

The Structure of Azoester-Modified Polybutadiene Elastomers

C. M. ROLAND, G. G. A. BÖHM, and P. SADHUKHAN, *The Firestone Tire and Rubber Company, Central Research Laboratories, 1200 Firestone Parkway, Akron, Ohio 44317*

Synopsis

It is demonstrated that the improved tack and green strength accompanying the IAD modification of polybutadiene arise strictly from the introduction of bulky, polar groups. The fact that addition of 1,4-PB occurs in a blocked arrangement is not a factor in the development of high green strength, as can be seen by the large increase in strength of modified 1,2-PB, wherein the IAD groups are randomly attached. The tack is also elevated through random IAD addition; however, the relevance of blocked vs. random structure in this regard cannot be completely judged since it depends as well on the absolute IAD level and the polymer's T_g , as well as the test temperature. At high levels of IAD (about 38 mol %), the modified PB becomes a phase-separated material, exhibiting high stiffness and brittleness. This heterogeneous system is quite unlike the PB modified with only 15 mol % IAD. These latter elastomeric materials are homogenous, and remain so during deformation. The attainment of high tack and green strength relies upon maximal addition of the IAD groups, provided the molecules retain their flexibility. In blending the modified PB with other rubbers, optimum behavior in the blends appears to be achieved when the IAD-PB is present as a continuous phase.

INTRODUCTION

Among synthetic elastomers, the capacity for autoadhesion when unvulcanized specimens are plied together for a short duration under modest pressure is an oft-desired but seldom realized property. For a material to exhibit high tack it must be able to form a bond during the limited time (about 10 s) available in a typical autoadhesion test, and simultaneously be sufficiently resistant to deformation such that large separating forces can be supported without excessive flow or fracture of the material. These two requirements are to some extent mutually opposing in the sense that many of the obvious routes to improving a polymer's bond formation capacity (e.g., lower molecular weight, dilution of the polymer chains with plasticizer, or a reduction in glass transition temperature) will, of course, also reduce its ability to resist deformation. The grafting of diisopropylazodicarboxylate (IAD) onto 1,4-polybutadiene rubber (PB), however, has been demonstrated to greatly improve the tack, as well as producing a material of much improved green strength.¹ The mechanisms underlying these improvements have been the subject of a recent publication.² It was found that incorporation of 15 mol % IAD imparts to the PB a capacity for hydrogen bonding and strong polar interactions, while simultaneously reducing entanglement coupling of the chains. This latter effect results in a more compliant elastomer which, in combination with its polarity and hydrogen bonding ca-

pability, can then readily form strong autoadhesive bonds. The green strength enhancement reflects the strong interactions between chains, particularly as the flexible molecules uncoil at high magnitudes of strain. This note describes a study of the influence of microstructure and phase morphology on the tack and green strength of IAD-PB elastomer compounds. In the earlier study,² the IAD structures were added to the chain in a blocky fashion. At a sufficiently high level of IAD, a two-phase morphology develops. A purpose of the present work was to determine the significance of these features in obtaining modified polybutadienes of high green strength and tack.

EXPERIMENTAL

The grafting of IAD onto polybutadiene was accomplished by known methods.³ The polybutadienes employed in this work were Diene 35 (a 1,4-PB manufactured by the Firestone Tire and Rubber Co.) and 1,2-polybutadiene (85% and 99.8% vinyl content) synthesized at the Firestone Central Research Laboratories according to the method of Halasa et al.⁴

Tack testing and green strength measurements were done using an Instron Universal Testing Instrument at crosshead speeds of 5.0 and 51 cm/min, respectively.

Room temperature tack testing was done in the 90° peel geometry. A nylon mesh was imbedded in the samples in order to make the legs of the test pieces inextensible. For tack testing at elevated temperatures, cylindrical discs with a ridge on the back side were prepared by compression molding. The back side of the discs was then exposed to electron beam irradiation in order to stiffen the elastomer and thereby facilitate clamping. The front surfaces of a pair of discs were then brought into contact and maintained thusly for a fixed duration under specific loading conditions. The contacting of the surfaces was accomplished with the Instron tester under computer control.

The dynamic testing was accomplished with a Rheometric Mechanical Spectrometer Model 605. The transmission electron micrographs were obtained on a Phillips EM300 instrument. Shear viscosity data was measured in an Instron Capillary Rheometer Model 3211. The ESCA data was obtained on a System 578, Physical Electronics, with a 400-W Mg_{K α} source. A JEOL PFT 100 spectrometer was used to obtain the ¹³C spectra.

RESULTS

Microstructure and Properties

It has been previously shown that the addition of IAD onto 1,4-polybutadiene proceeds in a blocky fashion, whereas there occurs a random attachment to 1,2-PB.³ In order to determine if the improved properties of IAD-PB are dependent upon blockiness of the IAD groups, 1,2-PB's (of 85% and 99.8% vinyl content) were reacted with the IAD. When the 85% 1,2-PB was modified with 15 mol % IAD, it was interesting to find that the IAD had reacted almost exclusively with the 1,4-PB units; the vinyl monomer units were 97% unmodified. This can be seen in the ¹³C NMR spectrum

displayed in Figure 1. Absent are the peaks at 27 and 33 ppm (relative to TMS) associated with aliphatic *cis* and *trans* carbons. The weak resonances at 60 ppm correspond to these 1,4 carbons after the IAD modification, and this accounts for about 85% of the incorporated IAD. These results are congruous with an earlier study that found the 1,4 modification with IAD to be significantly faster than the IAD reaction with 1,2-PB.³ It was also shown therein that the IAD addition to high vinyl polybutadiene occurs randomly. Since the microstructure of the 85% 1,2-PB used here is random,^{5,6} the IAD-modified polymer produced is also random, even though in this case the attachment is to the 1,4 units.

Green strength and tack were measured for these materials, and the results are given in Tables I and II. Since the glass transition temperatures of these various polymers differ (due to differences in both vinyl and IAD composition³), the measurements were done at different temperatures such that the comparisons could be made at a fixed temperature increment above the respective glass transition temperatures. It can be seen that the random IAD addition gives rise to markedly improved green strength. An order of magnitude improvement is realized with the addition of only 23 mol % of the IAD. The tack is also increased by IAD modification, although only by a factor of about 2. That only this modest improvement could be realized is due to the dependence of tack on a complex interplay of various factors. As shown previously,² the IAD modification increases the cross-sectional area of the chains in such a fashion as to reduce their entanglement couplings. This results in a more compliant material that, under the conditions of a tack test, can achieve more extensive contact when test specimens are pressed together. Simultaneous with the decrease in chain entanglements, the IAD modification causes an elevation in the monomeric friction coefficient due to polar interactions and hydrogen bonding between different

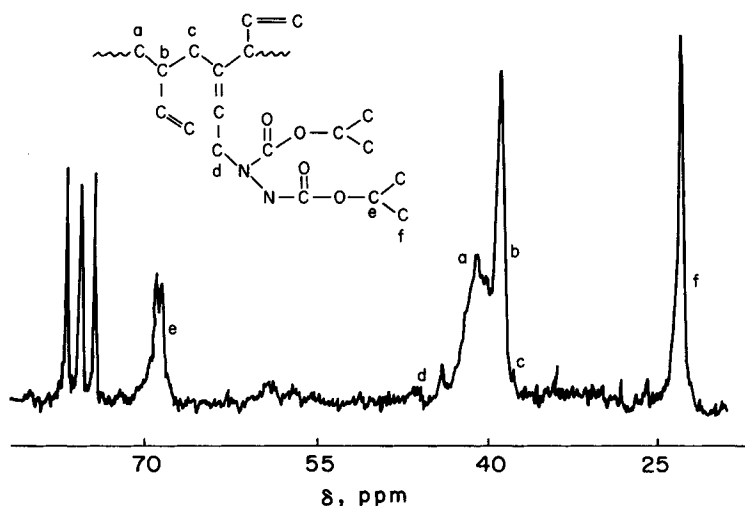


Fig. 1. ¹³ FT NMR spectrum at 25.15 MHz of an 85% 1,2-polybutadiene modified with 15 mol % of the isopropylazodicarboxylate group. CDCl₃ is the solvent. Although for the purpose of identifying the resonances a modified 1,2 unit is illustrated, in fact, as indicated in the text, the IAD addition was primarily to the 1,4 units.

TABLE I
Strain Energy Measured at Various Temperatures T Required to Fracture 1,2-PB
Containing the Indicated Level of Randomly Incorporated IAD^a

% vinyl	Wt % IAD	T (°C)	$T - T_g$ (°C)	Green strength (MJ/m ³)
99.8	0	27	34	0.92
99.8	54	50	32	14.60
99.8	0	50	57	0.35
99.8	54	75	57	> 2 ^b

^a The nominal elongation rate was 0.2 s⁻¹.

^b The elongation of the sample exceeded the dimensions of the testing oven.

hydrazoester groups. This effect is amplified as the chains uncoil at high strains and manifests itself in a strong resistance of the polymer to large deformation. These same interactions provide a mechanism for bonding at the interface between plied test specimens, even in the absence of any molecular interdiffusion. In the IAD modification of 1,4-PB, it was observed that the highest tack was obtained in a material with 15 mol % of the IAD. In view of the differences in T_g and the random mode of IAD incorporation into 1,2-PB, it is not expected that optimal tack properties would be obtained at this same level of IAD.

The point herein is that the addition to polybutadiene of polar groups capable of hydrogen bonding improves both tack and green strength, regardless of the nature of their distribution along the polymer backbone. This is in accord with previous work that demonstrated the connection between enhanced green strength and an elevation in the monomeric friction coefficient in IAD-PB, along with the development of adhesive properties due to interaction of the IAD structures.² The blockiness of the IAD groups in the previously studied materials is evidently incidental to their improved performance.

Phase Morphology in the Presence of Strain

It has been suggested that straining of IAD-PB elastomer may induce a phase separation.^{7,8} Since at very high levels of IAD (ca. 37 mol %) a two-phase morphology exists,³ it is conceivable that, at lower levels, a precipitation of IAD-rich domains could be effected by elongational deformation (the accompanying chain extension promoting unlike contacts and thereby

TABLE II
Tack Measured for Polybutadienes of the Indicated Microstructure and IAD Composition.^a

% vinyl	Wt % IAD	T (°C)	$T - T_g$ (°C)	Tack (J/m ²)
99.8	0	72	79	610
99.8	54	100	82	1100
85	15	75	80	580
10	0	0	89	210

^a The specimens were initially pressed together for 100 s under 22 kPa and then separated at a velocity of 5 cm/min at the indicated test temperature T .

shifting the equilibrium). Phase separation induced by the shearing of polymer solutions has, in fact, previously been observed.^{9,10}

Displayed in Figure 2 is the transmission electron micrograph of an OsO_4 -stained specimen of 38 mol % IAD-PB. The polybutadiene was of 1,4 microstructure, and, as noted above, the material exists as a phase-separated structure. This two-phase morphology is readily observable under the electron microscope; that is, the domains are of sufficient size, and, after staining, good electron scattering contrast exists between the phases. In order to determine if such a two-phase structure develops when 15 mol % IAD-PB is strained, specimens prepared from it were elongated to 1000% extension. In order to preclude redissolution of any phase-separated structures, the morphology of the strained elastomer had to be fixed. This was accomplished by two methods. In one experiment the sample after straining was quenched with liquid nitrogen, and then at 77 K irradiated with a 1.3 MeV electron beam. The dosage was sufficient to impart about 10 crosslinks per weight average molecule. The sample was then warmed slowly to room temperature, ultramicrotomed and then stained with OsO_4 . In a second experiment, the IAD-PB specimen was clamped at the 1000% strain and then exposed to OsO_4 vapor for 24 h. After this extensive staining, the sample was very rigid; in fact, no relaxation was observed after removal of the clamps. Ultramicrotoming was then accomplished on the stained sample. The transmission electron micrographs of both these highly stretched 15 mol % IAD-PB samples revealed no phase structure (see Fig. 3). The morphology in the presence of high strains remains homogeneous, at least on the scale probed by the electron microscope.

The actual block length of IAD at the 15 mol % level is not known, and it is reasonable to assume this microstructure differs from the PB modified to 38% IAD. Consequently, it is conceivable that domains hypothetically formed during straining of the initially homogeneous IAD-PB would not necessarily be as large and possess the well-defined interfaces seen in Figure

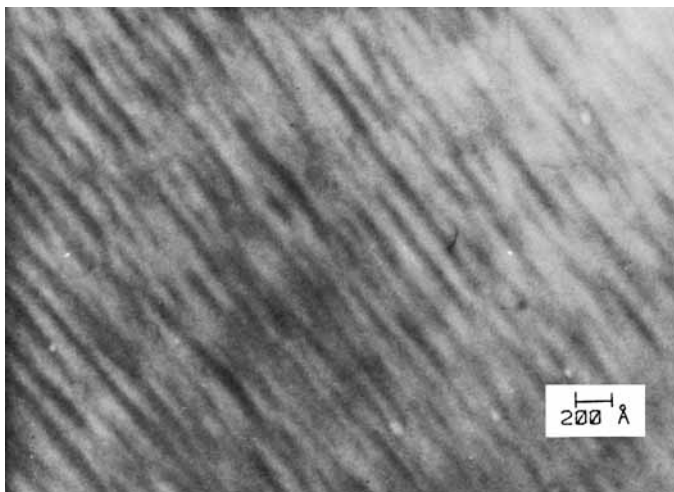


Fig. 2. Transmission electron micrograph of a stained specimen of 38 mol % IAD-PB. The original magnification was 55,000.

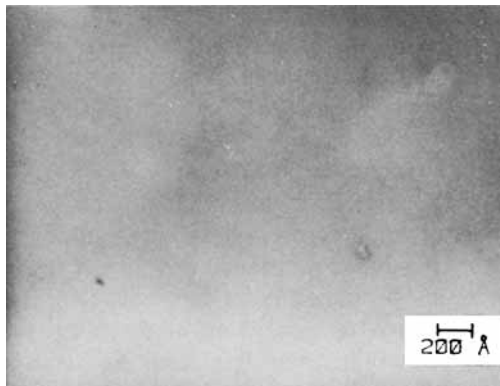


Fig. 3. Same as Figure 1, but the sample is now a 15 mol % IAD-PB that had a relative elongation of 1000% prior to electron beam irradiation.

2 for the 38% IAD-PB. Consequently, the homogeneity observed in Figure 3 does not preclude the possible existence of phase separated IAD-rich regions in the 15% IAD-PB. A particularly sensitive probe for the presence of such a two-phase structure would be detection of a pronounced maximum in the value measured for the mechanical loss tangent over a temperature range corresponding to the transition zone between rubbery and glassy behavior. Phase separated IAD-rich domains would exhibit a glass transition temperature around 80°C.^{3,8} Indeed, fluctuations in the DSC response of stretched IAD-PB have, in fact, been observed and attributed to a strain-induced phase separation phenomenon.^{7,8} In order to measure the loss tangent of the strained polymer, a sample of 15 mol % IAD-PB was mounted in the mechanical spectrometer, and the upper clamp then raised such that a relative elongation of 700% was imposed on the rubber strip. The specimen was then sinusoidally strained in torsion at 1 s⁻¹ at an average shear strain of 2%. The measured dynamic loss tangent is displayed in Figure 4. It can be seen that over the temperature range 47–127°C there exists only a monotonic increase in the loss tangent, which is associated with behavior in the terminal zone. No phase transitions are in evidence.

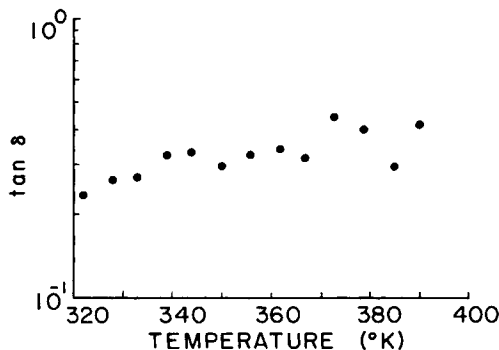


Fig. 4. Loss tangent measured for a 15 mol % IAD-PB which had a tensile prestrain of 700%. The shear strain was 2% imposed dynamically at 1 s⁻¹ rate.

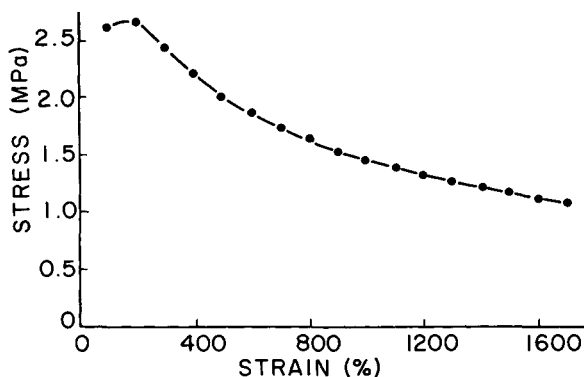


Fig. 5. Stress/strain curve obtained for 15% IAD-PB elongated at a constant crosshead velocity of 51 cm/min. Note that the stress decreases at high strain, indicative of flow rather than strain-induced reinforcement.

Among elastomers the classic example of a morphology which is altered by deformation is the strain-induced crystallization of natural rubber. This results in a markedly upturning stress/strain curve when the material is elongated in tension,¹¹ and also in a shear viscosity that becomes infinitely high at high shear rates.¹² In contrast to this, a 15 mol % IAD-PB exhibits a stress that declines with strain during tensile elongation (Fig. 5) and furthermore, during flow in a capillary die, behaves as a typical shear-thinning polymeric fluid (Fig. 6).

Properties of IAD-PB in Blends

Although the 15 mol % IAD-PB is a homogeneous material, it nevertheless is incompatible with the unmodified PB. This can be inferred from measurement of polymer-solvent interaction parameters for PB as a function of IAD level (Fig. 7), which suggests that a significant difference exists between solubility parameters of PB and IAD-PB when the IAD level exceeds 20% by weight. Also, when plied together for an extended period (16 h), PB and IAD-PB strips delaminate in a completely interfacial mode,

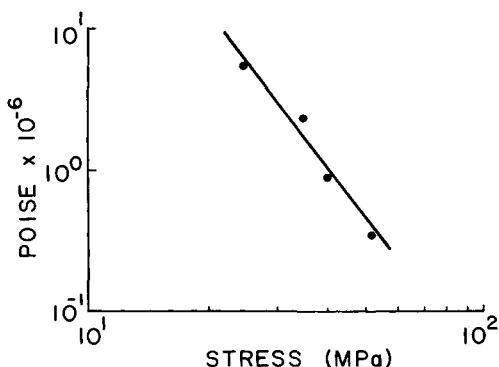


Fig. 6. Shear viscosity measurements for a 15% IAD-PB mixed with 40 phr N330 carbon black. The data was taken at 100°C over a range of nominal shear rates from 45 s⁻¹ to 1500 s⁻¹.

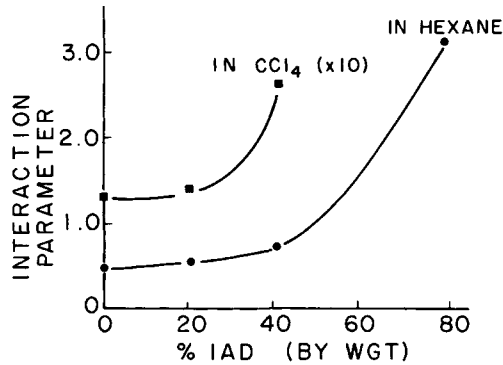


Fig. 7. Polymer-solvent interaction parameters measured for PB of various IAD contents. The solvents employed are as indicated.

suggestive of the absence of interdiffusion due to the thermodynamic incompatibility. When PB and IAD-PB are mixed together, it is therefore expected that the component present in lower concentration will exist as domains dispersed within the major component.¹³ ESCA analysis of the concentration of nitrogen and oxygen at the surface of blends of PB and 15 mol % IAD-PB showed, moreover, that the surface composition was reflective of the bulk; that is, there was no preferential migration of IAD-PB or of PB to the surface during blending. The tack of the various blends was then measured and these results are depicted in Figure 8. It can be seen that the increase in tack is a strong function of the concentration of modified PB present. If the level of tack were primarily dependent upon the extent to which IAD-rich regions at the two surfaces were brought into proximity, a quadratic dependence of autoadhesion on IAD concentration might be expected. This presumes the only effect of the IAD-PB is to promote interfacial bonding, and ignores its influence on the deformation characteristics of the material when plied test specimens are separated.

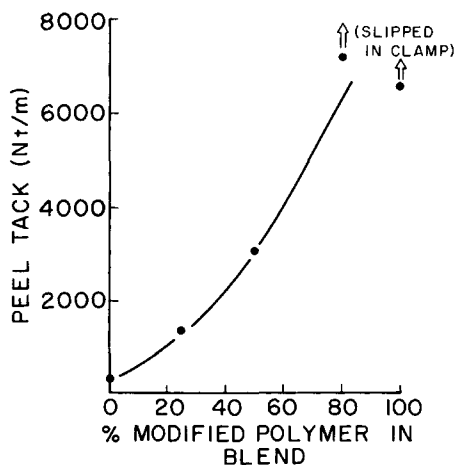


Fig. 8. Measurements of the tack of polybutadiene as a function of the level of IAD incorporated into the polymer.

TABLE III
Tack Measured for Blends of PB and IAD-PB^a

Level of IAD in IAD-PB (mol %)	Wt % PB in blend	Tack (J/m ²)
6.3	0	180
15	50	1000
38	71	10

^a The overall concentration of IAD was kept fixed at 20% by weight by adjusting the relative amount of the IAD-PB.

The data in Figure 8 reveals a weak dependence at low levels of IAD-PB, with the tack then steeply rising at higher IAD-PB concentrations. It seems likely that this marked increase corresponds to the development of an IAD-PB continuous phase. The nature of the morphology existing in these blends is not known and, given the complex dependence of the structure in heterogeneous blends on the details of the processing conditions and polymer rheological properties,^{13,14} it is difficult to draw general conclusions regarding the level of tack exhibited by IAD-PB containing polymer mixtures.

A given level of IAD can, of course, be present in a blend in different forms. For example, a lower concentration of highly modified IAD-PB could result in blend properties significantly different than a compound with a higher concentration of PB that had been modified to a low level of IAD. To examine this point, a series of blends were prepared in which the weight percent of IAD was maintained at 20%. The polymers used consisted of polybutadiene that had been reacted with 0–38 mol % IAD. The results of tack testing of these stocks are given in Table III. The highest tack is achieved in the blend containing the PB with the highest IAD content, provided it still remains a flexible-chain elastomer. Too high an incorporation of IAD results in a plastic material devoid of tack, while a lower level of IAD per IAD-PB molecule (the total IAD concentration in the blend is fixed) does not produce as large an enhancement in tack for the blend. In this latter case, it is seen that the development of autoadhesion does not simply parallel the IAD concentration, but is amplified at higher levels of IAD incorporation. This behavior is consistent with the data in Figure 8.

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