

Oxidative Degradation of Polydiene Vulcanizates*

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During the oxidation of polydiene vulcanizates at elevated temperatures, a combination of scission reactions and crosslinking reactions occur, which will either reduce the original rubbery network to a tacky semiliquid or to a brittle solid, depending on which reaction predominates. The relative importance of each reaction can be distinguished by the techniques of (I) continuous stress relaxation and (II) "intermittent" stress relaxation.^{1,2} In method (I), the decay of stress in samples held at constant extension measures scission alone when the crosslinking is not very extensive, since crosslinking on the average tends to occur in equilibrium with the stretched length. In method (II), samples are kept in a relaxed state except for very short intervals when the samples are stretched. The measured stress in these short intervals indicates the net effect of scission and crosslinking.

We have investigated, by such methods, the oxidation of vulcanizates of natural rubber and of polybutadienes, which were prepared by exposing the original unvulcanized polymer to high-energy electrons. The radiation vulcanization procedure has been selected because in this way no impurities are introduced into the network, i.e., this eliminates the usual procedure of adding chemicals to obtain cure, which may remain active as crosslinking agents after the vulcanization.

In Figure 1(A) are presented the data obtained by the two stress relaxation methods for radiation crosslinked natural rubber at 130°C. The near identity of the two curves indicates that, for this material, scission occurs with essentially no accompanying crosslinking reaction. The scission reaction has been shown to be a cleavage to polyisoprene chains induced by molecular oxygen.⁵ We have included, in Figure 1(B), the data of previous measurements taken in identical fashion for sulfur cures

of natural rubber.³ The sizable difference between the continuous and intermittent curves, in this case, shows that a crosslinking reaction does exist. By comparing with Figure 1(A), we can say that this reaction is not oxidative crosslinking of the pure hydrocarbon and must be caused by the presence of unreacted sulfur, accelerators, and their degradation products.

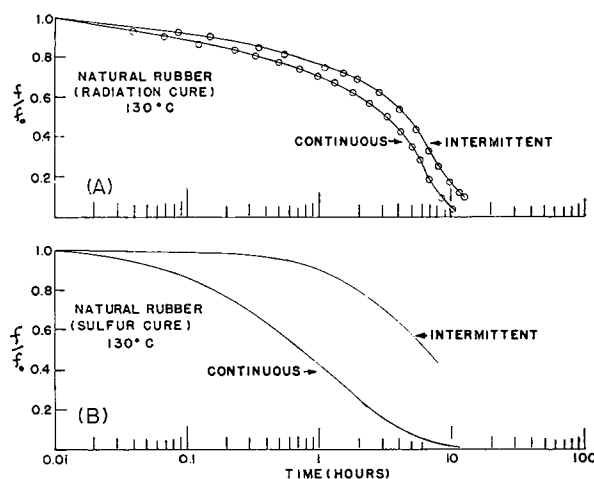


Figure 1.

Crosslinking reactions have been found to be strongly predominant in the synthetic rubber GR-S (a random copolymer containing 75% butadiene-25% styrene, prepared by emulsion polymerization). As shown in Figure 2(A), the stress measured intermittently for sulfur cures of GR-S rises steadily from the start of the experiment.³ Although it is evident from the continuous measurement that scission also takes place, this is more than compensated for by the faster crosslinking reactions. We have presented, in Figure 3(B), the behavior of the related emulsion polymerized polybutadiene (100%), which was crosslinked by radiation. In this case, the intermittent stress first decreases, then increases; finally a brittle solid is

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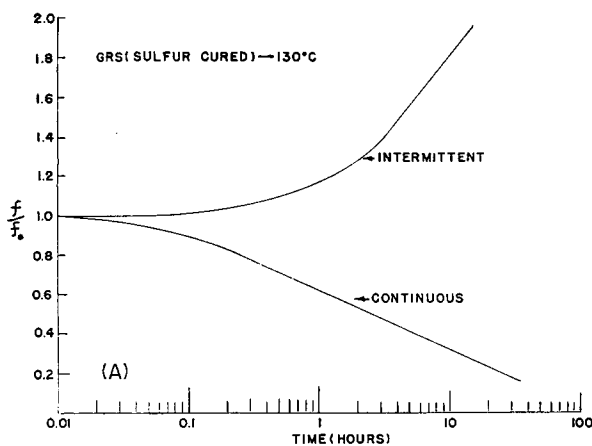


Figure 2.

obtained. This difference in behavior from the GR-S sulfur cure is partly due to a continued sulfur vulcanization in the sulfur cure. Nonetheless, it is clear that even in the absence of vulcanizing chemicals, polybutadiene exhibits a crosslinking reaction which must be related to the oxidation of the pure hydrocarbon.

Both GR-S and polybutadiene prepared by emulsion polymerization contain the diene in the 1,2-configuration (pendant vinyl group), and both the *cis* and *trans* 1,4-configuration. The emulsion polybutadiene contains 20% 1,2; 60% *trans*-1,4; and 20% *cis*-1,4, according to Binder.⁴ The butadiene portions of GR-S have similar proportions of these structures.⁴

In view of the results with emulsion polybutadiene and natural rubber, we performed similar experiments with all *cis* 1,4-polybutadiene obtained

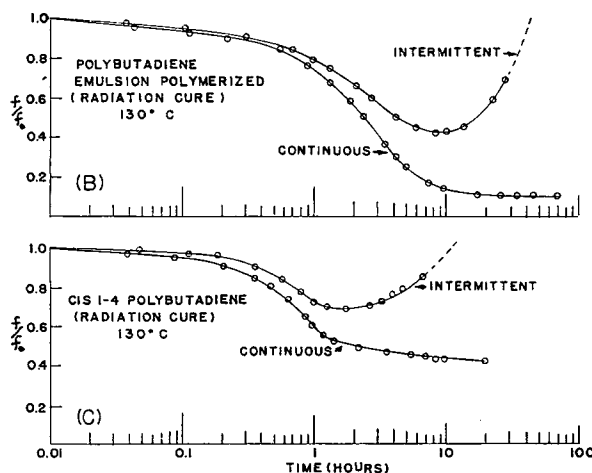


Figure 3.

from stereospecific polymerization. These data, as shown in Figure 3(C), demonstrate that all *cis* 1,4-polybutadiene also undergoes appreciable oxidative crosslinking in the pure hydrocarbon. This means that the oxidative crosslinking of GR-S and emulsion polybutadiene cannot be attributed exclusively to the 1,2-configuration.

EXPERIMENTAL

The polydienes were irradiated with 1 mev. electrons for 5 min. in a beam where they absorbed 195×10^{18} ev./sec./cc. of rubber. Further details are given in another article.⁵ The continuous and intermittent stress measurements were performed as described in references 1 and 2.

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References

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Synopsis

Intermittent and continuous stress relaxation measurements have been utilized to follow the oxidative degradation of vulcanizates of natural rubber, and of synthetically prepared polybutadienes. Vulcanizates were prepared by exposing samples to high-energy electrons. For natural rubber, only oxidative scission reactions were detected. Emulsion polymerized polybutadiene and all *cis* 1,4-polybutadiene exhibited both oxidative scission and oxidative crosslinking. With sulfur vulcanizates of these elastomers, there is superposed on the oxidation reactions a continued vulcanization caused by remaining curing agent.

Résumé

Des mesures de relaxation sous tension intermittente et continue ont été utilisées pour suivre la dégradation oxydative de caoutchoucs naturels vulcanisés et de polybutadiènes synthétiques vulcanisés. Les vulcanisats ont été préparés en exposant les échantillons à une source d'électrons à énergie élevée. Pour le caoutchouc naturel, on a détecté uniquement des réactions de scission dues à l'oxydation. Le polybutadiène polymérisé en émulsion et le 1,4 polybutadiène entièrement *cis* montrent et une scission à l'oxydation et un pontage dû à l'oxydation. Pour le cas des vulcanisats de ces élastomères au soufre, il se superpose aux réactions

d'oxydation, une vulcanisation continue due aux résidus de l'agent traitant.

Zusammenfassung

Zur Verfolgung des oxydativen Abbaus von Naturkautschukvulkanisaten und Vulkanisaten von synthetisch hergestellten Polybutadienen wurden intermittierende und kontinuierliche Spannungsrelaxationsmessungen herangezogen. Die Vulkanisate wurden durch Einwirkung hochenergetischer Elektronen auf die Proben hergestellt. Bei

Naturkautschuk konnten nur oxydative Spaltungsreaktionen festgestellt werden. Polybutadiene, die in Emulsion polymerisiert worden waren, sowie *cis*-1,4-Polybutadiene zeigten sowohl oxydative Spaltung als auch oxydative Vernetzung. Bei Schwefelvulkanisaten dieser Elastomeren ist den Oxydationsreaktionen eine weiter verlaufende Vulkanisation überlagert, die von Vulkanisationsmittelüberresten verursacht wird.

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