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Comparison of the Effect of a Hydrocarbon Oil and a Terpene Tackifier on the Autohesion of Styrene-Butadiene Rubber*

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Blends of uncrosslinked styrene-butadiene rubber (SBR) with a terpene tackifier resin or a naphthenic oil have been characterized, and their autohesion and cohesion determined using a T-peel geometry. SBR/oil blends are homogeneous at all proportions, while SBR/resin blends, based on DSC and DMA analysis, undergo *bulk* phase separation at about 50% resin. However, migration of tackifier to the surface region is proposed at much lower resin contents. Compositions diluted with oil have autohesion similar to the neat SBR. This is attributed to compensating effects; although oil hastens self-bond formation by increasing chain mobility, this is nearly equally balanced by more facile chain separation during bond rupture. In short, oil-diluted compositions are soft and weak. On the other hand, SBR compositions containing small amounts of resin have high autohesion. Resin-diluted specimens deform easily at low strain, just as those containing oil, but intertwined chains of the former have greater resistance to separation, due at least in part to higher glass transition temperatures. It is proposed that autohesion is further enhanced by migration of tackifier to the surface. This causes SBR/resin compositions to be both soft and strong—a necessary condition for high autohesion.

KEY WORDS T-peel geometry; cohesion; adhesion; phase separation; surface migration of tackifier; uncrosslinked SBR; SBR/oil blends; SBR/resin blends; glass transition temperature; solution cast sheets; mechanically mixed and molded sheets; thermal analysis; dynamic mechanical analysis; tensile properties.

INTRODUCTION

Autohesion is the resistance to separation that develops when two pieces of the same material are contacted. It is an important property of contact adhesives as well as for rubbery compositions used in the manufacture of multilayer composites such as tires.¹⁻⁵

When a conventional adhesive joint is formed, the adhesive is fluid to hasten wetting, and then sets by chemical or physical action to strengthen. However, in

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autohesion the material remains in the same state during, and subsequent to, bond formation. Thus, high autohesion requires sufficient compliance (liquid-like) and strength (solid-like) simultaneously. This condition is met only for polymeric materials in the rubbery state, where chain segments are mobile, but wholesale chain slippage is hindered by entanglements.

True molecular contact of surface chains involving flow and "impurity" displacement is the first step in autohesion; this is followed by chain interdiffusion.⁶ Autohesion is assessed after a specified contact time by loading a joint until it separates. A useful parameter is relative autohesion which is defined as autohesion divided by the cohesive strength, when both properties are measured in the same geometry. Relative autohesion can have values between zero and one and is a measure of the extent of bonding. Importantly, however, its value is not unique, rather it depends on the rate and temperature of separation.^{7,8}

Tackifiers are sometimes added to elastomers to improve autohesion.^{9,10} They often have limited solubility. Tackifiers have ring structures and are brittle glasses ($T_g \sim 50\text{--}125^\circ\text{C}$) with molecular weight typically in the range of 1000–3000.¹¹ It still is not well understood why tackifiers improve autohesion.¹² In this study, a comparison is made of the effect of a terpene tackifying resin and a hydrocarbon oil on the autohesion of a typical styrene-butadiene cold emulsion rubber.

EXPERIMENTAL

The elastomer used in this work was an amorphous styrene-butadiene rubber with 23.5% styrene prepared in cold emulsion (Krylene 1502, Polysar Ltd.). It has an ML 1 + 4 @ 100°C of 52 and a number-average molecular weight of about 10^5 . The oil, Sunthene 4130 (Sun Oil Co.), was a medium viscosity naphthenic oil with a molecular weight of about 380. The tackifier was Zonarez M-1115 (Arizona Chemical Co.), which is terpene resin produced by the cationic polymerization of β -pinene. It has a number-average molecular weight of about 1100 and a softening point of 115°C. All components are soluble in toluene, which was the casting solvent.

A silicone-coated release paper was the substrate for solution cast layers, and polyester film (Mylar®) was the substrate for compression-molded sheets. A woven cotton fabric was the backing for T-peel testpieces. The fabric was coated with an adhesive (Chemlok® 402, Lord Corp.) before making molded samples. This was done to prevent separation at the elastomer/fabric interface during peel tests.

Solution Casting

Solutions of SBR with either oil or tackifier were prepared by weighing the components into a glass jar, then adding toluene to form a 10% solution by weight. The solutions were allowed to stand for about 24 hours to allow the SBR to swell and soften before mixing by slowly stirring or by rotating the glass jar. After several days, all components completely dissolved. For casting sheets, release paper was folded into a rectangular trough and placed into a supporting tray with a smooth glass bottom. The tray then was placed on a balance, and the appropriate amount

of solution for the desired film thickness was poured into the trough. The filled tray was placed in a level position in a fume hood to allow solvent evaporation. Uniformity of the sheet thickness was improved by surrounding the tray with a foil barrier several inches high to reduce air flow on the surface. Backing was applied after the sheets had dried. The cotton fabric was soaked in a 10% SBR/toluene solution, then placed onto a dried sheet under light pressure. Solution-cast films were dried at room temperature to constant weight.

Mechanical Mixing and Molding

Mechanical mixing was done in two steps. First, a large batch of elastomer with no additives was mixed on a mill. Smaller portions of this batch then were mixed with tackifier or oil in an internal mixer (Brabender Plasticorder).

The following mixing procedure was used. Batches of 275 g were masticated on a water-cooled mill for 5 minutes. The nip (~ 2.5 mm) was adjusted to obtain a rolling bank. The front roll speed was 0.152 m/s, and the back roll speed was 0.213 m/s. If more than 275 g were needed, another batch was prepared. The two batches were then passed through the mill together and rolled up. The combined batches were then passed through the mill six times before the entire batch was sheeted.

The sheet was aged overnight before cutting into strips and feeding into the internal mixer. Blends weighing 63 g were mixed in the internal mixer at a rotor speed of 40 rpm. The wall temperature was controlled by circulating oil at 120°C. Half of the elastomer was added to the mixer, then all of the oil or tackifier, and finally the remaining elastomer. A batch containing only elastomer was mixed for 3 minutes after all elastomer had been added. The work per unit mass required to mix this batch was 0.26 MJ/kg. Other batches containing oil or tackifier were mixed to equal work input. After a batch was removed from the mixer and cooled, it was stored in a sealed polyethylene bag until molding.

For T-peel experiments, sheets of elastomer with a fabric backing were prepared using the mold configuration of Figure 1. The inside dimensions of the spacer were 0.18 m by 0.18 m, and the thickness was 0.8 mm. The ferrotype plate provided a very smooth molded surface. Molding was done for 20 minutes at 120°C under a force of 25 tons ($\sim 23 \times 10^3$ kg). Before molding, a volume of elastomer sufficient to fill the mold was passed through a mill several times to form a sheet slightly thicker than the mold spacer. After filling the mold, it was placed under light pressure for one minute prior to applying high pressure. This gave sheets of uniform thickness with few entrapped bubbles.

Testpieces for measuring cohesive strength had a fabric backing on both sides of the elastomer. First, two sheets with fabric on only one side were molded as described above, except that a Teflon® film was used in place of the lower Mylar film, and a molding time of 10 minutes was used. The two sheets were molded simultaneously in two compartments of the press. Teflon films were removed while the rubber still was hot, and the elastomer surfaces were contacted. A strip of Mylar was placed between the two sheets at one edge to form arms for peel tests. The plied specimens were then molded for an additional 10 minutes using a spacer of double thickness.

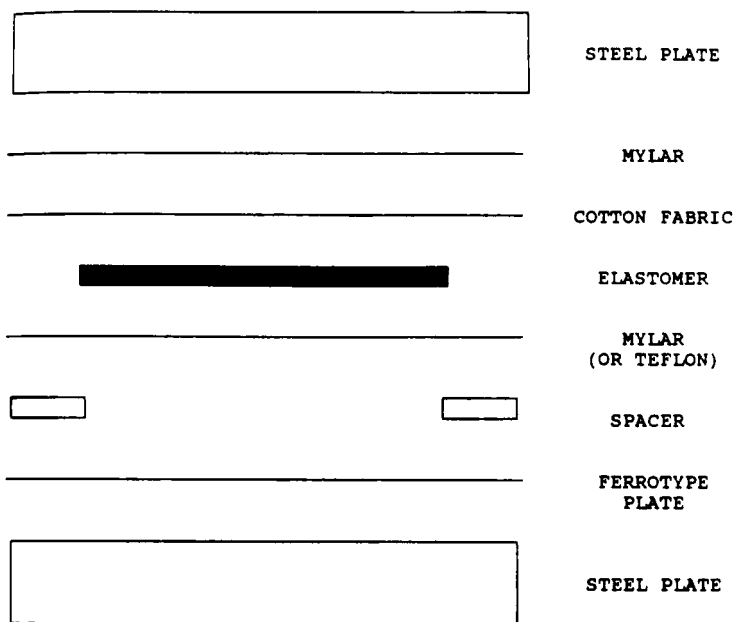


FIGURE 1 Mold configuration for preparing compression-molded specimens.

Thermal Analysis

Differential scanning calorimetry (DSC) was carried out using a DuPont Instrument with a scan rate of 20°C per minute. A sample was prepared by placing a drop of solution into an aluminum pan and allowing the solvent to evaporate.

Peel Tests

Both cohesive strength and autohesion were measured using a T-peel geometry (Figure 2). For autohesion tests, strips were cut from sheets which had fabric on

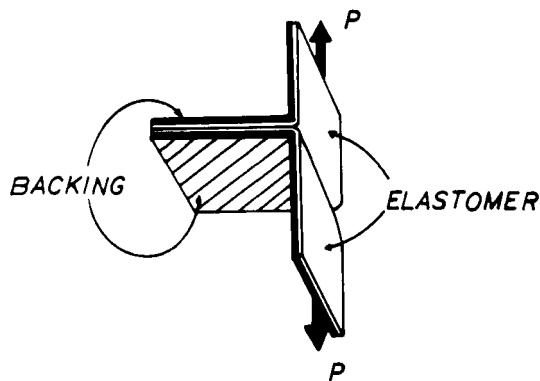


FIGURE 2 T-peel test geometry employed for measurement of both autohesion and cohesion.

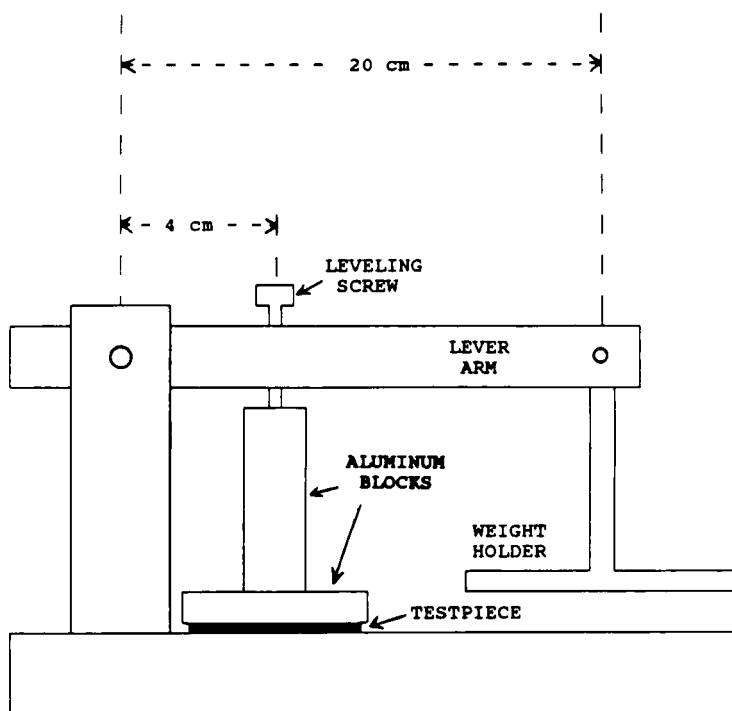


FIGURE 3 Apparatus for applying contact pressure to autohesion testpieces.

one side and Mylar or release paper on the other. Testpieces were formed by removing the cover layer from two strips, applying a thin layer of silicone grease at one end to provide test arms, and then placing the fresh elastomer surfaces in contact. The contact pressure was 0.573 MPa, and the contact time before peeling was one minute. Rectangular testpieces had dimensions of 10 mm \times 50 mm. Total thickness of the T-peel testpieces was about 2.4 mm, with the thickness of the elastomer about 1.5 mm. Contact pressure was applied using the apparatus of Figure 3 and was controlled by placing weights on the holder. The lever arm increased the force on the sample by a factor of 5. The mass of the weight holder was 6.3 N. The effect of the lever arm mass was equivalent to placing a weight of 2.0 N on the holder.

Testing was done at room temperature ($23 \pm 2^\circ\text{C}$) using an Instron testing machine with a crosshead speed 5.0 mm/min. For most samples, there was an initial peak in the peel force followed by steady-state peeling with small, random fluctuations. The peel force, F , was the average value, excluding the initial peak. Fracture energies, G , were determined by twice the average peel force divided by sample width.

Tensile Tests

Dumbbell-shaped specimens with a neck 5 mm wide and 25 mm long were used for stress-strain measurements. Ends of the specimens were wrapped with tape to pre-

vent sticking to the clamps. Clamping pressure was minimal to prevent squeeze-out of the soft compositions. The crosshead speed was 50 mm/min, corresponding to a nominal strain rate of 2 min^{-1} , and samples were run in triplicate.

Dynamic Mechanical Properties

Dynamic mechanical properties were measured using a Rheometrics Inc., Model RMS-800, dynamic mechanical spectrometer. Two different test geometries were used. In the temperature range from 0 to 120°C , sinusoidal shear deformation was applied to disc-shaped testpieces using parallel plates with a diameter of 8 mm and a plate separation of about 1.5 mm. At lower temperatures, slipping sometimes occurred between the testpiece and the plates. For this reason, rectangular testpieces ($50 \text{ mm} \times 5 \text{ mm} \times 1.5 \text{ mm}$) deformed in torsion were used in the temperature range from -80 to 20°C . The temperature scan rate was $5^\circ\text{C}/\text{minute}$, and the strain rate was 0.002 s^{-1} . The maximum strain was 0.005 for torsion tests, and 0.002 for the parallel plate tests.

RESULTS AND DISCUSSION

Autohesion

The autohesion, G_a , of SBR/oil blends is given in Figures 4 and 5 for samples prepared by *mechanical mixing-compression molding (MM)* and *solution casting (SC)*,

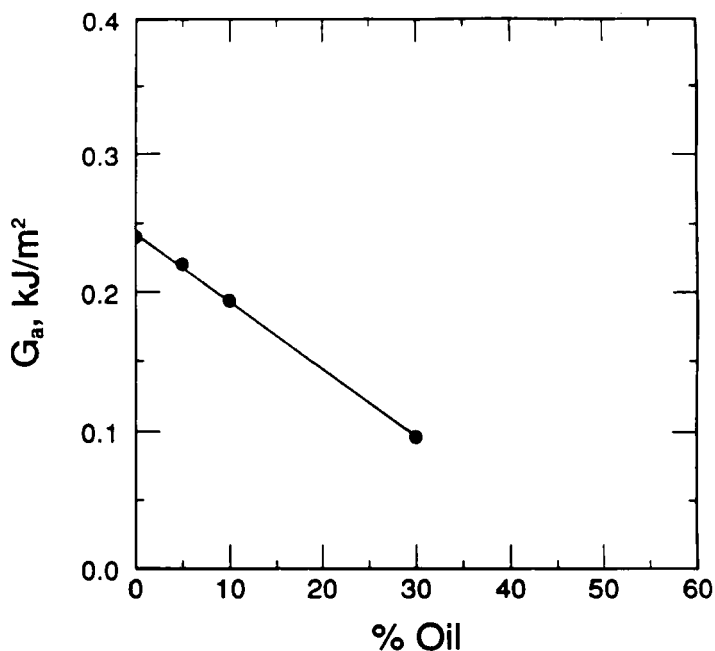


FIGURE 4 Autohesion of mechanically-mixed SBR/oil blends.

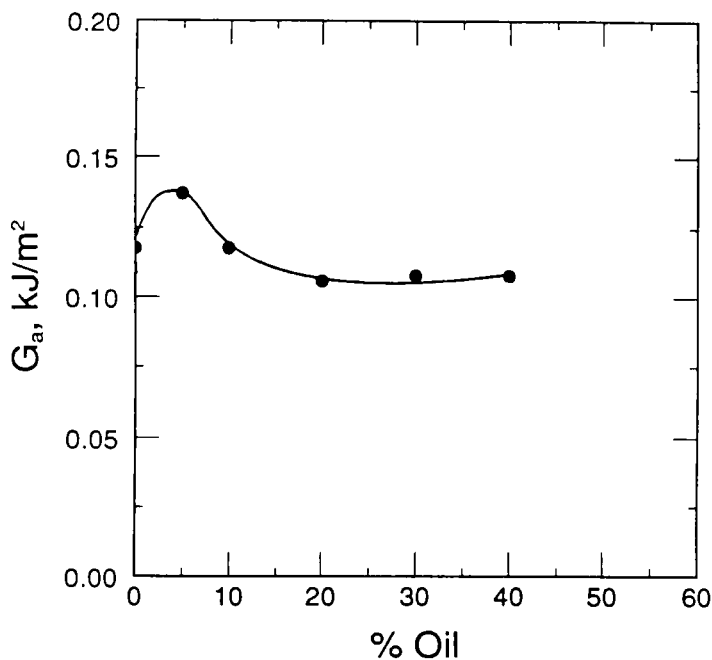


FIGURE 5 Autohesion of solution-cast SBR/oil blends.

respectively. With pure SBR, G_a (MM) is about twice G_a (SC). Oil addition causes a linear decrease in G_a (MM), while G_a (SC) is relatively independent of oil content, although data suggest that G_a (SC) may pass through a small maximum at low oil levels. At 30% oil, G_a (MM) \sim G_a (SC).

During MM, samples are subjected to intensive shear mixing, which undoubtedly results in some chain scission, especially of longer chains. Apparently, for the pure SBR, this enhances autohesion (relative to cast samples) by promoting viscous flow and increasing interdiffusion during bonding. Moreover, the difference between mechanically-mixed and solution-cast samples is expected to diminish when oil is added. Because of reduced internal friction and loss of entanglements with dilution, shear stresses during mastication are reduced and, consequently, so is chain scission. As noted already, at high oil content autohesion is similar for SC and MM samples, suggesting that chain scission is minimal during shearing of sufficiently diluted SBR.

When oil is added to an elastomer, autohesion is influenced by competing effects. Oil, by increasing chain mobility, is expected to facilitate bond formation. On the other hand, interdiffused, diluted chains should separate more readily when stressed. When the molecular weight of the rubber is not changing (*i.e.*, SC, Figure 5), these two factors seem to balance approximately, so that autohesion is weakly dependent on oil content. Next we consider experiments which provide evidence of changes in bond formation and rupture resistance with dilution.

Resistance to deformation at low strain and low strain rate provides one measure of chain mobility which is essential for good bond formation. Figure 6 is a schematic plot showing the general shape of stress-strain curves for the pure SBR and its

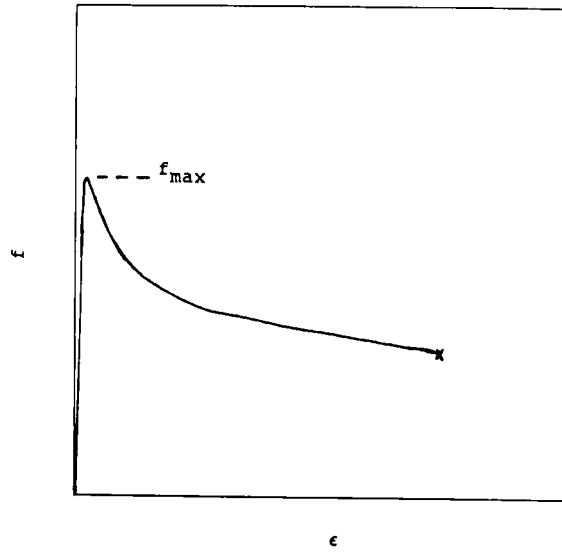


FIGURE 6 Typical stress-strain schematic for SBR or its blends with oil or resin.

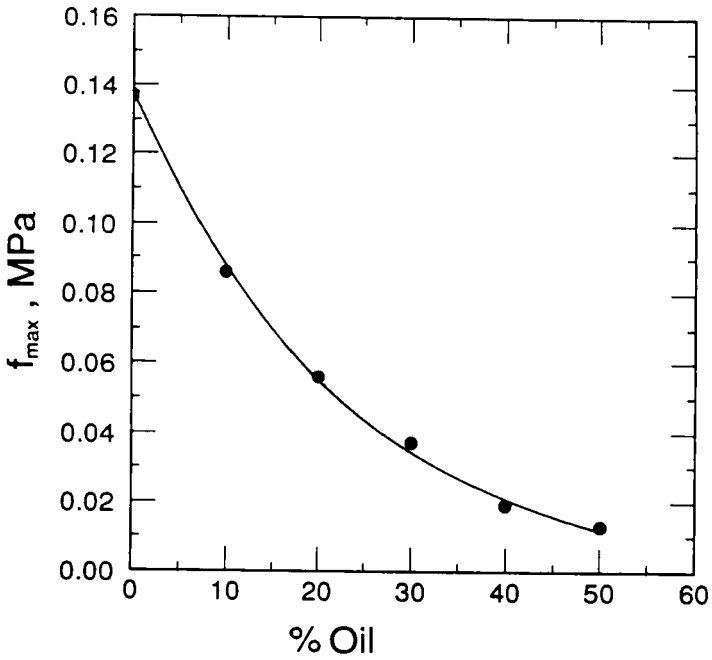


FIGURE 7 Yield stress as a function of oil content for SBR/oil blends.

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blends with tackifier or oil. There is an initial rapid increase in the engineering stress, f , to a maximum yield stress, f_{max} , followed by necking, marked strain-softening, and eventual fracture. With the pure SBR, tearing was preceded by the appearance and growth of numerous small cavities, causing substantial "whitening" in the region where fracture ensued. After fracture, samples exhibited high permanent set, indicating substantial chain disentanglement (and re-entanglement) had taken place. Figure 7 shows yield stress as a function of oil content for SC specimens. Flow occurs more readily with oil dilution as entanglement density is reduced. This coupled with an increase in chain self-diffusion rate with dilution will hasten bond formation.

To substantiate weakening caused by oil dilution, the cohesive strength, G_c , of SBR/oil blends was determined. Results are given in Figures 8 and 9 for MM and SC, respectively. G_c is the upper limit of autohesion, when bond formation is complete and the contact junction is indistinguishable from the bulk. G_c decreases steadily with increasing oil concentration.

If it is assumed (empirically) that autohesion is directly proportional to cohesion and inversely proportional to the square root of yield stress, *i.e.*,

$$G_a \propto \frac{G_c}{(f_{max})^{1/2}} \tag{1}$$

the effect of oil dilution on autohesion may be calculated. Table I shows that the experimented values of autohesion and those calculated from Equation (1) are in good agreement. Thus, Equation (1) satisfactorily accounts for the compensating

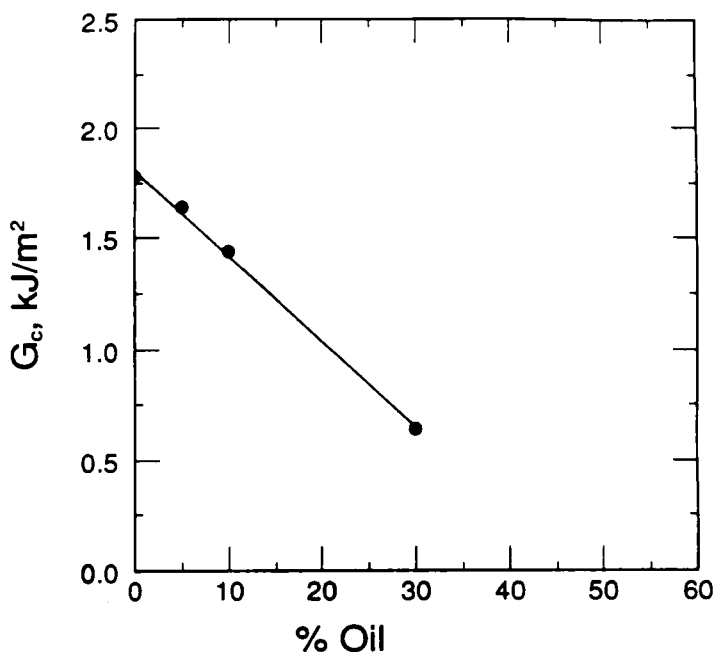


FIGURE 8 Cohesive strengths of mechanically-mixed SBR/oil blends.

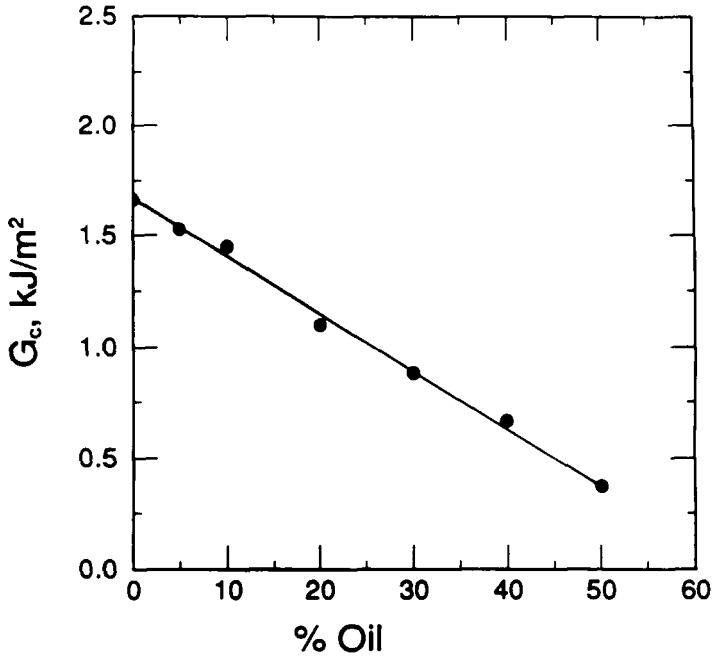


FIGURE 9 Cohesive strengths of solution-cast SBR/oil blends.

TABLE I
Experimental and calculated values of autohesion (kJ/m²) for various levels of oil dilution (solution-cast specimens)

% Oil	Experimental	Calculated
10	0.12	0.13
20	0.11	0.12
30	0.11	0.12
40	0.11	0.13

effects of increased bond formation, but more facile chain separation, with increasing oil content.

Insight to understanding the effect of oil on autohesion can be gleaned by considering relative autohesion, G_r ,

$$G_r \equiv \frac{G_a}{G_c} \tag{2}$$

G_r is a normalized value of autohesion and is a measure of the extent of completeness of bond formation. G_r can have values between zero and unity, corresponding to poor and extensive bonding, respectively. Figures 10 (MM) and 11 (SC) show the effect of oil on relative autohesion. In both cases, G_r increases with oil addition, illustrating, as expected, that bond formation is more complete when chains are diluted.

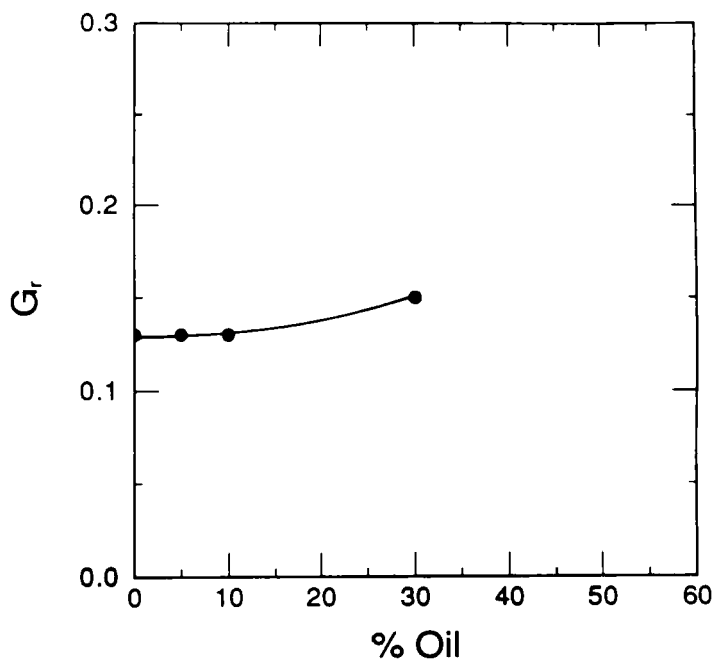


FIGURE 10 Relative autohesion of mechanically-mixed SBR/oil blends.

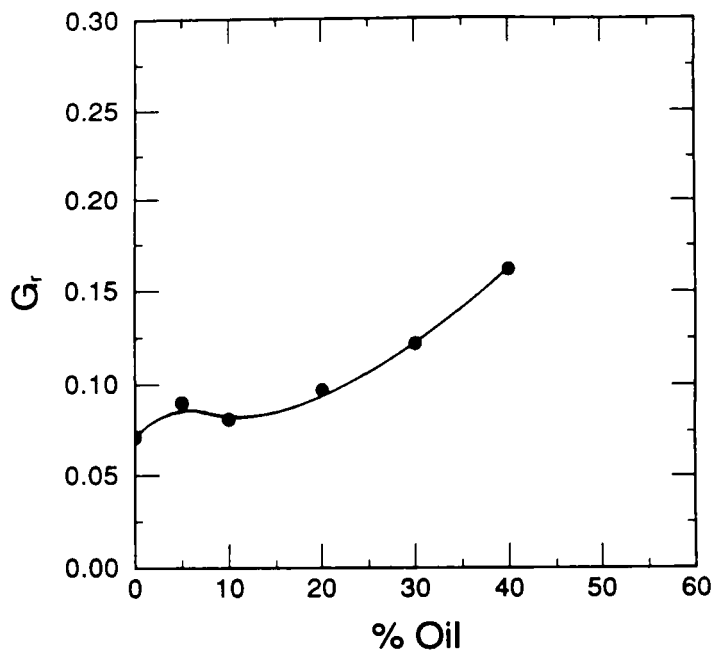


FIGURE 11 Relative autohesion of solution-cast SBR/oil blends.

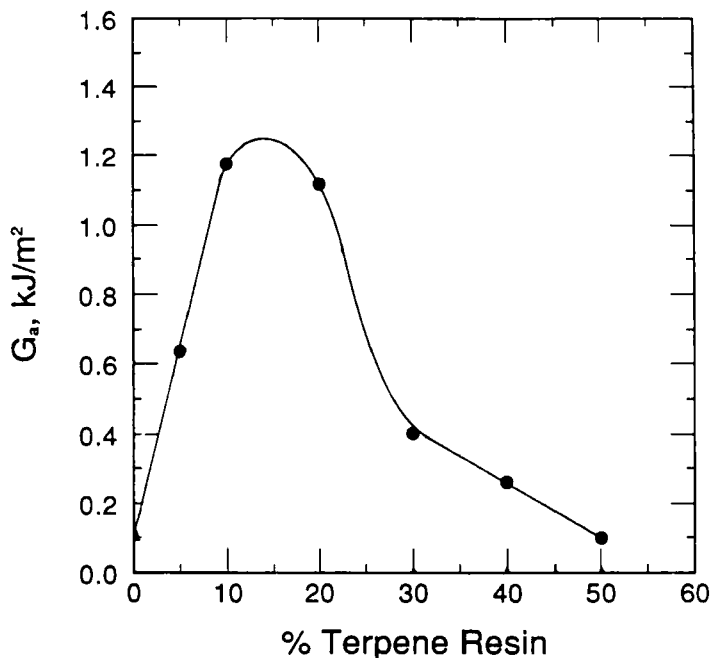


FIGURE 12 Autohesion of solution-cast SBR/resin blends.

We turn now to tackified compositions prepared by solution casting. Figure 12 shows G_a as a function of percent tackifier. Autohesion initially rises rapidly with tackifier addition and passes through a maximum at 10–20% tackifier. This behavior sharply contrasts with that of SBR/oil blends (Figure 5). Recall that oil had little effect on autohesion.

A loss of autohesion at sufficiently high resin concentration is expected, since the tackifier is a hard, glassy substance. When tackifier dissolves in an elastomer, chains are diluted (as with oil), but T_g increases. Previous investigators¹³ have used Equation (3) to analyze glass transitions for *homogeneous* elastomer/tackifier blends,

$$\frac{1}{T_{g,b}} = \frac{w_p}{T_{g,p}} + \frac{w_r}{T_{g,r}} \quad (3)$$

where

- $T_{g,b}$ = transition of blend
- $T_{g,p}$ = transition of polymer
- $T_{g,r}$ = transition of resin
- w_p = weight fraction polymer
- w_r = weight fraction resin

Equation (3) can be rearranged to give

$$\frac{1}{T_{g,b}} = \frac{1}{T_{g,r}} + w_p \left(\frac{1}{T_{g,p}} - \frac{1}{T_{g,r}} \right) \quad (4)$$

Accordingly, a plot of $1/T_{g,b}$ versus w_p should be a straight line. One (dynamic) measure of the glass transition of polymeric compositions is the temperature at which the loss tangent is maximized. With T_g defined in this way, data were graphed (Figure 13) as suggested by Equation (4). Up to 50% tackifier content, the plot is linear, but it deviates seriously at higher levels of tackifier. It is hypothesized that up to about 50% resin the blends are homogeneous, and then they undergo phase bulk separation at higher concentrations. Consistent with this, Figure 13 shows that T_g of the rubber phase depends weakly on tackifier level, for concentrations exceeding 50%. Corroboration of phase separation was obtained from differential scanning calorimetry (Figure 14). T_g increases steadily with resin addition to the SBR up to 40–50% resin. Again, above this level, the rubber phase T_g changes little, and a new high temperature transition appears (Figure 15).

Yield stresses for SBR/resin blends (Figure 16) show that, although the resin is a hard and brittle substance, *bulk* compositions are progressively softened (at least up to 50%) by addition of resin—much like the behavior of SBR/oil blends (Figure 7). This suggests that flow and chain interdiffusion (bond formation) are similar for blends diluted with equal amounts of oil or resin. For a given extent of self-bonding, will there be a difference in the resistance to separation of oil-diluted *versus* resin-diluted chains? The effect of resin on cohesive strength is shown in Figure 17. Unlike oil dilution, which was shown to decrease strength rapidly (Figure 9), tackifier addition slightly enhances G_c initially before strength slowly declines. Moreover, at all concentrations tackified compositions are significantly stronger than oil-extended ones. One reason for this is the higher T_g of SBR/resin blends. Both oil and tackifier soften the elastomer by reducing chain and entanglement densities, but oil markedly diminishes strength, whereas tackifier does not. In short, tackified blends are soft and stronger, compared with those diluted with oil which are soft and weaker. This is one factor which causes tackifier to increase autohesion, relative to oil addition.

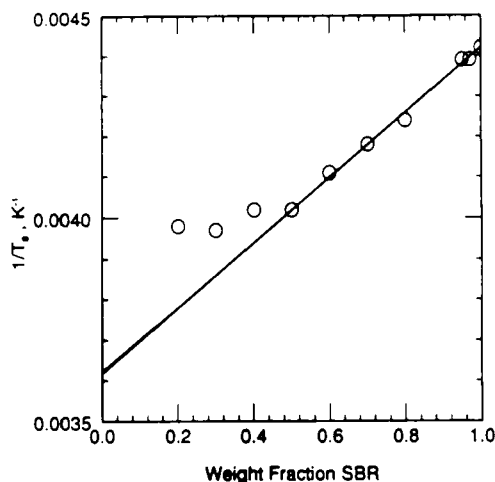


FIGURE 13 Glass transition data for solution-cast SBR/resin blends plotted according to Equation (3).

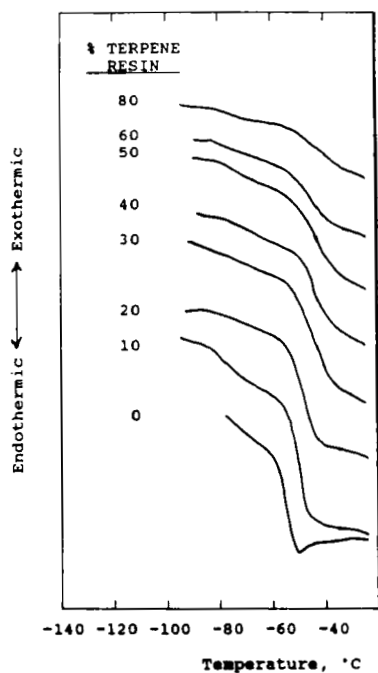


FIGURE 14 Low temperature region of DSC thermograms for solution-cast SBR/resin blends.

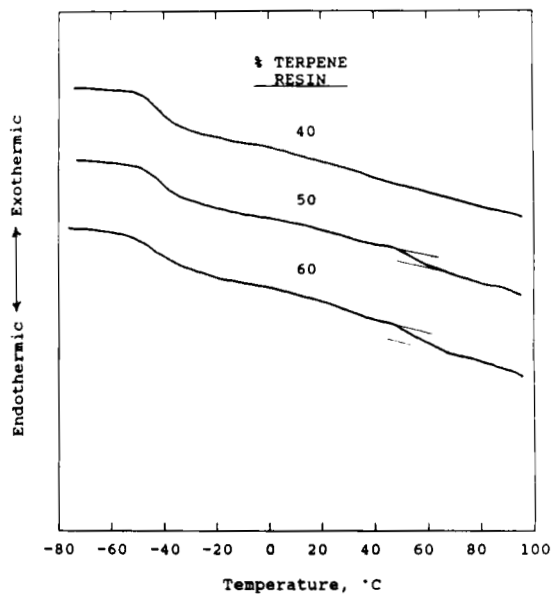


FIGURE 15 DSC thermograms showing the high-temperature region for solution-cast SBR/resin blends.

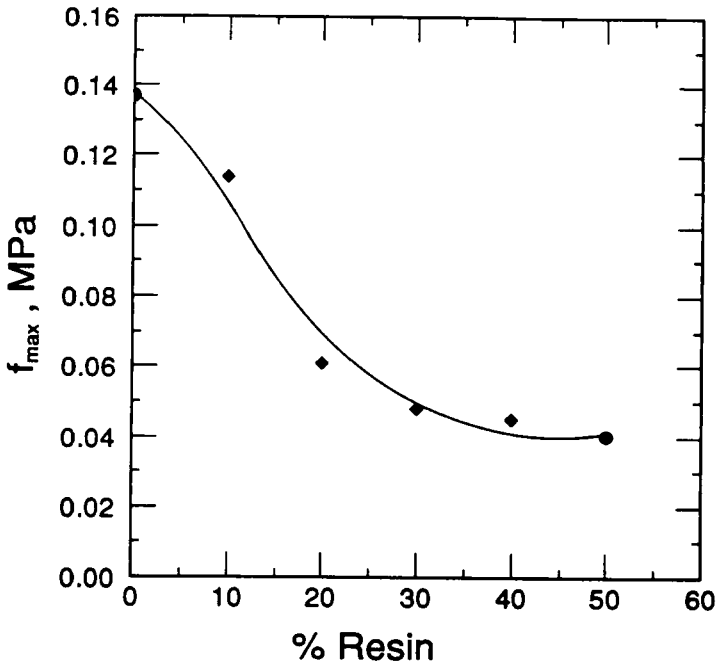


FIGURE 16 Yield stress as a function of resin content for SBR/resin blends.

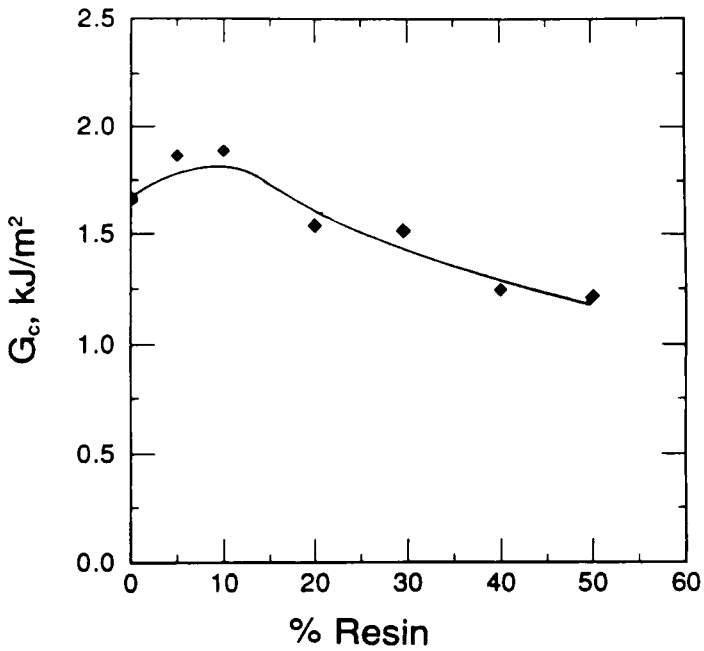


FIGURE 17 Cohesive strengths of solution-cast SBR/resin blends.

TABLE II
Experimental and calculated values of autohesion (kJ/m^2)
for various levels of tackifier dilution

% Tackifier	Experimental	Calculated
10	1.18	0.15
20	1.12	0.17
30	0.40	0.18
40	0.26	0.16

The magnitude of this effect may be determined by using Equation (1) to predict the autohesion of compositions diluted with tackifier (Table II). Calculated values of autohesion for tackified specimens are about 50% greater than those found for oil-diluted samples (Table I). This is entirely due to the greater cohesive strength after tackifier-dilution compared with oil-dilution. Note, however, that experimental values of autohesion, especially at low dilutions, are much higher than the calculated ones.

In Figure 18 we examine relative autohesion for SBR/resin blends. G_r increases sharply with tackifier addition, reaching a value of about 0.75, at 10–20% resin, before declining quickly at higher resin contents. It is interesting to compare G_r at low additive levels for SBR/oil (Figure 11) and SBR/resin blends. Pure, solution-cast SBR has a value of $G_r \sim 0.071$, *i.e.*, autohesion is about 7% of the (upper limit)

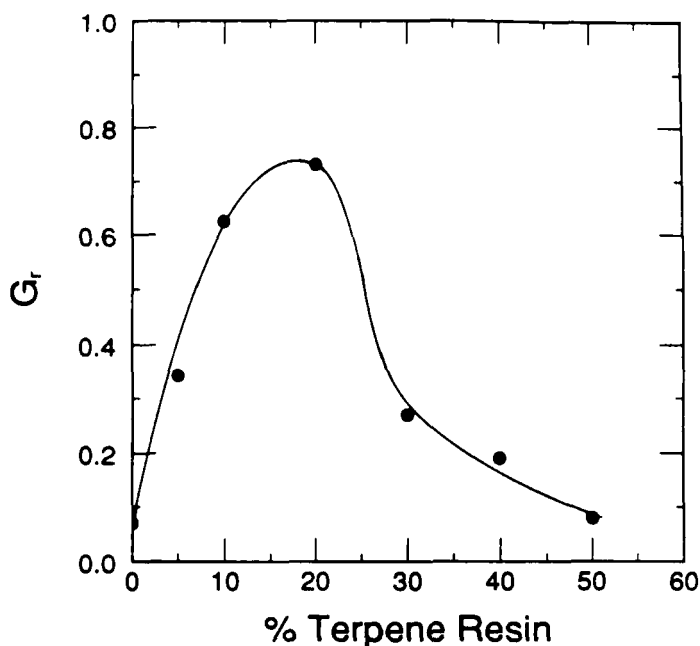


FIGURE 18 Relative autohesion of solution-cast SBR/resin blends.

cohesive strength. With 20% oil addition, G_r increases modestly to 0.097 while, with tackifier at this concentration, G_r becomes 0.731. It is concluded that tackifier addition somehow enables more complete bond formation (contact and chain interdiffusion). How does this happen?

The terpene resin is a substance of limited compatibility with the elastomer. Above about 50% resin content, there is *bulk* phase separation of the components (T_g , DSC results). However, it is well known¹⁴⁻¹⁸ that tackifier/rubber blends, which are compatible in the bulk, undergo tackifier migration to the surface region—thereby creating a layer rich in resin relative to the bulk. This can either help or hinder autohesion. As long as the surface layer remains rubbery, bond formation will be enhanced by increased chain dilution (entanglement loss and mobility increase). On the other hand, if the surface becomes glassy (or sufficiently stiff), then bonding will be hindered.

Bulk compositions with 50% overall resin content are soft (Figure 16), and maintain good cohesive strength (Figure 17). Nonetheless, Figure 12 shows that autohesion has dropped to a low value at this resin concentration. Figure 19 shows a photograph of the surface of a blend containing 50% tackifier. A thin surface skin has formed and developed small cracks with widths of about 5–20 μm . This is consistent with a surface layer which is stiffer than the bulk and may account for the rather low self-bonding.

Clearly, too much resin in the surface is detrimental to bonding, but a certain amount of tackifier enrichment in the surface may enhance autohesion. To illus-

50%

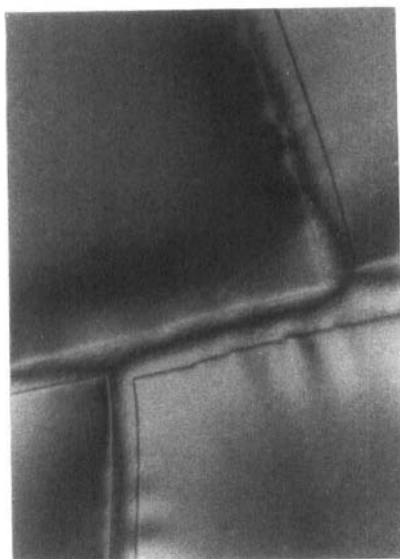


FIGURE 19 Optical micrograph showing surface cracking of a solution-cast SBR/resin blend with 50% resin.

trate, let us presume that the overall concentration of tackifier in a blend is 10%, but that there is a surface layer that contains, say, 40% resin. The chains in the surface would have high mobility and readily form a self-bond. However, once contacted there would be a redistribution of tackifier such that its concentration in the contact region would return to 10%. With this mechanism, bond formation commences with highly diluted, mobile chains, while, at a later time, when the joint is loaded to measure autohesion, chains are more entangled and resistant to separation. Softness and strength are achieved at the same time.

Commercially, there are several types of tackifier resins available including, *e.g.*, rosin derivatives, coumarone-indene resins, aliphatic petroleum resins, phenolic resins, and terpene resins (used in this research). All are polydisperse, lower molecular weight (~ 1000 – 3000), glassy substances, with softening points in the range of 60°C – 140°C . They are relatively poor solvents for the elastomers which they tackify and have somewhat higher cohesive energy density. Although tackifiers are glassy overall, they consist of a number of species; some are lower T_g liquids, while others are higher T_g solids.

In order to impart tack to an elastomer, at least some of the tackifier must dissolve in the elastomer (reduce entanglements) and soften it, ideally without weakening it. This requires careful control of the molecular weight of the tackifier. If it is too high, the tackifier becomes an incompatible filler—stiffening and perhaps strengthening, but hindering bond formation. On the other hand, if molecular weight is too low, such that compatibility is very high, the additive becomes a plasticizing solvent (soft and weak).

Marginal compatibility and the resultant tackifier migration seem to be a key aspect of tackification. Not only does (marginal) compatibility influence the overall dilution of chains in the surface *region*, but it also could control the true *surface* composition. Perhaps elastomers with added tackifier have surface chains which are highly diluted and “naked” (“non-solvated”)—a condition which would cause them to be readily adsorbed (adhesive tack) or interdiffused (autohesive tack). That is, tackifier-diluted compositions may have (lower energy) polymeric chains right at the surface so that the chain itself is readily adsorbed upon contact with a substrate. This may contrast to a solvent-diluted elastomer, which may have a layer of (relatively volatile) solvent molecules at the surface. Upon contact with a substrate, the solvent would become adsorbed first. Adsorption of a chain segment would then be hindered since it would require displacement of the solvent.

CONCLUSIONS

Autohesion of SBR diluted with a naphthenic oil or a terpene resin has been determined using a T-peel geometry and a contact time of one minute. Oil facilitates self-bond formation by diminishing entanglements, but diluted, interpenetrated chains are more easily separated upon loading than neat ones. These effects compensate such that oil addition has little effect on autohesion.

On the other hand, SBR/resin blends exhibit a sharp maximum in autohesion at low levels of resin. At low concentrations, resin, like oil, softens the elastomer;

however, intertangled chains diluted with resin resist separation significantly more than those diluted with oil. This is one reason that autohesion is greater with resin compared with oil dilution. An additional important factor is the migration of resin to the surface region, which further accelerates bond formation. Moreover, once contact takes place, redistribution of resin enhances resistance to bond separation. In this way, SBR/resin blends can be *both* soft and strong—a favorable condition for autohesion. The decrease in adhesion at higher resin contents is attributed to formation of a stiff surface layer hindering self-bonding.

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