

Morphology Studies of the Liquid-Induced Crystallization of Poly(ethylene Terephthalate): Effects of Polymer Blending, Nucleating Agents, and Molecular Weight

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Synopsis

The morphology associated with the liquid-induced crystallization of poly(ethylene terephthalate) (PET) blended either with poly(tetramethylene terephthalate) (PTMT), atactic polystyrene (APS), or polycarbonate of bisphenol A (PC) was studied, along with the effects of nucleating agents and polymer molecular weight on this type of crystallization in PET. It was found that melt-mixed blends of PET and either PTMT or PC led to an apparent well-mixed, two-component material in which some copolymer formation may be in evidence judging from the material superstructure. Blending PET with APS appeared to produce distinctly phase-separated materials in which PET could be crystallized and APS dissolved out of the structure as a result of treatment of the blend with certain types of liquid. The incorporation of nucleating agents into PET was shown to measurably influence the spherulitic character of the subsequently liquid-induced crystallized polymer. Finally, it was determined that liquid-induced crystallized PET samples with number-average molecular weights of 18,000 and 30,000 had identical characteristic morphology and apparent crystallization kinetics.

INTRODUCTION

The general morphological characteristics of initially amorphous, unoriented pure poly(ethylene terephthalate) (PET) that has undergone liquid-induced crystallization have been well studied in the past, and quite thorough summaries of this work exist.¹⁻³ Despite this, almost no studies exist detailing what effects variations in the initial state of the material may have on the resultant liquid-induced crystallization process. This is somewhat surprising in light of potential applications of this phenomenon, since very seldom in real situations does one deal solely with pure materials having a single given molecular weight distribution. Therefore, in this report we describe our attempts at characterizing the morphological effects of three different material variables on the liquid-induced crystallization of PET, viz., polymer blending, nucleating agents, and molecular weight.

For the case of PET blended with other polymers, no evidence exists in the literature concerning the behavior of such systems when undergoing crystallization induced by liquids. Nevertheless, the blending of two polymers is a very common way of engineering various performance characteristics into a given

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material. Clearly, this material performance is closely related to the degree of mixing between the two blended species. If the species are quite compatible with one another (as thermodynamically implied by a close match between their respective solubility parameters δ), a rather homogeneous blending can be accomplished in which little significant phase separation takes place between the two polymers. This homogenization is also greatly enhanced by specific interactions such as hydrogen bonding between the two polymers. On the other hand, if the polymers are incompatible, extensive segregation and phase separation can occur, in which case separate distinct domains of the two different materials would be in evidence.

In the present report, examples of both types of polymer blends will be discussed in reference to their morphology following liquid-induced crystallization. Specifically, blends (melt mixed) of PET with poly(tetramethylene terephthalate) (PTMT), atactic polystyrene (APS), and polycarbonate of bisphenol A (PC) will be investigated. The basis of selection of these systems was the desire to blend the liquid-induced crystallizable PET with (a) a chemically similar semicrystalline polymer that would be relatively impenetrable by the liquid (PTMT), (b) an amorphous, noncrystallizable, incompatible polymer (APS), and (c) a compatible polymer which could also undergo liquid-induced crystallization depending on the choice of liquid (PC). As will be noted in the results to be discussed, the realization of the ideal behavior of such systems was not achieved in all cases.

In addition to the blends study, some limited results regarding the effect of nucleating agents on the liquid-induced crystallization of PET will also be presented. Now the use of such agents for promoting the crystallization kinetics of polymer systems is quite common, particularly in the case of the thermal crystallization of PET.⁴⁻⁶ Such promotion is necessary because it is well known that PET crystallizes relatively slowly upon cooling from the melt and in fact can easily be quenched to below its T_g in the amorphous state. The use of nucleating agents has the specific effect of increasing the nucleating site density of the polymer, thereby increasing the frequency of nucleating and hence the number of growing crystalline entities. In this way, the overall crystallization kinetics of the polymer are enhanced, even though, strictly speaking, the actual crystal growth rates remain unchanged by the addition of the agents.⁷ Indeed, experimental studies of the effect of nucleating agents on the thermal crystallization kinetics of PET indicate that this increase of nucleating density alone is the mechanism operative for these systems,⁴ although other investigations maintain that the growth rate also appears to be enhanced by certain nucleating agents.⁵

The specific role played by the nucleating agent in providing nucleating sites for the polymer crystallization is a subject of considerable debate.⁸ Mechanisms proposed involve the nucleating agent having crystallite sizes closely comparable to the fold length of the polymer crystallite,⁹ a suspected particular chemical interaction between the nucleating agent surface and the polymer,^{4,8,10} and the presence of grooves or troughs on the surface of nucleating agent particles which enhance the degree of accommodation of the polymer molecule at the agent's surface and promote chain alignment.⁷ Also, it has been generally found that good nucleating agents are typically fine dispersions of small crystals that are insoluble in the polymer.⁸

Now, it is quite clear from past studies of the crystallization kinetics of liquid-induced crystallized PET^{3,11} that crystallization in these systems is extremely rapid even without the addition of nucleating agents. Therefore, further enhancement of the kinetics appears unnecessary for these systems. However, as implied earlier, the addition of effective nucleating agents results in the growth of smaller crystalline entities in the material, which in the case of liquid-induced crystallized PET would mean smaller-sized spherulites for a given supercooling. Since liquid-induced crystallized PET is quite turbid,^{3,12} due in part to the characteristic spherulite sizes being on the order of the wavelength of light, reducing the size of the crystalline entities may improve the transparency of these systems.¹³ It should also be noted that a high degree of surface cavitation or roughness and internal voids also contribute to the material's opacity. More importantly, reducing the size of the crystalline bodies may also reduce the noted brittleness of this material when thoroughly dried,¹⁴ a common trait of spherulitic polymers.¹⁵ To this end, the effect on the resultant morphology of incorporating nucleating agents in initially amorphous, unoriented PET undergoing liquid-induced crystallization will be discussed. Implications of this morphology regarding the improved transparency and suspected enhancement of mechanical behavior by the incorporation of such agents will be considered.

Finally, a very brief study concerning the effect of the molecular weight of PET undergoing liquid-induced crystallization will also be discussed. It is well known from observations regarding the thermal crystallization of a number of polymers that spherulite growth rates are a function of the molecular weight of the polymer,¹⁶ with the growth rate increasing with decreasing molecular weight. Further, it has also been noted that the average spherulite sizes of thermally crystallized poly(tetramethyl-*p*-silphenylene)siloxane¹⁷ and PET⁴ tend to decrease with increasing polymer molecular weight at a given crystallization temperature. In the PET case, however, this apparent molecular weight effect was suspected to be due to coincidental differences arising in sample fabrication rather than directly to molecular weight. In the present study, the liquid-induced crystallization behavior of two different molecular weight samples of PET will be reported with an eye toward elucidating any molecular weight dependence of this type of polymer crystallization.

EXPERIMENTAL

Materials

For the blending studies, PET/PTMT blends were prepared from PET pellets supplied by Allied Chemical Corporation and commercial-grade PTMT ("Tenite Polyterephthalate") formula 6PRO pellets obtained from Eastman Chemical Product, Inc. (Tennessee). The PET was stated to be pure. PET/APS and PET/PC blends were prepared from PET pellets supplied by E. I. du Pont de Nemours and Company, atactic polystyrene pellets (commercial grade) supplied by Monsanto Company (Springfield, Mass.), and Lexan polycarbonate resin (commercial grade) supplied by General Electric Company (Pittsfield, Mass.). The PET was again stated to be pure.

For the nucleating agent study, initially amorphous, unoriented quench-rolled pure PET films (6 mils, or 1.52×10^{-2} cm, thick) and PET films containing an

unidentified nucleating agent of known efficiency were obtained through the E. I. du Pont de Nemours and Company.* Their initial amorphous and unoriented nature was verified through wide-angle x-ray scattering (WAXS) and birefringence techniques. Also, the same PET pellets used to make up the PET/APS and PET/PC blends were blended with chemically pure sodium benzoate, a known nucleating agent for PET with high efficiency.

For the molecular weight study, initially amorphous, unoriented quench-rolled PET films with \bar{M}_n values of approximately 18,000 and 30,000 were again obtained through du Pont. Their amorphous and unoriented nature was again verified by WAXS and birefringence measurements.

The liquids used in all studies were reagent-grade dioxane, methylene chloride, acetone, nitromethane, and benzene. Their ability to readily induce crystallization in PET in the vicinity of room temperature has been well documented.^{3,18-20}

Apparatus and Procedures

All morphological investigations in this report were carried out by means of several rheoptical techniques, viz., optical microscopy (OM), small-angle light scattering (SALS), wide-angle x-ray scattering (WAXS), and scanning electron microscopy (SEM). The OM studies were carried out on a Zeiss polarizing optical microscope, and the SALS studies were carried out using a Spectra-Physics Model 115 He-Ne continuous gas laser as the light source ($\lambda = 6328 \text{ \AA}$) with the patterns recorded photographically. WAXS studies were carried out using a Philips x-ray diffraction unit with a Cu-Ni radiation source and pinhole collimation. Photographs were obtained of the patterns using Statton vacuum cameras (Warhus Co.). SEM studies were conducted using an ISI Super-Mini SEM, with samples coated with a thin layer (100 \AA) of gold-palladium to prevent charging, as is customary.

The PET blending studies were carried out in the following manner. Melt-mixed blends (coextruded) of PET/PTMT (75/25, 50/50, and 25/75 weight ratios) were retained from previous studies in this laboratory.²¹ Melt-mixed blends of PET/APS and PET/PC (weight ratios of 90/10 and 75/25 in both cases) were prepared by coextrusion of the PET/APS and PET/PC in a Mini-Max elastic melt extruder (Custom Scientific Corp.) at a temperature of approximately 270°C. This instrument is well known for its thoroughness of mixing with short material residence times.^{22,23} To ensure randomization and thorough mixing, the appropriate amounts of PET/APS and PET/PC pellets were physically well mixed prior to their introduction to the extruder, and following the first extrusion were pelletized and reextruded. All materials were stored at 80°C under vacuum for several days prior to extrusion to remove moisture and thus avoid hydrolysis in the melt state.

Following the two extrusions, all PET/PTMT, PET/APS, and PET/PC blends were again pelletized, stored for several days under vacuum at 80°C, and then compression molded into film form on a Preco Hydraulic Press (Los Angeles,

* Since this nucleating agent is unstated, any results regarding films containing this agent clearly suffer from a lack of specificity. However, results obtained with these films are deemed worthy of presentation as a general demonstration of nucleating agent capacity in the phenomenon of liquid-induced crystallization.

Calif.). Approximately 2 g of pellets were used per film, and the compression molding was performed at approximately 270°C to ensure thorough melting. Immediately following removal from the press, the films were quenched in an ice bath to avoid crystallization of the PET. Compression-molded films of pure PET, APS, and PC were also made under these same conditions.

The compression-molded films were then immersed in the previously cited liquids for various lengths of time at specified temperatures. Upon removal from the liquids, the samples were air dried and then investigated via OM, SALS, WAXS, and SEM. Selected cross sections (cryogenically fractured surfaces) of some samples were also investigated via SEM.

The weight loss due to the solvation of APS in the PET/APS blends was also determined after various immersion times in the liquids by noting the weight difference between samples before immersion and following immersion and drying for several days under vacuum at 120°C. Blanks and pure PET films undergoing similar liquid treatments were subjected to the same thermal cycle in order to correct for possible moisture removal and weight loss due to PET solvation.

Selected samples were also investigated by differential scanning calorimetry (DSC) using a du Pont 990 thermoanalyzer. DSC runs were performed on approximately 6 to 8-mg samples in a nitrogen atmosphere at a heating rate of 20°C/min.

For the nucleating agent study, pure PET films and PET containing 1% and 3% by weight sodium benzoate were prepared by melt mixing followed by compression molding in a manner exactly analogous to that used for the PET blend preparations. Similar storage conditions under vacuum were followed to prevent moisture buildup in the materials. After preparation, these films and the du Pont films with and without a nucleating agent were immersed for various lengths of time at specified temperatures in either acetone, dioxane, methylene chloride, or nitromethane liquid. Upon removal and air drying, the morphology of the samples was investigated via OM, SALS, WAXS, and SEM using the previously stated conditions and apparatus.

For the molecular weight study, the PET samples with \bar{M}_n values of approximately 18,000 and 30,000 were subjected to identical immersions in either dioxane, methylene chloride, nitromethane, or acetone liquid for various lengths of time at a series of temperatures in the vicinity of room temperature. Following removal from the liquids and air drying, their morphology was investigated by WAXS, SALS, and SEM.

RESULTS AND DISCUSSION

PET/PTMT Blends

The characterization of melt-mixed blends of PET/PTMT has been treated elsewhere.²¹ Specifically, it has been determined that following the coextrusion of these two polymers, rather extensive mixing is achieved, which may be expected on the basis of their similar chemical structure and total solubility parameter values ($\delta = 10.26$ for PTMT and $\delta = 10.7$ for PET^{21,24}). However, reheating these blends to temperatures of the order of 270° to 280°C results in some transesterification of the two components in the material yielding at first a block

copolymer which may in turn be transformed into a completely random copolymer if held for very long times at the reaction conditions. Thus, in the compression molding of the films under consideration in this report, some transesterification may take place, producing a limited amount of block copolymer material in the sample. However, the duration of time the original material was held at temperatures near 270°C during the molding cycle used was only of the order of 1 to 2 min. Therefore, it seems that some transesterification is probable for these systems but most likely is not extensive.

Due to the extremely rapid crystallization kinetics of PTMT, it is most difficult to quench this polymer from the melt to the glassy state without extensive crystallization of the polymer taking place. Indeed, under the molding procedure used in this study to fabricate the samples, pure PTMT undergoes quite substantial crystallization, as can be noted from its WAXS pattern. Also, PET, having much slower crystallization kinetics in comparison, is readily obtainable in the amorphous state upon quenching from the melt.

One would expect that since the PTMT crystallizes quite readily, it would be in the semicrystalline state in the blends as well, provided only limited transesterification took place during the compression molding of the films. Also, the PET should remain amorphous due to its slower crystallization rate provided that the suspected PTMT crystallites do not act as nucleation sites promoting PET crystallization during sample fabrication. The WAXS patterns of the 75/25, 50/50, and 25/75 PET/PTMT blends, however, provide little insight into this effect since they consist essentially of an amorphous halo. Clearly, the most intense reflections due to crystalline PTMT occur at the same radial angles as does the amorphous halo, and it may well be, therefore, that the halo masks these reflections in the pattern.

The surface morphologies of these films are perhaps more indicative of the presence of initially semicrystalline PTMT in the blends. For example, the SEMs of Figure 1 show the surfaces of PET/PTMT blends after they have been immersed in methylene chloride liquid for 10 min at 24°C. One can note that the degree of surface roughness is reduced substantially with increasing PTMT concentration in the blend. This effect may well be due to semicrystalline PTMT, relatively impenetrable to the liquid due to its crystallinity interspersed in the amorphous PET. Also, one can note from Figure 1 that the spherulites themselves appear to decrease in size with increasing PTMT concentration, possibly reflecting the reduced availability of PET to participate in superstructure formation with increasing levels of well-mixed PTMT in the blends.

SALS confirms that indeed the structures seen via SEM are optically anisotropic spherulites, and WAXS demonstrates that extensive crystallization is induced in these materials through the action of methylene chloride. Further, the WAXS intensities appear to increase measurably with increasing PTMT concentration in the blends, implying that as the amount of PTMT is increased, so too does its contribution to the overall crystallinity level of the entire sample. Thus, it appears that in these blends, the PET undergoes liquid-induced crystallization and the PTMT undergoes thermal crystallization upon quenching from the melt.

The behavior of the PET/PTMT blends in methylene chloride liquid is totally representative of the behavior of these blends in dioxane, nitromethane, and acetone liquid at 24°C. In short, for all the liquids investigated, increasing levels

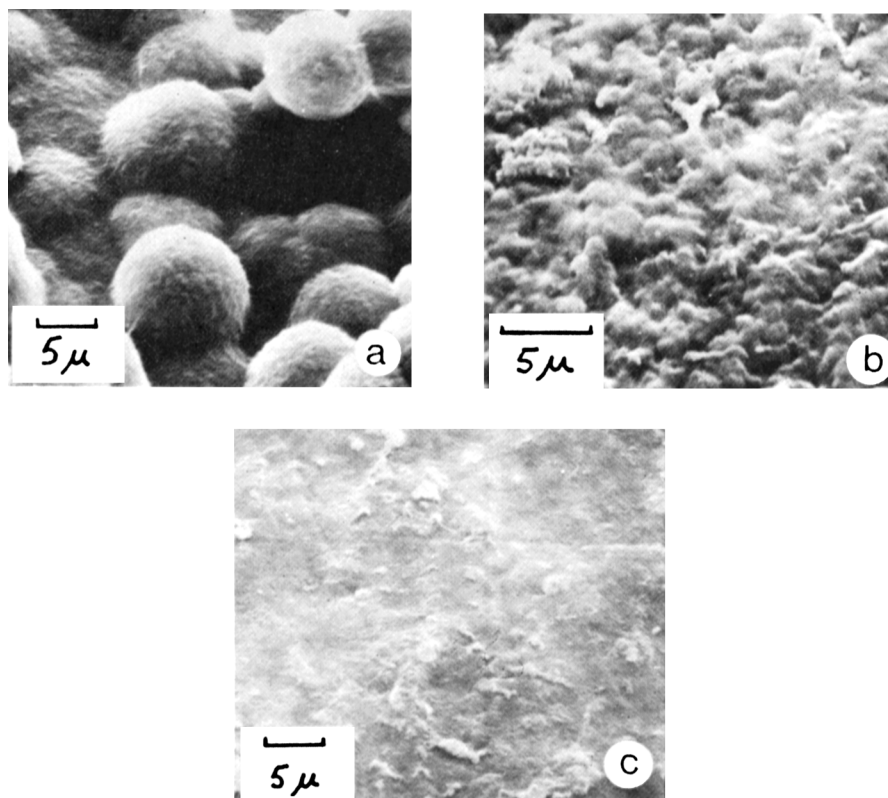


Fig. 1. Representative SEMs of the surfaces of PET/PTMT compression-molded films immersed in methylene chloride liquid for 10 min at 24°C: (a) 100% PET; (b) 50/50 PET/PTMT; (c) 100% PTMT.

of PTMT in the PET/PTMT blends suppress the amount of surface roughness induced through the action of the liquids. Characteristic spherulite texture is observed in all the blends containing PET, although the size of the spherulites appears to decrease somewhat with increasing PTMT concentration. Finally, based on visual inspection of the WAXS patterns, the apparent level of crystallinity in the blends following quenching and liquid treatments seems to increase commensurately with increasing PTMT concentrations.

PET/APS Blends

PET and APS are relatively incompatible with one another, as can be noted immediately by comparing their respective total solubility parameters ($\delta = 10.7$ for PET and $\delta \cong 9.0$ for APS²⁴). One would therefore expect distinct phase separation to occur between these two polymers upon blending, and in fact this has been observed directly via SEM of the fracture surfaces of the 90/10 and 75/25 PET/APS blends studied in this report. Figure 2 shows such behavior for the 90/10 blends, with the 75/25 samples also showing distinct phase separation. One can note the large spherical and ellipsoidal APS domains interspersed in the PET matrix in this micrograph. DSC scans also point up the distinct phase separation, as shown in Figure 3. Clearly, two glass transitions are in evidence in scans

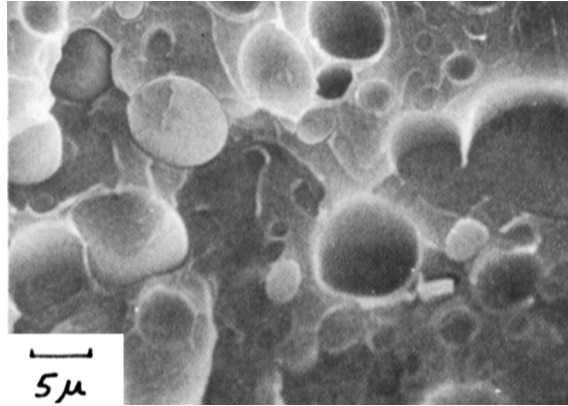


Fig. 2. Representative SEM of the fracture surface of a 90/10 PET/APS compression-molded film.

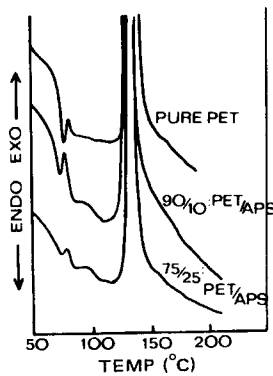


Fig. 3. DSC scans of pure PET and 90/10 and 75/25 PET/APS compression-molded films.

for the blended material: the endotherm at approximately 74°C due to PET and the endotherm discontinuity centered at approximately 100°C due to the APS. Glass transitions for the pure materials occur at approximately 70–75°C for PET and 100°C for APS.

Of the four liquids used in this report for treatment of the PET/APS blends, methylene chloride, dioxane, and benzene readily dissolved pure APS within 1 hr at 24°C, while nitromethane neither dissolved nor even swelled the pure APS even after several days of immersion at 24°C. On the other hand, as aforementioned, all four of these liquids readily induce the spontaneous crystallization of pure PET at 24°C.

To determine whether solvation of the APS and crystallization of the PET occur in the blended materials as well, Figure 4 shows representative SEMs of the fracture surfaces (after crystallization) of 90/10 PET/APS blends exposed to benzene, dioxane, and nitromethane at 24°C for 1 hr. It can clearly be noted in these micrographs that the APS domains have largely disappeared from the film matrix after the dioxane and benzene treatments, leaving behind many large holes or voids. Some of the larger holes are seen to contain some residual APS which apparently has not yet been completely solvated by the liquids. Similar behavior, although not shown here, can be observed for methylene chloride

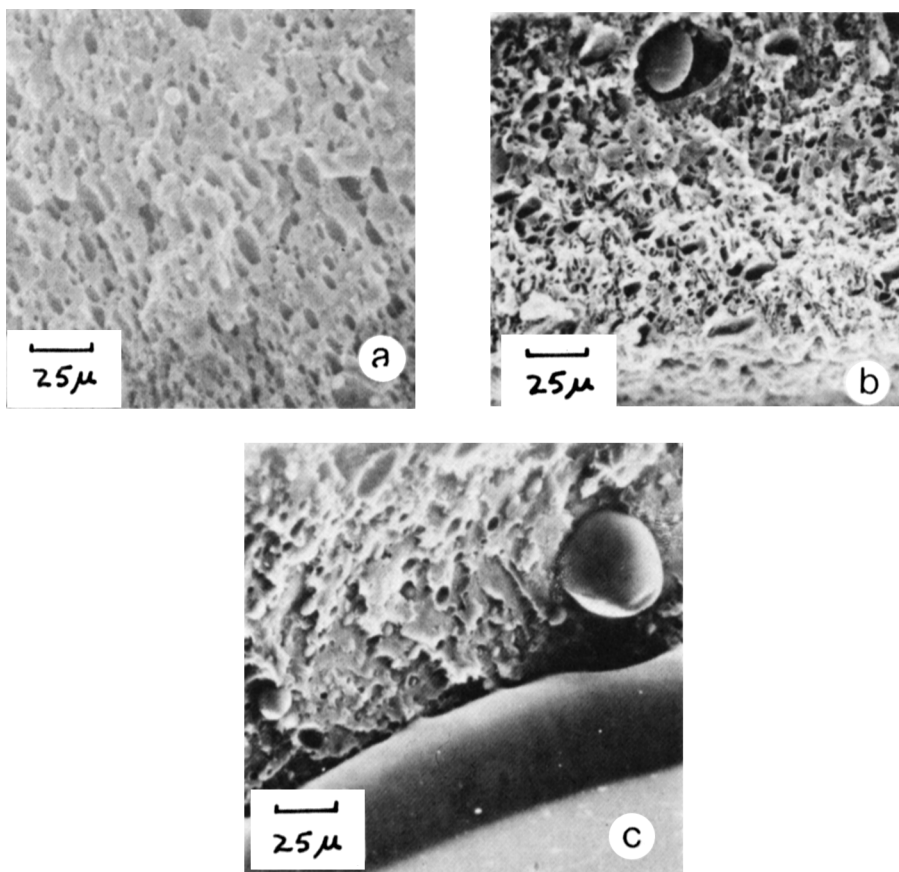


Fig. 4. Representative SEMs of the fracture surfaces of 90/10 PET/APS compression-molded films immersed for 1 hr at 24°C in: (a) dioxane liquid; (b) benzene liquid; (c) nitromethane liquid.

treatments of these blends. In the nitromethane case, on the other hand, these voided regions are not as prevalent, apparently because the nitromethane is not a solvent for APS and thus does not dissolve out this material. Other studies²⁵ indicate that 1-hr immersion times are more than sufficient to ensure complete penetration by these liquids of pure PET films of the same thickness [(5–8) $\times 10^{-3}$ cm].

Surface morphologies of these 90/10 PET/APS blends also imply solvation of the APS in dioxane, benzene, and methylene chloride, along with spherulitic crystallization induced in the PET by these liquids and nitromethane. Figure 5 shows representative SEMs of the 90/10 blends exposed to dioxane and nitromethane at 24°C for 1 hr. Spherulitic texture can be noted for both cases, and “holes” can also be seen on the surfaces for the dioxane treatment, again apparently due to the APS solvation. The spherulitic texture noted on the surface extends into the bulk of the film as well, as can be observed in Figure 5(b), which shows a magnified view of one of the “holes” on the surface of the 90/10 blend exposed to dioxane liquid. SALS studies confirm that these materials are in fact comprised of optically anisotropic spherulites.

In order to confirm that the APS is solvated and thus removed from the films

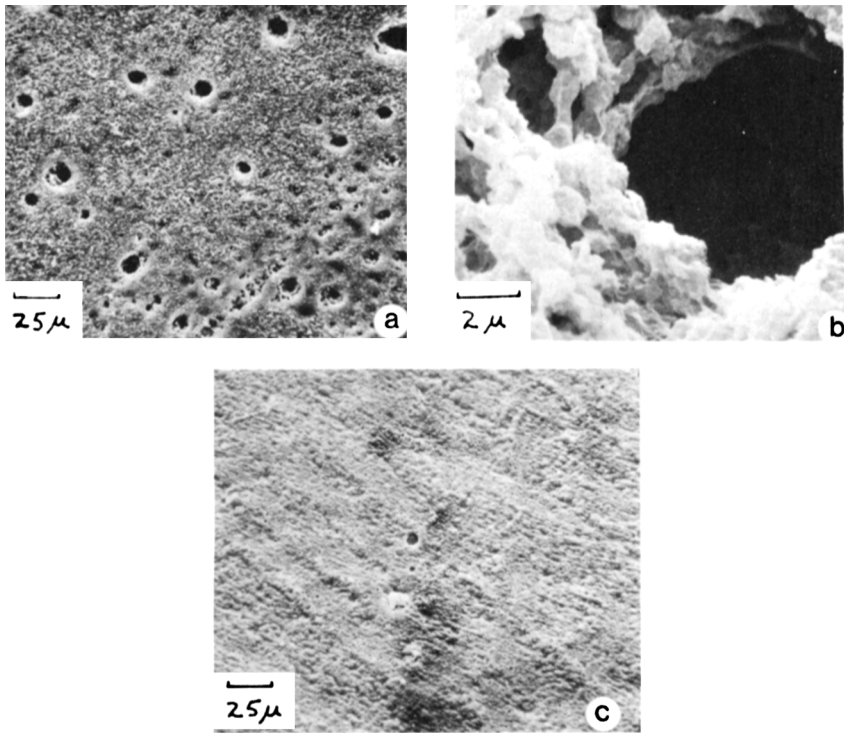


Fig. 5. Representative SEMs of the surfaces of 90/10 PET/APS compression-molded films immersed for 1 hr at 24°C in: (a) and (b) dioxane liquid; (c) nitromethane liquid.

in benzene, dioxane, and methylene chloride and not in nitromethane, weight loss studies were performed on the 90/10 blends. The results are tabulated in Table I. After the weight loss due to possible dissolution of low molecular weight PET is corrected for by exposing pure PET films to the same liquid treatments, the results clearly indicate that the APS is dissolved out of the films by the good solvents and is left relatively unperturbed by the nitromethane.

It can also be seen that the weight loss attributed to APS in the dioxane treatments is significantly greater than the nominal weight percent of APS initially in these films! Since the results listed are average values from several independent measurements, the hypothesis that the measurements were made on samples containing anomalously high initial amounts of APS can probably be discounted. It may therefore be that more low molecular weight PET is dissolved out of these films than may be observed and thus corrected for in the pure PET films. It may be recalled that these blends were exposed to temperatures of the order of 270°C several times during their fabrication. Thus, these thermal treatments may result in the loss formation of a higher content of low molecular weight PET material than has been observed during previous weight loss studies of pure PET,³ in which case the PET was not exposed to such repeated high-temperature thermal cycles. Perhaps the holes induced in the film surface and matrix through APS dissolution provide channels through which the PET dissolved in the bulk of the film can be removed. Such large holes are not observable in pure PET films treated with these liquids. The existence of such holes and channels also helps to explain the somewhat surprising facility

TABLE I
Weight Loss of APS in PET/APS Blends After Various Liquid Treatments at 24°C

PET/APS blend, weight ratio	Liquid	Immersion time, min	Wt. loss, APS, %
90/10	benzene	60	12.0
90/10	methylene chloride	1	5.0
90/10	methylene chloride	10	9.0
90/10	dioxane	1	2.5
90/10	dioxane	10	16.0
90/10	dioxane	60	14.0
90/10	nitromethane	1	—
90/10	nitromethane	10	—
90/10	nitromethane	60	0.5
75/25	benzene	60	25.5
75/25	methylene chloride	1	5.0
75/25	methylene chloride	10	11.0
75/25	dioxane	1	4.0
75/25	dioxane	10	14.0
75/25	dioxane	60	22.0
75/25	nitromethane	1	—
75/25	nitromethane	10	—
75/25	nitromethane	60	0.5

with which the APS is removed from these materials. Simple diffusion of APS through the bulk polymer would occur orders of magnitude more slowly than the rates at which APS apparently leaves the samples in these studies.

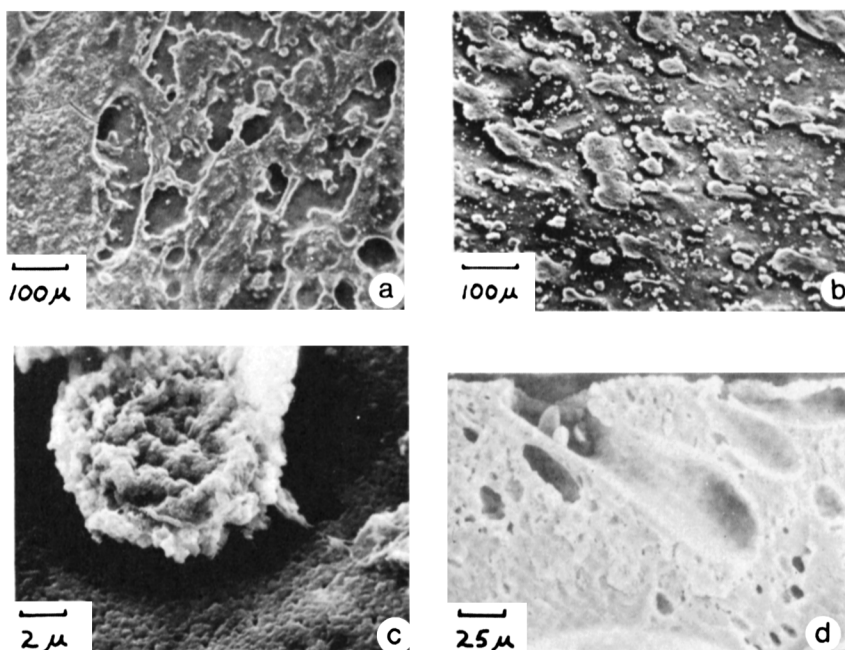


Fig. 6. Representative SEMs of the surfaces of 75/25 PET/APS compression-molded films immersed at 24°C in dioxane liquid for: (a) 1 min; (b) and (c) 60 min; (d) representative SEM of the fracture surface of sample shown in Fig. 6(b).

Similar effects of APS dissolution and PET crystallization can also be observed in the 75/25 PET/APS blends. In Table I are listed the weight losses due to APS in the 75/25 blends. Again it is apparent that nitromethane causes little solvation of the APS, whereas benzene, dioxane and methylene chloride cause extensive removal of this component from the blend.

The surface morphologies of these blends following liquid treatment are decidedly different from those observed in the 90/10 blends, however. Figure 6 shows representative scanning electron micrographs of the surfaces of the 75/25 blends after treatment in dioxane for varying lengths of time at 24°C. From these micrographs it seems that a layer of material on these surfaces is increasingly removed with increasing immersion times in these liquids, leaving behind small spheres and "islands" of apparently spherulitic PET material. The texture of these regions matches the texture of the underlying material, as can be noted by the highly magnified view of Figure 6(c). Fracture surfaces of these samples [an example is shown in Fig. 6(d)] also reveal that APS is again apparently removed from the bulk of the film as noted by the extensive interior voids in the sample.

The character of these surfaces thus seems to imply that the APS may be preferentially concentrated at the film surfaces. Although APS is the minor component in these blends, the surface layers behave as if the PET is the minor component dispersed in domains throughout an APS matrix. Treatments of the 75/25 blends in nitromethane bring out this effect more clearly. Figure 7 shows representative SEMs of the surface of a 75/25 blend before and after exposure to nitromethane liquid for 1 hr at 24°C. The texture here seems like a "complementary image" of the texture noted for the blends after long exposures

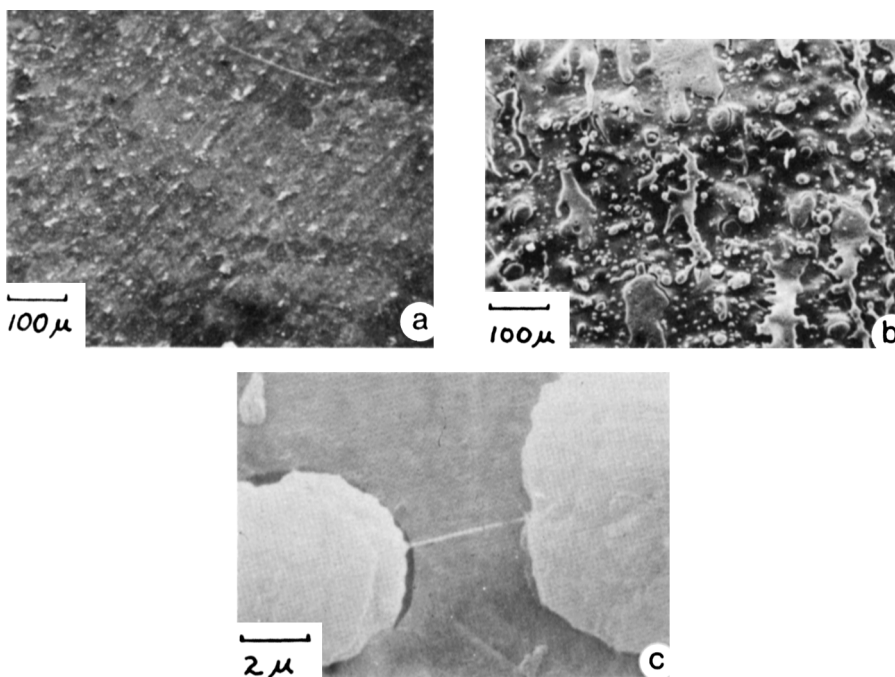


Fig. 7. Representative SEMs of the surfaces of 75/25 PET/APS compression-molded films: (a) with no liquid immersion; (b) and (c) immersed in nitromethane liquid 60 min at 24°C.

to dioxane [Fig. 6(b)]. In the nitromethane case, spherulitic domains, noted in the close-up of Figure 7(c), appear imbedded in an APS matrix that has been left relatively unaffected by the liquid treatment since nitromethane is not a solvent for APS. Again, SALS verifies that spherulitic crystallization is induced in the PET of these 75/25 blends by all the liquids studied.

The appearance of what seems to be an APS-rich surface layer in these 75/25 blends is at first surprising. A possible explanation may perhaps be found upon consideration of the fabrication procedures for these compression-molded films. Specifically, the molding procedure followed in this study involved the initial melting of pelletized, twice coextruded extrudate of the PET/APS blend. After melting, the material was then pressed out by means of a ram into film form. Clearly, it can be noted that this applied pressure must induce some shearing to the melt blend as it is transformed by some limited flow into a flat film of uniform thickness.

Now, from the most elementary considerations of fluid mechanics, it is well known that the highest shear would occur at the walls during such a flow as just described. Furthermore, in two-component, relatively immiscible systems, the component of lower viscosity is less able to resist the shearing and hence will tend to congregate preferentially in the vicinity of highest shear. Two-component polymer melts in which the two polymers are relatively incompatible tend to show such behavior when extruded and injection molded.²⁶

In the PET/APS blends, the two polymers are also incompatible, and APS has a lower viscosity at the molding temperatures than does the PET. Thus, one may expect that the APS may tend to accumulate at the surfaces of the compression-molded films since these surfaces are clearly under highest shear when the ram forces the melt into a uniform film. Due to the relatively short period of time that the blends are exposed to the pressure and flow is induced, this stratification effect is not complete, and much APS remains distributed throughout the bulk of the film. Also, this stratification effect is not manifest in the 90/10 PET/APS blends simply because so little APS is in the films initially.

PET/PC Blends

Melt-mixed blends of PET and PC have recently received some limited attention in the literature,²⁷ where it was shown that PET/PC blends containing PET as the major component (>50% by weight) appeared to display complete mixing in the amorphous phase as evidenced by dynamic mechanical property measurements. This result may be somewhat surprising based on the difference between the respective total solubility parameters of the two polymers, viz., $\delta = 10.7$ for PET and $\delta = 9.5$ for PC.^{24,28} Since these samples were mixed at temperatures on the order of 230–290°C, some transesterification may have taken place between the two polymers since PET and possibly PC as well are susceptible to this reaction at the higher mixing temperatures used.^{21,29} As a result of this interchange reaction, some limited amount of PET/PC copolymer may have been formed. Such a process may therefore contribute to the suspected complete mixing of the two polymers, just as has been demonstrated for the case of PET/PTMT melt-mixed blends.²¹

As stated previously, the PET/PC blends investigated in this report were also

melt mixed, in this case by coextrusion followed by compression molding into film form. Both procedures were carried out in the vicinity of 270°C, so the possibility of some limited copolymer formation in these blends as well cannot be discounted.

Bearing this possibility in mind, DSC runs of the PET/PC blends here indicate that thorough mixing is apparently achieved for these samples. Figure 8 shows the scan for pure PET, pure PC, and 90/10 and 75/25 PET/PC blends. The crystallization exotherm of pure PET, occurring at approximately 140°C, seems to be shifted upward in the blends to a temperature of approximately 155°C. This temperature is very near the glass transition of the pure PC sample (about 160°C) and seems to imply that the PC must achieve sufficient segmental mobility in order for the PET to crystallize. Based on this evidence, then, it thus appears that the PET and PC are well mixed, for if the two polymers formed extensive separate phases, the PET crystallization exotherms should occur quite independently of the segregated PC. The shift in the exotherm temperature implies that this is not the case. Based on this argument, however, it is somewhat difficult to account for the fact that the glass transitions of PET (denoted by the endotherms at approximately 75°C in the pure PET and the 90/10 and 75/25 PET/PC blends) seem unaffected by the presence of the PC in the blends. One would expect that, with thorough mixing between the two polymers, the PET glass transition would be shifted to higher temperatures with the addition of PC, since this polymer has a T_g in the vicinity of 150°C.

Scanning electron microscopy of the fracture surfaces of these PET/PC blends also reveals that no distinct phase separation between these two polymers occurs. An example is shown in Figure 9, which is a representative SEM of the fracture surface of a 90/10 PET/PC blend. The voids seen in this micrograph are artifacts due to air trapped within the film during molding.

Exposing these blends to liquids such as nitromethane, benzene, and acetone also tends to demonstrate the thoroughness of mixing between the two components. While pure PET and pure PC are both crystallized readily in these liquids in the vicinity of room temperature, the characteristic spherulitic morphology induced in the two cases is extremely different. For example, in the case of acetone liquid treatments at 24°C, pure PC crystallizes into approximately 6-micron-diameter spherulites, which themselves appear rather coarse and composed of distinctly fibrillar material. The film surface is also quite roughened.

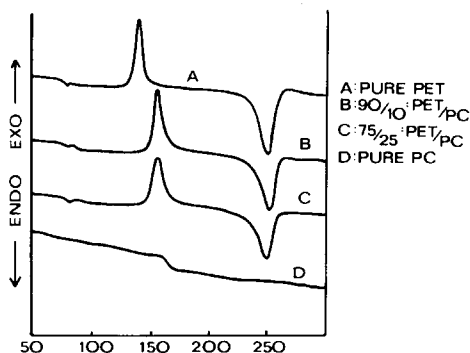


Fig. 8. DSC scans of pure PET, pure PC, and 90/10 and 75/25 PET/PC compression-molded film.

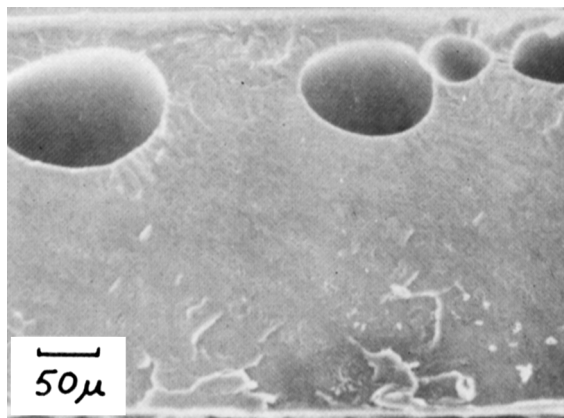


Fig. 9. Representative SEM of the fracture surface of a 90/10 PET/PC compression-molded film.

Pure PET, on the other hand, crystallizes under these same conditions into rather smooth-surfaced spherulites of about 2–3 microns in diameter, with very little surface roughness. Typical SEMs of such behavior, along with the corresponding SALS patterns, are shown in Figure 10. When the 90/10 and 75/25 PET/PC blends are exposed to the same liquid treatment, however, the resultant spherulitic texture induced in these blends appears to be the same as that induced in pure PET both via SEM and SALS.

Nucleating Agents

As mentioned in the introduction, relative spherulite size appears to be a good index of the nucleating capacity of the agent. On this basis, the results in this section indicate that nucleating agents can play a definite role in the promotion of crystallization in liquid-induced crystallized PET.

Specifically, considering first the case of the du Pont PET films both containing and free of a nucleating agent, the SEMs of Figure 11 demonstrate that the films containing the agent definitely have spherulites of smaller diameter than do the pure PET films when crystallized in various liquids at 24°C. The greatest size differential appears to occur in the nitromethane and acetone liquid cases, where it can be noted that the spherulites in the agent-containing films are smaller by a factor of approximately 8 than those seen in the pure films. In the dioxane and methylene chloride cases, the spherulite size differential between the agent-containing and pure PET films is about one half. Thus, while pure PET films show spherulite sizes of from 2 to 4 microns in diameter following crystallization in these liquids, the PET films containing the nucleating agents are composed of spherulites of from 0.5 to 1 micron in diameter following this crystallization.

In order to verify that the spherulite sizes observable via SEM on the sample surface are truly representative of the structure in the bulk of the film, SALS patterns were also taken of the materials just discussed. While patterns characteristic of spherulites consistent in size with those measured by electron microscopy were obtained for the pure PET crystallized in the four liquids (see the example in Fig. 12), no patterns were distinguishable for the film containing the

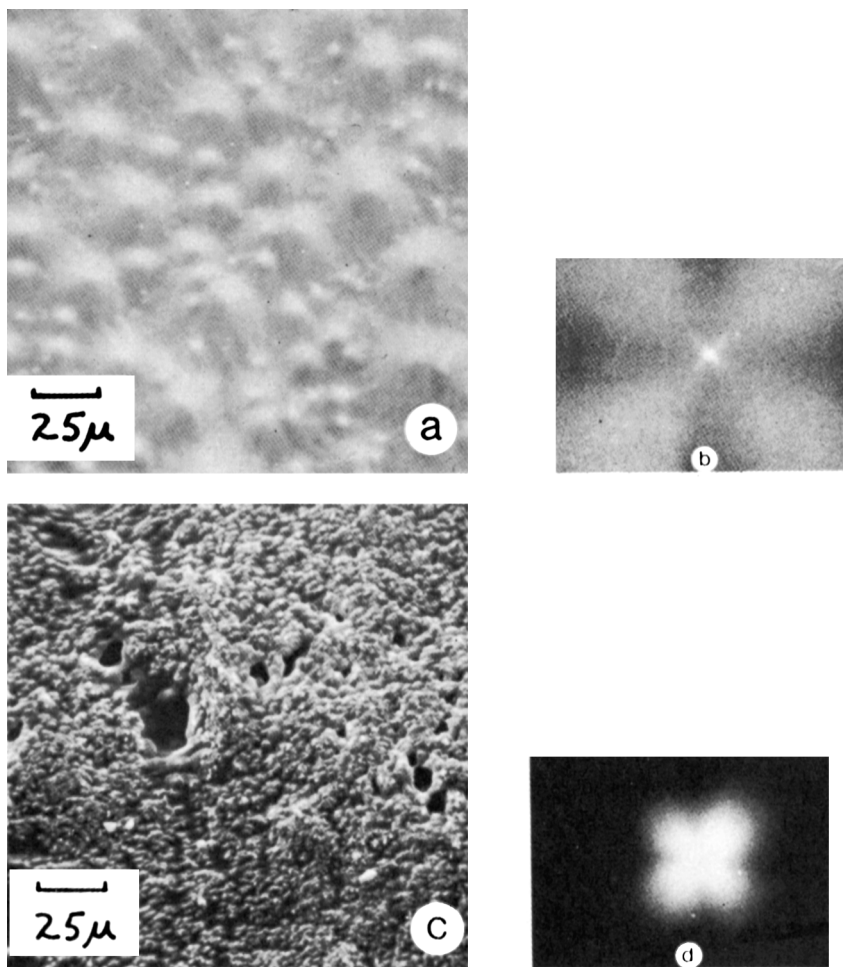


Fig. 10. (a) Representative SEM and (b) representative H_v SALS pattern of a pure PET film immersed in acetone liquid 10 min at 24°C; and (c) representative SEM and (d) representative H_v SALS pattern of a pure PC film immersed in acetone liquid 10 min at 24°C.

agents. Since these films definitely show spherulitic texture via SEM and crystallinity levels comparable to the pure PET films as noted by WAXS, it therefore appears that this absence of a distinct H_v cloverleaf scattering pattern may be due to the spherulites being smaller than the measuring limit of our SALS apparatus ($\sim 1.5 \mu$). This result, then, is consistent with the SEM finding that the spherulites in the agent-containing films are of the order of 0.5 to 1 micron in diameter.

The effect on the liquid-induced crystallization of incorporating a nucleating agent of known efficiency, sodium benzoate, into pure PET by melt mixing displayed the same general trends as were observed for the du Pont materials. (Sodium benzoate is insoluble in all four liquids under consideration.) For example, SEM studies of pure PET and PET containing sodium benzoate crystallized liquid induced in methylene chloride at 24°C resulted in spherulitic structure of characteristically smaller size in the sodium benzoate-containing films (see Fig. 13).

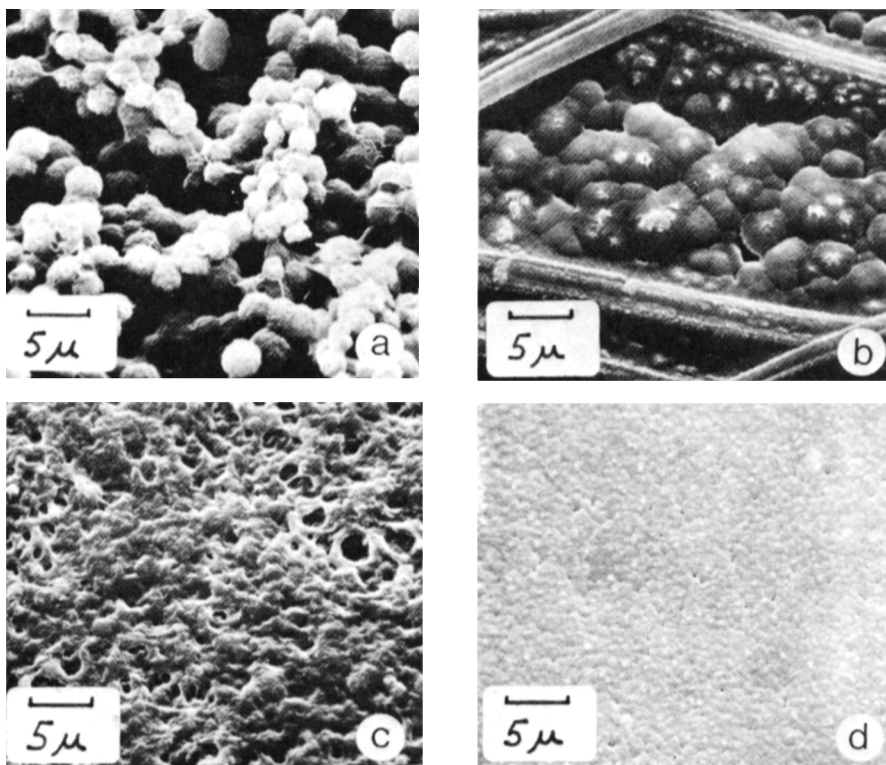


Fig. 11. (a) and (b) Representative SEMs of the surfaces of du Pont PET films without nucleating agent immersed at 24°C in (a) methylene chloride for 5 min and (b) acetone for 60 min. (c) and (d) Representative SEMs of the surfaces of du Pont PET films with nucleating agent immersed at 24°C in (c) methylene chloride for 5 min and (d) acetone for 60 min.

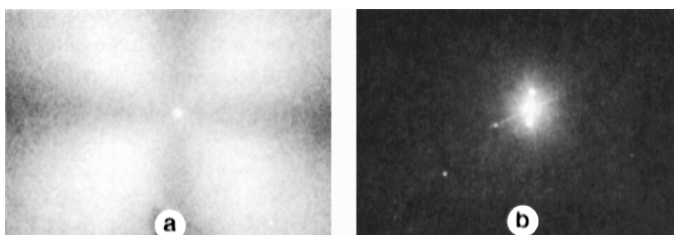


Fig. 12. Representative H_v SALS patterns for du Pont PET films (a) without nucleating agent and (b) with nucleating agent both immersed in acetone liquid 60 min at 24°C.

A number of SALS patterns were obtained for the pure PET and PET + sodium benzoate following liquid-induced crystallization at several temperatures in the four liquids studied. The characteristics of these patterns on the whole showed the same behavior as was seen in the du Pont materials. That is, the pure PET films showed patterns consistent with the spherulites of size comparable to that measured via SEM on the film surfaces. The PET + sodium benzoate films, on the other hand, showed no discernible pattern. Again, since the films were apparently spherulitic (as seen by SEM) and showed the same crystallinity levels as the pure films by WAXS measurements, the absence of a pattern may

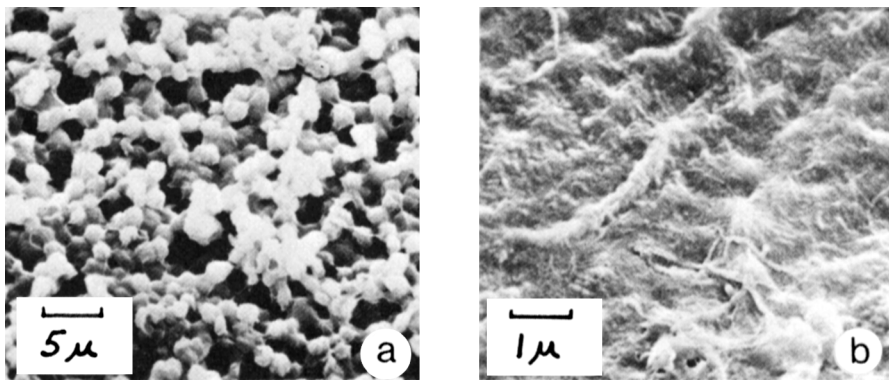


Fig. 13. Representative SEMs of the surfaces of PET films immersed in methylene chloride 5 min at 24°C: (a) pure PET film; (b) PET + 3% sodium benzoate film.

be due to spherulites smaller than the 1.5- μ measuring limit of our SALS apparatus. However, the presence of local large aggregates of crystalline sodium benzoate in some of the samples (as noted via OM) and their probable depolarization of light cannot be discounted. So at least by inference it appears that the sodium benzoate, even though poorly dispersed in certain samples, is still an effective nucleating agent for the liquid-induced crystallization of PET.

As a final observation concerning the effect of a nucleating agent incorporated into PET films prior to liquid-induced crystallization, the du Pont PET films containing a nucleating agent were slightly more transparent than the pure PET films following liquid-induced crystallization. However, probably due to the surface roughness evidenced in these films, they are still rather turbid.

The films containing sodium benzoate, on the other hand, showed no improvement in clarity over their pure counterparts following liquid-induced crystallization. Also, the PET + sodium benzoate samples were quite brittle both before and after crystallization. The local aggregation of this nucleating agent in some of the films probably influenced both of these effects. Perhaps some degradation of the PET occurred during the sample fabrication due to moisture content in the agent. This effect has been noted previously for PET + sodium benzoate systems.⁴

Molecular Weight

The resultant morphologies of the PET films with \bar{M}_n values of approximately 18,000 and 30,000, after exposure to the same liquid treatments at various times and temperatures near room temperature, were in all cases identical. Specifically, as measured by SEM, SALS, and WAXS, the degree of surface cavitation, the spherulite sizes, and the apparent level of crystallinity (as noted by the intensity and reflection breadth of the WAXS patterns) were the same for the two materials, no matter what the immersion conditions or the liquid used to induce the crystallization.

Furthermore, while specific spherulite growth rates were not measured in this report, inferential evidence indicated that these growth rates seemed comparable for the two different molecular weight materials. That is, distinct, fully developed spherulitic structure was observed on the surfaces of both film types after

treatment in either dioxane or methylene chloride for only several seconds at 24°C. Also, the overall crystallization of both materials in all the liquids was apparently completed in the same time scale as the diffusion process, indicating diffusion-limited crystallization kinetics for both cases. Taken together, both of these observations imply extremely rapid growth rates in both PET samples and infer that even if the higher molecular weight sample does have a slower spherulite growth rate (as suspected from thermal crystallization studies²⁴), it is not sufficiently slow to show a deviation from diffusion-limited crystallization kinetics.¹¹

SUMMARY

In this report some of the morphological consequences of variations in the initial state of PET subsequently undergoing liquid-induced crystallization have been discussed. First of all, it was found that melt-mixed blends of PET and either PTMT or PC showed no large-scale phase separation prior to liquid-induced crystallization. This was accounted for by copolymer formation due to interchange reactions occurring during sample fabrication. After exposing the PET/PTMT blends to suitable liquids, apparently increasing levels of crystallinity were revealed along with decreasing surface cavitation with increasing PTMT concentration, while the morphology of both pure PET and PET/PC blends after similar liquid-induced crystallizations appeared identical. Melt-mixed blends of PET and APS showed significant phase separation, and treatments with suitable liquids resulted in PET crystallization and APS dissolution in the blends.

Secondly, it was shown that nucleating agents appear to affect the liquid-induced crystallization of PET in the same manner that they affect this polymer's thermal crystallization. Specifically, PET films containing nucleating agents were characterized by spherulitic structure smaller in size than pure PET films undergoing the same crystallization by liquids. Finally, a brief study of the effect of molecular weight on the liquid-induced crystallization of PET showed that the characteristic morphology and apparent crystallization kinetics were the same for PET samples with \bar{M}_n values of 18,000 and 30,000.

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