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Thermal and Thermoelastic Properties of Fast Extrusion Furnace (FEF) Carbon Black Loaded SBR Vulcanizates

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Abstract: The effect of FEF carbon black as filler on the thermal capacity c, diffusivity a, and thermal conductivity λ, of styrene butadiene rubber (SBR) composites in the temperature range 300–420 K was studied. The filler strongly increases the thermal diffusivity, whilst strongly decreasing the thermal capacity and the thermal conductivity (except at high FEF content ≥ 80 phr).

The influence of the filler on the thermoelastic behaviour of the same composites was also investigated. It was found that the thermoelastic temperature change (ΔT) increased with carbon black concentration as well as the entropy change per unit extension.

Key words: thermal properties, fast extrusion furnace carbon black, rubber, thermoelastic properties, vulcanizate.

INTRODUCTION

Since physical changes in a polymer cause the thermal properties to change, thermal measurement can be used in polymer research to help to understand polymer structure–property relationships.

One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the physical mechanisms which determine these properties.

With the continuing effort to conserve energy, heat transfer properties of elastomers, additives and vulcanizates are attracting more attention throughout the rubber industry. Heat is the most important processing agent both in the manufacture of raw elastomers and in fabricating them to finished product. The rate at which heat can get into and out of rubber, i.e. its thermal conductivity, controls many applications, affects the design of processing machinery and controls the speed of many mixing, extruding and moulding processes.[1]

The measurement of thermal properties of polymeric materials and rubber composites has attracted the attention of many workers.[2–5] The thermoelastic effect, which was predicted by Thomson[6] and measured in iron and rubber by Joule[6] is an interesting field of research.[7–10]

Following a series of experiments aiming to study the effect of different parameters, such as mixing process

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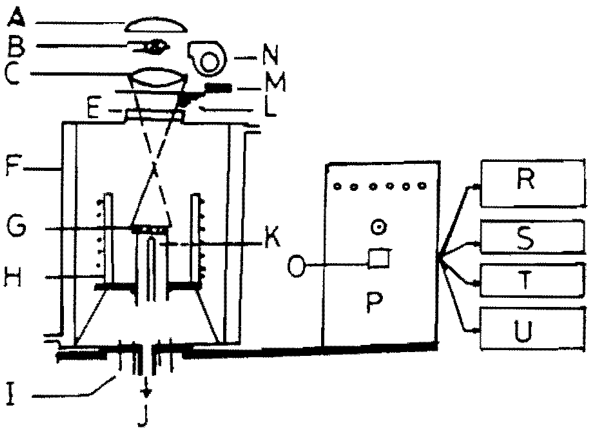

Fig. 1. Set-up used for fully automated measurements of thermal conductivity, diffusivity and thermal capacity. A, Reflector; B, lamp; C, lens; E, quartz window; F, stainless steel jacket; G, sample; H, heater; I, spark plugs; J, vacuum line; K, thermocouple; L, photodiode; M, shutter; N, blower; O, counter; P, programmed control unit; R, temperature controller; S, timer; T, DC amplifier; U, Y–t recorder.

and type of filler used, on the thermal properties of some polymeric materials by our group,[11–13] the present work aims to measure the thermal characteristics (thermal diffusivity a, thermal conductivity λ, and thermal capacity c) of a number of SBR (styrene butadiene rubber) samples mixed with different concentrations of FEF (fast extrusion furnace) carbon black, and also to elucidate the effect of dynamic cyclic extension on the thermoelastic effect ΔT of these composites.

EXPERIMENTAL

Specimens in the form of discs 2–3 mm thick and 15–20 mm diameter were used. The apparatus used for the thermal characteristic measurements (using the flash technique[14]) is shown in Fig. 1. One face of the specimen was subjected to a thermal flux produced by a powerful halogen lamp (1 kW) using a time-controlled shutter. The temperature of the second surface was measured by means of a fine thermocouple ($\phi = 0{\cdot}1$ mm) attached by silver paste. The two pens of a double Y–t recorder were attached, one to a photodiode placed underneath the shutter (which detects instantly the flash heating pulse), the other to the thermocouple, which was attached to the back surface of the specimen. Hence, the thermal capacity, diffusivity and conductivity can be computed.

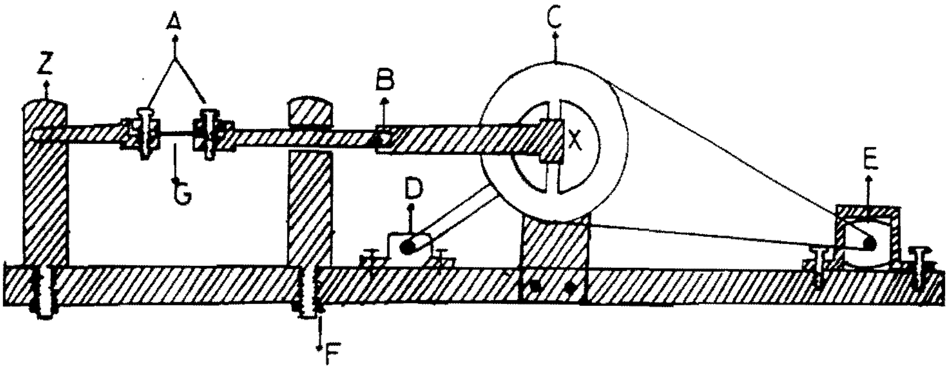

Fig. 2. Schematic diagram of constant strain fatigue tester. A, Clamps; B, joint; C, wheel; D, counter; E, motor; F, fixed nut; G, specimen; X, moveable nut; Z, Teflon rod.

TABLE 1. Formulations of styrene butadiene rubber (SBR) with Concentration (in phr) of FEF carbon black

Ingredients (phr)	Sample				
	S_1	S_2	S_3	S_4	S_5
SBR-1502	100	100	100	100	100
Stearic acid	2	2	2	2	2
ZnO	5	5	5	5	5
Processing oil	10	10	10	10	10
FEF black	—	30	60	80	100
MBTS[a]	2	2	2	2	2
PBN[b]	1	1	1	1	1
Sulphur	2	2	2	2	2

[a] Dibenzthiazyl disulphide.
[b] Phenyl-β-naphthylamine.

The temperature was varied in the range 300–420 K using a fully regulated electric oven. Heat losses due to surrounding cooling effects were minimized by making measurements in a vacuum (10^{-5} Torr) and over a short time interval.

The apparatus was tested using Al_2O_3. The results were in good agreement with published data.[15]

For thermoelastic measurements the rubber specimen was in the form of a sheet, 2·5 cm long, 0·26 cm wide and 0·17 cm thick, clamped at both ends in a holder attached to a cyclic extension fatigue machine (Fig. 2). The temperature of the periodically deformed sample was carefully measured using a calibrated Cu–constantin thermocouple, attached to a microvolmeter with sensitivity of 0·01 μV. Good care was taken during T measurements to ensure thermal insulation of test pieces from the surroundings.

The rubber used in the measurements was SBR, mixed with different concentrations of FEF carbon black (in phr, parts per hundred parts by weight of rubber) as a filler following the recipes given in Table 1. The test specimens were prepared on a two-roll mill, 170 mm diameter, working distance 300 mm and gear ratio 1.4.

The compounded rubber was left at least 24 h before vulcanization, which was conducted at 143 ± 2°C under a pressure of about 40 kg/cm^2 for 20 min.

RESULTS AND DISCUSSION

Thermal properties measurements

Unlike electrical conductivity, thermal energy is transmitted from molecule to molecule by a relatively slow diffusion–excitation process. A coherent theory that explains all aspects of thermal conductivity of polymers is not yet available. Debye[16] postulates that thermal excitation produces quantized elastic waves, or phonon scattering, at lattice imperfections, or other inhomogeneities. Intramolecular energy transfer is more efficient than intermolecular transfer since less phonon scattering is expected through covalent bonds than through the van der Waals type. Tightness of the bonds, or arrangement of the molecules, thus promotes thermal conductivity. A somewhat different approach has been advanced by Morgan & Scovell.[17] These authors postulate the existence of one-dimensional wave packets, which travel along the chains and have long mean-free paths. The wave packet may be scattered by chain ends, crosslinks, or interactions with other molecules.

Figures 3–5 present detailed results for the dependence of thermal capacity c, thermal conductivity λ, and thermal diffusivity a, on temperature, respectively, for the mixed rubber composites. As can be judged from Figs 3 and 4, the addition of FEF carbon black (as a filler) strongly lowers the thermal capacity c and the thermal conductivity λ. Meanwhile, it increases the thermal diffusivity a (Fig. 5). Figure 6 shows that the thermal conductivity λ of the SBR samples decreases with increasing carbon black concentration (at 300, 360 and 400 K) up to 80 phr with different sensitivities; at

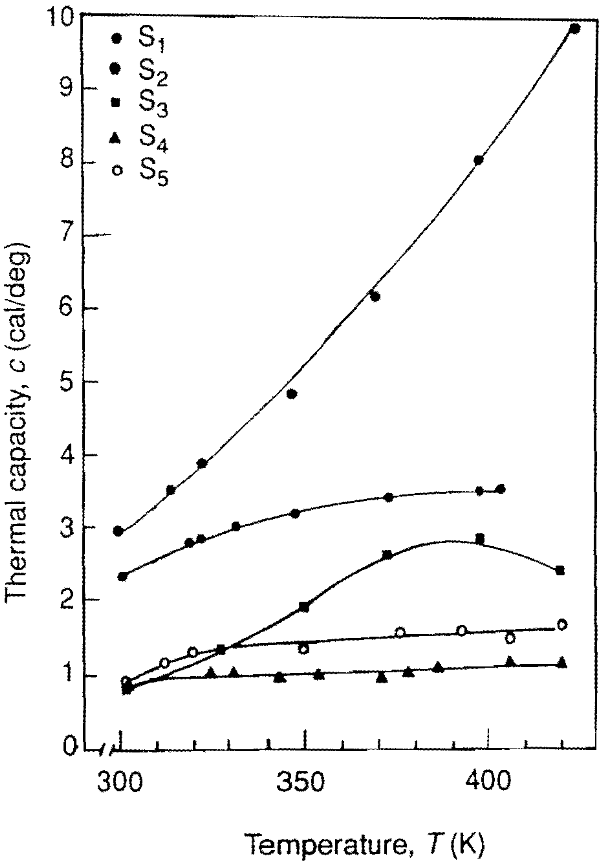

Fig. 3. Dependence of thermal capacity c on temperature for FEF/SBR composites.

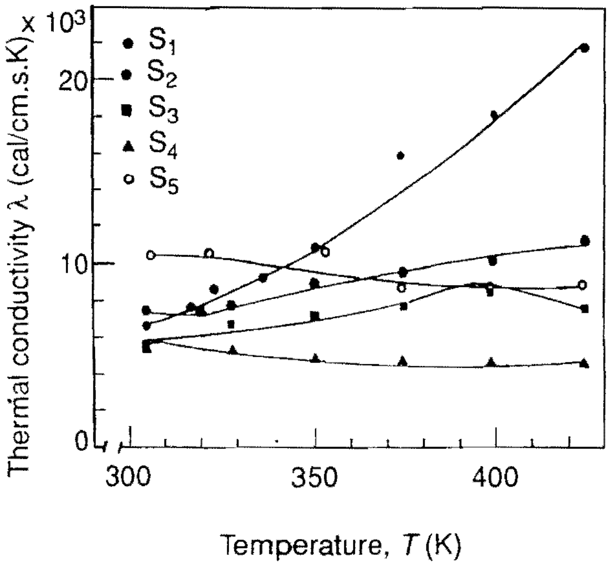

Fig. 4. Dependence of thermal conductivity λ on temperature for FEF/SBR composites.

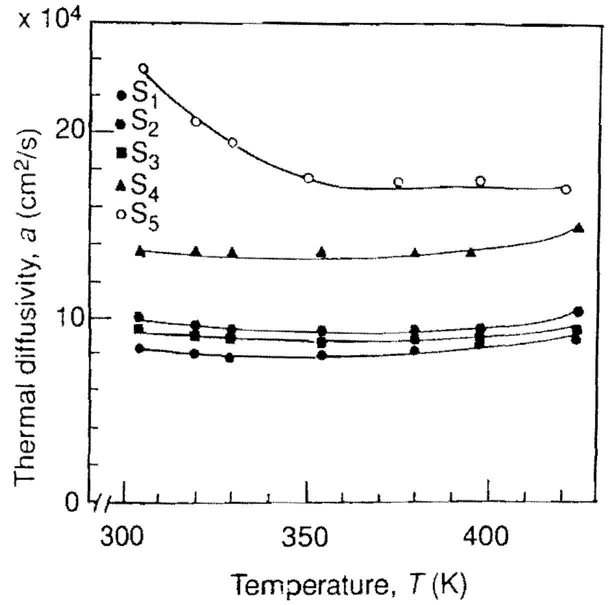

Fig. 5. Dependence of thermal diffusivity a on temperature for FEF/SBR composites.

high concentration (80 phr), λ begins to increase to the same extent in all cases. Sircar & Welss[1] support Gehman's contention[18] that the λ value of a composite is an assumed value in a particular recipe and not an additive function of the λ values of the components. This is clearly shown by the dependence of λ on FEF content in Fig. 6. This seems logical since carbon black conductivity depends on the polymer. It is now universally accepted that the transient (secondary) structure of carbon black varies with the nature of the polymeric medium.[19] This is expected to affect the thermal conductivity λ, as well as c and a.

Most of the processing operations in the rubber industry are done at temperatures between 100 and 160°C. Thermal conductivity values at higher temperatures are, therefore, more relevant to practical processing operations. Thermal conductivity, diffusivity and thermal capacity for unfilled samples are highly affected by temperature. In general, thermal conduction mechanisms in polymers filled with highly conductive particles vary with the volume content of particles and can be classified into two types. One is a system with low content of FEF filler particles (≤ 60 phr) in which dispersed particles hardly touch each other (dispersed system). The other is a system with higher content (≥ 80 phr of FEF) in which conductive chains are exponentially formed by particles (attached system). In the dispersed system, both λ and c increase with temperature, which is in accord with the theory of heat conduction in a glass, proposed by Klemens.[20] Over most of the temperature range (300–430 K) the phonons are scattered by the disordered, amorphous structure resulting in a constant mean-free path and a thermal conductivity proportional to the thermal capacity. In the attached system, λ of these composites decreases slightly with temperature, whilst c is independent of temperature. The slight decrease in λ with temperature is because the conductive chains formed are cut, or shortened, when thermal expansion of the polymer increases the distance between FEF particles.[21] The slopes in Figs 3 and 4 are steeper for the unfilled samples than the filled ones, and a relatively independent behaviour of a, λ and c on temperature was detected for carbon black concentrations of 60, 80 and 100 phr, which reflects the stable carbon black network configuration at each concentration.

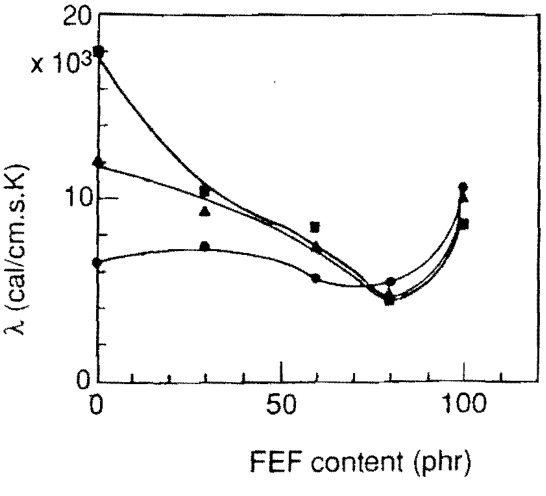

Fig. 6. Dependence of thermal conductivity λ on FEF content at ●, 300 K; ▲, 360 K; ■, 400 K.

Thermoelastic measurements

The temperature change that occurs when any Hookian solid is subjected to stress is known as the thermoelastic effect. The explanation of this effect is very simple, and follows directly from the basic concepts of kinetic theory, namely that the deformation of rubbers (at constant temperature) is associated with a reduction of entropy. The internal energy of a deformed rubber sample is purely kinetic and arises from the thermal agitation of the constituent atoms of the chains. This energy is a function of temperature only and is independent of the conformations of the chains, i.e. of the state of strain. Since the internal energy does not change, the work performed by the applied force in an isothermal deformation must be balanced by the emission of an equivalent amount of heat. If this heat is not emitted, but is retained, as in an adiabatic extension, the energy supplied by the applied force is used to increase the agitation, i.e. to produce a rise in temperature. The temperature rise is, therefore, $-\mathrm{d}Q/c_1$, where c_1 is the thermal capacity at constant length and $-\mathrm{d}Q$ is the equivalent heat emission for an incremental extension $\mathrm{d}l$ at constant temperature. Since the process is reversible we may put $dQ = T\,ds$ and hence obtain the entropy change per unit extension:

$$\frac{ds}{dl} = \frac{c_1}{T}\frac{dT}{dl} \qquad (1)$$

where c_1 is the thermal capacity of the composite, T is the ambient temperature, and dT/dl is the temperature change per unit extension.

In previous work,[22] some factors (e.g. amplitude and duration of dynamic cyclic strain) affecting the thermoelastic behaviour of 100 phr FEF carbon black loaded in different types of rubber (natural rubber, butyl rubber, butadiene rubber, styrene butadiene rubber and acrylonitrile butadiene rubber) were studied separately. It was found that an increase in the amplitude and duration of cyclic stress led to an increase in the thermoelastic temperature change ΔT. Moreover, the effect of frequency on the thermoelastic temperature change ΔT showed a linear proportionality for all rubber composites at constant strain amplitude (50%).

Figure 7 is a representative example for the temperature change ΔT, as a function of the duration of the periodic strain (at 22 Hz) at different strain amplitudes for 100 FEF/SBR samples. On applying periodic strain, the temperature change to a stable value depended on the applied strain amplitude. The experimental results were fitted to an empirical equation of the form

$$\Delta T = \Delta T_m\{1 - \exp(-t/\tau)\} \qquad (2)$$

where ΔT_m is the maximum attainable increase in the sample temperature and τ is a characteristic time. The value of T_m was found to be directly related to the applied strain amplitude through the relation

$$\Delta T_m = \alpha\varepsilon \qquad (3)$$

where the proportionality constant α was found to be a function of the carbon content in the rubber used. The fitting parameters ΔT_m, and the values of the coefficient τ for 100 FEF/SBR samples are given in Table 2. As the strain amplitude increases, the concentration of ruptured bonds together with free radicals increases, leading to intensified friction between particles and consequently to the observed rise in thermoelastic temperature change, as shown in Fig. 7.

TABLE 2. Values for T_m and τ in eqn (2) at different strain amplitudes for 100 FEF/SBR

ε	T_m (K)	τ (s)
0·1	5·5	14·3
0·2	12·5	13·5
0·3	19·0	12·5
0·6	24·5	8·2

Equation (1) may be used to calculate the change of entropy per unit extension in terms of the thermal capacity c_1 at constant length and ambient temperature (Table 3).

It was found that the sample temperature increased as the concentration of FEF carbon black increased, as shown in Fig. 8. This may be attributed to the presence of two kinds of bonds between carbon black and rubber, a weak bond and a strong one.[9,23] As a result of these bonds, the free movements of the system are

TABLE 3. Variation of entropy per unit extension with FEF carbon black concentration

Carbon black concentration (phr)	ds/dl (cal/deg)
30	0·89
60	0·683
80	0·93
100	1·32

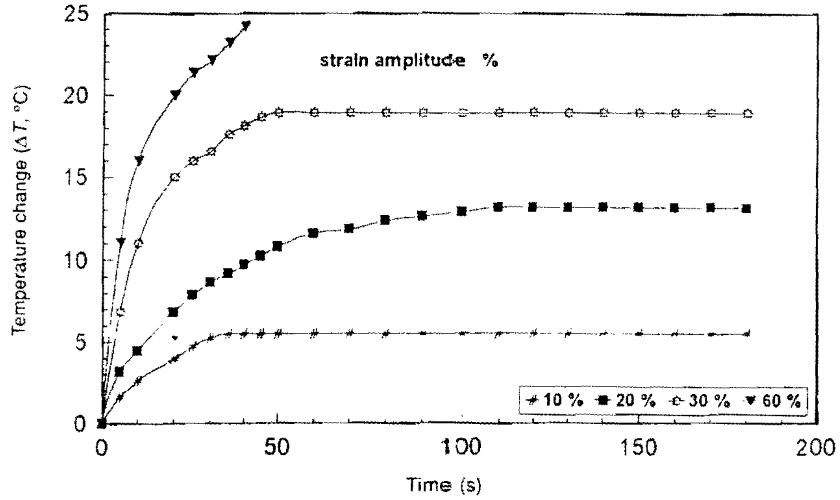

Fig. 7. Dependence of the thermoelastic temperature change (ΔT) for FEF/SBR composites (at constant strain amplitude and constant frequency 22 Hz) on duration of applied stress.

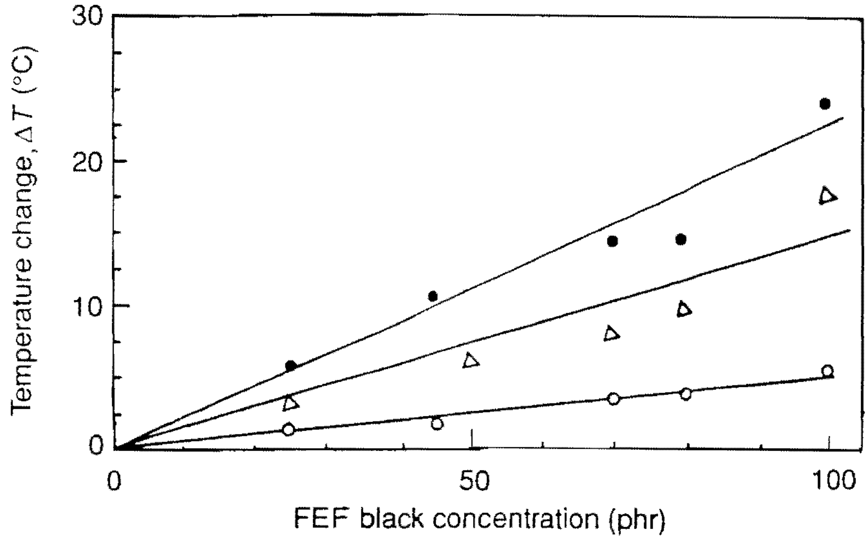

Fig. 8. Dependence of the thermoelastic temperature change (ΔT) on FEF carbon black concentration for SBR at ○, 10% strain amplitude; △, 30% strain amplitude; ●, 60% strain amplitude.

limited by the length of the chain segments in carbon black/rubber molecule bonds. This limitation creates a cohesive force, which in turn resists the applied periodic stress. Accordingly, in the case of strong bonds, the friction between carbon particles and molecules increases as the carbon black concentration increases. This eventually raises the temperature of the sample. Moreover, the weak bonds are ruptured and free radicals are created and set in random motion.

As the strain amplitude is increased the thermoelastic temperature change increases for all carbon black concentrations, as is clearly observed in Fig. 9.

CONCLUSIONS

The measurements carried out in this work lead to the following conclusions.

There is a marked decrease in the thermal conductivity λ on addition of FEF black up to 80 phr. Thereafter, λ increases with increasing FEF content (at 300, 360 and 400 K). Composites with FEF contents greater than 60 phr show almost temperature-independent behaviour of λ, thermal capacity c and thermal diffusivity a in the temperature range 300–420 K.

Thermoelastic experiments dealing with adiabatic heating under application of rapid strain (stress) afford an approach to evaluate the entropy change per unit extension. The increase in amplitude of cyclic stress leads to an increase in the thermoelastic temperature change (ΔT) due to fracture, either in the rubber matrix, or at the interface between the rubber and filler particles. The change of entropy per unit extension increases with FEF content. The effect of the addition of FEF as a filler on thermoelastic effects is linearly proportional for SBR composites.

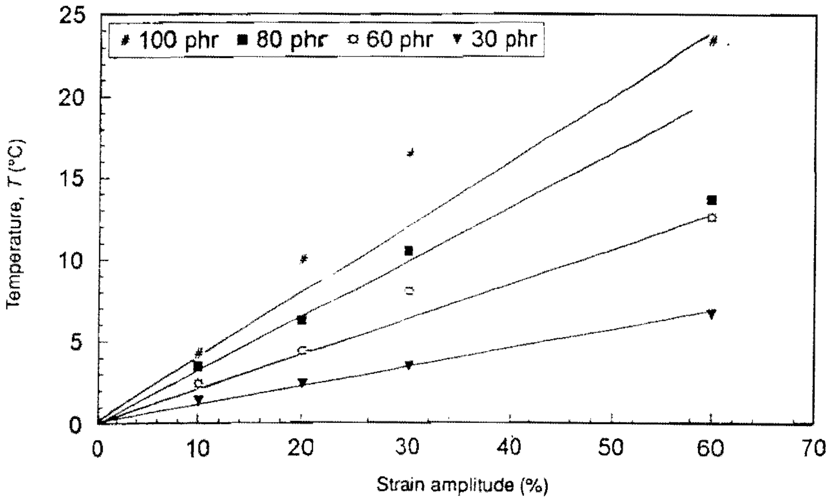

Fig. 9. Dependence of the thermoelastic temperature change (ΔT) on the strain amplitude for different carbon black concentrations.

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