

Thermal properties of carbon-filled silicone rubbers for use in thermal expansion moulding

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The pressure produced by the thermal expansion of silicone rubber on heating when enclosed in a steel mould can be used to fabricate complex shaped reinforced plastic components. To improve the thermal conductivity of the rubber, the effects have been studied of adding between 25% and 30% by volume of carbon, both as chopped carbon fibre and carbon black. Measurements have been made of the thermal conductivity between 30° and 170° C, and of the thermal expansion between 23° and 140° C. It was found that the chopped fibres were more efficient than the carbon black in increasing the thermal conductivity, giving approximately 100% increase in conductivity over that of the pure rubber for a 30% loading. The addition of carbon led to a decrease in the thermal expansion of the rubber by an order of 30%. The bulk modulus of the rubber was found to increase slightly, by less than 10%, when the carbon was added.

1. Introduction

A number of difficulties arise in the production of complex shaped or hollow reinforced plastic components using normal press-moulding techniques. In the first instance an intricately shaped, and thus expensive, mould may be required. In the case of a hollow component a method of exerting pressure on the inner walls of the component must be devised.

One method of overcoming these difficulties is to surround the uncured component with silicone rubber and enclose the system in a rigid mould. The application of heat then causes the rubber to expand, exerting a pressure on the composite. This method is known as thermal expansion moulding (TEM) and is used, for example, in the manufacture of fibre reinforced plastic sine-wave spars for aircraft wings.

Unfortunately, since rubber is such a poor conductor of heat, the "heating-up time" involved in TEM may be considerably longer than in conventional production methods. This situation can be improved by the inclusion of carbon in the rubber, which will increase its thermal conductivity and, hence, decrease the production time.

However, two other important properties of the rubber will be affected by carbon inclusions, namely, the volume thermal expansion coefficient β_r and the bulk modulus K_r . It can be shown [1] that the pressure, P , generated within a mould due to a temperature rise ΔT is given by

$$P = K_r \left[1 - \frac{V_{m0}(1 + \beta_m \Delta T)}{V_{r0}(1 + \beta_r \Delta T)} \right]$$

where V_{m0} and V_{r0} are the initial volumes of the mould and rubber respectively, and β_m is the volume thermal expansion coefficient of the mould. It can be seen that the values of K_r and β_r should be as large as possible to maximize the moulding pressure.

As the carbon content of the rubber is increased, it would be expected that the thermal conductivity and the bulk modulus would also increase, and that the coefficient of volume thermal expansion would decrease. Experiments are reported which have been made to investigate these changes in thermal properties, and to study the effects on the bulk modulus.

2. Materials studied

Two forms of carbon inclusion were investigated, namely, short chopped randomly oriented carbon fibre and carbon black. Silicon rubber specimens containing either chopped carbon fibres or carbon black were prepared at various volume fractions together with a number of unfilled silicone rubber samples to act as controls. Details of the five series of specimens studied are given in Table I. The unfilled silicone rubber was supplied by Dow Corning Ltd. The properties of the filled rubbers were assumed to be isotropic.

TEM is usually used for thermosetting composites requiring a maximum temperature of approximately 150° C. Thus, all high temperature measurements were kept below this temperature.

3. Thermal conductivity measurements

The thermal conductivities of the rubbers were measured using a "Dynatech" thermal conductivity

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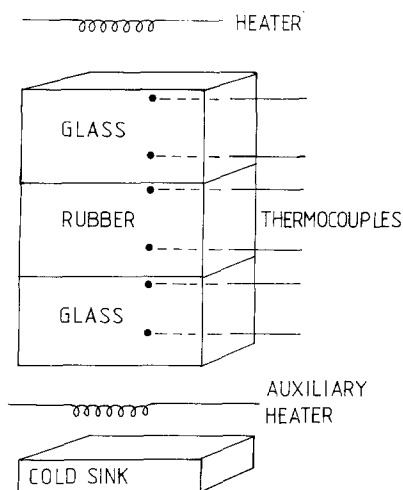


Figure 1 Schematic representation of the apparatus employed in the determination of the coefficient of thermal conductivity of rubber.

machine. A schematic representation of the machine is shown in Fig. 1. The system consists essentially of two glass blocks of known, identical dimensions and thermal conductivity, between which is sandwiched a test specimen possessing the same cross-sectional area as the glass blocks. Thermocouples embedded along this stack yield the temperature gradients across the test specimen and both the glass blocks. The stack is surrounded by a series of heaters of variable outputs which enable the heat flow through the stack to be controlled.

Ideally, the outputs of the heaters should be adjusted until the heat flows across the two glass blocks are equal. In practice, the heat flows across the glass blocks were not equal and, thus, the average of these two values was employed.

The results of the thermal conductivity measurements are displayed in Fig. 2. It can be seen that the addition of 30% chopped carbon fibre almost doubles the thermal conductivity of the silicone rubber. This is not an outstanding result when it is considered that the thermal conductivity of a carbon fibre is approximately 25 times greater than silicone rubber.

The chopped fibre inclusion is more effective than the carbon black in increasing the thermal conductivity of the rubber. However, the thermal conductivities of the rubber containing carbon black were virtually constant over the required temperature range, whereas the incorporation of the chopped fibres produced rubber composites whose thermal conductivities decreased with increasing temperature.

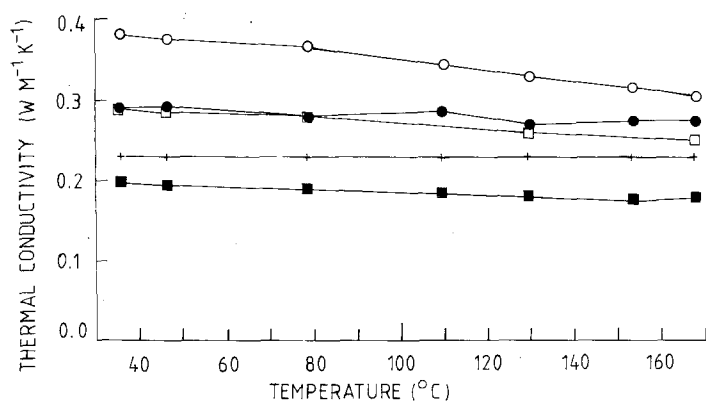


Figure 2 Thermal conductivity of carbon-filled silicone rubbers. ■, unfilled rubber; ○, 30% chopped fibre; ●, 30% carbon black; □, 25% chopped fibre; +, 25% carbon black.

TABLE I Materials studied; Silastic 35U* base rubber containing varying amounts of filler

Filler	Filler content (vol %)
None	0
Chopped carbon fibre	25
Chopped carbon fibre	30
Carbon black	25
Carbon black	30

*Trade name of Dow Corning Ltd.

4. Volume thermal expansion

The volume thermal expansions of the rubbers were obtained with the use of a simple, reusable glass dilatometer as shown in Fig. 3. The base of the dilatometer bulb was in the form of a threaded shaft, the mouth of which was ground flat. After filling the bulb with the rubber specimens (typically approximately 25 g) a ground glass disc was placed over the entrance of the shaft. The disc was held in place by means of a PTFE cap which screwed onto the shaft. This glass-to-glass seal simplified any corrections required to compensate for the expansion of the apparatus during the experiments. It was found that a rubber washer placed between the glass disc and the inner base of the cap ensured that leakage, due to the loosening of the cap at elevated temperatures, could be prevented.

Mercury was selected as the confining liquid since its volume expansion is well known and it did not attack the rubber. (A preliminary test conducted using silicone oil as the confining liquid proved unsatisfactory when the oil was observed to cause severe swelling of the rubber.) After the rubber specimens had been loaded into the dilatometer and the cap had been tightened, the system was evacuated. The top of the dilatometer was then opened to a mercury reservoir via a two-way tap and the mercury was allowed to fill the bulb via the capillary.

The dilatometer was placed in a glass-sided temperature bath containing a silicone oil which, in turn, was placed in a fume cabinet. The temperature of the system was monitored employing a thermocouple placed in the bath adjacent to the dilatometer bulb, the system being allowed to reach thermal equilibrium before a record of the temperature was made. The height of the fluid in the capillary was recorded with the use of a cathetometer equipped with a vernier scale capable of being read to 0.1 mm. The calculation of the true volume thermal expansion of the rubber was

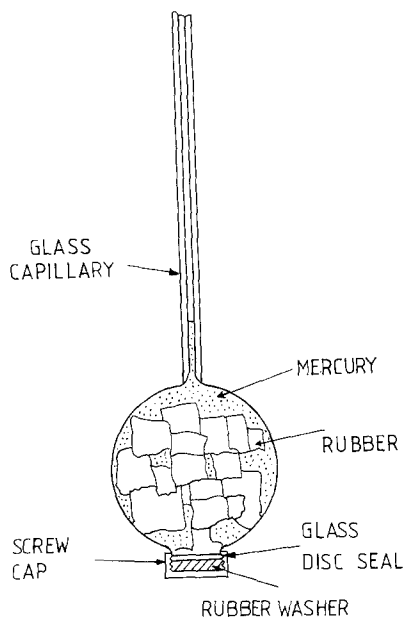


Figure 3 Construction of dilatometer employed.

simplified since only corrections due to the thermal expansion of the glass dilatometer and the mercury were necessary. The temperature bath was sufficiently deep to enable the majority of the capillary to be immersed and thus there was no temperature variation along the mercury column in the capillary.

The results of the experiments are displayed in Fig. 4. It can be seen that the volume thermal expansion of the unfilled silicone rubber increases over the temperature range 25° to 140°C. Values for the coefficient of volume thermal expansion of $7.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ and $9.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ were obtained for the unfilled rubber at 40°C and 120°C respectively.

The presence of the carbon black reduces the coefficient of volume thermal expansion by a percentage approximately equivalent to the content by volume of the filler, i.e. 30% carbon black reduces the thermal expansion by approximately 30%. A similar reduction in the volume thermal expansion of the rubber is associated with the presence of short chopped fibres, although the fibres appear to restrict the expansion of the rubber at high temperatures. This results in an almost constant value for the coefficient of volume thermal expansion being observed over the temperature range 25° to 140°C for the short fibre filled rubbers.

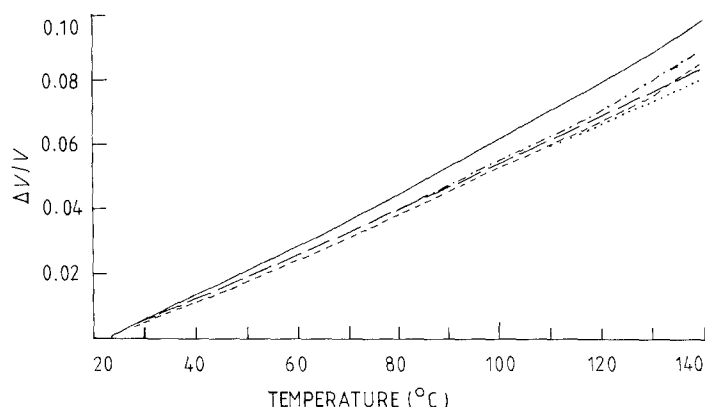


Figure 4 Thermal expansion of carbon-filled silicone rubbers. — unfilled rubber; - - - 25% carbon black, - · - 25% chopped fibre; · · · 30% carbon black; · · · · 30% chopped fibre.

TABLE II Measured values of the bulk modulus

Rubber	Bulk modulus (10^9 N m^{-2})
35U	0.9-1.1
35U/25% chopped fibre	1.0-1.2
35U/30% chopped fibre	1.0-1.2

5. Bulk modulus

The bulk moduli of rubbers are usually determined indirectly, but an attempt was made to make direct measurements by compressing the specimens in a simple piston-cylinder arrangement as shown in Fig. 5. The cylinder also acted as the mould during the manufacturing of the specimens. This ensured that the test specimens fitted tightly into the cylinder. The jig was placed on a Losenhausen UHS6 universal testing machine which enabled both the load being applied to the piston and the piston displacement to be monitored. After an initial "bedding in" period at low loads, a linear load displacement relationship was observed and thus, knowing the cross-sectional area of the cylinder the change in volume of the rubber could be indirectly read from the cross-head movement of the testing machine.

The thermal test results had indicated that the short chopped fibre filler was preferable to the carbon black and thus the bulk modulus measurements were restricted to those rubbers containing short chopped fibre only. The results of the bulk modulus measurements are given in Table II. Uncertainties in the values arise because of frictional effects and the encroachment of the rubber around the end of the piston.

It was found that the repeatability of the tests was poor and that, in general, a hysteresis effect was observed in all the tests. The test method adopted was unable to distinguish between the presence of 25% and 30% chopped fibre. Indeed, the general scatter in the results was greater than the difference in the average values obtained for the filled and unfilled rubbers.

The manufacturers of the unfilled rubber supplied a value for the bulk modulus of $1.1 \times 10^9 \text{ N m}^{-1}$, derived from other property measurements, which is close to the value obtained with the compression jig. Dow Corning Ltd also supplied information on the effects of other fibres on the bulk modulus of rubber

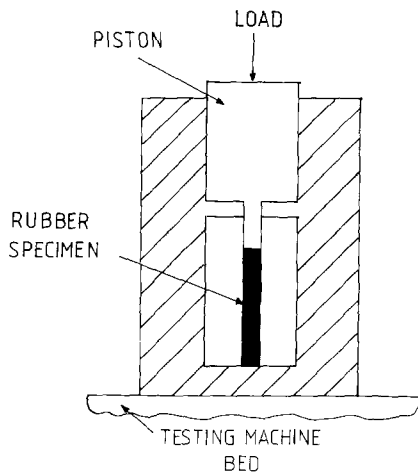


Figure 5 Rubber compression jig.

[2]. This information verified that, in general, the addition of fillers had little effect on the bulk modulus. For instance, the addition of 50% silica only increased the bulk modulus of the Silastic silicone rubber by approximately 8%. When one considers that the bulk modulus of silica is approximately 35 times greater than silicone rubber and that the bulk modulus of carbon is only approximately 3 times that of silica, it would not be expected that the presence of 25% carbon would increase the bulk modulus of the rubber by more than 10%.

The pressure exerting capability of the thermal expansion moulding system is far in excess of that required to press a composite. Variations in the bulk modulus will create differing pressure-temperature profiles for the TEM system. The temperature at which the desired pressure will be reached may be determined by the value of the initial gap in the system. It is apparent that the decrease in the volume thermal expansion coefficient of the rubber due to the presence of the carbon will be considerably more significant than the accompanying small increase in the bulk modulus.

6. Discussion

The present work has concentrated on the thermal properties of carbon-filled rubbers, but it is known that other factors are important in thermal expansion moulding. For example, it is desirable that a tooling rubber should have a long working life, which requires, among other factors, that it should have a high tear strength. Eccersley [3] has shown that the presence of chopped carbon fibre reduces the tear strength of silicon rubber, although the details of the system he studied are not known.

The effects of thermal cycling on carbon-filled rubber has not been investigated here. Work of Deutsch [1] indicates that cycling can lead to a significant reduction in the hardness of the rubber, and further assessment of this effect is needed.

The results obtained for the thermal properties of carbon-filled silicone rubber can be summarized as follows:

(a) The presence of carbon increases the thermal conductivity of the rubber and thus decreases the "heating up time" of a TEM system resulting in a reduced cycle time. Chopped carbon fibres are more efficient than carbon black at increasing the thermal conductivity of the rubber. Typical increases of 100% and 45% have been observed for a 30% loading of chopped fibres and carbon black, respectively.

(b) The presence of carbon inclusions decreases the volume thermal expansion of the silicone rubber. A decrease in the coefficient of volume thermal expansion of approximately 30% is observed for loadings of 30% carbon black or chopped fibres.

It was not possible to obtain a direct accurate determination of the effect of the carbon inclusions on the resultant bulk modulus of the rubber. However, it has been shown that the carbon will cause a slight increase in the bulk modulus of less than 10%.

The results indicate that a thermal expansion moulding system would benefit from the incorporation of carbon into the silicon rubber. The "heating up time" of the system would be approximately halved by the presence of 30% by weight loading of chopped carbon fibre. By selecting the appropriate initial dimensions of the rubber tool the required pressure profile could still be achieved.

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