

Evaluation of Natural Rubber Specific Heat Capacity at High Pressures from DSC Experimental Data at Atmospheric Pressure

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ABSTRACT: The natural rubber specific heat capacity dependence on pressure was estimated on thermodynamic grounds on the basis of the values empirically determined from differential scanning calorimetry data, (in the temperature range of -70 to 50°C), and by means of the Tait equation of state (in the pressure range of 0.1 – 240 MPa). It was found that the specific heat capacity decreases with pressure, being the dependency more pronounced at low pressures. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: natural rubber; specific heat capacity; differential scanning calorimetry; high pressure

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INTRODUCTION

Heat capacity is a key magnitude of the thermodynamic phase, because its entropy, enthalpy, etc., are derived from experimental data on isobaric heat capacity, $c_p(T, p = \text{constant})$. Data are usually collected at atmospheric pressure. An important issue is to obtain the specific heat at higher pressures. Experimental data on heat capacity of condensed matter under high pressure are scarce and inaccurate, because a direct and an accurate adiabatic calorimeter developed for ambient pressure can be hardly adapted to the devices generating high pressure.^{1–3} This lack of experimental data is filled with model relationships, allowing one to derive heat capacity from the equation of state (EOS), interatomic potential, molecular dynamics, etc. Specifically, heat capacity increases, decreases, or remains almost insensitive with pressure, depending on the applied model. It is difficult to recognize a general tendency in the changes of “model” c_p with pressure. For instance, heat capacity decreases with pressure for liquid SiO_2 ,⁴ and increases for liquid MgO .⁵ It is reasonable that pressure increases the frequency of atomic vibration in solids, increasing the Debye temperature and, hence, decreasing the heat capacity if the latter is less than the Dulong–Petit value ($3R$ per atom).^{6,7} The same is valid for organic solids and liquids, where c_p decreases with pressure.⁸

With regard to polymeric materials the information about the c_p dependence on pressure is also scarce. For this reason, it is convenient to elaborate a general strategy of calculation based on the classical thermodynamics, to extend the knowledge of the specific heat from room to higher pressures. In this way, it is advisable to use an EOS as a model of behaviour in connec-

tion with the classical thermodynamic relations, derived from the first and second laws of the thermodynamics. The purpose of this work is to propose a systematic calculation of the natural rubber (NR) specific heat capacity,⁹ at higher pressures than the atmospheric one, and in the experimental range of temperatures by means of a specific EOS (the Tait equation).

EXPERIMENTAL

Material

NR latex was obtained from Inducompre - Ind. Com. Prest. de Serviços Ltda. (Salvador, Brazil). Vulcanization additives used in the rubber formulation such as stearic acid (0.5 phr), zinc oxide (6 phr), sulfur (3.5 phr), *N-t*-butyl benzothiazole-2-sulfenamide (0.7 phr), and 4,4'-dioctyl-diphenylamine (1 phr) are present in the sample. The material was processed to obtain sheets with thickness of about 0.2 mm.

EXPERIMENTAL

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC)¹⁰ thermogram was obtained for the NR sample at $10^{\circ}\text{C}/\text{min}$ in a DSC-Q10 equipment from TA Instruments. The gas used in the DSC-Q10 to obtain an inert atmosphere was N_2 . The measurements were carried out in the range of temperature from -80 to 150°C . Uncertainty in the evaluated T_g is ± 0.1 . Figure 1 illustrates the DSC thermogram obtained for the NR sample, were it can be observed a sharp increase in the specific heat capacity as the NR is heated to a temperature above its glass transition temperature. The estimated NR T_g was of -60.2°C .¹¹ This value was evaluated as the temperature of the intersection of the glassy-

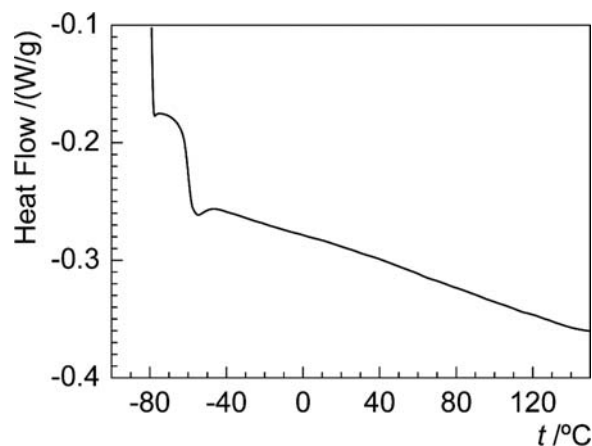


Figure 1. DSC curve taken at $10^{\circ}\text{C min}^{-1}$ for NR.

region baseline with the tangent to the endotherm in the middle point. It should be noted that strictly speaking, DSC data are not obtained in thermodynamic equilibrium. However, we can consider that the equilibrium is close to the experimental conditions due to the smallness of the sample.

RESULTS AND DISCUSSION

One of the more relevant findings arising from the rational thermodynamics methodology¹² is that the laws of the thermodynamics determine, at least partially, the constitutive structure of the material systems. This fact will be of usefulness in working on our problem. By considering a classical two-dimensional ideal system, with a state space in a (T, p) -plane, one can define the differential forms of the work and heat as

$$\begin{aligned} \bar{d}w &= v dp \\ \bar{d}q &= c_p dT + \lambda_p dp \end{aligned} \quad (1)$$

where $v(T, p)$ is the specific volume, $c_p(T, p)$ is the specific heat at constant pressure and $\lambda_p(T, p)$ is the latent heat with respect to pressure. Then, the first and second laws of thermodynamics can be written as

$$\begin{aligned} dh &= c_p dT + (\lambda_p + v) dp \\ ds &= \frac{c_p}{T} dT + \frac{\lambda_p}{T} dp \end{aligned} \quad (2)$$

where h and s are the specific enthalpy and entropy, respectively.

Equivalently to eq. (2) one can write

$$\begin{aligned} \frac{\partial c_p}{\partial p} &= \frac{\partial \lambda_p}{\partial T} + \frac{\partial v}{\partial T} \\ \frac{\partial c_p}{\partial p} &= \frac{\partial \lambda_p}{\partial T} - \frac{\lambda_p}{T} \end{aligned} \quad (3)$$

These coupled differential equations allow us to obtain the coefficients of the differential form of heat, λ_p and c_p , in terms of the coefficients of the differential form of work. Once more, it should be noticed the important consequence of the eq. (3),

i.e., the latent heat λ_p , as well as the specific heat c_p , can be predicted from the EOS [$v = v(p, T)$].

Solving eq. (3), the specific heat can be expressed in terms of the p, v, T parameters appearing in the EOS as:

$$c_p(T, p) = c_p^0(T, p_0) - T \int_{p_0}^p \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp \quad (4)$$

where $c_p^0(T, p_0)$ is the value of the specific heat capacity at the reference pressure, p_0 , as a function of the temperature. Here, $c_p^0(T, p_0)$ is taken from the calorimetric data.

The calculation of the NR specific heat capacity at higher pressures was carried out starting from the $c_p^0(T, p_0)$ values, that can be obtained by the Tait EOS¹³:

$$v(p, t) = v(p_0, t) \left\{ 1 - 0.0894 \ln \left[1 + \frac{p}{B(t)} \right] \right\} \quad (5)$$

where $v(p_0, t) = (T_a + T_b t + T_c t^2)$ [$\text{cm}^3 \cdot \text{g}^{-1}$] with t in $^{\circ}\text{C}$, is the specific volume at atmospheric pressure, and $B(t) = (B_a) \exp(-B_b t)$ [MPa] with t in $^{\circ}\text{C}$, are the parameters in the melt state for NR.

To obtain the five parameters of the Tait EOS, standard literature data¹⁴ of Pressure-Volume-Temperature (pvt) for NR were used. In Figure 2, are represented these NR pvt data and their corresponding fit to the Tait EOS. The fit was carried out by means of a multiple nonlinear regression analysis of the literature data, allowing the five characterizing parameters (i.e., T_a, T_b, T_c, B_a, B_b) to vary. The Tait parameters obtained in the fit were: $T_a = 1.09023 \pm 0.00031 \text{ cm}^3 \cdot \text{g}^{-1}$, $T_b = 5.6 \cdot 10^{-4} \pm 4 \cdot 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$, $T_c = 9.72 \cdot 10^{-7} \pm 1.3 \cdot 10^{-8} \text{ cm}^3 \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-2}$, $B_a = 218.77 \pm 1.43 \text{ MPa}$, and $B_b = 4.98 \cdot 10^{-3} \pm 3 \cdot 10^{-5} \text{ }^{\circ}\text{C}^{-1}$.

By means of eq. (5) and the obtained fit parameters, it should be possible to extrapolate the specific volume values of the polymer to higher pressures, as it is shown in Figure 2, where the isobaric curves from 0.1 MPa to 240 MPa are shown.

On the other hand, the specific heat capacity values, $c_p^0(T, p_0)$, were obtained from DSC measurements by means of the following relationship

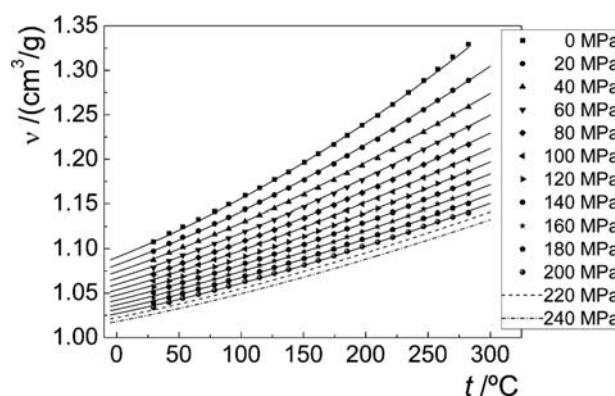


Figure 2. NR pvt data literature values (symbols). Solid lines represent the fit to the Tait equation.

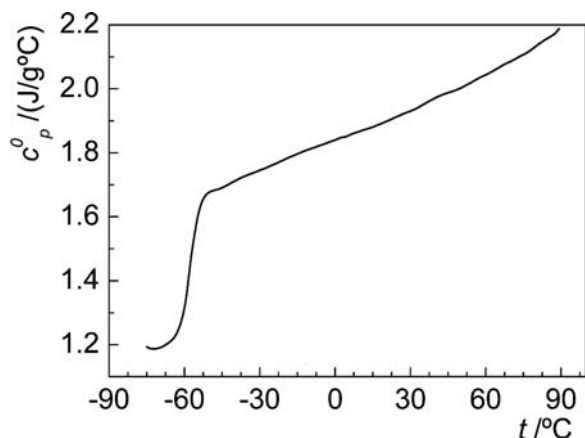


Figure 3. NR specific heat capacity as a function of temperature at atmospheric pressure.

$$c_p^0(T, p_0) = \frac{\dot{q}}{h} k \quad (6)$$

where $c_p^0(T, p_0)$ is in $\text{J g}^{-1} \cdot \text{°C}^{-1}$, \dot{q} is heat flow in W g^{-1} , h is the heating rate in °C min^{-1} (in our particular case was $10 \text{°C} \cdot \text{min}^{-1}$), and $k = 1.1007$ is the equipment calibration constant (dimensionless).

In Figure 3, is represented the temperature dependence of the specific heat capacity at atmospheric pressure, $c_p^0(T, 0.1 \text{ MPa})$, from DSC measurements. As we can see, the $c_p^0(T, 0.1 \text{ MPa})$ increases with the temperature, showing a jump near to the glass transition as correspond to a second-order phase transition.⁹

According to eq. (4), and to obtain the specific heat capacity, $c_p(T, p)$, it is necessary to evaluate the first and second partial derivative of the volume with the temperature at constant pressure. These partial derivatives are obtained by using the Tait EOS and they are

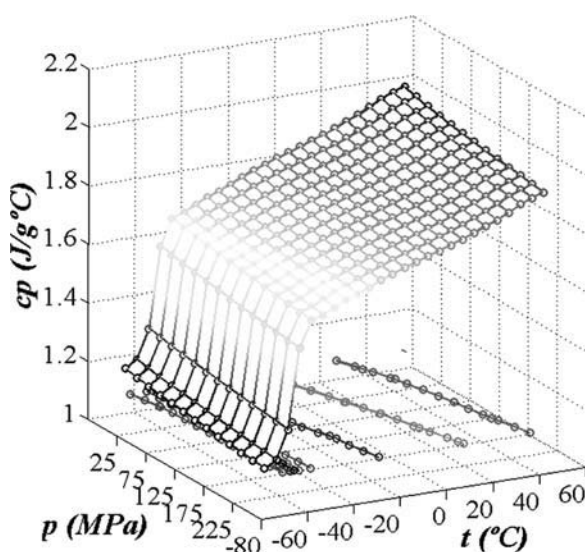


Figure 4. NR specific heat capacity as a function of temperature and pressure.

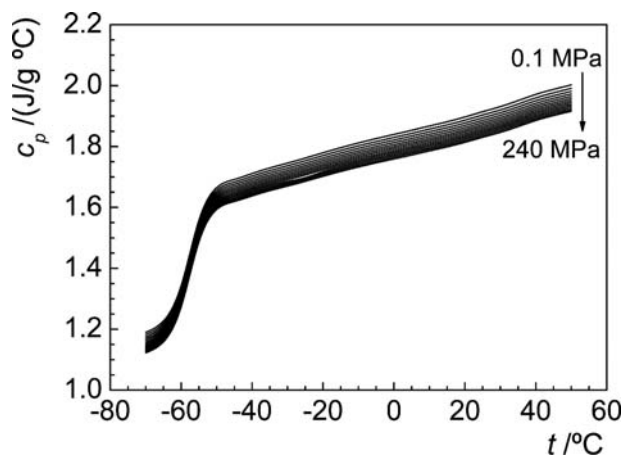


Figure 5. Temperature dependence of the NR isobaric specific heat capacity, $c_p / (\text{J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1})$ (from 0.1 to 240 MPa with a step of 20 MPa).

$$\left(\frac{\partial v}{\partial t}\right)_p = (T_b + 2 \cdot T_c \cdot t) \left(1 - N \cdot \ln\left(1 + \frac{p}{B_a \cdot \exp(-B_b \cdot t)}\right)\right) - \frac{(T_a + T_b \cdot t + T_c \cdot t^2) \cdot N \cdot p \cdot B_b}{B_a \cdot \exp(-B_b \cdot t) \cdot \left(1 + \frac{p}{B_a \cdot \exp(-B_b \cdot t)}\right)} \quad (7)$$

$$\left(\frac{\partial^2 v}{\partial t^2}\right)_p = 2T_c \left[1 - N \ln\left(1 + \frac{p}{B_a \cdot \exp(-B_b \cdot t)}\right)\right] - \frac{2(T_b + 2T_c t)N \cdot p \cdot B_b}{B_a \cdot \exp(-B_b t) \left(1 + \frac{p}{B_a \cdot \exp(-B_b t)}\right)} - \frac{(T_a + T_b t + T_c t^2) N p B_b^2}{B_a \exp(-B_b t) \left(1 + \frac{p}{B_a \exp(-B_b t)}\right)} + \frac{(T_a + T_b t + T_c t^2) N \cdot p^2 \cdot B_b^2}{B_a^2 \exp(-B_b t)^2 \left(1 + \frac{p}{B_a \exp(-B_b t)}\right)^2} \quad (8)$$

where $N = 0.0894$ and t is the temperature in °C .

After numerical integration¹⁵ of eq. (4) and using the $c_p^0(t, 0.1 \text{ MPa})$ values from the DSC measurements, specific heat capacity was calculated in the range of temperatures from -70 to 50°C and in the pressure range from 0.1 to 240 MPa. The results are shown in Figure 4. In this figure, we observe an increase of the specific heat capacity with temperature and a decrease with pressure, as the general tendency observed in solids.¹⁶

In order to a clear visualization of the specific heat capacity dependence on temperature and pressure, we have plotted in Figures 5 and 6, respectively, the c_p dependence on temperature for different isobars (from 0.1 to 240 MPa with a 20 MPa step) and the c_p dependence on pressure for different isotherms, above and below the glass transition (from -70 to 50°C with a 5°C step).

The same sharp increase of the specific heat capacity at temperatures near to the T_g is also clearly visualized in Figure 6, in which we have plotted the specific heat capacity dependence on pressure at several temperatures. A first glance, it is observed a roughly linear specific heat capacity dependence on pressure, in the sense of a c_p decrease with increasing pressure. However, a

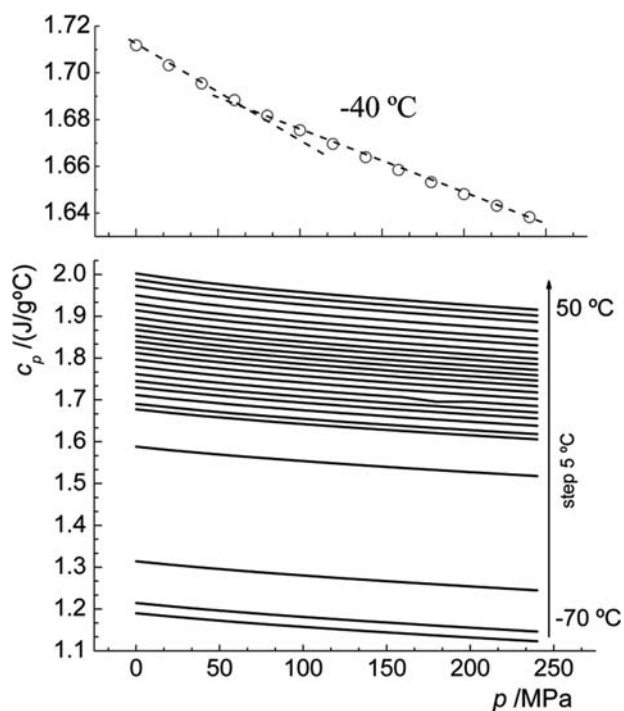


Figure 6. Pressure dependence of the NR isothermal specific heat capacity, c_p ($\text{J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$) (from -70 to 50°C with a step of 5°C).

closed inspection by means of a zoom of one isotherm (see the isotherm of -40°C in the top of the Figure 6) clearly shows that the c_p dependence on pressure is more pronounced in the low pressure zone.

CONCLUSIONS

Specific heat capacity of the NR at pressures above the atmospheric one, was estimated from a thermodynamic expression that combines, on one hand, experimental c_p data obtained by DSC and, on the other hand, c_p data evaluated by means of the Tait EOS.

Our results are in accordance with those ones reported by Andersson and Sundqvist¹⁵ regarding the relative specific heat capacity dependence on pressure for some polymers. Their results, as well as ours, show a nearly linearly decreasing of c_p with pressure, with a more pronounced dependency at low pressures.

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