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Oxidative stabilization of acrylic fibres

Part 2 *Stabilization dynamics*

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As acrylic fibres are heated in air to induce the stabilization reactions, the tension developed when stabilized at constant length and the instantaneous velocity of stabilizing fibres undergoing continuous processing both depend on the chemical composition, diameter, and orientation of the precursor fibre. An orientated fibre will tend to shrink when heated in the range 130 to 160° C, and hence will develop tension if restrained at constant length. Although this process has no direct relation to the stabilization process, it will influence the instantaneous velocity of the fibre during the later stages of continuous processing. As a fibre held at constant length is heated above 160° C the tension developed by entropic relaxation decreases and the fibre starts to undergo the prefatory and sequent reactions of stabilization described in a previous paper. If the prefatory reactions are rapid, a rigid structure is quickly established in the fibre and tension again increases rapidly. However, if the prefatory reactions are slow, select portions of the fibre react preferentially and the unreacted portions tend to relax to maintain a temporary quasi-equilibrium tension level. In both cases the fibres shrink at the later stages of stabilization because of chemical reactions. The shape of the tension–time curve is similar to the oxygen-uptake curves: The diffusion-limited mechanism of stabilization produces parabolic curves whereas the reaction-limited mechanism produces linear curves. Because each element of a fibre undergoing processing is subjected to the same tension at all times, previously orientated fibres first shrink, then stretch, and finally shrink again. These competing processes give rise to a changing instantaneous velocity. Data are presented for fibres of varying chemical composition, diameter, and initial orientation as well as for different conditions of stabilization.

1. Introduction

In the conversion of acrylic fibres to carbon fibres little is known about how variations in the stabilization process affect the mechanism of stabilization. Part 1 of this series of papers [1] describes the mechanism in terms of a series of unspecified reactions which lead up to and include the polymerization of the nitrile groups, called prefatory reactions, and a series of reactions that follow nitrile polymerization, called sequent reactions. The difficulty in specifying more precisely the chemistry of the system stems from the inability to characterize adequately the stabilized fibre. It is known that oxygen plays an important role in stabilization, yet it is not known how the added oxygen is incorporated into the fibre. It is probably present in a number of different structures; but the percentage of each functional group is unknown [2]. Part 1 further suggests that oxidative stablilization can occur under two different limiting conditions; a reaction-limited mechanism and a diffusion-limited mechanism.

In making carbon fibres, the acrylic fibres are usually heat-treated in air under conditions

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and for sufficient time to allow the fibre to be processed further at higher temperatures. Many studies have been carried out to determine the proper process conditions to improve the quality of the final yarns and to decrease their cost; yet it remains unclear how the process variations affect the chemistry and structure of the stabilized fibre. Two processes have been widely used to achieve stabilization: In one, the fibre is heat-treated while constrained to constant or nearly-constant length [3], analogous to a stress-relation experiment. In the other, the fibre is heat-treated while restrained by a constant force, analogous to a creep experiment. Constant force can be maintained either by using a riding pulley [4] by hanging weights from the end of the fibre [5, 6] or by continuous processing [7] in which the fibre is continuously fed into and removed from the heat-treatment zone.

Layden [5] suspended a known length of an unspecified acrylic fibre in the centre of a furnace and measured either the change in length under various loads or the change in tension. He found that for small loads, as the fibre was heated up to 270° C it initially shrank, then stretched, then shrank again; while for larger loads, the process was reversed: as the fibre was heated, it initially stretched, then shrank, then stretched again and finally broke.

Watt and Johnson [6] observed a different response when unspecified acrylic fibres were heated at 220° C in air under constant load: at low loads the fibres shrank, while at higher loads the fibres initially stretched and then shrank. In contrast, Fitzer and his colleagues [8–10] reported that only shrinkage occurred when polyacrylonitrile fibres were heated at various temperatures under a constant load. It was also reported, however, that under continuous process conditions, the fibres initially increased in length and later shrank.

Bahl and Manocha [11] observed the effects of oxidizing atmosphere and temperature on homopolymers and unspecified copolymers. An initial shrinkage was observed which was independent of atmosphere and could be eliminated with sufficient load. A secondary shrinkage was also observed and was dependent on the oxidizer content. Whereas Watt and Johnson take the position that shrinkage is caused by molecular relaxation, Fitzer and his colleagues and Bahl and Manocha suggest the occurrence of two distinct processes involving respectively a physical and a chemical mechanism.

The present paper is directed toward clarification of these issues. Both stress relaxation and creep measurements on different fibres will be used to provide insight into the processes of stabilization. The experiments show how information derived from stress relaxation can be used to understand the dynamic behaviour of fibres undergoing continuous processing.

2. Experimental procedure

Heat treatment of the acrylic fibres was carried out in the furnace shown schematically in Fig 1. Each of the four zones was independently maintained within ± 1° C of the set temperature by a Eurotherm series 96 controller. To minimize thermal gradients caused by the spacing of the heating elements, the furnace had an internal liner of copper tubing. A slot was milled the entire length of the copper tube so the fibre could be viewed at all times. In some runs, air was provided through the intake port (about 50 cm^3 sec^{-1}); in others, a pre-heated 5% hydrogen-forming gas was provided at a high flow rate (about 500 cm^3 sec^{-1}) to the centre of the furnace

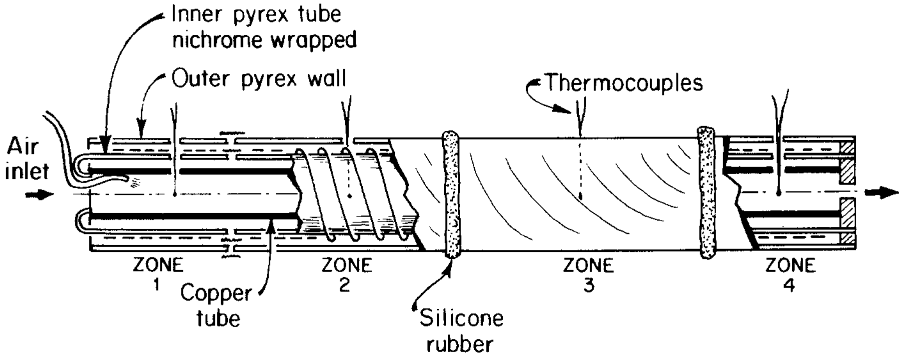

Figure 1 Schematic diagram of stabilization furnace.

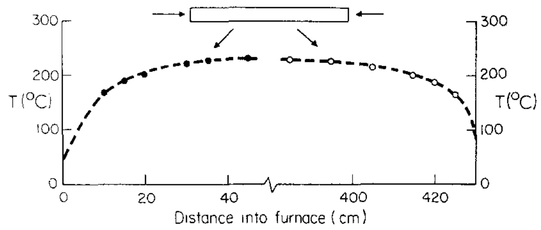

Figure 2 Temperature profile in stabilization furnace with temperature set at 230° C.

by a small-bore copper tubing inserted through the exit port. No attempt was made to use an oxidizing gas other than air. The temperature profile is shown in Fig. 2 for the case where all four zones of the furnace were set at 230° C. This figure illustrated typical temperature ramps at the entrance and exit of the furnace.

The fibres were processed in this furnace in either of two modes:

(1) In the stress relaxation mode, a length of fibre was held in the furnace by two fine copper wires. The shrinkage force developed by the fibre was monitored with a Zivy tensiometer as a function of time and temperature. Two non-idealities existed in the operation of this mode. First, the fibre was inserted at 20° C, and the temperature was raised over about 25 min to the desired temperature. During this heat-up period, the copper wires expand, reducing the shrinkage force. If the fibre shrinks less than 0.4%, a constant or a decreasing tension will be observed during the warm-up period. The curves of shrinkage force versus time have not been corrected for this effect because the total force decrease is the same in all cases, and only the data for the initial time period are affected. The main region of interest is that after thermal equilibrium has been established in the oven.

The second non-ideality arises from the mechanism of the Zivy tensiometer, which measures the force by allowing some length change, a maximum of 2.3% for 150 cm of fibre (corresponding to 100 g increase in tension). The fibre is permitted, therefore, to contract slightly with increasing shrinkage force. The maximum shrinkage allowed by the tensiometer is 10% or less of the unstrained shrinkage reported by Fitzer *et al.* [9, 10].

(2) In the continuous mode (creep mode) of furnace operation, a variable speed godet was used to control the speed of the fibre entering zone 1, and a variable speed synchronous motor connected to a take-up spool removed the fibre from zone 4. For a given fibre and temperature profile, the tension and the overall strain were determined by the differential motor speed. While operating in this mode, only steady state measurements were made. In order to eliminate fibre breakage during continuous processing, zone 1 was never set higher than 230° C. Therefore, heat treatment at, say 290° C, means zone 1 was at 230° C and the remaining 3 zones at 290° C. When the furnace was operating in this mode, the velocity of the fibre was determined by measuring its instantaneous speed as it underwent stabilization. This was accomplished with a cathetometer and a stopwatch.

Specifications of fibres M, O, D and C used in these investigations are given in Part 1 of this series [1]. The various deniers of fibre N, a Monsanto experimental acrylic fibre having the same composition as fibre M, were obtained by varying the draw ratio.

3. Results and discussion

3.1. Shrinkage force

Data on the dynamic shrinkage force measured for four fibres stabilized at constant length in air are shown in Fig. 3. The differences in behaviour observed for the different fibres are striking. As the temperature of the furnace approaches the glass transition temperature, fibres M, O and C

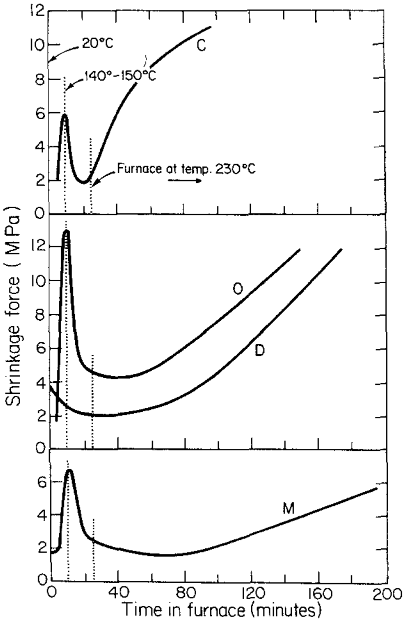

Figure 3 Shrinkage force curves for acrylic fibres heat-treated in air.

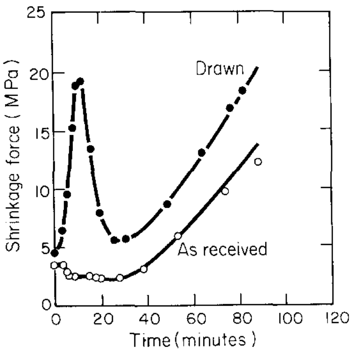

Figure 4 Effect of draw on the entropic shrinkage of fibre D heat-treated in air at 230° C.

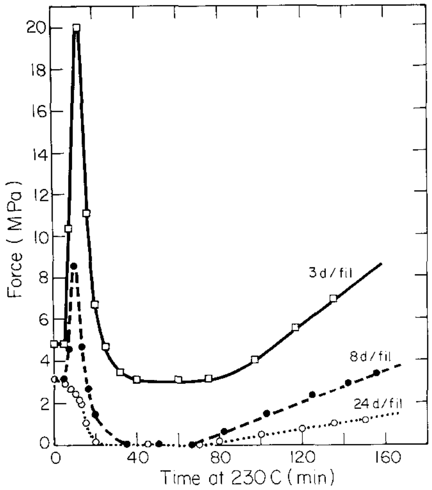

Figure 5 Effect of denier on the development of tension during the heat treatment of fibre N at 230° C.

start to shrink and develop tension. The maximum tension is attained in the region about 140 to 150° C and then declines to a "plateau region". The development of tension at temperatures about 140 to 150° C is due to entropic recovery of a drawn and quenched material. Fibre D does not develop tension in this region because it is essentially unoriented [12]. Shrinkage tension can be developed in fibre D by drawing it over a hot pin prior to the heat treatment (see Fig. 4). The initial development of tension (in the region of the glass transition) can be eliminated from all fibres by heat-setting the unrestrained material; further, the maximum tension is regulated by the draw ratio (see Fig. 5). Therefore, the behaviour of acrylic fibres up to temperatures where colour changes begin to occur (180° C) is related to processing details of the precursor fibres, and is not related to the stabilization reactions.

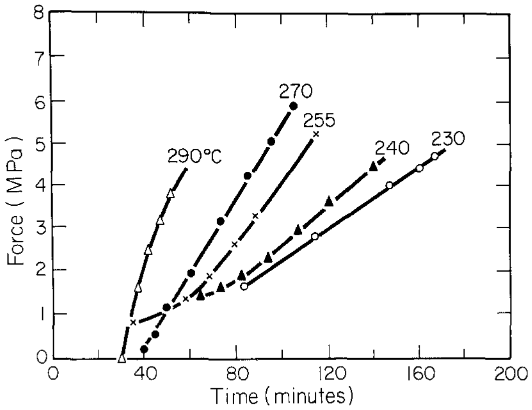

Figure 6 Effect of temperature on the shrinkage force curve for fibre M heat-treated in air.

The most important features of Figs. 3 and 4 concern the onset and shape of the second increase in shrinkage force (termed secondary shrinkage). In Fig. 6, only the secondary shrinkage is shown. The incubation time (when the tension starts to rise again) and the rate of secondary shrinkage depend upon the stabilization temperature for fibre M. All four fibres show a decrease in incubation time and an increase in secondary shrinkage rate with an increase in reaction temperature. More importantly, however, there is a temperature range for each type (and denier) of fibre below which the secondary shrinkage is linear with time and above which it is parabolic. For 1.23 denier fibre M, this temperature is about 285° C; for 4 denier fibre C, it is about 185° C. Examination of the cross-sections of these two fibres shows that when the rate of secondary shrinkage is linear, the fibre changes colour uniformly over the entire cross-sectional area as described in [1]. In contrast, when the rate of shrinkage is parabolic, the fibre cross-sections are characterized by the two-zone morphology [1].

The similarity in shape of the curves of secondary shrinkage versus time as well as the complementary observations of fibre cross-sections suggest a relation between reaction kinetics and secondary shrinkage [1].

Measurements of the shrinkage force during heat treatment of fibres in an inert atmosphere have helped in assessing the mechanism of secondary shrinkage. Considerable difficulty is encountered, however, during heat treatment in an inert atmosphere: At low temperatures (less than 230° C for fibre M) colour changes – and hence the reactions – proceed quite slowly, whereas at higher temperatures (in excess of 240° C), increased frequency of fibre breakage is observed

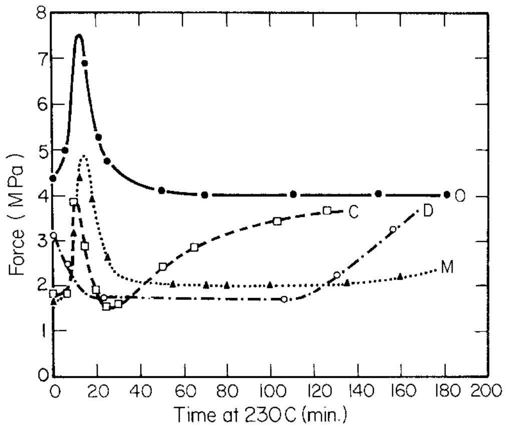

Figure 7 Development of shrinkage force in acrylic fibres with heat treatment time in an inert atmosphere.

because the exothermic reactions proceed in an uncontrolled manner.

The shrinkage force curves of the four fibres on treatment in forming gas at 230° C are shown in Fig. 7. Only at long reaction times, if at all, do fibres M, O and D show signs of shrinkage. On the one hand, the furnace was not completely airtight, and this shrinkage may have been related to air leaks and subsequent reaction, even though the fibres did not become black. On the other hand, shrinkage may be self-initiated under inert conditions given sufficient time. The rapid increase in secondary shrinkage force for fibre C suggests, however, that oxygen is not essential for shrinkage. When air is leaked into the oven subsequent to substantial prefatory reaction taking place, the fibre becomes black and further increases in tension result, as shown in Fig. 8. This behaviour indicates that oxygen catalyses or participates in the reactions which cause shrinkage.

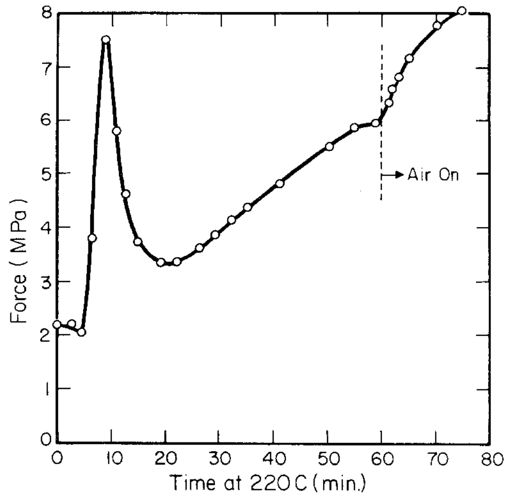

Figure 8 Effect of change from inert to oxidizing atmosphere on the shrinkage force of fibre C.

To complete the case for a direct correlation between secondary shrinkage force and reaction kinetics, it is necessary to explain the incubation period which is present in the tension measurements of fibres M, O nand D but not in their corresponding curves of oxygen uptake. To this end, observations of fibre cross-sections were correlated with the mechanism of stabilization [1]. Under conditions in which the rate-limiting step in stabilization is reaction-controlled, both prefatory and oxidative reactions occur slowly, at sites distributed throughout the fibre. Under conditions of diffusion control, on the other hand, prefatory reactions occur relatively rapidly throughout the fibre, and the rate of oxidation is limited by transport of oxygen through the outer oxidized layer. Once temperature is attained, the observed shrinkage of fibres stabilizing with a single-zone cross-section probably results from prefatory reactions as well as the sequent reactions in which oxygen plays a major role. In fibres that stabilize with the characteristic two-zone structure, however, the prefatory reactions are well underway in the time it takes to achieve uniform temperature and the secondary shrinkage results primarily from reactions involving oxygen.

At temperatures above 150° C, all virgin acrylic materials are easily extended: local extension can proceed within the acrylic regions in response to shrinkage induced by reactions in nearby volume elements; in contrast, the stabilized material cannot undergo differential extension–shrinkage. When stabilization is reaction-controlled, the prefactory and sequent reactions occur at sites well distributed through the fibre; after a continuum of material capable of bearing and transmitting load is established, realizable shrinkage can be measured and, hence, the incubation time ends. When stabilization is diffusion-limited, on the other hand, sequent reactions occur at the boundary of the outer layer of the fibre. In this way, shrinkage force is transferred along the fibre at all measurable times and, hence, negligible incubation times are observed.

The effect of fibre denier on the rate of secondary shrinkage for fibre N under conditions of reaction control, shown in Fig. 5, parallel the effect of denier on rate of oxygen uptake: A plot of the secondary shrinkage slope against the reciprocal of the square root of denier leads to a linear relationship. The consequences of this observation, that denier significantly affects the slope of secondary shrinkage via reaction rate, should not be ignored. It suggests, for example, that fibres of similar denier be used in effective comparisons of shrinkage behaviour of different types of fibres.

3.2. Continuous processing

When stabilization is achieved by heating a fibre fed continuously into one end of a furnace and removed at nearly the same rate from the other end, the local velocity of the fibre is not single-valued throughout the hot zone. Rather, the fibre responds to the constant force according to its local properties. Fig. 9 shows the behaviour of fibre M at steady state in a temperature gradient. There are three distinct regimes of response: first the fibre shrinks, causing an increase in its denier; then it draws; and finally it shrinks again. Due to the expansion and contraction of the fibre diameter, no simple correlation exists between the position-average velocity of the fibre and the average velocity calculated on the basis of (differential) input and output rates.

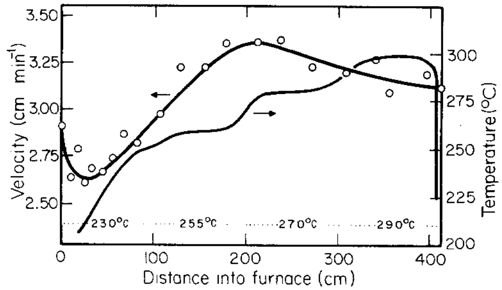

Figure 9 Local velocity of fibre M stabilizing in air in a temperature gradient.

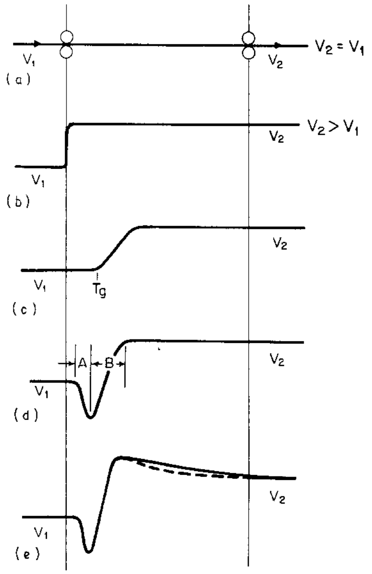

Figure 10 Predicted behaviour of model fibres under conditions of continuous processing.

To understand this behaviour, consider first an ideal elastomer being continuously drawn between two sets of pinch rolls, as shown schematically in Fig. 10a. If the speeds of the pinch rolls are equal, then the instantaneous velocity would be the same throughout the draw zone. If the exit speed is now increased, the elastomer will draw immediately after passing through the first set of rolls, giving rise to the local velocity curve shown in Fig. 10b. If an unoriented semi-crystalline polymer (say 40% crystallinity) is substituted for the elastomer and a suitable temperature gradient is added between the rolls, then (assuming homogeneous drawing occurs), the polymer will begin to draw near the glass transition, T_g. The presence of ordered regions in the polymer and the viscoelastic nature of the material above T_g is expected to extend the range of drawing. The behaviour expected for this material is illustrated is Fig. 10c, and that measured for an essentially unoriented fibre D is shown in Fig 11.

When a previously oriented semi-crystalline fibre is subjected to the same temperature gradient and draw ratio described above, it should first decelerate in the vicinity of T_g (region A, Fig. 10d) owing to entropic recovery, then accelerate in region B in order to obtain the final extent of orientation which is greater than the initial amount. The gradient between the input velocity and the minimum velocity should depend on the tension applied to the fibre. If the reoriented semi-crystalline fibre now undergoes a high temperature shrinkage-inducing reaction, a velocity profile of the form shown in Fig. 10e is expected.

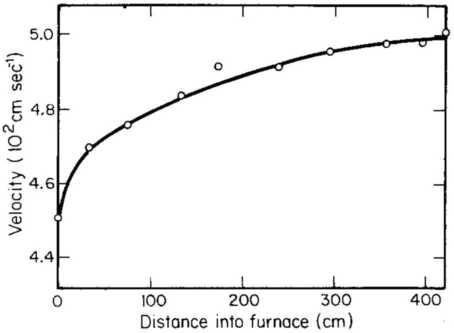

Figure 11 Local velocity of fibre D at 180° C.

The secondary shrinkage requires a compensating amount of additional draw; and it occurs at the region in the threadline where the fibre offers the least amount of resistance (i.e., in the unreacted acrylic material after entropic shrinkage and not in the stabilized material) to produce a maximum in the local velocity trace. Two conditions are shown in Fig. 10e: the solid line would result if the chemical reactions leading to shrinkage were incomplete, whereas the dashed line represents material in which stabilization is complete before the fibre emerges from the furnace. The expected behaviour shown in Fig. 10e corresponds excellently with the experimental results shown in Fig. 9 above.

The effect of temperature on the local velocity for underfeed and overfeed conditions has been studied. Generally the amount of draw (that is, the change in velocity from the minimum to the maximum velocity) increases with the amount of secondary shrinkage. However, when reaction rates are high, the early formation of ladder polymer and intermolecular cross-links limits the amount of draw. This is especially true when the oxidation process is limited by diffusion. At a given input speed, the local velocity will also depend on the take-up speed (to alter the overall extension). A higher process draw at a given temperature gives rise to a greater velocity maximum to compensate for the increased output speed.

The effect of temperature on the behaviour of 8 denier fibre N is shown in Fig. 12. Once again, high heat-treatment temperatures lead to large differences in local velocity. This is a result of additional extension when the fibre is extremely weak to compensate for the enhanced secondary shrinkage.

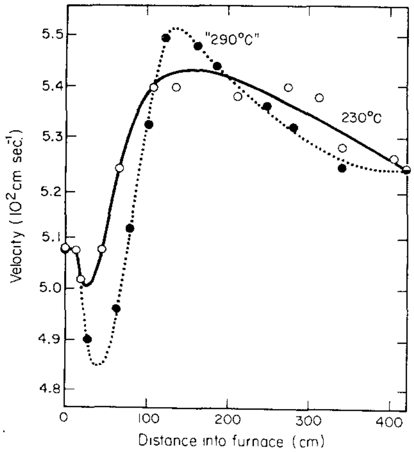

Figure 12 Effect of temperature on the local velocity of 8 denier fibre N.

The effects of process variables on the local velocity traces may be briefly summarized as follows: Entropic shrinkage produces a velocity minimum, and stabilization reactions produce a maximum, in velocity. Increasing the temperature generally depresses the minimum by lowering the overall tension and raises the maximum by promoting secondary shrinkage; the latter trend can be reversed at very high reaction temperatures by the occurrence of intermolecular reactions during extension. Increasing the denier decreases the rate, but increases the potential amount, of secondary shrinkage.

4. Conclusions

Two stabilization processes have been examined in detail: stabilization during which the fibre length is invariant (batch processing) and stabilization during which the fibre tension is invariant (continuous processing). Using the former (batch) process, two regimes of shrinkage force have been noted. During heat-up, the fibre tension rises as the glass transition is exceeded. This is associated with entropic recovery. Again at a later time, related directly to stabilization kinetics, the tension rises because of chemical reactions occurring in the fibres. Specifically, the shrinkage reactions can occur in the absence of an oxidizing gas, but oxygen present in the atmosphere has an accelerating effect on the rise in tension. A correlation between the development of shrinkage forces and the mechanism of stabilization has been demonstrated.

Under conditions of continuous processing, the velocity of the fibre varies with position in the reaction furnace. The precise form of the local velocity trace of a given fibre undergoing continuous processing is a function of the overfeed, the reaction temperature, the treatment time and, of course, the precursor and its draw history. When the overfeed is small or zero, fibres generally undergo an initial marked redrawing, but shrink during late stages of stabilization in response to stresses generated by chemical reactions. Again a correlation exists between the local velocity traces and the mechanism of fibre stabilization.

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