

Rheology, Composition, and Peel-Mechanism of Block Copolymer–Tackifier-Based Pressure Sensitive Adhesives

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SYNOPSIS

Three samples of styrene–isoprene–styrene (S–I–S) block copolymers were chosen; copolymer A had 25% styrene, and copolymers B and C had 14% styrene. Copolymers A and B contained 20% diblock polymer and copolymer C contained 40% diblock polymer. All copolymers were mixed with a terpene type tackifier to make 56% and 48% weight tackifier concentration. These represent our model samples of pressure sensitive adhesives. The determination of tack, room-temperature peel-strength, and failure temperature under static shear were performed. The above results have been interpreted with the basic rheological data. The dynamic viscoelastic measurements and tensile stress–strain measurements were used. The effects of tackifier on the rubbery plateau moduli were treated with the Guth–Gold-type equation. The implications of the deviation from the equation are discussed in terms of the connectivity between polystyrene domains and the stability of the hard domains affected by inclusion of rubber segments.

INTRODUCTION

The use of Styrene–Isoprene–Styrene (S–I–S) block copolymers in pressure sensitive adhesives (PSA) continues to increase.¹ PSAs are used in diverse industries as removable adhesives, medical adhesives, packaging adhesives, and electrical adhesives. The requirements demand higher temperature performance and higher peel values. The performance of PSA depends on the bulk properties and on the interfacial energies of the bonding surfaces. In practice, the performance is defined in terms of tack, peel, adhesion, and shear resistance. Adhesion values are dependent on time, rate, and temperature, as are the bulk properties. Correlation of the bulk rheological properties to adhesion values would provide invaluable insight into the end-use performance of the PSA, and would assist in the development and formulation of new PSAs. A number of studies already exist relating rheology and mechanical properties to the performance of PSA.^{2–6} This work attempts to extend these basic studies with an em-

phasis on the effect of styrene block concentration and of diblock concentration on the fundamental properties and the product performance of the PSA.

EXPERIMENTAL

Samples

Three S–I–S copolymers were chosen for the adhesive formulation. The major differences among these polymers are the styrene content and the percentage of diblock copolymer as shown in Table I. The minor differences in the molecular weight and its distribution are considered to be insignificant for the purpose of the relative comparison of their performance.

The S–I–S copolymers were mixed with a tackifier, Wingtack 95, a synthetic polyterpene, manufactured by Goodyear Tire and Rubber Company,⁷ in a 280 g Brabender Plastograph⁸ at 50 rpm with low shear mixing blades under a nitrogen blanket with a machine temperature of 150–155°C. First, the S–I–S copolymer and antioxidants were added. The antioxidants were 1 parts per hundred weight of rubber (phr) each of Irganox 1010 (Ciba Geigy) and Polygard (Uniroyal Chemical). When the co-

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Table I S-I-S Copolymers^a

Sample Code	A	B	C
Bound Styrene (%)	25	14	14
Diblock (%)	20	20	40
M_w^b	153,000	160,000	143,000
M_n^b	115,000	125,000	97,800
M_w/M_n	1.33	1.28	1.46
Trade Name	Sol T193A	Kraton 1107D	Kraton 1112D
Manufacturer	Enarco Elastomer Co.	Shell Chemical Co.	Shell Chemical Co.

^a Data supplied by the manufacturer.

^b Values are for triblock polymers. For diblock polymers values are about a half.

polymer became masticated and formed a homogeneous melt, the tackifier was slowly added until completion. Mixing time was 20 to 30 min.

The hot adhesive compound was deposited onto a silicone release paper.

ADHESION TESTS

Adhesive Film Preparation

The bulk adhesive compound, prepared as described, was placed on a laboratory scale knife-over-roll coater and spread to make a PSA film. The laboratory coater was equipped with a heated knife, a heated melt plate, and an overhead heating element. A differential silicone-coated, 80 lb., bleached Kraft paper was the carrier.

The adhesive was placed on the carrier, which was located on the melt plate, and was heated to 188–193°C until a flowable state was attained. When the adhesive was in a liquid state, it was passed under the knife at a predetermined gap setting to produce a thin film of PSA. The width and thickness of the film were adjustable. Test samples were prepared by placing 0.05 mm thick Mylar film (a product of duPont Company), resulting in a three layer, release paper-PSA-Mylar product. Test specimens of 25 mm × 200 mm were die-cut. The release paper was removed to apply the PSA film to the test substrate.

Shear Adhesion Failure Temperature⁹

The shear adhesion failure temperature is a measure of the ability of a PSA to withstand an elevated temperature under a constant force, which pulls the PSA tape downward from a vertically placed test substrate in a direction parallel to the surface of bonding. Test samples were prepared to form a 25.4 mm × 25.4 mm lap of specified thickness. After con-

ditioning for 24 h at 23°C and 50% relative humidity, the samples were placed in an oven set at 70°C. A load of 50 g was attached to one end of the lap shear, while the bonded area was adhered to an aluminum substrate. The temperature was raised in increments of 10°C per 0.5 h. The temperature at which the lower portion of the lap drops off describes the failure temperature. However, the highest temperature at which all specimens remained attached was recorded as the failure temperature.

Polyken Probe Tack Test¹⁰

The Polyken Probe Tack test provides a measure of the tackiness of a PSA and the PSA's ability to wet-out quickly a surface. The test is conducted on a Polyken Probe Tack testing machine, which is designed to measure the force required to break the adhesive bond (grams per square centimeter) resulting from placing the probe in contact with a flat film at controlled rates, contact pressures, and dwell times. The contact pressure was 100 g/cm², the dwell time was 1 s, and the rate of the test was 1 cm/s. The probe surface was No. 304 stainless steel.

Quick Stick¹¹

Quick stick is a property of a PSA film that causes it to adhere to another surface instantly, using no external force but only the weight of the film itself, to produce a contact. It is measured as the force in N/100 mm resisting peel of a tape at 90° angle from an aluminum surface.

Peel Strength¹²

The peel strength is a measure of the force required to remove a PSA film from another substrate. The film is applied to the test substrate, conditioned as

Table II Shear Adhesion Failure Temperatures

	Polymer A		Polymer B		Polymer C	
Wt % S-I-S	44	52	44	52	44	52
Failure Temp. (°C)	134	134	114	114	104	104

required, and then tested by peeling, at 180°, at the required speed and environmental condition. The PSA, coated on 0.05 mm thick Mylar film, was placed on an aluminum substrate. A 1 kg roller was passed twice along the test specimen; the specimen was then left at 25°C for 48 h for conditioning. The test was performed at 23°C with peel rates of 5, 30, and 51 cm/min.

FUNDAMENTAL PROPERTIES

Specimen Preparation

Test specimens of the PAS were prepared by compression molding between Mylar films. A dumbbell die, ASTM D1708-G6, was used to die-cut the tensile specimens.

Tensile Stress-Strain Measurements

An Instron tensile tester¹³ was used at room temperature and with strain rates of 0.0025, 0.025, 0.15, and 0.25 s⁻¹.

Viscoelastic Measurements

A Rheometrics Mechanical Spectrometer¹⁴ was used in the oscillatory mode with 25 mm parallel plates.

Some data were taken at room temperature using a frequency sweep. Most of the data were obtained at 1 rad/s under a temperature scan from the glassy region to terminal flow. A typical scan covered the range from -40 to 140°C.

RESULTS

Shear Adhesion Failure Temperature

The shear adhesion failure temperatures for six PSAs of this study are listed in Table II.

In the manner by which the test was performed, the failure temperatures listed in Table II are the highest temperature where all specimens remained attached. Therefore, actual failure temperatures were somewhat higher, that is, within a 10°C increment above those listed. In spite of this rather crude way of recording, the test was capable of ranking the performances of three polymers. In this test, the concentration range of 40–60% S-I-S polymer was covered. Within this range, no concentration dependence of the failure temperature was detected.

Polyken Probe Tack Test

Figure 1 illustrates the polyken tack results for polymers A, B, and C with the variable tackifier content. In general the tack increases with tackifier concentration until a maximum is reached; the tack then falls off with the further increase of tackifier concentration. Polymer A reached its highest tack at 40–44% polymer concentration; polymers B and C reached their highest tack at 36–40% polymer concentration.

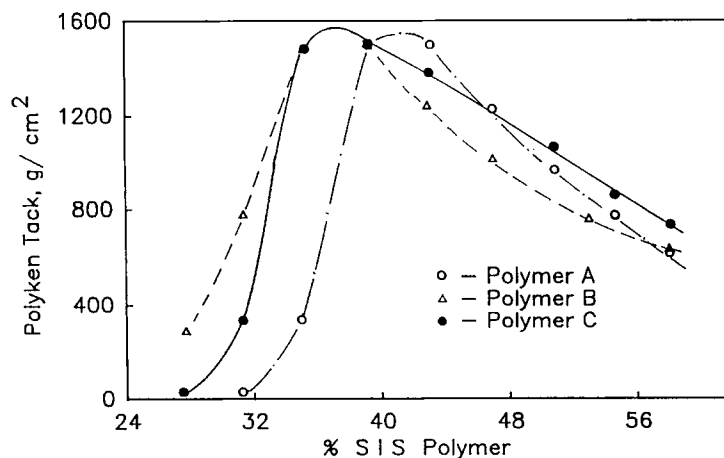


Figure 1 Polyken tack and optimum range in polymer-tackifier composition, S-I-S copolymers, A, B, and C.

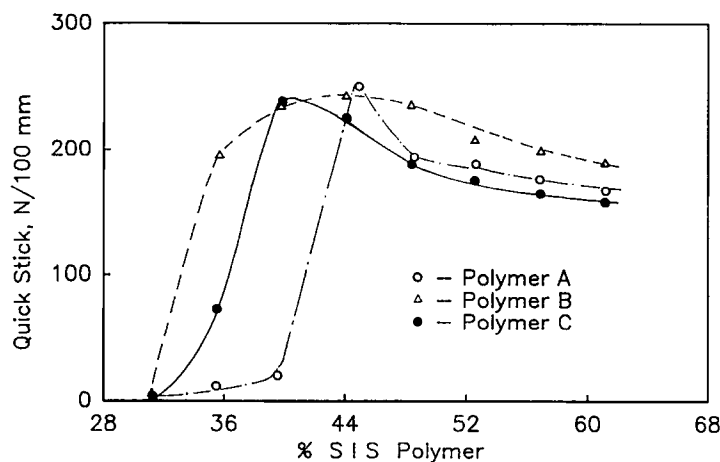


Figure 2 Quick stick and optimum range in polymer-tackifier composition, S-I-S copolymers A, B, and C.

Quick Stick

The quick stick results are very similar to the polyken tack profiles, as shown in Figure 2. At 32% polymer concentration, no quick stick properties are exhibited. Polymer A reaches the maximum value of quick stick at 43% polymer concentration and polymer B at 39%. Polymer C has a broad range of concentration where quick stick values remain high.

Peel Strength

As Gent and Hamed reported,¹⁵ peel strength may be dependent on thickness. The effect of adhesive thickness on peel strength was examined for Polymers A, B, and C at the 44, 48, and 52 wt % polymer concentration, the remainder being the tackifier resin. The peel strength-adhesive thickness curves showed an initial increase of the strength with

thickness and eventually attained a constant strength independent of thickness. The thickness at which this change occurred was clearly indicated for all samples, as shown in the example of Figure 3. The data are summarized in Table III.

As shown in Figure 4 for polymer A, the peel strength decreases with the polymer concentration in the range of 44–60% polymer. As the peel rate increases, the peel strength increases. The behavior of polymers B and C are very similar.

In all of the subsequent experiments, the thickness of the adhesive was between 0.45–0.50 mm. This eliminated the thickness dependence on the results.

Tensile Stress-Strain Measurements

The tensile stress-strain curves of polymers A, B, and C for a strain rate of 0.25 s^{-1} are shown in Figure

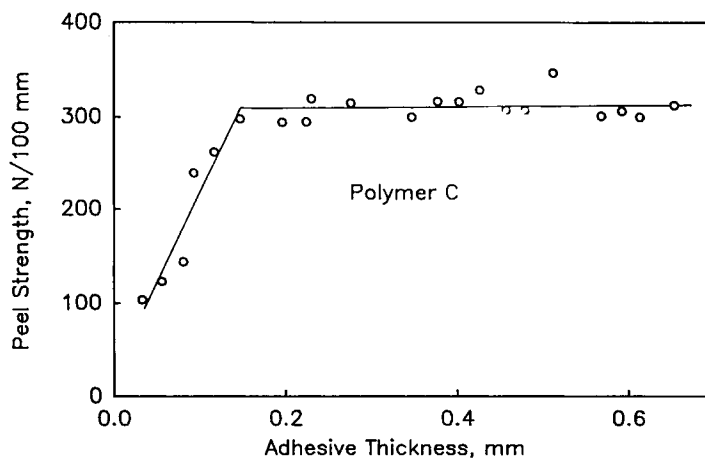


Figure 3 Dependence of peel strength on thickness of adhesive, 48% polymer C and 52% tackifier.

Table III Adhesive Thickness that Yields Optimum Peel Strength

S-I-S Polymer (%)	Polymer A (mm)	Polymer B (mm)	Polymer C (mm)
44	0.38	0.24	0.21
48	0.42	0.23	0.18
52	0.38	0.24	0.20

5. Significant differences in the modulus level are observed. In addition, polymer A extended uniformly until the specimen fractured, while polymers B and C exhibited a yield point corresponding to the visual observation of necking at some point in the specimen. The curves of polymers B and C are shown up to the yield points. The stress-strain curves of three polymers at other strain rates are similar to those shown in Figure 5.

The effect of strain rates on the stress-strain curves are shown in Figure 6 for polymer B. The rate effect is rather small until the strain becomes very large. Polymer A showed somewhat larger rate dependence.

The failure properties are summarized in Table IV. Although the failure-stress increased with increasing strain rate, the failure-strain remained independent of the rate.

Figure 7 shows the stress-strain curves of polymers A, B, and C at 44% polymer concentration in the PSA formulation. The strain rate was 0.15 s^{-1} . All three blends exhibited yield points, beyond which the specimen drew out nonuniformly at decreasing force levels.

The failure properties of the blends are compared to those of 100% polymers in Table V. The effect of tackifier is to decrease the failure stress and increase the failure strain.

Viscoelastic Properties

Figure 8 shows the viscoelastic properties of polymer A in terms of the shear storage modulus, G' , shear loss modulus, G'' , and $\tan \delta$ over the range of temperature. The glass-rubber transition is indicated at the lowest temperature, the rubber plateau in the middle, and the terminal flow region at the higher temperature. Although G' at the rubbery region is not exactly flat, the plateau modulus may be evaluated at the temperature, where G'' attains a minimum value. The $\tan \delta$ peak at -51°C corresponds to the T_g of the polyisoprene phase and the G'' peak at about 120°C corresponds to the T_g of the polystyrene phase. In addition, a small $\tan \delta$ peak was observed at about 0°C , which may correspond to the mixed zone at the boundary of two phases.

Qualitatively, polymers A, B, and C gave similar curves. The comparison of G' curves of these polymers is shown in Figure 9. The G' curve of polymer A, 25% polystyrene, is above the G' curves of polymers B and C, 14% polystyrene. The curve of polymer B, 20% diblock, is above that of polymer C, 40% diblock.

Figure 10 shows the viscoelastic properties of the 44% polymer A, 56% tackifier composition. The T_g of the tackifier-rubber phase is considerably higher than that of the rubber alone, because the tackifier is soluble in rubber and its T_g is 51°C . The polysty-

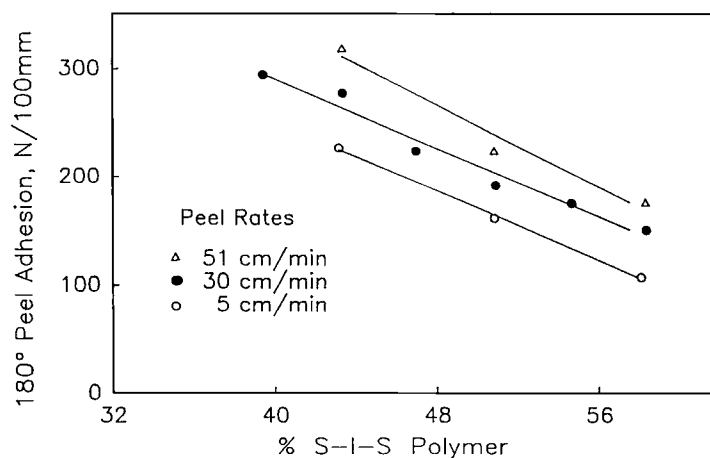


Figure 4 Peel strength and polymer-tackifier composition; also, effect of peel rate on peel strength, S-I-S copolymers A, B, and C.

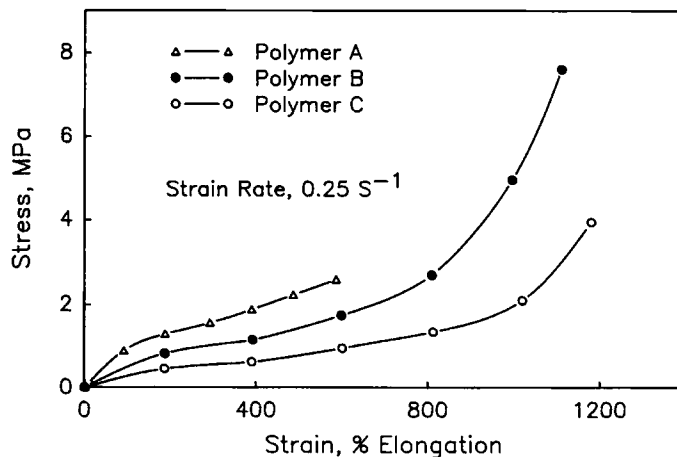


Figure 5 Tensile stress-strain curves of S-I-S copolymers A, B, and C.

rene phase is not affected by the tackifier, and the G'' peak remains unaffected. In the plateau region, the G' dips slightly and increases slightly when the polystyrene phase begins to soften. This result indicates that the morphology is not exactly in a stable state and some phase rearrangement is taking place as the temperature is raised. This phenomenon is more clearly shown in Figure 11, where the temperature sweep was repeated. However, in most cases, the plateau modulus was evaluated from a single temperature sweep as the G' corresponding to the temperature, where G'' attains a minimum value. Therefore, the plateau modulus is somewhat underestimated compared with values which would be obtained with annealed samples.

Figure 12 is a comparison of the G' curves of polymer A, which is mixed with the tackifier to make

52 and 44% polymer concentrations. The major effects of the tackifier are to raise the T_g of the rubber-tackifier phase and to lower the rubbery plateau modulus.

Qualitatively speaking, the temperature dependencies of viscoelastic properties of polymer A tackifier and polymer B tackifier are similar at both 52 and 44% levels. However, the behavior of polymer C tackifier is different, as shown in Figure 13, for the sample containing 52% polymer. In this case, the G' does not show a plateau; neither is there a G'' minimum. Therefore, the plateau modulus was evaluated as an inflection point of the G' curve, although it is an arbitrary choice. Evidently, in this system, the polystyrene domains are not firm cross-link junctions. Strictly speaking, there is no distinct plateau modulus.

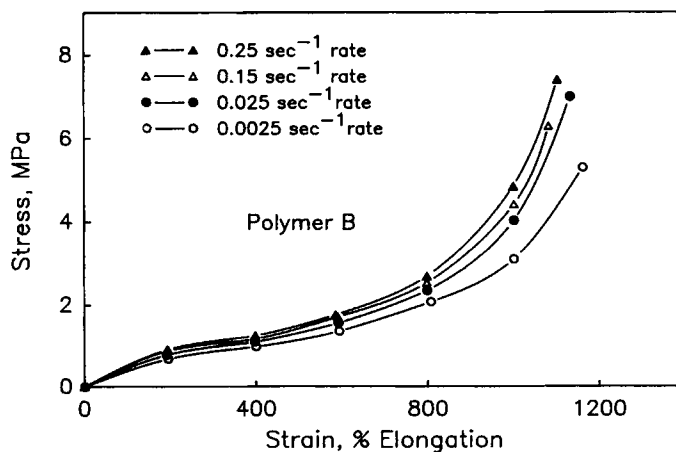


Figure 6 Tensile stress-strain curves of S-I-S copolymer B at different strain rates.

Table IV Tensile Failure Properties of Block Copolymers

Strain Rate (s ⁻¹)	Polymer A		Polymer B		Polymer C	
	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)
0.0025	1.9	650	5.3	1150	2.9	1230
0.025	2.3	640	6.3	1070	3.4	1180
0.15	2.5	590	7.0	1120	3.7	1180
0.25	3.3	650	7.4	1090	3.8	1180
Mode of Failure	Rupture		Yielding		Yielding	

DISCUSSION

Shear Adhesion Failure Temperature and Viscoelastic Properties

The shear adhesion data in Table II indicate a primary difference among polymers A, B, and C in shear adhesion holding power at elevated temperatures. Table VI contains information about the viscoelastic properties at the entrance to the terminal zone. This is defined here as the crossover temperature, where $G' = G''$ at the higher temperature end of the rubbery plateau. The volume fractions of polystyrene phases, ϕ_s and the elastomer phase, ϕ_R are also given.

Polymer A, with almost twice the polystyrene volume-fraction of polymers B and C, exhibited the highest shear adhesion failure temperature and crossover temperature. Polymers B and C contain the same volume fraction of polystyrene phase, but exhibited different failure temperatures. The crossover temperatures were the same for these polymers.

To determine which viscoelastic property relates to the shear adhesion failure temperature, a first attempt was to examine the crossover temperature. At temperatures above the crossover temperature, the viscous response (G'') becomes dominant over the elastic response (G'). However, the crossover temperature alone is evidently insufficient for distinguishing PSAs made with polymers B and C. The values of the moduli are different for formulations with polymers B and C.

The reason that the crossover temperature alone is insufficient for relating with the adhesive behavior may be as follows: whereas the shear failure temperature represents a failure behavior that presumably involves a large deformation, the crossover temperature represents a nondestructive behavior measured with a very small deformation. The difference of elastic modulus is expected to influence the failure behavior. Differences between the small shear deformation and large tensile deformation will be discussed later. However, formulations involving

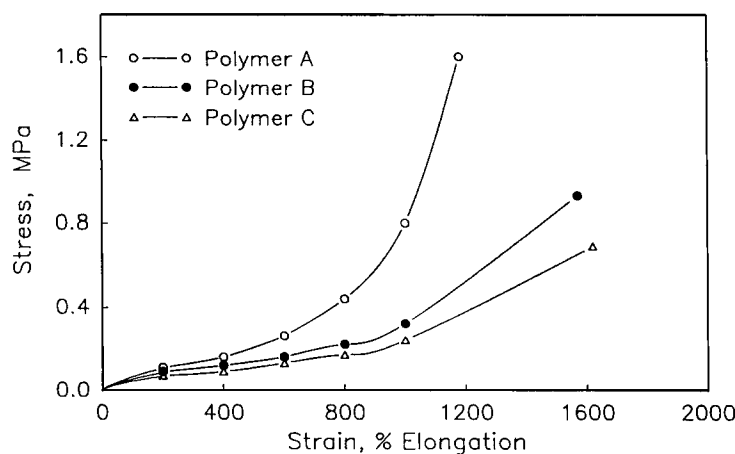


Figure 7 Tensile stress-strain curves of 44% polymer and 56% tackifier, S-I-S copolymers A, B, and C.

Table V Comparison of Tensile Failure Properties of 100% Polymer and 44% Polymer in PSA

Polymer Concentration Wt %	Polymer A		Polymer B		Polymer C	
	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)
100	3.4	650	7.1	1120	3.8	1180
44	1.9	1180	0.93	1570	0.69	1620

polymers B and C are clearly differentiated in the tensile deformation data.

Tack and Loss Modulus

The variation of the polyken probe tack and quick stick with tackifier concentration relates to the effect

of the tackifier on the viscoelastic properties. For good pressure sensitive tack and quick bond formation, the adhesive should be easily deformed in a time span on the order of a fraction of a second. The adhesive needs to make an intimate contact with the entire surface irregularities to form a quantifiable bond; therefore, viscous flow is required. The

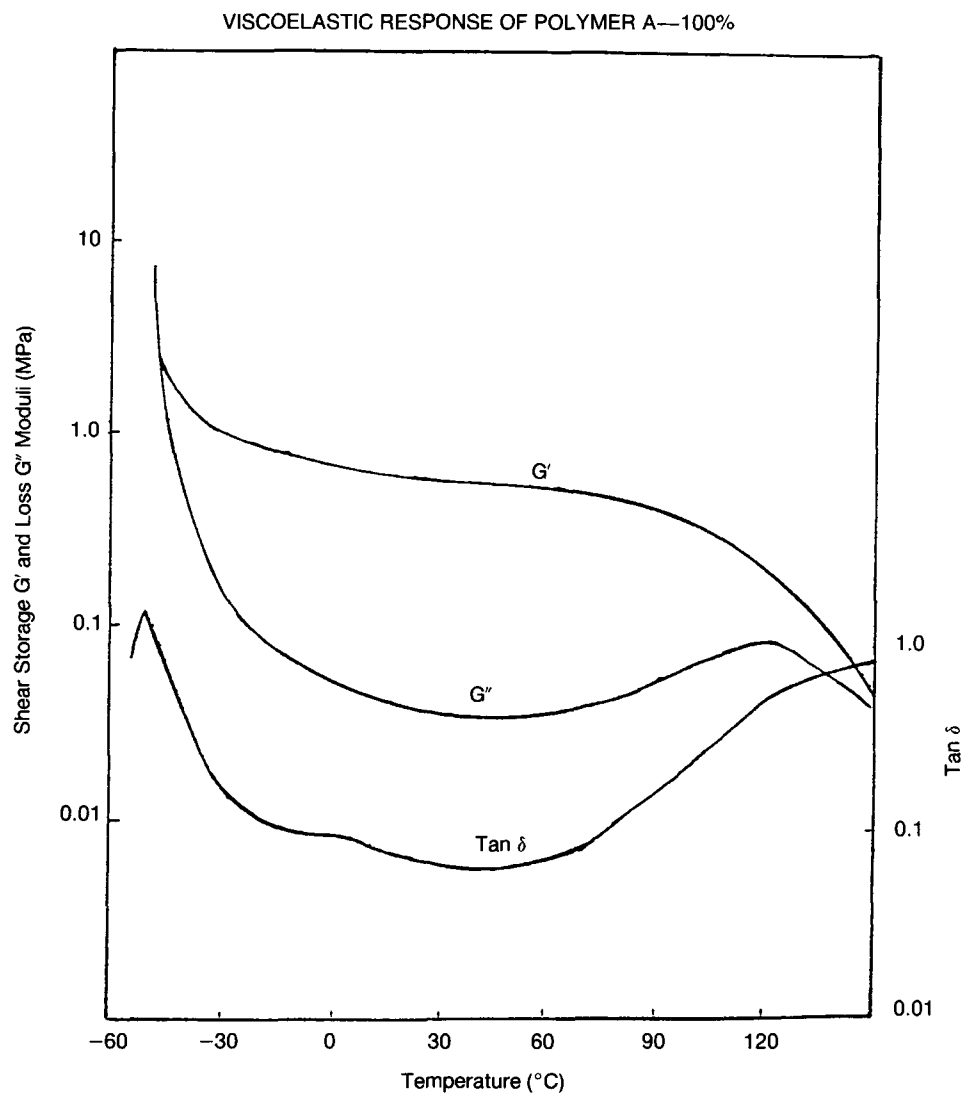


Figure 8 Viscoelastic property-temperature curves of S-I-S copolymer A at 1 rad/s.

100 % POLYMER COMPARISONS

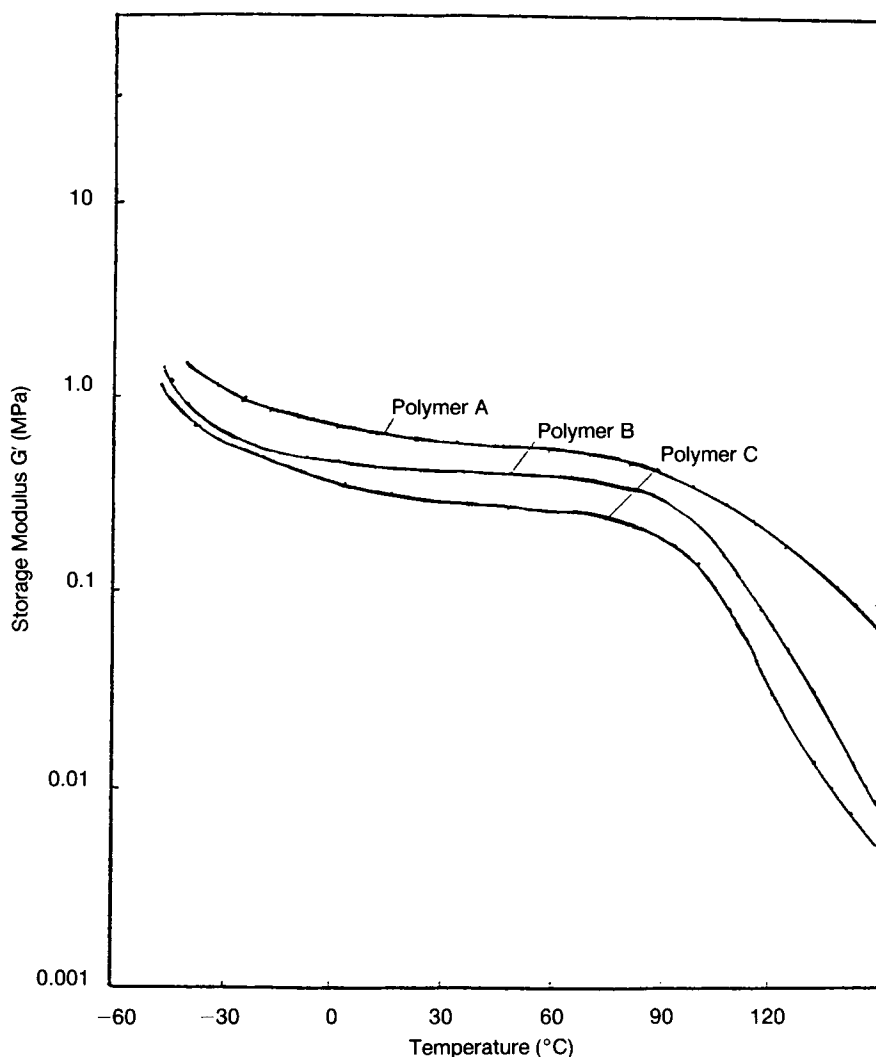


Figure 9 Storage modulus-temperature curves of S-I-S copolymers A, B, and C.

above requires a lower G' for the quick deformability and a lower G'' for the flow. However, these tests also require detaching the PSA from the surface. Therefore, the measured results reflect the resistance to the detachment also. For this, the higher values of G' and G'' are desired. Kraus et al.⁴ found a positive correlation between tack and loss modulus. Bates¹⁶ contends that dissipation energy is related to a loss factor that corresponds to $\tan \delta$. Table VII lists the tack values and viscoelastic properties. The values of G' and G'' were obtained at 23°C and 1 rad/s. Within the ranges of the material variables, the higher values of G' , G'' , and $\tan \delta$ tend to give the higher polyken tack. Therefore, the resistance to detachment is controlling the tack results. How-

ever, G' cannot increase indefinitely while maintaining good tack because too high a G' prevents the good wetting of the surface.³ The quick stick values do not correlate with viscoelastic properties, either because of the error in the measurements or because of the competition between the attachment and detachment mechanisms.

Peel Strength and Failure Energy

The adhesion data indicate that peel strength varies with peel rates and temperature. This is expected because the adhesive is a viscoelastic material, and the resistance to peeling separation is consistent with the energy criterion for adhesive failure. The

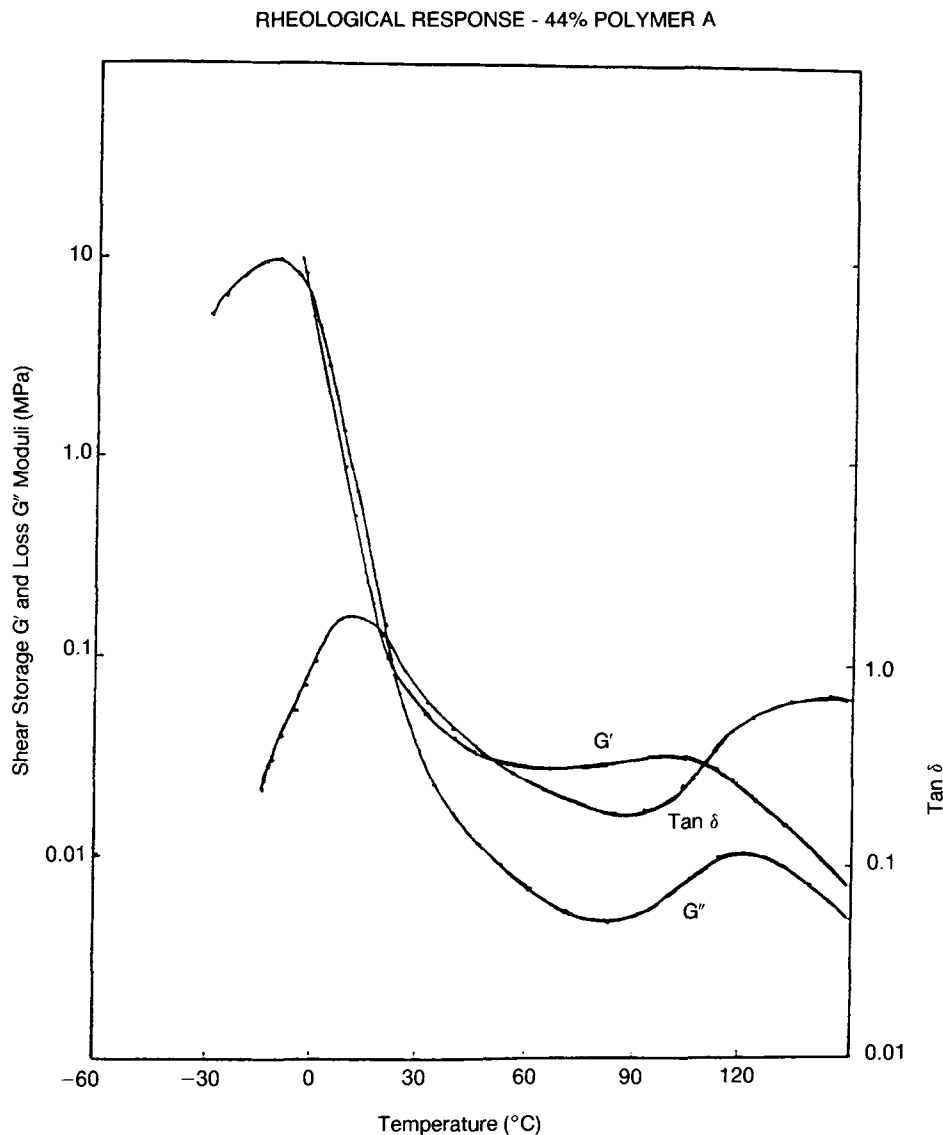


Figure 10 Viscoelastic property-temperature curves of 44% polymer A and 56% tackifier.

energy required for fracture of the elastomeric material is largely independent of the type of test piece and the way in which stresses are supplied and may thus be regarded as a characteristic measure of strength. This raises a possibility of relating peel strength with tensile stress-strain data through calculation of failure energy.

A characteristic amount of energy, W_a , per unit area of interface is required to bring about separation. For the present peel test,

$$W_a = P \quad (1)$$

where P is the peel force per unit width of adhesive-

adherent interface. The adhesive failure energy is equal to the sum of the different energy dissipations involved:¹⁷

$$W_a = W_0 + W_1 + W_2 + W_3 \quad (2)$$

and

W_0 = energy required to create new surfaces,
 W_1 = energy dissipated within the adhesive,
 W_2 = energy dissipated within the adherent,
 W_3 = strain energy in the newly detached strip.

For rubbery adhesives, W_1 is orders of magnitude

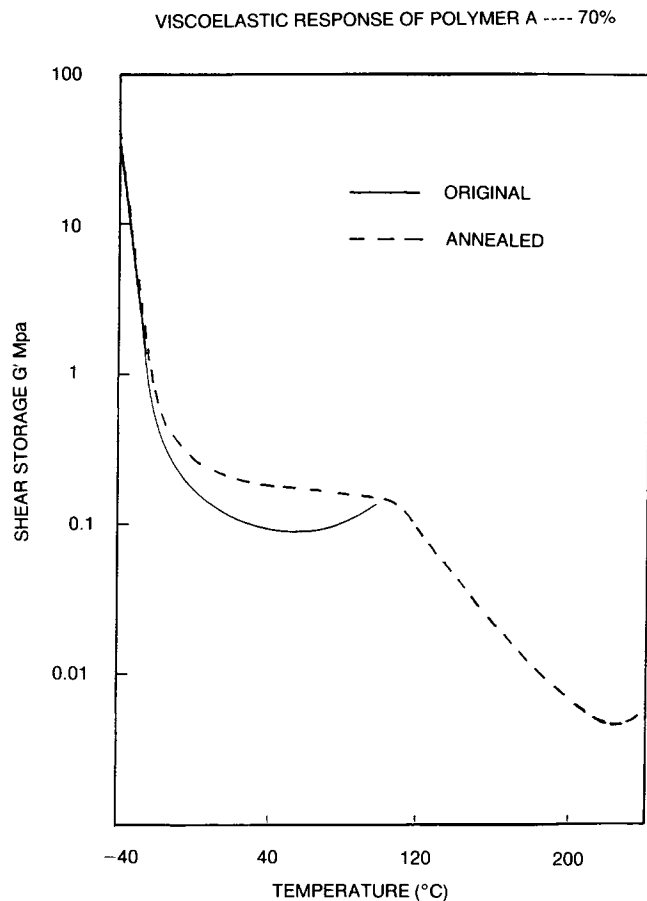


Figure 11 Annealing of morphology during measurement of viscoelastic properties, 70% polymer A and 30% tackifier.

larger than W_0 . In the present work, W_2 is small and negligible. Also, W_3 is small and may be neglected without any serious error.¹⁸

In order to estimate W_1 from the tensile stress-strain curve, the following scheme is used. Figure 14 is a schematic stress-strain curve, where B is the failure point. For PSAs made with Polymer A, point B corresponds to rupture and for those with polymers B and C it corresponds to yielding. Point A is the stress at any strain prior to failure, but may correspond to the stress at the detachment. Area 1 is the hysteresis area, which may correspond to W_1 if the hysteresis is the mechanism of the adhesive detachment. The areas 1 + 2 correspond to W_1 when the adhesive detachment involves a break of a sort including also a loss of the elastic energy. The area 1 + 2 + 3 represents the failure energy to the onset of yielding; the area 1 + 2 + 3 + 4 is the failure energy to an arbitrary point beyond the yield point,

and the area 1 + 2 + 3 + 4 + 5 is the failure energy beyond yielding at break.

Comparisons of the observed peel strength, and that calculated from tensile stress-strain curves, are given in Table VIII, where point A is chosen arbitrarily at the failure, σ_m , and also at $\frac{2}{3}\sigma_m$, and $\frac{1}{3}\sigma_m$. The PSA compositions of this part of the work are 48% polymer and 52% tackifier.

For calculating peel strength, the energies (per volume) evaluated from tensile measurements, U_1 and U_{1+2} , are multiplied by the effective thickness of the specimen. The effective thicknesses are those given in Table III; they are 0.40 mm for Polymer A, 0.24 for Polymer B, and 0.20 for Polymer C.

For Polymer A, the calculated results indicated that the adhesive failed (detached) at approximately $\frac{2}{3}$ of the failure stress. However, for polymers B and C, the calculated peel strengths are much smaller than the observed strengths. The possible expla-

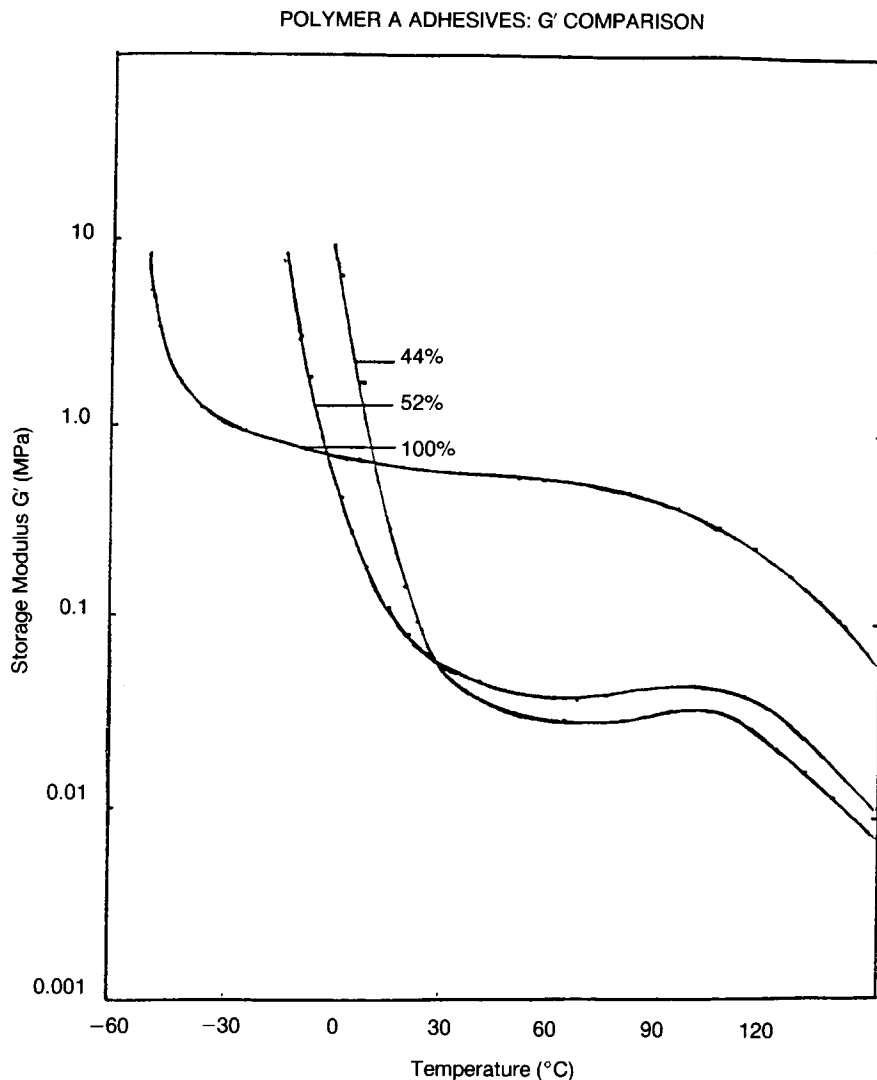


Figure 12 Storage modulus-temperature curves of polymer A with 0, 48, and 56% tackifier.

nation is as follows: At the peel failure, a considerable amount of material is seen to be drawn out for polymers B and C. This is more so for Polymer C than for Polymer B. This observation implies that the energy of drawing past the yield point may contribute to the peel strength including the area 1 + 2 + 3 + 4 for Polymer B and the area 1 + 2 + 3 + 4 + 5 for Polymer C. In addition to the drawing, it was noted that polymers A and B showed adhesive failure, whereas Polymer C failed cohesively. This might add support to the above interpretation of the difference between polymers B and C, where the latter, compared with the former, had a larger discrepancy between calculated and observed peel strength.

FUNDAMENTAL PROPERTIES

Glass Transition Temperature

The glass transition temperature, T_g , of the rubber phase for the S-I-S copolymers and the polymer-tackifier blends were estimated from $\tan \delta$ peaks in the viscoelastic data and are listed in Table IX as T_g observed.

The T_g values of the blends may be calculated according to the Fox equation,¹⁹ which had originally been devised for copolymers,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (3)$$

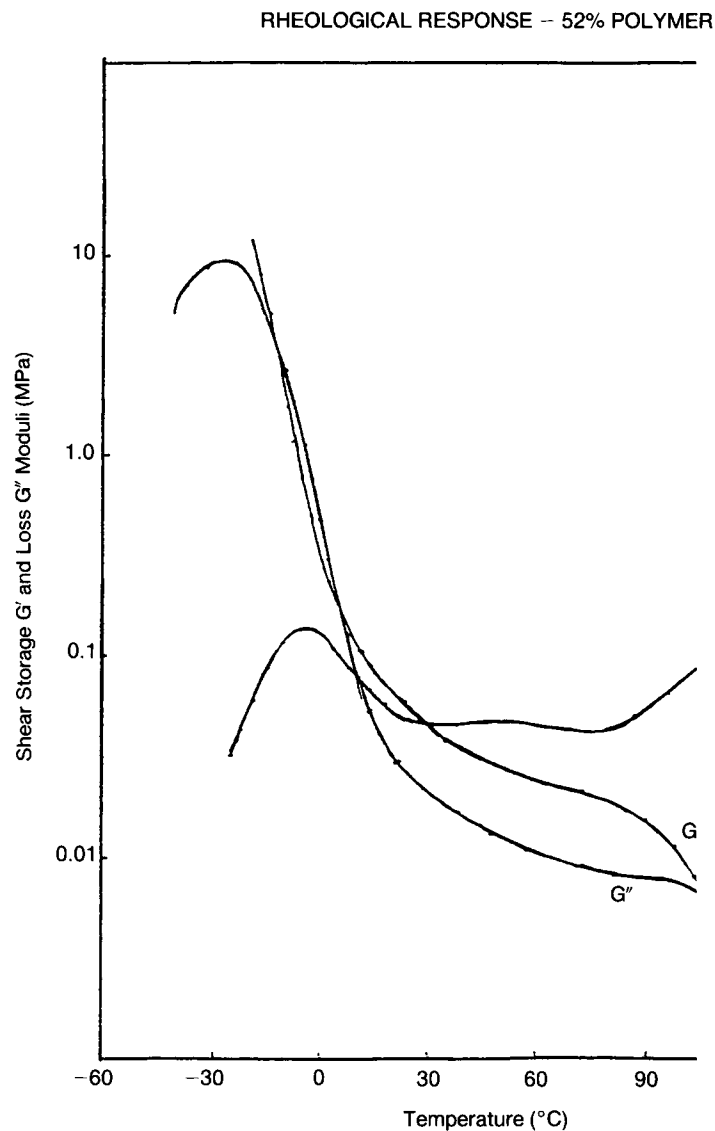


Figure 13 Viscoelastic property-temperature curves of 52% polymer C and 48% tackifier.

For this calculation, observed T_g values of the copolymers as listed in Table IX and the T_g of the tackifier, 51°C, were used. The observed T_g s are

several degrees higher than those calculated. This difference may be because eq. (3) is oversimplified, but it may also imply that the rubber and tackifier

Table VI Shear Adhesion and Viscoelastic Properties

Polymer in PSA	ϕ_s	ϕ_R	Shear Failure Temp. (°C)	$G' = G''$ (°C)	$G' (= G'')$ (kPa)
A-44%	0.10	0.33	134	> 150	—
A-52%	0.12	0.39	134	> 150	—
B-44%	0.06	0.38	114	105	8.5
B-52%	0.07	0.45	114	105	8.5
C-44%	0.06	0.38	104	105	5.5
C-52%	0.07	0.45	104	105	6.6

Table VII Tack and Viscoelastic Properties

Polymer in PSA	G' (10 ⁴ Pa)	G'' (10 ⁴ Pa)	Tan δ	Polyken Tack (g/cm ²)	Quick Stick (N/100 mm)
A-44%	8.7	8.6	0.988	1530	260
B-44%	6.6	5.5	0.833	1420	230
C-44%	5.2	4.1	0.789	1280	250
A-52%	6.3	3.0	0.476	1100	200
B-52%	5.7	2.7	0.473	1150	180
C-52%	5.5	2.5	0.455	870	200

are not completely miscible at the molecular level. The fact that the $\tan \delta$ peak broadens when the copolymer is mixed with the tackifier indicates somewhat poor mixing at the molecular level²⁰ (Figs. 7 and 9).

The T_g s of the polystyrene domains were estimated from the G'' peaks and are listed in Table X.

The T_g s of polystyrene domains in Polymer A and Polymer A-based PSA are rather high, *ca.* 120°C. The presence of tackifier does not affect the polystyrene domains, the T_g s being about the same for these PSAs. The T_g s of polystyrene domains of polymers B and C are considerably lower than that of Polymer A. The smaller domains appear less stable. With polymers B and C, the polystyrene domains are affected by the presence of tackifier, since their T_g s are lowered by several degrees. Also, the G'' peaks of these polymers become less distinct when the tackifier is present; with Polymer C they are more like shoulders than peaks (see Fig. 13).

The T_g of polystyrene is usually listed as about 100°C.²¹ However, somewhat higher values, for ex-

ample 116°C, are also reported.²² The T_g of natural rubber is reported to be -73°C.²³ However, the T_g of the polyisoprene domain in this work is -51 to -54°C (Table IX). The T_g s of both the rubber domain and the polystyrene domain of Polymer A appear to be about 20°C higher than those values reported elsewhere. The T_g s, of course, depend upon the time-scale of the measurements. In this work, the dynamic mechanical measurements were performed at 1 rad/s. Kraus and Hashimoto²⁴ reported the results of the dynamic mechanical measurements with a PSA formulation, which is similar to our Polymer B with the same tackifier. Their frequency of measurement was 0.6 rad/s, similar to ours. However, the T_g of the polystyrene domain, defined as the G'' maximum, was about 85°C, which is about 10°C lower than what we observed with our Polymer B. A primary difference here is the method of preparation of the blend; whereas our blends were prepared by melt-mixing, their sample was solution blended. There must be a significant difference in the morphology.

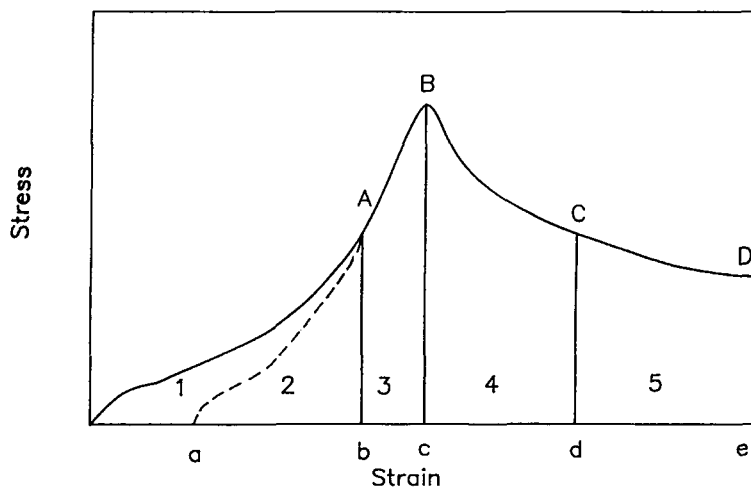


Figure 14 Schematic illustration of deformational energy corresponding to peel strength and estimated from tensile stress-strain curve.

Table VIII Peel Strength/Energy Criterion

0.15 s ⁻¹ ^a Strain Rate	Stree MPa	Elongation	N/mm ²		U ₁	Experimental ^a	U ₁₊₂
			U ₁	U ₁₊₂	Peel Strength N/100 mm	Peel Strength N/100 mm	Peel Strength N/100 mm
Polymer A (σ_m)	2.0	13.3	3.3	10.7	132	428	
(2/3 σ_m)	1.35	12.0	1.5	5.9	60	240	236
(1/3 σ_m)	0.67	9.4	0.8	3.2	32		128
Polymer B (σ_m)	0.74	15.3	1.9	5.2	46	250	124
Polymer C (σ_m)	0.46	15.5	1.4	3.4	28	375	68
0.25 s ⁻¹ ^b Strain Rate							
Polymer A (σ_m)	2.0	11.8	3.0	9.2	120		368
(2/3 σ_m)	1.35	11.3	1.9	6.3	76	275 ^b	252
(1/3 σ_m)	0.66	9.0	1.0	2.7	40		108

^a Experimental peel rate = 30 cm/min = 0.15 s⁻¹ strain rate: ASTM D638-82a, p. 239.

^b Experimental peel rate = 50 cm/min = 0.25 s⁻¹ strain rate: ASTM D638-82a, p. 239.

Rubbery Plateau

Kraus and Rollmann²⁵ tested the applicability of the following equation to the modulus values G_{en}^o at rubbery plateau;

$$G_{en}^o = (\rho/M_e)RT(1 + 2.5C + 14.1C^2) \quad (4)$$

where ρ is the density of rubbery phase, M_e is the molecular weight corresponding to the entanglement coupling distance, $(\rho/M_e)RT$ is the contribution from entanglement to rubbery modulus and C is the volume fraction of polystyrene domains. The quantity $(1 + 2.5C + 14.1C^2)$ is taken from the Guth-Gold equation.²⁶ For many samples of S-I-S and S-B-S types of triblock copolymers, Kraus and Rollmann found eq. (4) to give quantitative representation. However, they acknowledged the physical model of this equation to be an oversimplification. Among other things, the Guth-Gold equation is for a spherical dispersed-phase, which is wet with a

noninteracting medium. In the present case, the polystyrene domains are not exactly spherical. Moreover, they are connected to the medium with chemical bonds. In addition, the model ignores the interfacial zone of the mixed phase. In spite of these shortcomings, we use eq. (4) as a good "yard stick" for quantitative comparison, and as an interpretive aid.

The calculated results are compared to the observed data in Table XI.

The calculated values are almost twice as large as those observed. This finding is different from Kraus and Rollmann's results. Because our samples contain significant amounts of diblock copolymer, the lower moduli observed in our study may reflect decreases of entanglement density by the diblock copolymer. The extent of decrease in entanglement density may be estimated by taking a ratio of the observed over the calculated plateau modulus. With the 20% diblock content, the entanglement density

Table IX Glass Transition Temperature of Rubber Phase

	Polymer Type A			Polymer Type B			Polymer Type C		
Polymer (%)	100	52	44	100	52	44	100	52	44
T_g , obs., °C	-51		11	-51	-4	5	-54	-4	5
T_g , calc., °C	—	-4	4	—	-8	1	—	-10	-1
Rubber Fraction	1.00	0.448	0.370	1.00	0.482	0.40	1.00	0.482	0.40
Tackifier	0	0.552	0.630	0	0.518	0.60	0	0.518	0.60

Table X Glass Transition Temperature of Polystyrene Phase

	Polymer Type A			Polymer Type B			Polymer Type C		
	100	52	44	100	52	44	100	52	44
Polymer (%)	100	52	44	100	52	44	100	52	44
$T_g, ^\circ\text{C}$	123	123	120	107	96	98	100	94	95

was decreased to the 0.55–0.60 level for Polymers A and B. With the 40% diblock content, density was decreased to less than half. These results may reflect a loss of connectivity between the rigid domains rather than the loss of some of the entanglements. The connectivity is not considered in eq. (4).

When the tackifier is present, Kraus and Rollmann²⁵ tested a modified form of eq. (4).

$$G_{\text{en}}^{\circ} = V_2^2(\rho/M_e)RT(1 + 2.5C + 14.1C^2) \quad (5)$$

In eq. (5), C is the volume fraction of polystyrene domain in the entire composition and V_2 is the volume fraction of polymer in the tackified polyisoprene phase. The calculated and observed data are given in Table XII.

The calculated values from eq. (5) are 2.2 to 5.5 times larger than the observed ones. Kraus and Rollmann²⁵ also found discrepancies, but only by a factor of about 1.5. In our study, there were disagreements in the calculated and observed modulus of base polymers (Table XI). This implies a further loss of entanglement density or connectivity due to the dilution with tackifier. Also, somewhat larger factors for Polymers B and C suggest that the polystyrene domains of these polymers are somewhat affected by the tackifier. This was already noted in the examination of T_g s (Table X).

Log G'' vs. Log G' Plot

Presented in Figure 15 are plots of $\log G''$ vs. $\log G'$, constructed from the isothermal (room temperature) frequency sweep of dynamic measurements with 44% polymer PSAs. The curves of polymers A

and B are indistinguishable, whereas that of Polymer C lies to the left. Previously, it was found that the presence of long branches and gels shifts the curve to the right.^{27,28} In the present case, the major difference is the diblock content (Table I). Here, the degree of connectivity between polystyrene domains may be playing a role.

The data in the last column of Table XI also indicate that the loss of connectivity due to the diblock is about the same for polymers A and B, containing 20% diblock, but is significantly larger for Polymer C, containing 40% diblock. Although the data of Table XI are for the base polymers and those of Figure 15 are for the 44% polymer PSA, the relative extent of the loss of connectivity due to the presence of diblock is about the same.

Strain–Time Correspondence

Previously, it was discovered that the strain–time correspondence is an effective criterion for detecting a relative strength of network and pseudonetwork.²⁹ Here, the network is referred to as a chemically crosslinked structure. The pseudonetwork may be built by intermolecular association, highly branched gel molecules, or the hard domains of the triblock copolymers. In the absence of these networks, the strain–time correspondence given by the following forms apply; in the tensile stress–strain measurements, the stress based on the deformed cross-section, σ , and strain, ϵ , may be presented as modulus E , which is, in general, a function of time, t , and strain, ϵ .

$$\sigma/\epsilon = E(t, \epsilon) \quad (7)$$

When the strain–time correspondence is applicable,

$$\sigma/\epsilon = E(\alpha t) \quad (8)$$

where α is the extension ratio. This is a means of linearizing the otherwise nonlinear data. With Poisson's ratio of 0.5, the tensile modulus may be related to shear modulus, $G(\alpha t)$, by a factor of three. Because it is the linearized shear modulus, equivalent data may be obtained with dynamic measure-

Table XI Calculated and Observed Rubbery Plateau Modulus (MPa) of Block Polymers

Polymer	G_{en}° , Calculated	G_{en}° , Observed	G_{en}° (Observed) G_{en}° (Calculated)
	A	1.06	0.58
B	0.68	0.41	0.60
C	0.66	0.30	0.45

Table XII Calculated and Observed Rubbery Plateau Modulus (MPa) of PSA Formulations

Polymer	Polymer (%)	Calculated eq. (5)	Observed	Ratio of Moduli in Column 3/Column 4
A	44	0.089	0.040 ^a	2.2
	52	0.143	0.050 ^a	2.9
B	44	0.082	0.026 ^a	3.2
	52	0.122	0.028 ^a	4.4
C	44	0.081	0.019 ^b	4.3
	52	0.121	0.022 ^b	5.5

^a Observed data were corrected in the manner shown in Figure 11.

^b Estimated from the inflection point in G' curve.

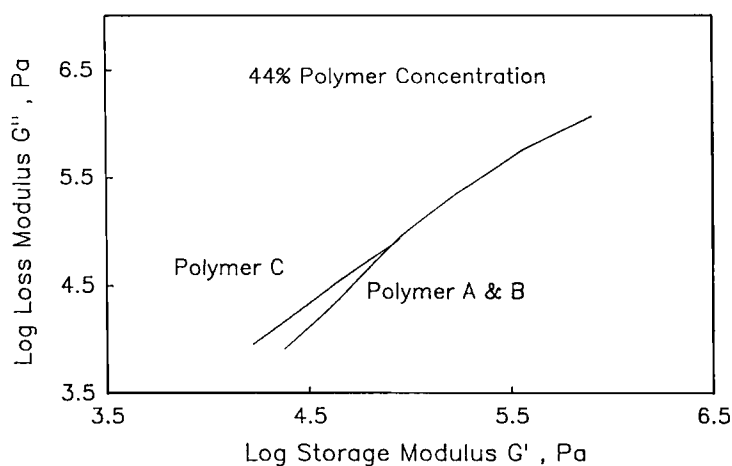
ment as the absolute value of complex modulus as a function of angular frequency, $|G^*|(\omega)$. Subsequently, the corresponding viscosities may be calculated from the tensile data as,

$$\eta_T = \frac{E(\alpha t)}{3} \times \alpha t \quad (9)$$

where $1/\alpha t$ is equivalent to the deformation rate. Then $\eta_T(1/\alpha t)$ may be compared to complex viscosity, $|\eta^*|(\omega)$.

Figures 16, 17, and 18 are η_T vs. $(1/\alpha t)$ plots for polymers A, B, and C, respectively. For Polymer A, the viscosities calculated from tensile data at different deformation rates do not form a master curve. The data of the higher deformation rate give a higher viscosity, a fact that indicates that the polystyrene domains are, to some degree, effective crosslink

points. On the other hand, for polymers B and C, the data form a master curve. This indicates that the polystyrene domains do not act like crosslink points at the large tensile deformation. In Figure 19, viscosities η_T and $|\eta^*|$ are compared for PSAs containing 44% each of polymers A, B, and C and 56% tackifier. With all three compounds, $|\eta^*|$ values are shown to be significantly higher than η_T values. Because $|\eta^*|$ s are measured at very small deformation, the polystyrene domains must be acting effectively as crosslink junctions, whereas the effectiveness of the junctions are significantly diminished at the large tensile deformation. However, the η_T curves are concave upward. Therefore, at the large deformation (at the left of the figure) either crosslink junctions reform or constraints develop against further deformation. This behavior is similar to the limited extensibility exhibited by the chemically crosslinked network.²⁹

**Figure 15** Plots of log loss modulus–log storage modulus, S–I–S copolymers A, B, and C.

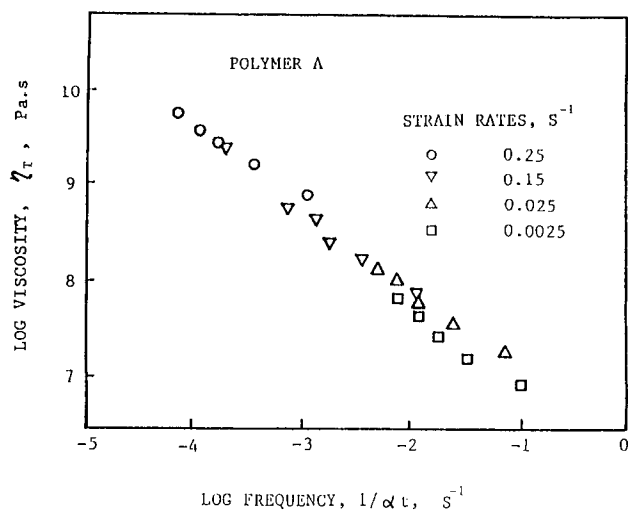


Figure 16 Inapplicability of strain-time correspondence, indicating presence of network junction formed by polystyrene block, S-I-S copolymer A.

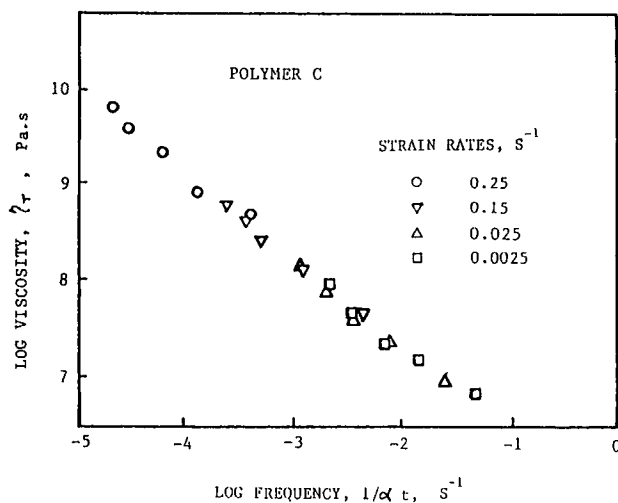


Figure 18 Applicability of strain-time correspondence, indicating that polystyrene blocks do not form effective network junctions, S-I-S copolymer C.

CONCLUSIONS

1. In contrast to the general belief that the polystyrene domains of S-I-S block copolymer forms network junctions, this is not always the case. With 14% polystyrene-block and 20–40% diblock, there was no indication of the network junctions in the tensile stress-strain behavior.
2. Comparison of dynamic shear data and ten-

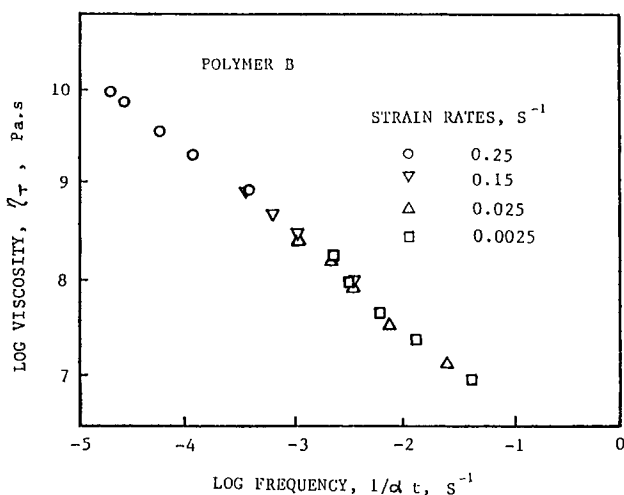


Figure 17 Applicability of strain-time correspondence, indicating that polystyrene blocks do not form effective network junctions, S-I-S copolymer B.

sile stress-strain data indicated that the polystyrene domains are effective network junctions at small deformation in the dynamic measurements. The styrene domains seem to be rather easily broken up in the large tensile deformation, not offering resistance as crosslink junctions. With the 44% polymer and 56% tackifier formulation, the block copolymers exhibited behavior like limited extensibility. This implies that the polystyrene domains set up increasing resistance before yielding.

3. The T_g of polystyrene domains depends upon the polystyrene content. The 14% polystyrene copolymers gave T_g s about 20°C lower than 25% polystyrene copolymer. The lower polystyrene content, that is, the lower polystyrene-block molecular weight, gives a smaller domain size. The polystyrene domain may contain rubber block segments. The fact that the T_g s of 14% polystyrene copolymers are lowered by several degrees in the presence of tackifier implies inclusion of rubber segments and tackifier in the polystyrene domains.
4. Loss of connectivity between the polystyrene domains is indicated when diblock content is increased from 20 to 40%. This was shown in the plots of $\log G''$ vs. $\log G'$.
5. The above observation shows that polystyrene content and diblock content are very ef-

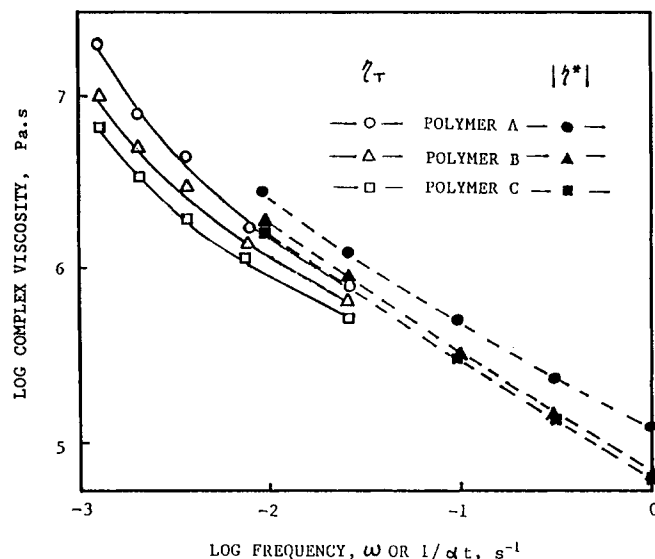


Figure 19 Comparison of viscosities calculated from tensile stress-strain measurements to dynamic shear viscosities. Disagreements indicate significant decrease of crosslink density at large tensile deformation.

fective material variables in controlling properties of pressure sensitive adhesives, when other variables, such as type of polymer, tackifier, and their proportion, are fixed. It also shows that, in addition to time-temperature dependencies, the type and magnitude of deformation must be considered in order to interpret the performance of pressure sensitive adhesives.

6. The shear adhesion failure temperature may be interpreted on the basis of (small deformation) dynamic mechanical properties. However, it is desirable to include information on the large deformation and failure behavior.
7. Tack and quick stick test results of the present study are influenced more by the detachment mechanisms than the attachment mechanisms. This conclusion may be altered if the range of the polymer-tackifier proportion is broadened beyond this work.
8. Peel strength may be calculated from tensile stress-strain data, if the deformation at the time of detachment is known. In the present study, the latter was estimated from the observed peel strength and tensile stress-strain data. It gave a reasonable result for 25% polystyrene copolymer at 48% polymer level. With the 14% polystyrene copolymer at the same polymer-tackifier proportion, the above

calculation was not successful because the adhesives drew out extensively after yielding.

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