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The effect of large strains on ageing of a filled elastomer

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Strain endurance experiments on a filled elastomer were performed at several temperatures. It was found that superimposed prestraining accelerated the ageing process. This process was caused by microstructural changes in the elastomer. In order to evaluate the mechanical properties of a filled elastomer it is necessary to take into consideration not only the ageing effects but also the loading history.

1. Introduction

During the ageing process of an elastomer, certain chemical and/or physical changes in its microstructure occur which, in turn, result in changes in its mechanical properties. It is common practice in the study of the ageing of elastomers to conduct accelerated ageing tests. In these tests specimens are examined after having been stored for relatively short periods of time at elevated temperatures. Accumulated experimental data may provide an empirical factor for relating the accelerated ageing period to real time at service conditions [1]. In spite of the fact that this factor may be questionable, accelerated ageing tests are widely used because of the great practical importance of the study of ageing processes.

Elastomers used for structural parts have to withstand different loading conditions. At the same time, the materials are ageing and internal structural changes may occur. These ageing effects may be accelerated since the internal free energy of the polymer is higher in the deformed state than in the unloaded state. Due to the imposed strain, new chemo-rheological processes may take place, thus changing the structure of the polymer network and its properties [2]. Therefore, even if the conversion factors were reliable, the accelerated ageing tests of unloaded systems would be still insufficient to determine the real behaviour of the elastomer after long service periods. In a previous study [3], we investigated the effect of prestraining on the mechanical behaviour of filled elastomers. It was found that prestraining may change the microstructure of the elastomer which in turn changes its mechanical properties.

In this work, efforts were made to investigate the superimposed effect of prestraining on the ageing of filled elastomers at different temperatures.

2. Experimental procedure

We studied the ageing of a composite material based on a hydroxyl-terminated polybutadiene-type elastomer, cross-linked by a diisocynate and filled with ammonium perchlorate with an average particle size of 10 μm (filler content, 50% vol).

The initial modulus and ultimate properties were determined by tensile measurements performed on dumb-bell-shaped specimens at constant strain rates of 0.7, 0.07 and 0.007 min^{-1}. The tests were conducted at various temperatures from -50° C to 100° C using an Instron testing machine. The data obtained was used in drawing the failure envelope.

The following strain Endurance tests were carried out:

2.1. Regular strain endurance tests

Regular strain endurance tests at strain levels of about 70% to 100% of the ultimate strain were conducted by means of the simple apparatus shown in Fig. 1. In this apparatus the specimens were subjected to constant strains for specified periods of time or until failure

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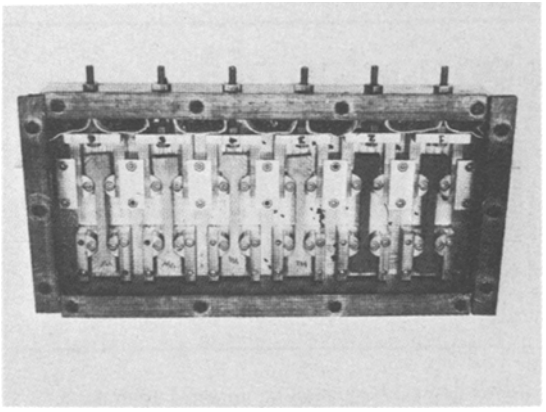

Figure 1 Apparatus for strain endurance tests.

occurred. The strain was applied by means of screw-operated jaws, turning the screw by hand at a uniform slow straining rate. The test apparatus was sealed and desiccated to avoid humidity effects. After a long period (usually 30 days) the specimens which did not fail were removed and strained at a strain rate of 0.7 min^{-1} until failure. This was done in order to evaluate the effect of prestraining on the mechanical properties of the investigated material.

2.2. Stepped strain endurance tests

In these tests our aim was to study the effect of stepped increases in strain magnitude. The specimens were initially subjected to 70 % of their ultimate strain and then their extension was increased in steps of 5, 10 or 15 % of their ultimate strain value until failure occurred. The samples were kept strained at each step for about 100 h before increasing the strain to the next step.

The strain endurance tests described above were performed at the following temperatures: ambient, 50° C, 65° C and 80° C.

3. Results

Fig. 2 illustrates the failure envelope [4–8] of the elastomer as determined by the uniaxial tensile tests. In the part of the failure envelope obtained from data characteristic of low rates of strain and high temperatures, failure occurred at constant strain which is almost equal to the maximum strain. This significant difference in behaviour between our curve and a failure envelope of ordinary shape [4], explains several phenomena in the ultimate behaviour of the material, as will be shown later in detail.

It was found in the strain endurance tests that the tested specimens did not fail unless their extension reached their ultimate strain value. As shown previously [3], the changes in the properties of the elastomer occurred during the first hours of the loading and these changes were irreversible.

In Fig. 3, Curve a shows schematically a failure envelope of ordinary shape and Curve b shows schematically a failure envelope of the investigated filled elastomer. When a specimen is strained until point A and then allowed to relax at a constant strain, as in the strain endurance tests, the stress in the elastomer decreases. When the stress value reaches the boundaries of the failure envelope, Point B, the specimen fails. Since the failure

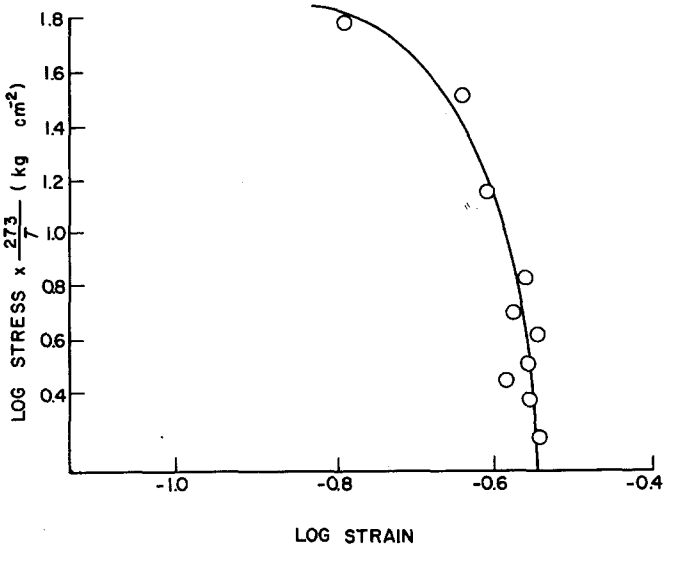

Figure 2 The failure envelope of the investigated elastomer.

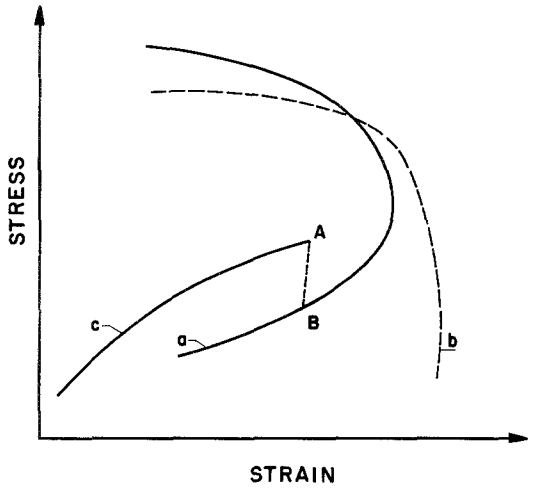

Figure 3 Schematic illustration of: Curve a, a failure envelope of ordinary shape; Curve b, the failure envelope of the investigated elastomer; and Curve c, the strain endurance experiments.

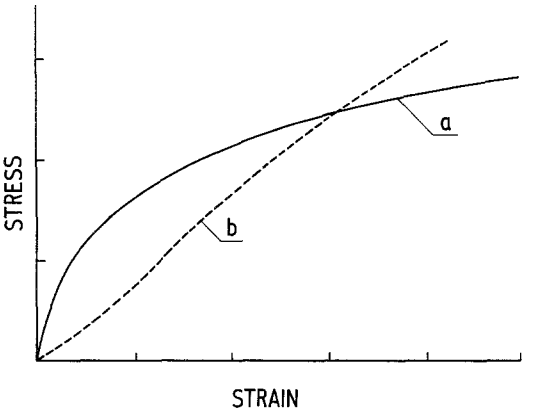

Figure 4 Typical stress–strain curves of: Curve a, reference specimen; and Curve b, a specimen which was prestrained in a strain endurance test.

envelope of the investigated elastomer is different in shape from that of ordinary materials at the lower part of the curve, the specimens do not fail unless the ultimate strain is applied. This phenomenon is unique because ordinary failure in strain endurance tests is expected at about 70 to 80% of the ultimate strain.

The samples which did not fail in the strain endurance tests were left free of strain for 3 h and were then strained to failure. In Fig. 4 two typical stress–strain curves are shown: Curve a of a reference (unstrained) specimen and Curve b of a specimen which was prestrained in a strain endurance test. In the initial part of the stress–strain curve of the prestrained specimen a softening effect is observed. At higher strains strengthening can be observed in the investigated material.

The stepped strain endurance tests show that the investigated elastomer has an unexpectedly high strain endurance capability and that its failure happens far outside the boundaries of the failure envelope, at about 140% of the ultimate strain. Changes in magnitude of the strain increment did not affect the results.

Similar results were obtained in the strain endurance experiments performed at elevated temperatures. The data obtained, given in Table I, indicate that significant strengthening of the material occurred in samples kept at elevated

TABLE I The effect of straining and ageing on the mechanical properties (tensile tests at ambient temperature at a rate of 0.7 min^{-1})

Ageing temperature (° C)	Ageing conditions	Maximum strain (%)	Maximum stress* (kg cm^{-2})	Modulus* (kg cm^{-2})
Ambient	Reference†	28.8	15	82
Ambient	30 days, unstrained	28.8	15	82
Ambient	30 days, strained at 0.7 ϵ_b‡	16.3	17	46
50	Reference†	28.0	16	86
50	30 days, unstrained	28.4	22	180
50	30 days, strained at 0.7 ϵ_b‡	22.0	28	250
65	Reference†	28.0	16	82
65	30 days, unstrained	13.5	26	200
65	30 days, strained at 0.7 ϵ_b‡	13.8	32	380
80	Reference†	27.1	14	66
80	30 days, unstrained	5.2	32	350
80	30 days, strained at 0.7 ϵ_b‡	4.6	42	715

*Based on cross-section measured before the final testing of the specimens.
†The reference specimens were strained at the ageing temperature at a constant rate of 0.7 min^{-1}.
‡ϵ_b is the strain at failure of the reference specimen.

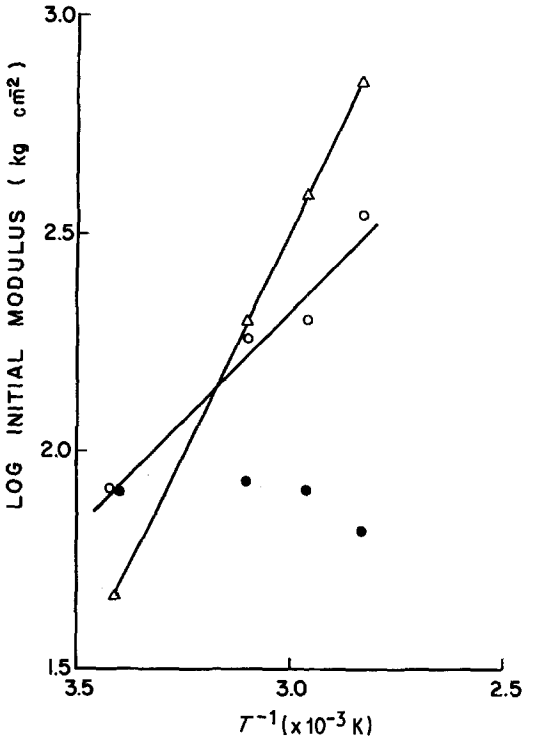

Figure 5 The effect of ageing and straining on the tensile modulus as a function of temperature. •, Reference specimen; ○, aged specimen; and △, aged and strained specimen.

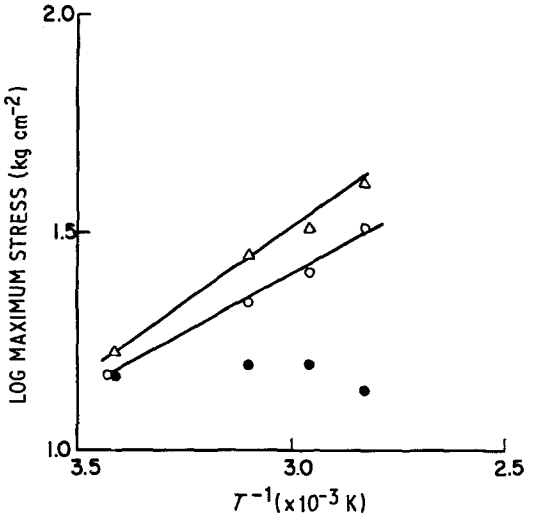

Figure 6 The effect of ageing and straining on the tensile stress as a function of temperature. •, Reference specimen; ○, aged specimen; and △ aged and strained specimen.

temperatures for different periods of time and that these changes were enhanced by superimposed prestraining.

The logarithmic plots of the initial moduli and maximum tensile stress against reciprocal value of the absolute ageing temperature, see Figs 5 and 6, are linear, indicating an Arrhenius-type relationship. From the slopes of these lines, the overall activiation energy of the ageing process was calculated and the values are presented in Table II.

4. Discussion

The mechanical behaviour of the investigated filler elastomer was found to differ significantly from the expected behaviour. Usually materials fail in the strain endurance experiments at about 70 to 80% of their ultimate strain, whether the strain is applied at once or in steps. The main effect of prestraining on the mechanical properties is a softening of the material, probably due mainly to de-wetting. In this work, however, the investigated elastomer failed in the strain endurance experiments only if the applied strain exceeded the ultimate strain, because of the unusual shape of its failure envelope. When the strain was imposed in steps, the elastomer withstood much higher strains, far beyond the boundaries of the failure envelope (140% of the ultimate strain).

It is known that the failure envelope is applicable in describing the ultimate properties of elastomers as long as the material remains basically (chemically and physically) unchanged during the investigation. It seems therefore that, in our case, when high strains were applied, internal structural changes occurred in the elastomer, and this in turn caused alternation in its mechanical behaviour, i.e., a strengthening of the material during its prestraining and ageing. The internal changes are also probably the reason why the ultimate behaviour of the elastomer could not be described by the failure envelope.

The data presented indicate that the internal structural changes in the material occurred almost immediately after application of the prestraining and that these changes seem to be of an irreversible

TABLE II Overall activation energies (kcal mol^{-1}) of ageing and straining

Properties	Ageing at elevated temperature	Ageing at elevated temperature and straining
Tensile strength	2.0	3.0
Tensile modulus	4.6	9.2

nature [3]. Our assumption that the changes occur in the early stages of the experiment is supported by the fact that, whenever samples ruptured in the strain endurance experiments, it happened shortly after strain application.

The differences in the overall activation energies obtained from the tensile strength and moduli measurements indicate, that the ageing process involved affect these two properties in different ways. The superposition of strain upon temperature increased the activation energy for the tensile strength by about 50% and by about 100% for the modulus. The moduli are determined by the initial part of the stress–strain curve; the softening in this part of the curve is of considerable importance. At ambient temperature the ageing effect is negligible and the softening effect is dominant. At elevated temperatures the situation becomes more complicated and the superposition of strain introduces additional difficulties. Our experiments show that ageing of the elastomer results in strengthening of the material, as was found earlier in other materials [2].

Some possible ageing processes that might be involved are the following:

(a) orientation of the elastomeric binder chains due to the applied strain;

(b) changes in the network structure of the binder;

(c) effect of microheterogeneity in the cured binder system; and

(d) changes in the interaction at the interphase between the binder and the filler particles.

In preliminary work, scanning electron microscope pictures gave no evidence of orientation and swelling experiments indicate that no significant changes in cross-link density occurred during prestraining and ageing.

5. Conclusions

The ultimate properties of filled elastomers used for structural parts, cannot always be determined by either testing the virgin material only, or by conventional accelerated ageing tests. To understand ageing effects properly, one should take into consideration not only time and environment conditions, but also the loading history of the elastomer. It is the combined effects of these factors that seem to produce the important structural changes in the composite, changes which are as yet unknown.

Further ageing studies of unfilled elastomers are in progress in order to investigate more carefully the possible ageing processes in the elastomeric binder. This may create a basis for a better understanding of the ageing processes of structural composite materials.

References

1. L. H. LAYTON, "Chemical Structural Ageing Effects", NTIS Technical Report number AD-A-002-836 (1974).
2. D. KATZ and A. BUCHMAN, *J. Appl. Polymer Sci.* **35** 491 (1979).
3. Y. DIAMANT, Z. LAUFER and D. KATZ, Proceedings of the 8th International Congress on Rehology, Naples, September 1980, Vol. 3, edited by G. Asterita, F. Marrucci and L. Nicolais (Plenum Press, New York, London, 1980) p. 243.
4. T. L. SMITH, *J. Polymer Sci.* **1** (1963) 3597.
5. T. L. SMITH and J. E. FREDICK, *J. Appl. Phys.* **36** (1965) 2996.
6. T. L. SMITH and R. A. DICHIE, *J. Polymer Sci.* **7** (1969) 635.
7. R. F. LANDEL and T. L. SMITH, *Amer. Rocket Soc. J.* **31** (1961) 599.
8. *Idem, Rubber Chem. Technol.* **35** (1962) 291.

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