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Evidence of Strain-Induced Phase Separation in Isopropyl Azodicarboxylate Modified Polybutadiene

G. R. Hamed[1], C.-H. Shieh[1] and D. N. Schulz[2]*

[1] Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA

[2] Firestone Central Research, Akron, OH 44317, USA

Summary

Polybutadiene (BR) has been modified by reaction with isopropyl azodicarboxylate (IAD). The reaction is quite efficient -- resulting in a structure in which there are pendant hydrazoester groups dangling from the BR backbone. The cohesive strength and autohesion of BR are increased by the IAD modification. It is proposed that this polymer is capable of strain-induced phase separation -- a mechanism of self-reinforcement. Evidence for this is the appearance of a new strain-induced thermal transition in the DSC scan of this material.

Introduction

Natural rubber strain-crystallizes when subjected to large deformation (KATZ 1925, TRELOAR 1941), because of its highly stereo-regular, cis-1,4 polyisoprene structure. This strain-induced strengthening mechanism is largely responsible for the simultaneous high tear strength and autohesion (tack) of unvulcanized natural rubber compared to stereo-irregular elastomers (e.g., styrene-butadiene rubber) which are incapable of hardening upon stretching (HAMED 1981 a).

Natural rubber can be processed to a relatively low molecular weight which facilitates the formation of an autohesive bond (contact and interdiffusion), but upon straining to measure autohesion, it strain-crystallizes and hence resists separation. A strain-induced strengthening mechanism is ideal for high autohesion since it is not active during contact and interdiffusion, which are low strain processes. Elastomers that have high cohesive strengths due to partial crosslinking or crystallinity in the unstrained state (e.g., some ethylene-propylene elastomers), have low autohesive properties (HAMED 1981 b) since the structures (i.e., crosslinks and crystallites) responsible for the high cohesion are present in the unstrained state and inhibit the formation of a tack bond.

In this paper, it is shown that the chemical addition of isopropyl azodicarboxylate onto polybutadiene (IAD-BR) via the ene reaction gives an elastomer with enhanced strength and

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* Current Address: Exxon Research and Engineering Company, Linden, New Jersey 07036, USA

autohesion. It is further shown that the IAD-BR exhibits a structural change upon stretching. It is suggested that this structural change is a strain-induced phase separation and contributes to the high cohesion and autohesion of this material.

Experimental

The elastomer which was modified by reaction with isopropyl azodicarboxylate (IAD) was Diene 35 NFA supplied by the Firestone Tire and Rubber Company. This is an anionically polymerized 1,4-polybutadiene (BR) containing primarily mixed *cis-* and *trans-* structures. The IAD was obtained from the Muskegon Chemical Company.

To synthesize the IAD-BR, the desired amount of IAD was added to a solution containing 15 weight percent BR at 80°C. The reaction was allowed to continue for 24 hours. After cooling to room temperature, the reaction mixture was coagulated with methanol in the presence of an antioxidant, di-*tert*-butyl-p-cresol. The coagulated product was then pressed into a thin sheet and dried in a vacuum oven for 48 hours at 37°C. This synthesis procedure is similar to that used previously (SCHULZ et al. 1980).

Osmotic pressure measurements to determine number-average molecular weight were run at 37°C using a Hewlett Packard Model 503 high speed membrane osmometer with toluene as the solvent.

Nitrogen analyses were performed with a Perkin-Elmer Model 240 elemental analyzer.

Differential scanning calorimetry (DSC) measurements were carried out with a Dupont Model 990 Calorimeter using a sample weight of 20-30 mg and a heating rate of 10°C/min. All specimens were first purified by dissolving 15 g of material in 100 ml of toluene at 40°C for 12 hours and re-precipitating into methanol. The purified samples were then pressed into thin sheets and dried in a vacuum oven for 72 hours at 37°C. The DSC scans of unstretched samples were then determined in the usual manner. To detect structural changes (if any) upon deformation, a relatively new technique (LYON et al. 1982) was adopted to examine the DSC thermal transitions of an elastomer while maintaining it in the stretched state. Here, a thin strip of an elongated elastomer is wound around a tiny brass spool (spool weight = 0.335 g) under a constant load. (The ends of the strip are secured to prevent retraction during testing.) The spool with the sample is then placed in the test pan opposite a reference spool, and the DSC scan run as usual. Unstretched samples were also run using the spool holder technique by loosely wrapping a sample on a spool before testing. The DSC scans of these samples were the same as those obtained by the normal technique of placing a specimen in an aluminum pan.

Dynamic mechanic tests were carried out using a Rheovibron DDV-II at a frequency of 110 Hertz.

Dumbbell test specimens were used to determine the stress-strain curves of the uncured elastomers at a strain rate of about 10 min.$^{-1}$.

Autohesion (tack) measurements were carried out using a T-peel geometry at a peel rate of 50 mm/min. Cloth-backed strips (0.8 mm thick) of the elastomer were prepared by compression molding specimens against Mylar for 10 minutes at 90°C. Subsequently, the Mylar was rapidly removed from two of the strips, whose fresh surfaces were immediately brought into contact under a pressure of 3.3 (10^4) Pa for one minute. Samples were then T-peel tested one more minute after removing the contacting pressure. Tack is given by the average peel force per unit width to separate the strips.

Results and Discussion

The modified BR has the general structure shown below (SCHULZ et al. 1980), in which there are pendant hydrazoester groups dangling from the BR backbone. Furthermore, it has been shown previously that the IAD adds to the BR in a blocky fashion, and, at sufficiently high IAD levels, the modified elastomer separates into two phases (SCHULZ et al. 1980, SPIEWAK et al. 1981).

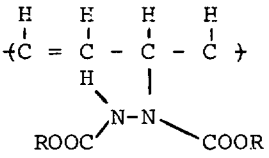

Figure 1. Structure of isopropyl-azodicarboxylate modified BR; R, CH_3-CH-CH_3.

The modification levels, number-average molecular weights from osmometry and the theoretical M_n's based on percent IAD incorporated are summarized in Table 1. There is reasonable agreement between predicted and direct measurements of M_n -- indicating that there is no significant crosslinking or chain scission accompanying the modification reaction.

Stress-strain curves

Figure 2 shows stress-strain curves for the IAD-BR's at various IAD levels. The ultimate breaking strength increases with modification level, whereas, the ultimate elongation at break passes through a maximum for a material with 36.7% IAD incorporated. This material remarkably shows a breaking

Table 1. Characterization of IAD-BR's

Sample	Wt. % IAD charged	Wt. % IAD incorp. (N analysis)	Osmometry $M_n \times 10^{-5}$	Calculated $M_n \times 10^{-5}$
BR	0	0	1.24	1.24
ID-9	9.1	7.7	1.30	1.34
ID-33	33.3	30.5	-	-
ID-40	40	36.7	2.02	1.96
ID-45	45	41.4	-	-
ID-50	50	46.4	2.16	2.31
ID-65	65	63.5	-	-

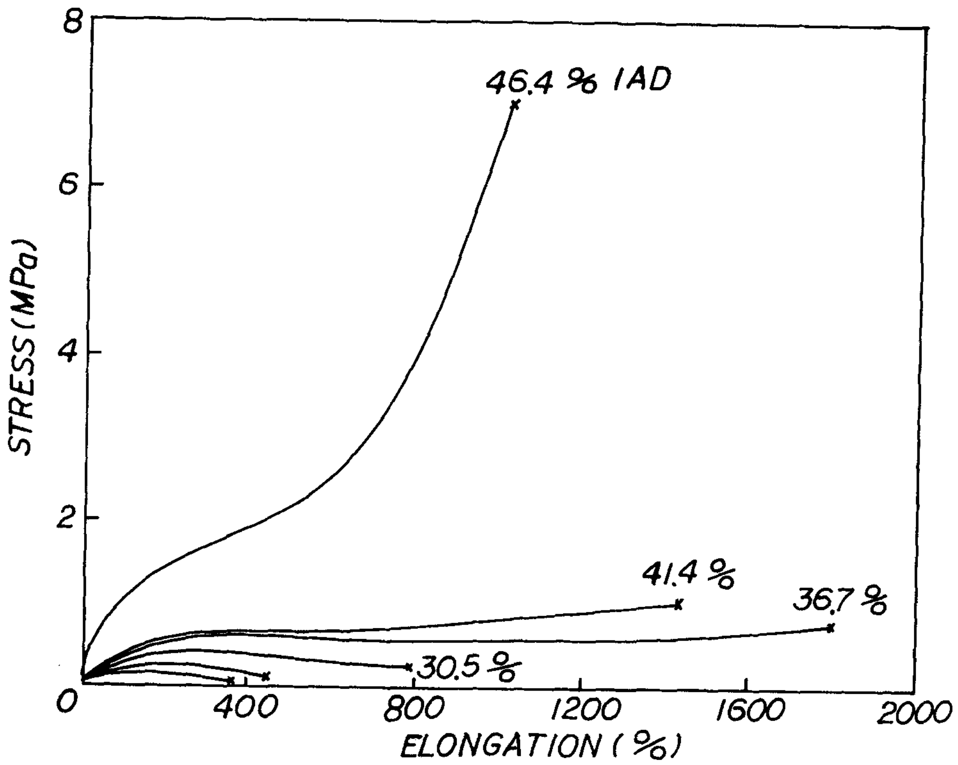

Figure 2. Stress-strain curves of uncured elastomer at various levels of IAD modification. (The weakest unlabelled curve is BR; curve immediately above this is 7.7% IAD modified.)

elongation of nearly 2000%. One striking feature in Figure 2 is the dramatic change in stress-strain response when the IAD incorporated increases from 41.4% to 46.4%. Beginning with the unmodified BR, there is a rather gradual increase in strength as the percent IAD incorporated increases up to 41.4%. This is likely due to the increased polarity and H-bonding capability imparted to the modified chains by the hydrazoester groups (SPIEWAK et al., 1981). Note, however, the abrupt increase in strength as the IAD level increases from 41.4% to 46.4% -- a small compositional change of only 5%. This behavior suggests that there also exists some abrupt morphological change at high IAD levels. Indeed, as will be shown in the next section, the highly modified BR exhibits a new DSC thermal transition when tested while sufficiently deformed. It is proposed, then, that the high strength of the highly modified BR is due, at least in part, to a structural change (perhaps a strain-induced phase separation) accompanying large deformation.

Morphological Changes Due to Straining

DSC scans for unstretched and stretched specimens of BR and ID-50 are shown in Figures 3 and 4.

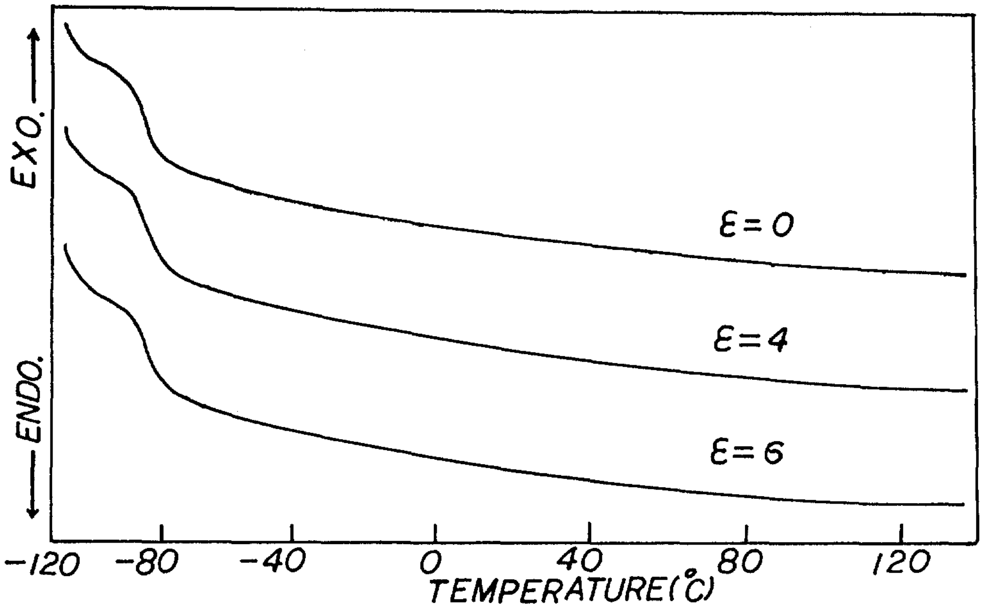

Figure 3. DSC scans of BR at various strain levels. (Very light crosslinking was needed to achieve a ε = 6.)

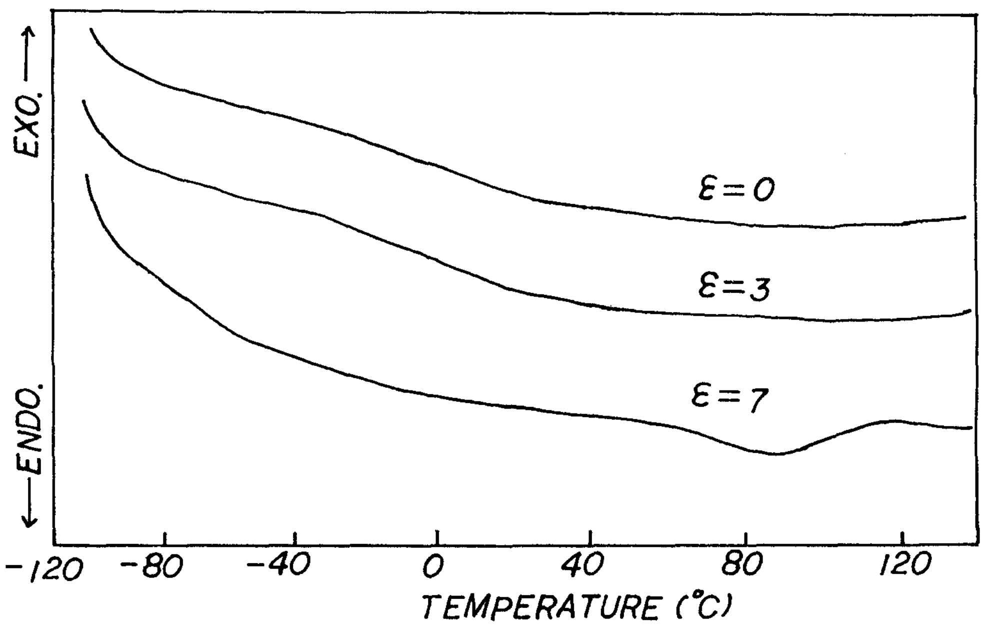

Figure 4. DSC scans of an IAD-BR (ID-50) at various strain levels.

Note that the thermal response of the BR does not change upon straining, whereas an endotherm develops upon straining the IAD-BR; i.e., there is a strain-induced structural change within this elastomer that self-reinforces (see Figure 2) it. It is significant to note that the temperature of this endotherm is similar to that of a tan δ peak (Figure 5), which appears in the dynamic mechanical response of the unstrained polymer at a substantially higher level of IAD.

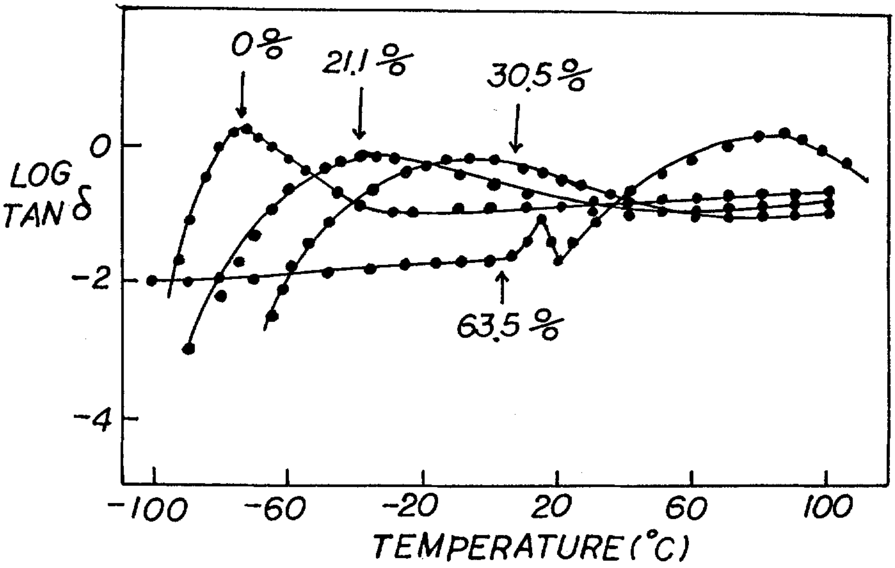

Figure 5. Damping response of IAD-BR's at various modification levels.

Apparently, the interaction of the IAD groups is entropically inhibited in the unstrained state as the rubbery chains tend to maximize their randomness. However, upon straining, the entropy decreases -- allowing these groups to interact more readily (i.e., form phase-separated domains) which strengthens the material. It is proposed that this phenomenon is favored (or perhaps possible) in this system because it is thermodynamically on the verge of phase separation. This is inferred, since, at high IAD levels, the unstrained IAD-BR has a two-phase morphology.

This is the first time to our knowledge that a material has been shown to exhibit strain-induced phase separation. (Note that strain-induced crystallization is highly unlikely here in view of the statistical process by which the IAD is added to the BR.) However, other authors have reported shear-induced phase separation upon shearing miscible polymer solutions (VERSTRATE and PHILIPPOFF 1974). It seems reasonable that for a system to exhibit a phase change with deformation or shearing that it must be thermodynamically "on the edge" of such a transition.

Autohesion

Typical high molecular weight elastomers containing polar moeities have high cohesive tear strengths but generally exhibit quite low values of autohesion. Examples include butadiene-acrylonitrile copolymers, chloroprene (non-crystallizing grades), and hydroxylated or carboxylated polybutadienes (HAMED 1981b). Indeed, a high cohesive strength can be achieved quite easily by light crosslinking or by polymerizing to a very high molecular weight. Again, however, tack remains low or is diminished. What is remarkable about the IAD modified BR is the dramatic enhancement in both the cohesive strength (shown earlier) and tack. Some tack data for BR and an IAD-BR are shown in Table 2.

Table 2. Autohesion of BR and an IAD-BR.

Sample	Peel Tack (k N/m)
BR	0.1
IAD-50	0.6

A possible reason for the enhanced tack of IAD-BR is that part of the strengthening mechanism in these materials is strain-induced, and, hence, inactive during the formation of the tack bond. This allows enough molecular mobility for flow and interdiffusion; but, at the same time, upon load application to disrupt the tack bond, the imposed strain induces domain formation, which enhances rupture resistance.

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