Cleavage in Urethane-Type Synthetic Rubbers

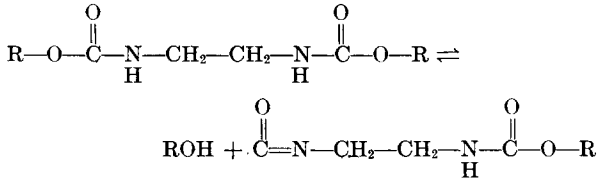
Chain scission of urethane-type rubbers was studied by stress-relaxation at constant elongation. Urethane rubber was made from the bischloroformate of tetrahydrofuran–alkylglycidyl ether copolymer extended with ethylene diamine or with piperazine (Research Division, Goodyear Tire and Rubber Company). These samples were vulcanized with:

	Parts per 100 rubber
Zinc oxide	5
Stearic acid	2
Benzothiazyl disulfide	2
Mercaptobenzothiazole	1
Tellurium diethyldithiocarbamate	0.5
Sulfur	1

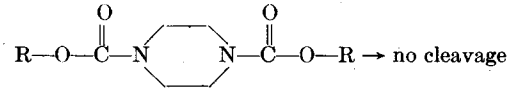
The following observation was made from stress-relaxation measurements of acetone-extracted samples at 120° C.

The piperazine-extended polyether chain is much more resistant to scission than the same chain extended with ethylenediamine.

This difference may be attributed to the fact that the ethylenediamine-extended chain contains normal urethane linkages with hydrogen on the nitrogen atom. This type of linkage is capable of a reversible cleavage back to isocyanate and alcohol:



This reaction is presumed to be responsible for chain scission in the ethylenediamine extended chain. On the other hand, the piperazine-extended chain contains *N*-alkyl-substituted urethane linkages which cannot undergo this same type of decomposition:



The stress-relaxation curves at 120° C. are shown in Figure 1. The time to relax to 36.8% of initial stress, i.e., the chemical relaxation time, is 4.8 hr. for the ethylenediamine-extended rubber and 165 hr. for the piperazine-extended rubber. It is noteworthy that the value obtained for the ethylenediamine-extended rubber is within a factor of 2 of that previously obtained for polyester rubbers containing similar urethane linkages, without any correction for the number of these linkages per network chain.[1] On the other hand, the value of the chemical relaxation time in the piperazine-extended rubber is about 35 times greater, and may well arise from (oxidative?) scission at linkages other than the substituted urethane linkage.

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Reference

1. Tobolsky, A. V., *Properties and Structure of Polymers*, Chapter V, p. 265, John Wiley & Sons, New York, 1960.

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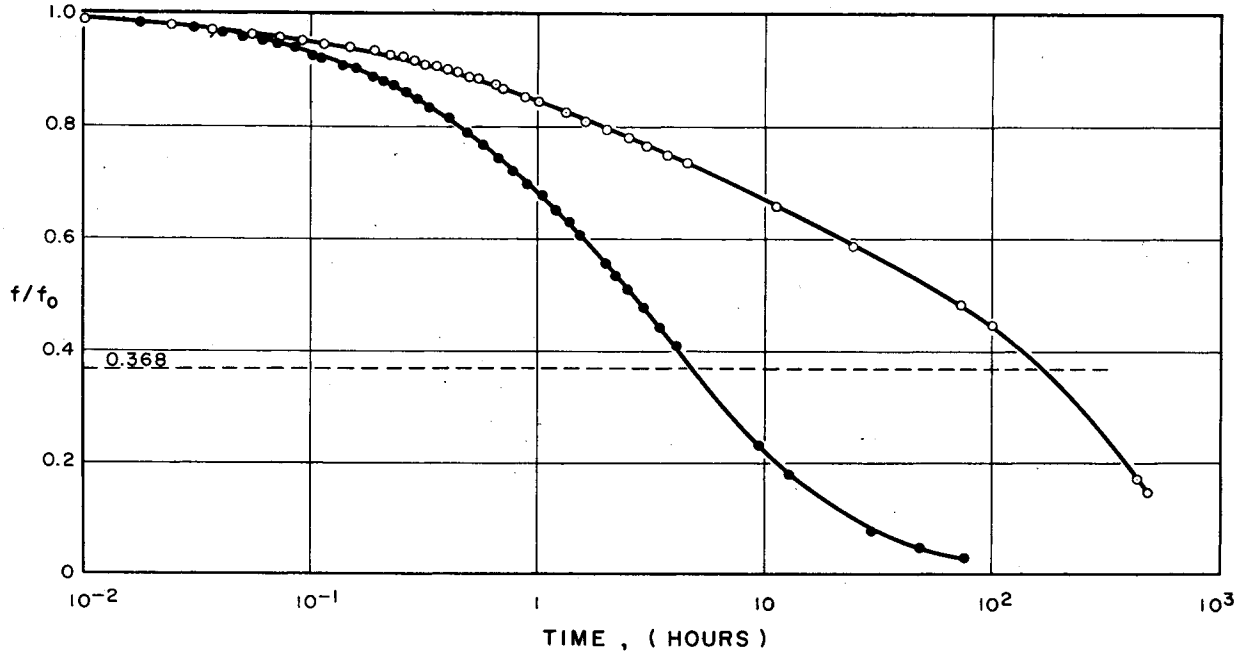

Fig. 1. THF-age copolymer: (O) extended with piperazine; (●) extended with ethylenediamine.