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Some Factors Affecting the Compression Set of Natural Rubber Vulcanisates

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Some physical factors that could affect the compression set at constant strain of two types of natural rubber (NR) vulcanisates were investigated. The two types of NR vulcanisates were those obtained during a conventional or normal vulcanisation (NV) and an efficient vulcanisation (EV). Special emphasis was paid to the comparison of the large and small recommended testpieces. The compression set was independent of the amount of compression for compression above 25% for both systems when the large testpieces were used. For the NV system, the compression set was independent of the shape factor of the testpieces in the range from 0.2 to 1.2. For the EV system, however, this region was from 0.6 to 1.2.

Generally, the large testpiece gave lower compression set values than the small testpiece and this difference was greater for the EV system than for the normal system. It was also shown that these differences could be attributed to the difference in ratio of the exposed surface area to volume of the two testpieces.

One important characteristic of vulcanised rubber is its ability to recover substantially to its original shape and size following the removal of deforming stresses. However, vulcanised rubber is not perfectly elastic and the recovery is usually incomplete; a permanent set develops. As many uses of rubber depend primarily on its ability to recover after stressing, it is important to be able to measure this property satisfactorily in the laboratory for predictions on its service performance to be made. As a consequence, tension and compression set tests[1,2,3] were developed and are now widely used in material specifications for rubber products.

This paper discusses some of the factors affecting compression set at constant deflection or strain. Although the compression set test is a fairly common one for rubber products and materials, there is little published literature on the factors affecting it. This paper presents the effects of some of the factors affecting compression set and compares the two types of testpieces recommended by the International Organisation for Standardisation (ISO), the British Standards Institution (BSI) and the American Society for Testing and Materials (ASTM).

MATERIALS AND EXPERIMENTAL

The base stock was prepared in a laboratory OOC (5 lb) Banbury and the curatives were added on an open two-roll mill. The formulations used are as shown in *Table 1*.

The cure characteristics of the mixes were determined using a Monsanto Rheometer at 150°C. The maximum torque T_{max} was reached in 20 min for the NV system and in 40 min for the EV system. The testpieces were compression moulded at 150°C to give different states of cure. The dimensions of the recommended testpieces are given in *Table 2*.

To study the effect of shape factor of the testpiece, samples with circular and square cross-sections having various shape factors were prepared. These samples were pre-

COMMUNICATION 648

TABLE 1. COMPOUND FORMULATIONS FOR THE NORMAL AND EFFICIENT VULCANISATION SYSTEMS

Compound	NV	EV
Rubber (RSS 1)	100.0	100.0
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
Nonox D (PBN)	1.0	1.0
FEF Black	40.0	40.0
Sulphu	2.5	0.2
VulkacitrCZ (CBS)	0.6	–
TMTD	–	2.8
t_{100} at 150°C (min)	20	40
Hardness (IRHD)	61	63

pared from the same slab of the vulcanisate to ensure that all the testpieces had the same state of cure. Square cross-sectional samples were preferred to the cylindrical type because the former could be cut more accurately. Cylindrical cross-sectional samples suffered from asymmetry when they were drilled out, especially those having low shape factors.

All compression set tests were performed in an air-circulating oven at 100°C and the test itself and calculation of the compression set values were carried out according to BS 903: Part A6 unless otherwise stated. Normally, the testpieces are compressed between two rigid parallel plates by 25%, the amount of compression being determined by the height of the spacers used between the plates. The compression set is defined by the following equation:

$$\text{Compression set (\%)} = \frac{t_o - t_r}{t_o - t_s} \times 100$$

where t_o = original thickness of testpiece
t_r = thickness of testpiece after recovery
t_s = thickness of spacer used.

RESULTS AND DISCUSSION

The hardness of the vulcanisates were measured using the large compression set testpieces. As shown in *Table 1*, the hardness of the two vulcanisates used are comparable and hence they have similar modulus.

Effect of Test Condition

The effect of test duration on compression set at 100°C is shown in *Figure 1*. The compression set, as expected, increased as the test duration was increased. For the large testpiece (button), the rate of increase of compression set was similar for both the NV and EV systems at cure conditions of 20 min at 150°C for the NV system and 40 min at 150°C for the EV system. However, when both types of testpieces were

TABLE 2. DIMENSIONS OF COMPRESSION SET TESTPIECES RECOMMENDED BY THE VARIOUS STANDARDS INSTITUTIONS

Testpiece	BSI	ASTM	ISO
Small testpiece			
Diameter (mm)	13.0 ± 0.5	13.0 ± 0.2	13.0 ± 0.5
Height (mm)	6.3[a] ± 0.3	6.0 ± 0.2	6.3 ± 0.3
Large testpiece			
Diameter (mm)	29.0 ± 0.5	29.0 ± 0.5	29.0 ± 0.5
Height (mm)	12.5 ± 0.5	12.5 ± 0.5	12.0 ± 0.5

[a]Samples of 6.0 mm height were also allowed so long as correct spacers were used to obtain the 25% compression.

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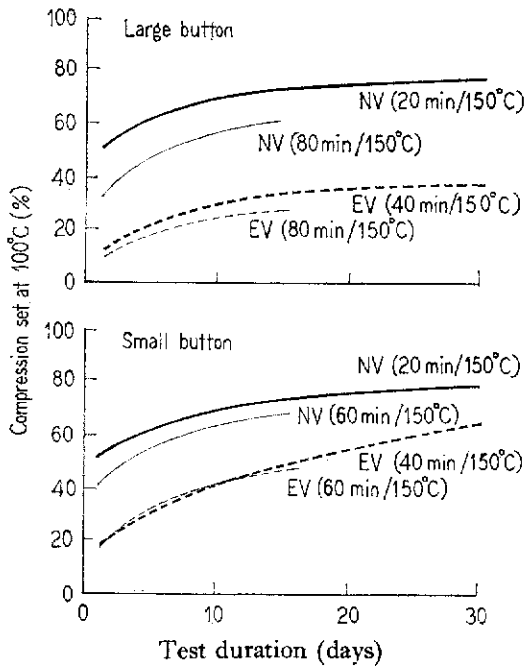

Figure 1. Effect of test duration on compression set at 100°C.

cured at 80 min at 150°C, the rate of increase of compression set for the NV was higher than that of the EV system. This is expected due to the post curing effects and the inherent thermal instability of the crosslinks in the normal vulcanisates. For the small testpiece, the EV system had a higher rate of increase of compression set compared to the NV system when cured to t_{100} at 150°C. At the overcure conditions, however, the rates were similar. These are rather unexpected observations since this type of EV system is known to produce vulcanisates which have good thermal stability. An attempt will be made later to explain this observation.

Effect of State of Cure

Compression set is known to decrease as the state of cure of the testpiece is increased. This expected trend was observed and is shown in *Figure 2* for the vulcanisates used in this experiment. The compression set (seven days/100°C) for the large button was unaffected by the cure time in the range of 50 min to 80 min while for the small buttons, this range was between 40 min and 60 min for the NV and 50 min to 80 min for the EV system.

The EV system appears less sensitive to variations of cure time above t_{100} than the NV system. A point to note is that small variations of cure time at t_{100} affected the compression set of both the large and small testpieces by similar amounts.

Effect of the Amount of Compression

The effect on compression set of the amount of compression imposed on the testpiece during the test was dependent on the size of the testpiece used. For the large testpiece, the compression set was independent of the amount of compression in the 20%–45% compression range as shown in *Figure 3*. This means that during normal

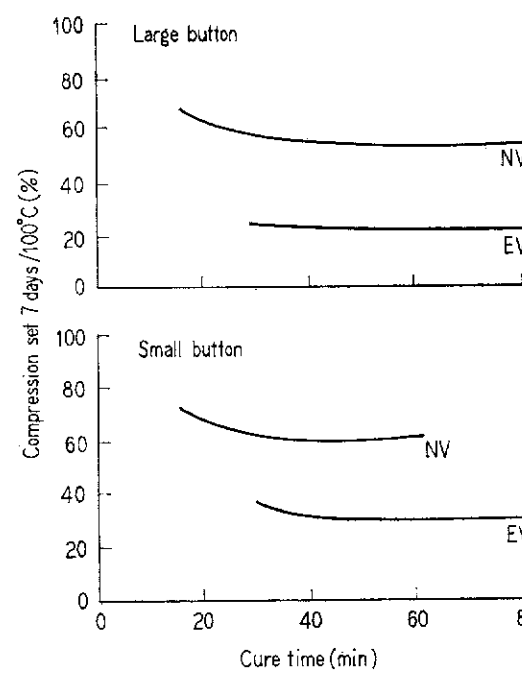

Figure 2. Compression set for seven days at 100°C as a function of cure time at 150°C.

compression set test, where up to four testpieces are compressed all at once between two plates to a predetermined height to give the required 25% compression, the compression set should be relatively unaffected by the variation in the initial height of the testpieces. For the small testpiece, however, the compression set was affected by the amount of compression. At the nominal 25% recommended compression for the standard testpiece, the actual compression on the individual testpieces may not be exactly 25%. This is because the moulded testpieces are usually not of the same height. This variation in compression set due to the amount of compression for the small testpiece could be one of the contributing factors to the variability in the test results when the small testpieces are used.

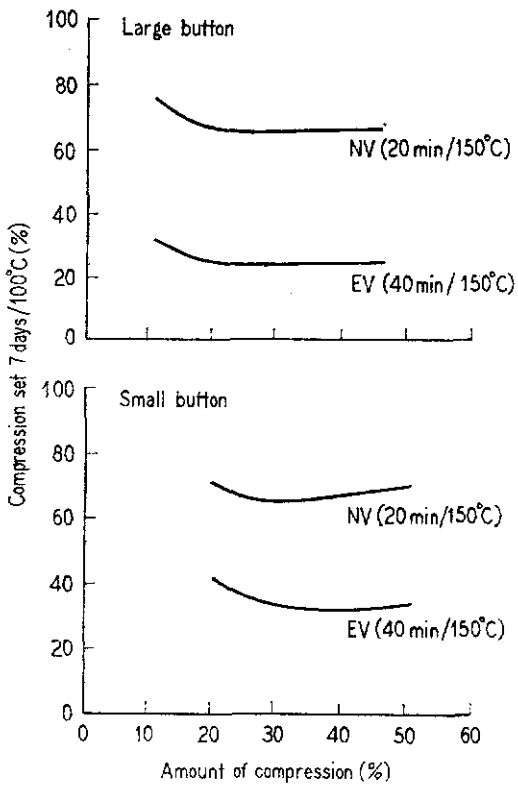

Figure 3. Variation of compression set (seven days/100°C) with amount of compression.

Effect of the Shape Factor of the Testpiece

The shape factor[4], *S*, defined as the ratio of one loaded area to the total force-free area, of a testpiece with its two ends bonded determines the shape of the compression stress-strain curve. Although, in the compression set test, the ends of the testpiece are lubricated with silicone oil, the shape factor is considered important since there is a possibility for this lubricant to be squeezed out when the testpiece is being compressed. Under this condition, incomplete slippage occurs at the ends of the testpiece. The shape factors of the large and small testpieces recommended by BSI are 0.58 and 0.52 respectively.

In this experiment, circular and square cross-sectional samples of height 13.3 mm were used and the results are shown in *Figure 4*. The height of the testpieces, although greater than that recommended, will not affect the general trend of the results. For the NV system, the compression set was independent of the shape factor from 0.2 to 1.2. This is consistent with the finding of the BSI Test Methods Committee as stated by Scott[5]. Their work was, however, limited to a narrow range of 0.5 to 0.6. For

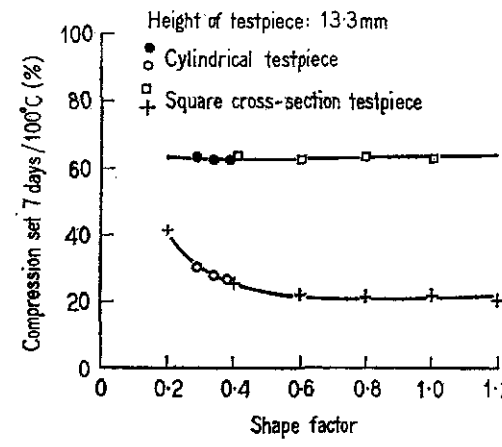

Figure 4. Effect on compression set (seven days/100°C) of the shape factor of the testpiece.

the EV system, there was a marked dependence of compression set on the shape factor of the testpiece in the region 0.2 to 0.6. Beyond this region, the compression set remained relatively independent of the shape factor. From the limited data in *Figure 4*, the compression set appears independent of the shape of the testpiece, at least, in the range of 0.2 to 0.4 of shape factor values.

Difference in Compression Set Between Large and Small Testpieces

The differences in compression set (seven days/100°C) for the large and small testpieces for the two systems cured to t_{100} at 150°C are shown in *Table 3*. The difference in compression set between the large and small testpieces was more pronounced in the EV system than in the NV system. A reason for this larger difference in compression set for the EV system is proposed. The amount of crosslinks formed and/or destroyed per unit volume of the testpiece due to heat during the compression set test is the same for both the large and small testpieces and is only a function of the test temperature, duration and the type of crosslinks. However, the amount of crosslinks that would be formed and/or destroyed due to oxidation will depend on the volume of rubber oxidised. It has been shown[6] that only a very thin layer of the testpiece surface is oxidised during ageing tests. In the efficient vulcanisates, the change in the bulk properties of the testpiece during the compression set test was small because of the highly thermally stable network structure. For the normal vulcanisates, there would be large changes in the bulk properties of the testpiece because of the less thermally stable network structure. Thus, the difference in the compression set between the two types of vulcanisates is primarily due to the difference in the stability of their network structures.

TABLE 3. DIFFERENCES IN COMPRESSION SET BETWEEN LARGE AND SMALL TESTPIECES

Testpiece	Compression set, 7 days/100°C (%)	
	NV	EV
Small testpiece	66.0	36.5
Large testpiece	67.0	26.5
Difference	1.0	10.0

An explanation for the difference in compression set due to a change in the size of the testpiece and why this difference is more pronounced for the EV system is as follows. The sizes of the two recommended testpieces were such that their shape factors were approximately the same. However, the testpieces have different exposed area to volume ratio, R, being 0.31 mm^{-1} for the small testpiece and 0.14 mm^{-1} for the large testpiece. It is proposed that the value of R is an important factor in the compression set tests conducted at high temperatures. Values of R for the testpieces used in this work have been calculated and were plotted against the corresponding compression sets. The plot is a smooth curve *(Figure 5)* indicating a relationship between compression set and R. It should be noted that the

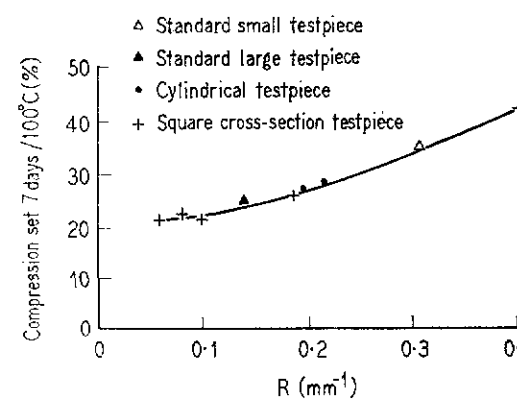

Figure 5. Dependence of compression set (seven days/100°C) of the efficient vulcanisate on the exposed area to volume ratio, R.

standard testpieces which have similar shape factors S but different R values also lie on this curve. The quality R can be made use of to explain the larger difference in compression set for the EV system between the large and small testpieces. Surface oxidation results in the formation of a skin[7] which will affect the shape of the end faces of the testpiece after the compression set test. This effect was more pronounced on the small testpiece than on the large one since the small testpiece had a higher value of R than the large testpiece. The ends of the large samples were relatively flat except for a slight curvature at the sides. The ends of the small samples, however, showed a slight convexity and this effect was more pronounced for the small sample of the EV than for the NV as shown in *Figure 6*. This effect was small for the NV system because the bulk of the testpiece set by a much greater amount than the EV system due to the thermal instability of its network. Hence, surface oxidation is not a major factor determining the compression set for the NV system but is an important factor for the EV system.

The skin formation on the testpieces which were tested at 150°C for 24 h is shown very clearly in *Figure 7*. For the large test-

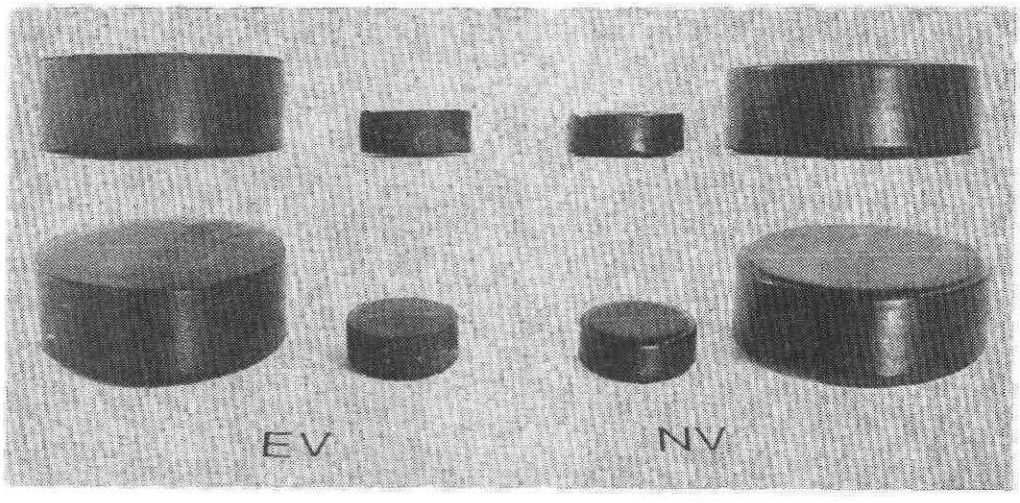

Figure 6. Shape of the compression set testpieces after the test (seven days at 100°C).

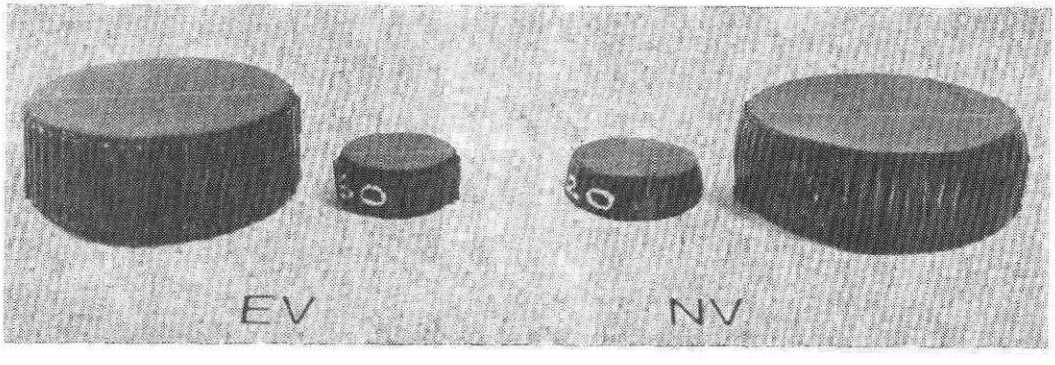

Figure 7. Skin formation on the compression set testpieces after 24 h at 150°C exposure.

pieces of EV system, where the skin had broken away from the bulk of the testpiece, the ends were relatively flat and the bulk actually had recovered more than the skin. For the small testpiece, however, the skin breakaway was not complete probably because of the smaller recovery forces than those of the large testpiece and a difference was observed in compression set values between the two. For the testpieces of the NV system, both the skin and bulk of the testpiece set by almost the same amount. The skin on these samples, which were tested at 150°C showed a rather corrugated appearance. Behind this skin, the rubber was porous and oxidised, consistent with the findings of Lindley and Teo[7].

CONCLUSION

The difference in compression set values obtained using the large and small testpieces and the effect of test factors on compression set depend on the type of cure system used. Results presented here show that the difference in compression set between the two recommended testpieces of the EV system can be attributed to the difference in the exposed area to volume ratio, *R*.

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REFERENCES

1. BS 903 Part A6 (1969) Methods of Testing Vulcanised Rubber. Part A6. Determination of Compression Set – Amended April 1974.
2. ASTM Standards (1969) *ASTM D395–67.*
3. ISO 815 – 1968
4. GENT, A.N. AND LINDLEY, P.B. (1957) The Compression of Bonded Rubber Blocks. *Proc. Inst. Mech. Engrs,* **173(3),** 111.
5. SCOTT, J.R. (1965) *Physical Testing ofRubbers.* MaClaren.
6. KNIGHT, G.T. AND LIM, H.S. (1975) Factors Influencing High Temperature Ageing of Large Natural Rubber Components. *Proc. Int. Rubb. Conf. Kuala Lumpur 1975,* **5,** 57.
7. LINDLEY, P.B. AND TEO, S.C. (1977) High Temperature Ageing of Rubber Blocks. *Plastics and Rubber : Materials and Applications,* **2,** 82.