

Thermal effects in styrene–butadiene rubber at high hydrostatic pressures

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The temperature changes as a result of rapid hydrostatic pressure applications are reported for unvulcanized styrene–butadiene rubber (SBR) in the reference temperature range from 292 to 405 K and in the pressure range from 13.8 to 200 MN m⁻². The thermal effects were found to be a function of pressure and temperature. A curve fitting analysis showed that the empirical curve $(\partial T/\partial P) = ab(\Delta P)^{b-1}$, described the experimental thermoelastic coefficients obtained from the experiments. The data were analysed by determining the predicted thermoelastic coefficients derived from the Thomson equation $(\partial T/\partial P) = \alpha T_0/\rho C_p$. The experimental and the predicted Grüneisen parameter γ_T were also estimated. Close agreement was found at low pressure but differences were observed at higher pressures between the experimental and expected values for the thermoelastic coefficients and the Grüneisen parameter.

(Keywords: styrene–butadiene rubber; adiabatic thermal effects; hydrostatic pressures; thermoelastic coefficient; Grüneisen parameter)

INTRODUCTION

In 1805 J. Gough¹ made two important observations related to the properties of rubber. Gough found that a stretched strip of rubber contracts reversibly upon heating and that a sudden stretching of a strip of rubber resulted in a rise of temperature. These observations were found to be very interesting and unusual because at that time it was also known that a stretched bar of metal elongated upon heating and a sudden stretching of a metal bar results in a decrease in temperature.

In the 1930's several authors^{2,3} began to develop quantitative theories based on the idea that the network chains undergo configurational changes by skeletal bond rotations in response to an applied stress. The important experimental observation made was that the deformation of rubbers occurred nearly at constant volume, therefore changes in entropy must involve changes in orientation or configuration of the network chains that build the rubberlike materials.

To develop the thermodynamic relationships for rubber elasticity, many investigators have carried out measurements of the stress as a function of temperature at fixed length to study the influence of temperature on the elasticity of rubber. The combination of the thermodynamic relationships and the statistical theory of rubber elasticity have resulted in mathematical expressions that can very well describe the theoretical equation of state for ideal rubbers. Many experiments conducted isothermally have confirmed the validity of these theories of rubber elasticity^{2,3,5}.

Contrary to the extensive research that has been done on the isothermally thermoelastic experiments, much less effort has been dedicated to the understanding of the thermal heating of rubber during rapid stretching. The reasons for that may be due to the fact that the initial

classical experiments showed that these temperature changes were relatively small at low percentages of elongation⁴.

Boone and Newman⁶ were the first to report that the temperature rise in vulcanized rubber during rapid elongation could be significant. An increase in temperature from 6°C to 12°C was recorded in the elongation range from 0 to 600%. Williams⁷ and Dart *et al.*⁸ confirmed Boone and Newman's observations for different vulcanized rubbers. These authors reported temperature changes from 0.1°C to 15°C for similar percentages of elongation.

Nearly all the experimental studies reported above have used rapid extension to determine thermal effects in rubbers. These thermal effects can also be evidenced under rapid compression or rapid hydrostatic deformations. The use of hydrostatic pressure deformation is a very attractive tool to study thermal effects because other important factors such as shear or plastic deformation can be substantially minimized. The importance of the quantitative measurements of the thermal effects lies not only in the thermodynamic information that they provide but also in the understanding of the final properties of the deformed material.

This work reports the finding of an experimental investigation on the temperature changes occurring during rapid applications of hydrostatic pressure in styrene–butadiene rubber. Uncrosslinked rubber was used and the thermal effects at different temperatures were measured.

EXPERIMENTAL

The styrene–butadiene rubber, SBR 1502 was obtained from BF Goodrich. Unvulcanized rubber was used in the

experiments. Samples were cut and shaped approximately to rubber rods of average dimensions 0.25 inches o.d. and 3.6 inches long (0.635 cm o.d. and 9.22 cm long). The rubber was used as received. The molecular weight and molecular weight distribution were unknown. The values of the heat capacity the thermal expansion coefficient and the density were obtained from the literature.

The apparatus and evaluation procedure for obtaining the temperature changes resulting from the rapid application of pressure were described previously⁹. Liquid mercury was used to transmit the pressure to the sample. Hydrostatic pressures were achieved by using a 1-hp air compressor and an air-driven high-pressure reciprocating pump. The pressure was measured with two Bourdon gauges, each with a maximum of 345 MN m⁻² and sensitivity of 3.45 MN m⁻². The temperature changes were recorded by using two iron-constantan thermocouples. The measuring junction was located in the geometric centre of the rubber sample, whereas the reference junction was located outside the high-pressure unit. This arrangement allowed us to measure directly only the temperature differences generated by the pressure variations and with maximum sensitivity since, when both junctions were at atmospheric pressure, the output of the differential thermocouple was virtually zero.

To record the thermal effects, the system was allowed to equilibrate to atmospheric pressure and to the reference temperature. Pressure was rapidly applied by opening a valve which caused the selected pressure to be transmitted instantaneously to the sample. An increase in temperature was recorded. The pressure was released by the rapid opening of a second valve to atmospheric pressure which resulted in a decrease in temperature in the rubber sample. Figure 1 shows a typical recording of the thermal effects.

RESULTS AND DISCUSSION

Figure 2 shows the temperature changes as a function of the applied pressure at different temperatures. The data is presented only for positive ΔP's and thus positive temperature increases, since the magnitude of the temperature decreases upon removal of pressure for the

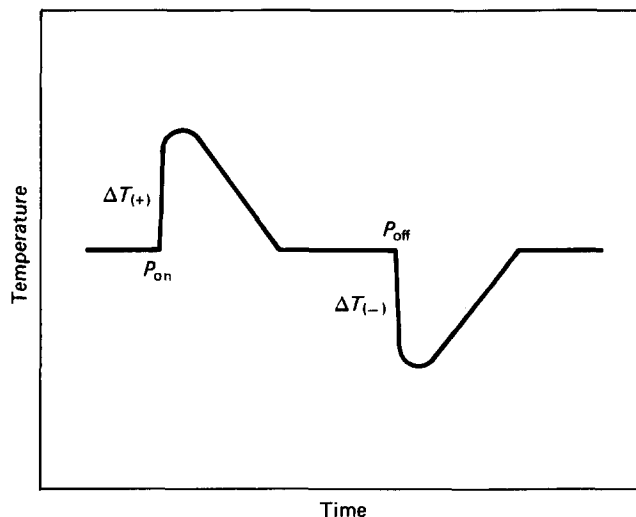


Figure 1 Representation of the reversible thermal effects resulting from the rapid application and release of hydrostatic pressure

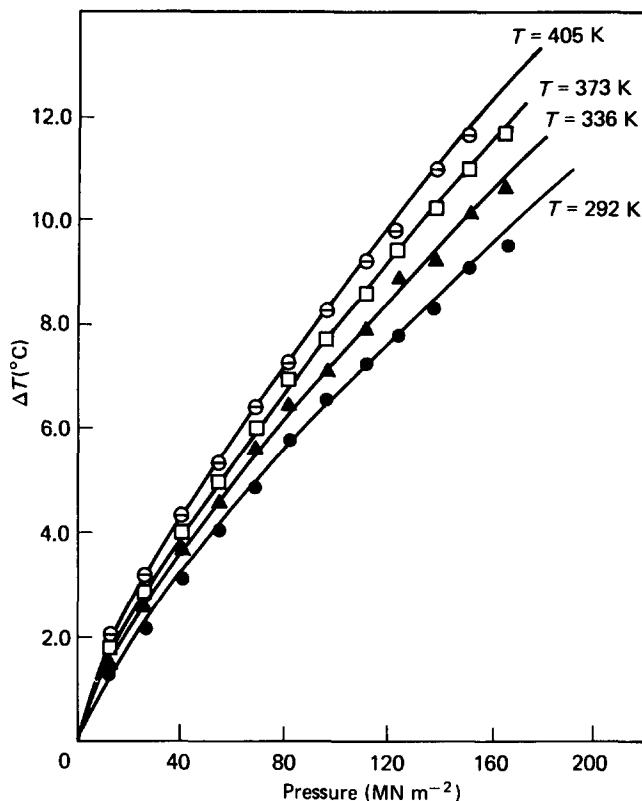


Figure 2 Temperature changes as a function of applied pressure for styrene-butadiene rubber at different reference temperatures

same pressure applied was identical. The magnitude of the temperature changes were found to be relatively significant. For example, for a pressure increase of 137.9 MN m⁻² and for the reference temperature T₀ = 405 K, the temperature change recorded was 10.8°C. For the same pressure applied but for the reference temperature T₀ = 292 K the temperature change was 8.5°C.

These temperature changes are in general agreement with the magnitude of the thermal effects observed during rapid stretching where temperature increases up to 14°C were observed at different percentages of elongation⁶⁻⁸.

Figure 3 shows the dependence of the temperature changes on the reference temperature at selected pressures. A linear dependence was found in the temperature range studied.

To evaluate our results, a curve fitting analysis was conducted. It showed that the best and simplest curve fit was obtained from the empirical equation ΔT = a(ΔP)^b. Table 1 shows the results of the curve fitting analysis. ΔT = T - T₀ and ΔP = P - P₀ where T₀ is the reference temperature and P₀ is the atmospheric pressure. Differentiating on both sides of the above empirical equation, we obtain:

$$\frac{\partial T}{\partial P} = ab(\Delta P)^{b-1}$$

This equation shows a clear dependence on the thermoelastic coefficients on the pressure applied. This equation is purely empirical and no effort was given to correlate it with thermodynamic variables. Table 2 gives the numerical expressions for (∂T/∂P) at certain reference temperatures and shows the thermoelastic coefficients

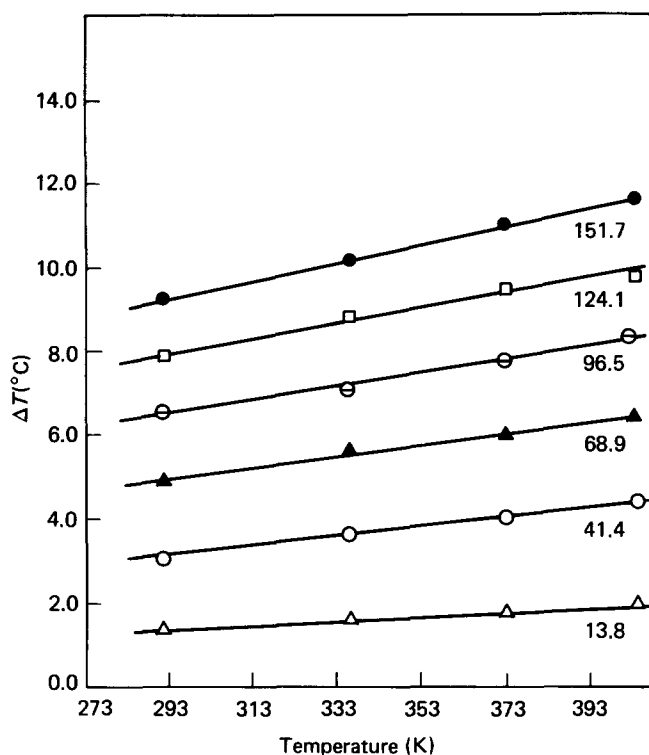


Figure 3 Temperature changes as a function of the reference temperature for styrene-butadiene rubber at selected applied pressures in MN m^{-2}

Table 1 Values for a and b in the empirical equation $\Delta T = a(\Delta P)^b$ obtained from the curve fitting analysis for SBR rubber

Reference temperature (K)	a	b	Coefficient of determination R^2
292	0.1678	0.7957	0.99
336	0.2018	0.7796	1.00
373	0.2169	0.7821	1.00
405	0.2603	0.7560	1.00

determined from selected pressures at the same reference temperatures.

From thermodynamic relationships, it is possible to derive an expression that describes the temperature changes during adiabatic deformation. It is important to define the type of deformation to be employed, that is, tension, compression or volumetric (hydrostatic pressure) deformation. Thomson¹⁰ proposed a general thermodynamic formula which describes the change in temperature as the result of rapid application of pressure. Later Joule⁴ verified Thomson's equation with an investigation of some thermodynamic properties of solids by measuring the temperature changes produced by sudden stretching or compression of a variety of materials at low stresses.

Swalin¹¹ has shown a recent and modern derivation of the Thomson equation to describe the thermoelastic effect. For hydrostatic pressure the Thomson equation can be written as:

$$\frac{\partial T}{\partial P} = \frac{\alpha_v T_0}{\rho C_p}$$

where α_v is the volume thermal expansion coefficient, C_p is

the specific heat at constant pressure, and ρ is the density. The term $(\partial T/\partial P)$ is usually called the thermoelastic coefficient. For small pressures or small deformations, the term $\alpha_v T_0/\rho C_p$ is assumed to be independent of pressure and temperature. Therefore, upon integration of the Thomson equation within reasonable limits, the temperature change ΔT , as the result of rapid pressure application of ΔP , can be estimated. This procedure may be valid for small pressure applications, but it would be limited in its usefulness in predicting changes resulting from relatively large pressure changes.

This limitation results from the parameters α_v , ρ and C_p being much more pressure sensitive for polymers than for either metals or ceramics. Recently, several authors¹²⁻¹⁴ have confirmed the validity of the Thomson equation in predicting thermal effects for the stress range from 2 to 42 MN m^{-2} . A study dealing with thermal effects in poly(tetrafluoroethylene) (PTFE) at high hydrostatic pressures showed that the solid-state transitions at 19°C and 30°C reported for PTFE substantially influence the temperature changes¹⁵. This indicates that the transitions and the viscoelastic nature of the polymeric materials are going to have an impact on the adiabatic heating phenomenon.

To evaluate the experimental data in terms of the predicted thermal effects from the Thomson equation, the values of the physical parameters were taken from the literature. For unvulcanized styrene-butadiene rubber the density is $0.933 \times 10^3 \text{ kg m}^{-3}$,¹⁶ the volume thermal expansion coefficient α_v is $660 \times 10^{-6} (\text{°C})^{-1}$,¹⁶ and the heat capacity C_p is $1.89 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$.¹⁷ Thus, the thermoelastic coefficient $(\partial T/\partial P)$ predicted from the Thomson equation could be estimated. They are shown in Table 3 where selected experimental values are also presented. Examining Table 3 an excellent agreement was found between the theoretical thermoelastic coefficient and the experimental coefficients at $\Delta P = 4 \text{ MN m}^{-2}$. However, deviations were found at other pressures. This confirms previous findings that certain properties of viscoelastic materials are very sensitive to pressure and temperature and therefore care should be taken in applying thermodynamic variables that are well

Table 2 Experimental thermoelastic coefficients $(\partial T/\partial P)$ determined for SBR rubber at selected pressures

Reference temperature (K)	$\frac{\partial T}{\partial P} = ab(\Delta P)^{b-1}$	ΔP (MN m^{-2})	$\frac{\partial T}{\partial P}$ (K/MNm^{-2})
292	$0.1335 \times (\Delta P)^{-0.2043}$	0.1013	0.2132
		4.0	0.1006
		20	0.0724
		100	0.0521
336	$0.1573 \times (\Delta P)^{-0.2204}$	0.1013	0.2606
		4.0	0.1159
		20	0.0813
		100	0.0570
373	$0.1696 \times (\Delta P)^{-0.2180}$	0.1013	0.2794
		4.0	0.1254
		20	0.0883
		100	0.0622
405	$0.1968 \times (\Delta P)^{-0.2440}$	0.1013	0.3440
		4.0	0.1403
		20	0.0947
		100	0.0640

Table 3 Experimental thermoelastic coefficients for styrene-butadiene rubber

Temperature (K)	$(\partial T/\partial P)_{\text{Theoretical}}^a$ (K/MNm ⁻²)	$(\partial T/\partial P)_{\text{Experimental}}^b$ (K/MNm ⁻²)
		ΔP (MN m ⁻²)
292	0.1093	0.1013 4.0 0.2132 0.1006
336	0.1258	0.1013 4.0 0.2606 0.1159
373	0.1396	0.1013 4.0 0.2794 0.1254
405	0.1516	0.1013 4.0 0.3440 0.1403

$$^a \frac{\partial T}{\partial P}_{\text{Theoretical}} = \frac{\alpha T_0}{\rho_v C_p}$$

$$^b \frac{\partial T}{\partial P}_{\text{Experimental}} = ab(\Delta P)b - 1$$

established for non-viscoelastic materials on reversible thermodynamics. However, these findings also show that the Thomson equation is still valid to estimate approximately the thermal effects during rapid deformation on polymeric materials.

Figure 4 shows comparatively the $(\partial T/\partial P)$ coefficients as a function of temperature for the predicted and experimental values at selected pressures. Interestingly a linear dependence was found in all of them.

The thermoelastic method (adiabatic heating) has been used to determine important thermodynamic properties. For example, Bottani^{18,19} measured the Grüneisen parameter and the thermal diffusibility coefficient in metals using the temperature increments obtained from rapid compression. Haward¹² reported the values of the linear coefficient of expansion and the Grüneisen constant at different stresses and temperatures in poly(methylmethacrylate) from thermoelastic experiments. Similar calculations have also been conducted for glassy polymers^{13,14}.

The macroscopic or the thermodynamic Grüneisen relationship γ_T can be estimated from the thermoelastic coefficients $\partial T/\partial P$ through the equation:

$$\gamma_T = \frac{\partial T}{\partial P} \frac{B_s}{T} = \frac{\partial T}{\partial P} \frac{1}{T} B_T (C_v/C_p)$$

where B_s is the adiabatic bulk modulus, B_T is the isothermal bulk modulus, C_v is the specific heat at constant volume and C_p the specific heat at constant pressure. The derivation of these relationships can be found in the literature^{11,14}. For unvulcanized SBR rubber the isothermal bulk modulus B_T reported in the literature is 1.890×10^3 MN m⁻².²⁰ The ratio C_v/C_p can be determined from the reversible thermodynamics equation:

$$\frac{C_v}{C_p} = 1 - \frac{T\alpha_v^2 B_T}{\rho C_p}$$

therefore allowing the determination of the Grüneisen coefficient. Using the experimental values and the predicted values from the Thomson equation for the thermoelastic coefficient, the Grüneisen parameter was calculated and the results are shown in Table 4.

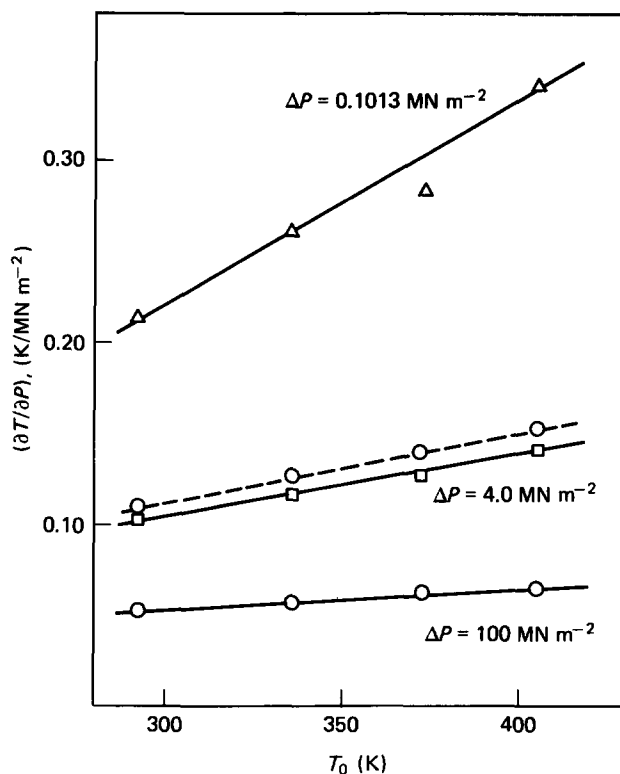


Figure 4 Thermoelastic coefficients $(\partial T/\partial P)$ as a function of temperature. Experimental (—) and predicted values (----)

Table 4 Values of the Grüneisen constant for unvulcanized styrene-butadiene rubber

Temperature (K)	$\frac{C_v}{C_p}$	From experimental coefficients		Predicted values from the Thomson equation
		ΔP (MN m ⁻²)	γ_T	γ_T
292	0.86	0.1013	1.187	0.6084
		4	0.560	
		20	0.403	
		100	0.290	
336	0.84	0.1013	1.231	0.5944
		4	0.548	
		20	0.384	
		100	0.269	
373	0.83	0.1013	1.175	0.5871
		4	0.527	
		20	0.371	
		100	0.262	
405	0.81	0.1013	1.300	0.5731
		4	0.530	
		20	0.358	
		100	0.242	

$$^a \text{Determined from } \frac{C_v}{C_p} = 1 - \frac{T\alpha_v^2 B_T}{\rho C_p}$$

Two interesting observations can be made from Table 4. First, the γ_T values determined from the experimental coefficients $(\partial T/\partial P)$ were found to be very dependent on pressure at constant temperature whereas at constant pressure less dependence was observed on the reference temperature. Second, the predicted γ_T values obtained via the Thomson equation were nearly independent of the reference temperature.

The low values for γ_T (for example 0.290) indicate relatively large thermal effects and high values of γ_T (for

example (1.187) indicate small thermal effects under the application of high hydrostatic pressures. Thus, the Grüneisen coefficient gives an estimation between mechanical and heat effects in materials^{21,22}. For metals the Grüneisen constant usually has a value between one and two whereas for glassy polymers, values below one are commonly found^{11,14}.

Experimental studies on the Grüneisen constant for unvulcanized rubbers are almost nonexistent, therefore a comparison cannot be made to further analyse our experimental results.

Finally, thermoelastic experiments dealing with adiabatic heating under rapid deformation afford a different approach to evaluate and perhaps further understand the thermal properties of viscoelastic materials. The simplicity of the experiment reported here may suggest a quick way to evaluate important thermodynamic variables.

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