

Effect of Swelling Process on Thermoelastic Temperature Change of Butadiene Acrylonitrile Rubber Filled with Polyvinyl Chloride

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ABSTRACT: Thermoelastic measurements dealing with adiabatic heating under application of rapid strain (stress) afford a new approach to evaluate important thermal properties of viscoelastic materials. The effects of both dynamic cyclic extension and swelling on the thermoelastic behavior of the acrylonitrile butadiene rubber (NBR) loaded with different concentration of polyvinyl chloride (PVC) 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. This temperature change decreases with increasing PVC concentration up to critical concentration.

Swelling behavior of samples was investigated. It was

found that swelling as well as diffusion coefficient has a higher level of solvent uptake in a fresh sample than in a strained sample. This can be attributed to the nature of the NBR and PVC blend. Also, the effect of swelling on the thermoelastic temperature change was studied. A remarkable decrease in the temperature change was shown for swelled samples as opposed to fresh samples. Both degradation and crosslinking may occur simultaneously, as was clearly detected for all samples with different sensitivities. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 916–921, 2005

Key words: swelling; rubber; polyvinyl chloride

INTRODUCTION

Polyvinyl chloride (PVC) contains highly polar chlorine atoms that mutually repel one another, and a substantial part of the macromolecules of this polymer have a relatively regular structure.¹ The unique ability to accept large amounts of plasticizer makes PVC one of the most commercially useful polymers. Generally PVC is plasticized with 20–70 parts of plasticizer per hundred parts resin (phr).²

The properties of PVC can further be modified by addition of other polymers, like butadiene acrylonitrile rubber (NBR). This polymer has two points of great chemical activity that either separately or jointly can easily lead to reaction with other substances. They are the C = C linkage of the polybutadiene part and the CN group of the polyacrylonitrile moiety.³ In the presence of suitable acceptors, the degraded NBR may then well act as a donor, whereas the thermally degraded PVC may serve as an acceptor. It is therefore anticipated that an intimate blend of NBR and PVC would mutually interact with each other.⁴

Khairy and Ateia⁵ 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 the Gruneisen constant.

It is well recognized that this rapid deformation of a solid usually results in a temperature change in the material. The rapid deformation is closely related to an adiabatic process whereby the heat absorbed or generated during the deformation changes the temperature of the material.⁶

For more explicit examination of thermoelastic phenomena, it is necessary to develop relations between force f , length l , and temperature T on the one hand, and the thermodynamic quantities, entropy S and internal energy E , on the other.^{7,8} These relations could be summarized in the following equations:

$$(\partial S / \partial l)_T = - (\partial f / \partial T)_l \quad (1)$$

$$(\partial E / \partial l)_T = f - T(\partial f / \partial T)_l \quad (2)$$

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TABLE I
Composition of NBR Samples with Different Polyvinyl Chloride Concentrations

Ingredients (phr) ^a	GH0	GH1	GH3	GH5	GH6
NBR	100	100	100	100	100
PVC	0	1	3	5	6
Stearic acid	2	2	2	2	2
Zinc oxide	5	5	5	5	5
HAF black	40	40	40	40	40
Processing oil	10	10	10	10	10
MBTS ^b	2	2	2	2	2
Sulfur	2	2	2	2	2

^aphr part per hundred parts of rubber by weight

^bDibenthiazyl disulfide

entropy and internal energy. Moreover, from the second law of thermodynamics, we can get

$$(\partial s / \partial l) = C_l / T (\partial T / \partial l) \quad (3)$$

where C_l is the heat capacity at constant length.

The present study describes the effect of both dynamic cyclic extension and swelling on the thermoelastic effect in NBR loaded with different concentrations of polyvinyl chloride.

EXPERIMENTAL

Sample preparation

NBR containing approximately 75% butadiene and 25% acrylonitrile, filled with different concentrations of polyvinyl chloride PVC, and loaded with 40 HAF carbon black—the percolation concentration⁷—were used in this study.

The rubber and other conventional additives were mixed according to the recipe illustrated in Table I. The test samples were prepared on a two-roll mill 170 mm diameter with work distance 300mm, at the speed of slow roll mill of 18 rpm and gear ratio 1.4. The rubber composites were left 24 h before being vulcanized at 152°C, and pressure about 1.17Mpa was fixed for an optimum time of 20 min.^{9,10}

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.¹¹ 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 (rang-

ing from 10 to 120%). The change in temperature (for every constant amplitude) was measured during cycles by using a copper constantan thermocouples with one junction fixed at the middle of the major surface and the other attached to a k-type micro-voltammeter with sensitivity of 0.1 degree. 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 s⁻¹.

Sorption measurements

Rubber blends were weighed and inserted into a test tube containing benzene at 30°C. Then they were removed from the solvent and blotted with filter paper to remove excess solvent on the surface of the samples. They 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.¹²

$$M_t = [(W_t - W_d) / W_d] / 100 \quad (4)$$

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 the swollen sample with time.

RESULTS AND DISCUSSION

Effect of amplitude and duration of dynamic cyclic strain on thermoelastic behavior of NBR/PVC: Before Swelling

Rubbers exhibit predominantly entropy driven elasticity. This was discovered by Gough¹³ and later by Joule¹⁴ through measurements of force and specimen length at different temperatures. They discovered the thermoelastic effects: that a stretched rubber sample subjected to a constant uniaxial load contracts reversibly on heating. Also, that a rubber sample gives out heat reversibly when stretched. These observations were consistent with the view that the entropy of the rubber decreased on stretching.

Figure 1 illustrates the effect of the duration of stress time (t) on the temperature change, for NBR loaded with different concentrations of polyvinyl chloride. All samples show the same behavior that the heat generated by cycling is 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.¹⁵ After a number of cycles, the temperature within the sample becomes nearly constant since the

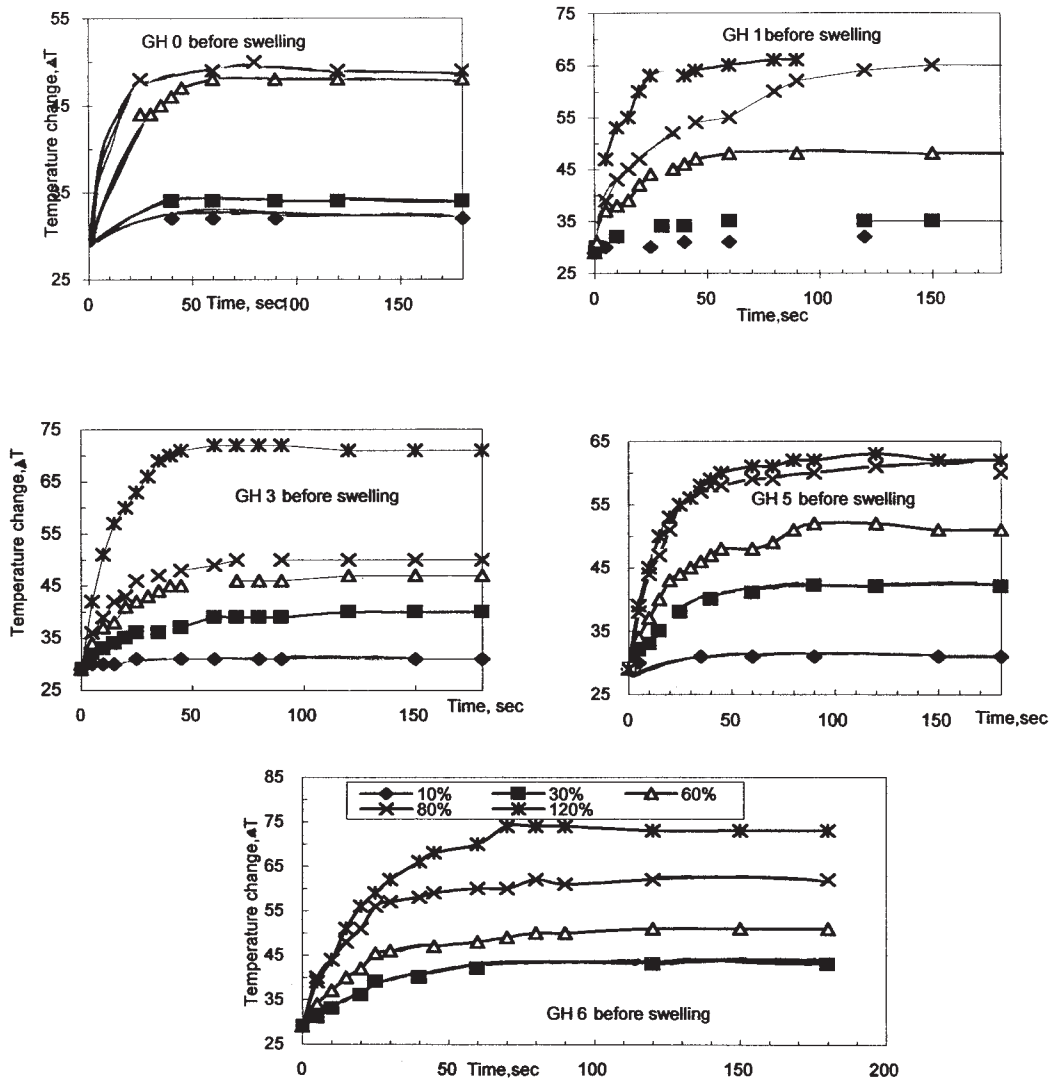


Figure 1 Dependence of the thermoelastic temperature change (ΔT) at various strain amplitudes (%) on the duration of stress time (t) for NBR samples loaded with PVC (before swelling).

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 figure), at constant time (90 s) when the strain amplitude increases, the concentration of 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. (3), one can calculate the change of entropy per unit extension, in terms of both heat capacity at constant length and ambient temperature, Table II.

Effect of PVC concentration on the thermoelastic temperature change for NBR samples

The thermoelastic temperature change in the deformed NBR samples as a function of PVC concentra-

tion is shown in Figure 3. The data shows that the temperature change decreases as the concentration of PVC increases, up to critical concentration, (GH3).

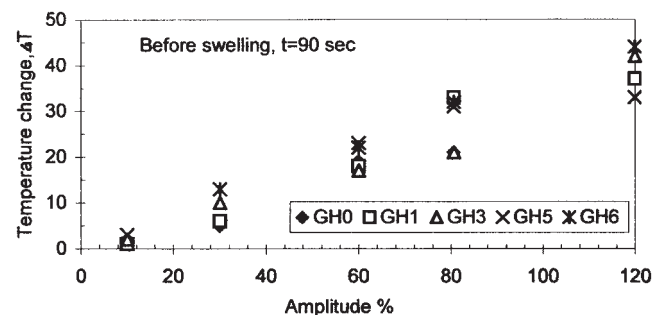


Figure 2 Dependence of the thermoelastic temperature change (ΔT) on the strain amplitude at constant time (90 s) for NBR samples loaded with PVC.

TABLE II
Variation of Entropy per Unit Extension
with PVC Concentration

PVC	$(\partial s/\partial l)$ cal/deg
0	0.504
1	0.446
3	0.427
5	0.446
6	0.637

This decrease may be due to the small amount of PVC as filler, which helps the nature of NBR to be predominant. In other words, the presence of polar substituents in the NBR chain increases the intermolecular forces that resist the applied periodic stress and consequently hinder the creation of free radicals. The increase in PVC concentration leads to increase in dipole density¹⁶ and formation of two types of bonds.¹⁷ Weak bonds are ruptured; the free radicals are created and set in random motion. This gives a contribution to the heat developed in the rubber matrix during the periodic deformation.

Effect of swelling on NBR samples loaded with different concentrations of polyvinyl chloride

The interaction of polymeric materials with different solvents is a problem from both the academic and technological points of view.^{18–20}

Crosslinked polymers brought in contact with different solvents during service applications usually exhibit the phenomenon known as swelling. The capacity of crosslinked polymers for the degree or the amount of swelling assesses swelling expressed as the amount of liquid absorbed by the polymer.

The percentage increase in weight due to swelling in benzene for all fresh samples is plotted against the square root of time in $\text{min}^{1/2}$. The curve is shown in Figure 4(A); the general features show that the linear region goes through the origin as expected for Fickian behavior.

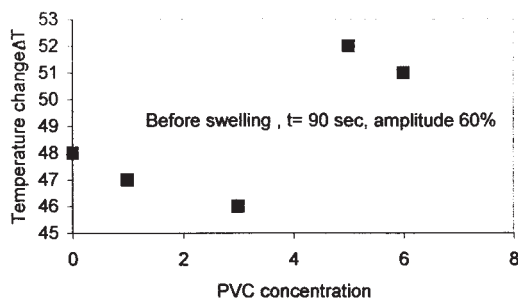


Figure 3 Dependence of thermoelastic temperature change (ΔT) on the polyvinyl chloride concentration for NBR samples.

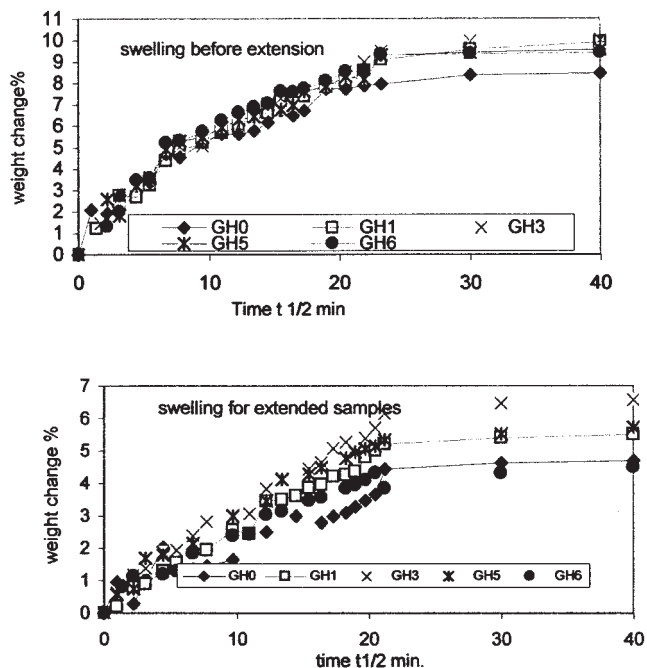


Figure 4 Solvent uptake percent versus square root of time for NBR loaded with PVC.

Figure 4(B) shows the same curve but for strained samples, which show the same trend as fresh samples but with a smaller level of solvent uptake. In general the blends are essentially incompatible; therefore, the degradation is the predominant process that increases the penetration of solvent into the rubber matrix. For strained samples, as shown in Figure 4(B), the straining process leads to both degradation and crosslinking that may occur simultaneously in rubber blends. Also, HAF carbon black, which was used, has a high ability to form aggregates.^{21,22} The mentioned reasons are the main expectation about lowering solvent uptake level in the extended samples with respect to a fresh one.

To investigate the type of diffusion mechanism, the sorption data of all investigated samples have been fitted to the following relation^{23,24}:

$$\log(Q_t/Q_\infty) = \log k + n \log t \quad (5)$$

where Q_∞ is the percent mass of solvent absorbed at equilibrium time, and k is a constant that depends on the structural characteristics of the polymer in addition to its interaction with the solvent.²⁵ The value of n indicates the type of the diffusion mechanism. From a least squares analysis of the $\log(Q_t/Q_\infty)$ data versus $\log t$, the values of k and n have been obtained and included in Table III.

The values of n in all samples are found to be around 0.5 ± 0.02 , which means that Fickian diffusion is implied. On the other hand, the values of constant k are dependent on the PVC concentration.

TABLE III
The Calculated Values of n , k , and Diffusion Coefficient D , NBR/PVC.

Sample	Extended samples			Fresh samples
	n	k (g/g min ⁿ)	$D(\text{cm}^2\text{sec}^{-1})\times 10^{-5}$	$D(\text{cm}^2\text{sec}^{-1})\times 10^{-5}$
GH0	0.48	4.89	1.72	2.29
GH1	0.50	4.50	1.56	2.00
GH3	0.40	7.58	1.09	1.76
GH5	0.24	1.31	1.50	2.04
GH6	0.60	2.88	2.00	2.17

The values of mutual diffusion coefficient D can be calculated from the initial slope of the sorption curves as

$$D = \frac{\pi}{t} \left[\frac{hM_t}{4M_m} \right]^2 \tag{6}$$

$$= \frac{\pi}{t} \left[\frac{h\theta}{4M_m} \right]^2$$

where h is the sample's thickness and M_m is the maximum equilibrium uptake of the solvent by 100 g of the polymer sample. The calculated diffusivity data for all PVC concentrations are given in Table III.

It is clear from the calculated data that the diffusion coefficient for both fresh and strained samples

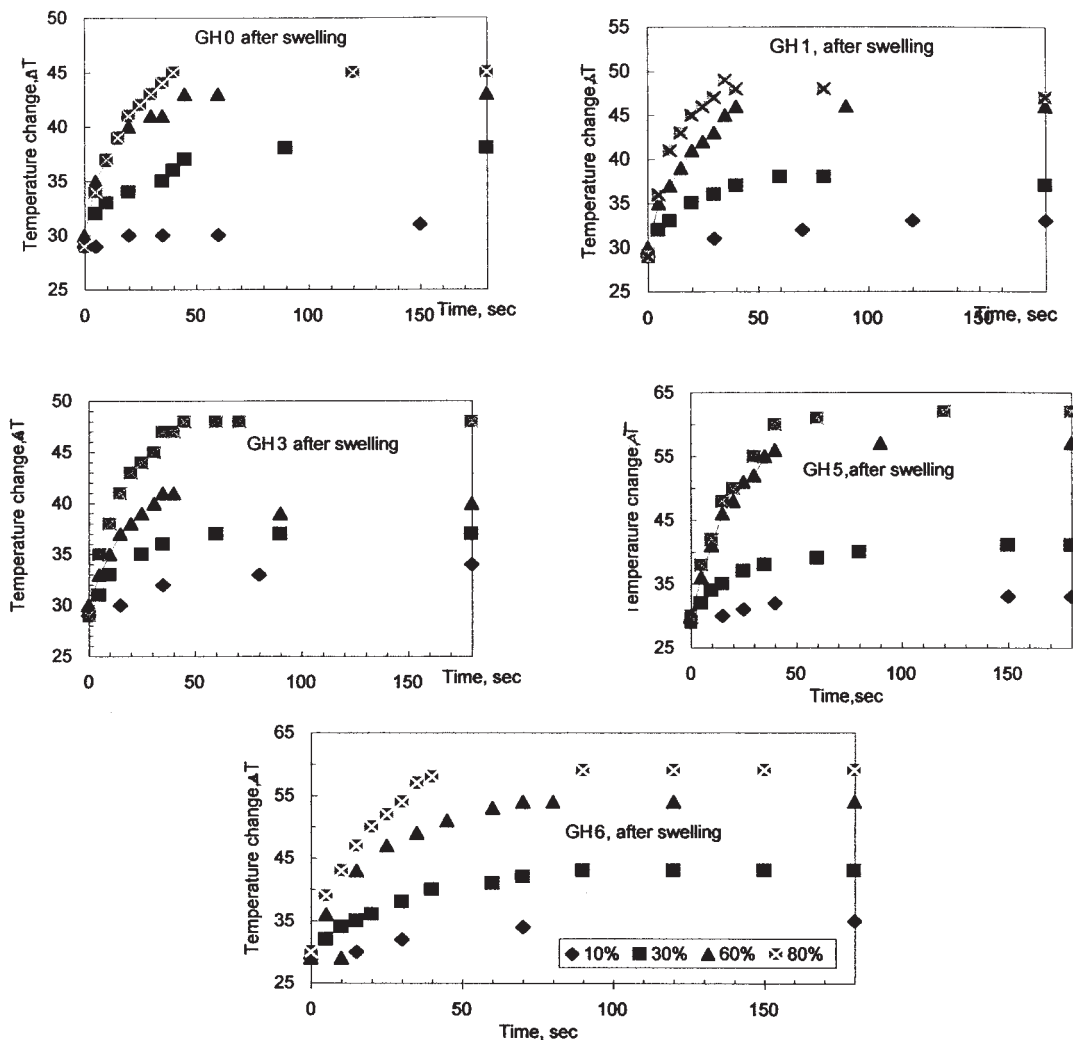


Figure 5 Dependence of the thermoelastic temperature change (ΔT) at various strain amplitudes (%) on the duration of stress time (t) for NBR samples loaded with PVC (after swelling).

decreases with increasing PVC concentration up to GH3, which is considered a critical concentration. Also, the fresh samples have a higher level of solvent uptake; this agrees with the previous discussion.

Effect of amplitude and duration of dynamic cyclic strain on the thermoelastic behavior of NBR samples: *After Swelling*

Swelling decreases the strength of rubber in different ways depending on the type of rubber,²⁶ the type of swelling liquid, and the nature of interaction between the rubber and liquid.²⁷

The effect of the duration time (t) on the thermoelastic temperature change for swelled NBR loaded with different concentrations of polyvinyl chloride is shown in Figure 5. It is obvious that when samples are subjected to the swelling process, the solvent molecules diffuse into the rubber matrix causing weakness and rupture of the rigid chain.¹² In general, swelled samples show a decrease in temperature change with respect to fresh samples (Fig. 1). This decrease is attributed to solvent diffusion into the rubber matrix forming insulating clusters around the free radicals. These clusters hinder free radical motion, leading to decrease in temperature change.

CONCLUSION

From the above results one can conclude that thermoelastic temperature change is mainly dependent on amplitude, duration of cyclic stress, and swelling process.

Also, thermoelastic experiments afford an approach to evaluate the entropy change per unit extension, which changes with PVC concentration.

Finally, the importance of the quantitative measurements of the thermal effects lies not only in the thermodynamic information that they provide but also in

understanding the final properties of the deformed material.

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