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A thermo-conductive approach to explain the origin of lamellar twisting in banded spherulites

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Abstract Thermo-conductive and morphological considerations have led to the conclusion that ribbon-like crystals developed in the presence of thermal gradients behave in the same manner of macroscopic cantilevers, whose deformation in a non uniform temperature field is a deeply examined issue in the continuum mechanics. Therefore, the well known concepts and principles of this science have been applied to a lower scale (Pitteri M, Zanzotto G (2002) Continuum models for phase transitions and twinning in crystals, CRC Press, London) to explain the origin of lamellar twisting during the growth of optically banded spherulites in polymer samples squashed between glass surfaces. The developed model considers that the torsional motion of the lamellae is caused by the presence of thermal gradients across the thickness of the samples and accounts for both morphological and optical characteristics of polymer spherulites.

Introduction

Polymers crystallized from melt show a typical spherulitic superstructure. Spherulites are built up of lamellar crystallites [1, 2] mostly shaped as ribbons, which radiate from the center and are separated by amorphous material. Many substances, from water to high polymers such as polyethylene (PE) [3–7], form optical banded spherulites whose band spacing is controlled by molecular characteristics and crystallization conditions. Banding in polymer spherulites has been explained in terms of periodic rotation of the optical indicatrix during the lamellar growth [2, 6], entailing that also the lamellae periodically twist.

Although it is well accepted that the twisting of the lamellae affects the optical properties of spherulites resulting in banding, a general reason for lamellar twisting seems to be still unknown [8, 9]. Many interpretations of lamellar twisting [10–18] have been reported as each theory relies on a specific property of a group of polymers and does not fit all the experimental observations on polymers, whilst the phenomenon of banding is not confined to polymers [4, 19].

Previous work [20–22] has shown that temperature gradients affect the morphology of spherulites. Foks [20] observed morphological differences in spherulites of polyethylene adipate when specimens were isothermally crystallized at three different temperatures. In particular, the author found that banded spherulites only form at low crystallization temperatures and he concluded that the fluctuation of the local temperature is responsible for the appearance of rings in the spherulites. The micrographs included in the study of Lovinger et al. [21] on the crystallization of isotactic polypropylene (iPP) also show that the β spherulites of iPP are banded when they originate in a temperature gradient. Moreover, stepwise crystallization of an ethylene–propylene copolymer (E/P) has shown that a characteristic band pattern of spherulites may be obtained under reiterated temperature changes [22], as shown in Fig. 1. The core of spherulites in Fig. 1 were formed at 130 °C, then the temperature of the hot stage was decreased to 120 °C to accelerate the

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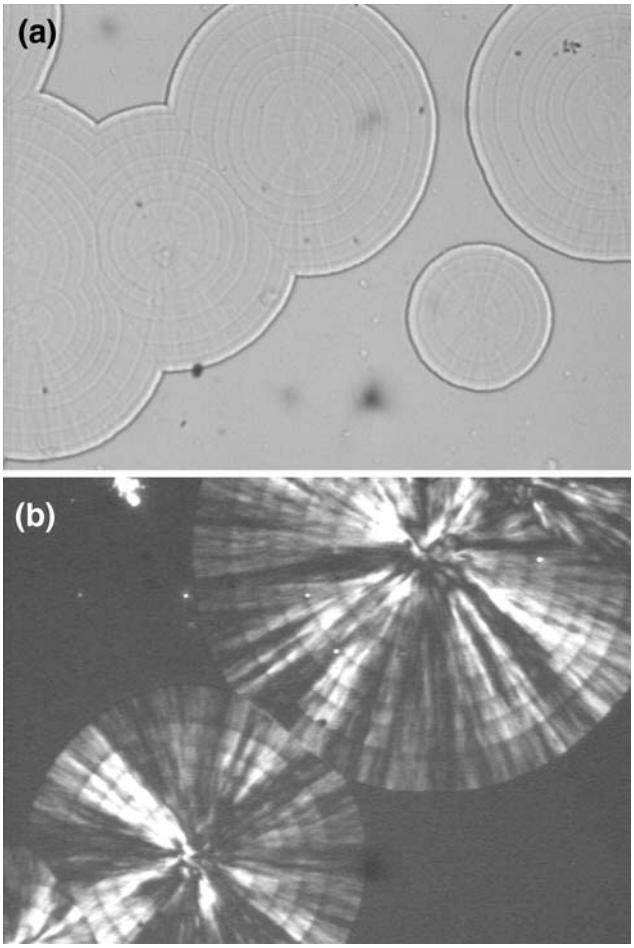

Fig. 1 Optical micrographs of E/P spherulites grown under a varying temperature field. (**a**) Unpolarized light. (**b**) Crossed polars

crystallization. Preformed spherulites were allowed to grow for 2 min, then the temperature was increased to 140 °C and, after 2 min more, reduced again to 120 °C. This temperature fluctuation from 120 °C to 140 °C was repeated many times and generated rings within spherulites.

As the existence of thermal gradients in crystallizing polymer films has been well recognized [23–25] and the possibility that gradients induce banding has also been suggested [20, 26], the influence of temperature gradients on deformation of lamellae has been modeled here. The main idea of this article is that it is essential to focus on the experimental crystallization conditions of polymers inside a hot stage in order to correlate the existence of banded spherulites to the temperature gradients. This model results from the effort to combine heat transport and elasticity theories on the bases of either early data and recent reports, and attempts to give a more general explanation for the regular twisting morphology of polymers starting from the idea that a body subjected to thermal gradients, which originate internal stress, is mechanically unstable and therefore warps [27]. For instance, a strong flexion of a parallelepiped lamella entails generally torsion, even in the absence of external torsional moments [27]. The torque stress acting on lamellae, accounting for twisting of lamellae and, hence, for the banded structure of spherulites, has been considered here to have a thermo-conductive origin [28] because of the existence of thermal gradients. Furthermore, a small temperature difference (even a tenth or hundredth parts of a degree centigrade) between opposite surfaces has been supposed to be sufficient to produce lamellar twisting because of the small thickness (tens of nm) of the lamellae. The main difficulties, connected to the complexity of a rigorous mathematical treatment leading to unsolvable differential equations, have been overcome by offering a qualitative model. To predict the influence of thermal gradients, on the shape and the optical morphology of growing lamellar crystals, the mathematical treatment proposed by Landau and Lifšits for a broad dimensional range varying from macroscopic beams to small structures like crystals, has been exploited. In particular, the twining of the lamellae is modeled by defining the deformation of a non-uniformly heated lamella as a torsion [28] and by studying the rate of propagation of the torsion wave along the growth direction of the lamella. This work offers a complementary view of optical banding and becomes a part of the current theories justifying banding when the existing interpretations are recognized to be seriously lacking, especially relative to polymers with helical conformations [9] and also in polymers and substances in general not included in previous explanations. Furthermore, the present model accounts for the previous observation that, at least for non chiral polymers, both right- and left- handed twisting occur with equal frequency, even in the same spherulite which may show opposite twisting sense in different sectors [7].

Theory

A crystallizing film observed by an optical microscope at a nominal constant temperature may be subjected not only to a temperature variation in the plane of the observation, but also to a temperature variation along its thickness. For instance, a temperature difference between the top and the bottom surfaces of a polymer sample could be due to the presence of two glass slides having different thicknesses and thus different insulating power from the external environment. Furthermore, the samples are actually three-dimensional and thus own a lateral surface that, differently from the base surfaces, is not in contact with glass but is surrounded by a gas medium. Therefore, during crystallization, thermal gradients may arise also because of the sensitivity of the convection mechanism towards local characteristics of the gas motion. In conclusion, crystallization studies carried out on polymers by an optical microscope should take into account the mechanisms of heat transfer among all the components (glass slides, heating resistors, air or nitrogen cooler, besides the polymer) involved in the system, disregarding some effects only when the investigated phenomenon does not critically depend on thermal gradients. Moreover, in polymer samples the heat developed during the crystallization is hardly dissipated because of their poor efficiency as conductors [29], also leading to thermal gradients.

Similarity between thermal and optical properties of lamellar crystals

Let us consider the deformation of a solid body occurring simultaneously to a temperature change, this latter being caused by the deformation itself or by other reasons. Assuming as non-deformed state that corresponding to the absence of external forces and to a temperature T_0, if the temperature of the body is $T \neq T_0$, it will change its dimensions as a consequence of thermal dilatation or contraction. If $T–T_0$ is low, the deformation tensor u_{ik} for a crystal is expressed by [28]:

$$u_{ik} = \alpha_{ik}(T - T_0)/3 \tag{1}$$

where α_{ik} is a second order tensor, symmetric with respect to the indices i and k, describing the thermal dilatation of the crystal in the space. Each symmetric tensor α_{ik} corresponds to a triaxial ellipsoid of equation $\alpha_{ik}x_i x_k = 1$, having in general three axes of different lengths. Like dilatation tensors of crystals showing anisotropy with respect to thermal deformation, optical indicatrices of birefringent crystals, showing different refraction indexes along the three spatial coordinates, are represented by triaxial ellipsoids. These latter solid figures have only two circular sections, the other possible sections being ellipses. The straight lines respectively perpendicular to each of the circular sections of the optical indicatrix and passing for the center of the circles, define the two optical axes. If a lamellar crystallite twists, the optical indicatrix rotates around the growth axes of the crystals. To explain optical banding, Keller [6] considered the succession of sections, lying in the microscope plane, of optical indicatrices along a radial direction of a banded spherulites. When the optical indicatrix is oriented in such a way that the plane of spherulites is perpendicular to one of the two optical axes, a circular cross section results from the intersection between the ellipsoid and the microscope plane, with extinction of the light. For all the other possible orientations of the optical indicatrix, allowing the light to pass, the cross sections are represented by ellipses. In a spherulite, the presence of concentric bands requires that for all the lamellar crystals growing radially from the center, the rotation of the optical indicatrices occurs in phase. Furthermore, the band spacings must correspond to the extinction period of the light.

It is worth noting the analogy between anisotropy of crystals with respect to dilatation and anisotropy of crystals with respect to light propagation. These two types of anisotropy are respectively connected to different percentages of dilatation and different propagation velocities of the light in the three spatial dimensions. As these two phenomena are described by similar mathematical equations, it is likely that they are also strictly interconnected in the explanation of the optical banding of spherulites.

Torsion of lamellae

Anisotropy with respect to heat propagation and/or a non-uniform way of heating may cause non-uniform dilatation, which, in turn, gives rise to mechanical tension. In the case of lamellar crystals, there is no reason to sustain anisotropy relatively to heat propagation, whereas a temperature difference between two opposite fold surfaces, perpendicular to the chain axes of the macromolecules, is likely to occur. A thermal gradient along the thickness of lamellae produces different extents of dilatation of the longitudinal sections of the crystals, generating a stress torque and thus a twisting of the lamellae [28]. In spite of the fact that heat is developed at the growing front of the lamellae because of the exothermicity of solidification, a temperature difference between the ends of a lamella can only change its length without causing shape variations and internal stress during the lamellar growth [28]. However, the release of latent heat during crystallization, especially at fast growth rates, may produce or enlarge thermal gradients across the thickness of samples.

The torsion of a thin lamella is characterized by the rotation φ of each rectangular section with respect to the adjacent sections, although the lamella maintains its general rectilinear shape on a larger scale. If one end of the lamella is fixed and a force couple acts at the other end, it is expected that the torsion angle τ (i.e. the angle between two sections at unit distance) is constant along the lamella. The torsion angle is proportional to the force moment M and inversely related to the torsional rigidity C of the lamella, as follows:

$$\tau = M/C \tag{2}$$

For a thin lamella a slight torsion moment M may be sufficient to cause a considerable relative rotation of two sections rather distant from each other. After the twisting, each transversally rotated section, originally flat, becomes bent and the two generatrixes of the lateral surfaces of the lamellae become helices, whose pitch corresponds to the band spacing of spherulites.

The wavelength λ of a torsion wave, running along a lamella that grows in an isotropic melt state, is given by the ratio between the phase velocity χ and the frequency v of the torsion wave:

$$\lambda = \chi / v \tag{3}$$

The present model is based on the following evident assumptions:

(I) the torsion moment M is generated by the temperature gradients along the thickness of lamellar crystals and produces banding only if it is intense enough to cause a rotation of 180°, corresponding to light extinction;

(II) the degree of winding of an individual helicoidal lamella is proportional to the frequency of the torsion;

(III) the distance between two subsequent extinctions of the polarized light along the radial direction of a banded spherulite (i.e. the band spacing) is assumed to correspond to the wavelength of the torsion wave that propagates along a growing lamella.

An increase of the band spacing with the crystallization temperature has been observed for PE , compatible in the present framework with a corresponding decrease of the thermal gradient along the thickness of the specimens.

This analysis also agrees with the observation [9, 30] that the plots of the experimental band spacing of both β-polypropylene (β-PP) and poly(3-hydroxybutyrate) (PHB) versus the crystallization temperature show a minimum.

Indeed, for a given polymer, the rate of propagation χ of the torsion wave along a lamella of certain dimensions is determined by the inherent properties of the polymer. The larger the thermal gradient, the higher the torsion frequency v and the lower the wavelength λ. Therefore, because of the model assumptions and the inverse proportionality between v and λ, the band spacing results are inversely related to the value of the thermal gradient across the lamellar thickness. To determine the trend of the band spacing, it is convenient to separate the two main variables taking into account first only the dependence of thermal gradients on the supercooling (defined as the difference between the melting temperature T_m and the crystallization temperature T_c), implicitly assuming that the width and the thickness of the lamellar crystals of a specific polymer is constant whereas actually they vary with the crystallization temperature. With this assumption, the thermal gradient across the thickness of a crystallizing film within a hot stage is expressed by the sum of two terms: the first term increases with the supercooling because of the greater jump between the initial and final temperatures of the device. Indeed, the acceleration of the crystallization with the supercooling causes an enhancement of the rate of heat evolution, increasing the thermal gradient during the solidification. On the other hand, when T_c approaches the room temperature T_{amb} the second term contributing to the thermal gradient, reflecting the rate of exchange between the sample in the hot stage and the surroundings, decreases as shown qualitatively in Fig. 2, according to the Newton's law of cooling. Therefore, the overall thermal gradient displays a maximum and, consequently, the wavelength λ and the band spacing display a minimum, as shown in Fig. 3. This model agrees with the general observation that banding of spherulites depends on experimental conditions, vanishing at high crystallization temperature (i.e. low supercooling), since it predicts that the band

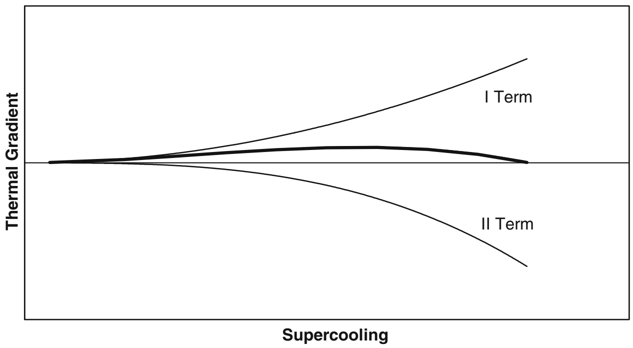

Fig. 2 The thick line qualitatively represents the trend of the thermal gradient across the thickness of a lamellar crystal versus the supercooling. The corresponding analytical equation is the sum of two terms, also shown in the graph

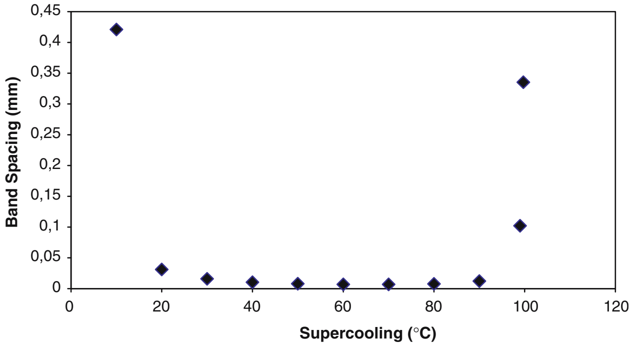

Fig. 3 General trend of the band spacing of polymer spherulites as a function of the supercooling, obtained, apart from an appropriate factor, as inverse function of the thermal gradient shown in Fig. 2

spacing tends towards infinite for T_m–T_c approaching zero. Furthermore, not for all polymers giving banded spherulites is it possible to achieve or even overcome experimentally the supercooling corresponding to the minimum in Fig. 3, as the crystallization may be too fast to be controlled in an isothermal manner owing to the presence of nuclei formed at higher temperature. Therefore, for polymers with very high crystallization rate such as PE, the present model predicts that the band spacing decreases monotonically with the supercooling. The achievement of the right-part of the graph shown in Fig. 3 may be possible only for polymers with a slow crystallization rate. This applies to both β-PP and PHB, which actually show a minimum in the plot of the band spacing versus crystallization temperature [9, 30].

Another factor affecting band spacing is the lamellar thickness, that also depends on the supercooling. If the lamellar thickness overcomes a certain value, the rigidity of the lamellae increases so that the torsion moment cannot induce 180° twisting causing the gradual disappearing of the band pattern in spherulites. In conclusion, in the present model the optical banding phenomenon of spherulites is considered to be a result of a delicate balance of thermal, kinetics and geometrical parameters involved in polymer crystallization. Other factors, such us composition, may become important in determining band spacing of spherulites of crystallizable components of polymer blends. The band spacing of polymer spherulites has been observed either increasing or decreasing upon addition of non-crystallizable diluents [19, 31, 32]. In this new outlook for spherulites banding, the influence of a diluent may be explained in terms of both its effect on the lamellar rigidity according to chemical structure and its allocation in interlamellar or intralamellar crystals, or even in terms of local temperature changes due to composition variation [33] during crystallization.

Conclusions

In this article a new approach to optical banding of spherulites has been proposed by considering thermal gradients existing within the samples and by applying the mathematical equation describing the propagation of torsion waves along lamellar crystals. The developed model ascribes the twisting of lamellae to thermal differences across their thickness that account for different dilatation level of longitudinal sections of the crystals. In this framework, thermal gradients determine the frequency of the torsion waves and hence are expected to affect the band spacing of spherulites. Furthermore, molecular characteristics of polymer chains, influencing the lamellar rigidity, also affect the wavelength of the torsion and thus the band spacing. In conclusion, for a fixed lamellar rigidity, there is a critical value of the thermal gradient across the thickness above which it is possible to observe banding. The present torsion model justifies the observed dependence of the band spacing on the crystallization temperature and has the merit to give a unique explanation for the optical banding in spherulites of all polymers. Furthermore, differently from previous models, its fundamental idea could be extended to all the non-polymeric substances forming banded superstructures.

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