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THERMAL ANALYSIS OF THERMOPLASTIC POLYMERS

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ABSTRACT

For the technologically important thermoplastic polymers, the basic transition analyses are those transitions with entropy and enthalpy change (first-order transitions) and of transitions with abrupt change only in heat capacity (glass transitions). A collection of critically reviewed thermodynamic properties for the thermoplastic polymers are now available. Those transitions do not only permit a quantitative assessment of mobility and order through their thermodynamic functions, they can also be characterized by their time-dependent, nonequilibrium behavior. For example, through its broadening over a large temperature range the glass transition gives phase-structure information, and through its hysteresis behavior, activation energy parameters. Kinetics and melting as well as crystallization can reveal special characterization of the materials. Combining both types of information on glass and melting transitions, a new characterization of the interface structure in the thermoplastic polymers has been studied: "rigid amorphous" fraction.

INTRODUCTION

Thermal analysis of the technologically important thermoplastic polymers has been carried out in our laboratories recently. Both solid (semicrystalline and glassy) and liquid state heat capacities have been established from experimental measurements [1-7] and calculations [8]. From heat capacity data it is not only possible to derive all thermodynamic properties, e.g., enthalpy, entropy, Gibbs free energy and residual entropy for amorphous materials at absolute zero, but also precise baseline can be established. Such baselines are fundamental for the study of transition phenomena in semicrystalline polymers [9]. The results we report here lead to a systematic discussion of thermal characterization in the thermoplastic polymers.

EXPERIMENTAL

The experiments were carried out with a DSC 2 in our laboratories. An IBM-PC LMS DSC data station was used for the treatment of the analog output.

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Both temperature and heat capacity calibrations followed our standard procedures. All heat capacity runs were made with 15 mg samples. Aluminum pans of similar mass (± 0.002 mg) were used for blank, reference and sample. The heating rate was 10 K/min, as usual. All measurements were made in a dry nitrogen atmosphere. The calorimeter is shielded in the Perkin Elmer dry box attachment. The samples were poly(thio-1,4-phenylene)(PPS), poly(oxy-1,4-phenylene)(PO), poly(oxy-2,6-dimethyl-1,4-phenylene)(PPO), poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)(PEEK), poly(4,4'-isopropylidenediphenylene carbonate)(PC), poly(ethylene-2,6-naphthalene dioxylate)(PEN), poly(ethylene terephthalate)(PET), and poly(butylene terephthalate)(PBT).

RESULTS AND DISCUSSION

Solid and Liquid Heat Capacities. Both solid and liquid heat capacities have been measured and calculated. Their relationship with temperature are as follows.

Solid heat capacities in J/(K mol):

PEEK: $C_p = \exp[0.1695(\ln T)^3 - 2.193(\ln T)^2 + 10.08(\ln T) - 11.63]$ (130-400 K) (1)

PPO: $C_p = \exp[-0.1322(\ln T)^3 + 2.230(\ln T)^2 - 1.168(\ln T) + 23.61]$ (220-480 K) (2)

PPS: $C_p = \exp[0.1090(\ln T)^3 - 1.785(\ln T)^2 + 10.774(\ln T) - 18.92]$ (220-330 K) (3)

PEN: $C_p = 0.0001616(\ln T)^2 + 0.7544T + 29.26$ (220-350 K) (4)

PO: $C_p = 0.337T + 7.95$ (300-350 K) (5)

PC: $C_p = \exp[0.04366(\ln T)^3 - 0.6603(\ln T)^2 + 4.2605(\ln T) - 5.1937]$ (120-410 K) (6)

PET: $C_p = 0.0006615T^2 + 0.7204T + 8.378$ (240-330 K) (7)

PBT: $C_p = 0.000713T^2 + 0.5203T + 52.16$ (210-300 K) (8)

PEEK: $C_p = 0.496T + 308.2$ (9)

PPO: $C_p = 0.2282T + 141.6$ (10)

PPS: $C_p = 0.1257T + 119.7$ (11)

PEN: $C_p = 0.4094T + 268.4$ (12)

PO: $C_p = 0.1425T + 99.01$ (13)

PC: $C_p = 0.559T + 249.2$ (14)

PET: $C_p = 0.282T + 237.0$ (15)

PBT: $C_p = 0.4622T + 219.6$ (16)

The liquid heat capacities of these thermoplastic polymers are substantially linear with respect to temperature.

Crystallization Behavior. The eight polymers we chose belong to three different types of crystallization behavior. Figures 1-3 show typical wide-temperature range DSC traces of PPS, PEN and PPO which were quenched from their melts to liquid nitrogen temperature before measurements. The first type, shown in Fig. 1, exhibits over a very limited temperature range a metastable liquid state above the glass transition for PPS [3] before a major exothermic crystallization peak occurs. A similar observation has been made with PEEK [1], PO, and PBT [7]. Therefore, these four polymers show fast crystallization. The second type is shown in Fig. 2 for the example of PEN [4]. An exothermic crystallization peak appears at a much higher temperature than T_g. In fact, it is just below the irreversible melting peak of PEN. A very slow and hindered crystallization is thus typical. PET belongs to this type of crystallization. The third type is represented, for example, by PPO and shown in Fig. 3 [2]. It is obvious that the quenched PPO does not show any crystallization. Above the glass transition range, the liquid state is metastable. PPO belongs thus to the category of polymers that are very difficult to crystallize. Polycarbonate (PC) also belongs to this category.

Glass Transitions. The glass transition region has to be characterized by five temperatures (T_b, T_1, T_g, T_2 and T_e) [1]. The heat capacity increases at T_g are calculated based on the solid and liquid heat capacities. They are listed in Table 1. Broadness of the glass transition region of the semicrystalline samples is generally observed due to the existence of crystals. The hysteresis is found for all the amorphous polymers as shown in Figs. 3-5 as three examples. Sometimes, the hysteresis can also be observed from semicrystalline samples such as PEEK (Fig. 4) [1], but with much less effect than one expects based on their crystallinity. The positive deviation from the linear relationship in Fig. 5 indicates that the freezing and unfreezing of motion of PEN at T_g is asymmetric, as well as in the case of PPO (Fig. 3). One can find that polymer chains with a backbone width larger than that of the phenylene group (0.5 nm) seem to often cause such positive deviation [2, 4].

Melting Behavior. A common observation of the thermoplastic polymers is the multiple melting peaks after isothermal crystallization as shown in Fig. 6 for PEN which indicates sequence of crystallization, recrystallization and reorganization. The low melting temperature peak is also closely related to the formation of "rigid amorphous" fraction in those polymers. Experimental observations of different heating rates indicates that the high melting materials do form during isothermal crystallization. Such conclusions can also be proven by the fusion behavior of two-step crystallization, and isothermal crystallization for different lengths of time [1, 3, 4, 7]. The ΔH_f of 100% crystallinity of the polymers are also listed in Table 1.

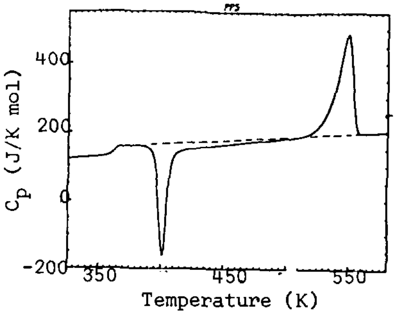

Fig. 1. DSC melting trace of quenched PPS.

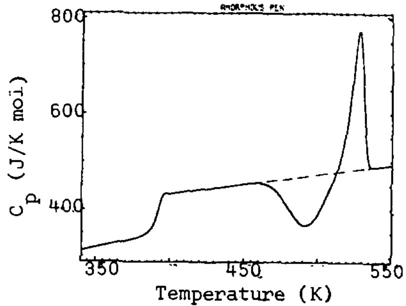

Fig. 2. DSC melting trace of quenched PEN.

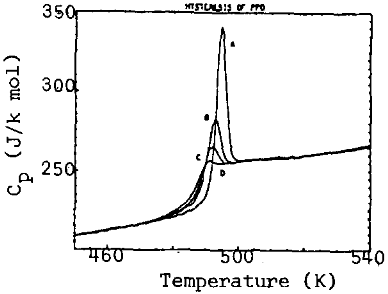

Fig. 3. DSC melting trace of PPO with different cooling rates (A: -0.31 K/min, B: -2.5 K/min, C: -10 K/min, and D: quenched to liquid N_2).

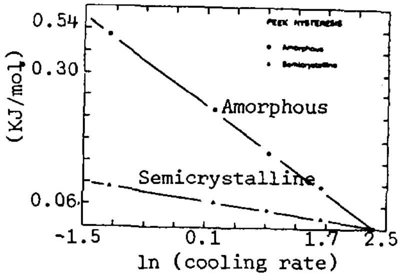

Fig. 4. Relationship of hysteresis peak Δh and ln (cooling rate) for PEEK.

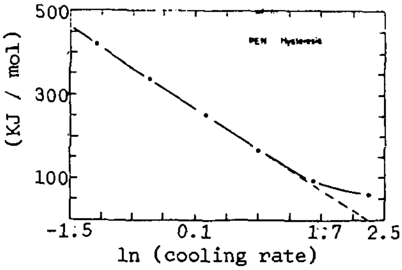

Fig. 5. Relationship of hysteresis peak Δh and ln (cooling rate) for PEN.

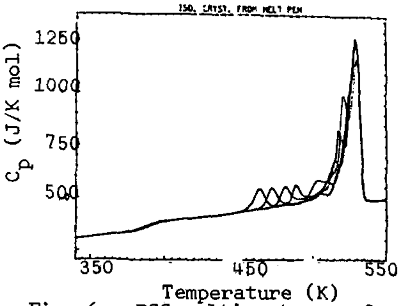

Fig. 6. DSC melting traces for isothermal crystallization of PEN at 450, 460, 470, 480, and 490 K (for low-temperature melting peaks from left to right, respectively).

TABLE 1

Thermodynamic properties of the thermoplastic polymers

Polymers	T_g (K)	ΔC_p J/(K mol)	T_m°	ΔH_f (kJ/mol)
PEEK	419	78.1	668	37.4
PPS	363	29.9	593	8.65
PO	358	21.4	535	7.82
PPO	483	32.0	580	5.95
PC	424	56.4	608	33.5
PEN	390	80.1	610	25.0
PET	342	77.8	553	26.9
PBT	248	107.0	518	32.0

Rigid Amorphous Fractions. For semi-crystalline samples of the thermoplastic polymers ΔC_p is not proportional to the amorphous weight fraction $(1 - \omega^c)$; i.e., from ΔC_p one can calculate only an overall "rigid fraction f_r" that remains solid beyond the glass transition region.

$$f_r = 1 - \Delta C_p(m)/\Delta C_p(a) \qquad (17)$$

where $\Delta C_p(m)$ and $\Delta C_p(a)$ are heat capacity increases at T_g for measured semi-crystalline and total amorphous samples, respectively. On the other hand, the area of the melting peak above the baseline gives the heat of fusion, usable for weight-fraction crystallinity determination

$$\omega^c = \Delta H_f(m)/\Delta H_f(c) \qquad (18)$$

where $\Delta H_f(m)$ and $\Delta H_f(c)$ are heat of fusions for measured semi-crystalline and 100% crystalline samples, respectively. We have found that $f_r < \omega^c$. It means that there is an extra metastable phase which neither contributes to ΔC_p at T_g, nor to ΔH_f at T_m, and it is now called a "rigid amorphous fraction." It has been observed that in the thermoplastic polymers, such "rigid amorphous fraction" can be as high as 30% of total amorphous materials, and may influence mechanical properties of the polymers [1-4, 7].

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