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Morphological changes in polyamide/ PVP blends

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Dramatic morphological changes have been found in the blend of an aliphatic crystallizable polyamide (nylon 6/6) with trace quantities of a polar non-crystallizable diluent (poly(vinyl pyrrolidone)). The influence of the addition of PVP on the crystal morphology of nylon 6/6 was studied using d.s.c., X-ray (small and wide angle) and hot stage optical microscopy. The addition of the diluent has a dramatic effect on the spherulitic morphology of nylon 6/6 by causing a striking reduction in the nucleation density of spherulites, modification of lamellar organization in spherulites (as evidenced by the occurrence of banding), and modification of interlamellar spacings. Furthermore, the effect of increasing diluent molecular weight was studied, and it was shown to have only a subtle affect on the system. © 1997 Elsevier Science Ltd.

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INTRODUCTION

There have been many studies of spherulitic crystallization of miscible blends from the melt in which an amorphous diluent is added to a crystallizable host polymer. Early investigations concentrated on blending atactic and isotactic[1] forms of the same polymer, and in further studies, chemically dissimilar polymers[1] were blended. In most of these works, diluent concentrations exceeded 10%, and it was found that the nucleation density and the growth rate of the spherulites can both be suppressed by as much as an order of magnitude by the presence of the diluent in such large quantities.

More recent studies have focused on blending chemically dissimilar polymers in small concentrations (~1%). For instance, Keith *et al.*[2] blended aliphatic polyesters with certain diluents, and, from these investigations, startling new observations and more subtle morphological changes were reported. Specifically, the incidence of nucleation was found to be extremely sensitive to the diluent concentration whereas the growth rates of the spherulites were not. Furthermore, the diluent induced more regular and well defined banding at temperatures where this did not normally occur in the host polymer, increased regularity of lamellar organization, modified interlamellar spacings, and in some cases, changed the molecular packing of the crystals. They concluded by stating that similar changes could occur in aliphatic polyamides when blended with an appropriate diluent at small concentrations.

The aim of this study, therefore, was to determine the effect of the addition of trace quantities of a polar amorphous diluent, poly(vinyl pyrrolidone) (PVP), on the morphology of a crystallizable aliphatic polyamide (nylon 6/6). The work consists of differential scanning calorimetry (d.s.c.) to investigate the thermal behaviour of the blends, an X-ray diffraction study to determine crystal structure and lamellar thickness alterations, and hot stage optical microscopy to reveal morphology changes. The results of this study will lead to a better understanding of the crystallization process and the mechanism by which small quantities of a diluent drastically affect polymer morphology. This understanding will help in 'tailoring' existing polymers to attain a specific morphology without adding large quantities of a second component.

This technique could also be applied to composite structures. Typically, when reinforcements are added to a semicrystalline matrix, a third phase (termed the transcrystalline region) is formed around the reinforcements. The formation of this region is a consequence of the profuse nucleation on the fibre surface. Therefore, applying a phenomenon which reduces nucleation density in this region could have a dramatic influence on the mechanical properties of these composites.

EXPERIMENTAL

Pellets of nylon 6/6 were purchased from Aldrich Chemical Company and two different molecular weights of PVP were purchased from BASF. The average molecular weights of the PVP were $M_w \approx 17\,000$ and $M_w \approx 1\,000\,000$. All polymers were placed in a vacuum oven at 105°C for 72 h before use, to remove any residual solvent or water vapour.

In order to study the crystallization behaviour of the nylon 6/6–PVP blends, solutions of 1% by weight of nylon 6/6 and its blends with PVP were prepared in formic acid. The blend compositions were 1–7% PVP (by weight) in nylon 6/6. Immediately following dissolution, samples for optical microscopy and d.s.c. were cast as thin films of melt on heated microscope cover slips in a Linkam hot stage (Model THMS 600) and maintained well above the melting temperature of the host polymer until solvent and residual nuclei were removed. Then specimens were quenched at a rate of 90°C min^{-1} and isothermally crystallized at 235°C. I.r. spectroscopy of the films showed no sign of residual solvent to within the resolution of the spectrometer ($\ll 1\%$).

To aid in the optical microscopy studies, an Olympus

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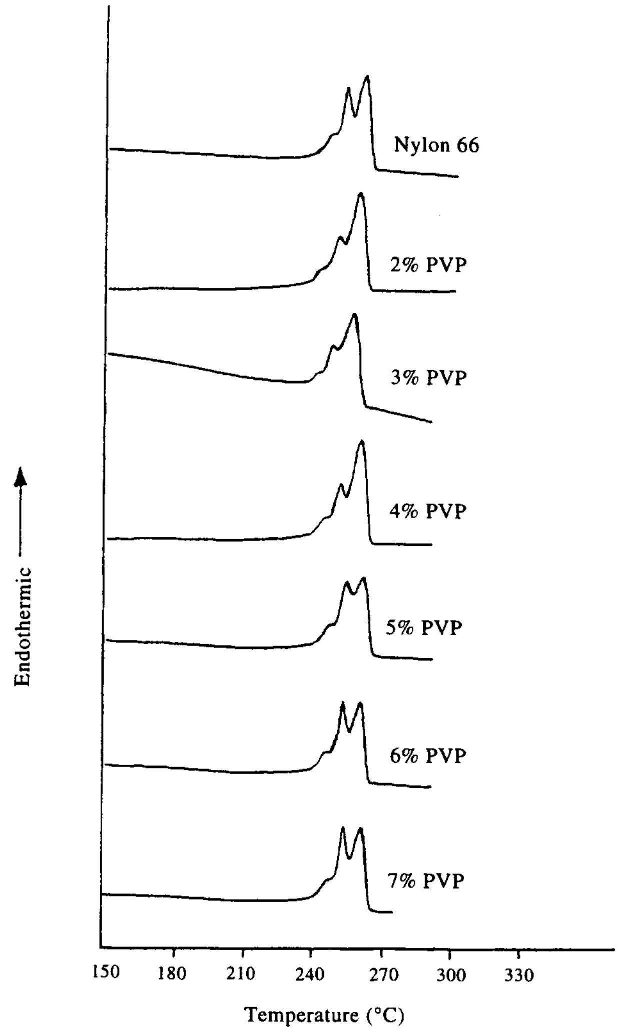

Figure 1 Melting endotherms for solution-cast blends of nylon 6/6–PVP crystallized at 235°C. Values of PVP concentrations are shown on the respective curves

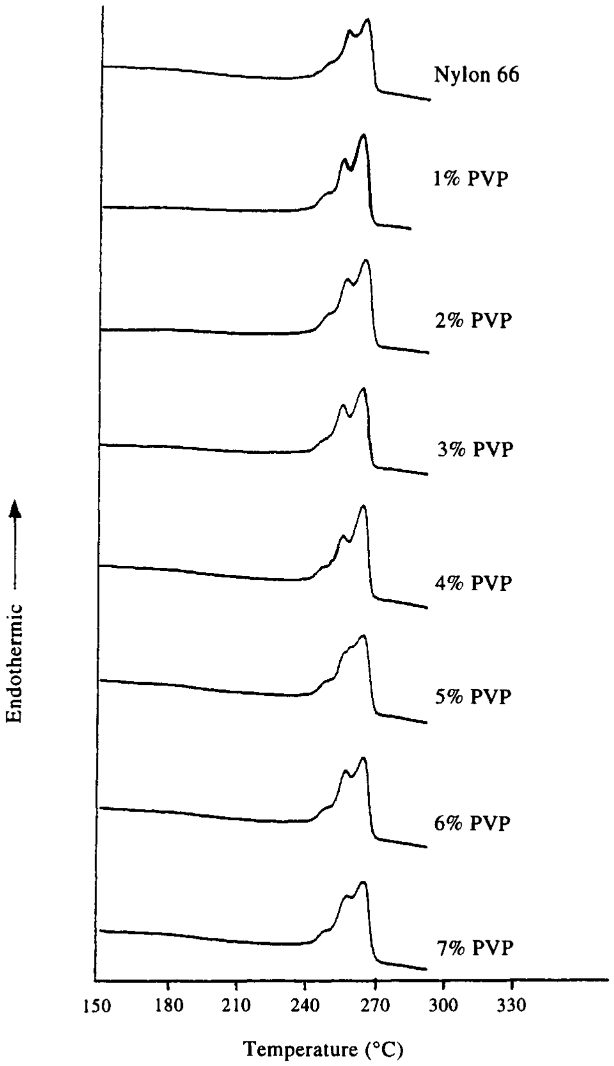

Figure 2 Melting endotherms for melt-processed blends of nylon 6/6–PVP crystallized at 235°C. Values of PVP concentrations are shown on the respective curves

polarizing microscope (Model BHSM) equipped with a 35 mm camera and a 530 nm compensator was used in conjunction with the hot stage.

Differential scanning calorimetry studies of the films (weighing 7–8 mg) were performed using a standard d.s.c. with an argon purge (Perkin-Elmer DSC-7). In all cases, the melting points were taken as the peaks of the individual melting endotherms. The instrument was calibrated for temperature and heat of fusion using indium and zinc. The heating runs were carried out at a rate of 10°C min^{-1} from room temperature to 300°C.

Films for wide angle X-ray diffraction (WAXS) and small angle X-ray diffraction (SAXS) studies were prepared using a second sample preparation technique. The dried nylon 6/6 and PVP were prepared by dry-mixing nylon 6/6 with 1–7% PVP (by weight) and then melt blending in a Haake melt blender (Model 600) for 3 min at 275°C. Neat nylon 6/6 was also melt processed to impart the same processing history as the blends.

These samples were then sandwiched between sheets of Teflon and melt pressed in a Pasadena Hydraulics hot press. The samples sandwiched in the sheets of Teflon were kept between two metal plates which were placed between the platens of the hot press. The platens were kept at a constant temperature of 275°C and minimum contact pressure was applied. When softening began, a load of 3000 kg was applied for a period of 5 min. Thereafter, the load was removed and the films were exposed to room temperature. The resulting films were homogeneous and of uniform thickness.

After attaining adequate size samples for WAXS and SAXS, the annealing cycle for these specimens had to coincide with the thermal history of the films cast from solution. Therefore, two Fischer isotemp programmable ovens (Model 838 F) were used to remelt and anneal the films formed in the hot press. Samples were placed in the first oven for 15 min at 300°C. The samples were then transferred to the second oven for 15 min and kept at the crystallization temperature of 235°C. Care was taken to minimize transfer time between the two ovens. The annealed samples were used for the WAXS and SAXS studies.

WAXS studies were carried out on both types of films: solution cast and annealed melt blended. The tests were carried out on a Philips Diffractometer operating at 40 kV and 30 mA, which uses Cu K_α radiation. The experiments on the diffractometer were carried out in reflection mode at room temperature.

In addition, SAXS was performed on the melt-blended specimens using a Siemens Kratky camera along with a position-sensitive detector system. The generator used was a

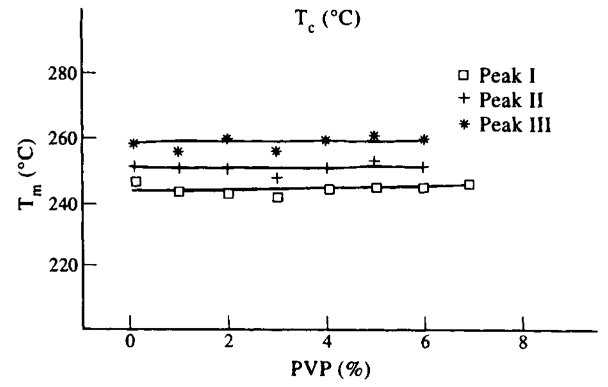

Figure 3 Peaks of the three melting endotherms as a function of PVP concentration at a crystallization temperature of 235°C

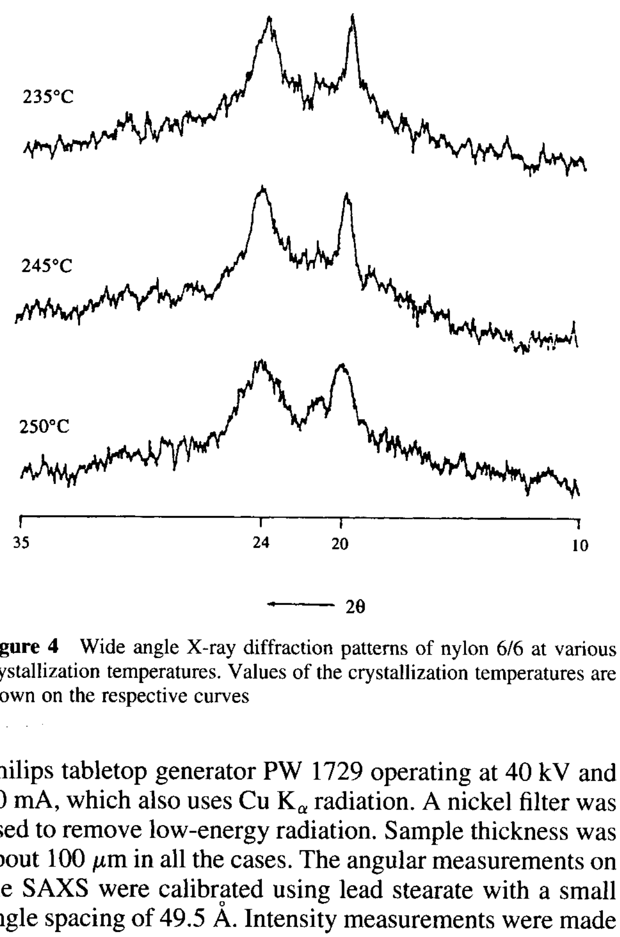

Figure 4 Wide angle X-ray diffraction patterns of nylon 6/6 at various crystallization temperatures. Values of the crystallization temperatures are shown on the respective curves

Philips tabletop generator PW 1729 operating at 40 kV and 20 mA, which also uses Cu K_α radiation. A nickel filter was used to remove low-energy radiation. Sample thickness was about 100 μm in all the cases. The angular measurements on the SAXS were calibrated using lead stearate with a small angle spacing of 49.5 Å. Intensity measurements were made using Lupolen. All measurements were made at room temperature.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Figure 1 shows the d.s.c. scans for solution-cast nylon 6/6 and its blends, crystallized at a temperature of 235°C. First, note the triple melting peak behaviour of pure nylon 6/6. This behaviour has been observed for a variety of polymers and was first detected in nylon 6/6 by Wilhoit and Dole[3]. Several additional works[4–9] followed this finding and concluded that the three peaks were a function of crystallization history and annealing time.

Furthermore, in *Figure 1*, it can be seen that addition of the diluent has the effect of increasing the size of the third melting peak relative to the second melting peak. This effect exists up to a concentration of 4% PVP. Any increased concentration of the diluent (5–7%) gives a d.s.c. trace similar to that of pure nylon 6/6. Since an increase in the size of the melting endotherm indicates an increase in the crystallinity of the sample, the results could imply that addition of the diluent up to a concentration of 4% somehow enhances crystallinity, and concentrations greater than 4% have no effect on the crystallinity of nylon 6/6. *Figure 2* shows d.s.c. traces for samples that were melt processed, and a similar behaviour was found.

Note that neither the presence of the diluent nor the sample preparation technique affected the positions of the melting peaks of nylon 6/6. The locations of all three melting peaks remained essentially unchanged for pure nylon 6/6 and its blends, as can be seen in *Figure 3* which shows the melting points of the three peaks of the solution-cast blends as a function of the PVP concentration. It can be seen in the figure that the melting points of the three peaks are essentially independent of PVP concentration. The position of the lower and upper tails of the melting endotherms were also found to be independent of the diluent concentration; i.e., no broadening or narrowing of the melting peaks occurred on addition of the diluent. This implies that the diluent does not affect the stability of the crystals which cause the melting peaks.

X-ray studies: WAXS

Nylon 6/6 samples which have been annealed at temperatures ranging from 175 to 250°C and studied at room temperature typically show the triclinic structure described by Bunn and Garner[10]. The four peaks usually seen correspond to the (001), (002) and (100) spacings and the (110), (010) doublet. The (001) and (002) peaks are due to order along the polymer chain, and their intensities are usually quite small. The two strong peaks [i.e. (100) and (010)] are due to lateral order. As the temperature is increased, the two strong peaks approach each other and merge at 175°C, the Brill temperature[11]. The equilibrium crystal structure is triclinic below the Brill temperature and pseudohexagonal above the Brill temperature.

Figure 4 shows the X-ray diffraction patterns of nylon 6/6 crystallized at various temperatures. Two major peaks are observed at 2Θ angles of 20° and 24° which correspond to the (100) and (010) spacings. A small shoulder is also seen on the peak corresponding to the (010) spacing which has been assigned to the (110) spacing. However, this assignment of the (110) peak cannot be definite due to the large amount of background scattering. The weak peaks corresponding to the (001) and (002) spacings also cannot be assigned because of the large amount of background scattering. On the basis of the X-ray diffraction patterns obtained, it can be concluded that the triclinic unit cell is the only unit cell structure observed at room temperature when nylon 6/6 is crystallized over the temperature range in this study. There is no previous evidence to suggest that different unit cell structures, apart from the pseudohexagonal structure, exist at high temperatures. In fact the presence of the pseudohexagonal structure as the only unit cell structure at high temperatures has been confirmed[11]. Therefore, it can be concluded that different unit cells do not contribute to the multiple melting peaks found for nylon 6/6 crystallized at these temperatures.

Figure 5 shows the X-ray diffraction patterns for solution-cast nylon 6/6 and its blends with PVP. Only two peaks, corresponding to (100) and (010) spacings, could be seen in the patterns. No other peaks could be resolved due to

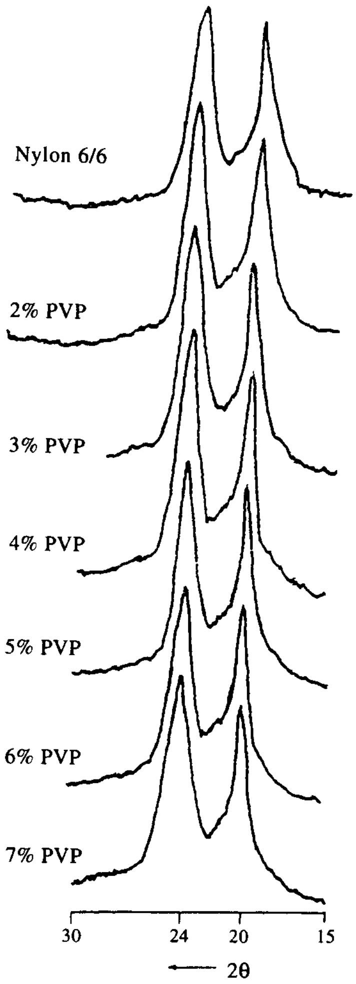

Figure 5 Wide angle X-ray diffraction patterns of solution-cast blends of nylon 6/6–PVP at a crystallization temperature of 235°C. Values of the PVP concentrations are shown on the respective curves

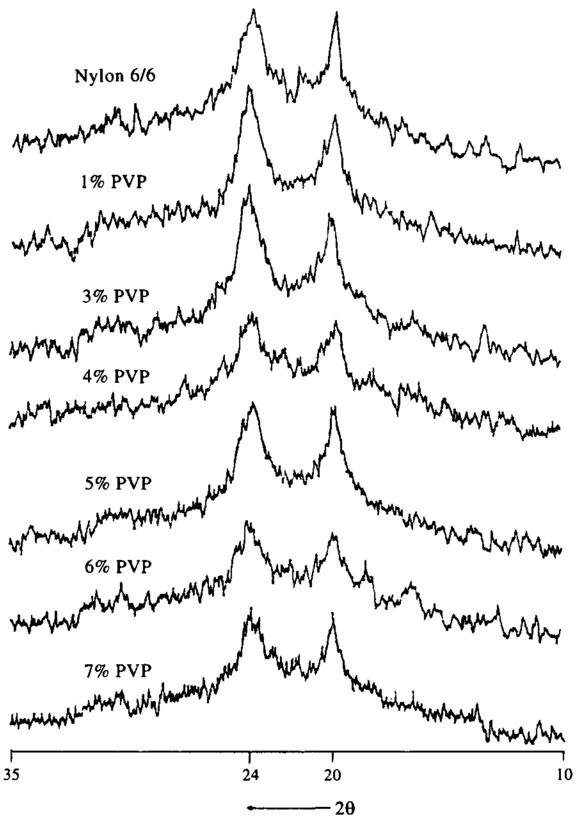

Figure 6 Wide angle X-ray diffraction patterns of melt-processed blends of nylon 6/6–PVP at a crystallization temperature of 235°C. Values of the PVP concentrations are shown on the respective curves

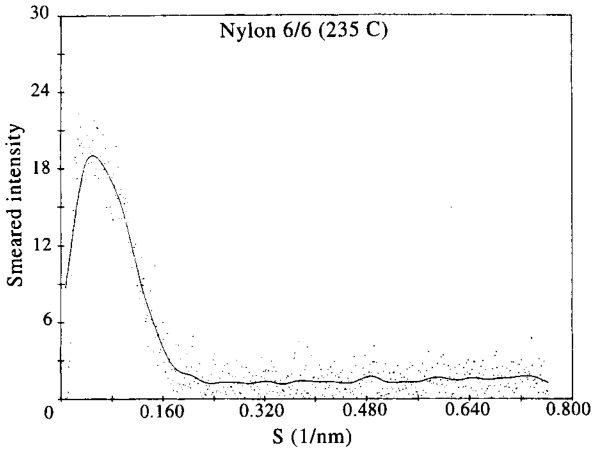

Figure 7 Small angle X-ray pattern for nylon 6/6 melt processed and crystallized at 235°C

the large amount of background scattering in the patterns. From this figure it can be seen that the unit cell structure in nylon 6/6 and all its blends is the triclinic structure described by Bunn and Garner[10]. The profiles show that there is no disordering of the lattice of nylon 6/6 due to the diluent. The fact that there is no disordering of the nylon 6/6 unit cell is acceptable because incorporation of PVP in the unit cell is virtually impossible due to its bulky side group. Although not found in this study, the occurrence of a diluent changing the unit cell parameters of a polymer, though uncommon, has been reported in the literature.

Figure 6 shows the diffraction patterns for melt-processed nylon 6/6 and its blends with PVP. The same results can be seen in the case of the melt-blended samples, in that the diluent does not perturb the unit cell dimensions of nylon 6/6.

X-ray studies: SAXS

Small angle X-ray studies were carried out on nylon 6/6 and its blends crystallized at 235°C. The X-ray long periods, indicative of interlamellar spacings, were determined from peaks in the small angle scattering profiles. *Figure 7* shows the SAXS pattern obtained after subtracting sample and parasitic position scattering patterns obtained for pure nylon 6/6 crystallized at 235°C. *Figure 8* shows the SAXS pattern for a blend of nylon 6/6 with 3% PVP which was also crystallized at 235°C. Although the data has not been desmeared, information concerning d-spacings can still be discerned. The variations in the X-ray long periods are strictly a measure of interlamellar spacing (d-spacings), but could also be indicative of changes in crystal thickness if we assume the thickness of the intervening amorphous layer to remain essentially constant. From a series of SAXS curves similar to *Figure 8*, d-spacings were obtained as a function of the PVP concentration and are plotted in *Figure 9*. From this figure it would appear that PVP is capable of modifying the interlamellar thickness of the nylon 6/6 crystals. If the diluent were to accumulate within the intervening amorphous layers, between otherwise unchanged crystals, small increases in the long period might be expected. However,

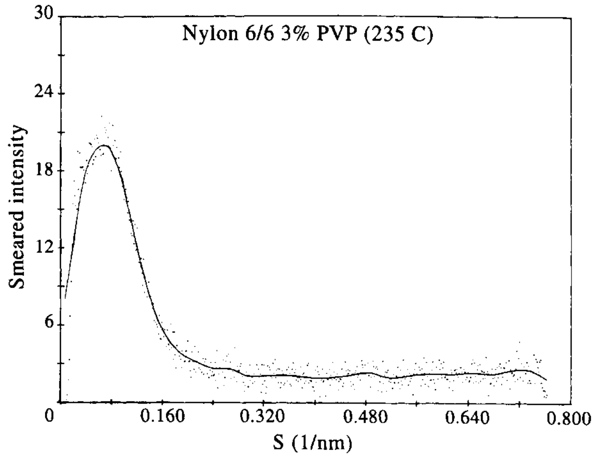

Figure 8 Small angle X-ray pattern for nylon 6/6–3% PVP blend, melt processed and crystallized at 235°C

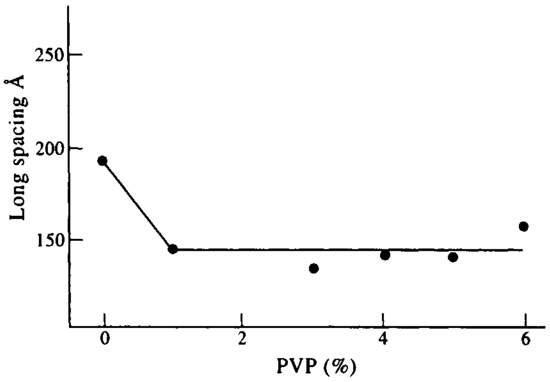

Figure 9 Long spacing obtained from SAXS *versus* PVP concentration

what is observed is a decrease in the long period upon adding the diluent. The decreased long periods could imply a decrease in the crystal thickness and in the lengths of molecular stems between folds. At concentrations of PVP above 1%, the values of the long periods are about the same as that for a 1% blend. This indicates that addition of 1% PVP modifies the lamella thickness, and that any higher concentrations of PVP have no additional effect. Although not completely understood, it has been speculated that the lamellar modifications are due to the diluent migrating to the crystal growth fronts of the host polymer.

Optical microscopy studies

Optical studies were carried out on pure nylon 6/6 and its blends with PVP, using hot stage polarized microscopy. The studies carried out on pure nylon 6/6 will be discussed first, followed by a discussion on the studies of the blends.

When nylon 6/6 is crystallized from the melt, positive spherulites are formed which, for crystallization temperatures below 250°C, show simple extinction crosses under the polarizing microscope (Maltese cross). The observed spherulites were identified as positive spherulites with the aid of a Michelle–Levy chart. *Figure 10* shows a micrograph of the positive spherulites of nylon 6/6 grown at 235°C. No evidence of any banded structure can be seen in the spherulites of nylon 6/6 grown at this temperature. Typically, spherulites of nylon 6/6 do not show the presence of banding if grown isothermally below a temperature of 250°C. However, simple extinction crosses are very much evident in the spherulites.

Nylon 6/6 crystallized at temperatures up to 250°C show similar spherulitic formation to those grown at 235°C. However, spherulites grown at higher crystallization temperatures exhibit banding, with radial separations in

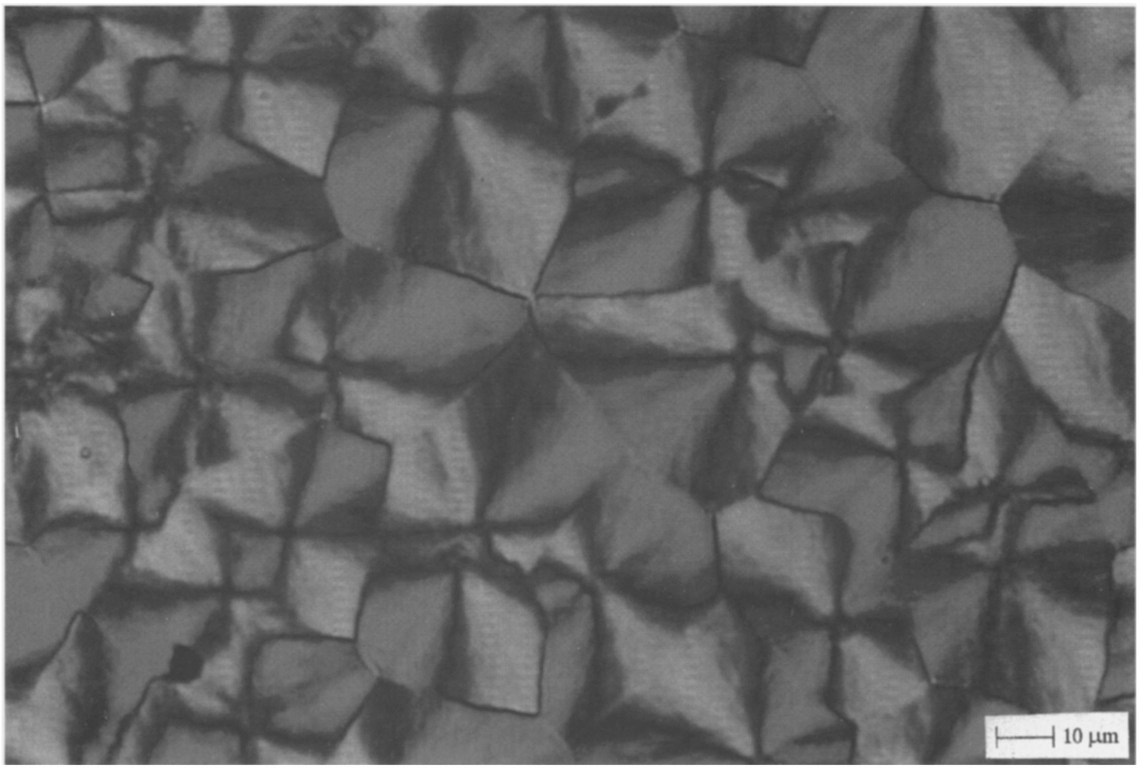

Figure 10 Nylon 6/6 solution cast and crystallized at 235°C

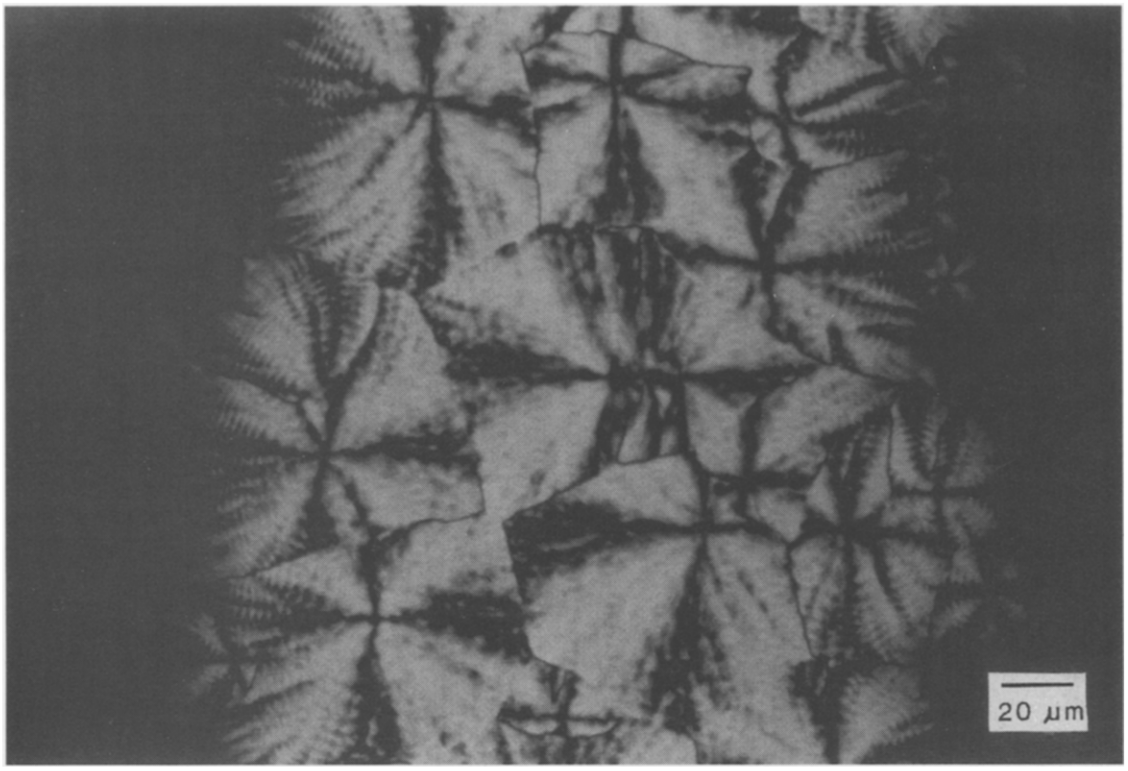

Figure 11 Nylon 6/6 solution cast and crystallized at 255°C

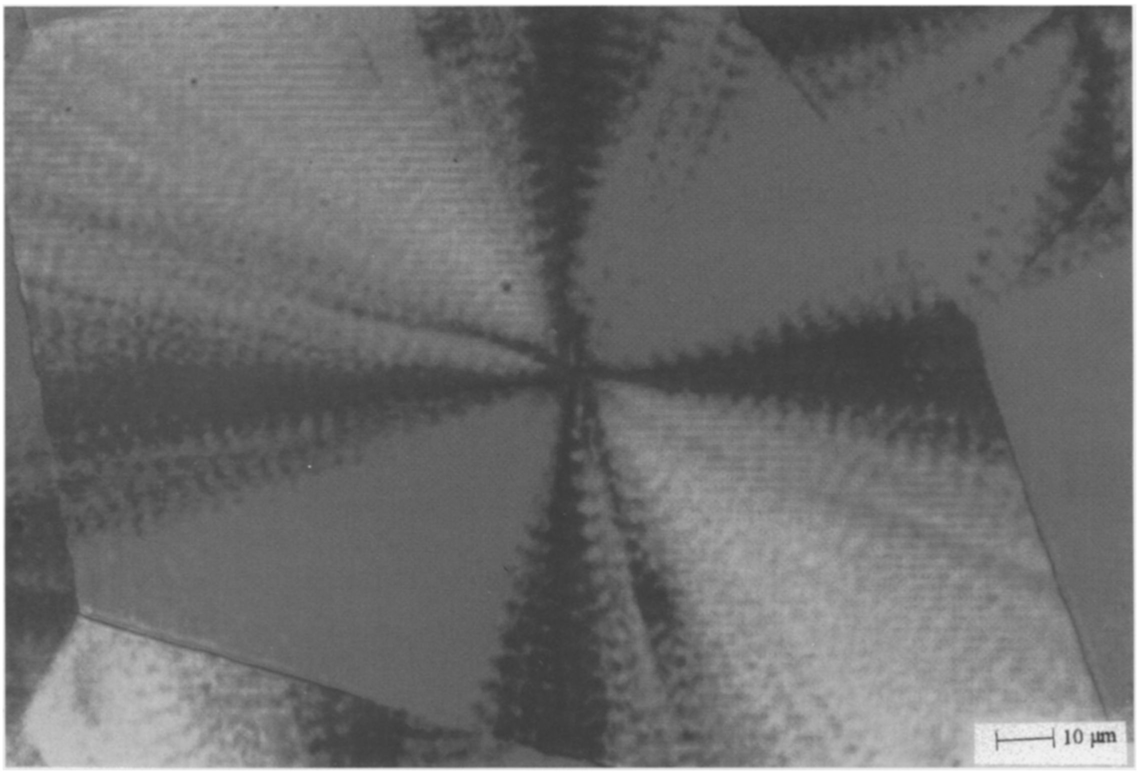

Figure 12 Nylon 6/6–1% PVP blend solution cast and crystallized at 235°C

the range of 1 μm. This is shown in the polarized photomicrograph of *Figure 11*. Such banding is common in polymer spherulites, and is attributable to a twisting or oscillation of crystallographic orientation about radii that reflects the cooperative twisting of radiating lamellae. Its occurrence implies a high degree of coordination in packing of lamellae within compact structures. Furthermore, it can be seen that samples crystallized at 255°C showed the presence of three distinct kinds of spherulites: banded spherulites, unbanded spherulites, and partially banded spherulites. The formation of partially banded spherulites can be attributed to the fact that at the

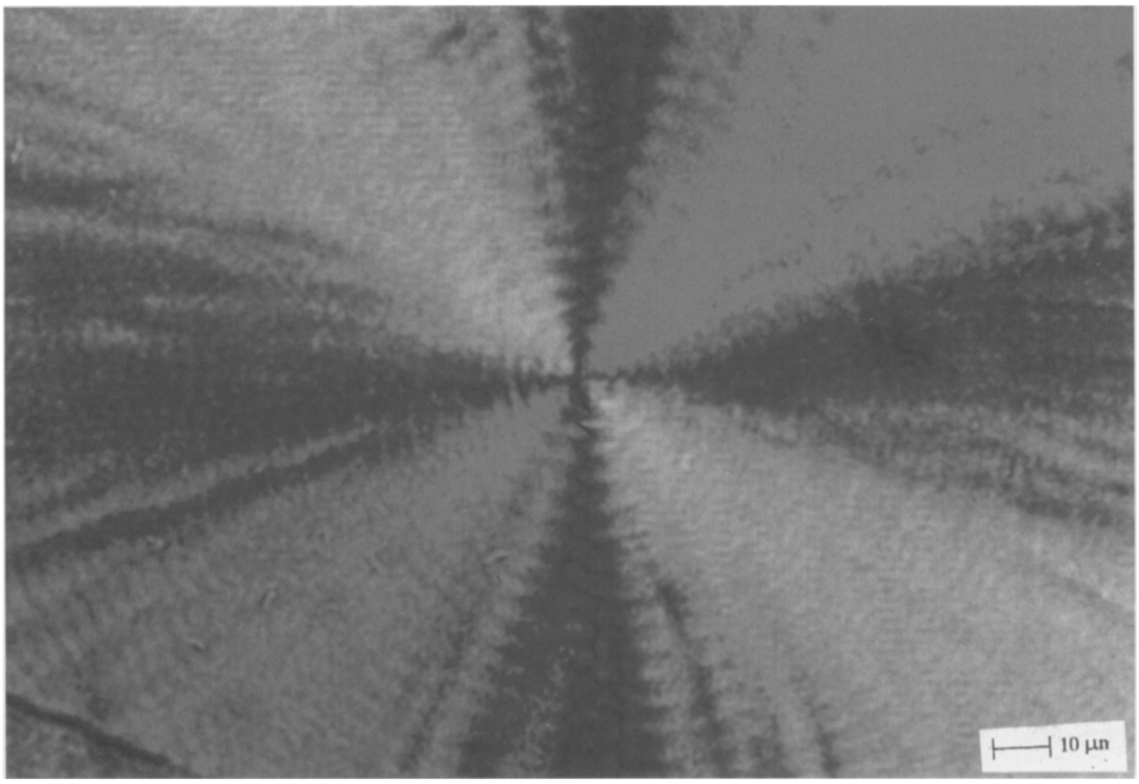

Figure 13 Nylon 6/6–3% PVP blend solution cast and crystallized at 235°C

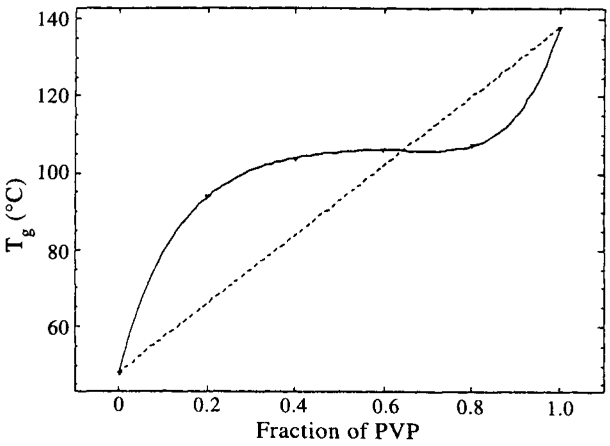

Figure 14 T_g *versus* composition (by weight) plot for nylon 6/6 and PVP

end of the annealing cycle, the samples were quenched to lower temperatures. Thus, spherulites which started growing as banded spherulites at the crystallization temperature continued to grow as unbanded spherulites when cooled to a lower temperature. Simple extinction crosses can be seen in all three kinds of spherulites. No negatively birefringent spherulites were formed under the crystallization conditions used in this study, confirming results of earlier studies on spherulitic formation in nylon 6/6[12].

The most notable effect of PVP as a diluent in nylon 6/6 is its remarkable potency in suppressing primary nucleation of spherulites. The micrographs in *Figures 12 and 13*, which are all taken at the same magnification (the size bar is shown in the bottom right of the micrograph), show nylon 6/6 blended with PVP at concentrations of 1 and 3, respectively, and isothermally crystallized at 235°C. It can be seen that the addition of 1% PVP has caused a striking reduction in the frequency of nucleation of nylon 6/6.

The addition of the diluent also induced banding in the blend at crystallization temperatures where it does not normally occur in pure nylon 6/6. These phenomena have been attributed to the fact that the diluent migrates to the crystal growth fronts of the lamella, therefore giving additional mobility to the polymer (allowing the lamella to twist). Furthermore, it can be implied that the addition of the diluent induced similar spherulitic morphology in the blend, similar to that in pure nylon 6/6 at higher crystallization temperatures. Namely, as diluent is added, the exhibition of twisted lamellae at 235°C suggests similar crystal propagation at what appears to be a faster rate on the crystallization rate curve. This seems unlikely since the melting temperature of nylon 6/6 does not change with the addition of the diluent. However, the glass transition temperature changes about 15°C over the composition range used, but the crystallization window between T_g and T_m is not affected significantly; i.e., ΔT changes from ~200°C to 180°C. Therefore, a shift to higher crystallization rates is not expected. *Figure 14* is a plot of the blend glass transition temperature as a function of PVP concentration. By studying the curve in the range of blend compositions that was used in this study, it can be seen that the glass transition is very sensitive to the addition of small amounts of diluent.

Higher concentrations of PVP in the blend increased the size of the spherulites somewhat, before plateauing at a 3% concentration of PVP, at which point additional diluent had no affect on the spherulitic growth. Furthermore, the banding in the spherulites seemed to become more regular as the PVP concentration was increased. This is most likely due to an increase in the number of PVP chains as the concentration is raised.

Figures 15 and 16 show micrographs of nylon 6/6

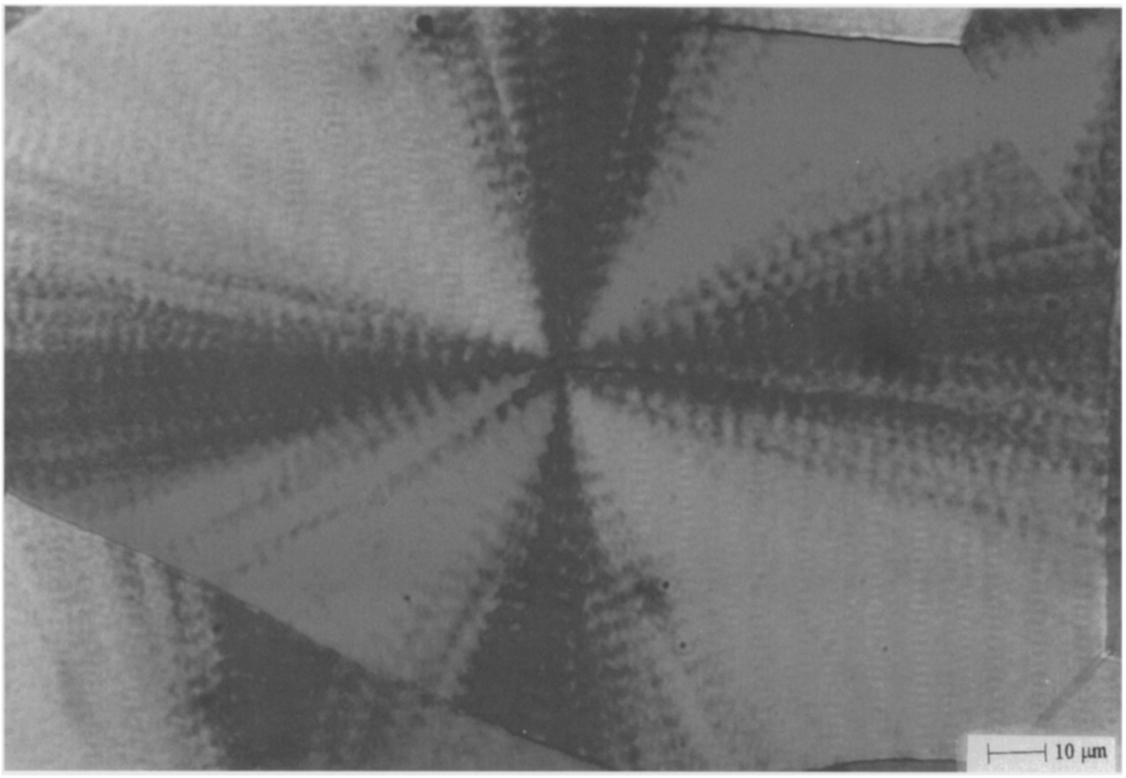

Figure 15 Nylon 6/6–1% PVP$_{(\text{high MW})}$ blend solution cast and crystallized at 235°C

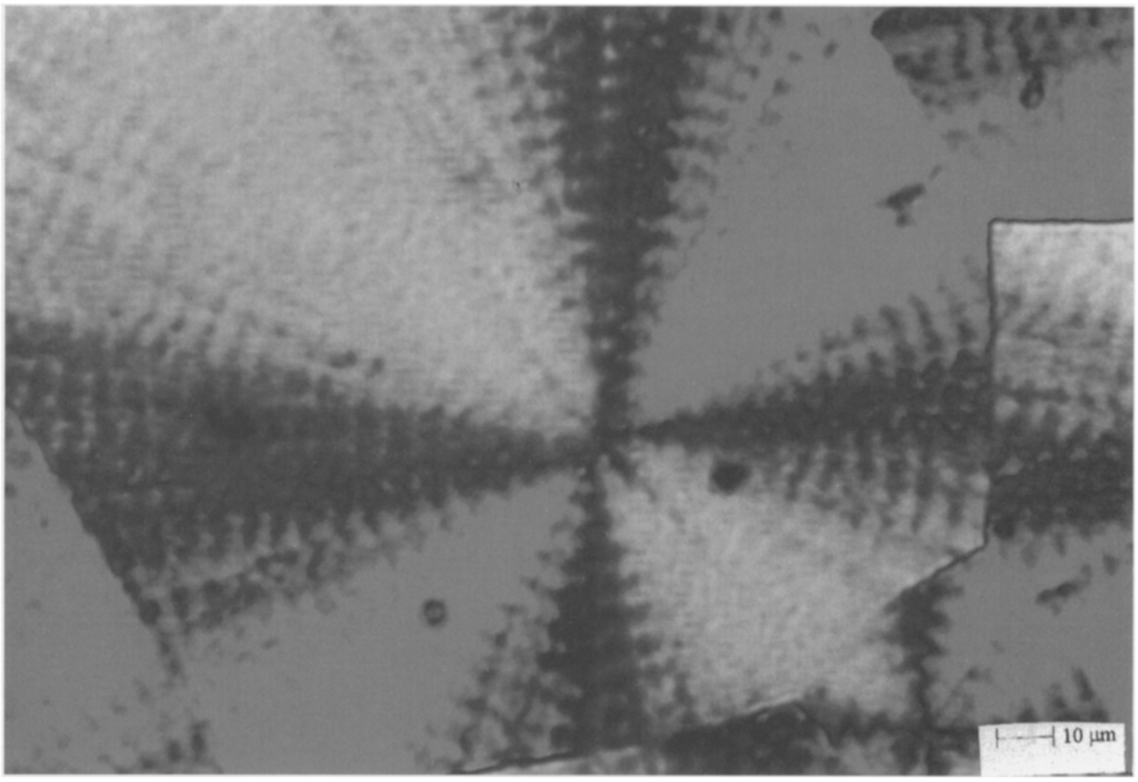

Figure 16 Nylon 6/6–3% PVP$_{(\text{high MW})}$ blend solution cast and crystallized at 235°C

blended with a high molecular weight PVP. A reduction in nucleation density is again seen, but not to the degree seen in the blends of nylon 6/6 and the low molecular weight PVP. This is due to the fact that since the concentrations are by weight, there are less high molecular weight PVP chains in the blend as opposed to low molecular weight chains in the previous samples. In other words, nucleation density dampening is a colligative property, and if the blend compositions were recalculated in mole fractions there would be sixty times more low molecular weight chains than high molecular weight chains at any given concentration. This reduction in the number of chains prevents the

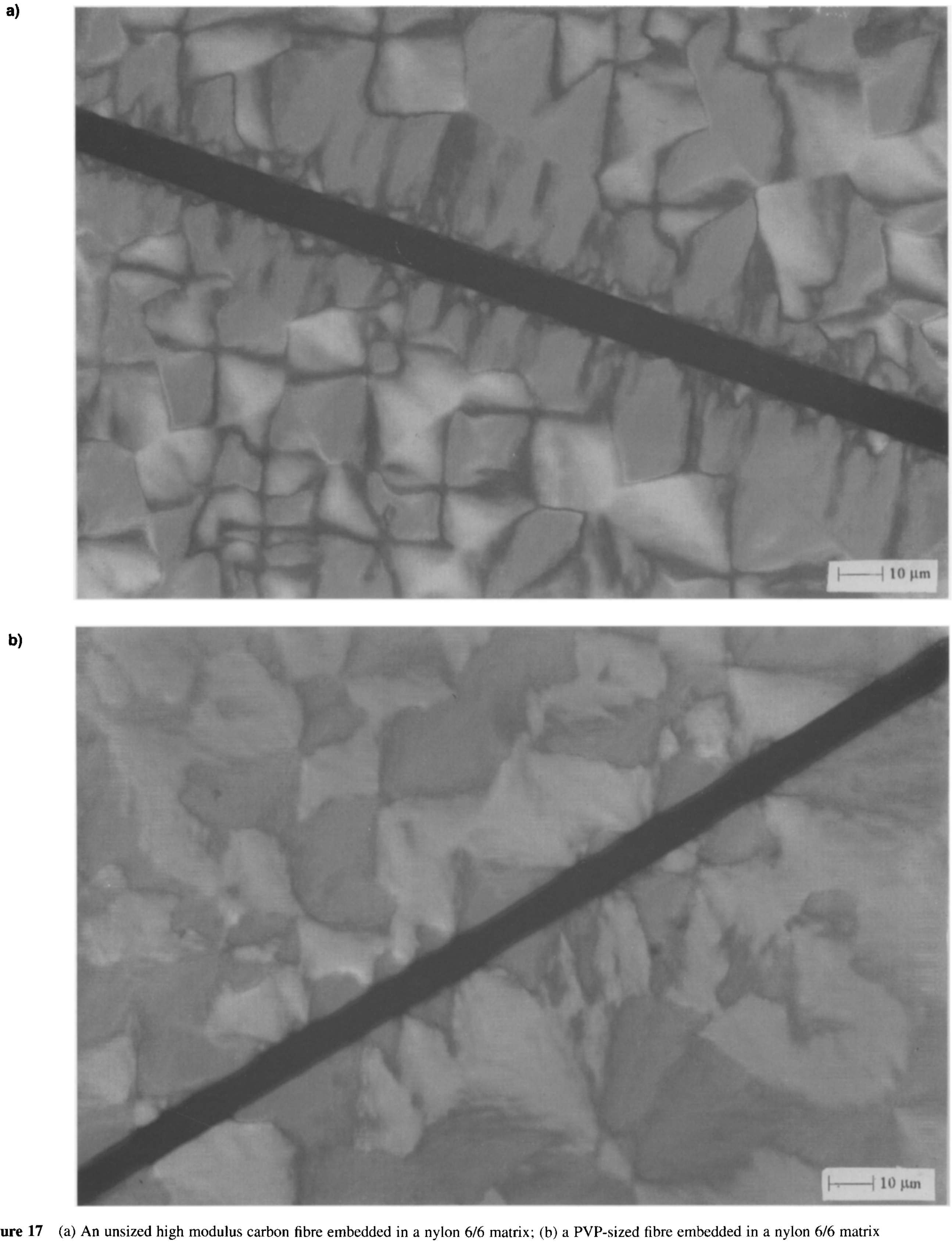

Figure 17 (a) An unsized high modulus carbon fibre embedded in a nylon 6/6 matrix; (b) a PVP-sized fibre embedded in a nylon 6/6 matrix

high molecular weight PVP from dampening nucleation as well as the low molecular weight PVP at a given concentration. Furthermore, the mobility of the high molecular weight PVP chains is much less than that of the low molecular weight chains, which can also account for the nucleation dampening difference between blends at a given concentration. This reduction in mobility can be coupled with the diffusion of the diluent in the blend. Several studies have determined the tracer diffusion coefficients, D^*, of melt blends of low and high molecular weight[13,14], and it was found that D^* decreased with increasing volume fraction of the diluent when the molecular weights of the two components exceeded the entanglement molecular weight of the blend. This result follows the reptation model for concentrated solutions. On the other hand, when one component had a molecular weight below the entanglement molecular weight of the blend, the D^* was virtually independent of volume fraction.

Although the molecular weight for entanglement has not been determined for the particular blend in this study, the low molecular weight diluent is most likely below this value, and therefore the diffusion of this species in the host polymer is much higher than the high molecular weight diluent and is not affected by concentration increases (increasing volume fractions). On the other hand, the high molecular weight PVP is almost certainly above the molecular weight for entanglement in the blend, and the diffusion is therefore much slower and concentration dependent.

CONCLUSIONS

Nylon 6/6 and its blends (1–7% PVP) were prepared by solution casting and melt blending. D.s.c., X-ray and hot stage microscopy studies were carried out to characterize the blends. From d.s.c. studies, several influences of the diluent on the triple melting of nylon 6/6 were found. For instance, the diluent did not remove the triple melting behaviour. Furthermore, addition of the diluent up to a 4% concentration enhanced the size of the third melting peak at 258°C relative to the other two (250°C and 243°C), and any increase in PVP above this amount produced a d.s.c. trace similar to that of pure nylon 6/6. Although the proportions of the three peaks changed, the positions of the peaks were not affected by the diluent. In addition, an increase in the glass transition temperature was observed with the addition of PVP. However, only a fifteen degree shift was found at the high PVP concentrations, i.e., 7% PVP, and this is not sufficient to cause a large shift in the crystallization rate. Nevertheless, an important finding for comparing d.s.c. and X-ray data was the fact that similar results were seen for both sample fabrication methods.

X-ray diffraction studies showed that the addition of the diluent did not affect the triclinic unit cell structure of pure nylon 6/6. There seemed to be no disordering of the lattice of nylon 6/6 on adding the diluent. Small angle X-ray studies showed that addition of PVP was very influential in changing the morphology of nylon 6/6. Furthermore, SAXS studies showed that PVP played an active role in associating with the non-crystallizable species during crystallization. The diluent caused an enhancement of lamellar organization in the spherulites and a modification of interlamellar spacings. The addition of 1% of the diluent caused the interlamellar spacings to decrease as compared to pure nylon 6/6. Therefore, the addition of PVP is associated with the amorphous layer reduction. Higher concentrations of the diluent did not seem to have any additional effect on the interlamellar spacings of the blend.

The most noticeable effects of the diluent on the structure of nylon 6/6 were seen in the optical studies. First, the structure of pure nylon 6/6 was observed. At temperatures below 250°C, the spherulites of nylon 6/6 show a simple extinction cross (Maltese cross) and no banding is evident at these temperatures. At temperatures above 250°C, the spherulites of nylon 6/6 additionally exhibit ringed extinction patterns (banding). The addition of the diluent results in a substantial reduction in frequency of nucleation of spherulites, such that the spherulites which form can grow to ten times the size of those found in pure nylon 6/6. Furthermore, the addition of the diluent caused nylon 6/6 to exhibit banding at temperatures where banding does not occur in pure nylon 6/6. In the range of blends tests, the nucleation density suppression plateaued at a 3% (by weight) diluent concentration level.

From this study, it can be seen that trace amounts of PVP have a dramatic effect on the morphology of nylon 6/6. Although the actual mechanism for these structural changes is not fully understood, the two following observations may play a role. Both the nylon 6/6 and PVP used in this study have a polar character, which could cause specific dipole interactions between the components and thus make the two polymers miscible. Alternatively, the adsorption of the diluent on the growth fronts and fold surfaces could be the cause of the effects described in this study.

As mentioned previously, this phenomenon, which reduces nucleation density, has been applied to semicrystalline polymer matrix composites. In these unmodified composites, an interphase is introduced due to the extremely high nucleation density on the reinforcing phase's surface, and the effect that the phenomenon described in this paper has on this region has been studied. Preliminary studies show that dramatic changes can be induced, and the micrographs in *Figure 17* exhibit this fact. *Figure 17a* shows an unsized high modulus carbon fibre embedded in a nylon 6/6 matrix, while *Figure 17b* shows a PVP sized fibre embedded in a nylon 6/6 matrix. Complete results from this study will follow in a subsequent paper.

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