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Heat Capacity

The Heat Capacity of Poly(Oxymethylene) as a Function of Crystallinity

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Dedicated to Professor Dr.-Ing. Georg Manecke on the occasion of his 70th birthday

Summary

The heat capacity of several poly(oxymethylene) (POM) samples with crystallinities between 50 and 80 per cent are determined by DSC in the solid (-100 to 70°C) and liquid state (170 to 240°C). Linear relationships between heat capacity and crystallinity are found, if premelting phenomena are excluded. The heat capacities of crystalline and liquid POM are obtained by extrapolation. They differ from the hitherto recommended data. Above the glass transition region the extrapolated heat capacity for zero crystallinity agrees with the heat capacity of the melt extrapolated to lower temperatures. This is in contrast to recent results of Suzuki et al., who assume the existence of a rigid amorphous fraction which does not contribute to the glass transition.

Introduction

The heat capacity c_p as a function of temperature for POM has been published by several authors (1-5), but with one exception (5) the crystallinity of the samples is unknown. In a recently published paper the crystallinity dependence of c_p for POM was investigated by Suzuki et al. (6). The discussion in (6) is based upon only few samples within a very narrow crystallinity range (56-67%) and upon questionable recommended data for crystalline POM (7). In this paper new experimental results will be presented.

Experimental

Compression moulded films of DELRIN 500 were quenched from the melt (200°C), followed by annealing for different periods of time at 160, 168 and 172°C, respectively. After storing the samples for several hours at room temperature, densities between 1.4077 and 1.4599 g/cm^3 were obtained, as measured at 20°C by the floating method, using mixtures of tetrachloroethane and n-heptane. Heat capacity measurements were performed with a computerized DSC-2-calorimeter

(Perkin-Elmer-Corp.) at a heating rate of 10 K/min and a sample mass of 12-14 mg. The samples were mounted in the DSC-cell at room temperature. The calorimeter calibration with pure standards revealed that the correction factor depends on the calorimeter block temperature, which for measurements in the solid state (-100 to 70 °C) is thermostated at -150 °C and for measurements of the liquid (167 to 240 °C) at -50 °C. The experimental heat of fusion ΔH^* was determined by integration between 30 and 200 °C.

Results

Crystallinity

The crystallinity w_c of semicrystalline polymers can be determined from the experimental heat of fusion ΔH^* or from the specific volume v, if the heat of fusion ΔH_M of the POM crystal and the specific volumes v_a and v_c of the undercooled melt and the crystal are known.

$$w_c = \frac{\Delta H^*}{\Delta H_M} \qquad [1] \qquad\qquad w_c = \frac{v_a - v}{v_a - v_c} \qquad [2]$$

From eqs. [1] and [2] a linear relation between ΔH^* and v is predicted, which is confirmed in Fig.1 for DELRIN 500®. By extrapolation to the amorphous state ($\Delta H^* = 0$) $v_a = 0{,}758$ cm³/g is obtained, which is in good agreement with (8).

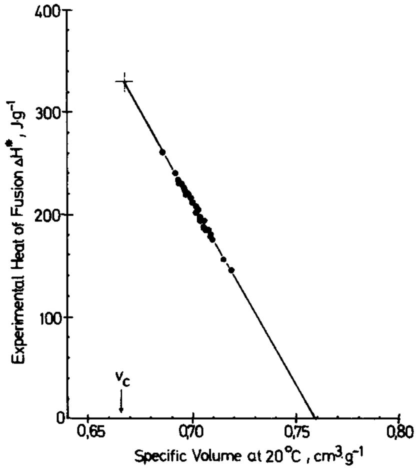

Figure 1
Relation between experimental heat of fusion and specific volume for DELRIN 500.

From several x-ray investigations (9-14) an averaged value of $v_c = 0.669\ cm^3/g$ is obtained for the elementary cell of POM. The extrapolation in Fig.1 to $v_c = 0.669\ cm^3/g$ results in $\Delta H_M = 330$ J/g for 100% crystalline POM. Within the experimental limits of error good agreement between the crystallinities from ΔH^* or from v is logically found.

Heat capacity

The heat capacity is plotted in Fig.2 as a function of crystallinity. Between -100 and 30°C c_p decreases linearly with increasing w_c. Above 30°C the linearity exists only for $w_c > 0.65$. Here samples with $w_c < 0.65$ show positive deviations over linearity. The heat capacities of the undercooled melt which are plotted in Fig.2 at $w_c = 0$ have been linearly extrapolated from the liquid state. Between 167 and 240°C the temperature dependence of c_p can be described by eq. [3] for ten independent measurements with a maximum deviation < 1%.

$$c_p = 1.329 + 1.67\ 10^{-3}\ T\ J/gK \qquad [3]$$

The measurements of Suzuki et al. (15) over the same temperature range obey eq. [4]. At 200°C the difference

$$c_p = 1.550 + 1.24\ 10^{-3}\ T\ J/gK \qquad [4]$$

between eqs. [3] and [4] is only 0.8%, but the decisive difference is the temperature dependence which effects the low temperature extrapolation.

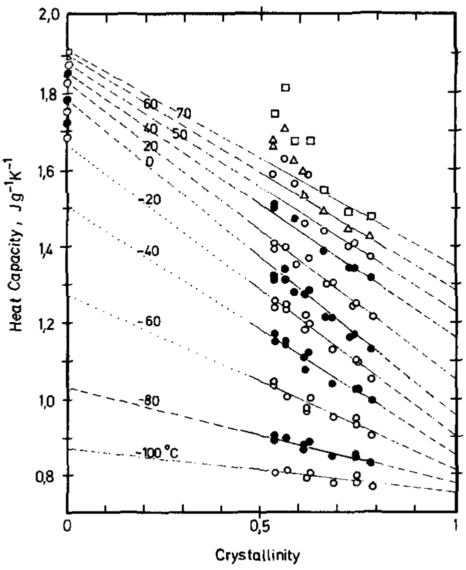

Figure 2
Heat capacity as a function of crystallinity at different temperatures for POM

The straight lines in Fig.2 extrapolate to the heat capacities given by eq. [3] for $w_c = 0$. No agreement between the extrapolated heat capacities and those of the undercooled melt is obtained within the glass transition region. DSC-measurements show, that on heating with 10 K/min the asymmetrie glass transition starts at about -80°C while the upper end is located near -20°C.

As shown in Fig.3 for $w_c = 0.58$ another apparent steplike increase of c_p occurs at about 30-40°C. Really this is no glass transition, but a premelting peak of small and/or imperfect crystals, which is responsible for the positive deviations from linearity in Fig.2 at > 30°C. Its intensity depends on the thermal prehistory.

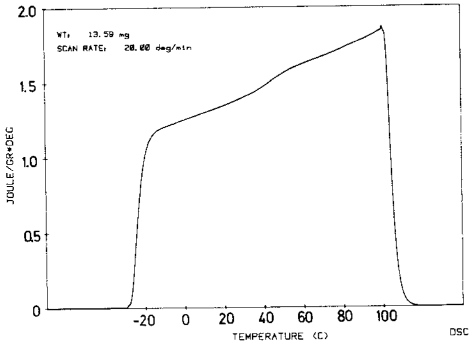

Figure 3
Heat capacity of POM. Crystallinity 0.58. Copy of computer printout

Discussion

The extrapolated heat capacities for 100% amorphous and 100% crystalline POM (Fig.2) are plotted in Fig.4 as a function of temperature, together with the recommended data (7, 15). Over the whole temperature range the heat capacity of 100% crystalline POM is considerably smaller as compared with (7). Between -83 and 27°C the recommended data in (7) are taken from (4) for a low temperature irradiation-polymerized trioxan crystal, the crystallinity of which has not been proved in (4). For temperatures between -70 and 0°C the differences between the DSC data in (4) and the very precise adiabatic c_p data in (5) for $w_c = 0.57$ are so small, that the assumption of 100% crystallinity for the irradiation-polymerized crystal (4) is strongly unprobable.

As a consequence of the too high c_p-data for the POM crystal the linear extrapolations to $w_c = 0$ in (6)

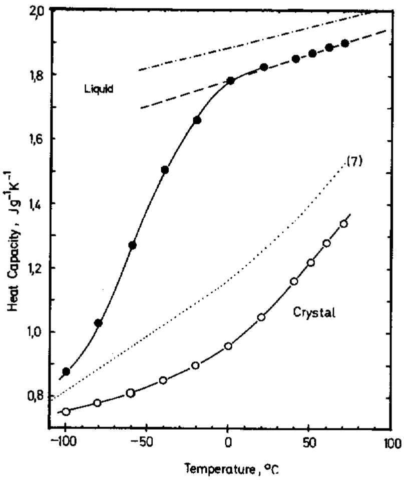

Figure 4
Heat capacities of the extrapolated 0% and 100% crystalline POM.

—●— extrapolated to w_c=0 (Fig.2)

— — — eq.3 (undercooled melt)

—·— eq.4 (undercooled melt)

······ recommended data for w_c = 1 (7)

—○— extrapolated to w_c=1 (Fig.2)

obviously yield too low heat capacities for the undercooled melt. It is this questionable extrapolation which led Suzuki et al. (6) to the conclusion, that semicrystalline POM contains a rigid amorphous fraction, which does not contribute to the glass transition. This concept cannot be supported by the present results which show, that outside the glass transition region the heat capacity of POM follows the two-phase model with linearity and additivity of the amorphous and crystalline contributions. Within the glass transition region an additive behaviour cannot be expected, especially if the glass temperature and the detailed form of c_p = f(T) change with crystallinity. It is therefore also questionable if the linear extrapolations at -20, -40 and -60°C (dotted lines in Fig.2) are allowed.

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