

Tensile Properties and Morphology of Blends of Polyethylene and Polypropylene

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Synopsis

The tensile behavior of blends of linear polyethylene (PE) and isotactic polypropylene (PP) was examined in relation to their morphology. Yield stress increases monotonically with increasing PP content, while true ultimate strength is much lower in all blends than in the pure polymers as a result of early fracture. The blends fail at low elongation because of their two-phase structure, consisting of interpenetrating networks or of islands of PE in a PP matrix, as shown by scanning electron microscopy of fracture surfaces and transmission electron microscopy of thin films. While spherulites in PP are very large (~100 μm in diameter), addition of 10% or more of PE drastically reduces their average size. This, together with the profusion of intercrystalline links introduced by PE, may be associated with maximization of tensile modulus in blends containing ~80% PP. Introduction of special nucleating agents to PP reduces average spherulite size and is accompanied by slight improvements in modulus. Thin films of blends strained in the electron microscope neck and fibrillate in their PE regions, but fracture cleanly with little fibrillation in areas of PP.

INTRODUCTION

Within the rapidly growing literature on polymer-polymer blends (see e.g., the recent reviews of Paul and Newman¹ and Manson and Sperling²), blends of crystalline polyolefins occupy only a very small part. The reason for this lies in the molecular incompatibility of the polymeric constituents³⁻⁵ which causes these blends to separate into individual phases. However, blends of polyethylene (PE) and polypropylene (PP) are now used commercially because of their high-impact strength and low-temperature toughness^{3,6}; furthermore, polyolefins are among the major constituents of plastic waste and scrap,^{7,8} and their recycling as a blend is of considerable value. For these reasons, melt-mixed blends of the two most common polyolefins—linear polyethylene and isotactic polypropylene—have been considered in this work.

Much of the research on polyolefin blends, particularly the works on melt mixing, compatibility, rheology, and applications, has been reviewed succinctly in a recent article by Plochocki.⁹ A few authors have also reported on the tensile properties of PE/PP blends. The earliest of such works are those of Slonimskii et al.¹⁰ and Plochocki,¹¹ who found a monotonic increase in tensile strength with PP content. On the other hand, Noel and Carley¹² obtained a maximum in ultimate strength and modulus at a composition of 90% PP, while Deanin and Sansone¹³ found similar results at 75% PP. We have, therefore, reexamined the tensile behavior of PE/PP blends in an attempt to reconcile these differences. Moreover, we have used optical and electron microscopy to investigate the morphology of our tensile specimens and of other PE/PP blends. Our results,

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together with a discussion on possible interrelationships between morphology and tensile properties in these blends, are presented in this article.

EXPERIMENTAL

The polymers used in this work were Dow high-density polyethylene 70065 ($\bar{M}_w = 132,000$, $\bar{M}_n = 12,500$, volume crystallinity = 76%) and Hercules Profax 6523 polypropylene ($\bar{M}_w = 217,000$, $\bar{M}_n = 21,000$, volume crystallinity = 58%); these molecular weight averages were calibrated against linear polyethylene fractions and thus represent absolute values for PE, but only relative ones for PP. Pellets of the two polymers were manually mixed to PE/PP compositions of 75/25, 50/50, 25/75, 20/80, and 10/90 by weight, and then blended in a two-roll mixer at 200°C for 15 min; in order to assure consistency of our data, the pure polymers were also subjected to this treatment. The milled samples were then compression molded to a nominal thickness of 1.25 mm. Tensile specimens were punched out from these sheets using a pneumatic die; their dimensions conformed to type IV specimens of ASTM Method D638 (width of narrow section = 6 mm, gauge length = 25 mm). Tensile tests were performed in accordance with this method on an Instron apparatus using a crosshead speed of 5 mm/min.

Morphological studies involved polarized-light microscopy of sections microtomed from our tensile specimens and scanning electron microscopy of fracture surfaces produced at liquid nitrogen temperatures; these surfaces were coated with a thin layer of evaporated carbon and examined at 20 keV using a secondary electron detector. In addition, very thin films of the polymer blends were also examined by transmission electron microscopy. The films were deposited on freshly cleaved mica from dilute solution of the polymers in decahydronaphthalene. After evaporation of the solvent, the films were remelted at 200°C and recrystallized at 100°C to approximate the conditions prevailing during crystallization of our tensile specimens. Finally, the films were shadowed with Pt/C and coated with carbon in a vacuum evaporator, floated off the mica in distilled water, and deposited on copper grids for examination at 80 keV in a JEOL 100-CX electron microscope.

RESULTS AND DISCUSSION

Tensile properties of our PE-PP samples were found to vary with aging time at room temperature in the manner described for pure PP by Remaly and Schultz.¹⁴ For this reason, all tensile data reported here refer to standard aging times, viz. 96-100 hr. The tensile behavior of our blends is summarized in Figures 1-3; its basic trends are in agreement with the findings of Noel and Carley¹² and Deanin and Sansone.¹³

Elongations at yield and at break are plotted against composition in Figure 1 (in this and other graphs, each point is shown as mean \pm standard deviation for seven or more measurements). Blending is seen to accelerate the occurrence of yielding only slightly: from $\sim 15\%$ elongation in the pure polymers down to $\sim 9\%$ at 75-80% PP. Incompatibility of PE and PP^{3,15} (see also the morphological evidence discussed below) is at the root of this early yielding. This incompatibility is reflected much more strongly in the ultimate elongation of all blends:

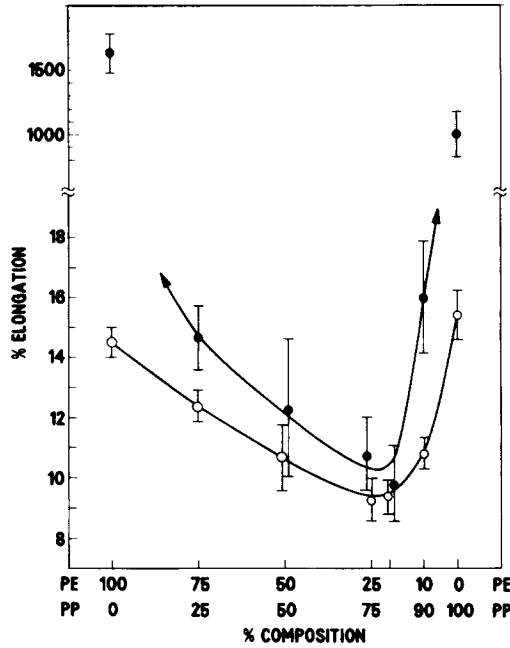


Fig. 1. Elongation at yield and at break of PE/PP blends: ○, yield; ●, break.

on the average, fracture takes place immediately after yielding (and sometimes even prior to yielding), in contrast to the behavior of the pure polymers which are drawn to ten or more times of their original length.

Variation of strength with composition is seen in Figure 2. Tensile strength at yield increases monotonically [Fig. 2(a)] despite incompatibility in the blends; this reflects the fairly narrow differences in elongation at yield at all compositions from 100% PE to 100% PP. Nominal tensile strength at break [Fig. 2(b)] is more interesting because it reaches a maximum between 75 and 90% PP, suggesting

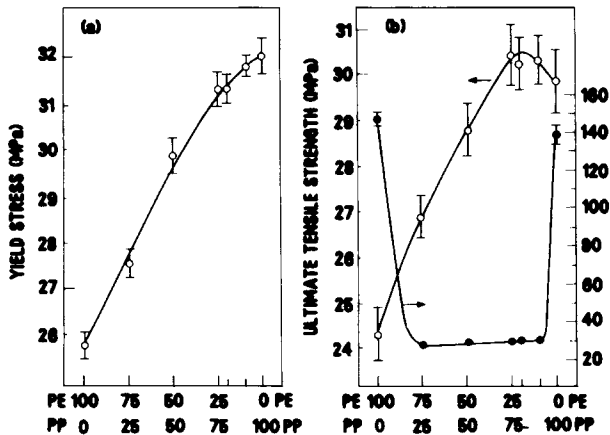


Fig. 2. Variation of tensile stress at (a) yield and (b) break with composition for PE/PP blends: ○, nominal stress; ●, true stress.

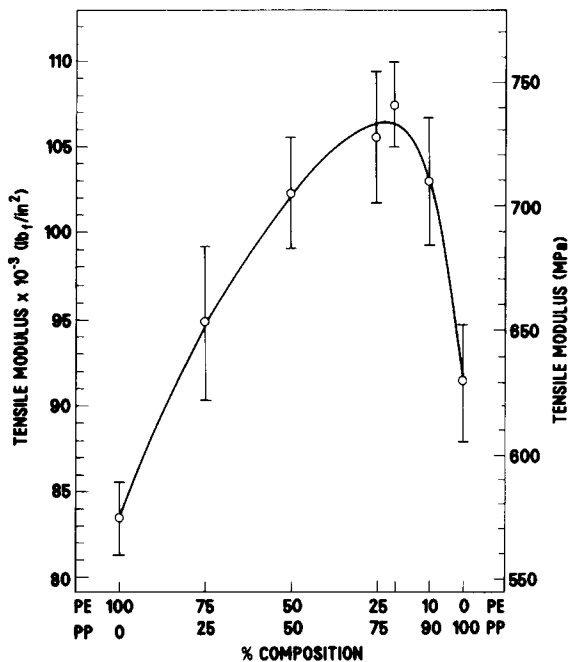


Fig. 3. Variation of tensile modulus (at 1% elongation) with composition for PE/PP blends.

some positive synergism of the polymeric constituents.^{12,13} However, this is misleading because nominal strength is computed from the *original* cross-sectional area of our specimens. Since the blends break very early, the force at fracture is sustained by much larger cross-sectional areas than in the case of the pure polymers; as a result, *true* strength, based on *actual* cross-sectional area, is vastly inferior in all blends.

In contrast to ultimate tensile strength, the modulus of the blends (measured at 1% elongation) reflects true positive synergism. This supports previous results of Noel and Carley¹² and Deanin and Sansone,¹³ who found maximization of modulus at 90 and 75% PP, respectively. In our samples, a distinct maximum is seen at 80% PP (Fig. 3).

To interpret these tensile results, we examined the morphology of our samples. The appearance of microtomed sections ($\sim 20 \mu\text{m}$ thick) between crossed polars is seen in Figure 4; here, the broad surfaces of the tensile specimens are horizontal and normal to the plane of the micrographs. These morphologies are typical of the entire specimen for PE and all blends; in PP, however, transcrystallization¹⁶ on the broad surfaces of the specimens caused formation of "skins" of oriented spherulites extending $\sim 30\text{--}40 \mu\text{m}$ inwards and occupying $\sim 4\text{--}6\%$ of the bulk of the samples. At this scale of magnification, the most obvious morphological features are spherulites; their sizes are known to be generally very small in PE as a result of high nucleation and growth rates, whereas the opposite is true for PP.¹⁷ In our specimens, the average diameters of PE spherulites are seen to be less than $10 \mu\text{m}$; on the other hand, PP spherulites (almost all of which belong to the α form¹⁸) are $\sim 100 \mu\text{m}$ or larger. The most important conclusion from the micrographs of Figure 4 is the very strong influence of PE in greatly

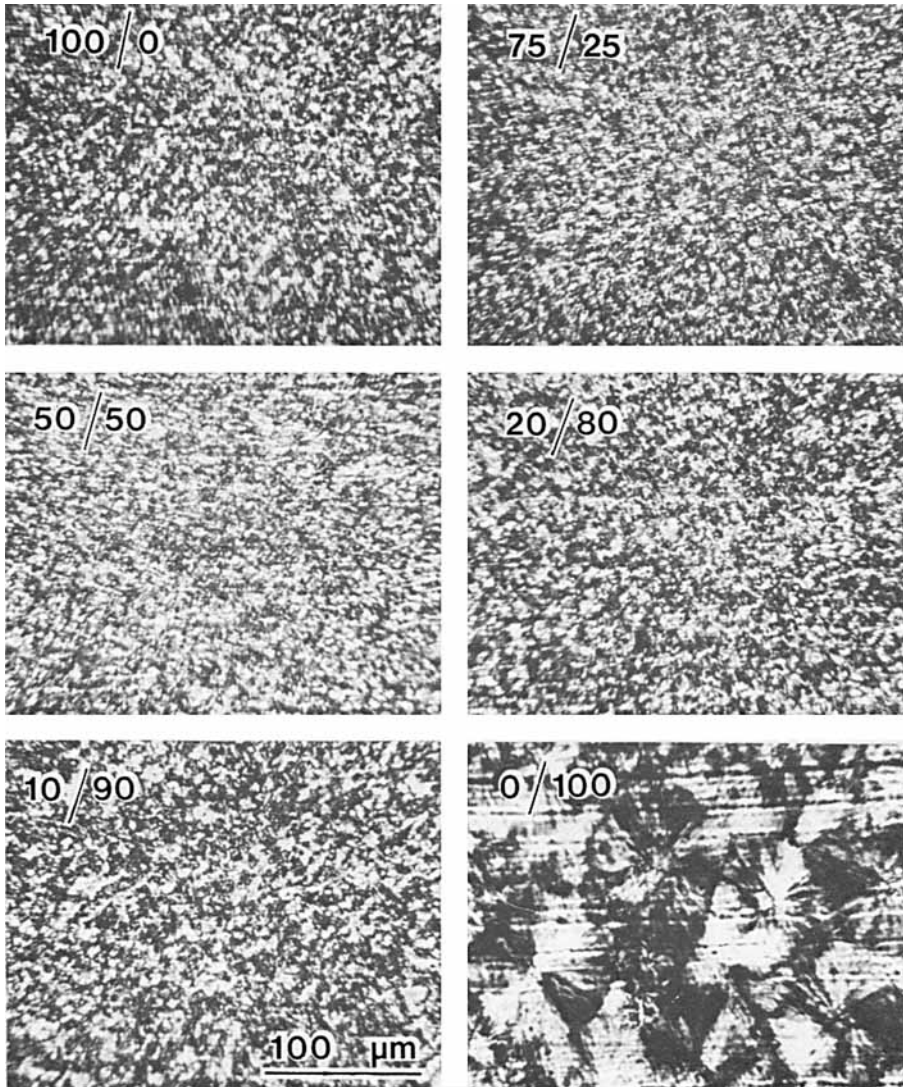


Fig. 4. Morphologies of microtomed sections from tensile specimens of PE/PP blends, as seen between crossed polars.

reducing the average spherulite size in all blends—even those containing 90% PP.

Significantly greater microstructural detail is seen in Figure 5, which depicts the bulk morphologies of our tensile specimens as revealed by fracture at liquid nitrogen temperatures. Very short lamellae ($1\ \mu\text{m}$ or less) are observed in PE [Fig. 5(a)], while those in PP are very broad and many micrometers in length [Fig. 5(d)]. The 50/50 blend [Fig. 5(b)] incorporates both these features and also shows clearly the two-phase structure of these samples. Islands of PE of the order of $2\text{--}10\ \mu\text{m}$ diam. are dispersed within the continuous matrix of PP in the blend. The same is true at higher concentrations of PP, but now the PE islands are smaller; in the 20/80 blend, their diameters are $1\text{--}2\ \mu\text{m}$ [Fig. 5(c)]. It is in-

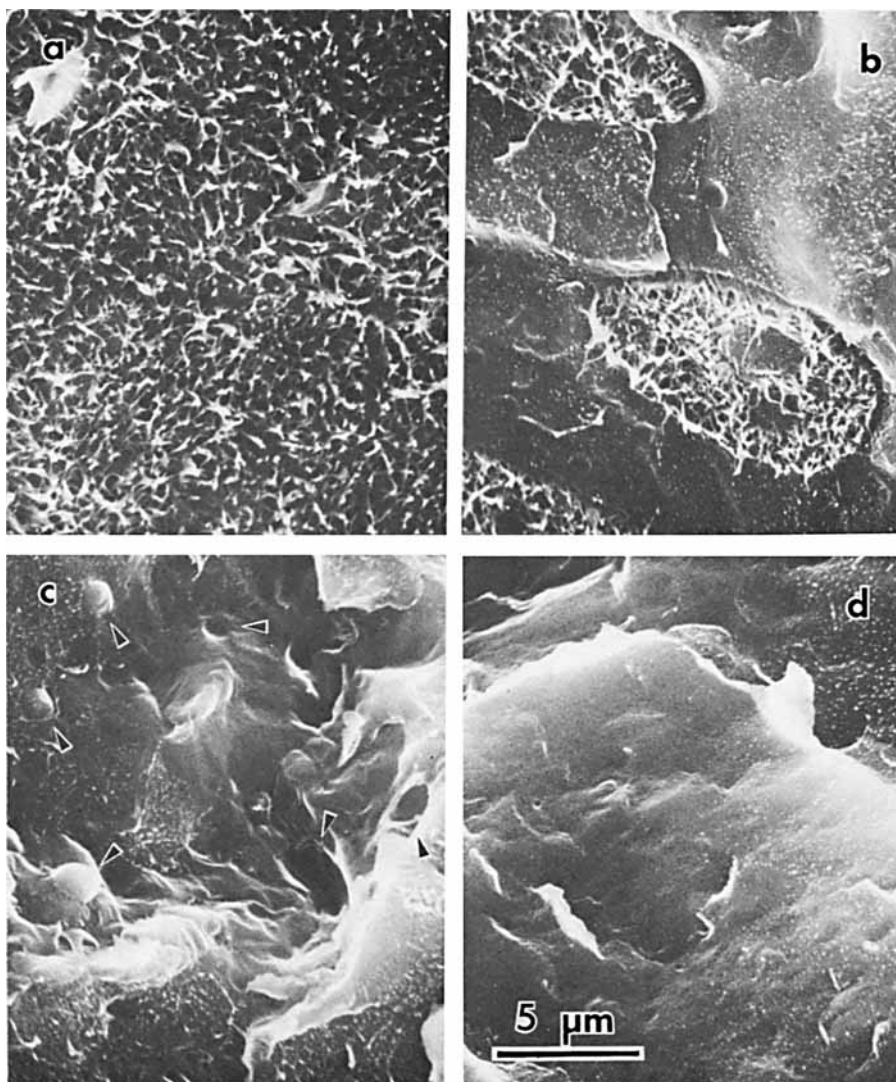


Fig. 5. Scanning electron micrographs (secondary electrons) of fracture surfaces obtained from tensile specimens of PE/PP blends: (a) 100/0; (b) 50/50; (c) 20/80; (d) 0/100.

interesting to observe in this micrograph that the PP lamellae are also smaller than those in the pure polymer; the rapidly crystallizing PE regions may be promoting nucleation of PP lamellae. Finally, Figure 5(c) also indicates that failure is initiated at the PE/PP boundaries: as pointed out by the arrowheads, some of the PE islands remain intact on the fracture surface shown, while others have been carried away on the mating surface, leaving voids behind.

Transmission electron microscopy probes structure on an even finer level than its scanning counterpart but requires specimens in the form of very thin films (less than ~ 100 nm). Such samples, prepared under conditions approximating crystallization of our tensile specimens, are seen in Figure 6. The regions shown in this figure were selected because they all show the effects of straining induced by the electron beam (these will be discussed presently). Concentrating for the

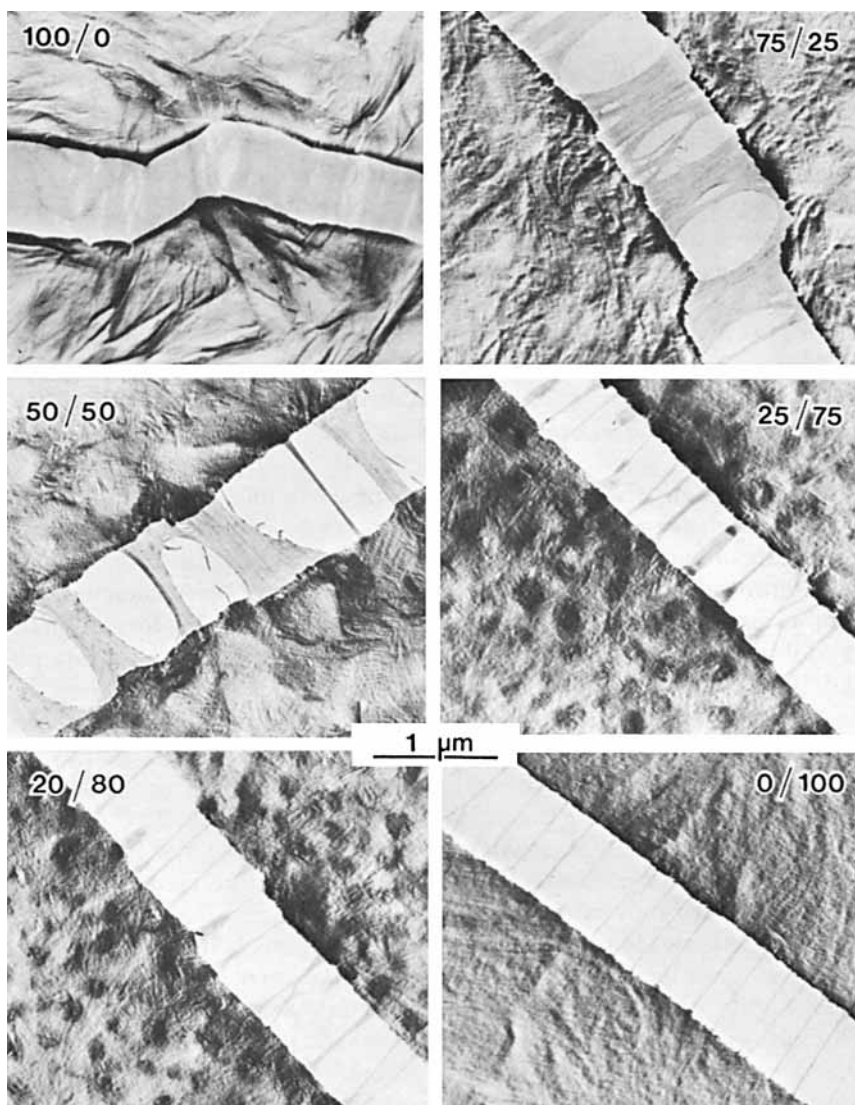


Fig. 6. Transmission electron micrographs of thin films of PE/PP blends crystallized at 100°C.

moment on the morphological features of Figure 6, we see that PE is distinguished by short ($\sim 1 \mu\text{m}$), sometimes curved lamellae, while PP now clearly displays the characteristically cross-hatched morphology described by Khoury¹⁹ and Padden and Keith.^{20,21} When blended together to a 75/25 ratio, PE and PP are seen to form interpenetrating networks without sharp boundaries. In the 50/50 blend, such regions are still the rule, but PE islands are also seen, while at higher concentrations of PP (e.g., 25/75 and 20/80) small PE islands with distinct boundaries are now in abundance. These islands are much smaller than their counterparts in bulk specimens (Fig. 5)—probably because of thin-film effects.

The response of these thin films to localized stresses owing to electron irra-

diation are of interest (see Fig. 6). PE yielded extensively throughout the sample, forming long, running necks; PP, on the other hand, yielded much less frequently and then with immediate fracture, exposing sharp boundaries bridged by only a few thin fibrils. The blends show intermediate behavior, the extent of fibrillation and necking decreasing with increasing PP content. As expected, the fibrils are seen preferentially to connect the PE islands in these blends.

The above describe our morphological evidence on PE/PP blends. To recapitulate, it was found that their structure up to 50% PP consists primarily of interpenetrating networks of the two polymers, while blends of 50% PP or more are typified by PE islands dispersed in a PP matrix. In all blends, PE serves to reduce the average spherulite size, probably acting as a nucleating agent for PP. This is supported by the findings of Olley, Hodge and Bassett,²² who observed copious nucleation of PP on an interphase boundary with PE. At this point, we should examine how this morphology might account for the mechanical behavior of PE/PP blends.

Broadly speaking, there are two competing morphological factors expected to affect the tensile properties of our blends: (1) deterioration of properties as a result of incompatibility and consequent two-phase structure of our samples; and (2) improvement of properties as a result of the role of PE in reducing average spherulite size, increasing overall crystallinity, and promoting formation of intercrystalline links. Incompatibility hastens yielding and fracture at interphase boundaries [see Fig. 5(c)]. On the other hand, numerous studies²³⁻²⁵ have shown that yield stress and ultimate strength are improved with decreasing spherulite size, primarily because yielding and failure are commonly initiated at interspherulitic boundaries.²⁶ Increases in overall crystallinity, such as would accompany addition of PE to PP, result in enhancement of modulus^{27,28} and possibly of strength,²⁶ as well. As regards tie molecules and intercrystalline links,^{29,30} their role in transmitting stresses between lamellae, and thus increasing strength, has been described by Vadimsky, Keith, and Padden.³¹

Therefore, at low elongations, these competing effects may account for the more-or-less linear increase of yield stress with PP content. With higher strains, incompatibility causes failure to occur early at interphase boundaries, thus precluding significant necking and drastically reducing true ultimate strength. The peak in modulus at 80% PP is not fully understood. However, at the small strains involved in modulus determination (1%), the influence of incompatibility is expected to be minimal, while the effect of tie chains and intercrystalline links should be significant. Padden and Keith²⁰ have shown that in contrast to PE in which there is a very high density of intercrystalline links, PP has only a few such links, primarily because of the slow growth of its spherulites. In this manner, and because of its higher crystallinity and role in reducing spherulite sizes, PE may be functioning as a stiffener for the PP matrix.

In order to isolate these factors, we tested the effects of decreasing spherulite size in PP on its tensile modulus. To avoid changes in crystallization temperature, special nucleating agents giving rise to the α form of PP were used; these were sodium benzoate¹⁴ and tertiary butyl benzoic acid.³² The first of these is a much stronger nucleating agent for PP, as seen in Figure 7, which depicts polarizing-light photographs of microtomed sections of these tensile specimens. Addition of only 0.01% sodium benzoate reduces the average size of PP spherulites from $\sim 100 \mu\text{m}$ [Fig. 7(a)] to $50\text{--}70 \mu\text{m}$ [Fig. 7(b)]; at 0.1 and 1% concentra-

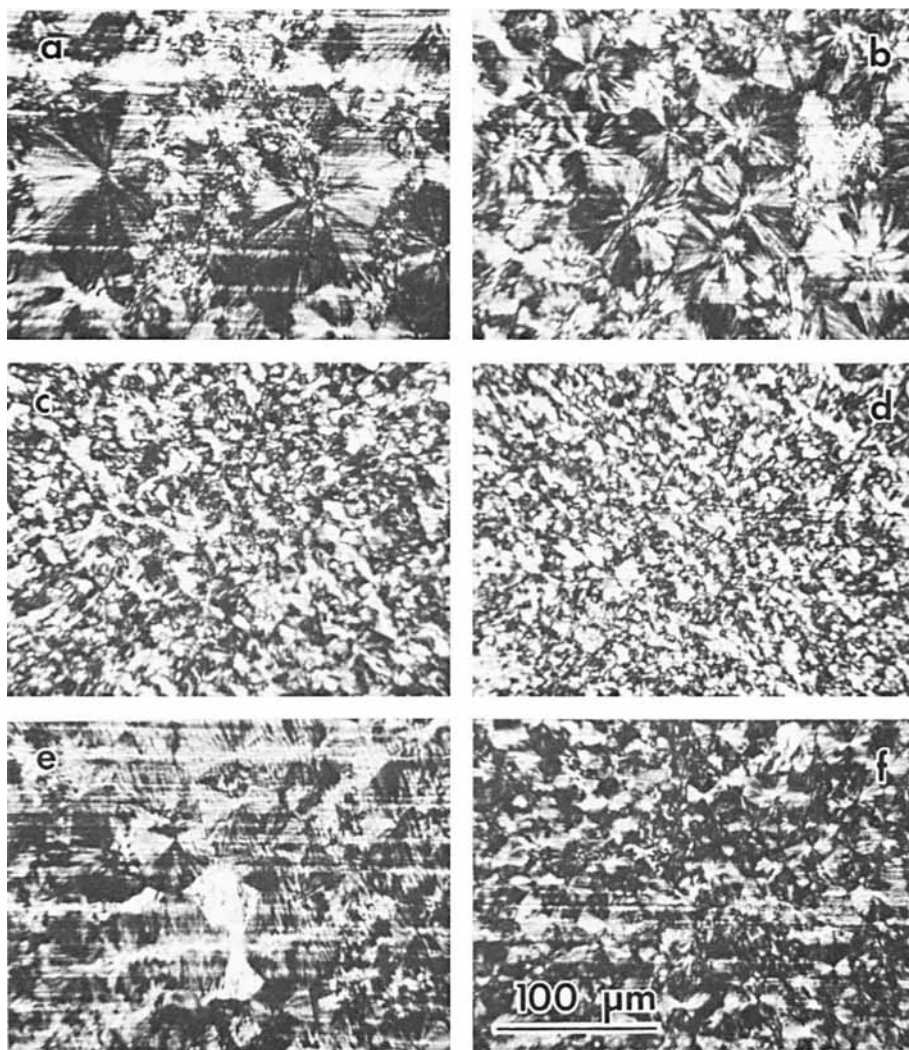


Fig. 7. Morphologies of microtomed sections from tensile specimens of PP with various nucleating agents, as seen in the polarizing microscope: (a) pure PP; (b) 0.01% sodium benzoate; (c) 0.1% sodium benzoate; (d) 1% sodium benzoate; (e) 0.1% *t*-butyl benzoic acid; (f) 1% *t*-butyl benzoic acid.

tions, spherulites become as small as 20–30 μm [Fig. 7(c)] and 5–10 μm [Fig. 7(d)], respectively. With 0.1% *t*-butyl benzoic acid, average spherulite size is reduced to 50–60 μm [Fig. 7(e)] and reaches 20–30 μm at 1% concentration of this nucleating agent [Fig. 7(f)].

There appears to be a tendency toward increasing modulus that parallels decreases in spherulite size in these samples, as seen in Figure 8. This tendency, however, is weaker than that seen when PE was used to reduce spherulite sizes to equivalent dimensions (Fig. 3). For example, even though a 20/80 PE/PP blend has the same average spherulite size as PP containing 1% sodium benzoate, its modulus is more than 30 MPa higher. It has been reported³³ that crystallinity in polystyrene and polypropylene decreases with increasing spherulite radius, primarily because of concentration of noncrystallizable species.³⁴ Therefore,

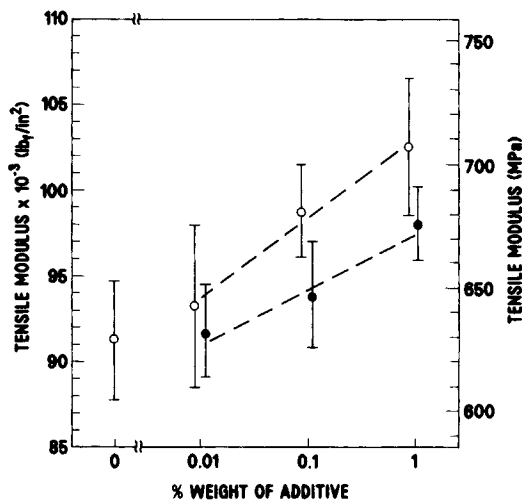


Fig. 8. Tensile moduli (at 1% elongation) of variously nucleated PP: O, sodium benzoate; ●, *t*-butyl benzoic acid.

all other factors being equal, a reduction in spherulite size might be expected to cause an improvement in modulus. The additional improvement obtained by incorporation of PE could then be attributed to increased concentration of intercrystalline links.

In summary, it was seen that morphological effects, such as spherulite sizes, intercrystalline links between lamellae, and the detailed structure of the two incompatible phases and of their mutual boundaries, may be correlated with the tensile behavior (distinguished by early fracture and by synergism in modulus) of PE/PP blends.

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