Morphology and Oxidative Stabilization of Acrylic Precursor Fibers

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We have shown earlier that the mechanical response and the changes in morphological parameters of acrylic fibers during a batch oxidative stabilization process support the morphological model proposed by Warner, et al. namely, connected alternating regions of lateral order and disorder in a fibrillar structure[1,2]. We describe here the results from additional experiments pertaining to the morphology of acrylic precursors and the progression of chemical and morphological changes during batch and continuous oxidative stabilization processes.

Experimental

The results reported here are from experiments conducted with fibers spun in our laboratory by redissolving a commercial acrylic fiber, Orlon-43, supplied by Du Pont. Fibers of different orientations and extents of lateral order were obtained through different combinations of drawing in a hot water bath(HWD) and through a high temperature tubular oven(HTD) (Table I). Results similar to those reported here have also been obtained with two other acrylic precursor fibers. The batch stabilization experiments were conducted in an air circulated oven at 265°C. Continuous stabilization was carried out in an 18-foot tubular oven at the same input and output velocities and with a flat temperature profile (265°C). The progression of changes here were monitored through measurement on a "process sample" obtained by cutting the filament bundle at the delivery end and rapidly pulling the sample out from the feed end.

Results and Discussion

1. Progression of Stabilization

The sonic modulus and WAXD data reveal clearly the presence of a higher overall orientation and lateral order in the HTD fibers than in the fibers drawn to the same extent in hot water(HWD) (table I). However, when the progression of stabilization is monitored through measurements of density and elemental composition (figs.1,2), little difference is seen between the responses in the two fibers.

When acrylic precursor fibers are heated to the temperatures involved in oxidative stabilization, whether dimensional constraints are imposed or not, a tendency toward increase in perfection and extent of the laterally ordered domains occurs in the early stages (fig.3), the extent of this increase decreasing with increasing order initially present in these fibers. The dramatic difference seen in the initial changes in sonic modulus (fig.4) between the presence and absence of dimensional constraints, with a pronounced drop in the absence of constraints indicates clearly the presence of an oriented but less ordered fraction, in which a majority of chain segments are connected to the ordered domains. The initial drop in the sonic modulus of HTD fibers (fig.4) and the rapid initial relaxation of shrinkage stress in both fibers (fig.5) reflect that some of the less ordered fractions do not bridge the ordered domains. The higher level of shrinkage stress but the lower shrinkage of HTD fibers (fig.6) is consistent with the higher orientational as well as crystalline order seen in these fibers.

The relative extents of the ordered fraction present at different stages of stabilization has been seen in the enthalpy of melting obtained through plasticization of the fiber with water. The monotonic build-up of shrinkage stress and shrinkage in the later stages of constrained and free heating respectively, and the results from WAXD measurements reflect this melting of ordered domains.

2. Morphology of Acrylic Precursor Fibers.

The following observations clearly show that the basic morphological unit in oriented acrylic fibers consists of a repeating sequence of oriented, laterally ordered and oriented but laterally disordered domains with a significant portion of the chain segments in the latter phase bridging the ordered domains.

(i) Clear WAXD evidence for the presence of laterally ordered domains.

(ii) Calorimetric evidence for "melting of crystals" when the melting is induced, through plasticization, at temperatures below those of degradation reactions.

(iii) Spontaneous shrinkage at high temperatures, without any loss of the extent of the orientation of the ordered domains.

Acrylic fibers with demonstrably different extents of order show little difference in density, indicating that the packing densities in the laterally ordered crystals and the laterally disordered "non-crystalline" regions are essentially the same. Confirmation of the existence of a long period in the precursor fibers has been obtained through SAXS studies of precursor fibers subsequent to impregnation with CuCl from a solution. Selective diffusion of CuCl into the disordered phase produces the electron density difference with the ordered domain, resulting in the appearance of the evidence for long period in SAXS.

References

1. M.K.Jain and A.S.Abhiraman, J.Mater.Sci., 18, 179, 1983.
2. S.B.Warner, D.R.Uhlmann and L.H.Peebles Jr, J.Mater.Sci., 14, 1893, 1979.

Table I. High Temperature Drawn Fiber Properties.

DRAW RATIO			DPF	SONIC MODULUS GPD	Fc	CRYSTAL SIZE A
HOT WATER	HOT OVEN	TOTAL				
3	-	3	3.	90	0.54	54
3	2.3	6.9	1.4	200	0.92	130
7.3	-	7.3	1.6	120	0.70	54

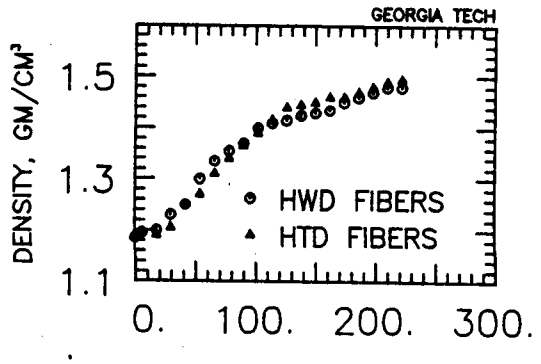

Figure 1. Density and continuous stabilization

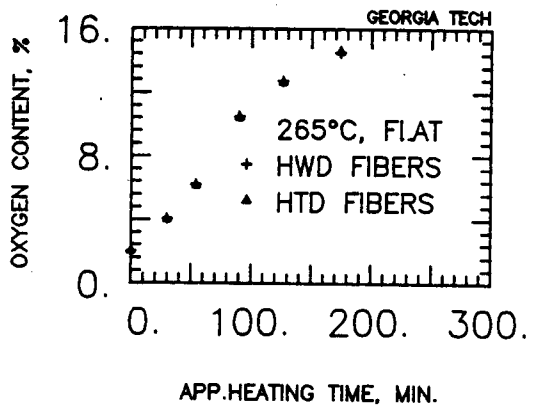

Figure 2. Oxygen pick-up in continuous stabilization

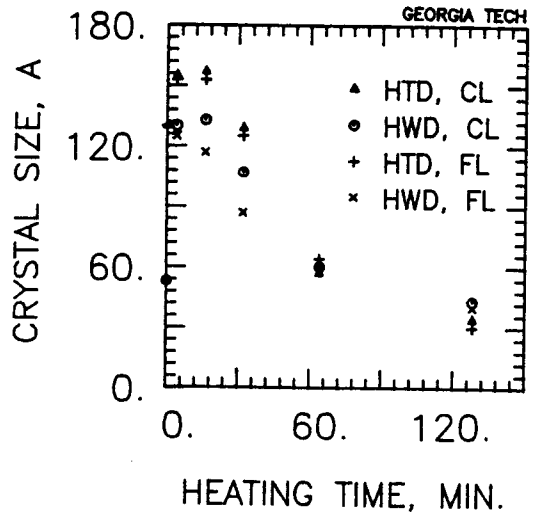

Figure 3. Crystal Size of batch stabilized fibers

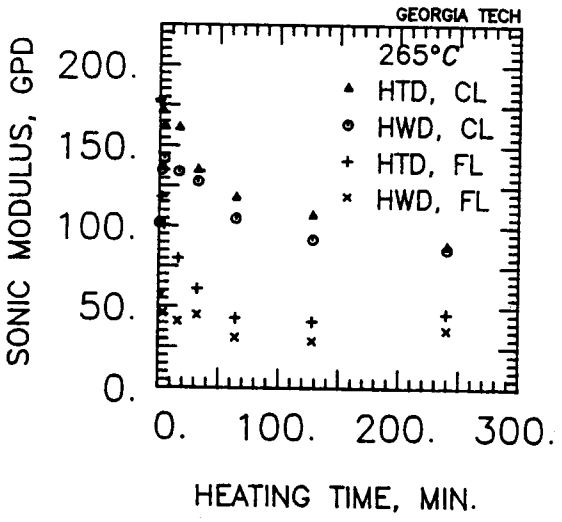

Figure 4. Sonic Modulus of batch Stabilized fibers

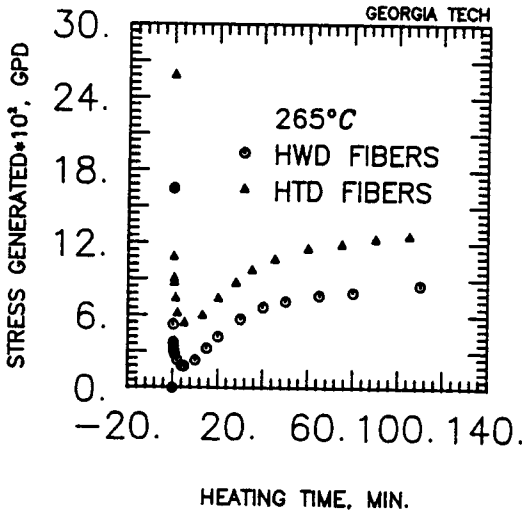

Figure 5. Shrinkage Stress in CL batch Stabilization

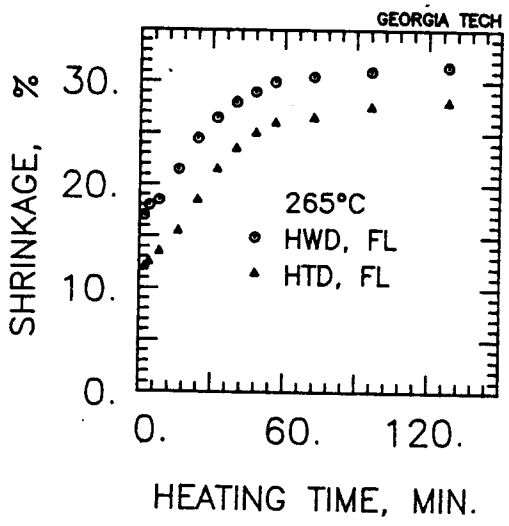

Figure 6. Shrinkage in FL batch Stabilization