*The Softening of Adiprene L Gum Stocks During Extension**

It has been known for many years that when a reinforcing filler is added to an elastomer, marked changes in the stress-strain properties take place. It has also been known that repeated deformation of such a material results in a decrease in the reinforcing action insofar as the modulus values are concerned. This softening of reinforced rubber on extension has been termed the "Mullins Effect" and has been the subject of several investigations.[1-3]

During measurements in this laboratory on the properties of a sample of Adiprene L (a commercially available[4] polyether with terminal isocyanate groups) cured with a diamine, it became apparent that this material also exhibited the Mullins Effect. Since this is believed to be the first reported case in which appreciable softening has been observed in the absence of reinforcing filler, the results are reported briefly here.

The gum stock was prepared from 100 g. of Adiprene L and 12.1 g. of 4,4'-methylene-bis-(2-chloroaniline) supplied by E. I. du Pont de Nemours & Co. Cure time was $3^1/_2$ hrs. at 212°F.

Stress-strain measurements on dumbbell samples were made on an Instron testing machine with an extension rate of approximately 1000%/min. All measurements were taken during the extension cycle. The sample was initially extended to 200% elongation, relaxed 10 min., and stretched again. The process was then repeated at the next higher elongation. It was found that essentially all of the softening took place during the first stretch to a given elongation.

The experimental results are shown in Figure 1. All of these results were obtained with a single sample but duplicate samples gave good agreement, even when the initial stretch was close to the breaking elongation.

The data have been analyzed following the quantitative, although semi-empirical, treatment of Blanchard and Parkinson.[2] Their approach involves a consideration of the weak (secondary) linkages which are broken by prestressing and strong (primary) linkages which survive prestressing. The extent of softening can be represented by an equation of the form:

$$G = G^* + G_r F(X) \qquad (1)$$

where G is the total modulus, G^* is the residual modulus due to strong linkages, G_r is the modulus due to secondary linkages, and $F(X)$ is a function that depends on the prestress and a strength distribution parameter K. This approach has been applied[2,5] to a number of elastomer–carbon black combinations, and it has been found that in all cases K = 0.28.

It was found that the data in Figure 1 could be treated in exactly the same manner and the final results, expressed in the form of eq. (1) above, are plotted in Figure 2. In the course of calculating the data required for Figure 2 it was found that K = 0.20. The effect of the variation of K on physical properties is not clear, but it is probable that the value of K influences the tensile and breaking elongation of an elastomer and that there is an optimum value of K for the attainment of best ultimate properties. It should be pointed out that samples of Adiprene L cured with a diol–triol mixture[4] do not exhibit any Mullins Effect. Such samples, even at optimum cure, have much lower modulus and tensile values than the diamine cured samples.

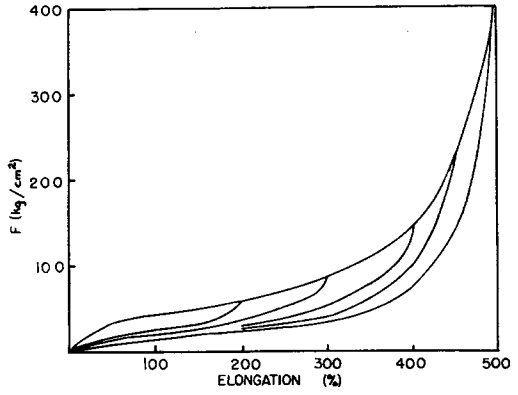

Fig. 1. Stress-strain curves for diamine cured Adiprene L showing change in modulus with prestress.

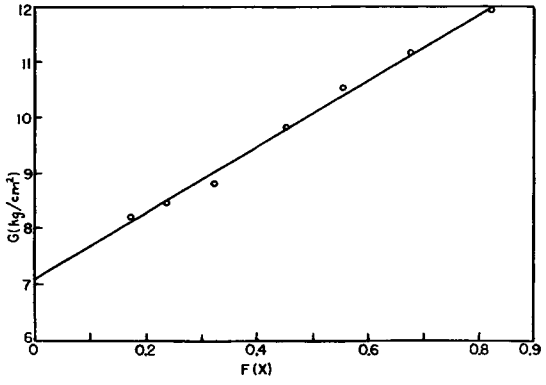

Fig. 2. Experimental results plotted in terms of eq. (1). G^* = 7.1 kg./cm.². G_r = 6.0 kg./cm.².

Although it has been established that Adiprene L cured with diamine behaves as a reinforced rubber, the source of the reinforcement has not been established. Work is in progress to determine the origin of this reinforcing action.

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