

# Effect of Swelling Process on the Thermoelastic Temperature Change of Ethylene Propylene Diene Rubber Filled with Carbon Black

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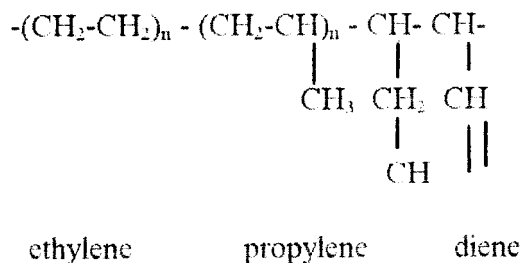
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**ABSTRACT:** The effects of both dynamic cyclic extension and swelling on the thermoelastic behavior of ethylene propylene diene rubber loaded with different concentrations of carbon black have been studied. As the strain amplitude increases, the concentration of the ruptured bonds increases, leading to more enhanced friction between particles and consequently to the observed rise in temperature. Temperature change was found to be highly dependent on the swelling and also on carbon black concentration. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1890–1897, 1999

**Key words:** thermoelastic effect; EPDM; swelling; fracture strength; temperature change

## INTRODUCTION

Ethylene propylene diene polymer (EPDM) has been used in a wide range of applications, so that it can be regarded as a general purpose material. One of the most recent uses of the material is for improved aging rocket<sup>1</sup> insulator compounds, filled with cork, asbestos fiber, and iron oxide. The basic structure of EPDM is represented by the following schematic configuration



Test samples (EH<sub>4</sub>, EH<sub>6</sub>, EH<sub>8</sub>, and EH<sub>10</sub>) were obtained by introducing different concentrations of carbon black HAF (high-abrasion furnace black) in ethylene propylene diene polymer.

Haward and colleague<sup>2</sup> studied the thermoelastic effect in poly(methyl methacrylate) (PMMA) under both tensile and compressive uniaxial stress; the resulting temperature change for a known applied stress has been used to calculate the linear expansion coefficient of PMMA over a range of temperatures from 295 to 355 K and uniaxial stress in the elastic range.

Khairy and Ateia<sup>3</sup> studied the temperature changes resulting from application of periodic strain (deformation), with strain amplitudes up to 60% for styrene butadiene rubber loaded with different carbon black concentrations. The method used involves deformation of the thermoelastic coefficient, change in entropy, enthalpy per unit length, and Gruneisen constant. It is well recognized<sup>4</sup> that the rapid deformation of a solid usually results in a change of its temperature. This rapid deformation is closely related to an adiabatic process, where the heat absorbed or

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**Table I The Physical Properties of Ethylene Propylene Diene Polymer (EPDM)**

Specifications	Vistalon 5600	
	Minimum	Maximum
Mooney viscosity	—	—
ML 1–8 min at 127°C	65	75
Vanadium, ppm	—	100
Ash, wt %	—	0.3
Water, wt %	—	0.5
Average molecular weight	1.89*10 <sup>5</sup>	—
Physical properties		
Tensile strength, MPa	10	—
Modulus, at 300% elongation, MPa	9.5	—
Color	Light gray	
Density at 35°C	0.86 g/ml	
Specific gravity	0.85	
Stabilizer, Nonstaining, wt	0.1	

generated during the deformation changes the temperature of the material. The present study describes the effect of both dynamic cyclic extension and swelling on the thermoelastic effect in ethylene propylene diene loaded with different concentrations of carbon black.

## EXPERIMENTAL

### Sample Preparation

Samples of ethylene propylene diene polymer (EPDM), filled with different concentrations of HAF carbon black, were used in this study. Its commercial name is Vistalone 5600. The physical properties of such commercial rubber<sup>5</sup> are listed in Table I. The rubber and other conventional additives were mixed according to the recipe illustrated in Table II. The usual ethylene content is 40 to 60%. A small proportion of diene, such as cyclopentadiene, cyclo-octadiene, or norbornadiene, yields a terpolymer that can be vulcanized with sulfur. The test samples were prepared on a two-roll mill (170-mm diameter), with a work distance of 300 mm and a slow roll speed of 24 rpm and gear ratio 1.4. The rubber composites were left for 24 h before being vulcanized at 152°C and pressure about 1.17 MPa were fixed for an optimum time of 20 min.<sup>6,7</sup> All materials used in this work were supplied from the Transport and Engineering Company (TRENCO; Alexandria, Egypt).

### Temperature Change Measurement

The cyclic fatigue machine used was discussed in a previous work.<sup>8</sup> Test samples were in the form of sheets of about 3 cm in length, 0.3 cm in width, and 0.2 cm in thickness. For experimental measurements, the specimen was clamped at both ends in a constant deformation fatigue tester. It was subjected to a given number of strain cycles of constant amplitude (ranging from 10 to 90%). The change in temperature (for every constant amplitude) was measured during cycles by using a copper–constantan thermocouple with one junction fixed at the middle of the major surface and the other attached to a *k*-type microvoltammeter

**Table II Composition of EPDM Samples with Different Carbon Black Concentration**

Ingredients (phr) <sup>a</sup>	Samples			
	EH4	EH6	EH8	EH10
EPDM	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	2	2	2
Processing oil	50	50	50	50
HAF Carbon black	40	60	80	100
MBTS <sup>b</sup>	1.5	1.5	1.5	1.5
TMTD <sup>c</sup>	2	2	2	2
Sulfur	3	3	3	3

<sup>a</sup> phr = part per hundred parts of rubber by weight.

<sup>b</sup> Dibenzothiazyl disulfide.

<sup>c</sup> Tetramethyl thiuram disulfide.

with sensitivity of 0.1 degree. Good care was taken during temperature change measurements to ensure thermal insulation of the test samples from the surroundings. The frequency of the fatigue tester was 17.2 sec<sup>-1</sup>.

### Sorption Measurements

Rubber blends were weighed and inserted into a test tube containing motor oil at 25°C. The rubber blends were removed from the solvent and blotted with filter paper to remove excess solvent on the surface of the sample. The rubber blends were then weighed to an accuracy of 0.1 mg at a given time and at a fixed temperature. The weight change was calculated by using the gravimetric method<sup>9</sup>

$$M_t = [(W_t - W_d)/W_d]/100 \quad (1)$$

where  $M_t$  is the percent mass of solvent absorbed at time  $t$ ,  $W_d$  is the dry weight, and  $W_t$  is the weight of swollen sample with time.

## RESULTS AND DISCUSSION

### Effect of Amplitude and Duration of Dynamic Cyclic Strain on the Thermoelastic Behavior of EPDM: *Before Swelling*

The temperature change that occurs when any Hookean solid is subjected to stress is known as the *thermoelastic effect*.<sup>10</sup> It was predicted by Thomson<sup>11</sup> and measured in iron and rubber by Joule.<sup>11</sup> The internal energy of a deformed rubber sample is purely a kinetic phenomenon 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, that is, of the state of strain. Since the internal energy does not change, the work performed by the applied force is an isothermal deformation that 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, that is, to produce a rise in temperature. The temperature rise is therefore  $(-dQ/C_l)$ , where  $C_l$  is the heat capacity at constant length and  $(-dQ)$  is the equivalent heat emission in an incremental extension  $dl$  at constant temperature.

Since the process is reversible, we may write  $dQ = T ds$  and hence obtain

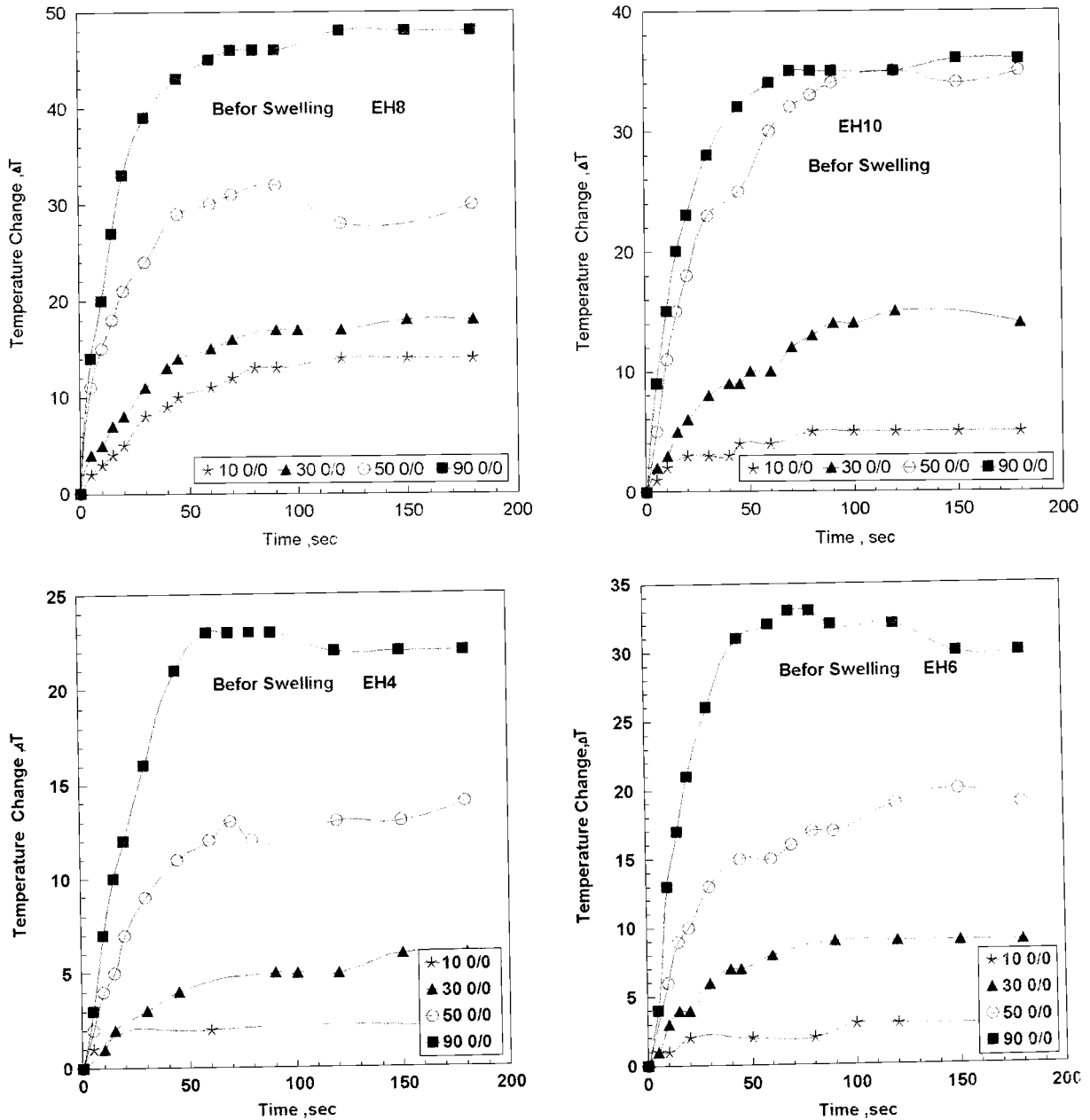
$$(ds/dl) = C_l/T(dT/dl) \quad (2)$$

Equation (2) gives the entropy change per unit extension in terms of heat capacity, which is, at the same time, equal to the temperature coefficient of tension at constant length  $(-df/dT)_l$ . It is to be noted that the change of heat capacity with carbon black concentration for all rubber composites is slight.<sup>12</sup>

Let us now try to follow the effect of the duration of stress time ( $t$ ) on the thermoelastic temperature changes for ethylene propylene diene loaded with different concentrations of carbon black, as shown in Figure 1. All samples show the same trend that the heat generated by cycling was a consequence of the creation of free radicals, which undergo random motion. This motion gives rise to the additional kinetic energy of the segments and hence to the rise in the temperature of the sample. This means that responsibility for the fracture either in the monomer matrix or at the interface between monomer and filler particles depends on the rubber type.<sup>13</sup> After a number of cycles, the temperature within the sample becomes nearly constant since the rate of heat generated is eventually balanced by the heat loss due to radiation and convection from the surface of the sample.

As shown in Figure 2 (deduced from the previous curve in Fig. 1), at constant time (120 sec), when the strain amplitude increases, the concentration of the ruptured bonds together with the free radicals increases, leading to intensified friction between particles and consequently to the observed rise in thermoelastic temperature change. By using eq. (2), one can calculate the change of entropy per unit extension, in terms of both heat capacity at constant length and ambient temperature. The thermoelastic temperature changes for EPDM samples with different carbon black concentrations are calculated from the slopes of Figure 2. These results show the simultaneous increase<sup>14</sup> of  $(ds/dl)$  according to carbon black concentration, except for the EH10 sample. This anomalous behavior of EH10 may be due to the closer packing of the filler particles.

It is impossible to know whether the observed temperature change is due to the magnitude of the strain amplitude or to the cycling process.<sup>6</sup> It may be assumed that the change in heat generated in the specimen during a cycle is related to the breakdown and reformation of structure during each cycle.<sup>6</sup>



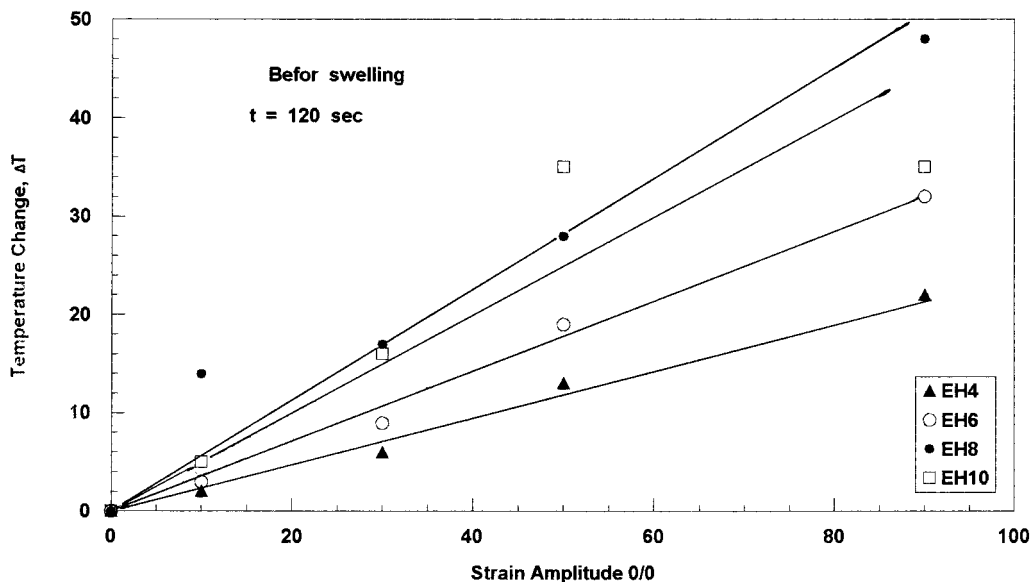
**Figure 1** Dependence of the thermoelastic temperature change ( $\Delta T$ ) at various strain amplitudes (%) on the duration of stress time ( $t$ ) for EPDM samples loaded with carbon black.

The breakdown is negligible at low-strain amplitude, and the reformation of the structure is negligible at higher amplitude (because it takes a long time).

**Effect of Carbon Black Concentration on the Thermoelastic Effect for EPDM Samples**

The thermoelastic temperature change in the periodically deformed EPDM sample was investigated as a function of carbon black filler concen-

tration. It was found that the sample temperature increases as the concentration of carbon black increases, as shown in Figure 3, which is taken from previous curves at constant time ( $t = 120$  sec), and constant amplitude (50%). This may be attributed to the nature of HAF carbon black<sup>15-16</sup> and also to the presence of two types of bonds between carbon black and rubber, a weak bond and a strong one.<sup>17</sup> As a result of these bonds, the free movement of the system is limited by the

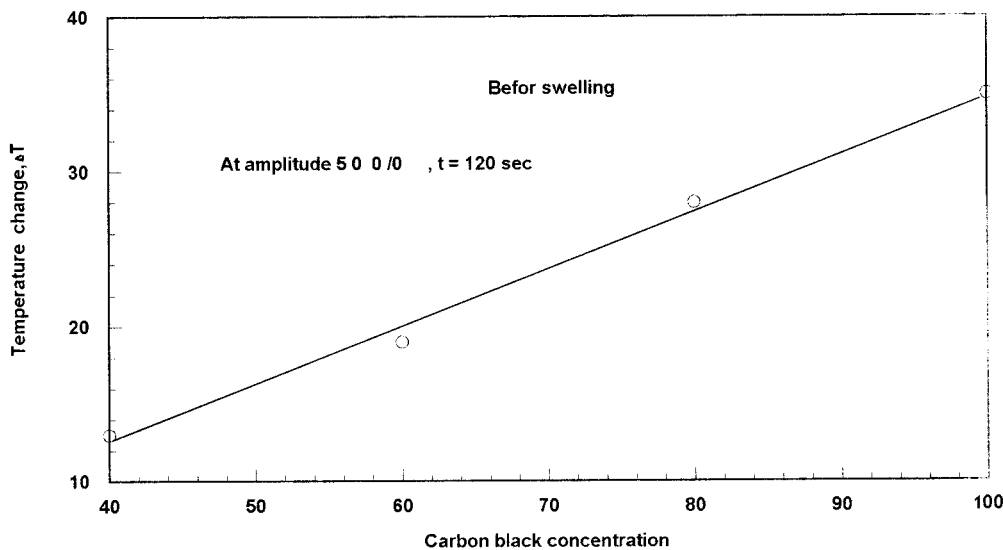


**Figure 2** Dependence of the thermoelastic temperature change ( $\Delta T$ ) on the strain amplitude at constant time (120 sec) for EPDM samples loaded with carbon black.

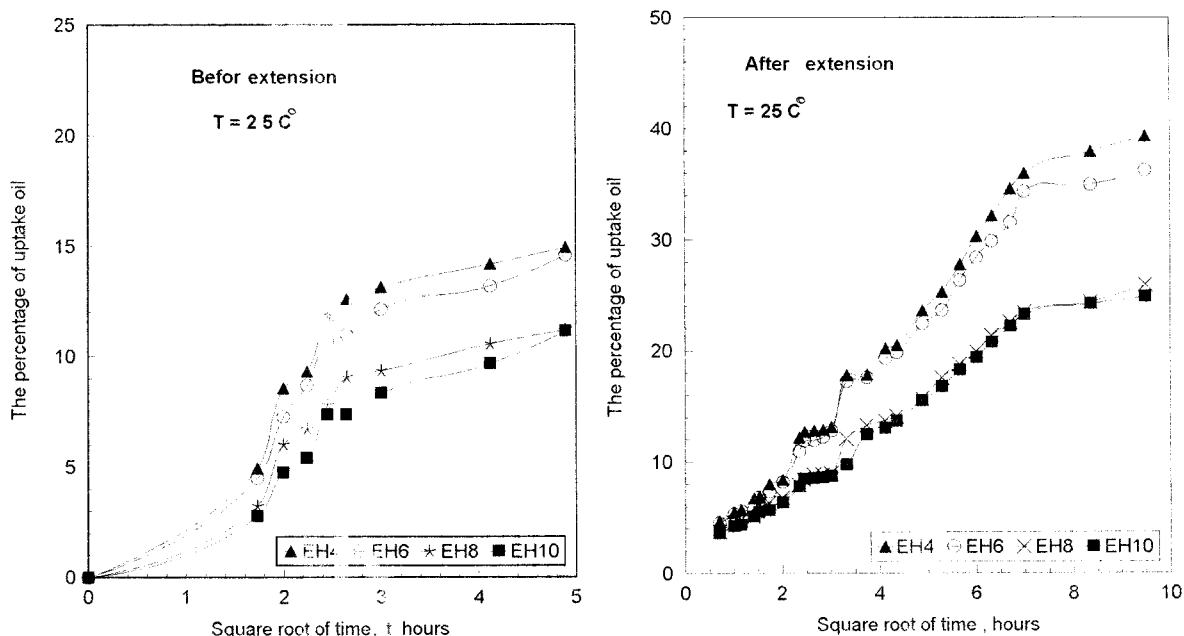
length of the chains. This limitation creates a cohesive force that, in turn, resists the applied periodic stress. Accordingly, in the case of strong bonds, the friction between carbon particles and molecules increases as carbon black concentration increases. This eventually raises the temperature of the sample. Moreover, the weak bonds are ruptured and free radicals are created and set in random motion. This also gives a contributes to the heat developed in the rubber matrix during the periodic deformation.

**Effect of Swelling on EPDM Samples Loaded with Different Concentrations of Carbon Black**

From a practical point of view,<sup>18</sup> it is very important to know the capacity of crosslinked polymer for swelling in various liquids. This capacity is assessed by the degree or amount of swelling, which is expressed as the amount of liquid sorbed by unit masses or volume of a given polymer. The degree of swelling may be taken as a measure of the degree of crosslinking. The percentage in-



**Figure 3** Dependence of the thermoelastic temperature change ( $\Delta T$ ) on the carbon black concentration for EPDM samples.



**Figure 4** Solvent uptake percent versus square root of time for EPDM loaded with carbon black.

crease in weight for all fresh samples, due to swelling in motor oil, is plotted against the square root of time in  $\text{min}^{1/2}$ . The curve is shown in Figure 4(a), the general features of which show that the linear region goes through the origin as expected for Fickian behavior. Figure 4(b) shows the same curve but for strained samples, which shows the same trend as fresh samples but with a higher level of solvent uptake. This may be attributed to the straining process causing degradation and destruction of the crosslinking rubber, leading to increases in the penetration rate of the solvent in rubber matrix. However, the increase in maximum equilibrium uptake of solvent (as obtained from the maximum point of the curves) is inversely proportional to carbon black concentration. This could be attributed to the nature of HAF carbon black used, which is distinguished by its fine particle size and its high ability to make aggregates.<sup>15-16</sup> This means that the penetration of oil into the matrix is difficult since these aggregations inhibit the diffusion of the oil molecules into the rubber matrix. The effect becomes clearer with increasing the black content, since the majority of pores disappear and the whole matrix looks like a solid block.

In order to investigate the mechanism of solvent transport in the polymer matrix we studied the relation between  $M_t$  and  $M_\infty$  according to eq. (3):

$$M_t/M_\infty = kt^n \quad (3)$$

where  $M_\infty$  is the percent mass of solvent absorbed at equilibrium time, and  $k$  is a constant that depends on the structural characteristics of polymer in addition to its interaction with solvent.<sup>19</sup> The value of  $n$  indicates the type of the diffusion mechanism. From a least squares analysis of the  $\log(M_t/M_\infty)$  data versus  $\log t$ , the values of  $k$  and  $n$  have been obtained and are included in Table III.

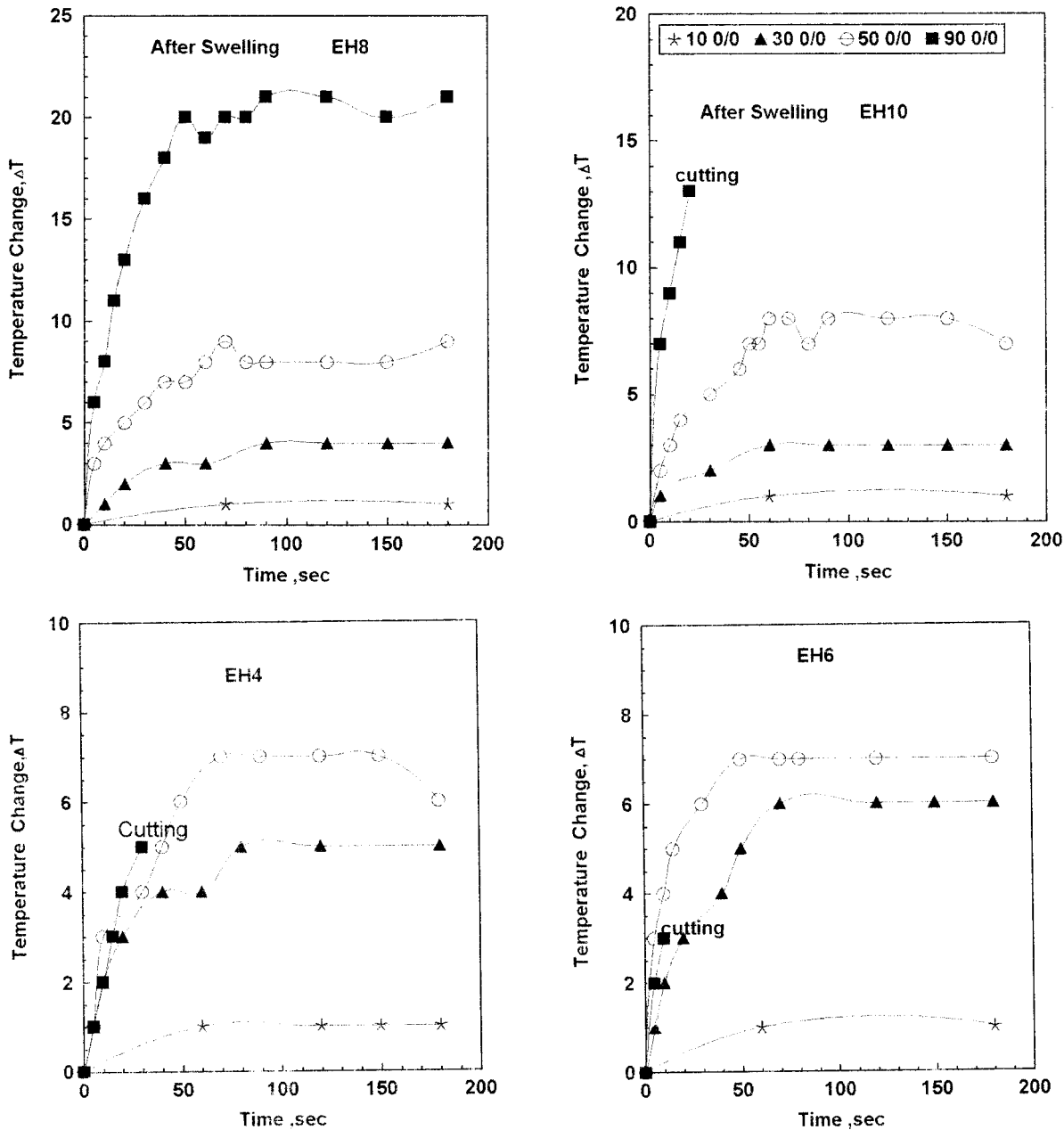
The values of  $n$  in all samples are found to be around  $0.49 \pm 0.02$ , which means that Fickian diffusion is implied. On the other hand, the values of constant  $k$  are highly dependent on the carbon black concentration. A decrease in  $k$  with increasing concentration of carbon black means that the excess of carbon acts as a reinforcing agent to resist the deformation or degradation that occurs in the polymer matrix during the swelling process.<sup>20</sup>

The value of the mutual diffusion coefficient  $D$ <sup>21</sup> can be calculated from the initial slope  $\theta$  of the sorption curves as

**Table III** Represent the Calculated Values of  $n$ ,  $k$ , and Diffusion Coefficient of EPDM Samples

Samples	$n$	$k \times 10^2$ (g/g min <sup>n</sup> )	Diffusion Coefficient, $D \times 10^8$ (cm <sup>2</sup> sec <sup>-1</sup> )
EH4	0.47	6.1	3.88
EH6	0.51	5.9	3.37
EH8	0.48	5.6	1.49
EH10	0.51	5.0	0.95





**Figure 5** Dependence of the thermoelastic temperature change ( $\Delta T$ ) at various strain amplitudes (%) on the duration of stress time ( $t$ ) for EPDM samples loaded with carbon black (after swelling).

$$D = \pi(h\theta/4M_m)^2 \tag{4}$$

where  $h$  is the sample's thickness and  $M_m$  is the maximum equilibrium uptake of the solvent by 100 gm of the polymer sample. The calculated diffusivity data for all carbon black concentrations are given in Table III, the general trend of which reflects the tendency of carbon black to form aggregates, and thus delays the oil molecules from penetrating inside the matrix.

**Effect of Amplitude and Duration of Dynamic Cyclic Strain on the Thermoelastic Behavior of EPDM Samples: After Swelling**

Swelling decreases the strength of rubber in different ways, depending on the type of rubber,<sup>22</sup> the type of swelling liquid, and the nature of interaction between the rubber and liquid.<sup>23</sup> It is obvious that in a first step, when samples are subjected to dynamic cyclic strain, this increases

the flexibility of a chain and also leads to breakdown of bonds. In a second step, samples were subjected to the swelling process in motor oil in which the solvent molecules diffuse into the rubber matrix and cause weakness and rupture of rigid chains.<sup>9</sup> Decreasing the crosslink density, as a result of the first step, increases the ability of the rubber to swell. In other words, the movement of molecules is now easier; that is, molecules do not need high energy to jump from one equilibrium site to another and the rubber is susceptible to degradation.

The effect of the duration time ( $t$ ) on the thermoelastic temperature change for swelled EPDM loaded with different concentrations of carbon black is shown in Figure 5. All swelled samples have the same trend as before, but show a decrease in fracture strength and in temperature change with respect to unswelled samples shown in Figure 1. This decrease may be attributed to the rupture of most bonds and chains that are responsible for the creation of the temperature change, and already done in the earlier steps (1 and 2) on the sample. Also the solvent is diffused into the rubber matrix and forms insulating clusters around the carbon black particles or aggregates,<sup>24</sup> where clusters hinder the motion of free radicals, leading to decrease in temperature change.

## CONCLUSIONS

1. It may be concluded that, for all these rubber composites, before swelling, the increase in amplitude and duration cyclic stress leads to an increase in the thermoelastic temperature change ( $\Delta T$ ) due to fracture either in the rubber matrix or at the interface between polymer and filler particles.
2. The calculated values of diffusion coefficient for swelled samples decreases with increasing carbon black concentration. This decrease was due to the tendency of carbon black to form aggregates that delay the oil molecules' penetration inside the matrix.
3. The effect of swelling on the thermoelastic effect shows a remarkable decrease in the temperature change with respect to the unswelled samples.

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