Notes

Acyclic Azoester Modification of 1,4-Polybutadienes. II. Green Strength and Tack Properties

INTRODUCTION

In a previous paper,[1] we presented evidence that, among other things, isopropyl azodicarboxylate (IAD)-modified 1,4-polybutadienes exhibit a blocky distribution of hydrozoester functionality and multiphase morphology. Macromolecules which show such molecular and supermolecular structures often exhibit enhanced mechanical properties.

Since amorphous synthetic elastomers are generally woefully deficient in two properties—green (uncured, cohesive) strength and tack (autoadhesion)[2–4]—we decided to evaluate these properties for the IAD-modified 1,4-polybutadienes. This paper describes our findings.

EXPERIMENTAL

Synthesis

IAD-modified 1,4-polybutadienes were prepared according to our previously published procedures.[1] The osmotic $\overline{M}_n$ of the unmodified 1,4 (mixed *cis*, *trans*)-polybutadiene was 107,000 and that of the one containing 15 mol % IAD repeat units was 177,000. All samples were gel-free.

Green Stress Strain and Tack Measurements

Green stress–strain measurements were performed on filled uncured rubber systems (100 phr rubber, 50 phr black, 10 phr oil, sulfur, and accelerator), using an Instron tester with an initial jaw separation of 1 in. (2.5 cm), a cross-heat speed of 20 in./min (5 mm/min), and a chart speed of 20 in./min (5 mm/min).

Tack measurements were made according to a previously reported method.[4] For example, plaques were first formed by pressing the test compound onto square woven nylon monofilament fabric at 93°C at a pressure of 4 MPa. Strips cut from the plaques were pressed together by winding a 25-mm-wide strip onto a 32-mm-wide strip which is clamped on the curved surface of a cylindrical drum, 63 mm in diameter and 40 mm long. The drum was rotated with a 4.5 kg load. The tack test was started 3 min after specimen preparation. For this operation, the drum and test specimen were transferred to an Instron tensile tester. The outer test strip was then unwound from the drum at a rate of 50 mm/min (2 in./min). The average force attained during the separation was determined graphically and expressed in N/m (lb/in.).

Dynamic Mechanical Measurements

Dynamic mechanical responses for IAD-modified polymers were obtained using a Rheovibron at constant frequency in the temperature range of −90–150°C. A computer program was used to convert the Rheovibron data into plots of dynamic modulus and tan δ vs. temperature.

RESULTS AND DISCUSSION

Two properties which are characteristic of natural rubber (NR) and generally absent in the case of amorphous synthetic elastomers (e.g., BR, SBR) are green strength and tack. The green strength of rubbers has been loosely defined as the ability of uncured rubber compounds to avoid rupture under steady strain at intermediate elongations without offering excessive resistance to deformation in material mixing, calendaring, and molding. A synonym for such green strength is cohesiveness.

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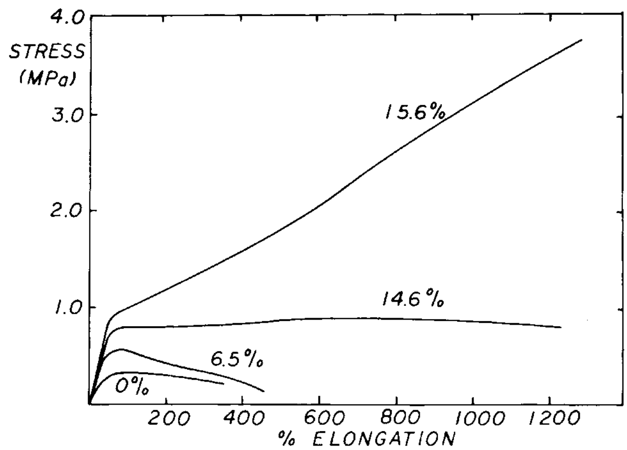

Fig. 1. Green stress–strain curves for various mol % of 1,4(*cis*, *trans*)-polybutadiene units which are IAD-modified.

A positive slope in the green stress–strain curve for rubbers is a common diagnostic test for this property.[2]

Tack is the ability of two similar surfaces to adhere strongly when brought into contact under a light pressure for a short time.[4] Tack or autoadhesion is distinct from stickiness to unlike surfaces. In tire making operations, one wants building tack but not stickiness (e.g., sticking to mill rolls). A number of tack tests for rubber compounds have been reported.[3,4]

In a previous paper,[1] we presented evidence that the isopropyl azodicarboxylate (IAD)-modified 1,4-polybutadienes exhibit a blocky distribution of hydrazoester functionality and microphase separation. It is known that polymers which evince such molecular and supermolecular structures often show mechanical property advantages over macromolecules without such structures. Indeed, such results are borne out by green stress–strain and tack measurements on IAD-modified 1,4-polybutadienes compared with those of unmodified 1,4-polybutadiene.

Figure 1 shows green (uncured) stress-strain curves for IAD-modified 1,4-polybutadiene compounds at various levels of IAD substitution. Unmodified and slightly modified 1,4-polybutadiene compounds exhibit the very low green strength expected for amorphous rubbers. However, at IAD contents above 15 mol %, there is a definite upturn in the green stress–strain curve or a strengthening of these elastomers. This effect is a reasonable consequence of blocky substitution and microphase separation. Such microphase separation is seen in the dynamic thermomechanical measurements

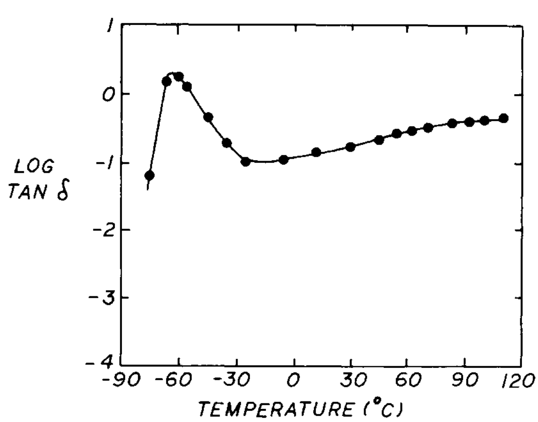

Fig. 2. Tan δ vs. temperature for unmodified 1,4(*cis*, *trans*)-polybutadiene.

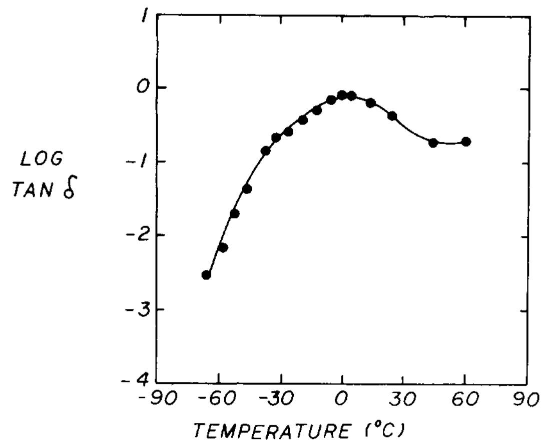

Fig. 3. Tan δ vs. temperature for 1,4(*cis, trans*)-polybutadiene in which 15 mol % of repeat units are IAD-modified.

for IAD-modified polymers; there is a broadening of the tan δ peaks with increasing IAD substitution until there is the ultimate emergence of two tan δ peaks or two polymer T_g's (Figs. 2–4).

Figure 5 shows tack comparisons between IAD-substituted 1,4-polybutadienes and 1,4-polybutadiene itself. It can be seen that amorphous 1,4-polybutadiene shows essentially no tack. Tack increases with increasing modified IAD repeat units and peaks about 11 mol % IAD repeat units. Such a substitution level is also characterized by substantial and broad mechanical losses at room temperature (Fig. 3). Tack maxima have been observed before for block polymers and frequently coincide with conditions of multiphase morphology and high energy losses.[5]

SUMMARY

Two properties of rubber compounds which are normally lacking for amorphous synthetic rubber are green (uncured cohesive) strength and tack (autoadhesion). We have found that isopropyl azodicarboxylate (IAD) modification of 1,4-polybutadienes results in significant improvements in these properties compared with the unmodified base polymer. At IAD contents above 15 mol %, there is a definite upturn in the green stress–strain curve of the modified polybutadienes. Also,

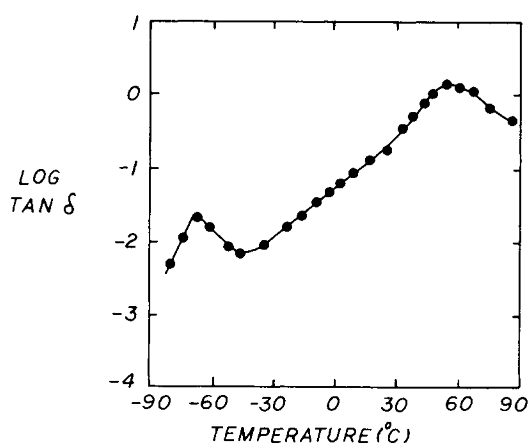

Fig. 4. Tan δ vs. temperature for 1,4(*cis, trans*)-polybutadiene in which 37 mol % of repeat units are IAD-modified.

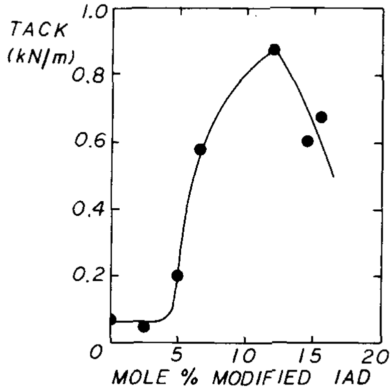

Fig. 5. Windup tack as a function of mol % of repeat units which are IAD-modified.

the rubber compound tack values increase with increasing IAD contents and peak about 11 mol % IAD. These property improvements are undoubtedly related to the previously described[1] unique molecular and supermolecular structures of IAD-modified 1,4-polybutadienes.

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J. W. SPIEWAK
L. A. BRYANT
D. N. SCHULZ

Central Research Laboratories
Firestone Tire and Rubber Co.
Akron, Ohio 44317

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