

Stress Relaxation of PVC Below the Yield Point

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SYNOPSIS

Stress relaxation of commercial poly(vinyl chloride) (PVC) is measured at strains below 3% and at different temperatures below the glass transition temperature. First it is shown that below the yield point the material follows a linear viscoelastic behavior. Then the data at a fixed deformation level (0.03) are fitted by considering a lognormal distribution function of relaxation times. Furthermore, from the measured stress-strain curves, the temperature dependence of the elastic tensile modulus is determined. The temperature dependence of the elastic modulus, the relaxation strength, and the parameters of the distribution: mean relaxation time, τ_m , and half-width, β , are given. Moreover, the distribution function and the temperature dependence of its characteristic parameters are discussed in terms of a cooperative model of the mechanisms involved in the mechanical relaxation of glassy polymers. Finally, the relationship proposed between the tensile modulus and the free volume helps explain the temperature dependence of the relaxation strength. © 1996 John Wiley & Sons, Inc.

Keywords: stress relaxation • PVC • lognormal distribution • cooperative model

INTRODUCTION

The viscoelastic behavior of unplasticized poly(vinyl chloride) (PVC) has been reported by several authors. Becker¹ studied dynamical properties of PVC characterized by an average molecular weight of 35,000 and a glass transition temperature $T_g = 347$ K measured by dilatometric methods. He reported the real component of the dynamic modulus and the loss factor for frequencies between 2 and approximately 1000 Hz, and temperatures between 277.5 and 426 K. By using the method of reduced variables and the Williams-Landel-Ferry (WLF) relationship,² he obtained an activation energy depending on temperature above T_g . This activation energy decreases with temperature, reaching a value of the order 336 kJ/mol for temperatures above 283 K.

Sommer³ also studied the viscoelastic behavior of unplasticized PVC by making dynamic and quasi-

static experiments in samples with the same transition temperature and average molecular weight as those used by Becker. Sommer reported the tensile modulus as a function of time for temperatures between 297 and 399.5 K. The real component of the dynamical modulus and the loss factor were also reported in the same temperature range, for frequencies between 10^{-5} and 10^4 Hz. Sommer used also the time-temperature superposition to build master curves for the measured mechanical properties and determined the corresponding spectra. From a shift of the spectra with temperature he obtained a temperature-dependent activation enthalpy which increased with temperature, reaching a maximum of 335 kJ/mol at 353 K, both for quasistatic and dynamic experiments.

Struik⁴ reported several creep data in commercial PVC, both at low and high strains. These experiments were mainly centered in the study of the aging behavior at different temperatures below T_g . The creep curves were interpreted in terms of the equation

$$J(t) = J_0 \exp[(t/t_0)^m] \quad (1)$$

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with $J(t)$ the creep compliance, J_0 its value at $t = 0$, t_0 and m structural constants, and t the time. Furthermore, according to this author, the stress relaxation for short times is described by

$$\sigma(t) = \sigma_0 \exp[-(t/t_0)^m] \quad (2)$$

where $\sigma(t)$ is the stress at the time t and σ_0 is the initial stress. The main effect of aging is to change t_0 , and for a long-term relaxation test started at an aging time, t_e , the stress will be given by

$$\sigma(t) = \sigma_0 \exp[-(t_e/t_0)^m] \{\ln(1 + t/t_e)\}^m. \quad (3)$$

Struik, however, does not give values of the physical quantities involved in the creep process, like activation enthalpy, distribution of retardation times, relaxation strength, etc.

More recently, Ngai and Yee⁵ analyzed some stress relaxation data in unplasticized and plasticized PVC. The torsional stress relaxation measurements were performed at a shear strain of 0.6% and at temperatures between 283 and 333 K.⁶ According to these authors, the shear relaxation modulus, $G(t)$, can be expressed by

$$G(t) = G_r + (G_u - G_r) \exp[-(t/\tau^*)^{1-n}] \quad (4)$$

where G_r and G_u are the relaxed (equilibrium) and the unrelaxed (glassy) moduli, respectively. τ^* is an average relaxation time and n is a parameter that depends on temperature. G_r was neglected in comparison with G_u and because n was slightly dependent on temperature, it was replaced by its mean value $n = 0.75$. With these assumptions, a master curve was built using the time-temperature superposition. Furthermore, for unplasticized PVC the WLF equation led to an activation enthalpy which increases from 135.6 to 288 kJ/mol, as the temperature rises from 313 to 333 K. However, below 313 K and down to 283 K the activation enthalpy was practically independent of temperature, with a value of the order of 135.6 kJ/mol. The material had a weight-average molecular weight $\bar{M}_w = 79,490$ and $T_g = 354.4$ K, as determined by differential scanning calorimetry (DSC) at 10 K/min.

It is the purpose of this article to present tensile stress relaxation data obtained in commercial PVC. The measurements were performed at strain levels below the yield strain and at temperatures below T_g . The data are interpreted in terms of a lognormal distribution of relaxation times and several physical parameters obtained from the experimental stress

relaxation curves are analyzed in terms of a cooperative model.

EXPERIMENTAL PROCEDURE

Material

The material used was commercial PVC-CAW, fabricated according to DIN 4102-B1 standard by SIMONA AG from Kim, Germany. The density and Young's modulus at room temperature are $\rho = 1.42$ g/cm³ and $E = 3.2$ GPa, respectively. We determined a weight-average molecular weight $\bar{M}_w = 71,837$ with a polydispersivity $\bar{M}_w/\bar{M}_n = 1.832$. The glass transition temperature, measured by DSC at 10 K/min, is $T_g = 349.1$ K.

Dogbone-type specimens were machined from the original 2-mm-thick sheet with a gauge length of 25 mm and a width of 4.2 mm.

Mechanical Tests

Previous to the tensile and stress relaxation tests, the specimens were located in a metallic capsule which was introduced in an oil bath and annealed in air at 393 K during 5 h. Afterwards, the specimens were slowly cooled by shutting of the power supply of the oil bath. Such a treatment ensured reproducibility both in the tensile and stress relaxation tests.

During the mechanical tests, performed in air above room temperature, the specimens were located in a test chamber heated by an oil bath. In this way the samples were heated without being in contact with the oil. The temperature was measured with two thermocouples located in the grips in contact with the heads of the specimen. Through this measurement homogeneity in temperature can be ensured, as well as stability, with fluctuations lower than 0.25 K during the whole stress relaxation test, which lasted for several hours. The measurements below room temperature were performed in vacuum to avoid absorption of water, which appears at 273 K, affecting the results.

The tensile and stress relaxation tests were performed in an Instron 1122 tensile machine, with an automatic data acquisition system which allowed measurements of the stress relaxation for times from 10^{-1} to near 10^6 s. At each temperature, for the stress relaxation tests, the machine was stopped at different strains below the yield point and the stress was measured as a function of time.

RESULTS

Tensile Modulus

The tensile modulus of the PVC used in this work was measured by using the following procedure. During a tensile test, in the elastic regime of the tensile curve, the rate of change of the load, $\dot{P} = dP/dt$, where P is the load, is given by⁷

$$\dot{P} = \nu C \quad (5)$$

with ν the velocity of the crosshead of the tensile machine and C the elastic constant of the machine and the sample. Because both machine and sample are submitted to the same load, that is, are disposed "in series," it follows

$$\frac{1}{C} = \frac{1}{K} + \frac{L}{AE} \quad (6)$$

where K is the elastic constant of the machine (load cell plus grips and loading bars), A and L are the initial cross section area and length of the sample, respectively, and E is the Young's modulus of the specimen. K can be determined by measuring a specimen of known E in the linear region at the beginning of the P against t curve. This was performed by using a characterized specimen of stainless steel leading to

$$K = 1.67 \text{ MN/m} \quad (7)$$

Once K is known, it is possible to determine E for PVC by using eq. (5) to eq. (7) with the load rate \dot{P} measured at the beginning of the tensile curve. The results obtained are shown in Figure 1, together with some results published in *Polymer Handbook*,⁸ by Pink,⁹ and the one provided by the supplier of the material. It is seen that our data have a linear dependence with temperature, which is expressed as

$$E(T) = E_0 - \xi T \quad (8)$$

with $E_0 = 13.3 \pm 0.7$ GPa and $\xi = 34 \pm 2$ MPa/K. It is noticed that the linear regression is fairly good with a linear correlation coefficient of -0.991 . With respect to the values published in Collins and Daniels,⁸ only the one measured at 293 K was obtained by stress-strain measurements at a strain rate of $2.5 \times 10^{-3} \text{ s}^{-1}$. The other values were obtained in creep at 0.2% strain. It is seen that our data are quite similar to those published, except at high temperatures where we believe ours are more reliable,

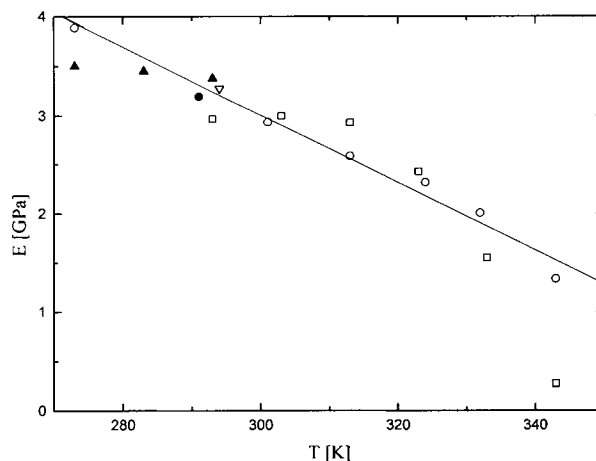


Figure 1. Tensile modulus of PVC as a function of temperature: (○) this work; (□) data from ref. 8; (▽, ▲) data from ref. 9 in tension and compression at a strain rate of $3.4 \times 10^{-4} \text{ s}^{-1}$; (●) data from the supplier of PVC. The linear regression is given by eq. (8).

because our lower deformation levels guarantee no contribution from anelastic components.

Time Dependence of the Stress Relaxation Curves

Figure 2 shows the true stress-strain curves against the absolute temperature obtained at an initial strain rate, $\dot{\epsilon} = 6.6 \times 10^{-4} \text{ s}^{-1}$. Figure 3 shows the stress against $\log(\text{time})$ curves at different temperatures and strains up to 0.03 which, according to Figure 2, are clearly below the yield point.

Stress relaxation tests above T_g could not be done with a tensile machine because the sample is deformed even when no external stress is applied, only due to the weight of the supporting system. Nevertheless, previous stress relaxation tests above T_g reported in the literature¹⁰ show that the relaxation is very fast (lasted less than an hour) and even at very low initial deformations the stresses are above the yield point. Therefore, these curves could not be included in the analysis presented in this article.

Strictly, "in a stress relaxation experiment a constant strain ϵ_0 is imposed on the specimen at the time $t = 0$ and maintained for $t \geq 0$ while the stress σ is observed as a function of time. Thus: $\epsilon = 0$, for $t \leq 0$; $\epsilon = \epsilon_0$, for $t \geq 0$. By linearity requirements $\sigma(t)$ will be proportional to ϵ_0 ." Then, the stress relaxation function $M(t) = \sigma(t)/\epsilon_0$ is given by¹¹

$$M(t) = M_e + \delta M \varphi(t) = M_e [1 + \Delta \varphi(t)] \quad t \geq 0 \quad (9)$$

where $M(t)$ is independent from ϵ_0 . M_e is the equilibrium (relaxed) modulus and

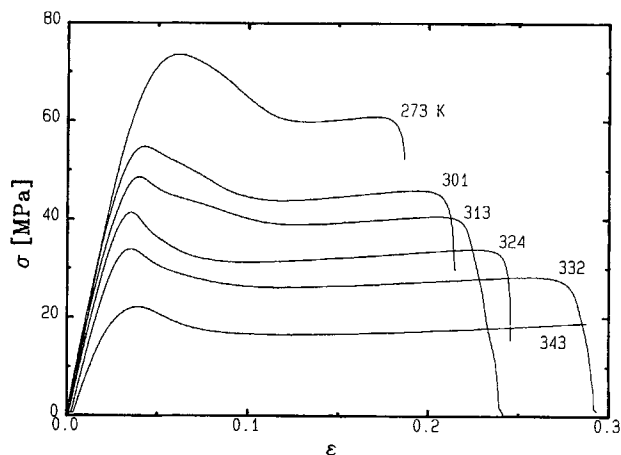


Figure 2. True stress-strain curves for unplasticized PVC, measured at different temperatures and at the strain rate of $6.6 \times 10^{-4} \text{ s}^{-1}$.

$$\delta M = M_g - M_e \quad (10)$$

with M_g the glassy (unrelaxed or instantaneous) modulus. The relaxation strength, Δ , is defined by

$$\Delta = \frac{M_g - M_e}{M_e} \quad (11)$$

The quantities M_g , M_e and, consequently, Δ should not depend on strain in the case of a linear viscoelastic material. $\varphi(t)$ is the stress relaxation function which goes from 1 at $t = 0$ to 0 at $t \rightarrow \infty$. In terms of the stress, eq. (9) can be written as

$$\sigma(t) = \sigma_e + \delta\sigma\varphi(t) \quad (12)$$

with

$$\sigma_e = M_e \epsilon_0 \quad (13)$$

$$\sigma_g = M_g \epsilon_0 \quad (14)$$

and

$$\delta\sigma = \sigma_g - \sigma_e \quad (15)$$

Then, in order to show that the material behaves as linear viscoelastic below the yield point, it must be demonstrated that the relaxation curves of Figure 3 obey eq. (12), independently from the strain level. The problem is that these curves were determined by interrupting a tensile test at a certain deformation. In fact, the sample was elongated using a tensile machine whose crosshead was moving at a given velocity. In other words, the relaxation tests were not

performed by imposing a given strain at $t = 0$. Then, the initial stresses in Figure 3 are not σ_g of eq. (15) but the stresses corresponding to the given strain in the tensile curve of Figure 2, where the stress relaxation started. These stresses will be named σ_0 .

The differential equation corresponding to the three-parameter standard anelastic element (SAE)¹¹ is

$$\sigma + \tau \dot{\sigma} = M_e \epsilon + M_g \dot{\epsilon} \tau \quad (16)$$

where τ is the relaxation time and the dot indicates the derivative with respect to the time. At the beginning of the tensile test $\dot{\epsilon} \approx \text{constant}$, so that

$$\epsilon \approx \dot{\epsilon} t \quad (17)$$

and, on integrating eq. (16), leads to

$$\sigma(t_m) = \sigma_0 = \dot{\epsilon} t_m \left[M_e + \delta M \frac{1 - e^{-(t_m/\tau)}}{t_m/\tau} \right] \quad (18)$$

where t_m is the time elapsed from the beginning of the tensile test to the initiation of the stress relaxation. Equation (18) is valid for the viscoelastic description of the material with the single relaxation time. In the case of a distribution of relaxation times

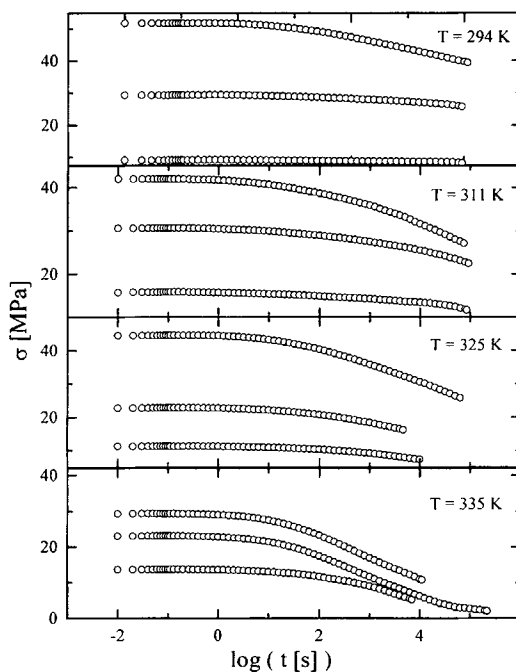


Figure 3. Stress relaxation curves at the true strain levels of 0.01, 0.02, and 0.03 for temperatures of 311, 325, and 335 K. The measurements at 294 K were performed at the strains: 0.005, 0.015, and 0.03.

eq. (16) becomes more complicate. It has been shown¹² that the time dependence of the relaxation modulus—usually written as an integral relationship of the relaxation spectrum—can be expressed by

$$M(t) = M_e + \delta M \exp\left[-\frac{t}{\tau(t)}\right] \quad (19)$$

where $\tau(t)$ is the relaxation time of a modified anelastic element (MAE). Particularly, the quasistatic mechanical properties associated to a lognormal distribution—used subsequently in this article—can be very well approximated on considering

$$\tau(t) = \tau_0^\gamma t^{1-\gamma} \quad (20)$$

with $0 < \gamma \leq 1$. It is noticed that $\gamma = 1$ corresponds to the SAE. On using this time dependence of τ , eq. (18) changes to

$$\sigma_0 = \dot{\epsilon} t_m \left[M_e + \delta M \frac{1 - e^{-(t_m/\tau_0)^\gamma}}{(t_m/\tau_0)^\gamma} \right] \quad (21)$$

where τ_0 is the average relaxation time and γ is related to the width of the distribution function for the MAE. Furthermore, τ_0 and γ are related to the parameters of the lognormal distribution.¹³

An apparent relaxation strength, Δ_a , can be defined as

$$\Delta_a = \frac{\sigma_0}{\sigma_e} - 1. \quad (22)$$

Then, on considering eqs. (11) and (21) it follows

$$\Delta_a = \Delta \frac{1 - e^{-(t_m/\tau_0)^\gamma}}{(t_m/\tau_0)^\gamma}. \quad (23)$$

If $t_m \ll \tau_0$, which is the case for the experiments performed in this work, eq. (23) reduces to

$$\Delta_a \approx \Delta \quad (24)$$

that is, the apparent relaxation strength coincides with the true relaxation strength. In summary, if the relaxation curves of Figure 3 correspond to a linear viscoelastic material, then they should be described by

$$\sigma(t) = \sigma_0 - (\sigma_0 - \sigma_e)[1 - \varphi(t)] \quad (25)$$

with $\varphi(t)$ independent from the strain level. Therefore, on taking the logarithm of eq. (25), the strain

dependence of the curves can be easily separated. In fact, eq. (25) can be written as

$$\log(\sigma_0 - \sigma) = \log(\sigma_0 - \sigma_e) + \log[1 - \varphi(t)] \quad (26)$$

in such a way that, at a fixed temperature a plot of $\log(\sigma_0 - \sigma)$ against $\log t$ should lead to a set of parallel curves when φ does not depend on strain. In other words, the curves of Figure 3 at each temperature should be superposed one to another by only a vertical translation. This is illustrated in Figure 4, where the relaxation curves at 325 K for strains of 0.01 and 0.02 are translated vertically onto the curve for 0.03, leading to a single relaxation curve. Analogous results were obtained for the other curves of Figure 3. The deviations at short times are magnifications of the experimental error due to the logarithm dependence of eq. (26). In addition, small variations in the temperature of the represented curves affect a complete matching.

In conclusion, PVC is linear viscoelastic below the yield point. Even when the parameters of the relaxation are independent from the strain level, smaller experimental errors are involved when higher deformations are considered. Consequently, the characteristic parameters of the relaxation behavior were obtained from the experiments performed at a strain of 0.03 shown in Figure 5. These curves were analyzed using the formalism developed previously.¹⁴ In fact, if the material behaves as linear viscoelastic the stress relaxation curves are described by

$$\sigma(t) = \sigma_e + \delta\sigma\varphi(t) \quad (27)$$

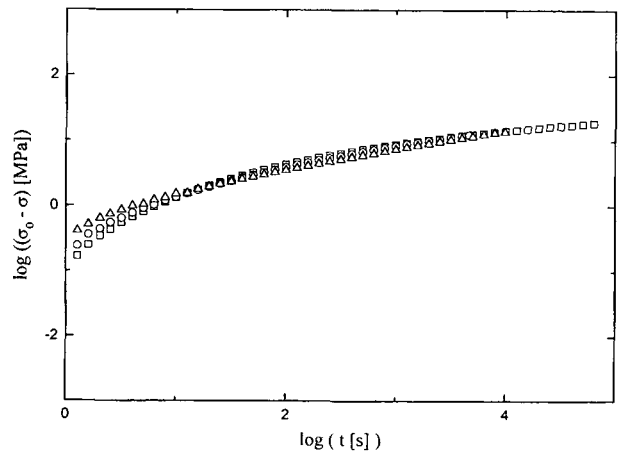


Figure 4. Superposition of the $\log(\sigma_0 - \sigma)$ against $\log t$ curves corresponding to the ones at 325 K of Fig. 4. (Δ) $\epsilon = 0.01$; (\circ) $\epsilon = 0.02$; (\square) $\epsilon = 0.03$.

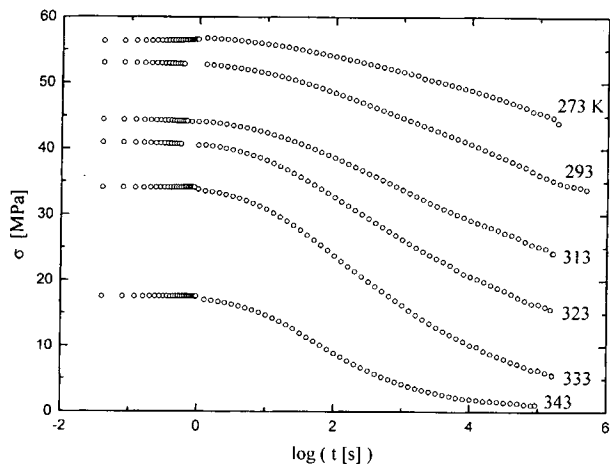


Figure 5. Stress relaxation curves for PVC, at different temperatures and at a true strain of 0.03.

where $\delta\sigma = \sigma_0 - \sigma_e$, σ_0 and σ_e are the initial stress and equilibrium stress reached at long times, respectively, and $\delta\sigma = \sigma_e \Delta$. Particularly, for a lognormal distribution of relaxation times, eq. (27) changes to¹¹

$$\sigma(y) = \sigma_e + \delta\sigma \varphi(y, \beta) \tag{28}$$

where

$$\varphi(y, \beta) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[-e^{y-\beta w}] e^{-w^2} dw \tag{29}$$

β is the half width of the lognormal distribution, and

Table I. Parameters Obtained by Fitting the Stress Relaxation Data of Fig. 5 to Eq. (28)

T (K)	σ_0 (MPa)	σ_e (MPa)	Δ	$\ln(\tau_m/s)$	β
273	56.34	34.37	0.64	12.11	9.0
293	53.55	26.51	1.02	10.20	7.3
313	44.40	21.30	1.09	7.63	5.7
323	41.34	14.33	1.89	6.86	4.8
333	34.46	5.80	4.94	6.21	4.1
343	17.68	1.75	9.10	4.87	2.8

$$y = \ln(t/\tau_m) \tag{30}$$

with τ_m the average relaxation time of the lognormal distribution. The derivative of eq. (28) with respect to $\log t$ is

$$\sigma_{\log t} = 2.303 \delta\sigma \varphi(y, \beta). \tag{31}$$

Figure 6 shows, as an example, the good quality of the fitting of eq. (28) and eq. (31) to the experimental stress relaxation curve measured at $T = 313$ K and its derivative, respectively. The fitting of the rest of the curves is similar. Table I gives the values of the different parameters obtained from the data of Figure 5 fitted by eq. (28).

Temperature Dependence of Δ , τ_m , and β Relaxation Strength

The values of Δ , obtained by fitting the data of Figure 5, are also indicated in Table I. On assuming

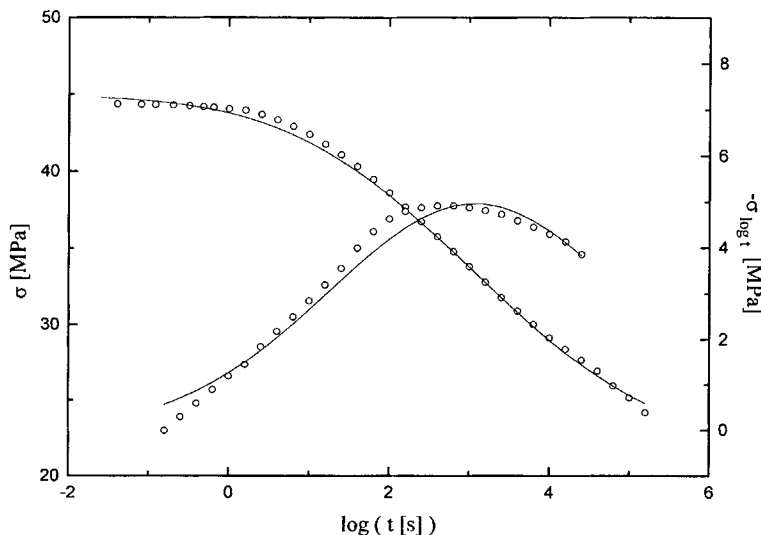


Figure 6. Fitting of the stress relaxation curve at $T = 313$ K of Figure 5 and of its derivative to eqs. (28) and (31).

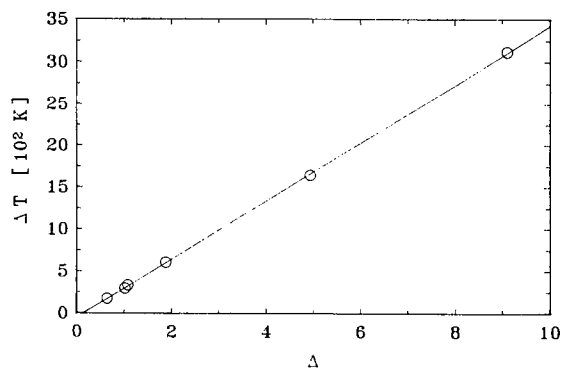


Figure 7. Relaxation strength for the data of Figure 5, plotted according to eq. (33).

that Δ changes with temperature according to a Curie-Weiss law, that is,

$$\Delta = \frac{\Delta_0}{T_c - T} \quad (32)$$

where T_c is a critical temperature and Δ_0 is a constant which involves the employed experimental procedure, the type of specimen, and the material. Equation (32) can be rewritten as

$$T\Delta = T_c\Delta - \Delta_0. \quad (33)$$

Then, a plot of $T\Delta$ against Δ should give a straight line of slope T_c and intercept Δ_0 . This plot is given in Figure 7 showing that an excellent straight line is obtained with

$$T_c = 347.2 \text{ K} \quad \Delta_0 = 49 \text{ K}. \quad (34)$$

T_c is very close to the glass transition temperature as determined by DSC, namely $T_g = 349.1 \text{ K}$. A similar situation was encountered by using an equivalent analysis for the loss tangent measured in atactic polystyrene.¹⁵

Mean Relaxation Time

On assuming that the average relaxation time changes with temperature according to an Arrhenius law, that is,

$$\tau_m = \tau_{m_0} \exp[\Delta H_m/kT] \quad (35)$$

with τ_{m_0} an average preexponential factor, ΔH_m an average activation enthalpy, and k Boltzmann's constant, a plot of $\ln \tau_m$ against $1/T$ should give a straight line of slope $\Delta H_m/k$ and intercept $\ln \tau_{m_0}$.

Such a plot, for the data indicated in Table I, is shown in Figure 8, leading to

$$\tau_{m_0} = 1.13 \times 10^{-10} \text{ s} \quad \Delta H_m = 79.4 \text{ kJ/mol}. \quad (36)$$

The value of τ_{m_0} is reasonable when compared with the reciprocal of the Debye frequency (of the order of 10^{-13} s). The value of ΔH_m is lower than the ones obtained when the time-temperature superposition principle (TTSP) is used. A discussion of this difference in the enthalpy as well as the applicability of the TTSP is presented in the following section.

Half-Width of the Distribution

The values of τ_{m_0} and ΔH_m given in eq. (36) are only average values. In fact, according to Table I, β changes with temperature, indicating how the shape of the distribution function changes with temperature. Nowick and Berry¹¹ have shown that when the relaxation time changes with temperature as

$$\tau = \tau_0 \exp[\Delta H/kT] \quad (37)$$

and τ is distributed according to a lognormal distribution with parameters β and τ_m , the distribution can be in τ_0 , in ΔH , or in both. Furthermore, if τ is distributed in a lognormal way then τ_0 and ΔH must be distributed in the same way. If the distribution is only in τ_0 then

$$\beta = \beta_0 \quad (38)$$

where β_0 is the half-width of the lognormal distribution in $\ln \tau_0$, with an average value $\ln \tau_{m_0}$. If there is only one value of τ_0 and the distribution is in ΔH , then

$$\beta = \beta_{\Delta H}/kT \quad (39)$$

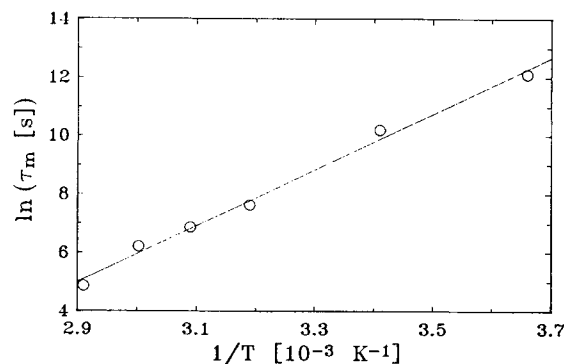


Figure 8. Average relaxation time against the reciprocal of the absolute temperature for the data of Figure 5.

where $\beta_{\Delta H}$ is the half-width of the Gaussian distribution in ΔH with average value ΔH_m .

When there are distributions for both ΔH and $\ln \tau_0$ and both do not vary independently but depend linearly on a single internal variable which is distributed in a Gaussian manner, both ΔH and $\ln \tau_0$ will have a Gaussian distribution and

$$\beta = \left| \beta_0 \pm \frac{\beta_{\Delta H}}{kT} \right|. \quad (40)$$

The plus sign occurs if the quantities $\ln \tau_0$ and ΔH both increase and decrease together with a change in the internal variable, while the minus sign occurs when $\ln \tau_0$ and ΔH vary oppositely from each other.

If $\ln \tau_0$ and ΔH are distributed independently of each other, each in a Gaussian manner, then

$$\beta^2 = \beta_0^2 + \left[\frac{\beta_{\Delta H}}{kT} \right]^2. \quad (41)$$

The plot of β from Table I against the reciprocal of temperature does not give a straight line, as illustrated in Figure 9, showing that eq. (40) is not obeyed. Nevertheless, the representation of β^2 against $1/T^2$ given in Figure 10 can be linearly correlated. That is, eq. (41) is obeyed and, consequently, the distributions of $\ln \tau_0$ and ΔH are both Gaussian and independent of each other. Of course, this behavior is valid in the glassy region, that is, for $T < T_g$. Thus, it is more convenient to rewrite eq. (41) as

$$\beta^2 = \beta_g^2 + \left(\frac{\beta_{\Delta H}}{k} \right) \left[\frac{1}{T^2} - \frac{1}{T_g^2} \right] \quad (42)$$

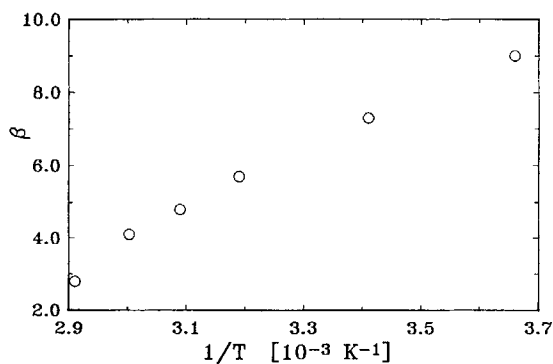


Figure 9. Half-width of the lognormal distribution against the reciprocal of the absolute temperature for the data of Figure 5.

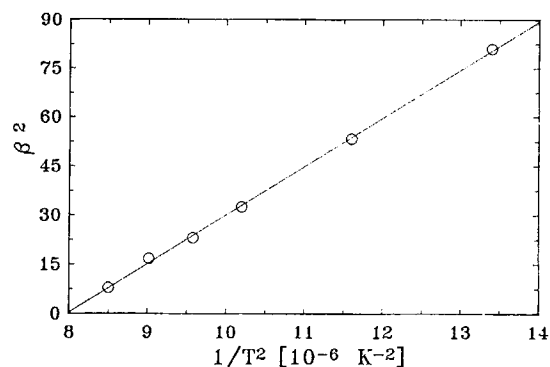


Figure 10. Square of the half-width of the lognormal distribution against $1/T^2$, for the data of Figure 5. The linear regression corresponds to eq. (42).

where β_g is the half-width of the distribution at T_g . In this way, the linear regression of the points represented in Figure 10 gives

$$\beta_g = 2.26 \quad \beta_{\Delta H} = 32 \text{ kJ/mol.} \quad (43)$$

DISCUSSION

The stress relaxation curves measured at different temperatures were fitted using a lognormal distribution function, finding the temperature dependence of its parameters and of the relaxation strength. Other expressions used in previous works, such as eqs. (2) and (4) with $G_r = 0$, did not provide a good description of our data. In fact, the stress relaxation curves reach an equilibrium value σ_e , as it is observed in Figure 5. Table I shows the temperature dependence of σ_e as well as that of β . Particularly the changes in β correspond to changes in the shape of the distribution function. That is, both the limiting stresses σ_0 and σ_e as well as the shape of the spectrum of relaxation times vary with temperature. This disables the matching of the individual segments to form a master curve.¹⁷ However, in several works assumptions such as $\sigma_e = 0$ or a slight temperature dependence of the parameters of the distribution were considered in order to build "pseudo-master curves."¹⁷ Because of this apparent but not true superposition, extremely high values of Δ and ΔH were found. For a complete discussion about these and other inconsistencies of the pseudo-master curves we refer the reader to ref. 17 and 18.

Going back to the curve fits proposed in the literature for the stress relaxation data, eq. (4) can be deduced from the MAE.¹² This element provides a good approximation of statistical systems characterized by a Gaussian distribution of the micro-

mechanisms involved not only in stress relaxation but also in creep and dynamical tests. Even when the MAE is a useful tool to deal with known mathematical expressions for the time or frequency dependence of the mechanical properties, the lognormal distribution is more suitable to interpret the physical mechanisms involved. Effectively, in what follows the parameters of the distribution will be related to the structure of glassy polymers by considering the concept of ordered domains.¹⁹

When a stress is applied over a polymer chain, the free enthalpy increases and the molecular segments reorient in order to relieve the stress. This reorientation is not instantaneous but depends on the "ability" of the segments to undergo configurational changes. Each segment is called conformer because its movements contribute to the conformation of the polymer chain. Then, on one hand, the reorientations are limited by the potential energy of internal rotation of each conformer. On the other hand, each conformer is connected to others so its rotational relaxation requires also the movement of its neighbors. The group of conformers which evolves cooperatively will be called domain. The size of the domain depends on the temperature in such a way that for $T > T_g$ each conformer can relax independently of the others, only overcoming the barrier of intramolecular rotation.

If c is the number of states a conformer can take, the entropy of N_z domains, each with z conformers, is given by

$$\Delta S = N_z k \ln c. \quad (44)$$

Furthermore, the probability of simultaneous relaxation of z conformers assumed to be independent is the z th power of the probability of the relaxation of only one conformer. Therefore, the activation energy will be z times the potential barrier of internal rotation of each segment, Δh , i.e.,

$$\Delta H = z \Delta h. \quad (45)$$

In the Mean Relaxation Time section it was established that the relaxation time follows the Arrhenius law, that is,

$$\tau = \tau_c \exp\left[\frac{\Delta G}{kT}\right] \quad (46)$$

which can be rewritten as

$$\tau = \tau_0 \exp\left[\frac{\Delta H}{kT}\right] \quad (47)$$

with $\tau_0 = \tau_c \exp[-\Delta S/k]$. Then, from eq. (44) it follows

$$\tau_0 = \tau_c c \exp[-N_z]. \quad (48)$$

In the Half-Width of the Distribution section it was shown that $\ln \tau$ is characterized by a Gaussian distribution both in $\ln \tau_0$ and ΔH . Then, according to eq. (48), the number of domains N_z is distributed following a Gaussian law with a mean value $N_{zm} = \ln(c\tau_c/\tau_0)$ and a dispersion $\beta_N = \beta_0$.

On the other hand, from eq. (45) it follows that the Gaussian distribution in ΔH corresponds to a distribution in the number of conformers integrating each domain. Furthermore, on considering that each conformer is one of the monomers of the polymeric chain ($-\text{CH}_2-\text{HClC}-$) whose barrier of internal rotation is,²⁰

$$\Delta h = 14.9 \text{ kJ/mol}$$

it results in a mean number of conformers $z_m = 5.3$ for each domain, with a dispersion $\beta_z = 2.1$. These values were not previously obtained in the literature. However, a comparison can be done with the number of conformers determined for a cooperative model in PMMA below its T_g ,²¹ $z = 6.65$. Similar values in other glassy polymers can be calculated from the mechanical model proposed by Argon and Bessonov.²²

Finally, the dependence of the relaxation modulus on time and temperature is related to the changes in the domains according to

$$E(t, T) = E_0 \left[\frac{v_f(t)}{v_f^{(e)}} - \alpha_m \frac{T}{T_g} \right] \quad (49)$$

where α_m is a constant and $v_f(t)$ is the free volume of the system at the time t . As the conformers reorient to its equilibrium state, the free volume reduces until an equilibrium value $v_f^{(e)}$ is reached. It is noticed that at $T = 0 \text{ K}$ all the mechanisms are "frozen" and no relaxation is possible, that is, $v_f(t) = v_f^{(e)}$. Moreover, the thermal expansion coefficient of the free volume, that is, the relative change of the free volume with temperature, is typically of the order of 10^{-4} K^{-1} .²⁰ Because this change can be neglected when compared with the linear dependence of E on T given in eq. (49), only the dependence of v_f on time will be considered. This assumption agrees with

the linear dependence of $E(T)$, given in eq. (8), determined from our measurements.

Once the equilibrium is reached, eq. (49) reduces to

$$E_e(T) = E_0 \left[1 - \alpha_m \frac{T}{T_g} \right] \quad (50)$$

which was previously employed by Gilbert et al.²³ in their work about modulus maps for amorphous polymers in the glassy regime. This equation is a first-order approximation of a more complex expression for $E_e(T)$ derived by Yannas and Luise²⁴ when the intra- and intermolecular potentials in the chains of amorphous polymers are considered. α_m is related to the potential barriers and to the dimensions of the conformers—named strophons in Yannas and Luise.²⁴ On considering the experimental data given in ref. 24 $\alpha_m = 0.8$ results.

On comparing eqs. (8) and (50) it is found $\alpha_m = 0.9 \pm 0.1$, which is similar to the value calculated from ref. 24. Because there are no measurements of the tensile modulus at 0 K, α_m and E_0 are replaced in eq. (50) in order to calculate the modulus at 77 K, obtaining: $E(77 \text{ K}) = 9.3 \text{ GPa}$. The reported modulus at that temperature,⁸ $E(77 \text{ K}) = 7.6 \text{ GPa}$, shows the good agreement of our results.

Because in a stress relaxation test the deformation, ϵ , remains constant, eq. (49) can be rewritten in terms of the stress as

$$\sigma(t, T) = \epsilon E_0 \left[\frac{v_f(t)}{v_f^{(e)}} - \alpha_m \frac{T}{T_g} \right]. \quad (51)$$

Then the initial and equilibrium stresses at the temperature T are

$$\sigma_0(T) = \epsilon E_0 \left[\frac{v_f(0)}{v_f^{(e)}} - \alpha_m \frac{T}{T_g} \right]$$

and

$$\sigma_e(T) = \epsilon E_0 \left[1 - \alpha_m \frac{T}{T_g} \right]$$

respectively, leading to

$$\Delta(T) = \Delta_v \frac{T_g}{\alpha_m} \left/ \left(1 - \frac{\alpha_m}{T_g} T \right) \right. \quad (52)$$

where $\Delta_v = (v_f(0) - v_f^{(e)})/v_f^{(e)}$ is the relative change in the free volume of the system. This equation has

the same temperature dependence as the empirical relationship determined from our data in eq. (32), with $\Delta_0 = \Delta_v T_g / \alpha_m$ and $T_c = T_g / \alpha_m$. Replacing the values of Δ_0 and T_c , given in eq. (34), it results $\Delta_v = 0.14$ and $\alpha_m = 1.005$. This value of α_m agrees with the one determined from eq. (50).

Finally, on comparing eqs. (27) and (51) it follows that

$$v_f(t) = v_f^{(e)} + [v_f(0) - v_f^{(e)}] \varphi(t) \quad (53)$$

that is, the time evolution of the free volume during the stress relaxation test. The discussion of changes in the activation volume with time and also with frequency in the case of dynamical tests as well as the stress relaxation data measured above the yield point²⁵ at the different temperatures are beyond the scope of this work and will be presented in forthcoming papers.

CONCLUSIONS

In this work tensile stress relaxation data in PVC below the glass transition temperature were presented. These curves, measured below the yield point, could be fitted by considering a lognormal distribution function of relaxation times. Moreover, the temperature dependence of the tensile elastic modulus was calculated from stress-strain data at very low deformation levels.

The temperature dependence of the relaxation strength as well as of the parameters of the distribution function were determined and explained in terms of a cooperative model of the micromechanisms involved in the relaxation process. These micromechanisms or conformers are the monomers of the polymeric chain. The reorientation of each conformer implies the movement of other neighbors, that is, the relaxation of a domain. It was demonstrated that the distribution in the size of the domain, z , determines a distribution in the activation energy while the number of domains in the structure, N_z , is related to the mean relaxation time. Finally, the relationship between the free volume and the tensile modulus proposed in this article explains the empirical dependence of the relaxation strength on temperature for PVC. Similar experiments on other linear polymers are under way in order to determine the applicability of the results shown in this work.

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