Crosslink Density of Elastomers.   A New Gas-Chromatographic Method

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Synopsis

The crosslink density of small microtomed samples of rubber vulcanizates has been determined using a gas-chromatographic method for estimating the amount of solvent in the swollen rubber.   The method may be used for determining the variation in crosslink density through thick rubber articles, for determining the change in crosslink density after aging service, or, for the investigation of rubber bonds and interfaces.

INTRODUCTION

Information concerning the state or degree of vulcanization of rubber products is often desired.   This is because most products are compounded and cured to a specific hardness or modulus depending on the end use. For example, stocks used in mechanical goods usually have a higher hardness than goods where fatigue resistance is important, such as tires.   If the modulus changes, however, during the life of the article, this is usually reflected in a shortened service period.   For general-purpose diene rubbers, this change depends on the type of polymer—polyisoprene rubbers such as natural rubber tend to soften slightly on aging or service, whereas rubbers derived from butadiene such as styrene–butadiene copolymer tend to harden considerably.[1]   Typical physical test methods are usually out of the question.   The determination of crosslink density by equilibrium swelling measurements is the only practical method that is presently available.   Moreover, any size or shape of sample may be used, which makes the method adaptable to routine measurements for new or aged products.

The usual procedure for the determination of crosslink density involves the swelling of a weighed sample of rubber in a suitable medium such as benzene for approximately 48 hr.[2]   The rubber is removed, blotted quickly with filter paper, and weighed in a tared weighing bottle.   After removal of the solvent in a vacuum oven, the weight of imbibed solvent is obtained as the difference between the weight of swollen sample and dried sample. The swelling value Q, defined as the grams of benzene per gram of rubber hydrocarbon, is readily calculated:

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{\text{original weight} \times \dfrac{100}{\text{formula weight}}}$$

where formula weight is the total weight of the rubber plus compounding ingredients based on 100 parts of rubber. A comparison of the crosslinking may then be made from the reciprocal swelling value, $1/Q$, and correlated with modulus if desired. Calculation of the actual number of crosslinks may be made for unloaded vulcanizates by using the Flory-Rehner equation.[3] For carbon black-loaded vulcanizates, the calculations are less certain due to assumptions and corrections that must be made.[4]

An adaptation of this method for very small samples is illustrated below by using microtomed samples $3 \times 5 \times 0.02$ mm in size. Accurate weighing of these small swollen samples is very difficult.[5] A rapid and accurate GC method was developed, therefore, for determining the amount of solvent in the swollen rubber. An optical method for thin samples whereby the area of the swollen specimen is magnified and traced on paper has previously been described by Coran.[6]

EXPERIMENTAL

The apparatus used was a Leitz sledge-type microtome, a Cahn electrobalance, and a Hewlett-Packard 7620A chromatograph with a 10-ft column containing 20% UCW-98 on Chromosorb W.

Microtomed samples approximately 20 μ thick were cut from a 3×5 mm billet of rubber that had been previously frozen in liquid nitrogen. Methanol was used as a wetting agent; and after cutting, samples were placed in 15×45-mm vials each containing 1 to 2 ml methanol and extracted at room temperature, preferably overnight. After drying in a vacuum oven for 4 hr at 50°C, they were weighed on a Cahn electrobalance (average weight was 0.5 mg) and placed in 28×60-mm vials each containing 3 to 4 ml reagent-grade p-xylene. It was found that swelling of these thin films was complete in 5 min. The swollen sample was removed with small metal forceps and the surface dried quickly with filter paper using a light rolling motion with minimum pressure. Xylene or other high boiling solvent is preferable as evaporation is minimized.

The swollen sample was placed immediately in a 15×45-mm vial which contained exactly 1 ml of a chloroform solution containing 1 mg cumene (1 g/l.). Volumetric flasks, 1 ml, may be used instead of glass vials if available. It was determined that the solution had come to equilibrium after 30 min. The amount of xylene in the solution was determined by gas chromatography, the cumene being used as an internal standard. The flow rate was adjusted so that the xylene peak appeared after 4 min and the cumene peak, after 5 min at 80°C. Areas were determined and the amount of xylene found was used to calculate the swelling value Q. The weight of rubber hydrocarbon was obtained by subtracting the weight of fillers and other insoluble nonrubbery materials from the weight of the methanol-extracted samples.

RESULTS AND DISCUSSION

Data obtained with the above GC method were comparable to those obtained using the conventional macromethod of weighing the swollen sample, $Q = 3.27$ versus 3.29. Typical data obtained on a tire tread are given in Table I.

With crosslink density measurements, the critical part of the procedure is wiping the swollen samples to remove the surface solvent. Although this operation is rather crude, precision was surprisingly good.

The above method may also be used to follow the hardening of polybutadiene-type elastomers upon accelerated aging, as shown in Table II.

The crosslink density in the vicinity of the boundary layer of bonded rubber vulcanizates may be studied by the above method.[7] It may also be used to study the bonding of dissimilar materials having vastly different crosslink densities. Figure 1 shows the crosslinking at the boundary layer of a typical carcass stock and tire cord adhesive. A film of the adhesive (cord dip without carbon black) was made by casting on a glass plate and allowing to dry overnight at room temperature. The film, approximately 0.1 mm thick, was dried in a vacuum oven, sandwiched between two 1-mm sheets of carcass stock, and cured. Samples were microtomed down through the carcass compound, the boundary layer, and into the adhesive. At the interface, it was difficult to obtain microtomed sections 20 μ thick that did not contain both carcass and adhesive.

Results show that the crosslink density of small samples of rubber vulcanizates can be determined accurately using a GC method for estimating the amount of solvent imbibed by the rubber. Microtomed samples were used to illustrate the adaptability to very small samples, but any size sam-

TABLE I
Crosslink Density of a Tire Tread

Tread Position	Q^a	$1/Q$	Std. dev., %
Outer	3.299	0.303	1.0
Middle	3.679	0.272	1.2
Inner	3.617	0.277	0.9

[a] Average of six determinations.

TABLE II
Effect of Aging in Air at 100°C on the Crosslinking of a SBR Tread Vulcanizate[a]

Days aged	Crosslinking, $1/Q$	Stress at 200% elong., psi	Hardness Shore A
0	0.322	1240	67
0.5	0.359	1620	70
1	0.371	1760	72
2	0.387	2020	73
4	0.402	2250	75

[a] 1.50 phr Sulfur and 1.00 phr Santocure NS, [N-t-butyl-2-benzothiazole sulfenamide].
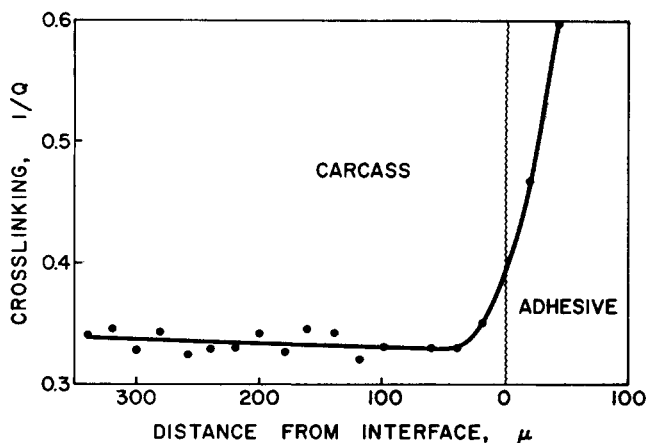
Fig. 1. Crosslink density near rubber–adhesive interface.

ple may be used.   For thicker samples, longer times should be employed for swelling and for equilibrium with the chloroform solution.   The method may be used for determining the variation in crosslink density through thick rubber articles, for determining the change in crosslink density after aging, and for the investigation of rubber bonds and interfaces.

References

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