

Dielectric study of poly(methylacrylate) plus poly(4-hydroxystyrene) or plus poly(4-hydroxystyrene-co-4-methoxystyrene) blends near the glass transition

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The dynamics of blends of poly(methylacrylate) (PMA) + poly(4-hydroxystyrene) (P4HS) and poly(4-hydroxystyrene-co-4-methoxystyrene) (MP4HS) have been studied by dielectric relaxation in the frequency range $20 < \omega/\text{Hz} < 10^5$. The results have been analysed in terms of the Havriliak–Negami function plus a conductivity contribution. The time–temperature superposition principle breaks down for the blends, while it seems to be valid for PMA. The width of the relaxation region increases with the content of P4HS or MP4HS, in accordance with previous dynamic mechanical relaxation data. For a given composition, the data of the blends follow the scaling curve proposed by P. W. Dixon (*Phys. Rev. Lett.*, 1990, **42**, 8179), however in the low frequency region each sample follows a different scaling curve, which slope is related to the α parameter of the Havriliak–Negami function. The increase of the width of the relaxation curves with decreasing the PMA content can be well correlated by the coupling model when a gaussian distribution of coupling parameters is taken into account. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The appearance of several theoretical models¹, as well as recent computer simulation results^{2,3}, have provided important insights upon the physical mechanisms underlying the Glass Transition (GT). In particular they support the stretched exponential behaviour of the relaxation function found in a wide variety of systems near the GT. In general, for real systems, it is not possible to make first principle predictions with those models, being necessary to resort to some adjustable parameters characteristic of each system.

The relaxation behaviour of polymer blends usually differs significantly from that of the components. The segmental relaxation dispersion for blends is usually broader than in the pure components, and in addition to the characteristic asymmetry towards high frequencies, some blends show a marked low-frequency tail, that is more marked as the temperature is lowered⁴.

A first mechanism that might result in the broadening of the relaxation spectrum in blends is the existence of

intrinsic differences in the relaxation properties of the components^{5,6}. A second mechanism is the existence of concentration fluctuations. Several theoretical models have been presented to account, in an approximate way, for the effect of concentration fluctuations on the dynamics of relaxation processes in polymer blends^{7–11}. Recent two-dimensional nuclear magnetic resonance (n.m.r.) experiments have made it possible to follow the dynamics of each of the two components of blends, confirming that while the first mechanism dominates in some cases¹², the second is more important in others^{13,14}. Zhang *et al.*¹⁵ have carried out a ¹³C CP/MAS n.m.r. study of blends containing poly(hydroxystyrene) (P4HS) and poly(methylacrylate) (PMA). From their results, Zhang *et al.* concluded that both components are intimately mixed in the blend with no detectable domains on a scale of 20–30 Å at all compositions. Based on the Donth fluctuation formula¹⁶, Zetsche and Fischer¹¹, and Katana *et al.*¹⁷ have calculated the size of the domains of cooperativity, i.e. volume elements characterized by a unique T_g . For the thermodynamically compatible blends studied in refs 11 and 17, the radius of such domains range from 20 to

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Table 1 Parameters of the WLF equation. Values in parentheses correspond to d.m.t.a. experiments (ref. 15)

w	T_g (K) ^a	C_1	C_2 (K)	T_0 (K)
w PMA + (1 - w) P4HS				
1	291	13.00 (8.53)	44.84 (31.66)	277.72 (290.35)
0.9	298	13.30 (9.69)	46.30 (39.60)	293.87 (296.15)
0.8	308	12.88 (13.29)	45.95 (47.26)	298.10 (310.95)
0.7	313	11.88	37.02	302.36
w PMA + (1 - w) MP4HS				
0.9	294	12.92	42.41	291.31
0.8	297	11.61 (13.35)	41.80 (66.51)	301.06 (298.15)
0.7	302	11.20	45.03	308.32

^a T_g (P4HS) = 426 K, T_g (MP4HS) = 373 K

100 Å, thus being even larger than those existing in the P4HS + PMA blend. Moreover, even the size of the domains in the pure components (arising from density fluctuations), is of the order of that reported by Zhang *et al.* (e.g. polystyrene, Katana *et al.*¹⁷ report volumes of 45 Å average radius). Since the size of such domains is directly linked to the concentration fluctuations¹⁶, one might, in principle, expect that broadening in the PMA + P4HS blends could arise mainly from differences in the T_g of the pure components.

From their n.m.r. studies, Zhang *et al.*¹⁵ also concluded that the motional state of PMA is greatly affected by blending with P4HS at low temperatures, while at higher temperatures the blending effect on molecular motion is observable for both components. Moreover, these blending effects seem to be composition dependent.

We have studied the PMA + P4HS and PMA + poly(4-hydroxystyrene-co-4-methoxystyrene) (MP4HS)

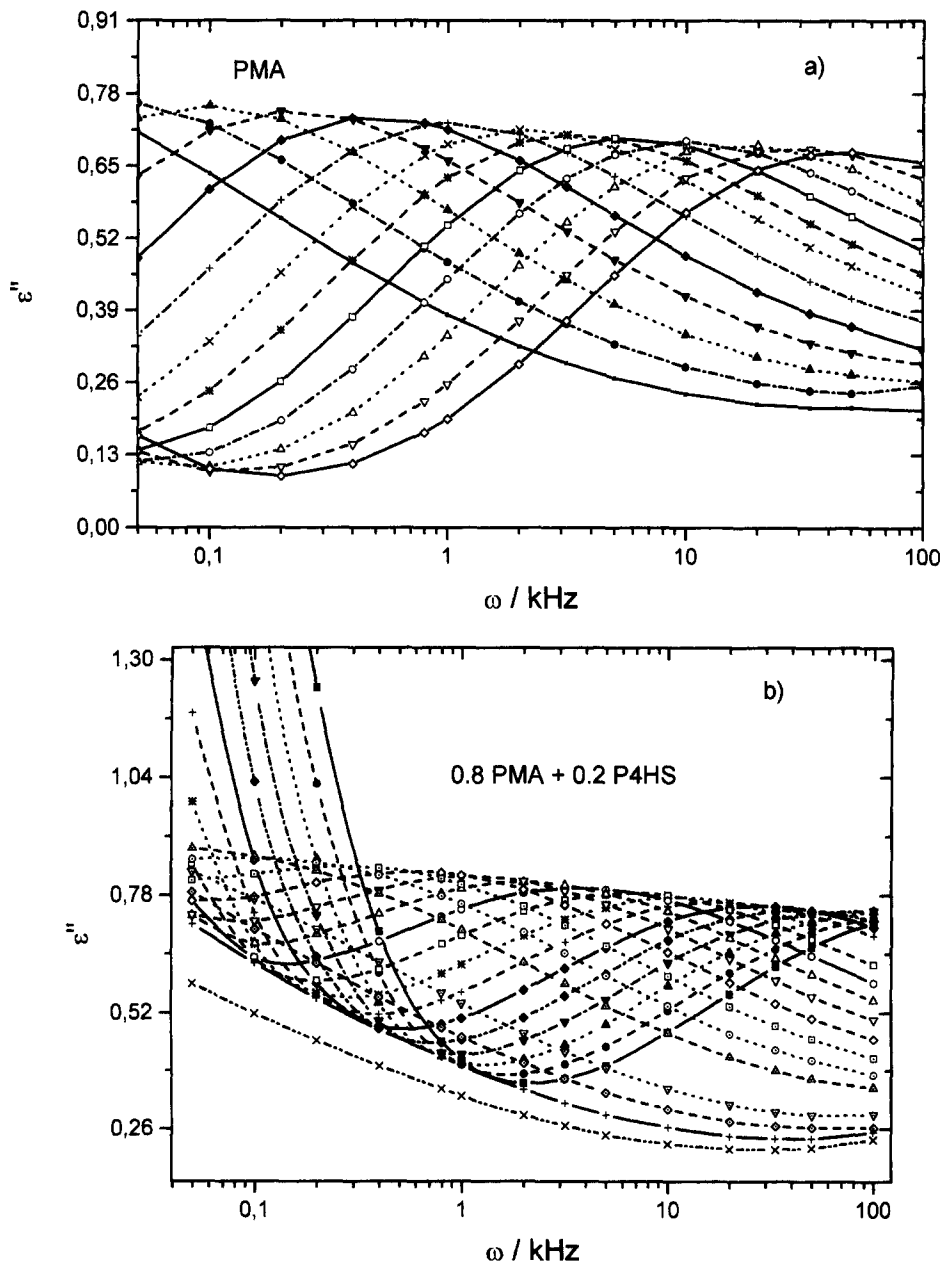


Figure 1 Dielectric loss curves for two of the systems studied. Isotherms differ by 2°. (a) PMA between 286 and 310 K. (b) 0.8 PMA + 0.2 P4HS between 300 and 339 K

systems using dynamic mechanical relaxation (d.m.t.a.)¹⁸, and found that the width of the loss curves increases with the weight fraction of P4HS or MP4HS. Moreover, when some of the hydroxyl groups of P4HS are methoxylated (thus decreasing the degree of miscibility¹⁹), the loss curves become wider, despite that the T_g s of both components are closer (see Table 1), thus suggesting a stronger weight of the concentration fluctuations in this blend than in the P4HS + PMA blend.

One might expect that both concentration fluctuations and differences in intrinsic mobilities lead to a breakdown of the time-Temperature Superposition Principle (tTSP)²⁰. Nevertheless, within the experimental uncertainty, it was possible to superimpose the d.m.t.a. data of each sample in a master curve¹⁸. However, the narrow frequency window available in our d.m.t.a. experiments might mask departures from the master curve in the high and low frequency limits. Therefore it seemed convenient to carry out a dielectric relaxation study of the dynamics of P4HS + PMA and MP4HS + PMA blends (MP4HS being a modified P4HS with 67% of the hydroxyl groups methoxylated).

EXPERIMENTAL

P4HS was the same as was used in previous works^{18,19,20}, with a number-average molecular weight, $M_n = 5100$ and $M_w/M_n = 2$. PMA was the same as was used in ref. 14, with $M_n = 1.5 \times 10^4$ and $M_w/M_n = 2$, as determined by gel permeation chromatography (g.p.c.) using tetrahydrofuran as solvent. P4HS was methoxylated according to the method proposed in ref. 22. The reaction conditions were adjusted in order to modify 67% of the hydroxyl groups of the original P4HS. The dielectric relaxation experiments were carried out in the frequency range 20 Hz to 100 kHz, using a GENRAD 1689M bridge. A two parallel plate cell from Polymer Labs. (Loughborough, UK) was used. Experiments were carried out in the isothermal mode, with temperature stability better than $\pm 0.1^\circ$.

The blends were prepared by casting from acetone, and were 33 mm in diameter and 0.15 mm thick. The thermal treatment of the samples was the same as in the d.m.t.a. experiments¹⁸, and they were kept at 10°C above the T_g during 30 min, within the electrodes, before starting measurements at the lowest temperatures. No differences were found between the raw samples and samples with metallized surfaces (silver painted), thus indicating good electrical contacts. Each isotherm is the average of at least three runs.

Due to the noticeable conductivity contribution to the dielectric loss ϵ'' in blends containing either P4HS or MP4HS, and to the limited frequency window available, it was not possible to obtain reliable values of the dipolar contribution to ϵ'' for blends with weight fraction of PMA, w , below 0.7.

RESULTS AND DISCUSSION

Since ϵ' and ϵ'' contain the same dynamical information, in this work we will focus our attention on the ϵ'' results. Figure 1 shows a typical set of results for two of the systems studied in the temperature range where the segmental dynamics, i.e. the α transition, is active within the available frequency (ω) window. In all the blends there is a noticeable conductivity contribution to ϵ'' at

low frequencies. At given T and ω , this contribution increases with the content of P4HS or MP4HS. At low T , a high-frequency contribution appears. It is related to the β -relaxation, and will not be studied here.

In order to discuss the dynamics associated with the α transition it is necessary to isolate the dipolar contribution ϵ_d'' associated with the segmental dynamics. We have followed the procedure described by Parthun and Johari²³. We have assumed that $\epsilon_d^* = \epsilon_d' + i\epsilon_d''$ can be described by the Havriliak–Negami (HN) function²⁴

$$\epsilon_d^* = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^{1-\alpha}]^\gamma} \quad (1)$$

with $0 < (1 - \alpha), \gamma \leq 1$, where α and γ are dimensionless parameters describing the asymmetric and symmetric broadening of the loss function, respectively. $\Delta\epsilon$ is the dielectric relaxation strength of the process, defined as $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, where ϵ_0 and ϵ_∞ are the low- and high-frequency limits for the real part of the dielectric constant. For the conductivity contribution to ϵ'' we have found that

$$\epsilon_{dc}'' = C_0/\omega \quad (2)$$

leads to satisfactory results in all our blends²³, C_0 being a temperature dependent parameter. No significant contribution for electrode polarization was found to be necessary. This is consistent with values of ϵ' which are almost frequency independent in the low frequency range.

We have discarded any isotherms for which a noticeable contribution from the β process can be detected, since there is no possibility of determining the corresponding parameters for a Cole–Cole function. In general, the quality of the fits is very satisfactory; as an example, Figure 2 shows the results for the blend 0.9 PMA + 0.1 MP4HS. Blends with $w < 0.7$ have not been studied since these show very important conductivity contributions through most of the frequency window. For such systems, no reliable sets of parameters for equation (1) can be determined, unless measurements at higher frequencies can be done, and therefore the values of ϵ_d'' cannot be calculated.

Figure 3 shows the values of $\tau_m = (2\pi\omega_m)^{-1}$, where ω_m is the frequency at which the maximum of ϵ_d'' is observed, for the blends at different temperatures. It can be observed that, for a given value of w and T , the τ_m s for the blends with MP4HS are lower than for the blends with P4HS. This can be understood in terms of the different T_g s of the polymers: 153°C for P4HS and 100°C for MP4HS.

The τ_m s have been fitted to the Williams–Landel–Ferry (WLF) equation

$$\log \tau_m = \log \tau_0 - \frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (3)$$

where C_1 , C_2 and T_0 are adjustable parameters given in Table 1, together with those previously obtained from the d.m.t.a. data¹⁸. The predictions of the WLF equation are included as dashed lines in Figure 3. The relaxation times obtained from dielectric relaxation data are larger than those previously obtained from d.m.t.a. Discrepancies between the values of τ_m obtained from different experimental techniques have been reported in the literature^{25,26}, and in particular for PMA, they have been previously discussed by Ngai *et al.*²⁷. This behaviour has been attributed to the different molecular mechanisms

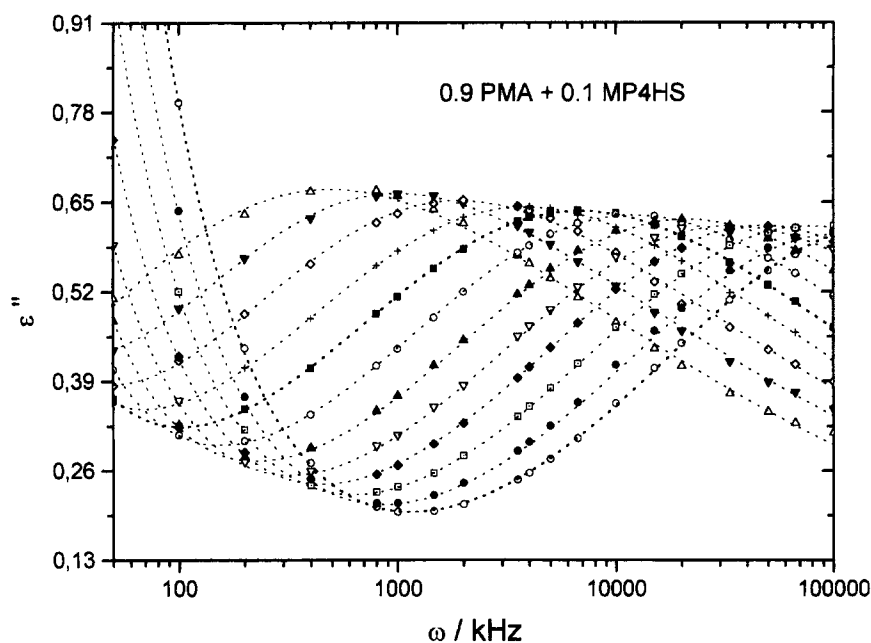


Figure 2 Loss curves for the blend 0.9 PMA + 0.1 MP4HS. Symbols are experimental data. Curves are fits to the HN function (equation (1)). Temperature range: 291–313° in 2° increments

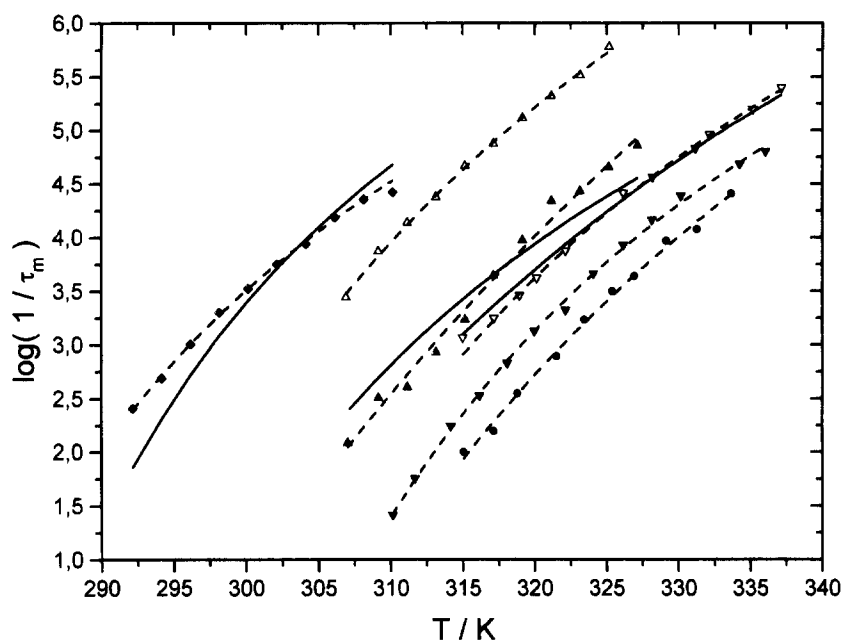


Figure 3 Relaxation times for the blends. $\tau_m = 1/2\pi\omega_m$, ω_m being the frequency at which the ϵ'' vs ω curve presents the maximum. Dashed curves are the best fits to the WLF equation. For the sake of comparison, the continuous lines correspond to the shift factors determined by d.m.t.a. for some of the blends (ref. 19). The data for the blend 0.7 PMA + 0.3 MP4HS have not been included to avoid confusion, since they are very close to those of the 0.8 PMA + 0.2 MP4HS blend

contributing to the elastic modulus and to the dielectric loss.

The values of C_1 and C_2 obtained from dielectric relaxation show a smaller composition dependence than those from d.m.t.a., which leads to non-negligible differences in the temperature dependence of the τ_m s obtained by the two methods; the differences are larger for the blends with P4HS than for those with MP4HS (see Figure 3, in this figure the curve corresponding to d.m.t.a. has been shifted along the $\log(1/\tau_m)$ - axis

for ease of comparison). Colmenero *et al.*²⁶ have discussed the temperature dependence of the relaxation times of pure polymers obtained by different techniques, pointing out that while in some cases the same temperature dependence is found, in others there are significant differences. In our case, it must be recalled that the parameters C_1 and C_2 from d.m.t.a. were obtained from the shift factors, i.e. assuming that the tTSP holds, and that a master curve can be constructed from the different isotherms. As will be discussed below,

Figure 4 Temperature dependence of the HN parameters for the w PMA + $(1-w)$ P4HS blends. T_0 is given in Table 1. The lines represent the best fits to the data with parameters given in Table 2. Similar results are obtained for the blends with MP4HS

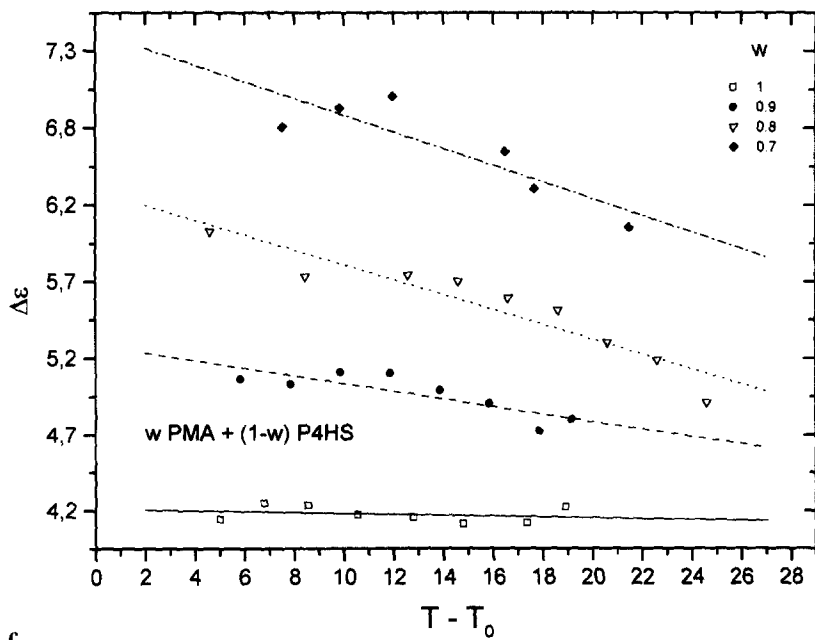
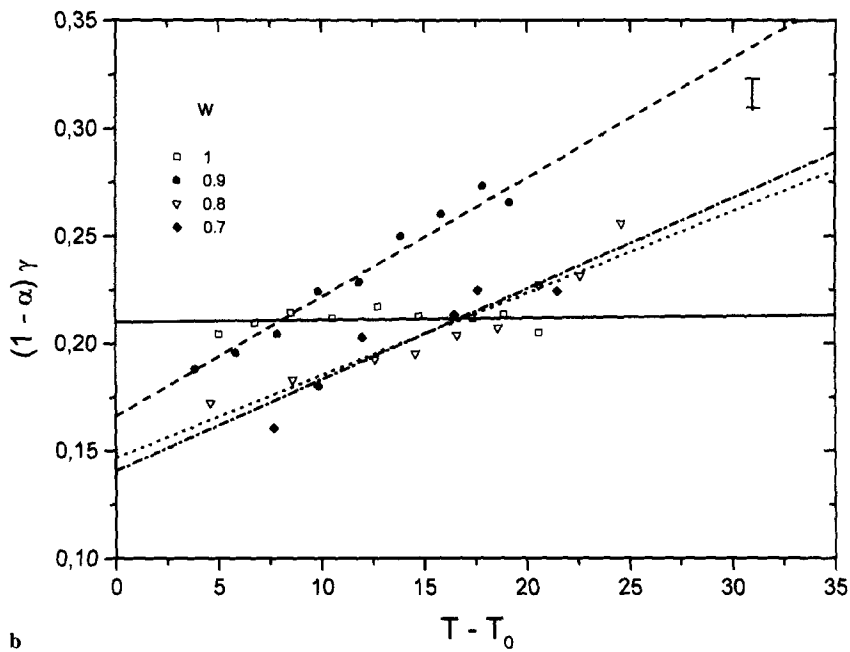
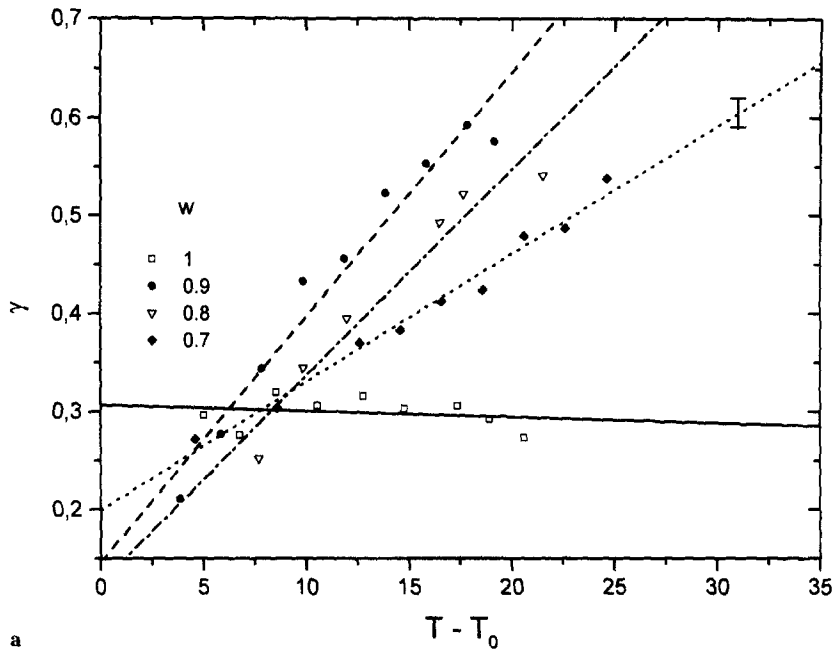


Table 2 Parameters for the equation $\lambda = \lambda_0 + \lambda_1(T - T_0)$ for the blends. λ represents any of the parameters of the HN $\Delta\epsilon$, γ or $\gamma(1 - \alpha)$, and T_0 is given in *Table 1*

Parameter	w PMA + $(1 - w)$ P4HS		w PMA + $(1 - w)$ MP4HS	
	λ_0	λ_1	λ_0	λ_1
$w = 0.9$				
$\Delta\epsilon$	5.28 ₈	-0.025 ₈	5.15 ₇	-0.059 ₃
γ	0.14 ₆	0.025 ₀	-0.012 ₈	0.021 ₂
$(1 - \alpha)\gamma$	0.16 ₃	0.003 ₈	0.10 ₈	0.006 ₇
$w = 0.8$				
$\Delta\epsilon$	6.34 ₂	-0.050 ₄	5.19 ₅	-0.036 ₅
γ	0.12 ₅	0.021 ₁	-0.005 ₄	0.021 ₈
$(1 - \alpha)\gamma$	0.14 ₇	0.003 ₈	0.07 ₁	0.007 ₇
$w = 0.7$				
$\Delta\epsilon$	7.41 ₂	-0.056 ₃	4.40 ₁	-0.049 ₆
γ	0.19 ₉	0.013 ₁	0.27 ₆	0.034 ₀
$(1 - \alpha)\gamma$	0.13 ₅	0.004 ₆	0.15 ₁	0.011 ₉

the dielectric data show that this may be satisfactory for PMA but not for the blends. The parameters of *Table 1* indicate that in general, the fragility of the systems tend to increase very slightly with the composition of P4HS or MP4HS, though the differences are small.

In general it is expected that T_0 is lower than the calorimetric T_g , which seems to be the case for the dielectric results of the PMA + P4HS blends, but not for all the blends PMA + MP4HS nor for the d.m.t.a. data¹⁸. It must be stated that due to our limited frequency (and therefore temperature) range, the values of C_2 and T_0 are quite sensitive to the τ_m s of the lowest and highest isotherms of each sample, which are the ones for which the uncertainty of τ_m is the largest. As a consequence, our results cannot be conclusive at this point.

A further aspect to be considered is the shape of the loss curves, which is governed by the parameters α and γ of equation (1). *Figure 4* shows the temperature dependence of γ , $\gamma(1 - \alpha)$ and $\Delta\epsilon$ as a function of

$(T - T_0)$ for the blends with P4HS; similar results were obtained for those with MP4HS. The order of magnitude of the uncertainties of these parameters is ± 0.03 for $\Delta\epsilon$, ± 0.02 for γ , and $\pm 0.01_5$ for $(1 - \alpha)\gamma$. It can be observed that while for PMA they can be considered as temperature independent, there are significant changes for the blends, the change being larger for the blends with MP4HS than for those with P4HS. An immediate consequence is that it is possible to build a master curve with the PMA data, as was the case for the d.m.t.a. data. This curve can be accurately described by a Kohlraush-Williams-Watts (KWW) relaxation function with a stretching parameter $\beta_{KWW} = 0.33$, a value slightly smaller than the one obtained from d.m.t.a. data ($\beta_{KWW} = 0.37$). The behaviour of γ and $\gamma(1 - \alpha)$ for the blends indicates that the width of the relaxation process increases as the temperature is decreased, thus no master curve can be built up by shifting the $\log(\omega)$ axis for the different isotherms. Moreover, the use of the KWW function does not describe in a satisfactory way the shape (width and asymmetry) of the ϵ'' vs $\log(\omega)$ curves, even for rather low values of β_{KWW} . Linear dependencies of the parameters of the HN function with $(T - T_0)$ have already been reported for other polymers²⁸. *Table 2* gives the characteristics of the linear fits of $\Delta\epsilon$, γ and $\gamma(1 - \alpha)$ vs $(T - T_0)$.

Dixon²⁹ has proposed that taking into consideration the temperature dependent width of the ϵ'' vs $\log(\omega)$ (normalized to the width of a simple Debye process: 1.14 decades) $\bar{v}\bar{v}$ it should be possible to build universal relaxation curves. More specifically, the master curve is obtained by plotting $\{\bar{v}\bar{v} \log[\omega_m \epsilon'' / (\Delta\epsilon \omega)]\}$ vs $\{\bar{v}\bar{v}(1 - \bar{v}\bar{v}^{-1}) \log(\omega/\omega_m)\}$. This universal curve describes quite accurately the behaviour of cyclo-octanol³⁰, but seems to fail in the high frequency region for 1-propanol³¹. It must be stressed that for the non-polymeric fluids for which Dixon's scaling has been tested the relaxation curves were accurately described by

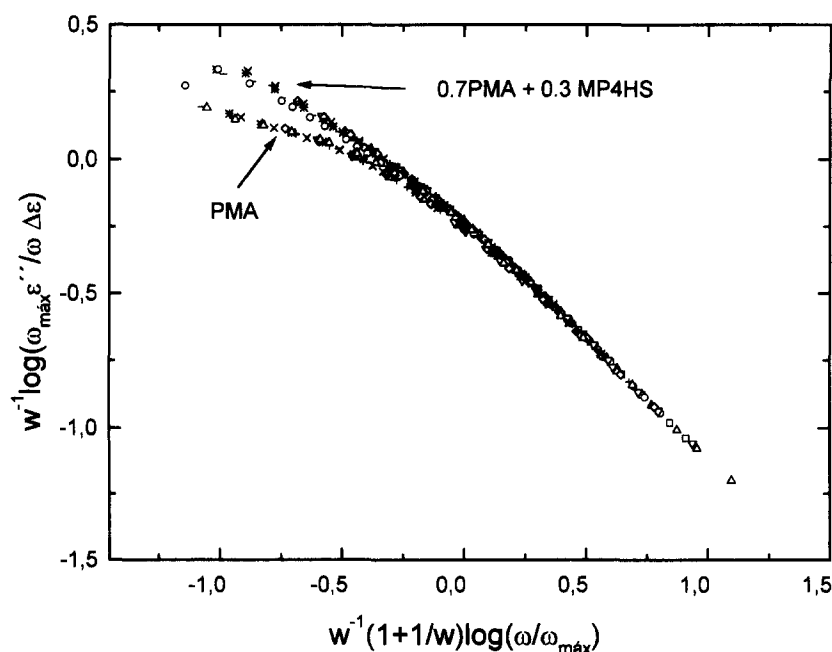


Figure 5 Dixon's scaling curves for the data of PMA and the blend 0.7 PMA + 0.3 MP4HS. The curves for the other blends lie between those shown. Notice that a universal curve seems to hold for frequencies larger than that of the maximum of the ϵ'' vs $\log(\omega)$ curves. The slope of the curves in the $\omega \rightarrow 0$ limit is related to the α parameter of the HN function

KWW functions at all the temperatures studied. Schönhals *et al.*³² have found that Dixon's scaling works quite well for pure polymers, although in the low frequency region each polymer seems to follow a separate curve. Using the HN parameters of our blends we have calculated $\bar{\nu}$ at each temperature³³. $\bar{\nu}$ increases as the temperature decreases, for a given value of $(T - T_g)$ increases with the content of P4HS or MP4HS, and is larger for the blends with MP4HS than for those with P4HS. This behaviour is in agreement with the width of the glass transition region, as measured by differential scanning calorimetry¹⁹. Figure 5 shows the scaling curves for two extreme cases: pure PMA and 0.7 PMA + 0.3 MP4HS, the curves for the rest of the blends lie between the two curves shown. It can be observed that for frequencies larger than ω_m the data of all the systems collapse into a unique curve, while at low frequencies each blend follows a different curve. This behaviour agrees with that reported by Schönhals *et al.*³². It is not difficult to show that in the $\omega \rightarrow 0$ limit, the slope of Dixon's scaling curve is related to the $(1 - \alpha)$ parameter of the HN function. Therefore, it must be expected that for systems that show a strong temperature dependence of $(1 - \alpha)$ the scaling behaviour will necessarily break down at low frequency. Despite that the temperature dependence of $(1 - \alpha)$ in our blends is larger than for the pure polymers of Schönhals *et al.*³², we find no disagreement with Dixon's scaling for each of the blends, most probably because our experimental set-up does not allow us to measure at frequencies low enough. These results are not surprising, since Dixon's scaling is a single parameter model, while the HN equation is a two-parameter one.

Even though effects from differences in intrinsic mobilities may be a source of dynamic heterogeneity in these blends, the fact that the relaxation curves for the systems with MP4HS are wider than those for systems with P4HS despite that the T_g s of the pure polymers are closer, seems to indicate that concentration fluctuations are the dominant effect in our blends. As a consequence, a rigorous analysis of ϵ'' vs $\log(\omega)$ curves for the blends would imply the use of a distribution of relaxation functions that follow the concentration fluctuations.

As already mentioned, there are three main approaches in the literature. One was proposed by Liu *et al.*⁷ and Cauley *et al.*⁸, another one was proposed by the group of Fischer^{11,17}, and the third one by the group of Ngai^{9,20}. The model of Fischer has been developed for mixtures in which one of the polymers is not dielectrically active, and it is necessary to know the parameters of equation (3) for both pure polymers, in order to apply it to blends. In our blends both polymers are active, and, as mentioned in the Experimental section, it has not been possible to study either pure P4HS or MP4HS, due to their high d.c. conductivity. The approach of Liu *et al.* is based on a lattice model for the polymer blend, and describes the relaxation spectra as the sum of several contributions of the KWW type (up to five contributions for a square lattice)¹³. For the reasons mentioned above, we have no objective way of calculating the parameters of each contribution, and we have therefore chosen to follow the approach of Ngai, although it seems reasonable to expect that the model of Liu *et al.* would lead to similar results.

The starting point of the model of Roland and Ngai⁹ is the description of the relaxation curves for a homogeneous system by a stretched-exponential relaxation function. For a binary blend, one can write:

$$\epsilon'' = \omega \int_0^\infty C(t) \cos(\omega t) dt \quad (4)$$

with

$$C(t) = \sum_{i=1}^2 C_i(t) \quad (5)$$

and

$$C_i(t) = C_{i,0} \exp\{-(t/\tau_i^*)^{1-n_i}\} \quad (6)$$

where the coupling parameter n_i is related to the usual stretching parameter of the KWW relaxation function by $1 - n_i = \beta_i$. For a blend, the concentration fluctuations impose a distribution of coupling parameters ranging from $n_i = 0$ to 1. Assuming a gaussian distribution for the concentration fluctuations, and thus for the coupling parameter, one may write

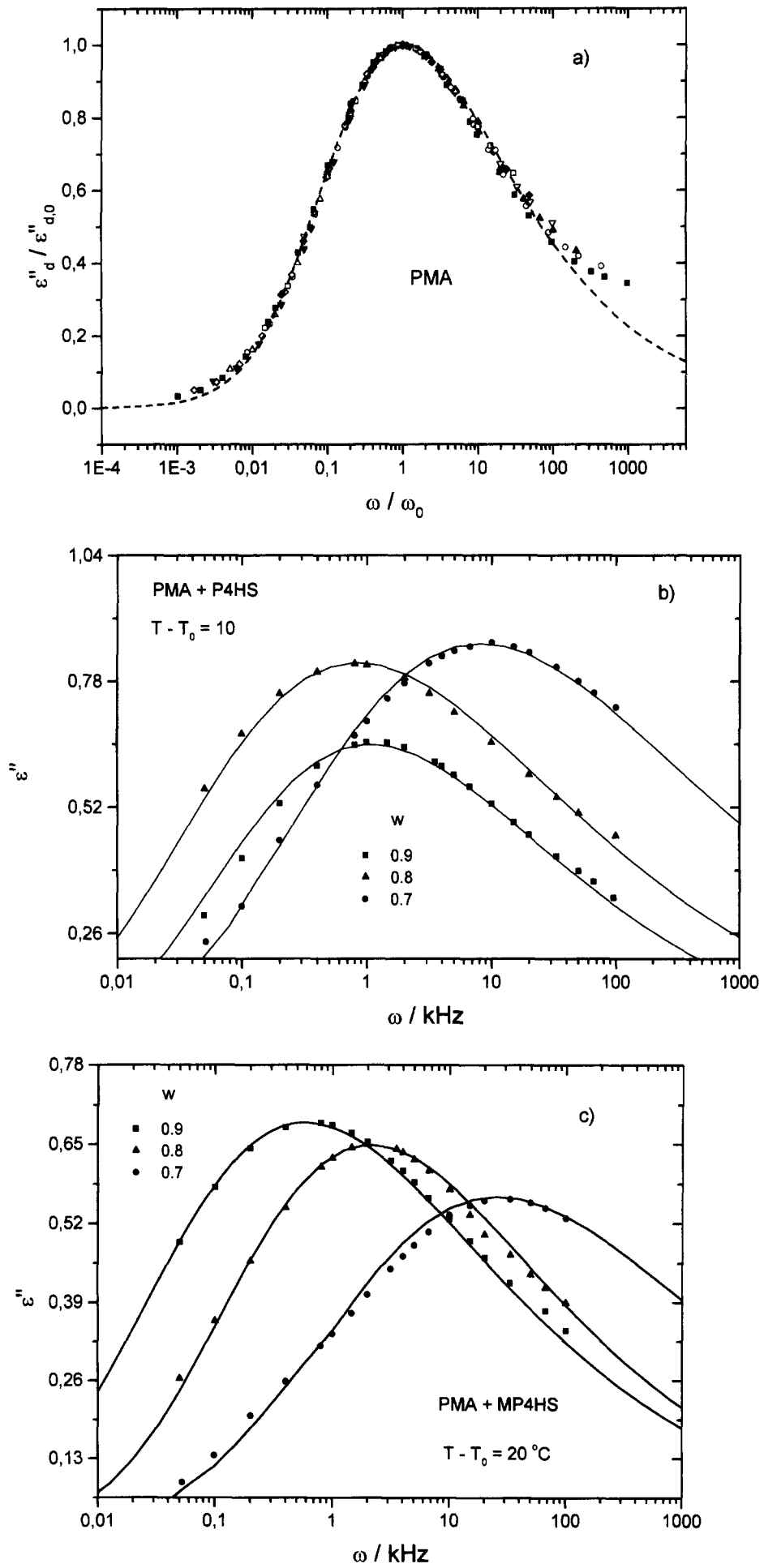
$$C_i(t) = C_{i,0} \int_0^1 \exp\{-a_i(n - n_i)^2\} \exp\{-[t/\tau_i^*(n)]^{1-n}\} dn \quad (7)$$

a_i being the width of the gaussian distribution.

It is important to note that in principle the values of all the parameters will change from one composition to another for a given blend. Since there is no a priori way to calculate such a dependence, in practice one has to deal with a large number of adjustable parameters. In order to reduce such a number, we have assumed a constant $\beta_1 = 1 - n_1$ for PMA in all the blends. This value has been taken as temperature-independent, since, as already seen in Figure 3, the shapes of the ϵ'' vs $\log(\omega)$ curves do not change in the temperature range studied. Figure 6 shows that a value of $\beta_1 = 1 - n_1 = 0.35$ describes accurately the master curve built for PMA. Figure 6 also shows the predictions of equations (4)–(7) for blends PMA + P4HS at $T - T_g = 10$ K, and for PMA + MP4HS at $T - T_g = 20$ K. As can be observed, the description is satisfactory. For the composition range studied, the coupling parameter of P4HS ranges from $1 - n_2 = 0.32$ for $w = 0.9$ to 0.28 for $w = 0.7$. A similar change is found for MP4HS: from 0.29 to 0.27. These changes are consistent with the increase in the width of the relaxation curves as w is decreased. It is also found that the values of a_i increase slightly with decreasing w , thus indicating that the weight of the concentration fluctuations grows with the concentration of either P4HS or MP4HS. This is consistent with the width of the glass transition region, as measured by d.s.c. through the same concentration range¹⁹. We consider that the present results must be considered as a further proof of the flexibility of equations (4)–(7). However, due to the significant number of adjustable parameters, unless a more theoretically sound method is devised for calculating some of the parameters, much care has to be taken in discussing the trends of the parameters.

CONCLUSIONS

The dynamics of blends formed by PMA + P4HS or + MP4HS has been studied in the glass transition region



using a dielectric relaxation technique. Once the conductivity contribution to ϵ'' has been accounted for, the dipolar contribution has been analysed in terms of the HN function. The results point out the existence of a noticeable temperature-dependence of each of the HN parameters, except for pure PMA. A consequence is that while it is possible to build up a ϵ'' vs ω master curve, this is not the case for any of the blends.

The width of the loss curves increase with the content of either P4HS or MP4HS, and, for a given composition, it is larger for the blends with MP4HS. The characteristic relaxation times can be well described with the WLF equation, and seem to indicate that the fragility of the system increase with the content of P4HS or MP4HS, in accordance with previous d.m.t.a. data for the same systems. Nevertheless, there are significant differences between the temperature dependence of the relaxation times obtained by dielectric relaxation and by d.m.t.a.

For any given composition of the blends, the relaxation data follow quite accurately the scaling function proposed by Dixon²⁹. However, in the low frequency region, the slope of the scaling curve corresponding to each sample is different, and it is related to the value of the α parameter of the HN function.

At each composition, the width of the relaxation curves of the blends with MP4HS are larger than those of the blends with P4HS. Since $[T_g(\text{P4HS}) - T_g(\text{PMA})] > [T_g(\text{MP4HS}) - T_g(\text{PMA})]$, this behaviour seems to indicate that for these blends, concentration fluctuations are the most effective mechanism in the broadening of the relaxation curves. The experimental data can be correlated with the coupling model when a gaussian distribution of coupling parameters is taken into account.

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Figure 6 Correlation of the dielectric data by the coupling model, including the effect of concentration fluctuations. (a) Master curve for pure PMA. The dashed curve corresponds to a coupling parameter $1 - n_i = \beta_i = 0.35$. (b) Correlations for the PMA + P4HS blend at $T - T_0 = 10$ K using equations (4)–(7). (c) Same as (b) for the PMA + MP4HS blends