Influence of Spinline Stress on Release Properties of a Coaxial Controlled Release Device Based on EVA Polymers

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Purpose. To investigate the influence of the extrusion parameters on the polymeric structure and release properties of polyethylene vinyl acetate (EVA) coaxial fibers, used for controlled release of steroids.
Methods. Coaxial fibers were prepared under various extrusion conditions. Both spinline stress and release properties were determined. The polymeric structure of the membrane was investigated with wide angle X-ray scattering (WAXS).
Results. Upon leaving the spinneret, the polymeric fiber exhibits a large die swell. As a consequence, it is necessary to apply a force to draw the fiber to its desired diameter. A larger drawing force is needed at lower extrusion temperature, at a smaller air gap, or at a higher spinning velocity. It was found that the release rate of a steroid from the coaxial fiber increases, when the fibers are prepared at a higher spinline stress. X-ray measurements reveal that at higher spinline stress, the crystalline volume fraction of the membrane decreases. As a result of a decreasing crystallinity, the permeability of the polymer increases.
Conclusions. It is demonstrated that the extrusion parameters and spinline stress have a significant influence on the polymeric structure of the membrane and hence the release properties. Higher spinline stress results in a higher release rate.

INTRODUCTION

Polyethylene vinyl acetate (EVA) copolymers are very suitable for the production of controlled release systems. In this report, a controlled release system is described that is manufactured from two types of polyethylene vinyl acetate copolymers by means of a coaxial melt spinning process. With this process, coaxial fibers are obtained that can be used for controlled release of steroids. Because the release from this type of system is influenced by the polymeric structure, it is essential to investigate the parameters that affect the polymeric structure.

The properties of the polymer can be adapted by varying the amount of vinyl acetate (1,2,3). By increasing the amount of vinyl acetate, the crystallization process of the polyethylene segments is disturbed. As a consequence the copolymer becomes less crystalline and therefore more permeable (4,5).

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The polymeric structure of the fiber is also influenced by the process parameters of the melt spinning process. During the melt spinning process the polymer emerges from the die into an extensional flow field (or shear free flow). The velocity profile changes from a parabolic profile in the die to a flat profile in the extensional flow field. Several authors have described the mechanics of steady spinning of both Newtonian and non-Newtonian melts (6,7). As a consequence of the viscoelastic properties of the polymer, the polymeric fiber expands to a diameter larger than the diameter of the die. In order to achieve a fiber diameter that is smaller than the die swell it is necessary to apply a drawing force. Crystallization kinetics of a polymer under these circumstances can be quite different than under quiescent conditions. Ziabicki and Kedzierska (8,9,10,11,12) studied the influence of spinline stress on the polymeric orientation of polyethylene. Other authors (13,14,15) used wide-angle and small-angle X-ray diffraction and other measurements to study the influence of the process parameters on the structure development during melt spinning of polypropylene and polyethylene fibers.

Although the influence of process parameters on the polymeric structure during the melt spinning process has been investigated extensively, the influence on the release properties of a controlled release system prepared by this process has received less attention. In Ref. 16 it has been reported that films and coaxial fibers based on EVA polymers displayed different permeability properties. It was suggested that this was probably due to differences in the polymeric structure.

The aim of this paper is to discuss the influence of the process parameters and spinline stress during the melt spinning process on the release properties of a steroid from a coaxial fiber.

THEORETICAL BACKGROUND

The principle of a reservoir system is that the drug is incorporated in a bulk polymer that is surrounded by a permeable membrane polymer. As a consequence of the concentration difference over the membrane, the drug that is dissolved in the core will diffuse through the membrane. The diffusion rate is dependent on the concentration in the core, the partition coefficient between core and membrane, the thickness and surface area of the membrane and the diffusion coefficient of the drug in the membrane. In order to achieve a constant release profile the permeability of the core polymer should be much higher than the permeability of the membrane polymer.

In order to predict the release rate from a cylindrical reservoir system (or coaxial fiber) the following model has been derived from literature (17):

$$\frac{dM_t}{dt} = \frac{2\pi LDK\Delta C}{\ln(r_0/r_i)} \tag{1}$$

where dM_t/dt = release rate (kg/s), L = length of the cylinder (m), D = diffusion coefficient of the drug in the membrane (m²/s), K = partition coefficient between membrane and core ($K = C_{membrane}/C_{core}$), ΔC = concentration gradient over the membrane (kg/m³), r_o = outer radius (m), and r_i = inner radius (= outer radius − membrane thickness) (m).

The fibers described in this report are prepared by a melt

spinning process. Both membrane and core polymer are melted and pumped to a spinneret. Upon leaving the die, the fiber expands to certain diameter (die swell) as a consequence of the viscoelastic behavior (18) of both polymers (Fig. 1).

If the die swell results in a fiber diameter larger than the anticipated diameter, it is necessary to apply a force in order to draw the fiber to the desired diameter. Immediately after leaving the die, the coaxial fiber is cooled in an air gap and subsequently in a water bath. Because the air gap applied in this study is relatively small (5 to 150 mm) the fiber will finally solidify at a short distance below the water surface.

During the melt spinning process several forces are involved. The most significant forces are the rheological force and the force needed to draw the fiber through the water bath (resistance transport wheels, bending force fiber, etc.). In this report, only the rheological force (or drawing force) is considered because of its influence on the polymeric structure of the fiber.

At a certain distance z from the spinneret, the stress (σ_z) on a cross sectional area (A_z) of the fiber is:

$$\sigma_z = \frac{F_{rheo}}{A_z} \qquad (2)$$

The relation between stress and the deformation of the fiber at a certain point z from the spinneret is described by:

$$\sigma_z = \eta_e \cdot \dot{\varepsilon} = \eta_e \cdot \frac{dv_z}{dz} \qquad (3)$$

where η_e = elongational viscosity (Pa·s), $\dot{\varepsilon}$ = elongational rate (1/s), and v_z = fiber velocity at distance z (m/s).

By adding the volume flow ($Q = v_z \cdot A_z$) and considering the boundary conditions the following relation can be deduced from Eqs. 2 and 3 (12):

$$F_{rheo} = \frac{Q\eta_e \ln\left(\dfrac{v_1}{v_0}\right)}{L} \qquad (4)$$

where F_{rheo} = rheological force (N), Q = volume flow (m³/s), v_1 = fiber velocity fiber at distance $z = L$ (take up velocity) (m/s), v_0 = fiber velocity fiber at distance $z = 0$ (velocity at spinneret surface) (m/s), and L = drawing distance (m).
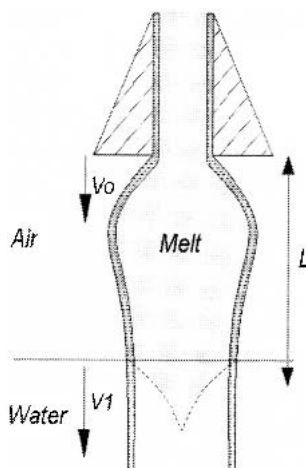

Fig. 1. The rheological behavior of the coaxial fiber in the air gap and water bath.

MATERIALS AND METHODS

Materials

Etonogestrel, as obtained from Diosynth B. Oss, The Netherlands, was used as a model steroid. The melting temperature of etonogestrel is 199°C. Two types of polyethylene vinyl acetate polymers were used in this study. Both EVA 28 and EVA 9 are random copolymers and have a melting temperature of respectively 80 and 100°C. EVA 28 contains 28 wt% vinyl acetate and is used as core material in the coaxial fiber because of the higher permeability. EVA 9 contains 9 wt% vinyl acetate and is applied in the membrane because of the lower permeability properties. The crystallinity of both polymers is about 20 and 38%, respectively (1,2,3). The molecular weights are given in Table I.

Methods

Manufacturing of Coaxial Fibers

Coaxial fibers with a diameter of 4 mm were produced with a fixed concentration of etonogestrel in the core (0.69 wt%). The thickness of the membrane was adjusted to 110 μm. In order to prepare a coaxial fiber, a steroid loaded core granulate was manufactured by mixing micronized steroid and ground EVA 28 in the desired ratio. Subsequently, the powder mixture was blended in a Berstorff ZE25 (Hanover, Germany) blend extruder at a temperature of 120°C. After leaving the blend extruder the strands were cooled to room temperature and granulated using a Scheer (Stuttgart, Germany) strand granulator, thereby forming steroid loaded pellets.

The coaxial fibers were prepared with a Plastik Maschinenbau (Kelberg, Germany) extrusion installation that consists of two single screw extruders that are connected to a spinning block. The molten polymers are delivered to two gear pumps, which assure an accurate flow of both polymers to the spinneret. The thickness of the membrane polymer is determined by the ratio between rotation speeds of both pumps. Subsequently, the membrane and core polymers are combined in a spinneret, thereby forming a coaxial fiber. The diameter of the die was 3.6 mm. In order to cool the fiber to room temperature a water bath was positioned below the spinneret. The outer diameter of the fiber after the water bath was measured on-line using a Mitutoyo laser scan micrometer. The fibers were prepared under various process conditions, that is, extrusion temperature, air gap, and spinning velocity.

Determination of the Fiber Diameter in the Air Gap and Below the Water Surface

The diameter of the coaxial fiber in the air gap and below the water surface was determined using a digital camera. By moving the camera in a vertical direction, digital pictures were made of the fiber at various distances from the spinneret. The exact diameter was determined by enlarging these

Table I. Molecular Weights of EVA 28 and EVA 9

	M_w	M_n	M_w/M_n
EVA 28	50,000	14,700	3.4
EVA 9	83,500	15,500	5.4

Mw = weight-average molar mass.
Mn = number-average molar mass.

pictures and measuring the dimensions of the fiber. A reference was used with a diameter of 4.0 mm. In order to examine the diameter of the fiber below the water surface a small window was mounted in the wall of the water bath.

Determination of the Drawing Force

The drawing force needed to draw the fiber to its desired diameter, was determined using a Schmidt (Waldkraiburg, Germany) tension meter.

Polarized Light Microscopy

A Jenaval light microscope was used to examine differences in the polymeric structure of the coaxial fibers. Small coupes were cut from the fibers and were examined by polarized light microscopy.

Determination of the in Vitro Release Rate

An automated release control system was used to measure the *in vitro* release rate of the coaxial fibers. Samples were cut from the fibers (157 mm) and the ends were sealed with Loctite acrylate glue, which is impermeable for steroids. The samples were immersed in 200 ml water of 37°C under continuous stirring (750 rpm). The steroid concentration of the release medium was determined daily by HPLC, using a Novapak C18 column of 3.9 × 150 mm at column temperature of 30°C, a mobile phase of acetonitril:water (30/70 v/v%), a flow rate of 1.5 ml/min, and an injection volume of 10 μl. Detection was carried out by UV detection at 205 nm.

In order to maintain sink conditions, the water in the containers was refreshed daily. Typical release curves from these fibers have been reported in a previous study (16). On the first day a burst release is observed that is followed by a gradual decrease in release rate. In order to study the effect of spinline stress on the release properties of the coaxial fiber average release rates have been calculated (days 2–21).

Wide Angle X-ray Scattering

The polymeric structure of both core and membrane polymer as a function of process parameters has been investigated with wide angle X-ray scattering (WAXS). The measurements were performed using a Philips X'pert-diffractometer. Because no differences were observed in the polymeric structure of the core polymer, the investigation was focused on the membrane polymer. Slices of membrane polymer of about 100 μm were cut from the fiber in axial direction. Two separate parallel layers of membrane slices were placed on both sides of an X-ray sample holder. Subsequently the polymeric structure of the membrane was investigated with both mapping (a compilation of radial scans with varying azimuthal angle) and azimuthal scans.

For the azimuthal scans the detector angle 2θ was set at 21.3°, being the maximum intensity of the [110] reflection of the unit cell of the polyethylene crystals. The sample was set at θ = 10.65°. Subsequently, the sample was rotated between φ = −90° and φ = 90°. The angle φ = 0° corresponded to the direction parallel to the fiber axis.

For each sample, four azimuthal scans were made each with a different position of the sample holder. From these four scans an average azimuthal scan was calculated.

For the mapping scans, the azimuthal angle was initially set at φ = −90° while the detector angle 2θ was programmed from 8° to 32°. Hereafter, the azimuthal angle was increased 5° and another radial scan was performed. This was repeated for 36 times so that radial scans at 37 different azimuthal angles (from −90° till 90°) with 5° intervals were performed.

The diffractograms were fitted using Pearson VII functions (Fig. 2). The diffraction pattern is composed of reflections of the crystalline [110] and [200] planes and of an amorphous contribution. By determining the surface area of the [110], [200] and amorphous contribution the crystalline volume fractions (V_c) were calculated using following equation.

$$V_c = \frac{\Sigma A_{110} + A_{200}}{\Sigma A_a + A_{110} + A_{200}} \quad (5)$$

where A_{110} is area [110] peak, A_{200} is area [200] peak, and A_a is area amorphous peak

RESULTS AND DISCUSSION

The Influence of Process Parameters on the Drawing Force

In order to determine the die swell, the fiber was allowed to flow freely out of the spinneret into the water bath. The fiber diameter was measured afterwards. The diameter of the die was 3.6 mm. In Table II, typical die swell values of the coaxial fiber are given for an extrusion temperature of 105°C. In the presence of the membrane polymer, which is about three times more viscous than the core polymer, the die swell of the coaxial fiber is enhanced significantly.

In order to achieve a desired fiber diameter of 4 mm it is necessary to apply a drawing force. In Fig. 3, an overall picture (compilation of three pictures) of the coaxial fiber between spinneret and water surface is shown. Similar pictures were prepared under various process conditions. By determining the fiber diameter from these pictures, Fig. 4 was obtained. Here the fiber diameter between spinneret and water surface is plotted as a function of distance from the spinneret. The extrusion temperature and spinning velocity were respectively 105°C and 3 m/min. Each curve is associated with a different air gap. The last point of each curve indicates the diameter of the fiber upon entering the water surface.

Before solidification of the polymer, the anticipated fiber diameter should be approximately 4.1 mm. During solidification the fiber finally shrinks to the desired diameter of 4.0 mm. At an air gap of 80 mm, the fiber enters the water bath at a diameter of approximately 4.2 mm, which is almost equal to 4.1 mm. However, at an air gap of 6 mm, the fiber enters
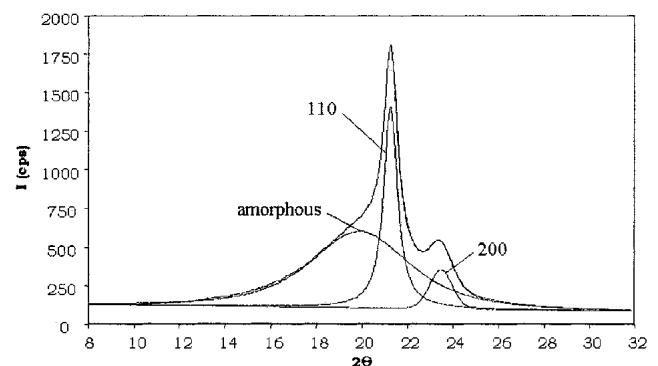

**Fig. 2.** Typical radial scan of the EVA 9 membrane.

Table II. The Die Swell Upon Freely Leaving the Die (∅3.6 mm) at 105°C (n = 3)

Spinning velocity (m/min)	Core + skin (mm)	Core only (mm)
1	6.7	5.6
3	6.8	5.3

the water bath at a much larger diameter of 4.5 mm. This means that for a small air gap, the fiber is also stretched in the water bath. Measurements below the water surface revealed that the fiber is stretched in the water bath over a distance of approximately 5–10 mm. Therefore, the drawing distance (L) in Eq. 4 is the total of the air gap and the drawing distance below the water surface.

It can be deduced from Eq. 4, that the force needed to draw the fiber to the anticipated diameter increases with decreasing air gap. In order to examine the relationship between the process parameters of the extrusion process and the drawing force, coaxial fibers were manufactured with various process parameters and the drawing force was measured (extrusion temperature 105, 110, and 130°C; air gap 5, 10, 20, 30, 50, 100 and 150 mm; spinning velocity 1 and 3 m/min). In Fig. 5, the measured drawing force is depicted as a function of temperature, air gap and spinning velocity. Figures 5a and 5b consist of 21 and 14 data points, respectively, that were fitted with a Lorentzian 3D function. It can be seen that the drawing force increases significantly with decreasing air gap. Also temperature of the spinneret and the spinning velocity have a significant influence on the drawing force. By decreasing the temperature and increasing the spinning velocity respectively, both viscosity and volume flow increase. As a consequence the drawing force increases.

It is well-known that polymeric crystallization under stress may influence the microstructure of the membrane. This could already be observed from the appearance of the fiber. An opalescent appearance was observed for the fibers prepared at a higher spinline stress. At low spinline stress the fibers were more transparent. In order to visualize differences in the polymeric structure of the coaxial fibers, thin cross-sectional coupes of the fibers were examined with polariza-
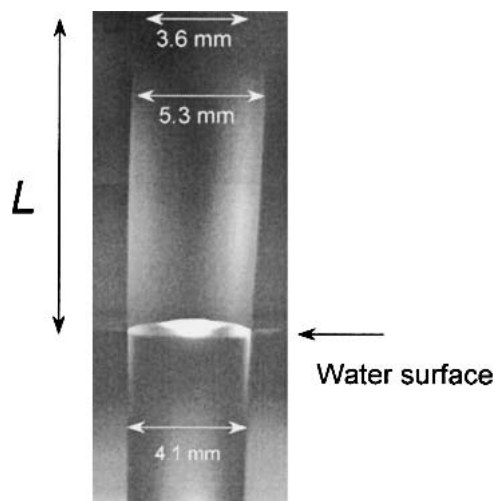
Fig. 3. Compiled picture of the fiber diameter in the air gap.
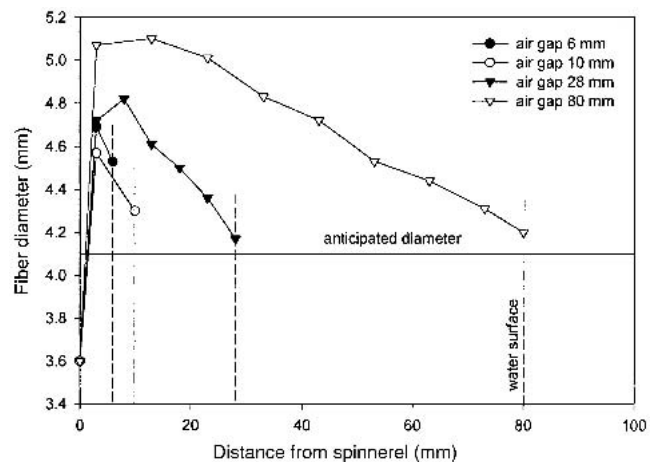
Fig. 4. The diameter of the fiber in the air gap (extrusion temperature 105°C, spinning velocity 3 m/min).

tion microscopy. The microscope is focused inside the bulk of the polymer. In Fig. 6a, large structures are visible in the membrane of the fibers produced at a high spinline stress. These structures were not present in samples produced at low spinline stress.

Wide Angle X-ray Scattering

Polymeric Orientation

In Fig. 7, average azimuthal scans are plotted of the fiber membranes that were obtained at different extrusion temperatures (105–130°C). The drawing force varied from 65 to 25 cN, respectively.

The detector angle was set at the maximum intensity of the [110] reflection.

It can be seen that by rotating the sample in the X-ray beam, the intensity of reflection is not constant in all directions. Apparently, all fibers are more or less orientated in the direction parallel to the fiber axis. Most likely the opalescent appearance observed at higher spinline stress is related to an increasing orientation of the polymeric structure of the membrane. Furthermore two additional peaks are formed at ± 25° from the symmetry axis at decreasing temperature (increasing drawing force). The appearance of these peaks has also been observed by others for polyethylene (14,19,20) and are attributed to the radial symmetry of the b-axis axis of the unit cell of a polyethylene crystal. Depending on the spinline stress, the a- and c-axes are orientated around the b-axis.

Keller and Machin (21,22) proposed a model for the way crystallization proceeds under stress. They described a two-stage nature of crystallization. First crystals are formed of which the c-axis is orientated parallel to the stress field. Subsequently, these crystals serve as nuclei of a secondary crystallization process.

This phenomenon during melt spinning of polymeric fibers has been investigated extensively by other authors. Dees and Spruiell (14) describe the influence of stress on the structure development during melt spinning of polyethylene fibers. By increasing the spinline stress the polymeric morphology of the polyethylene segments changes from a spherulitic structure to a row nucleated lamellae structure. Wide-angle X-ray measurements were performed to measure the orientation of
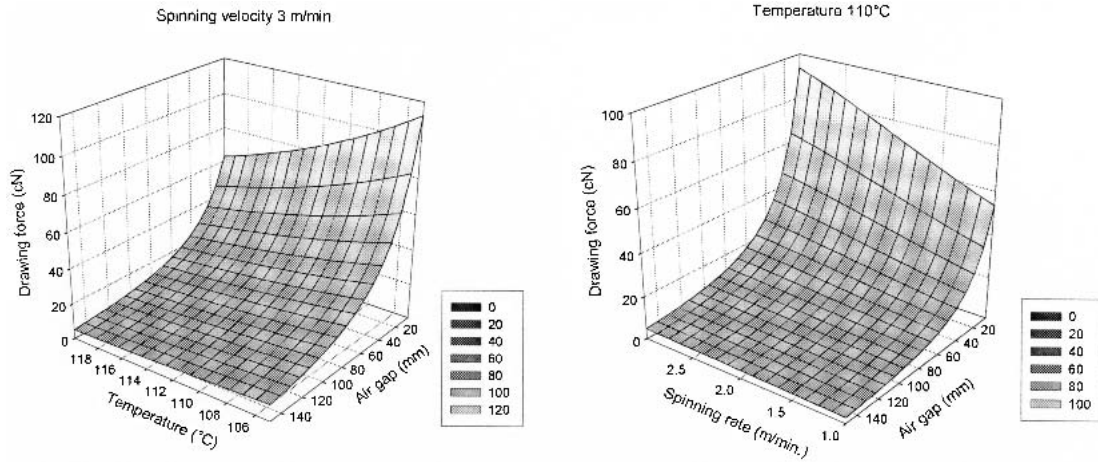
Fig. 5. The influence of temperature of the spinneret, air gap, and spinning velocity on the drawing force during melt spinning of the coaxial fiber.

the a-, b-, and c-axes of the unit cell of polyethylene as a function spinline stress.

Crystallinity

From the azimuthal scans it appeared that the polymeric structure of the fibers is orientated in axial direction. This means that the radial scans presented in Fig. 2 vary as a function of the azimuthal angle. This also implies that the volume crystalline polymer (V_c) is not constant in all directions. In order to determine the crystallinity of the membrane, 37 radial scans, with varying azimuthal angle, were performed for each sample. From these mapping scans the average crystalline volume fraction polymer was calculated using Eq. 5. In Fig. 8, the crystalline volume fraction is shown vs. the average release rate of the fibers that were manufactured under various process conditions and spinline stresses.

It can be seen that the crystalline volume fraction decreases with increasing spinline stress. Most probably the crystallization process of the polyethylene vinyl acetate membrane is hindered with increasing spinline stress. At the same time the permeability (expressed as release rate) increases. When the crystalline volume fraction decreases, the amorphous volume fraction increases. Because the steroid can only dissolve in the amorphous regions, an increasing amorphous fraction results in a higher solubility and therefore higher release rate.
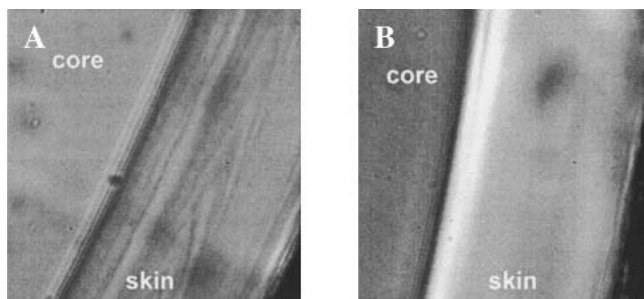

Fig. 6. Cross-sectional pictures of the membrane of coaxial fibers made with polarization microscopy: (a) high spinline stress; (b) low spinline stress.
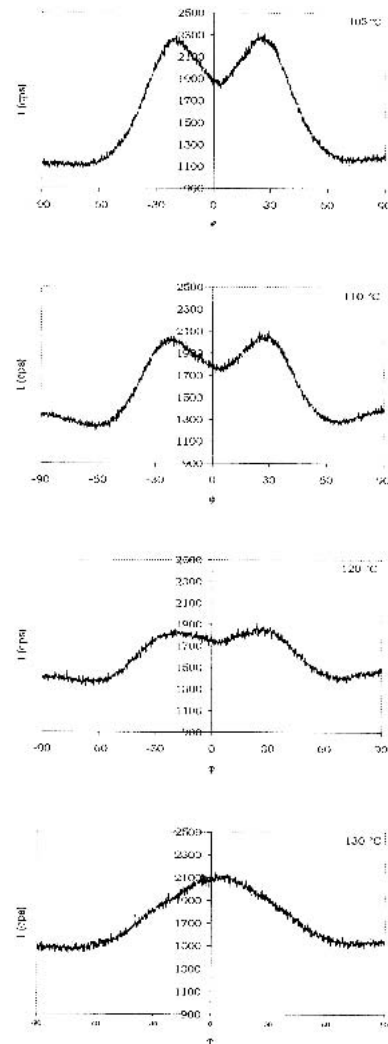

Fig. 7. The influence of the extrusion temperature on the orientation of the membrane. The intensity of the [110] reflection is plotted vs. the azimuthal angle.
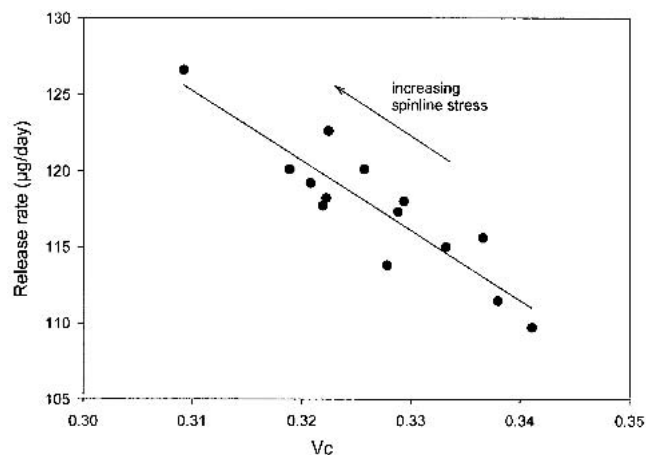
Fig. 8. The average crystalline volume fraction (V_c) as a function of the average release rate (day's 2–21, n = 6) of fibers prepared at various process conditions (temperature, air gap, spinning velocity).

The Relationship of Spinline Stress and Release Properties

In order to study the effect of spinline stress on the in-vitro release properties of a coaxial fiber, the in-vitro release rate at 37°C has been determined for fibers that were prepared under various process conditions (temperature, air gap, spinning velocity).

As a consequence hereof the drawing force varied from approximately 35 to 110 cN. In Fig. 9, the average release rate has been plotted as a function of the drawing force.

The figure suggests a linear relation between the drawing force and the in-vitro release rate. It is shown that the average release rate increases with increasing drawing force. It was demonstrated above that an increasing spinline stress results in orientated polymeric structure. Furthermore, it was found that the crystallinity also decreases with increasing spinline stress. It is expected that the combination of these findings results in the higher release rate.

CONCLUSIONS

It was demonstrated in this paper that the extrusion parameters and spinline stress have a significant influence on
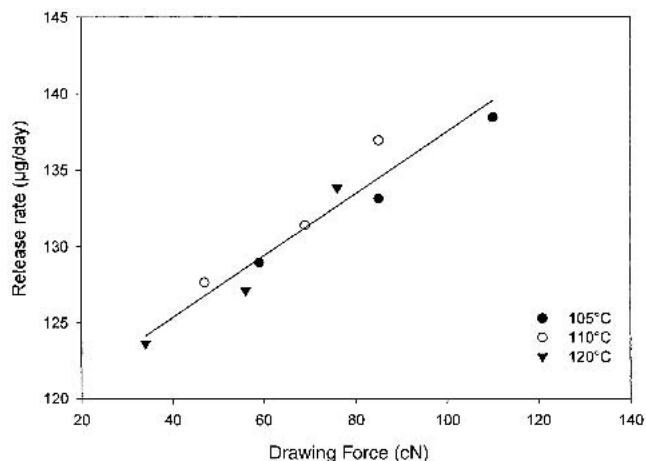

Fig. 9. The influence of the drawing force on the average release rate (day's 2–21, n = 3) of etonogestrel.

the release properties of a coaxial controlled release system based on EVA polymers. As a consequence of the viscoelastic behavior of the EVA polymers used, the polymeric melt exhibits a die swell upon leaving the die. Because the die swell is larger than the desired diameter, it is necessary to apply a force to draw the fiber to its desired diameter. By decreasing the spinning temperature and air gap or by increasing the spinning velocity, a larger drawing force (or spinline stress) is needed. It was found that the *in vitro* release rate of etonogestrel from the coaxial fiber increases with increasing drawing force.

It was demonstrated with polarized light microscopy and WAXS measurements that the membrane polymer is orientated as a consequence of higher spinline stress.

WAXS measurements also reveal that the crystalline volume fraction in the membrane polymer decreases with increasing spinline stress. The combination of these findings results in the observed differences in the release properties of the coaxial fibers that are produced under various process conditions.

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