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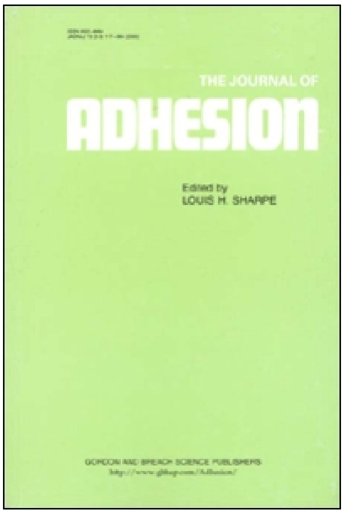

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Morphology and Viscoelastic Behavior of Styrene–Diene Block Copolymers in Pressure Sensitive Adhesives

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Linear (SDS) and radial $(SD)_x$ block copolymers of styrene (S) and dienes (D = butadiene or isoprene), varying in composition and molecular weight, were formulated as pressure sensitive adhesives. The morphology of these compositions was determined by electron microscopy of ultra-thin sections and dynamic viscoelastic measurements were made at 35 Hz between −90° and +140°C or higher. Pressure sensitive tack and holding power were determined and interpreted in terms of morphological and rheological properties.

A high degree of tack resulted only when the tackifying resin was compatible with the polydiene segments of the block polymer and incompatible with the polystyrene segments, provided also that the polydiene-tackifier phase was the continuum with the polystyrene phase forming spherical domains. All effective tackifying resins raised the glass transition temperature (T_g) of the rubbery phase, but plasticized the polymer at temperatures well above T_g. Polystyrene domain connectivity was found to lead to diminished tack in block polymers containing more than 30% styrene, a result of decreased creep compliance on the time scale of the bonding process and failure to achieve full contact with the substrate. For adhesives not limited by contact, tack increased with the loss modulus of the adhesive on the time scale of the debonding process. Holding power (shear resistance) increased with polymer styrene content and molecular weight, the polystyrene domain structure effectively inhibiting viscous flow at temperatures sufficiently below T_g of the styrene blocks.

I. INTRODUCTION

Thermoplastic elastomers are an increasingly important class of materials, both industrially and scientifically. One of the most interesting varieties is the type resulting from block copolymerization of styrene with a diene such as butadiene or isoprene. In the past few years these materials have become particularly important in the areas of adhesives and thermoplastic molding compositions.

One of the foremost adhesive applications for the styrene–diene block copolymers is in the area of pressure sensitive compositions, where interest is developing rapidly in solventless hot melt systems. Moderate knowledge exists concerning selection and formulation of styrene–diene block copolymers for use in pressure sensitive adhesives, most of it having been learned by largely Edisonian extension of earlier work with random styrene–diene copolymers and natural rubber. However, a number of peculiarities have been noted in the tackification and handling of block polymer-based systems which prompted the current investigation of the fundamental relationships between polymer morphology, viscoelastic behavior and adhesive performance.

II. BACKGROUND AND EXPERIMENTAL METHODS

The copolymerization of styrene with butadiene or isoprene can be controlled to provide a variety of polymer types, including segmented blocks of each monomer.[1, 2] Using organometallic polymerization initiators and a suitable polymerization solvent, polymers can be readily prepared with terminal

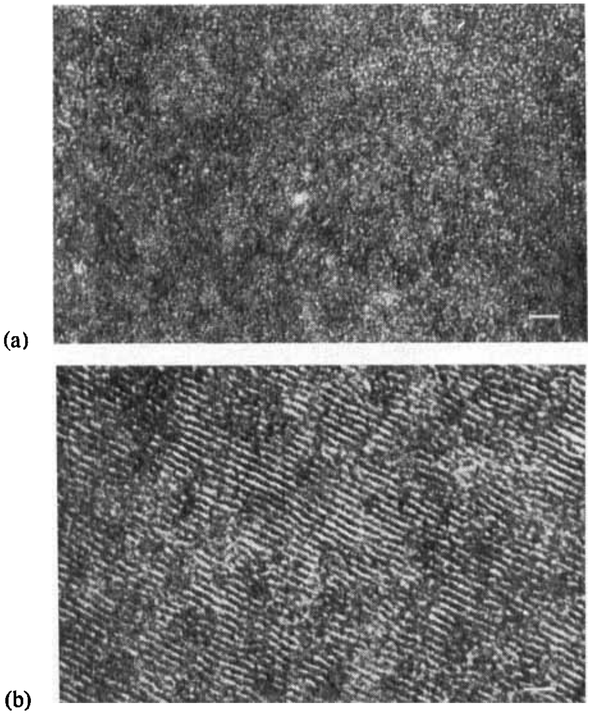


FIGURE 1a Rod-like form of styrene–butadiene teleblock copolymers (scale bar = 100 nm). (a) Sample sectioned normal to axis of rods. (b) Sample sectioned parallel to axis of rods.

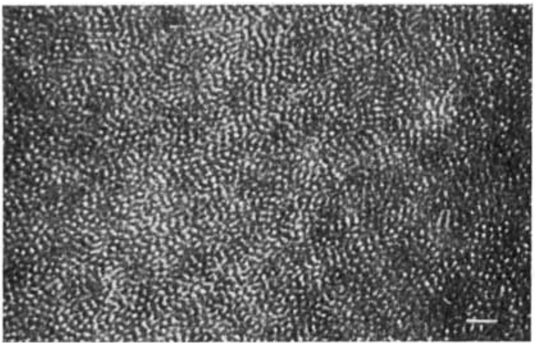


FIGURE 1b Spherical form of styrene–butadiene teleblock copolymers (scale bar = 100 nm).

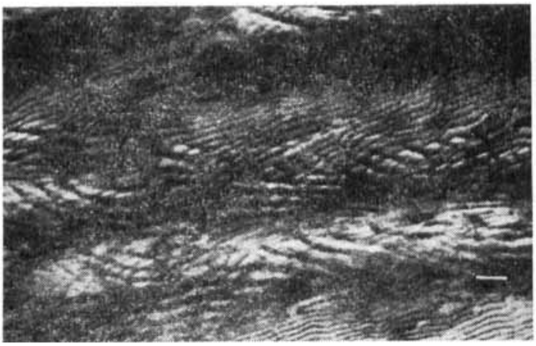


FIGURE 1c Lamellar form of styrene–butadiene teleblock copolymers (scale bar = 100 nm).

polystyrene blocks linked together by a polydiene block and are commonly referred to as ABA polymers or, sometimes, as "teleblock" polymers. Here A refers to polystyrene and B to polydiene. The polydiene can be linear or branched in a radial configuration, $(AB)_x$, where x is usually a small integer representing the functionality of the branch point. Numerous studies have shown [1-9] that these polymers, depending on composition, molecular weight and other parameters, exist as two-phase systems in which one of the block components forms discrete domains in a continuous matrix of the other block component, or in which both phases are continuous.

In general, five basic morphologies have been observed, the perfection of which is very much dependent on the method of sample preparation. Figure 1 shows electron photomicrographs of some of these morphological forms. In Figure 1b, spheres of polystyrene are dispersed in a continuum of polybutadiene. This morphology is *usually* observed up to about 20 weight % styrene in the system. Through the use of osmium tetroxide staining, the polybutadiene phase shows as the darkened region. The spheres of polystyrene are of the order of 13 nanometers in diameter in the present example; their size generally varies with block length. As the styrene content is increased the spherical domains develop an increasing degree of connectivity, so that in the range of 20–35% styrene a cylindrical or rod-like morphology is favored, as shown in Figure 1a. In the composition range of 35–65% styrene alternating lamellae are formed (Figure 1c). At still higher styrene contents, the polystyrene phase becomes continuous while the polybutadiene forms discrete domains; either rod-like in the range 65–80% styrene, or as spheres of polybutadiene when the styrene content is above 80%. More complex morphologies are also possible.[5, 6, 10] The typical composition limits mentioned are subject to considerable variation depending on sample preparation, particularly in films prepared by solution casting from different solvents.[4, 5] To a considerable extent the mechanical behavior of block polymers is governed by their morphology, and this would be expected to be equally true of adhesive compositions formulated from them.

In the present study, interaction between several polymer and formulation variables were considered:

1) Styrene/butadiene ratio.
2) Polymer molecular weight.
3) Butadiene versus isoprene.
4) Solvent.
5) Modifying resin and concentration.

A. Polymers

The polymers studied were of the radial, $(AB)_x$ type, prepared by solution polymerization techniques described previously.[1, 11] Radiality was slightly less than 4. Composition and molecular weights are shown in Table I.

Molecular weight distributions were determined using a Waters Model 100 gel permeation chromatograph. Weight and number average molecular weights were calculated from calibration curves derived from analyses of polybutadiene and polystyrene of known molecular weights, taking into account long chain branching.[12]

B. Adhesive formulations

The adhesive formulations used are shown in Table II. For hot melt blends the rubber and modifying resins were mixed in a Brabender plastograph at 180°C for a total of 30 minutes. For tack measurements small portions of the mixed formulation were pressed against 2 mil Mylar backing between

TABLE I Styrene/diene polymers and properties

Diene/styrene ratio	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
	Butadiene/styrene		
100/0	115	93	1.24
	223	173	1.29
	298	228	1.31
90/10	107	88	1.22
	199	157	1.27
	276	216	1.28
80/20	103	87	1.18
	149	120	1.25
	204	163	1.25
	314	241	1.30
70/30	109	88	1.24
	203	160	1.27
	288	229	1.26
60/40	105	89	1.19
	202	163	1.24
	284	225	1.26
	Isoprene/styrene		
85/15	314	217	1.45
85/15[a]	130	83	1.58

[a] Linear SIS.

TABLE II Adhesive formulations

	Formulation, parts A	Formulation, parts B
Block polymer	10	10
Rosin ester[a]	10	—
Rosin ester,[a] synthetic polyterpene,[b] or coumarone–indene[c] resin	—	7.5
Antioxidant[d]	0.1	0.1

[a] Foral 85 (Hercules Inc.).
[b] Wingtack 95 (Goodyear Tire and Rubber co.).
[c] Cumar LX 509 (Neville Chemical Co.).
[d] Irganox 1010 (Ciba–Geigy Corp.) or Butyl Zimate (R. T. Vanderbilt Co.).

Teflon-coated foil at 150°C to form 1–2 mil films. The films were tested at room temperature one day after preparation using the probe tack method of Wetzel [13] with a polished stainless steel probe, a contact time of 1 second, contact pressure of 100 gm/cm^2, and separation rate of 1 cm/sec.[14] Test results are average of five specimens.

C. Electron microscopy

For examination of morphological detail, ultra-thin sections were prepared by cryomicrotomy and stained by the osmium tetroxide method of Kato.[15] They were then examined under a Philips EM 300 transmission electron microscope.

D. Dynamic viscoelastic measurements

The viscoelastic behavior of the polymers and adhesive formulations were studied as a function of temperature at a fixed frequency of 35 Hz using a Vibron Model DDV-II Viscoelastometer from Toyo Instrument Co. Most of the measurements were in the shear mode, some in the tensile mode. Use of the shear mode was a matter of necessity in handling some of the highly deformable adhesive compositions. Measurements on tackifiers proper were made by impregnating the resins in fiber glass cloth; these materials were too brittle to be tested in unsupported form. This method is effective for determination of transition temperatures, but does not permit quantitative measurement of the complex dynamic modulus.

The shear test specimen was a 3 mm square of 0.4–0.5 mm thickness, bonded between brass plates. This sample is subjected to a sinusoidally applied strain of the desired frequency and amplitude at a controlled temperature and the resulting sinusoidal force amplitude is measured

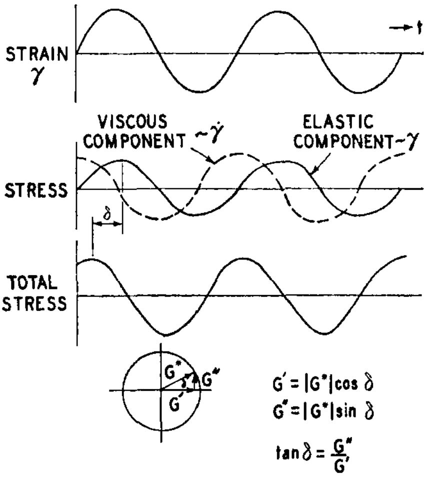


FIGURE 2 Viscoelastic property relationships.

together with the phase angle δ between the applied strain and the resulting stress (Figure 2). The absolute magnitude of the complex dynamic shear modulus $|G^*|$ is calculated from the strain and force amplitudes and sample dimensions. Values for the storage and loss components, G' and G'', respectively, and of the loss tangent are obtained by the well known relationships shown in Figure 2. Throughout this paper the data are displayed as plots of G' (E' for tensile data) and tan δ against temperature at a fixed frequency of 35 Hz.

III. EXPERIMENTAL RESULTS

A. Adhesive properties

1. *Effect of polymer composition and tackifier level on tack*

Various properties such as tack, peel strength, holding power, environmental resistance, etc., are commonly used to characterize pressure sensitive adhesives.[16] Figure 3 shows measured tack as a function of butadiene–styrene ratio for mixtures of block polymer ($M_w \cong 200{,}000$) with 100 phr of a rosin ester tackifier (Formulation A, Table II). Note that tack reaches a pronounced maximum at about 30 weight % styrene. The relative tackifier content based *on the polybutadiene phase* increases with the styrene content of the polymers in this experiment. Perhaps a more logical basis for comparison of the polymers would be to hold the ratio polybutadiene:tackifier constant. The result of doing this (data not shown) does not alter the general picture, except that the maximum tack value is shifted toward the polymer containing 20 weight % styrene.

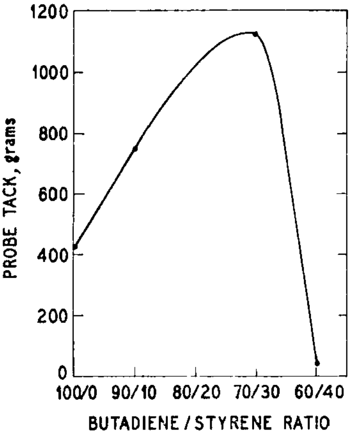


FIGURE 3 Tack response of block polymer–rosin ester adhesives at different butadiene/styrene ratios (polymer $M_w \sim 200{,}000$).

2. *Effect of block polymer molecular weight on tack*

In the range covered by this study the effect of block polymer molecular weight on the probe tack of mixtures containing the rosin ester is relatively minor, as seen in the upper curve of Figure 4.

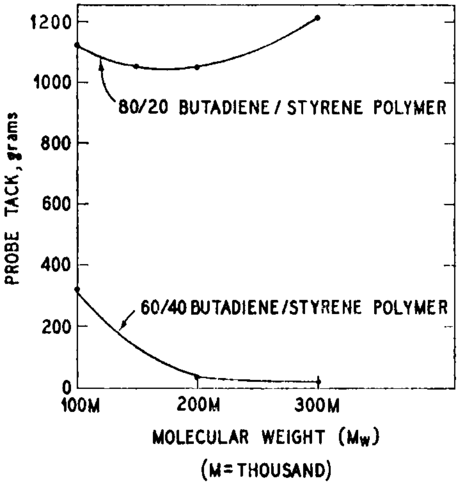


FIGURE 4 Tack response of 60/40 and 80/20 butadiene/styrene block polymer-based adhesives with varying molecular weight.

For the 60/40 polymer, however, the trend appears to be definitely toward higher tack with decreasing molecular weight.

3. *Effect of tackifier type on tack*

Various tackifiers such as the rosin esters are effective with both butadiene–styrene and isoprene–styrene block copolymers. Others, such as certain synthetic polyterpenes are effective with the isoprene–styrene copolymer only, and a third group represented by the cumarone–indene resins produce tack in neither polymer. These effects are seen in the data of Table III.

TABLE III Tack response of butadiene/styrene and isoprene/styrene polymers with different tackifiers

	Probe tack, grams	
Tackifier	Butadiene/styrene polymer[a]	Isoprene/styrene polymer[b]
Rosin ester (Foral 85)	850	920
Synthetic polyterpene (Wingtack 95)	0	1090
Coumarone–indene (Cumar LX 509)	0	0

[a] Butadiene/styrene ratio, 80/20; M_w 150,000.
[b] Isoprene/styrene ratio, 85/15; M_w 310,000.

4. *Effect of polymer and processing variables on holding power*

The effect of block polymer composition on adhesive holding power or shear resistance is seen in Figure 5. Determination of adhesive holding power involved a test configuration patterned after the Pressure Sensitive Tape Council Method PSTC-7. The adhesive mixture was dissolved in toluene, cast on 1-mil Mylar backing, and dried at room temperature in a dust-free cabinet to form 1-mil dry adhesive layers. Test strips 2.54 cm wide were bonded to a 2.54 cm wide stainless steel strip and loaded in shear with a 454-gram weight at the indicated temperature. Time to slip 1.6 mm was reported as the failure time. Holding power increased sharply with styrene content of the block polymer; in fact with the 70/30 and 60/40 polymers no significant amount of viscous flow was observed at 60°C under the conditions of the test and holding power may be regarded as effectively infinite. These polymers can be made to creep only at temperatures closely approaching or exceeding the glass transition of the styrene blocks, e.g., in the vicinity of 90°C.

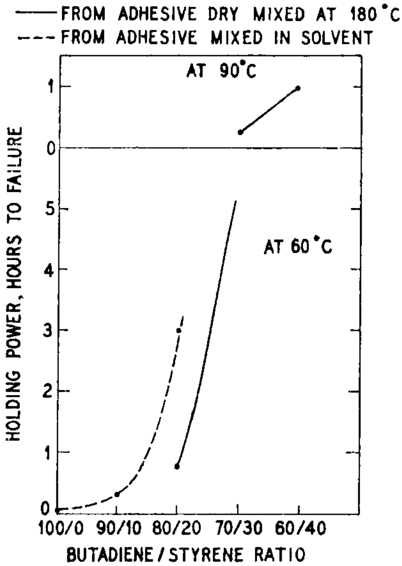


FIGURE 5 Holding power of block polymer–rosin ester adhesives at different butadiene/styrene ratios (polymer $M_w \sim 200{,}000$).

The sharp drop in holding power occurring near the 20 weight % styrene level is real and may be explained in terms of the shorter polystyrene block lengths for polymers in this composition region, i.e., $M_w \leqq 10{,}000$ (100 monomer units). The shorter the block, the easier is its detachment from the polystyrene domains under applied stress, a necessary requirement for true flow.

It is evident from the curves that the two preparation techniques studied provide films with somewhat different properties—the hot melt mixes exhibiting lower holding power. This is believed to be the result of modest degradation during the hot mixing step.

From the data shown several questions are apparent. Why are certain known tackifiers effective for styrene-diene block polymers and others either ineffective or very dependent on the nature of the diene structure? Why does tack, even with effective tackifiers, show such a pronounced maximum in the region of 20–30% styrene content? The morphological uniqueness of these materials in terms of domain formation was suspected as being a place to look for answers.

B. Viscoelastic properties and morphology

Unformulated block polymers of the type discussed here have been the subject of many morphological studies by electron microscopy,[3, 6] small angle x-ray scattering,[7-9] and viscoelastic behavior.[4-6] On the other hand there have been few published reports relating polymer morphology to performance properties in systems containing large amounts of additives. In the following paragraphs morphology and viscoelastic properties are described, both for the pure block polymers used in this study, and for the adhesives formulated from them and discussed above.

1. *Radial versus linear block polymers*

The linear viscoelastic behavior of ABA linear block copolymers of styrene and dienes has been extensively discussed in the literature. Much less has been said about multichain or "radial teleblock" copolymers.

Studies in our laboratories [17, 18] have shown that the viscoelastic behavior of linear and radial teleblock styrene–diene copolymers is basically similar, with differences arising primarily from the redistribution of the total styrene content over a larger number of blocks in the case of the radial copolymers. With polymers of high molecular weight these differences are small, except in polymer melts.[17] Figure 6 shows dynamic shear storage moduli and loss tangents plotted versus temperature for 85:15 isoprene/styrene block polymers of both linear and radial structure. The curves for the two structures nearly coincide. Similar results have been obtained with butadiene–styrene block copolymers and with polymers of higher styrene content. This similarity suggests that most of the observations on viscoelastic behavior of radial structures can be generalized to linear polymers.

2. *Behavior of radial structure block copolymers*

a) *Composition effects* The effect of composition on the viscoelastic properties of radial structure polybutadiene and a series of styrene–butadiene radial block copolymers is seen in Figure 7. Molecular weight for all of the polymers is about 200,000, narrowly distributed. Note that the 70/30 and 60/40 copolymers exhibit the glass transitions of the two phases as resolved maxima in tan δ and as steps in the storage modulus curves. The upper (polystyrene) transition is not well resolved in the 90/10 or 80/20 block polymers where a peak of much diminished height is superimposed on a rapidly rising tan δ approaching the melt region. The level of the storage modulus between the two glass transitions is closely related to morphology. Note that G' in the region rises slowly up to the 80/20 composition and then very rapidly above 20% styrene. This corresponds to the appearance of increasing connectivity of the styrene domains.

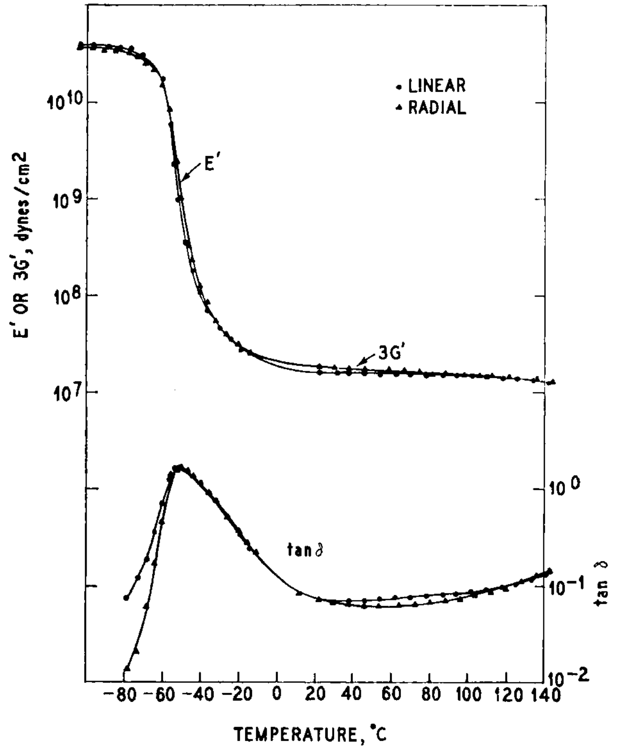


FIGURE 6 Viscoelastic properties at 35 Hz of linear and radial styrene–isoprene block polymers (15% styrene).

As shown by the photomicrograph of an 80/20 butadiene/styrene block copolymer (Figure 1b) the polystyrene domains are isolated spheres of about 13 nm diameter. In the 70/30 polymer (Figure 8a) and the 60/40 polymer (Figure 8b) it is apparent that the styrene domains are beginning to merge into more complicated shapes approaching that of short rods. Connectivity of the hard (polystyrene) phase must result in a higher modulus as this phase becomes increasingly load-bearing.[4]

b) Molecular weight effects Another significant variable is block polymer molecular weight. This effect is seen in Figure 9 showing G' and $\tan\delta$ of a series of 60/40 butadiene–styrene copolymers. The principal effect of molecular weight is a shift in the polystyrene domain glass transition, seen most

TABLE IV Adhesive properties of 80/20 butadiene/styrene block polymer in various formulations

Ingredients	1	2	3	4
80–20 butadiene–styrene	100	100	100	100
Rosin ester tackifier[a]	80	100	80	100
Coumarone–indene resin[b]	—	—	20	40
Liquid plasticizer[c]	—	—	—	60
Holding power, hours to failure at 60°C, 100 gram wt.	4	1	>24	1
Probe tack, grams	860	990	1070	730

[a] Foral 85
[b] Cumar LX 509
[c] Shellflex 371 oil.

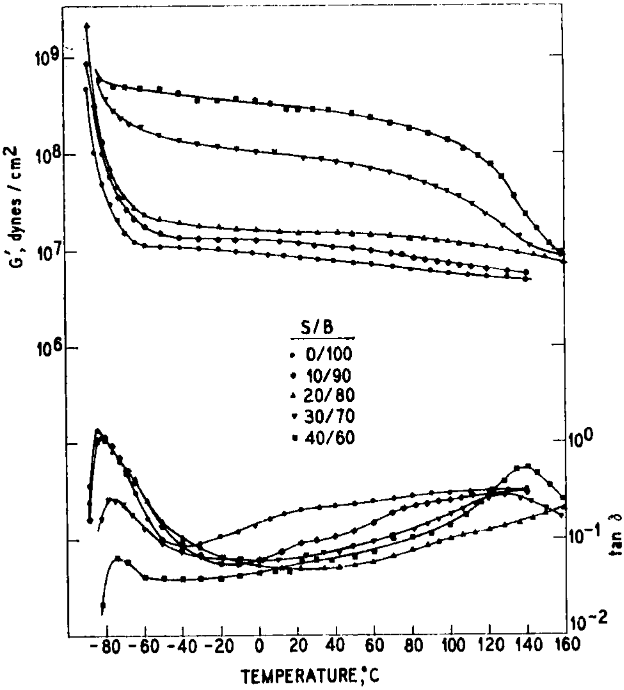


FIGURE 7 Viscoelastic properties of butadiene/styrene radial block polymers.

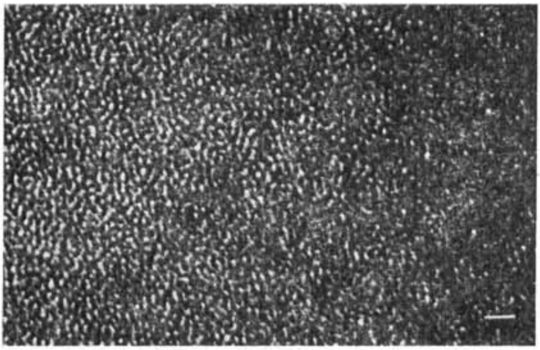


FIGURE 8a Effect of composition on morphological forms of styrene–butadiene teleblock copolymers: 70% butadiene–30% styrene (scale 100 nm).

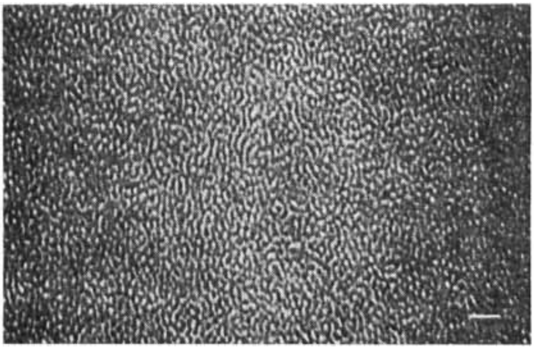


FIGURE 8b Effect of composition on morphological forms of styrene–butadiene teleblock copolymers: 60% butadiene–40% styrene (scale bar = 100 nm).

clearly in the tan δ curves. It is small between 300,000 and 200,000 molecular weight, but large between 200,000 and 100,000. Kraus and Rollmann[18] have shown that this shift occurs at a rapidly increasing rate when the styrene block molecular weight falls below 20,000 and is the result of intermixing of polybutadiene and polystyrene blocks in still predominately polystyrene domains. The approximate polystyrene block lengths for the tetra-chain radial 60/40 block polymers are 10,000, 20,000 and 30,000, respectively. There are also differences in this series which must be attributed to morphological detail; that is, connectivity of the polystyrene domains. This is most clearly seen in G' of the 100,000 molecular weight sample whose plateau modulus is only about 1/6 of the value for the other polymers. Moreover, the loss tangent in domain-forming polymers is most heavily weighted by the load-bearing phase. Consequently polystyrene domain connectivity not only raises the tan δ maximum of the polystyrene domains but concurrently decreases that of the polybutadiene phase.

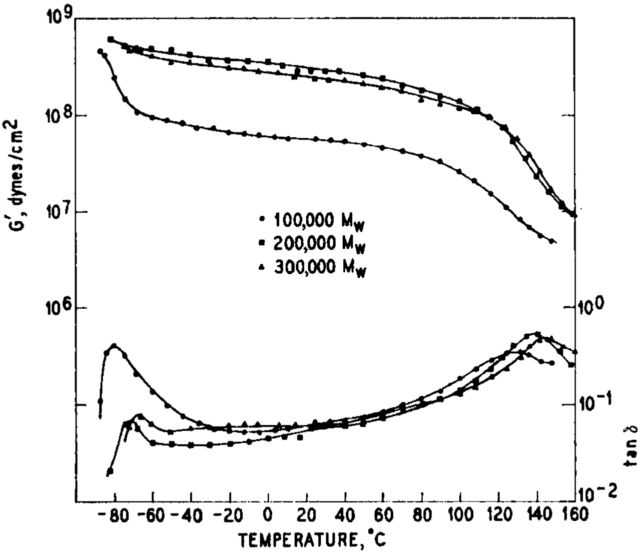


FIGURE 9 Effect of molecular weight on viscoelastic properties of 60/40 butadiene/styrene radial block polymers.

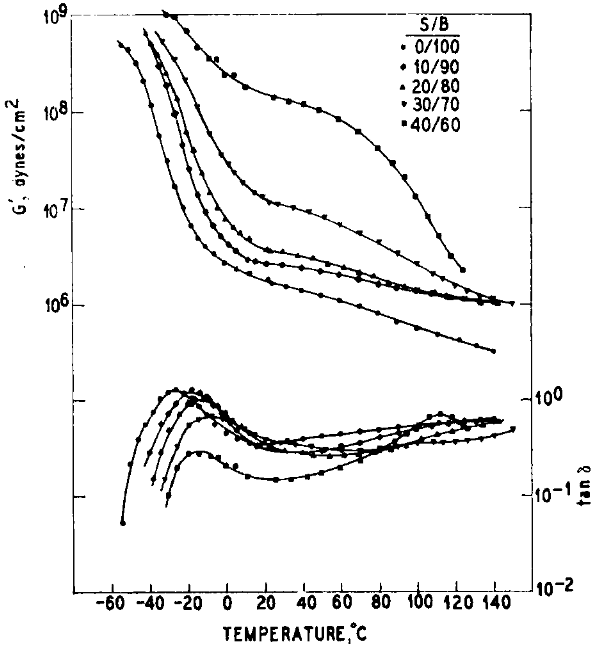


FIGURE 10 Viscoelastic properties of adhesives formulated from polymers of Figure 7 with rosin ester tackifier (100 phr).

c) Effect of a polybutadiene-compatible tackifier Figure 10 shows the consequences of adding to a styrene–butadiene block copolymer a substantial amount of a typical rosin ester tackifier (Foral 85); the data are for hot-mixed samples. These results are to be compared with those of Figure 7. The additive exerts its most pronounced effects on the rubbery phase. It raises T_g of this phase by some 60 degrees and, lowers G' in the plateau region of the curves. The magnitude of the shift in T_g increases slightly with styrene content.

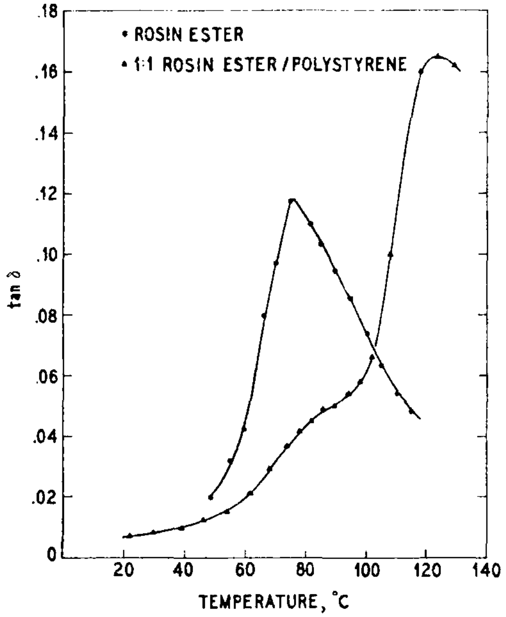


FIGURE 11 Loss tangent of rosin ester and rosin ester/polystyrene blend.

Since tackifiers are materials of high T_g relative to polybutadiene or polyisoprene their effect on the rubbery phase, if compatible, will be to increase T_g and, by the dilution effect, to lower the storage modulus in the plateau zone, precisely as observed. Moreover the shift in T_g will be dependent on the tackifier concentration in the rubbery phase, which increases with styrene content of the block polymer in this series. Because of its low molecular weight, the tackifier produces a relative increase in energy dissipation resulting in an increase in tan δ in the plateau region of G'.

Figure 11 shows tan δ at 35 Hz of the rosin ester tackifier alone and in admixture with polystyrene measured by the glass fabric impregnation method. These data establish the 35 Hz temperature of maximum loss tangent of this tackifier as 76°C. In the curve for the rosin ester/polystyrene blend, transitions for both components are clearly identified, indicative of incompatibility. Based on these data it is concluded that the rosin ester is compatible with the polybutadiene phase but essentially incompatible with the polystyrene phase. Similar results were obtained for the styrene–isoprene copolymer.

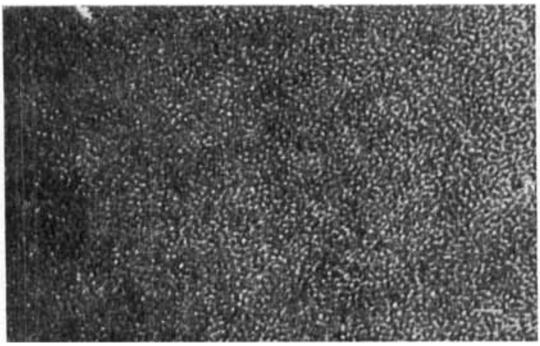


FIGURE 12 70–30 butadiene–styrene teleblock copolymer with rosin ester tackifier (scale bar = 100 nm).

Electron photomicrographs of styrene–butadiene block copolymers mixed with a rosin ester tackifier show no startling changes from incorporation of the additive. Comparing the photomicrograph of the 70 butadiene-30 styrene block polymer mixed with rosin ester tackifier (Figure 12) with that of the pure polymer (Figure 8a), it can be seen that the polystyrene domains are somewhat smaller and connectivity appears slightly diminished. The latter observation is not unexpected in view of the increase in the abundance of the rubbery phase resulting from admixture of the (compatible) tackifier.

d) *Formulations with polybutadiene-incompatible tackifiers* There are two possibilities involving additives which are incompatible with the rubbery phase; either the additive is also incompatible with polystyrene and forms a third phase, or the additive is fully or partly compatible with polystyrene.

The addition of the synthetic polyterpene resin (Wingtack 95) to a styrene–butadiene block copolymer does not produce measurable tack (Table III). The 35 Hz loss maximum of this resin impregnated on glass fabric was located at 111°C. This is too close to the polystyrene maximum to permit conclusions about compatibility on the basis of dynamic measurements. The behavior of the resin in an 80/20 butadiene–styrene block copolymer, as shown in Figure 13, shows that it is at best only sparsely soluble in polybutadiene, producing a much smaller shift in the lower loss maximum than the rosin ester and a sharp *increase* in the level of the plateau storage modulus. The electron photomicrograph in Figure 14 shows clear evidence of a third phase in this system. Note the large inclusions of resin which contain streaks of block polymer. At this low magnification the block polymer domain structure is not resolved and the block polymer shows up uniformly dark.

Results with Cumar LX-509, a coumarone–indene resin, are shown in Figure 15. This resin has been suggested as being polystyrene compatible.[19] By the glass fabric impregnation technique, its 35 Hz loss maximum was located at 178°C. In our work, binary blends of this resin with a high molecular weight polystyrene (Dow Styron 678) showed complex behavior suggesting partial miscibility only. This would not preclude compatibility with relatively low molecular weight polystyrene blocks. Such compatibility should result in a single T_g for the "hard phase", located somewhere between the component T_g's and responsive to the concentration of the components in height and position of the tan δ peak. Indeed, increasing amounts of Cumar LX-509 do progressively raise the upper T_g. At the higher additive concentrations a shoulder appears on the low temperature side of the maximum. Also a secondary loss region is evident near room temperature, the nature of which is not clearly understood. The effect of this resin on the polybutadiene transition is small.

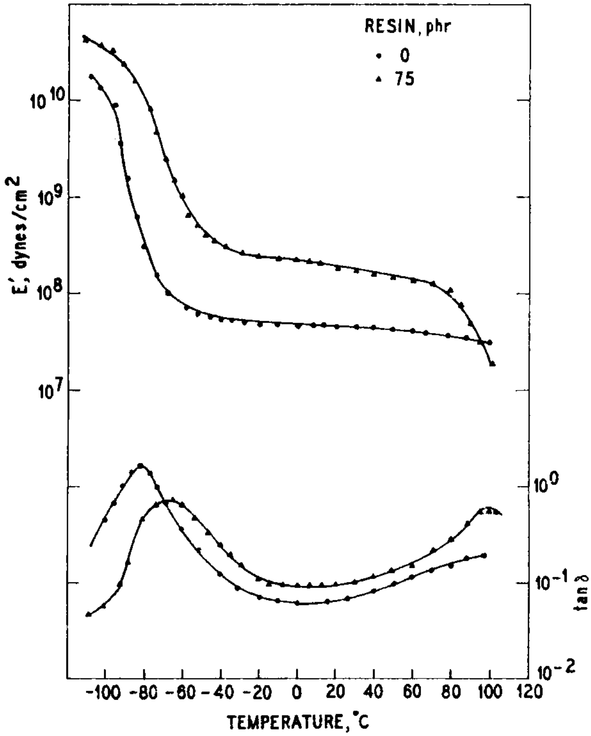


FIGURE 13 Viscoelastic properties of 80/20 butadiene/styrene block polymer with and without synthetic polyterpene resin (data obtained in tensile mode).

FIGURE 14 80/20 butadiene–styrene block polymer containing synthetic polyterpene resin (scale bar = 1000 nm).

An electron photomicrograph of an 80:20 butadiene–styrene block polymer mixed with 75 phr Cumar LX-509 is shown in Figure 16. A fibrillar morphology is suggested with the fibres viewed first end-on (Figure 16a) and then as viewed in the plane of the section (Figure 16b). There are no

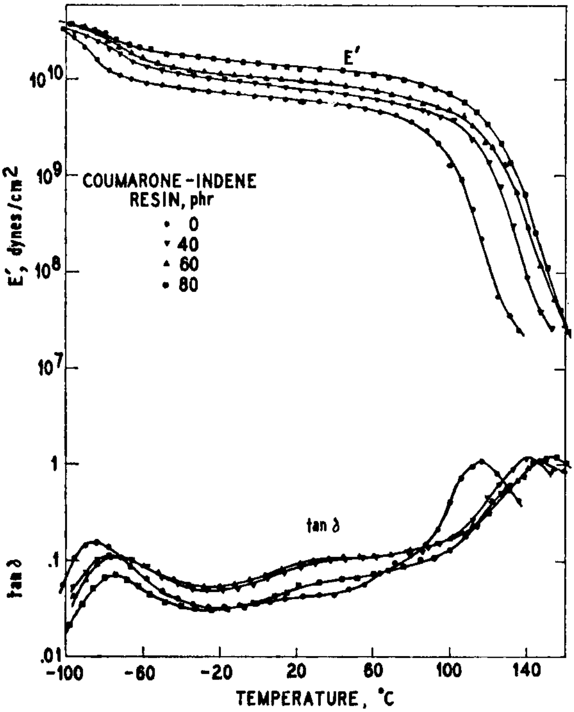
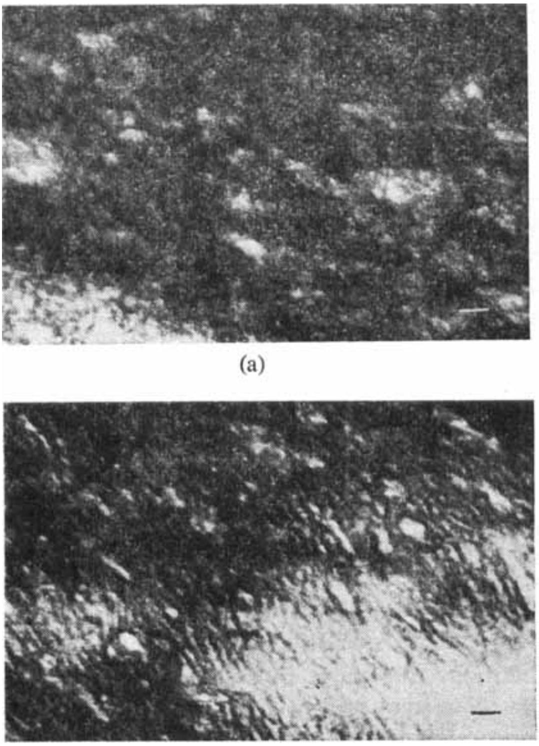


FIGURE 15 Viscoelastic properties of 60/40 butadiene/styrene block polymer with coumarone–indene resin (data obtained in tensile mode).

large inclusions of a separate phase, like in the example of the polyterpene resin (Figure 14). The incorporation of substantial amounts of resin in the polystyrene domains would be expected to produce a change from the spherical morphology of the pure block polymer to one in which both phases are continuous.



(a)

(b)

FIGURE 16 80/20 butadiene–styrene block polymer containing coumarone–indene resin (scale bar = 100 nm). (a) Sample sectioned normal to axis. (b) Sample sectioned parallel to axis.

IV. DISCUSSION

Probe tack is a complex phenomenon which depends on a combination of factors, including the bonding qualities of the adhesive and forces that develop during the unbonding or separation process.[16] Bonding is controlled by the wetting characteristics of the adhesive to the substrate and the viscoelastic properties of the adhesive material on the time scale of the bonding operation. After bonding, forces during separation likewise depend on the rheological properties of the adhesive, which are again rate- and temperature-dependent.

According to current theories of tackification[16,20] involving rubbery homopolymers and random copolymers, an increase in T_g coupled with a lowering of the modulus in the plateau region of E' or G' is an essential criterion of an effective tackifier. We have found no exception to this rule in our work with block copolymers. All rubbery phase-compatible resins have shown this behavior and are effective tackifiers; all rubber-incompatible resins are largely ineffective as tackifiers as they *increase* the plateau storage modulus and do not materially affect T_g of the rubbery phase.

As pointed out by Dahlquist[16] and Sherriff *et al.*,[20] the tackification phenomenon can be ascribed to characteristic time responses of the material to the establishment and breakage of an adhesive bond. Applying this idea, in a straightforward manner, to block polymer-based adhesives with dynamic viscoelastic data of the type developed here unfortunately runs into complications. In the probe tack test a bond is formed in a time of about one second. The relevant material property would thus be the one-second creep compliance at the bonding temperature. This can be determined from dynamic viscoelastic data obtained at a frequency of about 0.15 cycle per second, which however, lies outside the frequency range of the Vibron apparatus. For thermorheologically simple systems the one-second creep compliance can also be calculated from dynamic measurements at different temperatures and frequencies, applying the well-known time (frequency)-temperature superposition principle and converting the dynamic compliances to the creep compliance by known mathematical methods. However, as shown by Fesko and Tschoegl[21] this does not succeed for block polymers of the present type, because the conditions for simple time-temperature superposition are not fulfilled; that is, all relaxation times do not have the same temperature dependence. Simple behavior is only observed for these materials well below the glass transition of the polystyrene domains where these domains act essentially as rigid filler particles whose molecular motions are frozen in. Similar or even more complex behavior might be expected in adhesive systems formulated from block polymers. Nevertheless, some reasonable estimates are possible.

Dahlquist[22] has shown that a serious loss of tack results when the adhesive is unable to flow and make total contact with the microscopically rough substrate surface in the relatively short time span of the bonding process of about one second. He established a general criterion that the one-second compressive creep compliance for the adhesive must not fall below 10^{-7} cm^2/dyne to avoid contact limitation. A tensile or compressive creep compliance of 10^{-7} cm^2/dyne is approximately equivalent to a shear creep compliance of 3×10^{-7} cm^2/dyne. A criterion similar to Dahlquist's can be developed for the block polymer adhesives of the present study, based on the shear storage modulus at 25°C and 35 Hz.

Using the approximation method of Riande and Markovitz[23] and fundamental viscoelastic property relationships, we can arrive at an expression approximating creep compliance in terms of shear storage modulus and tan δ for which we have direct data at 35 Hz.

Shear compliance at time t

$$J(t) \cong \{[J'(\omega)]^2+[J''(\omega)]^2\}^{\frac{1}{2}} \tag{1}$$

where $\omega = 1/t$. Since

$$J' = \text{shear storage compliance} = \frac{G'}{(G')^2+(G'')^2}, \tag{2}$$

$$J'' = \text{shear loss compliance} = \frac{G''}{(G')^2+(G'')^2}. \tag{3}$$

and

$$G'' = \text{shear loss modulus} = G' \tan\delta, \tag{4}$$

it is easily shown that

$$J(t) \cong [G'(\omega)\times\sqrt{1+\tan^2\delta}]^{-1}. \tag{5}$$

In the present study tan $\delta \leqslant 0.35$ for all butadiene–styrene adhesives based on block polymers of less than 30% styrene content at 35 Hz and 25°C. Consequently,

$$\sqrt{1-\tan^2\delta} \leqq 1.06 \tag{6}$$

and hence

$$J(t) \cong \frac{1}{G'(\omega)}, \qquad \omega = \frac{1}{t}. \tag{7}$$

For these same adhesives we also find at 25°C

$$G'(35\text{ Hz}) \leqq 4\times10^6\text{ dynes/cm}^2 \tag{8}$$

or

$$J(0.0045) \geqq 2.5\times10^{-7}\text{ cm}^2\text{/dyne}. \tag{9}$$

Since

$$J(t=1) \gg J(t=0.0045) \tag{10}$$

we see that for butadiene–styrene block polymers not exceeding 20% styrene with a rubber compatible tackifier, any adhesive satisfying Eq. (8) will also have a 1-sec creep compliance greater than 3×10^{-7} cm^2/dyne as prescribed by Dahlquist. We conclude that all the adhesives prepared from radial polybutadiene, radial block copolymers of 90/10 butadiene–styrene, 80/20 butadiene–styrene, or 85/15 isoprene–styrene with rubber-compatible tackifiers are not limited in tack by incomplete contact with the substrate. For these adhesives tack *increases* with the styrene content of the block copolymer.

The viscoelastic function most relevant to the improvement in tack with styrene content is the loss modulus, G'', since it is proportional to the energy dissipated in one cycle of deformation. At fixed frequency it is also proportional to the real part of the dynamic viscosity. Dissipation of strain energy is, of course, a key factor in both adhesive and cohesive failure.[24] In Figure 17, tack values are shown as measured for rosin ester tackified block butadiene–styrene and butadiene–isoprene copolymers, prepared by the hot mix technique, as a function of G'' at 35 Hz at 25°C.† There is a positive correlation between tack and loss modulus for polymers containing up to 20 weight % styrene, which is attributable to increased ability to dissipate strain energy. The loss modulus is seen to increase beyond 20% styrene. However, as the result of increased reinforcement by the polystyrene domains the storage modulus G' undergoes an even more rapid rise, leading ultimately to loss in tack because the Dahlquist criterion will no longer be met. In other words, above 30% styrene the estimated one-second creep compliance begins to fall below 3×10^{-7} cm²/dyne suggesting that incomplete substrate contact becomes a limiting factor. Lack of contact eventually dominates, leading to extremely low tack values for the 60/40 butadiene–styrene block polymers.

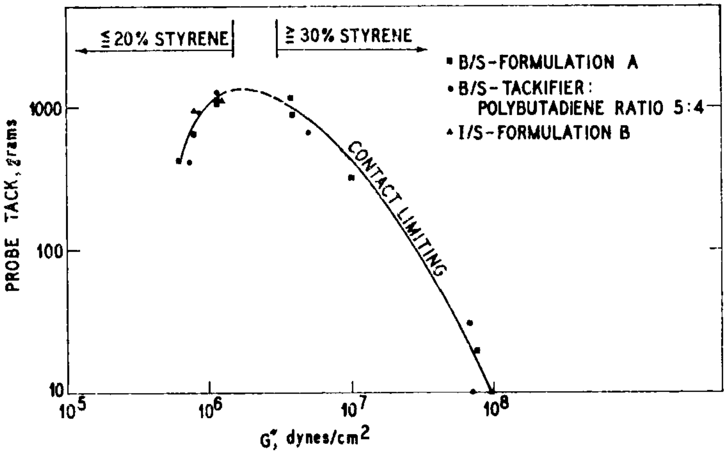


FIGURE 17 Tack versus loss modulus for rosin ester tackified block polymer adhesives (hot mixed).

Rubber-incompatible resins raise the storage modulus, G', over and above the value of the raw polymer. The resulting storage moduli are of the order

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† The time scale of the debonding step in the probe tack test has been estimated to be of the order of 0.01 sec.[16, 22] This is roughly comparable to 35 Hz in a dynamic test, as $t \approx 1/\omega = 0.0045$ sec. Thus, 35 Hz dynamic moduli should be fairly representative of the consistency of the adhesive during debonding.

of 10^8 dynes/cm^2 which translates into creep compliances of the order of 10^{-8} cm^2/dyne, far below the limit set by the Dahlquist criterion. As a consequence tack is virtually nil.

Regarding adhesive holding power, the time scale of the laboratory test is so great that any extrapolation from dynamic viscoelastic data at 35 Hz would be meaningless. However, the holding power data shown earlier are readily interpreted by the known behavior of block polymers under the conditions of the test. The test failure criterion is creep to a distance of 1.6 mm using an adhesive layer thickness of about 0.025 mm. To obtain 1.6 mm creep under this condition clearly requires true viscous flow. Domain forming styrene–diene block copolymers can only undergo viscous flow by detachment of styrene blocks from domains and subsequent re-attachment to other domains. This process depends to a considerable extent on the length of the polystyrene blocks.[17] Therefore, at constant total molecular weight, lengthening the styrene block (increasing styrene content) increases holding power. In Figure 4, showing the progression of holding power with block polymer composition, the styrene block length increases from zero to 20,000 in increments of 5000. Similarly, styrene block length can be increased by raising the total molecular weight at fixed styrene content and this, too, is found to lead to greater holding power.

In pure block polymers a styrene block length of 20,000 is sufficient to totally inhibit viscous flow at temperatures below the T_g of styrene homopolymer. This behaviour is undoubtedly moderated somewhat by the presence of a rubber-compatible tackifier, but the qualitative behavior remains similar.

One would expect holding power to be increased by polystyrene-compatible resins of high T_g, since this would stabilize the polystyrene domains. This suggests that an adhesive might be optimized by use of a combination of a rubbery phase-compatible tackifier (Floral 85) and a high softening point resin (Cumar LX 509) which exhibits polystyrene compatibility. Table IV shows an example of this effect. Note that the combination of these resins in formulation number 3 leads to a most interesting balance of good tack with greatly increased holding power. It is greatly superior to the formulation employing the coumarone-indene resin with a liquid plasticizer.

V. CONCLUSIONS

The conclusions of this work are that the formulation of a successful butadiene–styrene or isoprene–styrene block polymer pressure sensitive adhesive requires:

1) Use of a tackifying resin that is compatible with the rubbery blocks, but incompatible with the polystyrene blocks.

2) A rubber-continuous morphology of the adhesive. Connectivity of the polystyrene domains leads to low creep compliance and loss in tack, but higher shear resistance.

3) Development of tack requires a high creep compliance to permit the establishment of full contact with the substrate during the short bonding time.

4) Whenever full contact with the substrate is established, the probe tack value is governed by dissipation of strain energy which increases with styrene content of the block polymer.

5) Effective rubber-compatible tackifiers significantly raise T_g of the rubbery phase. By doing so the adhesive moves into a region of higher mechanical loss, resulting in increased dissipation of strain energy.

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