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Thermophysical properties of elastomers

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The following account describes investigations of dimensional and stiffness characteristics of representative polyacrylic and silicone rubbers over the approximate temperature range 20 °C–175 °C. The results have led to a quantitative understanding of distinctive features in the behaviour of these elastomers, encountered during the course of their repeated use as tool materials in composite component manufacture, conforming with an explanation in terms of thermally induced cross-linking. It is concluded that silicone rubber offers more promise than polyacrylic rubber in applications where behavioural stability and a reasonable degree of control are required.

1. Introduction

One method of manufacturing components from carbon-fibre-reinforced plastics (CFRPs) employs elastomers which are used as tools in the fabrication process. After observing that the ability of some elastomeric tools to reproduce fine details in the profiles of composite components was reduced by temperature cycling, it was decided to investigate the influence of thermal history upon those physical properties of two representative elastomers which governed performance when used in composite tooling.

Factors influencing the behaviour of these materials when used as a mould have been reported [1]. In the present application the materials are used both in moulds where the pressure exerted upon the CFRP component, on heating, is constrained by the container, and in the form of inflated bags within aircraft wings, where they are pressurized to consolidate the constituent members of the assembly. Thermal expansion and stiffness were recognised as the predominant physical properties governing performance in both applications and accordingly investigations were undertaken to determine the influence of temperature–time programmes upon the linear thermal expansion coefficient and Young's modulus of a polyacrylic rubber and a silicone rubber.

2. Experimental details

2.1. The apparatus

Measurements of linear thermal expansion coefficient and Young's modulus were made using a Mettler TA 3000 thermomechanical analysis system, incorporating a TA 4000 microprocessor and printer. The principle of operation involved the employment of disc-shaped specimens, diameter approximately 4 mm and thickness 1.5 mm. A specimen was mounted on a platform, the temperature of which could be controlled, and length measurements were effected with the aid of a probe which rested upon the upper face of the specimen. A static force of 0.1 N was applied in order to maintain stability, and an oscillatory force of ± 0.05 N was superimposed on it. Measurements of movements of the mean position of the probe accompanying changes of temperature gave the expansivity of the specimen, while associations of the amplitude of vibration with applied force gave the Young's modulus.

2.2. Standardization of the apparatus

2.2.1. *Linear thermal expansion coefficient*

Preliminary measurements of the influence of cycling over the approximate temperature range 20–175 °C on the temperature dependence of the linear thermal expansion coefficient of polyacrylic rubber produced results which caused a detailed evaluation of the reliability of the instrument to be undertaken. A *modus operandi* was eventually formulated, subsequent to which experimental results for the linear thermal expansion coefficient of standard fused silica SRM 739, obtained from the National Bureau of Standards, were produced with a precision and absolute accuracy of $\pm 0.4 \times 10^{-6}\ \mathrm{K}^{-1}$. Corresponding results for copper, which has a thermal expansion closer to that of polyacrylic rubber, were produced with an internal precision of $\pm 0.5 \times 10^{-6}\ \mathrm{K}^{-1}$; these results deviated from results published by the National Bureau of Standards in a known, systematic way – not exceeding 4% at any temperature and permitting corrections to be applied to subsequent measurements made with the Mettler system. This preparatory work provided the basis of the derivation of the temperature dependence of the linear thermal expansion coefficients of specimens of rubber from measurements made during the course of the main investigation.

2.2.2. *Young's modulus*

In the absence of an appropriate standard reference material, strips of polyacrylic rubber were cut from a sheet of the material from which specimens were prepared for the dynamic measurements and simple stretching measurements were made at room temperature. Although the temperature dependence of the dynamic results was of greater immediate interest than their absolute values, agreement to within a few per cent between the room-temperature results obtained by the two methods was taken as providing a measure of the confidence which might be placed in the results of the subsequent investigation.

3. Results

3.1. Thermal expansion

3.1.1. *Polyacrylic rubber*

The results of a series of temperature excursions (henceforth called cycles) between approximately 20 and 175 °C are displayed in Fig. 1. It may be seen that there was a large increase in the linear thermal expansion coefficient between the results of cycles 1 and 2, between approximately 20 and 100 °C, whereas there was very little change between the results over cycles 2 to 50. There was a fall by about 25×10^{-6} K^{-1}, as the temperature rose through the approximate range 80–110 °C, in the linear thermal expansion coefficient which was otherwise sensibly independent of temperature over the range 20–175 °C, averaging approximately 290×10^{-6} K^{-1}. This effect was reproducible from cycle to cycle.

Successive cycles between 20 and 175 °C and back to 20 °C were accompanied by specimen shrinkage. The averages of results for two specimens, in which the temperature was raised at the rate of 1 °C min^{-1} and reduced at the rate of 2 °C min^{-1}, are summarized in Fig. 2. (These measurements were preceded by subjecting a specimen of copper to the same cycling. No evidence of shrinkage was found in these measurements, confirming that the behaviour subsequently observed when investigating polyacrylic rubber was not instrumental in origin.) No evidence of weight loss from the specimens was detected during the course of these experiments. The dimensional change in a specimen throughout the course of a series of temperature cycles clearly depends upon the rate at which the temperature range is swept. Fig. 3 shows length changes in a specimen executing a series of cycles corresponding to a cure cycle consisting of heating to 175 °C at a rate of 1 °C min^{-1}, dwelling at 175 °C for 2 h and cooling to 20 °C at a rate of 2 °C min^{-1}. An exploratory excursion to 210 °C revealed that any potential commercial advantages to be gained by holding the rubber for extended periods at this temperature, the post cure temperature of the composite resin matrix; could not be exploited because of the development of cracks in the rubber.

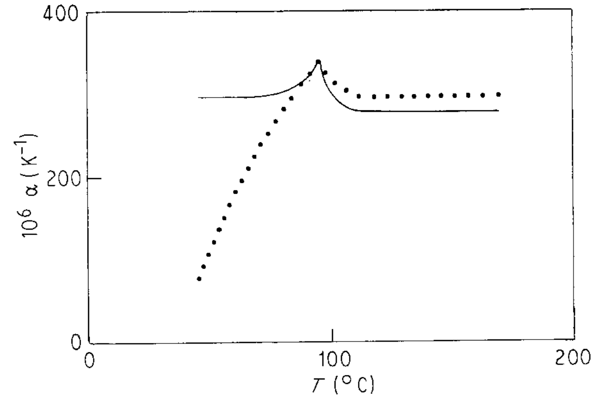

Figure 1 The linear thermal expansion coefficient, α, of polyacrylic rubber: (●) cycle 1, (——) cycles 2–50.

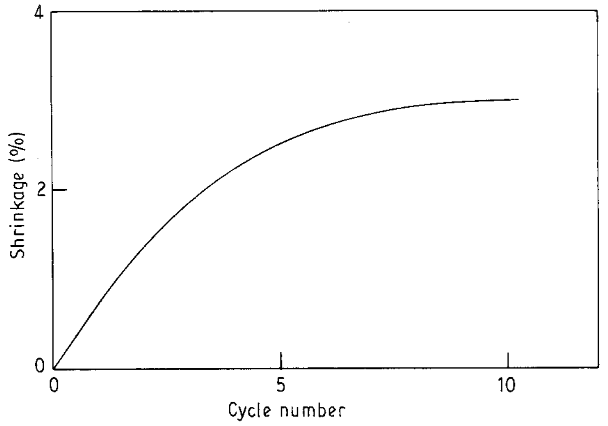

Figure 2 The influence of successive cycles between 20–175 °C upon the linear dimensions of polyacrylic rubber at 20 °C.

3.1.2. *Silicone rubber*

Results of a series of similar temperature cycles applied to silicone rubber are displayed in Fig. 4. Two differences between these results and the corresponding results for polyacrylic rubber, displayed in Fig. 1, are immediately apparent. Firstly, there is no evidence of a large difference between the results obtained in cycles 1 and 2, and, secondly, there is no sign of a discontinuity in the linear thermal expansion coefficient, as there was between 80 and 110 °C in the earlier results. The linear thermal expansion coefficient of the silicone rubber was some 12% higher than that of the polyacrylic rubber and the silicone rubber displayed no influence of cycling upon the magnitude of its linear thermal expansion coefficient or its independence of temperature above approximately 60 °C.

The cycles within the sequence represented in Fig. 5 were the same as those described in Section 3.1.1., for polyacrylic rubber. Comparing these results with those displayed in Fig. 3 it may be seen that the shrinkage accompanying repeated cycling is lower in silicone rubber than it is in polyacrylic rubber and that it levels off after about four cycles, whereas polyacrylic rubber was still shrinking after nine cycles.

3.2. Young's modulus

3.2.1. *Polyacrylic rubber*

The results of a series of excursions between room temperature and 175 °C upon the Young's modulus of a specimen of polyacrylic rubber are summarized in

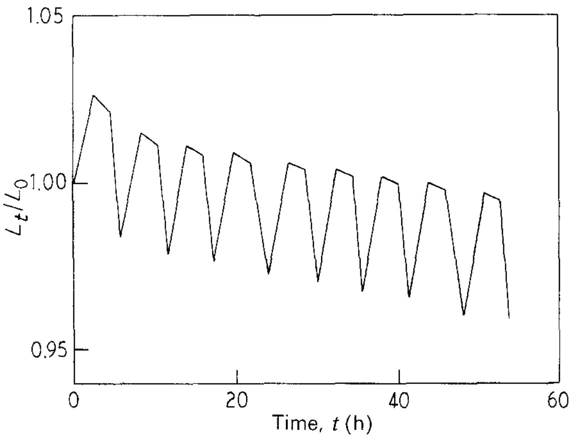

Figure 3 The influence of repeated applications of the temperature–time programme described in the text upon the linear dimensions of polyacrylic rubber.

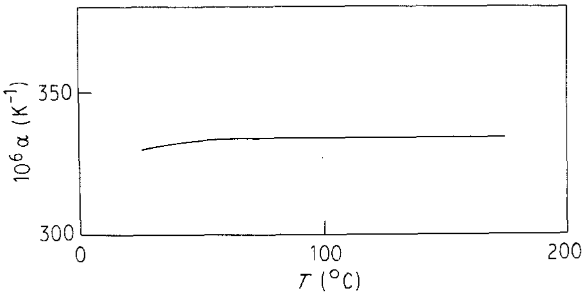

Figure 4 The linear thermal expansion coefficient, α, of silicone rubber, over cycles 1–40.

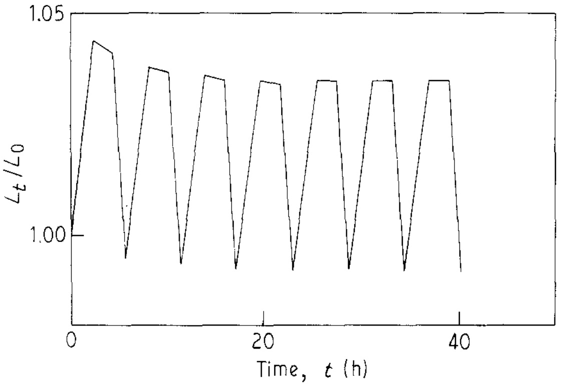

Figure 5 The influence of repeated applications of the temperature–time programme described in the text upon the linear dimensions of silicone rubber.

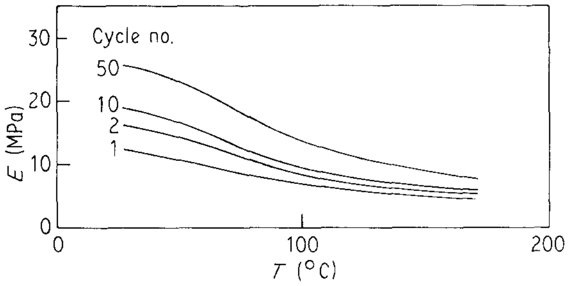

Figure 6 The influence of cycling upon the Young's modulus, E, of polyacrylic rubber.

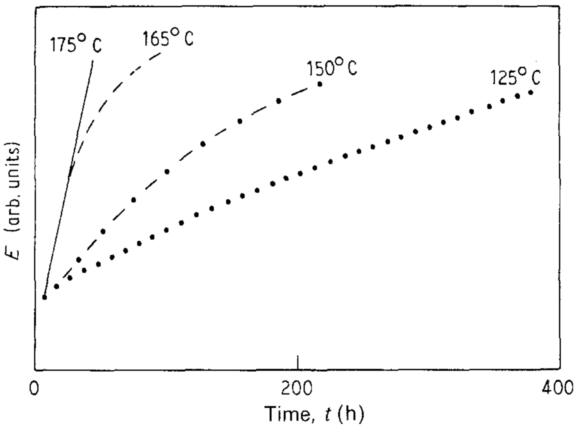

Figure 7 The influence of prolonged exposure to elevated temperatures upon the Young's modulus, E, of polyacrylic rubber.

Fig. 6. It may be seen that the Young's modulus falls with rising temperature and that a change in the sense of the curvature of the graphs, from concave downwards to concave upwards, occurs in the approximate temperature range 80–110 °C. One may also observe that, in contrast to the thermal expansion coefficient, the Young's modulus increases continuously with successive cycling over 50 cycles. It may be seen further that the modulus at room temperature increases considerably more rapidly with cycle number than the modulus at 170 °C. Representative results of prolonged exposure to constant elevated temperatures, summarized in Fig. 7, show that the modulus of a specimen exposed to an elevated temperature increases with time and that the rate of the increase of the modulus with time also increases with the conditioning temperature. Observations such as these provide the data from which the variation of the modulus of an elastomeric tool with time may be predicted throughout the course of the curing programme of a composite component, fabricated with its aid.

3.2.2. *Silicone rubber*

The temperature dependence of the Young's modulus of the silicone rubber, throughout the course of a programme of temperature cycling similar to that given to the polyacrylic specimen, is illustrated in Fig. 8. Comparing this with the results presented in Fig. 6 it may be seen that the dependence of modulus upon temperature is qualitatively similar in both systems, but the results for silicone rubber are significantly lower in magnitude.

3.3. The effect of mechanical constraint upon Young's modulus

All the results reported so far refer to specimens of rubber which were completely free to expand or contract laterally, corresponding to in-plane directions of the sheet from which they were cut, while their behaviour was studied in directions perpendicular to the plane of this sheet. In order to explore the behaviour under conditions resembling those within a mould, specimens were cut from sheets with the aid of a series

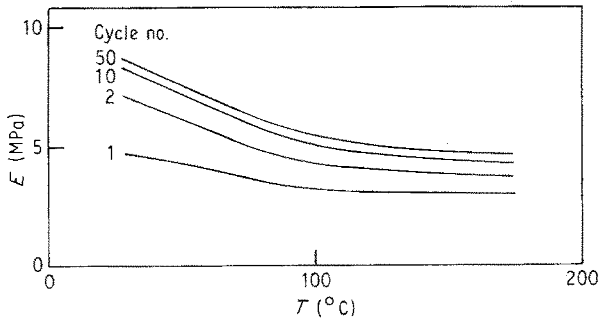

Figure 8 The influence of cycling upon the Young's modulus, E, of silicone rubber.

of short metal tubes, the lengths of which were the same as the thicknesses of the sheets and the rims of which were sharpened to facilitate cutting. The constrained specimens were subjected to programmes of temperature cycling resembling those employed earlier, producing results which were qualitatively similar to those displayed in Figs 6 and 8, but greater in magnitude, i.e. the effect of a constraint resembling that produced by a mould is to increase the modulus of the specimens. The effects of this constraint are illustrated in Fig. 9.

4. Discussion

It is of some interest to speculate upon the processes which may be responsible for the behaviour observed in the physical properties of the elastomers forming the subjects of the investigation.

The simplest situation to consider is that of isothermal changes in Young's modulus with increasing time, as illustrated by the results for the polyacrylic rubber displayed in Fig. 7. The increase in modulus with increasing time could be assumed to be due to an increase in cross-linking, and such a process can be described quantitatively by a rate equation involving a thermally activated cross-linking mechanism. If the degree of cross-linking is denoted by x, where $0 \leq x \leq 1.0$, then work on the curing of resins [2, 3] suggests that for an isothermal process the rate of change of x with time, t, is determined by an equation of the form

$$\frac{dx}{dt} = D\exp(-A/T)(1-x) \quad (T = \text{constant}) \tag{1}$$

where A and D are constants. In the absence of experimental data, it will be assumed in the following that the Young's modulus of the rubber is proportional to the degree of cross-linking, i.e. that $E = E_m x$, where E_m is a theoretical maximum value of E at temperature T. With T constant, and provided that $x = x_0$ is known at some time $t = t_0$, Equation 1 is readily integrated to give

$$\ln\left[\frac{1-x}{1-x_0}\right] = -D(t-t_0)\exp(-A/T) \tag{2}$$

which yields for x

$$x = \{1 - \exp[-D(t-t_0)\exp(-A/T)]\} + x_0\exp[-D(t-t_0)\exp(-A/T)] \tag{3}$$

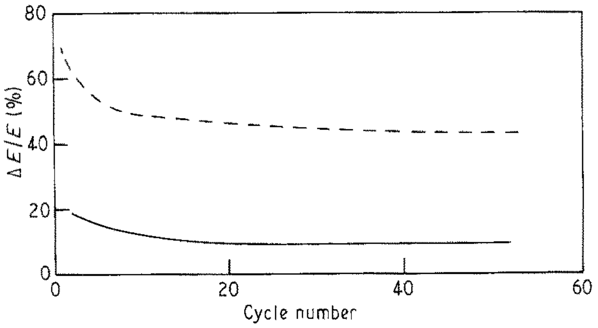

Figure 9 The percentage increase in Young's modulus, $\Delta E/E$, resulting from mechanical constraint as described in the text: (----) polyacrylic rubber, (——) silicone rubber.

Replacing x by E/E_m and x_0 by E_0/E_m in Equation 3 gives the variation of E/E_m with t. Rearranging Equation 2 and using E/E_m for x, the time t at which a given value of E is reached is given by

$$t - t_0 = \frac{1}{D}\exp(A/T)\ln\left[\frac{E_m - E_0}{E_m - E}\right] \tag{4}$$

Letting

$$B(T) = \frac{1}{D}\ln\left[\frac{E_m - E_0}{E_m - E}\right] \tag{5}$$

then

$$\ln(t - t_0) = \frac{A}{T} + \ln B(T) \tag{6}$$

The temperature dependence of the function $B(T)$ arises because E_m depends upon temperature. If it is assumed that the values E_0 and E correspond to degrees of cross-linking, x, which are much smaller than the maximum value $x = 1.0$, then

$$B \simeq \frac{1}{D}\ln\left[\frac{E_m}{E_m}\right] \rightarrow 0 \tag{7}$$

in which case

$$\ln(t - t_0) = \frac{A}{T} + \text{constant} \tag{8}$$

In order to test the validity of this equation, the results for the polyacrylic rubber obtained under isothermal conditions, displayed in Fig. 7, were used and a graph of $\ln(t - t_0)$ against $1/T$ was plotted in Fig. 10. In evaluating the ordinates, t was taken as the time at which a value of E was reached equal to that obtained at 125 °C after conditioning for 376 h, from the time t_0 at which E had its smallest value in Fig. 7. Some support for the validity of the thermally activated cross-linking mechanism assumed is provided by the fact that the form of the graph does correspond to that expected on the basis of Equation 8. Taking this interpretation a stage further, one may derive a value of $\ln B \simeq -17.8$ from Fig. 10; from which B is approximately zero. This is consistent with the approximation made in deducing Equation 8. Fig. 10 also yields a value of $A \simeq 9580$ K, from which it is possible to predict the approximate times it would take to achieve the arbitrary modulus increase employed here, by conditioning the rubber at different temperatures. For

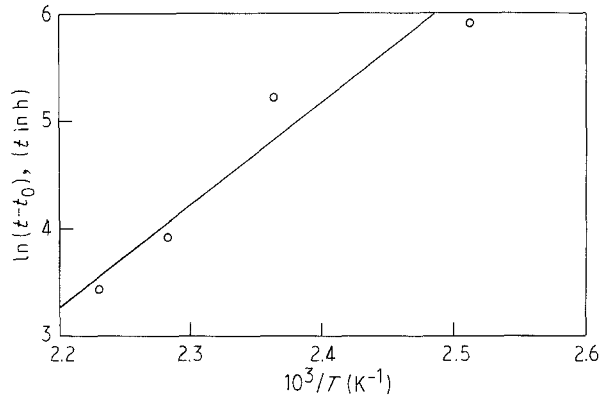

Figure 10 The time ($t - t_0$) required to increase the Young's modulus of polyacrylic rubber by a fixed amount by conditioning at different constant temperatures, T: (o) experiment, (——) theory.

example, at 220 °C it would take approximately 5 h to reach the same value of E that is reached after 31 h at 175 °C. This figure cannot be expected to provide more than an indication of the time required, because of the assumptions and approximations made and because of experimental uncertainties in the primary data, but the scheme clearly allows quantitative guidelines to be established, within which experimentally confirmed regimes might be developed.

5. Conclusion

The main purpose of the present investigation was to gain some understanding of the reasons for difficulties encountered in achieving a faithful reproduction of sharp contours when employing elastomers on a repetitive basis in the fabrication of CFRP components and structures. It is now clear that these arise mainly from progressive increases of stiffness which, it is believed, are to be associated with structural changes in the rubber promoted by increased temperatures. An additional increase of stiffness resulting from mechanical constraint has also been identified and there can be little doubt that a systematic quantitative development of this observation would provide a deeper insight into the mechanisms responsible for the increases of stiffness encountered. The development of a quantitative model to explain the observations would be assisted by repeating the experiments reported in this account with other specimens taken from other parts of the sheets of rubber employed and taking averages to allow for material variability and experimental uncertainties, although spot checks have indicated that this would be unlikely to produce any substantial changes.

On the basis of the observations recorded here, silicone rubber appears to offer a number of advantages over polyacrylic rubber as a tooling material. A discontinuity in the temperature dependence of the linear thermal expansion coefficient of the polyacrylic specimen in the temperature range 80–110 °C, which is presumably associated with some form of transition, does not complicate the corresponding behaviour of the silicone rubber. The greater influence of cycling upon the temperature dependence of the Young's modulus of polyacrylic rubber must make it more difficult to employ in a production line than silicone rubber. These difficulties of forward planning with polyacrylic rubber are compounded by the greater influence which physical constraint has upon the modulus of this material, compared with silicone rubber. Recalling that the shrinkage accompanying repeated cycling was lower in silicone rubber than in polyacrylic rubber and that it ceased fairly early in a sequence of cycling, whereas polyacrylic rubber was still shrinking after nine cycles, one may conclude that the pressure increase which would have to be applied during a sequence of moulding operations undertaken using a silicone rubber bag in order to fabricate a component of constant quality would be significantly less than would be required when using a polyacrylic rubber bag.

Detailed results from investigations such as the present one may be employed to calculate the increases of pressure which would be required to maintain consistent performance of pressurized bags in composite fabrication. In the case of applications of elastomers in moulds, progress could be made by employing the experimental data to provide guidelines within which an empirical approach might be developed to suit the needs of individual applications. Specifically, such information could be used to design an elastomeric tool for an identified application, to condition the rubber and then to produce a prototype composite component; with such familiarity, details of the design of the tool could be optimized to suit the particular circumstances of the component's function.

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