Control of Phase Separation and Voiding in Oil-Filled Polypropylene

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Synopsis

The physical properties, morphologies, and fracture characteristics of samples injection molded from blends of polypropylene and a low-viscosity hydrocarbon oil are described. Unexpectedly large improvements in mechanical and optical properties are found to occur on the addition of a nucleating agent (copper phthalocyanine). Both the ultimate tensile strength and the elongation of unnucleated samples are doubled by incorporation of as little as 0.01% of the nucleant. Similar increases in the properties of unnucleated blends are observed when the barrel temperature of the molding machine is reduced. In both cases, marked improvements in visual uniformity occur. It is shown that these gains can be correlated with improved dispersion of the oil as spherulite size is reduced.

INTRODUCTION

The properties of articles fabricated from polymer melts of more than one component are of increasing interest as new material blends are developed. To date, this interest has been centered primarily on noncrystalline polymers. Blends of these polymers with each other or with low molecular weight additives are often formulated to provide increased impact resistance or improved melt flow. Plasticized poly(vinyl chloride) is an important commercial example.

Plasticized or liquid-filled crystalline polymers have received much less attention. In general, the detrimental effects of noncrystalline additives on the properties of crystalline polymers are too severe to permit general use although inclusion of these substances is often desirable for other reasons. A major difficulty stems from massive phase separation and internal voiding in molded parts. We wish to report herein some recent studies on the relationship of phase separation to the morphology of samples molded from blends of a hydrocarbon oil and an ethylene–propylene copolymer. Our results indicate that control of morphology can be a powerful technique for reducing macroscopic phase separation in this blend.

EXPERIMENTAL

All samples were prepared from 70:30 blends of Amoco 20-9602 polypropylene (a 2% ethylene copolymer, melt flow = 4.0 g/min) and GE

10-C (GE registered trademark) oil (a 60 saybolt-second hydrocarbon oil). The polymer was prestabilized with 0.6% AGT antioxidant, a blend of 25 parts Irganox 1010, 30 parts distearyl thiodipropionate, and 5 parts calcium stearate. The two components were mixed on a two-roll mill to give a moderately dry, pourable powder. Nucleated blends were prepared by adding copper phthalocyanine in concentrations ranging from 0.005% to 0.1% based on the weight of the polymer.[1]

A $1/8$ in. by 2 in. dogbone (ASTM D-1822, Type L), a $1/8$ in. by 2 in. by $1/2$ in. flex bar and a 2 in. by 2 in. by $1/8$ in. plaque were injection molded directly from the polymer–oil blends using a Battenfeld 175-ton, 2.8-oz reciprocating screw injection-molding machine. The melt temperature was held at 180°C (except where otherwise noted), and the mold was held at 30°C. The injection time was 7 sec, the injection pressure was 700 psi, and the residence time in the mold was 33 sec for all samples.

All microtoming was done on a Porter-Blum MT-2 ultramicrotome using a diamond knife. The samples were held in a liquid nitrogen-cooled block during slicing to minimize deformation. Optical microscopy was carried out on a Zeiss polarizing microscope and scanning electron microscopy, on a JEOL SEM. Tensile data were taken on an Instron testing machine at a strain rate of 1.0 in./min and flexural data at 0.2 in./min.

RESULTS

Unnucleated Blends

The first series of test pieces was molded from the unnucleated polypropylene blend. On ejection from the mold, the specimens appeared to be void free and had the characteristic translucent appearance of the polypropylene copolymer. Within minutes, however, noticeable whitening of the samples began to occur first in isolated regions but eventually across the entire sample. Figure 1 shows a series of plaques held at room temperature for different times after molding. Since the samples are illuminated from behind for better contrast, the white areas appear dark in the picture. Note that the plaques become increasingly opaque over a period of many days. We attribute the decrease in transmittance to scattering from internal voids which continue to grow as phase separation proceeds.

It is well known that polymer crystallization from the melt proceeds with appreciable segregation of noncrystallizing (low molecular weight, low tacticity) species to the spherulite growth fronts during primary crystallization.[2] Oil is undoubtedly excluded in this way in the polypropylene–oil blends. The effects are manifested, however, only when strains set up by continued rejection of oil during secondary crystallization cause the samples to void at the weakened spherulite boundaries. It will be shown later that the way in which the oil is accommodated between neighboring spherulites is critical in determining the ultimate properties of these two-component systems.
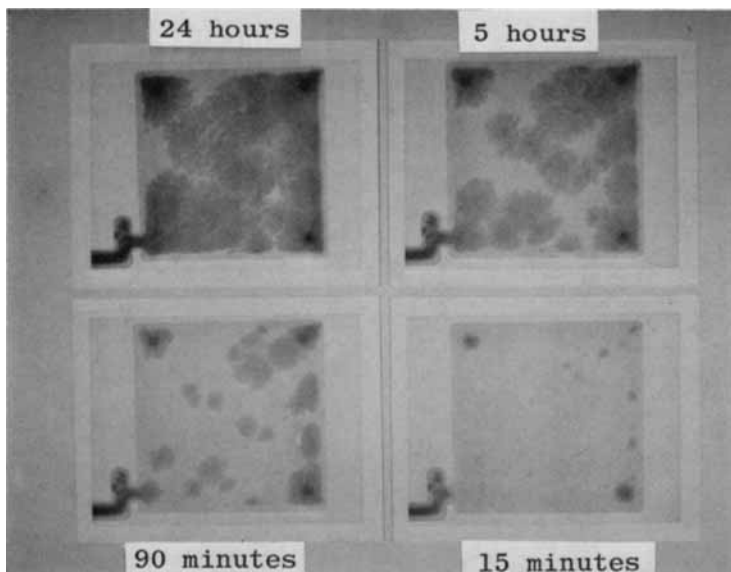
Fig. 1. Unnucleated, oil-filled, injection-molded plaque aged at room temperature for 15 min, 90 min, 5 hr, and 24 hr after molding at 180°C.

In each of the molded specimens it was found that little, if any, voiding occurred near the surface even after extended aging. This observation, together with several recent papers on the skin-core morphology of injection-molded polypropylene,[3,4,5] suggested that there was an excellent possibility for controlling macroscopic phase separation in moldings of oil-filled polypropylene by varying the morphology.

A light micrograph showing the morphology of a specimen molded from the unnucleated, two-phase blend is presented in Figure 2. This thin section was cut from the skin to the interior perpendicular to the flow direction. The four distinct morphological zones identified by Fitchman and Mencik[4] are clearly revealed. The first, or exterior zone, is a nonspherulitic but highly oriented skin. The second zone is made up of transcrystalline growths containing predominately type III spherulites. The third zone is composed of highly nucleated but nonoriented spherulites, while the fourth, or core zone, shows the well-developed type I spherulites characteristic of slowly cooled polypropylene.

Figure 3 is a photomicrograph of the surface of the block from which the section in Figure 2 was cut. With top illumination, the greater degree of phase separation and voiding in the core is clearly visible as the result of its greater light scattering ability. Comparison of Figures 2 and 3 shows that the region of greatest voiding terminates with the beginning of zone 3.

As noted above, voiding is believed to occur primarily between neighboring spherulites and results from strains set up during secondary crystallization. We propose that the relatively large spherulite diameter in the

core zone limits the interspherulitic area over which the oil can be distributed compared with the area available in the other zones. For this reason, voiding is observed in the core zone and not in the outer zones of the moldings.
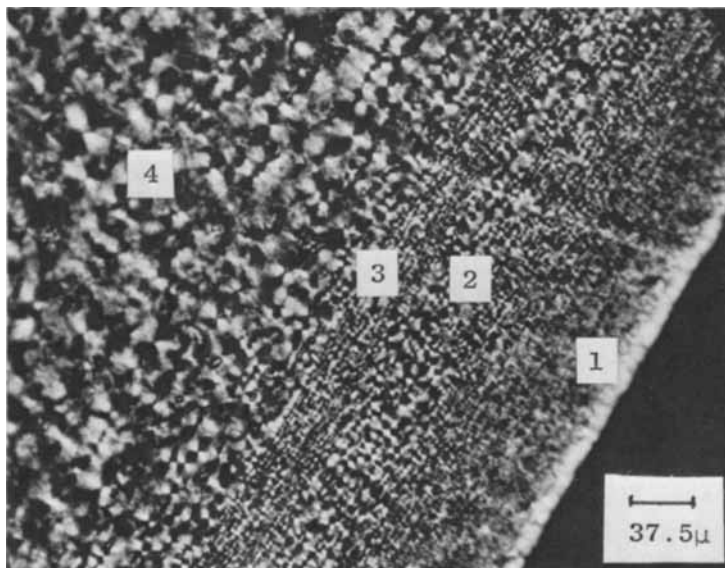

Fig. 2. Optical micrograph, crossed polarizers, showing distinct morphological zones in unnucleated, oil-filled molded bar.
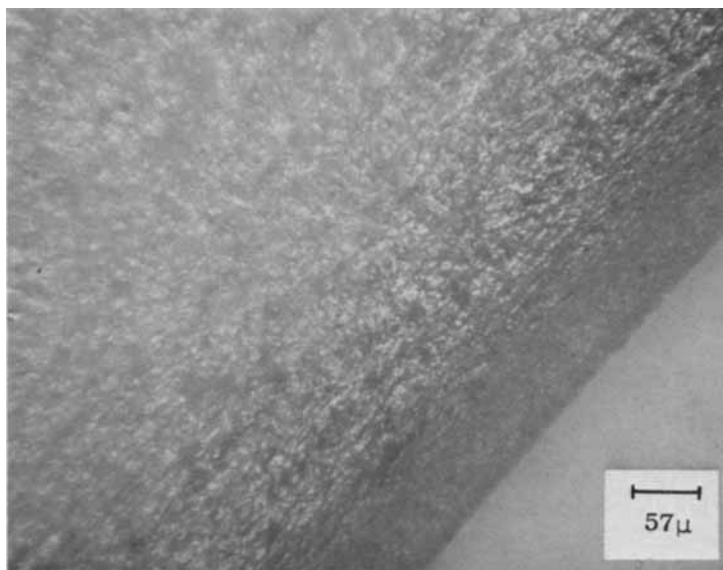

Fig. 3. Optical micrograph, incident steep illumination showing significant voiding in interior of molded bar.

TABLE I
Mechanical Properties of Injection-Molded Nucleated and Unnucleated,
Oil-Filled Polypropylene

Tensile Bars			
% Nucleant	Yield strength, psi	Ult. tensile strength, psi	Elongation, %
0	1577	1734	354
0.005	1625	2289	561
0.01	1654	2439	639
0.05	1747	2689	703
0.1	1647	2449	725

Flex Bars		
% Nucleant	Flexural modulus, psi $\times$ 10^{-4}	Flexural yield strength, psi
0	2.948	1361
0.005	3.241	1569
0.01	3.288	1581
0.05	3.588	1650
0.1	3.571	1609

There is substantial support for this hypothesis. For example, it is known that spherulite boundaries in polypropylene homopolymer are often the weakest areas of the material.[6] In the blends, this region is further weakened by a reduction in the number of interspherulitic links resulting from rejection of oil to the surface of spherulites during primary crystallization. Finally, as explained more fully below, we observe that an increase in nucleation density alone is enough to prevent macroscopic voiding in the core zone.

The size of the voids is readily revealed by extracting the oil with hexane and observing the samples with the scanning electron microscope. Figure 4 is an SEM photomicrograph taken between zones 3 and 4. The large pockets in the core zone are readily identified at the left side of the photograph.

The mechanical properties of all samples were measured approximately two weeks after molding in order to allow completion of secondary crystallization.[7] The results are reported in Table I. During testing the unnucleated, oil-filled bars continued to stress whiten up to the yield point. The average elongation at yield was approximately 40%. As the samples began to neck, however, large voids were observed to develop in the core zone. With further elongation, the skin and transcrystalline zones continued to elongate and thin as the internal voids agglomerated. At 100% elongation, the gauge section had been transformed completely into a hollow tube. Most samples failed at relatively low strain displaying the ribbon-like fracture surface shown in Figure 5.
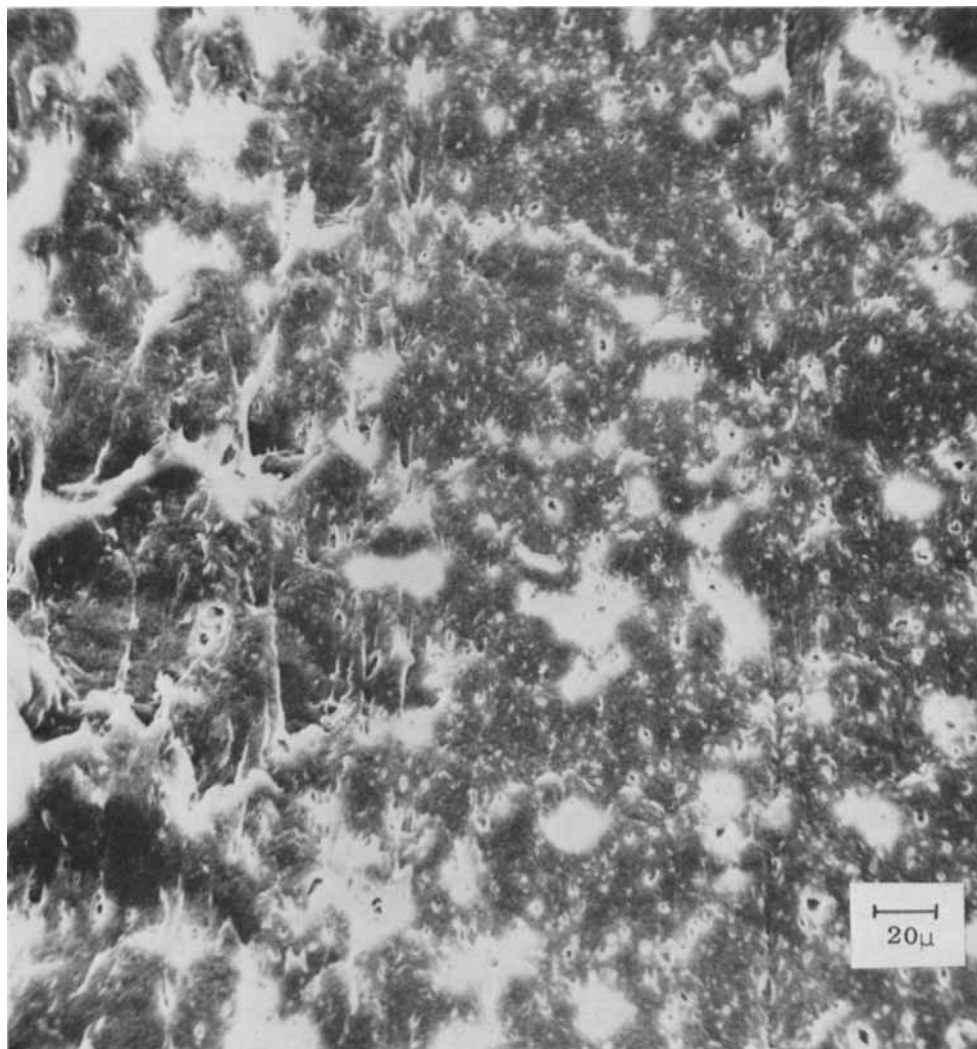
Fig. 4. SEM photograph of bar shown in Fig. 3 taken at junction of zones 3 and 4.   Note large voids in core zone.

Nucleated Blends

The second series of samples was fabricated under identical molding conditions from blends containing 0.005%, 0.10%, 0.05%, and 0.10% copper phthalocyanine, a nucleating pigment.   In contrast to the un-nucleated samples, these specimens remained translucent indefinitely after molding with no indication of massive oil agglomeration or voiding.   In thin sections cut from the molded bars, the various morphologic zones could still be readily identified although there was a marked decrease in the average spherulite size in each region, as shown in Figure 6.   The thick-
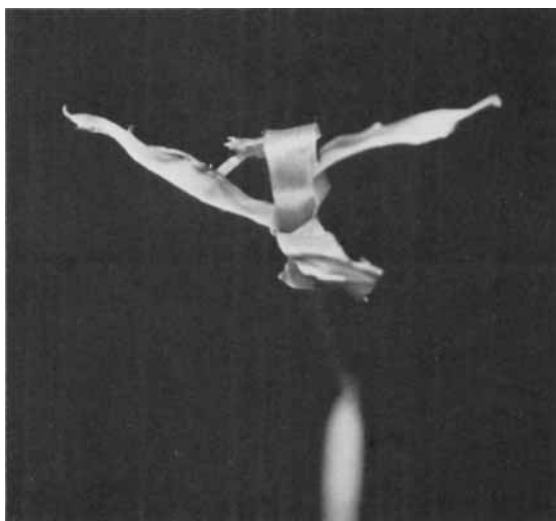
Fig. 5. Fractured end of unnucleated, oil-filled dogbone specimen showing ribbon-like
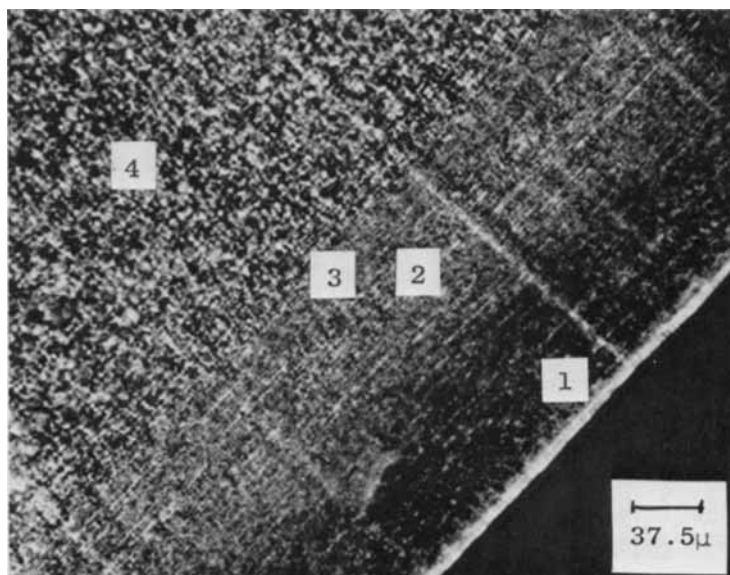failure and catastrophic voiding of core.

Fig. 6. Optical micrograph, crossed polarizers, showing distinct morphological zones in
nucleated, oil-filled molded bar.

ness of the skin, shear, and core zones remained constant, showing that
these features were responsive primarily to processing variables and in-
dependent of the amount of nucleant present.

Since heterogeneous nucleation only increases the number of primary
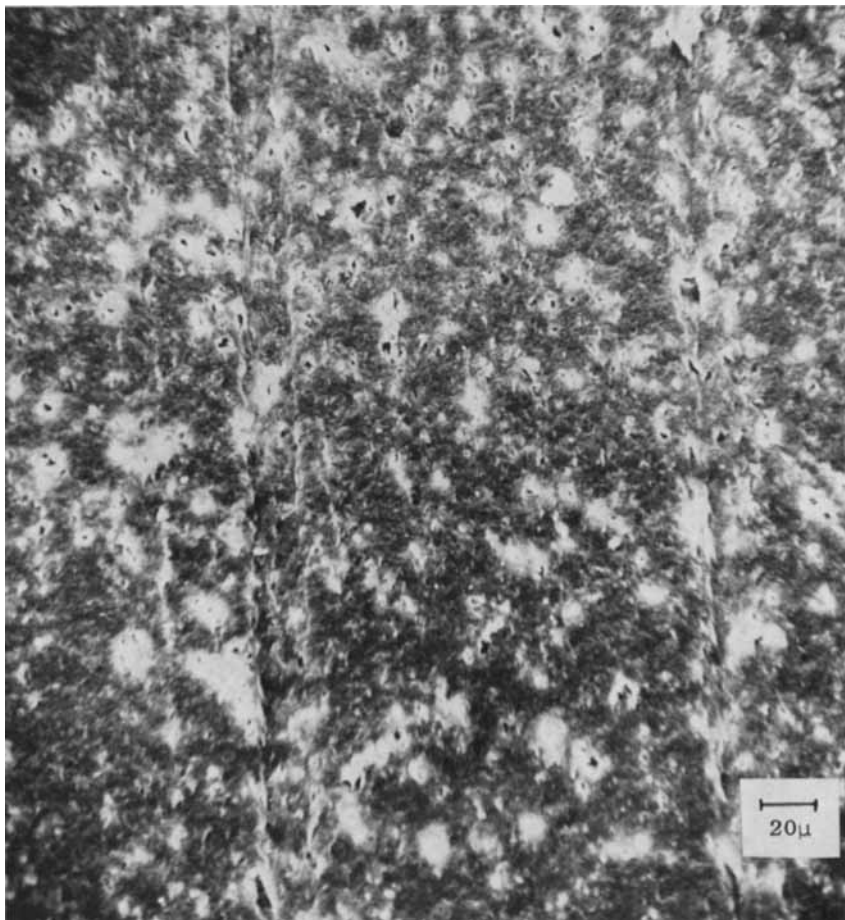nuclei and does not modify the sperulite radial growth rate or segregation

Fig. 7. SEM photograph of core of nucleated, oil-filled bar.   Compare with Fig. 4.

processes, we conclude that the large increases in interspherulitic surface area accompanying decreased spherulite size improve the ability of the matrix to accommodate oil at the spherulite boundaries.

Using the oversimplification that the surface area of a truncated spherulite is roughly that of a sphere, one calculates that a drop in the spherulite radius from 50 μ to 5 μ increases the interspherulitic surface area available for rejected oil by a factor of 100.   (This change in spherulite size is typical of that found on going from unnucleated to nucleated polypropylene.)   Furthermore, since the number of interspherulitic tie molecules per unit area is roughly constant, an increase in the total number of interspherulitic links is expected to accompany the decrease in spherulite size.   The improved physical properties reported below partially reflect this increase.

Figure 7 is an SEM photomicrograph of the core zone in an unstressed, nucleated specimen leached with hexane.   The dramatic drop in the size

Fig. 8. Fractured end of nucleated, oil-filled dogbone specimen showing fibrillar fracture.

of the internal voids resulting from nucleation is obvious in comparison with the left side of Figure 4. The two vertical striations are cutting artifacts.

It is well documented that nucleated nylons, polyesters, and polyolefins may exhibit physical properties superior to those of unnucleated materials but the gains are usually quite modest (10% or less).[8] The strengths and elongations of the nucleated, oil-filled specimens are presented in Table I for comparison with those of the unnucleated samples. Very substantial gains are observed in most properties. The ultimate tensile strength increases 40–50% and the elongation, 90–100% on adding 0.01% phthalocyanine. Although appreciable stress whitening was observed in the nucleated samples at modest strains (5%), there was no evidence of catastrophic voiding at the yield point. The tensile bars continued to elongate break without fracture in the core region. In contrast to the unnucleated specimens, failure was accompanied by fibrillation at the neck as observed for the oil-free polypropylene copolymer. A typical fracture surface is shown in Figure 8.

Variations in Mold Temperature

The absence of severe phase separation and voiding outside of the core region in unnucleated samples has been noted. It has been shown by Kantz et al.[3] that the thickness of the exterior zones (principally zone 2) can be increased substantially by reducing the melt temperature. It was our hope to reduce the degree of phase separation in the relatively thin ($1/_8$ in.) molded pieces by reducing the fraction of large core spherulites.

The third series of samples was molded from the unnucleated blend at successively lower melt temperatures from 180°C down to 140°C. At

TABLE II
Mechanical Properties of Injection-Molded Oil-Flled Polypropylene vs.
Melt Temperature

Melt temp., °C	DSC crystal-linity,[a] %	Yield strength, psi	Ult. tensile strength, psi	Elonga-tion, %	Flexural modulus, psi	Flexural yield strength, psi × 10⁻⁴
140	28	2056	2806	596	1714	3.734
150	33	2022	2325	560	1549	3.398
160	30	1843	1633	546	1421	2.825
170	31.5	1665	1243	341	1319	2.761
180	29	1558	1378	115	1261	2.600

[a] ΔH_f = 57 cal/g for 100% crystalline polypropylene [I. Kirshenbaum, Z. W. Wilchinksy, and B. Croton, *J. Appl. Polym. Sci.*, 8, 2723 (1964)].
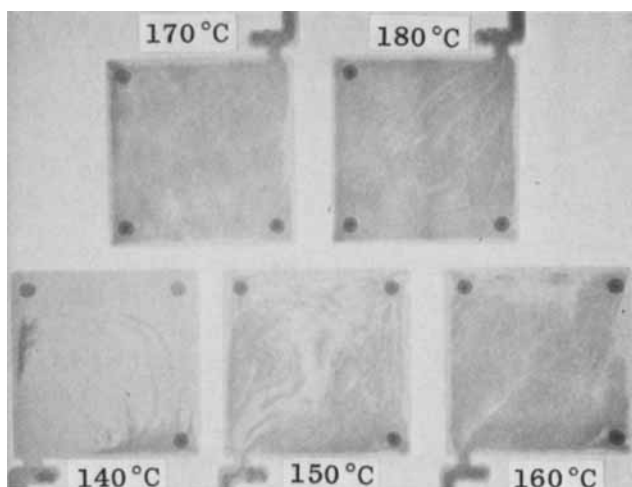

Fig. 9. Variation in internal voiding for samples molded at 140, 150, 160, and 170°C.

temperatures less than 140°C, the mold would not fill completely. Figure 9 shows the decrease in internal voiding resulting from reduced melt temperatures for samples aged for several weeks at room temperature. No increase in opacity is observed in large regions of the low-temperature samples. The different morphological zones could still be identified in thin sections cut from these specimens although the boundaries were not as distinct. The core zone had shrunk to one third of the sample thickness in bars molded from 140°C and 150°C melts and the average spherulite diameter in the core was roughly half that of samples obtained from the 180°C melt. Apparently, incomplete destruction of seed crystals at the lower temperatures increased the nucleation density in the core. The data in Table II show that there is no significant change in the level of crystallinity in the molded parts with melt temperature as determined by DSC. Furthermore, leaching of 20-μ sections taken at various levels from the exterior to the in-

terior of the bars showed the oil was distributed uniformly through all sections. This evidence indicates that a drop in melt temperature reduces the tendency toward phase separation and voiding by decreasing the thickness of the core and by reducing the average spherulite size in that core.

The results of mechanical tests on these samples are presented in Table II. In almost every case, higher melt temperature led to a drop in mechanical properties although, as noted above, there was little change in the overall level of crystallinity. Again, the most startling change in properties was in the elongation of the tensile specimens. An increase in melt temperature from 140°C to 180°C dropped the elongation to break from 600% to just over 100%. Ultimate tensile strength dropped 51% for the same temperature increase, while other properties fell 25–30% of their value at 140°C.

CONCLUSIONS

1. Injection-molded samples of unnucleated, oil-filled polypropylene show massive phase separation within 24 hr after molding. This phase separation results from rejection of oil to the spherulite boundaries in the core zone. It is undoubtedly accompanied by internal voiding as evidenced by the severe whitening and low strength of these samples.

2. The addition of a nucleating agent such as copper phthalocyanine dramatically reduces the degree of phase separation by increasing the interspherulite surface area. No voiding is observed for many months after molding and the physical properties are increased by an unexpected amount. In particular, the ultimate tensile strength is as much as 50% greater and the elongation is as much as 100% greater.

3. Reduction of the melt temperature also diminishes the observable phase separation in molded, filled polypropylene but not to the same extent as a nucleating agent. Improvement results both from an increase in the thickness of the outer zones where no voiding is observed as well as from a decrease in the size of core spherulites. Leaching experiments on thin sections show that in all cases oil is evenly distributed from the interior to the exterior of the molded bars.

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