JOURNAL OF MATERIALS SCIENCE 8 (1973) 1023–1029

Creep and stress relaxation of rubbers – the effects of stress history and temperature changes

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Two factors which affect the creep and stress relaxation of rubbers at room temperature are discussed.

The rate of relaxation in filled rubbers is dependent on the previous mechanical history of the specimen. Pre-stressing a rubber reduces the subsequent relaxation rate and this reduction is for most purposes permanent. Recovery can, however, be induced by swelling and deswelling the specimen.

A rise in temperature during a relaxation experiment is accompanied by a marked, short term, acceleration of the relaxation. The creep which this produces is not recovered when the temperature is reduced to its original level. The magnitude of the extra relaxation from this effect is greatest if the cycle occurs in the early stages of relaxation and also greatest during the first such cycle.

Both the effects are of importance in any consideration of the molecular nature of relaxation, and indicate that a simple network theory of viscoelasticity is inadequate. The effects are also of practical significance in that both of these factors should be well understood if laboratory testing is to be used for predicting the service behaviour of rubber components.

Abbreviations

CBS	– *N*-cyclohexyl-benzthiazole-2-sulphenamide
Nonox D	– phenyl-β-naphthylamine
Nonox ZA	– 4-isopropylamino diphenylamine
Nonox HFN	– arylamine blend

1. Introduction

The two closely associated phenomena of creep and stress relaxation are often among the most important considerations governing the design of elastomeric engineering components, and also the choice of polymer for a particular application. In addition they are very sensitive tests of changes in network structure and configuration.

Creep is the increase in deformation with time under a constant load, and stress relaxation is the decay in stress with time under conditions of constant deformation. The rates of these two processes can be related to one another if the shape of the force-deflexion curve is known [1].

The processes responsible for these two types of relaxation may be either chemical or physical in nature, and under all normal conditions both processes will occur simultaneously. However, at typical ambient temperatures the rate of chemical relaxation in general purpose rubbers (e.g., natural, butyl, polychloroprene, SBR etc.) is extremely small and the relaxation behaviour is dominated by physical processes except at very long times. These physical processes involve the reorientation of the molecular network, the disengagement and rearrangement of entanglements, and the breaking of bonds due to secondary valence forces.

On the simplest picture of viscoelasticity, the relaxation behaviour would depend mainly on the difference between ambient temperature and the glass transition temperature, but it is found that, for the general purpose rubbers

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mentioned above, the behaviour at room temperature, i.e., well above the glass transition region, is dominated by a number of other factors. Among these are the nature of the cross-link, the test strain, the test humidity, the previous mechanical history of the test piece, and the effect of fillers. These and other factors have been discussed in previous papers [2, 3]. In the present paper the last two of the effects just mentioned are discussed in more detail and results of experiments in which a temperature change occurs during relaxation are given.

For all of the experiments described in this paper on physical relaxation it is found that the amount of relaxation is directly proportional to logarithmic time. For this reason relaxation rates are quoted as "per cent per decade" – i.e., per cent relaxation per factor of ten increase in time.

2. The effect of fillers

Pure gum vulcanizates are rarely used in practical applications. Usually, some form of inorganic filler material, often some type of carbon black, is incorporated in the rubber. The presence of such material generally results in an increase in relaxation rates. A partial explanation of this follows from the theory of "strain amplification" [4]. This theory shows that, due to the inextensibility of the filler, the strain in the polymer phase of a filled material is greater than the overall strain. Stress relaxation rates, in general, increase with increasing polymer extension, thus filled rubbers would be expected to show higher relaxation rates. Other reasons for the higher relaxation rates in filled rubbers may, in some cases, be associated with filler-filler or filler-polymer breakdown. It has been shown [5] that the extent of such breakdown varies with different types of filler material. In particular, there is evidence of such breakdown contributing considerably to stress relaxation at low extensions [6]. Fig. 1 shows how the stress relaxation rate of a natural rubber vulcanizate (A – see Appendix) at 100% extension increases with increasing loadings of a semi-reinforcing carbon black filler [7].

It has been shown [2, 3, 8] that the stress relaxation rate of even a particular rubber test piece is not a unique quantity, but depends strongly on its previous stress history. Thus the results illustrated in Fig. 1 are for test pieces being deformed for the first time i.e., having no pre-stress history. If, however, any of the test pieces used is tested again, even after long periods of recovery, lower stress relaxation rates are recorded. Fig. 2 illustrates this effect for the samples containing 0 and 40 parts of carbon black respectively. Here, in each case, the same test piece is subjected to repeated testing. (Fig. 2 shows the creep rate rather than the stress relaxation rate, but this does not materially affect the picture.) Repeated stressing results in a progressive lowering of the creep rate, but the effect is very much more pronounced in the filled material. All tests are carried out at 100% extension and it has been shown previously hat the differences in behaviour between the gum and filled material can be explained mainly in terms of strain amplification [8].

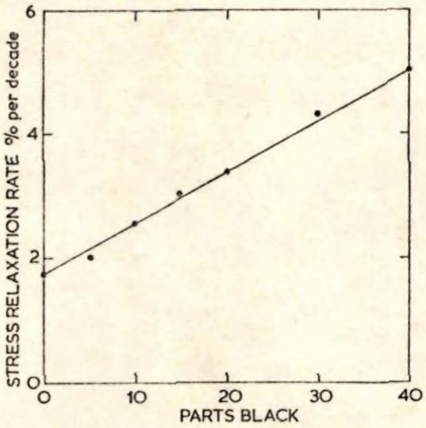

Figure 1 Variation of stress relaxation rate with amount of carbon black in a series of NR vulcanizates.

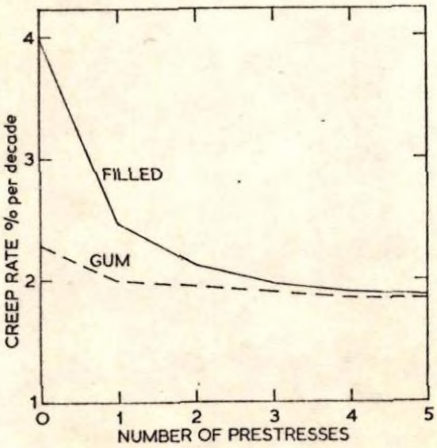

Figure 2 Decreasing creep rates shown by gum and filled NR vulcanizates as a result of pre-stressing.

2.1. Recovery

Studies have now been made of the recovery aspects of the phenomena. The rubber examined for this purpose was a dicumyl peroxide vulcanizate (B) of natural rubber containing 40 parts of a reinforcing black filler. New test pieces of this rubber show a stress relaxation rate of 3.38% per decade at 100% extension. This rate is reduced by over one fifth to 2.66% per decade by a prestressing procedure which consists of several short term extensions to 100%, followed by at least 24 h recovery unstrained before testing. If the test pieces which have been pre-stressed and tested are allowed to remain for 5 days unstressed at 30°C, some recovery might well be expected, but in fact the rate on subsequent testing is reduced still further to 2.31% per decade. This further reduction may be partly due to some chemical changes taking place in the rubber, although this has not yet been investigated, and partly due to further pre-stressing effects associated with the repeated testing.

It has been shown that the effects of stress softening (Mullins Effect) in filled rubbers can be largely recovered by swelling in a solvent and subsequently drying down [9]; this procedure was therefore applied to the pre-stressed rubber from the experiment above as it seems likely that the two effects may have similar origins. The rubbers are swollen in *n*-decane and this results in a weight loss of about 1.6% due to extraction of soluble material. The stress relaxation following this treatment is 3.13% per decade. Swelling and deswelling have brought about almost total recovery – the rate of 3.13% per decade being only 7% lower than the original rate for a new test piece.

A check was made to ensure that swelling and deswelling in itself brings about no change in the stress relaxation of new test pieces – and this is found to be the case even though soluble material was removed by extraction as before.

It seems that the change in network arrangement responsible for the reduction in relaxation rate after pre-stressing, is essentially irrecoverable under ordinary conditions and therefore, incidentally, that the "pre-working" often performed on rubber components before they are put into service, is of permanent benefit. The extreme treatment by swelling, which opens out the network and allows any strained regions to return to a lower energy configuration, does, however, produce recovery, indicating that the effects of pre-stressing are mainly topological changes in the network and not permanent cleavages of strong bonds.

We can imagine that these topological changes consist of non-affine displacement of network junctions and perhaps the pulling of entanglements through the network. The arrangement after pre-stressing will represent a higher energy state than the initial random state, but it is clear that there are energy barriers preventing a return to the random state and these are such that recovery, if it takes place at all, is extremely slow.

It should be remembered that these recovery experiments were carried out on peroxide-cured rubbers having stable carbon-carbon crosslinks. The experiments will now be repeated on conventional accelerated sulphur vulcanizates having mainly polysulphidic crosslinks. The extent to which the effects of pre-stressing in these vulcanizates are due to the lability of the polysulphidic crosslinks, as opposed to purely topological changes, should be apparent from the amount of recovery which can be induced by solvent swelling.

3. Effect of pre-stressing at different filter loadings

Although, as mentioned above, the effect of pre-stressing has been shown to be associated with changes in the polymer phase in filled materials, the strain amplification effects described make it much more noticeable as the filler level increases. This is illustrated in Fig. 3, where the creep rate at 100% extension is shown as a function of filler loading for both new and pre-stressed materials. The pre-stressing procedure is similar to that described above.

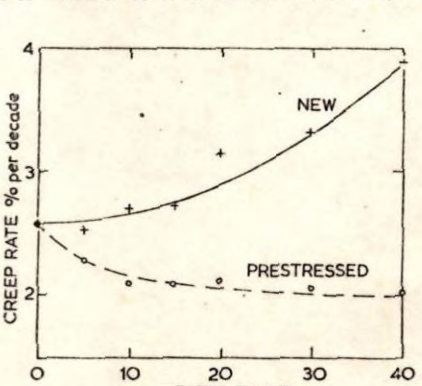

Figure 3 Creep rates for new and pre-stressed NR vulcanizates at a series of different filler loadings.

It is surprising to find that, after pre-stressing, not only is the creep rate lowered as compared with new test pieces, but actually falls with increasing filler loading. These results are for a conventional accelerated sulphur vulcanizate (A) of natural rubber, and are more easily understood if reference is made to the same experimental data plotted not in terms of creep rate but in terms of stress relaxation rate (Fig. 4). It is seen that the stress relaxation rate (generally taken as a more fundamental parameter) increases with increasing filler loading, for both the new and the pre-stressed material. The ratio between the creep rate and the stress relaxation rate depends upon the slope of the force-deflexion curve [1] and it is the change in this slope brought about by pre-stressing which leads to the apparently anomalous creep results.

4. Temperature cycling

The physical creep or stress relaxation rates of general purpose rubbers, are not strongly temperature-dependent in the region of room temperature. A conventional accelerated sulphur vulcanizate of natural rubber, for example, which shows a creep rate of 3.03% per decade at 40°C, shows a rate of 2.85% per decade at 60°C. This is only a 6% difference in rate for a temperature change of 20°C; the direction of the change should be particularly noted. Higher temperatures result in lower physical creep rates as predicted by viscoelasticity theory.

It might therefore be anticipated that a short term temperature rise during the course of the creep of a rubber specimen would not greatly affect the total creep observed. In certain circumstances this is found not to be the case.

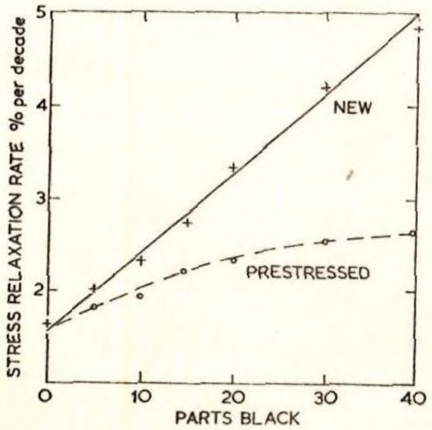

Figure 4 The creep data of Fig. 3 converted to stress relaxation rates.

Fig. 5 shows how the creep at 40°C of vulcanizate C is affected by a temporary rise in temperature to 60°C. The creep is expressed as the percentage change in extension referred to the extension 1 min after stretching. The procedure followed can be understood from the figure. From 1 to 20 min the test piece is held at 40°C and its creep shows the usual linearity with logarithmic time. The temperature is then raised as quickly as possible to 60°C, although in practice this takes several minutes. The temperature remains at 60°C for 1 h, after which it is lowered as quickly as possible to the original 40°C.

For the experiment illustrated, this procedure results in an extra 4.6% creep (equivalent to 1½ decades of time) at 80 min, associated with the temperature cycle. If no cycle takes place, this amount of creep at 80 min (10.35%) does not occur until 2300 min have elapsed.

The phenomenon is not unique to natural rubber and Fig. 6 shows the same effect for an SBR vulcanizate (D).

A good picture of the phenomenon is obtained by considering what should happen when the temperature is raised. The stress increases owing to the Joule Effect and the test piece shortens. The amount of this shortening may be found from stress versus temperature plots obtained from test pieces after all relaxation has ceased. It is assumed that this amount of shortening would occur in the temperature cycling experiment if it were possible to raise the temperature quickly enough. Various methods

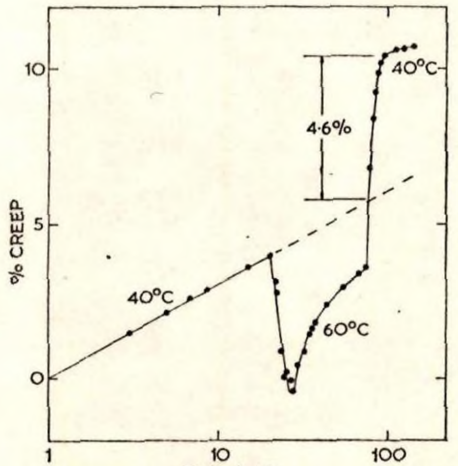

Figure 5 The effect of a temperature cycle starting at 20 min on the creep of an NR vulcanizate.

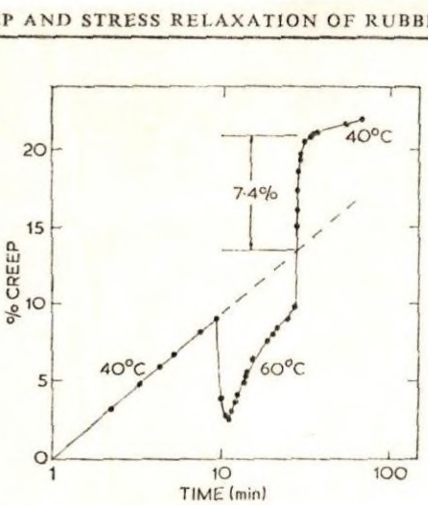

Figure 6 The effect of a temperature cycle starting at 20 min on the creep of an SBR vulcanizate.

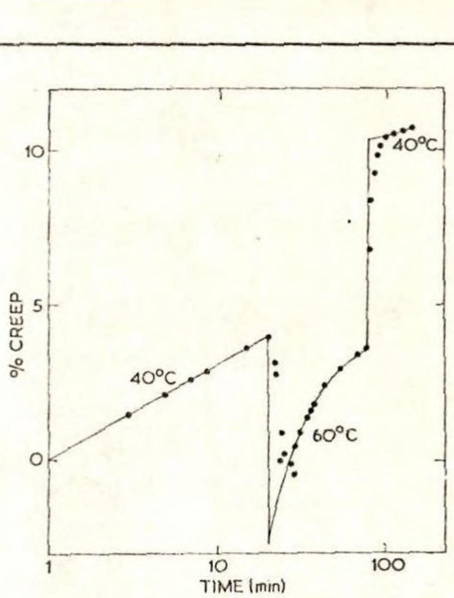

Figure 7 The full line shows the proposed behaviour for the temperature cycle shown in Fig. 8 if the temperature could be raised and lowered instantaneously. The changes in length shown are obtained from stress versus temperature measurements. The points are experimental.

of describing the behaviour immediately following the temperature rise have been considered and will be discussed in a later publication, but what is clear is that the temperature rise and shortening of the rubber are followed by a surge in the creep rate, the early stages of which cannot be seen experimentally. When the temperature is again lowered the change in length is about that which would be expected from stress-temperature considerations, so that the large amount of creep which occurred in the early stages at the higher temperature remains as a permanent addition to the length. This is illustrated in Fig. 7 where the full line indicates the length changes predicted from stress versus temperature plots and the points are experimental.

Further, the rate of creep now observed at 40°C is much higher than the rate would have been by the time the test piece had crept this amount in the absence of a temperature cycle. Thus in Fig. 5 the final creep rate at 40°C is approximately 0.005% per min – compared with a rate which would have been ten times lower than this at 2300 min if no cycle had taken place.

The relaxation mechanism can be thought of, in the loosest sense, as the breaking of some sort of bonds and at least some of these bonds must be temperature sensitive. Such bonds will not be chemical in nature but are probably due to Van der Waals type forces. There are then two alternative suppositions which can be made: either, these bonds would remain permanently stable in the absence of a temperature rise or, alternatively, they are bonds with relatively long relaxation times which would ultimately fail in time even at the lower temperature, but whose failure is accelerated by a temperature rise. Fig. 8 illustrates the results of an experiment to test these suppositions, in which the time before the temperature rise is very much greater than the 20 min of the previous experiments. The effect of the cycle is now very much reduced showing that the second of the alternatives mentioned above is probably the correct one. It also shows that the effect is likely to be of very much greater importance in short term

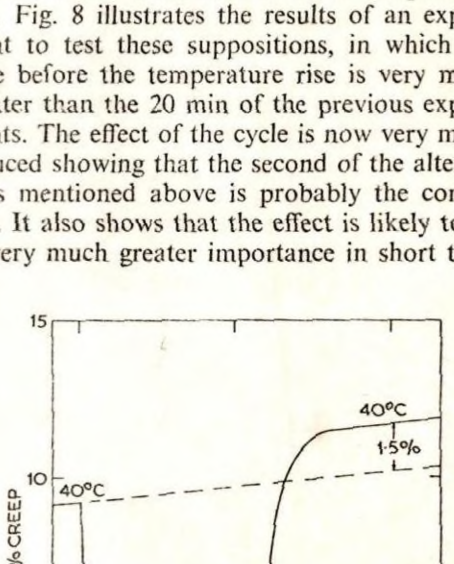

Figure 8 The effect of a temperature cycle starting at 1200 min on the creep of an NR vulcanizate.

laboratory testing than in actual service performance. The magnitude of the effect is such that it is obviously of even greater importance than was hitherto supposed to keep the temperature absolutely constant during creep and stress relaxation testing.

Discussion has so far been confined to the effects of a single temperature cycle. It is, however, found that the effect of an enhanced creep is not confined to the first cycle but is present in progressively diminishing amounts for several cycles. Fig. 9 illustrates the effect of a second cycle following on that already shown in Fig. 5. Because the absolute times are now extremely long it is shown for convenience on a linear time plot and it is clear that there is still some extra creep associated with the temperature cycle, but in this case it only amounts to just under 1 %.

After three or four cycles have been completed no further significant physical relaxation can be detected and reversible stress versus temperature cycles can then be obtained.

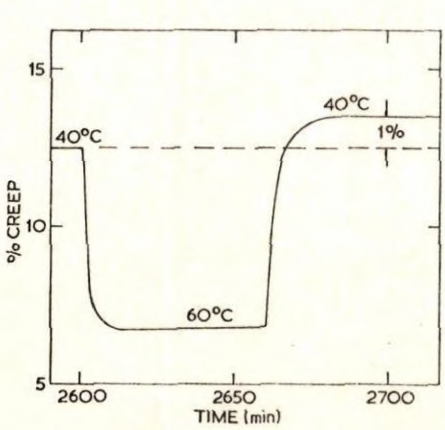

Figure 9 The effect of a second cycle starting at 2600 min on the creep of an NR vulcanizate. This experiment follows that shown in Fig. 5.

5. Discussion

The two effects described here indicate that a large part of the relaxation observed in rubber at room temperature is associated with rather weak interactions of a semi-permanent nature. It is clear, for example, that the fairly large change in relaxation rate brought about by prestressing, would not be accompanied by any significant change in glass transition temperature. The changes brought about by prestressing are, therefore, attributable to changes in intermolecular interactions different from those interactions which dominate in the glass transition region, and the change in relaxation rate cannot be explained simply, as in viscoelasticity theory, by a shift of the relaxation time spectrum.

The same weak interactions may well be responsible for the effects which occur when the temperature is increased. A number of questions are raised by the observations, which should be capable of clarification by further experiments. The "activation energies" could be obtained by carrying out the experiments at different temperatures and with different magnitude temperature changes, while the life times of the weak interactions can be studied by experiments having different time scales.

A further clue to the nature of the interactions may be given by the observation [2] that stress relaxation rate is dependent upon ambient humidity. The presence of a fraction of 1 % water in the rubber can increase the relaxation rate by up to, in extreme cases, a factor of two. This is different from the action of a plasticizer, the presence of which decreases the relaxation rate, and may well indicate that the weak interactions are unstable in the presence of water as well as unstable to temperature rises and to stress.

Acknowledgements

This work forms part of the research programme of the Natural Rubber Producers' Research Association. My thanks are due to Mr T. S. Pottle for experimental assistance and help in the preparation of this paper.

Appendix

Vulcanizate formulations

A	Natural rubber (CV)	100
	Zinc oxide	5
	Stearic acid	2
	Sulphur	2.5
	CBS	0.5
	Nonox D	1
	Magecol 888 carbon black	0 to 40
	Vulcanized for 35 min at 140°C	
B	Natural rubber (SMR5 RSS)	100
	Dicumyl peroxide	2.5
	HAF black	40
	Vulcanized for 10 min at 100°C plus 60 min at 150°C	

C	Natural rubber (SMR5 RSS)	100
	Zinc oxide	5
	Stearic acid	2
	Sulphur	2.5
	CBS	0.6
	Nonox ZA	1.5
	Vulcanized for 40 min at 140°C	

D	Polysar Krylene NS (SBR)	100
	Zinc oxide	3.5
	Stearic acid	2.5
	Nonox HFN	1
	Sulphur	2
	CBS	1.1
	Vulcanized for 60 min at 140°C	

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Received 24 November and accepted 11 December 1972.