Heat Treatment Studies of a TLCP Fiber

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SYNOPSIS

This work deals with the heat treatment of fibers and nonoriented specimens made of the thermotropic liquid crystalline polymer Vectra A900 in the light of tensile properties and DSC measurements. In calorimetric measurements, there seem to be some differences in the effects of the treatment between macroscopically isotropic (nonoriented) and highly oriented fiber specimens. Nonisothermal treatments also produce some effects on the tensile properties, which may be attributable to the thermal history of samples. Under the conditions of this study, a multistep treatment, ending at a final stage where the temperature was higher than the original melting point of the polymer, did not cause any acceleration in the rate at which tensile properties increase. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Different kinds of postspinning processing methods are an essential part of fiber manufacturing. In the case of flexible chain molecules, drawing and heat treatment of fibers may lead to a remarkable development in morphology and, at the same time, the mechanical properties may change essentially. The mechanical properties of liquid crystalline polymer fibers, with a rodlike molecular structure, do not change significantly as a consequence of the drawing process, because the initial structure is already highly oriented. On the other hand, thermal treatment has proven to be a successful method to increase the tensile properties of LCP fibers.[1-4]

The increase of molecular weight as a result of heat treatment has generally been used as an explanation for changes in tensile properties of thermotropic LCP fibers, and some experimental results indeed show a correlation between intrinsic viscosity and tensile strength.[5,6] However, the change in molecular weight provides an ambiguous explanation for the experimental results and, for example, the orientation of specimens may have its own effects.[7-11]

In our earlier work, we have found a remarkable increase of tensile strength as a result of the isothermal treatment of LCP fiber, carried out in vacuo.[12] Furthermore, the results show that elongation at break correlates with tensile strength. On the other hand, the abovementioned results show the treatment to have only a minor effect on the tensile modulus of fiber. Moreover, in the conditions used, the treatment time needed to reach an essential increase in tensile properties was long: at least ten hours. In this work, we consider the effects of some stepwise heat treatments.

The abovementioned earlier study shows that DSC traces of heat-treated oriented fibers are characterized by a wide melting endotherm that contains two peaks, and the results differ from the cases in which the initial specimens were not macroscopically oriented. Therefore, the results of heat-treated specimens without macroscopic orientation, treated in similar conditions as fiber, are presented.

EXPERIMENTAL

The fibers were spun of Vectra A900, consisting of p-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA).[13] The initial melting point of the copolymer was 280°C.[14] The spin draw ratio and the diameter of the as-spun fibers were 192 and 72 μm, respectively. The spinning process has been presented elsewhere.[15] The tensile strength of the

as-spun fiber was 1 GPa, and the elongation at break and modulus were 2% and 60 GPa, respectively. Thermal treatment was performed *in vacuo* and in the oven the fiber was wound, slightly tensioned, between two spools. The tensile specimens were cut from the part of fiber that was between the spools.

Tensile testing was performed using a JJ M30K-type universal testing machine. Specimen length and strain rate were 50 mm and 5 mm/min, respectively. The DSC analyses were performed using a Perkin–Elmer DSC-2 with a TADS data station. The scanning rate was 40° per min, which does not essentially destroy information during heating.[16] The fiber specimens were wound around a thin strip of aluminum to prevent the fiber from shrinking and moving during the measurements.

RESULTS AND DISCUSSION

Two-Step Treatment

The two-step treatment consisted of a 4 h treatment, either at 250 or 271°C ($= T_{A1}$), after which the temperature was raised to 280°C ($= T_{A2}$) for 4–24 h. As a result of the first step, the tensile strength increased from 1 to 1.3 GPa in both temperatures (Fig. 1). The increase of tensile strength in the second step at 280°C depends on the temperature used in the first step. The lower treatment temperature in the first step, 250°C, caused higher tensile strengths than those measured in samples treated at 271°C during the first treatment step. After a 28 h treatment, the tensile strength, measured at samples where T_{A1} was 250°C, was 2.5 GPa, while the measured values were 2.1 GPa in samples that were treated at first at 271°C. Elongation at break increased with increasing tensile strength.

A similar difference, due to the first treatment temperature, was noted in the modulus. Where the treatment started at 250°C, the measured values of modulus were slightly higher than the value of the as-spun fiber. The first step at 271°C caused a slight decrease of modulus compared to the original value (Fig. 1).

The above results show that a treatment, close to the original melting point, does not always favor the development of the measured properties. Similar results have been observed in the case of isothermal heat treatments.[12] The result of treatment depends on the previous thermal history of the specimen, which in this case is treatment temperature T_{A1}.

The DSC measurements indicate changes similar to those that were noted in isothermal treatments
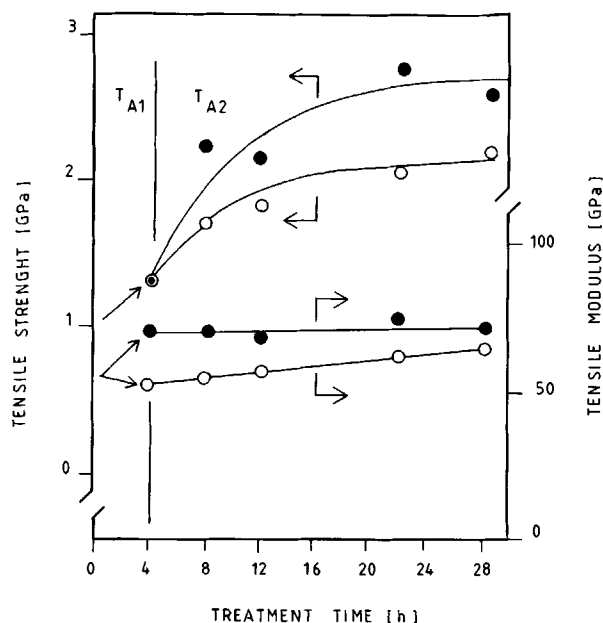

Figure 1 Tensile strength and modulus as a function of treatment time in a two-stage treatment, where the duration of the first stage is 4 h and the temperature, T_{A1}, is either 250 or 271°C. The temperature of the second treatment stage, T_{A2}, is 280°C. Closed symbols, T_{A1} = 250°C and open symbols, T_{A1} = 271°C.

at high temperatures. The vague melting behavior, typical of as-spun fibers, disappears during the first treatment step, and a wide endotherm, usually with two maxima, T_{M1} and T_{M2}, appears. Trace A in Figure 2 is an example of this melting behavior. With prolonged treatment and higher treatment temperatures, the endotherm shifts towards higher temperatures (Fig. 3).

The peak temperatures, measured after the first step, correlate with the treatment temperature. The next step, at 280°C, caused practically identical values to peak T_{M2}, which represents the final melting. The prolonged treatment caused slightly higher values for peak T_{M1} in samples treated at a lower temperature during the first step. On the other hand, the differences are small. Thus, the results measured from specimens, treated in the second step, show the thermal history formed during this step. The effects of the previous thermal history are minor. This is in agreement with what Sauer et al.[17] proposed. They noted that a stepwise increase of the heat treatment temperature results in a complete loss of previous thermal history.

The heat of fusion was small (1–3 J/g) in the abovementioned cases, and no systematic changes were observed. The crystallization temperature, T_c,

measured from the second cooling trace, started to decrease immediately after the treatment. In the light of our earlier results, it was already evident that the behavior of crystallization peak temperature displays a rapid change if the cooling rate is 40 deg/min. Due to the treatment, a distinct change appears in the crystallization peak temperature, resulting in the rapid stabilization of the temperature on a certain level. On the other hand, the used cooling rate does not permit a quantitative analysis of the crystallization behavior.

Treatment Above the Initial Melting Point

Our earlier study has shown the increasing effects of thermal treatment as a result of increasing treatment temperature.[12] In the treatment, the melting

Figure 3 Peak temperatures, measured from the first heating trace, and crystallization temperatures, measured from the second cooling trace, in a two-stage treatment. Closed symbols, T_{A1} = 250°C and open symbols, T_{A1} = 271°C.
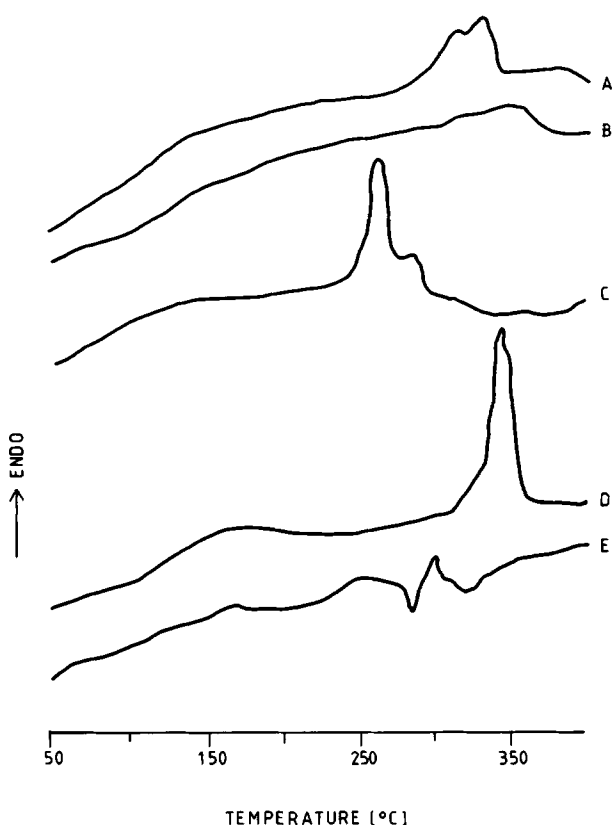
Figure 2 Examples of DSC traces of fibers. (A) Fiber subjected to a two-step treatment: first 4 h at 271°C and then 4 h at 280°C. (B) Fiber subjected to a two-step treatment: first 4 h at 280°C and then 4 h at 300°C. (C) The first heating trace of a nonoriented specimen, heat treated at a temperature of 198°C, treatment time 96 h. (D) As above, but treatment temperature is 271°C. (E) Isothermal heat treated fiber, treatment at 140°C for 96 h.
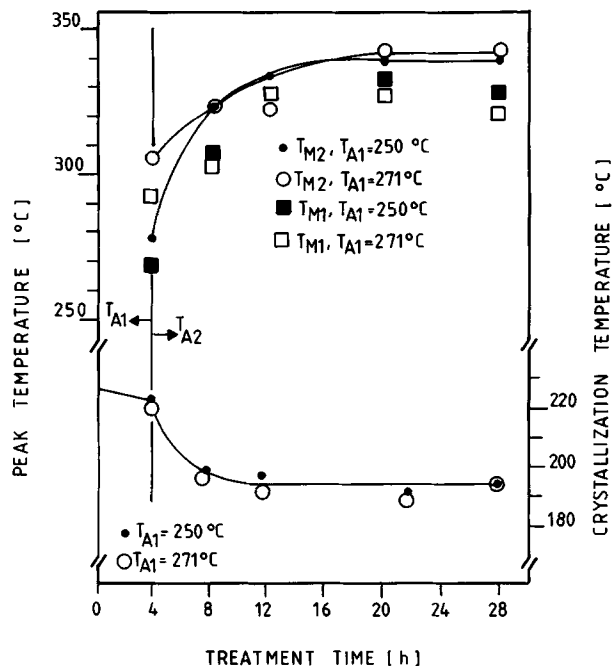
point of the treated fibers increased well above the original melting point. Thus, using a stepwise treatment, the stability of fibers can be increased to allow treatment at temperatures above the original melting point. A three-step treatment, which begins with 4 h at 271°C, continues for 4 h at 280°C and ends with 4–24 hours at 300°C, was used to examine the possibility of speeding up the treatment.

The first two steps yield a tensile strength of 2.1 GPa, but, as a result of the last step at 300°C, the tensile strength starts to decrease, and after a 24 h treatment at 300°C, the value for strength is 1.9 GPa. The effect of the last treatment step on modulus was similar and the measured value for the tensile modulus was 58 GPa. In DSC measurement, the first heating trace of samples, treated at 300°C, showed only a broad endotherm that does not contain the two distinct peaks that we have often encountered (trace B in Fig. 2). As a result of the prolonged treatment at 300°C, a weak increase of the maximum temperature of the endotherm was observed, from 333 to 340°C. The heat of fusion was low: 1–2 J/g. The cooling trace showed only a weak crystallization behavior and, after a 24 h treatment at 300°C, a weak peak was observed at a temperature of 180°C.

The treatment method used is limited, but some conclusions may be drawn on the basis of the results. The effect of treatment on the measured mechanical properties was negative. A treatment above the initial melting point (although DSC measurement shows that melting behavior exists at higher temperatures) starts a process that decreases the existing structure and properties of the specimen fibers. Although DSC traces show an increasing maximum temperature of the melting endotherm, the distinct peaks in the endotherm disappear. Thus, the development of crystallinity in samples may be equivocal.

Stability of Treatment

The purpose of the third, nonisothermal treatment was to observe the effects of the treatment at lower temperatures on samples treated effectively at a higher temperatures, which causes the observed changes in mechanical and DSC measurements, as compared to as-spun fiber. The specimens were first heat treated at 271°C for 24 h, and before the next step, at a lower temperature, they were kept 2 h at room temperature to separate the effects of the steps. The second step at a lower temperature was at 198–260°C for 48 h. Our earlier work has shown that a treatment above 220°C caused changes in both mechanical and thermal properties.[12]

In the treatment, mechanical properties were virtually unchanged, tensile strength was 2.1 GPA, and the modulus was 60 GPa in all cases. In other words, under the conditions used, the treatment of fibers, which have been treated earlier at a higher temperature, does not cause any further observable development in mechanical properties. This is because the earlier effective treatment had, for the most part, used up the preconditions that existed for structural development and, during the second step at a lower temperature, the process proceeds slowly.

Although tensile properties were practically unchanged as a result of the second step, the results of DSC measurements showed development in heating traces (Fig. 4). The second treatment step caused a weak, but observable, increase in melting peak, T_{M2}, which represents the final melting, and the shift was dependent on the treatment temperature. The melting endotherm after the first step includes two peaks, whose temperature difference is less that 10 degrees. After treatment at 198°C, however, the lower peak disappears and a new peak appears at a much lower temperature. Increasing treatment temperature increases peak temperature
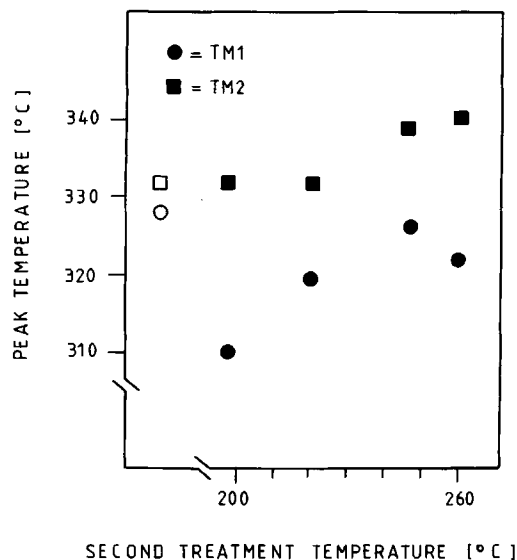

Figure 4 Peak temperatures of endotherms, formed in the further treatment of specimens treated first at 271°C for 4 h, as a function of treatment temperature. The second treatment time was 48 h in all cases.

T_{M1} remarkably. Thus, the behavior of peak T_{M1} evidently corresponds to the new structure formed during the second step.

Nonisothermal vs. Isothermal Treatment

In this work, high tensile strengths, 2.7 GPa, were attained using a two-step treatment, where T_{A1} was 250°C for 4 h and T_{A2} was 280°C, for 18 h, so the total treatment time was 22 h. On the other hand, the same tensile strength can be obtained in an isothermal treatment of 23 h at 271°C. Therefore, the nonisothermal treatment methods used in this work cannot be used to accelerate the development of tensile strength. Furthermore, the final melting peaks T_{M2}, measured by DSC for the two treatment methods, are located closely: at 339°C for the two-step treatment and at 334°C for the isothermal treatment; however, a difference is observed in the temperature of the T_{M2}, which here, too, correlates with the treatment temperature. On the other hand, there are some limitations caused by the test method.

Heat Treatment of Nonoriented Specimens

In our earlier work, DSC measurements revealed two closely located melting endotherms in fibers, caused by isothermal heating, which shifted with treatment time and temperature towards higher temperatures.[12] On the other hand, treatments at

low temperatures, and with short treatment times, the melting behavior is as vague as in the case of as-spun fibers. In general, the results differ from what has been obtained with macroscopically isotropic specimens.[17-19] To analyze possible differences, nonoriented specimens were prepared and subjected to thermal treatment.

For the test, DSC specimens were prepared using granulates and these were heated at a rate of 40 deg/min, to a temperature of 290°C using DSC; the specimens were then kept at this temperature for 3 min and were cooled down at the same rate to room temperature. The thermal history of the specimens roughly corresponds to the thermal history of the analyzed as-spun fibers. Even though the orientation of the specimens was not verified by any method, specimens prepared using this method can be considered practically nonoriented in comparison, for example, to fibers. The specimens were heat-treated in the same oven as the fiber specimens. The treatment temperatures were 160–271°C and the treatment time was 96 h in all cases.

The DSC traces for heat-treated specimens were clear. When the treatment temperature was less than 220°C, two endotherms, T_{M1} and T_{M2} occurred in the specimens (see trace C in Fig. 2. At higher treatment temperatures, only one endotherm occurs, which is trace D in Figure 2. The temperature of T_{M1} remained practically constant at 280 ± 2°C, and its heat of fusion was low: about 0.5 J/g (Fig.

Figure 6   Heat of fusion in nonoriented specimens as a function of treatment temperature.

5). On the basis of the temperature and the heat of fusion, this peak corresponds to the endotherm that is observed in nontreated samples.

The temperature and heat of fusion of peak T_{M2}, by contrast, depend on the treatment temperature. At the same time, the heat of fusion grows rapidly at the temperature range 189–200°C from approximately 2 J/g to approximately 10 J/g (Fig. 6). The treatment used had no effect on the crystallization behavior.

The measured behavior of peak temperatures, in this case, is similar to what was reported earlier.[17-19] On the other hand, our earlier results show that fiber samples, treated under the same conditions, have different kinds of melting behavior. As-spun samples and samples treated at a temperature of 220°C or below are characterized by vague melting, an example of which is trace E in Figure 2. Higher treatment temperatures caused in fibers an endotherm, generally with two separate peaks, both of which shift to higher temperatures as a result of prolonged treatment at higher treatment temperatures. To illustrate differences in melting behavior between these two kinds of specimens, Figure 7 presents peak temperatures for both fibers and nonoriented samples, treated in similar conditions at 271°C for 96 h. To explain the observed differences in melting behavior between these two kinds of specimens, a detailed morphological analysis is indispensable.

In fiber analysis, two typical phenomena may cause differences in DSC traces in the case of melting: reorganization and superheating.[20-22] The sam-
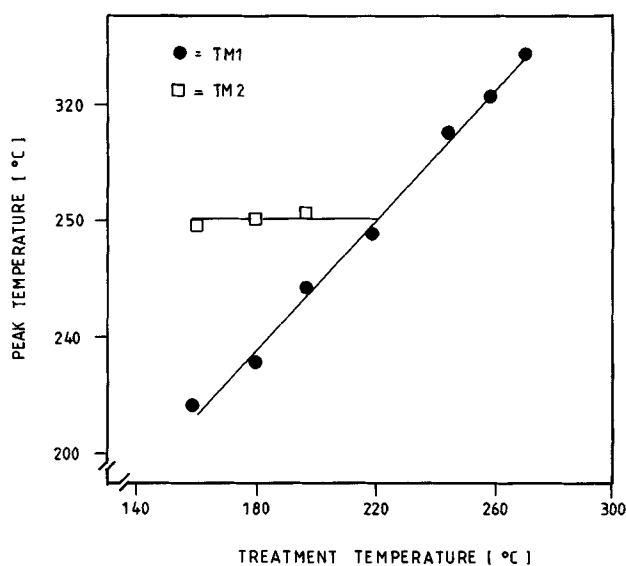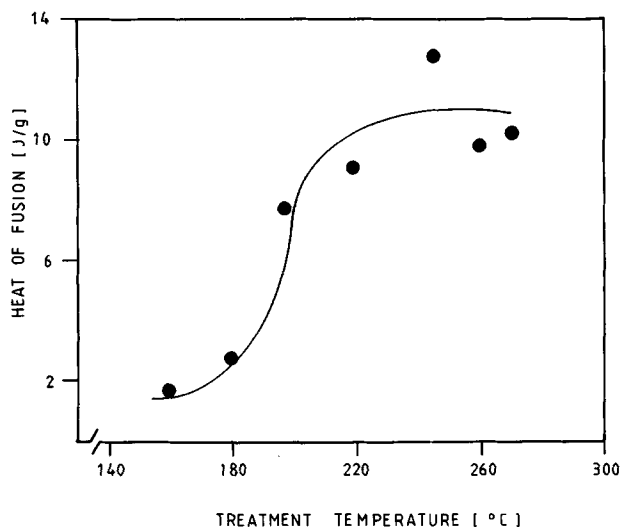

Figure 5   Peak temperatures, measured from nonoriented specimens, as a function of treatment temperature. Treatment time was 96 h in all cases.

ple preparation method may cause side effects, too.[23] In the case of fibers, spun from flexible chain polymers, shrinkage during melting causes a wider melting endotherm in DSC measurements than in the case where shrinkage is not allowed by the specimen preparation method. Figure 8 presents the melting endotherms of four identical specimens, treated for 48 h at 271°C. Only the heating rate and specimen preparation method were different.

No significant changes are observed in the starting and ending temperatures of the broad melting endotherm, regardless of whether shrinkage is allowed or not. At a high heating rate of 40 deg/min, the peak temperature of final melting is approximately 10 degrees higher than at a heating rate of 10 deg/min. At a slower heating rate, a splitting of the broad melting endotherm is observed. Moreover, at slow heating rates, the first part of the broad melting endotherm grows stronger in relation to the final melting endotherm. If fiber shrinkage is prevented, the final melting endotherm will be narrower.

CONCLUSIONS

In this work, we studied the nonisothermal heat treatment of fibers spun of liquid crystalline polymer
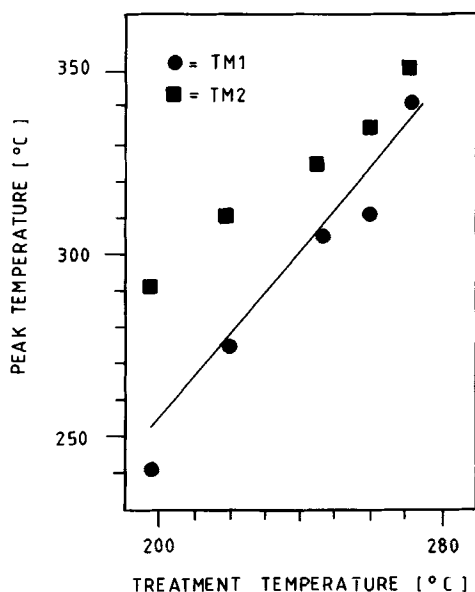
Figure 7 Peak temperatures, related to melting measured from isothermal heat-treated fiber specimens, as a function of treatment temperature. Treatment time in all cases was 96 h. The peak temperature, T_{M2}, measured from nonoriented samples treated at similar conditions, is presented as a correlation line.
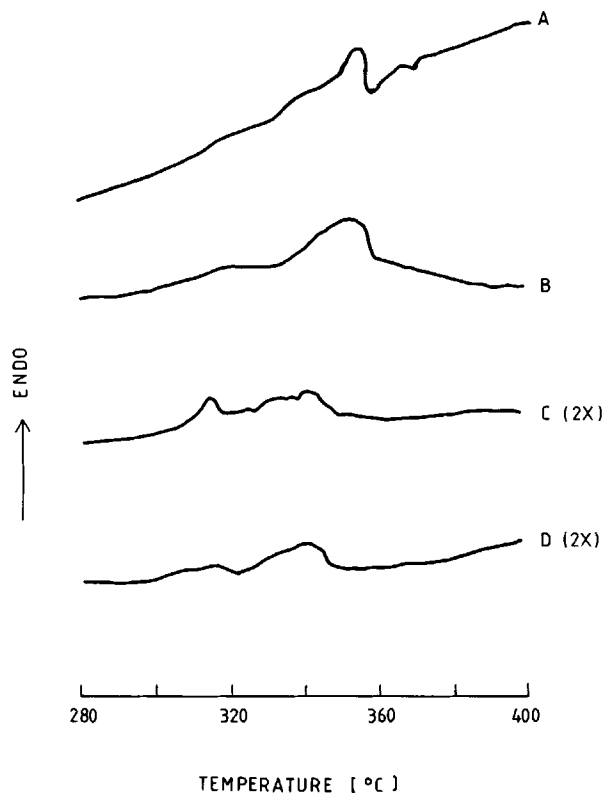
Figure 8 DSC traces, measured from heat-treated fibers around the melting endotherm. The treatments of fibers are identical; the only differences are measuring conditions. (Trace A) heating rate 40 deg/min, shrinkage of fiber not allowed (fiber tied around an Al strip), (trace B) 40 deg/min, shrinkage allowed, (trace C) 10 deg/min, shrinkage not allowed, and (trace D) 10 deg/min, shrinkage allowed.

Vectra A900 and the isothermal treatment of nonoriented samples, and the results were compared with the results of earlier isothermal treatments of fibers.

When comparing the results of this work to other results, at least two important things should be noted. In the present study, the treatment took place in a vacuum, while many results reported treatments in flowing inert gas or liquid. Second, the fiber studied in this work was thick: 72 μm.

To summarize, the next observations may be presented on the basis of the experimental results:

- Under the conditions of this study, the increase of mechanical properties is similar to that reached by an isothermal treatment with the same duration.
- In multistep treatments, with an increasing temperature, the specimen's properties, measured by the methods used, correlate with the

last treatment step. Only weak signs of previous thermal history may be detected. Properties formed at higher temperatures seem to be stable.

- A treatment at temperatures below, but close to, the initial melting point of polymer does not favor an unambiguous development of tensile properties. Furthermore, although temperatures of melting endotherms increase well above the initial melting point as a result of thermal treatment, a treatment above the mentioned temperature has no positive effect on the fiber properties. Thus, the effects of processes that decrease fiber properties increase as a result of increasing temperature in the temperature range mentioned. The processes may be, for example, relaxation mechanisms and/or chemical degradation.

- Comparing the measured mechanical properties and DSC traces, no unambiquous correlation may be drawn, although a limited correlation can be found.

- DSC traces showed differences in the results of highly oriented fiber specimens and nonoriented (macroscopically isotropic) specimens, due to the heat treatment.

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