Dielectric relaxations of microstructurally different latex polymer blends of poly(butyl acrylate) and poly(vinyl acetate)

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The dielectric permittivity and loss of latex films of poly(butyl acrylate), poly(vinyl acetate), their homogeneous blend and their core-shell structured particle blends were measured in the temperature range 80–360 K and frequency range 10–2 × 10^5 Hz. Poly(butyl acrylate) has two sub-T_g relaxations, namely β- and γ-processes. The presence of one polymer antiplasticizes the other in that their α-relaxation processes are shifted to higher temperatures in the blends. The homogeneous blends have relaxation features characteristic of both the poly(butyl acrylate) and poly(vinyl acetate) but at temperatures different from those of the pure polymer lattices. Only one β-relaxation is observed for the blend lattices. It has a very large half-width, and appears at a temperature intermediate to those of the β-relaxations in the pure polymers. The core-shell microstructure of the polymer particles produces a latex which shows evidence for the presence of a copolymer in its films, although the particles contained no copolymer in their emulsified state.

(Keywords: dielectric relaxation; latex blends; poly(butyl acrylate); poly(vinyl acetate)

INTRODUCTION

Emulsion polymerization is often used to produce structured, colloidally dispersed, latex particles with controlled core-shell morphology of the polymers. In addition to their obvious technical use, the controlled microstructure of such latex polymers facilitates a scientific study of (1) how the microstructure of the polymer particles controls the properties of latex and (2) whether or not the difference between their molecular kinetic behaviour can be related to the morphology of the polymer blends. One purpose of this study was to investigate these differences.

The morphology of particles in an emulsion can be satisfactorily studied by electron microscopy and other techniques. However, this morphology becomes altered during the formation of their latex films. For example, in the homogeneous blend of poly(butyl acrylate), PBA, and poly(vinyl acetate), PVAc, mechanical relaxation studies suggest that the latex film retains the former as inclusions in a matrix of the latter. These changes cannot be as easily determined in the latex film as in the emulsions from the usual microscopic techniques. A second purpose of this study was to dielectrically investigate such changes.

In an earlier paper[1], the dynamic mechanical behaviour of such latex films was reported. Here we report a corresponding study of their dielectric relaxation behaviour. During the course of our investigations we found that a complete study of PBA has not been made, though it is desirable for a scientific understanding of the chain dynamics of acrylic polymers. This too was done and the results are included.

EXPERIMENTAL

All polymers were in the form of thin films and were made by Laboratoire des Materiaux Organique, CNRS, 69390-Vernaison, France. These were prepared using the emulsion polymerization process and then evaporating the water. Homopolymer PBA was also washed using an ion-exchange process. It had $M_w > 10^6$, particle size of ~145 nm and dispersity of 1.06. Poly(vinyl acetate) had $M_n = 91 \times 10^3$, $M_w = 59.3 \times 10^4$, particle size 420 nm and dispersity of 1.02.

The blend of the homopolymers was prepared by mixing equal amounts by weight of PBA and PVAc followed by complete evaporation of water. The structured polymers were obtained by either a two-step or a three-step polymerization which led to a core-shell morphology of the particles. In the two-step process which led to a morphology with PBA core and PVAc shell, the morphology of the particles had a high radial gradient of composition. The particle size was ~175 nm and dispersity of ~1.07. This is referred to as core-shell polymer.

The structured copolymer obtained by the three-step polymerization had the core of PBA, followed by an inner shell of 50:50 by weight of PBA–PVAc copolymer and an outermost shell of PVAc. The mean composition of the particles is 50:50 by weight of PBA and PVAc, the fraction of copolymer is 20% by weight and the particle size is ~200 nm. This is referred to as structured core-shell copolymer.

The core-shell polymers were obtained by polymerization in emulsifiers, namely in 50:50 by weight mixtures of sodium dihexylsulphosuccinate and sodium dioctylsulphosuccinate. At the end of the polymerization, the amount of emulsifier in the particles was ~3% and this was partly removed by washing with

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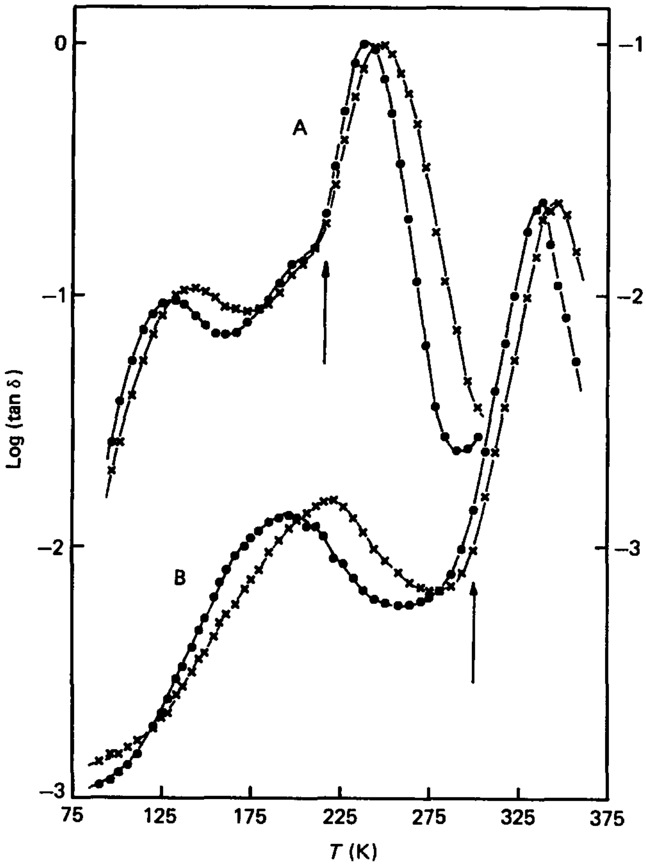

Figure 1 The tan δ of: A, PBA; B, PVAc measured at: ●, 1 kHz and ×, 10 kHz plotted against temperature. Arrows indicate T_g. For the curve A, the scale is on the right

water.Solid films were obtained by evaporation of the water at $\sim$298 K for a period of $\sim$3 weeks. Detailed procedures for the preparation are given elsewhere[2,3].

The opposite surfaces of $\sim 10 \times 25$ mm polymer films were vapour-deposited with aluminium and the film was sandwiched between two glass plates with copper interface between the aluminium and glass. This formed a three terminal dielectric cell. The cell was kept in a hermetically sealed glass jacket and its temperature was controlled by a thermostat assembly described before[4] within ± 0.1 K from 80 to 375 K.

The capacitance and the dielectric loss of the samples were measured at frequencies 12–200 000 Hz by means of a GR 1689 impedance bridge and a GR 1615 capacitance bridge assembly described before[5]. The temperature was measured by means of a thermocouple kept in contact with the polymer film.

RESULTS

In order to compare the behaviour of latex polymers with those of pure polymers and the various microstructurally and morphologically different blends, it was necessary to measure the dielectric relaxations in pure PBA and PVAc. The tan δ measured at 1 and 10 kHz for both PBA and PVAc are plotted against temperature in *Figure 1*, where their respective values of T_g are indicated. These isochrones show that, in their glassy states, two relaxation processes indicated by a shoulder at $\sim$200 K and a peak at $\sim$130 K for the 1 kHz measurements occur in PBA and one process indicated by a peak at $\sim$196 K for the 1 kHz measurements occurred in PVAc. Each of course has an α-relaxation process at $T > T_g$.

The tan δ of the 50:50 w/w PBA:PVAc blend, and of their core-shell polymer, measured at 1 and 10 kHz is plotted against temperature in *Figure 2*. For 1 kHz measurements, three relaxation processes at temperatures $\sim$124, 248 and 336 K and one low-temperature shoulder are observed in the polymer blend, two peaks and one shoulder at temperatures $\sim$130, 244 and 200 K, respectively, are observed in the core-shell polymer (i.e. without a copolymer).

The tan δ of the structured core-shell copolymer measured at 1 and 10 kHz is plotted against temperature in *Figure 3*. For 1 kHz measurements, the polymer has three relaxation processes indicated by three peaks at temperatures of $\sim$130, 188 and $\sim$238 K. These observations of the isochrones of the five polymers and their respective values of T_g are summarized in *Table 1*.

The isothermal spectra of tan δ for the α-relaxation process of PBA and of the relaxation process observed at $220 < T < 290$ K for the homogeneous blend are shown in *Figure 4*. The height of the high-temperature α-peak remains unchanged with changing temperature, but that of the low temperature α-peak decreases with decrease in the temperature. For the blend, the height of the α-peak due to PBA in *Figure 4* is $\sim$56% of the height of the corresponding peak for pure PBA. The frequency of the peak is $\sim$1.5 decades lower in the blend than in pure PBA when compared at the same temperature. The half-widths

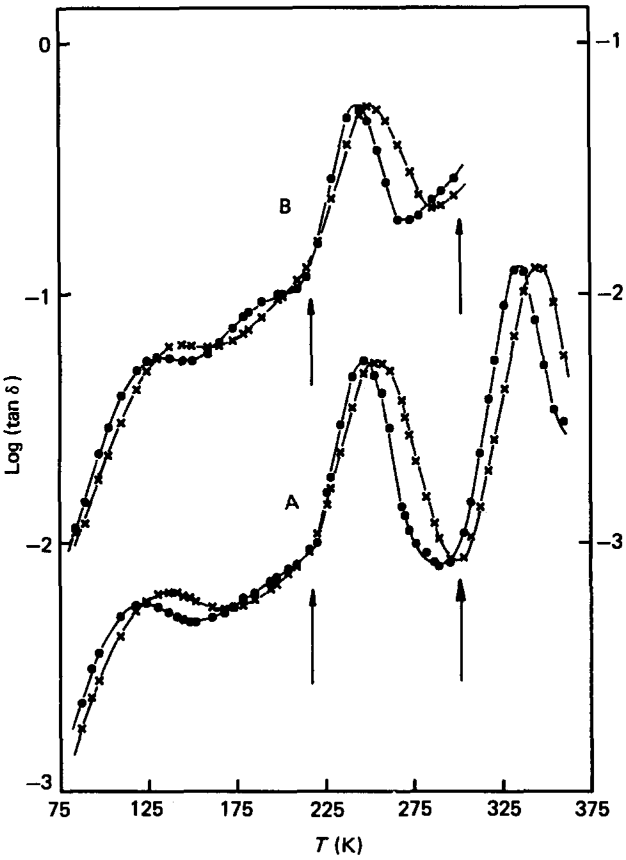

Figure 2 The tan δ of: A, the blend of 50:50 (w/w) PBA–PVAc; B, core-shell polymer obtained by a two-step polymerization measured at: ●, 1 kHz and ×, 10 kHz plotted against temperature. Arrows indicate T_g. For the curve B, the scale is on the right

of the peaks cannot be accurately estimated but approximate values of ~3.5 decades for pure PBA and ~4 decades for the blend suggest broadening of the spectra of PBA in the blend.

The tan δ spectra of pure PVAc for the α-relaxation region and the corresponding spectra for the blend are shown in *Figure 5*. The height of the α-peak for the blend is nearly half of that for the pure polymer, and the frequency of the peak is ~1.25 decades lower for the blend than for pure PVAc, when compared at the same temperature.

The tan δ spectra for pure PVAc and PBA at $T < T_g$ are shown in *Figures 6* and *7*, respectively. The height of the peak for the sub-T_g relaxation in PVAc remains unchanged with changing temperature and the estimated half-width is ~4 decades. The spectra for PBA in *Figure 7* show the presence of two relaxation processes, which become resolved at $T < 144.7$ K. Two relaxation processes at $T < T_g$ occur in the blend, as is seen in *Figure 8*. The heights of both the low- and high-temperature processes increase with increase in the temperature.

Both the core-shell polymer and the structured core-shell copolymer show the presence of two α-relaxation processes. Isothermal spectra of tan δ of the low-

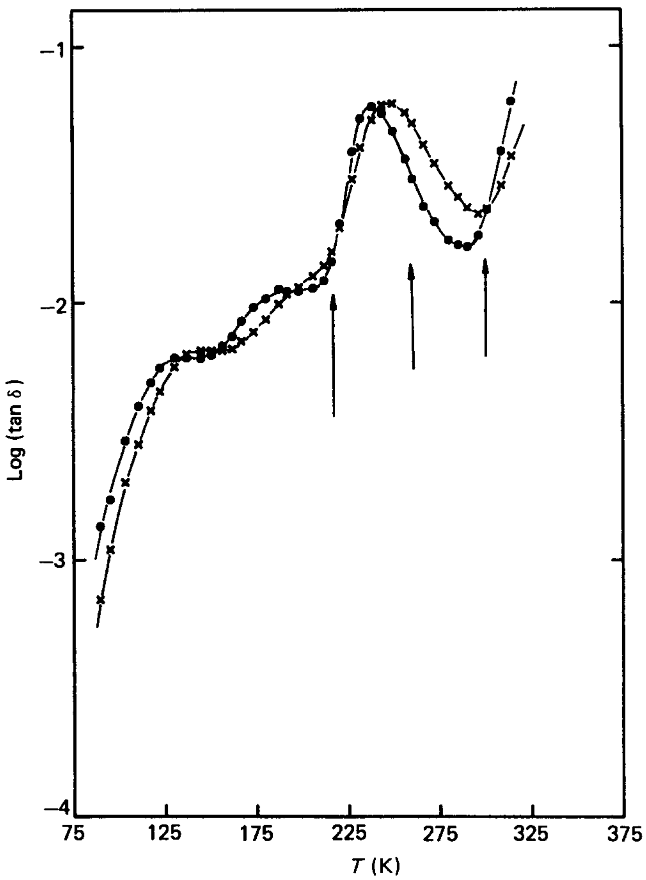

Figure 3 The tan δ of structured core-shell copolymer obtained by a three-step polymerization, measured at: ●, 1 kHz and ×, 10 kHz plotted against temperature. Arrows indicate T_g of the pure and the copolymers

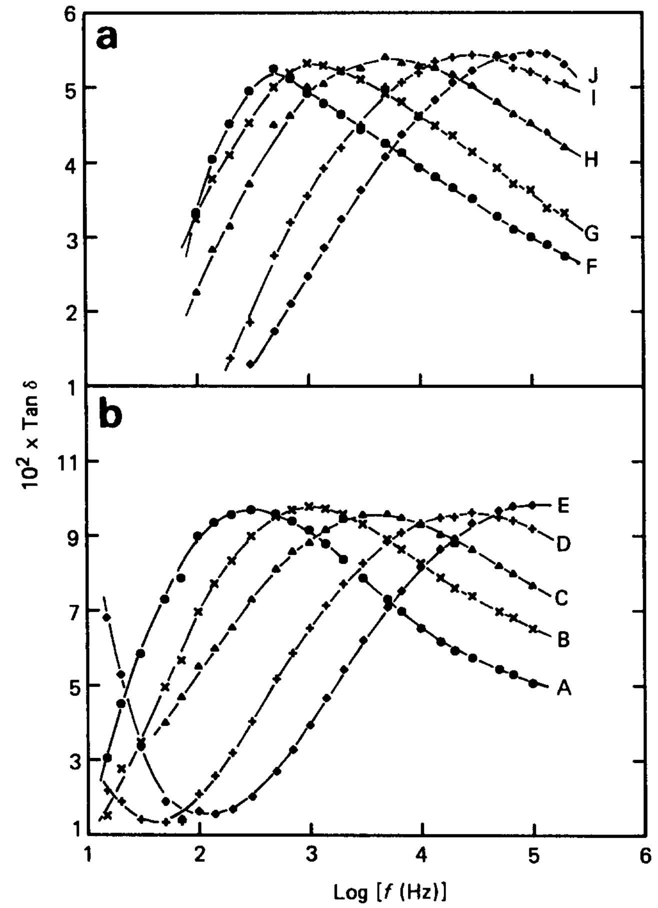

Figure 4 The tan δ of PBA in the α-relaxation region for (a) the blend and (b) the homopolymer plotted against logarithmic frequency at different temperatures. The temperatures for the curves are: A, 231.3; B, 235.3; C, 240.2; D, 245.3; E, 251.0; F, 242.7; G, 246.7; H, 251.6; I, 257.6; and J, 262.0 K, respectively

Table 1 Features of the isochrones of tan δ (measured at 1 kHz) at different temperatures for various polymers

Polymers	T_g (K)	Temperature and tan δ magnitude (given in parentheses) measured at 1 kHz			
Poly(butyl acrylate), PBA	218	130 K (p) (0.0096)	~200 K (s) (0.0135)	238 K (p) (0.10)	–
Poly(vinyl acetate), PVAc	301	–	196 K (p) (0.0133)	–	337 K (p) (0.24)
(Homogeneous) blend, 50 PBA–50 PVAc	218 301	124 K (p) (0.0057)	~200 K (s) (0.0075)	248 K (p) (0.054)	336 K (p) (0.132)
Core-shell polymer, 50 PBA–50 PVAc	218 301	130 K (p) (0.0056)	~200 K (s) (0.010)	244 K (p) (0.057)	–
Structures core-shell copolymer, PBA-50:50 blend:PVAc	218 264 301	130 K (p) (0.0061)	188 K (p) (0.0113)	238 K (p) (0.0585)	–

(p) denotes a peak and (s) a shoulder in the dielectric tan δ-temperature plots given in *Figures 1–3*

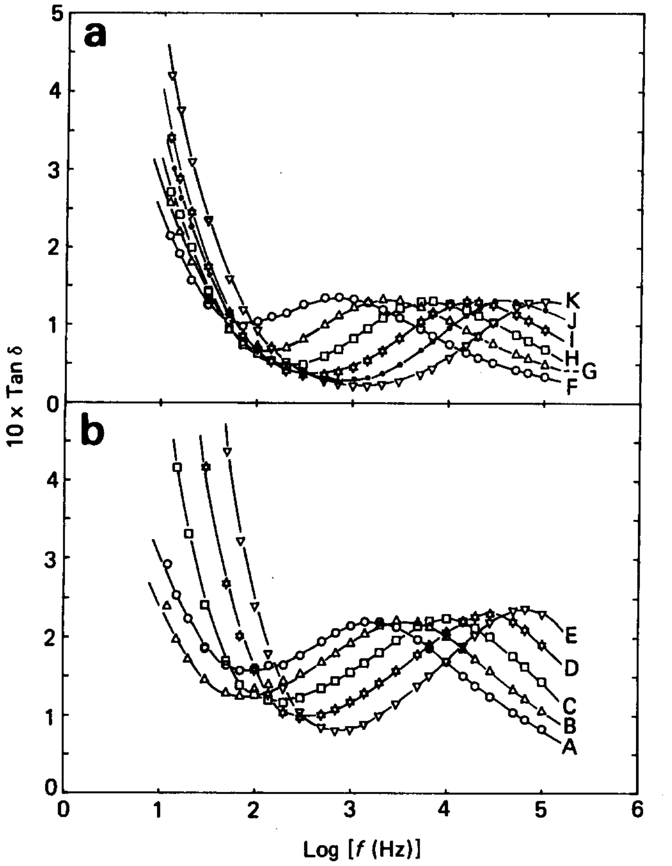

Figure 5 The tan δ in the α-relaxation region for (a) the blend and (b) the homopolymer plotted against logarithmic frequency at different temperatures. The temperatures for the curves are: A, 329.1; B, 332.5; C, 337.4; D, 342.9; E, 348.4; F, 341.9; G, 346.6; H, 351.4; I, 356.4; J, 361.4; and K, 367.0 K, respectively

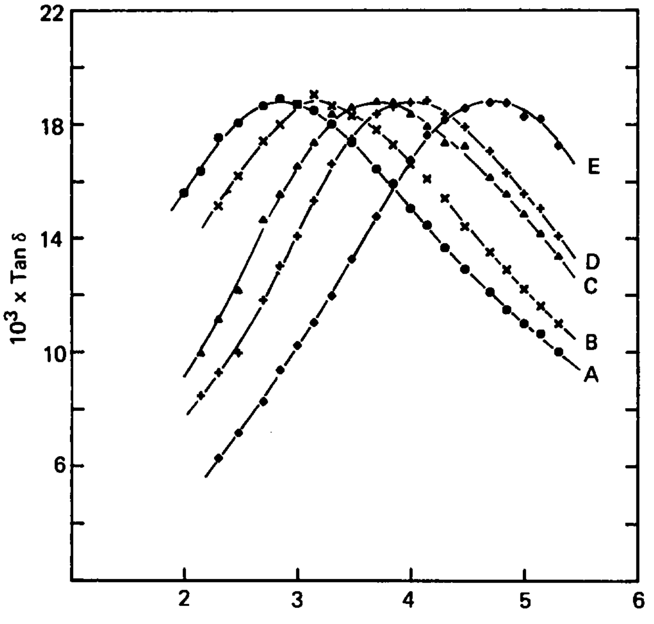

Figure 6 The tan δ of PVAc plotted against logarithmic frequency for its sub-T_g relaxation. The temperatures for the curves are: A, 184.5; B, 191.2; C, 200.0; D, 208.1; and E, 224.4 K, respectively

temperature α-process in the core-shell copolymer and of that of tan δ in the structured core-shell copolymer are shown in *Figure 9*. The heights of the peak remain unchanged with temperature. The estimated half-width

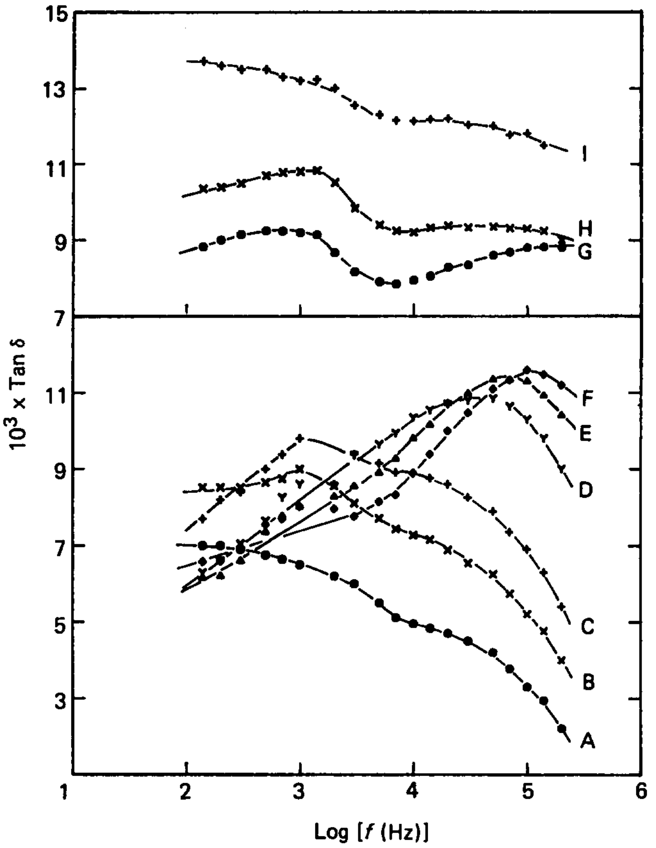

Figure 7 The tan δ of PBA plotted against logarithmic frequency for its two sub-T_g relaxations. The temperatures for the curves are: A, 113.1; B, 122.8; C, 130.0; D, 144.7; E, 151.2; F, 159.3; G, 187.5; H, 199.7; and I, 213.5 K, respectively

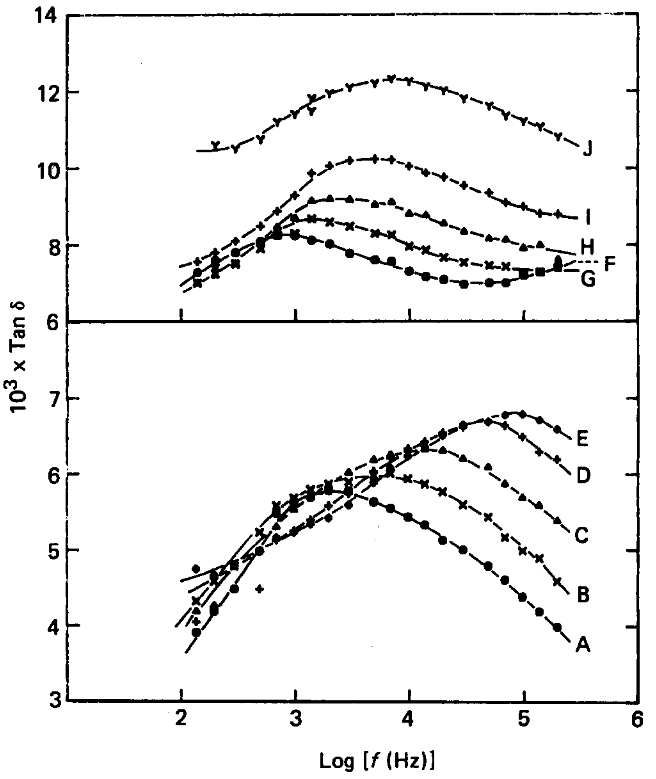

Figure 8 The tan δ of the blend plotted against logarithmic frequency for its two sub-T_g relaxations. The temperatures for the curves are: A, 119.7; B, 125.0; C, 131.4; D, 138.9; E, 144.6; F, 188.9; G, 195.0; H, 202.1; I, 210.2; and J, 218.3 K, respectively

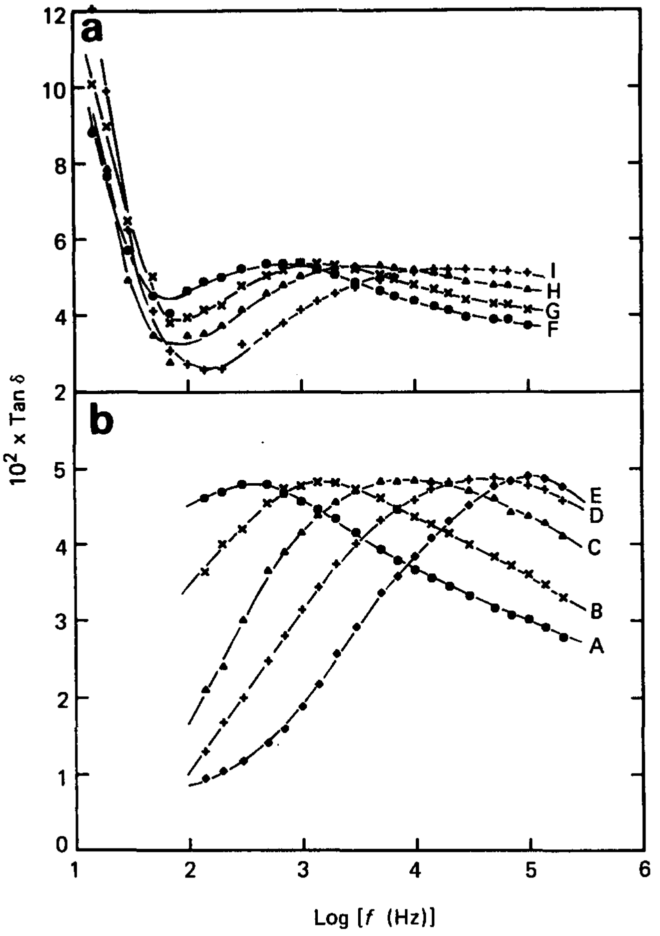

Figure 9 The tan δ of (a) the three-step structured copolymer and (b) the core-shell polymer in their α-relaxation regions corresponding to PBA plotted against logarithmic frequency. The temperatures of the curves are A, 238.4; B, 246.1; C, 249.8; D, 255.5; E, 261.7; F, 239.0; G, 241.5; H, 245.0; and I, 250.8 K, respectively

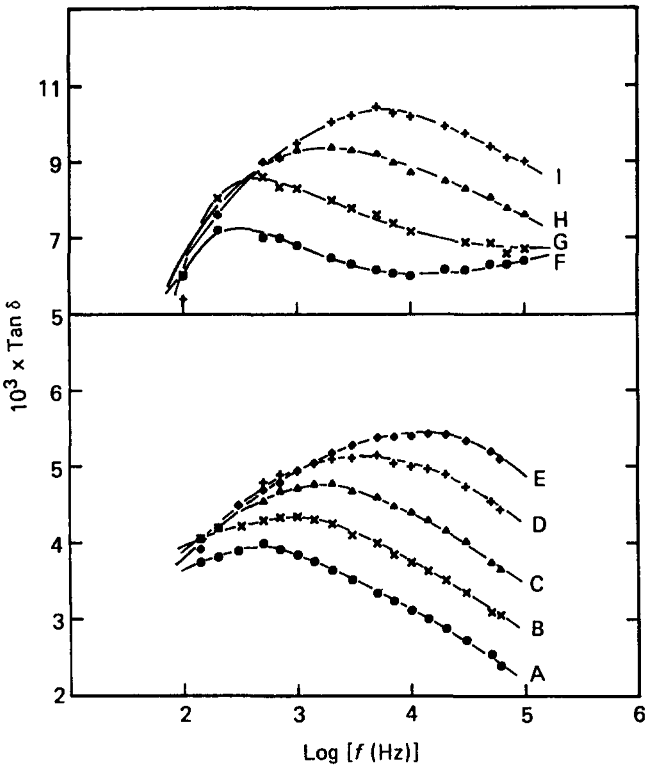

Figure 10 The tan δ for the core-shell polymer plotted against logarithmic frequency for the sub-T_g relaxations. The temperatures for the curves are: A, 114.2; B, 119.6; C, 125.3; D, 132.3; E, 138.1; F, 173.5; G, 186.8; H, 199.4; and I, 209.3 K, respectively

for the core-shell polymer is ~4.5 decades and for the structured core-shell copolymer is >6 decades. The tan δ spectra of the sub-T_g relaxation processes in the core-shell polymer are shown in *Figure 10*. The height of lowest temperature process ($110 < T < 140$ K) peak increased with increase in temperature. Its half-width is ~4 decades. The height of the high temperature process ($160 < T < 220$ K) also increased in a similar manner. Its half-width could not be accurately estimated.

The sub-T_g tan δ spectra for the structured core-shell copolymer seen in *Figure 11* show two relaxation processes at $110 < T < 150$ K, and a third clearly separated process at $180 < T < 220$ K.

The height of the α-peak for the core-shell polymer is about half the height of the corresponding peak for pure PBA in *Figure 4* and about the same as the height for the blend. The relaxation rate of the α-process in it is about 1.5 decades less than for the pure PBA, but is the same as for the homogeneous blend. The height of the α-peak for the structured core-shell copolymer is ~57% of that for the pure PBA and is almost the same as that for the homogeneous blend. At the same temperature, the α-relaxation rate in the structured core-shell copolymer is ~1.0 decades lower than in the pure PBA and ~0.4 decades higher than for the homogeneous blend. These features are summarized in *Table 1*.

The frequency for the tan δ peaks for all the relaxation

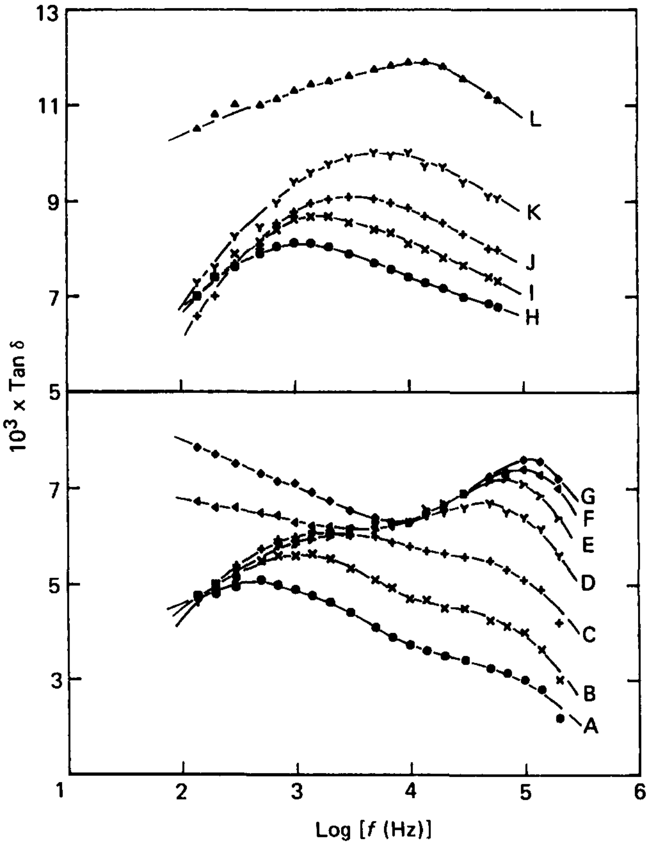

Figure 11 The tan δ for the structured core-shell copolymer plotted against logarithmic frequency for its sub-T_g relaxations. The temperatures for the curves are: A, 117.4; B, 124.2; C, 132.3; D, 142.0; E, 149.0; F, 156.4; G, 164.3; H, 188.7; I, 194.7; J, 201.0; K, 206.6; and L, 214.7 K, respectively

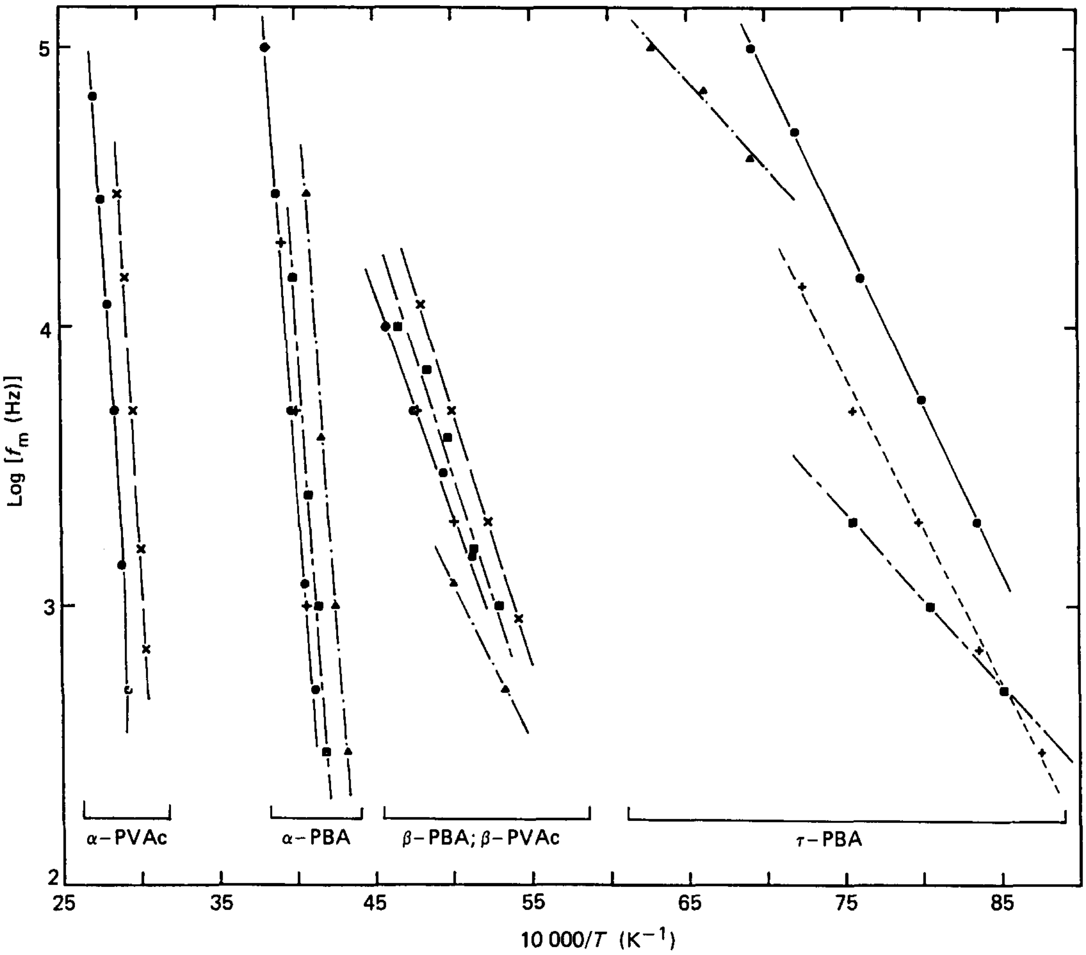

Figure 12 The frequency of maximum loss of the relaxations observed for the five polymers: ▲, PBA; ×, PVAc; ●, 50:50, PBA:PVAc blend; +, core-shell polymer; and ■, structured core-shell copolymer

Table 2 The values of the parameters of the equation $f_m = A\exp[-B/(T-T_0)]$ for the temperature range of relaxation in several polymers

Polymer	Temperature range (K)	A (Hz)	B (K)	T_0 (K)
PBA	230–250	1.75×10^{37}	185.5	0
PVAc	320–350	7.3×10^{7}	453.6	290
(Homogeneous) Blend: 50 PBA –50 PVAc	240–265 340–370	2.8×10^{34} 3.5×10^{10}	177.9 1211.9	0 275
Core-shell polymer	240–270	3.1×10^{9}	537.2	210
Structured core-shell copolymer	230–260	2.2×10^{10}	794.1	195

processes in the five polymers is plotted against the reciprocal temperature in *Figure 12* except for the α-process of PVAc in the blend and in pure PVAc, where f_m of the ε'' peak is plotted instead. The frequencies for the α-relaxation peaks were fitted to the Vogel–Fulcher–Tamman equation, $f_m = A\exp(-B/(T-T_0))$ and the values of the parameters are given in *Table 2*. The data for the sub-T_g relaxations were fitted to an Arrhenius equation, $f_m = f_0\exp(-E/RT)$. The value of the two parameters for the five polymers are given in *Table 3*.

DISCUSSION

Homopolymers

Poly(butyl acrylate). Two relaxation processes, referred to as β- and γ-, occur at $T < T_g$ in PBA, as is seen in *Figure 1*. Dynamic-mechanical study for a fixed frequency of 1 Hz has shown no β- or γ- relaxation peaks at $T > 125$ K. An extrapolation of the f_m to 1 Hz from the data in *Figure 12* indicated that the peak would appear at $T < 125$ K for a frequency of 1 Hz and therefore the sub-T_g processes were not observed in the limited temperature range of the dynamic mechanical study[1].

Wölf[6], and Thurn and Wölf[7] measured the dielectric and mechanical relaxations in PBA at two fixed frequencies. They reported no sub-T_g relaxations. The interpolated temperature for the α-relaxation from their measurement is higher than ours for the same value of f_m. This difference may partly be due to the difference in the molecular weights and partly to the difference in the constitution or microstructure of the studied samples. In view of the lack of knowledge of either of these factors, further discussion of this comparison seems inappropriate.

The occurrence of sub-T_g relaxations in poly(acrylates) is often related to the hindered rotation of the side group, or the side chain, attached to the polymer backbone[8]. Accordingly, the β- and γ-relaxations in PBA would be interpretable in terms of the motion of $-C(O)-O-C_4H_9$ group about the C–C bond and the motion of $-O-C_4H_9$ group about the C–O bond, respectively. It is now also

Table 3 The values for the parameters of the equation $f_m = f_0 \exp(-E/RT)$ for the temperature range of relaxation in several polymers

Polymer	Temperature range (K)	E (kJ mol^{-1})	f_0 (Hz)	Temperature range (K)	E (kJ mol^{-1})	f_0 (Hz)
PBA	140–160	12.0	8.7×10^8	180–220	22.3	8.4×10^8
PVAc	180–230	34.7	6.0×10^{12}	–	–	–
(Homogeneous) blend: 50 PBA–50 PVAc	110–150	22.7	1.6×10^{13}	180–220	29.0	8.4×10^{10}
Core-shell polymer	110–140	20.9	1.0×10^{12}	190–220	29.0	8.4×10^{10}
Structured core-shell copolymer	110–140	12.0	1.1×10^8	180–220	31.9	6.7×10^{11}

known that rigid molecular glasses[9] and amorphous polymers without a side group[8] also have β- and γ-relaxations at $T < T_g$ whose characteristics are remarkably similar to those observed for PBA. Therefore, it seems more appropriate to consider that the sub-T_g relaxations are associated with the low-density regions intrinsic to the amorphous packing, rather than to the hindered rotations of specific groups of a polymer molecule. This is particularly so when no independent means for identifying the motion of the various groups attached to a polymer chain are available.

Poly(vinyl acetate). Only one relaxation process at $T < T_g$ is dielectrically observed in PVAc, as is seen in *Figure 1*. Dynamic mechanical measurements[1] show the existence of two processes, one of which appears as a shoulder near 250 K for a measurement frequency of 0.01 Hz. The shoulder becomes less pronounced when the frequency of measurement is increased to 1 Hz and it is likely that in the kHz frequency range, the shoulder merges with the α-relaxation peak and therefore the relaxation process is not observable in our dielectric measurements.

Bulk PVAc has been dielectrically studied by several workers[10,11] but our results for its latex films are not expected to agree with those for the bulk PVAc. There is also a further difference which is due to the much lower molecular weight of our polymer since $M_n = 91\,000$ and $M_w/M_n = 6.51$, and to its large polydispersity. For example, the temperature for the same rate, or f_m, of our samples is ~10 K lower for the α-process and ~20 K lower for the β-process than those reported by Ishida *et al.*[10] and Saito[11]. Furthermore, the half-width of the β-relaxation peak is much higher in our latex than in the bulk samples[10,11]. For the latex, the height of the $\tan\delta$ peak for the α-process is ~34% as low, and that for the β-process nearly twice as high (*Figure 11*) as that observed for the bulk polymer.

The presence of water in the PVAc latex is likely to plasticize it and raise the height of its $\tan\delta$ peak for both the α- and β-processes. Since a decrease is observed for the former and an increase for the latter, we suggest that the difference between the observed dielectric behaviour of the latex and the bulk polymer is largely due to the high polydispersity of the former and not to small amounts of water. In an earlier study of the dependence of the height of the β-peak on the molecular weight of poly(propylene glycols)[12] we concluded that decrease in the molecular weight decreases the strength of the β-process. The effect of the polydispersity, which is equivalent to an increase in the fraction of the low-molecular weight PVAc here, on the strength of the β-process seems to be the opposite of that observed for poly(propylene glycols), and may be related to the presence of side groups in the PVAc (the latter has no dipolar side groups). We hope to examine this feature using pure polymers.

50:50, PBA:PVAc blend. The 50% PBA–50% PVAc homogeneous blend shows four relaxation processes as is seen in *Table 1* and *Figures 2* and *12*. Two of the processes, namely those observed as peaks at ~248 and ~336 K, are the α-processes for pure PBA and PVAc. The peak observed at 124 K is the lowest temperature peak for PBA seen in *Figure 1*. The shoulder observed at ~200 K is a combination of the shoulder at ~200 K, that appears in the isochrone for PBA in *Figure 1*, and the peak that appears for PVAc at ~196 K in *Figure 1*. The heights of the $\tan\delta$ peaks and of the shoulder for the blend are approximately half of those for the pure latex or homopolymers, as expected in view of the decreased concentrations of the more dipolar polymer in the blend, than in the homopolymers.

The mechanical relaxation studies for a frequency of 0.1 Hz have shown two peaks at ~240 and 310 K, a shoulder to the peak near 150 K and an increase of loss at $T < 120$ K. Since the increase of mechanical loss factor with decreasing temperature suggests the presence of another relaxation peak at $T < 100$ K, it seems that all four dielectrically observed processes are also mechanically observable. These are in addition to the process that is responsible for the appearance of a shoulder in the mechanical loss tangent observed near 250 K for both the pure PVAc and the homogeneous blend, which is dielectrically not observed here.

Clearly, the relaxation spectra of the blend is a weighted sum of the corresponding spectra of the pure or homopolymers with only slight change in the temperature and rate of relaxation of the various processes.

The α-relaxation for the blend, that corresponds to the motions of the PVAc chains, is shifted by ~10 K to higher temperatures as is seen in *Figure 12*. This implies that in the blend the PVAc is antiplasticized by the presence of PBA. Similar antiplasticization of PBA by ~11 K is also seen from the increase in the temperature of the α-process of PBA in the blend over that in the pure sample, as given in *Figure 12*. The half-width of the α-peak for the motions of the PVAc chains for the blend is ~0.8 decades less than for the pure polymer, but for the motions of PBA chains in the blend is 0.5 decade more than for the pure polymer. This clearly represents the interaction of one type of chain with the other in the relatively large interfacial regions. For polymer systems with limited compatibility, the relaxation temperature for each component is known to remain essentially unaffected by the presence of the other component, if the regions are sufficiently large for each polymer to retain its characteristic properties. The slight increase observed here in the temperature of the α-process may also be due to the partial homogeneous mixing of the two polymers, but not due to the presence of water in the blend sample. Reasons for the latter have been given in the preceding section.

The temperature for the β-relaxation in the blend in *Figure 12* is in between the two temperatures for the pure PVAc and PBA lattices. This is clearly due to the merger in the blend of the β-peaks for the two polymers whose frequencies differ by about a factor of 40 and whose half-widths are already large. Therefore, the β-process observed for the blend is a combined process for the two polymers. This is also evident from the observed half-width of the β-process seen in *Figure 8*, which for the blend is about twice as much as that for the pure polymers.

The γ-peak for the blend appears at a lower temperature than for pure PBA but at a $T > 130$ K, and has a higher activation energy. In view of the complex nature of the latex blends, it seems inappropriate to further discuss the reasons for this difference.

50:50 core-shell polymer. Since the microstructure or morphology of polymer particles is that of PBA core and PVAc-shell with a sharp concentration gradient at the boundary, one anticipates that the dielectric relaxation behaviour of the latex would be similar to that of the (homogeneous) blend. This is substantiated by the data in *Table 1* which show little change in the temperatures of the relaxation peaks from those observed for the homogeneous blend but there is a 30% increase in the height of the shoulder observed at ~ 200 K over that for the blend. This increase is attributable mainly to the change in the morphology from a random distribution in the blend to a spherical distribution of PBA in particles of smaller size in the core-shell polymer. In *Figure 12*, the temperatures of both the α-process in the PBA component and the combined β-processes in the PBA and PVAc components remain the same as in the homogeneous blend. However, the temperature of the γ-process in the core-shell polymer is raised by ~ 6 K.

Mechanical relaxation studies for frequencies < 1 Hz have shown no peaks due to the β- and γ-processes in the core-shell polymer. As discussed earlier here, this is mainly due to the fact that the two processes are too fast to be observable at 1 Hz at $T > 125$ K, the lower temperature limit of the mechanical relaxation measurements.

Structured core-shell copolymer. The structured core-shell copolymer particles, which have a PBA core, 50/50 by weight of PBA–PVAc copolymer inner shell and PVAc outer shell, have a mean composition of 50% PBA and 50% PVAc by weight. The fraction of the copolymer in it is 20% by weight. However, neither its isochrones nor isothermal spectra show a relaxation peak due to the copolymer. Mechanical relaxation studies[1] for frequencies of 1 and 0.01 Hz have also failed to show an α-process that could be associated with the copolymer, despite the relatively low T_g of 264 K for the copolymer[1].

When the tan δ values of the homogeneous blend and the core-shell polymer and structured core-shell copolymer are compared at temperatures between those of the α-peaks due to PBA and PVAc, significant increase of tan δ is seen (*Figures 1–3*) to occur in the latter two polymers. Specifically, for 290 K, the tan δ of the latter is twice as high as that of the blend. This increase is due to the contribution to tan δ from the relatively weak α-process of the copolymer which is expected to appear in this temperature range because of its lower T_g of 264 K. Furthermore, the increase of the heights of the β- and γ-peaks for the core-shell copolymer, which has the same average composition as the blend, and of those in the core-shell polymer, may be due also to the presence of an unresolved β-process in the copolymer anticipated in the temperature range 120–200 K. The contribution to tan δ from the α- and β-processes due to the copolymer in the particles of core-shell morphology would affect both the temperature and the position of the corresponding peaks associated with the molecular motions that occur in the pure or homopolymers in the same particles. This is evident from *Table 1* and *Figure 12.* We therefore conclude that the measured temperatures of the α-, β- and γ-peaks and their activation energies are all affected by the further contribution to tan δ from the presence of the copolymer at those temperatures where the copolymers own α- and β-relaxation peaks are expected to occur.

Since the tan δ at $T \simeq 290$ K for the structured core-shell copolymer (*Figure 3*) is about the same as for the core-shell polymer (*Figure 2*), it follows that both the two-step and three-step emulsion polymerization ultimately lead to an inner shell of a PBA–PVAc copolymer in the latex film, and that the concentration gradient in the latex film made from the core-shell polymer is not as sharp as is observed for its polymer particles in the emulsions. The latex films formed from the core-shell polymer and from the structured core-shell copolymer, have similar dielectric behaviours at $T \sim 290$ K, but one which is different from the corresponding behaviour of both the pure or homopolymers and the (homogeneous) blend lattices.

CONCLUSIONS

(1) The relaxation features of the PVAc latex differ from those of the bulk PVAc. The PBA latex has two relaxation processes at sub-T_g temperatures, namely β- and γ-relaxations. The activation energy for the low-temperature or γ-process is nearly half of that for the β-process.

(2) The presence of one polymer antiplasticizes the other in both the homogeneous and the heterogeneous (core-shell structured) latex blends.

(3) The latex blends have relaxation features of both homopolymers but at temperatures different from those for pure polymers. The β-relaxation in the blends appears at a temperature intermediate of that of the β-relaxations for homopolymers, and has a large half-width. Only one β-process is observed in the latex blends.

(4) Both the core-shell polymer and the structured core-shell copolymer lattices show evidence for the presence of a copolymer in its films, although the particles of the former in the emulisified state contained no copolymer.

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REFERENCES

1 Cavaille, J-Y., Jourdan, C., Kong, X. Z., Perez, J., Pichot, C. and Guillot, J. *Polymer* 1986, **27**, 693
2 Misra, S. C., Pichot, C., El Aasser, M. S. and Van der Hoff, J. W. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 567; *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 2383
3 Pichot, C., Kong, X. Z. and Guillot, J. *Polymer* submitted
4 Johari, G. P. *Polymer* 1986, **27**, 866
5 Pathmanathan, K., Johari, G. P. and Chan, R. K. *Polymer* 1986, **27**, 1907
6 Wölf, K. *Kunst. Plast.* (*Solothurn, Switz.*) 1951, **41**, 89
7 Thurn, H. and Wölf, K. *Kolloid Z.* 1956, **148**, 16
8 McCrum, N. G., Read, B. E. and Williams, G. in 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967
9 Johari, G. P. and Goldstein, M. *J. Chem. Phys.* 1970, **53**, 2372
10 Ishida, Y., Matsuo, M. and Yamafuji, K. *Kolloid Z.* 1962, **180**, 108
11 Saito, S. *Kolloid Z.* 1963, **189**, 116
12 Pathmanathan, K. and Johari, G. P. *Polymer* 1988, **29**, 303