 77
- 42 Witenhafer, D. E. in 'Encyclopedia of PVC' (Eds L. I. Nass and C. A. Heiberger), 2nd edn, Vol. 1, Marcel Dekker, New York 1986, p. 309 (see references cited therein)
- 43 Scherrenberg, R. L., Reynaers, H., Gondard, C. and Verluyten, J. P. *Macromolecules* 1993, **26**, 4118
- 44 Smith, G. D., Jaffe, R. T. and Yoon, D. Y. *Macromolecules* 1993, **26**, 298
- 45 Elicegui, A., del Val, J. J. and Colmenero, J. (unpublished results)
- 46 del Val, J. J., Colmenero, J., Rosi, B. and Mitchell, G. R. *Polymer* 1995, **36**, 3625 (see references cited therein)
- 47 Alegria, A., Guerrica-Echevarria, E., Goitiandia, L., Telleria, I. and Colmenero, J. *Macromolecules* 1995, **28**, 1516