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Investigation of factors affecting the thermal expansion of perfluoroelastomer seal materials

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The high thermal expansion coefficient of perfluoroelastomer materials can cause problems with the design of adequate seal grooves to cover both high and low temperature operation. Variations in filler shape and proportions have been shown to have a significant effect on thermal expansion over part of the temperature range. This feature describes an investigation of relevant literature that has been compared with experimental verification.

Nomenclature

α_V	= volumetric thermal expansion coefficient
α_L	= linear thermal expansion coefficient
C_V	= constant volume heat capacity
C_P	= constant pressure heat capacity
c	= composite (subscript)
E	= Young's Modulus
ϵ_{ij}	= internal thermal strain
f	= filler, (subscript)
K	= Bulk Modulus
K_S	= adiabatic bulk modulus
K_T	= isothermal bulk modulus
γ	= heat capacity ratio
Φ	= filler fraction
m	= matrix, (subscript)
T	= temperature, K
V	= volume

Introduction

It is well known that perfluoroelastomers expand significantly in volume with increasing temperature.^[1, 4] This is a phenomenon that must be taken into account when designing a seal, such as an O-ring, and the appropriate housing. Over-sizing a seal that has a high coefficient of thermal expansion (CTE), can often result in either extrusion of the material out of the gland, breakage of the seal, or both depending on the design of the seal and housing.

The effects of thermal expansion in sealing applications can be largely mitigated by appropriate design strategies, but many of the best properties of some key perfluoroelastomers are not fully exploited because of the need to do this. Principally, the requirement to undersize seals to accommodate thermal expansion creates the potential for seal leakage at lower temperatures because of insufficient interference and associated gland fill. If CTE could be reduced, the risk of such poor low temperature

performance could be considerably reduced, with the freedom to use higher gland-fill ratios.

The existence of elastomeric thermal expansion, while it is well known to sealing engineers, is less well understood. This paper discusses one of the key factors which contribute to thermal expansion in elastomers, namely the type and loading of filler materials used in the material formulation. This has been achieved partly through a survey of the literature in this area and supplemented by experiments and measurements undertaken at Precision Polymer Engineering Ltd (PPE).

Theory of thermal expansion in elastomers

In general, the thermal expansion coefficient of a material is a measure of the change in its size per degree Kelvin change in temperature at constant pressure with the dimension change measured either as a length or a volume increment. The volumetric thermal expansion coefficient may be expressed formally in three principal ways as shown in equation (1):^[9]

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{\gamma C_V}{K_T V} = \frac{\gamma C_P}{K_S V} \quad (1)$$

Here, V is the volume of the specimen, P the pressure of the system, T the system temperature, with C_P and C_V being the heat capacities at constant pressure and volume, respectively. $\gamma = (C_P/C_V)$ is the heat capacity ratio. K_T and K_S are the isothermal and adiabatic bulk moduli of the material, respectively. These are defined by equations (2a) and (2b):(2a)(2b)

$$K_T \equiv -V \left(\frac{\partial P}{\partial V} \right)_T \quad (2a)$$

$$K_S \equiv -V \left(\frac{\partial P}{\partial V} \right)_S = \rho \left(\frac{\partial P}{\partial \rho} \right)_S = K_T (1 + \alpha \gamma T) = \frac{C_P}{C_V} K_T \quad (2b)$$

The volumetric thermal expansion coefficient, α_V , is expressed in terms of the linear coefficient, as $\alpha_V = 3\alpha_L$.

This definition becomes important when it is considered that some materials expand at greater rates along one linear axis than another, i.e. they behave anisotropically. Thus, one material may have a lower value of absolute volumetric thermal expansion coefficient than another and still expand at a greater linear rate along one axis than another material. This is why a fundamental study of thermal expansion phenomena in certain mechanical applications should usually be directional and take linear coefficients into account. This becomes more relevant where non-spherical, high-aspect ratio filler particles are used to reinforce the elastomer matrix as described in the section below.

Effect of filler type and fraction on elastomer thermal expansion

A variety of models have been developed to explain the effect of fillers on the thermal expansion behaviour of the composites in which they are used. The simplest of these models simply moderate the contribution of individual component thermal expansion coefficients by their weight-loading in the composite. However there has been progressive development of more advanced models that use the fundamental mechanical properties of each phase to predict the expansion behaviour of the overall composite using mathematical analysis from first principles.

Iyer et al.^[5] used a simple correlation for the isotropic thermal expansion coefficient of a filled elastomer, α_c which is basically the rule of mixtures without modification. It requires knowledge of the relative concentrations of matrix and filler in the composite, the filler volume fraction, together with their respective known thermal expansion coefficients.

The rule of mixtures model was modified by Schapery, to take into account the mechanical interactions between different materials within a composite,^[8] producing a relationship that

also takes account of the Young's Modulus of the matrix and the filler.^[10]

Although this Schapery model represents a refinement in the rule of mixtures to balance the overall thermal expansion coefficient in terms of individual phase properties, it is in reality a mathematical averaging device which provides no fundamental insight into the causes of thermal expansion in the composite elastomer. In order for such a model to be credible it must be built from first principles by considering the internal strains caused by the differing physical and mechanical properties of the two composite phases, matrix and filler.

One of the most complete models of the interaction between matrix and filler, and its effect on thermal expansion was that of Chow.^[2] He reviewed the effect of particle shape and filler fraction on the mechanical and thermal properties of filled polymers, and developed expressions for a thermal expansion coefficient based on the strain of inclusions within the matrix providing expressions for the two cases of linear thermal expansion in the transverse and longitudinal directions.^[2, 10] This is in contrast to the isotropic models of Schapery which do not account for particle shape or directionality of thermal expansion.

This model takes the known volumetric thermal expansion coefficient of the elastomer matrix and filler, respectively, the bulk and shear moduli for the filler and matrix together with the filler volume fraction, the filler particle aspect ratio and the Poisson's ratio of the matrix.^[2, 10] In the model the aspect ratio is defined as the ratio of the major dimensional axis, with respect to the direction of expansion, to the minor one, transverse to the direction of linear expansion. Thus a fibre has $\rho > 1$, a sphere has $\rho = 1$, and a disc has $\rho < 1$. This permits the development of an equation to express the volumetric thermal expansion coefficient of an elastomer composite.^[2, 10]

This work was further developed by Lee et al,^[6] who modified Chow's model to derive expressions for longitudinal and transverse thermal expansion. This model is based on the fundamental mechanical observation that as the temperature changes in a two-phase composite an internal or thermal strain develops which can be expressed by:

$$\bar{e}_{ij} = (\alpha_{vf} - \alpha_{vm}) \Delta T \delta_{ij}$$

Here, e_{ij} is the internal strain, eigenstrain or thermal strain due to the difference between α_{vf} and α_{vm} .

This then led to the derivation of a fundamental statement of the model relating internal strain to the thermal expansion coefficient.^[3, 7, 10] The authors validated their model using data for a typical epoxy resin – glass fibre composite for which

the phase properties were known, see Figure 1.^[6] This shows results from the model compared with results using the earlier model of Schapery.

The principal points of the comparison may be summarised as follows:

- Spherical inclusions, corresponding to spherical filler particles, result in isotropic thermal

expansion coefficients which are a maximum of 70% the value of the unfilled matrix, at a filler loading of 25%.

- Fibre-shaped inclusions deliver the next best performance in reducing composite CTE; here maximum values of 95% of the unfilled matrix are recorded in contrast to 140% for disc-shaped inclusions.

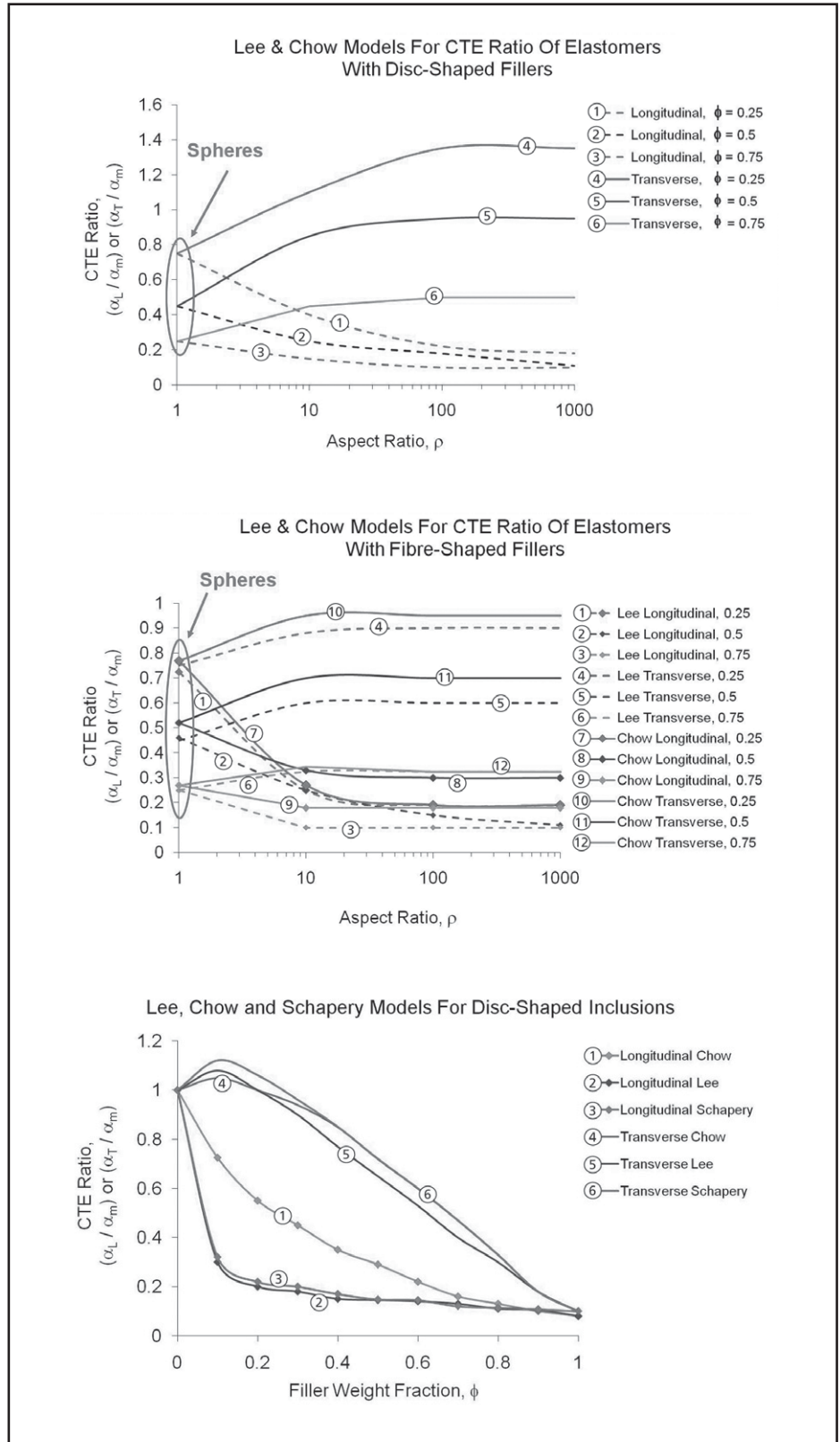


Figure 1. Comparison of Schapery,^[8] Lee^[6] and Chow^[2] models as calculated for epoxy resin–glass fibre system, for disc and fibre-shaped inclusions.

- For a spherical filler the thermal expansion coefficients decrease as filler ratio increases due to the dilution of the high CTE matrix with a low CTE filler, which is as may be expected. This relationship is intuitive for all morphologies and follows most closely the rule of mixtures and Schapery's model,^[8] both of which predict this scenario.
- As the aspect ratio increases, the linear coefficient of thermal expansion in the direction of filler alignment, decreases for all filler fractions, a phenomenon attributed by Lee^[6] to the mechanical constraint the filler provides against the expansion of the matrix.
- However, the transverse coefficient, undergoes the opposite trend of increasing with aspect ratio, as the particle inclusion becomes more needle-like in the direction of expansion. This is most probably because there is progressively less total interfacial surface area between the matrix and the filler particles in the transverse direction, so that the strain caused by increase in temperature is higher in this direction.
- The existence of contrasting thermal expansion behaviour in the longitudinal and transverse directions implies a much smaller effect on the volumetric expansion caused by the inclusions.

Comparing all three models the following trends are most apparent:

- In both the Lee and Schapery models the longitudinal expansion coefficient falls sharply from 1.0 to 0.2 over the first 20% of filler loading by weight. This is contrasted by little net change in the corresponding transverse coefficient at 20% loading, although the latter shows an intermediate spike to 1.1 at a loading of 5% filler, decreasing monotonically to unity as filler is raised to 20% w/w.
- The Chow model is distinct from the other two models in two significant respects: (a) The longitudinal curve is much higher, predicting greater CTE at all filler volume fractions, and (b) the transverse curve, while converging with that of Schapery for $0.35 < \Phi < 1.0$, does not exhibit the same local maximum at $\Phi = 0.05$ as the other two models.

It is not clear why the Chow model should diverge in these ways from the other two models, especially why it should exhibit more similarity with Schapery's model than Lee's which is more closely related in derivation and structure to it. It is clear however, that there is limited scope for reduction of volumetric thermal expansion coefficient by means of employing fibre or disc-shaped inclusions, since any reduction achieved in a longitudinal direction would be counter-acted by a persisting degree of expansion in the transverse direction. In contrast, there is a very obvious advantage to using spherical particles for the reduction of CTE.

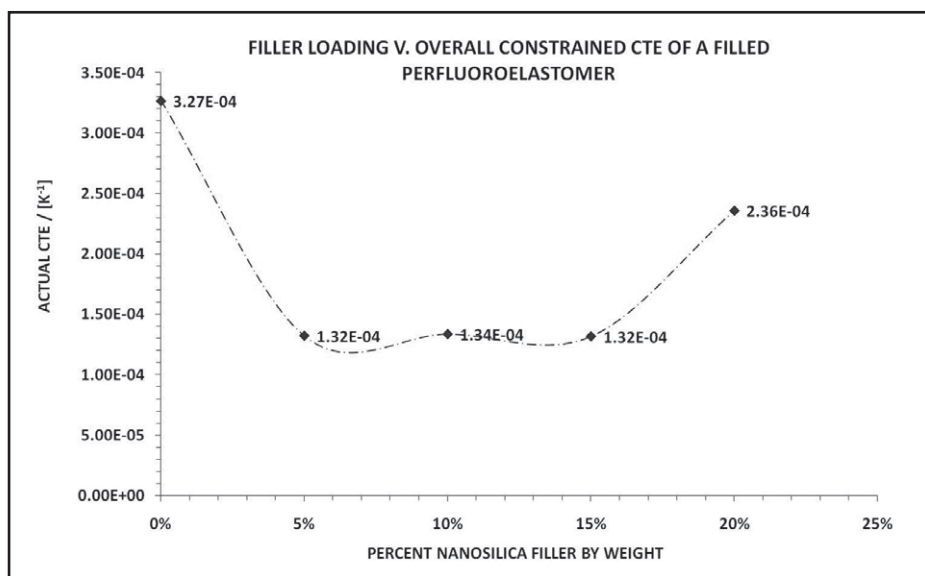


Figure 2. Filler loading versus overall constrained thermal expansion coefficient of perfluoroelastomer.

Experiments on a filled constrained perfluoroelastomer

The constrained thermal expansion of a typical perfluoroelastomer composition filled to different fractions with a high surface area amorphous silica nanofiller was investigated by experiment at PPE. A standard perfluoroelastomer base polymer filled to a known level with silica filler was moulded as an O-ring with a diametrical cross-section of 5.33 mm. Four silica loading levels were used, 0, 5, 15 and 20% w/w, respectively. A known length of O-ring was sectioned and inserted into a cavity of 5.34 mm in a brass test barrel, and the test cavity then sealed. The barrel was mounted vertically in a tensometer, within a heated chamber at thermal equilibrium of 298K. A piston was inserted into the other end of the cavity, until a minimum

reactive force of 1–2 N was registered on the tensometer, the force was then zeroed. The temperature within the chamber was increased at 5K per minute. The absolute strain in millimetres of the test piece expanding against the piston was recorded by the tensometer software as the temperature rose and a curve of temperature v. instantaneous thermal expansion coefficient was generated by calculation. The overall thermal expansion coefficient was also calculated from the data.

Results

The overall thermal expansion coefficients calculated as averages over the entire temperature range 293–473K for the four filled perfluoroelastomer mixes were recorded as illustrated in Figure 2.

This shows that the data follows the same general trend as the models of Lee and

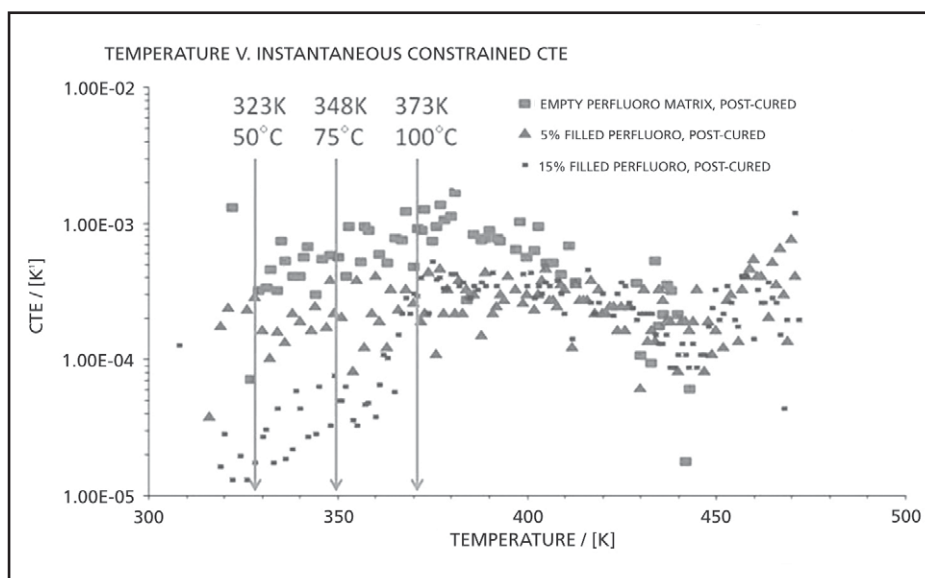


Figure 3. Instantaneous coefficient of thermal expansion of constrained silica-filled perfluoroelastomer mixes.

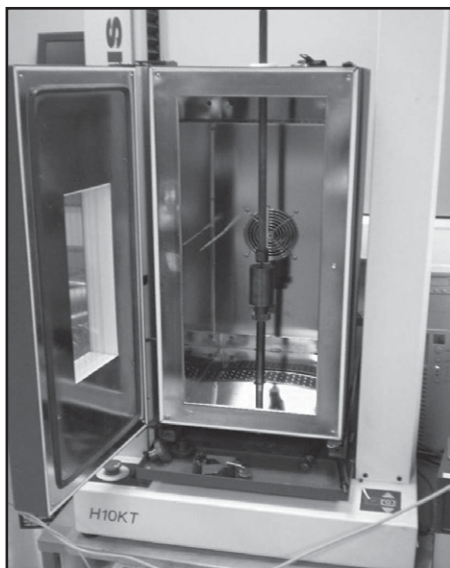


Figure 4a. General view of the thermal expansion cell in the oven.

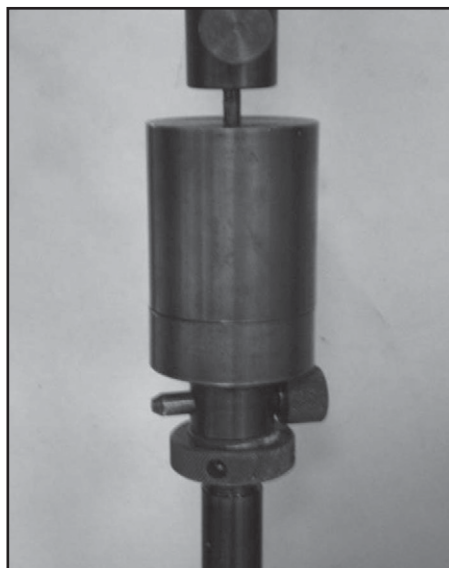


Figure 4b. Close-up of the cell for measuring thermal expansion coefficient.

Schaperly in Figure 1, indicating broad agreement with the literature. Implementing logarithmic and linear regression formulae on the data does not demonstrate a no close relationship between the overall thermal expansion coefficient and filler fraction. However, if the results for $\Phi = 20\%$ are excluded the data for $0\% < \Phi < 15\%$, provides a closer fit to an exponential model.^[10]

The increased thermal expansion coefficient at $\Phi = 20\%$ could be due to a failure of the interface between matrix and filler where the latter is present in excess. The response of instantaneous thermal expansion coefficient to temperature for the same constrained expansion experimental data is plotted in Figure 3, for three of the five perfluoroelastomer batches containing 0, 5 and 15% amorphous silica filler, respectively.

It can be seen that increased silica loading results in lower values of instantaneous thermal expansion coefficient, especially below a temperature of 373K, where a clear difference in CTE exists between all three batches.

A multifactor logarithmic and linear regression analysis of the instantaneous thermal expansion coefficient data with respect to the factors temperature and filler fraction does not provide any clear linear or logarithmic relationship, implying the effect of a more complex set of factors on the thermal expansion behaviour of these mixes. By taking vertical sections of the data at different temperatures and examining the effect of increased filler loading at constant temperature a more meaningful examination is possible. Thus at 323K a reduction in instantaneous CTE is observed from $4.0 \times 10^{-4}/\text{K}$ at $\Phi = 0\%$, to $1.05 \times 10^{-4}/\text{K}$ at $\Phi = 5\%$, to $1.05 \times 10^{-5}/\text{K}$ at $\Phi = 15\%$. Implementing a fit in this way to these three filler loadings at representative temperatures

can provide indicative models for instantaneous thermal expansion coefficient.^[10]

This analysis exhibits two trends:

- The empty perfluoroelastomer matrix has a CTE at 323K which is half that of the common value it exhibits at 348 and 373K, i.e. a pre-exponential constant of $4.0 \times 10^{-4}/\text{K}$ as compared against $8.0 \times 10^{-4}/\text{K}$.
- The magnitude of the exponential decay, as shown by the coefficient of Φ in the three equations, falls significantly with temperature, confirming that the suppression of instantaneous CTE with increased filler loading becomes progressively less effective with increasing temperature.

This demonstrates that there is a suppression effect of increased filler loading on instantaneous thermal expansion coefficient in the temperature range 298–373K. It appears that the restraining effect of filler on the expansion of the elastomer mixture is most effective at lower temperatures, whereas at higher temperatures, it is largely ineffective. This could be because restriction on expansion behaviour is shear-dominated by the silica filler in the lower temperature range, but limited by the micro-molecular structure of the polymer molecule matrix over the higher temperature range, where the shear effect of the filler phase has been overcome.

Conclusions

The effect of filler loading on the thermal expansion of unfilled and filled perfluoroelastomers has been quantified by experiment, using an amorphous inorganic nano-filler. It has been shown that an optimum filler loading of between 5 and 15% w/w amorphous silica nano-filler

reduces the overall thermal expansion coefficient of an FFKM formulation from $9.88 \times 10^{-4}/\text{K}$ to $3.35 \times 10^{-4}/\text{K}$. This implies there is no additional benefit of increasing filler to quantities in excess of 15% w/w unless other properties can be improved. Furthermore, it has been found that for filler loadings to 15% w/w, the largest filler-caused reduction in instantaneous thermal expansion occurs at temperatures less than 373K, with the effect diminishing to insignificance above this temperature. This may indicate that thermal expansion behaviour in filled perfluoroelastomer grades at higher temperatures is controlled by polymer structure rather than filler loading.

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