Crystallization Kinetics of a PEEK/LCP Blend

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SYNOPSIS

The crystallization kinetics of a polyetheretherketone (PEEK)/liquid crystalline polymer (LCP) blend was studied by using differential scanning calorimetry. Nonisothermal runnings were performed on heating and on cooling at different rates. Isothermal crystallization experiments at 315, 312, 310, and 307°C, from the melt state (380°C) were performed in order to calculate the Avrami parameters n and k and the fold surface free energy, σ_e. Polarized light optical micrographs were also obtained to confirm the Avrami predictions. It was observed that the LCP retarded the PEEK crystallization process and that the PEEK melting temperature decreased with the amount of LCP, but the LCP melting temperature increased with the amount of PEEK. Probably the PEEK improves the perfection of the LCP crystalline domains. A spherulitic morphology in pure PEEK and its blends was predicted by the Avrami analysis; however this morphology was only observed for pure PEEK and for the 80/20 composition. The other compositions presented a droplet and fibrillar-like morphology. The overall crystallization rate was observed to decrease with the crystallization temperature for all compositions. Finally, σ_e was found to decrease with the increase of LCP in the blends, having unrealistic negative values. Thus, calculations were made assuming σ_e constant at all compositions. It was observed that σ, the interfacial lateral free energy, decreased but still remained positive. It was concluded that in these blends neither σ_e nor σ could be considered constant. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The crystallization kinetics of a pure polymer has been traditionally studied by using the Avrami analysis, together with crystallization rates measured by polarized light optical microscopy, and the Hoffmann et al. kinetic theory of crystallization with chain folding, with[1,2] and without[3] reptation.

The Avrami approach has numerous disadvantages; however, the n and k parameters can be used to interpret qualitatively the nucleation mechanism and morphology and overall crystallization rate of the polymer, respectively. The Hoffmann et al. kinetic theory, on the other hand, allows the calculation of the overall crystallization growth rate of three theoretically defined crystallization regimes, each one ruled by a different nucleation mechanism from the melt.

In binary blends, the analysis is more complex. In the case of compatible blends,[4] for example, it is known that crystallization rates will be different from pure polymer due to a dilution effect; usually a decrease in crystallization rates is observed as the weight fraction of the noncrystallizable polymer increases.[5-7] It has also been observed that the fold surface free energy of the crystallizable polymer, σ_e, is constant at all compositions.[8] The kinetics in partially miscible or inmiscible blends has not been extensively studied as in completely miscible blends.

In a recent work,[9,10] the miscibility and crystallization kinetics of polyetherimide (PEI)/polyetheretherketone (PEEK)/liquid crystalline polymer (LCP) ternary blends were reported. It was observed that the cold crystallization temperature of the PEEK/LCP binary blends was constant; however, the cold crystallization temperature of the PEEK/PEI binary blends increased with the amount of PEI. The PEEK/LCP blends were found to be partially miscible before annealing, and the PEEK/PEI blends were miscible before and after the thermal

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treatment. In the ternary blends a similar behavior was observed. However, in this case, the LCP seemed also to affect this temperature in a nonpredictable way. The Avrami parameters changed with the crystallization temperature and composition; compositions with high concentrations of PEI or LCP needed higher times for crystallization to begin and higher times for maximum crystallization to occur. In some of the ternary blends a decrease was also observed in crystallization rates as the amount of PEI increased. Again, the influence of the LCP on the PEEK crystallization was observed, but no definitive conclusions could be obtained because being ternary blends, the PEI also affected the crystallization behavior. Thus, it was verified that in order to clarify this influence, it was necessary to study the crystallization kinetics of binary blends made solely of PEEK and LCP.

The objective of this work was to analyze in what ways the LCP influences the PEEK crystallization mechanism, by using the Avrami and Hoffmann et al. analyses.

THEORETICAL BACKGROUND

For homopolymers, the Avrami parameters n and k can be calculated from the equation[11]:

$$\ln\{[1 - X_c(t)/X_\infty\} = -kt^n \quad (1)$$

where $X_c(t)$ = degree of crystallinity as a function of time and X_∞ = ultimate crystallinity at very long times.

The calculations are made from data of isothermal crystallization experiments from the melt and/or glass-transition temperature, T_m and T_g, respectively.

σ_e is related to the free energy of formation of a crystal by the equation:

$$\Delta\phi_{crystal} = 4xl\sigma + 2x^2\sigma_e - x^2l(\Delta f) \quad (2)$$

where $\Delta\phi_{crystal}$ = free energy of formation of a single chain folded crystal; l = thin dimension of the crystal; x = large dimension of the crystal; σ = lateral surface interfacial free energy; and Δf = bulk free energy of fusion.

σ_e is also related to the overall crystallization rate, G,[3,6,7] by the following equation:

$$G = G_0\exp[-U^*/R(T - T_\infty)] \times \exp[-rb_0\sigma\sigma_e/(\Delta f)KT]$$

$$= G_0\exp[-U^*/R(T - T_\infty)] \times \exp[-K_g/T(\Delta T)f] \quad (3)$$

where G_0 = preexponential factor (independent of the temperature); U^* = activation energy for reptation in the melt; T_∞ = theoretical temperature at which reptation ceases; b_0 = thickness of the surface nucleus; K = Boltzmann constant; $f = 2T/T_m^\circ + T)$; K_g = nucleation constant; T_m° = equilibrium melting temperature; and r = parameter characteristic of the growth regime (4 for regimes I and III and 2 for regime II).

From the Avrami approach:

$$k \propto G^n \quad (4)$$

For miscible blends, the noncrystallizable component can be regarded as a diluent, and G can be calculated by[8]:

$$G = \varphi_2 G_0\exp\{-U^*/R[C_2 + T - T_g(\varphi)]\} \times \exp\{-rb_0\sigma\sigma_e T_m^\circ(\varphi)/[Kf\Delta H_m^\circ T\Delta T(\varphi)]\} \times \exp\{2\sigma T_m^\circ(\varphi)\ln\varphi_2/[b_0 f\Delta H_m^\circ\Delta T(\varphi)]\} \quad (5)$$

where φ_2 = volume fraction of the crystallizable polymer; $T_g(\varphi)$ = glass-transition temperature of the blend (composition dependent); C_2 = WLF constant = 51.6°C; $T_m^\circ(\varphi)$ = equilibrium melting temperature of the crystallizable component (composition dependent); ΔH_m° = equilibrium heat of fusion; and $\Delta T(\varphi) = T_m^\circ(\varphi) - T$ = actual undercooling.

By using eqs. (4) and (5) a final expression for the growth rate can be found[7,8]:

$$A = (\ln k/n) + \{U^*/R[C_2 + T - T_g(\varphi)]\} - [1 + 2\sigma T_m^\circ(\varphi)/b_0 f\Delta H_m^\circ\Delta T(\varphi)]\ln\varphi_2 = \ln G_0 - rb_0\sigma\sigma_e T_m^\circ(\varphi)/Kf\Delta H_m^\circ T\Delta T(\varphi). \quad (6)$$

Thus the slope of a plot of the left-hand term of eq. (6), A, as a function of $1/T\Delta T$ yields σ_e, if r, b_0, σ, $T_m^\circ(\varphi)$, and ΔH_m° are known. To evaluate σ, usually the Thomas–Stavely equation is used[7,8]:

$$\sigma = \beta\Delta H_m^\circ(A_0)^{1/2} \quad (7)$$

where β = 0.1 (polyolefins); β = 0.24 (for some polyesters); and A_0 = cross-sectional area of the chain in the crystal.

EXPERIMENTAL

Materials

The polymers used in this study were a PEEK (Victrex 450G) from ICI Co. and an LCP (HX4000) from DuPont. The LCP is a polyester based on terephthalic acid, phenylhydroquinone, and hydroquinone.

Blending

Before blending, the three polymers were vacuum dried at 120°C for 1 day. Each composition was first tumbled in a container on a weight ratio basis, then melt blended, pelletized, and finally injection molded. Melt blending was performed in a Killion extruder (model KL-100) at an average temperature of 370°C. Injection molding was performed in an Arburg injection molding machine (model 221-55-250) using the following barrel temperatures: zone 1, 350°C; zone 2, 380°C; zone 3, 385°C; zone 4, 390°C. The mold was held at 112°C. In a previous study,[12] an increase of the HX4000 viscosity with time was observed, but only at 385°C and after 4 min; however, because the residence times on the extruder and injection molding equipment were less than 2 min and the working temperatures were lower than 385°C, we assumed that there was not enough time for cross-linking or other significant chemical reactions to occur. Thus, four ratios of PEEK/LCP blends (80/20, 70/30, 50/50, and 30/70) were prepared.

Dynamic Mechanical Thermal Analysis (DMTA)

In order to confirm previous studies on miscibility,[9] DMT experiments were performed on the samples using a DMTA module from Polymers Lab. The scanning rate used was 2°C/min, at a frequency of 1 Hz, and strain of 4 (64 μm). The tests were done in the bending mode, before and after annealing (230°C, 48 h).

Differential Scanning Calorimetry (DSC)

A Perkin–Elmer DSC-7 was used to study the crystallization kinetics of the blends. The nonisothermal crystallization on heating was performed at 5, 10, and 20°C/min; on cooling from the melt (380°C, 5 min) the same absolute rates were used. The isothermal experiments were done at crystallization temperatures, T_c, of 315, 312, 310, and 307°C, from the melt (380°C, 5 min) under a nitrogen atmosphere.

Polarized Light Optical Microscopy (PLOM)

Films for PLOM were produced by melting at 380 ± 3°C and 400 ± 5°C, in a vacuum oven, during 30 min. After melting, the films were slowly cooled (~ 40°C/h) down to 315°C; the samples remained at this temperature during 5 h. The micrographs were obtained by using a Jenaval (Carl Zeiss) microscope.

RESULTS AND DISCUSSION

DMTA

Table I shows the DMT data for the blends, before and after annealing. The T_g values were taken at the maximum in E'' (loss modulus). Data before annealing was similar to previous studies,[9] in which a PEEK cold crystallization temperature (increase in E', the storage modulus) around 164.5°C, also appears. It can also be observed that, after annealing, only one T_g appears, indicating miscibility. Resolution of the T_gs can be poor due to three factors: the T_gs of the pure components are less than 20°C

Table I Dynamic Mechanical Thermal Data of Blends

	Before Annealing			After Annealing
Composition (PEEK/HX4000)	T_g PEEK (°C)	T_g HX4000 (°C)	T_c PEEK (°C)	T_g (°C)
100/0	142.8 ± 0.6	—	165.5 ± 0.7	157.2 ± 0.7
80/20	140.2 ± 0.2	—	164.5 ± 0.7	156.1 ± 0.3
70/30	142.2 ± 1.7	—	164.3 ± 0.4	154.0 ± 0.3
50/50	141.5 ± 4.5	162.2 ± 1.2	164.5 ± 0.7	153.7 ± 0.3
30/70	141.8 ± 0.8	161.5 ± 0.1	—	153.5 ± 3.8
0/100	—	158.9 ± 1.6	—	159.4 ± 0.3

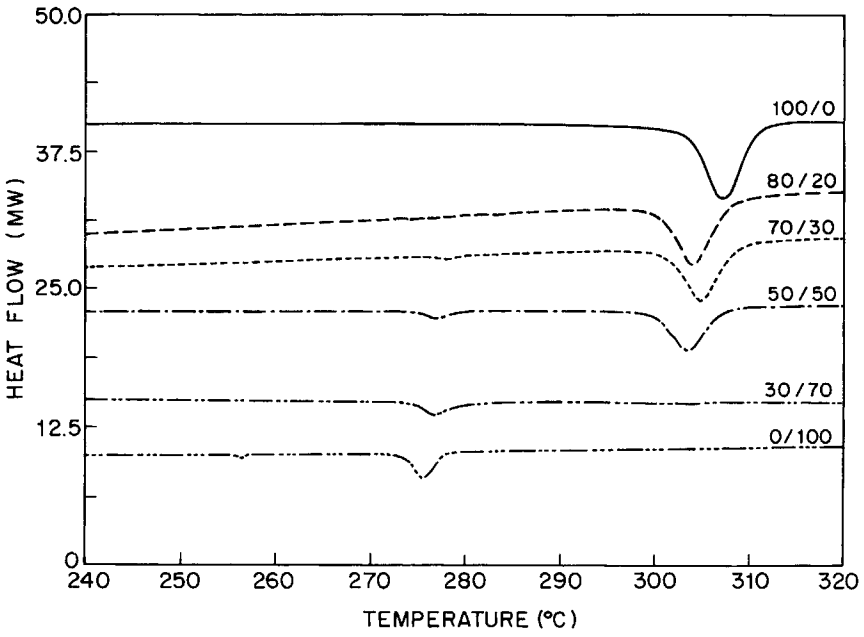


Figure 1 Typical nonisothermal crystallization curves of the blends on cooling from the melt (−5°C/min).

apart from each other; the HX4000 tan δ peak is small and broad; and cold crystallization occurs at temperatures intermediate to both T_gs. However, after annealing, besides this data, miscibility of the amorphous phases was also confirmed by scanning electron microscopy[9] and DMA using the torsion mode of the Rheometrics Mechanical Spectrometer 800.[9]

It was also observed that the T_g values, at all compositions, are lower than the T_gs of the pure components, which can be interpreted as a plasticization effect of the LCP on the PEEK.

Nonisothermal Crystallization

Figure 1 shows typical nonisothermal crystallization curves of the blends from the melt. Two crystallization peaks can be observed: the high temperature peak corresponds to the PEEK crystallization, the low temperature peak is due to the LCP. These values ($T_{c,c}$), along with the enthalphy of crystallization ($\Delta H_{c,c}$) as a function of the cooling rate are shown in Table II. The addition of the LCP in general decreases the PEEK crystallization temperature and retards the beginning of the crystallization probably due to partial or total miscibility of both components in the melt stage. One study[13] pointed out that a phase separated component can also influence the crystallization behavior; however, we believe that if the polymers were immiscible in the melt state, the noncrystallizable component probably would accelerate the beginning of the crystallization due to heterogeneous nucleation. This behavior has been confirmed by isothermal and nonisothermal crystallization studies of blends of PPS/HX4000.[14] On the other hand, the HX4000 crystallization temperature increases slightly with the increase of the amount of PEEK in the blend. The PEEK is probably acting as a nucleating agent for the LCP crystals.

The $\Delta H_{c,c}$ values of the HX4000 are much lower than of the PEEK, as expected. This has already been observed in other studies[15] and has been attributed to an imperfect packing of the chains and to the low conformational alteration that occurs during the nematic–crystalline solid transition.

In all these scannings, when it appeared, only one T_g was observed.

Figure 2 shows a typical heating scan of the blends and Table III summarize this behavior as a function of the heating rate. In general, two melting peaks and a cold crystallization peak can be observed. Some authors[16] have found two melting endotherms, at ~ 225 and 337°C, for pure PEEK, both varying with the heating rate. As the heating rate is increased, the heat of fusion of the low temperature endotherm increased and that of the high temperature endotherm decreased. However, in our studies, only the high temperature endotherm was observed. This last temperature decreases slightly with the addition of LCP; probably the LCP reduces the per-

Table II Values of $T_{c,c}$ and $\Delta H_{c,c}$ of Blends after Nonisothermal Crystallization on Cooling

PEEK/HX4000	Rate (°C/min)	$T_{c,c}$ (°C)		$-\Delta H_{c,c}$ (J/g)	
		PEEK	HX4000	PEEK	HX4000
100/0	−5	307.5 ± 0.4	—	40.0 ± 7.0	—
80/20	—	303.7 ± 0.5	276.4	45.0 ± 0.0	2.0
70/30	—	304.0 ± 1.0	277.3 ± 0.9	43.9 ± 0.3	3.3 ± 0
50/50	—	303.2 ± 0.4	276.6 ± 0.3	41.4 ± 0.0	5.0 ± 0.3
30/70	—	303.3 ± 0.6	276.2 ± 0.9	5.3 ± 2.0	8.6 ± 0.8
0/100	—	—	275.4 ± 0.1	—	8.2 ± 1
100/0	−10	301.1	—	39.7	—
80/20	—	290.0 ± 4.0	—	43.5 ± 0.8	—
70/30	—	295.0 ± 5.0	269.0 ± 4.0	45.1 ± 1.0	2.1 ± 0.4
50/50	—	299.8 ± 0.7	276.1 ± 0.3	48.6 ± 1.0	3.9 ± 0.7
30/70	—	298.9 ± 0.6	275.1 ± 0.6	5.6 ± 2.0	8.4 ± 0.3
0/100	—	—	275.0	—	7.9
100/0	−20	293.2 ± 0.3	—	41.9 ± 1.0	—
80/20	—	289.3 ± 0.1	270.1 ± 0.2	38.3 ± 0.2	1.8 ± 0.4
70/30	—	289.5 ± 0.1	270.7 ± 0.1	39.2 ± 0.1	3.3 ± 0.0
50/50	—	289.2 ± 0.5	270.2 ± 0.4	39.3 ± 0.1	5.3 ± 0.1
30/70	—	289.0 ± 0.9	269.7 ± 0.6	5.0 ± 3.0	8.2 ± 0.3
0/100	—	—	269.3 ± 0.7	—	7.5 ± 0.2

$T_{c,c}$, crystallization temperature on cooling and $\Delta H_{c,c}$, enthalphy of crystallization on cooling. Standard deviations of three separate measurements are also given.

fection of the PEEK crystals. On the other hand, the LCP melting temperature increases slightly with the increase of PEEK; in this case, PEEK probably increases the perfection of the LCP crystalline solid domains, altering its rotational and translational organization.

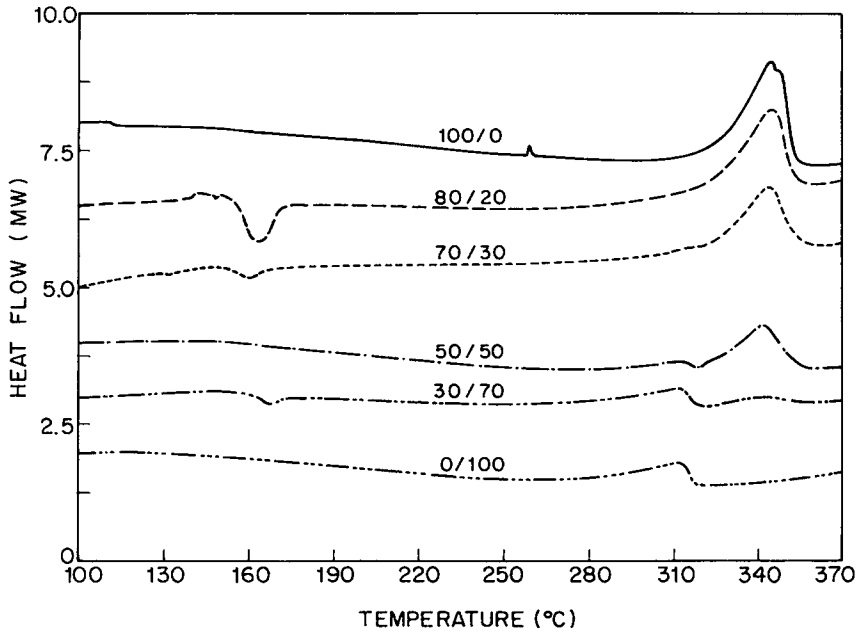


Figure 2 Typical nonisothermal crystallization curves of the blends on heating from above room temperature (5°C/min).

Table III Values of $T_{c,h}$ and $T_{m,h}$ of Blends after Nonisothermal Crystallization on Heating

PEEK/HX4000	Rate (°C/min)	$T_{c,h}$ (°C) PEEK	$T_{m,h}$ (°C) PEEK	$T_{m,h}$ (°C) HX4000
100/0	5	—	343.4 ± 3.7	—
80/20	—	161.7 ± 1.1	343.1 ± 3.0	—
70/30	—	159.6 ± 1.7	342.0 ± 3.8	312.0 ± 2.5
50/50	—	165	341.3 ± 2.9	311.3 ± 2.0
30/70	—	166.6 ± 1.2	340.0 ± 3.3	310.3 ± 2.0
0/100	—	—	—	310.2 ± 2.0
100/0	10	167.4 ± 1.3	342.3 ± 0.3	—
80/20	—	165.0 ± 1.0	340.6 ± 2.4	—
70/30	—	164.6 ± 1.0	339.8 ± 2.5	310.4 ± 2.3
50/50	—	169.2 ± 2.0	339.6 ± 1.0	311.1 ± 0.2
30/70	—	169.7 ± 1.9	337.4 ± 0.7	307.1 ± 0.6
0/100	—	—	—	307.4 ± 0.6
100/0	20	141.2 ± 3.0	346.2 ± 4.0	—
80/20	—	146.2 ± 167.8	343.6 ± 4.0	—
70/30	—	166.7 ± 3.4	340.9 ± 1.7	311.0 ± 0.8
50/50	—	171.2 ± 2.4	339.8 ± 1.8	310.9 ± 0.1
30/70	—	176.7 ± 1.4	337.8 ± 3.0	308.8 ± 3.0
0/100	—	—	—	309.6 ± 2.7

$T_{c,h}$, crystallization temperature on heating and $T_{m,h}$, melting temperature on heating. Standard deviation of three separate measurements are also given.

Isothermal Crystallization

Avrami Analysis

Figure 3 shows a typical isothermal crystallization scan of the blends at 315°C. From these curves, $X_c(t)$ and $X_c(\infty)$ can be calculated and a plot of $\{-\ln[1 - X_c(t)/X_c(\infty)]\}$ as a function of time can be drawn. Figure 4 shows a typical Avrami plot of the blends (315°C). It can be observed that the curves present two regions: one linear followed by a roll-off at longer times, each region giving a different value for n (n_1

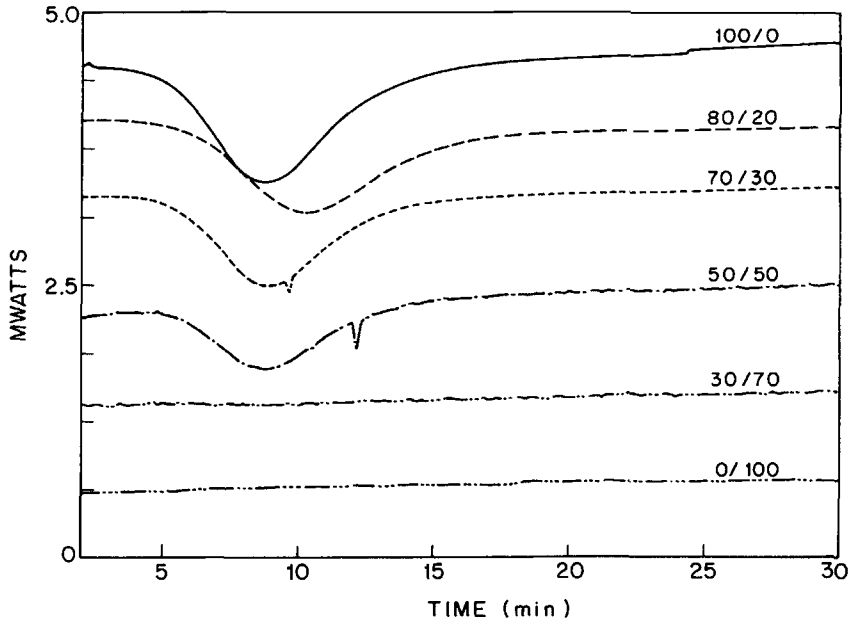


Figure 3 Typical DSC isothermal crystallization curves of the blends (315°C).

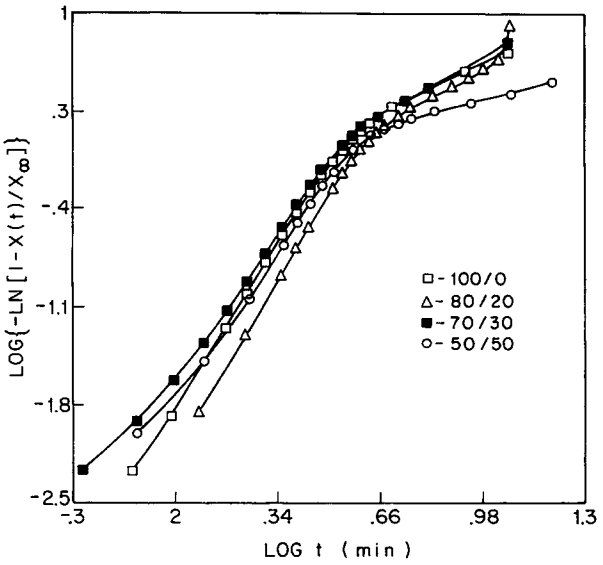


Figure 4 Typical Avrami plot of the blends (315°C).

and n_2) and k (k_1 and k_2). Two different values of n can represent two different crystallization mechanisms, the second one due to secondary crystallization or crystal perfection. This data is shown in Table IV.

The PEEK n_1 values (3.5–3.8) can be interpreted as representative of spherulitic growth from spo-radically formed nuclei.[17] It can be pointed out that n_1 can also change with the holding time in the melt, as observed in a recent study,[10] where PEEK was melted at 380°C for 2 min and n_1 was found to vary between 2.0 and 2.4. A previous study[16] relates this difference to the high viscosity and chain entanglements that occur in the melt, because it may take a long time for the crystalline regions in the bulk to lose order and become a completely homogeneous melt. In the blends, except composition 30/70, the n_1 values vary between 3.3 and 3.9, indicating that the crystallization morphology is the same as in pure PEEK.

Avrami analysis of the "roll-over" portion of the curves is not appropriate because secondary crystallization is not treated in the Avrami approach.

Figure 5 shows k_1 of the blends as a function of crystallization temperature. It can be observed that k_1 (or the overall crystallization rate) decreases with temperature, as expected. The overall crystallization rates of pure PEEK, at all crystallization temperatures, are higher than of the blends. However, a small amount of LCP (20 wt %) added to this polymer decreases its crystallization rate more strongly than a higher amount (50 or 70 wt %). It seems that 20 wt % of LCP in the PEEK acts as a more effective diluent (or plasticizer, as already reported[12]) than higher amounts.

Table IV n **and** k **(min^{-n}) Avrami Parameters of Blends as Function of Crystallization Temperature**

Composition (PEEK/HX4000)	Crystallization Temperature	n_1	k_1	n_2	k_2
100/0	315°C	3.5	2.9×10^{-3}	1.4	1.0×10^{-1}
80/20		3.4	6.8×10^{-4}	1.3	8.2×10^{-2}
70/30		3.8	8.6×10^{-4}	1.4	1.6×10^{-1}
50/50		3.5	1.6×10^{-3}	2.2	2.9×10^{-2}
30/70		—	—	—	—
100/0	312°C	3.7	1.1×10^{-2}	1.9	1.8×10^{-1}
80/20		3.7	3.1×10^{-3}	1.4	1.6×10^{-1}
70/30		3.5	5.6×10^{-3}	1.5	1.6×10^{-1}
50/50		3.3	1.5×10^{-2}	1.9	1.6×10^{-1}
30/70		—	—	—	—
100/0	310°C	3.7	3.2×10^{-2}	1.3	4.0×10^{-1}
80/20		3.9	6.3×10^{-3}	1.5	1.9×10^{-1}
70/30		3.6	1.4×10^{-2}	0.9	4.9×10^{-1}
50/50		3.5	1.2×10^{-2}	0.9	5.1×10^{-1}
30/70		2.7	4.9×10^{-2}	1.0	2.9×10^{-1}
100/0	307°C	3.8	1.3×10^{-1}	1.1	7.3×10^{-1}
80/20		3.7	3.2×10^{-2}	0.7	9.3×10^{-1}
70/30		3.9	2.7×10^{-2}	0.7	7.5×10^{-1}
50/50		3.7	4.0×10^{-2}	1.1	6.7×10^{-1}
30/70		2.8	9.0×10^{-2}	1.1	4.5×10^{-1}

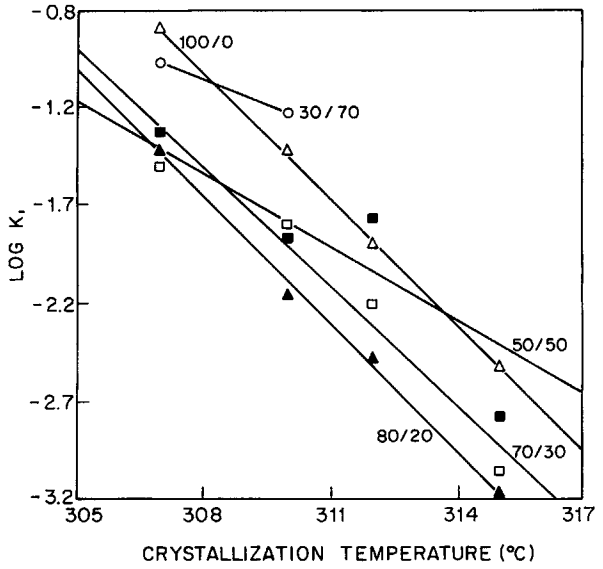


Figure 5 k_1 of the blends as a function of crystallization temperature.

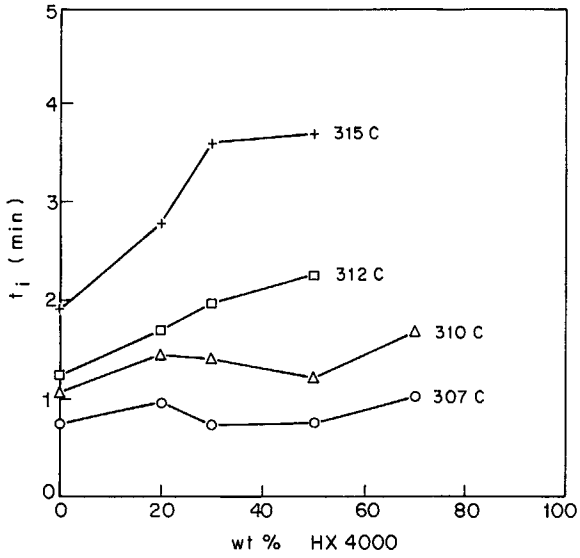


Figure 7 t_i of the blends as a function of composition and crystallization temperature.

Data of the time necessary for maximum crystallization to occur, t_{max}, is shown in Figure 6. This time corresponds to the point where $dQ/dt = 0$, $Q(t)$ being the heat flow rate. It can be seen that the 80/20 blend presents the highest t_{max}s, confirming that, at this composition, the LCP acts as a more effective diluent, retarding the PEEK crystallization in the blend.

The induction times, t_i, as a function of composition are shown in Figure 7. It is observed that t_i decreases as the crystallization temperature decreases, as expected. At 315 and 312°C, t_i increases with the amount of LCP. However, at 310 and 307°C the behavior of the curves changes, showing a maximum at the 80/20 composition. The LCP melts around 307–310°C. Thus, the PEEK crystallization kinetics will be different below 310°C because the LCP is changing from a solid crystalline to a nematic mesophase. This observation needs further studies.

Hoffmann et al. Analysis

Figure 8 shows a graph where the left-hand term of eq. (6), A, has been plotted as a function of $1/T\Delta T$ (φ). To calculate this expression the following pa-

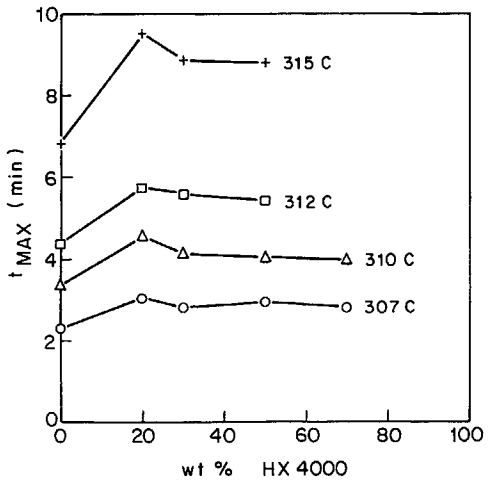


Figure 6 t_{max} of the blends as a function of composition and crystallization temperature.

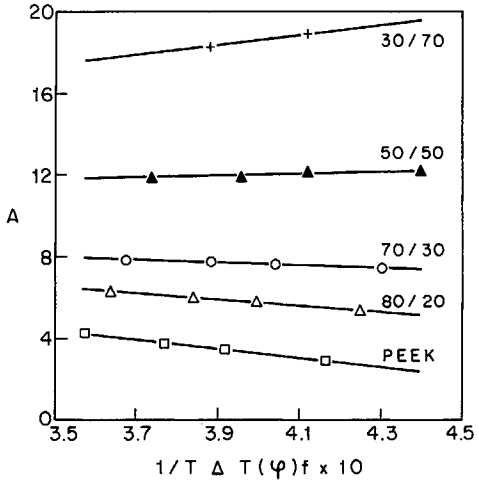


Figure 8 Left-hand term of eq. (6) as a function of $1/T\Delta T$ of the blends.

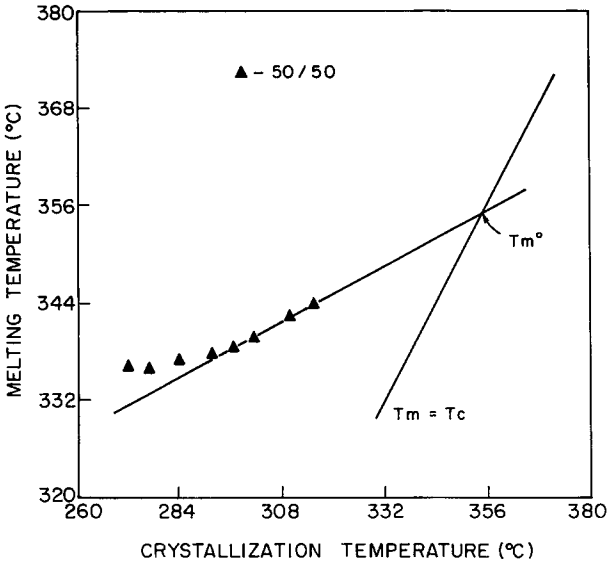


Figure 9 Typical plot for calculation of T_m° and α of the blends.

rameters were used[7-11]: U^* = 8.38 kJ/mol; C_2 = 51.6°C; b_0 = 0.2929 nm; β = 0.24; ΔH_m° = 130 J/g; ρ_{PEEK} = 1.263 g/cm^3, ρ_{HX4000} = 1.287 g/cm^3.

β was considered to be equal to 0.24, because as already pointed out by some authors,[8] "the presence of oxygen atoms on the lateral surfaces suggests that β for PEEK might be similar to that of polyesters."

The values of k_1 and n_1 are given in Table IV.

The values of T_m° were calculated by using the following eq.[4]:

$$T_m = T_m^\circ (1 - 1/2\alpha) + T_c/2\alpha \quad (8)$$

where α = lamellar thickening factor (the final lamellar thickness will be α times larger than the initial thickness).

A typical Hoffmann and Weeks plot of T_m vs. T_c, is shown in Figure 9. The deviation from a straight line of some of the data points can be caused by recrystallization or reorganization,[18,19] that usually occurs at low T_c values during the thermal analysis experiment. As a consequence, the T_m values obtained for high T_c values are apt to be more correct than those obtained for low T_c values. T_m° is the intercept of the extrapolated T_m values and the line $T_m = T_c$. The T_m° and α values are given in Table V. A slight depression of the equilibrium melting point was observed, indicating miscibility of both components, and as expected,[4] the final lamellar thickness of the PEEK crystals in the blends was larger than in the pure state due to a decreased supercooling. It is also known[19] that large α values can indicate that recrystallization has occurred.

The values of T_gs are given in Table I; σ was calculated from eq. (7), being equal to 19 erg/cm^2.

The values of σ_e were calculated from the slopes of the curves of Figure 8, assuming a regime III of crystallization kinetics[8] and are shown in Table VI. The σ_e value of pure PEEK (37 ± 5 erg/cm^2) is similar to the ones found in the literature.[6,8] However, in our case, this value decreases with the increase of LCP, even being negative at low concentrations of PEEK. It can also be observed that the correlation coefficient is close to 1 up to a 70/30 composition; however above this composition, this correlation coefficient decreases indicating an imperfect correlation. The 30/70 system did not present crystallization at 312 and 315°C, and only two points could be used to plot the data. The decrease of σ_e has been

Table V Extrapolated (T_m°) Values of Blends

Composition (PEEK/HX4000)	T_m° (°C)	α
100/0	357.3	1.52
80/20	356.4	—
70/30	355.9	—
50/50	355.0	1.81
30/70	353.2	1.85

Table VI. Fold Surface Free Energy, σ_e, as Function of Composition

Composition (PEEK/HX4000)	σ_e (erg/cm^2)	Correlation Coefficient
100/0	37 ± 5	−0.999
80/20	25 ± 4	−0.993
70/30	14 ± 4	−0.981
50/50	−8 ± 4	0.81
30/70	−41 ± 9	—

Table VII Lateral Surface Free Energy, σ, for σ_e = 37 erg/cm^2

Composition (PEEK/HX4000)	σ (erg/cm^2)
100/0	19.0
80/20	15.6
70/30	10.0
50/50	7.5
30/70	5.2

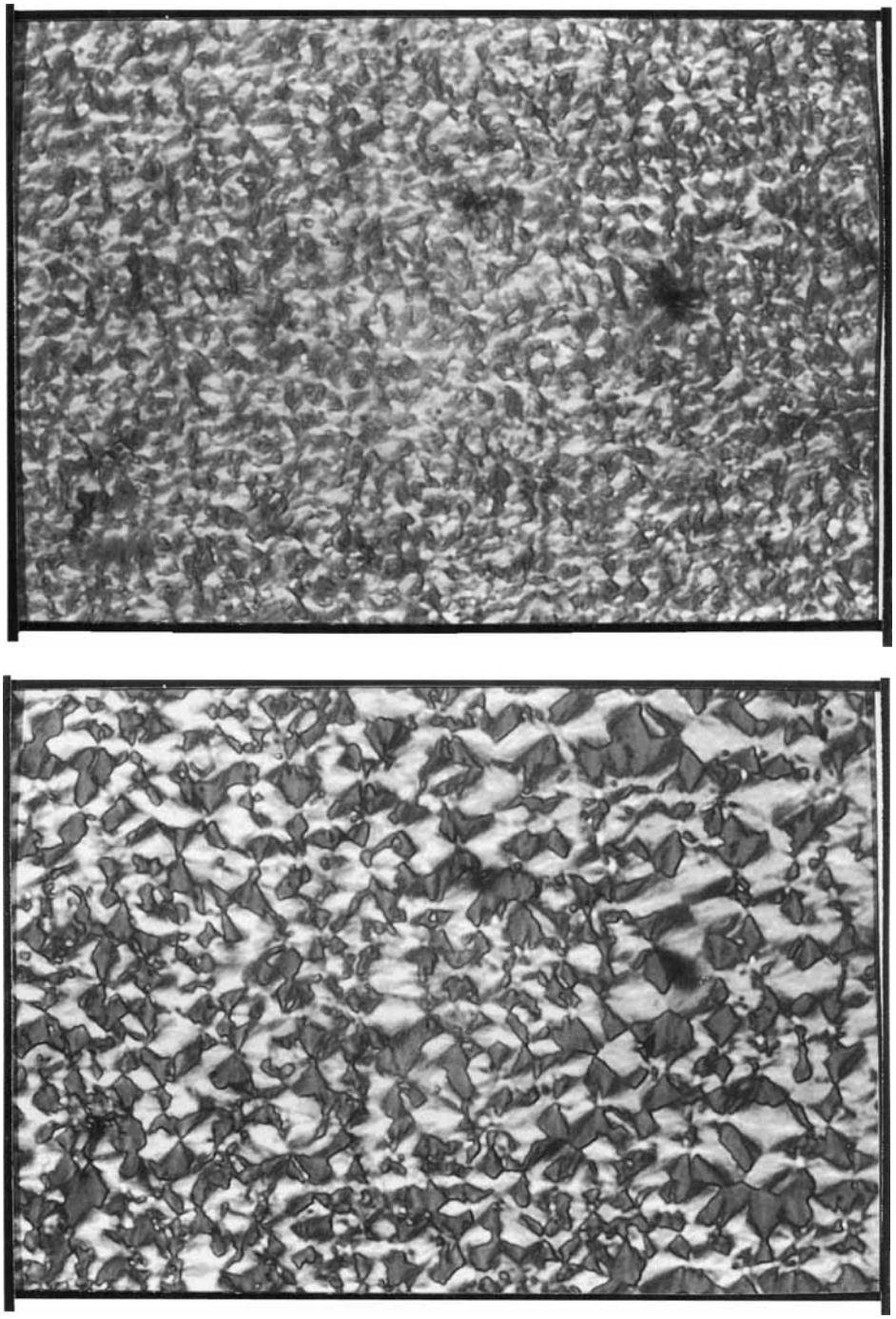


Figure 10 (a) PEEK isothermally crystallized at 315°C after melting at 380°C (magnification 1000×); (b) PEEK isothermally crystallized at 315°C after melting at 400°C (magnification 1000×).

observed[7] when a nucleating agent is added to an iPP/dotriacontane mixture. This lowering is explained[7] as a consequence of the occurrence of multiple nucleation, which leads to the formation of loops and tie molecules and dangling chain ends from cilia. Also, comparing two different poly(aryl ether ketones),[6] it was found that the product $\sigma\sigma_e$ was higher for PEEK than for polyetherketoneketone (PEKK); the discrepance was explained as due to the chemical structure of the PEKK that might

facilitate the chain folding mechanism, and consequently lower the crystal-surface free energy.

If we assume that eq. (6) is valid for our system and that the PEEK parameters are experimentally correct, then two factors can be considered responsible for these "anomalous" values of σ_e: the value of σ is not constant or the kinetic regime is not regime III, as assumed. In this last case, if a transition to regime II occurs, r would have to be equal to 2, σ_e would double, but still would decrease and would be negative. Regarding σ, it has been observed that almost all the literature on blends assume that in the case of PEEK, σ is equal to 19 erg/cm^2 and it is constant at all blend compositions. This last assumption is valid when the diluent is a noncrystallizable polymer that will also be a random coil in the melt state as the PEEK is. Thus σ will not be affected for the presence of other macromolecules with the same melt characteristics as that of the PEEK. However, the LCP is a rigid macromolecule that will not be a random coil in the melt state; its conformation will be more similar to the lateral surface of the PEEK crystallizing macromolecule. Thus, the LCP can affect the value of σ in the blend. To confirm this last hypothesis, we calculated the values of σ that would result if we took σ_e constant and equal to 37 erg/cm^2. The values are shown in Table VII. It can be observed that if σ_e is constant at all compositions, σ will decrease, but will be positive. In other words, the LCP rigid chains diminish the amount of lateral surface free energy that the PEEK macromolecules will expend to crystallize; this increased reduction in σ can eventually increase the thickness of the lamellae producing more extended PEEK crystals, as inferred from the calculated α values. As a matter of fact, we believe that in our systems neither σ nor σ_e can be considered constants; both probably change with composition.

PLOM

Two melting temperatures (380 and 400°C) were used because results of a recent study[10] showed that the PEEK spherulitic morphology was dependent on the melting temperature.

Figure 10 shows this difference; at 380°C [Fig. 10(a)], no spherulites (or very small spherulites) can be observed; at 400°C [Fig. 10(b)] a coarse texture and a spherulitic morphology is seen. Probably, at 380°C the PEEK did not melt completely and self-nucleation occurred, and at 400°C, it melted completely and heterogeneous nucleation happened.

Micrographs of the blends are also shown in Figure 11; the blend 80/20 has the same spherulitic morphology as pure PEEK, whatever the melting temperature [Fig. 11(a)]. This result confirms the Avrami analysis. However, the other compositions do not present this spherulitic morphology at any melting temperature [Fig. 11(b–d)]. Instead, a droplet and fibrillar-like morphology is observed. The HX4000 [Fig. 11(e)] showed a typical Schlieren texture, probably nematic. The "dark brushes" correspond to the extinction positions of the mesophases.[20] Evidently, this last micrograph shows the LCP in its solid crystalline form, because the nematic–solid transition of this polymer occurs around 270°C.

CONCLUSIONS

The nonisothermal crystallization experiments from the melt showed that the LCP retards the PEEK crystallization process, probably due to miscibility of both components in the melt state. The experiments on heating revealed that the PEEK melting temperature decreased with the amount of LCP, and on the other hand, the LCP melting temperature increased with the amount of PEEK. Thus, the PEEK probably improves the perfection of the LCP crystalline domains, while the LCP do not. The increase of an LCP melting temperature with annealing[21] has been attributed to "an ester interchange reorganization which induces the conversion of a random to block copolymer." In our case, probably two main factors contributed to increasing the HX4000 melting temperature: the annealing promoted by the DSC itself and the presence of the PEEK. Thus, this topic needs further research.

The isothermal crystallization Avrami analysis showed that a spherulitic morphology in pure PEEK and its blends with LCP should be expected, independent of the crystallization temperature. However, this spherulitic morphology was observed by PLOM only for pure PEEK and for the 80/20 composition. The other compositions presented a droplet and fibrillar-like morphology.

The overall crystallization rate was observed to decrease with the crystallization temperature for all compositions. There are two factors that can influence the PEEK crystallization: there is the effect promoted by the dilution of the PEEK, that will retard the crystal growth changing the crystallization peak to higher times and also the "plasticization" (or reduction of viscosity) of the PEEK promoted by the HX4000.[12] Thus the behavior of the crystallization peak with concentration will depend on the balance between these two factors.

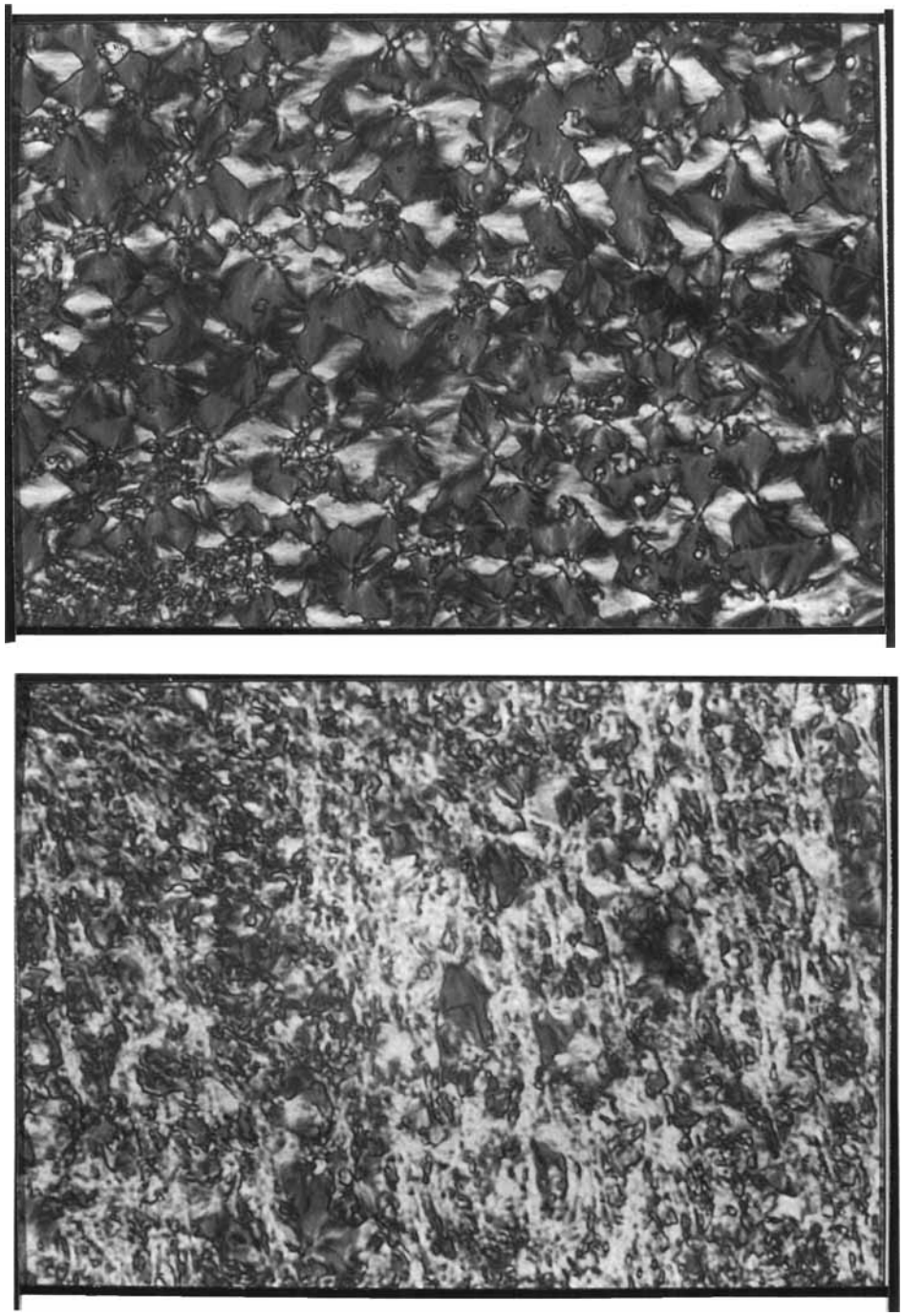
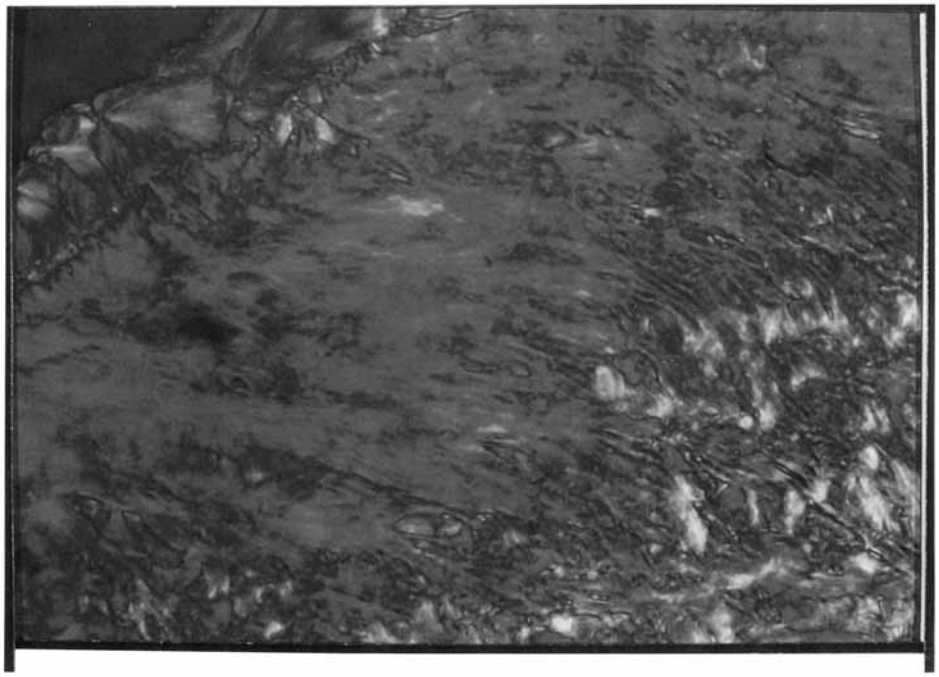
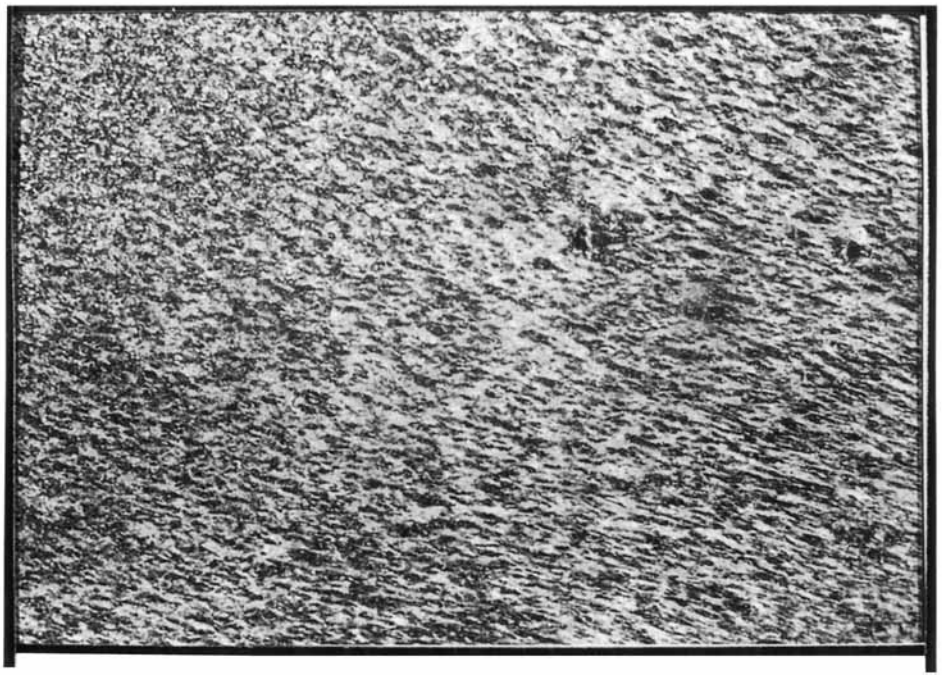


Figure 11 (a) 80/20 blend isothermally crystallized at 315°C after melting at 400°C (magnification 1000×); (b) 70/30 blend isothermally crystallized at 315°C after melting at 400°C (magnification 1000×); (c) 50/50 blend isothermally crystallized at 315°C after melting at 400°C (magnification 1000×); (d) 30/70 blend isothermally crystallized at 315°C after melting at 400°C (magnification 1000×); (e) HX4000 isothermally crystallized at 315°C after melting at 400°C (magnification 1000×).

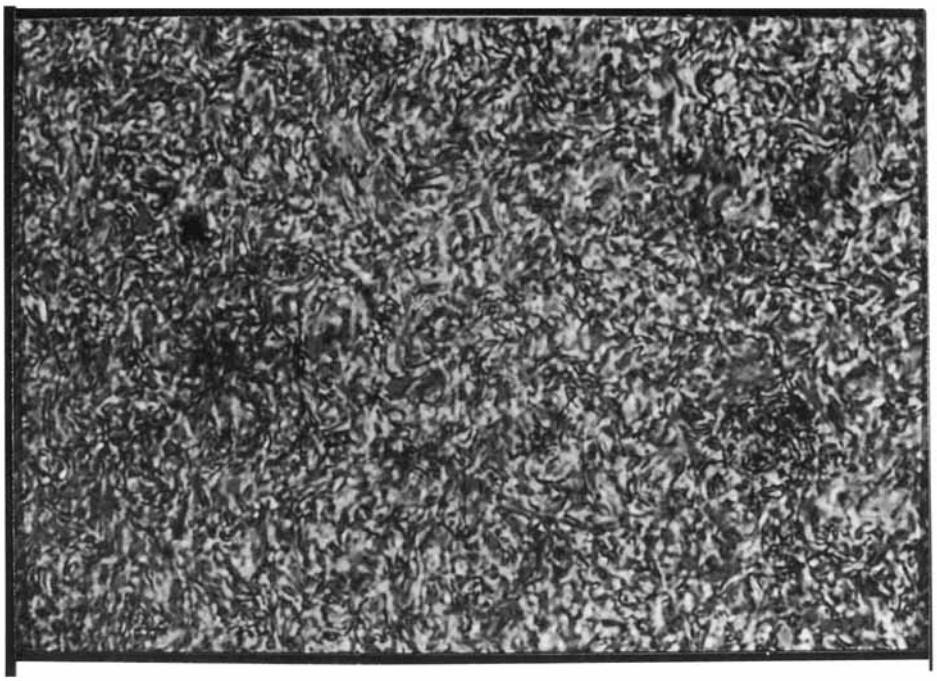


(C)



(D)

The value of σ_e for pure PEEK was found to be equal to 37 ± 5 erg/cm^2, similar to previous studies. However, it was observed that σ_e decreased with the increase in the amount of LCP, having unrealistic negative values. This discrepancy was attributed to the value of σ that in the calculations was maintained constant. Thus, it was observed that if we assumed that σ_e was constant, instead of σ, this last one would decrease, but still remained positive. Physically, this would mean that the presence of LCP rigid chains lowered the lateral surface free energy that the PEEK macromolecules would expend on crystallization, resulting in more extended crystals. As a matter of fact, we concluded that nei-



(E)

Figure 11 (*Continued from the previous page*)

ther σ nor σ_e can be considered constant for these blends. These last observations need further studies to be corroborated.

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