Physical Modification of Polyacrylonitrile Precursor Fiber: Its Effect on Mechanical Properties

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SYNOPSIS

Polyacrylonitrile precursor fiber of a special grade for making carbon fibers was modified by stretching in the prestabilization stage to various extents. The effect of such stretching on tensile properties of the original precursor fiber, intermediate (oxidized) fiber, and resultant carbon fiber prepared through a continuous process was monitored. Improvements in tensile modulus of fibers at various stages were observed with increasing stretch ratios. However, no obvious enhancement of tensile strength of final carbon fibers was found.

INTRODUCTION

It has been well established that polyacrylonitrile (PAN) is one of the most suitable precursors for manufacturing high-quality carbon fibers and that the mechanical properties of the resulting carbon fibers are significantly affected by the characteristics and quality of the precursors.[1-8] An early report by the Bahl research group established a correlation between the primary Young's modulus of PAN precursor fiber and the Young's modulus of the final carbon fibers.[9] More recently, several reports in the literature have revealed that, during the early stage of stabilization, PAN fiber, while under macroscopic restraints, underwent an ordering process termed "self-ordering," which led to improvements in the lateral and orientational order.[10-12] It is therefore inferred that a possible way to improve the morphological order, and thus the mechanical properties of the precursor, might be to modify the precursor by imposing stretch on the fibers well before stabilization takes place.[13] Through such a modification, we expect to obtain a carbon fiber with higher tensile properties. This study was devoted to surveying some aspects related to this consideration. A commercially produced PAN precursor was stretched to various extents at a temperature range between 175 and 195°C, within which PAN fiber undergoes plastic deformation.[13,14] The modified fiber was subsequently processed through continuous stabilization and carbonization. Tensile properties of fibers at various stages were then measured and compared in relation to the stretch ratio.

EXPERIMENTAL

A special grade of PAN precursor fiber tow (Courtelle fiber, Courtaulds Ltd., U.K.) containing 3000 filaments of 1.22 dtex was used in this work. The PAN precursor was first fed into a short furnace through a feeding godet, whose temperature was set constant. This stage was referred to as prestabilization. After such treatment, the modified precursor was then pulled out by a take-up godet and immediately fed into the first stabilization furnace. The schematic diagram of the whole process was detailed in our earlier report.[8] In the setup, stabilization constituted four furnaces while temperature increased from 215 to 265°C, corresponding to each furnace, respectively. During stabilization treatment, a compressed air flow of 4.0 L/min was tubed into the furnace. A total draw ratio of about 10% was imposed in stabilization that was established in our laboratory as suitable to make high-quality carbon fibers thereafter. Carbonization treatment was undergone under a temperature profile, gradually increasing from 300 to about 1300°C, and under the protection of argon. A processing speed of about 14 m/h was maintained in all the parallel experiments.

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A tensiometer was used to monitor the stress generated during the prestabilization stage while imposing stretch. An Instron Model 1122 testing machine was employed to measure the tensile properties of PAN fibers before and after modification as well as intermediate fibers (oxidized fibers) using the single-filament method and final carbon fibers using the impregnation method. For filament measurement, a gauge length of 2 cm and crosshead speed of 5 mm/min were used. An average of at least 30 independent measurements was recorded for the calculations. The diameter of individual filament was estimated by an optical microscope. For the carbon fiber measurement, a gauge length of 20 cm and a crosshead speed of 10 mm/min were used. The cross-sectional area was deduced by fiber density and linear density.

RESULTS AND DISCUSSION

Effect of Stretching on Tensile Properties of PAN Precursor

At a temperature of 185°C, three parallel experiments were run with the stretching ratio changing from zero to 4 and 8%. Data reflecting the variations in diameter, tensile strength, Young's modulus, as well as final elongation are plotted through Figures 1–4. Tension as a function of the fiber stretch ratio is recorded in Figure 5. It can be seen that with increase in the stretch ratio the stress generated shows approximately a linear increase (Fig. 5, temp 185°C). During this early and low-temperature prestabilization stage in which no detectable chemical reactions associated with stabilization were observed,[7] the stress could be attributed to two components: one comes from the shrinkage force induced by restraining the relaxation of the molecular chains; the other stems from the outside stretching force when imposing some draw ratios as in the case of the last two conditions. However, these two contributions to the overall stress can not be clearly divided. Potentially, they appear to interlink and interfere with each other. In addition, it can be inferred that the annealing temperature has an impact on the stress, since the temperature will be expected to influence the mobility of molecular chains. Later in this article, this aspect will be given a more detailed survey.

Examination of the data in Figures 3 and 4 shows that the Young's modulus demonstrates an evident increase with the stretch ratio and that the breaking elongation shows a general tendency to decrease with the stretch ratio. These changes can be explained on the basis of a "self-ordering" process occurring within the fiber while under macroscopic restraints as in this work,[10] which results in improvements in the lateral order and, thereafter, an increase in the Young's modulus and decrease in elongation.

The diameter of the precursor decreases with increase in the stretch ratio, from a value of about 12.3 μm dropping to 12.1 μm (Fig. 1). The tensile strength registers an obvious decrease initially after modification under lower stretch ratios, but when the larger stretch ratio of 8% was imposed, the tensile strength eventually improves compared with the original value (Fig. 2). Such a decrease in tensile

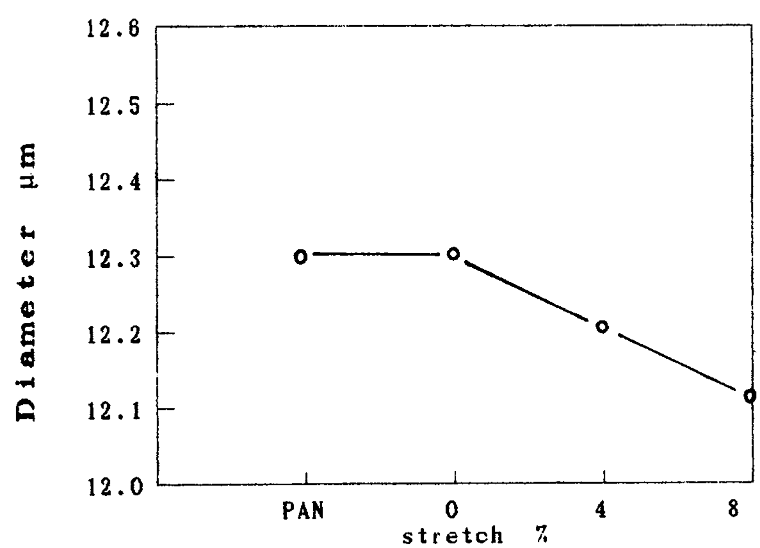

Figure 1 Variation of the diameter of the PAN precursor with the stretch ratio.

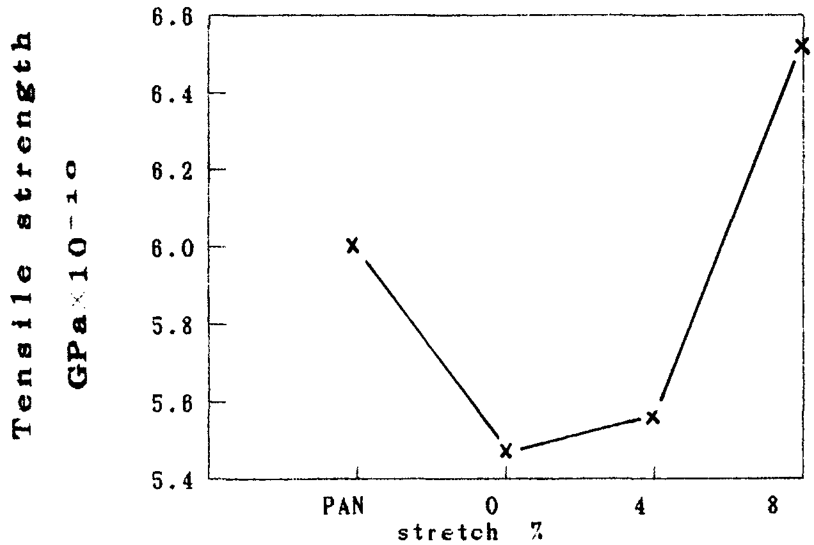

Figure 2 Variation of tensile strength of the PAN precursor with the stretch ratio.

strength in this early stage of processing was reported in our earlier article[8] and was observed by Ferguson and Mahapatro when studying the behavior of mechanical properties for a highly drawn PAN fiber under constant length.[15]

Back to the data in Figure 5, a large tension (about 6.5 MPa) was generated even when no stretch ratio was imposed (corresponding to constant length in a batch process). This development of tension is attributed to the "manifestation of the physical shrinkage force" because the entropic relaxation of molecular chains of the precursor is constrained in this case. With the ratio increasing to 4 and 8%, the tension increases to about 10 and 15 MPa, respectively (temp 185°C). Possible consequences of high stress within the fiber might be improving the orientation order both in the ordered region and less ordered regions[10]; increasing the number of ordered domains as some less ordered fractions rearrange into more ordered,[8,10] causing internal chain disruption or microfibrillar disruption as explained by Ferguson and Mahapatro[15]; and inducing higher plastic mobility among molecular chains that might then decrease the intermolecular interactions and thereafter decrease the cohesive energy.[16] All these possible effects will have impact on the tensile properties of the PAN precursor, especially on the strength, which is very flaw-sensitive.

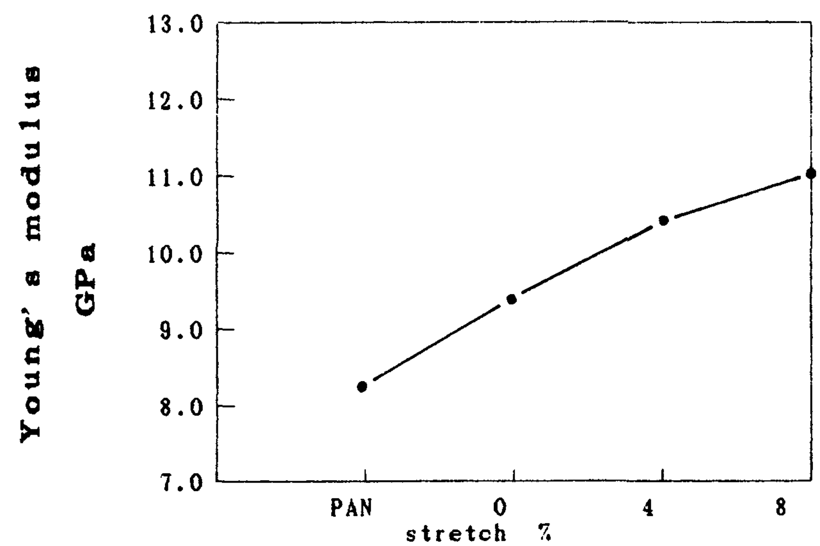

Figure 3 Variation of the Young's modulus of the PAN precursor with the stretch ratio.

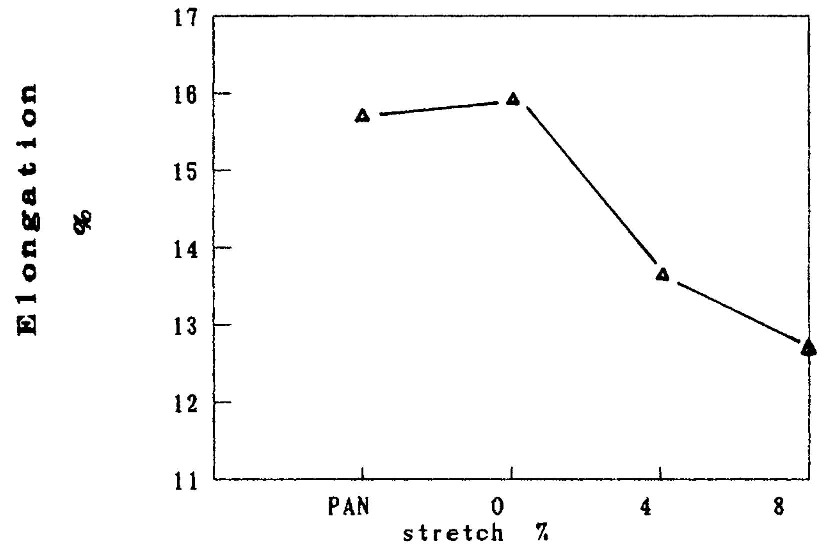

Figure 4 Variation of elongation at break of the PAN precursor with the stretch ratio.

However, to date, whether these effects all take place or some effects overshadow others at different levels of stress generated under outside stretch still remains to be elucidated.

Effect of Stretching on Tensile Properties of Intermediate Fibers

Figures 6 and 7 show the effect of stretching during the prestabilization stage on the diameter, tensile strength, and the Young's modulus of intermediate fibers after continuous stabilization. With increase in the stretching ratio, the diameter of the fiber decreases significantly, from a value of about 11.3 μm to a final 10.8 μm when stretch is increased to 8% (Fig. 6). The Young's modulus demonstrates a linear increase against the stretch ratio, a similar trend to that of modified PAN precursor. This suggests the influence of prestabilization stretching on the Young's modulus of the precursor sustains through the stabilization process. Moreover, the tensile strength shows a small tendency to increase with increasing stretch ratio.

Effect of Stretching on Tensile Properties of Carbon Fiber

To systematically survey the significance of stretching during the prestabilization stage on the me-

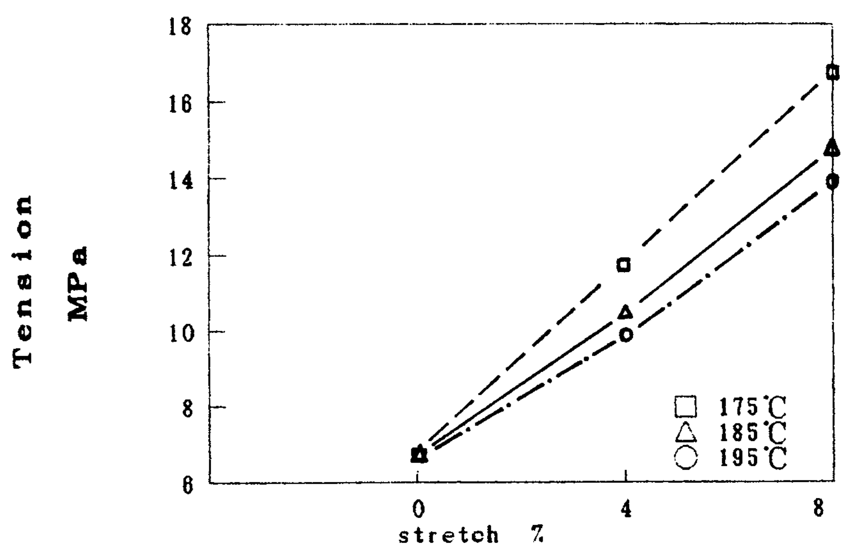

Figure 5 Tension as a function of the stretch ratio.

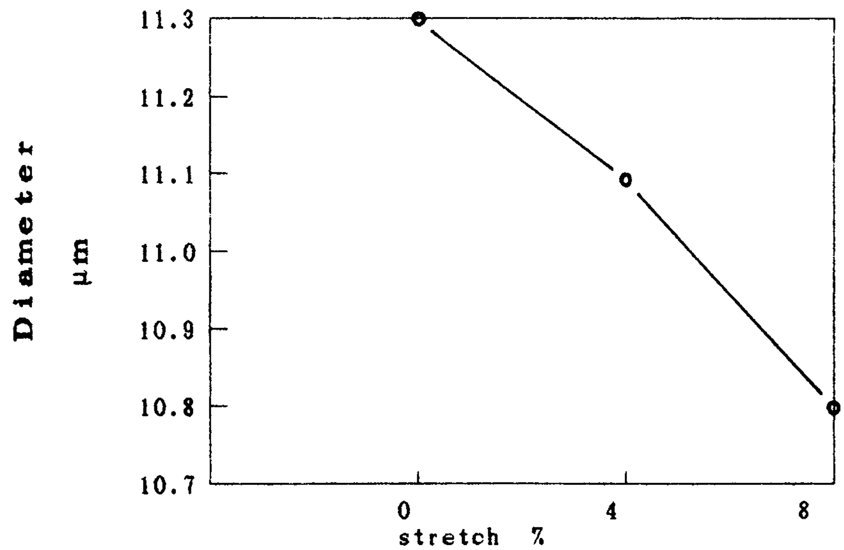

Figure 6 Effect of stretch on the diameter of the intermediate fiber.

chanical properties of the resulting carbon fibers through continuous, stepwise processing, three sets of parallel experiments, each with a specific temperature while changing the stretch ratio, were conducted. In each independent run, tension that was generated at this stage was measured by a tensiometer. The final carbon fibers were monitored by measuring the tensile strength and the Young's modulus as well as linear density. The data collected are plotted in Figures 5 and 8–10. It can be seen that the tension within the fiber during prestabilization increases very significantly with an increasing stretch ratio (Fig. 5). The other characteristic found in Figure 5 is that at the same stretch ratio the tension decreases with temperature increase. The higher the stretching, the more significant the decrease of tension. As discussed earlier in this article, the overall stress yielded in this stage can be ascribed to two contributions: One comes from the shrinkage force induced by restricting the relaxation of molecular chains; the other being the external stretching force imposed through controlling the speed difference of inlet and outlet rollers as in the cases of 4 and 8% stretching ratios. From this consideration, one would infer that by increasing the processing temperature the plastic deformation mobility of molecular chains will be increased somewhat under foreign restraints such as constant length or

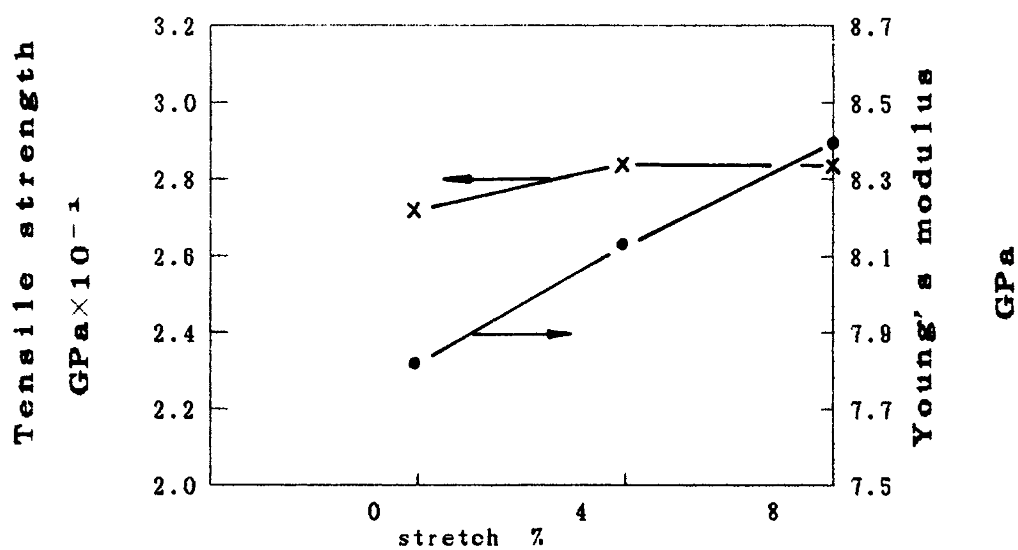

Figure 7 Effect of stretch on tensile properties of the intermediate fiber.

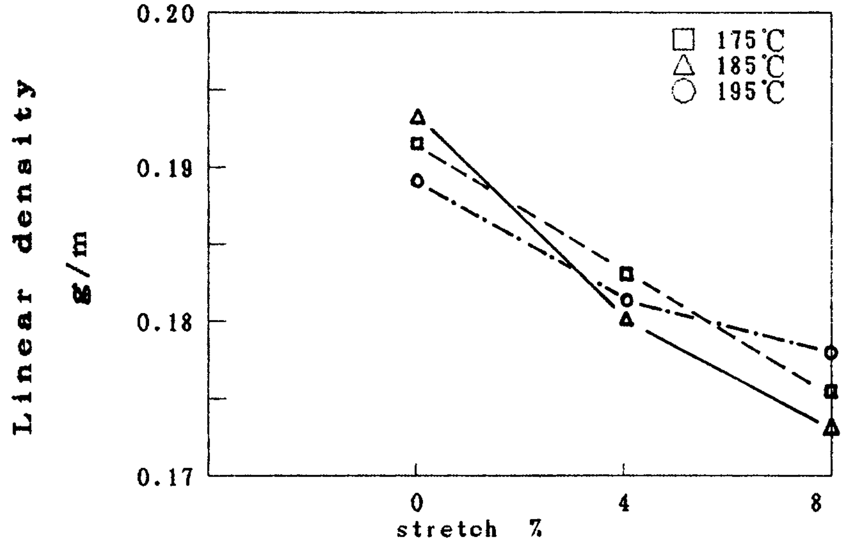

Figure 8 Linear density of carbon fibers as a function of the stretch ratio.

stretching. As a result, both the shrinkage force and the stretching force will be expected to decrease, which leads to an overall stress drop.

Examination of data in Figure 8 shows quite dramatic drops in linear density with increase in the stretching ratio for all three sets of runs. This suggests that a simultaneous drop in fiber diameter could be anticipated,[7] which reflects the influence of prestabilization stretching on the diameter of modified PAN precursor which is maintained in the final carbon fibers. The Young's modulus for these carbon fibers increases with the stretch ratio increase in all nine runs, a trend similar to that observed for the modified precursor and intermediate fibers. These results seem to con irm a correlation between the Young's modulus of t. e PAN precursor and of the resultant carbon fibers as established by Bahl et al.[9] This correlation has been attributed to better orientation obtained in the PAN precursor fibers while restricting shrinkage or extension and which is sustained throughout the whole process of carbon fiber manufacture and is retained in the final carbon fibers.[8,10]

Surveying the data in Figure 10, considerable scatter in tensile strength with stretch ratio is found whatever the temperature being used. No reasonable relation can be observed. All carbon fibers manufactured under the nine conditions yield tensile

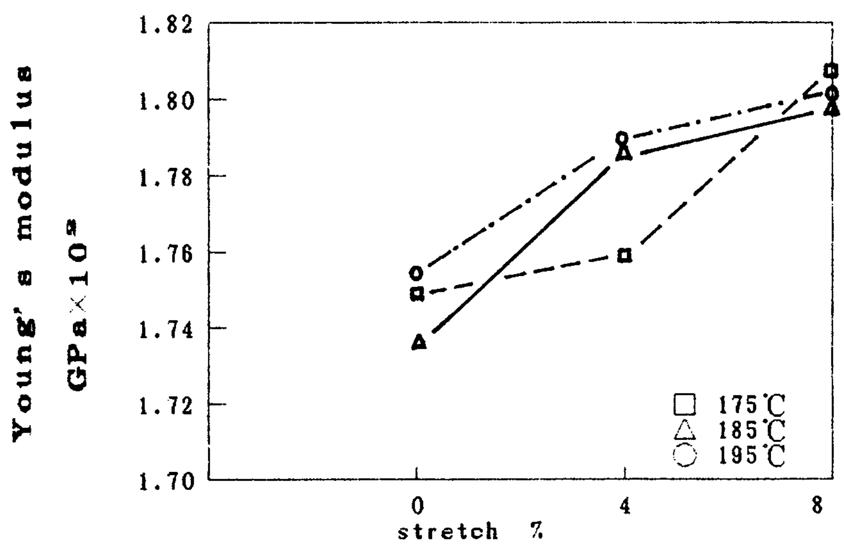

Figure 9 The Young's modulus of carbon fibers as a function of the stretch ratio.

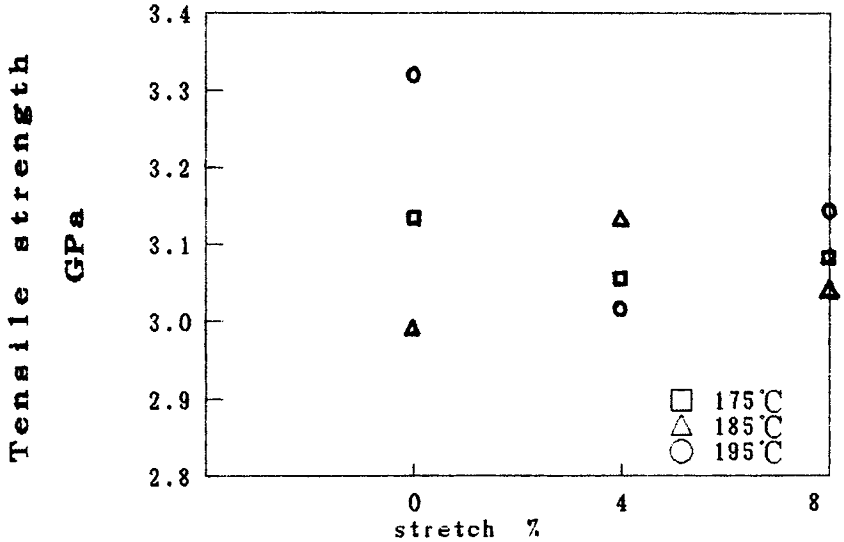

Figure 10 Tensile strength of carbon fibers as a function of the stretch ratio.

strengths varying around 3.0 GPa. The implication of this figure at least suggests the influence of stretching during the prestabilization stage on tensile strength of carbon fibers, while keeping the other parameters in stabilization and carbonization constant, is not as significant as with the Young's modulus.

Comparatively, the effect of stretching during stabilization can be said to have far more potential in the context of the mechanical properties of carbon fibers, as shown in our earlier study.[8] It should be pointed out here that the conclusion is based on the current processing conditions; i.e., the influence was studied while a certain extent of stretching was maintained during stabilization. If no stretching is imposed on stabilization, the effect of prestabilization might be more obvious whatever the strength and modulus being concerned. The second consideration is that after modification by stretching the modified PAN precursor takes on some variations in their characteristics, such as diameter, and possibly other features as reported by Bahl and Manocha.[11] Therefore, whether these variations need different processing conditions in subsequent treatment to optimize properties remains to be answered.

Finally, as generally believed, the tensile strength of carbon fibers is very sensitive to flaws and defects both internally and on the surface, either inheritable from the precursor used or subsequent processing. The prestabilization stretching, as has been shown, usually generates high stress within the precursor fiber. This high value of stress might have complex effects on the structure and texture of the precursor as discussed above, including possibly internal or microfibrillar disruption and larger intermolecular deformation, both being flaw or defect initiation sources. Therefore, it would be appropriate to carefully balance the extent of stretching to be chosen in early stages of processing on a wide range of considerations.

CONCLUSION

1. With increase of the stretch ratio at the prestabilization stage, the diameter of PAN precursor fiber gradually decreased and the Young's modulus of the precursor continually increased. The tensile strength of the modified PAN precursor first dropped to its lowest value under the condition of no net stretching and subsequently increased with the stretch ratio increase.
2. The tension generated within the fiber at the prestabilization stage showed a significant increase with stretching. This tension was due to the overall effects of relaxation force induced under the external restraints and stretching force imposed through the godet speed differences. Increasing temperature reduced the absolute value of the stress at the same stretching ratio.
3. The diameter of the intermediate fiber after stabilization gradually decreased with the stretching ratio. The Young's modulus increased, corresponding to that of modified precursor. The tensile strength showed a relatively small extent of improvement relating to stretching increase.

4. The influence of prestabilization stretching on linear density reduction and the Young's modulus increase of the resulting carbon fibers was quite evident and was thought to derive from the modified precursor. However, the data on tensile strength were quite scattered regarding the stretch ratio. This suggests that the effect of stretching at the prestabilization stage is not so obvious and significant as that at the stabilization stage from the viewpoint of tensile strength of carbon fibers.

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