Polymer Vol. 39 No. 1, pp. 129–134, 1998
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0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00237-1

Dielectric studies of specific interaction and molecular motion in single-phase mixture of poly(methyl methacrylate) and poly(vinylidene fluoride)

Takaaki Aihara[a], **Hiromu Saito**[a,*], **Takashi Inoue**[a], **Hans-Peter Wolff**[b] and **Bernd Stühn**[b]
[a]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan*
[b]*Faculty of Physics, Freiburg University, Hermann-Herder Strasse 3, D-79104 Freiburg, Germany*

(Received 17 January 1997)

It is well known that the miscibility of dissimilar polymers with high molecular weights arises from specific interaction, such as hydrogen bonding. To discuss the influence of the interaction on a side group rotation and main chain motion of poly(methyl methacrylate) (PMMA) in PMMA/poly(vinylidene fluoride) (PVDF) blends, we investigated the dielectric loss ε'' as a function of frequency f. $\varepsilon''(f)$ showed a peak at around 10^4 Hz, which is assigned to the β process characteristic of the side group rotation of PMMA below the glass transition temperature (T_g) and the $\alpha\beta$ process characteristic of the side group rotation cooperative with the main chain motion above T_g. Above T_g, the peak frequency f_{max} increased and then decreased with increasing PVDF content (ϕ); $f_{max}(\phi)$ showed a peak at $\phi \approx 10$ wt.%. The increase may be interpreted by the acceleration of main chain motion by lowering of T_g with increasing the content of the lower T_g component (PVDF). Increasing further the PVDF content, the specific interaction seems to restrict the main chain motion and prevails over the T_g effect so that the peak appears in the $f_{max}(\phi)$ curve. f_{max} decreased with increasing annealing time t_a, suggesting the increase in restriction with t_a. This may imply that the association of dissimilar polymers by the specific interaction is a very slow rate process on a time scale of thousand minutes. Also observed after annealing were broadening of the relaxation time distribution and the appearance of interfacial polarization, suggesting a change in chain conformation from random coil to a locally stretched state to form a nematic domain. © 1997 Elsevier Science Ltd.

(Keywords: poly(methyl methacrylate); poly(vinylidene fluoride); blend)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) are known to be molecularly miscible in the amorphous state by thermal analysis[1,2], dynamic mechanical spectroscopy[2,3], dilatometry[2,3], small-angle X-ray scattering[4], pulse and ^{13}C-NMR[5,6], and Fourier transform IR spectroscopy (FTIR)[7,8]. The miscibility of dissimilar polymers with high molecular weights arises from specific interaction, such as hydrogen bonding[9]. The presence of the specific interactions in PMMA/PVDF mixtures has been confirmed by FTIR[10]. The depolarized light scattering studies on the single-phase mixtures of PMMA and PVDF suggested the formation of local ordering in the mixtures, i.e. nematic alignments of the locally stretched dissimilar chains[11,12]. With decreasing temperature, the degree of specific interactions by FTIR increased and the degree of ordering increased[12]. This concept is consistent with the argument based on Monte Carlo simulation[13,14] and wide-angle X-ray scattering measurement[15].

In a single-phase mixture of PMMA and PVDF, the C=O stretching band of PMMA in FTIR spectra changes on adding PVDF, suggesting that the side group of PMMA interacts with PVDF[12]. Two-dimensional NMR analysis revealed that the side group rotation of PMMA is a 180° (± 20°) flip of the OCO plane accompanied by a main chain rearrangement, i.e. the side group rotation is cooperative with the main chain motion[16]. Then, the interaction between the side group and PVDF is expected to constrain the main chain motion.

Since the side group of PMMA has a large dipole moment, its rotation is expected to be very prominent in dielectric relaxation. The relaxation observed below T_g is the β process characteristic of the side group rotation, and that above T_g is the $\alpha\beta$ process characteristic of the side group rotation cooperative with the main chain motion[17]. Hence, to obtain a much deeper understanding of the constraint on the side group rotation and the main chain motion by the specific interaction in a single-phase mixture of PMMA and PVDF, we carried out dielectric relaxation measurements over a wide frequency range at various temperatures. The time variation of dielectric spectroscopy during the annealing was also investigated to understand the

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[*] To whom correspondence should be addressed

kinetics of the association of dissimilar polymers. The results are discussed in terms of the local ordering and inhomogeneity in the mixture.

EXPERIMENTAL DETAILS

Polymer specimens used in this study were commercial polymers. PMMA was supplied by Mitsubishi Rayon Co., Ltd.; MD 001, M_w = 75000. PVDF was by Kureha Chemical Industry Co., Ltd.; KF1000, M_w = 70000.

PMMA and PVDF were dissolved at 8 wt.% of total polymer in *N,N*-dimethylacetamide. The solution was cast onto a glass plate. The solvent was evaporated under a reduced atmosphere of 10^{-2} mmHg at room temperature. The cast film was further dried under vacuum (10^{-4} mmHg) at 70°C for 1 day, and then at 160°C for 5 h in order to remove completely residual solvent. The absence of residual solvent was confirmed by FTIR. Then a stack of thin cast films was compression moulded at 220°C into a film of about 0.125 mm thickness. The films thus prepared were used for dielectric measurements and differential scanning calorimetery (DSC).

The dielectric measurements were carried out with a Schlumberger 1260 impedance analyser equipped with an impedance transformer (Chelsea Dielectric Interface, Pugh Dielectric Instruments). The capacitor used in the dielectric experiments consisted of two circular gold-plated copper plates. They were separated by a polyimide spacer ring to define a fixed sample thickness of 0.125 mm. The filled capacitor was placed in a nitrogen-flooded container. The dielectric measurements covered the frequency range 1 Hz–$10^{5.5}$ Hz and the temperature range 60–140°C. Here the temperature fluctuation was less than 0.5 K.

Frequency-sweep runs were carried out at a fixed temperature. Then, another run was carried out at a higher temperature. In this way, the isothermal runs were repeated at appropriate temperature intervals during the heating process. Similar runs were carried out also during the cooling process. We also employed the time-resolved measurement of dielectric spectroscopy during annealing at a fixed temperature. The whole set-up was operated under microcomputer control and allowed automatic data collection for various temperatures and frequencies.

DSC thermograms were recorded by a Shimadzu thermal analyser DT-4 at a heating rate of 10°C $\min^{-1}$. The glass transition temperature T_g was defined as the point at the half-height of the heat capacity jump.

RESULTS AND DISCUSSION

Figure 1 shows the dielectric loss as a function of frequency $\varepsilon''(f)$ in neat PMMA and 80/20 PMMA/PVDF blend at various temperatures. $\varepsilon''(f)$ of neat PMMA shows a peak (*Figure 1*(a)). This relaxation peak is assigned to the β process characteristic of the side group rotation of PMMA when the main chain motion is frozen at low temperature below T_g. On the other hand, at high temperatures above T_g, the peak is assigned to the $\alpha\beta$ process in which the side group rotation is cooperative with the main chain motion. Owing to the cooperative motion, the peak height of ε'' above T_g is much larger than that below T_g[17]. A similar peak is seen also for the blend (*Figure 1*(b)). The peak position shifts to higher frequency with increasing temperature. The side group rotation and the main chain motion should be accelerated with increasing temperature. Hence, as a measure of the rate for the side group rotation associated with the main chain motion, one can employ the peak frequency f_{max}, i.e. the peak position is expected to become higher as the side group rotation is faster.

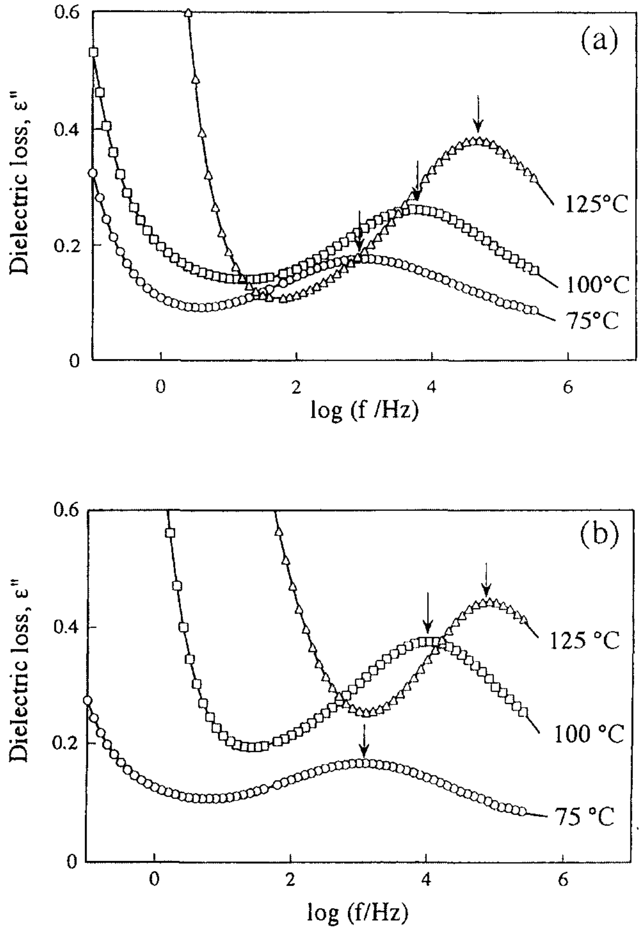


Figure 1 Frequency dependence of dielectric loss ε''. ○, 75°C; □, 100°C; △, 125°C during heating process; (a) neat PMMA and (b) 80/20 PMMA/PVDF blend

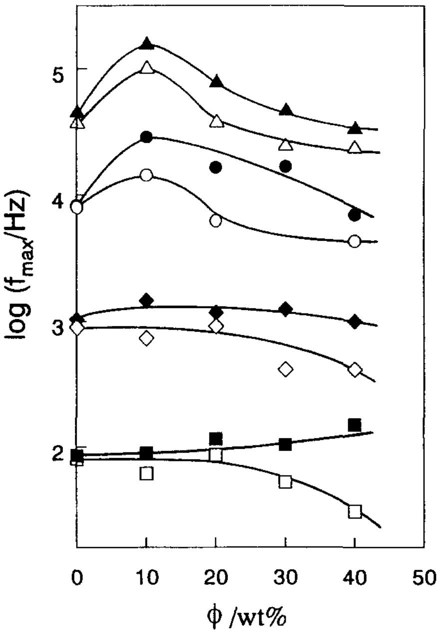


Figure 2 Peak frequency f_{max} versus PVDF content. ■, 45°C; ◆, 75°C; ●, 105°C; ▲, 125°C during heating process. □, 45°C; ◇, 75°C; ○, 105°C; △, 125°C during cooling process

Figure 2 shows the peak frequency f_{max} as a function of PVDF content ϕ. Here f_{max} was obtained from the fitting

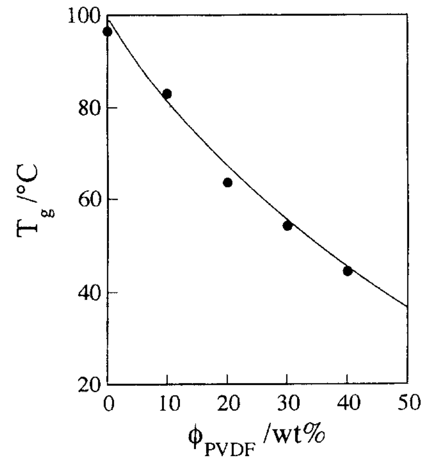


Figure 3 Glass transition temperature versus PVDF content

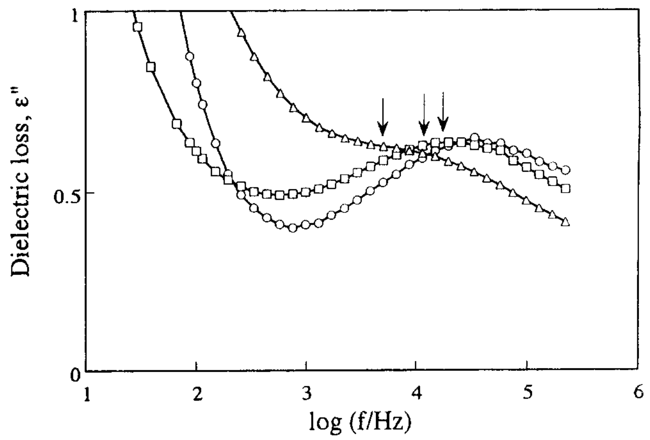


Figure 5 Frequency dependence of dielectric loss ε'' of 80/20 PMMA/PVDF blend at 100°C. Annealing time: ○, 90 min; □, 500 min; △, 1500 min

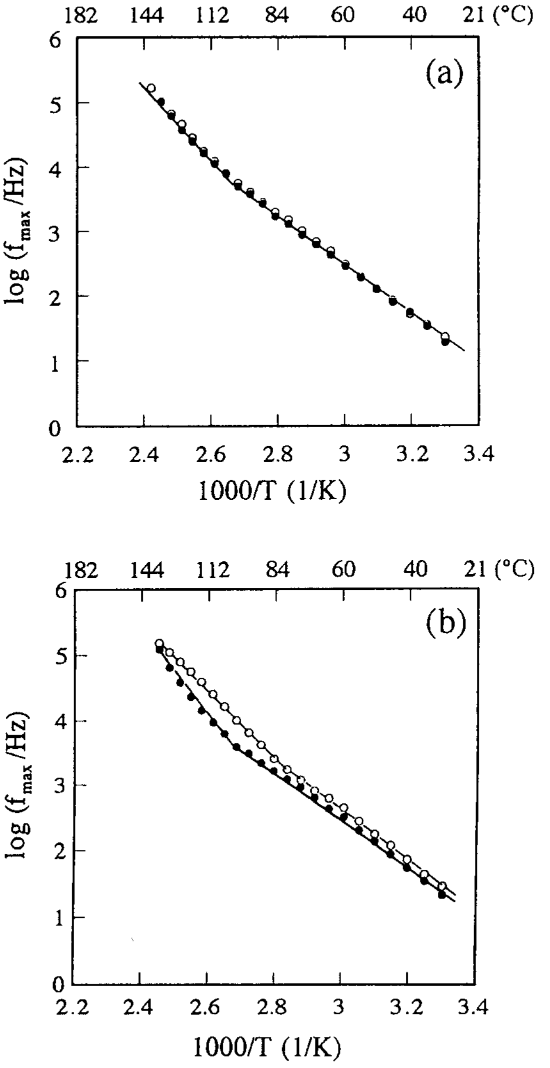


Figure 4 Temperature dependence of peak frequency f_{max}: ○, during heating process; ●, during cooling process; (a) neat PMMA and (b) 80/20 PMMA/PVDF blend

procedure of $\varepsilon''(f)$, demonstrated in *Figure 6*. Below T_g during the heating process, f_{max} hardly depends on ϕ (closed squares in *Figure 2*), suggesting that the side group rotation of quenched PMMA is hardly affected by blending PVDF. A similar result is reported for the local motion in the blend of bisphenol-A polycarbonate and tetramethylbisphenol-A polycarbonate[18]. However, f_{max} shows a peak above T_g (closed circles and triangles in *Figure 2*). One would expect the molecular motion would be activated by adding more mobile molecules with lower T_g. As shown in *Figure 3*, T_g decreases with added PVDF so that one would expect larger f_{max} of the $\alpha\beta$ process. Increasing further the PVDF content, f_{max} starts to decrease. The decrease could be interpreted by a restriction of main chain motion caused by the specific interaction. When the restriction prevails over the T_g effect, f_{max} may start to decrease and then show the peak in the $f_{max}(\phi)$ curve.

Another interesting result here is that f_{max} during the cooling process (open symbols in *Figure 2*) is smaller than that during the heating process in the blends (closed symbols in *Figure 2*). This indicates that the molecular motion on cooling is more restricted than that on heating. In contrast, no difference was observed in neat PMMA. The difference in the blends may be ascribed to slow association of dissimilar chains. That is, the association is expected to be weak in the melt-quench specimen and it becomes stronger during the heating and the cooling processes.

The values of f_{max} of neat PMMA and 80/20 PMMA/PVDF blend during heating and cooling are plotted as a function of temperature. The results are shown in *Figure 4*. In neat PMMA we see Arrhenius behaviour and a bend at around T_g (*Figure 4*(a)). The bend may arise from the change in the mode of motion at T_g, i.e. the motion above T_g is the $\alpha\beta$ process while that below T_g is the β process[17], as demonstrated before. The blend also exhibits Arrhenius behaviour and the plots also bend at around T_g (*Figure 4*(b)). Anyhow, f_{max} of the blend is smaller during the cooling process than during heating especially above T_g. The result suggests that the main chain motion becomes slower after the heating process. The change should be caused by a slow association of dissimilar chains and the association should be a very slow rate process.

Such a slow process can be justified by the time variation of $\varepsilon''(f)$ during isothermal annealing. As shown in *Figure 5*, the peak frequency clearly shifts to lower frequency with increasing annealing time t_a. Note also that the increase in ε'' with decreasing frequency at low frequencies becomes sharper with increasing t_a. Such a change can be discussed in detail by employing the curve fitting procedure of $\varepsilon''(f)$, shown as follows.

As shown in *Figure 6*(a), the $\varepsilon''(f)$ curve of neat PMMA can be well resolved into two parts: the $\alpha\beta$ relaxation and the d.c. conductivity. The $\alpha\beta$ relaxation can be described by

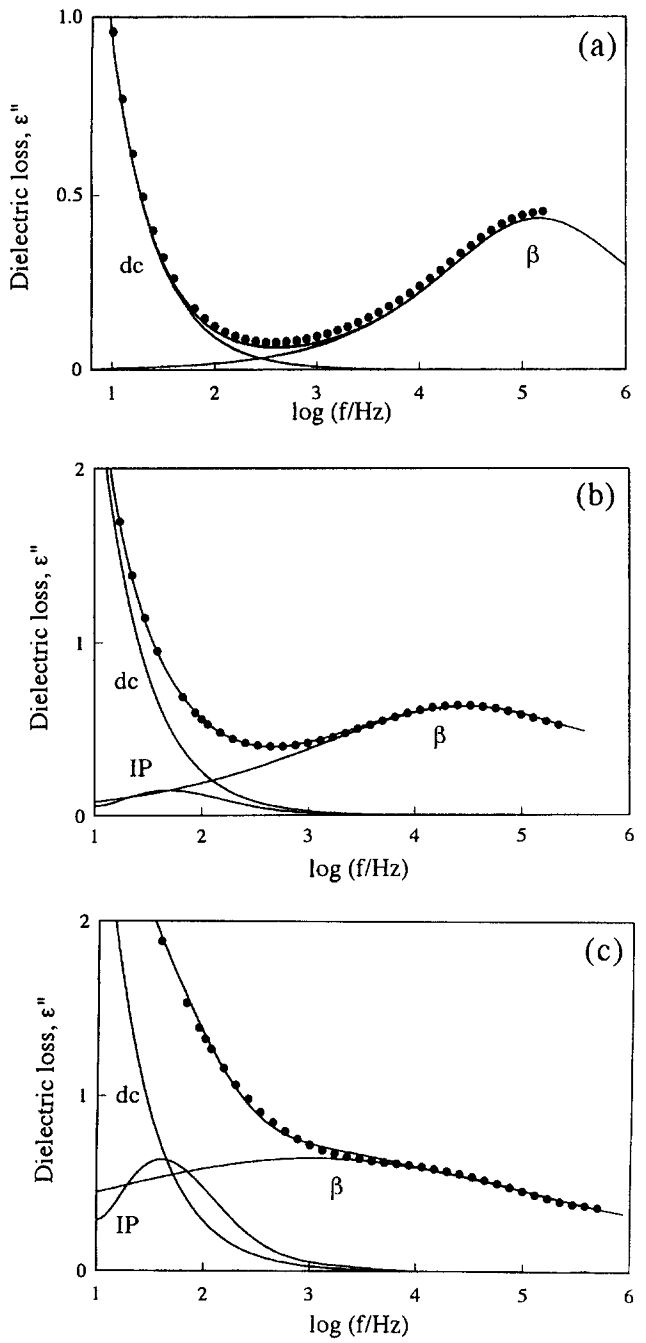


Figure 6 Frequency dependence of dielectric loss ε''. (a) The curve of neat-PMMA at 140°C was fitted by equation (1) ($\Delta\varepsilon = 1.734$, $\log f_{max} = 5.164$, $\alpha = 0.5911$, $\gamma = 1.0$) for the $\alpha\beta$ relaxation and by equations (2) and (3) ($\sigma/\varepsilon_0 = 9.311$) for the d.c. conductivity. (b) The curve of 80/20 PMMA/PVDF blend at 100°C at the early stage of annealing ($t_a = 218$ min) was fitted by equation (1) ($\Delta\varepsilon = 3.79$, $\log f_{max} = 4.48$, $\alpha = 0.41$, $\gamma = 1.0$) for the $\alpha\beta$ relaxation, by equations (2) and (3) ($\sigma/\varepsilon_0 = 25.8$) for the d.c. conductivity, and by equation (4) ($\Delta\varepsilon = 0.301$, $\log f_{max} = 1.72$) for the interfacial polarization. (c) The curve of 80/20 PMMA/PVDF blend at 100°C at the late stage of annealing ($t_a = 1725$ min) was fitted by equation (1) ($\Delta\varepsilon = 6.27$, $\log f_{max} = 3.05$, $\alpha = 0.258$, $\gamma = 1.0$) for the $\alpha\beta$ relaxation, by equations (2) and (3) ($\sigma/\varepsilon_0 = 28.6$) for the d.c. conductivity, and by equation (4) ($\Delta\varepsilon = 1.30$, $\log f_{max} = 1.64$) for the interfacial polarization

the Havriliak–Negami (HN) equation[19]

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1+(i\omega\tau)^\alpha\right]^\gamma} \tag{1}$$

where ω is the angular frequency ($\omega = 2\pi f$), τ is the relaxation time, the parameters α and γ are fitting parameters ($0 \le \alpha, \gamma \le 1$), ε^* is the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, and $\Delta\varepsilon$ is the dielectric strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, ε_∞ and ε_0 being the limiting low- and high-frequency permittivities, respectively. α and γ describe the broadness and asymmetry of the relaxation time distribution, respectively. The imaginary component of ε^* can be separated by

$$\varepsilon'' = \Delta\varepsilon \frac{\sin(\gamma\theta)}{1 + 2(\omega\tau)^\alpha \cos\frac{\pi\alpha}{2} + (\omega\tau)^{2\alpha}} \tag{2}$$

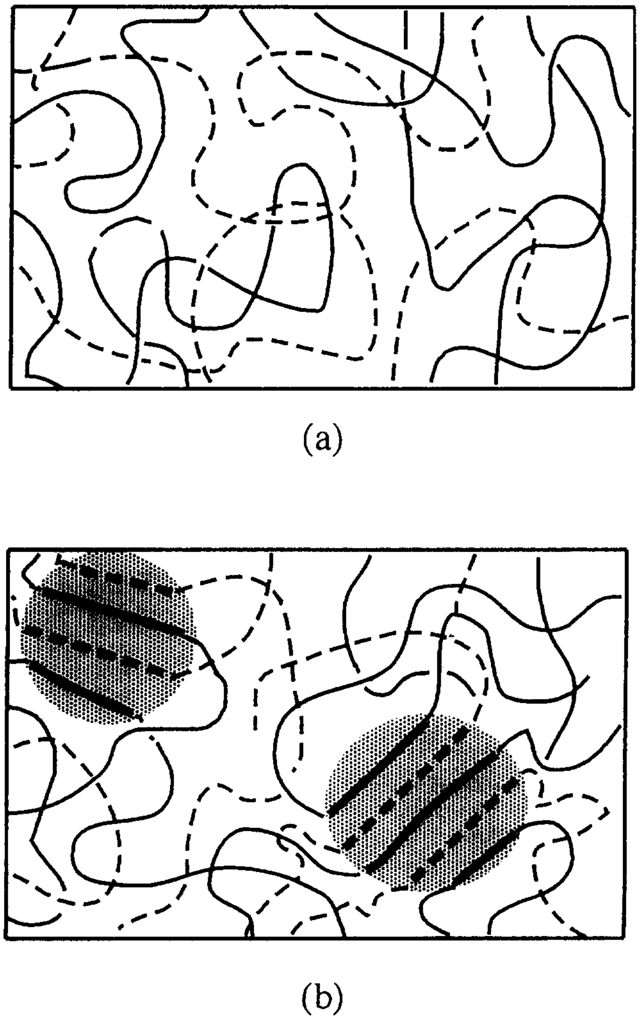
$$\theta = \arctan \frac{(\omega\tau)^\alpha \sin\frac{\pi\alpha}{2}}{1 + (\omega\tau)^\alpha \cos\frac{\pi\alpha}{2}} \tag{3}$$

On the other hand, the d.c. conductivity can be described by[20–22]

$$\varepsilon''_{dc} = \frac{\sigma_{dc}}{\varepsilon_0 \omega_p} \tag{4}$$

$$\omega_p = 2\pi(f)^p \tag{5}$$

where σ_{dc} is the d.c. conductivity and p is the parameter describing the broadening of the relaxation time distribution for the d.c. conductivity. A plot of $\log\sigma_{dc}$ versus $1/T$ exhibited a bend at around T_g, suggesting that the d.c. conduction is not induced by electronic conduction but by ion conduction. The value of p of the neat PMMA is equal to unity above T_g[21,22].



(a)

(b)

Figure 7 Chain conformations in the single-phase mixture of dissimilar polymers: (a) random coil chains and (b) locally ordered chains

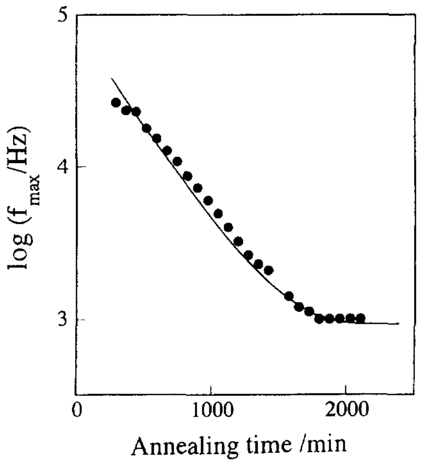


Figure 8 Time variation of peak frequency $f_{\max}$ of 80/20 PMMA/PVDF blend during annealing at 100°C

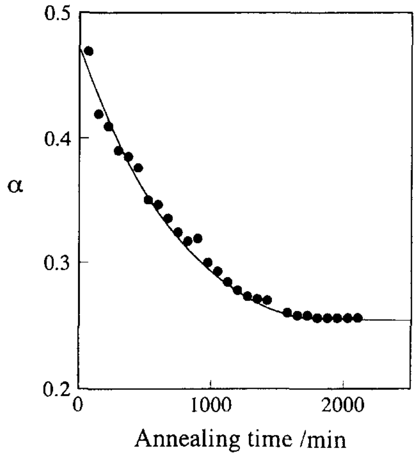


Figure 9 Time variation of fitting parameter α for 80/20 PMMA/PVDF blend during annealing at 100°C

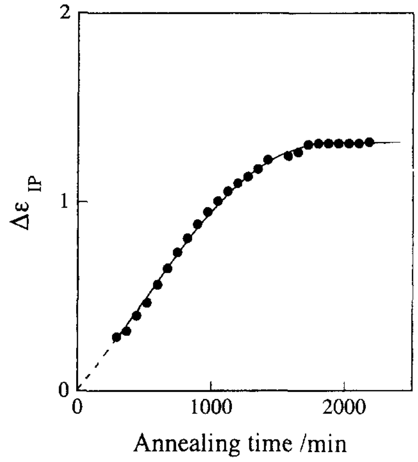


Figure 10 Time variation of dielectric strength $\Delta\varepsilon_{\mathrm{IP}}$ for the interfacial polarization of 80/20 PMMA/PVDF blend during annealing at 100°C

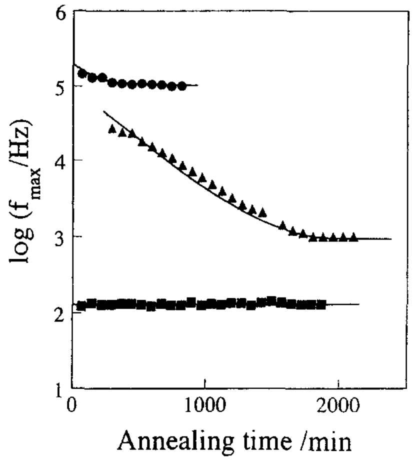


Figure 11 Time variation of peak frequency $f_{\max}$ of 80/20 PMMA/PVDF blend during annealing: ■, 75°C; ▲, 100°C; ●, 125°C

However, $\varepsilon''(f)$ of the blend specimen above T_g could not be nicely resolved into the two curves by assuming $p = 1$. The poor resolution was seen in the low frequency region and it increased with t_a. The resolution was improved by taking account of the third contribution, the interfacial polarization (IP) caused by the existence of the interface. However, the problem is what is the interface in the single-phase mixture. The depolarized light scattering results suggested that locally ordered regions exist owing to the specific interaction in PMMA/PVDF blends (see *Figure 7*)[11,12]. One could assign the interface to that between the ordered region and the random coil region. Assuming that the ordered domain is spherical with a dielectric constant ε_2 and conductivity σ_2, and is dispersed in a matrix of random coil region with a dielectric constant ε_1 and a conductivity σ_1, the complex dielectric permittivity due to the interfacial polarization is described by the Maxwell–Wagner equation[23,24]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_{\mathrm{IP}}}{1 + \mathrm{i}\omega\tau} \qquad (6)$$

$$\Delta\varepsilon_{\mathrm{IP}} = \frac{9(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)^2}{(2\varepsilon_1 + \varepsilon_2)(2\sigma_1 + \sigma_2)^2}\phi_{\mathrm{d}} \qquad (7)$$

where $\Delta\varepsilon_{\mathrm{IP}}$ is the dielectric strength of the interfacial polarization, and ϕ_{d} is the volume fraction of spherical domains.

As shown in *Figure 6*(b,c), $\varepsilon''(f)$ of the blends were nicely resolved into three curves by taking into account the $\alpha\beta$ relaxation (equation (1)), d.c. conductivity (equations (4) and (5)) and the interfacial polarization (equations (6) and (7)).

The peak frequency $f_{\max}$ of the $\alpha\beta$ relaxation processed by the fitting procedure is plotted in *Figure 8* as a function of annealing time t_a at 100°C for 80/20 PMMA/PVDF blend. $f_{\max}$ decreases with t_a and then levels off at *ca.* 1800 min, indicating that the restriction of the main chain motion becomes stronger with t_a during the annealing and then attains an equilibrium state. The association process seems to be very slow on a time scale of thousand minutes.

As was shown in *Figure 5*, the ε'' peak of the $\alpha\beta$ relaxation becomes broader with t_a. The broadening of the peak is ascribed to the relaxation time distribution for the main chain motion. The parameter α in equation (1) decreases as the relaxation time distribution becomes broader. *Figure 9* shows α as a function of t_a. α decreases with t_a, indicating that the relaxation time distribution becomes broader with t_a. The decrease of α levels off on the same time scale as that of $\Delta\varepsilon$. Thus the relaxation time distribution becomes broader during the slow association of the dissimilar chains. The broader distribution may be created by a dynamic heterogeneity in chain association, as demonstrated by CP-MAS solid state NMR[25,26]. That is, there should exist both highly associated chains and less associated ones, in which the component polymers possess intrinsic difference in mobility. The heterogeneity implies the locally nematic structure in which ordered domains coexist with the random coil region as shown in *Figure 7*(b).

The dielectric strength of the interfacial polarization $\Delta\varepsilon_{\mathrm{IP}}$ obtained from equation (6) is shown as a function of t_a in *Figure 10*. $\Delta\varepsilon_{\mathrm{IP}}$ increases with t_a and then levels off in the same time scale of $f_{\max}$ and α. According to equation (7), the increase of $\Delta\varepsilon_{\mathrm{IP}}$ may be ascribed to the increase of the volume fraction of the ordered domain ϕ_d. The result may be related to that of *Figure 9*. That is, one could have better understanding of the evolution of heterogeneous restriction on the basis of the formation of ordered domains and the increase in ϕ_d with t_a.

Figure 11 shows the time variation of $f_{\max}$ of the $\alpha\beta$ relaxation in the blend during isothermal annealing at various temperatures. $f_{\max}$ at 125°C decreases with the annealing time t_a and then levels off at *ca*. 700 min, while that at 100°C levels off at *ca*. 1800 min. The result suggests that restriction of the side group rotation proceeds faster at higher temperature, probably owing to higher mobility for the association. However, the change of $f_{\max}$ at 125°C is much smaller than that at 100°C. This suggests that less restriction is imposed at higher temperature. As demonstrated by FTIR, the specific interaction becomes weaker at higher temperature[14].

On the other hand, no time variation of $f_{\max}$ is seen at 75°C, suggesting that the restriction does not increase during the annealing at around T_g. As shown in *Figure 4*(b), the motion at 75°C is the side group rotation when the main chain motion is frozen. This may imply that the main chain motion is required for the association of dissimilar main chain and then for the restriction of the $\alpha\beta$ relaxation.

CONCLUSION

By adding the lower T_g polymer (PVDF), the $\alpha\beta$ relaxation of PMMA is expected to be accelerated above T_g of the blend owing to the increase in the main chain motion. However, the dielectric study showed the opposite result, i.e. the motion was depressed by adding PVDF ($\phi >$ 20 wt.%). This was ascribed to a restriction of main chain motion by the specific interactions between PVDF and PMMA. Further, by the curve resolution procedure of $\varepsilon''(f)$, it was shown that the association to yield the specific interaction is a very slow process on a time scale of thousand minutes and the association leads to heterogeneity in the single-phase mixture which may correspond to the formation of locally ordered domains.

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