Studies on heat capacity of cellulose and lignin by differential scanning calorimetry*

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Heat capacities (C_p) of wood cellulose, other natural celluloses having various crystallinities and of lignin are given for temperatures ranging from 330K to 450K using differential scanning calorimetry. The calculation of the C_p of completely crystalline cellulose is based on a two-state model of cellulose which assumes linearity between the crystallinity and C_p. The higher C_p found in the amorphous region compared with the crystalline region, is apparently due to differences in the frequency of molecular vibration in these two areas. The glass transition of lignin was observed as a sudden increase in C_p at 400K. The precise T_g of lignin was dependent on the sample's origin, characterization, thermal history etc. When annealed at around T_g enthalpy relaxation occurs, and this can be detected as an endothermic peak in the C_p curve at the transition temperature. Moreover, the C_p in the glassy state was found to decrease with both annealing time and temperature, suggesting that rearrangement of the local conformation of lignin molecules occurs in the glassy state temperature range.

Keywords Cellulose; lignin; differential scanning calorimetry; heat capacity; glass transition; annealing

INTRODUCTION

The molecular rearrangement of cellulose molecules is restricted by strong intermolecular hydrogen bonding. Moreover, even the main chain motion in the amorphous region of cellulose is rarely observed by thermal[1], mechanical[2] and dielectric[3] measurements when the cellulose is in a completely dry state. It is difficult to find any first order phase transition in cellulose in a temperature range lower than that at which decomposition starts.

However, lignin, another major component of wood, is a completely amorphous polymer having typical amorphous halo pattern when observed by X-ray diffractometry[4]. The glass transition may be observed by differential scanning calorimetry[5,6], viscoelastic methods[2,6,7] and broadline nuclear magnetic resonance spectrometry[6]. The glass transition of lignin was found to occur at around 400K; however, the transition region is quite broad which may reflect a complicated chemical structure.

It is interesting to find that the above two polymers, which have quite different physical properties, form a compatible composite material in nature. Two important factors in their mutual miscibility are the hydrogen bonding between the two components and the role of water molecules in the living tissue.

Here, we have investigated the thermal features of cellulose and lignin, and have discussed the compatibility of the two components from data on their heat capacities.

EXPERIMENTAL

Samples

The cellulose used in these experiments were wood cellulose, American cotton, jute[8] and amorphous cellulose prepared by the hydrolysis of cellulose triacetate[9]. α-D-glucose anhydride crystal and amorphous D-glucose were prepared as previously reported[10] for use as reference materials.

Dioxane lignin (DL) was prepared as previously reported[11]. All samples were kept in a desiccator with P_2O_5 and annealed at 423K for 5 minutes before the measurements were taken.

Crystallinities of the above samples were measured by X-ray diffractometry[8]. Crystallinities of celluloses were calculated by Hermans' method[12].

Measurements

A Perkin–Elmer differential scanning calorimeter (d.s.c.) model DSC-II equipped with a Textronic 31

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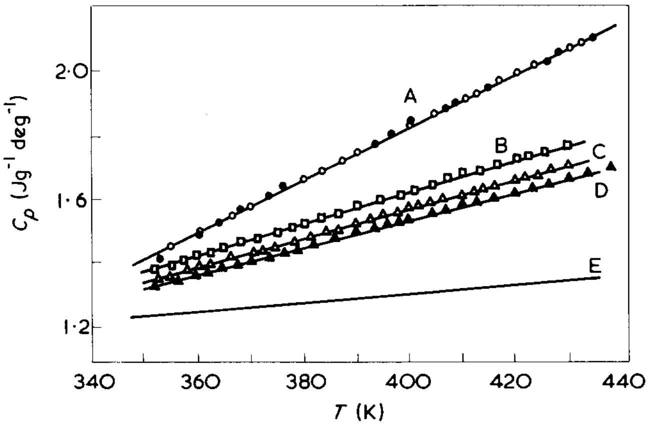

Figure 1 Heat capacities of cellulose samples: A, amorphous cellulose (○ Run 1, ● Run 2); B, wood cellulose; C, jute; D, American cotton; E, calculated values for 100% crystalline cellulose

calculater was used for the measurements. Heat capacities were obtained as reported previously[13]. About 7–10 mg of the sample was pressed, at room temperature, into a pellet so as to avoid thermal hysteresis caused by the delay of thermal conduction. A sensitivity of 2 mcal s^{-1} and a heating rate of 10K min^{-1} were applied. The samples were weighed using a Sartorius microbalance model 2405 before and after the measurement. Samples showing any weight loss by this check were omitted from the experiment. Samples containing a trace amount of moisture, which was easily distinguished by the endothermic deviation of the d.s.c. base-line owing to evaporation, were also omitted.

Before measuring the C_p of the cellulose samples used in this experiment, the d.s.c. curves of the samples were carefully checked under the above running conditions. However, neither exothermic nor endothermic deviations were detected.

A Rigaku Denki Co. X-ray diffractometer Rotaflex RU-100-PL was used. The X-ray diffraction patterns were recorded with a scintillation counter and a rate meter with Cu Kα radiation with a crystal monochromator operated at 42.5 kV and 30 mA.

RESULTS AND DISCUSSION

C_p *of cellulose with different crystallinity*

Figure 1 shows heat capacities (C_p) of celluloses of different origins: American cotton, jute, wood cellulose and amorphous cellulose. The crystallinities, as estimated by X-ray diffractometry, were 52, 46, 38 and 0%, respectively. The C_p curves for several different batches of amorphous cellulose were in close agreement with one another throughout the entire temperature range (two batches are shown in *Figure 1* curve A). The values obtained agreed well with those previously reported[14].

The above samples were carefully handled to avoid moisture absorption and, after annealing at 423K for 10 min, they were weighed for the C_p calculation. The presence of trace amounts of water in a sample caused an endothermic inflection to appear, from 350 to 450K, in the d.s.c. curve. Such samples could not be used, as reabsorption of moisture artifact would take place during cooling to room temperature, despite the continuous flow of nitrogen gas through the cell during the heating and cooling runs.

Figure 2 shows the C_p of cellulose as a function of crystallinity at several representative temperatures. As shown in *Figure 2*, the C_p varies linearly with the per cent of crystallinity. Although there may not be sufficient range of data points from which to extrapolate a straight line, it is rather difficult to obtain natural celluloses having a percentage of crystallinity outside the 40–60% range. Therefore, we have derived C_p values for completely crystalline cellulose by extrapolation to find the intercept at 100% crystallinity. The estimated values are illustrated in *Figure 1* (curve E). The slope of C_p for 100% crystalline cellulose was very small, 1.42×10^{-3} J g^{-1} deg^{-2} compared with the value for amorphous cellulose which was 8.08×10^{-3} J g^{-1} deg^{-2} (see *Table 1*).

The above result was supported by the C_p data for glucose, which are available in either completely amorphous or crystalline form. The slope for the α-D-glucose anhydride crystal yielded 1.76×10^{-3} J g^{-1} deg^{-2} and that for amorphous D-glucose 8.49×10^{-3} J g^{-1} deg^{-2}.

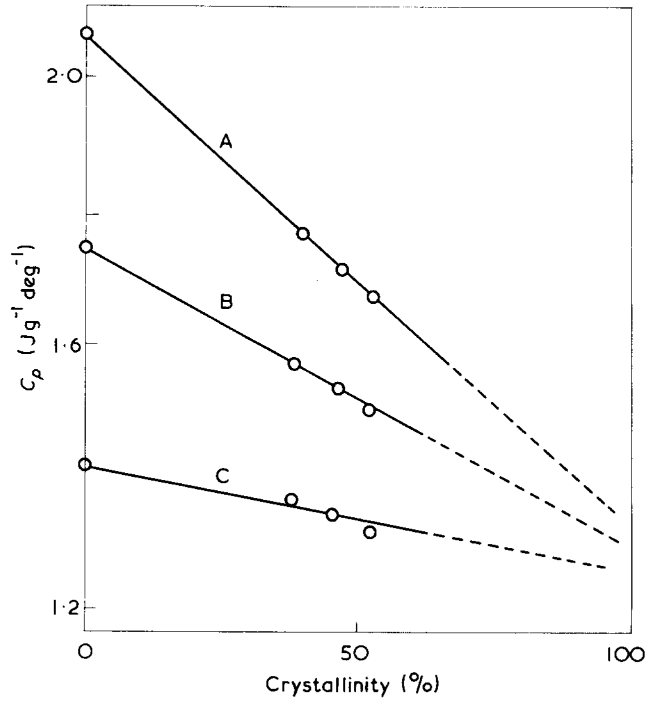

Figure 2 Relation between heat capacities and crystallinity of cellulose at various temperatures. A, 430K; B, 390K; C, 350K

Table 1 Heat capacities of celluloses and D-glucose with various crystallinities

Sample	Crystal-linity (%)	C_p at 350K (J g^{-1} deg^{-1})	$\alpha \times 10^3$ (J g^{-1} deg^{-2})
Amorphous cellulose	0	1.414	8.08
Wood cellulose	38	1.364	5.06
Jute	46	1.339	4.64
American cotton	52	1.318	4.27
100% crystalline cellulose*	100	1.230	1.42
Amorphous D-glucose	0	2.222	8.49
α-D-glucose anhydride crystal	100	1.351	1.76

* Calculated value

C_p values for celluloses between 350 and 440K are given by the following equation from the results shown in *Figure 1*:

$$C_p = C_{p350\mathrm{K}} + \alpha(T - 350) \qquad (1)$$

where $C_{p350\mathrm{K}}$ is C_p at 350K, α is $\Delta C_p/\Delta T$ and T is absolute temperature. The α and $C_{p350\mathrm{K}}$ values of all samples are presented in *Table 1* together with that estimated for 100% crystalline cellulose. Linearity between the C_p of amorphous cellulose and natural celluloses suggests that the two phase model is applicable. From this relationship we can easily derive the crystallinity of an unknown cellulose from the C_p data.

The difference in C_p's between crystalline and amorphous cellulose can be explained partly on the basis of theoretical arguements[15]. Omitting the zero point energy, the average energy of the linear harmonic oscillator, ε, can be expressed by the equation:

$$\varepsilon = R\frac{h\nu}{e^{\theta/T} - 1} \qquad (2)$$

where h is Plank's constant, ν is the frequency of the vibration, θ is $h\nu/k$, T the absolute temperature and k Boltzmann's constant. θ/T is large enough so that the minus one term may be ignored in comparison with $e^{\theta/T}$ in the denominator of equation (2). In this case we can write the equation for the C_p per degree of freedom as

$$C_i = R\frac{\theta^2}{T^2}e^{-\theta/T} \qquad (3)$$

which also makes the gross assumption that the major frequencies of vibration are all approximately the same. It is possible to express the C_v per gram by the equation

$$C_v = \chi Nk\frac{\theta^2}{T^2}e^{-\theta/T} \qquad (4)$$

where χ is the number of modes of vibration per gram of cellulose. We can rearrange equation (4) into a linear equation of the form shown

$$\ln C_v T^2 = \ln \chi R\theta^2 - \frac{\theta}{T} \qquad (5)$$

For convenience we have neglected the difference between C_p and C_v in the following discussion, as C_v cannot be measured by our methods. When $\ln C_pT^2$ is plotted against the reciprocal temperature, θ can be calculated from the slope of the curve. From θ, the major contributing frequency, ν, is derived by the assumption $\theta = h\nu/k$ in the equation (1).

The value of ν is $\sim$750 cm^{-1} in crystalline cellulose and $\sim$1100 cm^{-1} in amorphous cellulose. These values seem to be very reasonable if we keep in mind that natural cellulose shows a broad diffuse absorption at 500–800 cm^{-1} and 900–1200 cm^{-1}. However, the i.r. bands corresponding to those particular frequencies calculated from θ for cellulose, have not yet been identified with a particular molecular motion.

From the intercept of $\ln C_pT^2$ curve at $1/T$ extrapolated to zero, we can obtain the number of modes of vibrations; $\chi \simeq 0.32$ in crystalline cellulose. On multiplying by the molecular weight per repeating unit (=162), a value of $\sim$51 was obtained. The value calculated above does not agree well with theoretically expected value of 63, assuming each atom is a repeating unit ($C_6H_{10}O_5$) which has 3 degrees of freedom. However, if it is considered that the molecular structure of cellulose is very complicated and that we have made several assumptions in deriving our equations which might tend to cause discrepancies, the above disagreement may not be unreasonable.

Enthalpy relaxation of lignin

Lignin is an amorphous polymer in which several different kinds of monomer units are linked to each other[16]. An X-ray diffractogram of lignin shows a broad halo pattern indicating that inter- and/or intra-molecular distances are randomly distributed[4]. The rapid increase in the C_p curve and the α-dispersion in viscoelasticity suggest that lignin molecules transform from the glassy state into the rubbery state at about 400K. The precise temperature of the glass transition depends on the particular characteristics of each lignin, such as sample origin, molecular weight and molecular weight distribution, thermal history, etc.

Figure 3 shows the C_p of DL with different thermal histories as a function of temperature. The C_p values for the glassy and transition regions reflect directly the structural change in the amorphous state of lignin. The endothermic peak which appears at T_g in the heat-treated samples indicates that relaxation of the molecular chain takes place during annealing. For this to occur in lignin the duration of annealing must be long enough to produce a well defined C_p peak. The peak increase at T_g, caused by the annealing, relates with the enthalpy relaxation according to previous papers[17–20]. This suggests that the rearrangement of local order in the amorphous chain can

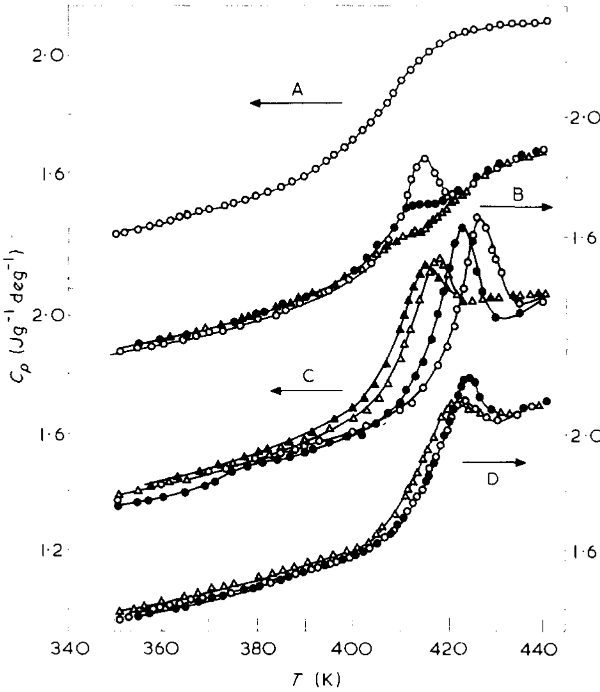

Figure 3 Heat capacities of DL annealed at various temperatures. A, original (quenched from 423K); B, 380K (○, 900 min; ●, 160 min; △, 60 min; ▲, 30 min); C, 395K (○, 1300 min; ●, 940 min; △, 100 min; ▲, 60 min); D, 400K (●, 140 min; ○, 95 min; △, 50 min) (n.b. change in scale in left and right scale axes)

be estimated by d.s.c. At a given temperature below T_g we find that variations in the rate of rearrangement of the polymer molecules are generally dependent on the characteristics of the particular sample being studied. For example, in the case of poly(4-hydroxystyrene), which, having 4-hydroxyphenyl groups, might serve as a model for lignin polymers, the rate of enthalpy relaxation is slower than that for polystyrene because the rearrangement of the local order in the chain molecules is restricted by hydrogen bonding[21]. In the case of lignin, the effects of the hydrogen bonding can be clearly seen in *Figure 3*. The transition from the original structure (A) to the stable glassy state was observed in the sample annealed at 380K (B). The shoulder peak found by annealing for a short time disappears and becomes a broad peak at a higher temperature with longer annealing time. We have discussed this phenomenon in a previous report[5]. The peak temperature for C_p shifts with temperature and time of annealing. The greatest temperature difference was observed in the sample annealed at 395K which is the T_g of the original sample. T_g was determined from the C_p curves as the intersection of the extension of the base-line with a line which is a tangent to the maximum slope of the endothermic peak. T_g increases with increasing annealing time and temperature. By annealing at 380K, T_g shifted to a temperature lower than that for the original sample. This suggests that rearrangement of the local order takes place in the lignin molecule in the amorphous state.

The enthalpy relaxation of amorphous polymers has been explained[22-24] by at least two concepts. (1) A glassy polymer cooled slowly from the molten state or annealed at about the T_g contains smaller amounts of free volume than expected from Doolittle's equation. The glass transition is known to occur when the free volume exceeds a certain theoretical limit, which would predict that in well packed glass, an endothermic peak would be observed at T_g. (2) Alternatively, this concept was not supported by observations of glass transition behaviour of densified polystyrene glass[25,26], which contains very small amounts of free volume. The densified glass showed at normal C_p increase at T_g instead of an endothermic peak. These data have led some researchers to support the iso-configurational[23] entropy theory, which assumes that the decrease in enthalpy of the glassy state occurring during slow cooling or annealing is the result of structural change occurring in the amorphous state. However, direct evidence, e.g. from X-ray diffractometry, has not been obtained owing to the molecular features of the amorphous state.

Our data show that C_p varies with temperature and duration of annealing as shown in *Figure 3*. For example, C_p of the original DL is 1.342 J g^{-1} deg^{-1} at 350K; however it decreases with annealing at 400K; 1.312 J g^{-1} deg^{-1} (annealed for 50 min) and 1.295 J g^{-1} deg^{-1} (annealed for 95 min). These data suggest that rearrangement of the local order takes place in lignin. Annealing seems to facilitate the molecular rearrangement of local order in the amorphous lignin chain, reflecting that this molecule is an assembly of different unit structures with a broad molecular weight distribution.

The vibrational frequency was calculated for DL at a temperature lower and higher than T_g by a procedure similar to that used for cellulose. Frequencies of 790 cm^{-1} (original sample), 750 cm^{-1} (annealed at 395K for 100 min) and 720 cm^{-1} (annealed at 395K for 940 min) in the glassy state and ~1000 cm^{-1} in the rubbery state were obtained.

CONCLUSION

Our results show that the C_p of lignin in the glassy state is similar to that of amorphous cellulose, moreover that the vibrational frequency of lignin in the glassy state is similar to that of crystalline cellulose. This vibrational frequency in the rubbery state is also similar to that of amorphous cellulose. These facts suggest that cellulose and lignin, which exist together in nature as composite materials in living wood, respond to thermal changes in the atmosphere in a similar manner, despite their having completely different chemical structures. In nature, of course, wood contains large amounts of water which serves to form and break hydrogen bonding in different phases.

Our data, *via* thermal analysis of dry cellulose, show that cellulose in the crystalline state is thermally stable and relatively uninfluenced by thermal stimulation. However, the lignin molecule changes its molecular conformation even when it is annealed at a temperature lower than T_g. The fact that the thermal properties of lignin are quite similar to those of amorphous cellulose suggest that lignin molecules would be likely to interact with the amorphous region of cellulose in living plant tissues.

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