Influence of Chalk and its Surface Treatment on Crystallization of Filled Polypropylene

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Synopsis

Isotactic polypropylene has been shown to crystallize from the melt spherulitically at intermediate undercoolings (100 - 130°C) in the presence of a high amount (40 wt %) of chalk (calcium carbonate). Linear growth rate is not remarkably affected by the presence of a filler. Both nonisothermal and isothermal crystallization DSC experiments indicate that chalk acts as a weak nucleant. Introduction of liquid [oligomer of ethylene oxide (OEO), $M_w = 300$] at polymer–filler interface lowers the nucleating activity of chalk. Analysis of crystallization kinetics in Avrami coordinates, followed by dimensional-analysis correction for the case of nonintegral values of exponents, indicates that the amount of extra "chalk nuclei" is approximately constant in the range of 100–130°C while the amount of OEO-modified "chalk nuclei" decreases with the increase of the crystallization temperature. Comparison of the melting endotherms indicates that filled melt-crystallized material contains higher fraction of lower melting crystallites than unfilled polypropylene. This fraction is also higher in the case of polypropylene filled with unmodified chalk. Nucleating activity of chalk has been shown to depend upon its crystal structure (calcite or aragonite), surface topography, and aggregation.

INTRODUCTION

Mineral fillers added to semicrystalline polymers usually cause deterioration of mechanical properties. This applies to such properties as ductility (elongation at break) and impact strength, i.e., the features which often decide the practical importance of these composites. Simple analogy to filled rubbery or glassy polymers would suggest dealing with this problem by increasing the polymer–filler adhesion. However, application of various coupling agents in systems consisting of semicrystalline polymers with mineral fillers gives only partially satisfactory results.[1] In a series of studies on polyolefins, starting with stress analysis around the filler particles,[2-5] we have shown that introduction of oligomeric liquid (e.g., oligomer of ethylene oxide) at polymer–filler interface gives much better results, leading to a significant improvement of tensile (elongation at break) and impact properties. Further investigations proved the correctness of the supposition for preferring a liquid interfacial agent, i.e., one incapable of transmitting static tension load. It has been concluded that it reduces the stresses arising around the filler particles in the polymer matrix subjected to deformation, thus preventing premature crack formation in these areas. The oligomeric nature of liquid has been shown to be the condition providing that it will not exhibit corrosive action towards the polymer matrix.

The present work deals with the problem of the influence of the liquid interfacial layer on polymer–filler interface morphology. Nucleating activ-

ity of chalk has been supposed to be the main factor controlling its influence on the supermolecular structure of the polymer–filler interface. Thus not only direct observation (TEM, optical microscopy) but also experiments giving information about the crystallization process (nonisothermal and isothermal crystallization in DSC) and about some parameters of the arising structure (DSC melting, X-ray diffraction) were performed. Isotactic polypropylene filled with precipitated chalk was used as the object of investigations. The reason for such a choice was not only the practical importance of both materials but also the relative ease of performing crystallization kinetics experiments with polypropylene (growth rate less temperature sensitive than in polyethylene), and well-defined crystal structure of chalk (calcium carbonate) makes it a good object of fundamental studies. As calcium carbonate exhibits crystallographic polymorphism calcite-aragonite (especially when obtained by precipitation), attention has been paid to the role of this polymorphism in the effects under discussion.

EXPERIMENTAL

Materials and Sample Preparation

Isotactic polypropylenes (PP), J-400 (Polish production), in the case of composites containing 40 wt % of chalk, and Moplen C-30-G (Montedison), in the case of composites containing 1.2 wt % of chalk, were used throughout the studies. Oligomer ($M_w = 300$) of ethylene oxide (OEO) (Polish production) was used as chalk modifier. Technical grade precipitated chalk (Polish production, factory Inowroclaw) was used as a filler. For the purpose of studying the nucleating activity of calcite use was made of large monocrystals of calcite.

Highly filled samples were prepared by threefold extrusion (in order to obtain good dispersion) at die temperature 200°C. Liquid modifier was added to polypropylene pellets in the relation of 10 wt % of chalk, following which wetted pellets were mixed with chalk and supplied to the extruder. The following compositions were prepared:

   100 wt % polypropylene (PP)
    60 wt % PP + 40 wt % chalk (PP + C)
    60 wt % PP + 40 wt %(90 wt % chalk + 10 wt % OEO) (PP + MC)
    90 wt % PP + 10 wt % OEO (PP + M).

Samples containing low amounts of the filler were prepared by means of Brabender mixer (mixing time 5 min, rotational frequency 100 rpm, 190°C). The filler and modifier were premixed with polymer pellets in the same way as in the case of extrusion of mixed samples. The following compositions were prepared:

   100 wt % PP C-30-G (PP1)
   98.8 wt % PP C-30-G + 1.2 wt % chalk (PP1 + C)
   98.8 wt % PP C-30-G + 1.2 wt %(90 wt % chalk + 10 wt % OEO
                 (PP1 + MC)

The samples were subjected to further preparation needed for each particular experimental techniques.

Methods

Optical Microscopy. For the purpose of simultaneous observation of the crystallization process of PP, PP+C, and PP+MC on the microscope hot stage, thin (20–30 μm) films were prepared and placed together on a single microscopic glass in such a way that they could be observed at the same time. The sample was first annealed at 230°C, and then cooled to the crystallization temperature (130, 120, or 110°C). The crystallization temperature has been set with the accuracy of 1°C and maintained within the interval $\pm$ 0.05°C. The crystallization process was recorded photographically, and the growth rates were determined.

Transmission Electron Microscopy. TEM observations were performed on thin films of PP1+C obtained by casting from 0.2 wt % solution in boiling xylene on hot (230°C) glycerol surface, annealed for 10 min, and transferred with the dish onto the hot stage kept at crystallization temperature (ranging from 110 to 130°C). Crystallized films were then carried onto the surface of distilled water from which they were picked on the microscope grids. Observations were carried out using Tesla BS-500 microscope at 90 kV.

Differential Scanning Calorimetry. Measurements were performed with the aid of Perkin Elmer DSC-2 apparatus on the samples of highly filled polypropylene (PP, PP+C, PP+MC, PP+M). Both nonisothermal (annealing for 10 min at 230°C and cooling rate 10°C min) and isothermal (annealing as before and crystallization at 110, 120 and 130°C) measurements were carried out. After each isothermal crystallization the samples were heated in DSC apparatus at the rate of 10°C/min, and melting endotherms were recorded.

X-Ray Diffraction. X-ray diffraction patterns were recorded by means of DRON 2 diffractometer using Ni-filtered CuK$_\alpha$ radiation.

RESULTS AND DISCUSSION

Optical microscopy observations indicate that, in the considered temperature range, PP and also PP+C and PP+MC crystallize spherulitically (see Fig. 1). It should be emphasized here that in the case of PP+C and PP+MC samples, spherulitic ordering and borders cannot be observed after completion of the crystallization. The reason for this is the presence of the large amount of birefringent chalk particles which makes observation of spherulitic ordering in polarizing microscopy impossible. The interspherulitic borders are also indistinguishable due to high interpenetration of spherulites caused by the presence of chalk particles. It seems that high interpenetration of spherulites may be partly responsible for the fact that the impact strength of polypropylene highly filled with OEO modified chalk exceeds that of pure polypropylene.[4] The influence of spherulites interpenetration on the mechanial properties has been demonstrated for the case of POM doped with POE by Galeski et al.[6]

Growth rate measurements performed with the aid of successively taken photographs show that in the considered temperature range the presence
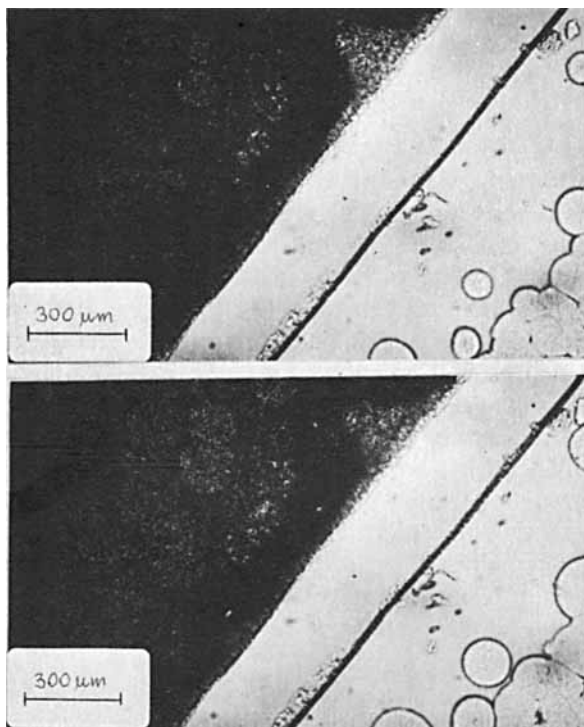
Fig. 1. Subsequent stages of spherulitic crystallization of PP+C (dark area, left) and PP (light area, right). Crystallization on the hot stage of the optical microscope, angle between polarizers $\neq 90°$. Contrast obtained by slight defocusing.

of chalk and of modified chalk within the limits of experimental error does not affect the rate of propagation of crystallization front. The average growth rates are listed in Table I. Such a results suggests that there are no strong interactions between polypropylene and chalk particles. (Strong polymer–filler adhesion would slow down the growth rate as it would act as a hindrance for transport of polymer molecules to the crystallization front.) In such a case the filler particles can be treated as inert entities. Theoretical considerations[7] show that the effect of the presence of such a medium on the growth rate is negligible even for high contents in the crystallizing polymer.

Careful examination of Figure 1 leads to the conclusion that the number of spherulites in chalk filled polypropylene is greater than in pure polymer. This suggests some nucleating activity of chalk. In order to compare its nucleating activity with the activity of commonly used nucleating agents

TABLE I
Crystallization rates of i-PP in the Presence of Chalk

Crystallization temperature (°C)	Growth rate (μm/min)
110	35 ± 4
120	24 ± 2
130	7.5 ± 1.5

for polypropylene, nonisothermal crystallization measurements were performed by means of DSC. Positions of the crystallization peaks are shown in Table II. In view of the results of growth rate measurements the shifts of DSC peaks are indeed indicative of the presence of nucleant in PP+C, PP+MC, and PP+M samples. The magnitude of its nucleating ability is small in comparison with the nucleating ability of good nucleating agents (see also Fig. 1 — the spherulites contain high amounts of chalk outside the center), e.g., Cu(benzoate)$_2$ added in the amount of 0.25 wt %[8] produces a comparable effect as chalk added in the amount of 40 wt %. The presence of liquid at the interface lowers the nucleating ability of chalk. Note that the addition of liquid alone causes a shift of nonisothermal crystallization DSC peak towards higher temperatures.

The results of DSC measurements of isothermal crystallization kinetics are plotted for the case of 130°C crystallization in Avrami coordinates in Figure 2. At other studied temperatures, the plotting of the degree of conversion in Avrami coordinates also resulted in straight lines. The trend observed in nonisothermal crystallization, i.e., nucleating activity of chalk and its lowering by liquid interface modifier is also observed here. The values of Avrami coefficients n and K are listed in Table III. Almost in all cases the values of n are close to 3, which together with the observation of the spherulitic character of crystallization suggests instantaneous nucleation to be predominant in the considered temperature range.

It is usually assumed that nonintegral values of n are caused by such factors as mixed nucleation modes, secondary crystallization, or intermediate dimensionality. Grenier and Prud'homme[9] have shown, however, that also experimental factors such as erroneous determination of the "zero" time and an overestimation of the enthalpy of fusion of polymer at the given moment or at the time when crystallization is completed can cause nonintegrality of n and large (several orders of magnitude) deviations of K. The values of K might be corrected if the true values of the exponent n are known. If we assume that the nucleation was purely instantaneous (true value of $n = 3$) the corrected value of K is approximately equal to

$$K = \frac{4}{3} \pi N G^3 \approx (K_{\text{expt}})^{3/n}$$

where n denotes the experimentally determined value of the Avrami exponent, N is the number of nuclei per volume, G is the spherulite growth rate, and K_{expt} is the value obtained experimentally. Let us denote the

TABLE II
Positions of the Crystallization Peaks of PP in the Presence of Various Additives

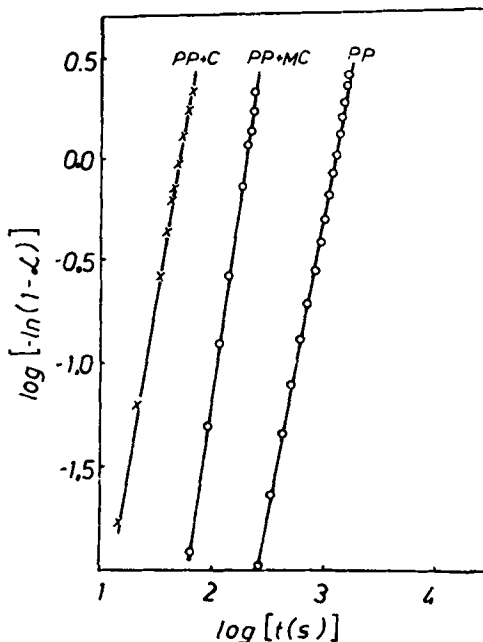| Sample	T_{max} (°C)
PP	108.3
PP + C	120.8
PP + MC	116.8
PP + M	110.8

Fig. 2. Results of DSC isothermal crystallization measurements at 130°C plotted in Avrami coordinates.

nucleation density in pure polymer by $N_p(T)$ and in filled sample by $N_f(T)$. This last quantity can be expressed as:

$$N_f(T) = \frac{N_p(T)V_p + F_s(T)}{V_s} = N_p(T)(1 - f) + F(T)$$

where V_p and V_s are the volumes of the polymer and of the whole sample, $F_s(T)$ is the number of nuclei connected with the presence of a filler (referred hereinafter as "filler nuclei"), $F(T)$ the number of "filler nuclei" per the sample volume, and f the volume fraction of a filler. The values of $N_p(T)$ and $F(T)$ calculated on the basis of growth rate and DSC crystallization kinetics measurements are plotted in Figure 3. For the sake of comparison, the number of chalk particles per sample volume calculated from the average dimensions of filler particles[3] equal to $(5\pm2) \times 10^{10}$ cm^{-3} has also

TABLE III
The values of Avrami coefficients for isothermally crystallized PP, PP+MC and PP+C

	Crystallization temperature					
	130°C		120°C		110°C	
Sample	n	K (s^{-n})	n	K (s^{-n})	n	K (s^{-n})
PP	2.71	2.84×10^{-9}	2.25	2.75×10^{-5}	2.49	6.90×10^{-4}
PP + MC	3.07	6.59×10^{-8}	3.65	5.68×10^{-6}	2.66	2.75×10^{-3}
PP + C	2.73	1.73×10^{-5}	3.43	7.13×10^{-5}	3.23	1.07×10^{-3}

been indicated in Figure 3. As can be seen, only about 5% of chalk particles act as spherulite nuclei in polypropylene.

The most important trend observed here is that unmodified chalk nuclei are practically insensitive to temperature in the considered range, while the amount of modified chalk nuclei decreases with the increase of temperature. Thus liquid modifier not only reduces the nucleating ability of a filler but also changes its character.

Further information about the differences in the nucleating activity of unmodified and modified chalk can be obtained from analysis of DSC melting data. Normalized melting endotherms (the area under the peak is equal to the degree of crystallinity) are shown in Figure 4. Such endotherms were obtained by substraction from the base line drawn as a straight line between the points of the melting onset and end. As such a procedure always involves some ambiguity, especially when recognizing melting onset point, the data were analyzed numerically. The treatment applied was as follows: One end of the baseline was fixed at the "crystallization end" point (easily recognizable), and second was continuously changed from lower temperatures to higher, and for each case the surface under the peak was computed. The point at which the change of slope of peak surface vs. baseline "low temperature end" was observed has been recognized as the melting onset point. The estimated accuracy of such a procedure was about 2°C. Crystallinity degrees are listed in Table IV (heat of fusion of polypropylene 209 kJ/kg was assumed in calculations after Ref. 10.) In all cases considered PP+C samples have the highest crystallinities, PP+MC intermediate, and PP the lowest, but these differences were within the limits of possible estimated
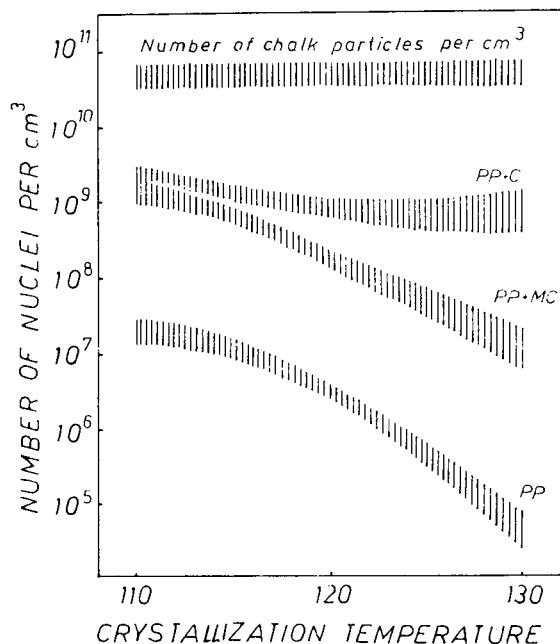

Fig. 3.   Nucleation density in PP and the number of "filler nuclei" per cm^3 in PP+C and PP+MC. The number of chalk particles per cm^3 is indicated for the comparison.
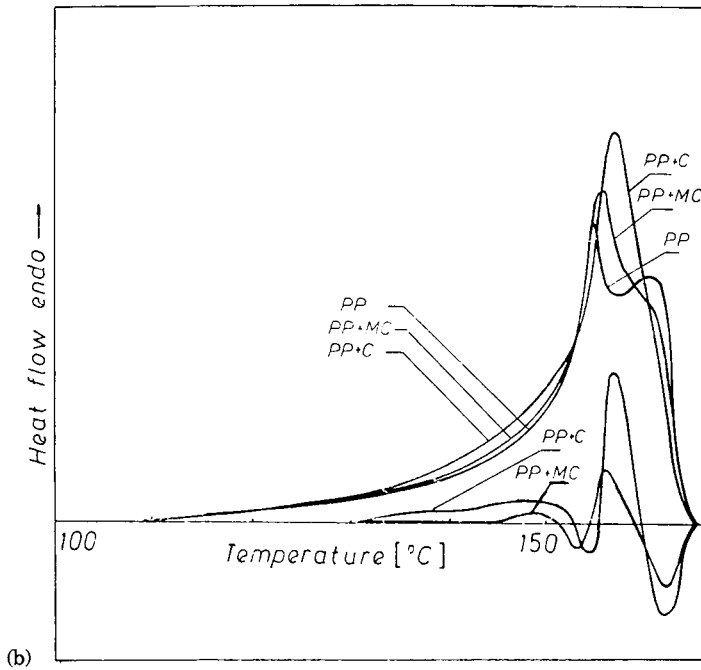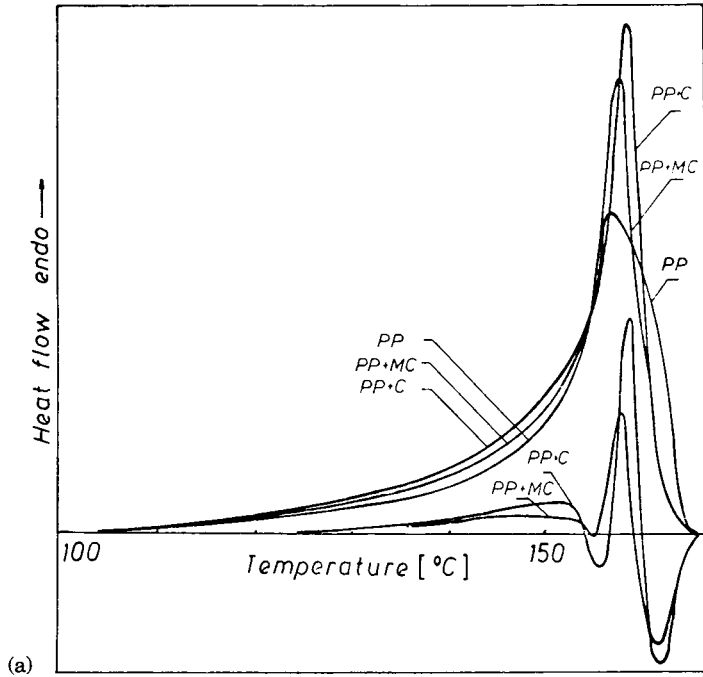
Fig. 4. Normalized (see text) melting endotherms and "difference curves" of PP, PP+C, and PP+MC: (a) crystallized nonisothermally; (b) crystallized at 110°C; (c) crystallized at 120°C; (d) crystallized at 130°C.
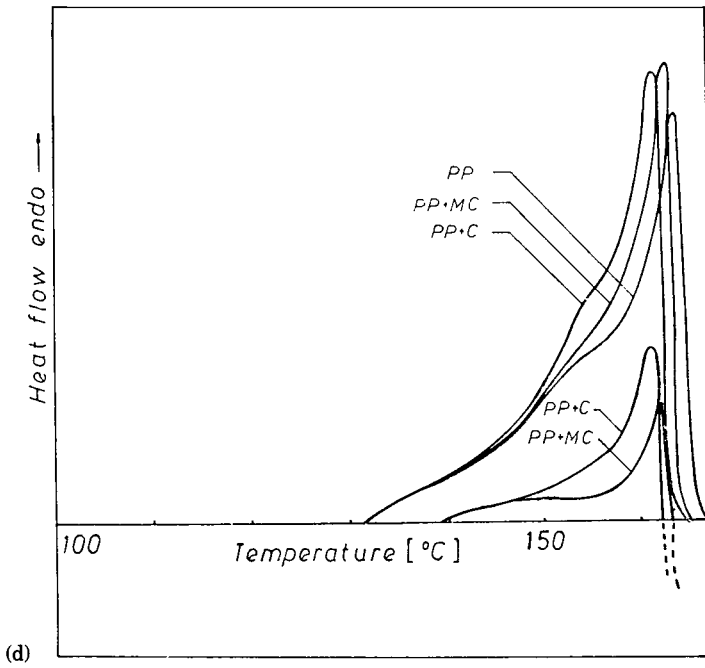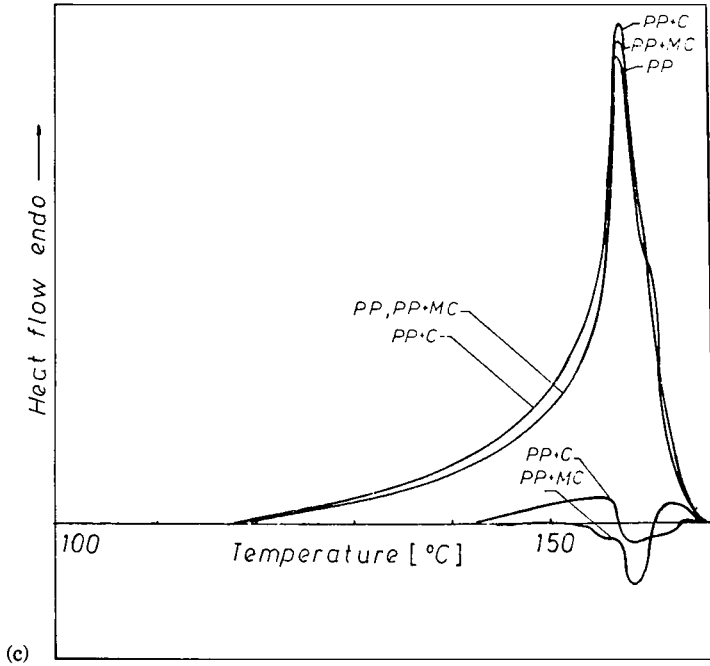
Fig. 4. *(Continued from previous page.)*

TABLE IV
DSC Crystallinity Degrees of PP, PP+C, and PP+MC after Various
Crystallization Conditions

	Temperature of crystallization			
Sample	130°C	120°C	110°C	Nonisoth.
PP	0.453	0.438	0.435	0.460
PP + C	0.460	0.465	0.481	0.507
PP + MC	0.460	0.430	0.435	0.485

experimental errors ($\pm$ 0.02 line thickness error; + 0.003/1°C and -0.01/
1°C errors due to inaccuracy in melting onset recognition below and above
real melting onset point, respectively).

The differences between the considered systems are much more pronouced
if we analyze the shifts of the melting endotherms of filled samples with
respect to the endotherms of pure polymer crystallized under the same
thermal conditions. The curves for filled samples are shifted to lower tem-
peratures, the magnitude of the shift being higher in the case of PP+C
samples. The shift can be characterized by the "difference" curves obtained
by subtraction of pure polymer endotherms from the filled sample (see Fig.
4). Since x-ray diffraction shows that in considered temperatures polypro-
pylene crystallized only in monoclinic form, the difference curves contain
information about the differences of the distributions of crystallite melting
temperatures in the compared samples. Polypropylene filled with unmo-
dified chalk contains, in all investigated cases, more lower melting crys-
tallites than pure polypropylene crystallized in the same way. The same
trend is observed for polypropylene filled with modified chalk, but the
difference is about two times lower. The ratio of the area under the positive
portion of the "difference" curve to the endotherms area indicates that the
lower melting crystallites occurring in the presence of a filler constitute in
the case of unmodified chalk up to 20% of all crystalline fraction in the
sample.

A possible explanation of the above observations is that some, quite large,
fraction of chalk particles causes the origination around them of a very
thin crystalline layer, which under the crystallization conditions has not
been able to become a spherulite nucleus.

As has already been mentioned, only some chalk particles are active
primary nucleation centers. Further information concerning this problem
can be obtained from TEM and electron diffraction data. It should be noted
here that exposure to electron beam causes complete damage of the original
morphological features of polymeric material. Low-dose exposition micro-
graph obtained with the smallest possible illumination of the sample [Fig.
5(a)] reveals real features of the sample morphology, as the sample gives
crystalline electron diffraction pattern after taking the picture [Fig. 5(b)].
If normal illumination picture is taken from the same place of the sample
(Fig. 6), electron diffraction reveals only diffused scattering rings, but the
direction of the lamellae is properly represented on the micrograph. Such
pictures may thus be used to identify the spherulite centers and borders.

The samples of PP1+C prepared in the way described in the previous
section were examined under a transmission electron microscope and a

A)

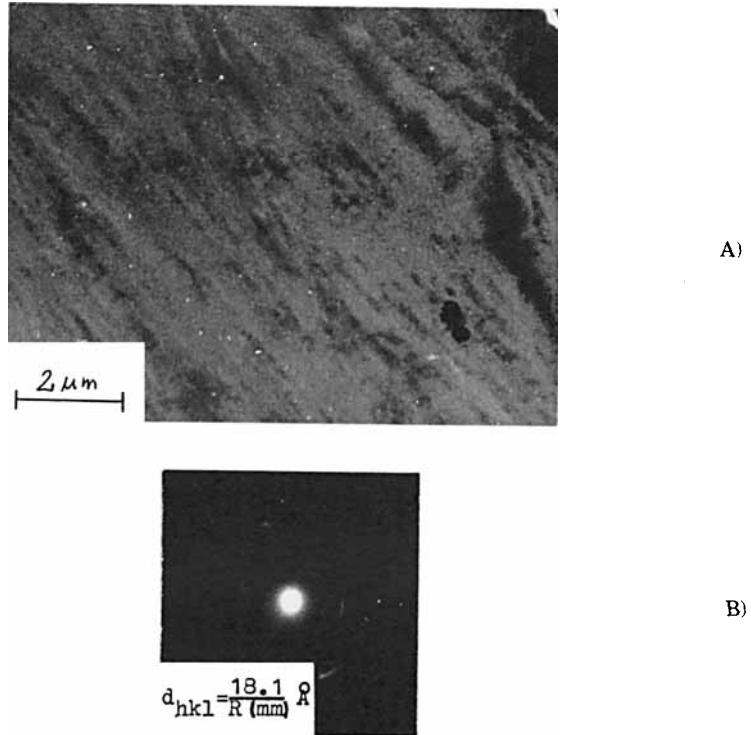$$d_{hkl} = \frac{18.1}{R \text{ (mm)}} \text{ Å}$$

B)

Fig. 5. (a) "Low dose" electron micrograph of a thin polypropylene film. Dark areas are diffracting crystallites. (b) Selected area diffraction pattern from the film shown in Figure 5(a).

large number of spherulite centers has been analyzed. Four typical types of spherulites were identified in respect to their centers: with no heterogeneous nuclei; with large aggregates of chalk particles in the center (Fig. 7); with small (two to three particles) aggregates of chalk (Fig. 8); with single chalk particles in the center (Fig. 9).
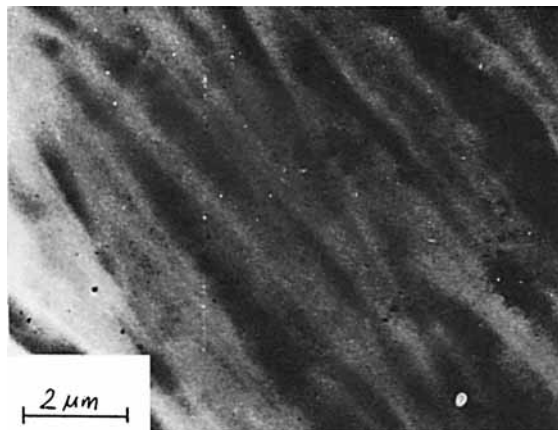
Fig. 6. The same place as in Figure 5(a) but after hard illumination with the electron beam.
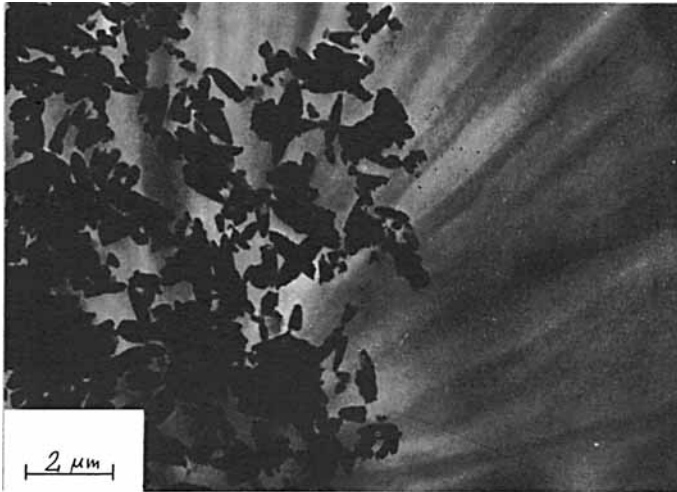
Fig. 7. TEM of a large aggregate of chalk particles in the spherulite center.

Needle-shaped particles seen in Figure 7 are most likely aragonite chalk particles as crystals of this modification crystallize in such a form. It is seen that these particles are capable of nucleating the spherulite only if they occur in a larger number together. (They are very often found outside the spherulite centers if they are single.) Electron diffraction shows that single chalk particles in the centers are always very small (below 1 μm) calcite crystals (see electron diffraction pattern in Fig. 9) while aggregates consist mainly of aragonite (e.g., electron diffraction pattern in Fig. 8). The
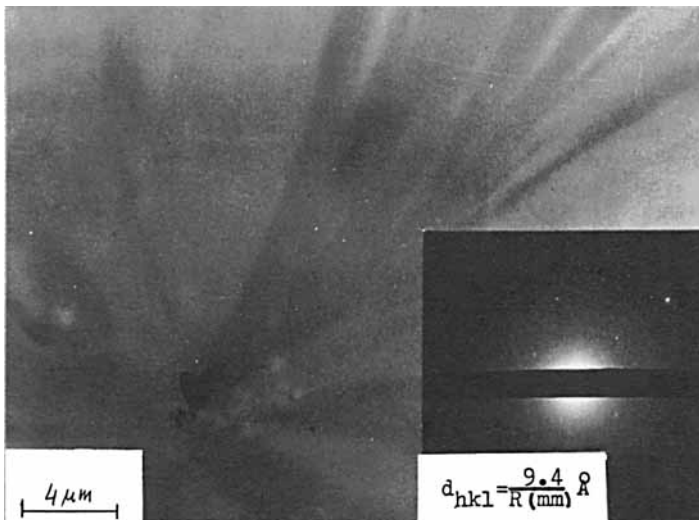

$$d_{hkl} = \frac{9.4}{R \, (mm)} \, \mathring{A}$$

Fig. 8. TEM of (at least) two-particle aggregate of chalk in the spherulite center. Insert: electron diffraction pattern from {111} and {021} or {002} or {121} planes of aragonite. (The difference between the interplanar spacings of these lays within the limits of experimental error.) The angle between these two reflections (85°) indicates that they must originate from the two different crystals.
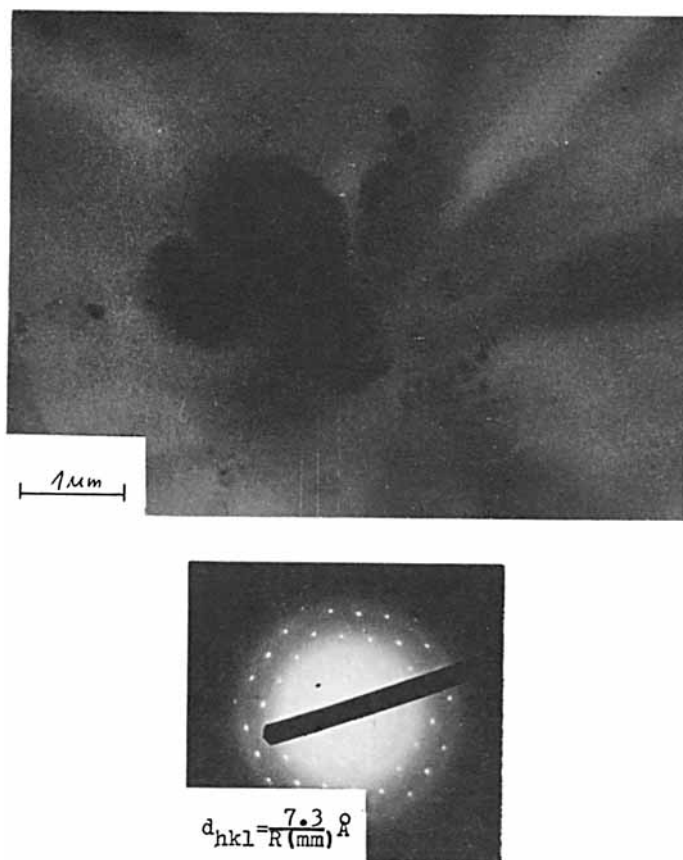
Fig. 9.   TEM of a single chalk particle in the spherulite center. Electron diffraction pattern from {121} plane of a single crystal of calcite in the center. (These reflections are normally forbidden, but they may appear if the crystal is sufficiently thin.[11])

above results indicate that the primary nucleation ability of chalk depends on its crystal structure and size, and on its agglomeration. Aragonite crystals can act as nucleation centers only if they lie close enough to one another, thus increasing the surface at which the crystal nucleus is in contact with the substrate. Small calcite crystals can act as single nucleation centers.

X-ray diffraction revealed that the chalk used throughout these experiments consisted mainly of calcite. The fact that only some fraction of chalk is active in primary spherulitic nucleation suggests that only some crystal faces of calcite (which do not occur commonly) can act as spherulite nucleation substrates. In order to prove this hypothesis experiments were performed on the cleavage surfaces of large calcite monocrystals. Calcite monocrystals were cleaved along different planes and then embedded in molten PP1, which after 10 min annealing at 230°C was crystallized isothermally at 130°C. From the obtained planes the {10$\bar{1}$1} (indexed in hexagonal system) plane known as pronounced cleavage plane could be easily distinguished. (If chalk particles undergo cleavage in the field of shear forces these planes should be most often found in the considered samples.) After crystallization, the samples were cut, calcite crystals were removed, and
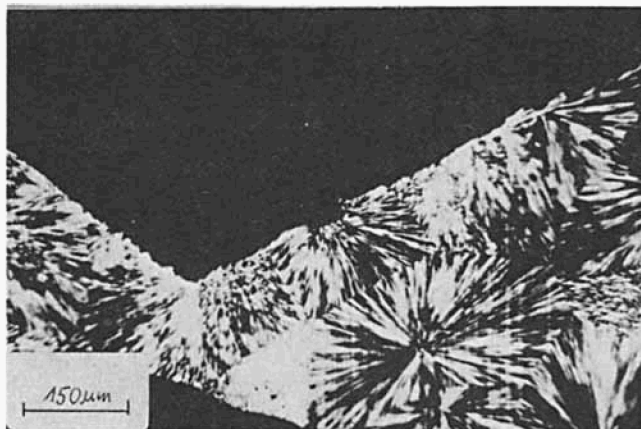
Fig. 10. Morphology of PP1 crystallized in contact with the best cleavage plane of calcite single crystal.

thin sections were microtomed perpendicularly to the given cleavage plane. The sections were then examined in a polarizing microscope.

Figure 10 shows that cleavage plane does not cause transcrystallinity (which would indicate nucleating activity) and only few spherulites are nucleated at polymer–crystal interface, presumably on some steps or other surface defects. All other planes exhibit high nucleating ability as illustrated in Figure 11. The most possible reason for this is that they contain a very high concentration of surface defects (cleavage occurs probably along many best cleavage planes changing from place to place).

Difference in the nucleating ability of calcite and aragonite can be explained in terms of the differences in the structure of those two modifications of $CaCO_3$. It is known that the substrate structure may play the decisive role in determining its nucleating ability (the need for epitaxial fit[12]). It has been shown that epitaxial crystallization of polyolefines occurs most likely on the surfaces consisting of alternating rows of positive and
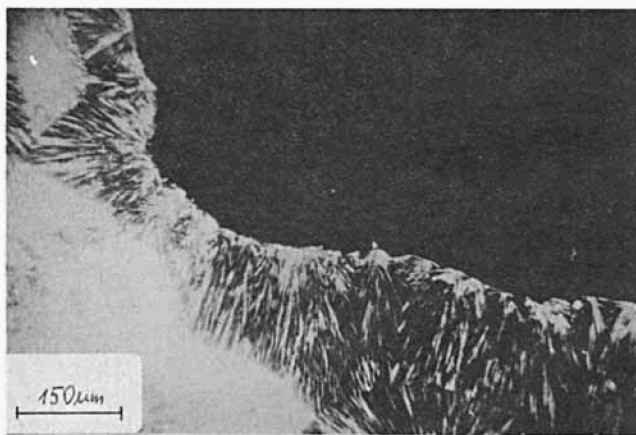

Fig. 11. Morphology of PP1 crystallized in contact with another undefined plane of calcite single crystal.
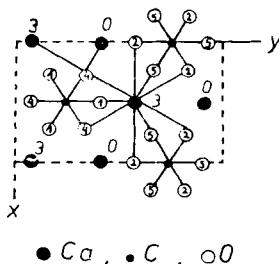
$\bullet\, Ca\, ,\, \bullet\, C\, ,\, \circ\, O$

Fig. 12.   Crystal structure of aragonite.

negative charges.[13] Such surfaces are very hard to find in aragonite crystals, the structure of which is shown in Figure 12. The crystal structure of calcite resembles the structure of NaCl perturbed by the planar CO_3^{2-} ions (Fig. 13). Here such planes are found easily, i.e., the cleavage plane fulfills this condition.

Without a remarkable concentration of defects, the calcite cleavage plane is not capable of causing spherulite nucleation. DSC melting data indicate, however, that quite a high fraction of chalk particles is capable of causing origination around them of thin crystalline layers. The fact that these layers cannot become spherulite nuclei suggests that the crystallite nucleated on a large flat surface of calcite (e.g., cleavage plane) can continue to grow only parallelly to the substrate. Such a situation is observed in the case of epitaxial growth, where the crystals can grow only to some limited height (several hundreds of Å above the substrate (e.g., Ref. 14). In the presence of defects such as steps, etc., the secondary nucleation and growth in another direction (which is the necessary condition for the spherulite origin) becomes possible. Let us note that such a result explains some discrepancy between the number of spherulites in the samples of PP+C calculated from Avrami analysis and observed in optical microscopy. As lower melting crystallites constitute about 20% of all crystalline polymer, the values of N computed from the Avrami equation assuming spherulitic growth only would be too high.

CONCLUSIONS

Chalk influences the crystallization of polypropylene showing nucleating activity. Some small fraction of chalk particles may act as spherulite nuclei. It seems that a much larger fraction of chalk particles causes origination
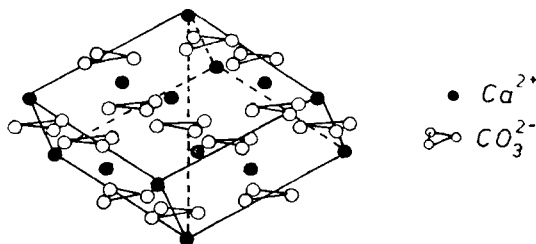

$\bullet\ Ca^{2+}$

$\text{\scriptsize 8}\!\!\!\infty\ CO_3^{2-}$

Fig. 13.   Crystal structure of calcite.

around them of a thin epitaxial layer of polypropylene. Thus polypropylene–chalk interface morphology is determined to some extent by the nucleating acitivity of the filler.

The nucleating activity of chalk is lowered in the presence of liquid at the polymer–filler interface, which also leads to changes in the interface morphology.

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