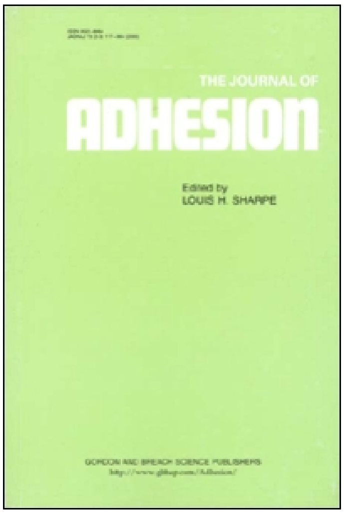

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Adhesion Properties of Rubbers Modified by Surface Active Substances

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The introduction of anionic surface active substances into butadiene-styrene rubbers doubles or trebles the work of delamination (A) for fabric-rubber bonds. The increase of A is due to a rise in mechanical loss through a higher rate of relaxation of a polymer adsorbed by a filler (τ_H). A linear dependence between A and $\log \tau_H$ is found.

INTRODUCTION

Surface-active substances (SAS) make it possible to regulate supermolecular structures,[1] control the rate of crystallization of polymers,[2] change the strength of compounded polymers[3] and their wettability.[4] No special investigation into the effect of SAS on the work of delamination of polymers was undertaken.

In this paper basic factors governing the work of delamination of glue joints and its increase through modification of polymers by SAS are revealed.

Delamination is a particular case of the rubber tear strength testing. The work of tear dA is $dA = dE + dW$, where dE is the work expended in tearing, which is attended with the formation of new surfaces, and can be expressed in terms of the characteristic energy of tear, T_*; dW is the work of deformation of the specimen ends which can be expressed in terms of the equilibrium modulus of rubber, E_∞.[5]

The change in the work of tear is governed by changes of the characteristic energy of tear on condition that rubbers with uniform cross-links density, that is equimodulus rubbers, are tested.

The characteristic energy of tear T_* appears to be the sum of two terms: $T_* = \alpha + q$, where α is the free surface energy of solid, q is the scattered heat during the formation of a unit of new surface or mechanical loss.

As the analysis showed,[6] the T_*/α ratio for solids close to ideal elastic bodies is 1.5–2 and for high elastic materials equals 10^4–10^5. Clearly T_* is basically determined by the mechanical loss in the course of fracture.[7]

The mechanical loss comprises three main components:[7] (1) deformation (relaxation) loss resulting from local inelastic deformations, viscous, plastic (or forced elastic) flow at stress points; (2) dynamic loss developing during the motion of crack walls and unloading of the specimen areas around the crack; (3) dissipation of elastic energy during bond breaking at the apex of a growing crack (the Bartenev–Razumovskaya effect). The latter process is not connected with the mechanical loss within the volume of the material, but is a fine surface effect. The first component of the loss is several orders of magnitude more than the two others taken together. Thus, the work of tear and hence of delamination is determined for the most part by the deformation loss which in turn depends upon relaxation properties of high elastic materials. The experimental data available on the relation between these characteristics is scarce.

Of some interest was an investigation on the work of delamination versus relaxation properties of the rubbers modified by SAS.

EXPERIMENTAL

The following formulations of rubbers (weight percent per 100 parts of polymer by weight) were studied: BS (butadiene–styrene)—45k–70, SKS-30A–30 (a butadiene–styrene copolymer containing 30% styrene), sulfur—2.6, Captax—1.4, diphenyl guanidine—1.4, zinc oxide—5, carbon white "Y-333"—40, vaseline oil—15, SAS—from 0.2 to 5. Physical modification of the rubbers was performed using anion-active SAS of the sulfonol type with varying structure of the hydrocarbon radical: tetrapropylenebenzenesulfonate (NP–I) and dodecylbenzenesulfonate (KB).

The powdery SAS was introduced into rubber mixes in the process of polymer thermal plasticization on mill before fillers. Optimum cure was carried out at 145°C, thus ensuring constant concentration of active chains of vulcanizing network. The rubber under study was bonded to a cotton fabric (Russian Standard 4108) using a polychloroprene adhesive. The bond strength was tested on strips 10 × 100 mm by the delamination method. Delamination was carried out at 20°C using a sensitive tensile testing machine with peel angle of material 90° and rate of grip motion 0.2; 2; 20; 200 mm/min (designed at the Polymer Physics Problems Laboratory of the "V. I. Lenin"

Moscow State Teachers' Training Institute). Stress relaxation curves were taken on an axial stress relax meter with 20% strain. The experimental data processing was made by the method suggested in Refs. 8–10. The method is based on the assumption that real processes of relaxation are composed of individual elementary process and for a preset deformation are expressed by the sum of n-exponents:

$$\sigma(t) = \varphi(\varepsilon_0, t) = \varepsilon_0 \sum_{i=1}^{n} E_i e^{-t/\tau_i}$$

where ε_0 is the preset deformation; $\varphi(\varepsilon_0, t)$ is the relaxation function depending for non-linear processes not only upon time t, but also on deformation ε_0; τ_i is the relaxation time of ith elementary mechanism of relaxation entering into the relaxation time discrete spectrum; E_i is the factor whose value is indicative of the contribution of ith relaxation process.

RESULTS AND DISCUSSION

The dependence of the work of delamination upon the rate of delamination in semilogarithmic coordinates for fabric-unfilled rubber specimens (Figure 1a) is linear. The work of delamination increases with the rate of delamination

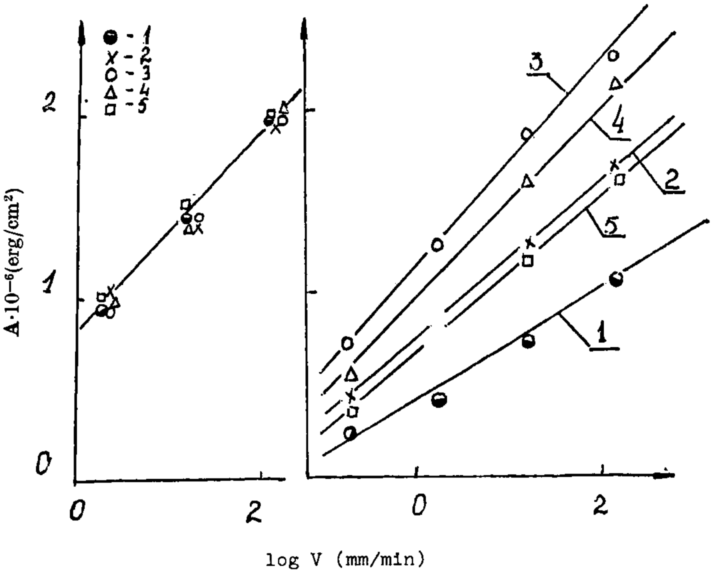

FIGURE 1 Work of delamination of unfilled (a) and filled (b) rubbers with different content of NP-1 versus the rate of delamination. 1 – 0.0; 2 – 0.2; 3 – 1.0; 4 – 2.0; 5 – 3, 0 parts by weight of SAS per 100 parts by weight of rubber.

and does not depend upon the presence of SAS in rubber. A similar dependence for filled rubbers with a different SAS content is presented by a family of divergent straight lines (Figure 1b). The higher the rate, the greater the effect of an increase in the work of delamination with the introduction of SAS into rubber. With optimum content of SAS in rubber, the work of delamination can be increased by a factor of 2–2.5.

This dependence of the work of delamination upon its rate is relaxative in nature. In filled cross-linked rubberlike polymers stress relaxation is related to four major processes[11] set out below. (1) Orientation and displacement of free segments in chain molecules occurring very fast with the relaxation time of 10^{-4} to 10^{-6} sec at 20°C. (2) Rearrangement of elements in supermolecular structures with the relaxation times of 10^2 to 10^4 sec. (3) Breaking away and adhesion of polymer macromolecules to filler particles with the relaxation times of 10^5 to 10^6 sec. (4) Rearrangement of transverse and chain chemical bonds both in the chemical relaxation process and under the influence of stress with the relaxation times of 10^7 to 10^9 sec at 20°C. The first two process relate to fast and slow stages of physical relaxation of a free polymer, respectively, the third process to the slow stage of physical relaxation of a filler-absorbed polymer and the fourth one to chemical relaxation.

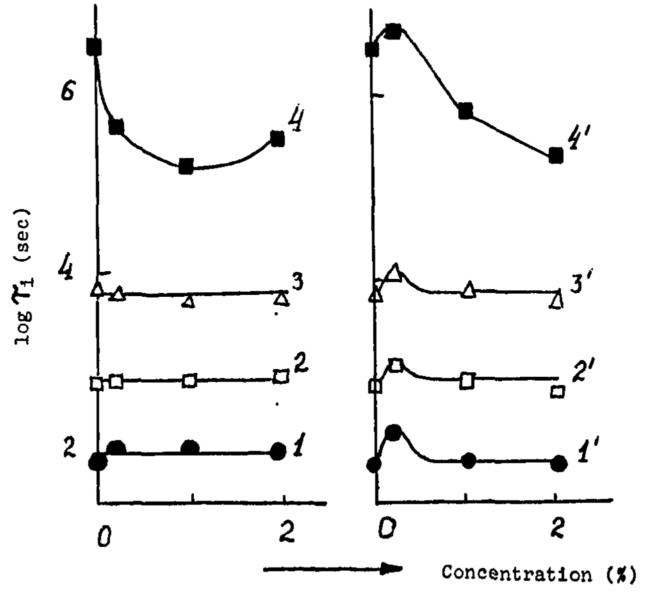

FIGURE 2 Time for the slow stage or rubber physical relaxation process versus SAS concentration: 1–4 for NP-1; 1′–4′ for KB. 1,1′–τ_1; 2,2′–τ_2; 3,3′–τ_3; 4,4′–τ_4 time of *i*th elementary mechanism of relaxation entering into the relaxation time discrete spectrum for filled rubber.

The time for experimental fracture of glue joints is commensurable with that for the slow stage of physical relaxation and hence the latter has been studied. The results of processing of the experimental data on stress relaxation are presented in Figure 2. It is seen from Figure 2 that the relaxation times from 10^2 to 10^4 sec characteristic for properties of the polymer proper are practically independent upon the SAS content in rubber, while the relaxation times τ_H from 10^5 to 10^6 sec determining the properties of a filler-adsorbed polymer have extremum dependence upon the SAS concentration in rubber. With optimum SAS content, τ_H can be reduced by an order of magnitude. When adsorbing on the polymer-filler interphase boundary, the SAS is likely to act as an interstructural plasticizer making it possible to control the rate of polymer relaxation in the rubber carbon component.

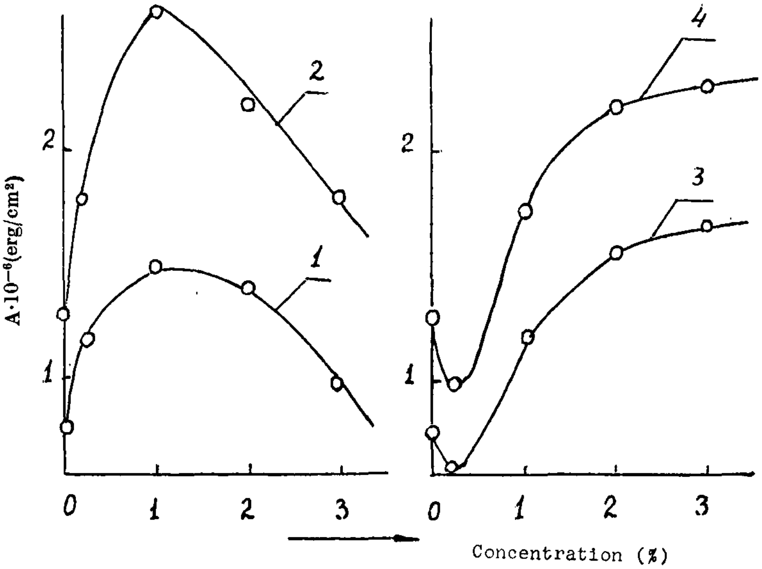

FIGURE 3 Work of delamination versus SAS concentration in rubber: 1,2 – NP-1; 3,4 – KB at the rate of delamination 1,3 – 20; 2,4 – 200 mm/min.

The dependence of the work of delamination upon the SAS concentration is also extremum (Figure 3). It is interesting that in this case the maximum of the work of delamination fits the maximum on the curve of τ_H against the SAS concentration. The change in the rate of relaxation for compounded rubbers modified by SAS apparently shifts the maximum of mechanical loss in delamination towards lower temperatures, with the result that the work of delamination increases so long as the mechanical loss in rubber rises at a given rate of fracture. The maximum work of delamination should obviously follow the maximum mechanical loss and maximum rate of relaxation. In semilogarithmic coordinates the dependence of the work of delamination upon $\log \tau_H$ is linear (Figure 4), that is, the greater the time for polymer relaxation in the rubber carbon component, the less the work of delamination. The increase in the rate of relaxation heads to the reduction of overstress concentrations at an apex of a growing crack and to the increase the work of delamination. This increase of the rate of relaxation is particularly important for the surface layer of a polymer because relaxation processes in it involve difficulties, as compared to its volume.[12] The increase in mobility of the surface layer molecules apparently promotes a deeper course of diffusion processes which play a significant part in the formation of an adhesion contact.[13]

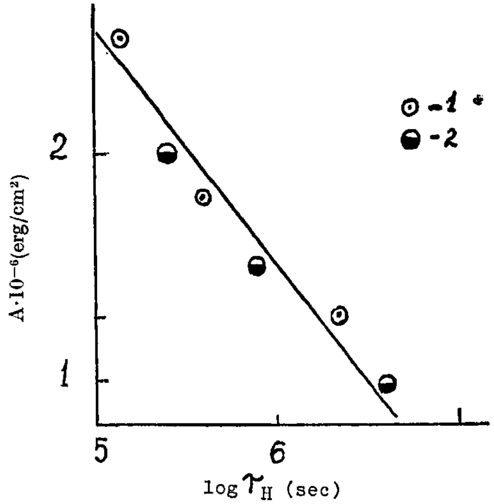

FIGURE 4 Work of delamination for fabric—unfilled rubber specimens versus the time of physical relaxation: 1 - NP-1 ; 2 - KB.

CONCLUSIONS

1) The introduction of anionic SAS into butadiene–styrene rubbers doubles or trebles the work of delamination for fabric–rubber bonds.

2) The direct experiments have demonstrated that the increase in the work of delamination (A) is due to a rise in mechanical loss through a higher rate of relaxation of a filler-adsorbed polymer (τ_H). A linear dependence between A and $\log \tau_H$ is found.

3) With the optimum content of SAS in rubber, the value of τ_H may be reduced by more than an order of magnitude.

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