Effect of moisture on stabilization of polyacrylonitrile fibers

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The method of modification through pre-stabilization stretching in the presence of plasticizers, such as succinic acid [1], boracic acid [2], dimethylformamide [3] and zinc chlorid [4] etc., has been adopted to prepare small-diameter carbon fibers, which contain fewer defects per unit volume. But the method is relatively complicated and at risk of introducing new flaws. To overcome the above drawbacks, the authors have introduced a modification into the stabilization process, and have chosen moisture in air as the plasticizer. The process is easy to control by damping the atmospheric air and facilitated to applied to continuous process. Foremost in importance is that the new species has not been used, which guaranteed the required cleanliness in the process.

Experiments were performed on a PAN-based 3000-filament batch, and the shrinkage of PAN fibers was monitored by the displacement of weight. Stabilization was carried out between the temperatures of 180–220 °C, air flow of 0.3 m^3/h. The stabilized fibers were then introduced into the carbonization furnace. The carbonization furnace was heated in high-purity nitrogen from room temperature to 1000 °C at a rate of 5 °C/min, and heating ceased when the temperature was reached. Finally the fibers were taken out when cooled down to room temperature. Experimental details have been published elsewhere [5] and the experimental setup was shown in Fig. 1. A special barothermohygrograph was utilized to examine the amount of moisture in damp air.

The result from Fig. 2 show that the fibers can be more easily elongated with increasing R.H. in air. The total amount of length elongation was about 0.2% at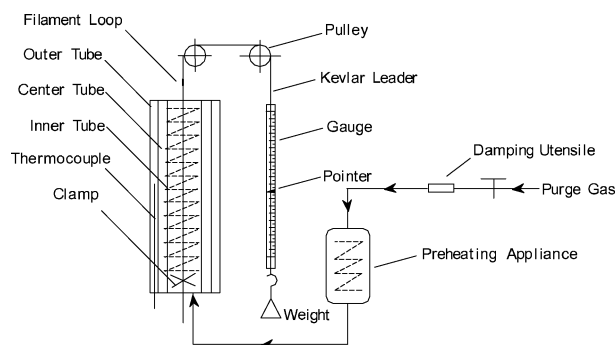 40% of R.H. as compared with 0.8% at 80%. This means that moisture serves as a plasticizer in reduce Van de var force between nitrile chains.

Table I lists data of various physical characteristics of oxidized fibers. The results show that increasing density and aromatization index (AI) increase initially with increasing R.H., displaying that the presence of moisture favored the formation of a heteroaromatic, cyclic structures (frequently referred as "ladder structure"). A decrease in tensile strength is also clearly seen, this is because when linear PAN chains are transformed into heteroaromatic cyclic structures, the cohesive energy between the chains will drop resulting in a decrease in tensile strength [6]. The sudden decrease in density may be due to excess moisture that contained in stabilized fibers, because the fibers have not been dried before density measure.

TABLE I Properties of oxidized fibers

Sample code	R.H. (%)	Density (g/cm^3)	Diameter (microns)	AI (%)	Tensile strength (MPa)
OF-50	50	1.381	11.61	35.53	308.28
OF-60	60	1.380	11.41	50.40	306.59
OF-70	70	1.385	11.49	52.43	299.23
OF-80	80	1.386	11.04	52.67	291.36
OF-90	90	1.396	11.12	58.14	286.15
OF-100	100	1.377	11.32	35.53	282.59

Note. If not specially emphasized, R.H. means the amount of moisture in air in stabilization process.

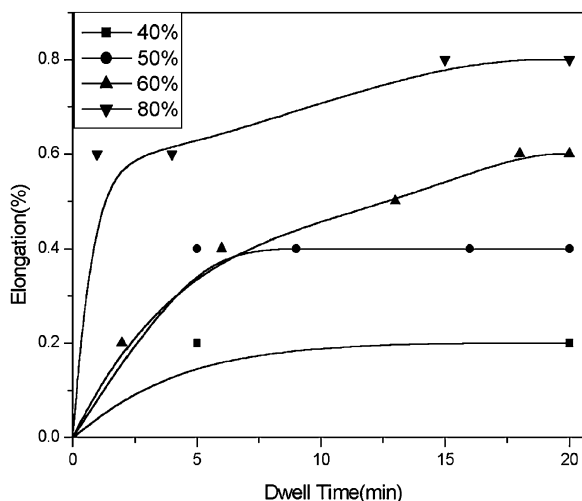*Figure 1* Schematic diagram of apparatus used for stabilization.

Figure 2 Changes in elongation of PAN fibers during stabilization. Condition: stabilization temperature, 180 °C; tension, 0.045 g/d.
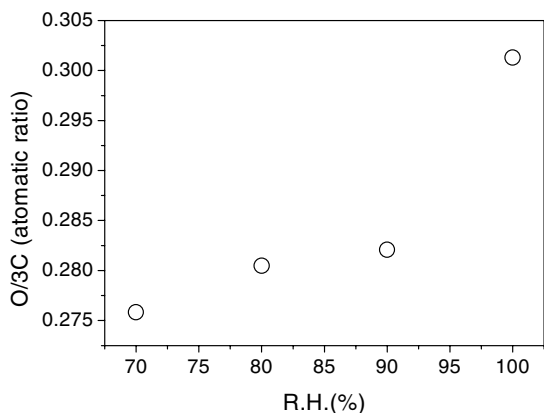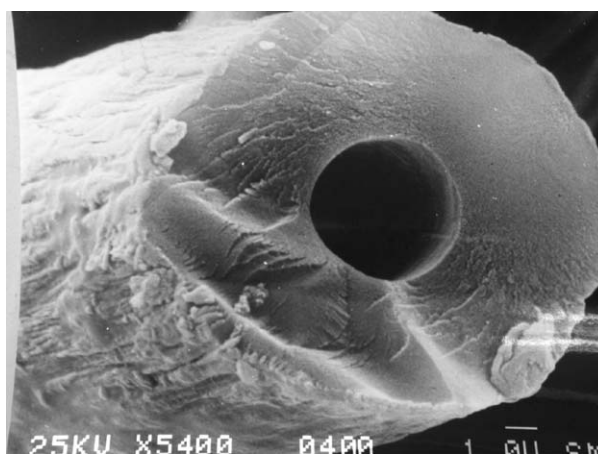
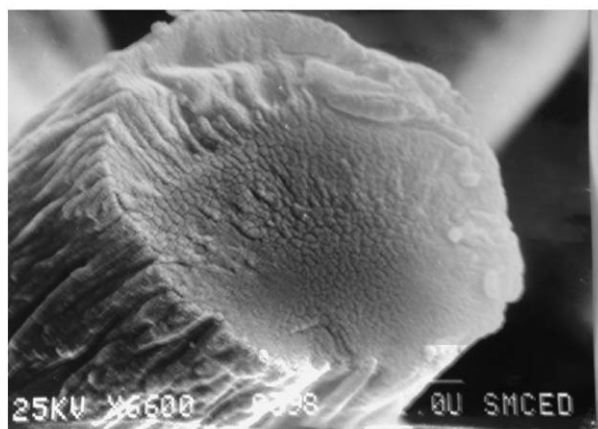*Author to whom all correspondence should be addressed.

Figure 3 Change of O/3C and H/3C value when stabilized at different R.H. conditions.

(a)

(b)

Figure 4 Typical transversal surface of stabilized fibers: (a) stabilized at 50–60% (R.H.) in air and (b) stabilized at >100% (R.H.) in air.

Fig. 3 shows that both oxygen and hydrogen contents increases rapidly with increasing R.H. in air. This further confirms that moisture is helpful for the full stabilization of PAN fibers. All the fibers were well dried (100 °C for 4 h) before measurement, and thus increasing O and H can be attributed to be "chemically" linked to the fibers. Previous workers suggested that oxygen is incorporated into fiber and reactions leading to nitrone [7], ketone [8], epoxide [8], lactone [9], lactam [9] and other structures [10]. The increasing oxygen content means that oxidative stabilization may proceed
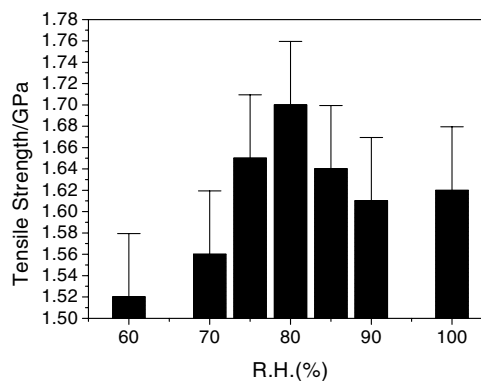

Figure 5 Change in tensile strength of ultimate carbon fibers with R.H. in air.

as "reaction-limited" kinetic process in high R.H. as compared with low one.

Fig. 4 shows scanning electron micrographs of the section of the fibers. The authors used 50% (wt) of sulfuric acid in flux for 24 h to etch off the not-fully-stabilized component. Fig. 4a shows a hollow tube of stabilized fiber, and its inner core has been eroded. In the case of Fig. 4b, the surface remains intact, indicating that it is composed of fully-stabilized materials.

Fig. 5 shows the variation of tensile strength of ultimate carbon fibers (no tension has been applied during carbonization). The results show an initial steady increase with increasing moisture in air. Above 80% (R.H.), a significant decrease was observed. This can be interpreted as over-oxidized (AI > 55%, Table I).

From the above results, it can be inferred that moisture plays an important role in the mechanical properties of ultimate carbon fibers. During stabilization in air, moisture acts as a plasticizer to reduce the Van de var force between molecular chains. In addition, the presence of moisture favors the diffusion of oxygen into the inner core of the fiber, which causes the process to proceed in a "reaction-limited" route and results in fully-stabilized fibers. The effect has lead to a significant improvement of final carbon fibers. The influence of moisture on mechanism of stabilization reactions will be further discussed in a future paper.

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