JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 3311–3318 (1977)

The Entanglement Plateau in the Dynamic Modulus of Rubbery Styrene–Diene Block Copolymers. Significance to Pressure-Sensitive Adhesive Formulations

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Synopsis

Styrene–diene (butadiene or isoprene) block copolymers of the SDS or $(\mathrm{SD}\rangle_x$ type exhibit a plateau in the dynamic storage modulus located between the glass transitions of the polydiene and polystyrene domains. When the polydiene is the continuous phase, the height of this plateau can be estimated with good success from the entanglement spacing molecular weight of the polydiene and the filler effect of the polystyrene domains. The effect of introduction of a center block-compatible diluent can also be calculated, although the simple procedure used here tends to underestimate the plasticizer effect, particularly at high diluent concentration. Nevertheless, the calculation furnishes a useful criterion of compatibility of the polydiene center blocks and low molecular weight resins used commonly as tackifiers in pressure-sensitive adhesives. Center block compatibility is essential for the development of tack in these compositions.

INTRODUCTION

The dynamic storage modulus of high molecular weight SDS block polymers (S = styrene, D = butadiene or isoprene) exhibits a plateau region between the two domain glass transitions. The height of this plateau is governed mainly by the connectivity of the glassy polystyrene domains. However, when the polystyrene domains are spherical, which is usually the case when the styrene content does not exceed 20% by weight, the plateau modulus may be expected to be determined by the density of the entanglement network of the rubbery center blocks, augmented by the reinforcing effect of the polystyrene domains. It is shown that this is true not only for the pure block polymers, but also for their blends with center block-compatible diluents. The latter case has important implications in the use of these polymers in pressure-sensitive adhesives.

THEORETICAL CONSIDERATIONS

The quasiequilibrium shear modulus of an entanglement network is given by application of the theory of rubber elasticity as

$$G_{eN}^{0} = (\rho/M_e)RT \tag{1}$$

where ρ is the density, M_e is the entanglement spacing molecular weight, and R and T have their usual meaning. High molecular weight homopolymers and random copolymers exhibit a plateau in the (isothermal) G'-versus-frequency curve at the level of G_{eN}^0. In dynamic data at fixed frequency and varying temperature, this plateau is also discernible, at least as an inflection point which occurs *near* the minimum in tan δ. In block polymers, there is additional reason for selecting G' at the minimum in tan δ to compare with G_{eN}^0—it is the point on the curve least affected by the two domain glass transitions and represents the closest approach to a quasiequilibrium state. However, before a valid comparison can be made it is necessary to introduce the filler effect. As shown by Holden,[1] for spherical polystyrene domains the Guth and Gold[2] equation should apply, hence,

$$G_{eN}^0 = (\rho/M_e)RT(1 + 2.5c + 14.1c^2) \cong G'(\tan \delta_{\min}) \tag{2}$$

where c is the filler (polystyrene) volume fraction and T is now the temperature at the minimum in tan δ.

The effect of a diluent on the entanglement plateau modulus is to reduce it by $v_2{}^2$, the square of the volume fraction of polymer.[3] Thus, if all the diluent is assumed to enter the rubber phase of the block polymer,

$$G'(\tan \delta_{\min}) \cong v_2{}^2\,(\rho/M_e)RT(1 + 2.5c + 14.1c^2) \tag{3}$$

Note that v_2 is the volume fraction of polymer in the rubbery phase alone, while c is the volume fraction of polystyrene in the entire composition. Also, ρ/M_e is the entanglement density in the *undiluted* rubber. Values of M_e for the homopolymers are given by Ferry[3] as follows: polybutadiene, 1900; polyisoprene, 5750. We assume that these values apply also to long sequences of butadiene and isoprene units in block polymers.

The block copolymers used in this study were products of alkyllithium polymerization and were either of the linear (SDS) or of the radial multichain $(\mathrm{SD}\!\!\rightarrow)_x$ type. In the latter, the functionality of the central branch point was approximately 4. The presence of a single crosslink per molecule has no discernible influence on the entanglement network, and its effect was neglected.

EXPERIMENTAL

Polymer characterization data are given in Table I. Molecular weights were determined by gel permeation chromatography using universal calibration and do, where applicable, take into account long-chain branching.

Commercial polymeric resins of low molecular weight, commonly used in formulation of pressure-sensitive adhesives, were used as diluents. Diluent concentration was varied from 43% to 56% by weight. Resins investigated are shown in Table II.

Films approximately 0.05 cm thick were compression molded at 153°C between silicone release paper. From these, small (0.318 × 0.318 cm) test pieces were cut for determination of the complex dynamic moduli. The latter were measured with a Vibron Model DDV-II viscoelastometer (Toyo Instrument Co., Tokyo, Japan) at 35 Hz in the shear mode.

For electron microscopy, ultrathin sections were prepared by cryomicrotomy and stained by the osmium tetroxide technique of Kato.[4] They were then examined under a Philips EM 300 transmission electron microscope.

TABLE I
Polymer Characterization Data

No.	Diene	Styrene, %	Structure[a]	$M_w/1000$	$M_n/1000$
1[b]	Isoprene	0	L	1963	626
2	Isoprene	15	L	130	83
3	Isoprene	15	R	314	217
4	Butadiene	0	R	223	173
5	Butadiene	0	R	298	228
6	Butadiene	10	R	199	157
7	Butadiene	20	R	103	87
8	Butadiene	20	R	149	120
9	Butadiene	20	R	204	163
10	Butadiene	20	R	314	241

[a] L = Linear; R = radial.
[b] *cis*-Polyisoprene.

Pressure-sensitive tack was measured on 0.003–0.005-cm-thick films using a Polyken Probe Tack Tester. The probe material was No. 304 stainless steel. Contact time was 1 sec, contact pressure, 10 kPa, and probe separation rate, 1 cm/sec. Test results given are averages of five specimens.

RESULTS

Figure 1 shows the storage modulus and loss tangent of polymer 9, a butadiene–styrene block polymer of 20% styrene content, as a function of temperature. The plot is typical of the data obtained for all block polymers of this study. Note the pronounced plateau in G', extending from about −20°–+60°C, and the minimum in tan δ locating the approximate center of the plateau. Data for the same polymer blended in equal weights with the rosin ester diluent (resin A) are shown in Figure 2. The effect of the diluent is to shift the low-temperature maximum in tan δ from −82° to −12°C and to lower the value of G' at temperatures exceeding −8°C. There no longer exists a real plateau, only a region of diminished slope. Whereas with the pure polymer the definition of the "plateau modulus" by the minimum in tan δ is not critical to the evaluation of G_{eN}^0, it is so with the diluted polymer and introduces an element of uncertainty.

For the undiluted homopolymers, there is very good agreement between G' (tan $\delta_{\min}$) and G_{eN}^0 calculated from eq. (1):

	$T(\tan \delta_{\min})$, °C	$G'(\tan \delta_{\min}) \times 10^{-6}$, dyn/cm²	G_{eN}^0 (calc.) $\times 10^{-6}$, dyn/cm²
Polybutadiene (#4)	−40	11.0	9.1
Polyisoprene (#1)	24	3.9	3.9

Figure 3 shows a comparison of $G'(\tan \delta_{\min})$ calculated by the appropriate equation, (1), (2), or (3), with experimental values. Satisfactory agreement is obtained also for the block polymers, but for compositions containing large amounts of diluent, the calculation overestimates the "plateau" modulus by a factor of roughly 1.5.

TABLE II
Resins Investigated

Resin	Trade Name	Type	Source
A	Foral 85	Rosin ester	Hercules, Inc.
B	Wingtack 95	Polyterpene	Goodyear Chemical Co.
C	Super Sta-Tac 80	Polyolefin	Reichold Chemical Co.
D	Zonarez 7085	Polydipentene	Arizona Chemical Co.
E	Zonarez B-85	Poly(β-pinene)	Arizona Chemical Co.
F	Picco Alpha 115	Poly(α-pinene)	Hercules, Inc.
G	Resin 18-240	Poly(α-methylstyrene)	Amoco Chemical Co.
H	Cumar LX-509	Coumarone-indene	Neville Chemical Co.

Electron-microscopic examination showed spherical polystyrene domains in all the block polymers. Not all the block polymer/diluent mixtures were examined, but those that were and for which data are displayed in Figure 3 likewise exhibited spherical morphology.

DISCUSSION

For the homopolymers $G'(\tan \delta_{\min})$ not only shows good formal agreement with the calculated G_{eN}^{0}, but the frequency and temperature of measurement is easily shown to place the data squarely into the entanglement plateau region for these rubbers as determined by Ferry and associates.[5,6] The success of eq. (2) for the pure block polymers (unflagged points in Fig. 3) thus supports the contention that the height of the plateau in G' is governed by the entanglement network of the center blocks augmented by the filler effect of the spherical polystyrene domains. It also supports the assumption that normal (homopolymer) entanglement spacings prevail in the polydiene continuum of the block polymers.

There are several reasons why the calculation for the diluted block polymers provides less satisfactory agreement. The entanglement region of viscoelastic response is not as well defined, and the procedure for locating its center by the minimum in tan δ is only an approximation. Also, this minimum is shifted toward higher temperature, where the segmental motions of the polystyrene blocks may no longer be frozen in, particularly in the interphase region between the matrix and the polystyrene domains. The effect of this would be a decrease in the observed storage modulus. Finally, the v_2^2 relation, eq. (3), for the diluent effect has not been extensively tested experimentally and may well be an oversimplification. Consequently, the prediction of $G'(\tan \delta_{\min})$ to within $3/2$ of the observed value without the use of adjustable parameters must be regarded as a successful confirmation of the basic ideas underlying the extremely simple theory. Moreover, the calculation can serve as a simple practical test for compatibility of a diluent with the diene portion of block polymers of the present type and has important implications in their use in adhesives.

When a polymeric diluent of $T_g \gg T_g$ (polydiene) is polystyrene-compatible or is incompatible with either phase of the block polymer, the result must be an increase in G' in the plateau region—not only can there be no plasticization of the rubbery matrix, but the effective total filler content is increased.

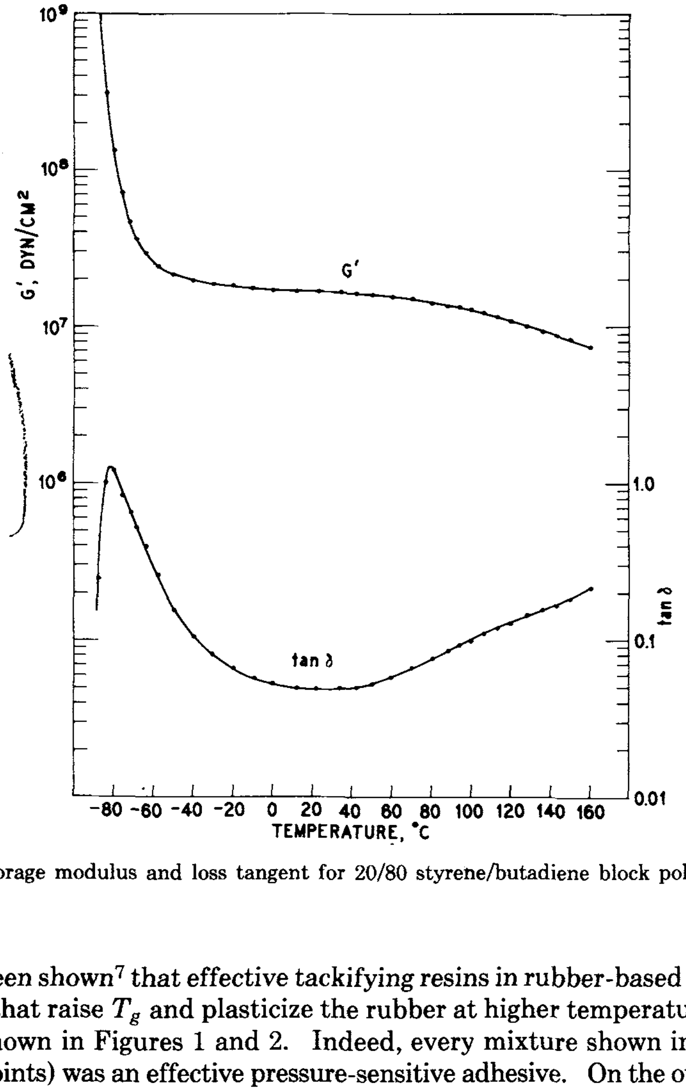

Fig. 1. Storage modulus and loss tangent for 20/80 styrene/butadiene block polymer (polymer 9).

It has been shown[7] that effective tackifying resins in rubber-based adhesives are those that raise T_g and plasticize the rubber at higher temperatures in the manner shown in Figures 1 and 2. Indeed, every mixture shown in Figure 3 (flagged points) was an effective pressure-sensitive adhesive. On the other hand, resin B was not an effective tackifier for butadiene–styrene block polymers and was shown to be incompatible with both phases[8]; $G'(\tan \delta_{\min})$ for polymer 9 containing 43% of this resin was 7.02×10^7 dyn/cm^2, well in excess of the value of the pure block polymer.

The ratio of the experimental value of $G'(\tan \delta_{\min})$ to that calculated by eq. (3) appears to be a remarkably accurate criterion for polydiene center block compatibility of a resin and, together with the shift in T_g, for effectiveness as a tackifier. Some illustrative examples are shown in Table III. In every case where $G'_{\text{obs}}G'_{\text{calc}} > 1$, little or no tack is observed. Resin E in the butadiene–styrene block copolymer seems to be an example of partial compatibility as judged by the large shift in T_g, together with the modestly large G' ratio. Nevertheless, its tack value is low.

The success of the G' ratio as criterion of tackifier effectiveness appears to be founded in the following. First, the stainless steel substrate (probe) is a high-energy surface, while the adhesives are nonpolar or at best very weakly polar

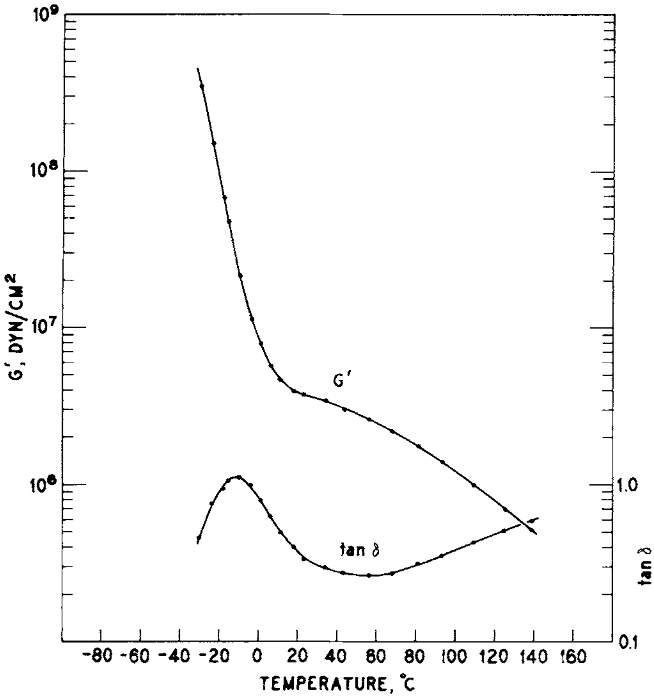

Fig. 2. Storage modulus and loss tangent for 50/50 blend of polymer 9 with resin A.

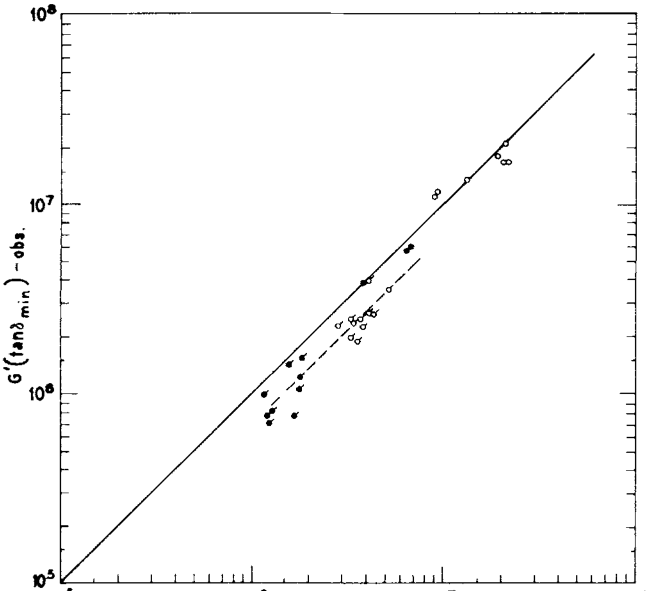

Fig. 3. Storage modulus at the minimum in the loss tangent. Open circles: Polybutadiene and butadiene–styrene block polymers. Closed circles: Polyisoprene and isoprene–styrene block polymers. Flagged circles denote mixtures with center block-compatible polymeric diluents of low molecular weight.

TABLE III
$G'(\tan \delta_{\min})$ and Pressure-Sensitive Tack

Block polymer	Resin	%	$G'_{\mathrm{obs}}/G'_{\mathrm{calc}}$ (at $\tan \delta_{\min}$)	ΔT_g[a], °C	Probe tack,[b] g
Butadiene–styrene (#10)	A	50	0.65	69	1240
Butadiene–styrene (#9)	A	50	0.65	70	1050
Butadiene–styrene (#9)	A	43	0.69	55	850
Butadiene–styrene (#9)	B	43	15.6	18	0
Butadiene–styrene (#9)	C	50	0.71	76	1270
Butadiene–styrene (#9)	D	50	0.53	76	930
Butadiene–styrene (#9)	E	50	3.5	61	32
Butadiene–styrene (#9)	F	50	0.61	98	1310
Butadiene–styrene (#9)	G	50	15.2	27	26
Butadiene–styrene (#9)	H	43	15.0	16	0
Isoprene–styrene (#3)	A	43	0.85	36	920
Isoprene–styrene (#3)	B	43	0.68	42	1090
Isoprene–styrene (#3)	C	50	0.84	51	1420
Isoprene–styrene (#3)	D	50	0.59	54	1430
Isoprene–styrene (#3)	E	50	0.58	56	1502
Isoprene–styrene (#3)	F	50	0.68	72	1560
Isoprene–styrene (#3)	G	50	7.4	16	110
Isoprene–styrene (#3)	H	43	67	2	0

[a] ΔT_g = shift in maximum in tan δ.

[b] Polyken tack tester, 25°C, 1 sec dwell time, 1 cm/sec probe withdrawal rate.

compositions of relatively low free surface energy. They undoubtedly spread on the substrate, and the thermodynamic work of adhesion would not be expected to vary widely from one example to another. Consequently the probe tack value is governed mainly by the rheological properties of the adhesive layer.

As Dahlquist[9] has shown, a necessary requirement of tack is the establishment of extensive (preferably full) molecular contact with the microscopically rough substrate surface, which generally will be assured if the 1-sec compressive creep compliance is ca. 10^{-7} cm^2/dyne or more. This is equivalent to a shear compliance of $J(1) \geqq 3 \times 10^{-7}$ cm^2/dyne for rubbery materials on Poisson's ratio 1/2. According to Riande and Markovitz,[10]

$$|J(t)| \cong |J^*(\omega)| \qquad \omega = 1/t \tag{4}$$

where $|J^*(\omega)|$ is the absolute magnitude of the complex dynamic shear compliance. If tan δ is not large (say, $\leqq 0.35$),

$$|J^*(\omega)| \cong 1/G'(\omega) \tag{5}$$

is a good approximation. For 35 Hz, $\omega = 220$ rad/sec and $t = 0.0045$ sec, so that

$$J(1) > J(.0045) \cong 1/G'(35\ \mathrm{Hz}) \tag{6}$$

At 25°C, the requirement that $J(1) \geqq 3 \times 10^{-7}$ cm^2/dyne will be met conservatively if

$$G'(35\ \mathrm{Hz}) \leqq 3.3 \times 10^6\ \mathrm{dynes/cm^2} \tag{7}$$

The adhesive compositions of Figure 3 generally fulfill this condition at the minimum in tan δ. However, since G' is relatively flat at the minimum in tan

δ, $G'(\tan \delta_{\min}) \approx G'(25°\mathrm{C})$, and the adhesive will not be seriously contact-limited in the 25°C probe tack test.

The second requirement of a tackifier, that it raise T_g, has to do with the value of the force measured on withdrawal of the probe once full contact has been established. Since the prevailing strain rate is rather high, the viscoelastic behavior of the adhesive on a shorter time scale (than the 1-sec dwell time for establishment of full contact) becomes important.[7,9] A high loss modulus reflecting ability to dissipate strain energy is required. On isochronal plots like Figures 1 and 2, shorter response times are represented by lower temperatures. Obviously, a large upward shift in T_g moves the adhesive into a region of greater modulus and increased mechanical losses.

This discussion not only furnishes a rationale for the observation of Table III, but also makes clear the limitations of the G' ratio as a criterion of tackification. It is based specifically on the condition of temperature and time of the probe tack test. The extent to which it can be applied to tack measured under other conditions may be expected to depend on how far these deviate from the present ones.

The authors are indebted to O. L. Marrs for the preparation of the adhesive formulations and for the measurements of adhesive tack.

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Received September 21, 1976
Revised October 19, 1976