

Comparison of micromechanical properties of latex films obtained by different emulsion copolymerization pathways

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A comparative study is reported on the micromechanical behaviour of polymer films made from vinyl acetate-butyl acrylate (VAc-BuA) copolymer latices prepared by different emulsion processes: (i) conventional batch, (ii) two-step polymerization, (iii) corrected batch, and (iv) mixture of the two corresponding homopolymers. Using special equipment well adapted for micromechanical analysis, the real and imaginary parts of the dynamic shear modulus (G' and G'' respectively) and the internal friction ($\tan \delta = G''/G'$) of these films were measured as a function of temperature (from 100 K to 340 K, i.e. in the glass temperature zone of both homopolymers) and of frequency (from 5×10^{-5} Hz to 5 Hz). Results are compared and discussed in relation to particle morphology of the latex from which the polymer films were obtained. An analysis of the results confirms that the plots of $\tan \delta$ would clearly show the inadequacy of time-temperature superposition for the dynamic mechanical behaviour of polymer blends in the range of the glass transition temperature.

(Keywords: polymer; polymer blend; poly(butyl acrylate); poly(vinyl acetate); emulsion polymerization; morphology; dynamic mechanical analysis)

INTRODUCTION

Micromechanical measurement aspects

It is well known that mechanical pressure applied to a material can be used as either a treatment to modify the material structure or morphology, or a measurement probe¹; in the latter case, there are two ways of studying the mechanical properties of a material.

The first consists in using large strain, e.g. in the case of glassy materials in a temperature range far below the glass transition temperature. Analysis of the strain as a function of the stress applied to the material can be done to determine thermodynamical parameters². Secondly, mechanical properties are used as a non-destructive probe, i.e. in a strain range in which it can be assumed that no modifications in structure or in morphology are induced, which is the case in micromechanical spectroscopy; this implies the measurement of dynamic shear modulus as a function either of temperature or of frequency.

The micromechanical spectrum generally shows different relaxation processes; in the case of a glassy material the main or ' α '-relaxation appears at the glass transition temperature; generally it is assumed that above this temperature, when the material is a supercooled liquid (i.e. in metastable equilibrium), its dynamical behaviour can be described by a Williams-Landel-Ferry (WLF) equation³. At sufficiently low temperature, because the mobility of structural units decreases with decreasing temperature, experiments can be done in an isoconfigurational state (i.e. where no morphological evolution can occur), depending upon the thermal

history⁴; each secondary relaxation process (' β '-relaxation) can be described by an Arrhenius law with a specific activation energy. It is generally agreed that this approach includes glassy homopolymers and compatible polymer blends⁵⁻⁷.

It appears from literature reviews that many attempts have been made to associate each process with microstructural motion^{8,9}. To determine micromechanical properties increasingly accurately, a new apparatus has been designed in the authors' laboratory that allows measurement of the dynamic shear modulus with change of temperature (100-700 K) or frequency (10^{-5} to 5 Hz), or both, for a very low relative strain ($\sim 10^{-5}$)¹⁰⁻¹². Glassy homopolymer behaviour seems well understood and there is increasing interest in polymer blends, so that the same approach has been used in the case of emulsions.

Emulsion aspects

Emulsion polymerization is a unique process that allows the preparation of colloidal dispersed polymer particles. In the last decade, structured latices have been recognized as very useful for technical applications and scientific investigation, owing to the potential versatility of their properties. Among the various pathways commonly carried out to synthesize 'structured' latex particles, emulsion copolymerization is of particular interest because of the wide range of achievable particle morphologies. Many parameters have been found to control particle morphology, such as the nature of the binary monomer system, polymer compatibility,

polymerization sequences, crosslinking agent, etc.¹³. Batch emulsion copolymerization of the vinyl acetate-butyl acrylate (VAc-BuA) system results in particles with core-shell morphology, owing to widely different reactivity ratios and water solubilities of the monomers; whereas, with semicontinuous monomer addition the comonomers are more uniformly distributed within particles¹⁴. Such differences in the morphology have been found to affect the mechanical behaviour of films^{15,16}.

As part of a study of structure-property relations in emulsion copolymers, the effect of particle morphology on the micromechanical behaviour of latex films (dynamic shear modulus, $\tan \delta$) has been examined as a function of temperature or frequency, or both. This paper reports work on the same basic system (VAc-BuA) in which particle morphology was varied according to the type of emulsion process.

EXPERIMENTAL

Preparation of latices

Four series of latices were synthesized by different emulsion polymerization pathways:

(1) Conventional batch copolymerization, from which different particle-average copolymer compositions were obtained (0–100 wt%), i.e. from pure VAc to pure BuA; the monomer concentration gradient in the particles was estimated by a model calculation¹⁸.

(2) Two-step emulsion polymerization in which the more hydrophilic monomer (VAc) was polymerized on a poly(BuA) seed latex, which leads to core-shell morphology^{14,15}; the monomer concentration gradient in particles changes abruptly for this pathway.

(3) A corrected batch process¹⁷, which produces polymer particles of nearly uniform composition.

(4) A simple blend of the two homopolymer latices obtained as in (1), without any further copolymerization.

The emulsion polymers were characterized by particle size (by quasielastic light scattering or transmission electron microscopy) and copolymer composition (by proton nuclear magnetic resonance).

Average particle size was ~ 200 nm; average copolymer composition and average particle size data are given in Table 1.

Micromechanical measurements

The polymer film samples were prepared from latex by a standard evaporation technique, to achieve homogeneous solid films¹⁷. The samples were cut to a dimension of $\sim 1 \times 6 \times 40$ mm for measurement of the real and imaginary parts of the modulus with an inverted forced oscillation pendulum¹².

Measurements were repeated for each frequency and temperature to test the reproducibility of the results, which was within a few parts per cent. As the temperature

of the sample remained constant to ± 0.2 K, error arising from temperature variation was minimal. Observed viscoelastic and relaxation behaviour showed no dependence upon applied stress over strain amplitudes of the order of 5×10^{-5} .

RESULTS

In a preliminary study, the real and imaginary parts of the dynamic modulus, G' and G'' , respectively, and the internal friction, $\tan \delta$ ($=G''/G'$) were plotted versus temperature. The following systems were investigated:

- (1) BuA and VAc homopolymers and 20/80, 40/60, 70/30 wt/wt BuA-VAc copolymers (simple batch process);
- (2) 60/40 core-shell copolymer;
- (3) 50/50 uniform composition emulsion (corrected batch process);
- (4) 50/50 blend of homopolymers.

Results are shown in Figures 1 to 4. In Figure 1, G'/G_0 and $\tan \delta$ variations are presented for both poly(BuA) and poly(VAc) latex films, in the temperature range 100–350 K and for 0.01, 0.1 and 1 Hz. (G_0 is the value of G' measured at 100 K.) Each film exhibits (i) a main or α -relaxation, which corresponds to its own glassy transition, and (ii) one or two secondary relaxations (e.g. β -). In Figure 2, G'/G_0 and $\tan \delta$ for copolymer system (1) and polymer blend (4) are given in the same temperature range and for 0.1 Hz. These spectra show two main relaxation processes, which correspond to those of pure poly(BuA) and pure poly(VAc).

In Figures 3 and 4, the values of G'/G_0 and $\tan \delta$ at different frequencies are plotted against temperature for copolymer systems (2) and (3). For core-shell copolymer, observations are similar to those reported for batch copolymer and homopolymer blend. On the other hand, in the case of corrected batch copolymer, for which the local BuA-VAc composition is uniform throughout the whole particle and is close to the average composition of the sample, the curves show only one main relaxation process at an intermediate temperature between the main relaxation temperatures for poly(BuA) and poly(VAc).

To obtain more accurate information on these different systems, G'/G_0 , G''/G_0 (G_0 as above defined) and $\tan \delta$ were measured as a function of frequency between 5×10^{-5} Hz and 5 Hz for different temperatures for BuA and VAc homopolymers (Figures 5 and 6), 60/40 core-shell copolymer (Figure 7), 50/50 corrected batch copolymer (Figures 8 and 9) and 50/50 homopolymer blend (Figures 10 and 11).

Then, as is usually done in such studies¹, an attempt was made to superimpose the curves by simply shifting them along the frequency axis; because of the large number of data, only the master curves obtained by such a treatment are given, except in cases of pure poly(BuA) and pure poly(VAc), where experimental data are given

Table 1 Copolymer composition and average particle size

	Batch				Corrected batch	Core-shell	Blend
% Mol%	0	14.4	31	61	100	31	40.1
Weight%	0	20	40	70	100	40	50
Volume%	0	22	43	72.5	100	43	53
T_g (BuA)	218	—	223	229	—	243	220
T_g (VAc)	—	301	302	293	302	—	306

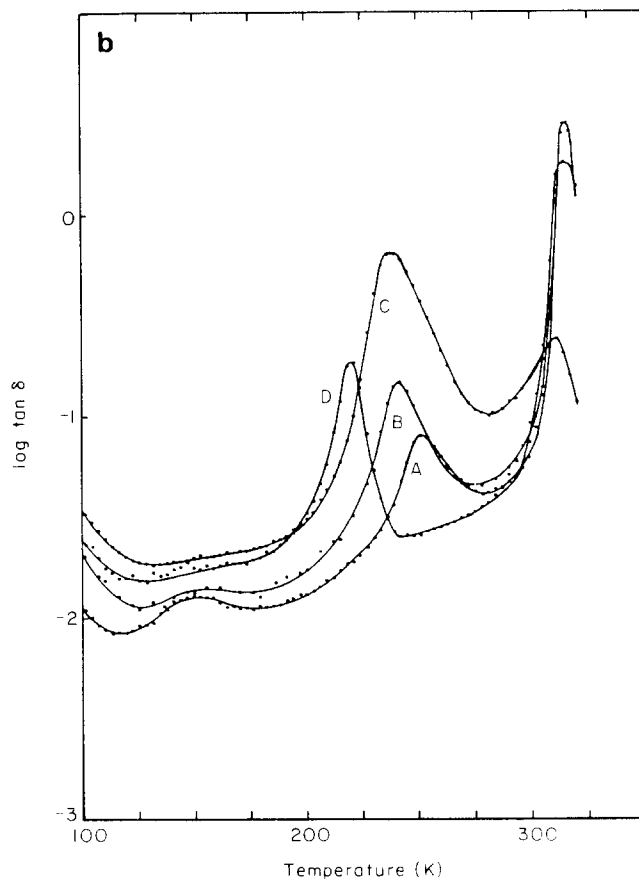
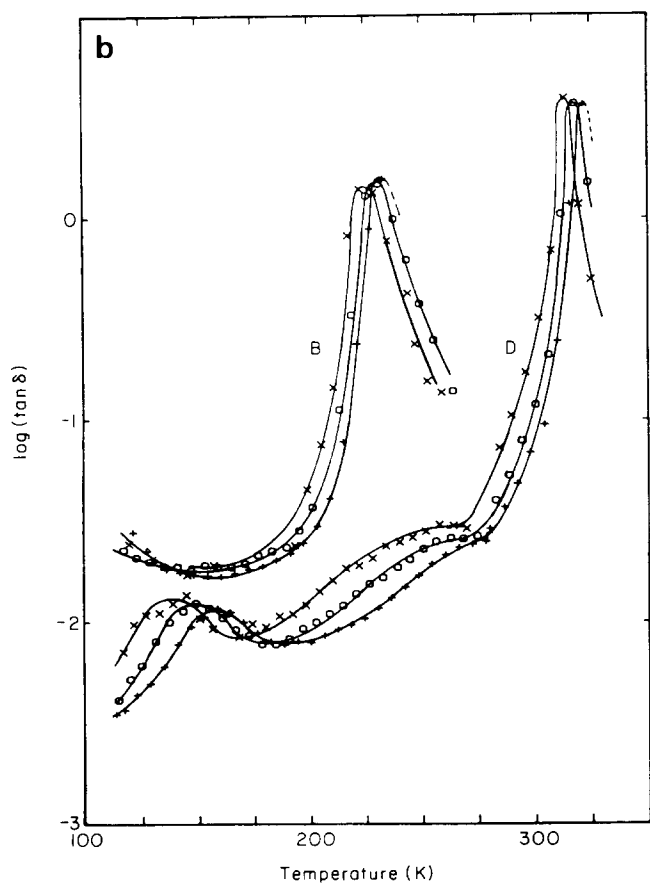
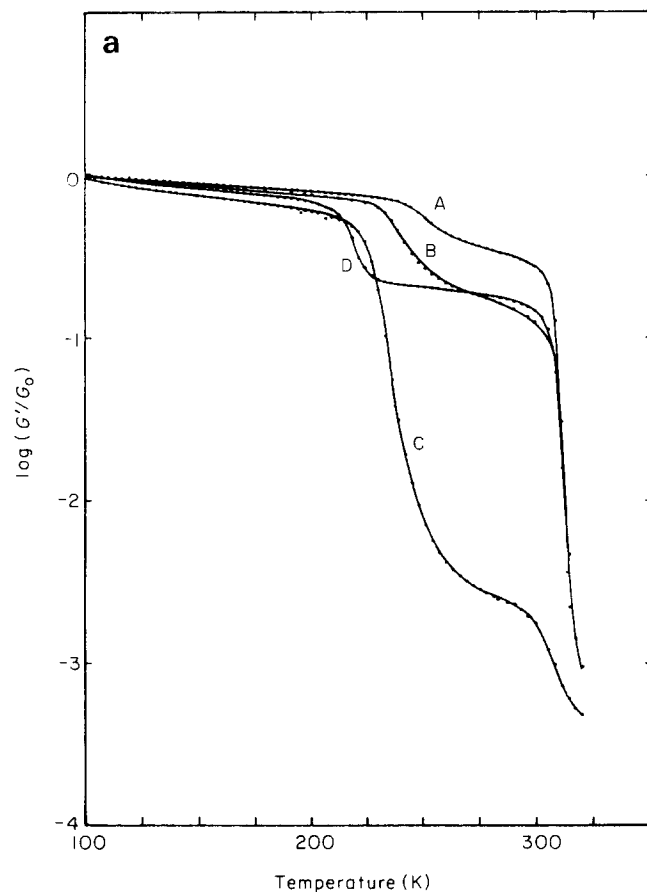
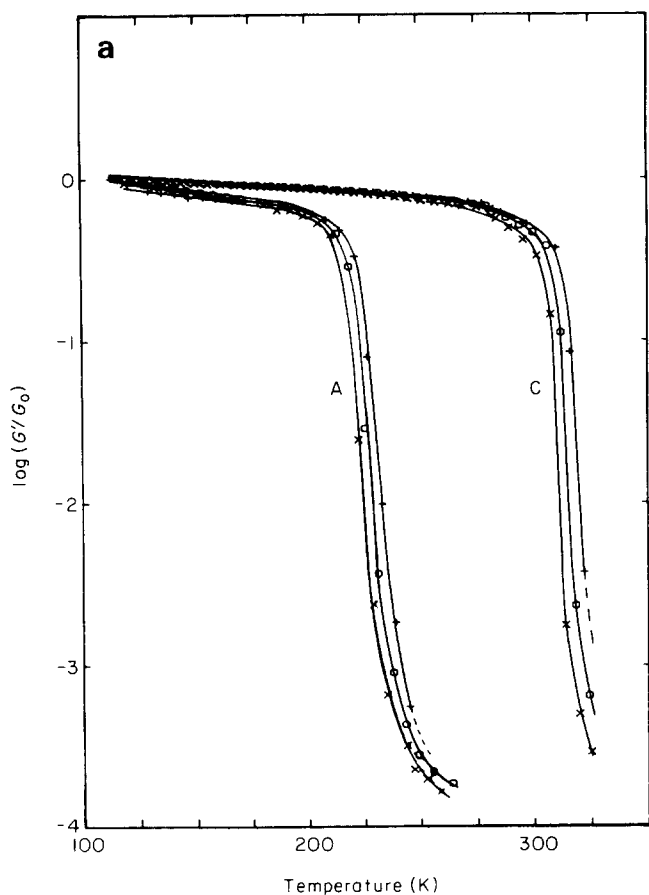


Figure 1 (a) and (b) Micromechanical property-temperature spectra, different frequencies, of BuA and VAc homopolymers. (A) G'/G_0 , (B) $\tan \delta$ for pure poly(BuA)—($G_0 = 1.5 \times 10^9$ Pa at 100 K); (C) G'/G_0 , (D) $\tan \delta$ for pure poly(VAc)—($G_0 = 1.5 \times 10^9$ Pa at 100 K). Frequency: \times , 0.01 Hz; \circ , 0.1 Hz; $+$, 1 Hz

Figure 2 Micromechanical property-temperature spectra at 0.1 Hz of batch copolymer and simple blend systems. (a) $\log(G'/G_0)$; (b) $\tan \delta$. A, 20/80; B, 40/60; C, 70/30 BuA/VAc batch copolymers; D, 50/50 simple blend

Figure 3 (a) G'/G_0 , (b) $\tan \delta$ versus temperature spectra for coreshell polymer. Frequency: \times , 0.01 Hz; \circ , 0.1 Hz; $+$, 1 Hz

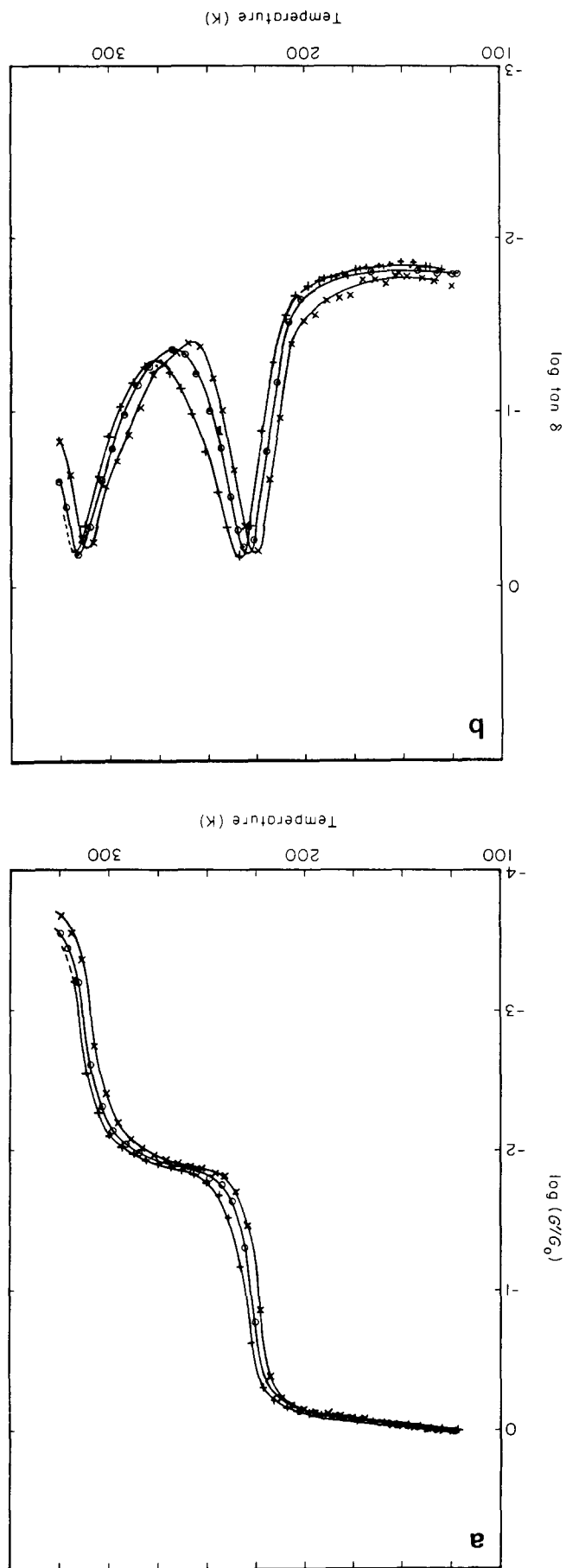
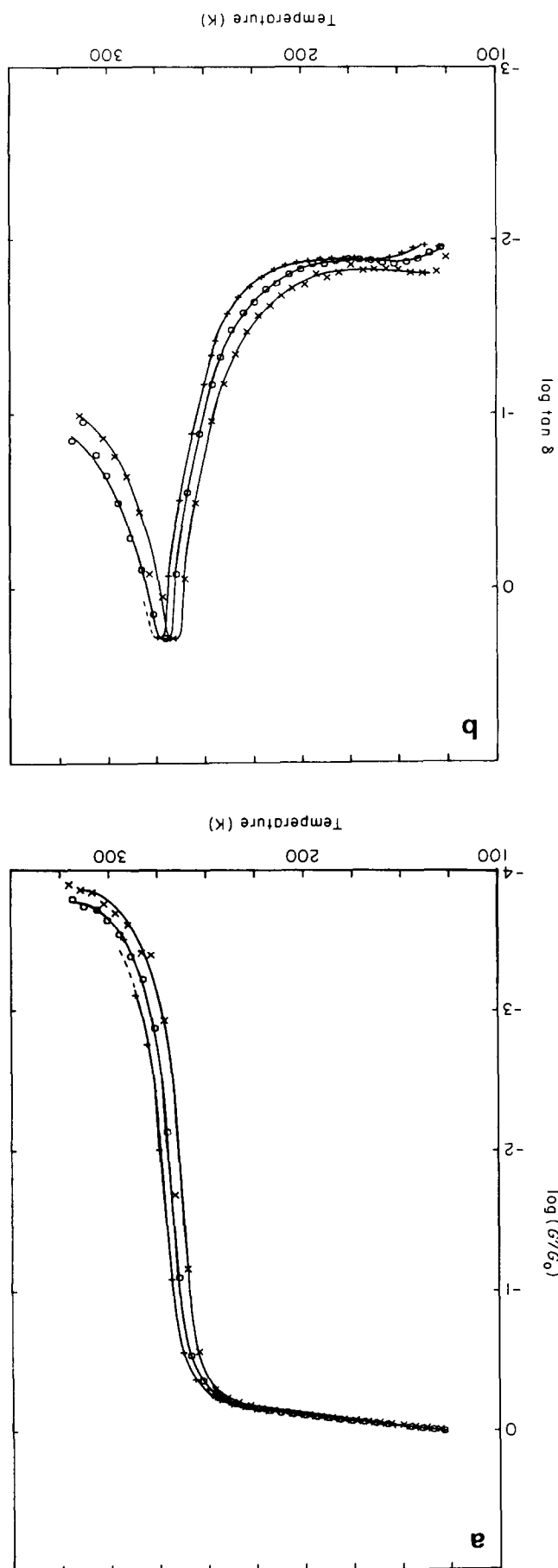


Figure 4 (a) G'/G_0 , (b) $\tan \delta$ versus temperature for corrected batch process copolymer. Frequency: \times , 0.01 Hz; \circ , 0.1 Hz; $+$, 1 Hz



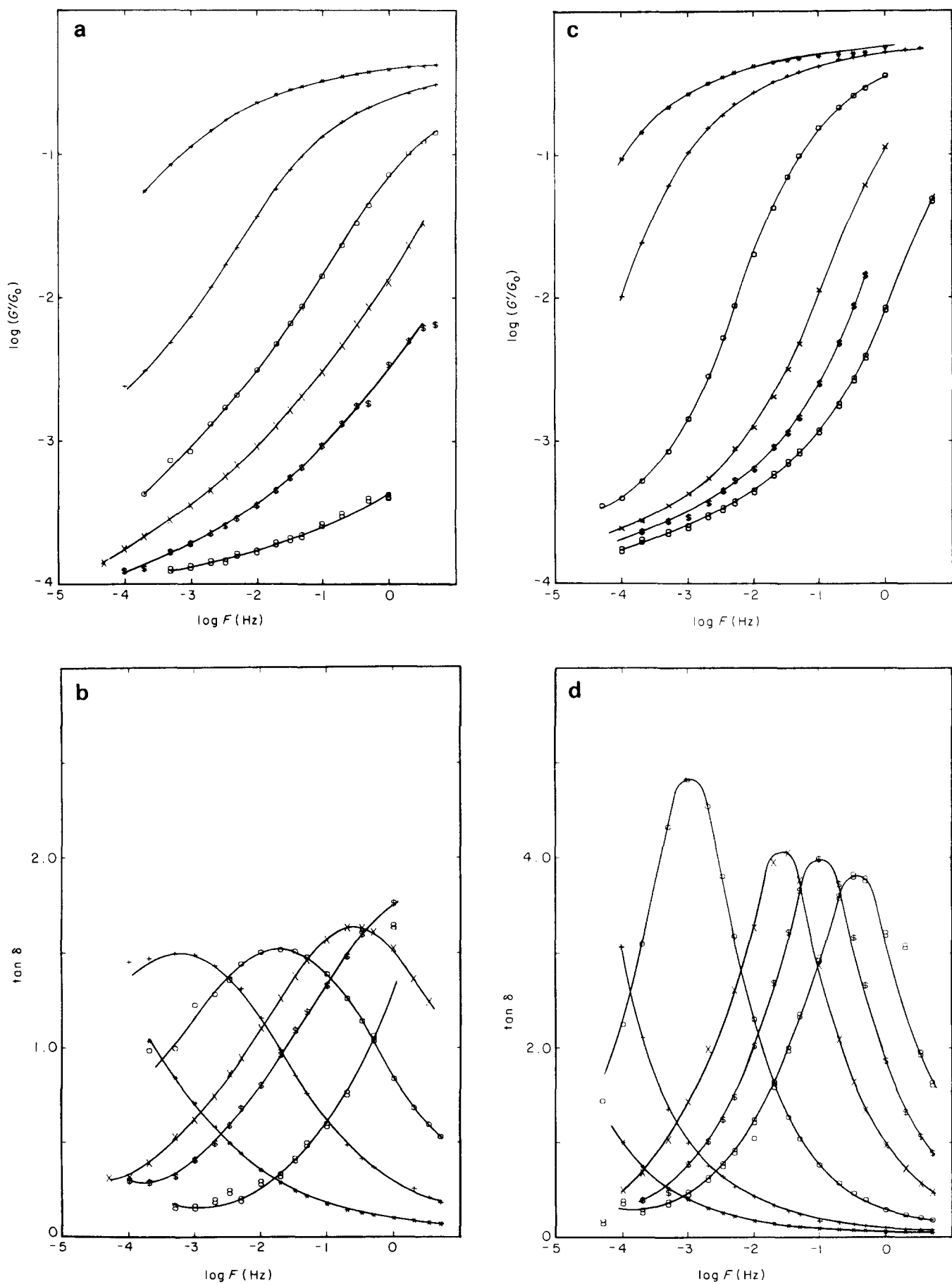


Figure 5 Log G'/G_0 versus frequency for (a) pure poly(BuA) and (c) pure poly(VAc); $\tan \delta$ versus frequency for (b) pure poly(BuA) and (d) pure poly(VAc). (a), (b): ★, 217 K; +, 222 K; ○, 227.5 K; ×, 233 K; §, 236 K; 8, 245 K; (c), (d): ★, 305 K; +, 307.5 K; ○, 312.5 K; ×, 317.5 K; §, 320 K; 8, 322.5 K

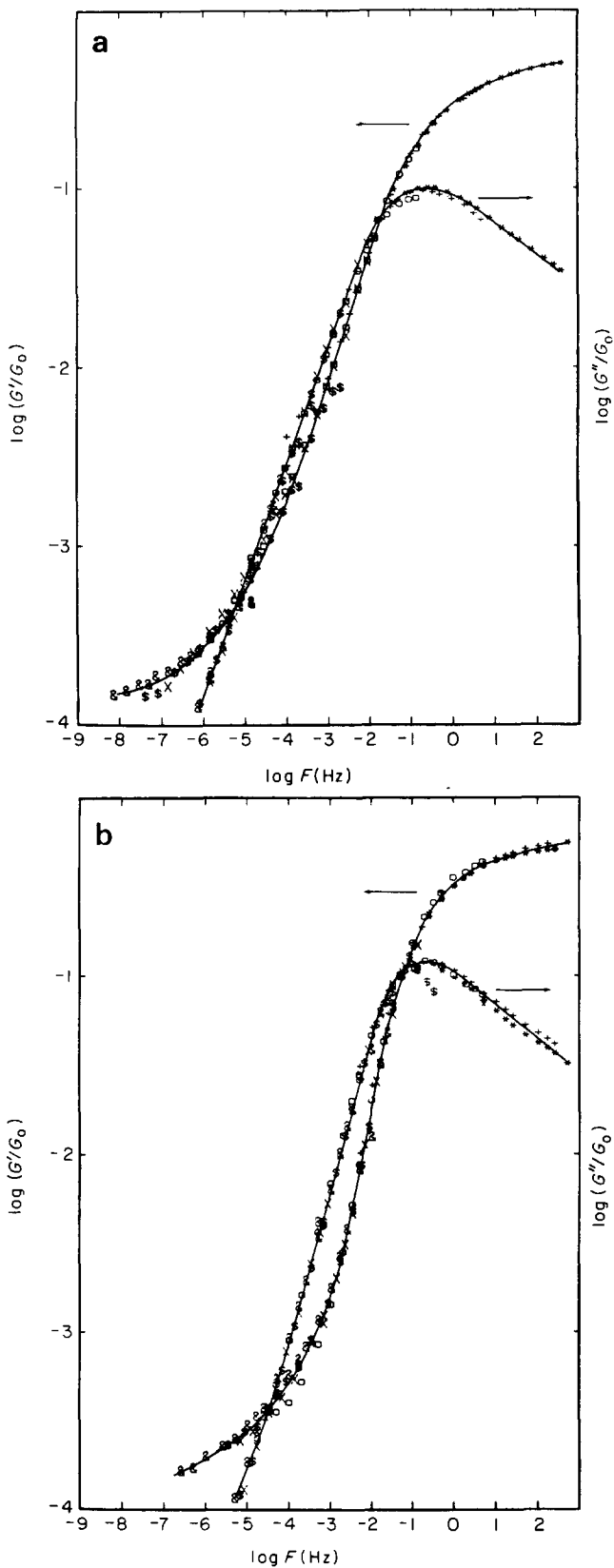


Figure 6 G'/G_0 and G''/G_0 master curves plotted against frequency for: (a) pure poly(BuA), (b) pure poly(VAc). (a): Δ , 217 K; +, 222 K; \circ , 227.5 K; \times , 233 K; $\$$, 236 K; 8, 245 K; (b): Δ , 305 K; +, 307.5 K; \circ , 312.5 K; \times , 317.5 K; $\$$, 320 K; 8, 322.5 K

(Figure 5). The shift factors, $\log \alpha_T$, are given in each case (see Table 2 and Figure 12), with reference to the temperature where $\tan \delta$ is a maximum at 10^{-3} Hz: two groups of curves were considered for each sample, except for the corrected batch copolymer, where only one transition was observed.

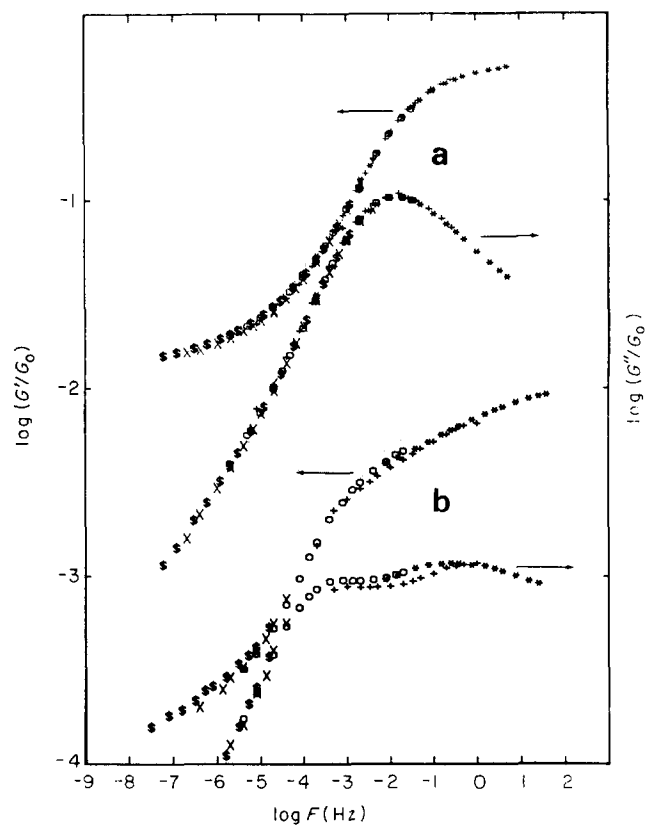


Figure 7 Master curves of G'/G_0 and G''/G_0 versus frequency for coreshell copolymer. (a) BuA glass transition: \star , 220 K; +, 224 K; \circ , 227 K; \times , 230 K; $\$$, 232 K; (b) VAc glass transition: \star , 293 K; +, 298 K; \circ , 300.5 K; \times , 311.5 K; $\$$, 313 K; &, 315 K

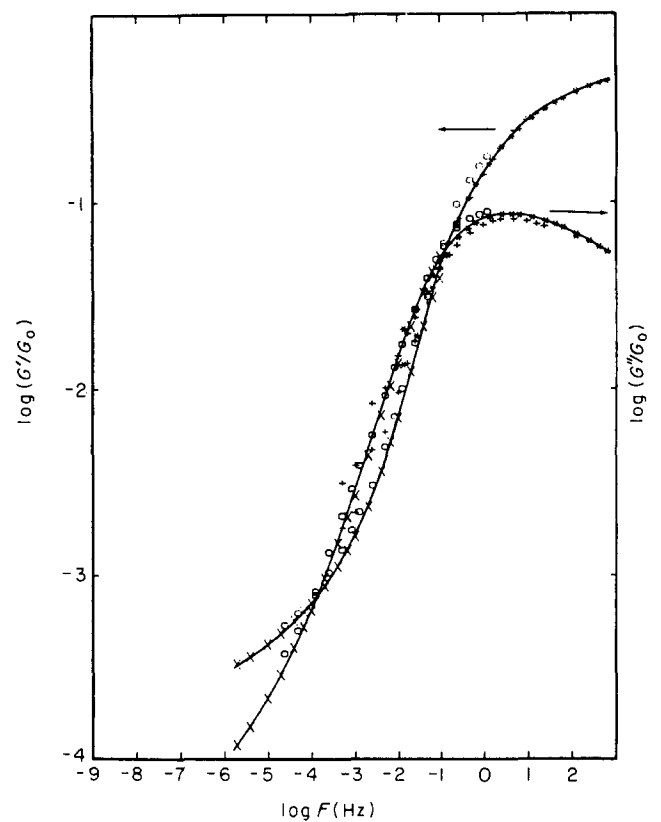


Figure 8 Master curves for G'/G_0 and G''/G_0 versus frequency for corrected batch copolymer in the range of the glass transition: \star , 257 K; +, 261 K; \circ , 267 K; \times , 272 K

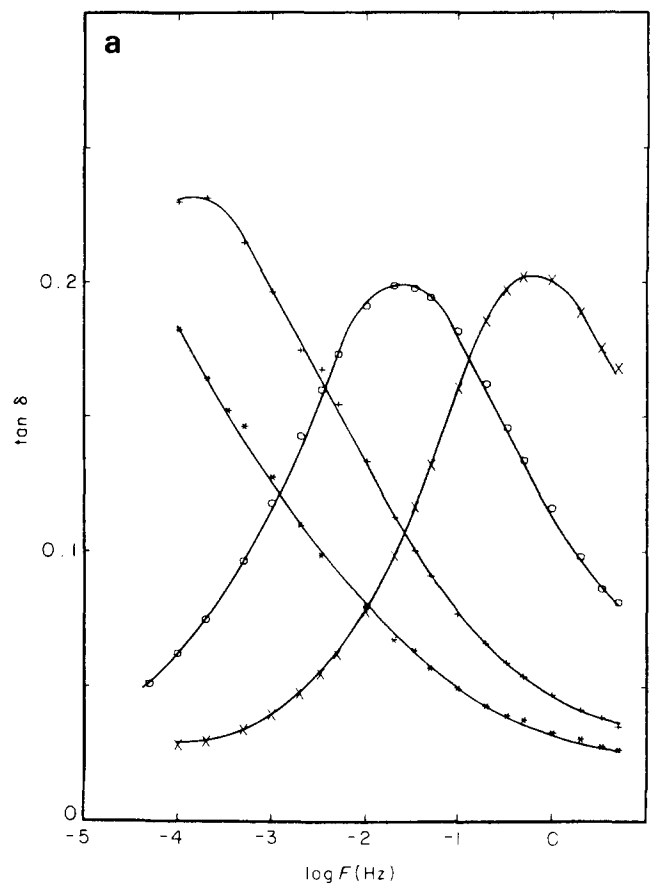
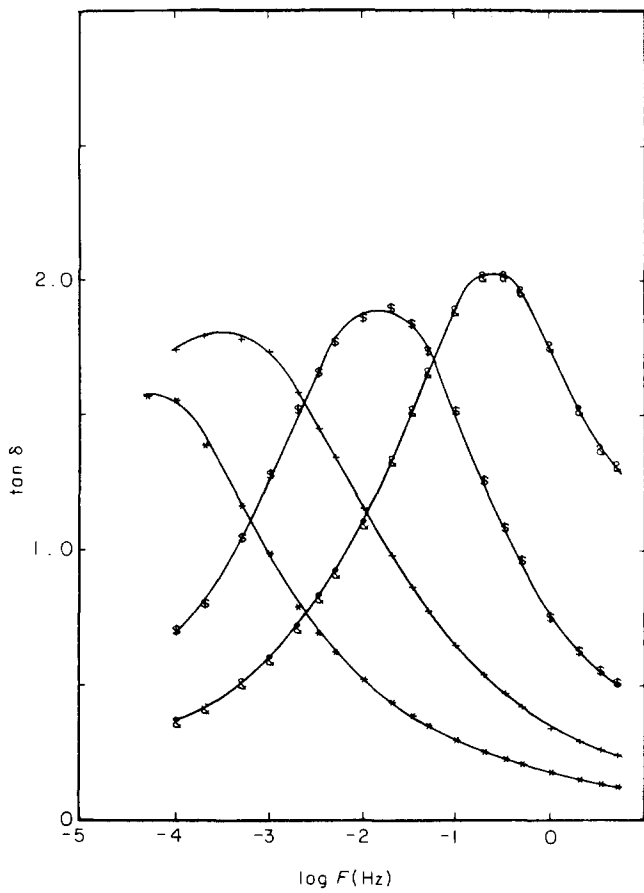


Figure 9 $\tan \delta$ versus frequency for corrected batch copolymer: \star , 257 K; +, 261 K; \circ , 267 K; &, 272 K

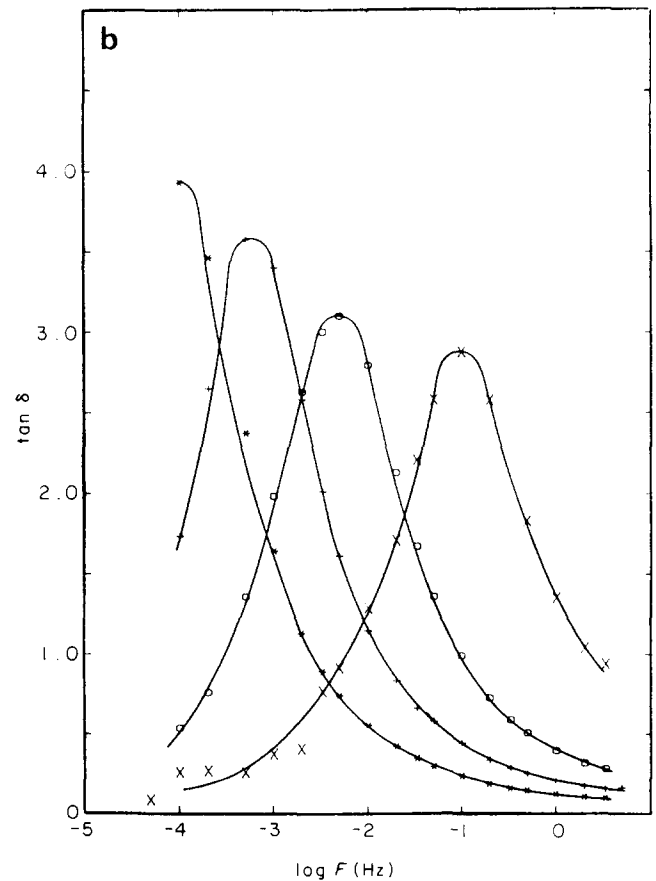
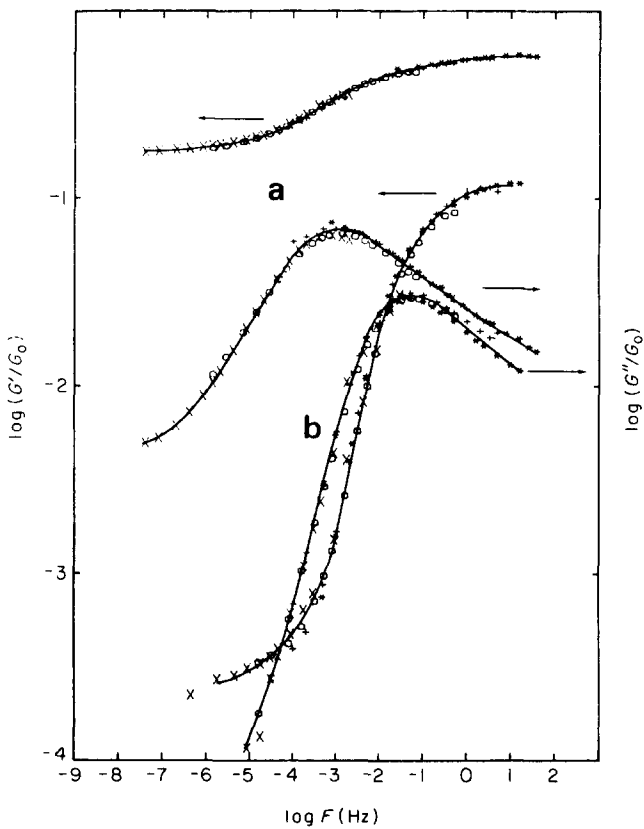


Figure 10 Master curves of G'/G_0 and G''/G_0 versus frequency for simple blend sample. (a) poly(BuA) glass transition: \star , 210 K; +, 215 K; \circ , 220 K; \times , 225 K; (b) poly(VAc) glass transition: \star , 310 K; +, 312.5 K; \circ , 315 K; \times , 320 K

Figure 11 $\tan \delta$ versus frequency for simple blend sample. (a) poly(BuA) glass transition: \star , 210 K; +, 215 K; \circ , 220 K; \times , 225 K; (b) poly(VAc) glass transition: \star , 310 K; +, 312.5 K; \circ , 315 K; \times , 320 K

Table 2 Shift factors, $\log \alpha_T$, at various test temperatures for polymers

Sample	Test temperature and ($\log \alpha_T$) ^a						Temperature of $\tan \delta_{\max}$ at 10^{-3} Hz
Pure poly(BuA)	217 (1.88)	222 (0.00)	227.5 (-1.56)	233 (-2.56)	236 (-3.40)	245 (-4.84)	222
Pure poly(VAc)	305 (2.72)	307.5 (1.72)	312.5 (0.00)	317.5 (-1.17)	320 (-1.77)	322.5 (-2.29)	312.5
Blend	BuA	210 (0.89)	215 (0.00)	220 (-1.86)	225 (-3.40)	— (—)	215
	VAc	310 (0.68)	312.5 (0.00)	315 (-0.80)	320 (-2.06)	— (—)	312.5
Core-shell	BuA	220 (0.00)	224 (-1.10)	227 (-2.02)	230 (-2.70)	232 (-3.24)	220
	VAc	293 (3.58)	298 (3.28)	300.5 (2.76)	311.5 (0.00)	313 (-1.80)	311.5
Corrected batch	257 (2.10)	261 (0.67)	267 (-0.63)	272 (-1.72)	— (—)	— (—)	264

^aThe test temperature is followed by the $\log \alpha_T$ value in parentheses, e.g. 217 (1.88)

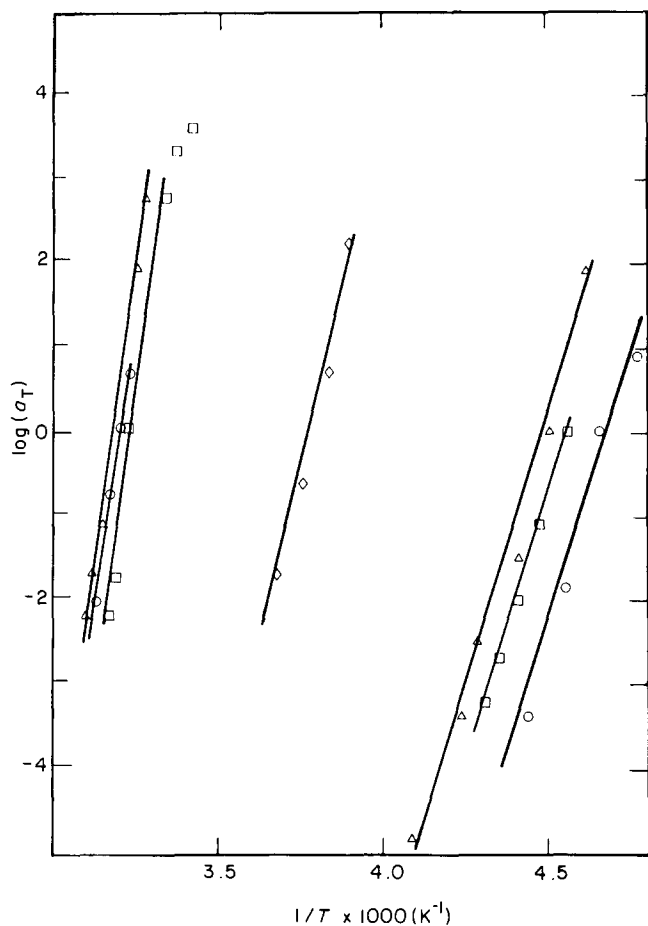


Figure 12 Shift factor versus inverse temperature. Δ , homopolymers; \circ , simple blend; \square , core-shell copolymer; \diamond , corrected batch

DISCUSSION

Micromechanical spectra versus temperature

For batch copolymer systems, two peaks are observed (Figures 1 and 2), the first corresponding to the BuA-rich phase glass transition, the second to the VAc-rich phase glass transition; moreover, these spectra exhibit shifts along the temperature axis that depend upon sample composition and type of morphology, as well as variations of maximum height in $\tan \delta$ peaks; the values are reported in Figure 13, in addition to values corresponding to the core-shell copolymer sample: $\tan \delta$ peak temperatures are given as a function of the particle-average composition. For the 'BuA peak', temperature increases from 232 K to 253 K as BuA content decreases from pure BuA to 20% BuA/80% VAc; (2) on the other hand, the 'VAc peak' temperature decreases from 318 K to 308 K as VAc content decreases from pure VAc to 70% BuA/30% VAc; such behaviour has already been observed

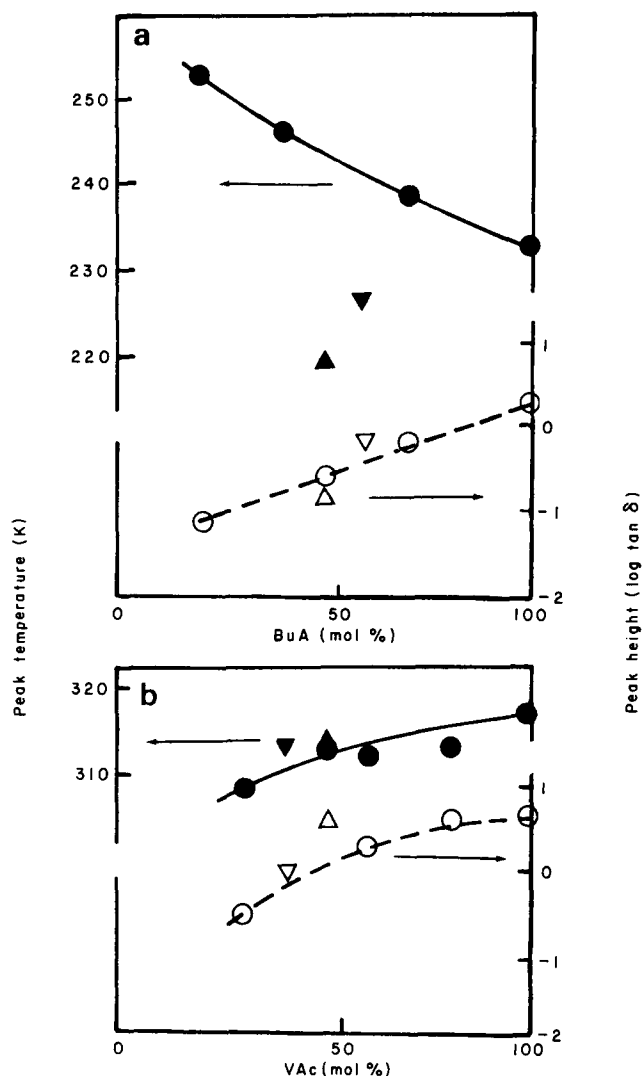


Figure 13 $\tan \delta$ peak temperatures and height at 0.1 Hz as a function of mean composition of particles, for different systems. (a) corresponding to BuA ' α '-relaxation; (b) corresponding to VAc ' α '-relaxation; \bullet , \circ , batch copolymer; \blacktriangle , \triangle , simple blend; \blacktriangledown , \triangledown , core-shell morphology

in different systems¹⁴.

In a simple blend system, the poly(BuA) $\tan \delta$ peak temperature does not follow the same pattern as for the 50% BuA/50% VAc blend—it is lower than for pure poly(BuA); the same behaviour can be seen for the core-shell copolymer 60% BuA/40% VAc. On the other hand, no noticeable effect is seen on the 'VAc peak'. The glass transition temperature does not change as observed in calorimetric experiments¹⁷.

In order to interpret the differences between the temperature shifts of the 'BuA peak', in batch-process copolymers and in the simple blend, variations in the

morphology have to be considered. As mentioned above, the simple blend systems contain no copolymer; moreover, the homopolymers do not seem to be compatible¹⁹ and, because films were made at low enough temperature (room temperature) in order to avoid volume diffusion, it can be assumed that both phases remained separate in the sample; this has also been observed in other similar systems²⁰.

In the case of core-shell copolymer, film morphology would be nearly the same except that a copolymer zone might exist between quasipure BuA and quasipure VAc, as will be discussed later.

For such systems of inclusions in a matrix, many experiments and calculations have been performed which show the shift of $\tan \delta$ peak towards lower temperatures for the dynamical behaviour of the glass transition of the inclusion^{21,22}. As mentioned above, this shift does not imply a shift of glass transition temperature, but results from mechanical interactions between inclusions and matrix.

Moreover, in *Figure 13*, the peak height corresponding to each polymer is a maximum for homopolymers and decreases as the concentration of this polymer decreases; since this behaviour does not depend upon the morphology, the relaxation intensity would be a function of the average composition only in the material.

In the corrected batch process copolymer (*Figure 4*), only one main transition is observed at a temperature between the poly(BuA) and the poly(VAc) transition temperatures. If T_1 , T_2 and T are $\tan \delta$ peak temperatures of poly(BuA), poly(VAc) and copolymer respectively, W_1 and W_2 the average weight composition of BuA and VAc respectively, using the Fox relation²³, $1/T = (W_1/T_1) + (W_2/T_2)$ $T = 274$ K (by experiment $T = 270$ K). This relation, although valid only for the glass transition temperatures T_g , is also applicable to $\tan \delta$ peak temperatures, which are shifted from T_g .

Micromechanical spectra versus frequency

As mentioned above, measurements have been performed as a function of frequency for different temperatures. As shown in *Figures 6, 7, 8 and 10*, the time-temperature superposition³ seems appropriate for a description of the viscoelastic behaviour of the different materials. But as reported elsewhere⁷, an appropriate method of testing the applicability of time-temperature superposition is by plotting $\tan \delta$ as a function of frequency for different temperatures. This has been done in *Figures 5b, 5d, 9 and 11*. *Figures 5b and 5d* show different behaviour for pure poly(VAc) and pure poly(BuA). The lower the temperature, the higher the $\tan \delta$ peak for poly(VAc); the opposite for poly(BuA). However, in both cases it is clear that the time-temperature superposition for the plots of dynamic shear behaviour in the glass transition zone is unsatisfactory. Although it appears to be adequate for G' and G'' , its adequacy must also be tested for $G''/G' = \tan \delta$, as here. The difference observed between (1) G' and G'' , and (2) $\tan \delta$ is due to the choice of scales: the logarithmic scale over four decades for G' and G'' obscures the departure from superposition but the linear scale of $\tan \delta$ clearly shows it.

To compare the transition characteristics of homopolymers with copolymer or blends, different parameters were measured such as $\tan \delta_{\max}$, $\tan \delta$ halfwidth and G'' halfwidth, and apparent mean activation energy obtained from master curve plots (see *Table 2*).

Homopolymers

As shown in *Table 2*, the $\tan \delta$ peak for pure poly(VAc) is much higher and sharper than for pure poly(BuA), which has to be correlated with the local order in the material⁹; in other words, the higher is the disorder, the larger is the relaxation time distribution, which must be considered in a mechanical process. Differences in the disorder could be attributed to the structure of BuA monomer, which is more asymmetric and bulky than that of VAc monomer, which reduces the mobility of the units.

Constant-composition emulsion copolymers

The single main relaxation for this material is quite similar to the relaxation of pure poly(BuA), except for the $\tan \delta$ peak temperature, as discussed above. Hence, it may be concluded that the disorder in the glassy material is predominantly controlled by the BuA sequence arrangements in the copolymer.

Simple blend

This material shows two main relaxations, corresponding respectively to poly(BuA) and poly(VAc) main or α -relaxations. In the blend each of them has similar features (see *Table 3*) as in homopolymers, but with different intensity in relation to mean overall composition: the same apparent activation energy (300 kJ mol^{-1} and 600 kJ mol^{-1} respectively), same G'' and $\tan \delta$ halfwidth; $\tan \delta_{\max}$ is 0.2 instead of 2 for pure poly(BuA) relaxation (*Figure 11*). The variation in $\tan \delta$ as a function of frequency with temperature is found to be different; the higher the temperature, the lower the peak, which differs from the behaviour of pure poly(BuA). This can be explained by taking into account the β -relaxation of pure poly(VAc), which occurs in the same range of temperature and frequency. It can also be deduced from *Figure 1* that the poly(VAc) β -process contribution is larger at $T = 215 \text{ K}$, $F = 10^{-2} \text{ Hz}$ ($\tan \delta \sim 0.03$) than at $T = 225 \text{ K}$, $F = 1 \text{ Hz}$ ($\tan \delta \sim 0.01$). This can explain the difference between $\tan \delta$ height at 225 K and $\tan \delta$ height at 215 K, as observed in *Figure 11*.

Thus it can be concluded that micromechanical behaviour of poly(BuA) is the same in the simple blend as in pure poly(BuA). The same is true for poly(VAc), which confirms that both homopolymers are incompatible in this type of system.

Core-shell copolymer

Core-shell copolymer exhibits two main relaxation processes like classical batch-process copolymers or simple blends (*Figure 7*). Whereas the 'BuA relaxation' resembles that in BuA homopolymer, the 'VAc relaxation' appears different: it has two peaks, the former corresponding to the VAc homopolymer at low frequencies, the latter at higher frequencies. This is probably related to the core-shell morphology.

The sample used in experiments, BuA/VAc = 50/50 (mol/mol) represents a volume ratio of 63/37; as the initial seed latex was poly(BuA), the core radius is slightly smaller than the overall particle radius (200 nm), whereas the shell thickness is about 15% of this radius.

The copolymer zone was probably formed during the synthesis, because the conversion was not complete in the BuA seed latex (97%). A ¹³C n.m.r. analysis of the sample¹⁷ showed that ~5–10% of the total VAc was incorporated in the form of short sequences.

The second peak (observed in high frequency range of

Table 3

	T_{\max}^{\dagger} (K)	G' slope (dec/dec)	G'' slope (dec/dec)	$\tan \delta_{\max}$	$\Delta\omega_{1/2}$ G''	$\Delta\omega_{1/2}$ $\tan \delta$	H_a kJ mol^{-1}
Pure poly(BuA)	231	0.7	0.7	1.5-2	3.5	4.0	300
Pure poly(VAc)	319	1.2	1.0	4-5	3.0	2.0	560
Blend	poly(BuA)	222	0.1	0.4	0.2	3.5	300
	poly(VAc)	320	1.0	0.8	3-4	3.0	560
Core-shell	BuA	228	0.5	0.5	0.7	3.2	300
	VAc	316	0.4	0.5	0.8	3.8	560
Corrected batch	270	0.8	0.7	2.0	7.0	3.0	375

$\dagger T_{\max}$: temperature of $T_g \delta_{\max}$ at 0.1 Hz

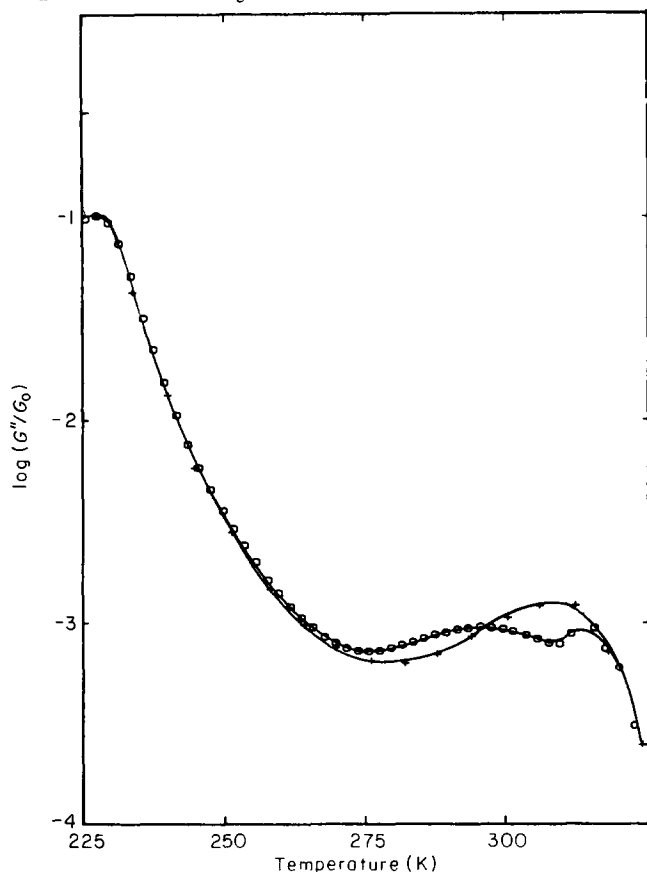


Figure 14 $\log G''/G_0$ versus temperature for core-shell copolymer: +, after an annealing at room temperature for several months; O, after a second annealing at 315 K for 48 h

the VAc transition spectrum) should correspond to the copolymer zone: this peak position is intermediate between poly(BuA) and poly(VAc) relaxations, as would be the case for homogeneous VAc-rich copolymer. On the other hand, as shown in Figure 14, a shift of this peak towards lower temperatures (higher frequencies) occurs after annealing at 315 K for 48 h. This indicates that some physical changes occur in the copolymer zone.

CONCLUSIONS

The results show the significance of micromechanical analysis, especially frequency scanning, in studies of the influence of the polymer film morphology. First, it has been pointed out that differences exist between the behaviour of batch copolymer and simple blend (e.g. relaxation peak shifts). Secondly the uniform-composition emulsion copolymer spectrum indicates that the disorder is mainly due to BuA arrangements. Finally the frequency scanning study applied to material of core-shell morphology shows the presence of a copolymer zone.

From these results two points arise: (1) Complete understanding of the core-shell copolymer zone

behaviour needs more kinetic studies coupled with thermal treatments, as well as the synthesis of 'perfect' core-shell polymer lattices, i.e. without any copolymerization; and (2) it is of interest to relate more quantitatively the micromechanical spectra to the morphology of the simple blend and of the core-shell materials. By using mechanical models (Kerner²⁴, Dickie²¹, Takayanagi²⁵), and clarifying the physical hypothesis, it is for instance deduced that for the simple blend the film morphology might comprise poly(BuA) inclusions in a poly(VAc) matrix: further work by the authors on this is currently in progress.

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