

Orientation in Composite of Polypropylene and Talc

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Synopsis

X-ray diffraction and microscopical investigation of test samples prepared by injection molding from composites of isotactic polypropylene with talc revealed a preferred orientation of the talc and polypropylene matrix. Contrary to the situation in polypropylene alone, the preferred orientation in polypropylene-talc composites survived melting and a new crystallization. Crystallization rate measurements confirmed the nucleation activity of talc for polypropylene crystallization.

INTRODUCTION

In studying the structure and morphology of polymers modified by mineral fillers some problems may arise. These concern the character and the extent of interaction at the polymer-filler interface and the homogeneity of filler distribution and eventually filler orientation in the case of filler anisometric particles.¹ In this paper a new effect is noticed, concerning polymer and filler orientation in the isotactic polypropylene (PP)-talc system. PP filled by talc is an important commercially distributed composite. Earlier, we have studied this system investigating the homogeneity of filler distribution and the effect of talc on PP morphology and crystallization.² We have established that talc represents a nucleation active filler for PP, increasing its overall crystallization rate. We have also noticed the tendency of PP to line regularly on the basal planes of talc sheet particles; however, this tendency was lower than in the case of polyethylene.³

In this article we present the results of structure characterization obtained with injection-molded test samples of PP-talc composites.

EXPERIMENTAL

Materials. Measurements were performed with samples of composite PP Mosten 52 492 having $\bar{M}_w = 385 \times 10^3$, $\bar{M}_n = 69 \times 10^3$, and 99% isotacticity (Czechoslovak production) with 5-50% (w/w) of talc EKI and 0.15% of Irganox 1010 stabilizer. Injection molding of standard test samples in form of dumbbell or beam was done at 210°C and 82 MPa. Experiments were performed mostly with composite containing 5% of talc. Test samples and composites were prepared in the Research Institute of Macromolecular Chemistry Brno.

X-Ray Measurements. The structure and orientation of the PP-talc composite was investigated using the x-ray diffractometer Micrometa 2E with a goniometer (Chirana, Czechoslovakia) equipped with a heating chamber (of

TABLE I
Isothermal Crystallization Rate of PP and Its Composites with Talc

Talc (%)	T_c (°C)	$\tau_1 \pm 1$ (min)
0	139	28
5	139	4.3
10	139	4.5

our own construction) for measurements at higher temperature. The CuK_α radiation was monochromatized by a quartz monochromator.

Crystallization characteristics were measured with composites containing 5 and 10% talc; samples with a higher talc content were not convenient for a high x-ray absorption. For comparison PP alone was also measured.

RESULTS AND DISCUSSION

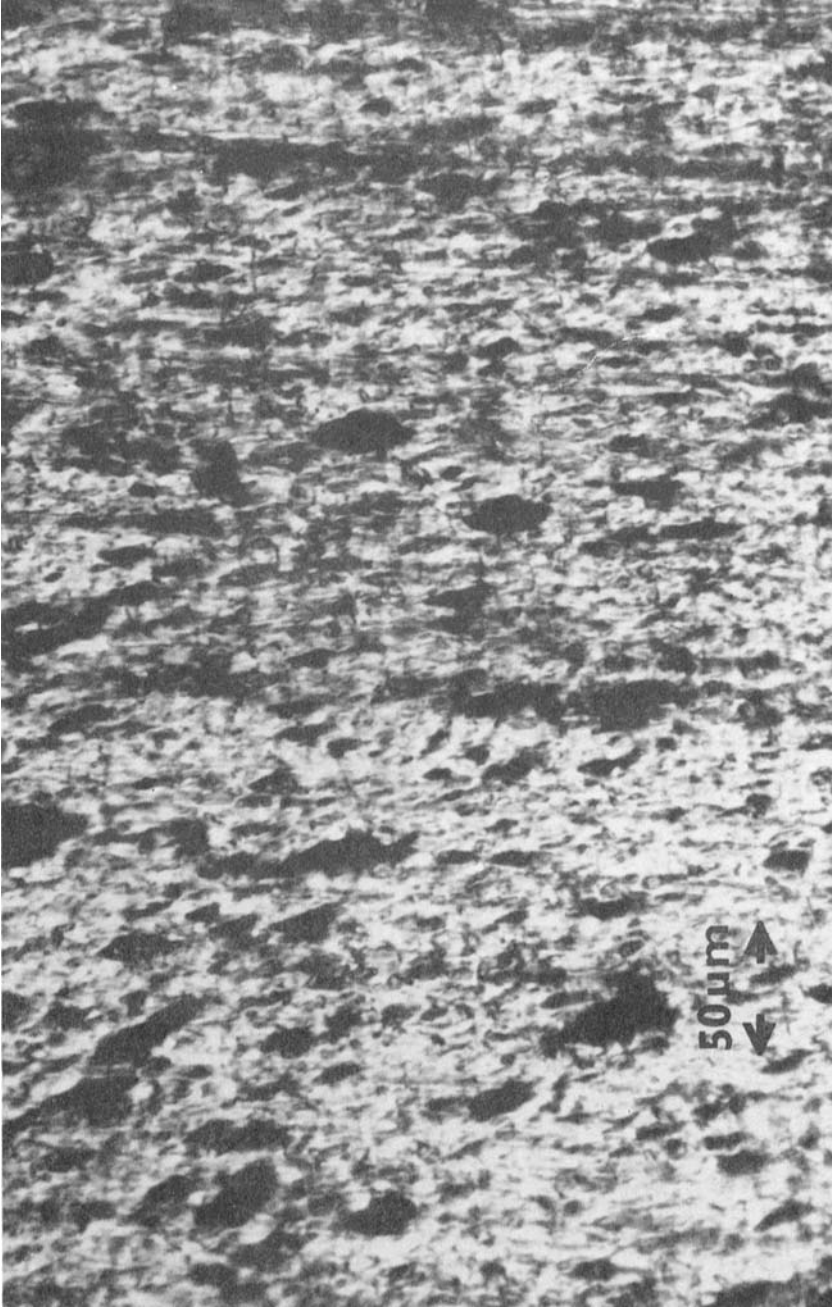
The results of the overall crystallization rate at 139°C after the standard melting 14 min at 220°C are listed in Table I. The crystallization rate is characterized by the crystallization half-time τ .

The data shown in Table I clearly confirm our earlier results proving a moderate nucleation activity of talc for PP crystallization. The PP composites crystallize much faster than PP alone. Comparing results for composites with 5 and 10% talc, we may notice that a limiting concentration of crystallization nuclei was reached, because a twofold increase in talc concentration did not result in a further increase of the crystallization rate. Therefore, the investigation of the crystallization rate in composites with higher talc content made no sense. On the other hand, we can see that only a small fraction of talc particles is nucleation-active. From this it follows that there is a certain limit in any intention to reduce the spherulite size using a high concentration of nucleation-active additives down to crystallite size approaching the dimensions of critical-size crystallization nuclei.

Contact x-ray radiography has confirmed a nearly homogeneous distribution of talc particles in composites; there were no particle aggregates or places with markedly lower filler concentration.

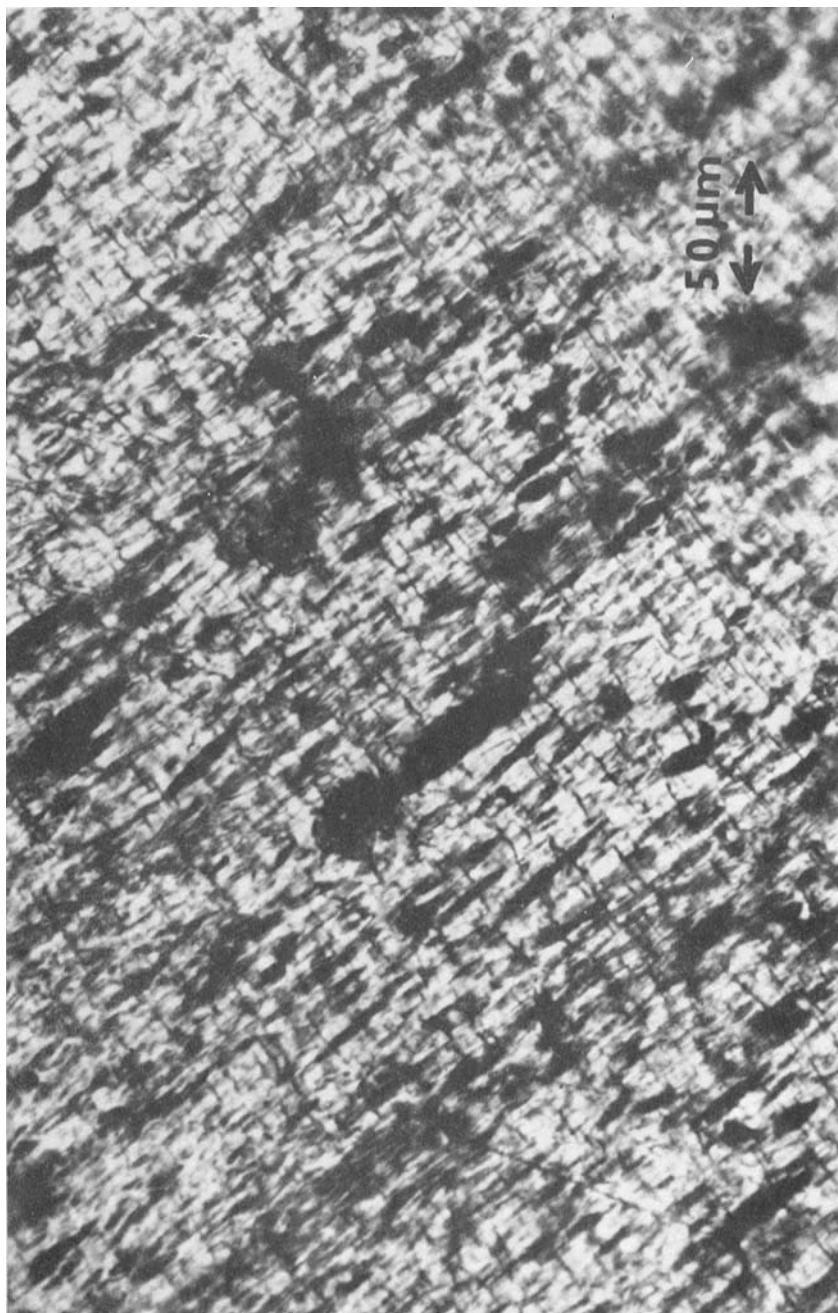
Examination by polarizing light microscopy has revealed the anisotropy in talc and PP orientation. Talc particles were oriented with their basal sheet planes mostly parallel to the larger dumbbell surface. This is apparent from micrographs in Figures 1(a) and (b), showing the transverse and longitudinal section respectively (direction D shown in Fig. 2) of the remelted and isothermally crystallized test sample. Also the PP matrix is highly oriented and the spherulitic texture, typical for the unfilled sample [Fig. 1(c)], disappeared.

Preliminary x-ray diffraction measurements fully confirmed the preferred talc and PP orientation. Therefore, we have performed a detailed study of sample diffraction spectra on sample places and directions marked out in the scheme in Figure 2. Arrows indicate the incidence of the line-shaped x-ray beam on the sample. Some typical diffraction spectra for PP and its composites with 5% talc are shown in Figure 3. The evaluation of the intensity ratio of two prominent reflections of PP (110 and 040) and of talc (002 and 020) is summarized in Table II.



(a)

Fig. 1. Polarizing light micrographs of the transverse (a) and longitudinal (b) sections of the composite PP + 5% talc and of the transverse section of PP alone (c). Samples were melted 14 min at 220°C and isothermally crystallized at 139°C.



(b)

Fig. 1. (Continued from the previous page.)



(c)

Fig. 1. (Continued from the previous page.)

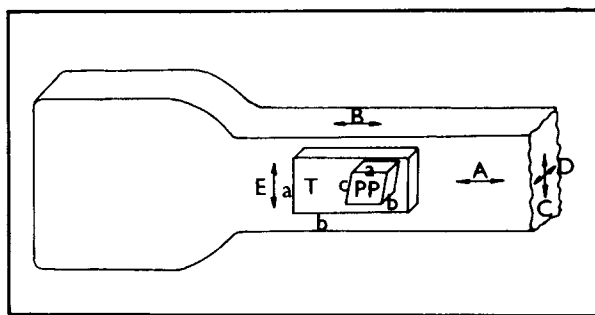


Fig. 2. Scheme of the test sample showing places and directions of the x-ray diffraction spectra measurements and the mutual orientation of the talc (T) and PP crystal unit cells.

In isotropic PP samples the ratio I_{110}/I_{040} lies in the range 1.3–1.5. The diffraction spectra and data of Table II indicate that the original test samples of PP alone are far from being homogeneous. Further we may trace a small amount of the metastable β -modification of PP crystallites. However, after melting and isothermal crystallization at 139°C, the PP samples are characterized by a higher crystallinity, by absence of β -crystallites, and mainly by the fact that the sample is isotropic, the ratio I_{110}/I_{040} now being in the range typical for isotropic samples.

Composites of PP with 5% talc (likewise with a higher talc content) show not only a preferred orientation of PP crystallites but also of talc and this is true not only for original but even for recrystallized samples, as is apparent from Figure 3 and Table II. And further, it is clear that the degree of PP orientation is in composites considerably higher than in PP alone.

Based on these results, one can deduce the average mutual crystallite orientation of PP and talc in test samples as sketched in Figure 2. Due to melt flow during injection molding the talc sheets orient themselves with the a, b crystal planes predominantly parallel to the upper or lower dumbbell surface, the orientation of a and b crystal axes in this plane being random. PP tend to crystallize with a, c planes laying in a, b planes of talc, the b -axis of PP being normal to a, b plane of talc. This type of PP and talc orientation corresponds to a reasonable expectation. The exact orientation of the PP c -axis in the a, b talc plane was not yet determined. In this plane, however, there is not apparent any simple epitaxial relation of both crystal cells, nor is there obvious any possibility of a topographically favorable placement of PP chain segments on the talc substrate. In this connection the question arises how to explain the mechanism of the incontestable high nucleation activity of talc for PP crystallization. One explanation might be based on the assumption that for the nucleation action of solid surfaces their irregularities (steps, ridges, dislocations, stacking faults, etc.) are much more important than epitaxial relations.⁴

The analysis of given results brought about two important aspects:

1. The Extent of Orientation. One would hardly expect that 1.84 vol% of talc may influence the orientation of practically all PP crystallites. It is clear that talc is an effective nucleation agent for PP, but morphological studies did

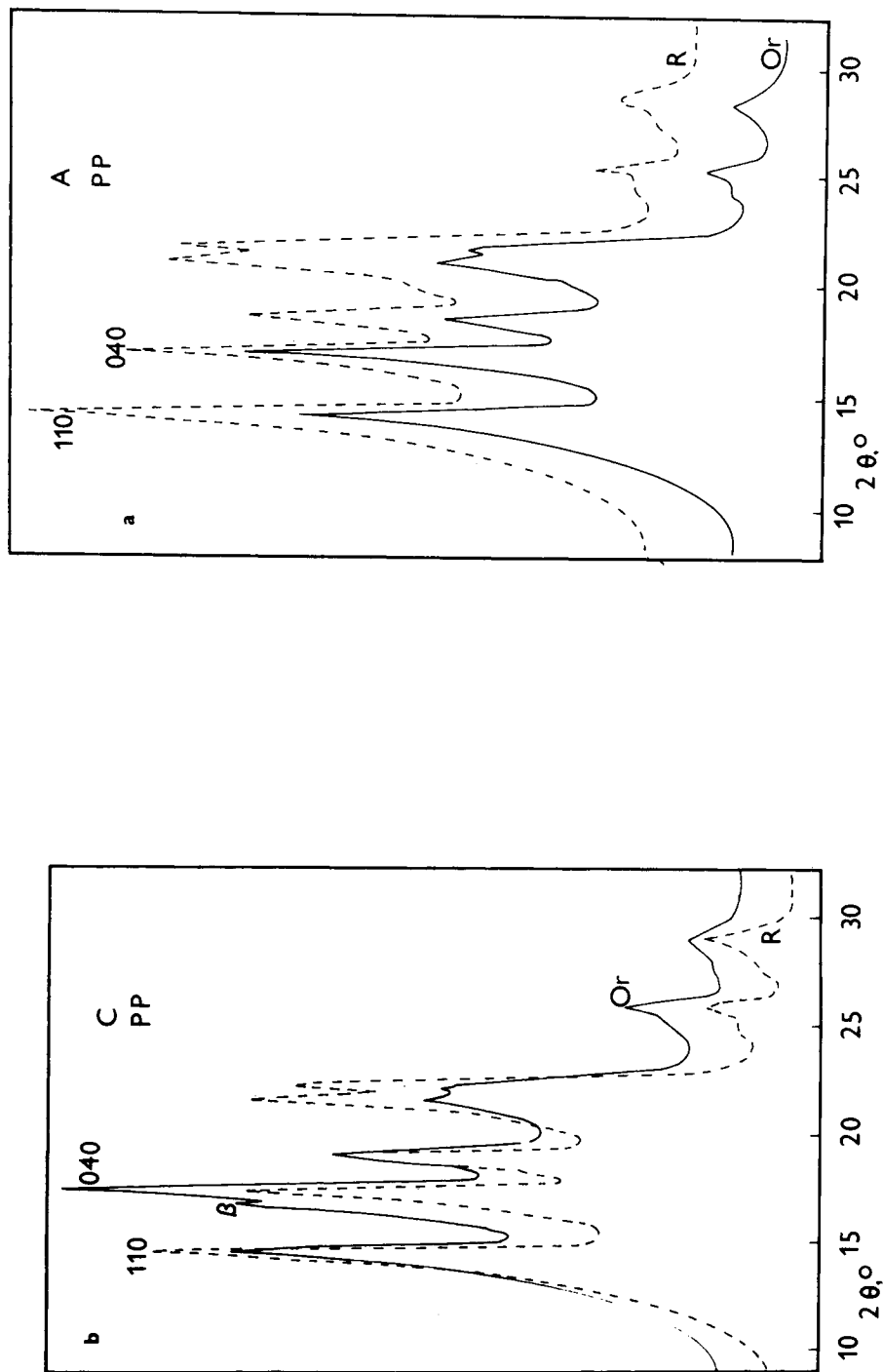


Fig. 3. Typical x-ray diffraction spectra of test samples injection molded from PP (a, b, c) and composite PP + 5% talc (d, e, f), measured in various directions with original (Or) and samples isothermally crystallized at 139°C after melting 14 min at 220°C (R).

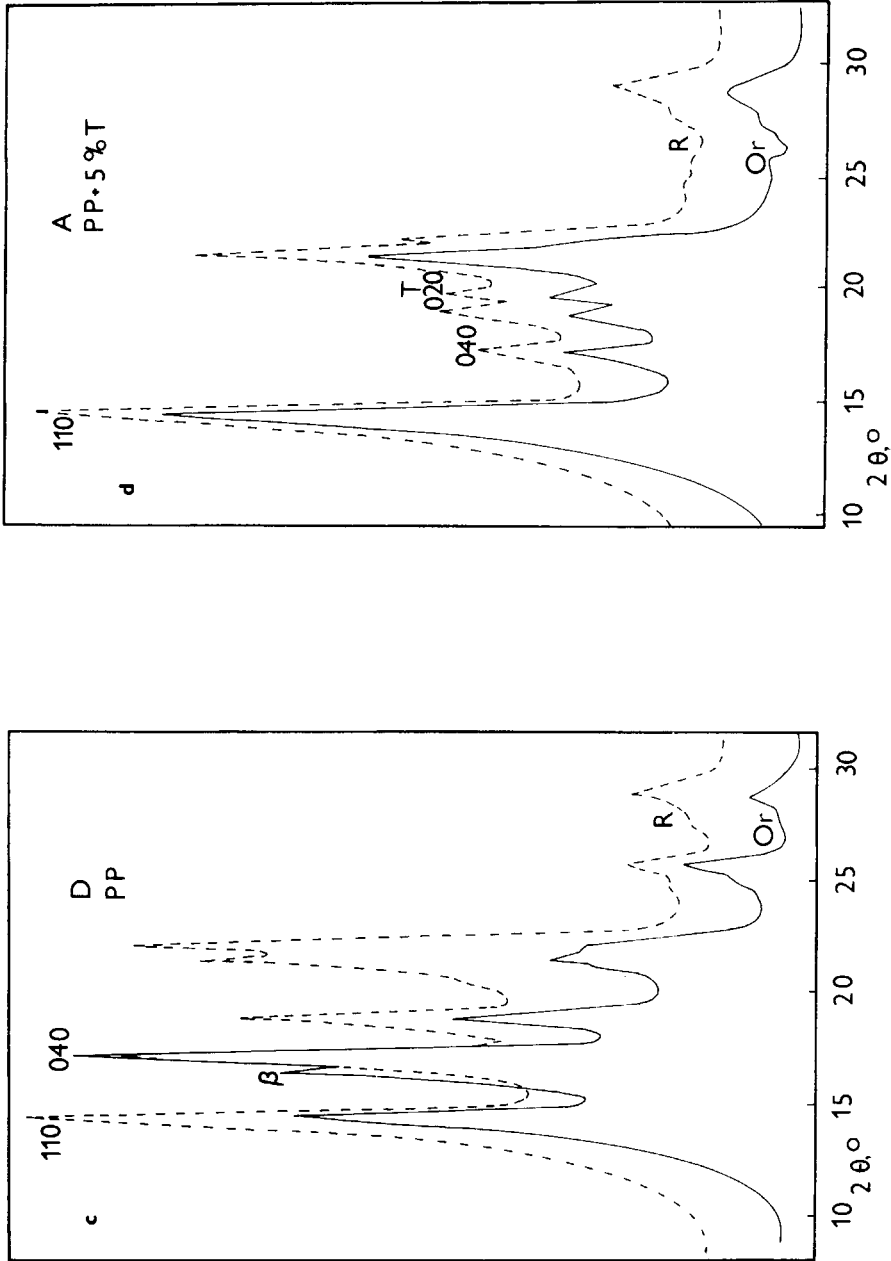


Fig. 3. (Continued from the previous page.)

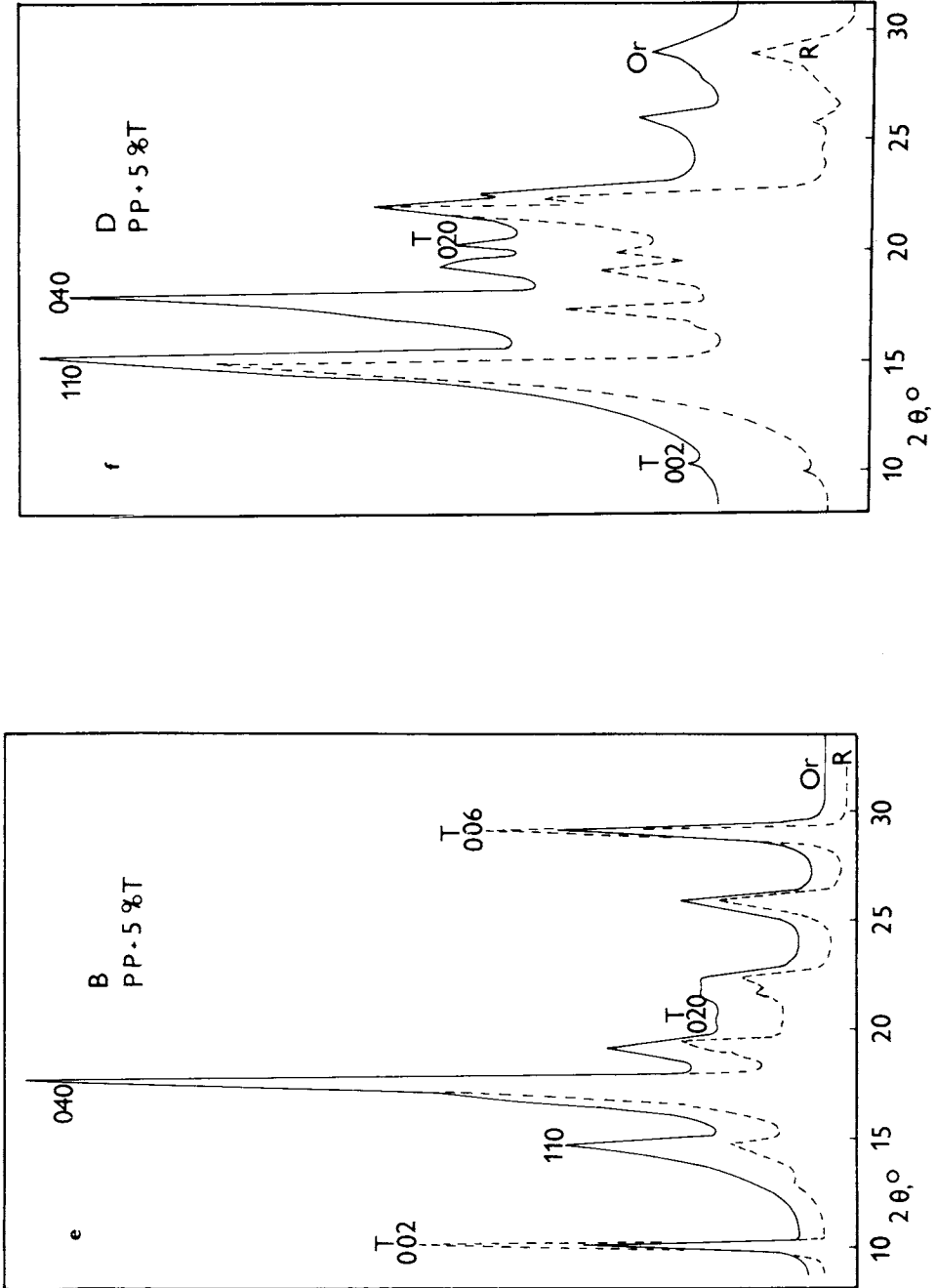


Fig. 3. (Continued from the previous page.)

TABLE II
Intensity Ratio of PP I_{110}/I_{040} and of Talc I_{002}/I_{020} Reflections in PP and Its Composites
with 5% Talc, Measured in Various Directions

Talc (%)	Place of measurement	PP I_{110}/I_{040}		Talc I_{002}/I_{020}	
		Or ^a	R ^b	Or ^a	R ^b
0	A	0.95	1.5		
0	B	0.59	1.35		
0	C	0.71	1.45		
0	D	0.62	1.39		
0	E	22			
5	A	5.3	6.1	0.17	0.23
5	B	0.24	0.076	11.1	20
5	C	0.28	0.37	36	14
5	D	1.1	3.3	0.32	0.31
5	E	18		7.2	

^aOr = original sample.

^bR = sample remelted 14 min at 220°C and isothermally crystallized at 139°C.

not reveal the preferred orientation also in places remote more than about 10^2 nm from the talc surface.

2. The Stability of Orientation. During injection molding of polymer composites, logically, orientation of the polymer matrix and of the filler takes place. With PP alone we have noticed after remelting and crystallization that the preferred orientation disappeared resulting in an isotropic structure. A different situation was established in PP-talc composites where after melting and crystallization the original mutual orientation of PP and talc crystallites remained not only preserved but even increased. As far as the talc particle orientation is concerned, we understand that the change of their position in the viscous PP melt is difficult. On the other hand, it is very surprising to find that also the orientation of PP crystallites remains unaffected by melting. Because most of the PP crystallites are relatively distant from the talc surface, we must take into consideration the action of substrate attraction forces of far reach, their existence being well known but less understood.⁵

The talc particles evidently influence also the fracture pattern even at the liquid nitrogen temperature on a relatively large distance from the filler, as is shown on the electron micrograph in Figure 4. Another explanation based on chemical bonding between talc and PP seems to be less probable.

Based on established facts, the composite PP-talc manifests itself as a system which is firmly interconnected by directionally oriented physical forces of far reach, rendering the change of the original preferred orientation of PP and talc impossible.

Finally we may state that the situation at the PP-talc interface brings about some new suggestions for further studies of interaction, structure, and morphology, which are of prime importance for understanding properties of this interesting and practically important polymer composite.



Fig. 4. Electron micrograph of the fracture surface of the PP-talc composite fractured at liquid nitrogen temperature. T = talc particle; PP = polypropylene matrix.

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