Dynamic–mechanical properties of polybutadiene rubbers

M. A. Mohsin, J. P. Berry and L. R. G. Treloar*
Department of Polymer Science and Technology, University of Manchester Institute of Science and Technology, Manchester, M60 1QD, UK
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The dynamic properties of high-*cis* (98%) and *cis–trans* (42% *cis*) polybutadienes, crosslinked with 0.1 to 1.0% of crosslinking agent, have been studied using a torsion pendulum method over the temperature range −170 to +20°C. For the high-*cis* rubber plots of damping factor (tan δ) against temperature showed the expected peak in the glass-transition region with an additional peak in the neighbourhood of 0°C attributable to crystallization. The *cis–trans* rubber showed two damping maxima in the transition region, separated by 30 to 40°C (depending on the degree of crosslinking), suggesting incipient phase separation of the component structures. The rebound resilience of the high-*cis* rubber at room temperature exceeded that of the *cis–trans*, reaching 92% at the highest crosslink density. Plots of resilience *versus* temperature for both rubbers showed a single minimum in the glass transition region.

(Keywords: polybutadiene; torsion pendulum; rebound resilience; dynamic modulus G'; loss modulus G''; loss tangent tan δ)

1. OBJECTIVES AND EXPERIMENTAL METHODS

Polybutadiene rubbers are of particular interest on account of their exceptionally high rebound resilience at room temperature, which is directly related to their extremely low glass-transition temperature (T_g). The object of the present work is to explore the relation of their rebound resilience to the more general dynamic-mechanical properties over a wide range of temperature (both above and below T_g), with particular reference to the effects of differences in molecular structure and the degree of crosslinking.

For this purpose two types of polybutadiene have been examined. These are Cariflex 1220 (supplied by the Hubron Rubber Company), stated to be of 98% *cis* configuration, and Intene 50NF (supplied by the International Synthetic Rubber Company), having the approximate composition 42% *cis*, 48% *trans* and 10% vinyl configuration (by weight). For each of these materials measurements of dynamic modulus and loss were made by means of the torsion pendulum over the temperature range −170 to +20°C and of rebound resilience over the range −100 to +20°C. The degree of crosslinking was varied by the use of 6 different concentrations of crosslinking agent in each case. Associated data on transition temperatures were also obtained from d.t.a. measurements.

2. TORSION PENDULUM METHOD

(*a*) *Apparatus*

The essentials of the torsion pendulum apparatus are shown in *Figure 1*. The specimen (A), of length 25 mm and approximate cross-section 10 × 4 mm, was held between a lower fixed clamp and an upper clamp rigidly connected to the inertia bar (B), which was suspended by the steel wire (C), carrying the counterpoise weight (E). The hand-operated lever (G) enabled the lower clamp to be momentarily rotated through a small angle to initiate the oscillations. These oscillations were detected by the capacitative proximity gauge (H), connected to an amplifier and pen-recorder. The temperature was reduced to a low value by charging the chamber (J) with liquid nitrogen, recordings being taken at intervals of 5°C, as measured by the thermocouple (K). During the subsequent warming-up period, the rate of warming was maintained approximately constant (at 1°C min^{-1}) by a controlled power input to heating coils (not shown) surrounding the chamber. The pendulum assembly was enclosed by a Perspex cabinet to eliminate draughts.

The period of oscillation varied between 0.5 s and 9 s approximately over the range of temperature covered by the experiments.

(*b*) *Calculations of* G′, G″ *and tan* δ

The period P and logarithmic decrement Δ were obtained directly from the pen-recorder trace. The in-phase and out-of-phase components G' and G'' of the complex shear modulus were obtained from the relations[1]

$$G' = (Il/kP^2)(4\pi^2 - \Delta^2) \qquad (1)$$

$$G'' = 4\pi Il\Delta/kP^2 \qquad (2)$$

in which I is the moment of inertia, l the specimen length, and k a shape factor given by

$$k = 1/3bh^3(1 - 0.63h/b) \qquad [h/b < 0.5] \qquad (3)$$

where b is the width and h the thickness of the specimen. The damping factor is represented by

$$\tan\delta = G''/G' \qquad (4)$$

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* During publication of this paper it was learned of the untimely death of Professor L. R. G. Treloar. A series of papers commemorating his contribution to polymer science will be published in Polymer early in 1986.

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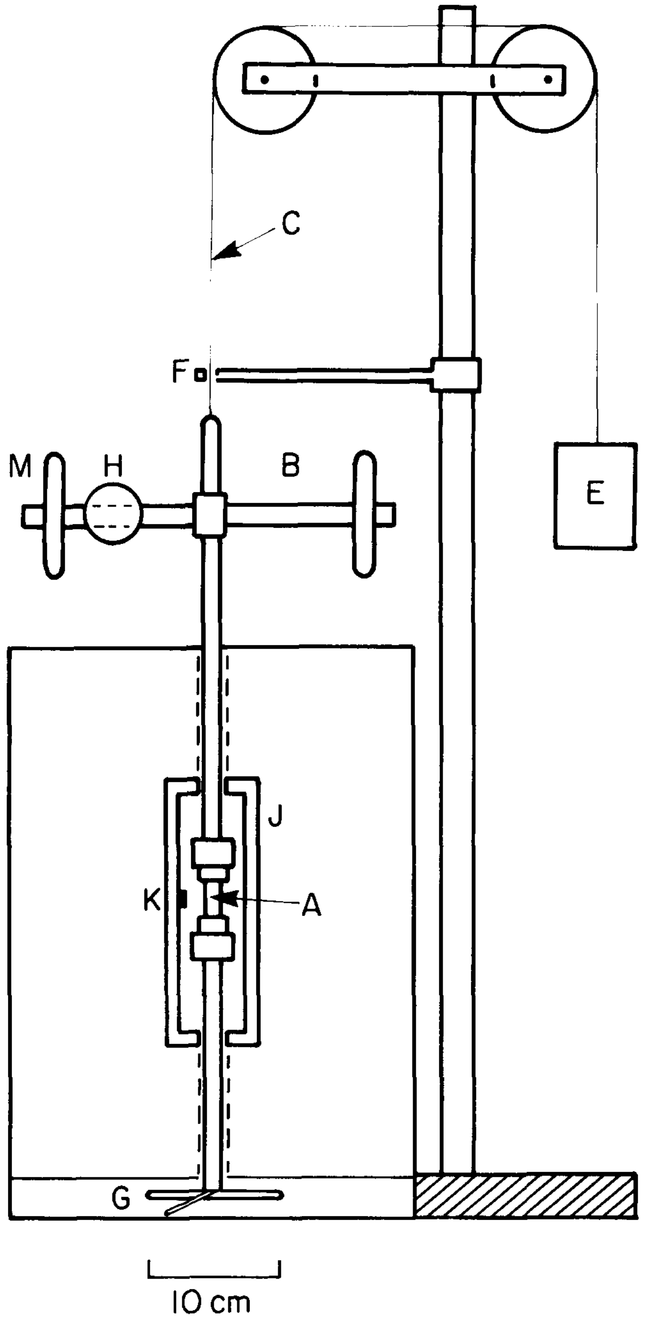

Figure 1 Torsion pendulum apparatus: Specimen (A); inertia bar (B); steel wire (C); counterpoise weight (E); teflon bush helps to reduce parasitic oscillation (F); hand-operated lever (G); capacitative proximity gauge (H); chamber (J); thermocouple (K); mass (M)

3. TORSION PENDULUM DATA

(*a*) Cis–trans *polybutadiene*

Sheets of approximate thickness 4 mm were press-cured for 15 min at 165°C with tert-butyl perbenzoate (TBPB) at concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 wt%. Plots of log G' and log tan δ for selected samples are shown in *Figures 2* and *3* respectively. The most noticeable feature of these results is the presence of two separate maxima in the curves for log tan δ *versus* temperature. Corresponding, though less striking, effects are visible also in the log G' curves, in which a definite shoulder is observed in the region of the second damping peak.

The positions of the two peaks for all the samples studied are listed in *Table 1*, from which it is seen that the lower-temperature peak (T_1) moves progressively to higher temperatures with increasing concentration of TBPB. The second peak (T_2) on the other hand, shows at first a slight shift towards lower temperatures with increasing TBPB concentration, followed by a displacement in yhe opposite direction at higher concentrations. The resultant separation of the two peaks is reduced from 40°C at 0.1% to 28°C at 1.0% concentration.

The variation of G', G'' and tan δ with concentration of crosslinking agent at 20°C is shown in *Figure 6*.

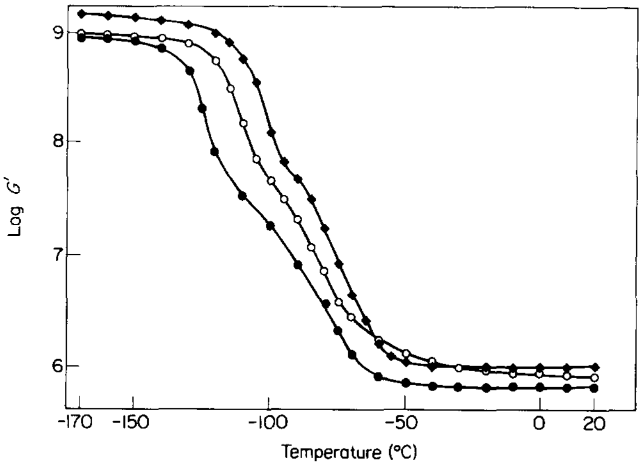

Figure 2 *Cis–trans* polybutadiene. Variation of log G' with temperature for TBPB concentrations of 1.0% (●), 0.4% (○) and 1.0% (◆). (G' in N m^{-2})

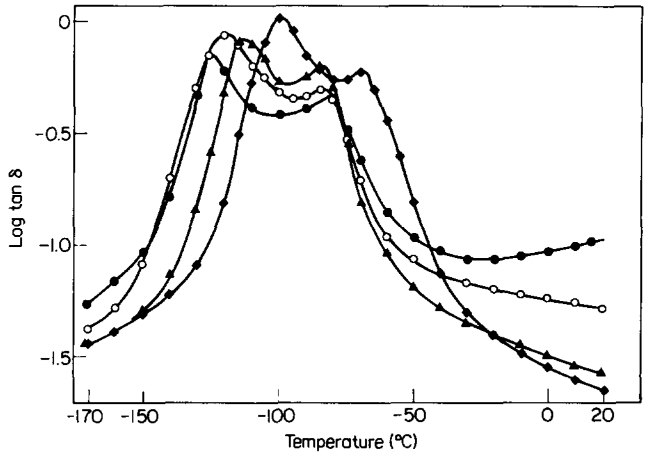

Figure 3 *Cis–trans* polybutadiene. Variations of log tan δ with temperature for TBPB concentrations of 0.1% (●), 0.4% (○), 0.6% (▲) and 1.0% (◆)

Table 1 *Cis–trans* polybutadiene. Positions of maxima in tan δ and d.t.a. curves (°C)

% TBPB	tan δ		d.t.a.	
	T_1	T_2	T_1	T_2
0.1	−122	−82	−96	−77
0.2	−119	−88	−89	−73
0.4	−116	−84	−86	−65
0.6	−111	−83	−80	−55
0.8	−109	−82	−77	−52
1.0	−98	−70	−70	−45

(*b*) *High*-cis *polybutadiene*

Samples of high-*cis* polybutadiene were prepared in the same way as the *cis–trans* samples, except for the use of dicumyl peroxide (DCP) as crosslinking agent. The curing conditions were identical.

Data for log G' and log tan δ for samples of different DCP concentration are shown in *Figures 4* and *5*. In contrast to the *cis–trans* polymer this material showed only a single peak in the log tan δ curves in the region of -100°C, though for DCP concentrations of 0.6% or less a small 'shoulder' was apparent in the region of -150°C. However, at the lower DCP concentrations a second peak was present at temperatures between -5 and $+5$°C (*Table 2*). This peak decreased in intensity and merged with the main peak as the DCP concentration was increased, finally disappearing at 1.0% concentration. The corresponding log G' curves show a complex pattern of variation, with a reduction of slope or 'plateau' appearing at around -50°C for the lower DCP concentrations. With increasing DCP concentration this developed into a definite peak, as shown by the 0.6 and 1.0% curves in *Figure 4*. These features, together with the secondary peak in the damping curves, are believed to be associated with crystallization. This is discussed more fully in the Discussion.

Table 2 High-*cis* polybutadiene. Positions of maxima in tan δ and d.t.a. curves (°C)

% DCP	tan δ T_g	tan δ Crystal melting	d.t.a. T_g
0.1	-105	$+5$	-95
0.2	-105	-5	-92
0.4	-102	0	-86
0.6	-102	–	-79
0.8	-100	–	-77
1.0	-100	–	-75

The positions of the observed peaks in the log tan δ curves for all the samples studied are included in *Table 2*.

The variation of G', G'' and tan δ at 20°C with DCP concentration is shown in *Figure 6* for comparison with the corresponding *cis–trans* polymer. For both materials G' increases with concentration of crosslinking agent, while G'' and tan δ decrease. The values of G'' and tan δ, however, are consistently lower for the high-*cis* than for the *cis–trans* material.

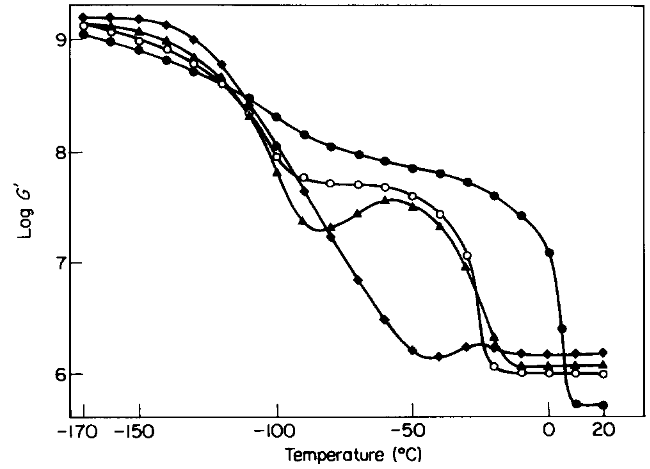

Figure 4 High-*cis* polybutadiene. Variation of log G' with temperature for DCP concentrations of 0.1%, (●); 0.4%, (○); 0.6%, (▲); 1.0%, (◆). (G' in N m^{-2})

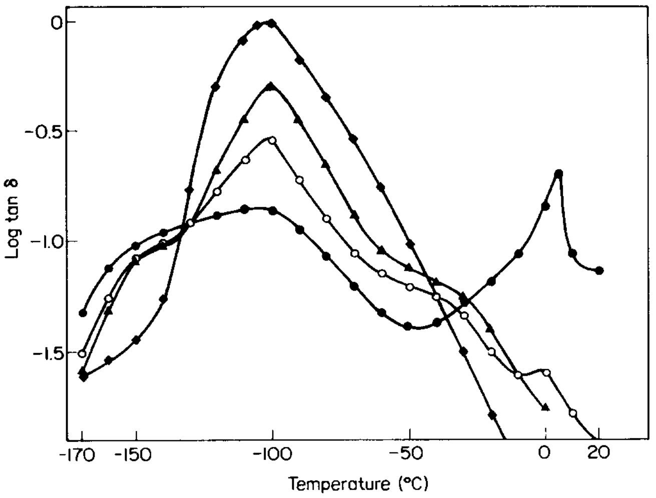

Figure 5 High-*cis* polybutadiene. Variation of log tan δ with temperature for different concentrations of DCP. (0.1%, (●); 0.4%, (○); 0.6%, (▲); 1.0%, (◆) (G' in N m^{-2})

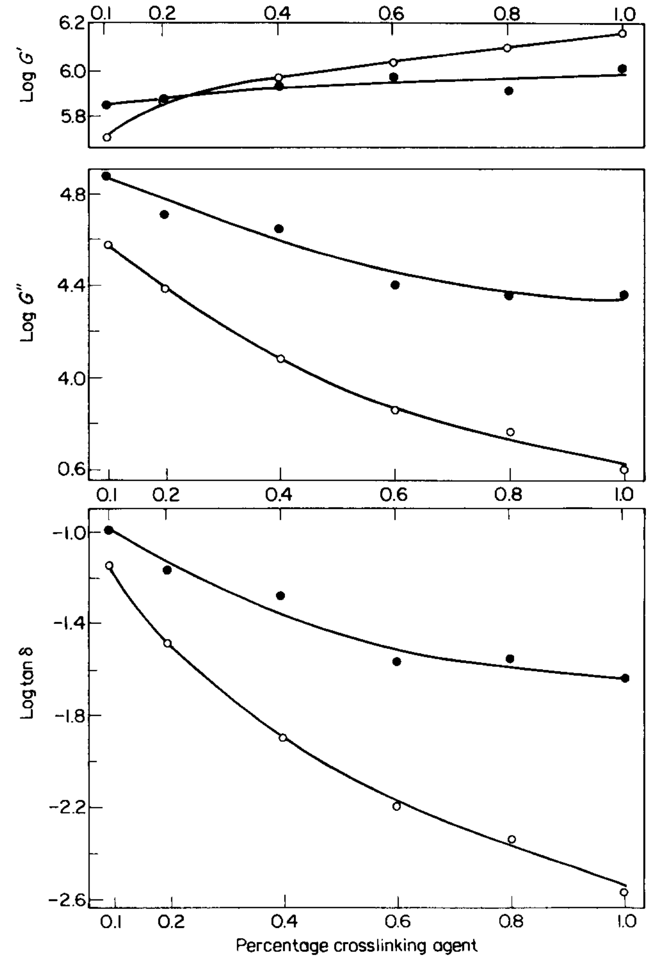

Figure 6 Dependence of log G', log G'' and log tan δ at 20°C on concentration of crosslinking agent. *Cis–trans* polybutadiene (●). High-*cis* polybutadiene (○)

DIFFERENTIAL THERMAL ANALYSIS

All the samples of both types of polybutadiene were examined using a DuPont 990 Differential Thermal Analyser, at a heating rate of 20°C min^{-1}. This instrument recorded automatically both the ΔT curves and their differentials.

The results obtained confirmed the torsion-pendulum data in showing two clearly separated relaxation peaks in the case of the *cis–trans* samples, but only a single peak (with a minor hump at a lower temperature) for the high-*cis* samples (*Figure 7*). For each type the pattern obtained was not affected by the degree of crosslinking of the sample except for a displacement along the temperature scale. The positions of the peaks for all the samples examined are included in *Tables 1* and *2*.

REBOUND RESILIENCE

The rebound resilience of a rubber passes through a minimum at a temperature corresponding to the maximum energy loss, i.e. to the maximum in the tan δ curve. However, owing to the shorter time-scale involved, corresponding to periods in the millisecond region, the minimum resilience occurs at a significantly higher temperature than the maximum damping obtained from torsion-pendulum data.

Measurements of resilience were made by direct observation of the height of rebound of a falling steel ball on to the rubber specimen. Details of the apparatus are shown in *Figure 8*. The test specimen S, of diameter 22 mm and thickness 12 mm, was mounted within the cylindrical brass block (A), which was surrounded by the copper coil (E) for the circulation of liquid nitrogen. Heating elements (B) were provided to enable the rate of temperature rise to be maintained approximately constant, at 2°C min^{-1}. The temperature at 5 mm below the specimen surface was measured by a thermocouple (C). The steel ball (K), of diameter 3.5 mm, was released electromagnetically from the top of the graduated glass tube (D), giving a height of fall, h_0, of 44.5 cm. The range of temperature covered was from −100 to +20°C.

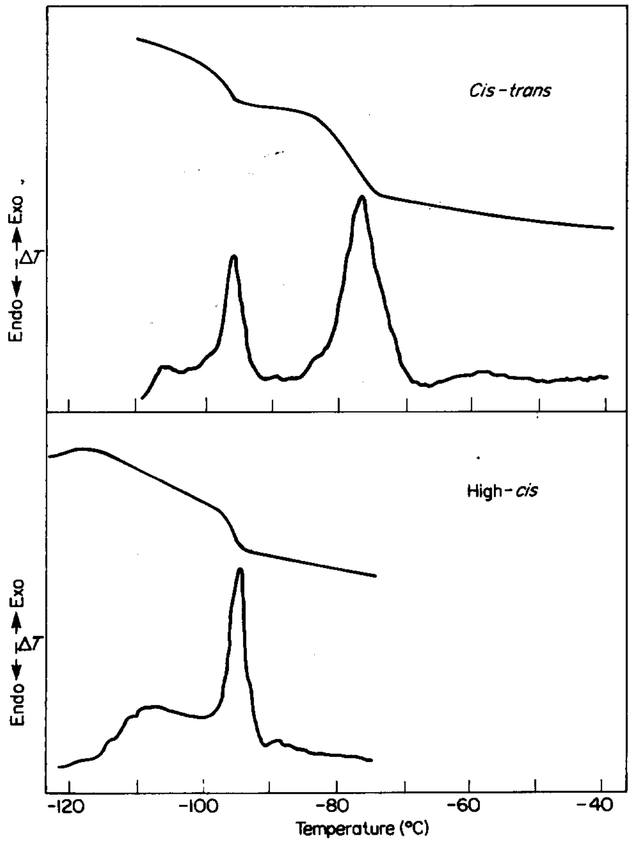

Figure 7 D.t.a. records of ΔT (upper curves) and their derivatives (lower curves) for *cis–trans* and high-*cis* polybutadienes at 0.1% concentration of crosslinking agent

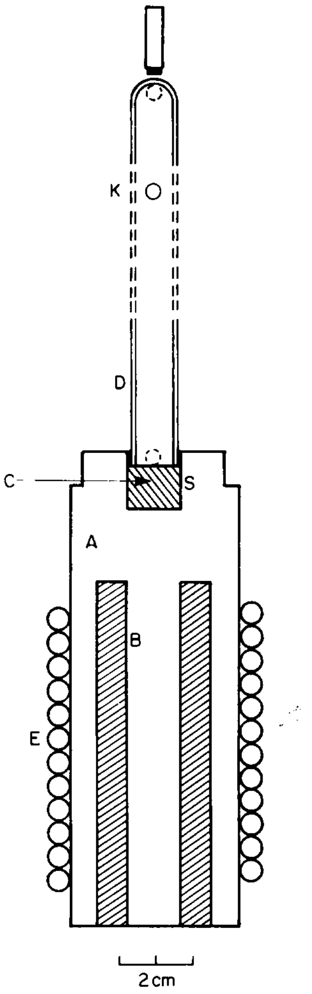

Figure 8 Rebound resilience apparatus

The specimens used for the resilience measurements were moulded as an integral part of the sheets used for the torsion-pendulum experiments by suitably shaping the mould; this eliminated possible variations in curing conditions between the samples. Plots of resilience *versus* temperature for the two polybutadienes studied are shown in *Figure 9*; these relate to the highest concentrations (1.0%) of crosslinking agent employed. For all the samples examined the curves were of this type, showing only a single minimum with no peculiar features of any sort. A comparison of the positions of these minima with the higher of the two torsional damping peaks (T_2) for the *cis–trans* polybutadiene shows a fairly consistent displacement, averaging 20°C (*Table 3*). For the high-*cis* polymer the displacement from the (single) torsional damping peak is rather greater, averaging 28°C. Displacements of this magnitude are consistent with the data of

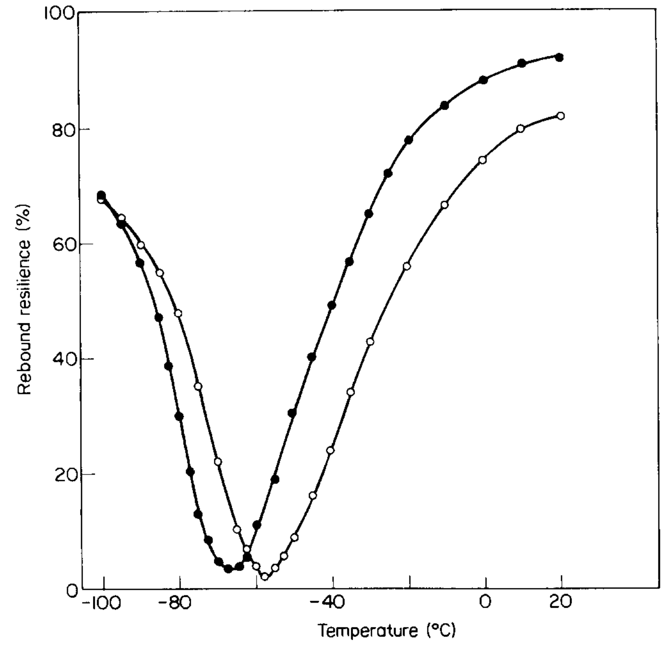

Figure 9 Variation of rebound resilience with temperature for *cis–trans* (○) and high-*cis* (●) polybutadienes at 1.0% concentration of crosslinking agent

Mullins[2] on a variety of rubbers using a pendulum rebound technique.

Table 3 lists also the values of resilience at room temperature (~20°C) for all the samples. These show a continuous increase of resilience with increasing concentration of crosslinking agent, in accordance with the corresponding reduction in tan δ obtained by the torsion-pendulum method (*Figure 6*). Similarly, the values of resilience are consistently higher for the high-*cis* than for the *cis–trans* material, and are greater than 90% in the former case at the highest degrees of crosslinking.

6. DISCUSSION

The principal results which require discussion are:

(a) the presence of a double peak in the damping curve for the *cis–trans* polybutadiene;

(b) the absence of any corresponding effect in the resilience-temperature curves; and

(c) the appearance of a secondary (higher-temperature) peak in the damping curves for the high-*cis* polybutadiene, which is believed to be associated with crystallization.

Table 3 Temperatures of minimum resilience compared with maxima in tan δ for *cis–trans* and high-*cis* polybutadienes (°C)

Type	% TBPB	Temp. of minimum resilience	tan δ T_2	Resilience (%) at 20°C
Cis–trans	0.1	−62	−82	70.5
Cis–trans	0.2	−66	−88	72.0
Cis–trans	0.4	−63	−84	75.0
Cis–trans	0.6	−61	−83	76.0
Cis–trans	0.8	−60	−82	79.0
Cis–trans	1.0	−58	−70	82.0
	% DCP		tan δ T_g	
High-*cis*	0.1	−81	−105	72.0
High-*cis*	0.2	−78	−105	75.0
High-*cis*	0.4	−76	−102	80.0
High-*cis*	0.6	−75	−102	84.0
High-*cis*	0.8	−70	−100	88.0
High-*cis*	1.0	−67	−100	92.0

Double maximum in cis–trans *polybutadiene curves*

The double maximum obtained from the torsion-pendulum data is confirmed by the d.t.a. measurements, though with some displacement along the temperature scale, which may reasonably be attributed to the difference in time-scales of the two methods of measurement. However, the absence of a comparable double minimum in the resilience-temperature curves is surprising. This cannot be attributed to the fact that the lowest temperature attained in the resilience measurements was only −100°C, compared with −170°C for the torsion pendulum data, on account of the displacement of the position of the minimum in the resilience curves by some 20°C compared with the higher of the two maxima in the tan δ curves. This would have given an adequate range for the observation of a second minimum, had such been present.

It has been noted by McCrum[3] that, owing to differences of activation energy associated with different relaxation processes, damping peaks tend to become narrower the higher the temperature of observation. However, it seems unlikely that an effect of this kind could produce a sufficiently drastic change in the form of the damping curves as to cause complete coalescence of the two maxima for a change of temperature of about 30°C only. Moreover, there is no evidence of any such effect in the d.t.a. traces, which are similarly displaced to higher temperatures.

The existence of the double peak in the log tan δ curves for the *cis–trans* polybutadiene suggests the presence of some degree of agglomeration or incipient phase separation of the structural components of this material, presumably between the *cis* and *trans* components. This in turn would seem to imply some departure from a completely random succession of these units in the chain, it being generally accepted that the glass transition is a cooperative process involving a significant number of chain segments. Whether any such structural non-randomness is to be expected on the basis of the polymerization process employed is an open question.

*Secondary peak in high-*cis *polybutadiene curves*

In Section 3(b) (high-*cis* polybutadiene) attention was drawn to the secondary peak in the damping curves at about 0°C and the associated anomalies in the log G' curves at somewhat lower temperatures. The latter effects, which involve an actual *rise* in log G' with rising temperature for certain DCP concentrations (e.g. 0.6%, *Figure 4*) cannot be attributed to a relaxation effect in the usual sense, since any such effect must necessarily lead to a *reduction* of modulus with rising temperature. The phenomenon can, however, be explained if the rise of temperature is accompanied by a change of structure, e.g. crystallization. In a rubbery polymer which is capable of crystallization, a rapid cooling to a temperature below T_g results in a freezing-in of the amorphous structure; subsequent heating at a slow rate enables crystallization to take place over a range of temperature between the T_g

and the crystal melting point[4]. In a study of *cis* polybutadiene by differential thermal analysis Cooper and Smith[5] observed a broad melting peak over the range −20 to −5°C, while Trick[6,7], using a dilatometric method, reported a final melting point of −8°C. These observations support the interpretation of the secondary peak in the present work as an effect of crystallization.

Finally, it may be mentioned that X-ray diffraction studies of the high-*cis* polybutadienes in the stretched state at room temperature showed a strong crystalline 'fibre' pattern at the lowest DCP concentration (0.1%). This diminished in intensity as the DCP concentration was increased, and was absent at concentrations exceeding 0.4%, for which only the amorphous 'halo' was observed. The *cis–trans* polybutadienes showed only the amorphous pattern at all concentrations of cross-linking agent. These observations, while having no direct bearing on the interpretation of the dynamic-mechanical properties, do nevertheless confirm the potential crystallizability of the high-*cis* material under suitable conditions.

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