Thermochimica Acta, 80 (1984) 287–296
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF VARIATION IN THE VALUES OF THE THERMAL PROPERTIES OF RUBBER ON THE VULCANIZATION OF THIN AND THICK SHEETS

M. ABDUL, B. ROCHETTE, A. SADR and J.M. VERGNAUD

Laboratory of Materials and Chemical Engineering, UER of Sciences, 23 Dr. P. Michelon, Saint-Etienne 42100 (France)

(Received 4 May 1984)

ABSTRACT

The effect of a 30% variation around a mean value of thermal property values on the vulcanization of 1 and 2 cm thick rubber sheets is studied, by using a molding process at 40 ° C for the initial rubber and 120 ° C for the injected rubber. The thermal properties chosen are the diffusivity and the product of density and heat capacity. This variation in thermal properties has a slight effect on sheets $\leqslant 1$ cm thick, but becomes significant when the thickness is $\geqslant 2$ cm. This must be taken into account when calculating the time necessary for the state-of-cure to reach 90% at the midplane of the sheets.

INTRODUCTION

As shown previously by considering the heat evolved by the overall reaction of cure [1,2], this reaction is an important step for the vulcanization of rubber in molds, and some parameters of interest were found: the cure enthalpy [3,4], and kinetic data including the constant, activation energy [5] and reaction order. However, the heating of rubber is the first step in the vulcanization process and, the rate at which heat can penetrate the rubber controls the rate of the extruding and molding operations.

It has been shown recently that the temperature gradients developed in the rubber mass can be calculated by several mathematical models [1–3, 6–10] by considering the balance of internal heat generation from the cure reaction, or conduction through the rubber mass. A profile of the extent of the cure reaction, an expression of the state-of-cure, can also be calculated by using the same heat balance [1–3].

Values of thermal properties of rubber, i.e., the thermal diffusivity, α, thermal conductivity, λ, specific gravity, ρ, and specific heat at constant pressure, C, are needed for heat-flow calculations. As indicated several years ago [10–12], hardly any thermal diffusivities exist, and the reported values of thermal conductivity show a very large scatter. Not only do the values differ

0040-6031/84/$03.00

at some temperatures by more than 100%, but different trends are indicated throughout the temperature range. However, diffusivity is the essential parameter for transient-flow calculations. The thermal properties are temperature-dependent. Both the diffusivity and conductivity of black-loaded NR compounds were found to decrease with increasing temperature; this decrease, over the temperature range from ambient to 170 °C, can be as much as 35% [11]. The temperature variation of thermal conductivity is rather small for NR. The thermal conductivity of raw materials and their gum vulcanizates are very similar [10].

The purpose of this work was to study the effect of a variation in the thermal properties (thermal diffusivity, α, and the product ρC) on the vulcanization process of rubber, by considering the profile of temperature and extent of cure obtained at the midplane of rubber sheets of different thicknesses. These thermal properties are considered since they are concerned with the equations of heat transfer. As the injection molding process is of interest for rubber, this study was conducted by choosing two different temperatures for the rubber at injection (40 and 120 °C), while the mold temperature was kept constant. On the one hand, the thermal properties considered vary with the temperature [1], on the other hand, they are non-temperature dependent; the values chosen are varied from their mean value by 30% whereas this mean value is calculated at 120 °C from the above temperature-dependent thermal properties.

THEORETICAL

Mathematical treatment

The differential equation governing transient one-dimensional heat conduction with internal heat generation from the cure reaction is written as follows

$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}x}\left(\lambda\frac{\mathrm{d}T}{\mathrm{d}x}\right)}_{\text{(conduction heat)}} + \underbrace{\frac{\mathrm{d}Q}{\mathrm{d}t}}_{\text{(reaction heat)}} = \rho C\frac{\mathrm{d}T}{\mathrm{d}t} \tag{1}$$

where Q is the heat source term due to the vulcanization.

The thermal diffusivity of rubber is represented either by constant, as in the present study, or by a linear function of temperature

$$\alpha = 3.12\times 10^{-3}(1-10^{-3}\,T) \tag{2}$$

The density decreases and the heat capacity increases with increasing temperature; in the present study, the product ρC in eqn. (1) is either constant or barely sensitive to temperature

$$\rho C = 0.35\left[1+1.6\times 10^{-3}(T-293)\right] \tag{3}$$

Initial and boundary conditions are as follows

$$\begin{array}{llll} t=0 & 0<X<L & T=T_0 & \text{rubber space} \\ t=0 & X<0 \text{ and } X>L & T=T_{\mathrm{m}} & \text{mold space} \\ & 0<X<L & T=T_x,\, t & \text{rubber space} \end{array} \qquad \begin{array}{r} (4) \\ (5) \end{array}$$

The overall cure reaction can be described by a single first-order reaction for this particular rubber compound, as previously shown [1,5].

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = K_0(Q_\infty - Q_t)\exp(-E/RT) \tag{6}$$

where Q_t is the heat of cure reaction evolved up to time t, and Q_∞ the total heat of cure reaction, in the unit volume of rubber.

Numerical calculation

The exact mathematical solution for the heat equation is entirely intractable for this particular problem. A numerical method with finite differences is therefore applicable.

The cross-section of the slab is divided into equal intervals intervals of thickness, ΔX, while a small enough time interval, Δt, is chosen so that

$$M = \frac{(\Delta X)^2}{\Delta t}\,\frac{1}{\alpha} \tag{7}$$

where M is a dimensionless number.

The temperature at a particular reference point, n, at a particular time, $i\Delta t$, is designated with two subscripts, the first identifying the time and the second the point. The heat balance written on the plane n enables us to find the equation

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}\right] + \frac{1}{\rho C}\,\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{8}$$

The heat generated by the cure reaction on plane n during the time Δt is calculated at the time $i\Delta t$ by the following equation

$$\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t = Q_\infty\left[\exp(-S_i) - \exp(-S_{i+1})\right] \tag{9}$$

where $S_i = \int_0^{i\Delta t} K\,\mathrm{d}t$, and S_{i+1} is given by the approximative recurrent relation

$$S_{i+1} = S_i + K_{T_{i\Delta t}}\Delta t \tag{10}$$

EXPERIMENTAL

Properties of rubber compounds

A rubber powder (150–200 μm grain size) having the following composition was used: 55% rubber hydrocarbon; 14% acetone extractable; 25%

TABLE 1

Thermal properties of rubber and kinetic data

(1)	$\rho C = 0.41\,[1+2.5\times10^{-3}(T-293)]$	cal cm^{-2} K^{-1}
	$\alpha = 3.1\times10^{-3}(1-10^{-3}T)$	cm^2 s^{-1}
(2)	$\rho C = 0.406$ cal cm^{-2} K^{-1}	$\alpha = 1.89\times10^{-3}$ cm^2 s^{-1}
(3)	$\rho C = 0.52$	$\alpha = 2.46\times10^{-3}$
(4)	$\rho C = 0.28$	$\alpha = 1.32\times10^{-3}$
$n = 1$	$K_0 = 3\times10^9$ s^{-1}	$E = 25.400$ cal mol^{-1}

carbon black; and 6% ash. The rubber hydrocarbon is a mixture of NR and SBR in the ratio of about 2/3. This rubber powder and 2% sulfur as vulcanizing agent were mixed.

The enthalpy of reaction, Q_∞, and the heat capacity, C, were measured by calorimetry [1]. The results obtained are in good agreement with those found in the literature [13]. The diffusivity, α, was measured by a flash method [14]; the face of the rubber sample is subjected to a thermal impulsion of short duration and the evolution of temperature is recorded on the other face. The diffusivity of the rubber was found to vary slightly with temperature [10,11] as shown in Table 1 (first values). However, constant values were calculated for α and the product ρC from these values at a temperature of 120 °C, as well as other values differing by 30% from the above mean value.

The kinetic parameters in eqn. (6) were determined by microcalorimetry working under isothermal conditions at temperatures ranging from 140 to 170 °C [1,2]. The overall rate of cure was found to follow a first-order reaction with a constant activation energy.

Temperature profiles at the midplane of rubber sheets

The rubber compound was pressed into the slabs of a $10\times10\times L$ cm stainless-steel mold at a temperature of 170 °C. Three series of temperature measurements were determined: the temperature of the mold; the temperature of the rubber just before its introduction into the mold; and the difference between the temperature of the mold and that measured at the midplane of the rubber sheets.

RESULTS

The purpose of this work was to give new information on the effect of a variation in the thermal properties (diffusivity, the product ρC) on vulcanization at the midplane of rubber sheets. As many other parameters are also of interest in the vulcanization process, an additional investigation considered the effect of the above-mentioned parameters by using different rubber-injection temperatures (40–120 °C) and rubber-sheet thicknesses (1–2 cm).

We have examined two different ways for the variation in thermal properties: (1) concerned with a variation of 30% in thermal properties around the average value, by keeping them non-temperature dependent; (2) by using thermal properties expressed as a linear function of temperature (eqn. 2; Table 1). The average for the non-temperature dependent thermal properties was calculated from this linear function at a temperature of 120 °C.

Effect of a variation in thermal properties on vulcanization in thin rubber sheets (1 cm)

Figures 1 and 2 represent the variation of the temperature and state-of-cure determined at the midplane of a 1 cm thick rubber sheet, when the temperature of the rubber at the beginning of the process, T_{ir}, was 40 °C. Of course, the lower values of the thermal properties were responsible for the higher temperature at the midplane and shorter time for the state-of-cure to achieve certain values, but these differences are not as sensible.

Similar results are shown in Figs. 3 and 4 for 1 cm thick sheets when the temperature of the injected rubber was 120 °C, leading to the same conclusions as for $T_{ir} = 40$ °C.

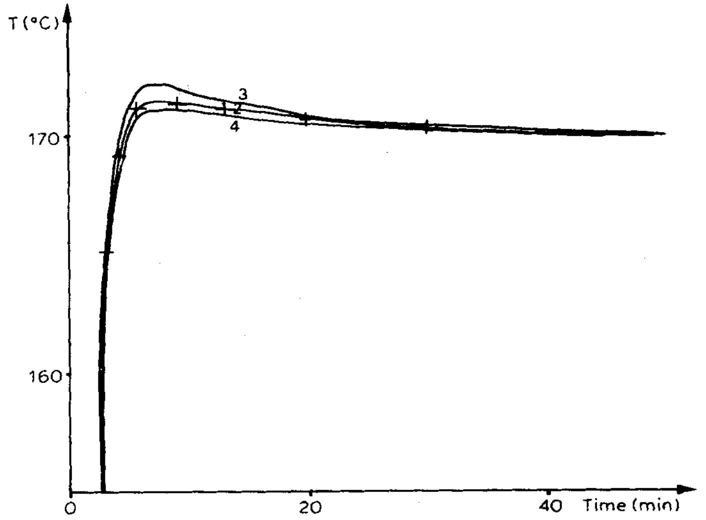

Fig. 1. Midplane temperature vs. time for different values of heat transfer parameters. (2) $\alpha = 0.4$, $\rho C \times 10^3 = 1.89$; (3) $\alpha = 0.52$, $\rho C \times 10^3 = 2.46$; (4) $\alpha = 0.28$, $\rho C \times 10^3 = 1.32$; (+) α and ρC are a function of T. $T_{ir} = 40$ °C, $L = 1$ cm.

Effect of a variation in thermal properties on vulcanization in thick rubber sheets (2 cm)

In order to appreciate the effect of a variation in thermal properties on the vulcanization process, experiments and calculations were carried out using 2 cm thick rubber sheets.

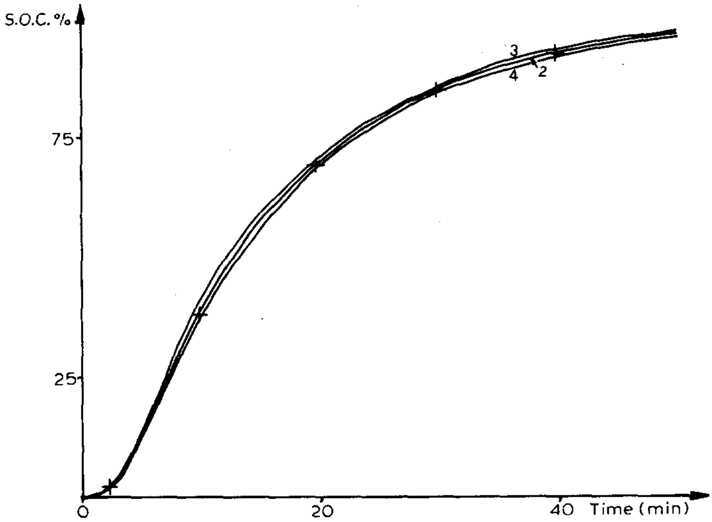

Fig. 2. State-of-cure (SOC) at the midplane vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1.

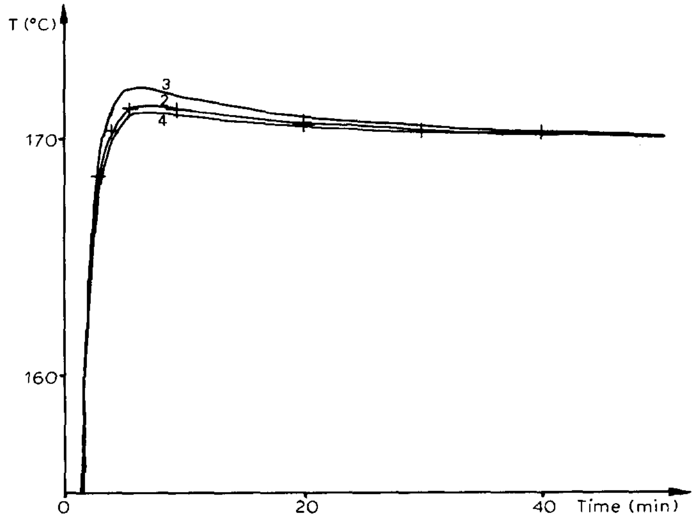

Fig. 3. Midplane temperature vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1. $T_{ir} = 120\,°C$, $L = 1$ cm.

The profiles of temperature and state-of-cure at the midplane are shown in Figs. 5 and 6 when the initial temperature of the rubber was 40 °C. and in Figs. 7 and 8 when it was 120 °C. The effect of a variation in thermal properties on the vulcanization process becomes significant for the thick sheet. A decrease in thermal properties by 60% is responsible for an increase of about 3 °C in the maximum value reached by the temperature at the midplane. The state-of-cure–time curves in Figs. 6 and 8 are not parallel to

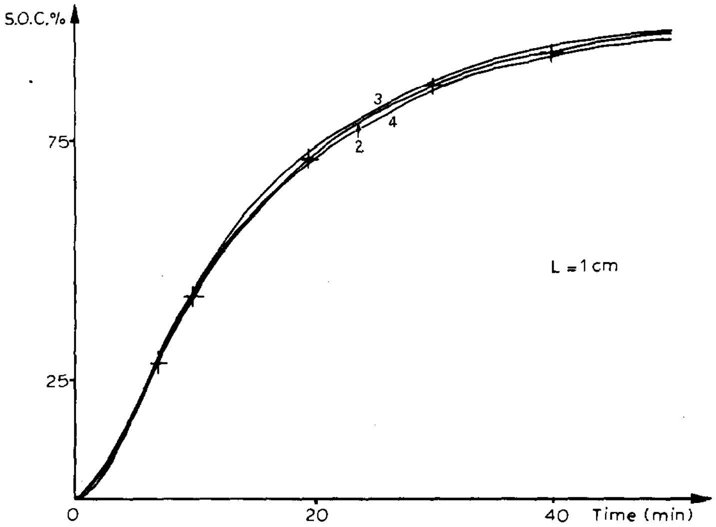

Fig. 4. SOC at the midplane vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1.

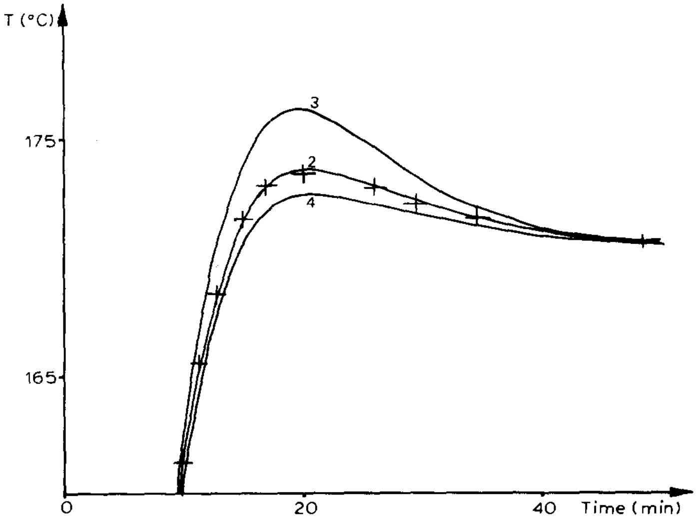

Fig. 5. Midplane temperature vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1. $T_{ir} = 40\,°C$, $L = 2$ cm.

each other, and the retardation in the state-of-cure due to an increase in the thermal properties varies with the value of the state-of-cure. As a 90% state-of-cure is often considered to be of interest, the times necessary for the state-of-cure to reach this value are collected in Table 2 for different thermal properties.

The following conclusions have been drawn from this Table concerned

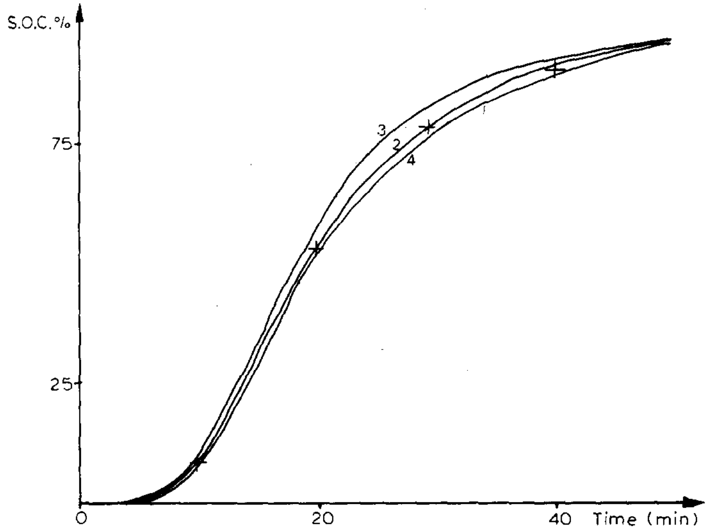

Fig. 6. State-of-cure (SOC) at the midplane vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1.

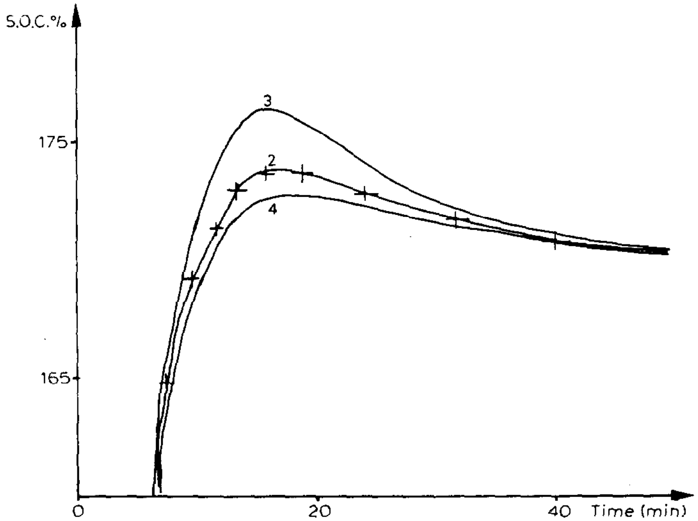

Fig. 7. Midplane temperature vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1. $T_{ir} = 120\,°C$, $L = 2$ cm.

TABLE 2

Time necessary (s) for state-of-cure to reach 90%; $L = 2$ cm

	$\alpha \times 10^3 = 1.32$ $\rho C = 0.28$	1.89 0.41	2.46 0.52	function of T function of T
$T_{ir} = 40\,^\circ C$	2184	2364	2436	2451
$T_{ir} = 120\,^\circ C$	1980	2124	2244	2260

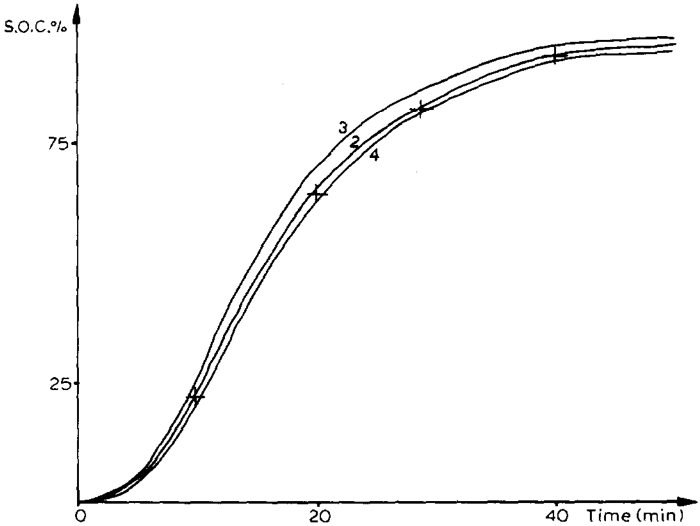

Fig. 8. State-of-cure (SOC) at the midplane vs. time for different values of heat transfer parameters. For thermal properties, see Fig. 1.

with the effect of the values chosen for the thermal properties on the retardation in the state-of-cure at the midplane.

(1) A decrease in the thermal properties must be considered as responsible for a shortening of the time necessary for the state-of-cure to reach selected values.

(2) A variation in thermal properties of 30% around the mean value produces a variation of about 4–6% in the time necessary for the state-of-cure to reach 90%.

(3) A linear function with temperature for the thermal properties gives about the same results as for constant values, when these constant values were calculated from the linear function at 120 °C.

(4) The effect of a variation in thermal properties on the above-mentioned time is about the same in injection molding as in classical molding.

RESULTS

As it has been often taken for granted that a variation in thermal properties on the vulcanization process was of slight importance, we decided to approach the problem by using several thicknesses of rubber sheets.

The results obtained in this paper demonstrate that a variation in thermal properties of 30% around the mean value has no effect on the vulcanization of sheets of $\leqslant 1$ cm, but it becomes significant for sheets of $\geqslant 2$ cm. The choice between a linear function with temperature or a constant value for the thermal properties did not affect the vulcanization at the midplane if the constant value is calculated from the linear function at 120 °C. The effect of a variation in thermal properties on vulcanization is about the same when a higher initial temperature is used for the rubber at injection.

REFERENCES

1 A. Accetta and J.M. Vergnaud, Thermochim. Acta, 59 (1982) 149.
2 A. Accetta and J.M. Vergnaud, Rubber Chem. Technol., 56 (1983) 689.
3 A. Accetta, B. Bouzon, A. Sadr and J.M. Vergnaud, J. Chim. Phys., 80 (1983) 691.
4 A. Sadr, M. Hivert and J.M. Vergnaud, Thermochim. Acta, 71 (1983) 237.
5 C. Ferradou and J.M. Vergnaud, Thermochim. Acta, 68 (1983) 283.
6 S.Y. Pusatcioglu, J.C. Hassler, A.L. Fricke and H.A.Mc Gee, J. Appl. Polym. Sci., 25 (1980) 381.
7 W.E. Claxton and H.C. Holden, Rubber Chem. Technol., 56 (1973) 1103.
8 G.A. Prentice and M.C. Williams, Rubber Chem. Technol., 53 (1980) 1023.
9 D. Hands and F. Horsfall, Kautsch. Gummi, Kunstst., 33 (1980) 440.
10 S.D. Gehman, Rubber Chem. Technol., 40 (1967) 36.
11 D. Hands, Rubber Chem. Technol., 50 (1977) 480.
12 A.K. Sircar and J.L. Wells, Rubber Chem. Technol., 55 (1982) 191.
13 R.H. Normand (Ed.), Proc. RAPRA Meet., Shawbury, Shrewsbury, Gt. Britain, 1975.
14 N. Bekhedahl and J.J. Weeks, J. Res. Natl. Bur. Stand., Sect. A, 73 (1969) 221.