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Dynamic mechanical thermal analysis of homopolymeric and diblock polybutadienes and polybutadiene blends

S. Poshyachinda, H. G. M. Edwards and A. F. Johnson*
IRC in Polymer Science and Technology, Chemistry and Chemical Technology, University of Bradford, Bradford, West Yorkshire, BD7 1DP, UK
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The dynamic mechanical properties are reported for polybutadienes with different vinyl contents, of poly(1,4-butadiene-*b*-1,2-butadiene) copolymers with various compositions, block molecular weights and overall molecular weights, and of a number of different blends of the homopolymers. The microstructure of the polymers has been obtained by Raman spectroscopy and the molecular weights by gel permeation chromatography. The morphology of the diblock copolymers, as perceived using dynamic mechanical thermal analytical methods, has been found to be a function of the molecular weight of the individual blocks and the overall molecular weight of the copolymers. The extent of phase separation in the polymer blends is greater than that seen in the diblock copolymers. The glass transition temperature has been shown to be a function of vinyl content in homo-polybutadienes. Comparisons have been drawn between the dynamic mechanical properties of the diblock copolymers and those of polymer blends which have a similar overall microstructural composition. Copyright © 1996 Elsevier Science Ltd.

(Keywords: anionic polymerization; diblock copolymer; glass transition temperature)

INTRODUCTION

Anionically initiated polymerization of butadiene by organolithium initiators in hydrocarbon solvents gives rise to polybutadienes with predominantly 1,4 units in the polymer chain. However, in the presence of polar modifiers such as THF, diglyme or 1,2-dipiperidinoethane (DIPIP), polymers with a largely 1,2 (vinyl) content are produced[1,2].

The preparation of poly(1,4-butadiene-*b*-1,2-butadiene) copolymers (PBB) by the sequential addition of monomer to cyclohexane containing butyllithium as initiator or DIPIP as a complexing modifier has been described elsewhere[3]. Three block copolymers were produced with each of the blocks having different molecular weight but the overall molecular weight of the copolymer being similar. In this work, the dynamic mechanical thermal (d.m.t.a.) behaviour of these polymers is described and compared with those of the blends of low- and high-vinyl polybutadienes which have similar overall microstructural compositions. The dynamic mechanical properties of homo-polybutadienes with various vinyl contents in the range 17–96% are also reported.

EXPERIMENT

Poly(1,4-butadiene-*b*-1,2-butadiene) copolymers were prepared as described earlier[3]. Polybutadienes with various vinyl contents in the range 17–96% have been prepared using cyclohexane as solvent, *n*-butyllithium as initiator, and complexing modifiers such as diethylether, monoglyme, diglyme and DIPIP to control the microstructure of the polymer. Similar experimental methods have been used to those described previously[3].

The microstructures of the polymers were characterized by Raman spectroscopy using the $\nu(C = C)$ stretching vibrational bands and the molecular weights of the products determined by gel permeation chromatography[4]. In this work, the gel permeation chromatograph (Waters Associates) was fitted with two PL gel 10 μm mixed bed columns (Polymer Laboratories Ltd.) and a refractive index detector (Waters, Model 410) was employed in the present work. Tetrahydrofuran was used as eluant with a flow rate of 1 ml min^{-1}. The instrument was calibrated with low-vinyl polybutadiene standards (Polymer Laboratories).

A dynamic mechanical thermal analyser (Polymer Laboratories, Mark II) has been used to carry out measurements over a range of temperatures between -100 to 50°C at a scan speed of 3°C min^{-1} on films which were produced by casting from cyclohexane solution (of appropriate composition in the case of the polymer blends) onto a polytetrafluoroethylene plate. The stress was applied in the shear mode of deformation at a frequency of 1 Hz.

RESULTS AND DISCUSSION

Glass transition temperature of vinyl polybutadienes characterized by d.m.t.a.

The dependence of the loss tangent, $\log \tan \delta$, on

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* To whom correspondence should be addressed. Present address: IRC in Polymer Science and Technology, School of Chemistry, University of Leeds, Leeds LS29 9AT, UK

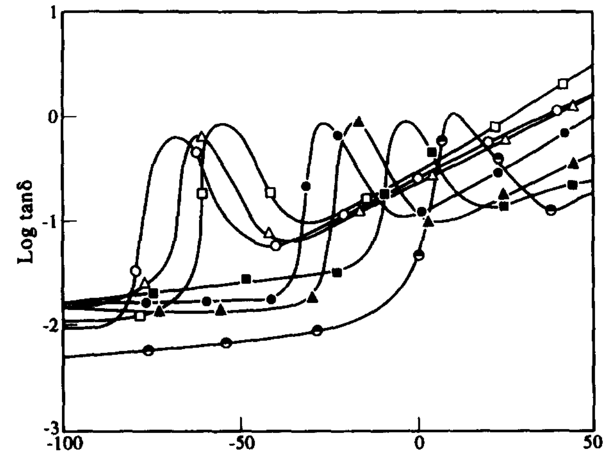

Figure 1 Temperature dependence of log tan δ of ○ DEE-1, △ DEE-2, □ DEE-3, ● MG-1, ▲ MG-2, ■ DG-1, and ◓ DP-1

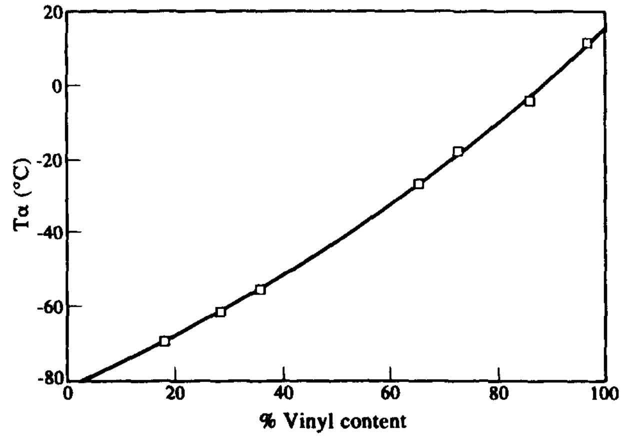

Figure 2 The variation of $T\alpha$ with vinyl content of vinyl polybutadiene sample

temperature is displayed in *Figure 1*. The temperature-peak maximum was taken to be the glass transition temperatures ($T\alpha$). The observed glass transition temperatures of polybutadienes with different vinyl contents are shown in *Table 1*. The polymers have number average molecular weights in the region of 100 000 to 120 000 with polydispersity indices lower than 1.10. It can be seen that ($T\alpha$) increases steadily from −69.5 to +12.0°C when the vinyl content increases from 17.8 to 96.4%. It is to be expected that the $T\alpha$ of the polymers will increase when side groups are incorporated into a flexible polymer chain such as 1,4-polybutadiene (both *cis*-1,4 and *trans*-1,4) since they will restrict the motion of the polymer backbone, necessitating higher temperatures for the free movement of the backbone as the number of side groups increases.

The homo-polybutadienes can be regarded as copolymers containing three types of microstructure, *cis*-1,4 and *trans*-1,4 and vinyl units. Only one $T\alpha$ is observed as might be expected from a polymer containing an essentially random distribution of units in the polymer chain. The variation of $T\alpha$ with vinyl content is displayed in *Figure 2*.

For a statistical copolymer comprising two components, it is assumed that the specific volume–temperature behaviour of the two components in the rubbery and glassy states remains the same in the copolymer as in the homopolymers [5] and it has been shown[6,7] that the $T\alpha$ is related to composition by the expression

Table 1 Glass transition temperatures of vinyl polybutadienes characterized by d.m.t.a.

Sample	% Vinyl	$T\alpha$ (°C)
DEE-1	18	−70
DEE-2	29	−62
DEE-3	36	−56
MG-1	65	−27
MG-2	73	−18
DG-1	86	− 4
DP-1	96	12

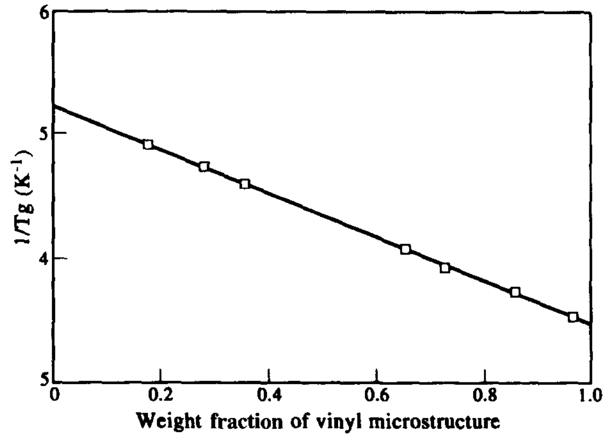

Figure 3 The plot of $1/T\alpha$ against weight fraction of vinyl units

$$\frac{1}{T\alpha} = \frac{1}{(w_1 + B'w_2)}\frac{w_1}{T\alpha_1} + \frac{B'w_2}{T\alpha_2} \tag{1}$$

where w_1 and w_2 are the weight fractions of the two components whose homopolymers have transitions at temperatures $T\alpha_1$ and $T\alpha_2$, respectively, and B' is a constant which is close to unity.

Since $w_2 = (1 - w_1)$ and $B' \approx 1$, the above equation may be rearranged to

$$\frac{1}{T\alpha} = \frac{1}{T\alpha_1} - \frac{1}{T\alpha_2} w_1 + \frac{1}{T\alpha_2} \tag{2}$$

If it assumed that polybutadienes are statistical copolymers comprising vinyl and 1,4-addition units (even though the latter may be a mixture of *cis*-1,4 and *trans*-1,4), it is meaningful to plot $1/T\alpha$ against w_1, the weight fraction of vinyl microstructure for the polybutadienes listed in *Table 1*. *Figure 3* shows that this plot is linear and from the intercept and slope, respectively, the $T\alpha$ of 1,2 polybutadiene is found to be 18°C and that of 1,4-polybutadiene is − 82°C. Equation (2) works well for the polybutadienes examined here because the ratio of the *trans*-1,4/*cis*-1,4 units is almost constant in all the polymers studied and not because the $T\alpha$ values of the *cis*-1,4 and *trans*-1,4 polymers are the same. It has been established[8] that the *trans*-1,4/*cis*-1,4 ratio changes only slightly with vinyl content, regardless of the complexing agent used in the preparation (except DIPIP)[8]. The reported $T\alpha$ value for *cis*-1,4 polybutadiene (− 106°C) as measured by differential thermal analysis (d.s.c.) is the same within experimental error[9] thus making any distinction between the two isomeric forms immaterial

Table 2 Microstructures of poly(1,4-butadiene-*b*-1,2-butadiene) characterized by Raman spectroscopy[4]

			% Microstructure					
			First block			Second block		
Sample	% Weight LVPB	HVPB	Vinyl	*Trans*	*Cis*	Vinyl	*Trans*	*Cis*
PBB-100/0	100	0	9.9	46.4	43.5	–	–	–
PBB-90/10	92	8	9.0	47.1	43.9	91.3	7.9	0.8
PBB-80/20	84	16	8.8	46.5	44.7	94.4	5.4	0.2
PBB-70/30	70	30	9.2	46.8	44.0	93.7	5.9	0.4
PBB-60/40	59	41	9.5	46.7	43.8	94.9	5.1	0.0
PBB-40/60	38	62	9.2	47.0	43.8	94.7	5.3	0.0
PBB-30/70	29	71	9.1	47.7	43.2	95.2	4.8	0.0
PBB-20/80	20	80	8.9	46.9	44.2	94.8	5.2	0.0
PBB-10/90	10	90	9.7	47.0	43.3	94.9	5.1	0.0
PBB-0/100	0	100	–	–	–	96.1	3.9	0.0
PBB-50/50-1	51	49	9.5	47.3	43.2	95.0	5.0	0.0
PBB-50/50-2	54	46	9.0	47.6	43.4	93.1	6.4	0.5
PBB-50/50-3	49	51	9.2	47.3	43.5	94.7	5.3	0.0

Table 3 Average molecular weights of poly(1,4-butadiene-*b*-1,2-butadiene) and peak molecular weights of the first and second blocks

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Mp_1[a]	Mp_2[a]
PBB-100/0	337 000	301 000	1.12	314 000	–
PBB-90/10	508 000	382 000	1.33	380 000	52 000
PBB-80/20	371 000	267 000	1.39	232 000	69 000
PBB-70/30	425 000	315 000	1.35	224 000	120 000
PBB-60/40	430 000	307 000	1.40	191 000	150 000
PBB-40/60	539 000	382 000	1.41	165 000	263 000
PBB-30/70	477 000	346 000	1.38	96 000	288 000
PBB-20/80	620 000	422 000	1.47	80 000	423 000
PBB-10/90	558 000	407 000	1.37	32 000	431 000
PBB-0/100	316 000	287 000	1.10	–	292 000
PBB-50/50-1	476 000	333 000	1.43	207 000	236 000
PBB-50/50-2	131 000	96 000	1.37	48 000	62 000
PBB-50/50-3	62 000	48 000	1.30	24 000	27 000

[a] Mp_1 = peak molecular weight of the first block
Mp_2 = peak molecular weight of the second block

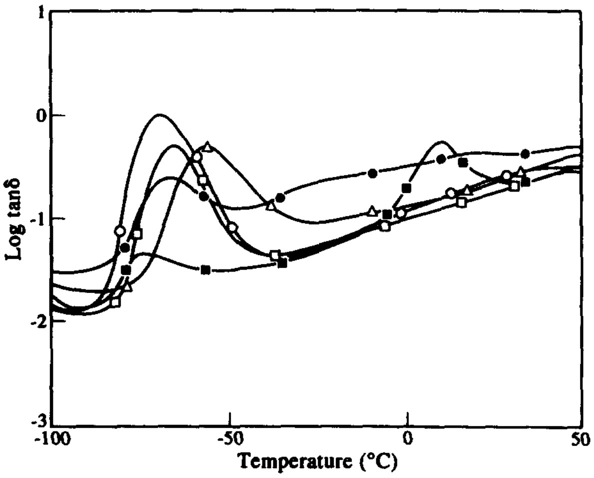

Figure 4 Temperature dependence of log tan δ of ○ PBB-100/0, □ PBB-90/10, △ PBB-80/20, ● PBB-70/30, and ■ PBB-60/40

as far as the use of equations (1) and (2) are concerned. However, it should be noted that no difference can be seen between the *T*αs of the *cis*-1,4 and *trans*-1,4 polybutadienes using d.m.t.a.

Table 4 Glass transition temperatures of low- and high-vinyl phases in poly(1,4-butadiene-*b*-1,2) and polymer blends

Sample	*T*α(LVPB) (°C)	Tα(HVPB) (°C)
PBB-100/0	−72	–
PBB-90/10	67	–
PBB-80/20	−58	–
PBB-70/30	−68	–
PBB-60/40	−74	9
PBB-50/50-1	−74	12
PBB-40/60	−70	10
PBB-30/70	−70	7
PBB-20/80	−61	10
PBB-10/90	–	7
PBB-0/100	–	12
BL-80/20	−70	13
BL-60/50	−70	10
BL-50/50	−70	10
BL-40/60	−72	9
BL-20/80	–	8

*Poly(1,4-butadiene-*b*-1,2-butadiene) (PBB)*

The molecular characteristics of the PBB diblock copolymers examined are summarized in *Tables 2* and *3*. The code names used for the copolymers, e.g. PBB-60/40, signify that a PBB diblock containing 60% by weight of low-vinyl polybutadiene (LVPB) and 40% by weight of high-vinyl polybutadiene (HVPB) was the target in the polymerization experiment. The copolymer compositions actually obtained differ slightly from the target, as can be seen in *Tables 2* and *3*.

Dynamic mechanical thermal analysis (d.m.t.a.) of PBB

The PBB copolymers have weight fraction ratios of low-vinyl/high-vinyl components in the range 90/10 and 10/90 and overall number average molecular weights (M_n) in the range 300 000 to 600 000 but with different molecular weights for the individual blocks (*M*p1 and *M*p2). *Figures 4* and *5* show the temperature dependence of the loss tangent and *Figures 6* and *7* the temperature dependence of the storage shear modulus for the materials as measured by d.m.t.a. The effect of the

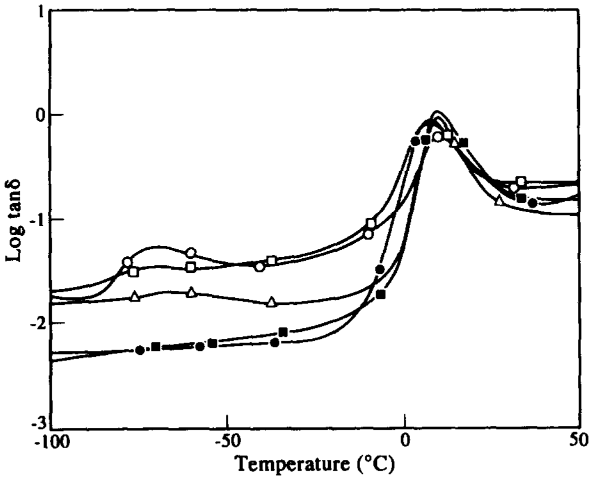

Figure 5 Temperature dependence of $\log\tan\delta$ of ○ PBB-40/60, □ PBB-30/70, △ PBB-20/80, ● PBB-10/90, and ■ PBB-0/100

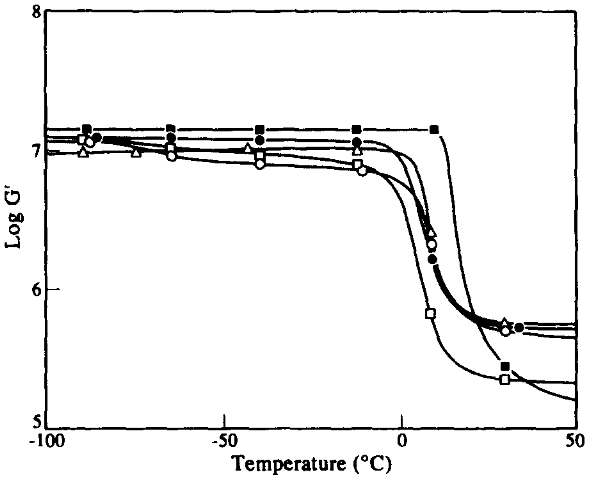

Figure 7 Temperature dependence of $\log G'$ of ○ PBB-40/60, □ PBB-30/70, △ PBB-20/80, ● PBB-10/90, and ■ PBB-0/100

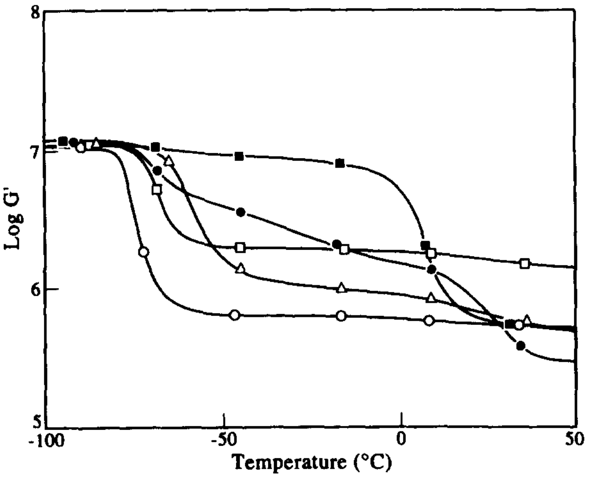

Figure 6 Temperature dependence of $\log G'$ of ○ PBB-100/0, □ PBB-90/10, △ PBB-80/20, ● PBB-70/30, and ■ PBB-60/40

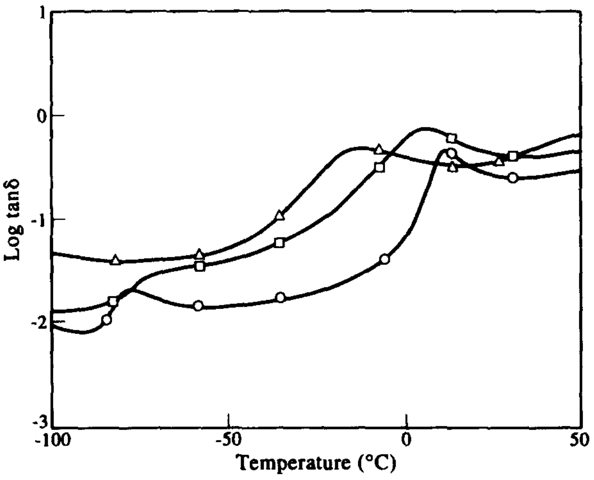

Figure 8 Temperature dependence of $\log\tan\delta$ of ○ PBB-50/50-1, □ PBB-50/50-2, and △ PBB-50/50-3

molecular weight on $\log\tan\delta$ and $\log G'$ was examined by fixing the lengths of the two blocks and varying the overall molecular weight of the polymers. *Figures 8* and *9* illustrate the results obtained for copolymers with equimolar (or weight) compositions (PBB-50/50) but with different overall molecular weights.

The homo-polymers (PBB-100/0 and PBB-0/100) were examined by d.m.t.a. in order to compare the dynamic mechanical properties with those of the block copolymers. The blended polymers are coded in a similar manner to the copolymers; BL indicates a blend and the numbers which follow indicate the weight percentage of the low-vinyl and high-vinyl polybutadiene components (see *Table 4*). The plots of $\log\tan\delta$ and $\log G'$ against temperature of these blends are shown in *Figures 10* and *11*, respectively.

The $T\alpha$ of PBB-100/0, a low-vinyl polybutadiene, is −72°C as determined by the peak of the loss tangent plot. By introducing 10% of high-vinyl block into the chain (PBB-90/10) the observed $T\alpha$ shifts to −66°C. The $T\alpha$ increases further to −57°C for PBB-80/20, in which the peak of loss tangent appears to be much broader than for the previously mentioned polymers. However, with longer high-vinyl blocks, e.g. PBB-70/30, $T\alpha$ decreases again to −68°C. This sample also exhibits a higher value for $\log\tan\delta$ in the range −40 to 0°C. In addition, there appears to be a small peak near −30°C. The $T\alpha$ again reduces to −74°C, for PBB-60/40, with a second peak appearing at 8°C. When the high-vinyl component of the block copolymers increases even further (PBB-40/60), the lower temperature $T\alpha$ increases slightly to −70°C and the higher $T\alpha$ to 10°C. The lower $T\alpha$ temperature remains essentially unchanged for PBB-30/70, but the higher $T\alpha$ decreases to 7°C. When the high-vinyl content of the copolymers increases from PBB-100/0 to PBB-20/80, the loss tangent peak height at lower temperature decreases significantly. In PBB-20/80 the lower $T\alpha$ appears at −60°C and the higher $T\alpha$ at 9°C. The lower $T\alpha$ in PBB-10/90 can no longer be detected and the higher $T\alpha$ is seen at 8°C, which shifts to 12°C for PBB-0/100.

Figure 6 shows that for PBB-100/0 there is a sharp decrease in the $\log G'$ curve starting at −80°C, which corresponds to the $T\alpha$ seen in *Figure 4*. There is little change in the $\log G'$ with increasing temperature until a temperature of about −20°C is reached at which point a further decrease in $\log G'$ occurs. Similar behaviour is observed for PBB-90/10 as the temperature is increased, but after the first sharp drop in $\log G'$, the curve then decreases slightly. For PBB-90/10, the curve starts to

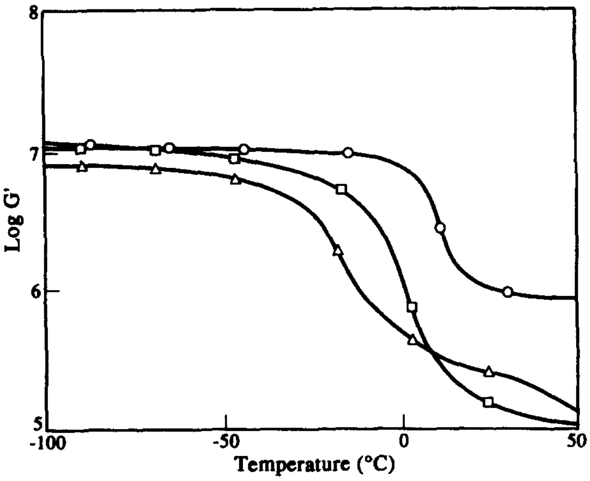

Figure 9 Temperature dependence of log G' of ○ PBB-50/50-1, □ PBB-50/50-2, and △ PBB-50/50-3

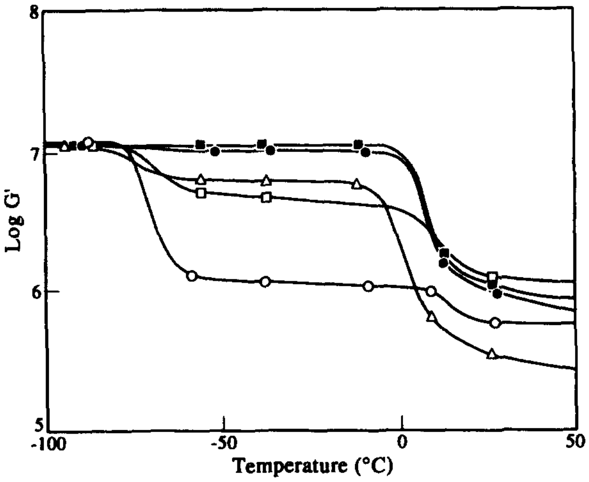

Figure 11 Temperature dependence of log G' of ○ BL-80/20, □ BL-60/40, △ BL-50/50, ● BL-40/60, and ■ BL-20/80

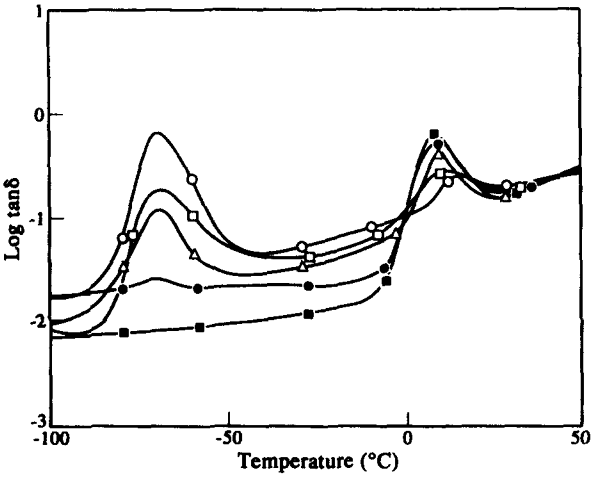

Figure 10 Temperature dependence of log tan δ of ○ BL-80/20, □ BL-60/40, △ BL-50/50, ● BL-40/60, and ■ BL-20/80

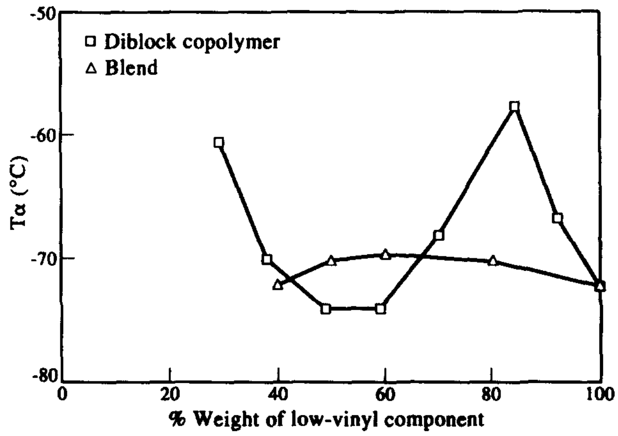

Figure 12 The variation of $T\alpha$ of the low-vinyl phase in PBB diblock copolymers and polymer blends with weight percentage of LVPB component

drop at higher temperature than PBB-100/0 and PBB-90/10 and from −45°C the log G' gradually decreases until 10°C from which the curve declines a little faster. Complex behaviour can be seen in PBB-70/30 in which, after the first sharp drop in log G' at about −70°C, is followed by a steady decline until 10°C where another sharp drop is observed. PBB-60/40 exhibits a small drop in log G' at −70°C, the log G' value then declines slightly with temperature until 0°C, where the curve drops sharply. The log G' plots for PBB-40/60 and PBB-30/70 are similar to those for PBB-20/80 and PBB-10/90 which exhibit only significant change in log G' at 0°C. However, for PBB-0/100, high-vinyl polybutadiene, the log G' remains constant until a temperature of 10°C is reached, above which it steadily decreases.

When the molar or weight ratio of the components in the block copolymers is fixed and the overall molecular weight of the copolymers is varied, two $T\alpha$s are detected, at −74°C and 12°C for PBB-50/50-1 (*Figure 8*), which has the highest molecular weight. When the overall molecular weight decreases, the $T\alpha$s are seen at −70°C and 5°C whereas for PBB-50/50-3, which has the lowest molecular weight, only one $T\alpha$ is observed at −15°C and the log tan δ peak of this sample is broad.

Figures 10 and *11* show the plots of log tan δ and log G' with temperature for the polymer blends in the compositions range from BL-80/20 to BL-20/80. These blends exhibit a rather more consistent behaviour than the block copolymers. The $T\alpha$ of the blends does not shift far from −73°C, which is the $T\alpha$ observed in PBB-100/0, one of the components used in the blends. The $T\alpha$ at a higher temperature shifts insignificant from that of the high-vinyl polybutadiene (PBB-0/100) when the weight fraction of the high-vinyl component is varied.

Two distinct changes in the magnitude of log G' for BL-80/20, BL-60/40, BL-50/50 and BL-40/60 at −70°C and 0°C, and these correspond to the two peaks found in the log tan δ plots for these polymer blends.

The behaviour of the blends and block copolymers are compared in *Figure 12*. The absolute differences are very small and care should be taken not to read too great a significance into these data.

Since the $T\alpha$ value of high-vinyl polybutadiene (HVPB) is higher than that of the low-vinyl polymer, when a small block of HVPB is chemically linked to LVPB the $T\alpha$ of LVPB increases in a similar manner to that observed for random copolymers. This indicates that the HVPB block is able to disperse totally in the

LVPB, results in the $T\alpha$ shifting to a higher temperature (PBB-90/10). When the HVPB block is longer (PBB-80/20), this effect is larger but since the HVPB block is probably not completely soluble in LVPB a broadened loss tangent is seen (*Figure 4*). When the molecular weight of the HVPB block increases further, the incompatibility of the two blocks becomes significant and phase separation takes place, resulting in the $T\alpha$ shifting to a lower temperature (as seen in PBB-70/30). The separation is clearly observed in the dynamic thermomechanical plots for the material PBB-60/40, where the $T\alpha$ of HVPB phase can be detected. At this composition the HVPB phase can be considered to be dispersed as separate domains in an LVPB matrix since the LVPB block is still the continuous phase. However, the phase separation is not thought to take place completely since there must be some degree of interphase penetration of the HVPB block into the LVPB phase due to chemical linkage between the two blocks. The observed trends in $\log G'$ with temperature for PBB-70/30 and PBB-60/40 support this suggestion, i.e. the decrease in low temperature transition corresponding to the $T\alpha$ of the LVPB block, the higher temperature transition to the $T\alpha$ of the HVPB phase. This behaviour is characteristic of two-phase polymers where the phase boundaries are diffuse; in this case the diffuse layers containing both LVPB and HVPB units[10]. When the phase separation is complete, the variation of the $\log G'$ plot with temperature between the two $T\alpha$s of the two blocks should be insignificant[10,11].

When the HVPB block is the continuous phase (as is the case for PBB-40/60 to PBB-10/90), the LVPB phase becomes the dispersed phase and the $\log \tan \delta$ decreases with increasing HVPB content. Phase separation becomes insignificant when the molecular weight of the LVPB block is low and the observed physical properties are dominated by the longer HVPB block. The $T\alpha$ of the LVPB phase starts to rise again as the molecular weight decreases until the LVPB block becomes completely soluble in HVPB, resulting in the disappearance of the $T\alpha$ of LVPB as can be seen for PBB-10/90. The change in $\log G'$ with temperature for PBB-40/60 and PBB-30/70 shows that the phase separation between the two blocks must be incomplete since $\log G'$ changes gradually between the two distinct $T\alpha$s.

The $T\alpha$ of PBB-0/100 at 12°C decreases to 8°C when 10% of the LVPB block is incorporated into the chain (PBB-20/80). The introduction of the LVPB block may be considered as a plasticizer reducing the $T\alpha$ of the polymer. However, the mixing of the blocks in this case must be incomplete since the loss tangent peak appears to be broad. For PB-20/80, the measured $T\alpha$ increases to 9°C; and the $T\alpha$ of the LVPB block can also be seen. However, the $T\alpha$ decreases again for PB-30/70 to 7°C but becomes significant for PB-40/60, resulting in an increased value of the $T\alpha$ of the HVPB block.

The polymer blends exhibit quite different behaviour to the diblock copolymers. The $T\alpha$ of the LVPB component is almost constant, indicating that phase separation is more clearly defined than is the case for the PBB diblock copolymers, presumably the direct consequence of the two polymers not being chemically linked in the blend. Only for BL-60/40 is a gradual decrease in $\log G'$ between the two $T\alpha$s seen, showing that some inter-phase penetration is present in the material. That interphase penetration is possible, is manifest by the observed decrease in the $T\alpha$ of PBB-0/100 when a small weight fraction of PB-100/0 is introduced into the block copolymer (PBB 10/90).

The effect of the overall molecular weight of the polymers on the phase separation can be seen in *Figure 8*. For PBB-50/50-3, the two blocks are too short for any substantial phase separation to take place. However, phase mixing is not complete as the loss tangent peak is quite broad. The $\log G'$–temperature profile for this copolymer (*Figure 9*) supports the hypothesis that only bundles of like units are formed, too small to be seen as fully phase separated by d.m.t.a. The blocks of PB-50/50-1 are phase separated and two loss tangent peaks attributable to the $T\alpha$s of the two components can be seen. Intermediate properties are observed in PBB-50/50-2, which has a molecular weight between that of PBB-50/50-1 and PBB-50/50-3. The $T\alpha$ of the HVPB block can be seen, although the phase boundaries must be diffuse since the $\log G'$–temperature plot decreases with increasing temperature. The $T\alpha$ of the LVPB block can also be identified.

CONCLUSIONS

The dynamic mechanical properties of the PBB diblock copolymers depend on their morphology, which is itself related directly to the molecular structure of and composition of the copolymers. Phase separation is a function of the overall molecular weight of the diblock copolymers and the molecular weight of each block since, for a given overall molecular weight, an increase in the block length of one block results in a decrease for the other. For the copolymers examined, the composition determines the block length, whereas for the polymer blends, a change in composition has not influenced the molecular weights of the two homopolymers used.

The compatibility of HVPB and LVPB is undoubtedly enhanced by linking the two polymers together in a block copolymer.

Yoshioka *et al.*[12] reported that a vulcanized product of vinyl polybutadienes having approximately 70% vinyl content is suitable for passenger-car tyres. Blends of *cis*-1,4-polybutadiene and high-vinyl polybutadiene also exhibit an excellent balance between rolling resistance and wet-skid resistance. Odar and Von Hellens[13] support these claims. In fact, the dynamic mechanical properties of a 50/50 blend of 77.8% vinyl polybutadiene with *cis*-1,4-polybutadiene[12] resemble those of PBB-50/50-2, which has also a similar value of the molecular weight. Further experiments are required to establish the utility of the block copolymers described in this work for tyre applications. In particular, it is necessary to investigate the physical properties of the vulcanized copolymers.

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