polymer communications

The use of two-component Einstein specific heat models to investigate the structure of dioxane lignin

Peter J. Hall
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
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Specific heat data for dioxane lignin (DL) over the range 350–440 K is interpreted using a two-component Einstein specific heat model. There are two major contributions to the vibrational spectrum of DL: one is associated with one degree of freedom and has a low Einstein temperature; the other is associated with two degrees of freedom and has a high Einstein temperature. The higher Einstein temperature reduces when the DL is above its glass transition temperature.

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It has been shown that the variation of specific heat capacity (C_p) with the temperature of coals can be modelled by two-component Einstein specific heat models[1]. One component represents one-third of the total vibrational spectrum and is associated with low Einstein temperatures (Θ_1) and therefore with easily excited vibrations. The other two-thirds of the vibrational spectrum is associated with high Einstein temperatures (Θ_2) and therefore with macromolecular vibrations that are harder to excite. The total C_p of coal at any temperature is given by:

$$C_p = \left(\frac{R}{a}\right)[1/3g_1(\Theta_1/T) + 2/3g_2(\Theta_2/T)] \qquad (1)$$

where $g(\Theta/T)$ is the Einstein C_p function[2], defined by:

$$g(\Theta/T) = \frac{\exp(\Theta/T)(\Theta/T)^2}{[\exp(\Theta/T) - 1]^2} \qquad (2)$$

and a is the mean atomic weight for the coal. This is a function of the ultimate elemental analysis.

Coal consists of aromatic units and other cyclic functionalities of varying condensation arranged randomly throughout the macromolecular matrix[3]. The physical interpretation of two-component Einstein C_p theories applied to coals is that the vibrations associated with Θ_1 are those perpendicular to the aromatic units which tend to be associated with weak bonding in this direction. Similarly, the vibrations associated with Θ_2 tend to be those in the plane of the aromatic units, and are associated with relatively strong bonding. Θ_1 is associated with one degree of freedom and Θ_2 is associated with two degrees of freedom. This explains the weighting in equation (1). Hall and Larsen[4] have shown how Θ_1 and Θ_2 change following coal solvent treatment and how they may be used to follow changes in coal structure. Equation (1) provides a good fit to experimental data from 150 K to pyrolysis temperatures[4].

The question arises as to whether two-component Einstein temperatures can be used to investigate the structure of other polymer-like materials that are structurally similar to coal. Lignin is a precursor material for lignitic coal and has certain structural similarities. Hatakeyama *et al.*[5] have presented a d.s.c. study of dioxane lignin (DL) in which C_p data between 350 K and 450 K were measured. This showed the existence of a broad glass transition at ~410 K. Hatakeyama *et al.*[5] calculated mean vibrational frequencies for DL from the C_p data using an approximated one-component Einstein model. Hatakeyama *et al.*[5] derived the following relationship to predict the mean atomic vibration frequency:

$$C_v = \chi N k\left(\frac{\theta}{T}\right)^2 e^{\theta/T} \cong C_p \qquad (3)$$

where χ is the number of modes of vibration per gram of material. This is an approximation to the Einstein theory when $\theta/T \gg 1$. Equation (3) contains no term to represent mean atomic weight.

Equations (1) and (3) have been fitted to the experimental data of Hatakeyama *et al.*[5]. A comparison of the respective models is shown in *Figure 1*. Hatakeyama *et al.*[5] give no information concerning the chemical structure of their DL. The mean atomic weight has been taken as 7.9, which represents a mean for similar lignins[6]. The exact value of this is unimportant since it acts as a scaling factor in equation (1). The best fit for the one-component model has Θ_1 = 1155 K and the best fit for the two-component model has Θ = 380 and 1630 K. The value of 1155 K for Θ_1 in the one-component theory corresponds well to the equivalent value of 1137 K given by Hatakeyama *et al.*[5]. This further corroborates the choice of 7.9 as the mean atomic weight. *Figure 1* shows that the one-component model predicts that C_p rises more quickly than is observed. The deviation between theory and experiment is expected to be greater at lower temperatures. The two-component theory gives a much better agreement with the measured C_p. The deviation at 390 and 400 K is because the structure of the DL is changing. This is shown more clearly in *Figure 2*. As the DL goes through its glass transition macromolecular motion increases, and macromolecular vibrations become easier to excite. This

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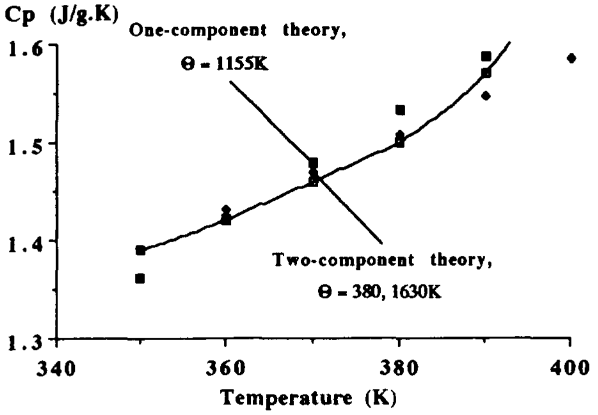

Figure 1 Specific heat data for DL over the range 350–400 K together with one- and two-component Einstein specific heat model fits to the data: (□) experimental data of Hatakeyama *et al.*[5]; (■) one-component Einstein model fit to the data from equation (3) with an Einstein temperature of 1155 K; (◆) two-component Einstein model fit to the data from equation (1) with Einstein temperatures of 380 K and 1630 K

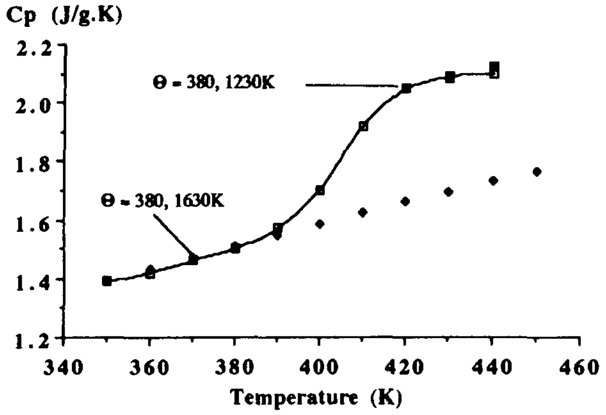

Figure 2 Specific heat data for DL over the range 350–440 K together with a two-component Einstein specific heat model fit to the data: (□) experimental data of Hatakeyama *et al.*[5]; (◆) two-component Einstein model fit to the specific heat data below the glass transition from equation (1) with Einstein temperatures of 380 K and 1630 K; (■) two-component Einstein model fit to the specific heat data above the glass transition from equation (1) with Einstein temperatures of 380 K and 1230 K

is manifested as a decrease in Θ_2 to 1230 K, a decrease of 400 K as a result of the transition. This is equivalent to a decrease in the mean atomic vibrational frequency.

At this point there is a fundamental disagreement with the interpretation of Hatakeyama *et al.*[5], who predict that the mean atomic vibrational frequency increases following the glass transition. The equivalent Einstein temperature changes from 1137 to 1439 K as a result of the glass transition.

The key to understanding this difference lies in the χ parameter in equation (3). It is defined by Alford and Dole[7] as the number of modes of vibration per unit weight of material. It is assumed to be constant for polymers below their glass transition temperatures (T_gs) and be a different, though constant, value for the same polymer above its T_g. Alford and Dole[7] do not give an explicit physical interpretation of χ. Physical models of C_p are based on the assumption that there are three degrees of freedom and that the maximum C_p occurs when all possible vibrational modes are excited, in agreement with the Dulong–Petit law[2]. Equation (3) does not generalize to the Dulong–Petit law at high temperatures. In addition to this, the classical expression for the energy of a linear harmonic oscillator[2]:

$$\varepsilon = \frac{h\nu}{(e^{\theta/T} - 1)} \qquad (4)$$

predicts that as ν or θ are increased at any temperature T then the energy associated with the vibration should decrease, which would be manifested as a decrease in C_p.

The available evidence therefore suggests that equation (1) provides a better model for interpreting C_p data both in accuracy of fit and in terms of understanding the vibrational physics that occurs during glass transition phenomena.

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