

The Mechanism for Enhanced Autoadhesion in Azoester-Modified Polybutadienes

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Synopsis

The addition of IAD pendant groups to PB molecules results in a larger effective chain cross-sectional area with consequent decrease in chain entanglements. This causes the rubber to be more compliant at low strains and strain rates. Simultaneously, the IAD structures give rise to polar and H-bond interactions which cause the material to exhibit strong adhesion and to possess high green strength. As a result, the IAD-PB is a relatively rare example of a synthetic polymer with good autoadhesive properties.

INTRODUCTION

The autoadhesion (tack) of diisopropylazodicarboxylate-modified 1,4-polybutadiene (IAD-PB) has been shown to greatly exceed that exhibited by unmodified polybutadiene (PB) elastomers.¹ It is generally accepted that in order for an uncured elastomer to resist separation when two pieces are brought into contact for a short time under modest pressure, three requirements must be met²⁻⁴: (1) sufficient wetting to ensure that contact on a molecular scale is attained, (2) bond formation at the interface either through molecular diffusion or the development of large attractive forces, and (3) sufficient cohesive strength in the bulk material to resist fracture or flow. In this paper the underlying factors which give rise to the high autoadhesion in IAD-PB are discussed. Specifically, it will be shown that the grafting of isopropylazodicarboxylate onto polybutadiene chains enhances the behavior of the material in each of the three aforementioned aspects of autoadhesion.

EXPERIMENTAL

The 1,4-polybutadiene used in this study was Diene 35 made by the Firestone Tire and Rubber Co. The IAD- modification (via the ene reaction) was accomplished by published procedures.⁵ Except where noted, a 40% by weight (15 mol %) incorporation of IAD was utilized. The level of IAD was determined by nitrogen analysis using a Perkin-Elmer Model 240 Elemental Analyzer. Molecular weight determinations were accomplished with a Wescans Instruments Model 231-230 Membrane Osmometer and with a Waters Associates Model 200 Gel Permeation Chromatograph.

Dynamic mechanical testing was carried out on a Rheometric Mechanical Spectrometer Model 7200.

Peel and tensile strength measurements were done using an Instron Universal Testing Instrument. Nominal deformation rates for the peel adhesion

and tensile testing were 0.6 s^{-1} and 0.2 s^{-1} , respectively. A Surfalyzer 2000 marketed by Federal Products Co. was used to characterize the roughness of specimen surfaces.

RESULTS AND DISCUSSION

The fundamental rheological and adhesive properties of IAD-PB have been characterized in order to elucidate the mechanism whereby the material exhibits high autoadhesion. These properties will now be presented and discussed in terms of the aforementioned requirements for high elastomer tack.

DEVELOPMENT OF INTERFACIAL CONTACT

It has long been recognized that, for any adhesive type of bonding, contact on a molecular scale must exist between the adherends. Indeed, the ability of many elastomers to readily autoadhere (in the "tack" sense) arises in part from their high compliance (relative to plastic or crystalline polymers). In particular, a more compliant elastomer can exhibit high levels of autoadhesion even when the initial surfaces of the plied rubber pieces are not microscopically smooth.

Displayed in Figure 1 are the in-phase shear moduli G' for PB and IAD-PB. These measurements were made over a frequency range of 10^{-1} – 10 Hz and from -90°C to $+100^\circ\text{C}$. The depicted data are the results after time-temperature superpositioning according to the WLF theory⁶ using experimentally determined shift factors. It is interesting to observe that the plateau modulus of the modified elastomer is less than that of the PB. This plateau modulus reflects the pseudoequilibrium network resulting from entanglement couplings, and it is immediately obvious that the *IAD modification has reduced this entanglement density*. Because the plateau modulus is not strictly independent of frequency, a quantitative estimation of M_e , the molecular weight between entanglements, cannot be made directly from the data of Figure 1. An estimate of the shear modulus due to the

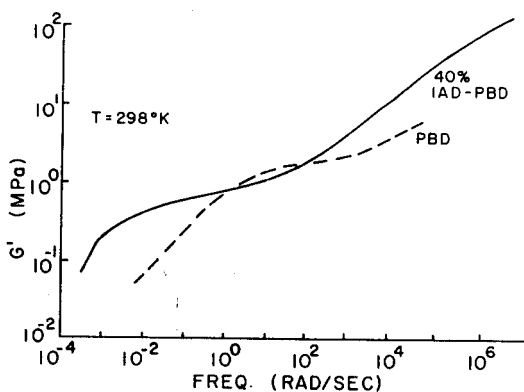


Fig. 1. Master curves of the elastic shear moduli measured for PB and IAD-PB.

entanglement network, G_n , can be obtained by assuming a uniform spacing of these couplings, for which a phenomenological theory predicts^{7,8}

$$G_n = G''_m/0.207 \quad (1)$$

where G''_m designates the maximum value of the loss modulus in the terminal region.

An alternate means for extracting a value for G_n is by integration of the loss modulus from infinitely low frequency, ω , through the rubbery plateau^{6,9}

$$G_n = 2/\pi \int_{-\infty}^a G'' d \ln \omega \quad (2)$$

where a corresponds to an extrapolated intercept with the abscissa. The extrapolation provides a convergence of the integral at the minimum in G'' .

Dynamic loss moduli for the PB and IAD-PB are shown in Figure 2 (again after WLF shifting) and the respective values for the pseudoequilibrium moduli calculated according to eq. (1) and (2) are listed in Table I. The value obtained for the unmodified polybutadiene is about 30% higher than previously published values for polybutadienes of approximately similar microstructure,¹⁰ which can be attributed at least in part to the error associated with assuming a uniform distribution of strand lengths or in extrapolating the G'' spectrum in the region of overlap with the transition zone. The lower magnitude found for the modulus of the IAD-PB reflects directly the reduced density of entanglements, J_e , resulting from the IAD modification⁶

$$J_e = G_n/gRT \quad (3)$$

(where the front factor g can be assumed equal to unity). The relative change in the number average molecular weight between entanglements is then just the ratio of the equilibrium moduli times the inverse ratio of the densities of the two polymers. By using the values tabulated in Table I, it can be seen that a 40% by weight addition of IAD increases M_e by about a factor

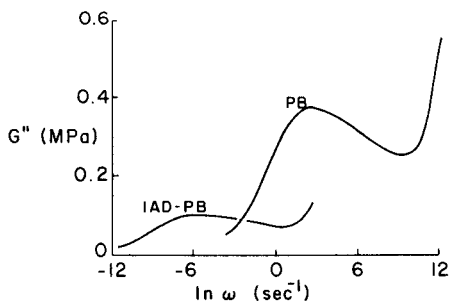


Fig. 2. Master curves of the loss moduli measured for PB and IAD-PB.

TABLE I
The Effect of IAD Modification on Modulus Due to Entanglements in Polybutadiene

		PB	IAD-PB
G_n	[eq. (1)]	1.8 MPa	0.52 MPa
G_n	[eq. (2)]	2.1 MPa	0.93 MPa
J_e	($\text{cm}^{-3} \times 10^{-20}$)	4.4 ± 0.7	1.3 ± 1.0
ρ	(g/cm^3)	0.93	1.02
M_e	(g/mol)	1300	4700

of 4 (only a 60% increase results simply from the increase in average monomer molecular weight itself).

This reduction in entanglements is primarily a consequence of the lower concentration of chains in the IAD-PB melt as opposed to unmodified PB. In fact, the reduction in G_n (by a factor of 3.6 in Table I) is equal to that which would be predicted from the simple decrease in chain concentration, whereby the modulus would scale quadratically with the volume fraction of polymer.¹⁰ While this agreement may be fortuitous (since the IAD modification may alter both chain contour length and the Kuhn step length), it does indicate that the decrease in chain contour length per unit volume due to the grafting of bulky side groups can lead to a reduction in modulus of the polymer.

The consequence of a lower plateau modulus with regard to autoadhesion is that greater wetting can be achieved when two pieces of the modified elastomer are brought into contact.

The creep compliance of stocks based respectively on PB and IAD-PB were measured under conditions appropriate for tack considerations (11 KPa compressive loading for ten seconds). These stocks were compounded with 40 phr N330 carbon black and 5 phr processing oil. The results are given in Table II. Although the reinforcing filler makes a significant contribution to the creep behavior, it is observed that the IAD-PB-based stock is, nevertheless, more compliant than the PB compound. The topography of a rubber stock molded against Holland cloth (which imparts a surface roughness pertinent to practical applications) is displayed in Figure 3. The height of the asperities is about 25 μm , so that, for a rubber sheet of typical thickness, compressive strains of a few percent must be attained during typical testing, i.e., 10 s loading at 11 kPa. It can be seen, therefore, that the difference in compliance between the IAD-PB and PB stocks is in the range whereby a significant improvement in wetting can be realized for

TABLE II
Effect of IAD Modification on Creep Compliance (Measured at 10 s under 11 kPa) of Filled Stocks and on Tack of Polymers When Molded against Rough and Smooth Surfaces

	PB	IAD-PB
Creep compliance (MPa^{-1})	3.3	4.2
Autoadhesion ($\text{N}/\text{m} \times 10^{-3}$)		
Holland molding	0	3.9 ± 0.8
Mylar molding	0.1	3.7 ± 0.8

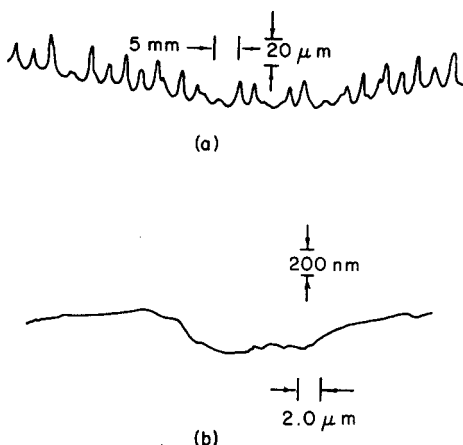


Fig. 3. Surface profile resulting from molding a rubber specimen against (a) Holland cloth and (b) Mylar.

the modified polymer. The effect of better contact can be seen in the tabulated values given in Table II for the autoadhesion measured for IAD-PB. When the stock is given a smooth surface by molding it against Mylar, there is negligible change in tack compared to specimens molded against the rougher Holland cloth. Due to the high compliance of IAD-PB, the level of tack is not being limited by the degree of microscopic contact. Contrarily in PB, although wetting itself does not ensure autoadhesion (i.e., tack between Mylar-molded surfaces is still low), there is a modest increase when the surface topography of the PB is made smoother.

Bond Formation at the Interface

Contact on a molecular level between two plied rubber sheets will promote their adhesion only insofar as an adhesive force develops at the contact loci.

In natural rubber or *cis* polyisoprene based stocks a high level of tack is realized (or at least not limited) by the diffusion of polymer chains across the interface.^{11,12} Interfacial bonding results from entangled macromolecules. Contrarily, diffusion of polybutadiene chains across the interface, formed when a pair of PB specimens are brought into intimate contact, is sufficiently slow with respect to the time scale of a tack experiment that negligible bonding takes place. This behavior can be observed in Figure 4, where the autoadhesion of PB sheets (molded against Mylar and then plied together for 300 s under a compressive loading of 20 kPa in order to ensure extensive wetting) is observed to increase with time after removal of the load. This increase, which is accompanied by a change of failure mode from adhesive to cohesive failure, is indicative of a coalescence of the contacting surfaces resulting from interdiffusion. It is not to be inferred from data such as this that self-diffusion of PB chains (of $M_n \simeq 125,000$) is anomalously slow compared to polyisoprene. Retarded diffusion across an interface, notwithstanding an ostensibly sufficiently large diffusion constant, has simi-

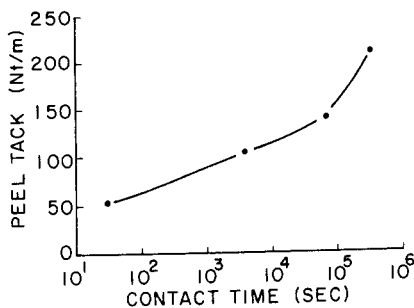
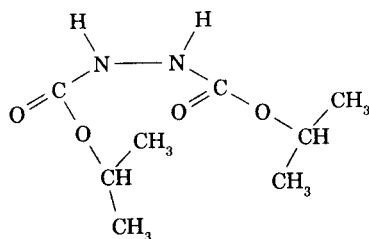


Fig. 4. Tack of PB vs. time after removal of compression loading. The increase reflects the development of coalescence between the two surfaces.

larly been observed for styrene-butadiene copolymers.¹³ The important point is that significant improvement in the tack of PB can be achieved only by providing a mechanism for its bonding at the interface.

Although the lower entanglement density resulting from IAD modification may facilitate chain diffusion, we observe during tack testing that the IAD-PB stocks, nevertheless, fail in an *adhesive* mode; that is, the locus of failure is the original interface. The IAD modification has not significantly enhanced the interdigitation of chains from either side. The polarity of the ester functionality along with a capacity for H bonding suggests that the diisopropyl hydrazodicarboxylate structure



can give rise to interfacial bonding via attractive forces.

A measure of this increased capacity for surface interaction in the modified polymer can be noted in the adhesion of the elastomer to plastic substrates (where any interdiffusion between the two surfaces is prohibited both kinetically and as a result of polymer-polymer incompatibility). Table III lists peel adhesion values for both IAD-PB and PB to polystyrene and to a 70% by weight IAD-modified PB. Both these materials are hard plastics, the former relatively nonpolar, the latter polar in nature (it is a brittle

TABLE III
Adhesion Measured between Polybutadienes and Rigid Adherends

Adherend	Adherend	180° peel force (N/m)
PB	Polystyrene	140
PB	70% IAD-PB	35
IAD-PB	Polystyrene	1100
IAD-PB	70% IAD-PB	1100

solid as a consequence of its two-phase structure, which consists of rigid IAD-rich domains and pure PB regions⁵). It is observed that the IAD-PB adheres strongly to both substrates, whereas unmodified PB exhibits little attraction.

Evidently the IAD-PB is capable of coupling to these surfaces via hydrogen bonding and polar attractions (the latter resulting from the induction of dipoles in the polystyrene). The fact that the polar nature of the plastic adherent has negligible effect on the measured adhesion of the IAD-PB is due primarily to the nature of the peel experiment.⁴ This peel force measures the energy expended when the elastomer is subjected to a cyclic tensile deformation in which the maximum stress is that at which separation occurs. The stress-strain curve of the IAD-PB (Fig. 5) is essentially that of a polymer undergoing flow (i.e., the stress is declining with elongation, and the ultimate strain is quite high). Consequently, the measured peel adhesion will be roughly the area under the stress-strain curve, taken up to the level of stress the interface is capable of supporting. This peel energy (or force per unit width) will be relatively insensitive to the interfacial bond strength when the polymer exhibits flow. On the other hand, it is, of course, expected that the surface interaction per se is greater when the rigid adherend itself is polar.

An interesting consequence of a tack mechanism involving only interfacial forces and not molecular diffusion across the interface is that an increased molecular weight will not reduce tack due to slower interdiffusion. Thus, whereas the tack of natural rubber exhibits a maximum when plotted against molecular weight due to the simultaneous elevation of cohesive strength but reduction in bond formation ability,¹⁴ the tack of IAD-PB is observed to increase up through a number average molecular weight of 450,000 (Fig. 6). The mode of failure remains interfacial. The greater autoadhesion reflects the increasing cohesive strength of the IAD-PB as the material is subjected to the stresses accompanying peeling.

Cohesive Strength

Although the attractive forces present at the interface when IAD-PB specimens are plied together are primarily responsible for the high autoadhesion, a rubber stock must also possess sufficient cohesive energy

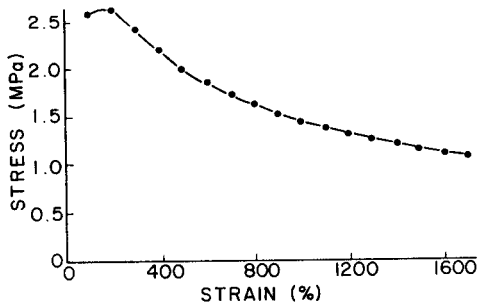


Fig. 5. Stress (based on the initial cross-sectional area) of IAD-PB as a function of the relative change in specimen length.

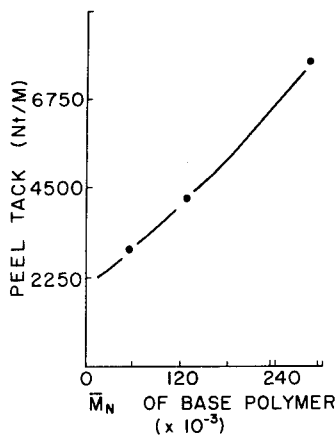


Fig. 6. Effect of the molecular weight of the precursor PB on the autoadhesion of the IAD modified material. These samples were molded against Mylar to minimize the influence of the stock's compliance on tack. Note that the last point corresponds to an M_n for the IAD-PB of 450,000 (15 mol % modification level).

density ("green strength") such that cohesive failure does not occur at relatively low values of applied load. In fact, the level of peel tack exhibited by IAD-PB gum rubber (Table II) exceeds the peeling green strength of the unmodified PB (which is only about 500 N/m). Thus the elevation in cohesive strength which accompanies IAD modification of PB is a necessary but insufficient condition for high tack in this elastomer. Displayed in Figure 7 are the values of cohesive energy density measured in tension for PB as a function of the level of IAD grafted onto the PB backbone. The improvement in green strength is nonlinear with respect to IAD content, and there is roughly a 35-fold increase from 0% to 40% by weight of the IAD. It is interesting to note that in this experiment the elevation in energy to break is due both to a higher level of stress (at strains > 100%) as well as to a higher elongation at break.

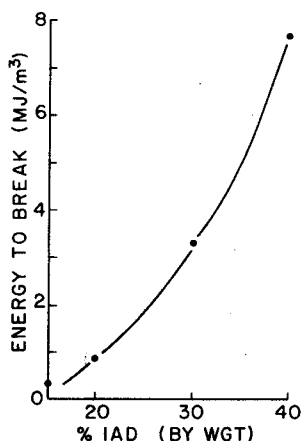


Fig. 7. Green tensile energy to break measured as a function of the level of IAD incorporated onto the PB.

The source of this green strength is related to the same factors which give rise to tack bonding at the interface, that is, the enhanced polarity and H-bonding capacity of the modified polymer. As the elastomer is pulled in tension (directly or via a peel adhesion experiment), the slippage of flowing chains past one another is resisted by the frictional forces existing between chain segments. An increased friction coefficient will lead to larger drawing stresses, which in turn manifests itself in the form of higher green strength. A measure of the monomeric friction coefficient, ξ_0 , can be obtained from the transition zone of the viscoelastic spectrum, where the dynamic behavior is not influenced by macromolecular topology, but reflects only local motions. Specifically in the frequency region where the elastic and loss moduli are proportional to the half power of frequency⁶

$$G' = G'' \propto \xi_0^{1/2} \quad (4)$$

As can be seen in Figure 1, despite exhibiting a lower modulus at slow frequencies due to reduced entanglement couplings, at the higher frequencies associated with the glass transition, IAD-PB is significantly stiffer than PB. It can be estimated from this data that the IAD modification of the PB increases ξ_0 by about a factor of 7. Of course, the changes in entanglement coupling also affect the measured tensile strength. Evidently the tensile viscosity (at strains $\gg 1$) is more reflective of the frictional interactions of chains than to their topological constraints. It may also be that polar interactions are promoted by the uncoiling of elastomer chains which accompany tensile straining. This could increase the number of molecular contacts which give rise to the enhanced frictional drag. (In this regard it has been suggested that increased interactions at high strains may effect phase separation in IAD-PB.¹⁵ The structure of IAD-PB, including the effect of strain on morphology, will be considered elsewhere; in particular, it will be shown that the green strength of IAD-PB is not a consequence of the blocky structure, nor is it related to any phase transformation.¹⁶

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