

Note

THERMAL PROPERTIES OF POLYVINYL ALCOHOL

CHINNASAMY THANGAVEL VIJAYAKUMAR * and
HARIMURTHI KOTHANDARAMAN

*Department of Physical Chemistry, A.C. College of Technology Campus, University of Madras,
Madras-600 025 (India)*

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The thermal properties of polymers are of interest because of their influence on the processing conditions and on the end applications. On heating, polyvinyl alcohol (PVAL) undergoes glass, structural and melting transitions and decomposes at elevated temperatures. Thus, in addition to the first- and second-order transitions (T_m and T_g), at about 403 K the specific volume, temperature coefficient of specific heat and the mechanical properties of PVAL show a discontinuous change [1]. It has been demonstrated by X-ray diffraction [1], infrared [2] and nuclear magnetic resonance data [3] that the transition occurring at about 403 K is due to the increased mobility resulting from the relaxation of the inter- and intramolecular hydrogen bonds between the hydroxyl groups of PVAL, which in turn allows rapid crystallization of an incompletely crystallized sample [4]. The present study has been applied to monitor this structural change in PVAL through annealing studies using a differential scanning calorimeter (DSC).

EXPERIMENTAL

The PVAL sample was supplied by the SD's-Lab. Chem. Industry, Bombay, India (molecular weight 125,000, acetate content 12%). Weighed quantities of PVAL were annealed in the DSC cell in an oxygen-free nitrogen stream at 323 and 333 K for a variety of predetermined time intervals. After the specific period of annealing, the samples were quenched in an ice-salt bath and the specific heat (C_p) measurements were carried out in a Perkin-Elmer DSC-1B calorimeter, using alumina as the enthalpy calibrant.

* To whom all correspondence should be addressed. Present address: Institut für Chemische und Physikalische Technologie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben, Austria.

The calorimeter temperature was raised from a steady value of 309 K to 401 K in the sequence: (i) empty, (ii) reference and (iii) sample, which is the usual procedure followed for C_p measurements. The values of (i) and (ii) gave the area-to-enthalpy conversion factor and the reference data for specific heats, which in conjunction with (i) and (iii), led to the total enthalpy change in the polymer in the temperature range 309–401 K, as well as the specific heats. The computer program [5] transformed the DSC output into the specific heat values ($\text{cal deg}^{-1} \text{g}^{-1}$). The computer procedure was based on an isothermal temperature calibration and a correction for thermal lag due to the finite heating rate, which was derived from the sample curve itself [6]. All the specific heat measurements were performed at a heating rate of 8°C min^{-1} and the thermal lag observed was 1.8°C .

RESULTS AND DISCUSSION

Polyvinyl alcohol, when heated at 8°C min^{-1} showed a transition around 370 K, the peak being at 371.5 K. In addition, there are two endotherms, one

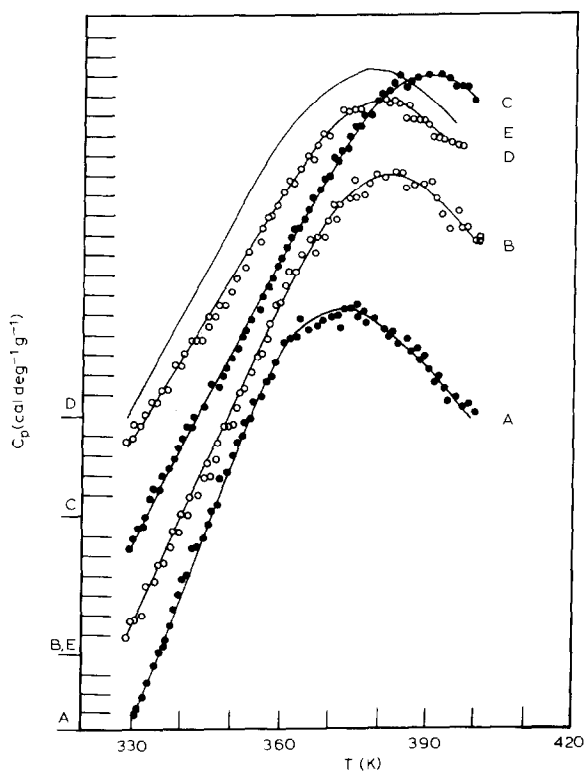


Fig. 1. The effect of annealing temperature (333 K) on the C_p of polyvinyl alcohol. A, Unannealed sample; B, annealed 1 h; C, annealed 3 h; D, annealed 14 h; E, annealed 23 h. The starting point on the C_p axis for the different curves are A, 0.560; B and E, 0.600; C, 0.400; D, 0.500. Each division on the C_p axis corresponds to 0.010 unit.

TABLE I

The variation of specific heat and peak temperature of polyvinyl alcohol with annealing temperature and time

| Curve | Annealing time (h) | C_p (cal deg ⁻¹ g ⁻¹) | | Peak temp. (K) |
|--|-----------------------|--|---------|-------------------|
| | | At 350 K | At peak | |
| <i>Annealing temperature: 323 K (Fig. 2)</i> | | | | |
| A | 1 | 0.490 | 0.604 | 380.5 |
| B | 3 | 0.570 | 0.683 | 383.5 |
| C | 5 | 0.638 | 0.722 | 372.5 |
| D | 15 | 0.594 | 0.688 | 370.5 |
| E | 24 | 0.513 | 0.612 | 378.5 |
| <i>Annealing temperature: 333 K (Fig. 1)</i> | | | | |
| B | 1 | 0.721 | 0.844 | 382.0 |
| C | 3 | 0.479 | 0.626 | 390.0 |
| D | 14 | 0.568 | 0.662 | 380.0 |
| E | 23 | 0.816 | 0.898 | 378.0 |
| A | Unannealed PVAL | 0.693 | 0.774 | 371.5 |

at 479 K and the other at 626 K. The lower-temperature endotherm is attributed to melting, while the higher-temperature endotherm is due to decomposition of the polymer. Severe exothermic decomposition of the polymer starts at 718 K. The C_p measurements of the unannealed PVAL indicate that the C_p increased rapidly, went through a maximum at 371.5 K and then decreased (Fig. 1, curve A). It is clear that the variation of C_p with temperature is very steep in the case of PVAL. The values of C_p for PVAL at 350 K and at the peak temperatures are 0.693 and 0.774 cal deg⁻¹ g⁻¹, respectively, for the unannealed PVAL (Table 1).

Annealing at 323 K

From Fig. 2, it is evident that the values of C_p at 350 K for PVAL annealed for different time intervals, viz. 1, 3, 5, 15 and 24 h, at 323 K were 0.490, 0.570, 0.638, 0.594 and 0.513 cal deg⁻¹ g⁻¹, respectively. When PVAL was annealed for 1 h, the C_p value decreased in comparison with the unannealed sample showing an increased order due to co-arrangement of the chains.

When the annealing time was increased from 1 to 3 h, the C_p value increased from 0.490 to 0.570 but was still lower than the C_p value of the unannealed PVAL. This increase in C_p value persisted up to 5 h of annealing. But on increasing the annealing time from 5 to 24 h, the C_p value decreased from 0.638 to 0.513. Thus, during the first hour of annealing there

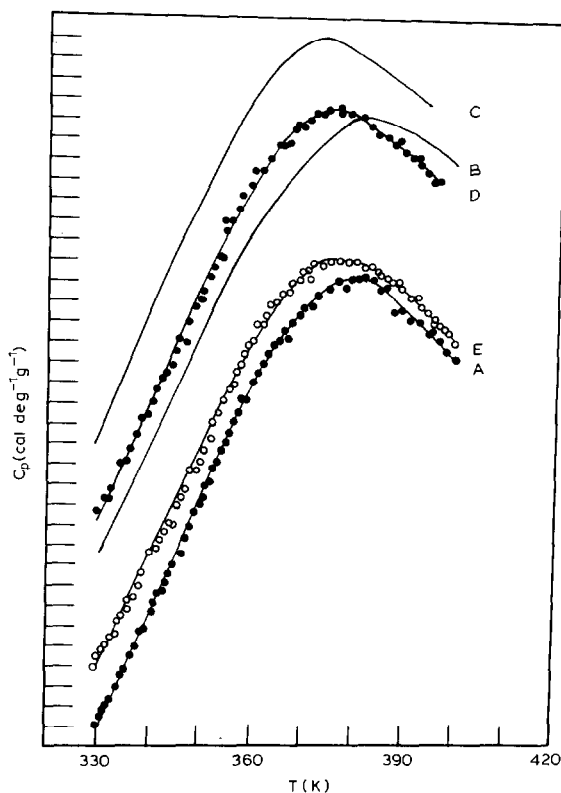


Fig. 2. The effect of annealing temperature (323 K) on the C_p of polyvinyl alcohol. A, Annealed 1 h; B, annealed 3 h; C, annealed 5 h; D, annealed 15 h; E, annealed 24 h. The C_p axis starts at 0.370 for all the curves. Each division on the C_p axis corresponds to an increment of 0.010 unit.

should be some sort of chain realignment, which can be explained in terms of increased inter- and intramolecular hydrogen bonding, leading to a decrease in the amorphous content and hence a decrease in the C_p value. But when the annealing time is increased from 1 to 3 h, because of the continuous thermal energy input into the system by the way of annealing, the ordering process is disrupted owing to the increase in the molecular motions, leading to a thermodynamically more stable state. Once the annealing time is further prolonged, say 15 and 24 h, again the phenomenon of ordering of chains proceeds and leads to the decrease in the C_p value.

The variation of C_p with annealing time at the peak temperature follows the same trend as the C_p variation at 350 K (Table 1). From Table 1, it is evident that the peak temperature increased from 371.5 to 380.5 K during the 1 h annealing and increased to 383.5 K during the 3 h annealing. It then decreased to 372.5 K (5 h annealing) and then steadily increased to 378.5 K (24 h annealing). This reverse order of the peak temperature variation also

supports the foregoing explanation. Thus there is a complex interplay of thermodynamic factors governing the ordering or the local alignment of the chain segments by breaking and making of the inter- and intramolecular hydrogen bonds present in the bulk PVAL sample and the kinetic factors governing the thermal motions of the chain segments during annealing.

Annealing at 333 K

When the annealing temperature was raised from 323 to 333 K, the variation of C_p with annealing time was different (Fig. 1, Table 1). The C_p value of the sample annealed at 333 K for 1 h was almost the same as the unannealed sample. Annealing for 1 h at 333 K does not result in any increased order which may be due to the increased thermal mobility at the higher temperature. This is in contrast to the increased order on annealing PVAL for 1 h at 323 K. At higher temperatures, the hydrogen bonds are not so stable as at lower temperatures. Hence annealing does not result in an increase of order as was observed at the lower temperatures. A decrease in C_p value was seen for the sample annealed for 3 h. When the annealing time was increased to 23 h, the C_p regularly increased. The increase in intrinsic viscosity of PVAL solutions with time [7,8] was attributed to the formation of intermolecular hydrogen bonds leading to the association of polymeric chains in solution. This view is analogous to our observations on the effect of annealing time at 323 K.

Thus the annealing studies of PVAL showed that the alignment of chain segments due to the reorganization of the inter- and intramolecular hydrogen bonds depends both on the annealing temperature and the annealing time.

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