Dynamic Mechanical Behavior of Poly(vinyl chloride)/Poly(methyl methacrylate) Polymer Blend

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SYNOPSIS

A poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) (80/20 w/w) polymer blend was studied by mechanical spectroscopy. Two relaxations can be distinguished: in the glassy state, a very large secondary relaxation in the range of 100 K to 325 K which results from the combination of secondary relaxations of PVC and PMMA; and only one main relaxation at 364 K associated to the glass rubber transition. The relaxation spectrum in the range of the β relaxation has been described by a relaxation time distribution function based upon a Gaussian function and a series-parallel model. The α relaxation was studied by means of a theoretical approach for the nonelastic deformation of polymers. We found that the miscibility of this blend appears to be a function of the observation scale: the PVC/PMMA blend is heterogeneous at the scale of molecular movements involved for the β relaxation process but homogeneous at the scale of the chain segments responsible for the α relaxation dynamics. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years the blending of polymers has gained significant interest. The advantage of blending polymers is that properties of commercially available polymers may be adjusted without the laborious development of new macromolecules. There are several possibilities for the preparation of polymer blends. Mixing of polymers in the molten state is the method most often applied in polymer material processing. Limiting factors of this method are the thermal or mechanical degradation of the polymers and the effectiveness of the mixing of the melt. Investigating the miscibility of a polymer system is usually one of the first experiments performed with a blend. Miscibility of polymers depends on thermodynamics and kinetics. The thermodynamics of polymer mixtures can be described by the Gibbs free enthalpy. The basic equation was derived by Flory[1]:

$$\Delta G_m = NRT\left(\frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi_{12}\phi_1\phi_2\right) \quad (1)$$

where ΔG_m is the Gibbs free enthalpy of mixing, N is the number of moles, ϕ_i is the volume fraction of polymer i ($i = 1, 2; \phi_1 + \phi_2 = 1$), r_i is the number of segments of polymer i, and χ_{12} is the interaction parameter. Because the two first terms become negligible for polymers with high degrees of polymerization, their miscibility requires χ_{12} close to or smaller than zero. Thus, for a blend of two polymers, miscibility will generally result from specific intermolecular interactions (such as dipole–dipole forces).

Poly(vinyl chloride) (PVC) is one of the most important thermoplastics. Several polymers are currently mixed with PVC to improve high-impact behavior and its heat resistance temperature. Poly(methyl methacrylate) (PMMA) is generally used to form blends

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with PVC because it improves the viscoelastic properties and the thermal stability of the melt.[2] Most of the literature about PVC/PMMA blends discusses the miscibility of this system. Wlochowicz and Janicki[3] concluded by means of infrared spectroscopy, differential calorimetry, and wide angle X-ray scattering measurements that PVC/PMMA blends at all compositions are wholly amorphous two-phase systems. Li and colleagues[4] reached the same conclusion and also suggested that intermolecular forces between the two polymers are very weak. On the other hand, Kögler and Mirau[5] and Shen and Torkelson[6] observed that PVC/PMMA blends are miscible at all compositions if they are prepared between T_g and their lower critical solution temperature (LCST $\approx$ 450 K). Preparation of blends is another factor which determines compatibility of the system. Schmidt and coworkers[7] reported that PVC/PMMA blends cast from methyl ethyl ketone have a greater degree of miscibility that the blends resulting from tetrahydrofuran casting. The tacticity of PMMA seems also to have a great influence on its miscibility with PVC. However, Lemieux and colleagues,[8] from a large study of PVC/PMMA blends prepared from PMMAs with greatly differing tacticity, concluded that all PMMA, whatever their tacticity, can be set miscible with PVC under proper thermal treatments. Miscibility is maintained as long as these blends are annealed between T_g and the temperature of phase separation. This temperature varies with PMMA tacticity and composition of the blend, so the temperature range of this system's miscibility lies between 370 K and 450 K. The PVC/PMMA blend is a well-known system in which hydrogen bonds involving the α hydrogen and the carbonyl group of PMMA are expected. It has been reported[8] that this type of interaction is competing along with dipole–dipole interactions between the H—C—Cl and C=O groups to ensure miscibility.

In fact, almost all information about PVC/PMMA blends concerns their miscibility. Only few data about their mechanical properties are available. Thus, the purpose of this paper is to study the mechanical relaxations of a PVC/PMMA blend by mechanical spectroscopy and to compare the properties of the blend with those of the parent homopolymers. Moreover, by analyzing those relaxations we attempt to determine the scale over which the molecular motions correspond to a single phase or two-phase blend.

EXPERIMENTAL

PVC and atactic PMMA was provided by Elf–Atochem (France). The average molecular weights of both polymers were determined by gel permeation chromatography (GPC) in THF at 298 K, using a standard Waters GPC apparatus. For PVC, $\overline{M_n}$ = 54,100 and $\overline{M_w}/\overline{M_n}$ = 2; and for PMMA, $\overline{M_n}$ = 46,600 and $\overline{M_w}/\overline{M_n}$ = 1.8. In order to process the blends, the following formulation was used: PVC, 100 phr; PMMA, 25 phr; dialkyltin dioctylthioglycolate (Ciba-Geigy, France) as stabilizer, 2 phr; waxes of polyethylene, 0.7 phr, and stearic acid (Merck–Clevenot, France), 0.1 phr, as lubricants. After dry mixing in a Henschel mixer at high speed (1,000 rpm) for a few minutes at 383 K, the mixture was extruded in a Leistritz LSM 30–40 mm intermeshing, counter-rotating, twin-screw extruder at 453 K, molded at 473 K and cooled at room temperature. Thus the PVC/PMMA blend has a composition close to 80/20 (w/w), and is referred to PVC/PMMA in the following.

Mechanical behavior was measured with the help of a mechanical spectrometer developed in GEMPPM[9] and available from Metravib SA (Ecully, France); it consists of a forced oscillation pendulum, working in the temperature range 100 to 700 K and frequency range 5×10^{-5} to 5 Hz. The maximum strain was less than 10^{-4} and the viscoelastic behavior of the polymer materials appeared to be independent of the applied stress over the whole strain amplitude range in all temperature ranges used for the experiments. 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 f (under isothermal conditions) or temperature T (for one or several fixed frequencies). Resolution was better than tan $\phi = 5 \times 10^{-4}$. For isothermal experiments, the sample temperature remained constant to within 0.2 K.

RESULTS

Figure 1 shows G' and tan ϕ as functions of temperature for PVC/PMMA. Two relaxations are exhibited: the main or α relaxation (at 364 K) and, at low temperature, a broad secondary or β relaxation (between 100 and 325 K). At higher temperatures than 400 K the flow of polymer is observed.

β Relaxation: Experimental Results

The β relaxation in the range 175 to 280 K was studied under isothermal conditions every 5 K. In order to avoid problems for the understanding of figures,
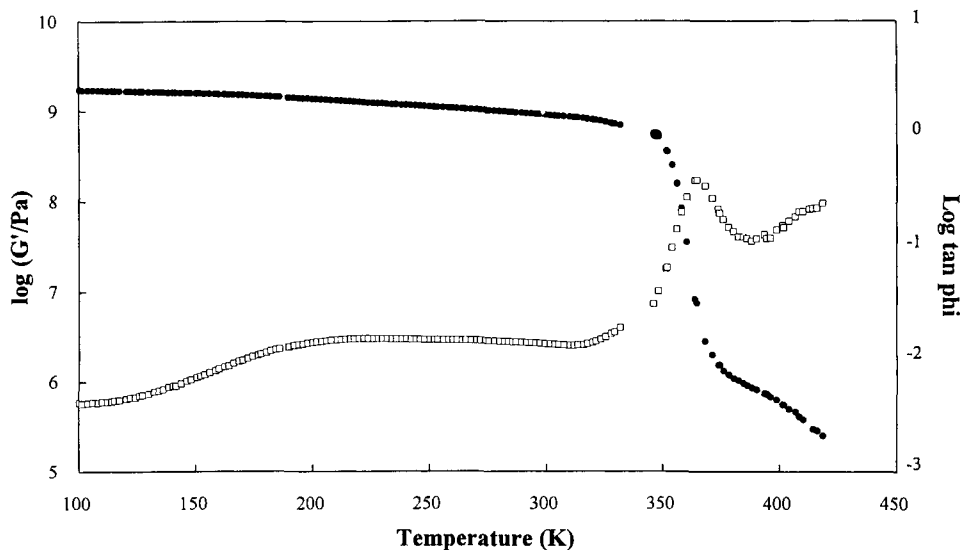
Figure 1 Isochrones at 0.1 Hz of G' (●) and tan ϕ (□) for PVC/PMMA blend (80/20 w/w).

we have plotted only five curves for the G' and G'' isothermal behavior of the blend in Figures 2 and 3. These figures show that as temperature increases, G' decreases and its spectrum shifts toward the high-frequency side. It is difficult to distinguish a peak in the $G''(f)$ curve because the relaxation is very broad: the β relaxation of the blend seems to result from the combination of secondary relaxations of PVC and PMMA as seen in Figure 4, where we have plotted the variation of tan ϕ versus temperature for PVC, PMMA, and PVC/PMMA.

Mechanical spectroscopy at low frequency is a powerful tool for the study of mechanical relaxations because it allows the separation of several relaxations. For this reason, drawing master curves from isothermal data would make it possible to see more clearly the PVC and PMMA contributions in the β relaxation of the blend. So, after construction of the G'' master curve, the variation of the shift factor is plotted against the reciprocal temperature. Figure 5 shows these results. Two ranges can be distinguished, the first at low temperature (175–230 K)
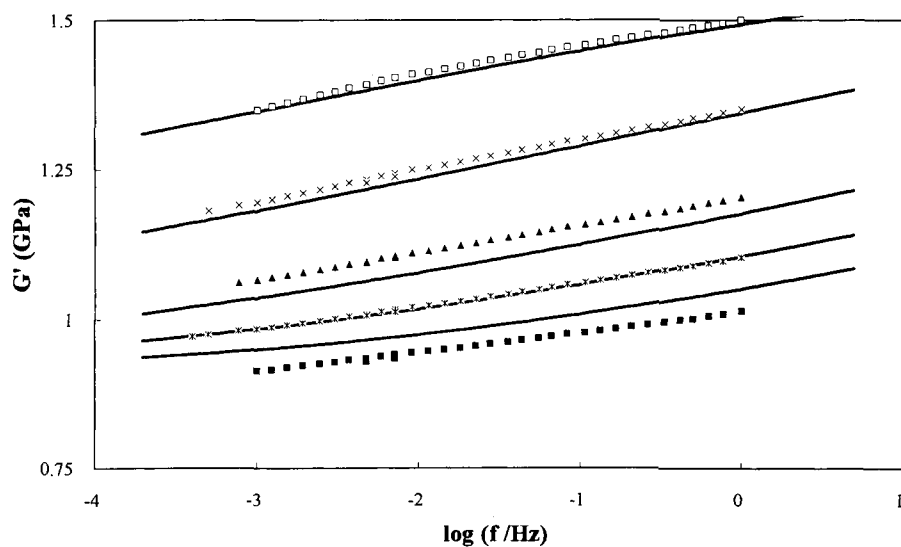
Figure 2 Isothermal spectrum of G' for the β relaxation process in PVC/PMMA at: (□) 175 K, (×) 205 K, (△) 240 K, (∗) 260 K, (■) 280 K. (—) Calculated curves (see text and Table I for parameters).
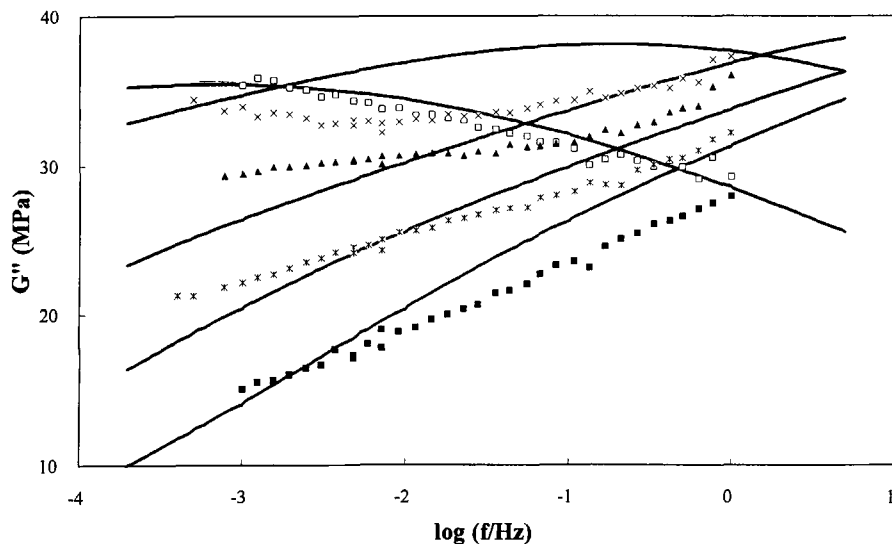
Figure 3   Isothermal spectrum of G'' for the β relaxation process in PVC/PMMA. Same symbols as Figure 2.

with an activation energy of 55 ± 3 kJ/mol; and the second at higher temperature (230–280 K) with an activation energy of 80 ± 3 kJ/mol. These values are similar to those obtained for homopolymers: $E_{\beta PVC} = 62$ kJ/mol[10] and $E_{\beta PMMA} = 78$ kJ/mol.[11] However, there is a slight modification of the activation energy for homopolymers in the blend since the activation energy for pure PVC is lower and the one for pure PMMA is higher.

Interpretation of the β Relaxation

Viscoelastic relaxations in solids are always broader than a Debye relaxation. This broadening is often described by a distribution of relaxation times[12] or, alternatively, by a stretched exponential function.[13] A distribution of relaxation times might in turn reflect a distribution of activation energies, a distribution of preexponential factor (entropy), or both.
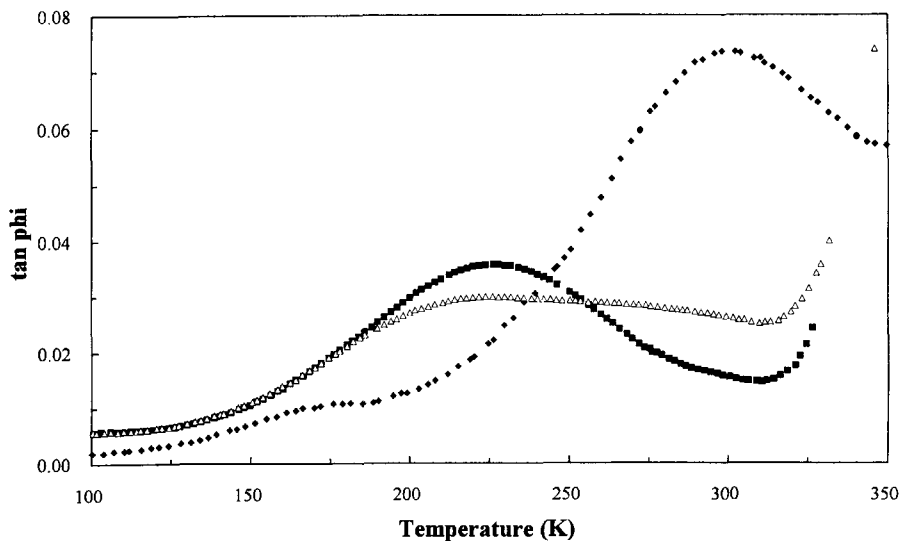
Figure 4   Tan ϕ versus temperature for PVC (■), PMMA (♦) and PVC/PMMA (△) in the range of the β relaxation processes.
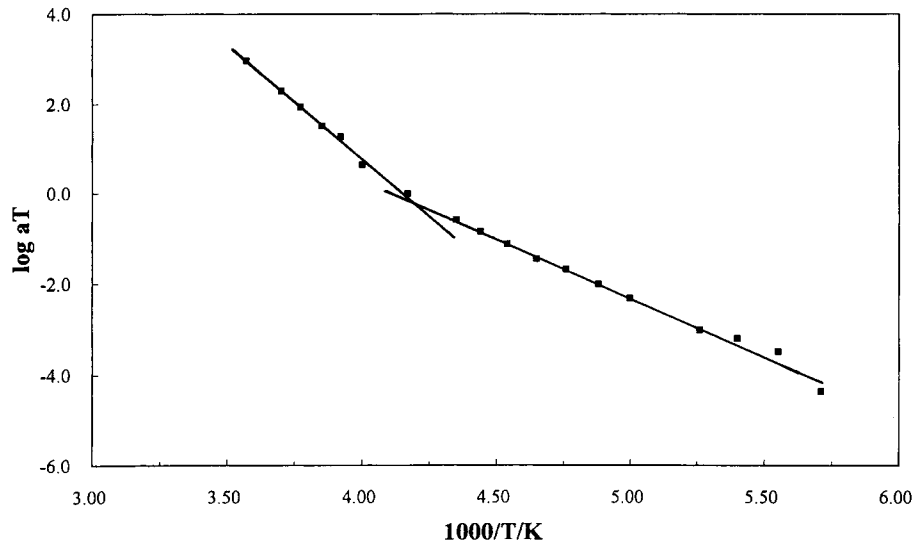
Figure 5 Variation of the shift factor with temperature in the range of the β relaxation of PVC/PMMA.

Following several previous works,[10,11] we can describe the shape of the β relaxation spectra by a distribution function of relaxation time (Ψ), based upon a Gaussian function:

$$\Psi\left[\ln\left(\frac{\tau}{\tau_m}\right)\right] = \frac{1}{B\pi^{1/2}} \exp\left(-\left[\frac{\ln\left(\frac{\tau}{\tau_m}\right)}{B}\right]^2\right) \quad (2)$$

where B is the Gaussian distribution width, and τ_m is the most probable value of τ which corresponds to f_m, the frequency at the maximum of the G'' spectrum:

$$\tau_m = \frac{1}{2\pi f_m} = \frac{1}{2\pi f_o} \exp\left(\frac{E_\beta}{RT}\right) = \tau_o \exp\left(\frac{E_\beta}{RT}\right) \quad (3)$$

where E_β is the average activation energy of the β relaxation process and τ_o is the preexponential factor.

Thus the storage and loss moduli G' and G'' in a dynamic mechanical experiment can be described as follows:

$$\frac{G'(\omega) - G_R}{G_{U\beta} - G_R}$$

$$= \frac{\sum_i \left(\frac{(\omega\tau_i)^2}{1 + (\omega\tau_i)^2} \exp\left[-\left(\frac{\ln(\tau_i/\tau_m)}{B}\right)^2\right]\right)}{\sum_i \left(\exp\left[-\left(\frac{\ln(\tau_i/\tau_m)}{B}\right)^2\right]\right)} \quad (4)$$

$$\frac{G''(\omega)}{G_{U\beta} - G_R} = \frac{\sum_i \left(\frac{\omega\tau_i}{1 + (\omega\tau_i)^2} \exp\left[-\left(\frac{\ln(\tau_i/\tau_m)}{B}\right)^2\right]\right)}{\sum_i \left(\exp\left[-\left(\frac{\ln(\tau_i/\tau_m)}{B}\right)^2\right]\right)} \quad (5)$$

where G' and G'' are the real and imaginary components of the shear modulus, respectively; $G_{U\beta}$ and G_R are the unrelaxed and relaxed moduli, respectively, in the range of the β relaxation; and ω is the angular frequency.

Nowick and Berry[14] have proposed that if $\ln \tau_o$ and E_β depend on a single internal parameter (e.g., local order) and if they are temperature-independent, B can be expressed by

$$B = B_o + \frac{B_U}{RT} \quad (6)$$

where B_o is a dimensionless quantity representing the width of the distribution of the temperature-independent parameter, $\ln \tau_o$, and B_U has the dimension of energy and represents the width of the E_β distribution.

From these considerations, simulation of relaxation spectra in the range of the β relaxation can be made as explained in refs. 10 and 11. Using eqs. (4) and (5), the best fit of G' and G'' versus frequency is obtained from the adjustment of $\Delta G_\beta = G_{U\beta} - G_R$, G_R and B. This leads to tan ϕ. The variation of $G_{U\beta}$,

G_R, ΔG_β, and B with temperature can be determined and by means of this analysis, it is possible to predict the β relaxation behavior at any temperature or frequency (in isothermal and isochronal conditions as well). This method has been successfully applied to PVC[10] and PMMA.[11]

For modeling the dynamic behavior of the blend, we must take several points into account:

(1) Values for ΔG_β, $G_{U\beta}$, B, and τ_m versus temperature for PVC and PMMA were taken from literature.[10,11]

(2) The simplest models which describe the mechanical coupling of two-phase systems are the parallel (Voigt's model) or series (Reuss's model) associations of the two phases. However, the behavior of materials generally takes place between these two limiting cases. The simple phenomenological model previously proposed by Takayanagi and colleagues[15] and based on a mixing rule of the Voigt and Reuss equations has been chosen for this work. It consists of the parallel connection of a PVC element with a series of PVC and PMMA elements as shown in Figure 6. Thus, the modulus can be written as:

$$G_{\text{blend}} = \frac{\varphi G_{\text{PVC}} G_{\text{PMMA}}}{(1 - \lambda)G_{\text{PMMA}} + \lambda G_{\text{PVC}}} + (1 - \varphi)G_{\text{PVC}} \quad (7)$$

The parameters λ and φ are characteristic of the contribution of each component. Moreover, the determination of only one of them is enough because they are related to the volume fraction of PMMA ($v_{\text{PMMA}} = 0.23$) by $v_{\text{PMMA}} = \lambda\varphi$. Thus, the complex modulus of the blend can be expressed by

$$G^*_{\text{blend}} = \frac{\varphi G^*_{\text{PVC}} G^*_{\text{PMMA}}}{\left(1 - \dfrac{v_{\text{PMMA}}}{\varphi}\right)G^*_{\text{PMMA}} + \left(\dfrac{v_{\text{PMMA}}}{\varphi}\right)G^*_{\text{PVC}}}$$
$$+ (1 - \varphi)G^*_{\text{PVC}} \quad (8)$$

where $G^*_{\text{PVC}} = G'_{\text{PVC}} + iG''_{\text{PVC}}$ and $G^*_{\text{PMMA}} = G'_{\text{PMMA}} + iG''_{\text{PMMA}}$.

(3) Special care of the PVC crystallinity in the blend must be taken. In fact, PVC involved in the blend appears to have a smaller crystallinity than pure PVC as displayed by X-ray patterns (Fig. 7). As a very rough approximation, the crystallinity ratio can be estimated between 10 and 15% and between 5 and 10% for pure PVC and for PVC included in the blend, respectively. Because PVC in the blend is more amorphous, the contribution of this polymer to the relaxation process should be higher than that
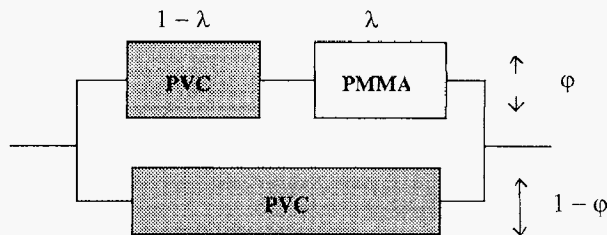
of pure PVC. The variation of the secondary relaxation intensity with the crystallinity has been observed by Fulchiron and coworkers[16] in the case of poly(ethylene terephthalate). To take into account this variation, we have increased by 5% the value of ΔG_β and decreased by 5% $G_{U\beta}$ of PVC.

(4) Molecular interactions between polymers must be considered as well. As previously pointed out, there is a slight modification of the respective activation energies for both homopolymers in the blend. In fact, we have observed that the blend shows a decrease of $E_{\beta\text{PVC}}$ of about 4 kJ/mol, and an increase of $E_{\beta\text{PMMA}}$ of about 4 kJ/mol. A lower value of $E_{\beta\text{PVC}}$ in the blend can be explained by a perturbation of intermolecular forces between PVC chains owing to the presence of PMMA. On the other hand, the increase of $E_{\beta\text{PMMA}}$ can be understood by considering interactions of the α-hydrogen of PVC and the carbonyl groups of PMMA (Cl—C—H---

sible for slowing the motion of the ester group which is considered to be the origin of the β relaxation in PMMA.[12,17]

The isothermal behavior of the blend was calculated as follows: (1) ΔG_β, $G_{U\beta}$, G_R, B, and τ_m are calculated for PVC and PMMA at several temperatures with parameters given in Table I; (2) G' and G'' for PVC and PMMA are then obtained using eqs. (4) and (5); (3) G' and G'' of the blend are now calculated by means of eq. (8) with $\varphi = 0.3$.

The G' and G'' calculated spectra are shown in Figures 2 and 3. Theoretical curves are in reasonably good agreement with experimental ones, since the discrepancy is never higher than 15%. The self-consistency of this can be tested by calculating G' and G'' versus temperature (isochronal behavior) from eqs. (4), (5), and (8) and with the parameters given in Table I. Results are given in Figures 8 and 9. Calculated curves correspond fairly well to experimental data, and this supports the validity of our
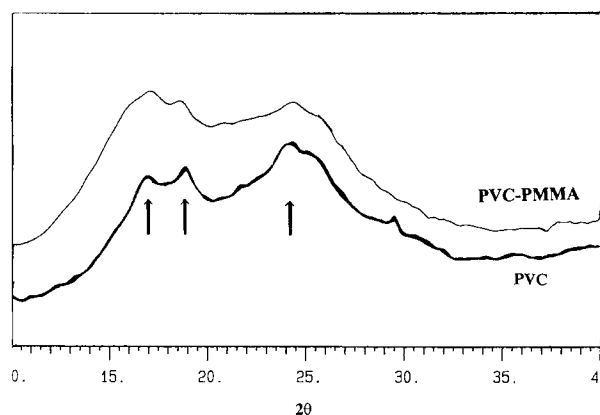
Figure 7 X-ray patterns for PVC and PVC/PMMA.

analysis. It is noteworthy that from the knowledge of the variation of ΔG_β, $G_{U\beta}$, G_R, and B for homopolymers and of the activation energies of each polymer in the blend, and using Takayanagi's model, it is now possible to predict the β relaxation process of PVC/PMMA at any temperature or frequency (in isothermal and isochronal conditions as well).

A Cole–Cole plot gives useful information on secondary relaxations, especially when the relaxation intensity changes because of material evolution during experiments. Moreover, it is possible to distinguish the contributions of each component in the blend as it is made with the master curves. Cole-Cole plots in the range of the β relaxation for PVC/PMMA in isothermal and isochronal conditions are displayed in Figure 10. Figure 10(a) shows that PVC/PMMA changes with temperature, which indicates that this material is not thermorheologically simple. A similar observation was made by Flores and Perez[10] and by Havriliak and Shortridge[18] in the case of PVC. In the same figure we have plotted theoretical results obtained by the method described here before. There is a good agreement between calculated and experimental results, since the maximum discrepancy is not larger than 15%. As was previously pointed out,[10] the use of the parameter B could suggest some similarities with Havriliak's function with a parameter β equal to 1. This would be the case if B were constant. In fact, since B is a function of temperature for PVC as well as for PMMA, this results in a slightly asymmetrical curve in the Cole-Cole plot as shown in Figure 10.

In conclusion, the β relaxation of PVC/PMMA results from the combination of secondary relaxations of PVC and PMMA. The presence of PMMA in the PVC matrix results in a slight decrease of the β relaxation activation energy of PVC, as well as a

slight increase in E_β of PMMA. Interactions between the two polymers could be responsible for this behavior.

α Relaxation: Experimental Results

The variation of G' and tan ϕ as a function of frequency in the temperature range 348 K to 375 K for the blend is shown in Figure 11. In spite of a slight discrepancy in the tan ϕ maxima plotted on a linear scale, the construction of master curves for G', G'', and tan ϕ is satisfactory as shown in Figure 12.

DISCUSSION

In order to relate the macroscopic behavior (as measured by the spectrometer) to specific molecular motions, the mechanical behavior through the glass transition range (α relaxation) of homogeneous amorphous materials has been analyzed with the help of a molecular model developed by Perez and colleagues[19-23] based on three main assumptions, namely:

(1) The polymer is considered as a packing of repeat units linked together through intra- and intermolecular forces. The concept of "defect" is introduced in the case of repeat units that exhibit, with their first neighbors, an increment of enthalpy or entropy. 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 $T > T_g$. When $T < T_g$, $C_d(T) = C_d(T_g)$; unless physical aging has to be taken into account, leading to a change of C_d as a function of time, $C_d(T, t)$.

(2) When submitted to a stress σ, the nonelastic deformation of the polymer results first from the thermomechanical activation of some of defects;

Table I Parameters and Variation of $G_{U\beta}$, ΔG_β, B, and $\tau_m = \tau_0 \exp(E_\beta/RT)$ with Temperature Used for Modeling the Secondary Relaxation in the 80/20 PVC/PMMA Blend

Parameters	PVC[10]	PMMA[11]
E_ρ (KJ/mol)	58*	82*
τ_0 (s)	$1.5 \ 10^{-16}$	$2.6 \ 10^{-16}$
$G_{U\beta}$ (Pa)	$1.9 \ 10^9 - 1.7 \ 10^6 \ T$	$1.3 \ 10^9 - 6.5 \ 10^5 \ T$
ΔG_β (Pa)	$9.8 \ 10^8 - 2.1 \ 10^6 \ T$	$4.3 \ 10^8 + 3.5 \ 10^5 \ T$
B	$1.35 + 2254/T$	$6.14 - 421/T$

* Results obtained from Figure 5.
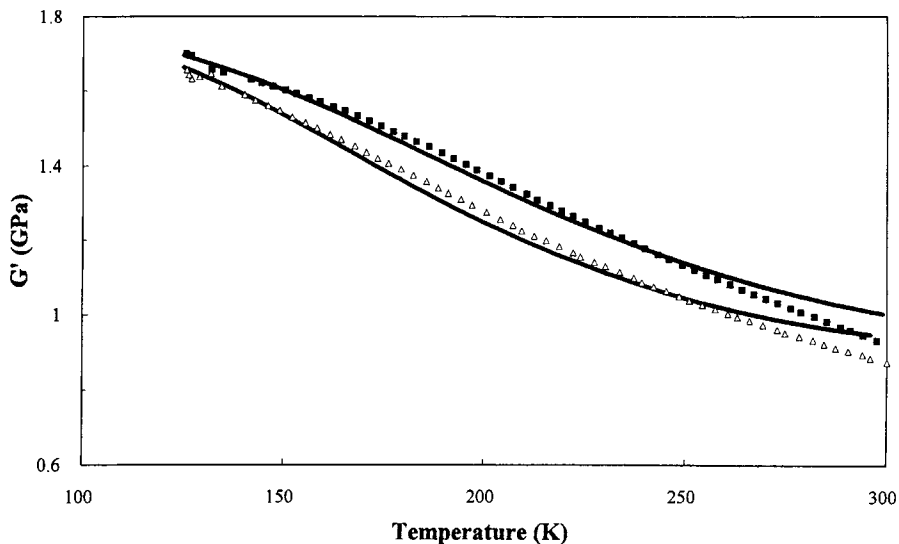
Figure 8 Isochrones of G' for the β relaxation process in PVC/PMMA at 1 Hz (■) and 0.01 Hz (△). (—) Calculated curves (see Table I for parameters).

then these defects, once activated, become sheared microdomains (smd).

(3) If the applied stress remains, this elementary process could be followed by the expansion of smd, owing to correlated movements of units (hierarchical correlation). The characteristic time depends on the duration of application of the stimulus, and the theory yields a value characterizing the whole process:

$$\tau_{mol} = t_o\left(\frac{\tau_\beta}{t_o}\right)^{1/x} \tag{9}$$

where $0 < X < 1$ is the correlation parameter (X increases with C_d); τ_β is the characteristic time of local motions identified with molecular movements responsible for the β relaxation; and t_o is a scaling parameter. For experimental time lower than τ_{mol}, the deformation $\varepsilon(t)$ is mainly anelastic (the system recovers its previous configuration); whereas for a longer time, internal stresses all along the lines bordering smd are suppressed, thanks 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[19–23]:

$$J(t) = \frac{1}{G_{U\alpha}} + A\left\{1 - \exp\left[-\left(\frac{t}{\tau_{mol}}\right)^x\right]\right\}$$

$$+ A'\left(\frac{t}{\tau_{mol}}\right)^{x'} \tag{10}$$

where $G_{U\alpha}$ is the unrelaxed (or elastic) modulus in the range of the α relaxation, and A and A' are parameters corresponding to the relaxation strength and proportional to C_d. $X'(0 < X < X' < 1)$ relates the change of X with strain ($X' = 1$ for molecular glasses).[22] It is noteworthy that X' is very sensitive to the presence of crosslinking nodes or crystallites.[24] 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 angular frequency ω), taking into account the rubber elasticity.

$$G^* = G_C + \frac{G_{U\alpha} - G_C}{1 + (i\omega\tau_{mol})^{-X} + Q(i\omega\tau_{mol})^{-X'}} \tag{11}$$

where G_C is the rubber plateau modulus; Q is a function of A and A' and is generally close to unity.
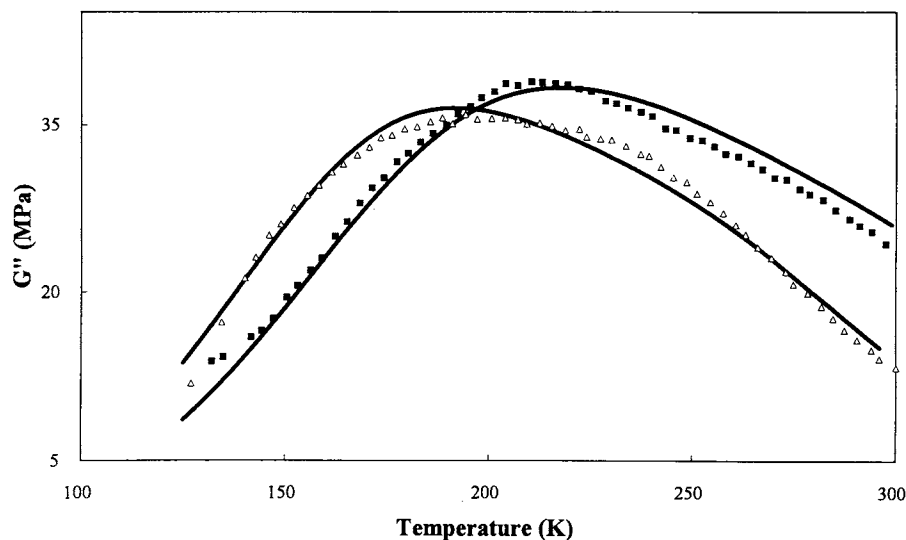
With the purpose of taking into account the terminal zone, and since the effect of the flow of chains remains weak in the temperature range corresponding to our data, it is assumed that the modulus $G_C^*(i\omega)$ corresponding to this zone can be written as[25,26]

$$G_C^*(i\omega) = G_C \sum_{j=1}^{n} \frac{i\omega\tau_{e,j}}{1 + i\omega\tau_{e,j}} g_i \tag{12}$$

with

$$\tau_{e,j} = \tau_{mol} f_e 2^j \tag{13}$$

Figure 9 Isochrones of G'' for the β relaxation process in PVC/PMMA; same symbols as Figure 8.

where $\tau_{e,j}$ is the characteristic time of the flow of chains (f_e factor depending on molecular weight, i.e., of the degree of polymerization). The distribution function g_j of $\tau_{e,j}$ is approximated by a box. This approach has been used extensively to interpret experimental data from mechanical spectrometry.[27]

The comparison of the theory with experimental data requires the determination of $G_{U\alpha}$, G_C, X, X', Q, τ_{mol}, and f_e. Each of these parameters is determined independent of the others. The complex plane plot of G'' versus G' (Cole-Cole plot) provide most of them[22]: the maximum value of G'' is related to Q; $G_{U\alpha}$ and G_C are given by the high and low frequency limits, respectively; $X = 2\theta/\pi$ and $X' = 2\theta'/\pi$, where θ and θ' are the angles made by the plot at the low and high frequency intercepts, respectively (a more accurate determination of X' is obtained by fitting the linear plot of tan ϕ versus log[f]). f_e can be determined by fitting experimental data in the high temperature range; for isothermal G' and tan ϕ, because of a lack of data close to the terminal zone, f_e has been arbitrarily chosen very large (see Table II).

Figure 12 exhibits calculated master curves for PVC/PMMA. There is good agreement between experimental data and calculated curves in both cases. The corresponding parameters are shown in Table II.

The temperature dependence of X (or τ_{mol}) can be determined from measurements in the metastable equilibrium and under isoconfigurational conditions, i.e., for $T < T_g$. We have verified that two parts can

be distinguished, corresponding respectively to the Arrhenius regime ($T < T_g$) and to the so-called "WLF" regime ($T > T_g$) (Fig. 13). In the former case, X has been considered constant: $X = X(T_g)$. Eq. (9) indicates that the origin of the WLF law is due to the temperature dependence of X. This dependence has been taken as[28]

$$X(T) = \frac{1}{1 + \{X(T_g)^{-1} - 1\}\exp[-C(T - T_g)]} \quad (14)$$

where $X(T_g)$ is the value of X for isoconfigurational conditions (Arrhenius range, $T < T_g$) and C is a constant determined by fitting experimental data to a calculated curve in the WLF range. It is noteworthy that, having obtained the relationship between X and temperature (or τ_{mol} and temperature; see eq. [9]), it is easy to calculate the isochronal thermograms. However, τ_{mol} as indicated by eq. (9) needs the determination of τ_β, the characteristic time of the β relaxation which, for the blend, results from the combination of secondary relaxations of PVC and PMMA. In order to determine which of the two β processes is responsible for the α relaxation, we have compared the isoconfigurational behavior of the blend with the expected behavior of PVC and PMMA alone. This comparison is made in Figure 13: for $T < T_g$, theoretical straight lines are drawn with a slope equal to $E_{\beta PMMA}/X(T_g)$ and to $E_{\beta PVC}/X(T_g)$ (see eq. [9]). Obviously, the blend has a behavior controlled by the β movements of PVC. We can conclude from
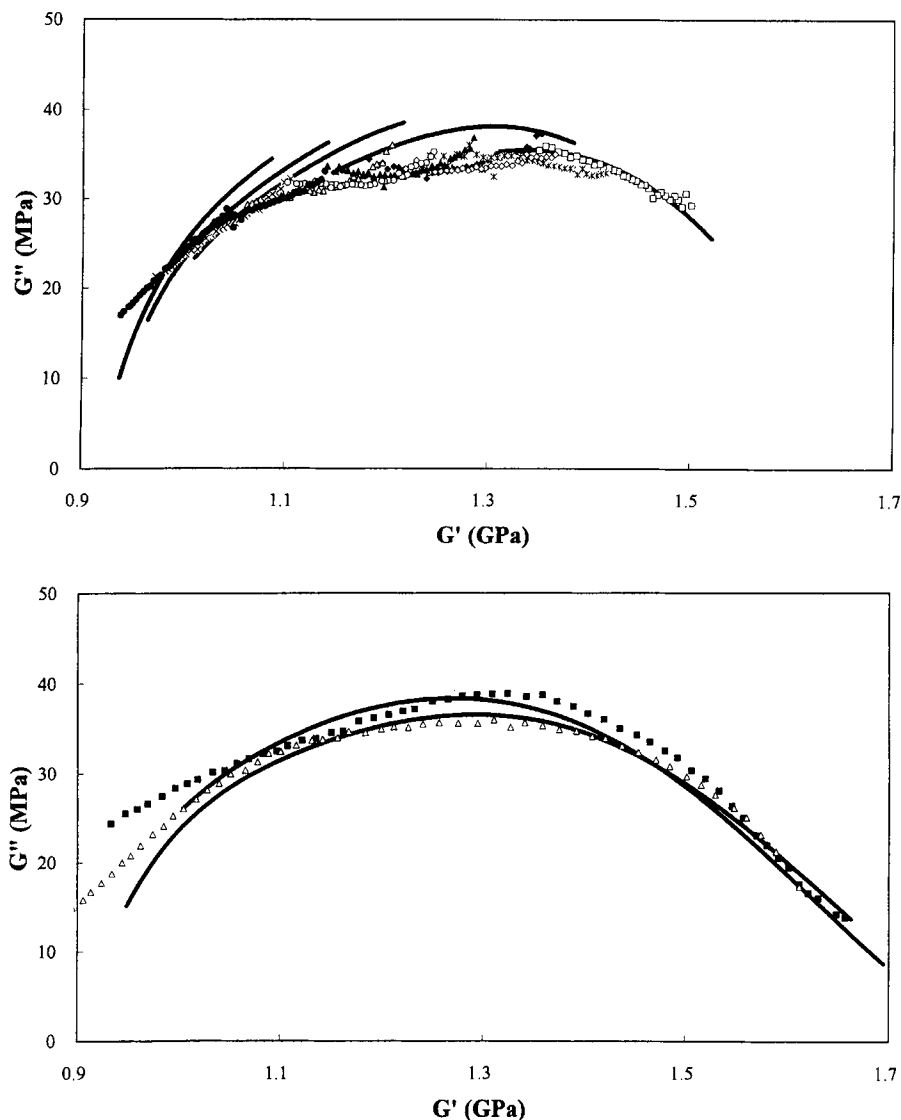
Figure 10 Cole-Cole plot in the β relaxation range for the PVC/PMMA: (a) Isothermal conditions; symbols: experimental data as in Figure 2, (—) calculated curves. (b) Isochronal conditions: (■) 1 Hz, (△) 0.01 Hz, (—) calculated curves.

this result that PVC drives the anelastic deformation of PVC/PMMA. Recently a similar conclusion has been inferred from compression tests and calculation of the activation volume for PVC, PMMA, and the same blend.[29]

Once we have determined that τ_{mol} requires, in the range of the α relaxation, the use of τ_β of PVC, it is possible to calculate the isochronal thermogram. Results for PVC/PMMA calculation are presented in Figure 14 and corresponding parameters are displayed in Table II. In the same table we have included parameters obtained for modeling the behavior of pure PVC using the same molecular

model.[30] It is noteworthy that f_e used for modeling the isothermal behavior is wrong, because the experimental temperature range is not large enough to see the flow of chains.

As seen in Table II, under isochronal conditions PVC/PMMA shows a different behavior from PVC because $G_{U\alpha}$ is higher and G_C and f_e decrease. PMMA is responsible for this behavior since PMMA has a higher $G_{U\alpha}$ modulus than PVC, and it seems that PMMA hinders crystallization of PVC. In fact, the crystallinity of PVC in the blend appears to be different from that of pure PVC, since the blend has a smaller relaxed modulus and it flows more easily
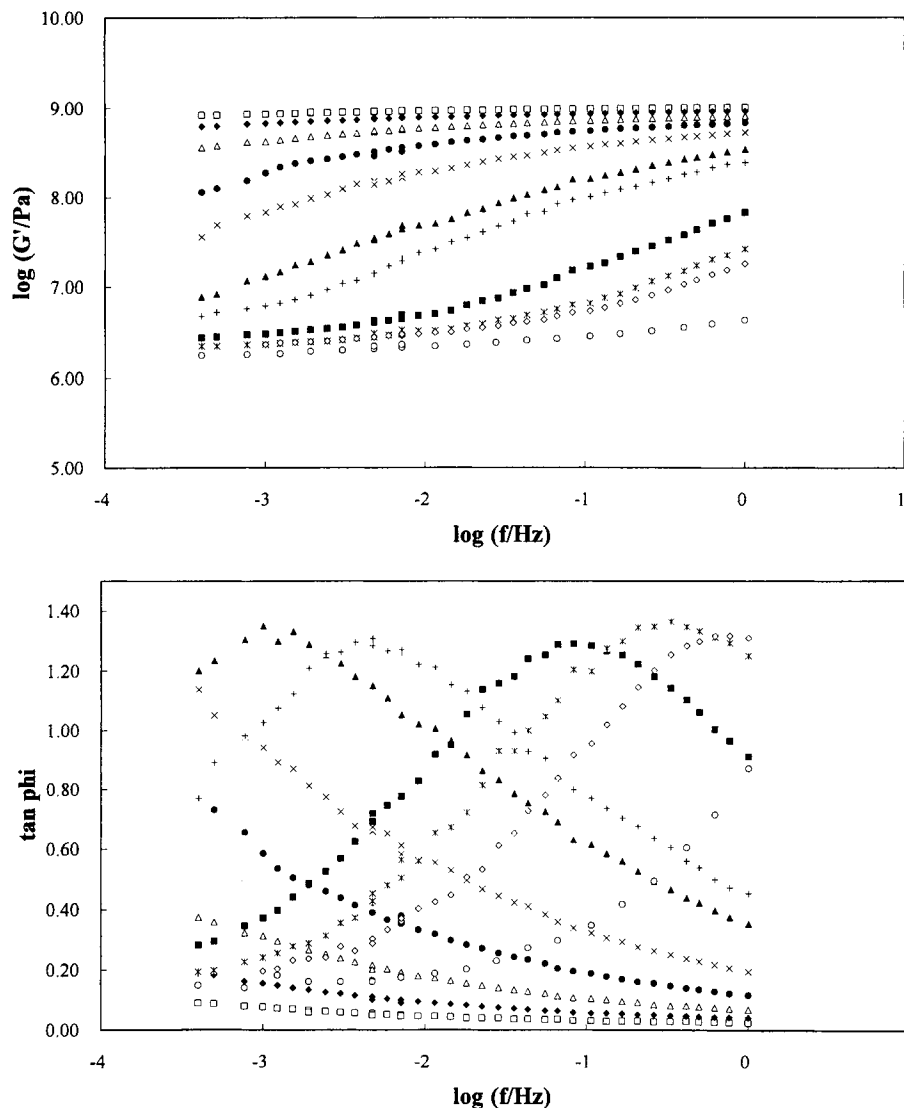
Figure 11 Isothermal plots of (a) G' and (b) tan ϕ against frequency for the α relaxation process in PVC/PMMA at several temperatures: (□) 348 K, (◆) 351 K, (△) 354 K, (●) 357 K, (✕) 359 K, (▲) 361 K, (+) 363 K, (■) 367 K, (✱) 369 K, (◇) 371 K, (○) 375 K.

at high temperature than PVC. This conclusion agrees well with results observed in X-ray diffraction (see Fig. 7), as discussed above.

Isothermal and isochronal parameters used for calculating curves for PVC/PMMA have different values. In fact, it seems that the blend has the behavior of a crosslinked polymer under isothermal conditions, as G_C is higher and χ' decreases. This means that the average length of subchains inside the blend is shorter than in pure PVC. It can be reasonably assumed that, during isothermal measurement, a change in structural order occurs and this change brings out a decrease in tan ϕ (increase

of G_C) (see Fig. 11). In order to check this idea, isothermal experiments at 360 K ($T > T_g$) over 5 days were performed and G', G'', and tan ϕ were measured each day. Results for G' and tan ϕ given in Figure 15 indicate that there is a microstructural change of PVC/PMMA during aging. In addition, aging is at least partly thermoreversible, as the polymer was rejuvenated at 423 K for 30 min and the initial state was almost regained (see Fig. 15). These changes probably result from an increase of local order in PVC, sometimes discussed in terms of "paracrystallinity" or "mesomorphic state": they can be induced in PVC by annealing procedures above T_g,
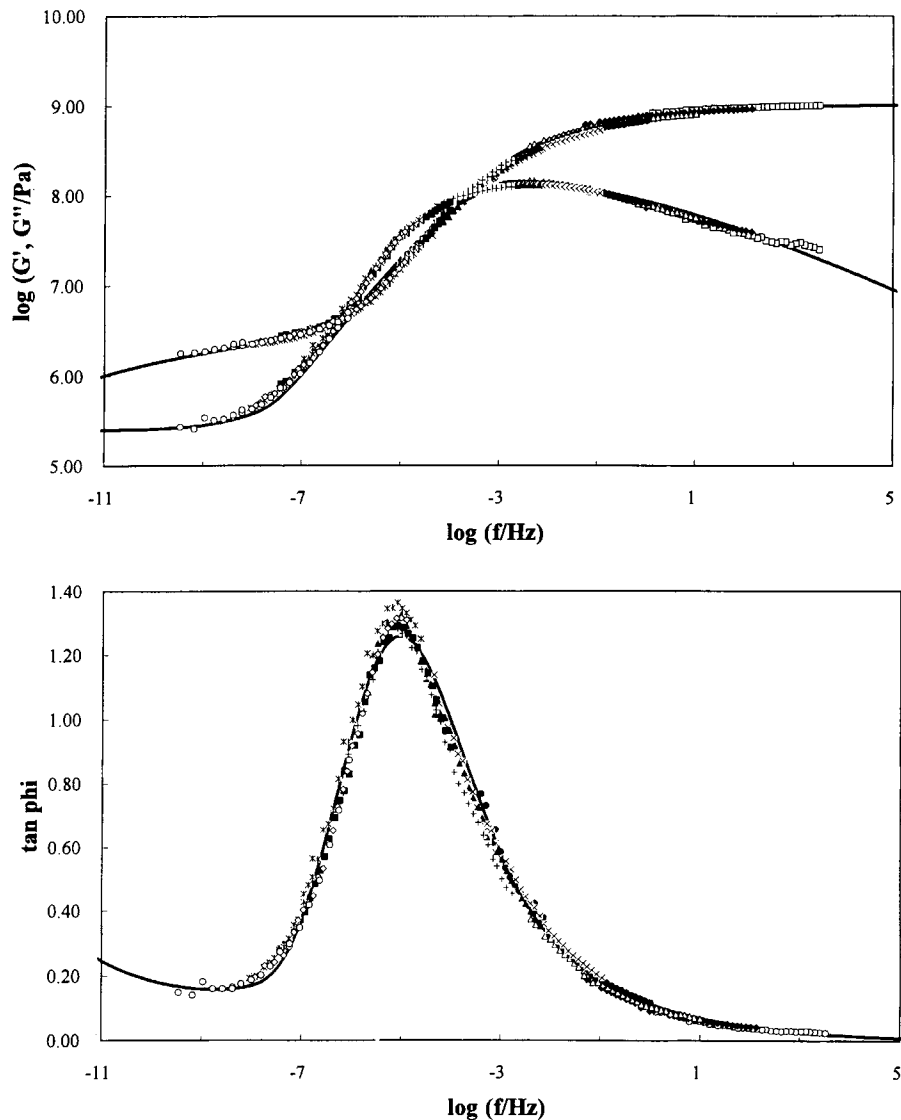
Figure 12 Master curves of (a) G' and G'' and (b) tan ϕ for PVC/PMMA: experimental data (symbols) and calculated curves (solid lines). See Table II for parameters.

and the existence of such an ordered state acts as a physical network. The same phenomena were observed[30] for pure PVC. The observed changes were attributed to the reinforcement of the physical net-

work formed either by crystallites, by local order, or by both.

Even if PVC/PMMA shows the same behavior at $T > T_g$ as pure PVC, the blend at the beginning

Table II Parameters for Modeling the α Relaxation of PVC and of 80/20 PVC/PMMA

	$G_{U\alpha}$ (GPa)	G_c (MPa)	χ	χ'	Q	f_e (10^4) [see eq. (13)]
PVC/PMMA Master Curves	1.05	2.2	0.24	0.69	0.20	80
PVC/PMMA Isochronal	0.80	1.7	0.31	0.82	0.20	0.008
PVC Master Curves	0.80	3.5	0.23	0.60	0.20	80
PVC Isochronal	0.8	2.0	0.31	0.76	0.20	3

is more amorphous than pure PVC. After a thermal aging at 360 K for 5 days, it does not reach the same ordered state as pure PVC. In fact, the comparison between the maximum of tan ϕ for PVC and for PVC/PMMA after 5 days at $T > T_g$ shows that pure PVC could be better ordered than PVC in the blend (tan ϕ for PVC after 5 days at 356 K = 0.9[30]; tan ϕ for PVC/PMMA after 5 days at 360 K = 1.4). And the same conclusion can be made if we compared χ' for PVC with χ' for the blend under isothermal conditions (see Table II). Then, although PVC in the blend is more amorphous than pure PVC, the thermal effect is less pronounced in the former material. This could suggest that PMMA limits the crystallization or at least the formation of a local order in PVC. Such behavior has been reported for blends of amorphous and semicrystalline polymers having a miscible amorphous phase.[31]

CONCLUSION

It appears that the miscibility of PVC and PMMA in 80/20 w/w blend depends on the observation scale of molecular movements. Below T_g, using a Gaussian distribution function for the relaxation time spectrum of homopolymers, we predict the dynamic mechanical behavior of PVC/PMMA over the range of the β relaxation in isothermal or isochronal conditions as well (in other words, at
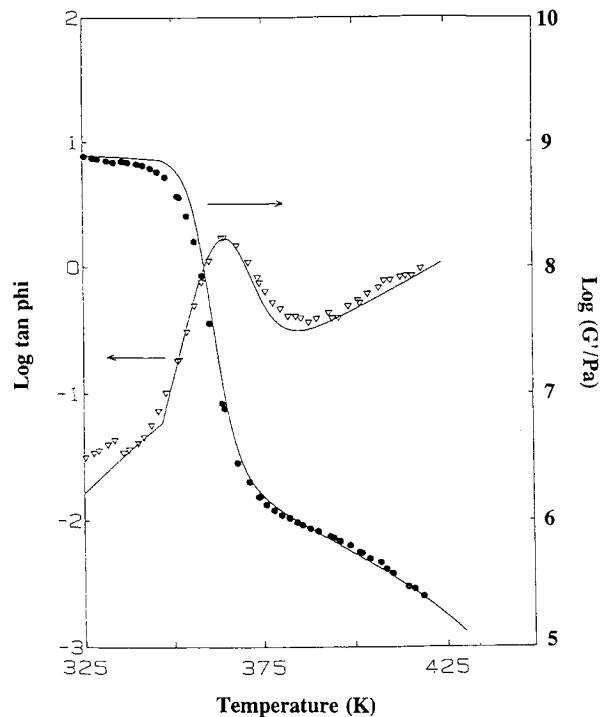

Figure 14 Isochrones of G' (●) and tan ϕ (∇) for PVC/PMMA at 1 Hz in the α relaxation range. (—) Calculated curves.

any temperature or frequency). Moreover, the dynamic mechanical behavior of PVC/PMMA can be described by a series-parallel model which is
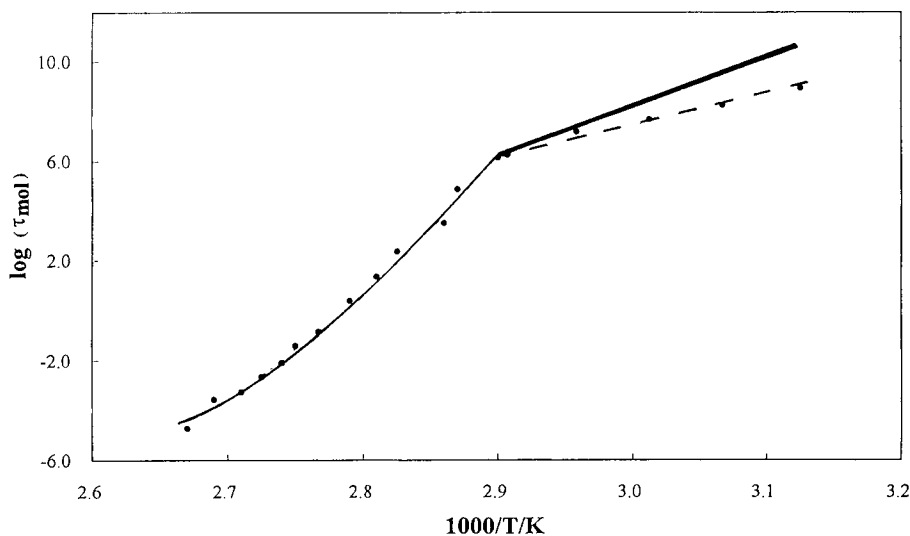
Figure 13 The relaxation time for the α relaxation process for PVC/PMMA plotted against the reciprocal temperature: experimental data (●) and calculated curves considering either U_β of PVC (- -) or that of PMMA (—); for $T > T_g$: calculated curve with $C = 0.04$ and $\chi(T_g) = 0.24$ [eq. (14)].
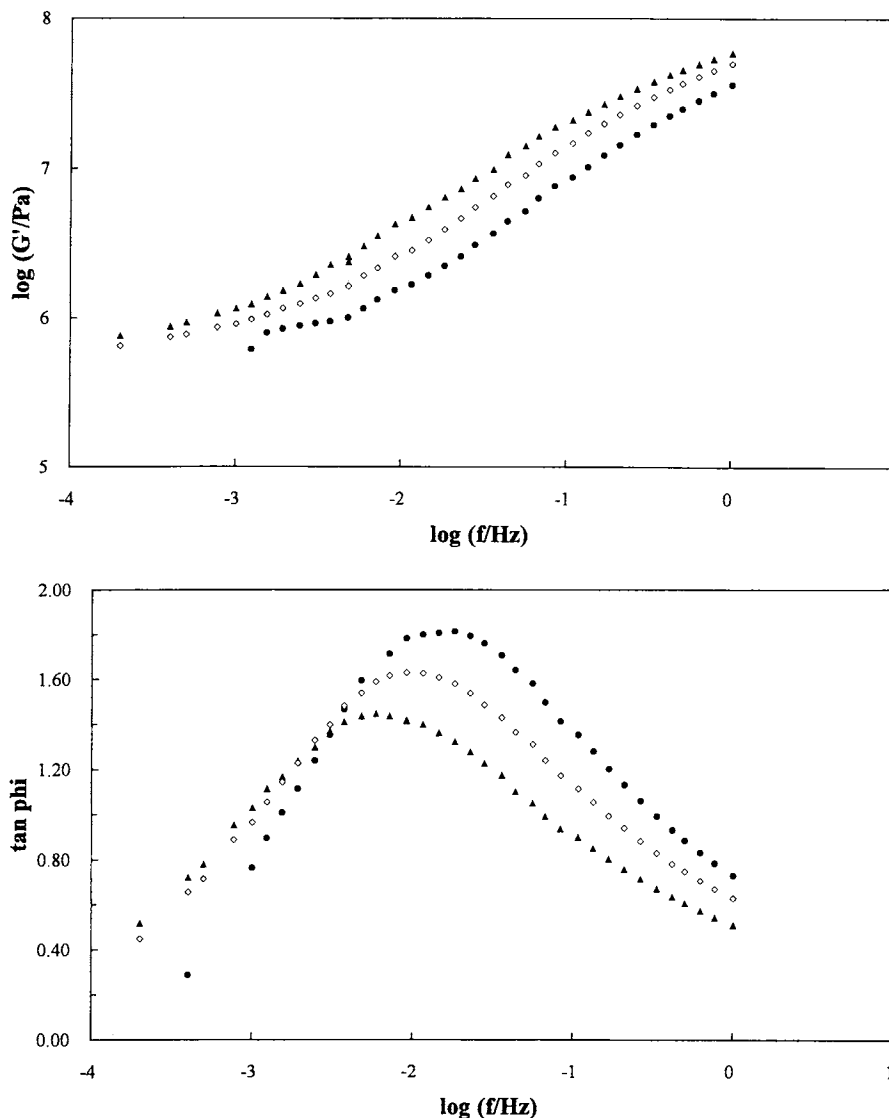
Figure 15 Isothermal plots of (a) G' and (b) tan ϕ against frequency for PVC/PMMA at 360 K versus time: (●) day 1; (△) day 5; (◇) results after aging at 360 K for 5 days and then "rejuvenated" by heating at 423 K for 30 min.

intermediate between the two limits (parallel and series). This is consistent with the common idea that the β relaxation concerns some repeat units (5 or 7) and at this scale the blend appears heterogeneous.

On the contrary, if movements of chains become collective (which is the case in the α relaxation), there is no more distinction between PVC and PMMA macromolecules and the blend appears homogeneous. Moreover, it has been shown that the α relaxation data of PVC/PMMA can be described by theoretical relationships involving parameters that have a precise physical meaning. The analysis

of the parameters used in calculation gives information on the microstructure and mechanical properties of a polymer. In particular, PVC seems to control the mechanical behavior of the whole material.

Finally, we have shown that, when PVC/PMMA is submitted to aging at $T > T_g$, local ordering of PVC occurs, resulting in a modification of the physical network. This process is thermoreversible and is less pronounced than in pure PVC; the presence of PMMA decreases the crystallinity of pure PVC and thus its capability of reorganization (formation of local order) in the blend.

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