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THERMAL ANALYSIS OF VECTRAN® FIBERS AND FILMS

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Abstract

Vectra® liquid crystalline polymers (LCP's) were introduced as commercial products in the mid-1980's. The first of these (Vectra A130) was a wholly aromatic thermotropic copolyester of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. Vectra A130 is a thermotropic LCP that can be melt spun into filaments that on heat treatment are characterized by high strength and high modulus. Vectra resin can also be extruded into films. In the fiber or film form this material is commercially known as Vectran®. Heat treatment enhances the tensile strength of Vectran fiber variants. Because of this, the elucidation of the physical transformations taking place in the internal structure of the material during heating has always been an important subject. Several thermal techniques are used to indicate clearly that what is observed as a "glass transition" is unlike the conventional glass transition in typical semicrystalline polymers. There is also an indication of the presence of multiple states of mesophase aggregation that collapse into a single state when taken to high enough temperatures.

Keywords: liquid crystalline polymers, Vectran® fibers and films

Introduction

Copolymers of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic (HNA) are the basis for the commercial products sold by Hoechst Celanese as Vectran films and fibers. At high temperatures these thermoplastic materials become liquid crystalline melts. The elongational flow generated during the fiber spinning and film extrusion can result in unusually high molecular orientation. This high orientation greatly influences the tensile properties of these materials. For example, the as-spun copolymer fiber of HBA/HNA with a molar ratio of 73/27 has a tensile modulus of 62GPa and a tensile strength of about 1 GPa. Thermal conditioning of fibers on an industrial, commercial scale involves using temperatures in the range of 230–300°C for times in the range of 2 to 16 h, and this treatment can increase the tensile strength to 3–4 GPa. The thermomechanical and calorimetric behavior of these materials under both static and dynamic conditions is of interest because of the information they may provide about the internal structure of the material that is responsible for the development of these properties.

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Experimental

The DSC measurements were performed using a TA Instruments 3200 controller and 2920 modulated DSC cooled by a mechanical cooling accessory. In the modulated DSC experiments the heating rate was 2 and 5°C $\min^{-1}$ (the heat flux scale in the figures given in this paper are different for the reversing and non-reversing signal in order to maximize the signals). In the traditional DSC measurements the heating rate was 2, 5, 10, 20 and 40°C $\min^{-1}$, the cooling rate was also varied between 2 and 40°C $\min^{-1}$. For the DSC measurements the Vectran fiber was chopped up to short pieces, then crimped in standard DSC pans.

The DMA measurements were carried out on a Perkin-Elmer DMA7e and a Rheometrics RSA2 in autotension mode. The static force was determined from stress-strain measurements. The average scanning rates were 2 and 3°C $\min^{-1}$.

High temperature wide angle X-ray diffraction experiments in the transmission mode were carried using the one dimensional INEL 120 curve position sensitive detector which was mounted on a Philip goniometer. Monochromatized CuK_α from the rotating anode generator was utilized. The film sample was oriented in such a way that the extruded direction is perpendicular to the scattering plane and the detector captured the diffraction in the equatorial direction. A specially designed furnace utilizing radiant heating from copper blocks which were heated via cartridge heaters was used. The temperature of the furnace was controlled by OMEGA 2010 temperature controller.

As extruded Vectran films, as well as as-spun and plant heat treated Vectran fibers were studied.

Results and discussion

Differential scanning calorimetry

Detailed DSC measurements on Vectra have been reported before [1, 2], therefore, only the special properties associated with Vectran films and fibers will be discussed here. The modulated DSC curves of as-extruded Vectran film, as well as the total heat flow curves of the as-spun and heat treated fibers are shown in Figs 1 and 2. The three peaks found on the total heat flow curves for the as-extruded and as-spun samples (Figs 1 and 2), as well as on the reversing and non-reversing heat flow curves of the as-extruded film (Fig. 1), in agreement with heating rate dependence of the traditional DSC curves (Fig. 3) indicate order perfection during heating (second and third peaks). The question of the first, lowest temperature peak is more complicated because its relative intensity does not change with the heating rate. Nevertheless, an exotherm in the reversing heat flow in the temperature range of the lowest temperature disordering peak implies a process accompanied with order increase. This peak may also have heating rate dependence, but at rates much higher than the ones used in this series of experiments. These conclusions are in agreement with the X-ray results. The major scattering equatorial intensity is attributed to the (110) peak (heating rate is ~2.5°C $\min^{-1}$). The "crystal" size (order)

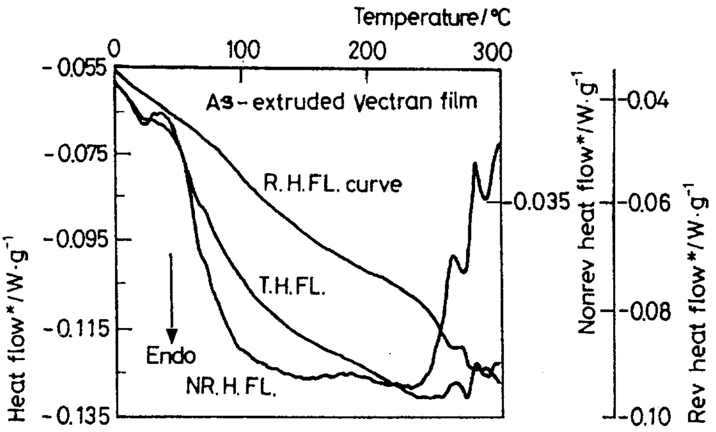

Fig. 1 The MDSC curve of as-extruded Vectran film

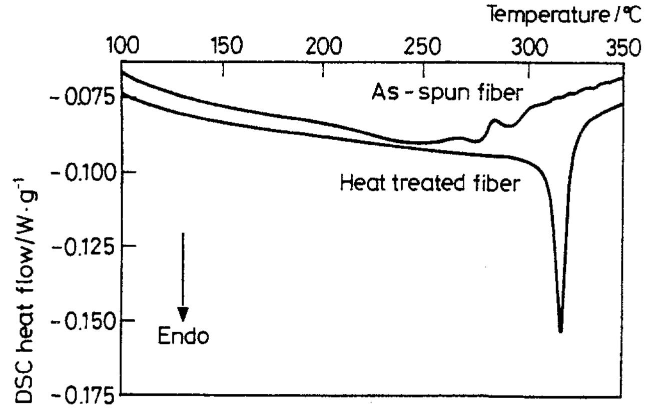

Fig. 2 The heating DSC curves of as-spun and heat treated Vectran fibers

calculated from the established peak width-crystal size relationship: it is improving with increasing temperature, and at about 260°C, a loss of crystal order was observed. This is probably due to orthorhombic to nematic transition.

The DSC traces in Fig. 2 illustrate the usefulness of the industrial heat treatment process: the mechanical properties of the fibers are vastly improved and the temperature range of use is increased: the temperature of the disordering process is increased by ca. 26°C (the peak temperature of the disordering process increases from 292.5 to 318.5°C).

Thermomechanical processes in single filaments

Figures 4a and 4b show the DMA traces for an as-spun (unannealed), and a heat treated (annealed) filaments. The experiments involved cyclic heating and cooling between –45 to 160°C. The filaments were heated at 3°C min^{-1} from –45 to 160°C followed by cooling back to –45°C and the heating-cooling cycle was then repeated.

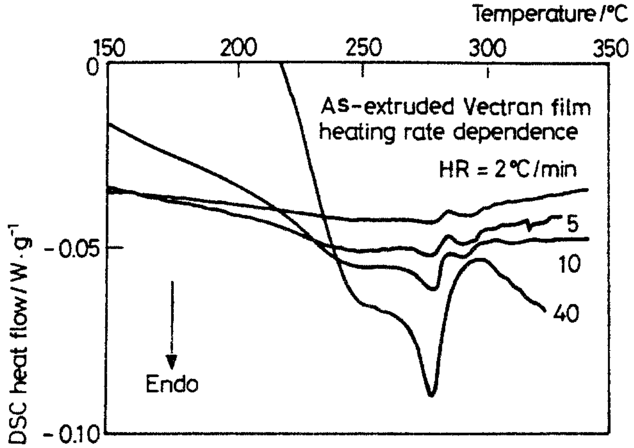

Fig. 3 The heating DSC curves of as-extruded Vectran film at different heating rates

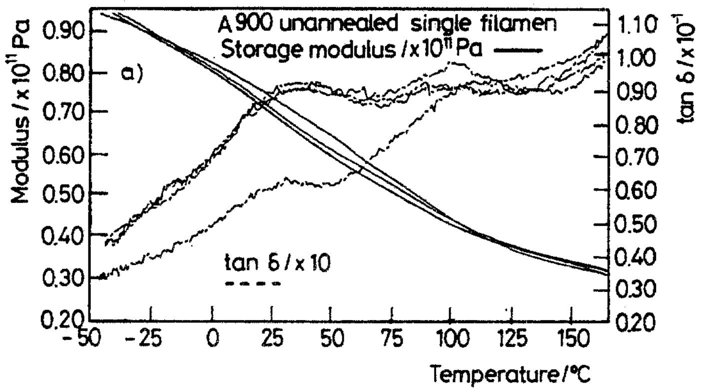

Fig. 4a DMA of as-spun (unannealed) Vectran fiber with cyclic heating-cooling between the temperatures –45 to 150°C

Figures 5a and 5b show the profile of the probe position during the DMA experiments of as-spun and heat-treated single fibers in the heating-cooling cycles. These data provide information on the thermally induced changes in the filament specimen length during the course of the heating and cooling cycles. For both the as-spun (Fig. 5a), and the heat treated filaments (Fig. 5b), there is a uniform contraction as they are heated from –45°C to about 50°C. On the first heating for the as-spun filament, there is a change in the apparent rate of contraction at about 50°C; for the heat treated filament there is a slight elongation at about 50°C before contraction resumes at higher temperatures. While the change in the rate of contraction on the first heating can be identified with the β loss process, there is no dimensional change that can be identified with the α process. For the as-spun filament there is some slight elongation as the temperature approaches 160°C, but clearly the contraction on heating and extension on cooling is quite uniform. Similarly with the

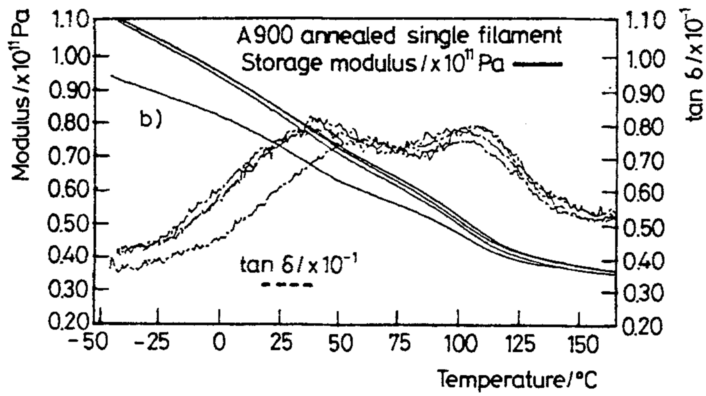

Fig. 4b DMA of commercial heat treated (annealed) Vectran fiber with cyclic heating-cooling between the temperatures –45 to 150°C

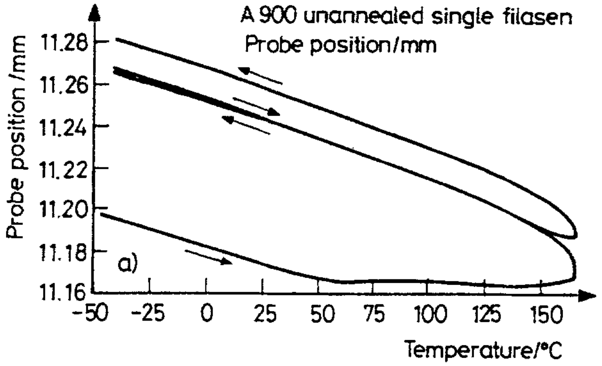

Fig. 5a Probe position (filament specimen length) during DMA of as-spun (unannealed) Vectran fiber with cyclic heating-cooling between the temperatures –45 to 150°C

heat treated filament, the contraction on heating and extension on cooling is quite uniform after the first heating. For both as-spun and heat treated filaments after the first heating, there is no indication of the loss processes that continue to be observed in the DMA on subsequent heating and cooling.

The overall contraction on heating and extension on cooling is what would be expected for a highly oriented macromolecular system that undergoes conformational disordering on heating and reordering on cooling. We suggest that the process occurring in the 50°C range in the profile of the filament dimension on the first heating is "slip" in the sense described by Takayanagi [6]. Slip can be either opposing translation of individual molecules relative to each other or the opposing translation of assemblies of molecules relative to each other. The internal arrangement of the macromolecules is such that once this slip is accomplished, it cannot be observed on subsequent heating and cooling. Under the conditions of these experiments, the loss processes that continue to be observed in the DMA after the first heating cannot be related to relaxation processes that involve the longitudinal trans-

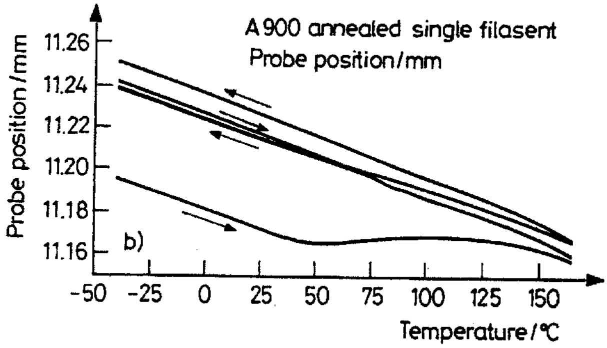

Fig. 5b Probe position (filament specimen length) during DMA of heat treated (annealed) Vectran fiber with cyclic heating-cooling between the temperatures –45 to 150°C

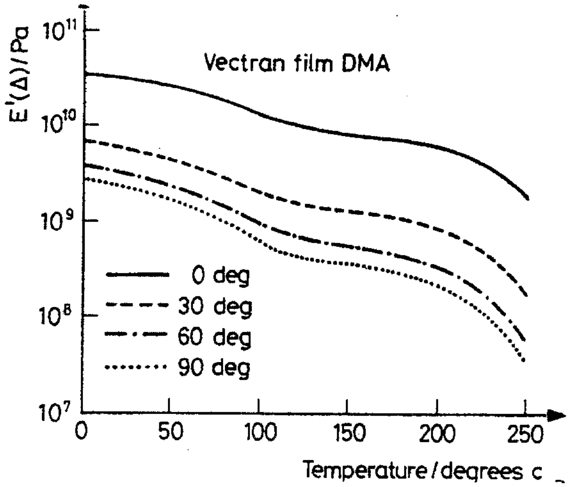

Fig. 6 Storage modulus profiles from DMA on Vectran film samples cut at four different angles relative to the direction of molecular orientation (0, 30, 60, 90°C)

lation of macromolecules or macromolecular assemblies along the fiber axis. Indeed, the uniform, nearly reversible contraction and extension suggest that in the experimental temperature range, the internal structure is such that the positions are fixed and the thermally induced change in end-to-end length produced as a result of conformation changes is mechanically transmitted along the length of the filament. The DMA loss processes that continue to be observed after the first heating must represent rotational relaxation processes that occur without diffusion of the macromolecules. Rotational relaxational processes in the materials have been previously examined using static field dielectric relaxation techniques [7].

Thermomechanical processes in films

Figure 6 shows the DMA profiles for film specimen cut at four different angles relative to the direction of molecular orientation: 0, 30, 60 and 90 degrees. The modulus profile for the film cut at in the direction of molecular orientation (0°), is similar to that observed for the single filament. There is not a precipitous loss in modulus in the expected α transition region of about 100°C; instead, there is a gradual loss in modulus that occurs over the temperature range of 40 to 110°C (similarly as the "glass transition" was evaluated from DSC experiments in [1]). Film cut at increasing angles each show an overall decrease in modulus over the entire temperature range. As discussed for filaments, in the molecular direction, the macromolecules behave as if they are relatively fixed, so that the modulus is expected to be higher. At 90°, the chains can undergo a lateral, flexural deformation that increases the amplitude of their sinuous trajectory. This mode of deformation is expected to result in a lower modulus.

Conclusions

The presence of three distinct and reproducible peaks have been observed in the DSC of Vectran fibers and films. The behavior of these peaks with the variation of heating rate along with their behavior in modulated DSC, suggests that these peaks represent multiple states of mesophase ordering. Reorganization to states of increasingly higher order during heating of film samples appears to be consistent with increasing order with heating as measured by wide angle X-ray experiments. The DMA results indicate clearly that there are distinguishable dynamic processes initiated when the temperature is increased. After an initial slip of chains or aggregates of chains that occurs on the first heating. These processes are highly reversible suggesting no large loss of chain configuration during heating and cooling. Based on this, it is suggested that the loss processes observed in the DMA are rotational in nature. If the thermally induced dynamic processes are constrained to be rotational, then the reorganization observed in the DSC and MDSC experiments is conformational reordering. TMA results on film mounted at 0° and 90° to the molecular orientation suggests that with increased temperature, the Vectran macromolecule contracts along the direction of molecular orientation and increases its sinuous amplitude in the lateral direction. This strongly indicates that although the molecule retains a high orientation even at elevated temperatures, it is not behaving strictly as a rigid rod. Instead, the assembly of molecules represented in the film, while retaining a high degree of orientation, behave as if they have a sinuous trajectory.

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