Molecular Orientation in the Amorphous Fraction of Poly(ethylene Terephthalate) and Polyamide 6 Fibers

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Synopsis

Comparison of the Hermans orientation functions of the amorphous fraction of PET and PA6 fibers oriented by stretching to various degrees was made. The orientation functions obtained by different methods enable one to draw conclusions about the acceptability of different methods and their correlation with each other.

INTRODUCTION

The molecular orientation of the amorphous fraction of fibers, i.e., the ordering of kinetic chain segments in relation to the geometric axis of the fiber, is widely accepted as a decisive factor determining many important physical and physicochemical properties of fibers. The amorphous orientation strongly affects among others the mechanical response to an imposed force and the tenacity,[1] transport processes such as the migration of water or dyestuff molecules and electric charge carriers. The amorphous orientation also affects the diffusion kinetics of different chemical agents, which, in turn, modify the rate of chemical reactions.

The examination of amorphous orientation has become one of the most important questions in fiber fine structure investigations. Unfortunately, the hitherto known methods of quantitative evaluation of amorphous orientation are still far from perfect. The results obtained by application of various measuring techniques are very often controversial and do not allow unequivocal appraisal of amorphous orientation. In such situations it seems to be useful and advisable to compare results achieved for the same samples by using different methods. Such collation should create a proper base for drawing conclusions about the usefulness and adequacy of individual methods and should help to develop a universal method that would precisely evaluate the amorphous orientation in fibers.

In fulfilling this aim, an attempt has been made to compare methods enabling direct appraisal as well as indirect assessment. Two different X-ray methods and the IR-spectroscopy method have been considered as representatives of the first type of method; whereas the complex method based on the well-known equation of Stein[2] and the method based on measurements of the dichroic ratio of the standard dyed fiber (DRSDF method) have been taken into consideration as representatives of the second type of methods. In order to ensure proper conditions for a relevant comparison of results from all

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methods, the same amorphous orientation index had to be chosen. That was the Hermans orientation function f_a.

The comparative study should provide information on how various methods quantitatively assess the amorphous orientation and how they reflect the changes in orientation. Such an analysis should also yield information about the mutual consistency and compatibility of particular methods.

EXPERIMENTAL

Materials. The materials used were samples of continuous PET and PA6 filaments, manufactured at industrial conditions with differentiated draw ratio. In the case of PET fibers samples of draw ratio 1.0 ×, 2.65 ×, 3.62 ×, and 4.38 × have been investigated. PA6 fiber samples with draw ratios 1.0 ×, 1.5 ×, 2.0 ×, 2.5 ×, 3.0 ×, and 3.52 × have been investigated.

Measurements.

X-Ray. The evaluation of the amorphous orientation has been based experimentally on the determination of the azimuthal intensity distribution of the X-ray radiation scattered on the amorphous fraction of the investigated samples $I(\delta)$. The $I(\delta)$ distributions have been established for the scattering angle 2θ, corresponding to the maximum value of the scattered intensity, i.e. $2\theta = 21.5°$ in the case of PET fibers and $2\theta = 20.8°$ in the case of PA6 fibers (amorphous halo). The $I(\delta)$ intensity distributions have been established indirectly by radial scans, at various constant azimuthal angles differing by $\Delta\delta = 5°$ similarly to the procedure developed by Jellinek.[3] The radial scans have been performed on the DRON-3 diffractometer by employing CuKα radiation. The values for amorphous orientation function $f_{a,r}$ have been calculated from the $I(\delta)$ intensity distributions, applying two procedures: the method developed by Hargat and Oswald,[4] and the method proposed by Biangardi.[5] In the case of the Hargat–Oswald method the volume fraction of the isotropic and anisotropic amorphous phase of the fibers have been additionally computed.

IR Spectroscopy. The amorphous orientation functions $f_{a,\text{IR}}$ have been established on the base of measured values of the dichroic ratios R of selected "amorphous" absorption bands. The R values have been calculated as the quotients of the extinction values of an absorption band for parallel and perpendicular vibration direction of the IR. The following "amorphous" bands have been chosen as relevent, for PET fibers the bands 898 and 1042 cm^{-1}, for PA6 fibers the bands 712 and 1171 cm^{-1}. The values of amorphous orientation function $f_{a,\text{IR}}$ have been calculated by the equation[6]

$$f_{a,\text{IR}} = \left(\frac{R-1}{R+2}\right)\bigg/\left(\frac{R_0-1}{R_0+2}\right) \tag{1}$$

where R_0 is the dichroic ratio of the absorption band for an ideal amorphous orientation. For bands of π-type dichroismus $R_0 = \infty$ for bands of σ-type dichroismus $R_0 = 0$.

DRSDF. This method used in the case of PET and PA6 fibers is experimentally founded on measurements of the directional optical densities of the

fibers[7] which have been previously dyed under special conditions with the standard dyestuff DisperseYellow/ColorIndex 3(11855).

The values of the amorphous orientation function $f_{a,d}$ have been calculated from the relationship given by Patterson and Ward,[8]

$$f_{a,d} = \frac{D_\parallel - D_\perp}{D_\parallel + 2D_\perp} \qquad (2)$$

where $D_\parallel$ and $D_\perp$ are the directional optical densities for the standard dyed fiber, respectively, for visible light vibrating parallel and perpendicular to the fiber axis.

Complex Method. The values of amorphous orientation functions $f_{a,c}$ have been calculated from measured birefringence Δn, crystallite orientation function f_k, crystallinity x, and values of the intrinsic amorphous and crystalline birefringence Δn_a Δn_k from the transformed Stein equation

$$f_{a,c} = \frac{\Delta n - f_k \cdot x \cdot \Delta n_k}{(1-x) \cdot \Delta n_a} \qquad (3)$$

Two sets of values of intrinsic birefringences Δn_a and Δn_k have been regarded: for PET fibers after Dumbleton[9] $\Delta n_a = 0.253$, $\Delta n_k = 0.220$ and after Okajima[10] $\Delta n_a = 0.216$, $\Delta n_k = 0.210$; for PA6 fibers after Urbańczyk[11] $\Delta n_a = 0.078$, $\Delta n_k = 0.084$, and after Jambrich[12] $\Delta n_a = 0.078$, $\Delta n_k = 0.0675$.

RESULTS AND DISCUSSION

The values of the amorphous orientation function referring to the examined PET and PA6 samples are shown in Tables I and II and are demonstrated graphically in Figures 1 and 2. The results obtained from all methods used confirm that an increase in fiber draw ratio causes an increase in the amorphous orientation function for both fibers. The results exhibit a specific differentiation in respect to the magnitude of the f_a values and a specific variation of f_a within the considered range of draw ratios. This indicates that each of the methods evaluates properly, and specifically, the amorphous orientation occurring in drawn PET and PA6 fibers.

For PET as well as for PA6 fibers the smallest f_a values have been obtained by the DRSDF method, and the largest f_a values result from the X-ray methods, especially by applying the procedure of Biangardi.[5] Intermediate values have been reached from the IR spectroscopy and the complex methods.

The differences in the level of f_a values acquired by different methods seem to be fully justified. It can be assumed that the smallest values which have been obtained from the DRSDF method are a consequence of the fact that the spatial distribution of dyestuff molecules is mainly determined by least ordered amorphous regions. Due to their smallest density, the dyestuff diffusion, and the uptake of dyestuff will be greater than in more ordered amorphous regions.

The reason for the largest f_a values achieved by X-ray methods is that the anisotropy of the intensity distribution within the amorphous halo is determined first of all by the best ordered amorphous regions (the s.c. anisotropic

TABLE I
Values of the Hermans Orientation Function in the Amorphous and
Crystalline Fraction of PET Fibers[a]

Evaluation method / Draw ratio	DRSDF method $f_{a,d}$	IR spectroscopy method $f_{a,IR}$		X-ray method			Complex method		X-ray method crystallite orientation, f_k
		Absorp. band 1042 cm^{-1}	Absorp. band 898 cm^{-1}	After Biangardi, $f_{a,r}$	After Hargat–Oswald, $f_{a,r}$	Anisotropic amorph. phase (%)	$f_{a,c1}$	$f_{a,c2}$	
1.00 ×	0.015	0.013	0.016	0.258	0.303	27.3	—	—	—
2.65 ×	0.047	0.048	0.050	0.393	0.336	43.1	0.134	0.157	0.8142
3.22 ×	0.089	0.222	0.088	0.589	0.446	63.7	0.172	0.201	0.8812
3.62 ×	0.156	0.317	0.150	0.632	0.483	76.3	0.530	0.621	0.8814
4.38 ×	0.130	0.238	0.130	0.654	0.526	80.0	0.707	0.816	0.8810

[a] $f_{a,c1} = \Delta n_a$, Δn_k after Dumbleton[9]; $f_{a,c2} = \Delta n_a$, Δn_k after Okajima.[10]

TABLE II
Values of the Hermans Orientation Function in the Amorphous and
Crystalline Fraction of PA6 Fibers

Evaluation method / Draw ratio	DRSDF method $f_{a,d}$	IR spectroscopy method $f_{a,IR}$		X-ray method			Complex method		X-ray method crystallite orientation, f_k
		Absorp. band 1042 cm^{-1}	Absorp. band 898 cm^{-1}	After Biangardi, $f_{a,r}$	After Hargat–Oswald, $f_{a,r}$	Anisotropic amorph. phase (%)	$f_{a,c1}$	$f_{a,c2}$	
1.0 ×	0.064	0.180	0.167	—	—	—	0.036	0.127	0.8143
1.5 ×	0.100	0.199	0.226	0.757	0.498	55.0	0.311	0.421	0.8567
2.0 ×	0.137	0.324	0.253	0.756	0.506	56.2	0.315	0.437	0.8601
2.5 ×	0.171	0.409	0.286	0.770	0.525	59.3	0.380	0.511	0.8753
3.0 ×	0.215	0.494	0.326	0.814	0.560	64.3	0.393	0.534	0.8927
3.52 ×	0.252	0.583	0.406	0.818	0.563	65.2	0.489	0.645	0.8933

[a] $f_{a,c1} = \Delta n_a$, Δn_k after Urbańczyk[11]; $f_{a,c2} = \Delta n_a$, Δn_k after Jambrich.[12]
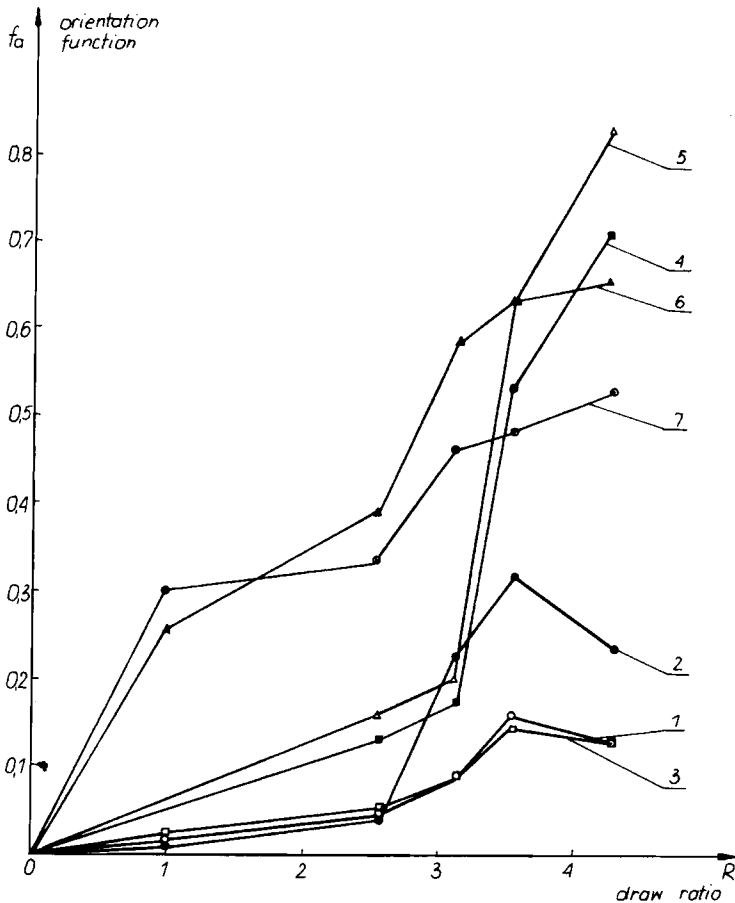
Fig. 1. Values of the orientation function for the amorphous fraction of differently stretched PET fibers: (1) dichroic ratio of standard dyed fiber method; (2) IR spectroscopy method 1042 cm^{-1} absorption band; (3) IR spectroscopy method 898 cm^{-1} absorption band; (4) complex method due to the Stein equation $\Delta n_a = \Delta n_k$ after Dumbleton[9]; (5) complex method due to the Stein equation $\Delta n_a = \Delta n_k$ after Okajima and Keyama[10]; (6) X-ray method procedure after Biangardi[5]; (7) X-ray method procedure after Hargat and Oswald.[4]

amorphous phase). The $f_{a,r}$ value increases rapidly for PET fibers after the draw ratio exceeds 2.65 × and somewhat slower for PA6 fibers when the draw ratio exceeds 2.5 ×. It is well known that above the mentioned threshold draw ratio values there occurs an intensive increase in the anisotropic amorphous phase content in drawn fibers.

The variation of $f_{a,r}$ in the region of the threshold value of the draw ratio enables us to conclude that X-ray methods lead to an appraisal of amorphous orientation which depends not only on the average orientation of the kinetic chain segments but is also very sensitive to the content of the anisotropic amorphous phase.

The results obtained from IR spectroscopy and complex methods exhibit that the values of amorphous orientation function vary. In the case of IR
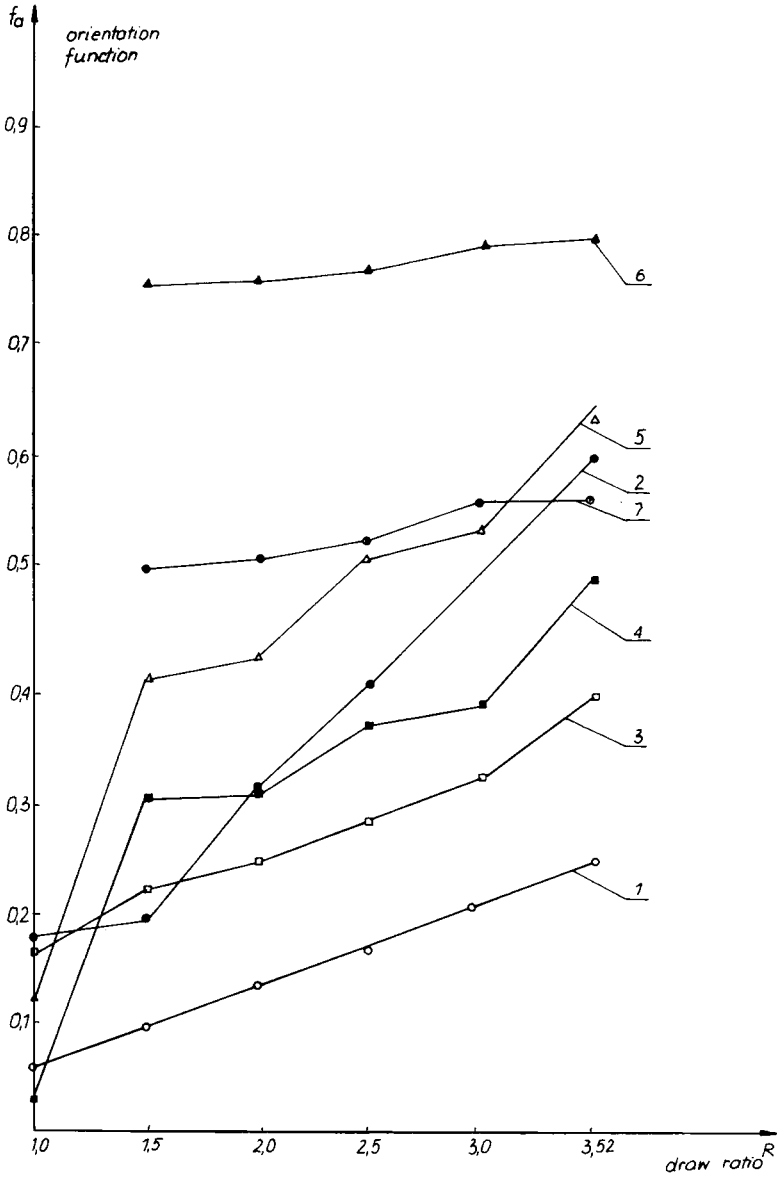
Fig. 2. Values of the orientation function for the amorphous fraction of differently stretched PA6 fibers: (1) dichroic ratio of standard dyed fiber method; (2) IR spectroscopy method 712 cm^{-1} absorption band; (3) IR spectroscopy method 1171 cm^{-1} absorption band; (4) complex method due to the Stein equation $\Delta n_a = \Delta n_k$ after Urbańczyk[11]; (5) complex method due to the Stein equation $\Delta n_a = \Delta n_k$ after Jambrich[12]; (6) X-ray method procedure after Biangardi[5]; (7) X-ray method procedure after Hargat and Oswald.[4]

spectroscopy method they depend on the type of "amorphous" band; in the case of the complex method on the assumed Δn_a and Δn_k values.

For PET fibers, for the majority of draw ratios, comparatively larger $f_{a,\,\mathrm{IR}}$ values are attributed to the 1042 cm^{-1} band than to the 898 cm^{-1} band and for Δn_a and Δn_k after Okajima and then after Dumbleton. For PA6 fibers, for the majority of draw ratios, relatively larger values refer to the 712 cm^{-1} band than to the 1171 cm^{-1} band and to Δn_a and Δn_k given by Jambrich and then by Urbańczyk.

The methods noted reveal a visible differentiation in respect to their sensitivity to reflect alterations of the amorphous orientation. Assuming the fluctuation interval of f_a, corresponding to the full range of regarded draw ratios, as a measure characterizing the sensitivity to amorphous orientation changes, the following conclusions can be drawn. PET fibers are most susceptible to changes in amorphous orientation by the complex method and in diminishing order by X-ray, IR spectroscopy, and finally DRSDF. In the case of PA6 fibers the sequence begins with the IR spectroscopy method and later on there follows successively the complex, DRSDF, and X-ray methods. Striking features of these juxtapositions are the comparatively high susceptibility of the complex method and the discrepancy in sensitivity of the X-ray methods in the case of each kind of fiber. One can suppose that the high susceptibility of the complex method is only apparent, artificially enhanced as a result of assuming constant values for Δn_a for samples with various draw ratios. Analyzing equation (3) it can be seen that assuming increasing values for Δn_a for enhancing draw ratio would be more appropriate to obtain smaller $f_{a,\,c}$ values.

The reasons for the uneven sensitivity of the X-ray methods in the case of PET and PA6 fibers can be explained by two factors. The first consists in differences of the evaluation accuracy of the azimuthal distribution of the scattered intensity for both types of fibers. In the case of PA6 fibers the evaluation is less precise, due to the influence of crystalline reflexes situated near the amorphous halo. Secondly, as a result of a larger content of the anisotropic amorphous phase at the small draw ratio the differentiation of the $f_{a,\,r}$ values for PA6 fibers is less pronounced than in case of PET fibers.

The comparison of results obtained from all methods in question enables us to infer about their mutual compatibility and adequacy. Assuming as a compatibility criterion the value of correlation factor r between sets of values corresponding to two compared methods and further on assuming that for $r = 0.88–0.99$ there exists a good compatibility, for $r = 0.77–0.87$ a relatively good compatibility and for $r < 0.77$ a poor adequacy, one can draw the following conclusions.

For PET fibers there exists good compatibility between DRSDF, IR spectroscopy and X-ray methods and a relatively good compatibility between DRSDF and complex methods. Small adequacy pertains to the IR spectroscopy and X-ray methods. For PA6 fibers a very good adequacy refers to the DRSDF and IR spectroscopy methods, a relatively good compatibility pertains to DRSDF and complex and X-ray methods. An inadequacy occurs, however, between DRSDF and X-ray methods and between X-ray and complex methods.

CONCLUSIONS

The amorphous orientation functions for PET and PA6 fibers established by the application of different evaluation methods show a broad differentiation in the case of the same samples.

The smallest f_a values have been obtained from measurements of the dichroic ratio of standard dyed fibers, the largest from X-ray methods. Intermediate values have been obtained from the IR spectroscopy method and the complex method based on the Stein equation. Methods differ with respect to their susceptibility to the changes in the amorphous orientation in the fiber. The relation between susceptibilities of particular methods is different in the case of PET and PA6 fibers. The susceptibility of the complex method seems to be artificially enhanced as a result of assuming constant values of Δn_a for fibers with different draw ratio. The discrepancy in sensitivity of the X-ray methods in the case of PET and PA6 fibers can be explained by an unequal accuracy of the evaluation of the azimuthal intensity distribution within the amorphous halo and by the different content of anisotropic amorphous phase in both kinds of fibers. The results obtained indicate that among some of the methods there is good correlation. In the case of PET fibers, the dichroic ratio of standard dyed fiber method, the IR spectroscopy, and the X-ray methods, and in PA6 fibers the DRSDF and the IR spectroscopy method can be included in the methods that correlate very well with each other.

The results of our investigations lead to the conclusion that there still is a need to develop a universally valid method free of uncertainties and ambiguities in the quantitative appraisal of amorphous orientation in fibers.

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