Broadband Dielectric Spectroscopy for Poly(methyl methacrylate)/ Poly(α-methyl styrene-co-acrylonitrile) Blend

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ABSTRACT: Blends of poly(methyl methacrylate), PMMA, and Poly(α-methyl styrene-co-acrylonitrile), PαMSAN, random copolymer have been studied by broadband dielectric relaxation spectroscopy and differential scanning calorimeter (DSC). The dielectric measurements were carried out over a wide range of frequency (10^{-1} to 10^6 Hz) and temperature (30–155°C). The molecular dynamics of the glass relaxation process, α-process, was investigated as functions of composition, frequency and temperature. It has been found that, only one common α-relaxation process has been observed for all measured samples, its dynamics and broadness were found to be composition dependent. The existence of only one common α-relaxation process located at a temperature range between those of the pure polymer components was taking as a strong evidence for the miscibility of the blend over the entire range of composition. The miscibility was also confirmed by measuring the glass transition temperatures of the blends, T_gs, calorimetrically using DSC and dielectrically from the activation curves of the α-relaxation processes of the blends. The T_gs of the blends were found to follow Fox-equation. The composition dependence of the dielectric relaxation strength, $\Delta\varepsilon$ has been also examined for α and β-relaxation processes. In addition, the blending was found to have no effect on the kinetics and broadness of the β-relaxation processes of the PMMA, indicating that blending does not change the local environment of each component in the blend. This also led to in turn that the mixing of the two polymer components should take place on a structure level bigger than the segmental level to keep the local environment unchanged and small enough to have the same volume as the cooperative dipoles, which are related to the single T_g of the miscible blend.

KEY WORDS Poly(methyl methacrylate)/Poly(α-methyl styrene-co-acrylonitrile) (PMMA/ PαMSAN) / Miscibility / Molecular Dynamics /

Physical or chemical combination of two structurally different polymers can be used to obtain materials with properties which differ from those of the constituent components and which can be optimized to meet specific needs, like chemical resistance, impact strength, flexibility or weatherability. The final properties of the blend depend on the properties of the pure polymer components, miscibility and adhesion between the phases as well as the size and uniformity of the phase texture or morphology. Many techniques have been extensively used to investigate the miscibility and molecular dynamics of polymer blends, such as, differential scanning calorimetry (DSC),[1,2] NMR,[3–6] dielectric spectroscopy,[7–12] and mechanical measurements.[13–17]

The dielectric relaxation spectroscopy is a powerful tool cable of providing information about the molecular dynamics and the nature of the interactions in blends by monitoring the motion of dipolar groups attached to molecular chains. The dielectric spectroscopy has been widely used in polymer relaxation analysis and has the advantage over the dynamic mechanical methods in that it covers a much wider frequency range. Although dielectric spectroscopy requires that at least one of the species possesses a permanent dipole moment,

this can be also advantageous in blends in which one of the blend component is non-polar and thus invisible to the dielectric technique, allowing specific monitoring of the motion of the polar component. This is not the case in the current work, where both components of the blends are polar. In this case the dielectric behavior is therefore more complex because both of the blend component should contribute in the dielectric relaxation of the blend. However, on the other hand, only poly(methyl methacrylate) (PMMA) has strong local process (β-relaxation process), therefore poly(α-methyl styrene-co-acrylonitrile) (PαMSAN) will be inactive to the electromagnetic field at a temperature range lower than the T_g (the range of β-relaxation process). Thus it is advantage for the current blend to investigate the effect of blending on the local dynamics of PMMA regardless of the PαMSAN component. This seems to be industrial important, since the local relaxation process is greatly related to the mechanical properties of polymers.

In this paper, the broadband dielectric spectroscopy for PMMA/PαMSAN blends will be investigated over a wide range of frequency (10^{-1}–10^6 Hz) and temperature (30–155°C). These temperatures and frequency ranges are good enough to allow the observation of the α and β-relaxation processes in the blends and pure

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components. The miscibility was examined dielectrically by consider the change in the molecular dynamics of the α-relaxation process (which is related to the T_g of the blend) as functions of blend composition, frequency and temperature. The T_gs of the blends were also measured calorimetrically using DSC and dielectrically from the activation curves of the α-relaxation process. In addition, the relaxation strengths ($\Delta\varepsilon$) of the α and β-relaxation processes were also calculated as a function of composition from the analysis of dielectric relaxation spectra. The variation of the dynamical constraints or the change in the distribution of relaxation times caused by blending for the α and β-relaxation processes was also studied.

EXPERIMENTAL

Materials and Samples Preparation

The PMMA was obtained from Sumitomo Chemical Co., Japan. The M_w and M_w/M_n of PMMA were 14000 and 2.1, respectively. The PαMSAN was kindly obtained from Prof. Cakmak, University of Akron. The M_w and M_w/M_n of PαMSAN were 96500 and 2.26, respectively. The PαMSAN sample contained 31 wt% acrylonitrile as detected by elemental analysis.

The blends were prepared by dissolving the corresponding weights of the two polymer components in tetrahydrofuran. The blend solutions were then cast onto a petri-dish and left to dry at room temperature for about three days, after that, complete drying of the blends until a constant weight was accomplished under vacuum for another three days at 90°C. About 0.1 g of the blend was taken and pressed between two cooper electrodes at a temperature higher than the T_g of the corresponding blend composition by 30°C. The pure samples pressed directly without dissolution. The capacitance of the condensers used in the dielectric measurements was about 30 pF.

Measurements

The dielectric set-up contains an impedance/gain analyzer SI1260 (schlumberger), an electrometer amplifier and a measuring cell, which was very similar to that used in literature.[18] The effective diameter of the sample was 24 mm, and the blend thickness was about 0.1 mm. The measurements were carried out over a wide range of frequency (10^{-1}–10^6 Hz) and temperature (30–155°C).

The calorimetric glass temperatures of the blends (T_gs) were determined using modulated DSC, Seiko Instruments EXSTAR6000. The measurements were carried out at 10°C min^{-1} heating rate. The T_g was defined as the temperature of the half of the step height in specific heat curves.

RESULTS AND DISCUSSION

We start the discussion by investigating the various types of relaxation in the pure components and then proceed with the blends of different composition.

Pure PMMA

The dielectric behavior of pure PMMA has been received much attention recently [19–24] and the studied published before 1967 have been reviewed.[25] The aim here is not a comprehensive study of the dielectric response of PMMA but merely the identification of major relaxations in the sample that would help us understand its behavior in the blend. Figure 1 represents the dielectric measurements for pure PMMA as the values of dielectric loss (ε'') vs. frequency at different temperatures in a double logarithmic scale. This figure shows the dielectric spectra of PMMA at a temperature range lower than the T_g, therefore, only the local relaxation process (β-relaxation process) can be observed. Obviously, the PMMA has strong local process, the origin of this process is the partial rotation of the –COOCH$_3$ side groups around the C–C bonds linking these side groups to the main chain. With increasing the temperature from 30 to 80°C, the loss peak maximum shifts to a higher frequency, the peak intensity increases and the distribution sharpens. The shift of the peak maximum to higher frequency is a consequence of the high mobility with increasing temperature. The increase in the peak intensity is associated with an increased in the numbers of the relaxed dipoles with increasing temperature.

Figure 2 shows the dielectric spectra of PMMA at a higher temperature range above the T_g. One can see that the α-relaxation process appears at a lower frequency than the β-relaxation process. The α-relaxation is a cooperative process related to the micro-Brownian
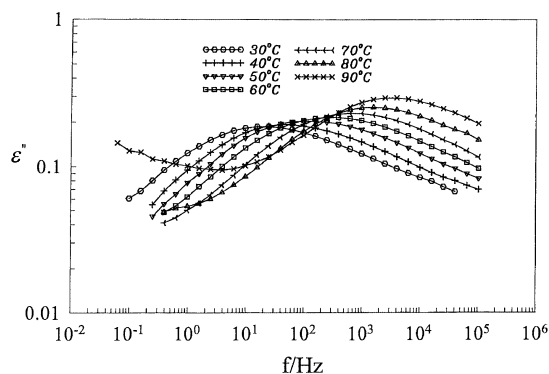

Figure 1. Dielectric loss (ε'') of the local process of PMMA as a function of frequency at different temperatures.

Figure 2. Dielectric loss (ε'') of PMMA as a function of frequency at different temperatures.
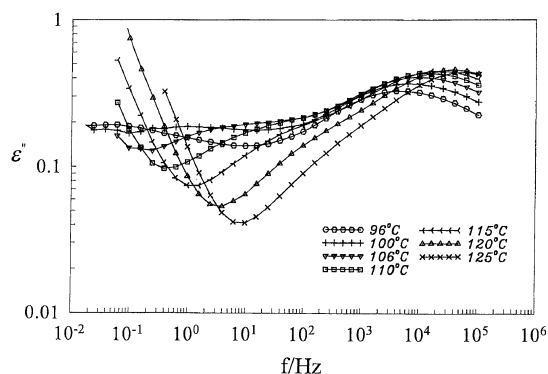

Figure 3. Dielectric loss (ε'') of PαMSAN as a function of frequency at different temperatures.

motions of the main chain backbone. At high temperature, the α-process merges with β-process into a complex $\alpha\beta$-process, in which the side group rotation is cooperative with the main chain motion. An abrupt increase in the dielectric loss values is clearly observed at high temperatures and low frequency range in Figure 2. This indicates the existence of space charge polarization and free charge motion within the materials and also related to the so-called conductivity current relaxation process. The behavior of pure PMMA (Figures 1, 2) is in good agreement with the literature studies, however, most of the published data for the dielectric behavior of pure PMMA observed $\alpha\beta$-process merged together.[19–24] The ability to resolve these two relaxation process is strong function of the frequency and temperature. In the current case, the measurements in Figures 2 were carried out over 10^{-1}–10^{6} Hz and $5°C$ increment in the temperature, therefore, for example, at $96°C$ one can clearly observe two resolved α and β-relaxation processes at low and high frequencies, respectively. However, on the other hand, only one merged $\alpha\beta$-process detected at temperatures higher than $115°C$. Most of literature data reported the dielectric behavior of PMMA either over a narrow frequency range or at a high temperature increment, therefore, only a single $\alpha\beta$-process detected. Based on the above it is recommended for such kind of materials which have two consecutive relaxation processes to study over a wide range of frequency with small temperature increment.

Pure PαMSAN

In order to investigate the molecular dynamics of the β-relaxation process of PαMSAN, the dielectric measurements were started at temperatures lower than the T_g. It has been found that the PαMSAN has a very week β-relaxation process its loss maximum peak is too low to preciously detect dielectrically. Figure 3 illustrates the dielectric spectra of pure PαMSAN, the figure
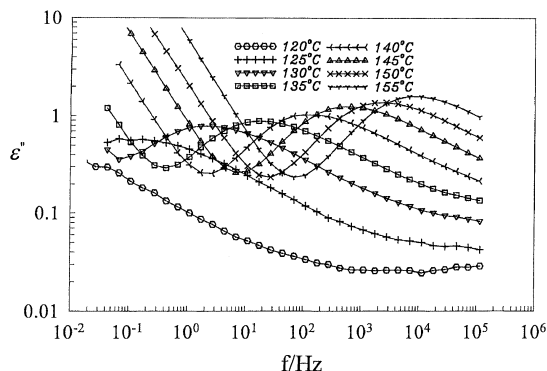
shows the α-relaxation process with a very week tail of the β-relaxation process observed at high frequencies. The α-relaxation process of the PαMSAN is located at a temperature range higher than that of PMMA due to the T_g of PαMSAN is higher than PMMA. As usual in the molecular dynamics of the α-relaxation process, the loss maximum peak shifts to higher frequency with increasing temperature. In addition, the dielectric spectra of PαMSAN showed a contribution to the ionic conductivity process at low frequencies and high temperatures, indicating the presence of space charge polarization and free charge motion. Furthermore, the height of the α-relaxation process of PαMSAN is slightly higher than that of PMMA due to the higher polarity of the segments in PαMSAN than that in PMMA.

PMMA/PαMSAN Blends

All the prepared samples of PMMA/PαMSAN blends were optically clear at room temperature after evaporation of the solvent until constant weight. In addition, the sample sheets were also still optically clear at the end of the dielectric measurements (about $30°C$ above the T_gs of each blend). This may indicate that, the two components make a miscible blend within the temperature range of the measurements. Representative dielectric spectra for different compositions of PMMA/PαMSAN blends are shown in Figures 4–6. One can detect in each blend composition a single α-relaxation process at a temperature range located between the T_gs of the two pure components. This finding implies that, the two components are miscible and the molecular dynamics depends on the blend composition. At higher frequency range of the dielectric spectra in the Figures 4–6 (higher than those of the α-processes of the miscible blends), one can also detect the β-relaxation processes (see for example Figure 4 at $115°C$). The change in permittivity of the β-process is directly proportional to the amount of PMMA in the blend, since PαMSAN does not undergo a β-relaxation
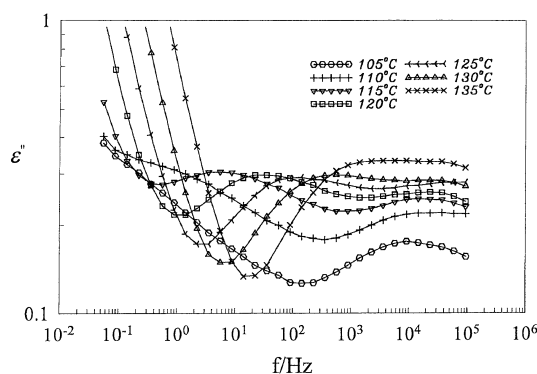
Figure 4. Dielectric loss (ε'') of PMMA/PαMSAN = 75/25 blend as a function of frequency at different temperatures.

Figure 6. Dielectric loss (ε'') of PMMA/PαMSAN = 25/75 blend as a function of frequency at different temperatures.

Figure 5. Dielectric loss (ε'') of PMMA/PαMSAN = 50/50 blend as a function of frequency at different temperatures.

Figure 7. Frequency at maximum loss as a function of reciprocal temperature for PMMA/PαMSAN blends of different composition.

in the same temperature range as mentioned above. The height of the β-relaxation process is strongly decreased with decreasing the PMMA content due to the dilution effect of PαMSAN component in the blend. However, on the other hand, the position and broadness of the β-relaxation process in the blend is almost the same as in the pure PMMA (will be discussed in the next section). At low frequency range, one can clearly detect the ionic conductivity process in all measured blends.

The frequencies of the maximum loss f_{max} as a function of the reciprocal temperature, $1/T$, for the α-processes of all measured samples are shown in Figure 7. These curves can help for judging the miscibility of the blends. Obviously the activation curves systematically shifted to lower temperature with increasing the PMMA contents. This systematic variation of the molecular dynamics with composition can be taken as strong evidence for the miscibility of the blend over the entire range of composition. The T_gs can be detected from the activation curves of Figure 7 by reading the temperatures corresponding to the dielectric relaxation frequencies.[26–29] The dielectric relaxation frequencies corresponding to the calorimetric T_gs were found to be 0.006 Hz and 0.5 Hz for PMMA and PαMSAN, respectively. One can draw straight line between these two frequencies of the pure components which can inter-
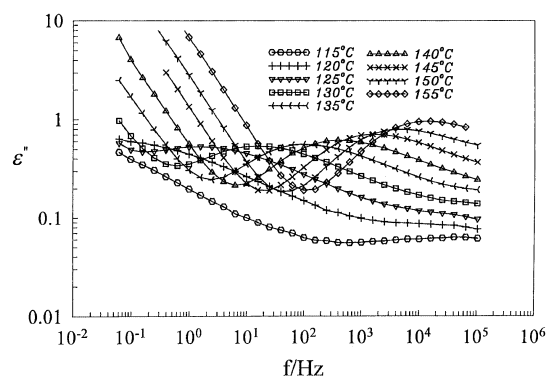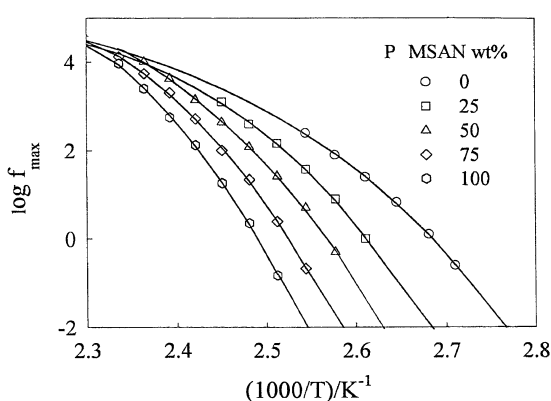
sect the other activation curves of the different composition at different frequencies. The dielectric T_gs predict by extrapolating the different intersects to the x-axis to read the correspond temperatures. The accuracy of the extrapolation is quite good as shown in Figure 8 (good agreement with DSC as will be discussed). This method has been derived by considering that the distance along the logarithmic frequency (or time) scale in the activation diagram is nearly constant between the curves which were determined by different experimental methods.[26–29] The current method has been successfully used for detecting the dielectric T_gs for some of plasticized polymers.[26] Extrapolation of the activation curves (to make the solid lines in Figure 7) can be done either by WLF-equation or more precisely by fitting f_0, Q_γ, Q_s and $3r/d$ in the Meander model equation [27–29]

$$f_m = \frac{f_0}{\pi} \exp(-Q_\gamma/RT)$$

$$\times \{1 - (1 - \exp(-Q_s/RT)^{3r/d}\}^{3(d/s)(3r/d)^2}, \quad (1)$$

where f_0 is the local vibration frequency of a segment, Q_γ is the local activation energy of a segment, Q_s is the dislocation energy, s is the segmental length, r is the bundle diameter and d is the inter chain distance. This

Table I. Fitting parameters obtained from the analysis of activation curves (α-relaxation processes) of PMMA/PαMSAN blends to the Meander model (eq 1)

PMMA, wt%	$f_0 \times 10^{13}$ (Hz)	Q_γ (kJ mol^{-1})	Q_s (kJ mol^{-1})	$3r/d$
100	5	65	5.4	45
75	4	60	5.25	40
50	4	55	5.15	37
25	4	55	5.05	35
0	5	50	4.99	34
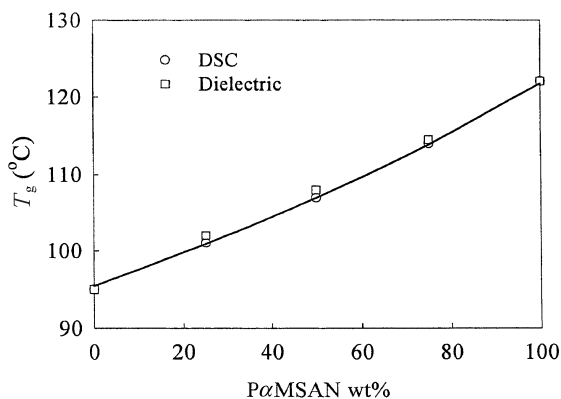
Figure 8. Composition dependence of glass transition temperatures detected by dielectric and DSC measurements. The line passing through the symbols is a fitting line using Fox-equation.
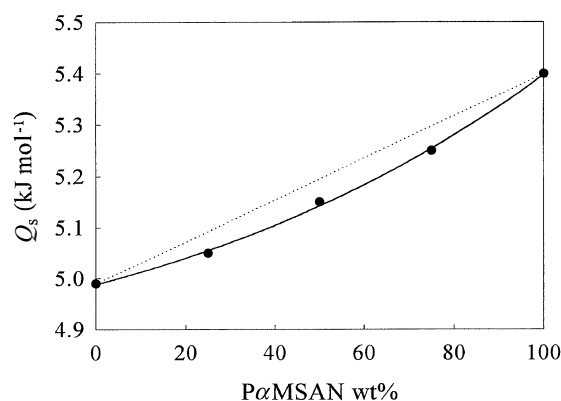

Figure 9. Dislocation energy, Q_s, as a function of composition.

model was derived by considering the dislocation concept and described elsewhere.[27–29] One can fit this Meander model to the experimental activation curves using the non-linear regression technique. Table I represents the fitting parameters obtained from the regression. An excellent description of the data was obtained as shown in Figure 7. Here the lines are computed from eq 1 using the parameters listed in Table I, while the symbols are experimental.

The calorimetric T_gs of the blends detected by DSC were in good agreement with that measured dielectrically. For each blend, only one common T_g was detected its value located between the T_gs of the pure components. Figure 8 depicts the composition dependence of the T_gs detected dielectrically and calorimeterically. The experimental values of the T_gs detected by the two different methods can be well described by Fox-equation, which was derived originally for copolymers and widely used for polymer blends.[30]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

Where $w_{1,2}$ and $T_{g1,2}$ are the weight fractions and the glass transition temperatures of polymer 1 and 2, respectively.

The fact that, the T_gs of the blends follow Fox-low (negative deviated from the simple mixing rule) might be attributed to the difference in the molecular architecture of the PMMA and PαMSAN. Therefore, large numbers of structure defects (quasi-dislocations) would

be created in the blends. The values of dislocation energy, Q_s obtained from fitting the activation curves of the α-relaxation process to Meander model (see Figure 7 and Table I) might support this suggestion. Figure 9 demonstrates the composition dependence of the Q_s. Obviously, the behavior of Q_s with composition is similar to that detected for the T_g with composition. It must be stated here that, this negative deviation in the behavior of Q_s was not observed for other blends, such as, TMPC/PC, since both polymer components have similar molecular architecture and a linear relation of T_g versus composition was detected.[31] The similar molecular architecture of TMPC and PC leads to better packing of the polymer chains without creation additional structure defects over those existing in the pure polymers.[31] The total number of quasi-dislocations per segment is given by

$$N = \sum_i w_i N_i \tag{3}$$

where

$$N_i = \exp(-Q_s/kT) \tag{4}$$

w_i is the weight fraction and N_i is the number of quasi-dislocation per segment in the pure state.

The variation of the dipole interaction of the polymeric segments with blending can be evaluated from the analysis of the dielectric relaxation process. The dielectric relaxation spectra of PMMA/PαMSAN blend can be resolved into three processes, α, β-relaxation processes and ionic conductivity. The α, β-relaxation processes can be simulated using Havrillak–Negami
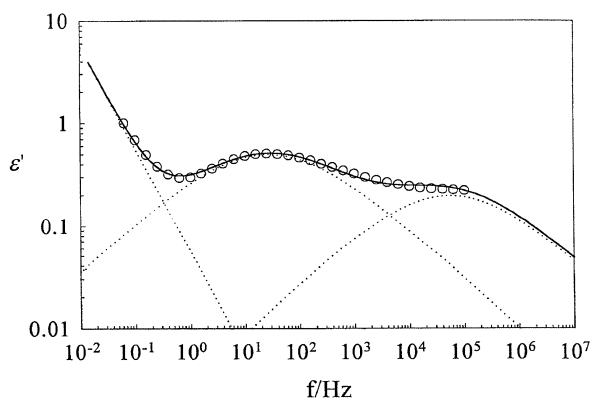
Figure 10. Analysis for the dielectric spectrum of PMMA/PαMSAN = 50/50 blend at 125°C.

Figure 11. Relaxation strength, $\Delta\varepsilon$, of α and β-relaxation processes as a function of composition.

equation:[32]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau)^b]^c} \quad (5)$$

Where ω is the angular frequency ($\omega = 2\pi f$), b and c are parameters which describe the shape of the relaxation time distribution function, τ is the relaxation time, ε^* is the complex dielectric permittivity, ε_0 and ε_∞ are the limited low-and high-frequency permittivities, respectively. In our case the best fit of the experimental results was obtained at $c = 1$, i.e., eq 5 reduces to Cole–Cole relashionship [33] (symmetrical curves). At low frequencies, the contribution of ionic conductivity to the measured dielectric loss describes by $\varepsilon'' = \sigma_{dc}/\varepsilon_0\omega^c$ where σ_{dc} is the d.c. conductivity and c is the parameter describing the broadening of the relaxation time distribution for the d.c. conductivity. The dielectric relaxation parameters, i.e., relaxation strength, $\Delta\varepsilon$, maximum relaxation frequency, f_m and distribution parameters of each process can be obtained from this analysis. Figure 10 illustrates the analysis of PMMA/PαMSAN = 50/50 blend at 125°C. The circular symbols in this figure represent the experimental data, while the dotted lines represent the contribution of each relaxation process according to the Cole–Cole and ionic conductivity relationships. The solid line passes through the experimental points is the total sum of the three processes. Obviously, a good description of the data was obtained as shown in the figure.

The composition dependence of $\Delta\varepsilon$ for both α and β-relaxation processes are shown in Figure 11. One can see that, the $\Delta\varepsilon$ varies linearly with composition for the two relaxation processes within the accuracy range of the measurements and the analysis ($< 10\%$ for $\Delta\varepsilon$). The $\Delta\varepsilon$ at a given temperature can be obtained according to Kirkwood–Fröhlich [34]

$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty \propto \frac{n}{T}g(T)\mu^2(T) \quad (6)$$

where n is the number density of dipole moments and μ is the dipole moment. This approximation gives $\Delta\varepsilon$
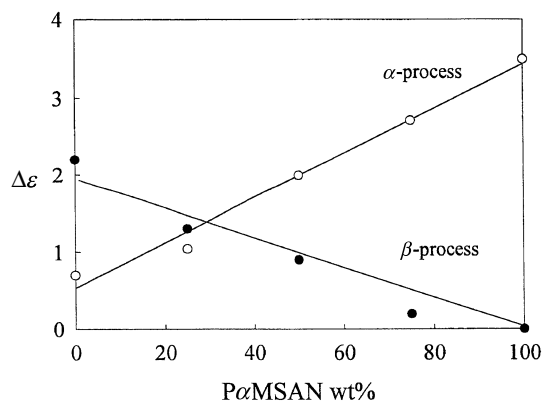
which at a given temperature is proportional to the number of dipole moments. To a first order approximation (neglecting the dipolar interaction), the total relaxation strength of the miscible blend, $\Delta\varepsilon$, equal to the sum of dipolar contributions of each component:

$$\Delta\varepsilon_B = \sum_i \phi_i\Delta\varepsilon_i \quad (7)$$

In the case of α-relaxation process, the composition dependence of $\Delta\varepsilon$ at 125°C is a linear behavior and the experimental data can be fitted nicely with the above equation as shown in Figure 11 (the solid line). However, on the other hand, the values of $\Delta\varepsilon$ in the case of β-relaxation process is directly related to the concentration of PMMA in the blend because PαMSAN has no β-relaxation process as mentioned above. Thus the decreasing of $\Delta\varepsilon$ with composition for β-relaxation process is mainly due to the dilution effects caused by the presence of unrelaxed segments of PαMSAN at 30°C.

The linearity in the variation of $\Delta\varepsilon$ with composition for α-relaxation process means that the orientation correlation factor, g, in the Fröhlich–Onsager equation [35] remains unchanged upon blending, i.e., there is no variation in the dipole–dipole interaction. This finding is surprising since it was expected that the blending of two polar segments would cause a change in the dipolar interaction. Therefore, it is necessary to investigate the variation in the dynamical constraints caused by blending. It is well established that the dynamical constraints could be monitored by following the change in the distribution of relaxation times (peak width) of the process under consideration. The greater the variation in the dynamical constraints the broader the relaxation process will be. Figure 12 demonstrates the normalized curves for the α-relaxation process of different blend composition. It is apparent that blending led to a great change in the width of the relaxation spectrum. This behavior is well known and was detected previously for several polymer blends.[36, 37] This broadening can be attributed
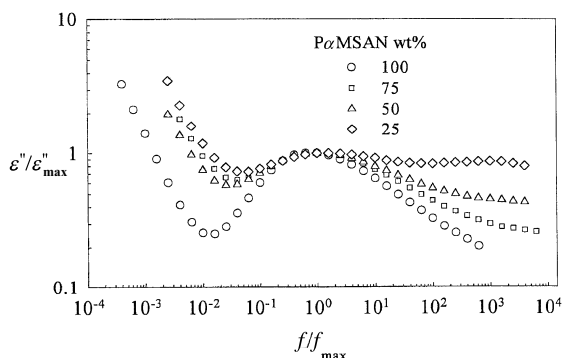
Figure 12. Normalized frequency dependence of ε'' for the α-relaxation process as a function of composition.

Figure 13. Normalized frequency dependence of ε'' for the β-relaxation process as a function of composition.

Figure 14. Activation plot for the β-relaxation process of various PMMA/PαMSAN blend composition.

to a concentration fluctuations, which would lead to a variation in the consistency of the cooperative regions and in turn produce a greater variation in the dynamical constraints of segments as a result of blending. However, on the other hand, this behavior was not observed in the case of the ideal blend of TMPC/PC[31] due to the similar molecular architecture of the two components of the blend.

Molecular Dynamics of β-Relaxation Process

The β-relaxation process is believed to be correlated with the mechanical properties of the blends such as ductility, impact strength and toughening. Studies of the blend dynamics of the β-relaxation process are of considerable practical interest and have received much attention recently.[38–41] Figure 13 shows the normalize curves of the local process of PMMA in the blends at 50°C. One can see that this local process is much broader than the α-relaxation process (Figure 12). This is believed to be due to the disorder structure of amorphous materials, in the glassy state, there exists a range of different environments surrounding the chemical units that undergo molecular motion. This heterogeneity generates a distribution of potential energy barriers hindering the reorientation motion, which is reflected experimentally in the broad distribution of relaxation frequencies. One can see that there is no any difference in the broadness of the β-relaxation process with blending, *i.e.*, the distribution of relaxation time of the local process of PMMA in the blend seems to be identical as in pure component.

Figure 14 represents the activation curves for the β-relaxation processes in the blends of different composition. It is apparent that the β-relaxation process of PMMA has almost same activation curve regardless of the blend composition. However, it has been found in the previous section that the dynamics of the α-relaxation process of the blend strongly influenced by blending. Based on the above it is clear that the absence of any blending effect on the local dynamics of
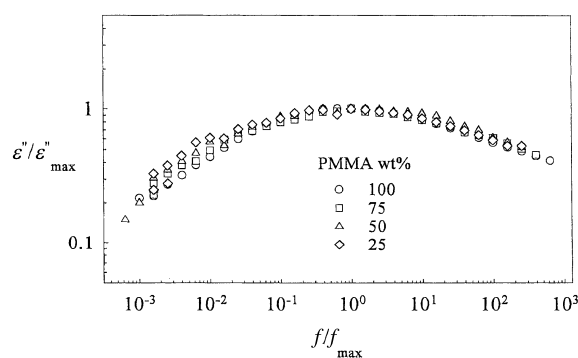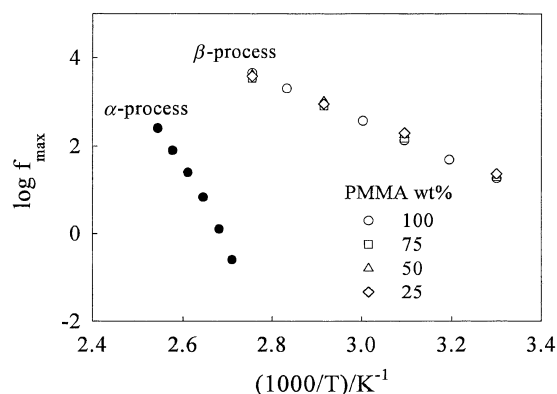
PMMA implies that the local environments of the two components of the blend are unchanged by blending and consequently miscibility at the segmental level is not achieved. The miscibility should take place on a level somewhat between the segmental and molecular level, this level must be big enough to maintain the local environment unchanged and in the same time small enough to give only one glass relaxation process for the miscible blend. This behavior is in good agreement with the previous data for TMPC/PC[31] and TMPC/PS[42] blends, where the dynamics of the β-relaxation process of TMPC was unchanged by blending.

CONCLUSION

The molecular dynamics of PMMA/PαMSAN blends have been investigated by broadband dielectric spectroscopy over a wide range of frequency (10^{-1} to 10^6 Hz) and temperature (30–155°C). All the bends exhibited mainly two relaxation processes, one for α-relaxation process of the miscible blend and the other for the β-relaxation process of PMMA. The kinetics of the molecular dynamics of the α-relaxation process was found to be composition dependent and well described by Meander model. The T_gs of the blends calculated from the activation curves of the dielectric

spectra are in good agreement with the calorimetric T_gs determined by DSC. This experimental fact indicates that the PMMA/PαMSAN blend is miscible over the entire range of composition. Although the molecular dynamics of the glass relaxation process (α-relaxation process) was changed strongly by blending there was no any change observed in the kinetics of the local processes (β-relaxation processes) of PMMA. Based on the last finding it is concluded that the local environment of each component does not change by blending and the miscibility of the blend on a segmental level is not achieved. The miscibility should take place on a structural level bigger than the segmental level to maintain the local environment unchanged and should be small enough to give only one common T_g for the miscible blend. This fact is consistent with the previous measurements for TMPC/PC[31] and TMPC/PS[42] blends.

REFERENCES

1. C. A. Trask and C. M. Roland, *Macromolecules*, **22**, 256 (1989).
2. V. A. Bershtein and V. M. Egorov, "Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis Technology", Ellis Horwood, Chichester, 1994.
3. C. Le Menestrel, A. M. Kenwright, P. Sergot, F. Laupretre, and L. Monnerie, *Macromolecules*, **25**, 3020 (1992).
4. Y. H. Chin, C. Zhang, P. Wang, P. T. Inglefield, A. A. Jones, R. P. Kambour, J. T. Bendler, and D. M. White, *Macromolecules*, **25**, 3031 (1992).
5. G. C. Chung, J. A. Kornfield, and S. D. Smith, *Macromolecules*, **27**, 964 (1994).
6. G. C. Chung, J. A. Kornfield, and S. D. Smith, *Macromolecules*, **27**, 5729 (1994).
7. E. W. Fischer and A. Zetsche, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **33**(1), 78 (1992).
8. A. Zetsche and E. W. Fischer, *Acta Polym.*, **45**, 168 (1994).
9. A. Alegria, J. Colmenero, K. L. Nagai, and C. M. Roland, *Macromolecules*, **27**, 4486 (1994).
10. F. Alvarez, A. Alegria, and J. Colmenero, *Macromolecules*, **30**, 597 (1997).
11. G. S. Rellick and J. Runt, *J. Polym. Sci., Polym. Phys.*, **24**, 279 (1986).
12. G. S. Rellick and J. Runt, *J. Polym. Sci., Polym. Phys.*, **24**, 313 (1986).
13. J. A. Zawada, G. G. Fuller, R. H. Colby, L. J. Fetters, and J. Roovers, *Macromolecules*, **27**, 6851 (1994).
14. J. A. Zawada, G. G. Fuller, R. H. Colby, L. J. Fetters, and J. Roovers, *Macromolecules*, **27**, 6861 (1994).
15. B. H. Arendt, R. Krishnamoorti, J. A. Kornfield, and S. D. Smith, *Macromolecules*, **30**, 1127 (1997).
16. J. Roovers and P. M. Toporowski, *Macromolecules*, **25**, 3454 (1992).
17. R. Colby, *Polymer*, **30**, 1275 (1989).
18. A. A. Mansour, R. Junge, B. Stoll, and W. Pechhold, *Colloid Polym. Sci.*, **270**, 325 (1992).
19. R. Bergman, F. Alvarez, A. Alegria, and J. Colmenero, *J. Non-Cryst. Solids,* **235–237**, 580 (1998).
20. T. Aihara, H. Saito, T. Inoue, H-P. Wolff, and B. Stuehn, *Polymer*, **39**, 129 (1998).
21. J. W. Sy and J. Mijovic, *Macromolecules*, **33**, 933 (2000).
22. I. M. Kalogeras and A. Vassilikou-Dova, *J. Phys. Chem. B,* **105**, 7651 (2001).
23. I. M. Kalogeras, A. Vassilikou-Dova, and E. R. Neagu, *Mater. Res. Innovations*, **4**, 322 (2001).
24. M. Dionisio, A. C. Fernandes, J. F. Mano, N. T. Correia, and R. C. Sousa, *Macromolecules*, **33**, 1002 (2000).
25. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effect in Polymeric Solids", Dover Publications, Inc., New York, N.Y., 1991.
26. A. A. Mansour and B. Stoll, *Colloid Polym. Sci.*, **271**, 834 (1993).
27. W. Pechhold and B. Stoll, *Polym. Bull.*, **7**, 413 (1982).
28. W. Heinrich and B. Stoll, *Prog. Colloid. Polym. Sci.*, **78**, 37 (1988).
29. W. Pechhold, E. Sautter, W. Von Sonden, B. Stoll, and H. P. Grossmann, *Macromol. Chem. Suppl.*, **3**, 247 (1979).
30. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
31. A. A. Mansour and S. A. Madbouly, *Polym Int.*, **36**, 269 (1995).
32. S. Havriliak and S. J. Negami, *J. Polym. Sci., Part C*, **14**, 99 (1966).
33. R. H. Cole and K. S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
34. P. Hedvig, "Dielectric Spectroscopy of Polymers", Adam Hilger Ltd., Bristol, 1977.
35. H. Fröhlich, "Theory of Dielectric", 2nd ed., Oxford University Press, Oxford, 1958.
36. F. E. Karasz and W. J. Macknight, in "Polymer Compatibility and Incompatibility", K. Sol, Ed., MMI Press, Symposium Series, vol. 2, 1982.
37. K. Naito, G. E. Johnson, D. L. Allara, and T. K. Kwei, *Macromolecules*, **11**, 1260 (1978).
38. J. T. C. Landry and P. M. Henrichs, *Macromolecules*, **22**, 2157 (1989).
39. J. C. Brauwens, *J. Polym. Sci.*, **33**, 123 (1971).
40. R. F. Boyer, *Polym. Eng. Sci.*, **8**, 161 (1968).
41. G. D. Butzbach and J. H. Wendorff, *Polymer*, **32**, 1155 (1991).
42. A. A. Mansour and S. A. Madbouly, *Polym Int.*, **37**, 267 (1995).