Longitudinal Growth of Polymer Crystals from Flowing Solutions. XI. The Friction with the Rotor Surface

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Synopsis

During the formation of ultrahigh modulus fibers by the "surface-growth process," the takeup stress is the main limiting factor lowering the attainable takeup speeds. This paper presents an investigation into the relative importance of the various factors contributing to takeup force and stress. Equations for force and stress have been derived which appear to agree with measurements. It has been concluded that the major part of the stress stems from the friction with the rotor surface and a smaller contribution arises from the coil deformation due to the flow. The equation for the stress has been employed to compute the maximum takeup speed.

INTRODUCTION

Previous work has dealt with the "surface-growth process" for the preparation of polyethylene fibers.[1-7] It was found that one of the basic factors in this crystallization process is the takeup stress. From a fundamental point of view, it has been remarked that the takeup stress is related to the degree of chain extension.[7] The large chain extension is responsible for the typical features of the surface-growth process, such as the very rapid longitudinal crystal growth, and the exceptionally high strength and modulus of the structures produced. From a practical point of view, it has been concluded that takeup stress is one of the most important factors determining the limitations of the surface-growth process.[8]

It is clear that to improve this process it is useful, if not indispensible, to have a thorough understanding of the factors involved in the buildup of the takeup stress. There are several contributions to the stress. One is associated with the elastic deformation and crystallization of polymeric coils adhering to the fiber. Another stems from the friction between the fiber and the rotor surface. A third one arises from the friction in the takeup tube. This third contribution can be eliminated by the use of a horizontal rotor apparatus, as has been shown earlier,[6] and will not be dealt with in this study.

This paper presents an investigation into the relative importance of the various contributions to the takeup stress. An equation for the takeup stress is derived and compared with a number of measurements. This equation is employed to predict the limiting conditions for the surface-growth process. The predictions are compared with experimental results reported previously.[5-9]

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EXPERIMENTAL

Materials

The linear polyethylene used throughout this work, Hostalen Gur, had an intrinsic viscosity of 15 dL/g in decalin at 135°C, an M_n of 10^5 g/mol as determined by osmometry, and an M_w of 1.5×10^6 g/mol as determined by light scattering in α-chloronaphthalene at 135°C. This polymer was dissolved in the high purity solvent p-xylene at a concentration of 0.5 wt %. Furthermore, 0.5 wt % of the antioxidant ditertiarybutylparacresol was added, and all solutions were kept under purified nitrogen in order to prevent oxidative degradation of the polyethylene. The EPDM rubber had an M_w of 7×10^6 g/mol.

Couette Apparatus

Frictional forces were measured in a modified Couette apparatus described in detail elsewhere.[7] The apparatus consisted of an inner rotor of Teflon with a diameter of 115 mm, placed in a vessel with an internal diameter of 130 mm. The annular gap was filled with the aforementioned solution. The apparatus was immersed in a silicone–oil bath, the temperature of which was controlled to within ±0.05°C. The takeup force was measured by means of a Statham strain gauge (Model UC-3), which has been described elsewhere.[10]

RESULTS AND DISCUSSION

First of all, an equation for the takeup force will be derived. This equation will be compared with force measurements, and will subsequently lead to the calculation of the takeup stress.

Takeup Force

Starting point for the calculation of the takeup force is the mechanism for this longitudinal growth process according to which the fiber is a flat ribbon, and the section sliding over the rotor is tapered, as in Figure 1(a).[7]

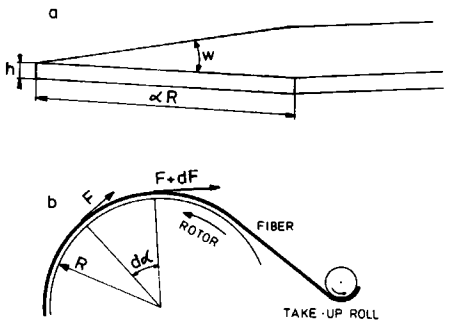

Fig. 1. (a) A schematic representation of the ribbon-shaped fiber with its tapered end having a length αR, a variable width w, and constant height h. (b) A sketch of the development of the takeup tension F in the fiber as a result of the friction and the adherence to the rotor surface. The discussion of the figure is elaborated in the text.

The mechanism additionally states that the rotor surface is covered with a layer of adsorbed macromolecules. The length of the tapered end in contact with this adsorbed gel layer is αR, where R is the radius of the rotor and α is the contact angle over which the ribbon is attached to the rotor surface. The height of the ribbon is indicated by h and the width, which varies along the tapered end, by w. A schematic representation of the fiber gliding over the rotor surface is given in Figure 1(b). The fiber is thought to be pulled against the rotor surface by the dragging force of the moving fluid, τ_{flow}, and by the attachment of the lateral sides of the tapered fiber due to the entanglements of the cilia with the adsorbed gel layer. This attachment gives rise to a retractive force as a result of coil deformation when the fiber slides over the rotor surface, τ_{def}, which is reduced by the stress relaxation due to oriented crystallization and slippage of chains past each other, τ_{relax}. There may also be a contribution to the adherence from surface charges arising from friction.

The addition of these contributions leads to an increase in force from the fiber tip to the location where the fiber leaves the rotor surface. The infinitesimal increment in the fiber force F by an amount dF over a length $Rd\alpha$ arises from the friction between the fiber and the rotor surface and from the drag force and the adherence. To reduce mathematical complexity, we consider the drag force as an adherence force. The frictional contribution to dF is proportional to the coefficient of gliding friction, μ, and the normal force, which is equal to $Fd\alpha$. The other contributions are proportional to the total adherence force per unit area and to the adherence surface area. This area is supposed to be the lateral fiber surface area. A number of observations[7] have shown that the ribbon height is constant, and therefore it is assumed that the fiber adherence is also constant over the entire fiber length, and is given by [see Fig. 1(a)]

$$2hRd\alpha \tag{1}$$

the force increment dF may be expressed as

$$dF = \mu Fd\alpha + 2hR\tau d\alpha \tag{2}$$

where $\tau = \tau_{\text{flow}} + \tau_{\text{def}} - \tau_{\text{relax}}$. The differential equation (2) can be integrated over the total fiber length α according to well-known procedures given in Ref. 11, leading to the equation for the takeup force F

$$F = 2hR\tau[(e^{\mu\alpha} - 1)/\mu] \tag{3}$$

In this equation h can be regarded as a constant.[7]

Obviously it will be difficult to verify eq. (3), because the shape of the ribbon, its length, and the coil deformation and stress relaxation due to oriented crystallization are interrelated and the magnitude of the contributions to the adherence force τ does not seem to be amenable to a simple theoretical assessment. Nevertheless, some information as to the validity of eq. (3) could be obtained by measuring the tension in a polyethylene macrofiber that is submerged in the Couette instrument containing pure p-xylene at 21°C. The fiber tension turned out to be independent of the rotor speed.[5] The tension, however, increased with fiber length (rad), as is illustrated in Figure 2. These data can be compared with eq. (3) for $\mu = 0.28$ and $2hR\tau = 0.42$ mN. Similar data for a 0.5 wt % solution of EPDM rubber in p-xylene having a viscosity of 1.89 cP at 21°C exhibit a considerably higher frictional force which can be calculated using eq. (3) with

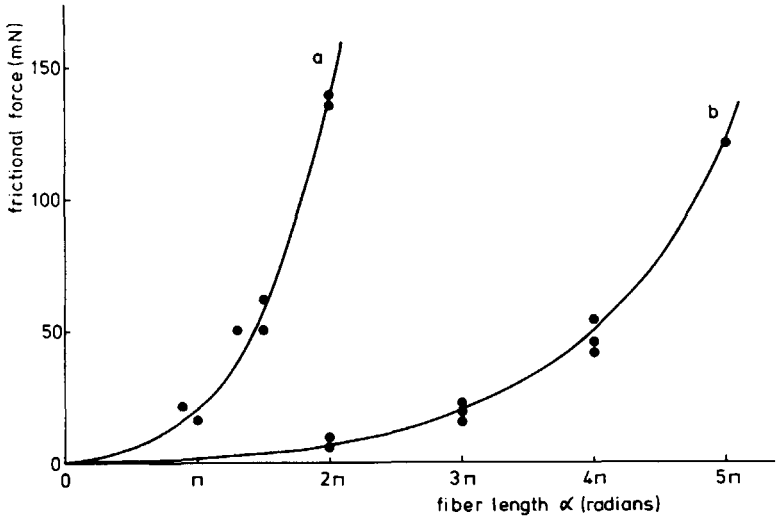

Fig. 2. Plot of frictional force between a polyethylene fiber and a Teflon rotor surface, against the fiber length (rad). (a) The Couette apparatus was filled with a 0.5 wt % solution of EPDM rubber in p-xylene; rotor speed: 117 mm/s. (b) The Couette apparatus contained pure p-xylene; rotor speed was 250 mm/s. The curves were calculated from eq. (3), using, $a - \mu = 0.55$ and $2hR\tau = 2.48$ mN, $b - \mu = 0.28$, and $2hR\tau = 0.42$ mN.

$\mu = 0.55$ and $2hR\tau = 2.48$ mN. Figure 2 reveals that eq. (3) agrees well with these experimental data.

In order to approach the actual surface-growth conditions closer, the frictional force was also assessed in the solution of 0.5 wt % polyethylene normally used for surface growth. Effects of crystallization were avoided by increasing the temperature beyond levels where crystal growth may occur. Under these conditions polyethylene fibers would dissolve, so that cotton threads with diameter of 0.3 mm were used. Figure 3 shows the dependence of force on α for mea-

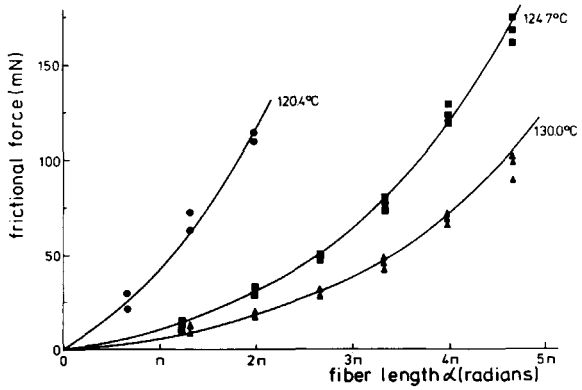

Fig. 3. Frictional force between a cotton thread and a Teflon rotor vs. thread length α (rad). The rotor was immersed in the solution of 0.5 wt % high-molecular-weight polyethylene in p-xylene that is usually employed for surface growth. The points are experimental data, and the curves were calculated according to eq. (3) with $\mu = 0.17$, and $2hR\tau$ equal to 10.25 mN for 120.4°C, 2.69 mN for 124.7°C, and 1.60 mN for 130.0°C. Rotor speed was 80 mm/s; diameter 115 mm.

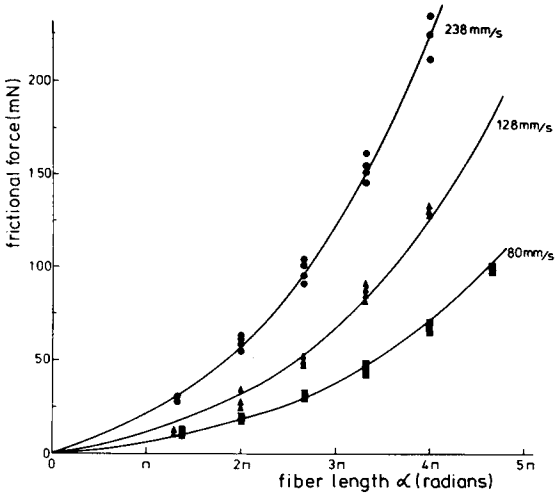

Fig. 4. Frictional force between a cotton thread and a Teflon rotor vs. thread length α. Same solution and rotor as in Figure 3 and temperature of 130.0°C. For the various rotor speeds, the points are experimental data, and the curves were calculated using eq. (3) with $\mu = 0.17$, and $2hR\tau = 1.60$ mN for a rotor speed of 80 mm/s, 2.81 mN for 128 mm/s, and 5.16 mN for 238 mm/s.

surements at various temperatures. The data corresponded well with eq. (3) using $\mu = 0.17$ for all temperatures, and $2hR\tau$ equal to 1.60, 2.69, and 10.25 mN for 130.0°C, 124.7°C, and 120.4°C, respectively. The strong effect of temperature on the adherence force suggests that at lower temperatures entanglements have longer relaxation times as a result of enhanced formation of temporary embryonic crystallites, in agreement with the earlier proposed mechanism of fiber formation.[7] Figure 4 displays the dependence of force on α at 130.0°C, for various rotor speeds of 80, 128, and 238 mm/s. Equation (3) agrees satisfactorily with the experimental data for the same $\mu = 0.17$. The front factor of eq. (3), $2hR\tau$, increases with rotor speed. This effect is clearly illustrated in Figure 5, which shows the force as a function of rotor speed for constant α equal to 2π rad and for 130.0°C and 124.7°C. The increase of force with rotor speed is linear up to 200 mm/s, but levels off at higher speeds. The increase of force with rotor speed in these crystallizable polymer solutions may be attributed to the formation of embryonic crystallites, as is suggested by the observation that force is not affected by rotor speed in the noncrystallizable solution of EPDM rubber or in pure xylene. In case of the measurements of Figure 5 carried out at the lower temperature of 124.7°C, the plot of force vs. rotor speed additionally shows an upward curvature above 400 mm/s. This seems related to the observation that in this experiment a polyethylene fiber had crystallized, which stuck to the cotton thread. Such a fiber adhering to the thread makes α effectively larger, so that the force becomes greater.

Takeup Stress

One may assess the takeup stress by dividing the force by the fiber cross section ϕ_c, which is given by

$$\phi_c = 2RhG_{lat}\alpha/V_t \tag{4}$$

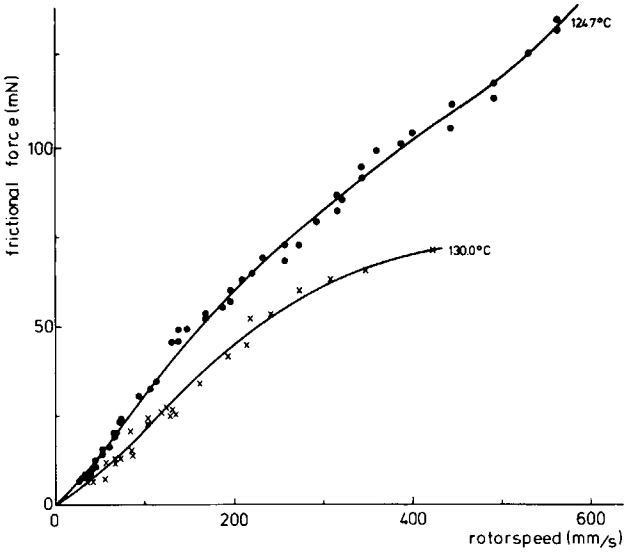

Fig. 5. Frictional force between a cotton thread and a Teflon rotor, as a function of rotor speed, for 124.7°C and for 130.0°C. Same solution and rotor as Figure 3. The thread length corresponded to one rotor circumference (2π rad).

as has been derived previously.[7] In this equation G_{lat} denotes the lateral growth rate, or the rate at which the fiber edges grow in a direction perpendicular to the fiber direction and parallel to the rotor axis. An expression for the takeup stress σ results from dividing eq. (3) by eq. (4)

$$\sigma = \frac{\tau V_t}{G_{lat}} \left(\frac{e^{\mu\alpha} - 1}{\mu\alpha} \right) \tag{5}$$

The first part of the right-hand side of eq. (5) may be regarded as the contribution to the stress due to adherence, whereas the second part, in parentheses, originates from the friction. The latter becomes evident when setting μ equal to zero, which reduces the part in parentheses to 1, so that it vanishes. The friction part must be considered to be a multiplier for the stress. The magnitude of the multiplier amounts to 2.97, using $\mu = 0.3$, which is an average of the aforementioned values of 0.55, 0.28 (Fig. 2), and 0.17 (Figs. 3 and 4), and setting $\alpha = 2\pi$, which holds for a grooved rotor and under some conditions for a smooth one. This indicates that $^2/_3$ of the takeup stress arises from friction. The employed value of 0.3 for μ is in agreement with a number of earlier reported values.[12,13] Equation (5) should be compared with previously published relationships between stress and the variables of the growing process.

The influence of takeup speed on stress was determined in experiments using a rotor modified with a groove, such that the fiber length α was constant and equal to 2π. It was observed that also the lateral growth rate G_{lat} and the force F were approximately constant,[7] and therefore the adherence force τ may also be considered to be invariant. Under these conditions eq. (5) predicts a direct proportionality between takeup stress and takeup speed V_t, corresponding well with the observed relationship.[8] Furthermore, according to this same equation, the stress should be inversely proportional to the lateral growth rate, G_{lat}, as is

confirmed by experiments showing the decrease of fiber cross section due to the diminishing lateral growth rate, and the simultaneous increase of stress.[8] These experiments were also carried out at constant takeup force and using a rotor with groove, so that τ and α were constant. G_{lat} could also decrease by increasing the crystallization temperature. This should lead to an increase in takeup stress, as has indeed been observed,[5,8] again in agreement with eq. (5).

Derivation of the Takeup Speed Limits

Equation (5) for the takeup stress appeared to be in full agreement with experiments. Using this equation, it will presently be attempted to predict the upper and lower limits of the takeup speed as a function of a number of other process variables.

The ultimate takeup speed V_t^{max} can be found from eq. (5) by making σ equal to the strength at breakage of the fibers, σ_{br}:

$$V_t^{max} = \frac{\sigma_{br} G_{lat}}{\tau} \left(\frac{\mu\alpha}{e^{\mu\alpha} - 1} \right) \tag{6}$$

Since the lateral growth rate is directly proportional to the cross section[7] and the latter increases linearly with the rotor speed,[5], the ultimate takeup speed V_t^{max} is proportional to rotor speed V_r:

$$V_t^{max} \sim V_r \tag{7}$$

if τ and α are unaffected by V_r, i.e., if the force F is independent of V_r. It was found that F is indeed independent of V_r in the range of low rotor speeds.[8] Equation (7) is in agreement with measurements in this range carried out in our laboratory,[8] which display a linear relationship between the maximum takeup speed and rotor speed. This eq. (7) is also confirmed by similar experiments carried out by Barham and Keller.[9] Equation (6) suggests that an increase of lateral growth rate should imply a rise of the maximum takeup speed. The lateral growth rate may be increased by lowering the temperature. It was found that a temperature reduction from 118°C to 110°C led to a rise of maximum takeup speed from 2 to 16 mm/s, in line with eq. (6).[8] The lateral growth rate may also be influenced by switching from a Teflon rotor to a brass one; in this case the lateral growth rate diminished as a result of the reduced adsorption of polymer on a brass rotor surface. Concomitantly, the maximum takeup speed decreased,[9] in line with eq. (6).

Another method to increase lateral growth rate is by sweeping the fiber up and down the rotor in order that the fiber constantly meets a fresh adsorbed layer.[9] This is expected to leave the adherence force virtually unchanged, because fiber length should not alter too much. This method caused a fourfold increase of lateral growth rate and a corresponding 2.5 times increased maximum takeup speed. Also this observation emphasizes that eq. (6) is essentially correct.

In the range of low takeup speeds, fracture occurs as a result of loop formation.[8] This phenomenon takes place when the longitudinal growth rate of the fiber tip is greater than the takeup speed, which leads to the wrapping of two or three windings around the rotor. It may be calculated from eq. (5) that in the case of

two windings ($\alpha = 4\pi$), and again using $\mu = 0.3$, the stress is four times larger than normally, and 90% of it comes from the greatly increased friction. This illustrates that friction is a major factor responsible for fiber breakage as a result of loop formation.

The limitation imposed on the takeup speed as a result of loop formation may be derived in the following way. It has been found that mass growth rate is directly proportional to rotor speed. It is conceivable that also the longitudinal fibrous crystallization rate G_{long} would be proportional to rotor speed.[14] Furthermore, it has been demonstrated clearly[8] that, for a set rotor speed, the takeup speed may be varied by a factor of 3 without causing breakage. This indicates that the growth process is not only governed by an intrinsically high longitudinal growth rate G_{long}, which is in line with a study of seeded crystallization in Poiseuille flow,[15,16] but is also influenced by a so-called regulating mechanism. The regulation presumably arises from the impediment of the tip growth by the section of the fiber that is about to leave the rotor, from depletion of the adsorbed layer and from the influence of the takeup speed on the crystallization rate. The regulating mechanism is evidently capable of slowing down the intrinsic growth rate in such a manner that the actual growth rate does not exceed the takeup speed. This observation, that the takeup speed also affects the intrinsic growth rate, may be expressed by the following relationship:

$$V_t^{\min} = G_{\text{long}}/C \tag{8}$$

where C is a constant and $V_t^{\min}$ the minimal takeup speed. For takeup speeds below $V_t^{\min}$, loop formation will occur. If we now employ the linear proportionality between G_{long} and the rotor speed V_r, eq. (8) reduces to

$$V_t^{\min} \sim V_r \tag{9}$$

in other words, the above considerations lead to a linear proportionality between the minimum takeup speed $V_t^{\min}$ and the rotor speed, in agreement with experimental observations.[8]

CONCLUSIONS

The main conclusion of this work is that a large part of the takeup stress in surface growth is due to the friction of the polyethylene fiber with the teflon rotor surface. This frictional factor substantially contributes to interruption of the growing process as a result of fiber fracture.

The present results indicate that under steady state growing conditions ($\alpha = 2\pi$) about $\frac{1}{3}$ of the stress stems from the deformation of polyethylene molecules. This contribution is inherent to surface growth, because longitudinal crystal growth occurs as a result of the coil extension. The remaining $\frac{2}{3}$ of the stress arise from the friction with the rotor surface, and may be regarded as a drawback of the process. In case of loop formation the frictional contribution increases, so that the total stress may rise by a factor of 4. This explains that loop formation causes fracture of the fiber.

The work done to reach the above-mentioned conclusions has yielded an equation for the takeup stress, which appeared to correspond well with the variation of takeup stress with takeup speed, temperature, and crystallization time. Moreover, this stress equation is used to compute the limits of the takeup

speed. It was predicted that the maximum and the minimum takeup speed both increase linearly with rotor speed, and that the maximum takeup speed is proportional to the lateral growth rate. The equations derived contribute to the understanding of this peculiar surface growing process, and support the earlier presented mechanism of fiber formation.[7]

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