Enthalpy relaxation in amorphous and crystalline polymers.
Polyaryl ether ether ketone blends

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Abstract: The kinetics of enthalpic relaxation in compatible blends of polyether ether ketone, PEEK and polyetherimide, PEI have been measured by DSC, and interpreted in terms of a broad spectrum of relaxation processes, in that the overall fractional extent of conversion \( \phi(t) \) at time \( t \) obeys the relationship,

\[
1 - \phi(t) = \exp\left(-t/\tau\right)^\beta,
\]

where \( \tau \) is the relaxation time and \( \beta \) is a measure of the reciprocal breadth of the relaxation spectrum. Similar analysis has been carried on the dynamic and dielectric response of the blends, but there is little similarity in the \( \beta \) values so determined. Although the 50:50 blend exhibits a single glass transition temperature, the observed value of \( \beta \), 0.2 for the dielectric relaxation spectra is consistent with some heterogeneity developing at the molecular level.

Key words: Physical aging; DSC; dielectric relaxation; polyetherimide; PEEK; blends

Introduction

Organic glasses are not normally in thermal equilibrium but approach it over extended periods in a temperature region below but close to the glass transition temperature, \( T_g \). Physical aging is attributed to the progressive change in the glass towards equilibrium, the restricted mobility of chain segments as the temperature is reduced below the transition, and is associated with the formation of the glass from the liquid on cooling.

Since the material properties of the quenched glass change progressively the process has considerable commercially importance and has been widely studied. Conventionally it has been observed that there is an increase in the yield stress and tensile modulus, and a decrease in enthalpy, specific volume and fracture toughness of the glass with increasing extent of physical aging. Changes in material characteristics, such as specific volume, enthalpy and creep compliance, are conveniently used to follow the process of physical aging, but exact correlation between the experimental procedures have not been observed. This was stressed recently [1] when the difference in the temperature range over which physical aging can be detected by creep measurements, over 250 K, and by changes is enthalpy, about 50 K were discussed. under these circumstances, it is convenient to use the term enthalpic relaxation and restrict it to calorimetric studies of physical aging. Differential scanning calorimetry appears to be best suited for such studies.

We have used enthalpy relaxation to probe the microtexture of compatible blends, and the present report investigates the miscibility of polyether ether ketone/polyetherimide compatible blends as a function of composition.

Experimental

A commercial grade of PEI was used, Ultem 1000, manufactured by GEC. The polymer has a number average molecular weight of about 20 000. It was
dried at 150°C for 4 h prior to use. A commercial grade of PEEK was also used, as supplied by ICI Polymer and Chemicals Ltd. It was used and characterised as described elsewhere [2]. Blends were produced by weight, on dried polymer, using an APV model MP2000 twinscrew extruder at 380°C. Sheets, 1 x 150 x 150 mm, of amorphous blends were moulded at 350°C using a hydraulic press, dried, and quenched directly into ice/water. Required samples were cut directly from these sheets.

Thermal analysis was carried out on a Perkin-Elmer differential scanning calorimeter, model DSC-2C, interfaced to and controlled by a BBC Master computer. Details of the procedures involved in measuring the glass transition temperature and following the kinetics of physical ageing have been discussed elsewhere [1].

Results and Discussion

The blends were initially examined by DMTA between 20° and 250°C at a range of frequencies between 1–10 Hz, and a heating rate of 3 Kmin⁻¹. The peak temperature in tanδ at 1 Hz was taken to define the Tg and this changed progressively with composition between the homopolymer values (see Fig. 1). Crystallization of PEEK from the blend occurred immediately above Tg with a corresponding increase in modulus and tanδ values. Crystallisation increased the Tg due to the amorphous phase containing less PEEK and the reinforcing effect of the PEEK crystals. The values of the Tg of the amorphous samples were substantially different from those calculated by the Fox relationship.

\[
(T_g) = x_1/T_{g1} + (1-x_1)/T_{g2},
\]

where \(x_1\) is the weight fraction of homopolymer 1, and \(T_{g1}\) and \(T_{g2}\) the glass transition temperature of the two homopolymers 1 and 2 respectively. The negative deviation is consistent with specific interactions between the components, and the presence of a single Tg is consistent with miscibility of the two homopolymers over the total composition range.

A single Tg was observed for all blend compositions by DSC and the progress of enthalpic relaxation was monitored by the development of the endothermic peak (see Fig. 2). The relaxation of the