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# Comparative study of the crystallization of poly(aryl ether ketone) in binary blends, with poly(ether sulfone) and poly(ether imide)

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The influence of the amorphous polymers poly(ether sulfone) (PES) and poly(ether imide) (PEI) on the crystallization of the semi-crystalline poly(ether ketone ether ketone ketone) (PEKEKK) was investigated by optical microscopy, d.s.c. and wide-angle X-ray scattering. The miscibility was estimated by measuring the glass transition temperatures. The different miscibilities of the investigated polymer systems were correlated to their crystallization behaviour. The half-time of crystallization of PEKEKK is increased in the miscible system PEKEKK/PEI whereas in the immiscible system PEKEKK/PES the half-time of crystallization runs through a maximum. Compared to pure PEKEKK the normalized crystallinity is higher in PEKEKK/PEI blends and slightly lower in PEKEKK/PES blend. The unit cell parameters of the crystalline PEKEKK phase are not changed in the blends. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: poly(ether ketone ether ketone ketone); poly(ether sulfone); poly(ether imide))**

## INTRODUCTION

Blending polymers is a useful way to get materials with certain properties for special applications. Generally, the properties of a blend are strongly dependent on the resulting structure after processing. If the blend is homogeneous, i.e. the components are miscible at the molecular level, the properties are showing a continuous change with the concentration. Otherwise, if the blend is heterogeneous the properties of the pure components are unchanged and preserved in the blend. In spite of a miscibility or separation of the amorphous phases, blends of a crystallizable and a non-crystallizable component are always heterogeneous because of a crystallization-induced phase separation. The kinetics of the crystallization as well as the final crystallinity are controlled by the miscibility and morphology before the crystallization process in the molten state. Crystallizable poly(aryl ether ketone)s show a different miscibility with other high-temperature resistant and non-crystallizable polymers such as poly(ether imide) (PEI) and poly(ether sulfone) (PES). It is our goal to show the influence of a different miscibility and morphology to the crystallization of a poly(aryl ether ketone). Because the selected polymer systems poly(ether ketone ether ketone ketone) (PEKEKK)/PEI and PEKEKK/PES are completely miscible and completely immiscible, respectively, they can be used as model systems. The practical interests from complementary properties of the pure components as described in the literature[1].

While the miscibility, morphology and crystallization of the polymer system poly(ether ether ketone)/PEI have been studied by many authors[2-6], polymer systems with PEKEKK as the crystallizable component and with PES as the amorphous component have not been investigated in such an intensive way until now. Therefore, in this work the crystallization of PEKEKK in binary blends with PEI and PES was characterized. In particular, isothermal crystallization experiments were carried out to prove theoretical considerations. Further experiments give information about the crystallinity and the crystalline structure in the blend.

## THEORETICAL BACKGROUND

The crystallization rate $v$ at a definite temperature is controlled by the free energy to activate the transport process of crystallizable segments from the amorphous phase to the crystalline/amorphous interface ($\Delta G_\eta$) and by the free energy to form nuclei of a critical size ($\Delta G_N$)

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according to the Turnbull-Fisher equation[7]:

$$v = v_0 \exp\frac{-\Delta G_\eta}{RT} \exp\frac{-\Delta G_N}{kT} \qquad (1)$$

where $R$ is the molar gas constant, $k$ is the Boltzmann constant and $T$ is the absolute temperature. $v_0$ is a complicated pre-exponential factor only weakly dependent on temperature. It can be approximated by $b_0kT/h$ ($b_0$ is the thickness of a monomolecular layer and $h$ is Planck's constant)[8,9]. The free energy for the activation of the transport of crystallizable segments to the crystalline/amorphous interface ($\Delta G_\eta$) can be approximated by the WLF equation, i.e. the temperature dependence of the diffusion process is equal to that of the macroscopic viscosity:

$$\frac{\Delta G_\eta}{RT} = \frac{C_1}{R(C_2 + T - T_g)} \qquad (2)$$

where $C_1$ and $C_2$ are constants and $T_g$ is the glass transition temperature.

$\Delta G_N$ contains the thermodynamic driving force for the crystallization process $\Delta g_c$ (the difference between the free energies of the amorphous and crystalline phase at a temperature below the equilibrium melting point $T_m^0$) and the interfacial free energies of the nucleus. $\Delta G_N$ is proportional to $\Delta T^{-2}$ ($\Delta T = T_m^0 - T$) in the case of the formation of a three-dimensional nucleus (primary nucleation) while $\Delta G_N$ is proportional to $\Delta T^{-1}$ for a two-dimensional nucleus (secondary nucleation). In general, secondary nucleation can be assumed for spherulitic growth due to the existence of phase or particle boundaries. If the existing boundary consists of the same material, the nucleation is homogeneous, otherwise the nucleation is heterogeneous. The final expression for $\Delta G_N$ (secondary homogeneous nucleation) is given by

$$\frac{\Delta G_N}{kT} = \frac{4b_0\sigma\sigma_e}{kT\,\Delta g_c} = \frac{4b_0\sigma\sigma_e T_m^0}{kT\,\Delta h_m^0\,\Delta T} \qquad (3)$$

where $\sigma$ and $\sigma_e$ are the free energies of the lateral and fold surfaces of the crystal, respectively, and $\Delta h_m^0$ is the heat of fusion of the crystal[7-10].

Because of the contrary influence of the diffusion term (equation (2)) and the nucleation term (equation (3)) on the crystallization rate, the temperature dependence shows a maximum in a bell-shaped curve.

In a molecular-homogeneous blend the situation for calculation of the crystallization rate is changed due to the variation of (1) the glass transition temperature, (2) the equilibrium melting point depression, and (3) the dilution effect of the second component. If the glass transition temperature $T_{g,mix}$ is decreased in the blend the crystallization rate will be higher and if the glass transition temperature is increased in the blend the crystallization rate will be lower at a certain crystallization temperature (equation (2)). The equilibrium melting point will be depressed from $T_m^0$ to $T_{m,b}^0$ because of the changed free energy of the amorphous phase. This melting point depression reduces the undercooling $\Delta T$ and so the thermodynamic driving force $\Delta g_c$ (equation (3)). Furthermore, a second term must be added in equation (3) considering the dilution effect by the non-crystallizable component. This term is proportional to $\ln V_c$ and represents the probability of selecting the required number of crystalline sequences from a mixture. The volume fraction $V_c$ of the crystallizable component also acts as pre-exponential factor because the rate of nucleation is proportional to the concentration of crystallizable units[11-15]. Therefore, in the case of molecular-homogeneous blends the crystallization rate can be calculated by

$$v = v_0 V_c \exp\frac{-C_1}{R(C_2 + T - T_{g,mix})} \exp\frac{-4b_0\sigma\sigma_e T_{m,b}^0}{kT\,\Delta h_m^0\,\Delta T} + \frac{2\sigma(\ln V_c)T_{m,b}^0}{b_0\,\Delta h_m^0\,\Delta T} \qquad (4)$$

But, also in immiscible blends the linear crystallization rate can be changed. It was shown by Martuscelli[16] and Bartczak and co-workers[17] that for spherulitic growth, additional energy must be dissipated for rejection or for occlusion and deformation of dispersed particles in the crystallizing matrix. It is dependent on which of the following processes takes place: (1) the difference of the interfacial free energies between the particle and crystallizing solid on one side and the particle and amorphous melt on the other side, (2) the spherulitic growth rate and (3) the particle size. Therefore, in the case of immiscible blends, equation (1) must be completed by a third exponential term containing the energy $E$ for the processes described above:

$$v = v_0 \exp\frac{-\Delta G_\eta}{RT} \exp\frac{-\Delta G_N}{kT} \exp\frac{-E}{kT} \qquad (5)$$

The linear crystallization rate $v$ can be estimated by measurement of the spherulitic growth rate whereas, by means of other methods such as d.s.c., wide-angle X-ray scattering (WAXS) or dilatometry, an overall crystallization rate can be determined via measurement of the converted volume fraction or fractional crystallinity $\alpha$. The linear crystallization rate $v$ and the overall crystallization rate $k$ are correlated by

$$k = gNv^m \qquad (6)$$

where $g$ is a constant depending on the shape and density of the growing unit, $N$ is the nucleation density in the case of an athermic (instantaneous) nucleation and $m$ is the dimensionality of the growth. The nucleation density $N$ (number per volume) must be replaced by the nucleation rate $\mathrm{d}N/\mathrm{d}t$ (number per volume and time) if the nucleation is thermic (sporadic). From equation (6) it can be seen that $k$ is proportional to the nucleation density. So, the crystallization can be strongly accelerated in heterogeneous systems with finely dispersed particles which act as nucleating agents. $k$ and $m$ in equation (6) can be determined by fitting experimental data (fractional crstyallinity $\alpha$ *versus* time $t$) to the well-known Avrami equation:

$$\alpha = 1 - \exp(-kt^n) \qquad (7)$$

The Avrami exponent $n$ depends on the dimensionality of the growth $m$ and the nucleation mechanism (athermic $n = m$, thermic $n = m + 1$)[9,10]. Therefore, by measuring the overall crystallization rate the geometry of the growing units and the nucleation mechanism cannot be determined separately.

## EXPERIMENTAL

The materials used were Ultrapek A-2000 (PEKEKK) and Ultrason E-1010 (PES) from BASF and Ultem 1000 (PEI) from GEP. Blending was performed by melt mixing in a twin-screw extruder after drying the components. From the extrudates, tensile test specimens were injection moulded. PEKEKK/PES blends were prepared in the ratios 100/0, 70/30, 65/35, 60/40, 50/50 and 0/100 wt% and PEKEKK/PEI blends in the ratios 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 wt%.

Isothermal crystallization experiments were carried out on a DSC 2920 (TA Instruments). Tensile test specimens were thinned down to a thickness of 0.5 mm, and then samples were punched out with a diameter matching the dimensions of the aluminium pans of the calorimeter. By this preparation technique for d.s.c. samples a constant sample weight of 20 mg and a constant geometry with good thermal contact for heat transfer between the sample and pan was guaranteed. Samples were heated at $10\,\mathrm{K\,min^{-1}}$ to 420°C, held for 5 min in the molten state and then cooled stepwise down to the crystallization temperature $T_c$ ($-60\,\mathrm{K\,min^{-1}}$ down to $T_c + 5\,\mathrm{K}$ and $-10\,\mathrm{K\,min^{-1}}$ down to $T_c$) to minimize the temperature oscillations around the final temperature. Melting temperatures and crystallization temperatures were taken from non-isothermic d.s.c. measurements as the peak maximum and the peak minimum of the heat flow. The midpoint temperature was defined as the glass transition temperature.

Optical microscopy was used for investigating the morphology of the system PEKEKK/PES. Thin sections with a thickness of 5–10 $\mu$m were prepared by a microtome using glass knives. These thin sections were investigated by a Leitz Orthoplan microscope in polarized light.

WAXS diagrams were measured using an URD 63 diffractometer (Präzisionsmechanik Freiberg) with Ni-filtered $\mathrm{CuK}_\alpha$ radiation. Data were collected by a position-sensitive detector in the $2\theta$ range from 10 to 42° with a $2\theta$ increment of 0.02°. Samples were investigated in the transmission mode.

In general, if an error bar is not shown in a figure then the error is smaller than the symbol. In isothermic experiments the number of values is three, and in non-isothermic experiments it is 10.

## RESULTS AND DISCUSSION

### *Glass transition temperatures*

In *Figure 1* the glass transition temperatures of the blends are plotted against the blend composition. The glass transition temperature of PEKEKK is 172.5°C and the glass transition temperatures of PES and PEI are 219.5 and 213.9°C, respectively. In the system PEKEKK/PES the two separate glass transition temperatures of PEKEKK and PES remain constant in the investigated concentration range while in the system PEKEKK/PEI only one transition can be detected lying between those of the pure components. From this result we conclude that the system PEKEKK/PEI is miscible, similar to the system PEEK/PEI[2,3,5], and that the system PEKEKK/PES is immiscible.

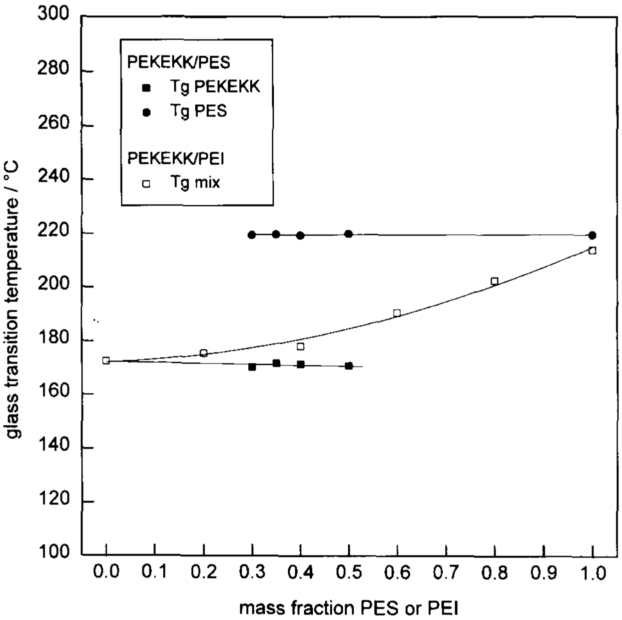

**Figure 1** Glass transition temperatures as functions of the concentration of the amorphous component in the polymer systems PEKEKK/PES and PEKEKK/PEI

### *Crystallization rate*

Because the glass transition temperature of the blend with PEI is increased, the chain mobility of PEKEKK molecules is reduced at a certain temperature. The free energy for the activation of the transport of PEKEKK molecules to the front of the growing lamella is increased, resulting in a lowered crystallization rate. Additionally, the dilution effect of the amorphous PEI will reduce the crystallization rate. In contrast to the miscible system PEKEKK/PEI, for the immiscible system PEKEKK/PES $\Delta G_\eta$ is constant at all concentrations, and the term containing $\ln V_c$ in equation (4) is zero. Here, we have to apply equation (5) for an explanation of the crystallization behaviour of PEKEKK. To verify these assumptions, isothermal crystallization experiments were carried out by d.s.c. The lowest crystallization temperature was chosen as that at which the induction time was about 10 min. This procedure confirmed that we were in thermal equilibrium at the beginning of the crystallization process. Because it is difficult to reproducibly determine the time when thermal equilibrium is reached, we have taken as the zero point of the time-scale the start of the cooling process. In *Figure 2* typical d.s.c. crystallization isotherms—heat flow *versus* time—for different crystallization temperatures are shown for the blend PEKEKK/PES 65/35. Crystallization temperatures were varied between 355 and 370°C with an increment of 2.5°C. With increasing crystallization temperature the maximum of the crystallization isotherm appears at longer times, i.e. the crystallization rate is reduced. From these data, fractional crystallinity–time plots were calculated by

$$\alpha(t) = \frac{\int_0^t \mathrm{d}h/\mathrm{d}t\,\mathrm{d}t}{\int_0^\infty \mathrm{d}h/\mathrm{d}t\,\mathrm{d}t} \tag{8}$$

where $\alpha(t)$ is the fractional crystallinity or the conversion at time $t$. The integrals are the crystallization enthalpies d$h$ at time $t$ and at the end of the crystallization process ($t \to \infty$). The result of this calculation for the d.s.c. scans

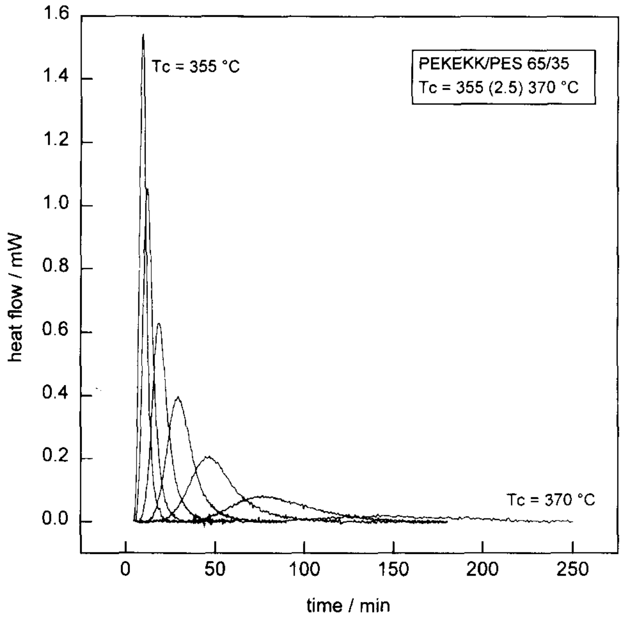

**Figure 2** Crystallization isotherms of the blend PEKEKK/PES 65/35

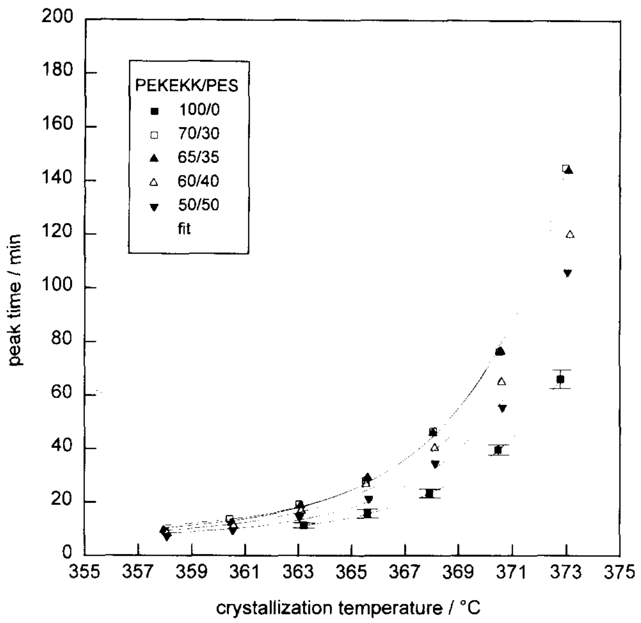

**Figure 4** Dependence of the peak time on the crystallization temperature for PEKEKK/PES blends

shown in *Figure 2* is illustrated in *Figure 3*. From these plots the half-time of crystallization (fractional crystallinity = 0.5) and the peak time for each crystallization temperature were determined. The peak time was calculated as the maximum of the heat flow–time curve by a third-degree polynomial regression (crystallization isotherms are always asymmetric due to secondary crystallization). The peak time is more reliable than the half-time of crystallization because of uncertainties in drawing the baseline, especially at high crystallization times, which results in an error in the fractional crystallinity–time plot and the determination of the half-time of crystallization. Therefore, the peak times are plotted for the system PEKEKK/PES in *Figure 4*. If we look at one blend composition, then a decrease of the peak time with increasing crystallization temperature can be observed. This behaviour is in accordance with the Turnbull-Fisher equation (equation (1)), which predicts a bell-shaped dependence of the crystallization rate on temperature. Blending PEKEKK with small amounts of PES results in a drop of the crystallization rate to lower values, but at higher concentrations of PES the crystallization rate increases again, i.e. the crystallization rate runs through a minimum. As an illustration, the depend-ence of the peak time on the concentration of PES for different crystallization temperatures is shown in *Figure 5*. In general, reasons for such a behaviour can be a change of the phase composition (concentration-dependent miscibility) or

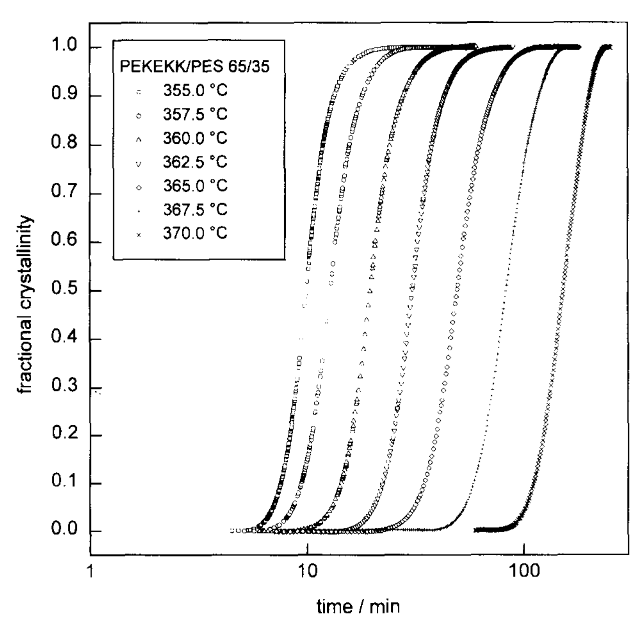

**Figure 3** Fractional crystallinity as function of time for the blend PEKEKK/PES 65/35

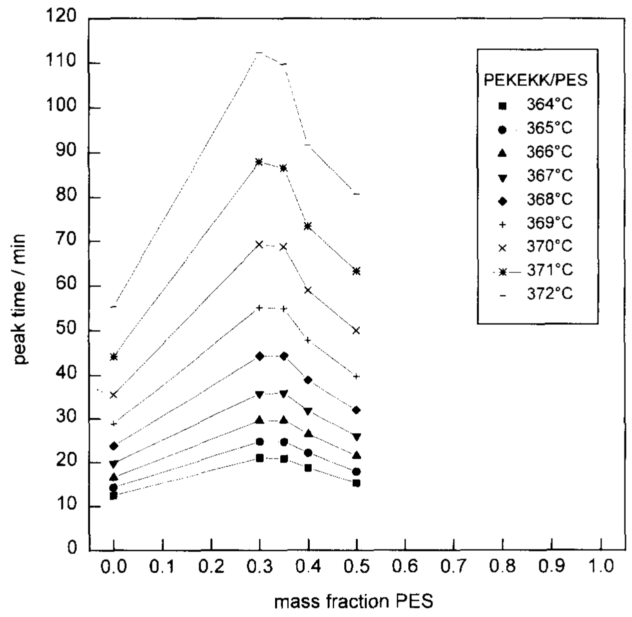

**Figure 5** Dependence of the peak time on the concentration of PES in the system PEKEKK/PES for different crystallization temperatures

phase distribution (morphology). Because we know from the glass transition temperatures that the system PEKEKK/PES is immiscible over the whole concentration range, a changed morphology must be taken into account in order to explain this behaviour.

In contrast to the immiscible system PEKEKK/PES, the peak times continuously increase with increasing content of PEI in the miscible system PEKEKK/PEI (*Figure 6*). Therefore, the temperature range for the measurement must be shifted to lower crystallization temperatures compared to pure PEKEKK. The reason for this behaviour can be seen in the changed glass transition temperature and the dilution effect of PEI, as indicated by equation (4).

### *Phase morphology and crystallite morphology of the system PEKEKK/PES*

In *Figures 7a–7e*, optical micrographs are shown for PEKEKK and the PEKEKK/PES blends. It can be seen that the morphology of PEKEKK is unchanged in the blend PEKEKK/PES 70/30. The same volume-filled fine-spherulitic morphology is visible in this blend. PES particles are finely dispersed in interspherulitic regions and cannot be observed by this method but can be seen using scanning electron microscopy[18]. If the concentration of PES increases, the particles will become larger and larger until PES is the matrix in the blend PEKEKK/PES 50/50. The spherulitic structure of the crystallized matrix is not visible in *Figures 7c* and *7d* because the polarizer and analyser are not perpendicular for better contrast between the different phases. Furthermore, it should be noted that the particle size is dependent on the position in the sample. The particles are smaller in the region near the surface and larger in the inner region of the tensile test specimen. Considering the dependence of the particle size on the concentration of PES there is a qualitative change in the morphology in the concentration range of about 30–35 wt% of PES. Because the growth rate is the reciprocal of the particle size, the maximum of the peak time in *Figure 5* can be related to the change in the morphology.

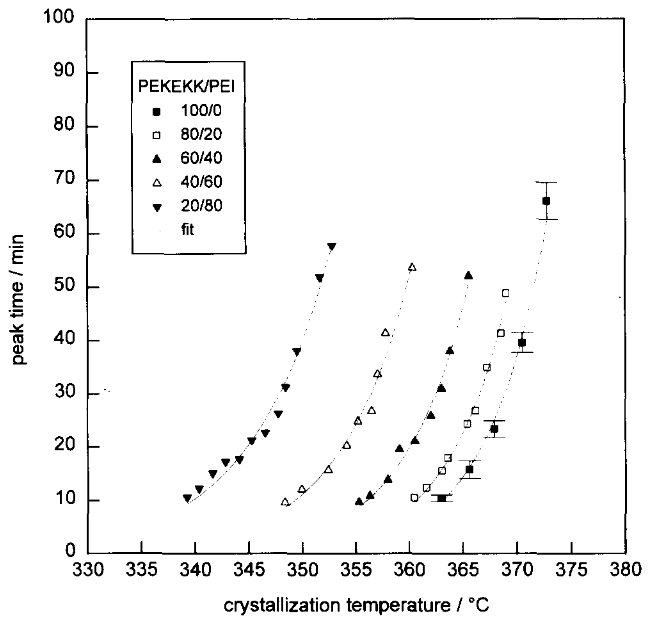

**Figure 6** Dependence of peak time on the crystallization temperature for PEKEKK/PEI blends

Furthermore, we have estimated the Avrami exponent *n* of equation (7) to get information about possible changes of the crystallite morphology and the nucleation mode. Raw data were taken in the range of 0–0.4 fractional crystallinity because of the shortcomings of the Avrami equation regarding the secondary crystallization[19]. Additionally to the Avrami constants k and n we have introduced a third parameter $t_0$ to fit also the induction period of the crystallization process. The induction period, i.e. the time until the crystallization starts, must be subtracted from *t* in equation (7) to get correct values of *k* and *n*. To avoid an unbalanced weight of data points, a non-linear least-square fit based on the Levenberg–Marquardt algorithm (MicroCal Origin, Version 3.5, MicroCal Software, Inc., 1994) was used instead of the linear regression of data in the classical Avrami plot[20]. Calculations were performed until the $\chi^2$ value was minimized. In *Figure 8* the fractional crystallinity–time plot of the blend PEKEKK/PES 65/35 is shown, including the fitted function. The good fit to the experimental data is clearly seen. In *Table 1* the dependence of the Avrami exponent *n* on the concentration of PES and on the crystallization temperature is shown. Although *n* is lower at higher crystallization temperatures (mean $\langle n \rangle = 2.6$ at 370°C and $\langle n \rangle = 3.2$ at 363°C) there seems to be no systematic concentration dependency. From these values of *n* we can only assume a spherulitic growth, which is in accordance with the results on pure PEEK[21,22]. The slight decrease of *n* at higher crystallization temperatures ($T_c \geq 368$°C) cannot be explained by our measurements.

### *Crystallization and melting temperature*

The non-isothermic crystallization temperatures of the system PEKEKK/PES shown in *Figure 9* are in accordance with the isothermal experiments. The crystallization temperature runs through a minimum at 30–35 wt% of PES, and the melting temperature is only slightly decreased (< 5 K in the blend PEKEKK/PES 50/50).

The melting temperature of PEKEKK is also depressed in blends with PEI, which can be caused by different reasons. Frequently discussed reasons are the equilibrium melting point depression[14], the crystallite size, i.e. the thickness of the lamella, and the state of order of the crystallites[9]. According to the reduced crystallization rate observed by isothermal crystallization experiments, the crystallization temperature during cooling is also strongly decreased due to the kinetic hindrance of the diffusion of PEKEKK molecules.

### *Crystallinity*

The different miscibilities of PEKEKK with PES and PEI also influence the relative crystallinity of PEKEKK in the blends. The crystallinity was calculated on the basis of the heat of fusion using a value of $\Delta h_m^0 = 130\,\mathrm{J\,g^{-1}}$ [23]. Furthermore, a crystallinity index was determined by WAXS. For WAXS measurements, samples were isotropized by melting and then slowly cooled to room temperature. In *Figure 10* the relative crystallinity determined by d.s.c. is shown for the systems PEKEKK/PES and PEKEKK/PEI. The PEKEKK crystallinity is only a little affected by blending with

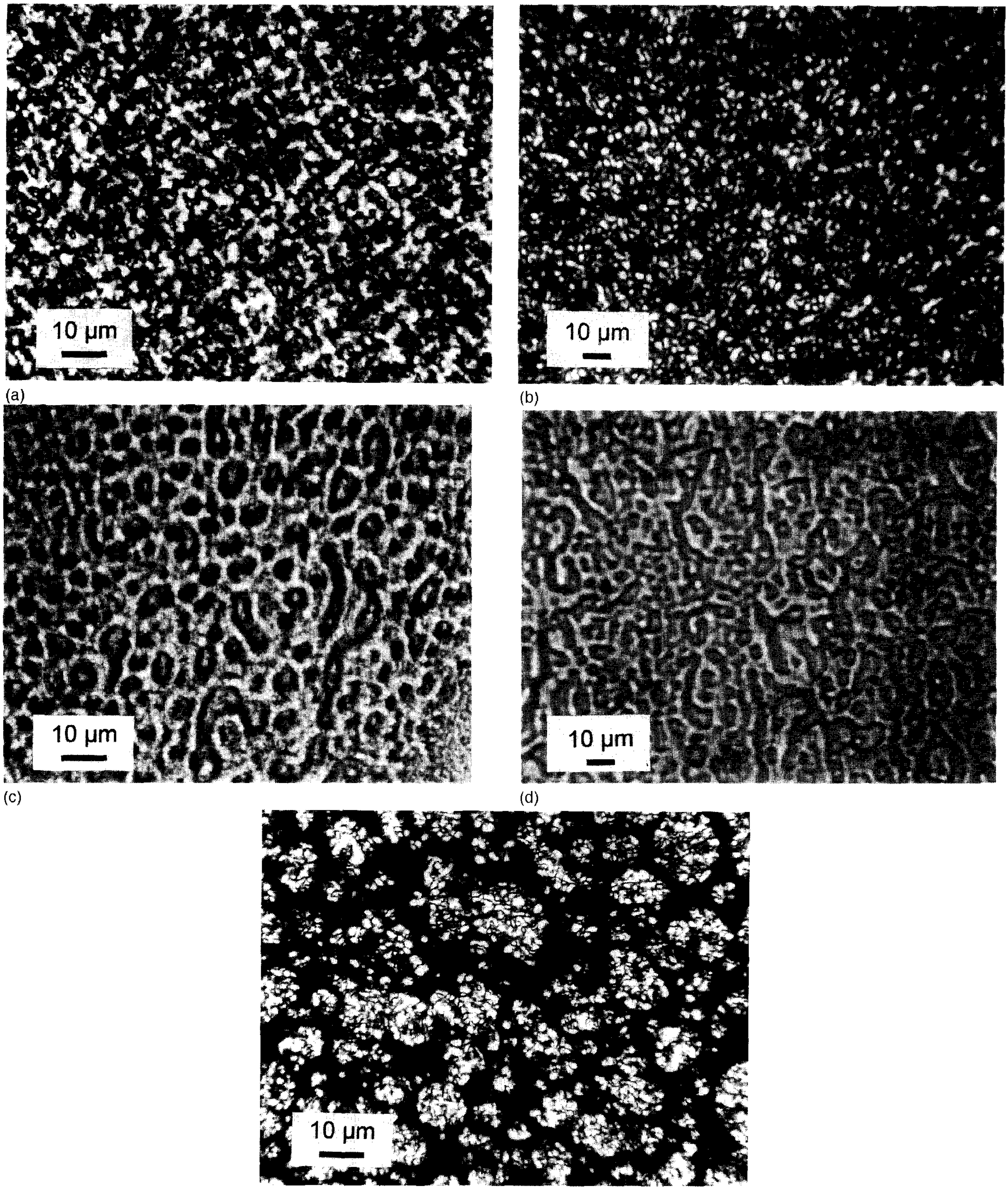

**Figure 7** Optical micrograph of (a) PEKEKK, (b) the blend PEKEKK/PES 70/30, (c) the blend PEKEKK/PES 65/35, (d) the blend PEKEKK/PES 60/40 and (e) the blend PEKEKK/PES 50/50

PES. However, there seems to be a slight minimum at 35 wt% PES, which is reproducible by WAXS measurements (*Table 2*). This minimum in the relative crystallinity can be connected with the minimum in the crystallization rate.

Compared to the rather small differences in the relative crystallinity of PEKEKK in blends with PES, the relative crystallinity in blends with PEI is clearly increased up to values higher than 40% in PEI-rich blends. This increase is not easy to explain because the overall crystallization rate is drastically reduced in the blends. While Harris and Robeson[2] measured a maximum of the relative

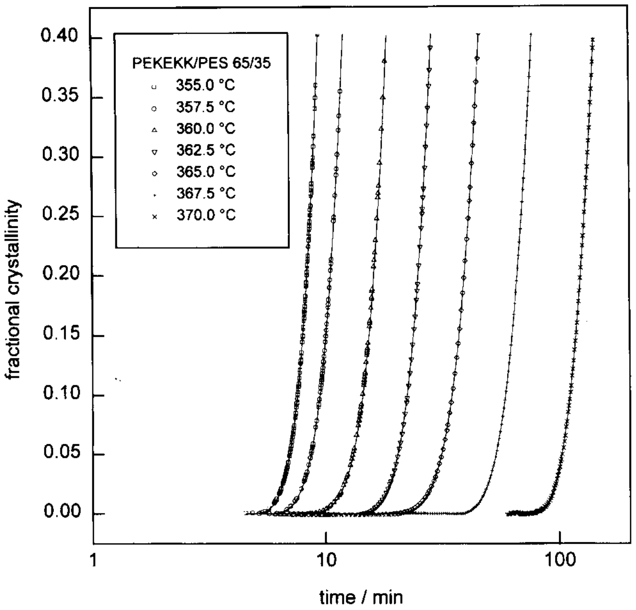

**Figure 8** Fractional crystallinity as a function of time for the blend PEKEKK/PES 65/35 with the Avrami function fitted

**Table 1** Dependence of the Avrami exponents *n* of PEKEKK in the system PEKEKK/PES on the concentration of PES and on the crystallization temperature

| PES fraction | *n* (363°C) | *n* (365.5°C) | *n* (368°C) | *n* (370.5°C) |
|---|---|---|---|---|
| 0.00 | 3.1 | 3.4 | 2.7 | 2.6 |
| 0.30 | 3.2 | 3.3 | 3.1 | 2.7 |
| 0.35 | 3.5 | 3.1 | 3.0 | 2.7 |
| 0.40 | 3.4 | 3.8 | 3.2 | 2.6 |
| 0.50 | 2.8 | 3.3 | 2.6 | 2.4 |

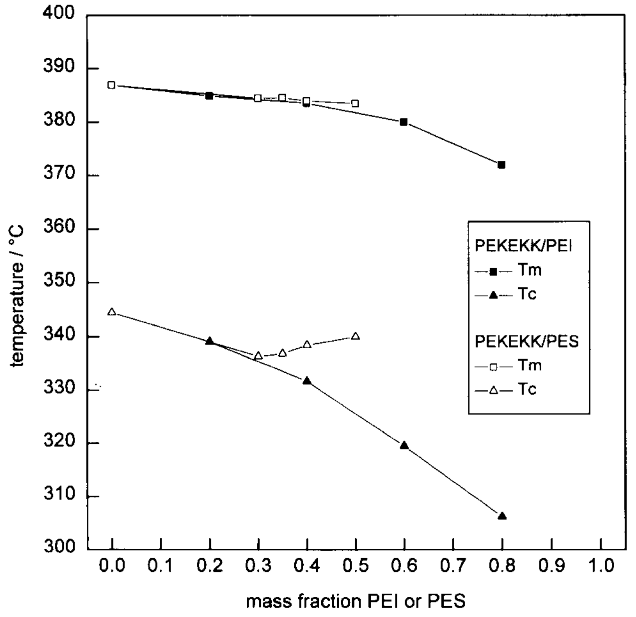

**Figure 9** Crystallization and melting temperatures of the systems PEKEKK/PES and PEKEKK/PEI from non-isothermic d.s.c. experiments

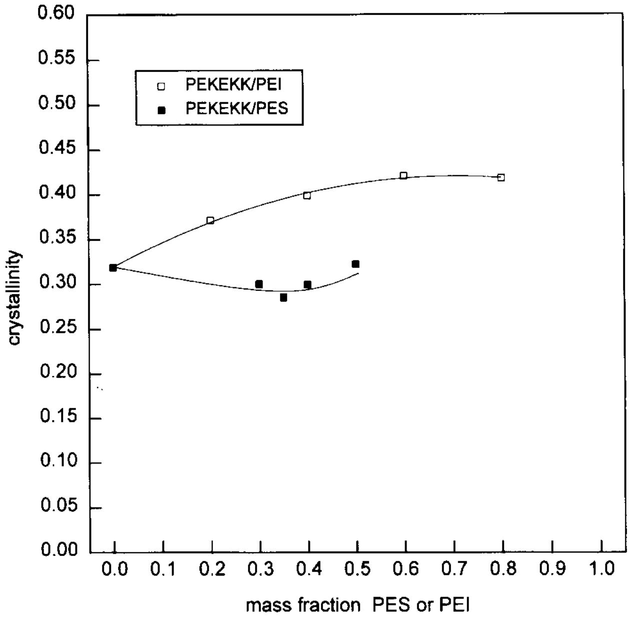

**Figure 10** Crystallinity of PEKEKK in blends with PES and PEI

**Table 2** Crystallinity of PEKEKK measured by d.s.c. and WAXS for the system PEKEKK/PES

| PES fraction | Crystallinity by d.s.c. | Crystallinity index by WAXS |
|---|---|---|
| 0.00 | 0.320 | 0.330 |
| 0.30 | 0.300 | 0.270 |
| 0.35 | 0.285 | 0.260 |
| 0.40 | 0.300 | 0.295 |
| 0.50 | 0.320 | 0.280 |

crystallinity in PEEK/PEI blends at a concentration of 40 wt% of PEI, Crevecoeur and Greoninckx[3] found a continuous increase of the relative crystallinity in PEEK/PEI blends. Harris and Robeson[2,24] explain such a behaviour by an increased mobility in the interlamellar regions due to the presence of the non-crystallizing diluent and the increased volume for the growth of spherulites.

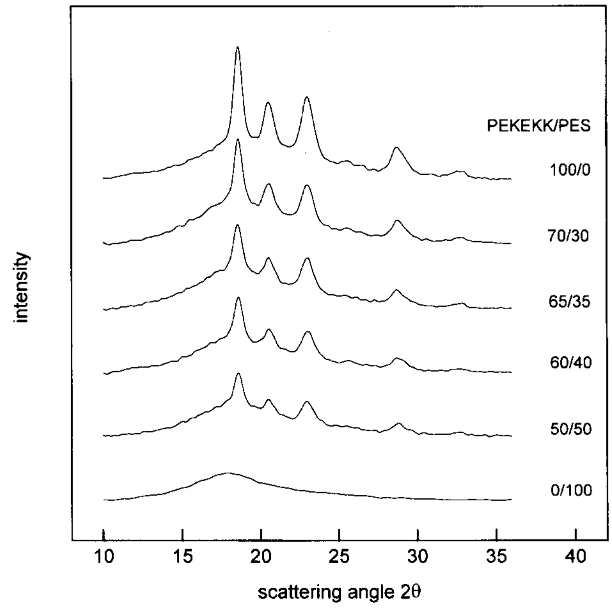

**Figure 11** WAXS diagrams of PEKEKK/PES samples

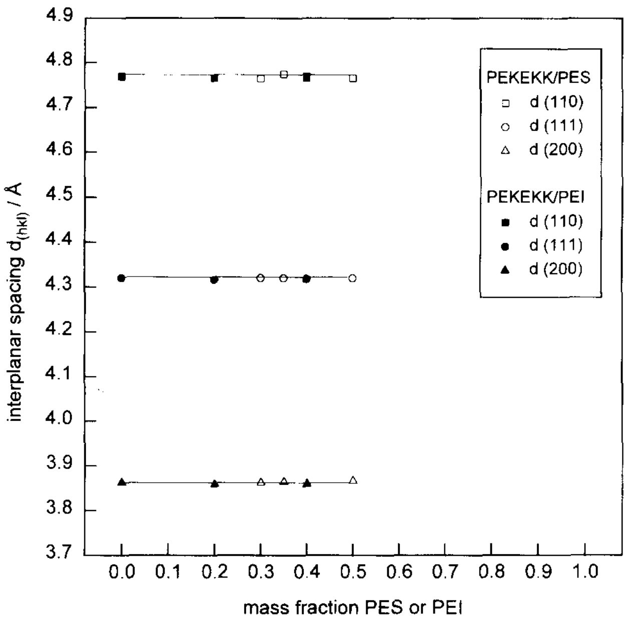

**Figure 12** Interplanar spacings of the crystalline phase of PEKEKK in dependence on the concentration of PES and PEI

### *Unit cell dimensions*

Finally, interplanar spacings $d_{(hkl)}$ were determined to get information about possible changes of the unit cell, especially in the system PEKEKK/PEI. In *Figure 11* only the WAXS diagrams for the system PEKEKK/PES are shown, which are similar to those of the system PEKEKK/PEI. The peaks were indexed on the basis of the lattice constants given by Blundell and Newton[25]. From *Figures 11* and *12* it can be seen that the unit cell dimensions remain constant at all concentrations of the amorphous component. The unit cell dimensions of PEKEKK are independent of the chemical nature of the amorphous component, the miscibility and the morphology.

## CONCLUSIONS

In this work the crystallization behaviour of PEKEKK in binary blends with PES and PEI was investigated by d.s.c., optical microscopy and WAXS. Differences in the crystallization rate and crystallinity can be explained by different miscibilities of PEKEKK with PES and with PEI. The decrease of the crystallization rate in the miscible system PEKEKK/PEI agrees with the theory given by the Turnbull–Fisher equation. The crystallization rate in the immiscible system PEKEKK/PES can be understood by assuming a particle size-dependent kinetic hindrance of the spherulitic growth in matrix–particle systems. The Avrami evaluation of d.s.c. data indicates an unchanged crystallite morphology and nucleation mechanism in PEKEKK/PES blends compared to PEKEKK. The measured relative crystallinities are in accordance with a lot of measurements on other miscible and immiscible polymer systems. The crystallinity of PEKEKK is nearly unchanged in the immiscible system PEKEKK/PES but clearly increases in the miscible system PEKEKK/PEI. The dimensions of the unit cell of the crystalline phase are not affected by blending PEKEKK with the non-crystallizable polymers PES and PEI.

## ACKNOWLEDGEMENTS

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