

Interactions in the System Isotactic Polypropylene–Calcite

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SYNOPSIS

Interaction in the system isotactic polypropylene–calcite was investigated using X-ray diffraction and transmission electron microscopy. Calcite acts as a weak nucleation agent for polypropylene crystallization and its activity could be increased or decreased by a suitable surface treatment. Investigation of the morphology on the polypropylene–calcite interface using calcite single crystals disclosed the tendency of polypropylene for epitaxial crystallization along preferred substrate crystallographic directions. This tendency was analogous to polymer crystallization on other ionic crystals.

INTRODUCTION

The properties of filled polymers differ in many respects from those of unfilled ones. The structure, morphology, and resulting properties depend mainly on the size, shape, orientation, amount, and distribution of filler particles and on the interaction of polymer and filler. For a given filled polymer system, knowledge of these factors is of great importance. It is relatively easy to gain information on filler structure and morphology. Problems arise in evaluating the interaction between a crystalline polymer and a solid filler.^{1,2} According to their action, fillers are usually classified as inert or active. In case of active fillers, one can expect the filler influencing not only the process of polymer crystallization and melting but also the structure and morphology at the polymer–filler interface. This effect depends mainly on the character of the bond between polymer and filler. In polymers without functional groups which are capable of forming chemical bonds with the filler substrate (which is, e.g., the case for polyolefines filled with mineral fillers), bonding is realized by weak intermolecular forces (electrostatic, induced dipole, and dispersion forces). Their energy is low and consequently the interfacial adhesion is lower than inside the polymer, where physical chain entanglements increase the cohesion.

It is not yet understood whether the first mono-

molecular polymer layer on the filler surface has an amorphous, mesomorphous, or crystalline character. Nevertheless, the setting down of molecular segments in an extended conformation with various perfection of lateral order could be assumed. Epitaxial overgrowth of the same polymer on substrates with different lattice parameters indicates that the polymer surface layer has an amorphous or mesomorphous structure.^{3,4} Usually, on this layer the polymer crystallizes in a stable crystal modification.⁵

Our investigation of the crystallization of linear polyethylene and its composites with solid fillers has shown the nucleation activity of talc and kaolin.² Morphological examination proved that polyethylene tends to crystallize on the basal planes of sheet silicates, epitaxially, in such a way that a system of parallel lamellae, oriented perpendicular to the basal plane of the substrate, grows out from the filler surface. Epitaxial lamellae tend to be aligned in a pseudohexagonal array, suggesting that polyethylene lamellae nucleate along rows of equally charged ions in the basal plane of sheet silicates. Further, we have found that isotactic polypropylene (PP) crystallizes on the talc surface in the same way as polyethylene does, in spite of differences in chain conformation.⁶ Figure 1 shows PP epitaxial overgrowth on a flat talc particle.

Therefore, we decided to investigate whether such crystallization of PP might be typical, also, for other filler surfaces. In this contribution, we report on crystallization, nucleation, and morphology in the system PP–calcite, which is widely used in practice.

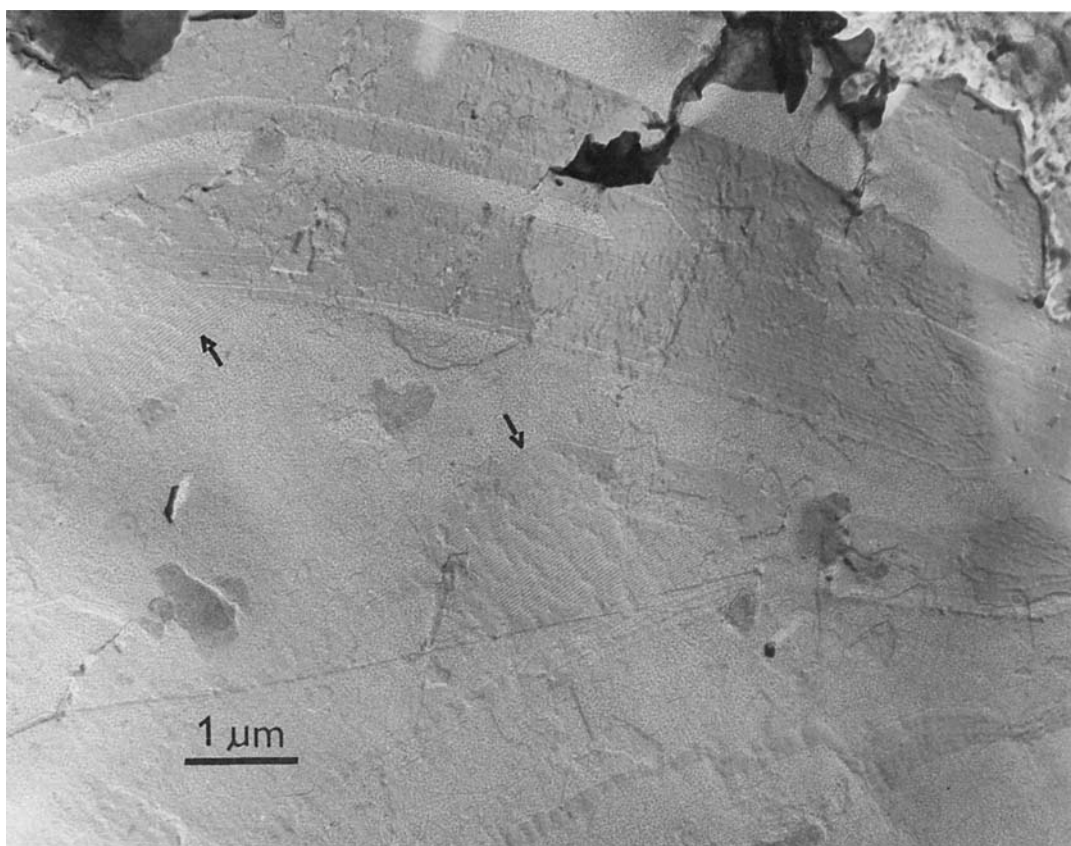


Figure 1 Fracture surface of the composite PP-talc. Arrows point to places with PP epitaxial overgrowth. Au-decoration.

EXPERIMENTAL

Materials

The polymer was commercial PP Mosten 58412 (Czechoslovak product) with melt flow index 3.5,

98% isotacticity, and $\bar{M}_w/\bar{M}_n = 9$. The filler was CaCO_3 Durcal (Omya, France) of the calcite type with particle size in range 1–10 μm . Compositions were prepared by mixing polymer powder with filler and subsequent melt pressing to sheets. Calcite single crystals were supplied by Monokrystal (Turnov,

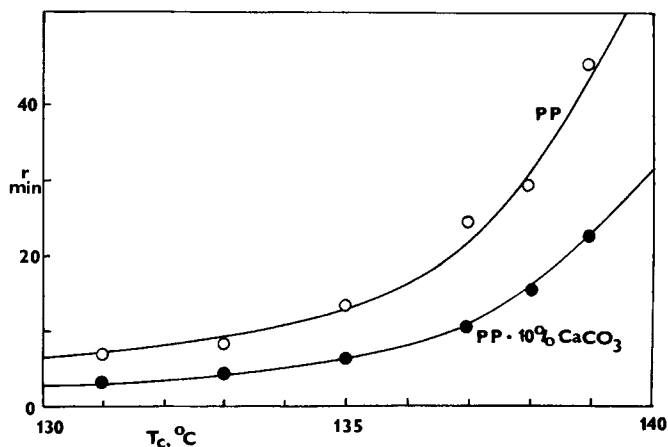
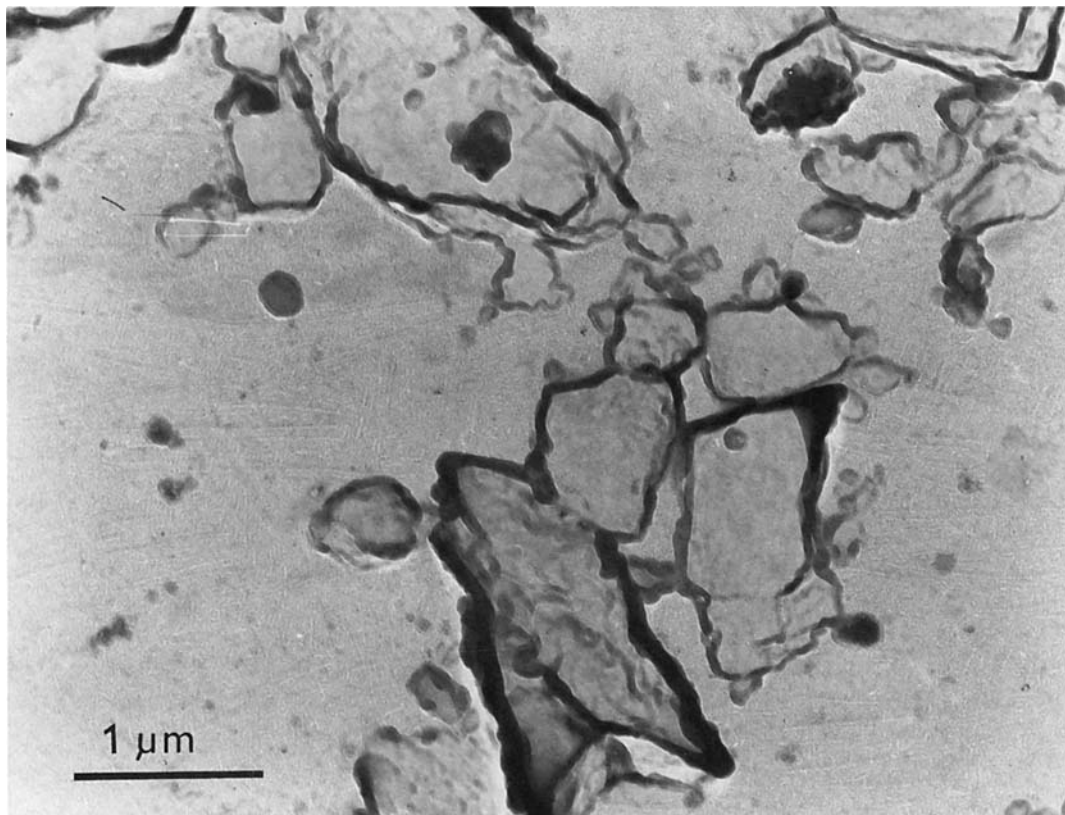


Figure 2 Temperature dependence of the isothermal crystallization half-time r of PP (O) and its composite with 10% (w) of CaCO_3 (●).

Table I The Effect of Various Additives on the Number of Heterogeneous Nuclei (N) in the Composite PP + 10% CaCO₃^a

Sample	Additive, 0.5%	$N \times 10^{-5}/\text{cm}^3$	Type of Action
PP	O	1.38	
PP	Phthalic acid	134	Primary nucleation agent
PP	Benzoic acid	20.4	Secondary nucleation agent
PP	Slovasol O	3.27	Secondary nucleation agent
PP	Ca-stearate	1.37	Inert
PP	Stearic acid	0.48	Destroys or blocks heterogeneous nuclei in polymer
PP	KOH	0.49	Destroys or blocks heterogeneous nuclei in polymer
PP	Mg-stearate	0.006	Destroys or blocks heterogeneous nuclei in polymer
PP	CaCO ₃	11.95	Weak primary nucleation agent
PP + 10% CaCO ₃	O	10.58	Weak primary nucleation agent
PP + 10% CaCO ₃	Phthalic acid	707	Increases nucleation of CaCO ₃
PP + 10% CaCO ₃	Benzoic acid	67	Increases nucleation of CaCO ₃
PP + 10% CaCO ₃	Slovasol O	2.15	Decreases nucleation of CaCO ₃
PP + 10% CaCO ₃	Ca-stearate	1.04	Decreases nucleation of CaCO ₃
PP + 10% CaCO ₃	Stearic acid	0.707	Decreases nucleation of CaCO ₃

^a Crystallization temperature 138°C.

**Figure 3** Free surface of the PP-CaCO₃ composite. Au-decoration.

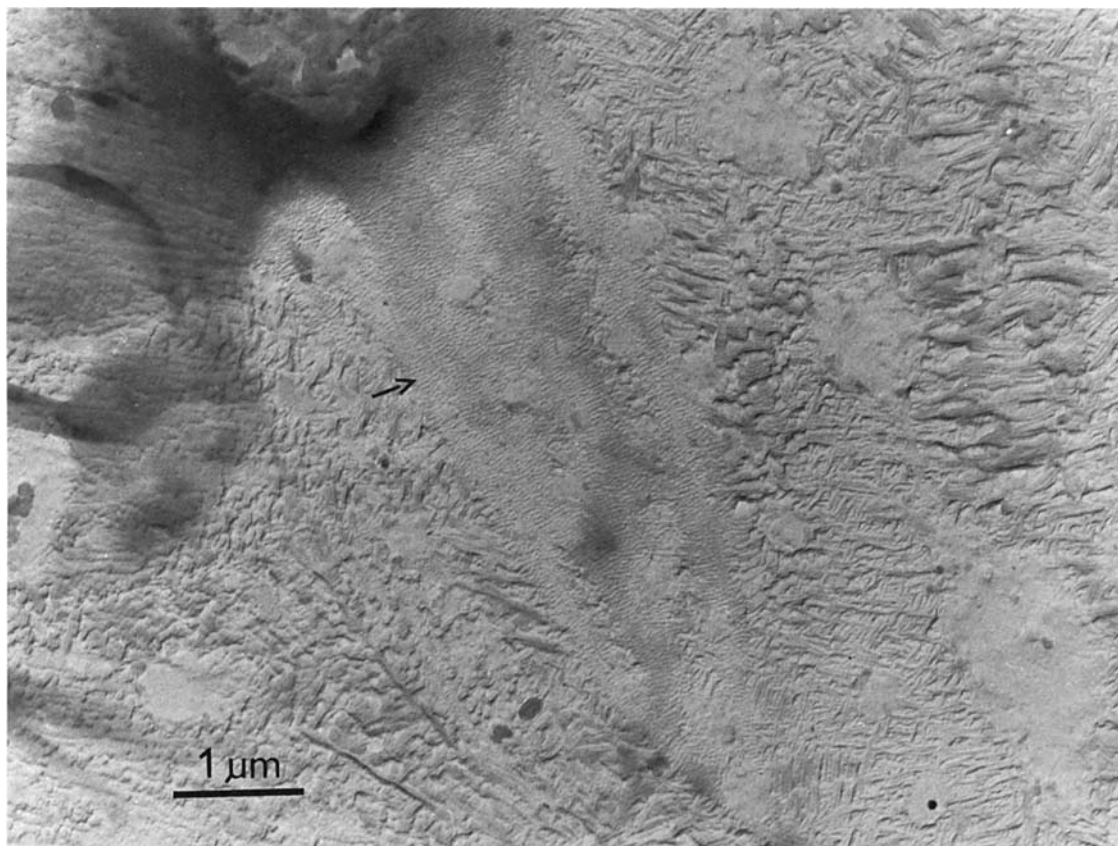


Figure 4 Free surface of the composite PP-CaCO₃. The arrow marks parallel PP lamellae on the filler surface. Pt-shadowing.

Czechoslovakia). All other materials were of chemical purity.

Isothermal Crystallization

The isothermal crystallization rate of PP and its composites with calcite was measured by X-ray diffraction and thermo-optical methods, as described earlier.² Samples were melted for 14 min at 220°C and cooled down to the isothermal crystallization temperature T_c . The crystallization rate was characterized by the half-time, $r \pm 1$ min. The number of crystallization nuclei, N , was determined from the r values and the spherulite growth rate v . In a spherulitic crystallization, controlled by heterogeneous nucleation, where the Avrami exponent $n = 3$,

$$N = 3 \ln 2 / (4\pi v^3 r^3).$$

Morphology Examination

Sample morphology was examined by light and transmission electron microscopy. For electron microscopy, replicas of fracture-free or selectively

etched⁷ surfaces were used. Crystallization of PP on calcite single crystal cleavage surfaces was done as follows: On the fresh surface of a small calcite cleavage rhombohedron (approx. dimensions 10 × 10 × 1 mm), a piece of PP sheet (0.5 mm thick) was laid down and the composite was melted *in vacuo* for 14 min at 220°C and crystallized at a chosen T_c , in the range of 130–160°C. After stripping the PP layer

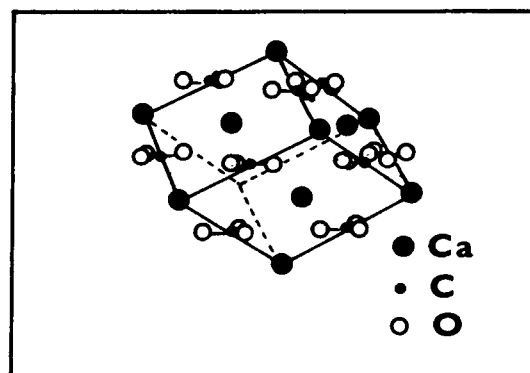


Figure 5 Scheme of the calcite cleavage rhombohedron atomic structure.

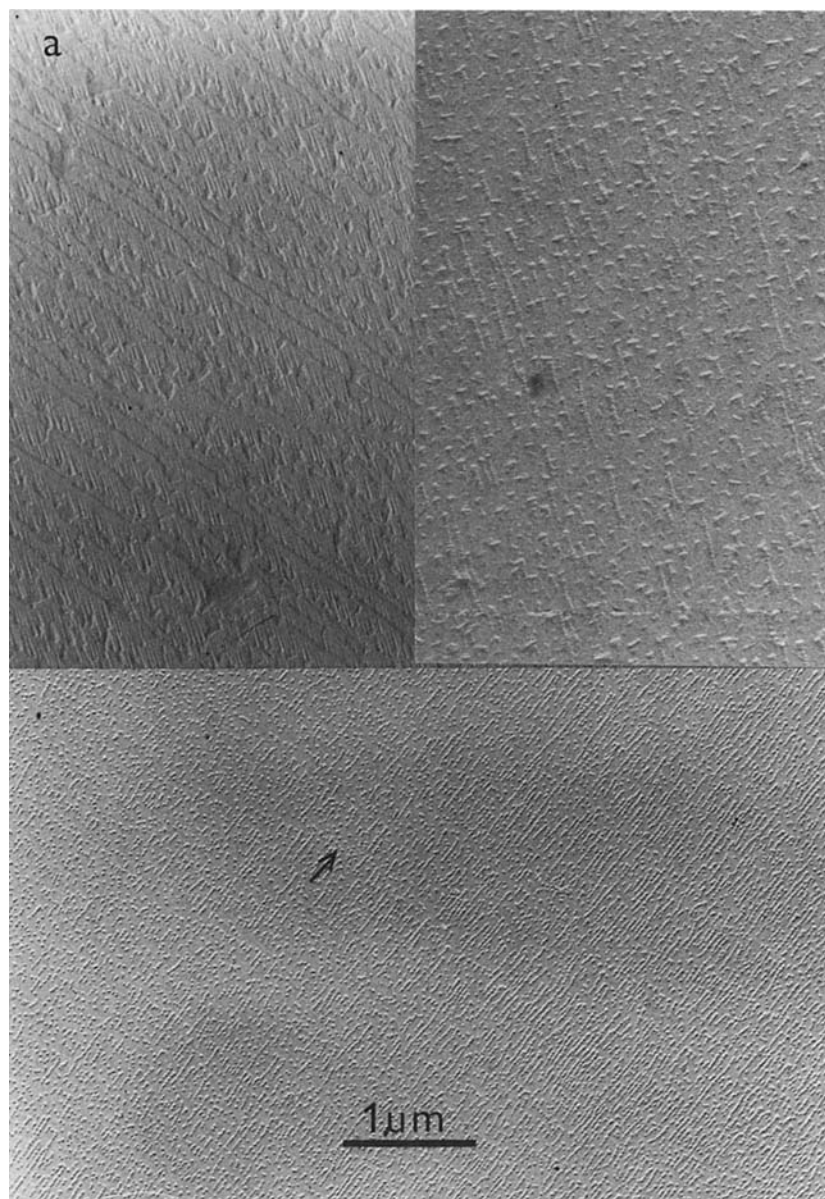


Figure 6 (a, b) Typical interfacial morphology of PP on the calcite single crystals. Arrows show principal substrate directions. Pt-shadowing.

off the calcite, the morphology of both contact planes was replicated. A thin PP overgrowth was prepared, either by vacuum evaporation of PP on calcite single crystals or by melt crystallization of an ultrathin PP film deposited on a calcite single crystal from 0.5% xylene solution.

RESULTS AND DISCUSSION

Isothermal Crystallization

Figure 2 shows isothermal crystallization rate measurements for PP and its composite with 10% (w)

of CaCO_3 , at various T_c 's. From r values, it follows that filled samples crystallize much faster than PP alone. The calcite particles evidently increase the number of heterogeneous crystallization nuclei, and this results in a higher crystallization rate. From the known distribution of filler particle sizes, it follows that the composition of PP with 10% CaCO_3 , contains approximately 10^{11} particles per cm^3 . The addition of this amount of CaCO_3 particles leads to an increase in heterogeneous nuclei (N) from about 10^5 to $10^6/\text{cm}^3$ in the composition, at $T_c = 138^\circ\text{C}$. This means that only a small fraction of filler particles acts as nuclei. The filler did not influence the

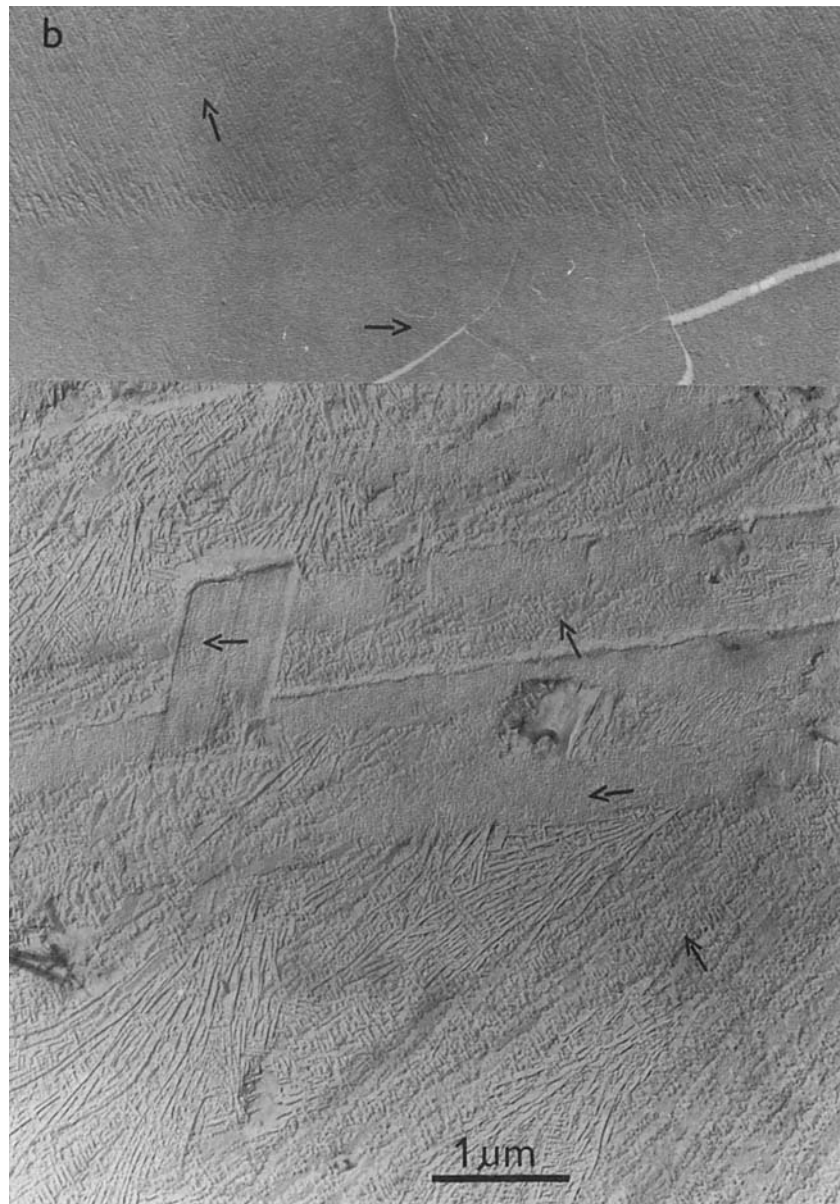


Figure 6 (Continued from the previous page)

crystal structure of the PP matrix, which was the stable monoclinic α -modification.

In technical practice, surface modification of fillers is often applied by various additives. The aim of such surface modifications is to reinforce the bond between polymer and filler. This is analogous to the preparation of emulsions using emulsifiers. Additives serve to overcome the low compatibility of blend components, forming a monomolecular layer on the filler surface, oriented with the polar part of the molecule toward the filler surface, and the nonpolar part toward the nonpolar polymer. For example, stearic acid is often used in blends of PP

with CaCO_3 . Even though this idea is correct, cohesion between the impregnated filler and polymer matrix would not be increased, because the bond between the nonpolar additive part and the polymer results from weak intermolecular dispersion forces. As long as macromolecular chains, compatible with the polymer matrix, are not chemically bonded to the filler surface, interfacial adhesion cannot be increased. In nonpolar polymers, there always will be the problem of polymer immiscibility. The improvement of some properties of blends with surface-modified fillers could be due rather to other effects (e.g., to a better filler dispersion or wetting). Instead

of influencing the tie between polymer and filler, low molecular weight additives may affect the nucleation and crystallization process. The effect of various additives on polymer nucleation may be manifold.^{8,9} Omitting the case of inert additives, additives may increase or decrease the number of active nucleation centers. Table I shows some examples of divergent additive effects in the composite PP + 10% CaCO₃.

In elucidating such effects one has to be careful, because they may result from interaction of the additive with both the filler and/or with original heterogeneities present in the polymer. As the additive can migrate from the filler surface into the polymer, it is also useful to examine its action in the neat polymer. Increased nucleation ability is usually due to the introduction of new solid nucleation centers by the additive (phthalic acid, CaCO₃), but nucleation activity may be also due to the additive being liquid at crystallization conditions, which enables better wetting of the filler or otherwise inactive heterogeneities in the polymer. By such a secondary action it is possible to explain the nucleation action of benzoic acid (melting temperature 122.4°C) in

PP alone and in its composite with CaCO₃ at $T_c = 138^\circ\text{C}$. Common surfactants (Slovasol O) may act similarly. Additives that do not influence the original heterogeneities in the polymer, may decrease nucleation by the filler (Ca-stearate). Some additives block or destroy nucleation centers in PP and/or in the filler (stearic acid). As the original nucleation centers in PP are mainly polymerization catalyst residues,⁶ it is possible to markedly decrease their number by alkali reagents.

The results shown indicate that the situation, concerning the interaction at the PP-CaCO₃ interface, may be considerably complicated. With active fillers, such as CaCO₃, we are able to classify the type of their action and to increase or decrease their nucleation activity. However, efforts to increase the adhesion between polymer and filler merely by a physical surface modification using low molecular weight substances seem less likely.

Morphology of the Composite PP-Calcite

The morphology of PP is characterized by a lamellar spherulitic texture consisting mainly of α -spheru-

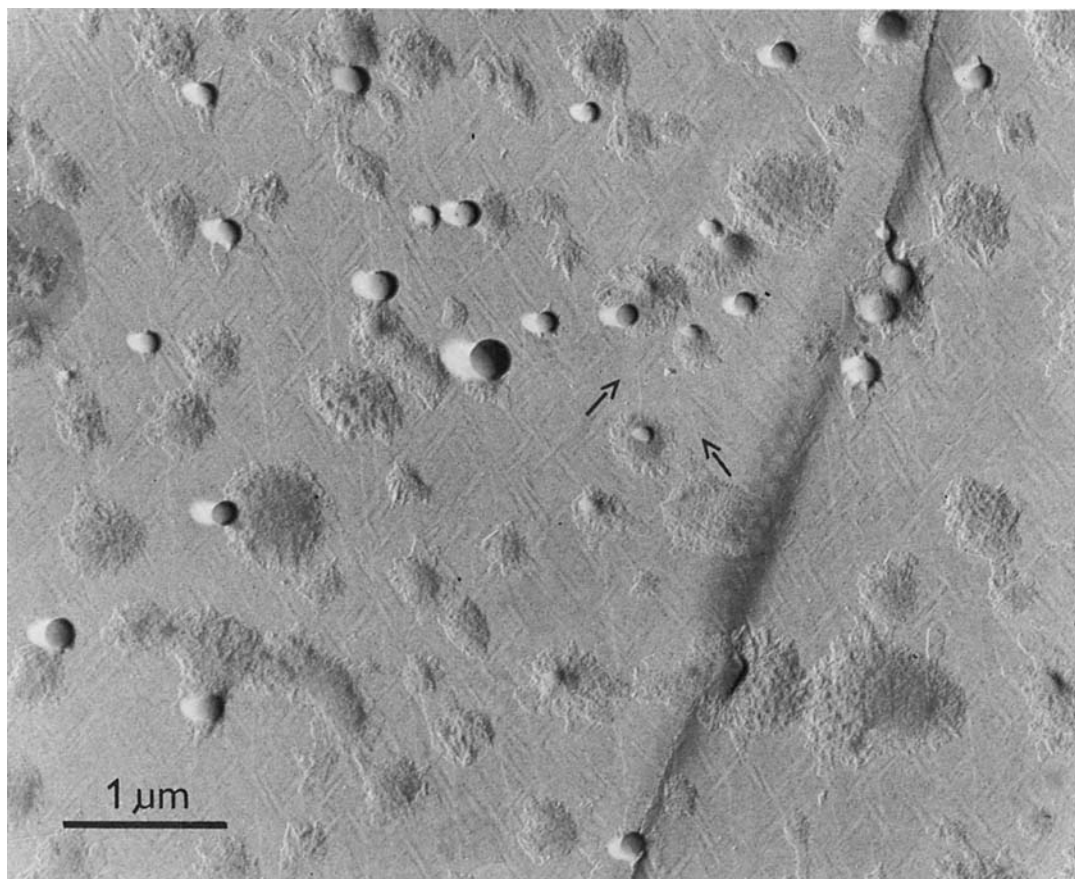


Figure 7 Morphology of thin PP film evaporated in high vacuum on the calcite cleavage face. Arrows show substrate directions of equally charged ion rows. Pt-shadowing.

lites with the typical crosshatched lamellar texture.¹⁰ With increasing amounts of CaCO_3 in the composite, the spherulite number increased and finally at about 40% (w) of CaCO_3 no individual spherulites were seen; the morphology was characterized by randomly oriented lamellar stacks. Filler particles were distributed evenly in the polymer matrix and there was no preference for being situated in central or marginal spherulite parts. Since PP wets CaCO_3 particles well, there were no voids or gaps on the PP- CaCO_3 interface and no separation tendency was observed. The interfacial layer was clearly distinct and its thickness was about $0.1 \mu\text{m}$ (Fig. 3). Beyond this layer no influence of the filler on PP morphology was observed.

Generally, small irregular filler particles are not favored for the study of interfacial morphology. In spite of this, we were able to observe, with some larger, flat CaCO_3 particles, the tendency for PP to exhibit regular lamellar ordering, different from the texture of the surrounding PP matrix. On the CaCO_3

surface, PP forms parallel lamellar striations (Fig. 4).

A detailed investigation of the structure and morphology at the interface was possible only with calcite single crystals. Calcite crystallizes with a hexagonal unit cell ($a = 0.4989 \text{ nm}$, $c = 1.7062 \text{ nm}$) and could be cleaved to rhombohedra along the $10\bar{1}1$ face (Fig. 5). The cleavage faces are not ideally smooth; they often contain fine striations and steps. We have investigated the morphology of both contact faces. This was possible because, on the calcite surface, small amounts of PP remained firmly attached after stripping off the polymer layer. The morphology on both sides of the interface was essentially identical, although it varied slightly from place to place. The cleavage surface was covered unevenly; there were areas with different degrees of polymer ordering, but in some places a general tendency for parallel alignment of lamellar rows was apparent (Fig. 6). A detailed inspection of such striations disclosed that they are formed by the co-

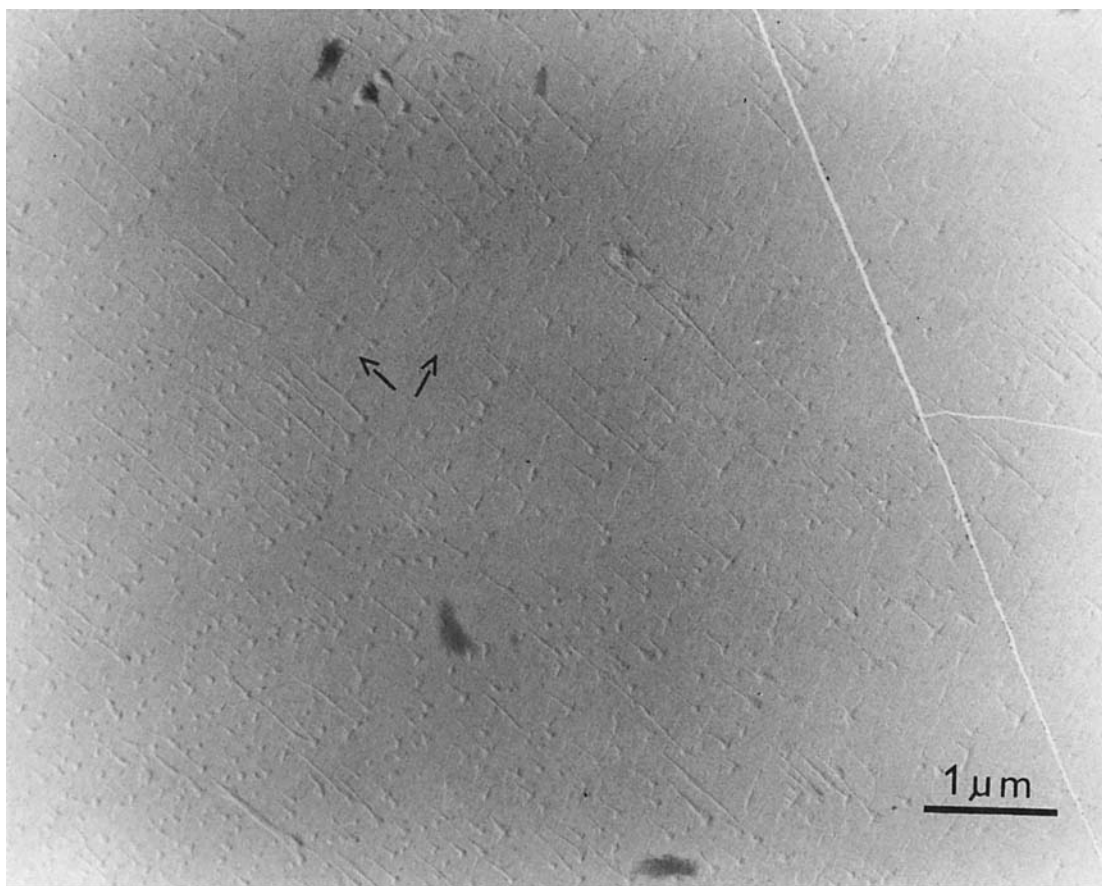


Figure 8 Morphology of thin PP film on the calcite cleavage face, prepared from dilute xylene solution and subsequent melt crystallization. Arrows show directions of substrate equally charged ion rows. Pt-shadowing.

alescence of small lamellar blocks [Fig. 6(a)] oriented perpendicular to the striation direction and to the calcite surface. The lamellar blocks nucleate on the most active substrate locations. The detailed structure of the calcite surface, where epitaxial crystallization (and we believe also preferred PP nucleation) starts, remains to be elucidated.

The orientation of small blocks and large striations agrees mostly with important substrate crystallographic directions, namely along diagonals and sides of the cleavage rhombohedra. These directions represent rows of equally or oppositely charged ions

respectively (Fig. 5). It seems that the first PP overgrowth takes place along equally charged ion rows of the substrate [along diagonals of the cleavage rhombohedra as may be seen on calcite surfaces where PP has crystallized in a thin layer either by vacuum evaporation of PP (Fig. 7) or by melt crystallization of an ultrathin film prepared from a dilute xylene solution (Fig. 8)].

In this respect, the situation in the system PP-CaCO₃ does not differ from that with other ionic substrates (NaCl, KCl, KI, etc). Figure 9 shows that the morphology of PP crystallized on NaCl single

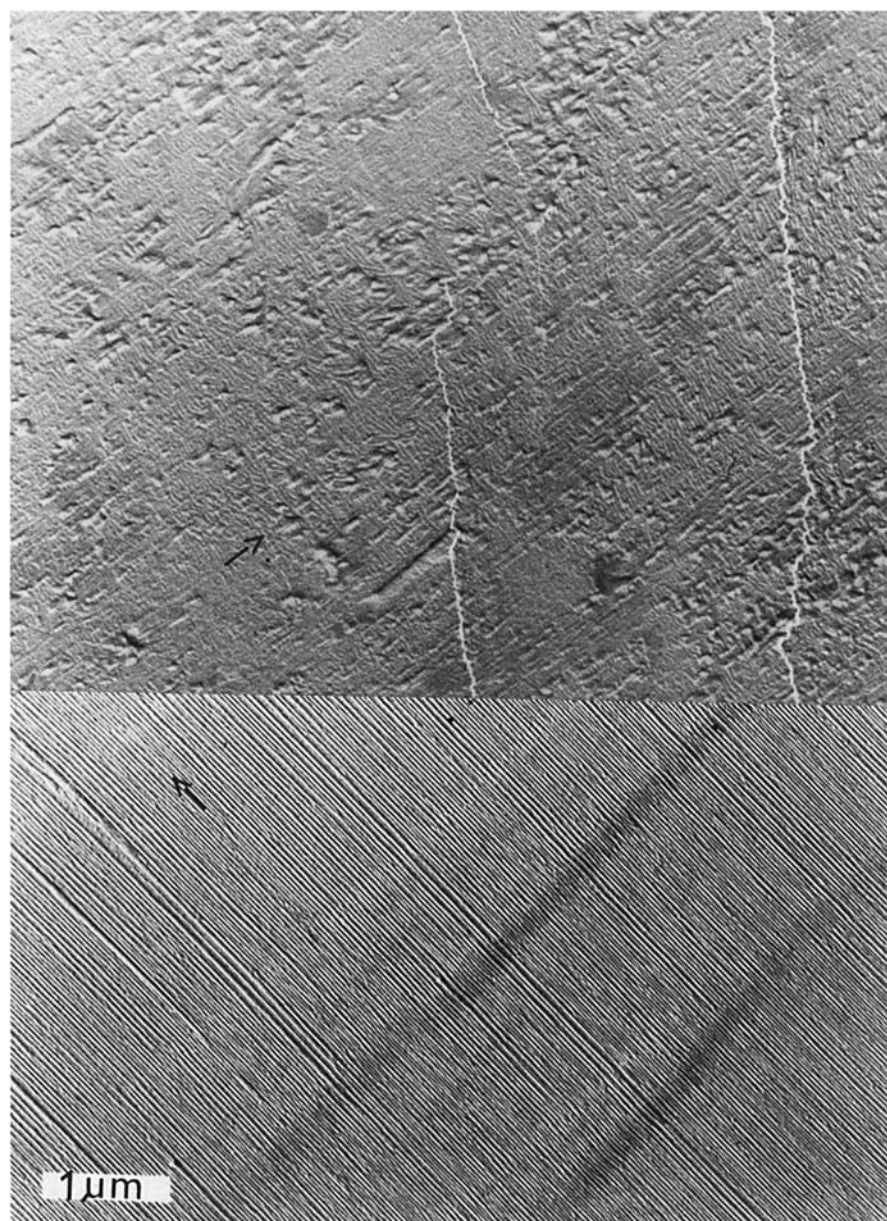


Figure 9 Morphology of PP crystallized on NaCl single crystal cleavage face. Arrows show the 110 substrate direction. Pt-shadowing.

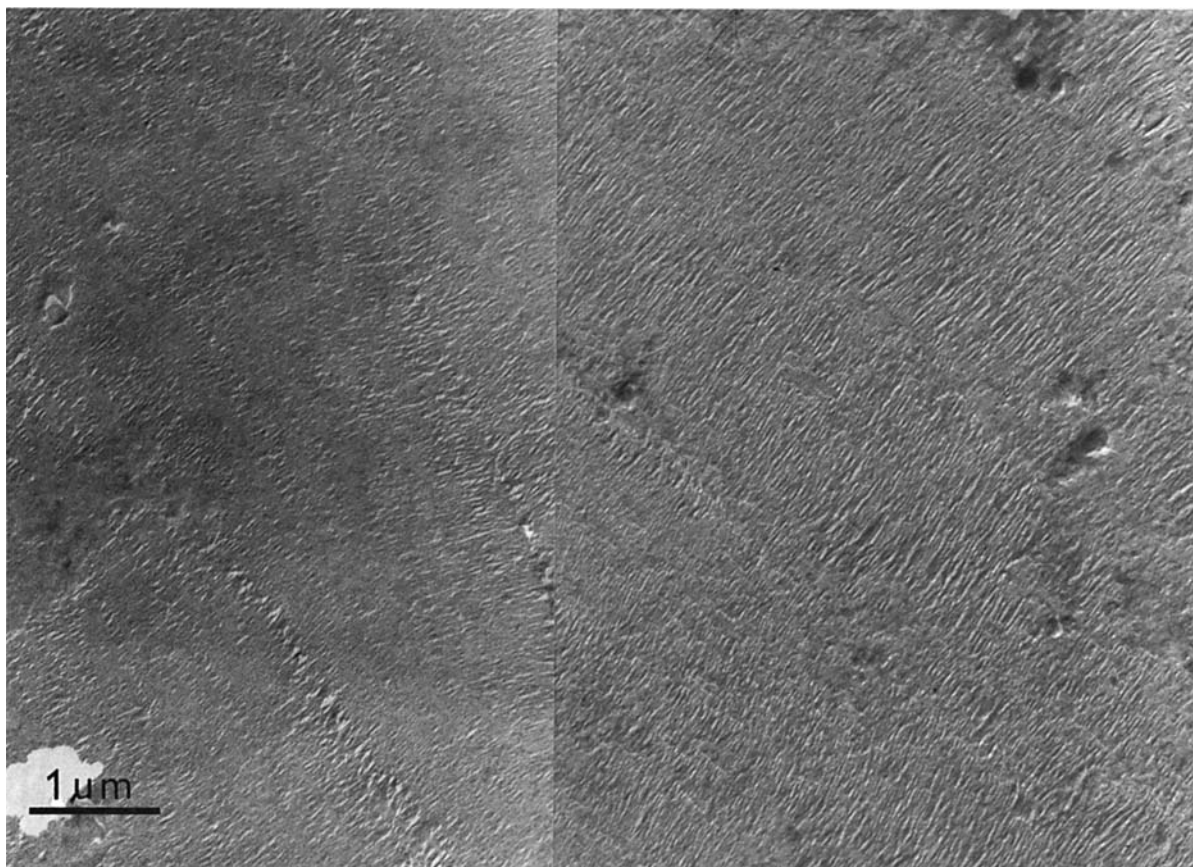


Figure 10 Morphology of PP crystallized on NaCl single crystal cleavage face covered by a thin carbon film. Pt-shadowing.

crystals does not differ from that seen on the calcite single crystals. In addition to the regular deposit mentioned, we have observed on the calcite surface, also, long and thick polymer striations situated along cleavage steps and surface irregularities.

Considering the regular epitaxial crystallization of polymers, we must bear in mind that the surface of ionic crystals is far from being smooth and homogeneous. Polymer crystallization takes place, preferentially, on minute surface steps,⁶ running parallel to ionic rows, formed in places where spiral dislocations intersect the cleavage surface. Such intersections represent local charges, discontinuously changing along the step. Such charges, together with a more efficient action of intermolecular forces along the steps, cause a preferred nucleation on the steps. Dislocations in ionic crystals are sources of vacancies with a charge and so the cleavage surface of the crystal is electrically heterogeneous. The vacancies of the same electric charge organize themselves into domains with dimensions about $0.1\text{--}1\ \mu\text{m}^2$. On the border of domains with opposite charges, a marked gradient of the electric field is formed which exer-

cises an induction influence on polymer segments. Besides, further localized forces, with a markedly long range ($\sim 10\ \text{nm}$) influence a preferred nucleation above the substrate surface.^{4,5} This effect may be traced by a local thick overgrowth and by the fact that their influence is not stopped by a relatively thick (5–10 nm) amorphous carbon interlayer (Fig. 10).

From these facts, it follows that the interaction between polymer and a solid filler depends mainly on two factors: substrate attraction forces and substrate topology and roughness.

CONCLUSION

Investigation of the crystallization behavior and morphology of PP filled by calcite has shown a weak nucleation activity of calcite for PP crystallization. This activity could be increased or diminished by calcite surface modification by a suitable additive.

The morphology at the PP–calcite interphase proved the tendency of PP to epitaxial ordering in

parallel lamellae growing out of the calcite cleavage face, oriented in significant substrate crystallographic directions. On the unevenly covered calcite cleavage surface, the effect of surface topology and locally different attraction forces was apparent.

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