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A Simple Stress Relaxometer and Its Use with Vulcanized Nitrile Rubber/PVC Compounds

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Synopsis

An easily constructed, cheap and compact stress relaxometer has been designed for aging tests on elastomers. Its construction is such as to allow it to fit inside a multicavity metal block oven commonly used for aging tests. The instrument works well on continuous and intermittent cycles and its action is illustrated by a brief examination of the stress relaxation properties of vulcanized nitrile rubber/PVC blends. The presence of PVC increases the initial (physical) relaxation both at high and normal temperatures under conditions of continuous stress. The rate of relaxation thereafter increases with increase in PVC content. Under intermittent conditions the PVC seems to encourage a crosslinking reaction, as does carbon black.

1. INTRODUCTION

Stress relaxation studies are being used increasingly to study the aging properties of rubbers,[1] and various designs have been suggested. However, no design of stress relaxometer was previously available which would allow rapid construction in a laboratory, hence the design described below was developed with particular consideration of the necessity for operating the instrument in a metal block aging oven.

Very few data are available on the relaxation behavior of PVC/nitrile rubber blends, and hence these were chosen to illustrate the operation of the instrument. These blends are being used in increasing quantities and would be expected to have unusual properties due to the combination of thermoplastic and thermosetting materials.

2. CONSTRUCTION AND OPERATION OF THE RELAXOMETER

The instrument (Fig. 1) is similar in principle to the helical spring relaxometer designed by Berry,[2] but it has been constructed so that its base fits inside a glass tube in a multicavity metal block aging oven (Fig. 2). Previous instruments of this type could not be set up, after conditioning of the specimen, without removal from the oven. The instrument described below is readily tensioned from above, at the test temperature and the initial relaxation can be measured. Further, the present instrument is more easily constructed and does not require an electrical make and break system to be operated in the metal block type of aging oven.

The relaxometer is constructed from two silica rods held at fixed centers between the brass base block and a brass holder for the micrometer head. A central guide block with spring steel brace serves to hold the instrument centrally in the glass tube. One intermediate block carries the zeroing point and another the bottom specimen clamp. Both intermediate blocks can be locked in any position by means of screws. The upper specimen clamp is free to move and is attached to the coil steel spring by means of a draw bar which carries the zero pointer. The extension of the spring is measured by means of the 1-in. micrometer head, reading ×0.001 in. A selection of springs with different tensions is required to cater for rubbers of different moduli. The percentage extension of the spring should be small compared with that of the specimen, which is usually 50–100%.

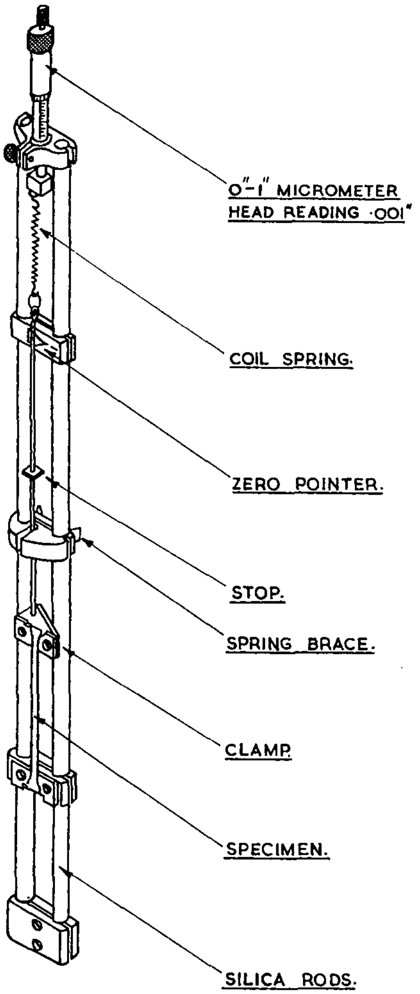

Fig. 1. Stress relaxometer.

The specimen is prepared as described in the next section and is clamped in the relaxometer, as shown in Figure 1, but in a relaxed state. Fine parallel lines (4 cm. apart) are drawn on the surface of the specimen, with suitably colored rubber ink, to facilitate extension measurements. The micrometer head is adjusted to zero and the intermediate block is moved until the zero on the block coincides with the zero pointer. The bottom clamping block is next moved so as to produce the required extension with the zero pointer on zero. The draw bar is then disconnected from the spring so that the stop rests on the center guide block and the rubber specimen is relaxed. The relaxometer is then placed in the oven, to condition for 30 min. at the required temperature. To start the test the draw bar is reconnected to the spring and the zero pointer adjusted to zero by means of the micrometer. This reading of the micrometer equals the initial extension of the spring f_0 and is directly proportional to the tension in the rubber. Subsequent readings of spring extension f_x are taken at suitable time intervals and expressed as a fraction of f_0. These ratios are plotted against log time to give stress relaxation curves.

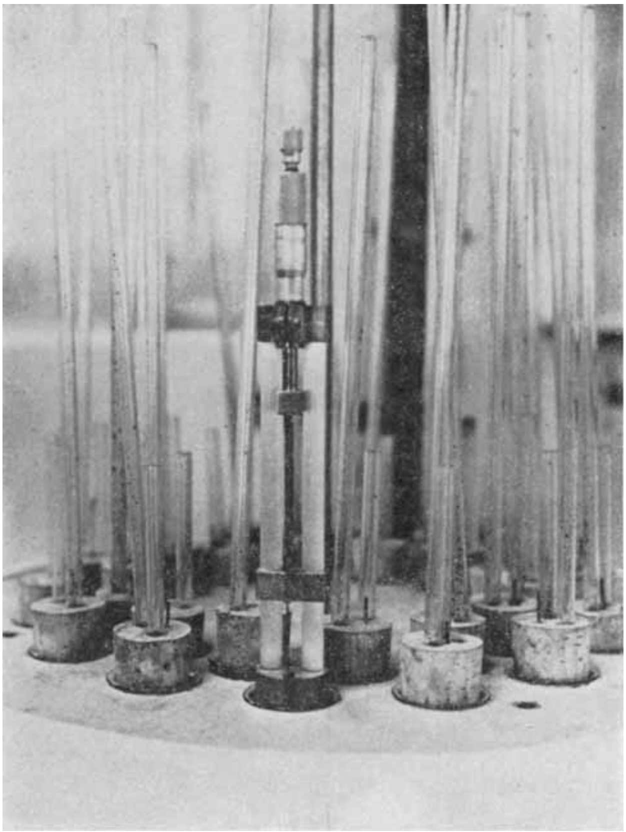

Figure 2.

3. EXPERIMENTAL

The compounds shown in Table I were prepared by mixing on a 12-in. laboratory mill. The properties of these compounds are shown in Table II. The following mixing procedure was adopted with the nitrile rubber/PVC compounds. The nitrile rubber and the PVC were fluxed together on the mill for a few minutes at 150°C. The mix was then cooled and the remaining ingredients added in the normal way.

The sample sheets were press-cured in a special mold to a thickness of 0.2 mm. Test pieces (8 cm. × 0.5 cm) were cut from these sheets with a special cutter.[2] All tests were carried out at 50% elongation. In continuous tests the second reading was taken after 3 min. and the tests were continued for approximately 1000 min. With the intermittent tests the sample was tensioned for 5 sec. prior to taking the reading and then immediately released. The second reading was taken after 15 min. On the graphs intermittent tests are drawn with a dotted line and continuous tests with an unbroken line.

In order to follow the state of cure during the test period, free sulfur contents were carried out by the bromine method[3] on the test samples

TABLE I

	Parts by weight				
Ingredients	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5
Hycar 1042	100.0	80.0	70.0	60.0	70.0
Corvic H.55/34	—	20.0	30.0	40.0	30.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Tetramethylthiuram monosulfide	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5
Calcium stearate	1.0	1.0	1.0	1.0	1.0
Stearic acid	0.5	0.5	0.5	0.5	0.5
SRF Black	72.0	72.0	72.0	72.0	—
Di(2-ethylhexyl)phthalate	10.0	10.0	10.0	10.0	10.0
Press-cured 30 min. at 155°C.					

TABLE II

Physical properties	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5
Tensile strength, psi	2160	2195	2455	2615	1120
Elongation at break, %	300	220	180	140	380
Modulus at 100%, psi	580	1135	1885	2465	270
Hardness, Shore A2	70	79	83	86	56

TABLE III

Compound no.	Free sulfur after aging, %		
	0 hr.	1½ hr. at 120°C.	16 hr. at 120°C.
1	0.23	0.16	0.04
2	0.15	0.09	0.05
3	0.13	0.11	0.05
4	0.12	0.11	0.03
5	0.29	0.22	0.01

before, during, and after aging at 120°C. The results are given in Table III.

4. RESULTS

Continuous Relaxation at Room Temperature

Tests were carried out on nitrile rubber and nitrile rubber/PVC formulations at constant temperature and humidity (20°C., 65% R.H.) and the relaxation curves are shown in Figure 3. The initial relaxation (3 min.) increases with PVC content, as does the rate of relaxation thereafter.

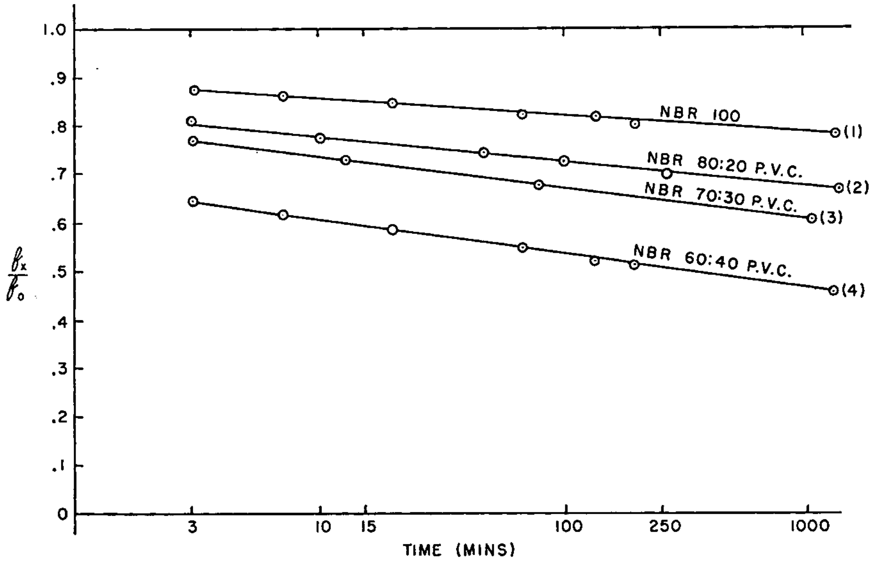

Fig. 3. Continuous relaxation at 20°C.

This latter effect was noticed by Ross, Sharp, and Pedley[4] in tests on considerably larger test pieces. The relaxation curves are straight lines and thus exhibit normal relaxation for rubber vulcanizates at room temperature.

Effect of PVC Content on Relaxation at Elevated Temperatures

The relaxation properties of nitrile rubber and nitrile rubber/PVC compounds were compared at 120°C. and the stress relaxation curves are shown in Figure 4. In the early stages of the test (up to 100 min.) the continuous curves approximate to straight lines and follow a similar pattern to those at room temperature, where the initial relaxation and rate of relaxation thereafter increases with increase in PVC content. The initial relaxation (3 min.) at 120°C. is considerably less than that at room temperature (Fig. 3), and this is attributed to the higher rate of relaxation which may occur at the higher temperature during initial tensioning on starting the test.

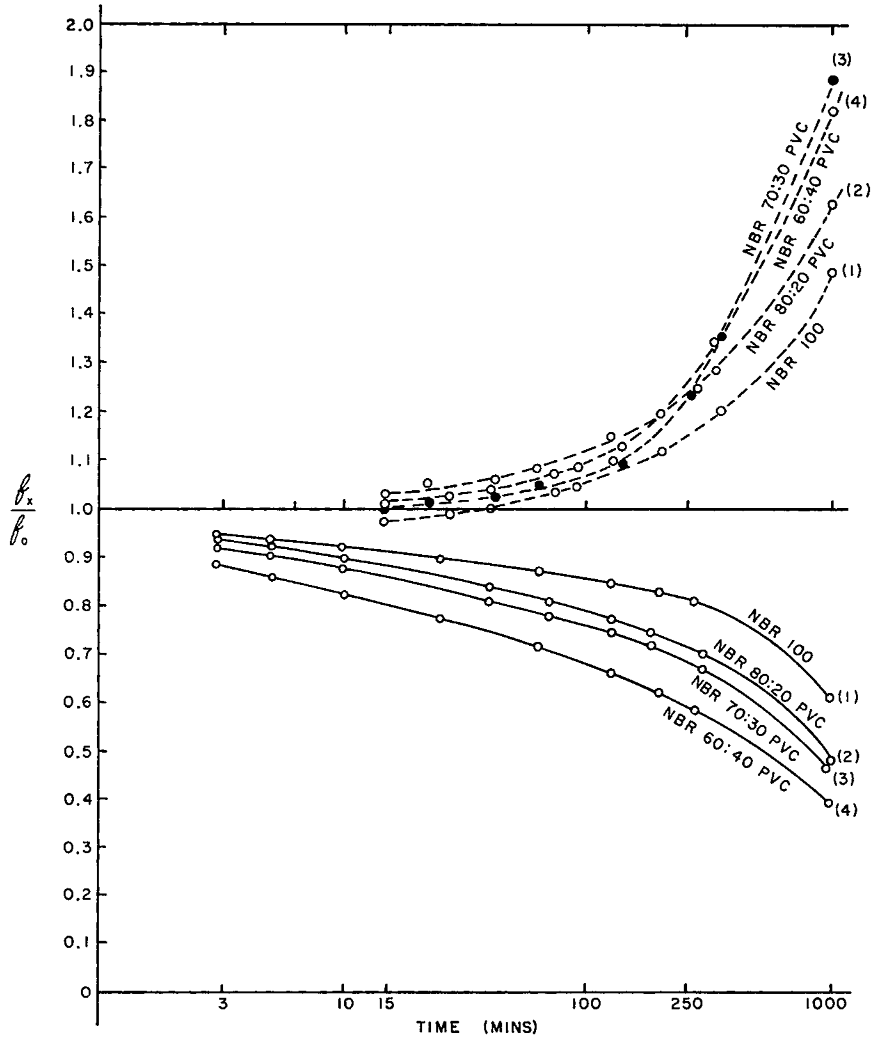

Fig. 4. Continuous and intermittent tests at 120°C.

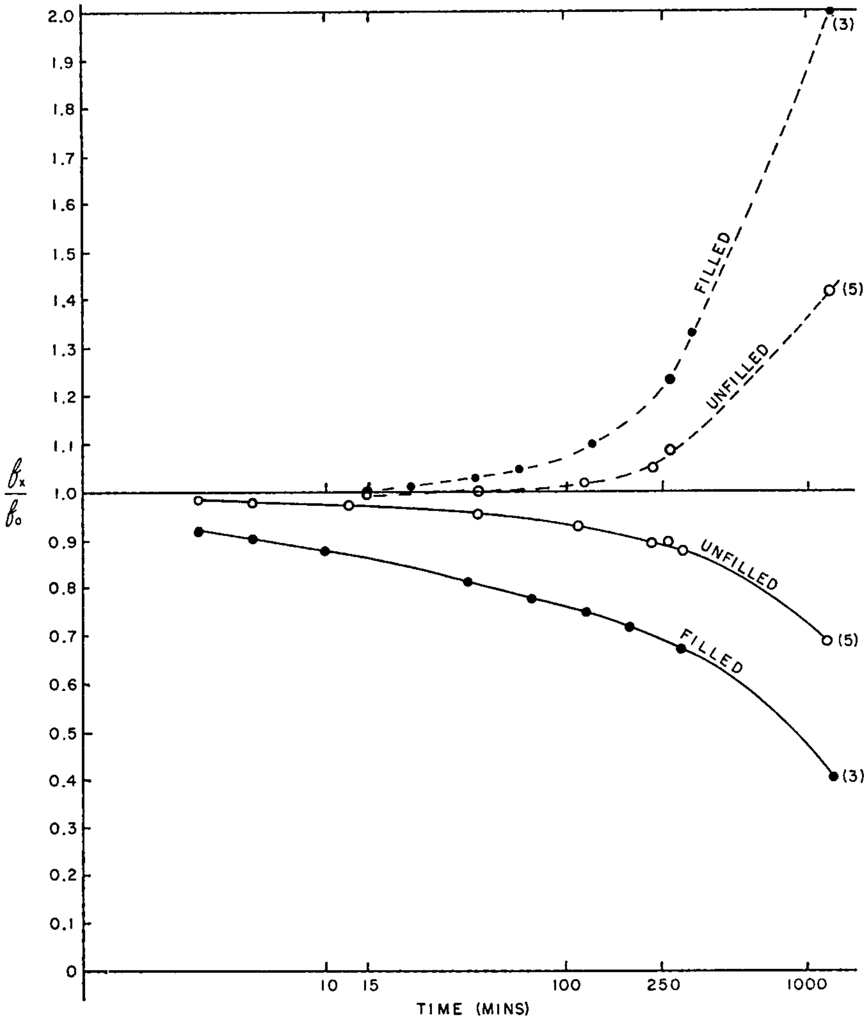

Fig. 5. Effect of carbon black reinforcing filler at 120°C.

In the latter stages (100–1000 min.), however, the curves fall off more quickly at the higher temperature.

In the intermittent tests the result of crosslinking is apparent after approximately 15 min. (total of 45 min. if the conditioning period is included.) Thereafter the crosslinking reaction predominates in all the compounds, but up to 250 min. the curves do not differ significantly. From 250 min. until completion of the test at 1000 min. the crosslinking reaction increases with PVC content up to 30 pph polymer and thereafter is reduced presumably due to the increasing thermoplastic nature of the system.

The increased crosslinking could be due to the reaction of excess vulcanizing ingredients, but the free sulfur determinations in Table III indicate otherwise. Although reduction of free sulfur content occurs, the rate is fairly constant for each compound. In fact, the nitrile rubber compound which exhibits the least crosslinking also shows the greatest reduction in free sulfur content.

Effect of Carbon Black

From a consideration of the relaxation curves in air at 120°C. for a carbon black-filled and an unfilled nitrile rubber/PVC compound (Fig. 5) it is apparent that the action of carbon black is similar to that of PVC. Under continuous stress carbon black increases the initial relaxation (3 min.) and likewise the rate of relaxation thereafter, which indicates a filler relaxation effect. With intermittent tests the presence of carbon black increases the crosslinking reaction which effect has been observed in other polymer systems.[5]

References

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Résumé

Une balance de relaxation facile à construire, économique et compacte a été désigné pour étudier le vieillissement des élastomères. Sa construction est telle qu'on peut l'adapter à l'intérieur d'une étuve composée d'un bloc de métal à plusieurs cavités ordinairement employée pour les essais de vieillissement. Cet instrument peut travailler aussi bien en continu qu'en cycles intermittents et son action est illustrée par un bref examen des propriétés de relaxtion de la tension de mélanges caoutchouc nitrile vulcanisé/PVC; la présence de PVC augmente la relaxation initiale (physique) aussi bien à température élevée qu'a température normale dans des conditions de tension continue. La vitesse de relaxation en conséquence augmente avec l'augmentation de la teneur en PVC. Dans des conditions intermittentes, le PVC semble favoriser une réaction de pontage comme le fait le noir de carbone.

Zusammenfassung

Es wurde ein einfach gebautes, billiges und kompaktes Spannungsrelaxometer zur Ausführung von Alterungsprüfungen an Elastomeren entwickelt. Seine Konstruktion erlaubt seine Anbringung im Inneren eines der üblicherweise für Alterungsprüfungen verwendeten Mehrkammer-Metallblocköfen. Das Instrument arbeitet sowohl bei kontinuierlicher als auch bei intermittierender Beanspruchung einwandfrei und seine Arbeitsweise wird durch eine kurze Prüfung der Spannungsrelaxationseigenschaften von vulkanisierten Nitrilkautschuk/PVC-Mischungen demonstriert. Bei Anwendung kontinuierlicher Spannung wird durch die Anwesenheit von PVC die anfängliche (physikalische) Relaxation sowohl bei hohen als auch bei normalen Temperaturen erhöht. Die Geschwindigkeit der darauffolgenden Relaxation nimmt mit steigendem PVC-Gehalt zu. Bei intermittierender Beanspruchung scheint das PVC ähnlich wie Russ eine Vernetzungsreaktion zu fördern.

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