

ANALYSIS OF THE ORIENTATION OF POLYPROPYLENE-BASED SHEETS SUITABLE FOR FIBRILLATED YARN PRODUCTION

By

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Introduction

The physical-mechanical properties of polypropylene (PP)-based sheets suitable for fibrillated yarn production are fundamentally determined by the production parameters of the film strips besides the chemical structure and the molecular parameters of the base components used.

The spherulitic structure of the primary films formed as the first step of production is abundantly reported in literature.

The spherulitic structure of primary sheets was examined by MENGES and HORN [1] as functions of the molecular weight of the polyolefine base materials, crystallinity and the method of cooling the sheet (direction and rate of cooling). The effect of the temperature of cooling air on the formation of spherulitic primary sheets of PP, and on the possible formation of smectic structure was examined by BODOR [2, 3]. The spherulitic structure of polyethylene was reported by MUZZY and HANSEN [4].

The physical-mechanical properties of sheets are fundamentally determined — among the production parameters — by the drawing of primary sheets. The spherulities in the primary sheets become oriented in the course of drawing by lamellar slip. The orientation of isotactic sheets was first analyzed in detail by SAMUELS [5].

In this work the oriented system was characterized by Herman's function:

$$f = \frac{3 \overline{\cos^2 \Theta} - 1}{2} \quad (1)$$

where f — Herman's orientation function,

Θ — the angle formed by the polymer chain axis and the drawing direction.

For a random orientation:

$$f = 0$$

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For a polymer chain parallel to the direction of deformation i.e. to the drawing direction:

$$f = 1.$$

For polymer chains normal to the direction of deformation:

$$f = -0.5$$

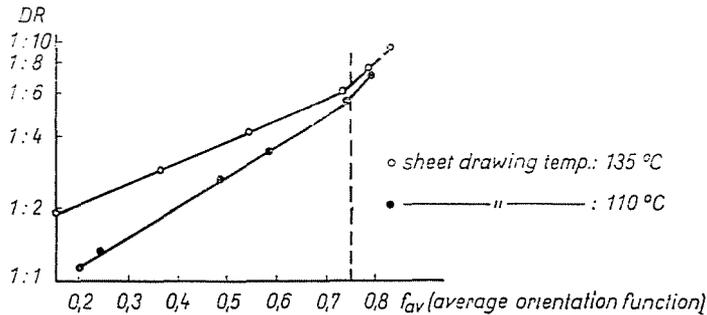


Fig. 1

The mean orientation of polymeric macromolecules containing both crystalline and amorphous phases can be expressed in the form:

$$f_{av} = \beta f_c + (1 - \beta) f_{AM} \quad (2)$$

where f_{av} — mean orientation function,
 β — crystallinity percentage,
 f_c — orientation function of crystalline parts,
 f_{AM} — orientation function of amorphous parts.

The orientation function of amorphous parts was also examined by SAMUELS in another paper [6]. He succeeded in establishing a direct relationship between the drawing ratio (DR) and the mean, crystalline, and amorphous orientation functions.

In Fig. 1, data are presented after SAMUELS. The temperature of drawing was 135°C, and 110°C. In Fig. 1, the tensile strain ratio is shown as a function of the mean orientation function.

A linear relationship is seen to exist between the strain ratio and the orientation function. At $f_{av} = 0.76$ the function has a turning point. Until $f_{av} = 0.76$ which is attained at 135°C for DR = 1 : 6, and at 110°C for DR = 1 : 5, the value of the orientation function rapidly increases upon further

drawing. Beyond that value, however, i.e. for $DR = 1 : 5$ or $1 : 6$, an increase in DR will result in less increase in the value of the orientation function (until $DR = 1 : 10$), and at the same time the temperature difference will also become insignificant.

The folding length of the isotactic PP molecules, i.e. thickness of the lamellae, or long period ($L/\text{\AA}$) increases until $f_{av} = 0.76$. For identical DR values the increase of temperature will greatly increase the long period of the PP chains [7].

BODOR [2] examined the orientation, crystallinity, crystalline particle size, as functions of DR for PP, and for sheet strips containing high-pressure polyethylene in the range of $DR = 1 : 5.8$ to $1 : 11.7$.

He has concluded that in the examined range the increase of DR will hardly change the value of the orientation function (in the order of a few per cent). The crystallinity will remain identical, while the crystalline particle size suffers a 20% break-up during drawing.

The quoted authors have examined the structure of PP sheets by means of X-ray diffraction and electron microscopy.

The present analysis is concerned with the study of the orientation of PP sheet-strips type DM 55 for $DR = 1 : 6.8$.

The second moment of the NMR signal for strips was measured as a function of the angle between the drawing direction and the external magnetic field.

NMR measurements

According to the classical description of the magnetic resonance the core of the hydrogen atom i.e. proton proceeds at a frequency $w_0 = \gamma H_0$ in an external magnetic field, H_0/γ is a material constant characteristic for one proton. The proton so proceeding will follow its angle of incidence, when influenced by another magnetic field H normal to H_0 , and is of high frequency, simultaneously energy will be absorbed from H , which can be detect-

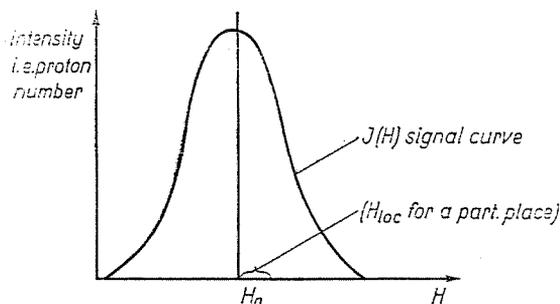


Fig. 2

ed. Thus the magnetic field at the site of protons can be measured. Due to dipole—dipole interaction, the individual protons do not feel the external field H_0 alone, but also the local dipole field generated by its neighbours. The signal curve shows the proton number distribution vs. H_{loc} , characteristic for a given material structure [8].

The shape of the signal curve cannot be deduced directly from the structure of the material, only its statistical second and fourth moment M_2M_4 , resp. using formula [3]. The n -th moment of resonance signal described by the shape function $f(H)$

$$M_n = \frac{\int_{-\infty}^{\infty} F|H| |H - \langle H \rangle|^n dH}{\int_{-\infty}^{\infty} f|H| dH} \text{ gauss}^n \quad (3)$$

where $\langle H \rangle$ is the probable values of magnetic field [9].

The wide-signal NMR spectrometer is suitable to measure the shape signal function $f(H)$, thus M_2 and M_4 can be calculated, consequently comparable values are obtained for moments M_2 and M_4 calculated with the use of a presumed structure.

The second moment can be calculated with the help of a presumed structure by the expression:

$$M_2 = \frac{9}{80} \gamma^2 h^2 N^{-1} \sum_{j=1}^N \sum_{k=1}^N |3 \cos^2 \Theta_{jk} - 1| r_{jk} \quad (4)$$

where

γ — the gyromagnetic factor of a proton;

h — Planck constant;

N — sum of all protons in the mathematical model;

j and k — running parameters for two particular protons;

r_{jk} — distance between protons j and k ;

Θ_{jk} — the angle between r_{jk} and external magnetic field H_0 [13].

The interactions between the protons of the unit PP spirals considerably contribute to the second magnetic moment [10]. This contribution was estimated to be of the order of 8 G² applying formula 2.10 in Ref. [10].

It should be noted that for the liquid phase the above dipole—dipole contribution is cancelled and the chemical shift appears which contains more structural information, and which is measured by high resolution magnetic resonance spectroscopy.

The structure of PP and the orientation dependence of the second moment

The location of atoms was determined by NATTA and CORRADINI [11] for polypropylene. The present calculations were carried out for the structural group C2/c not significantly different from the structural group C/c, consequently there would be no difference in the second moment calculated.

Fig. 3 shows the main axis of the PP chain (C), for the strips, (Z), the external magnetic field (H_0), and angles (γ) formed by H_0 and Z, and (Δ) formed by Z and C.

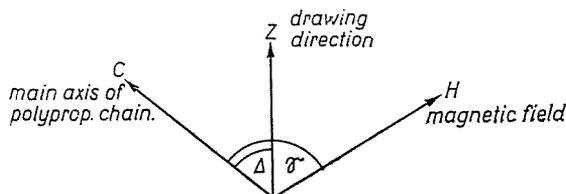


Fig. 3

It was attempted to determine the probability of occurrence of a given polypropylene chain including an angle Δ with the drawing direction. In other words the orientation distribution of strips was determined.

The calculation of the orientation dependence of the second moment according to formula (4) is rather tedious.

MCBRIERTY and WARD [12] applied the following expression making use of spherical harmonic functions.

Ideally

$$M_2 = 4 \left| \frac{G}{N} \right| \sum_{l=0,2,4} a_l s_l P_l |\cos \gamma| |P_l| |\overline{\cos \Delta}| \quad (5)$$

where

$$s_l = \sum_{j>k} P_l |\cos \theta_{jk}| r_{jk}^{-5}$$

$$a_0 = 1/5$$

$$a_2 = 2/7$$

$$a_4 = 17/35$$

$$G = \text{material constant} \left(G = \frac{9}{80} \gamma^2 h^2 \right),$$

h — Planck's constant

s_l — lattice sum

γ — angle between magnetic field H and the drawing direction

Δ — angle between the axis of the polypropylene chain and the drawing direction.

a_0, a_2, a_4 constants formed by LEGENDRE polynomial expansion of these functions.

Experimental, procedure, results

The proton resonance measurements were carried out by a wide-signal NMR spectrometer [12] in a magnetic field of 4500 G (H_0) applying 1 G modulating field using the facilities of the Hungarian Central Research Institute of Physics.

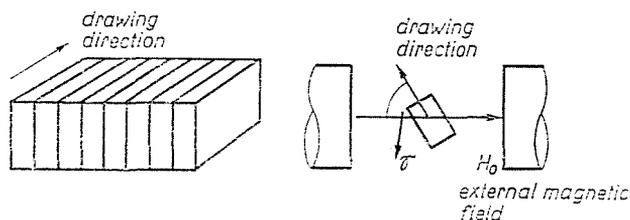


Fig. 4

The PP strips were cut up to 2×4 mm pieces, piled up to make a stack with dimensions $10 \times 2 \times 4$ mm³ (Fig. 4).

The NMR spectrum was recorded in the $\gamma = 0^\circ$ to 180° interval (the angle between the drawing direction and the external magnetic field H_0), whereas the external magnetic field was 4500 G. Four measurements were recorded at each angle position. Signals were read by a mm square-net. After calibration the second moment was calculated by expression [3] using a TPA computer.

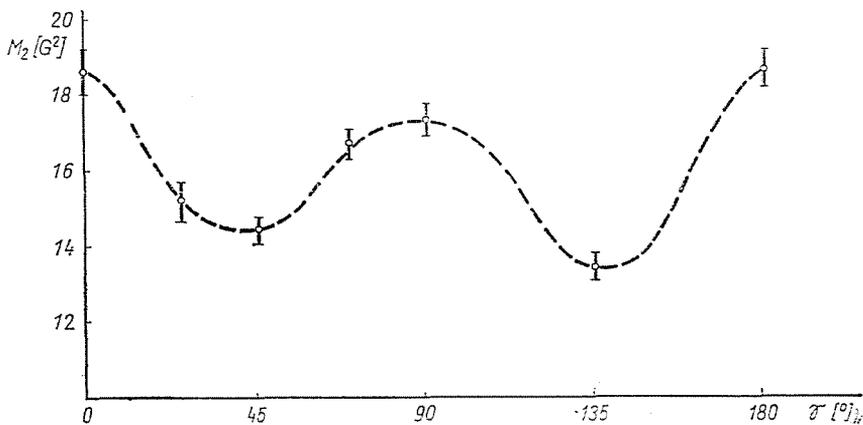


Fig. 5

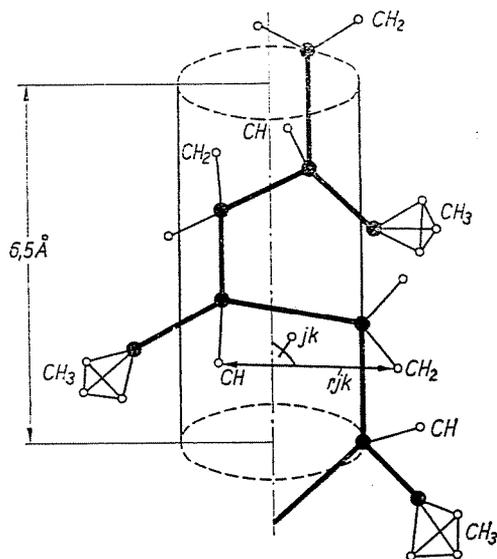


Fig. 6

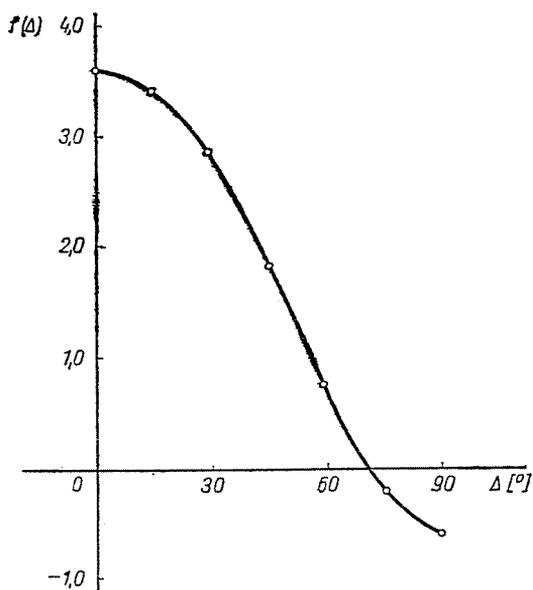


Fig. 7

The results are shown in Fig. 5.

For the theoretical calculation of the second moment (formula (5)), the identity period of PP was constructed from wire by geometric scaling ($1 \text{ \AA} = 50 \text{ mm}$).

The identity period and angles, distances measured on the model are shown in Fig. 6.

The values of the respective 155 distances for the 18 protons found in the identity period of polypropylene, and the angles between distances and the chain axis θ_{jk} were read off the wire scale model.

Making use of the measured distances and angles according to formula (5), Legendre functions P_2 and P_4 were calculated and lattice sums S_0 , S_2 and S_4 were also obtained. Computations were carried out by a TPA computer of the Hungarian Central Research Institute of Physics.

In expression (5) the terms $P_2/\cos \Delta$ and $P_4/\cos \Delta$ are unknown. These, however, can be calculated from NMR measurements by solving the system of equations. Measured and calculated results are given in Table 1.

Table 1
Results of NMR measurements

Measured second moment at 0° (G ²)	18.6
Measured second moment at 45° (G ²)	14.4
1 = S_0 lattice sum at 0	0.5942
1 = S_2 lattice sum at 2	-0.0084
1 = S_4 lattice sum at 4	-0.0655
$P_0 \overline{ \cos \Delta }$	1
$P_2 \overline{ \cos \Delta }$	1
$P_4 \overline{ \cos \Delta }$	-0.366
Contribution of second moment due to molecular interaction (G ²)	8

The distribution of unit chains according to the angle $|\Delta|$ i.e. the angle between them and the drawing direction is as follows [11]:

$$F|\Delta| = \sum_{l=0}^{\infty} \left| 1 + \frac{1}{2} \right| P_1 \overline{|\cos \Delta|} P_1 |\cos \Delta| \quad (6)$$

The distribution function $f/|\Delta|$ expressed in formula (6) was calculated using data in Table 1. The calculated results are plotted in Fig. 7.

Conclusions

It is seen from Fig. 7 that for DR exceeding 1 : 6.8 the unit spirals of the PP split fibres become oriented with the highest probability in the drawing direction. The orientation range of 0° to 30° also has a rather high probability. This result agrees well with X-ray orientation analyses of PP strips (for DR = 1 : 5.8 the material is 90% oriented) [2, 3].

MCBRIERTY [12] has examined the orientation angle distribution for high pressure PE split fibres having variable DR values. He has examined the 1 : 1.3 to 1 : 3.7 range. His results are given in Fig. 8.

In Fig. 8 it seems clearly that in the lower DR range (1 : 1.3 to 1 : 3.7) the increase of DR is likely to entrain very rapid increase in the probability of the chains to become oriented in the direction of drawing.

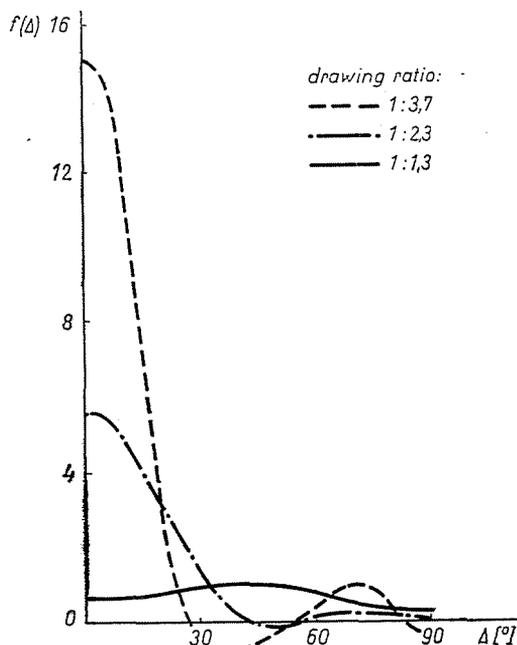


Fig. 8

In the range we studied (1 : 6.8), the PP spirals are already oriented in the drawing direction with the highest probability.

According to X-ray results discussed previously, upon a further increase of DR, the orientation may increase only by a few per cent [2]. This low increase percentage, however, may result in a marked change on the physical-mechanical properties of the split fibres. The maximal orientation percentage is attained for PP at the strain ratio of 1 : 10. Further increase of strain ratio will decrease the orientation percentage.

Analysis of orientation for PP split fibres with additives

Strips made of PP containing no additive are rather rigid and physically inelastic. For certain uses the material must satisfy special requirements, therefore the physical-mechanical properties should be modified by additives.

The application of rubbery-elastic polymers may help to make PP softer and more elastic.

Whether a macromolecular compound is rubbery-elastic at 20°C or not is dependent on the mobility of the polymer molecular chains.

The mobility of the molecular chains is determined by three factors:

- a) spatial retardation of substituted atom groups on the chain,
- b) forces operating among chain segments, with magnitudes also dependent on the nature of substituted atom groups,
- c) regularity of structure.

When free movement of chains is spatially retarded then mobility due to softening of the polymer will not be marked. Conversely, for such a polymer the loss of entropy is not too large, provided those transfer from the rubbery-elastic state into the glassy state. For a glassification or freezing process, as well as for any physical-chemical change the relationship

$$\Delta G = \Delta H - T\Delta S$$

holds. The process may only occur if the energy given off in the form of heat by the system ΔH is greater than $T\Delta S$, the entropy term.

Among the rubbery-elastic materials, polyisobutylene has a more regular structure in space than PP or polyethylene, however, the methyl group on polyisobutylene as compared to PP exerts extra shading effect thus retarding an optimal approach of chains. In this case the secondary bonding energies responsible for crystallization proportionally decrease with the inverse of the 7th or 8th power of the distance between the molecular chains. Due to this spatial hindering effect the softening region will drop to -70°C .

Polyisobutylene and PP do not form a separable system since cohesion energy densities are hardly different from that of PP in particular, and that of polyolefines in general. (For polyolefines: $7.9-8.1 \text{ cal}^{+1/2} \text{ cm}^{-3/2}$.) The two polymers become separated when the difference in cohesion energy density exceeds 1.2.

Since polyisobutylene forms a compatible system with PP, and polyisobutylene is a rubbery-elastic compound, therefore it can be used as such an additive that will make PP softer and more elastic.

The softening effect of polyisobutylene on PP was observed by measuring the respective stress-strain curves.

The effect of the polyisobutylene additive on the orientation process of PP was followed thermoanalytically and by X-ray diffraction analysis, noting that the process fundamentally determines the physical-mechanical properties of the PP film and split fibres. The analysis was made using a material containing 88% and 12% polyisobutylene with an average molecular weight of $1.5 \cdot 10^6$.

The softening effect of polyisobutylene

The softening effect of poly-isobutylene on PP was proven by recording the stress-strain curves both for the additive-free PP and for the mixture specified above, at a drawing temperature of 140°C, in an INSTRON instrument. The sample length was 25 mm, the rate of deformation was 20 mm/min. The value of DR was 1 : 8.

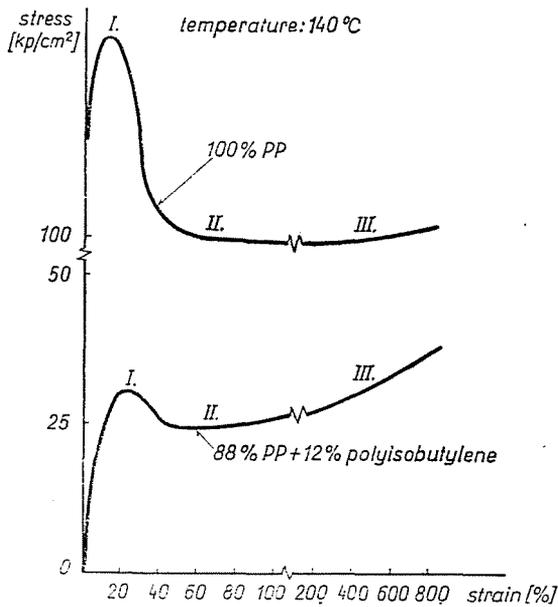


Fig. 9

The respective curves of the additive-free PP, and that of 88% PP + 12% polyisobutylene of $1.5 \cdot 10^6$ average molecular weight are shown in Fig. 9.

From the curves in Fig. 9, the following conclusions could be drawn:

1. The mixture containing polyisobutylene could be oriented just as well as PP. All three known stages of the stress-strain curve appeared.

2. For the mixture containing polyisobutylene there was a marked difference in the run of the stress-strain curve. No such marked drop of stress at the boundary between stages I and II was observed for PP.

3. The length of stage II shortened as compared to that of PP, and its slope was different as well. Stage III has started significantly earlier. That proves that the additive changed the crystalline structure and the process of orientation for PP. The system most likely attains the orientation maximum much sooner than for PP. (For this reason the orientation process was analysed by means of thermoanalysis and X-ray diffraction to be reported subsequently.)

4. The stress orienting the mixture containing polyisobutylene was significantly smaller than for PP. Hence, polyisobutylene appears to be an efficient plasticizer for PP. That seems to be important from the view of machining, since primary sheets can be drawn with relatively small forces, again, extrudability is also likely to improve.

*Thermoanalytical examination of the orientation tendency
of polyisobutylene-PP mixture*

From 88 to 12 mixtures of PP and poly-isobutylene of average molecular weight of $1.5 \cdot 10^6$ with DR = 1 : 2, 1 : 4, 1 : 6, 1 : 8, samples were prepared with the Instron instrument. The temperature was 140°C, the original length 25 mm, the rate of deformation 20 mm/min in each case.

With increasing strain ratio the percentage of orientation has also presumably increased. The goal of the thermoanalysis was to find out for varying DR values concomitant to different orientations and states of crystallinity, whether a characteristic change in the degradation kinetics can be detected

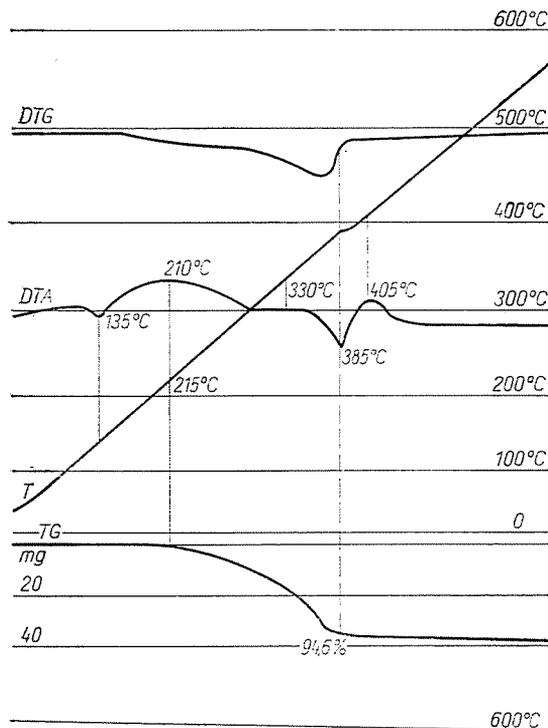


Fig. 10

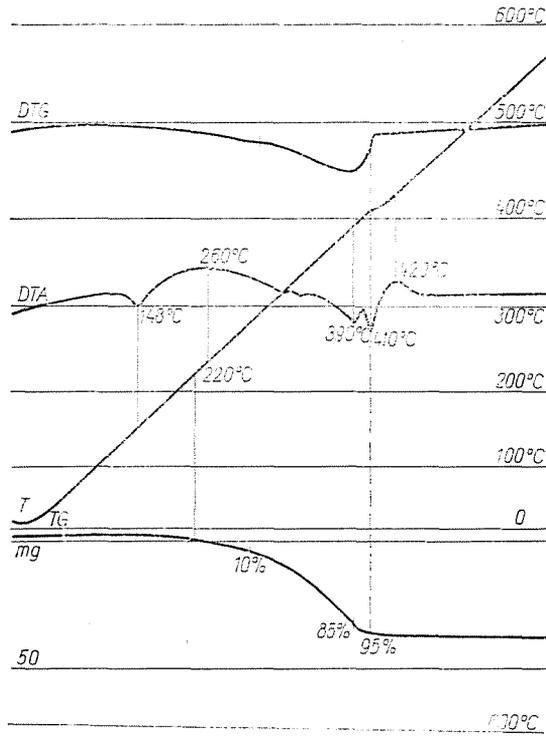


Fig. 11

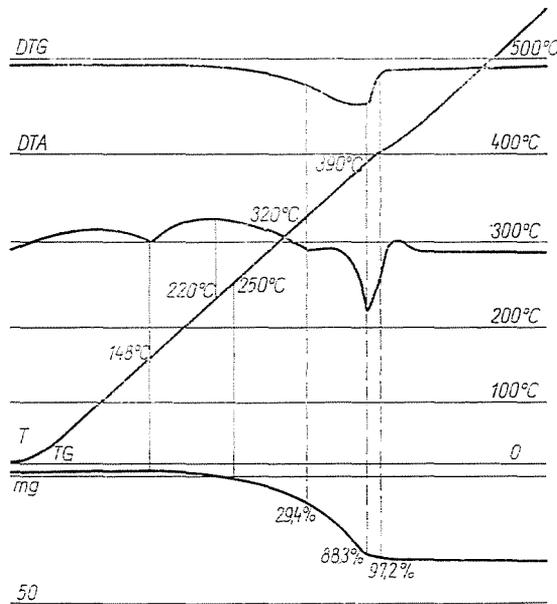


Fig. 12

depending on the percentage of orientation. Derivatograms for various DR values are presented in Figs 10 through 13.

The derivatograms show the first endothermal peaks not accompanied by loss in weight, to appear at temperatures characteristic for the phase transition of the mixture. For higher DR values, however, (1 : 6, 1 : 8) the peaks appear at higher temperatures. The characteristic temperature for the first

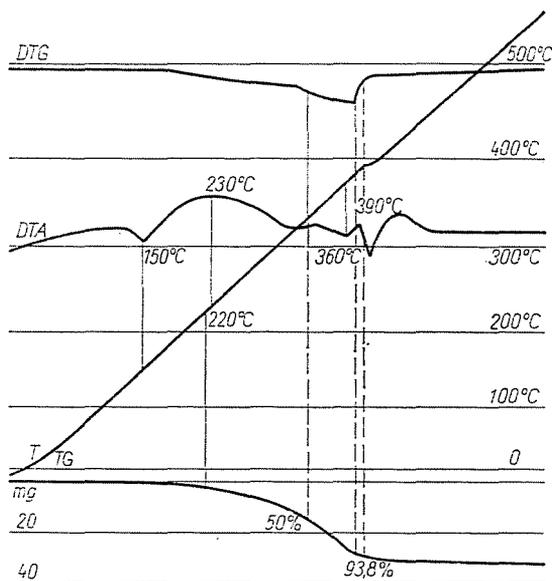


Fig. 13

endothermic peak for samples with DR = 1 : 2 is 135°C, for those with 1 : 6, or 1 : 8, 148 to 150°C. Another characteristic change is seen at the temperature of polymeric heat degradation. The sample with DR = 1 : 6 has shown the most stable structure in the range studied. Dissolution of the mixture starts at 250°C. Probably the mixture is most oriented at this value of DR (Fig. 12). Samples of higher or lower DR values will start to dissolve at 215 to 220°C. Measurements of dissolution kinetics above 300°C also suggest that different DR values will result in different orientation percentages.

X-ray diffraction analysis of polyisobutylene-PP mixture

The orientation of samples previously specified in the DR range of 1 : 2 to 1 : 8 was examined by X-ray diffractometry. The X-ray measurements were made by a Philips-Müller 111-type X-ray apparatus using CuK α radiation

kindly offered by the Hungarian Research Institute of Plastics Industry, Department Polymer Micromorphology. The orientation was determined on records of the run of equatorial blackening of the fibre. The intensity distribution with respect to the equator of the (110) reflection $2\theta = 14^\circ$, was measured by CDC microdensitometer. The orientation parameter ($\bar{0}$) can be calculated from the half-value-width of the maximal blackening (A):

$$\bar{0} = \frac{180 - A}{180}$$

The possible maximum value of $\bar{0}$ is 1.0, corresponding to 100% orientation.

Records of samples with DR = 1 : 2, 1 : 4, 1 : 6, 1 : 8 are given in Figs 14 through 17.

Quantitative evaluation of the X-ray records are given in Table 2.

Table 2

Drawing ratio	Orientation percentage
	%
1 : 2	64.5
1 : 4	92.5
1 : 6	95.2
1 : 8	91.5

Data in Table 2 help to conclude that in the studied DR range the ratio 1 : 6 has given the highest orientation percentage.

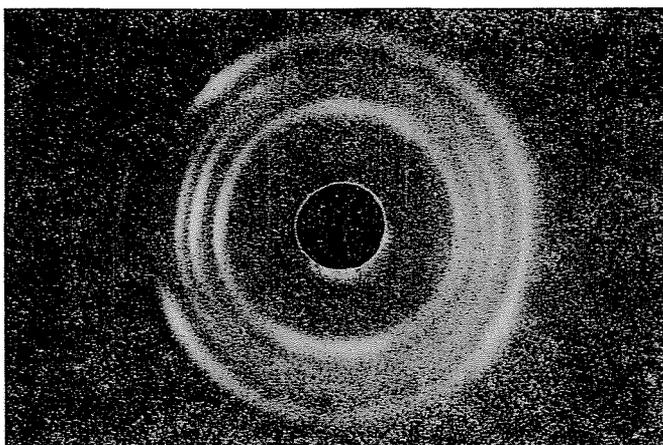
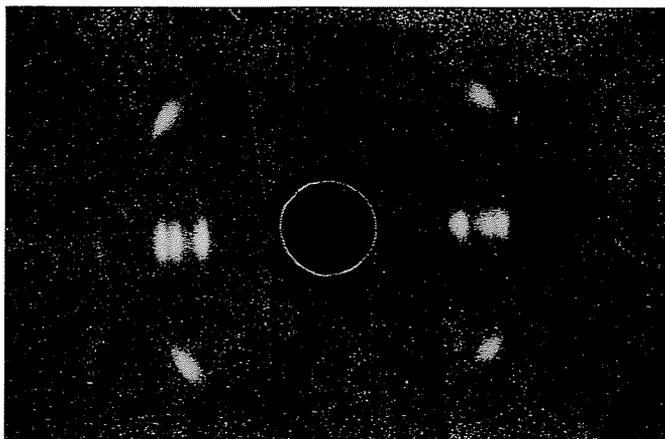
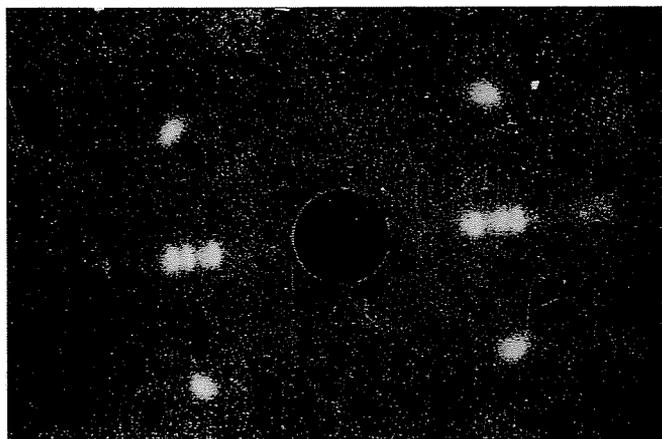
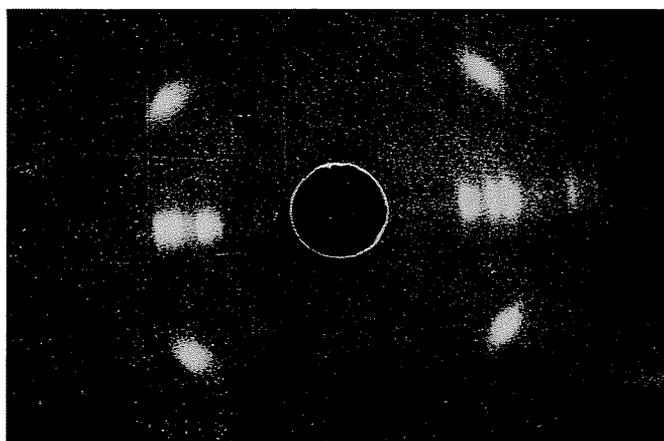


Fig. 14

*Fig. 15**Fig. 16**Fig. 17*

This result is different from the change of the orientation parameters of additive-free PP. In that case the maximum of the orientation parameter was observed at $DR = 1 : 10.4$, and a further increase of DR resulted in a decrease of orientation down to 92.5% [2].

This observation indicates that the crystalline structure of the polyisobutylene-PP system differs from that of the additive-free PP.

Summary

The orientation process fundamentally determining the physical-mechanical properties of fibrillated fibres is different in the case of PP with and without an additive. For the additive-free PP at $DR = 1 : 6.8$ the macromolecular chains are most likely to be oriented in the tensile stress (drawing) direction. Applying higher DR values, for $DR = 1 : 10.4$ an orientation maximum is obtained. Admixing polyisobutylene as an additive will change the orientation process of the system. The process will take place at stresses lower by several orders, consequently the orientation maximum will be at $DR = 1 : 6$.

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