Monomeric friction coefficient of a styrene–butadiene copolymer

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The monomeric friction coefficient (MFC) of a copolymer of styrene and butadiene (styrene, 11; 1,2-butadiene, 42; 1,4-butadiene, 47 mol%) has been determined by two experimental techniques. Four low molecular weight polymers with similar microstructure but with no molecular entanglements were synthesized. From the zero shear viscosities of these samples, the values of MFC obtained was 1.9×10^{-9} N s m^{-1}. The MFC was also obtained from rheological measurements on the bulk polymer and the value obtained was 2.8×10^{-9} N s m^{-1}. The agreement between the two values is comparable to the agreement reported in the literature for other polymers. By comparing the values obtained with MFC of other polymers, it is demonstrated that the experimentally obtained MFC is consistent with the microstructure of the polymer.

(Keywords: monomeric friction coefficient; Rouse theory; styrene–butadiene copolymer; linear viscoelastic spectrum)

INTRODUCTION

In analysing the viscoelastic behaviour of a polymer, the monomeric friction coefficient (MFC) is an important and useful parameter. The molecular theories of viscoelasticity such as the Doi–Edwards theory[1] and the Rouse theory[2] make use of the monomeric friction coefficient. If the monomeric friction coefficient is known, it is sometimes possible to predict the linear viscoelastic behaviour of a polymer. On the other hand, sometimes the viscoelastic experimental data is used to obtain the MFC. The two are thus intimately related.

MFC is indicative of the resistance encountered by a segment of polymer molecule moving through its surroundings and, hence, is indirectly related to the glass transition temperature. In elastomer science, several properties may be related to the MFC. Recently, a hypothesis has been proposed[3,4], which demonstrates that wet skid resistance (friction between the tyre and the road surface under wet conditions upon application of brakes) may be strongly influenced by the MFC and M_e, the molecular weight between the entanglement points. Hence the MFC takes on an added significance.

MFC and M_e for many rubbers have been documented in the literature[5]. However, no information appears to be available for some of the more recent elastomers. One such polymer is a copolymer of styrene, 1,4-butadiene and 1,2-butadiene. The 1,4-butadiene units may be present in *cis* or *trans* configuration. This polymer was proposed by Bond *et al.*[6] as having excellent tyre tread properties, and similar polymers are currently used commercially in tyre treads. In this paper, we report the MFC of a similar copolymer, which is referred to as VSBR (vinyl styrene butadiene rubber) in the rest of the paper.

Several methods have been described in the literature for experimental determination of MFC[5]. One method is to obtain the MFC from the dynamic mechanical spectrum. In the relaxation (or retardation) spectrum of many polymers, there is usually a small region where the storage modulus (G') or the loss modulus (G''), or both, are proportional to the square root of the applied frequency. In this region, the Rouse theory may be used to obtain the MFC from the viscoelastic data.

Another method involves measurement of zero shear viscosity of polymers of low molecular weight. The molecular weight must be smaller than M_c, the molecular weight above which entanglements influence viscosity. The zero shear viscosity measurements of such polymers are usually straightforward. From viscosity measurements, MFC may be obtained. Reference 5 also lists other methods. It is, of course, desirable to use more than one method to obtain the MFC, so as to have reasonable confidence in the results. In this study, both methods described above were used.

EXPERIMENTAL

The VSBR used in this study was Cariflex 1215, with composition: styrene, 11; 1,2-butadiene, 42; 1,4-butadiene, 47 mol% (obtained from nuclear magnetic resonance (n.m.r.) measurements).

Viscoelastic measurements were made on a RMS 800 Rheometrics mechanical spectrometer. Entanglement molecular weight, M_e, was obtained from the viscoelastic data. Four low molecular weight polymers were synthesized in our laboratory, each having a molecular weight $< M_e$.

The low molecular weight polymers were synthesized by anionic polymerization in cyclohexane. Appropriate amounts of cyclohexane, styrene and butadiene were charged into the reactor. Butyllithium was used as the initiator. Methoxybenzene was used as the modifier, to randomize the microstructure of the polymer and to control the 1,2-butadiene:1,4-butadiene ratio. The polymerization was done at 30°C for 2 h. The reaction was terminated by addition of methanol. The resulting copolymers were centrifuged and dried in a vacuum oven. The microstructure was determined using n.m.r. and

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Fourier transform infra-red (*FT*i.r.) and was found to be comparable to that of Cariflex 1215. Molecular weight distributions were determined by gel permeation chromatography (g.p.c.).

Roughly 10 g of each polymer was synthesized. The zero shear viscosity measurements were made using a falling ball technique. A ball bearing is dropped into the jar containing the polymer and the time required for the ball to fall through a specific distance is measured. The zero shear viscosity is proportional to this time and is calculated according to Stoke's law. The technique has been documented in the literature[7] and is considered to be accurate within ±5%. The glass transition temperature was determined by using a differential scanning calorimeter (d.s.c.) Du Pont 9900, with a heating rate of 10°C min^{-1}.

RESULTS

Figure 1 shows the molecular weight distribution (obtained by g.p.c.). The distribution is bimodal, with each peak having a fairly narrow molecular weight distribution. The number average and weight average molecular weights for the low molecular weight peak were 96 400 and 107 000, respectively, while for the high molecular weight peak, they were 356 000 and 392 000, respectively.

Figure 2 shows the viscoelastic behaviour of VSBR. The master curve represents the combination of experimental data at several temperatures (−30, −20, 0, 30 and 60°C). The experimental data at different temperatures was physically shifted to obtain the master curve. This mainly involved a shift along the frequency axis, with a slight shift along the modulus axis. A characteristic feature of the terminal region (low frequency) behaviour appears to be that the two curves (G' and G'') run parallel to each other over a limited frequency range (0.1–0.001 rad s^{-1}). This contrasts with the behaviour of a linear polymer, where the two curves (G' and G'') cross at an intermediate frequency, before the storage modulus reaches a plateau. In *Figure 2* there is no crossover. At low frequency, the two curves appear to be slowly coming together and there may be a crossover at very low frequencies (assuming the sample contains no gel). This type of behaviour has been documented in the literature for polybutadiene and is usually indicative of the presence of some long range branching in the polymer[8].

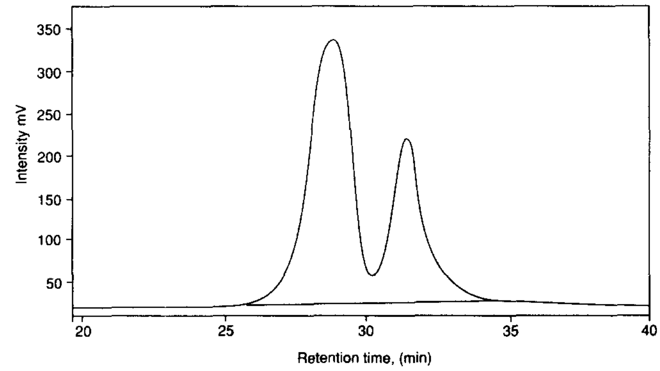

Figure 1 Molecular weight distribution of VSBR (obtained by g.p.c.)

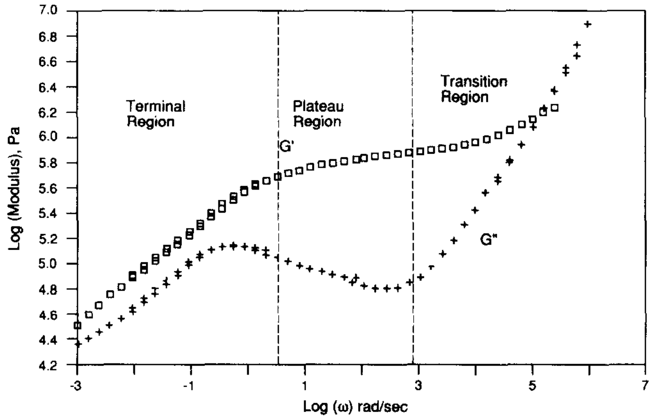

Figure 2 Linear viscoelastic behaviour of VSBR at 25°C. G', storage modulus; G'', loss modulus; ω, frequency

The plateau modulus is the limiting value of the storage modulus at the completion of the terminal region relaxation. Calculation of the precise value of plateau modulus is not straightforward. However, an approximate value may be obtained from the plateau in the G' curve in *Figure 2*. From the plateau modulus (G_∞), M_e can be determined by the simple equation,

$$M_e = dRT/G_\infty \qquad (1)$$

where d, R and T are the density, universal gas constant and temperature, respectively. The value of M_e obtained in this manner was 3250. This value is comparable to the M_e of linear poly(1,2-butadiene) and also that of a linear (styrene–butadiene) copolymer (*Table 1*). The presence of long term branching, if any, does not appear to influence M_e significantly, which is consistent with findings in the literature[8].

The low molecular weight polymers should have molecular weights $<M_c$, the critical molecular weight influencing the zero shear viscosity by entanglement coupling. While M_c and M_e are related, the relationship is not simple and varies from one polymer to another. It is probably advisable to stay well below M_c, to avoid the possibility of going into the entangled region (unless M_c is known precisely). However, $M_e < M_c$, for almost all the polymers reported on in the literature. Hence the low molecular weight polymers were synthesized so that the number average molecular weight $(\bar{M}_n) < M_e$. In addition, it is important that these polymers have a narrow molecular weight distribution. *Table 2* lists the $\bar{M}_n$ and polydispersity index $(\bar{M}_w/\bar{M}_n)$ obtained from g.p.c. measurements. The zero shear viscosity obtained by the falling ball technique is also recorded in *Table 2*.

Table 1 Microstructure, entanglement molecular weight, M_e, and monomeric friction coefficient (MFC) of various polymers

	Microstructure (mol%)				
		Butadiene			log(MFC)
				M_e	at 25°C
Polymer	Styrene	1,4	1,2	at 25°C	(N s m^{-1})
VBR1		8.5	91.5	3550	−7.11
SBR	12	88		3000	−9.11
VSBR	11	47	42	3250[a]	−8.71[b] −8.56[a]
VBR2		58	42	2730[c]	−9.83[c]
polystyrene	100			16 000 at 100°C	−0.94 at 100°C

[a] Obtained from rheological measurements

[b] Obtained from the zero shear viscosity of low molecular weight polymers

[c] Obtained by extrapolation[11]

All other data is from Reference 5

DISCUSSION

From the linear viscoelastic spectrum, MFC is obtained by using the Rouse theory. In the transition region, the relaxation times are sufficiently short that the following approximate expression is obtained for G', G'' from the Rouse theory[5]:

$$G''=G'=\left(\frac{a\rho N_0}{4M_0}\right)(\zeta kT/3)^{1/2}\omega^{1/2} \qquad (2)$$

where ρ is the density, N_0 is Avogadro's number, M_0 is the monomer molecular weight, ζ is the MFC, a is the characteristic length, k is the Boltzmann constant and ω is the frequency. In the transition region viscoelastic spectrum of many polymers, there is usually a small frequency range where $G'=G''$ and both are proportional to the square root of frequency. If G' or G'' is known in this region, the MFC may be calculated. This approach is subject to several approximations, e.g. the exact value of a may not be known. For a copolymer such as VSBR, the precise value of M_0 may also be unknown. However, this method is widely used for estimating the MFC[5].

In principle, G' and G'' are equal and are given by equation (2). In practice, however, G'' starts showing this dependence at a much lower frequency than G'. In *Figure 2*, G'' shows this dependence over the frequency range $>1000\,\text{rad s}^{-1}$. G' is expected to show this dependence at higher frequency, which was not accessible experimentally.

Figure 3 shows a plot of G'' *versus* frequency over the range 1000–$100\,000\,\text{rad s}^{-1}$. The slope of the straight line is 0.58, which agrees reasonably well with the slope of 0.5 required for the application of Rouse theory. With this difference in slope, the values of MFC calculated at 1000 and $100\,000\,\text{rad s}^{-1}$ (the two extremes in *Figure 3*) according to equation (2) differ by ≈40%. The mid-point of this range ($10\,000\,\text{rad s}^{-1}$) was selected for calculation of MFC. The density was obtained experimentally. The parameters N_0 and k are available in the literature. M_0 was calculated from the microstructure. The characteristic length, a, is specific to a polymer. While a is not known for VBSR, it varies little from one polymer to another (e.g. for 28 plastics and rubbers listed in Reference 5, a ranges from 0.55 to 0.875 nm). The values of a for polystyrene, poly(1,2-butadiene) and poly(1,4-butadiene) are 0.7, 0.755 and 0.6 nm, respectively. Hence the value for VSBR is probably between 0.755 and 0.6 nm. For this calculation, $a=0.7$ nm was assumed.

Table 2 Viscosity and molecular weight data[a] for low molecular weight (styrene–butadiene) copolymers

Sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	η_0 at 25°C (Pa s)	log(MFC) at 25°C (N s m^{-1})
A	983	1.07	0.345	−9.79
B	1410	1.07	2.087	−9.16
C	1940	1.10	3.622	−9.06
D	3050	1.06	12.72	−8.71
Bulk polymer				−8.56

[a] $\bar{M}_n$, number average molecular weight; $\bar{M}_w$, weight average molecular weight; η_0, zero shear viscosity; MFC, monomeric friction coefficient

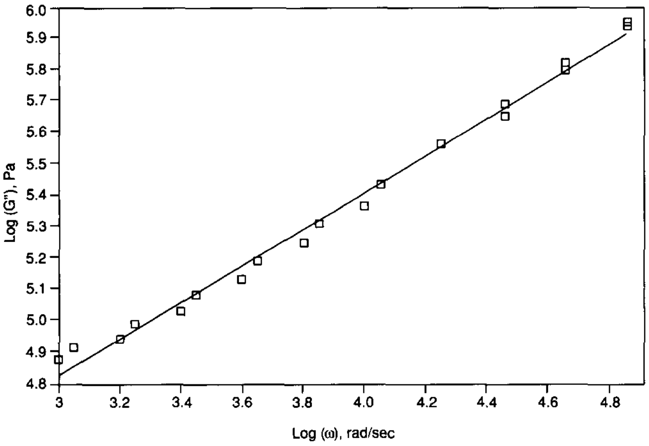

Figure 3 Dependence of the loss modulus (G'') on frequency for VSBR in the transition region at 25°C

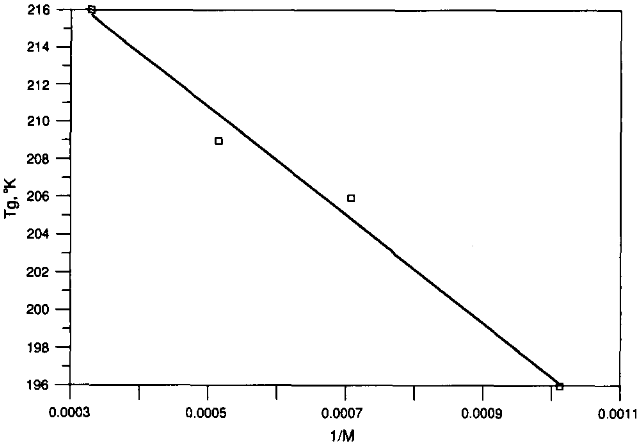

Figure 4 Dependence of glass transition temperature (T_g) on number average molecular weight (M) of low molecular weight polymers (described in *Table 2*)

All the quantities in equation (2) except MFC are known and hence MFC can be calculated. The value obtained was

$$\log(\zeta)=-8.56 \quad \text{or} \quad \zeta=2.76\times10^{-9}\,\text{N s m}^{-1} \qquad (3)$$

The other method for determining the MFC requires a study of low molecular weight polymers. *Figure 4* shows a plot of glass transition temperature (T_g) as a function of number average molecular weight. The four points lie on a straight line with a correlation coefficient of 0.984. Using a least squares fit, the empirical relationship between the two parameters may be obtained:

$$T_g=224-28\,000/M \qquad (4)$$

The prefactor to $1/M$ is 28 000, which is considerably smaller than that for polystyrene[9] but greater than that for 1,4-polybutadiene[10]. Extrapolation to infinite molecular weight gives 224 K, which is slightly smaller than the experimentally obtained value of 229 K for the bulk polymer. A similar discrepancy has been observed for 1,4-polybutadiene[10], which has been attributed to small differences in the microstructure.

From the zero shear viscosity data for low molecular weight samples, MFC is given by[5]

$$\zeta=36M_0^2\eta_0/\rho a^2 N_0 M \qquad (5)$$

The quantities have been defined above, except M, which represents the molecular weight (weight average molecular weight for a polydisperse polymer). The quantity η_0/M was evaluated separately for each polymer. The MFC thus obtained is listed in *Table 2* for each polymer. The MFC increases with molecular weight. The reason for this is that T_g increases with molecular weight and since the MFC is reported at 25°C for all the polymers, the polymer with higher molecular weight is closer to T_g. The MFC obtained from rheological measurements is also listed in *Table 2*. In the literature[5] the values of MFC obtained by both methods have been listed for several polymers, and the two methods agree to within a factor of ≈ 3. In view of that, the agreement obtained in this study (between the MFC of sample D and that of the bulk polymer) appears to be reasonable (*Table 2*). However, the difference between T_g of the bulk polymer and that of sample D is ≈ 13 K. This indicates that there is probably still some influence of chain ends on T_g and MFC for molecular weight as high as 3050. An extensive study of 1,4-polybutadiene[10] indicates that this influence may be felt at molecular weight M_c or higher.

A comparison of the value of MFC for VSBR with that for other polymers may be useful. *Table 1* lists the MFC of several polymers. The MFC for VSBR is significantly greater than that for polybutadiene with comparable microstructure but no styrene (VBR2). This is consistent with the well known fact that the butadiene unit is much more flexible than the styrene unit at any given temperature, and replacing butadiene by styrene (to obtain VSBR) results in a substantial increase in MFC. Hence the MFC of VSBR is greater than that of polybutadiene (with 42% 1,2-units), but is substantially less than that of polystyrene. The MFC of VSBR is also greater than that of SBR, which contains a comparable amount of styrene but a very small amount of vinyl (1,2-) butadiene groups. It has been well established that the vinyl butadiene group is much stiffer than the 1,4-butadiene group at any given temperature. The MFC of VSBR, however, is smaller than that of polybutadiene with a high amount of vinyl units (VBR1). This is also consistent with findings in the literature. It has been observed[11] that, in polybutadiene, changing the vinyl content from a very low value to $\approx 50\%$ leads to a moderate increase (a factor of ≈ 5) in MFC, while changing it from 50 to 90% results in a large increase in MFC (two orders of magnitude). Hence the increase in MFC of SBR as vinyl butadiene content is increased from a very low value to 47% is expected to be small. Thus the MFC values of SBR and VSBR in *Table 1* are comparable (that of VSBR being higher), both being substantially smaller than that of VBR1.

From this discussion, it is clear that the experimentally observed MFC of VSBR is roughly where it is expected to be based upon the consideration of the stiffness of the various groups composing the molecule. To my knowledge, this is the first time that the Rouse theory has been used to obtain the MFC of a random copolymer with three different structural units (copolymer of 1,2-butadiene, 1,4-butadiene and styrene) and it is encouraging to note that, even for such a complex polymer, the Rouse theory yields a reasonable answer, consistent with the microstructure.

CONCLUSION

The monomeric friction coefficient of VSBR has been obtained by two different experimental techniques. There is reasonable agreement between the values obtained by the two techniques. By comparing the values obtained with the monomeric friction coefficient of other polymers, it may be concluded that the experimentally obtained MFC is consistent with the microstructure of the polymer.

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