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Dynamic-Mechanical Study of the Dynamics of Polymer Blends near the Glass Transition

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ABSTRACT: Poly(methyl acrylate) (PMA) and its blends with poly(4-hydroxystyrene) and a poly(4-hydroxy-*co*-4-methoxystyrene) have been studied by dynamic-mechanical spectroscopy at temperatures close to the calorimetric glass transition temperature T_g and frequencies between 0.3 and 30 Hz. The results for the imaginary part of the elastic modulus lead to broad master curves, which width increases with the content of the concentration of the second polymer. Even though the results can be described reasonably well using a Kohlrausch–Williams–Watts relaxation function, rather low values of the stretching parameter β are necessary in order to obtain good agreement with the experimental data. The Havriliak–Negami relaxation function leads to slightly worse agreement with experiment. The fragility parameter of the blends decreases with the concentration of PMA. The qualitative trend of the results may be interpreted in terms of the existence of concentration fluctuations in the blends.

Introduction

The glass transition (GT) has been the object of experimental and theoretical studies for many years.[1] Recent theoretical approaches[2] provide new light upon the physical processes responsible for the behavior of systems near the GT. Most of the recent data favor the view of the GT as a dynamic transition, thus discarding the existence of any underlying high–order thermodynamic transition.[2]

Two of the most frequently used theoretical approaches are those of the coupling model of Ngai[3] and the mode–mode coupling theory (MCT).[4,5] In both theories the calculation of the properties of the system from first principles is not possible for real complex systems such as polymer blends. Therefore the use of fitting parameters is necessary in both cases. During the last years there have been many papers in which relaxation data are used to test some of the predictions of the MCT[4,6] (mainly dielectric relaxation data in the case of polymer systems).[7] Also, many papers have made use of the predictions of the coupling model to discuss the relaxation behavior of polymers and blends near the GT,[8] including the breakdown of the time–temperature superposition principle (tTSP),[9] which is assumed to hold in the MCT.

Recent works have pointed out disagreements with some of the predictions of the basic formulation of the MCT. Broad band dielectric relaxation experiments[10] and neutron scattering data[11] do not give any hint for the existence of a critical temperature T_c ($T_c \simeq 1.2\ T_g$), at which a dynamic transition is predicted. Moreover, in some systems different values of T_c are obtained from different techniques, or values $T_c < T_g$ are obtained.[12,13]

Recent multidimensional NMR experiments[14,15] indicate that for a polymer near the GT there exist a wide variety of local environments, leading to a distribution of relaxation times. Since such a distribution may change with the temperature, these results would point toward a failure of the tTSP. Although this effect has been discussed in several papers,[16,17] and might be taken into account within the mode coupling model, at least qualitatively, it is hardly compatible with the MCT.

Recently, we have reported light-scattering and dynamic–mechanical spectroscopic data on poly(vinyl acetate) + poly(4-hydroxystyrene) (P4HS).[13] In general, the results agree with the predictions of the MCT for the scaling of the susceptibility; however, they lead to $T_c < T_g$. Although there is some indication of the tendency of those two polymers to mix at the molecular level, as revealed by FT-IR data,[18,19] it is difficult to ensure that both polymers have the same dynamics in the blend. Zhang et al.[16] have studied the dynamics of blends with similar specific interactions like P4HS + poly(methyl acrylate) (PMA) and P4HS + poly(methyl methacrylate) (PMMA) using ^{13}C-NMR. Their results indicate that P4HS and PMA form blends that are homogeneous at scales of 30 Å or larger and that the blending process alters signfiicantly the motional state of PMA at low temperatures, hindering the whole segmental motion of the PMA chains. Nevertheless, the blending effect on the dynamics of P4HS is insignificant, only the environment of the phenolic –OH being affected. On the other hand P4HS + PMMA are homogeneous only at scales of 300 Å and both components have dynamics in the blend different from in the pure state.

FT-IR and NMR measurements confirm that the miscibility in P4HS + PMA is due mainly to the formation of hydrogen bonds between the hydroxyl groups of P4HS and the carbonyl ones of PMA.[16,18,19] Methoxylation of part of the hydroxyl groups reduces the ability to hydrogen bond, and as a consequence one can expect that P4HS modified in this way (MP4HS) will form blends with PMA that, even if they show a unique calorimetric T_g,[20] will have a higher degree of heterogeneity at the molecular level. Therefore this is likely to be a more difficult scenario for the tTSP.

In the present paper we study the dynamics of PMA and some of its blends with P4HS and MP4HS (67% of

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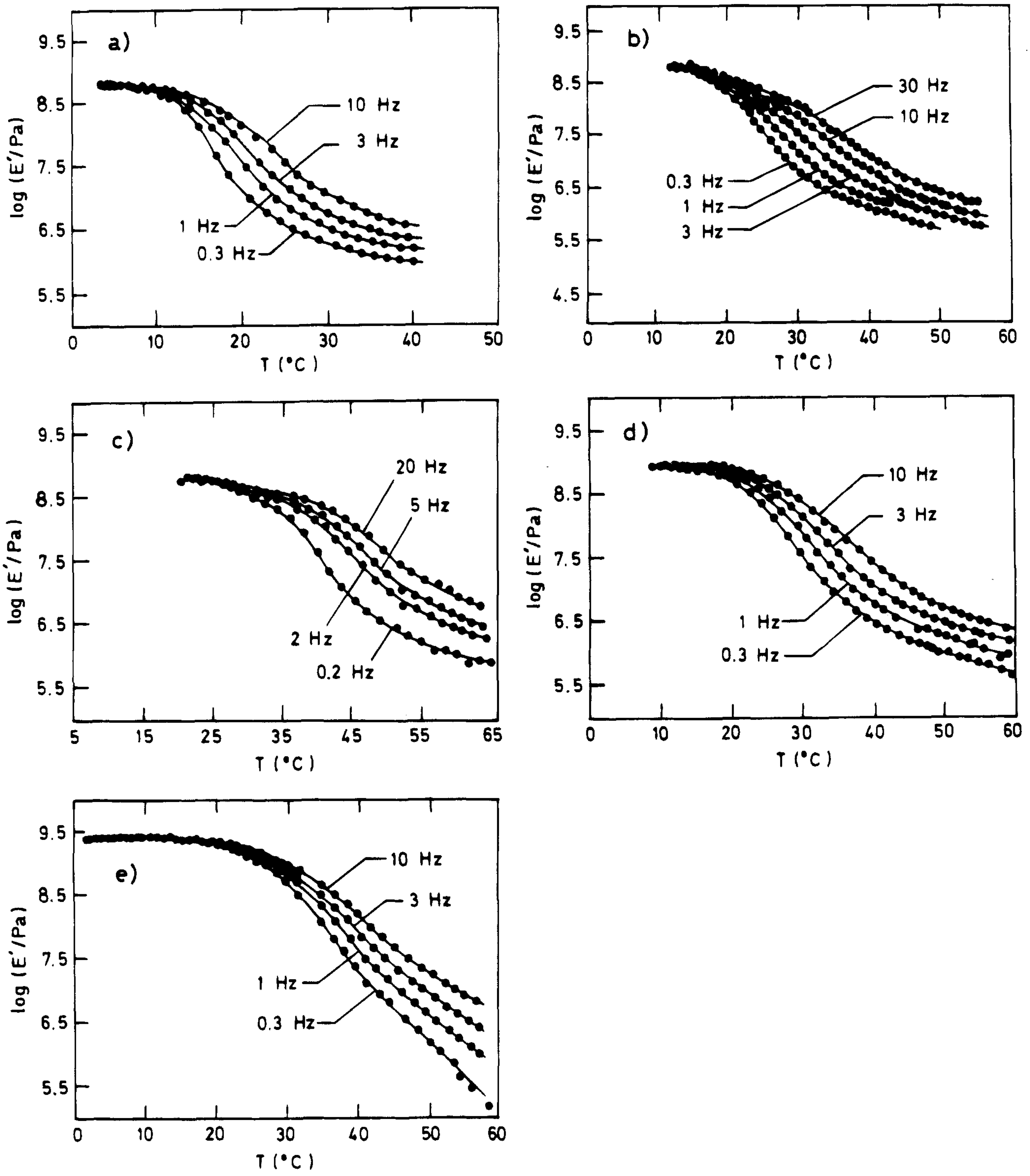

Figure 1. Real part of the elastic modulus E' for PMA and its blends with P4HS and MP4HS: (a) PMA; (b) PMA + P4HS, w = 0.9; (c) PMA + P4HS, w = 0.8; (d) PMA + MP4HS, w = 0.8; (e) PMA + MP4HS, w = 0.6.

the hydroxyl groups methoxylated) through dynamic-mechanical spectroscopy. The results will be used to compare the ability of some relaxation functions to describe the relaxation of these systems near the GT.

Experimental Section

Poly(4-hydroxystyrene) was the same used in previous works,[13,18] with a number average molecular weight $M_n = 5100$ and a polydispersity index $M_w/M_n = 2$. Poly(methyl acrylate) was purchased from Polysciences (U.K.) with a number average molecular weight $M_n = 1.5 \times 10^4$, and a polydispersity index $M_w/M_n = 2$, as determined by GPC using tetrahydrofuran as solvent.

P4HS was methoxylated according to the method proposed in ref 21. The conditions were adjusted in order to modify 67% of the hydroxyl groups of the original P4HS.

The dynamic-mechanical (DMTA) experiments were carried out on a Polymer Laboratory apparatus in the single cantilever bending mode, with a heating rate of 1 deg min^{-1} and with 2 × 6 × 20 mm probes. Several probes were measured for each composition. Each of the E'' presented in this work for each composition is the average of at least three samples whose

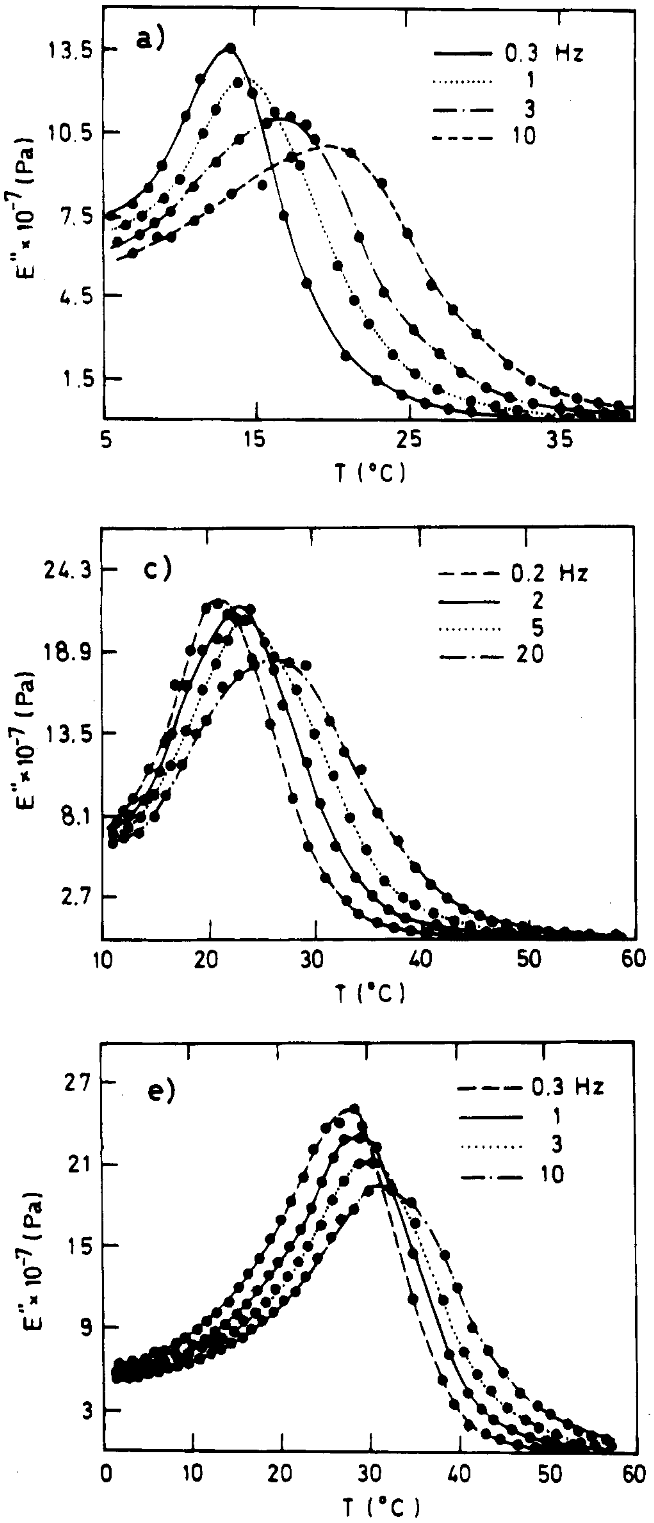

Figure 2. Imaginary part of the elastic modulus E'' for PMA and its blends with P4HS and MP4HS: (a) PMA; (b) PMA + P4HS, $w = 0.9$; (c) PMA + P4HS, $w = 0.8$; (d) PMA + MP4HS, $w = 0.8$; (e) PMA + MP4HS, $w = 0.6$.

results agreed within the experimental uncertainty (3% for E'' as revealed by the repetitivity of the results taken in the same probe going to 2 deg above T_g). Using the criterion, usually 80% of the samples measured lead to acceptable results. Special attention was paid to ensure that no hysteresis was observed. This is important because of the large change in sample stiffness and because the experiments were performed to well above T_g.

The precision in the temperature measurements was ±0.2 deg, and the experiments were carried out between 0.1 and 30 Hz. The thermal treatment of the samples and the method of preparation of the blends were the same as described before.[13,18] Experiments in the whole frequency and temperature range were only possible for blends rich in PMA. For blends rich in P4HS we did not succeed in preparing sample probes free of crazes. In effect, as the solvent was removed from the blend, crazes started to appear all through the sample. Even though annealing above the T_g led to the apparent disappearance of the crazes, it was not possible to obtain repetitive E'' curves for different probes of the same composition prepared independently according to this aging process. For the blends with MP4HS the concentration range was larger but it was also impossible to study the MP4HS homopolymer.

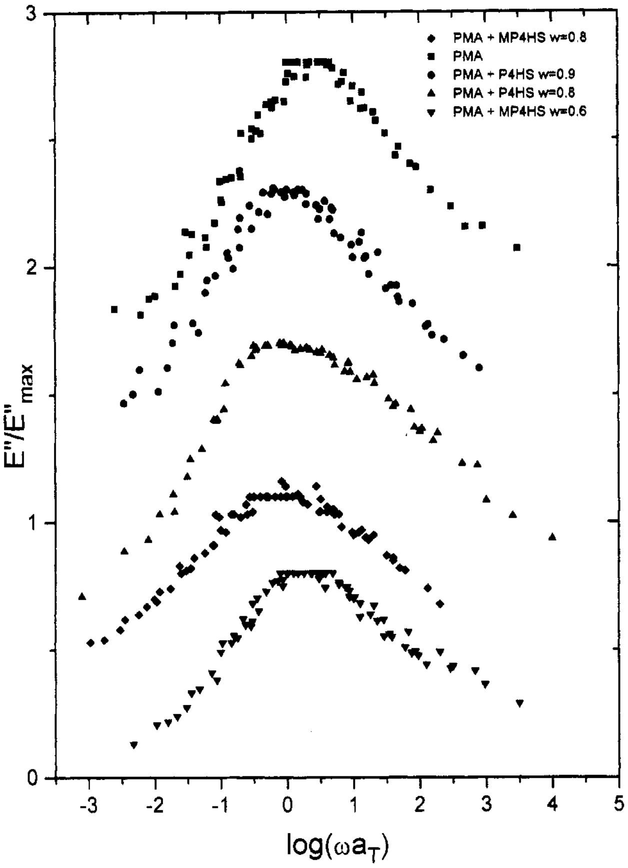

Figure 3. Normalized master curves of the imaginary part of the elastic modulus for PMA and the blends studied in this work.

Results and Discussion

Figures 1 and 2 show the results of E' and E'' obtained for the systems studies. The behavior is rather similar to those of other blends for which there is a noticeable difference between the T_g of the two homopolymers.[22] A decrease in the weight fraction of PMA leads to an increase in the maximum of E'' for each frequency, and to a decrease on the effect of frequency on the temperature of the maximum of the E'' curves. Also, as usually found in the literature, the temperatures of the maxima of the E'' curves are lower than those of tan δ ($=E'/E''$) curves.

According to the tTSP, it should be possible to construct a master curve from the data of a susceptibility like E'' at different temperatures and frequencies. The tTSP seems to hold in some polymers and blends while not in others. Figure 3 shows the master curves that have been obtained. In all the cases the temperature dependence of the shift factor along the frequency axis, a_T, has been described according to the Williams–Landel–Ferry (WLF) equation[22]

$$\log_{10} a_T = \frac{-(T - T_o)C_1}{C_2 + T - T_o} \qquad (1)$$

where C_1 and C_2 are constants characteristic of each polymer and T_o is a reference temperature that we have taken to be equal to the calorimetric T_g. Table 1 summarizes the parameters for each of the systems.

The scattering shown by the master curves is well within the uncertainty in the E'' measurements, and there is not a systematic trend for the data obtained at different temperatures or frequencies. While the present results are similar to those previously obtained for poly(vinyl acetate) + P4HS,[13] for other blends it has not been possible to build a master curve,[23,24] thus suggesting the breakdown of the tTSP.

Table 1. Calorimetric Glass Transition Temperature, T_g, and Constants of the Williams–Landel–Ferry Equation for the Different Polymer Systems

system	T_g/°C	T_o*/°C	C_1	C_2/°C
PMA	18.0	17.2	8.53	31.66
0.9PMA + 0.1P4HS	25.0	23.0	9.69	39.6
0.8PMA + 0.2P4HS	35.0	37.8	13.29	47.26
0.8PMA + 0.2MP4HS	25.0	25.0	13.35	66.51
0.6PMA + 0.4MP4HS	33.0	30.6	14.74	54.83

[a] The reference temperature T_o of the WLF equation has been taken as the experimental isotherm closest to the calorimetric T_g.

It is possible to calculate the master curve through[2,25]

$$\frac{E^*(\omega,T) - E(\infty,T)}{E(\infty,T) - E(0,T)} = \int_o^{\infty} \frac{d\phi(t)}{dt} \exp(-i\omega t)\, dt \qquad (2)$$

where $\phi(t)$ is the relaxation function and ω is the frequency. A striking fact is that despite the variety of materials used to study the GT and of the experimental techniques employed, the relaxation behaviors are very similar.[1,2,22,25] Almost all the experimental data for a relevant relaxation function $\phi(t)$ can be represented in terms of the so-called Kohlrausch–Williams–Watts (KWW) law

$$\phi(t) = A \exp\,[-(t/\tau_o)^{\beta}] \qquad (3)$$

A being a static correlation function and τ_o a characteristic relaxation time. The exponent β ($0 < \beta \leq 1$) measures the departure from the Debye pure exponential law ($\beta = 1$). The mode coupling model of Ngai[2] makes extensive use of eq 3, with τ_o related to microscopic variables through

$$\tau_o = [\beta \omega_c^{\,1-\beta} \tau^*]^{1/\beta} \qquad (4)$$

where ω_c^{-1} defines the inception of intermolecular constraints and τ^* is the noncooperative relaxation time prevailing at short times ($t < \omega_c^{-1}$) before torques and unbalanced forces from neighboring segments begin to retard the relaxation. The value of τ^* is mainly governed by the spectrum of skeletal bond conformational transition modes. The value of $(1 - \beta)$ is a measure of the severity of intermolecular constraints. Equations 2 and 3 cannot be solved in a close analytical form except for specific values of β. We have used the method suggested in ref 26, based on series expansion of the right-hand side of eq 2. It must be pointed out that the different types of series expansions have to be used for different intervals of ωa_T; the specific limits of such intervals are dependent on the value of β.

Figure 4 shows the best fits to some of the master curves obtained from eqs 2 and 3. The values of β are collected in Table 2, together with the value of τ_o and the average relaxation time $\langle\tau\rangle = \tau_o\Gamma(\beta^{-1})/\beta$, where Γ is the gamma function. Even though there is no clear trend in τ_o, it can be observed that β and $\langle\tau\rangle$ show the same trend. It must be remarked that in all the cases we have chosen the calorimetric T_g as the reference temperature in the WLF equation, and therefore, according to the definition of T_g as the temperature at which $\tau = 100$ s, one should expect almost the same $\langle\tau\rangle$ in all the cases, at least if the two polymers show the same dynamics and the concentration fluctuations are not too large. The values of β for PMA is almost the

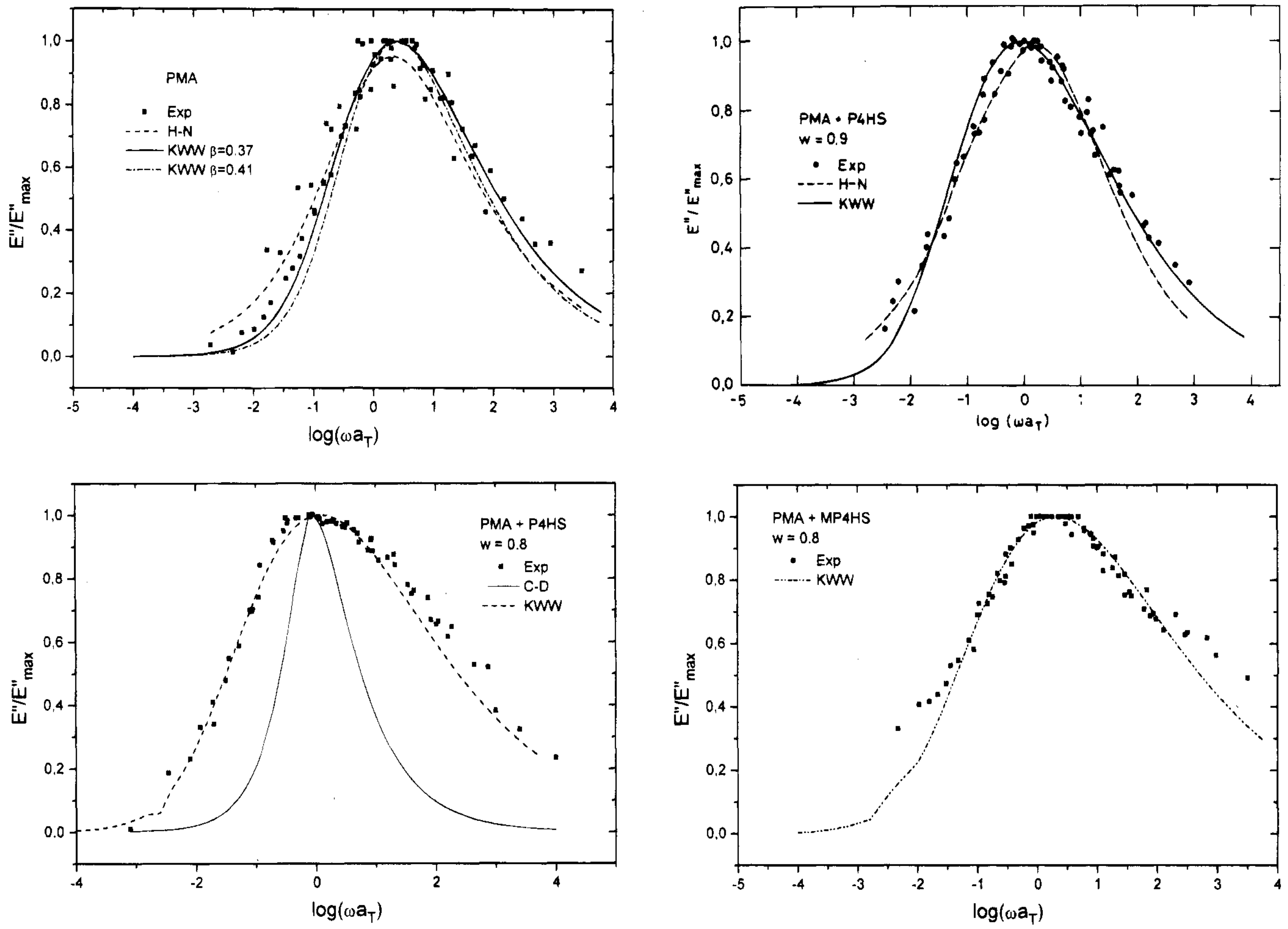

Figure 4. Comparison of the experimental master curves with those calculated with different relaxation functions. (a) Pure PMA. Symbols are the experimental points; the continuous and dashed lines are the best fits with the KWW and Havriliak–Negami relaxation functions, respectively. The dashed-dotted line represents the use of the KWW function with the value of β obtained from shear compliance experiments. (b) PMA + P4HS, $w = 0.9$. Symbols are as in part a. (c) Comparison of the experimental results with the best fit obtained from KWW and Cole–Davidson functions. (d) Results for a blend with a rather low value of β (0.26). For $-3 < \log(\omega a_T) < -2$ the calculation of E'' through series expansions of eq 2 and the KWW relaxation function was difficult due to the very slow convergence of the series.

Table 2. Parameters of the Kohlrausch–Williams–Watts Relaxation Function Average Relaxation Time Relative to That at the Reference Temperature (T_g)

system	β	τ_o	$\langle\tau\rangle$
PMA	0.37	0.045	0.15
0.9PMA + 0.1P4HS	0.34	0.125	0.13
0.8PMA + 0.2P4HS	0.28	0.085	0.09
0.8PMA + 0.2MP4HS	0.26	0.05	0.002
0.6PMA + 0.4MP4HS	0.23	0.270	0.008

same previously obtained for poly(vinyl acetate)[13] and compares quite well with the value of $\beta = 0.41$ obtained from viscoelastic shear compliance.[27] Figure 4 also shows the master curve predicted with $\beta = 0.41$ for PMA. Figures 4 shows that a KWW relaxation function underestimates the experimental results at high frequencies. This might be associated with some degree of overlapping of the α transition and the low-temperature β transition, as has been found in spectroscopic and neutron-scattering experiments.[7,28,29] However, it must be stressed that for PMA and the present blends, the β relaxation is found below −70 °C.[20] Also, in the case of blends with MP4HS, the KWW function underestimates E'' at the lowest frequencies. A similar behavior has been described by Alegría et al.,[24] and was attributed to the overlapping of the α transition with the terminal zone processes.

In order to test whether the discrepancies in the fits could arise from the use of the KWW form for the relaxation function, we have used the relaxation function proposed by Havriliak and Negami (HN),[30] that has been proved to be successful in describing dielectric relaxation data near the GT.[31] According to the HN relaxation function

$$\frac{E^*(\omega,T) - E(\infty,T)}{E(\infty,T) - E(0,T)} = [1 + (i\omega\tau_{\mathrm{HN}})^{1-\alpha}]^{-\delta} \qquad (5)$$

Due to the limited number of frequencies available for each temperature we have fitted only the master curve at the reference temperature to eq 5. Figure 4 shows the predictions for PMA ($\alpha = 0.55$, $\delta = 0.622$) and for 0.9 PMA + 0.2P4HS ($\alpha = 0.534$, $\delta = 0.748$). For the systems studied in this paper the HN function never leads to better descriptions of the master curves than the KWW one for our systems.

Alvarez et al.[32] have proposed a correlation between the parameter β of the KWW function and the parameters α and δ of the HN one

$$\alpha\delta = \beta^{1.23} \qquad (6)$$

When applied to the β's of Table 2, one observes that this relation does not hold satisfactorily ($\alpha\delta = 0.34$ for

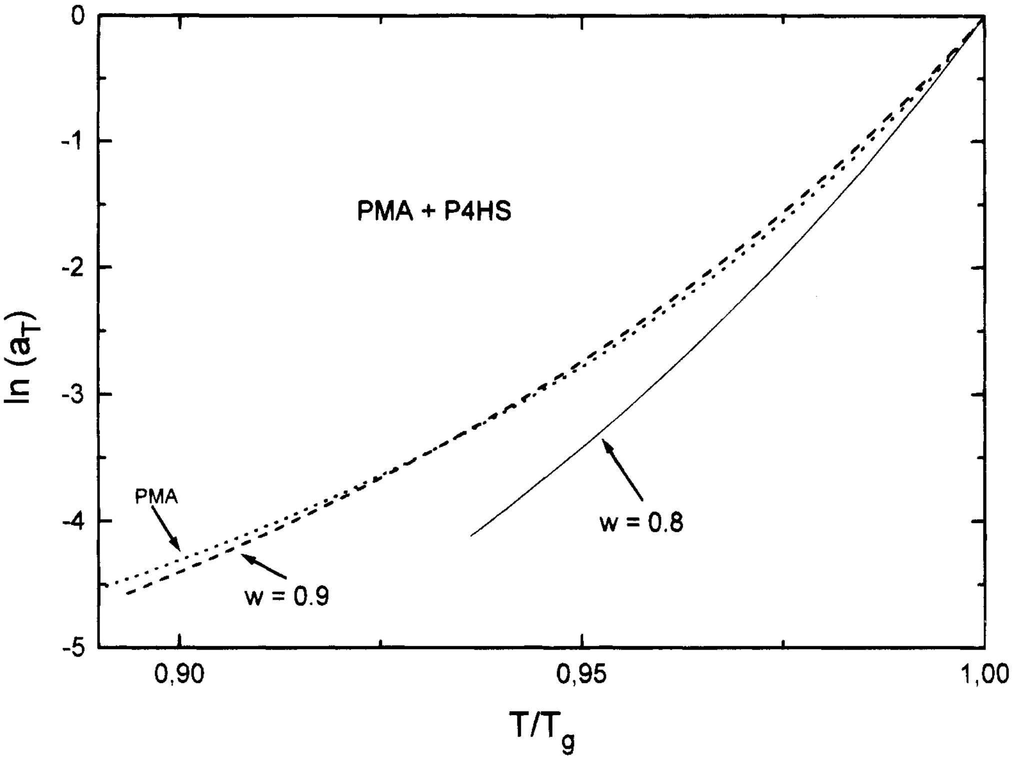

Figure 5. Cooperativity plots for the blends of PMA + P4HS.

PMA, while $\beta^{1.23} = 0.29$). As expected,[31] the use of the Cole–Davidson (CD) relaxation function leads to master curves narrower than the HN or the KWW ones. For the sake of example, Figure 4 compares the predictions of the KWW and the CD functions for one of the blends. Nevertheless, the parameters obtained for the CD satisfy quite well the relations with the β of KWW proposed in ref 33.

As Figures 4 and Table 2 show, increasing the concentration of P4HS leads to slightly lower values of β, i.e., broader master curves. Also, it can be observed that in the case of blends with MP4HS the β's are noticeaby lower than in those with P4HS. The stretched exponential relaxation function, eq 3, has been associated rather frequently with the existence of a broad distribution of relaxation times.[1,25] This interpretation seems to be supported by recent multidimensional NMR experiments.[15] Therefore, the decrease of β might be due in part to incomplete homogeneity at the microsocpic level.

Under these conditions, the interpretation of the relaxation function in terms of the coupling model cannot be done just by fitting the data to eqs 2–4. However, it has been shown than when the measured relaxation is inhomogeneously broadened, the degree of intermolecular cooperativity can still be assessed from the temperature dependence of the relaxation times. Employing an operational definition of T_g as the temperature at which the relaxation time equals 100 s, and considering that $a(T) = \tau(T)/\tau(T_g)$, eq 1 allows us to build the so–called cooperativity plots, i.e., Arrhenius–like plots with the temperature normalized by the T_g of each system. Figure 5 shows the plots for the blends of PMA and P4HS. In general, it can be said that the higher the influence of T upon τ, the higher the cooperative character of the glass transiton (more fragile the system). For the case of blends, it is also generally found that incompatible systems show a stronger temperature dependence than miscible ones. In our systems a decrease of the weight fraction of PMA increases the cooperative character of the transition. Using eq 1 and the constants C_1 and C_2 of Table 1, it is possible to calculate the fragility parameter $m = [d \log \langle\tau\rangle/d(T_g/T)]_{T=T_g}$ for the different systems studied. It must be remarked that there is a very good agreement with the correlation proposed by Böhmer et al.[22] according to which $m = (250 \pm 30) + 320\beta$.

Conclusions

The dynamic-mechanical spectra of PMA and its blends with P4HS and MP4HS have been obtained. Even though the results lead to broad master curves that can be described with a KWW relaxation function, the values of the stretching exponent β are rather low. The use of the Havriliak–Negami relaxation function does not improve the results obtained with the KWW one for any of the systems studied in this work. The width of the master curves increases and the fragility parameter decreases with the concentration of P4HS or MP4HS in the blends. These results might be explained qualitatively in terms of the existence of concentration fluctuations in the blends.

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