Periodic surface instabilities in stressed polymer solids

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The surface morphology of isothermally grown polymer single crystals of polypropylene is observed by atomic force microscopy. The distinguishing features of the polymer single crystals studied are periodic undulations and transverse fractures (cracks) across the single crystal laths. Up to 20 wrinkles are observed near the edges of the cracks. The periodicity of these surface perturbations is 400±100 nm and the amplitude is 6±3 nm. The formation of the periodic modulations and transverse fractures is attributed to surface stress relief caused by the uniaxial thermal contraction of polymer solids.

INTRODUCTION

Surface and interface stability of growing solid films is a vital issue for many technological applications. Formation of various perturbations of growing thin films under stressed conditions has been observed for various polymers.[1,2] Periodic surface perturbations and fractures have been very recently observed by electron microscopy in isothermally grown polymer single crystals of syndiotactic polypropylene (sPP) and associated with anisotropic thermal expansion.[3,4] The sPP single crystals are good objects to investigate the stability for several reasons.[3-8] First, the lathlike habits of sPP single crystals provide the possibility of unambiguous identification of surface features and their arrangement with respect to the crystal edges and the crystal lattice (Fig. 1). Second, x-ray data reveal a high anisotropy of thermal expansion coefficient. The thermal expansion coefficient, K, along the b axis of the unit cell is about 1 order of magnitude higher than along the a axes. Third, the surface of an unstressed polymer single crystal is very smooth, with a microroughness in the range 0.3–0.5 nm[9]. From experimental observations, undulation profiles should be obtained along with the widths of cracks, surface profiles close to the crack edges, and the period and amplitude of the undulations to characterize perturbed morphology. Atomic force microscopy (AFM) was selected as a primary method to investigate surface morphology in great detail.[9,10]

EXPERIMENT

Single crystals of sPP were prepared by isothermal crystallization of ultrathin films by Lovinger, AT&T, according to a procedure described earlier[3,4] [see sketch of the process in Figs. 1(a)–1(d)]. Cast polymer film was melted at high temperature (150 °C–170 °C is the melting range, T_m) and cooled to 130 °C–145 °C. Single crystals were grown during a definite period of time (3–24h) at this temperature, then rapidly cooled to room temperature. AFM images of the surfaces were obtained with an atomic force microscope, the Nanoscope II according to known procedures.[9,10] Heads J, D, and A were used for scanning with applied forces of 10^{-8} N in air and 10^{-9} N under water. Gold-coated optical grating with 1 μm spacing and grids with 10 μm cell size were used for calibration.

RESULTS AND DISCUSSION

Polymer single-crystals growing from a unique nucleus are usually formed by several lathlike single crystals up to 40 μm length of main axes and up to 15 μm across [Fig. 2(a)]. The height of these lamellar single crystal of sPP is in the range of 10.5±1 nm. Detailed discussion of the observed surface morphology will be published elsewhere.[11]

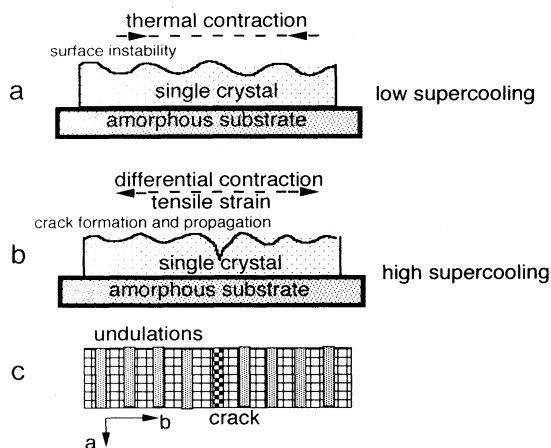Distinguishing features of the single-crystal surface are

FIG. 1. A general scheme of growth of a sPP single crystal: (a) formation of the undulations for growing single crystal exposed to modest thermal contraction at a low degree of supercooling; (b) formation of fracture caused by differential contracting during cooling process; (c) "top-view" of a sPP single crystal showing the orientation of the crystal lattice, the transverse crack, and undulations.
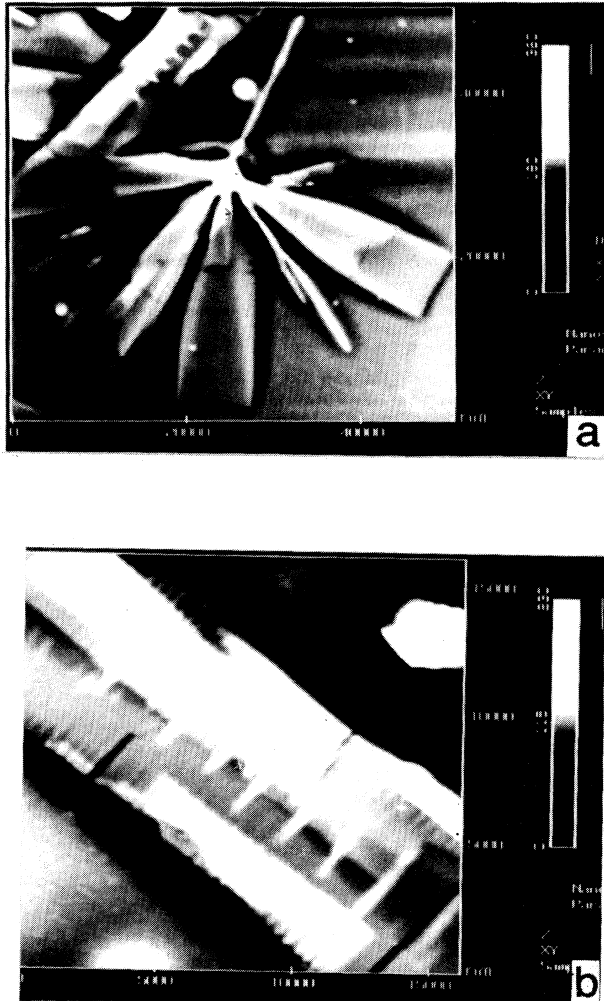
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FIG. 2. AFM images of sPP single crystals: (a) five single crystals grown from one nucleus, 50 μm$\times$40 μm; (b) cracks and wrinkles on crystal surface, 17 μm$\times$17 μm.
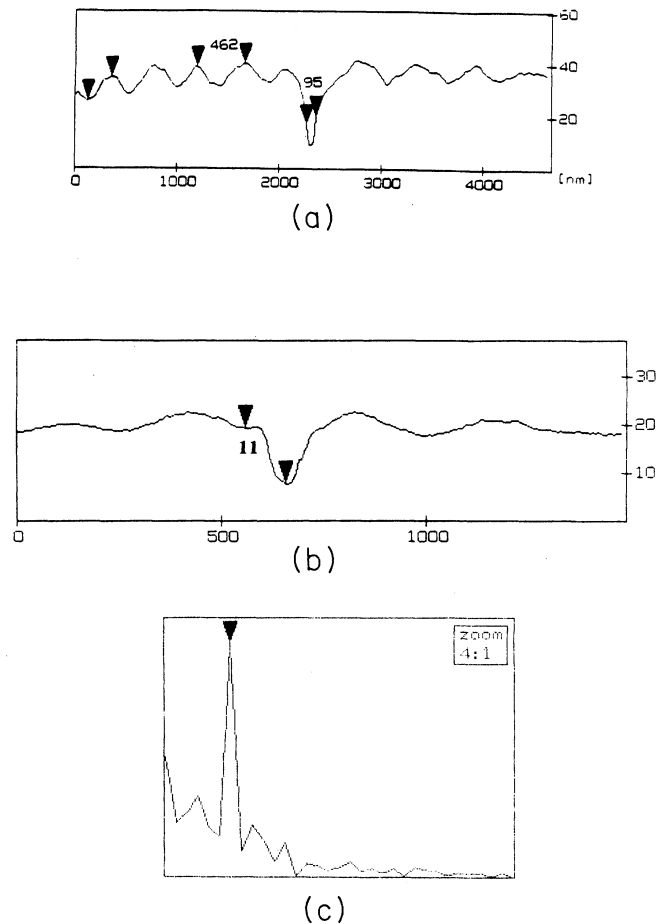

FIG. 3. Cross sections of single-crystal surface perpendicular to the undulations at various magnifications. (a) The numbers on the graph correspond to the horizontal distances between the nearest markers; (b) the numbers correspond to the vertical distances between the markers; (c) 1D Fourier spectrum of the cross section of an undulation with a period, d, of 411 nm.

periodic patterns which include many periods of wrinkles with straight microcracks running across the total width of crystals [Fig. 2(b)]. Periodic surface perturbations and microcracks run across the main axis of the lath crystals, that is transversely to the b axes of the crystalline lattice [Fig. 1(c)]. Three or four cracks were detected in a lath-like single crystal that was up to 40 μm long. Up to 30 periodic wrinkles running parallel to the microcracks were observed. Examples of the sinusoid-like profiles of the undulations are presented in Fig. 3(a). Presence of one intense peak on the corresponding 1D Fourier spectrum confirms the periodic nature of the undulations [Fig. 3(c)]. The periodicity, λ, and the amplitude, A, of these perturbations were obtained from images and 1D Fourier-transforms. Averaging over 10 crystals gives $\lambda=400\pm100$ nm and $A=6\pm3$ nm. The half-width of the microcracks is 90 ± 30 nm.

It is known that regular surface modulations can be created on a polymer surface by the AFM tip due to a

stick-slip instability.[12] To eliminate this possibility, we checked known features of this kind of process (see, for example, Ref. 13) and observed that: (a) the observed surface undulations do not depend upon scanning direction; (b) the periodicity and amplitude of the undulations are very stable and do not depend upon number of scans, scanning rate, or scanning direction; (c) imaging at a very low load (in water) reveals the same characteristic surface features. Thus, we can conclude that the observed undulations are real surface features and not an artifact produced by the AFM tip. The polymer *crystal* surface is much more stable under normal scanning conditions than surface of the *amorphous* polymers analyzed in Refs. 12 and 13.

The periodic surface pattern is very similar to those detected and discussed for polymerized diacetylene single crystals, for which surface instability mechanism was proposed.[14] We compare the AFM data with the results of nonlinear analysis of crack formation process in materials

controlled by stress-driven surface instabilities.[15,16] Recently, Grinfeld and Srolovitz[15-17] considered stressed growing solids and predicted that surface diffusion can lead to relaxation of stress via formation of periodic surface perturbations with characteristics wavelength λ_{max}. This could result in the formation of a periodic cracklike pattern with microcracks forming on the minima of periodic modulations. Experimental evidences of this process have been very recently observed for various compressed solids.[14,16,18]

Many features of surface undulations observed on sPP crystals agree with these theoretical predictions. The fact that all wrinkles run perpendicular to the direction of the b axes, along which the uniaxial stress is produced is as expected in the model. Several other features of the perturbed surface morphology are the shape of the surface profile across the crack edges $\rho(x)$; the wavelength of the surface undulations, λ_{max}; the temperature variation of λ_{max}; and the conditions for crack nucleation and propagation, that is the critical size l^*.

Surface profile. According to the theoretical predictions, the surface profile across crack edges has a few characteristic features which are attributed to diffusion controlled evolution of the surface. This includes the development of the bumps adjacent to the groove in which material diffusing out of the groove accumulate. In addition, the cracks should form and propagate at the positions of minima of surface profiles, this is at the bottom of the wrinkles. Our observations confirm both these features. First, the accumulated ridges of material can be seen in the cross section [Fig. 3(b)]. Second, the vast majority of the cracks on the surface actually occur at the minima of the undulations.

Period of undulations. According to the present theory,[15,16] the surface of a stressed growing solid is unstable for stresses higher than the critical stress:

$$\sigma \geq \sigma_{cr} = [\pi \gamma E / (1 - \nu^2)\lambda]^{1/2} , \tag{1}$$

where γ is surface free energy, E is elastic modulus, ν is Poisson's coefficient, and λ is the wavelength of the surface perturbations. At a given stress, σ, the elastically deformed surface becomes unstable for perturbations with a wavelength:

$$\lambda_{max} = \pi(1 - \nu^2)\gamma / E\varepsilon^2 , \tag{2}$$

The quantities used in Eq. (2) are rarely available from very limited experimental data for sPP and must be estimated from available data for isotactic PP. For estimation of λ_{max} we used the following set of parameters: for the elastic modulus along the b axes of the crystal lattice $E \sim 3 \times 10^9$ Pa[19]; for the surface energy γ of the axb face of the crystal lattice, $\lambda = 50$ N/m^2 for sPP from Ref 20; for the Poisson coefficient, a common approximation $\nu = \frac{1}{3}$; for the strain along the b axis, $\varepsilon = \delta b / b_0$, where δb is a variation of the edge of the unit cell and b_0 is the initial length of the edge of the unit cell.

To calculate strain resulting from thermal contraction, we used $\varepsilon = K \delta T$, where $K = \delta b / (b_0 \delta T)$ is the thermal expansion coefficient and $\delta = T - T_m$ is the degree of supercooling. From x-ray data[3,4] K is 1.6×10^{-4} K^{-1} for

the b axis. Thermal strain for the various degrees of supercooling was calculated by using this thermal expansion coefficient. The actual process of polymer solidification can be considered as occurring in two succeeding stages (Fig. 1): a steady single-crystal growth at low supercooling and fast cooling to room temperature. For these two different regimes strain levels associated with thermal contracting are $\varepsilon_1 \sim 5 \times 10^{-3}$ for the growth stage at 130 °C–140 °C and $\varepsilon_2 \sim 2.2 \times 10^{-2}$ after cooling to 25 °C. Respectively, stress along the b axes is $\sigma_1 \sim 16$ MPa for the first stage, and much higher for the cooling stage $\sigma_2 \sim 66$ MPa. From Eq. (2) we estimate the expected wavelength of the surface undulations as $\lambda_1 = 1700$ nm and $\lambda_2 = 100$ nm for two degrees of supercooling, respectively. These estimates fit very fair to the experimentally observed period of surface undulations within the range 600–200 nm.

The existing theory also predicts the dependence $\lambda(\varepsilon) \sim \varepsilon^{-2}$. In the case of thermally induced stress one could expect the relationship $\lambda \sim (\delta T)^{-2}$. We tried to verify this prediction by analyzing the period of surface undulations for polymer crystals grown at different degrees of supercooling. Unfortunately, the range of supercooling where flat lathlike single crystals can be grown and surface undulations observed is very narrow, only about 20 °C. Growth temperatures out of this range yield a spectrum of morphologies, from lathlike habits to spherulites. Variations of the period λ within the narrow accessible range of supercooling cannot be measured accurately enough to verify the expected relationship. Nevertheless, we observed that the periodicity of surface undulations increases for lower degrees of supercooling as expected.

Crack propagation. In the framework of brittle fracture mechanisms, newly created cracks are able to propagate through a material only if their depth exceeds a critical length l^*. In Griffith theory, for estimation of propagation, a simple relationship $l > l^* = 2E\gamma / \pi(\sigma)^2$ can be used. Estimated lead to significantly different critical lengths at two different degrees of supercooling: $l_1^* = 400$ nm and $l_2^* = 22$ nm. This difference is caused by the difference in stress levels. The probability of nucleation and propagation of the cracks caused by compressive stress at low supercooling ($T = 140$ °C) is very low because the compressive stress is low. The probability of nucleation and propagation of the cracks is much higher for the second stage of single-crystal formation. We can make a crude estimate of the probability of crack propagation at different stages using following simple arguments. Consider every minimum of the undulations as a "prospective crack nucleus" with the depth equal to the amplitude A ($l = 6$ nm). Let us assume Gaussian distribution for the probability p of crack propagation in the form $p = 1 - \exp[-(l/l^*)^2]$ with $l^* = 22$ nm. For the observed amplitudes of the undulations and the critical lengths, the probability of propagation of the cracks caused by compressive stress developing during isothermal growth is only 2×10^{-2}%. Contrarily, during second stage of cooling the probability of crack propagation is about 7%. As can be concluded from the AFM data, only one of 15 to 20 surface undulations contains

crack. This is fairly close to the above estimate. Thus, we suggest that the thinner regions of the undulations formed during crystal growth tend to crack during cooling to room temperature.

Occasionally we observed some other surface features. For example, the cracks sometimes run along the top of the surface undulations or an irregular crack propagates along the long axis of the lathlike crystals. High, periodic ridges than can be attributed to material pushed away from the crystal during growth are occasionally observed on top of the single crystals. For some specimens the undulations tend to concentrate along the edge of the single crystals. These features cannot be understood now and require further detailed investigations.

CONCLUSIONS

We observed several intriguing features of the periodic undulations and fracture surface of isothermally grown single crystals of syndiotactic polypropylene. The complex pattern of formation of the undulations and fracture surface in the polymer studied can be briefly described as follows. The Grinfeld-Srolovitz mechanism can account for the undulations of grown single crystal at low supercoolings. Within this approach, the undulations are formed by surface diffusion and provide stress relief for compressed interface. The source of the stress in this case may be the contraction of the lathlike crystal at lower supercooling. As the temperature falls as the sample is cooled to room temperature, the forces increase, but the diffusion coefficient of the polymer along the surface falls even faster. If the diffusion cannot keep up with the increasing stress, the Grinfeld-Srolovitz mechanism, which would eventually form cracks, may be overtaken by ordinary cracking. Because the lathlike crystals have a high thermal expansion coefficient along its long axis and are attached to an amorphous substrate with a much lower thermal expansion coefficient, the contraction of the crystals as it cools will be greater than the contraction of the substrate. This differential contraction produces high tensile forces in the lathlike crystals cooled to room temperature and the cracks form across its thinnest sections. These sections are at the minima of the undulations that formed during crystal growth. Since the cracks are narrow, it seems likely that ordinary cracks formed at the weakest sections during fast cooling.

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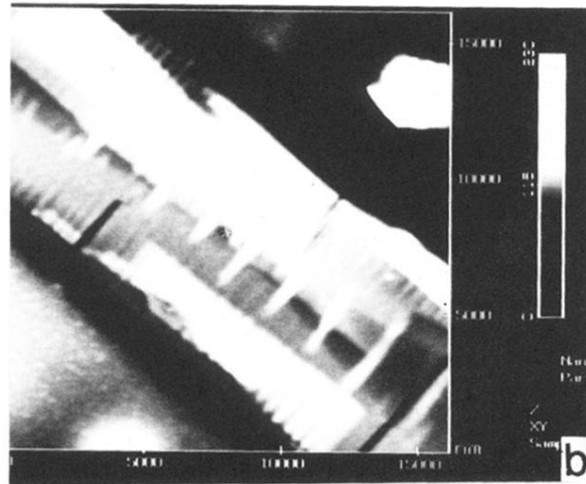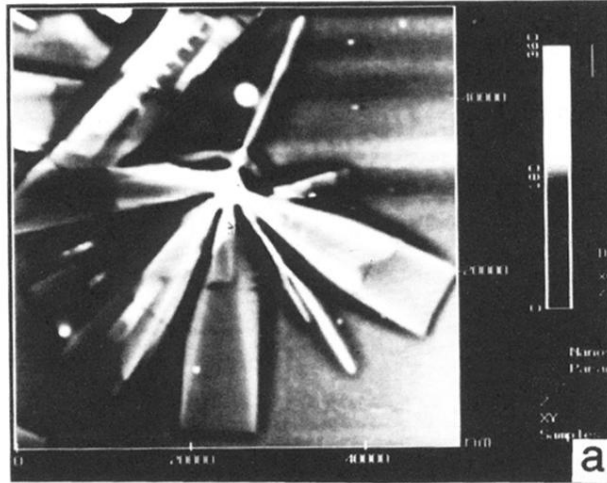[20] E. J. Clark and J. D. Hoffman, Macromolecules **17**, 878 (1984).

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