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THERMAL ANALYSIS OF CRYSTALLINE POLYMER BLENDS

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Abstract

PEI/PEEK blends have been prepared and analysed by DSC. The blends are compatible over the full composition range in that amorphous samples are transparent and exhibit a single T_g varying with composition between the limits of the two components. The crystallisation kinetics of PEEK from the blend melt has been measured by DSC but the technique is limited to blend compositions above 20% PEEK. The use of a polarised light microscope to measure crystallization kinetics and melting behaviour of blends with compositions as low as 2 and 5% PEEK is discussed. In general, since the extent rather than the rate of crystallization is measured directly, the polarised light microscopy extends the measurement to slower rates and so to a wider temperature range.

Keywords: blends, crystallisation kinetics, hot stage microscopy, polyether ether ketone, polyether imide

Introduction

Blending two thermoplastics can be a convenient method of creating new materials with a range of different properties as well as reducing cost without chemically modifying them. Blending can impart the improved properties of one component to those of the other. The aim of this paper is to assess the effect of blending on the thermal properties and mechanical behaviour of blends of two high temperature engineering polymers, polyether ether ketone, PEEK, and polyether imide, PEI. PEEK is expensive and so it is generally used in high technology applications as a high melting partially crystalline polymer, *m.p.* 360°C. It can also be used as an amorphous glass but the glass transition temperature, T_g, at 140°C, is quite low and it is sensitive to aromatic and chlorinated hydrocarbons. PEI is a tough amorphous thermoplastic with a higher T_g, i.e. 220°C. It is notch sensitive and prone to stress cracking with some organic solvents. Diluting PEI with PEEK should raise T_g and crystallisation of the PEEK should improve notch sensitivity, impact properties and the solvent resistance of PEI. Benefits were sought for minimal amounts of PEEK added, so only low compositions of PEEK were investigated.

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Experimental

Polyether imide was supplied by General Electric Ltd as the grade Ultem 1000. Its average molecular mass was 20 kg mol^{-1}. Polyether ether ketone, grade 450G, was supplied by Victrex Ltd. Its number average M_w was 40.7 and mass average M_w 99.2 kg mol^{-1}. Blends were prepared on an APV model MP2000 twin screw compounder at barrel temperature of 380°C. The pellets of PEI, PEEK and the blends were dried before processing.

A Leitz Dialux-Pol polarising light microscope was used with a Linkam TH600 hot-stage whose temperature was controlled with a Linkam PR600 temperature controller to ±0.1 K. The microscope was used with a constant wavelength light source from a sodium vapour lamp. A 50 ohm platinum resistance thermometer was used as the temperature probe, and calibrated from the *m.p.* of pure sodium nitrate. With this apparatus the temperature could be controlled from ambient to 770±0.1 K with heating rates from 0.1 to 90 K min^{-1} and cooling rates from 0.1 to 200 K min^{-1}. Cooling was achieved with nitrogen gas by passing over liquid nitrogen through internal cooling rings fitted to the hot-stage. The sample chamber was flushed with nitrogen.

The change in light intensity was followed using an ORP 12 photo-resistor cell. The resistance of this cell decreased as the light intensity increased. Variation in resistance was measured in a bridge circuit and the voltage changes recorded by the a/d conversion of the BBC Master microcomputer via an operational amplifier.

Initial studies were carried out to ensure that the photo-resistor circuit produced a linear response with light intensity, since this was essential for all subsequent analyses. Calibration was achieved using a relative area method. The light intensity was measured as a function of the sample area illuminated, and compared with photo-resist response.

Thin sections (20–40 μm thick) were prepared using a Leitz sledge microtome. These were placed between glass cover slips, inserted into the stage sample holder and then into the furnace. Samples were melted and held in the melt for various dwell times, before being cooled rapidly to the crystallization temperature.

The samples were subsequently melted at fixed heating rates to determine their *m.p.* In both types of experiments the light intensity was monitored as a function of time and temperature. The intensity/time/temperature data was stored directly on disc for subsequent analysis.

A Perkin-Elmer differential scanning calorimeter, model 2, was interfaced to an IBM compatible PC. The DSC was calibrated from the enthalpy of fusion of indium, and the m.p. of 99.999% purity indium, tin, lead and zinc. The DSC was used to follow crystallization kinetics as well as melting, using procedures outlined previously [1].

Results and discussion

The mechanical properties of the blends

Addition of PEEK to PEI resulted in a linear decrease in the yield stress between the limits of 93 and 63 Mpa corresponding to the yield stress of PEI and PEEK, (Fig. 1). All the blends in these tensile experiment were ductile, exhibiting a marked drop in load and local yielding due to neck formation. The ultimate elongation was about 130%. These samples were amorphous but annealing allowed some crystallinity to develop and this raised the yield stress of the blends to an optimum value of 92±2 MPa – close to the original value for PEI.

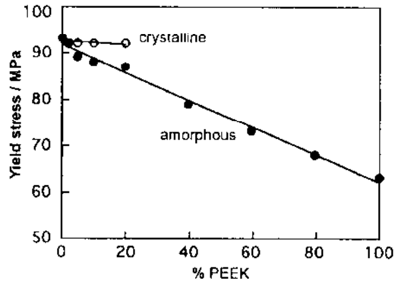

Fig. 1 Variation of yield stress with content

It was thus possible to add PEEK to PEI in small amounts of 5–20% to retain the tough ductile properties of PEI and high yield stress without making the product too expensive with use of too much PEEK. However, it was important to determine the temperature – time range for each blend to develop to an optimum degree of crystallinity.

DSC studies

DSC analysis of the quenched blends exhibited a step change in the heat capacity characteristic of a glass transition, followed by an exotherm and at a much higher temperature an endotherm – characteristic of crystallisation and melting respectively, (Fig. 2). The enthalpies of these transitions were consistent with the samples initially being completely amorphous [2] and with only the PEEK component crystallising. The T_gs of the blends varied linearly with composition between the T_g values of PEEK and PEI. It is apparent that the blends were compatible over the full range of composition.

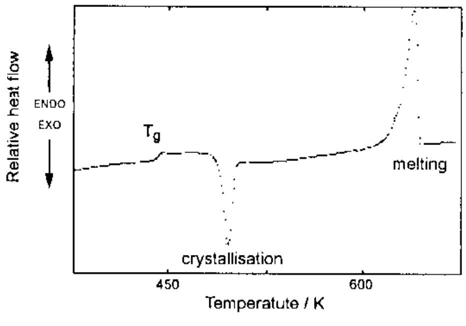

Fig. 2 DSC analysis of 50:50 PEEK/PEI blend

The development of crystallinity with time in the blends were carried out over a range of isothermal temperatures by DSC using techniques discussed in some detail previously [1]. Bulk isothermal crystallization kinetics are conventionally analysed by the Avrami equation, i.e.

$$1-X_t=\exp-Zt^n \qquad (1)$$

where X_t is the fractional extent of crystallinity which has developed at time t, Z is a composite rate constant and n an integer constant which is diagnostic of the crystallisation mechanism. The half-life, $t_{1/2}$, and n were used to characterise the rate and the mechanism of crystallisation (Table 1 and Fig. 3). The n values for the blends lay between 2 and 4 and are different from those observed for PEEK alone, 3.0–4.0. These values of n are consistent with the growth either of homogeneously or heterogeneously nucleated spherulites, but reduced in the case of the blends by the rejection of uncrystallisable PEI.

The temperature range over which the isothermal rate measurements were made severely limited to blends which contained more than 50% PEEK (Fig. 3), because of the reduced rate of heat evolution at longer half-lives and it was apparent that

Table 1 Crystallisation rate parameters

DSC blend composition PEEK/%	T_c/K	n	$t_{1/2}$/min
80	589.5	3.2	3.5
	595.1	4.0	9.7
	600.8	3.9	31.5
60	570.1	2.1	4.5
	573.4	2.2	6.8
	575.3	2.1	8.1
40	551.8	2.3	5.8
	557.4	2.0	7.3
	566.9	2.1	10.1

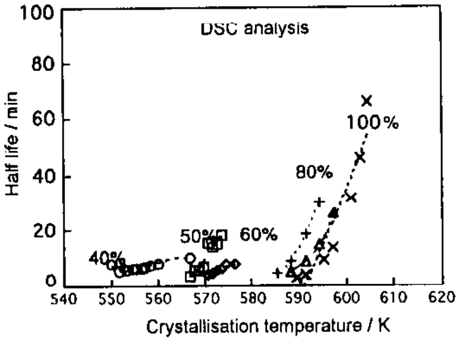

Fig. 3 T_c/K blends crystallisation half-lives

DSC could not follow the isothermal crystallisation at the lower compositions unless the half-lives were short.

Hot stage microscopy

The technique of hot stage microscopy was used to measure the crystallisation kinetics and the *m.p.* of the blends from the change in birefringence since it was apparent that DSC could not be used to measure the rate of crystallisation in blends below 40% PEEK content. Studies with polypropylene, polyethylene terephthalate and PEEK samples showed that measurement of the rate parameters by DSC and hot stage microscopy gave very similar results. Subsequent studies were limited to blends containing less than 20% PEEK.

Crystallisation rate studies were carried out isothermally after heating the samples to 5 K above the observed melting temperature for 5 min and cooling at 100 K min^{-1} to the crystallisation temperature. The change in light intensity was assumed to be a measure of the amount of crystallinity that had developed at time t such that,

$$X_t=(I_t-I_o)/(I_f-I_o) \tag{2}$$

where I_t, I_o and I_f are the measured intensities at time t, initially and finally.

The time dependence of X_t was measured by Eq. (1) and $t_{1/2}$ and n values determined (Fig. 4 and Table 2). From this data it was apparent that the maximum rate of crystallisation of the blends occurred at 550 K and that the rate decreased with increasing PEI content. This was consistent with the PEI acting as a non-crystallisable impurity and being rejected by the crystallising front. Raising or lowering the temperature reduced the rate of crystallisation. Although PEEK was the minor component, there is no evidence of diffusion controlled growth of the crystallites from the measured n values of 3.0±0.3. From the half-lives, the temperature range over which crystallisation occurred at acceptable rates could be determined.

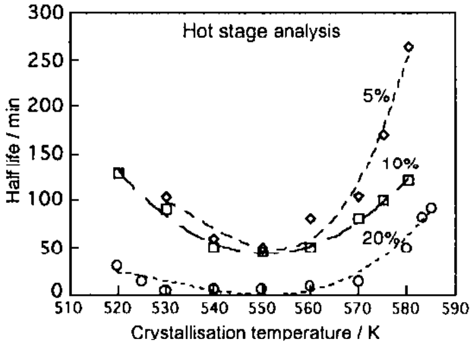

Fig. 4 T_c/K blends crystallisation half-lives

Table 2 Crystallisation rate parameters

Hot stage	T_c/K	n	$t_{1/2}$/min
20	520	3.0	30
	540	2.9	6
	560	3.0	10
	585	3.0	92
10	520	2.8	128
	540	2.6	50
	560	2.6	65
	580	4.0	120
5	540	2.9	103
	560	2.7	80
	580	2.8	260

Using the hot stage heating, the *m.p.* of the blends, T_m, were measured from the temperature corresponding to the last trace of crystallinity. These values varied with crystallisation temperature, T_c, following the Hoffman Weeks [3] relationship, i.e.,

$$T_m = T_m^o(1 - \beta/2) + T_c/2\beta$$

where T_m^o is the equilbrium *m.p.* of the blend and

$$\beta = l^*\sigma e/l\sigma^*$$

the ratio of the equilibrium and actual fold periods and surface free energies of the lamellae. At equilibrium β=1 and the slope of the plot of T_m *vs.* T_c is linear with slope 1/2. Within experimental error the experimental *m.p.* of the blends did not vary significantly from one another T_m^o=623±2 and 622 K for 10 and 5% PEEK respectively. These were much reduced from the value previously obtained for PEEK, i.e. 660 K, consistent with PEI depressing the *m.p.*

Conclusions

Measurement of the time dependence of crystallinity from changes in the polarised light intensity using a hot stage light microscope is more accurate for determining the kinetics of crystallisation of PEEK/PEI blends containing a small amount of the crystallising component than conventional DSC. The two methods appear to give very similar kinetic results with materials which can be studied by both techniques. The difference is attributed solely to the lack of sensitivity of DSC to measuring very low heat flows, i.e. below 1 J h^{-1}.

References

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