

Calculation of orientation factors for crystalline polymers from X-ray pole figure intensities

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Summary

The characterization of polymer orientation is discussed by expanding the orientation distribution function (ODF) for the crystalline phase into a series of generalized spherical harmonics (GSH) or into a series of symmetric generalized spherical harmonics (SGSH). A transformation relation is derived between the two expansions. By means of this transformation the orientation factors (moments of the ODF) can be calculated from the SGSH series expansion coefficients. As an example, this transformation is demonstrated for crystals of hexagonal symmetry and fiber texture.

Introduction

The anisotropic properties of a polycrystalline material are related to the orientation distribution function (ODF) of the crystallites [1]. For partially crystalline polymers, the amorphous orientation can be described independently from the orientation of the crystallites [1]. In this paper we consider only the crystalline orientation.

The material properties of an anisotropic sample measured in different directions are functions of only a few statistical averages (or moments) of the ODF which are called orientation factors. The connection between the ODF and the anisotropic material properties was treated previously by Roe and Krigbaum [2]-[3] and by Nomura and Kawai [4]. These authors made use of a series expansion and interrelated the coefficients of this expansion to the orientation factors. Another slightly different series expansion was developed independently by Bunge [5], [6] taking into account the crystal structure (crystal symmetry) and the sample orientation (sample texture). It is the purpose of this paper to express the orientation factors by the coefficients of the Bunge ODF series.

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The orientation factors can be determined from X-ray measurements by several ways:

- (a) - direct integration of the weighted scattering intensities over the orientation angles [7]-[9]. This procedure results in low order orientation factors only.
- (b) - measurement of the pole figure intensities, from which the coefficients of the ODF series can be determined [2]-[4]. The relation between the ODF series and the orientation factors is the subject of this paper.

The pole figures are defined as stereographic projections of the plane normal vectors of a crystal lattice [8]-[9]. A pole figure is measured at a fix Bragg angle by varying the sample position relative to the incident X-ray beam by using 4 axes texture goniometers [8]-[10]. For the determination of the ODF series expansion coefficients a certain number of complete pole figures have to be measured.

The determination of the ODF series expansion coefficients from pole figures is routine for metals, commercially available as ODF software TEX11/ODF11 developed by Siemens AG [10]. This software makes use of the ODF series expansion method of Bunge [5], [6] for cubic and hexagonal symmetry classes. The application of this software for polymers is limited, because they mostly belong to crystal classes with lower symmetry. Polyoxy-methylene (POM) is the only mass polymer which possesses a hexagonal crystal symmetry [8].

Series Expansion for the Orientation Distribution Function

The probability of finding a structural element (i.e. elementary cell) in the $d\vartheta d\psi d\phi$ angular range can be given by the orientation distribution function $w(\vartheta, \psi, \phi)$. This probability is equal to $w(\vartheta, \psi, \phi) d\vartheta \sin\vartheta d\psi d\phi$ where ϑ , ψ and ϕ are the Euler angles of the structural element with respect to the laboratory frame [6], [11]. We note, that the Euler angles in the two different ODF series discussed here, are defined in different ways [6].

ODF Series Expansion by Roe and Krigbaum

The ODF can be expanded in a series of generalized spherical harmonics [1]-[3], [9]:

$$w(\vartheta, \psi, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{n=-l}^l W_{lmn} Z_{lmn}(x) e^{-im\psi} e^{-in\phi} \quad (1)$$

with $x = \cos \vartheta$ and with the normalization condition

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} w(\vartheta, \psi, \varphi) \sin \vartheta d\vartheta d\psi d\varphi = 1 \quad (2)$$

$$w_{\text{random}} = 1/(8\pi^2)$$

where the functions $Z_{lmn}(x)$ have the following form:

$$Z_{lmn}(x) = \left[\frac{2l+1}{2} \frac{(l-m)!(l+m)!}{(l-n)!(l+n)!} \right]^{1/2} (1/2)^m (1-x)^{\frac{m-n}{2}} (1+x)^{\frac{m+n}{2}} P_{l-m}^{(m-n, m+n)}(x) \quad (3)$$

The explicit expression for the $P_s^{(\alpha, \beta)}(x)$ Jacobi polynomials will be shown later, the variables ϑ , ψ and φ correspond to the Euler angles as defined by Margenau and Murphy [11].

The W_{lmn} ODF coefficients can be separated into a real and an imaginary part [4]:

$$W_{lmn} = a_{lmn} + ib_{lmn}$$

The W_{lmn} ODF coefficients are explicitly the lmn -th orders of the moments of the ODF function. Due to specific symmetry properties with respect to the sample texture and the crystal system, some of the expansion coefficients in eq. (1) are zero and some are equal. Concerning the details, we refer to the literature [3].

As statistical averages of the ODF (labelled with $\langle \rangle$), the orientation factors are expressed in terms of $\sin^n \alpha$ and $\cos^n \alpha$. Here α is equivalent to either ϑ , or ψ or φ and n is a positive integer. The W_{lmn} coefficients of the ODF expansion by Roe result directly in the f_{lmn} orientation factors:

$$f_{lmn} = 4\pi^2 \left[\frac{2l+1}{2} \frac{(l+m)!(l+n)!}{(l-m)!(l-n)!} \right]^{1/2} W_{lmn} \quad (4)$$

Since the imaginary component of W_{lmn} vanishes for practical cases i.e. for texture with biaxial or uniaxial symmetry [4], explicit expressions for some orientation factors (as listed below) contain only the real part, a_{lmn} :

$$f_{200} = (2/5)^{1/2} 4\pi^2 a_{200} = (1/2)(3\langle \cos^2 \vartheta \rangle - 1) \quad (5)$$

$$f_{220} = (12/15^{1/2}) 4\pi^2 a_{220} = 3\langle \sin^2 \vartheta \cos 2\psi \rangle \quad (6)$$

$$f_{202} = (12/15^{1/2}) 4\pi^2 a_{202} = 3\langle \sin^2 \vartheta \cos 2\varphi \rangle \quad (7)$$

$$f_{400} = (2^{1/2}/3)4\pi^2 a_{400} = (35\langle \cos^4\vartheta \rangle - 30\langle \cos^2\vartheta \rangle + 3)/8 \quad (8)$$

$$f_{420} = 80^{1/2}4\pi^2 a_{420} = (15/2)\langle (\cos^2\vartheta - 1)\sin^2\vartheta \cos 2\psi \rangle \quad (9)$$

$$f_{440} = 16(35)^{1/2}4\pi^2 a_{440} = 105\langle \sin^4\vartheta \cos 4\psi \rangle \quad (10)$$

In addition to the X-ray procedure, there are other well established experimental methods to determine individual orientation factors. For example, f_{200} corresponds to the so-called Hermann's orientation parameter which describes e.g. the optical anisotropy of samples with cylindrical symmetry [1]. Stein used the f_{220} coefficients for biaxially oriented polymers for the description of dichroitic properties [1]. The characterization of the anisotropy of the elastic stiffness tensor needs information about the fourth order moments (see e.g. [12]). NMR methods result in orientation factors up to the eighth order [1]. Only wide X-ray diffraction gives in principle every order of the moments [1].

ODF Series Expansion by Bunge

According to Bunge [6], the ODF is defined slightly different from $w(\vartheta, \psi, \varphi)$ and denoted by $f(\varphi_1, \Phi, \varphi_2)$ where the Euler angles $\varphi_1, \Phi, \varphi_2$ differ from ϑ, ψ, φ . The Bunge series expansion is written as

$$f(\varphi_1, \Phi, \varphi_2) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{n=-l}^l C_l^{mn} T_l^{mn}(\varphi_1, \Phi, \varphi_2) \quad (11)$$

with the normalization condition (12)

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} f(\varphi_1, \Phi, \varphi_2) \sin\Phi d\Phi d\varphi_1 d\varphi_2 = 8\pi^2 \quad (12)$$

$$f_{\text{random}} = 1$$

where the spherical harmonics $T_l^{mn}(\varphi_1, \Phi, \varphi_2)$ are defined as follows:

$$T_l^{mn}(\varphi_1, \Phi, \varphi_2) = e^{im\varphi_2} e^{in\varphi_1} \frac{(-1)^{l-m} (i)^{n-m}}{2^l (l-m)!} \left[\frac{(l-m)!(l+n)!}{(l+m)!(l-n)!} \right]^{1/2} \cdot (1-\cos\Phi)^{-\frac{n-m}{2}} (1+\cos\Phi)^{-\frac{n+m}{2}} \frac{d^{l-n}}{d(\cos\Phi)^{l-n}} [(1-\cos\Phi)^{l-m} (1+\cos\Phi)^{l+m}] \quad (13)$$

The two sets of Euler angles are interrelated:

$$\varphi_1 = \psi + \pi/2 \quad \Phi = \vartheta \quad \varphi_2 = \varphi - \pi/2$$

The two ODF functions are simply related [6]:

$$w(\vartheta, \psi, \varphi) = \frac{1}{8\pi^2} f(\varphi_1, \Phi, \varphi_2) \quad (14)$$

Taking into account certain symmetry conditions, Bunge developed an expansion in a series using linear combinations of the T_1^{mn} functions. These combinations are called symmetrical generalized spherical harmonics, SGSH [5], [6]. The coefficients for the linear combinations are selected such that both the crystallographic symmetry and the sample texture symmetry are taken into account. The SGSG series expansion by Bunge has the general form:

$$f(\varphi_1, \Phi, \varphi_2) = \sum_{l=0}^{\infty} \sum_{\mu=1}^{M(l)} \sum_{\nu=1}^{N(l)} C_l^{\mu\nu} \dot{T}_l^{\mu\nu}(\varphi_1, \Phi, \varphi_2) \quad (15)$$

The number of independent spherical harmonics, - $N(l)$ for the texture and $M(l)$ for the crystall symmetry - are given for various l in the literature [6]. The dots over T mean that in the series expansion only the symmetric generalized spherical harmonics are kept, which are linear combinations of the non-symmetric T_1^{mn} generalized spherical harmonics:

$$\dot{T}_l^{\mu\nu}(\varphi_1, \Phi, \varphi_2) = \sum_{m=-1}^1 \sum_{n=-1}^1 \dot{B}_l^{m\mu} \dot{A}_l^{n\nu} T_1^{mn}(\varphi_1, \Phi, \varphi_2) \quad (16)$$

The symmetry operations S defined by the crystal structure and by the texture leave the "dotted" spherical harmonics invariant:

$$\dot{T}(S(\varphi_1, \Phi, \varphi_2)) = \dot{T}(\varphi_1, \Phi, \varphi_2) \quad (17)$$

The coefficients $\dot{B}_l^{m\mu}$ in eq. (16) express the crystal symmetry and $\dot{A}_l^{n\nu}$ has to be selected according to the texture symmetry. The values of these coefficients have been summarized by Bunge [6] in tables for different cases.

The advantage of the Bunge series expansion (15) is that, for a given error, fewer terms are required than for the expansion (1). Unfortunately, a direct physical interpretation of the expansion coefficients C by the orientation factors is not possible.

Transformation of ODF Coefficients of the Bunge Expansion to Orientation Factors

For the mathematical transformation, we make use of the Jacobi polynomials in the differential description as defined by Gel'fand and Shapiro [13]:

$$P_s^{(\alpha, \beta)}(\xi) = \frac{(-1)^s}{2^s s!} (1-\xi)^{-\alpha} (1+\xi)^{-\beta} \frac{d^s}{d\xi^s} [(1-\xi)^{s+\alpha} (1+\xi)^{s+\beta}] \quad (18)$$

with the substitution $\xi = \cos\Phi$.

Let us substitute in eq. (18) $s = l - \frac{1}{2} (|m+n| + |m-n|)$, $\alpha = |n-m|$, $\beta = |m+n|$ and multiply with

$$K(\xi) = \left(\frac{1}{2}\right)^m \frac{(1+m)!(1-m)!}{(1+n)!(1-n)!} (1-\xi)^{\frac{|n-m|}{2}} (1+\xi)^{\frac{|n+m|}{2}} \quad (19)$$

As a result, we obtain the individual terms of the series expansions, on the left-hand side the terms of Roe and on the right-hand side the terms of Bunge. It follows from this relation, that the expansion coefficients for the GSH series can be written as

$$W_{lmn} = \frac{i^{n-m}}{8\pi^2} \left(\frac{2}{2l+1}\right)^{\frac{1}{2}} \sum_{v=1}^{n_v(l)} A_1^{mnv} C_1^{mv} \quad (20)$$

The above relation gives a direct transformation between the coefficients of Bunge (measurable with the SIEMENS TEX11/ODF11 system) and the coefficients of Roe. The transformation coefficients A_1^{mnv} should be calculated for the different crystal systems and texture symmetries. For the hexagonal crystal system and fiber texture they have the following form (see [6], Table 14.4):

$$A_1^{mnv} = \frac{1}{2} (-1)^l \quad v=1 \quad (21.a)$$

$$A_1^{mnv} = \left(\frac{1}{2}\right)^{\frac{1}{2}} (-1)^l \delta_{6(v-1), m} \quad v > 1 \quad (21.b)$$

where $\delta_{i,k}$ is the Kronecker symbol with the value 1 or 0. The orientation factors f_{lmn} can be obtained with the eq. (20), by a substitution of the coefficients W_{lmn} into the equation (4). As an illustration, the Hermann orientation factor for a specimen with fiber texture and hexagonal crystals has the form:

$$W_{200} = \frac{1}{8\pi^2} \left(\frac{2}{5}\right)^{\frac{1}{2}} \cdot \frac{1}{2} \cdot C_2^{00}$$

(22)

$$f_{200} = \frac{1}{2} (3\langle \cos^2\theta \rangle - 1) = 4\pi^2 \left(\frac{2}{5}\right)^{\frac{1}{2}} W_{200}$$

In a forthcoming paper, we give the orientation factors determined from X-ray scattering data for POM with fiber texture.

Acknowledgement

The authors acknowledge financial support by the Swiss National Science Foundation (Grant No. 2.046-0.86). They are indebted to Dr. P.I. Welch, Technische Universität Clausthal, for the helpful discussions and to Mrs. A. Forster for typing the manuscript.

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