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Effects of Quasi-Carbonization Process on the Mechanical Properties of Spun Yarn Type Quasi-Carbon Fabrics

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Abstract: In this paper we have extensively studied what and how processing parameters for quasi-carbonization influence the breaking strength and modulus of resulting quasi-carbon fabrics that are prepared from stabilized PAN fabrics with a spun yarn texture. Seven processing parameters have been considered as follows: applied tension, final heat-treatment temperature, heating rate, heating step, holding time, cooling rate, and purging gas purity. The results indicate that optimal uses of applied tension, final heat-treatment temperature, heating rate, and heating step during quasi-carbonization process are primarily important to increase the tensile properties of quasi-carbon fabrics and holding time, cooling rate, and purging gas purity are less importantly contributed.

Keywords: quasi-carbonization, breaking strength and modulus, processing parameters, quasi-carbon fabrics.

Introduction

Carbon fibers have been importantly utilized as reinforcement for advanced composite materials in commercial and military aircraft and aerospace applications during the last three decades.[1,2] In general, commercial PAN-based carbon fibers of high performances are proprietarily manufactured through a series of heat-treatment processes above 1,400 °C in an inert atmosphere.[3] When stabilized or oxidized PAN fibers are treated at high temperatures, many chemical and physical characteristics and properties of the final carbon fibers obtained strongly depend on a variety of processing parameters involved.[4,5] Among the parameters, it has been known that final heat-treatment temperature is most critical.[6,7] Therefore, the properties of carbon fibers may be specifically controlled and designed by the variation of heat-treatment or carbonization processing conditions, depending on their purpose of use. That is, multi-grade carbon fibers or fabrics with a spectrum of properties may be obtained.

It has been reported that stabilized PAN fibers can be successfully transformed into quasi-carbon fibers or partially carbonized fibers when they are heat-treated at lower temperatures than that general grade carbon fibers experience.[6-10] Many properties of the fibers obtained significantly rely on the quasi-carbonization process. One of them is mechanical property including tensile one. It is known that quasi-carbon fibers generally show lower mechanical properties, lower thermal conductivity, and higher electrical resistivity than carbon fibers.[11] Therefore, it will be very desirable if quasi-carbon fibers with relatively low cost can replace carbon fibers for thermal insulation applications like in heat-sink or shielding and ablation resistant materials.[12] However, it is also important to minimize the reduction of tensile properties of quasi-carbon fibers and the composites with a polymer matrix for maximizing their performances. One practical approach for that is to optimize the processing parameters for quasi-carbonization, for example, final heat-treatment temperature (HTT), heating rate, heating step, holding time, tension, etc.[4,11]

Consequently, the objective of this study is to provide the optimal processing conditions for quasi-carbonization, which can contribute to minimizing the reduction of mechanical properties (breaking strength and modulus) of quasi-carbon fabrics with a spun yarn texture.

Experimental

Materials. The stabilized PAN-based woven fabrics composed of staple spun yarns and of an 8 harness satin texture, supplied from Zoltek Co., U.S.A., were used as a starting material for preparing quasi-carbon fabrics. A commercial

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roll of the fabric with a width of 1 m and with a length of 50 m was supplied. The length of a staple spun yarn is about 85 mm. The average diameter of a single filament of the stabilized PAN fiber was observed to be about 13.8 μm. The as-received woven fabrics were heat-treated without any further modification according to the scheduled processing conditions.

Quasi-Carbonization Process. The stabilized PAN-based woven fabrics were cut to be 300 mm(warp)$\times$ 50 mm(fill) in size. The thickness of a single ply of the fabric is about 0.64 mm. Eight plies of the fabrics were tightly gripped with a tailor made device for applying tension. Figure 1 shows the illustration of an assembly of fabrics gripped with tension devices. The tension was applied by screwing up a stainless steel rod directly attached to the grips in two opposite directions. The tension can be controlled from the outside of the furnace before heat-treatment and it is kept to be constant through quasi-carbonization process.

Quasi-carbonization was performed in a mullite tube-type Siliconit carbonization furnace (Figure 2) under an inert atmosphere varying processing parameters like final HTT, heating and cooling rates, heating step, holding time, the presence and absence of tension, and purging gas purity. The cylindrical heating zone in the furnace is 150 mm in length and 70 mm in height. The plied fabrics with grips were placed in the heating zone during the quasi-carbonization process. After quasi-carbonization, the fabrics in the heating zone were cut to be 130 mm in length and used for each measurement. The furnace was designed to manipulate all the processing parameters by programming temperature and time variables on purpose. Table I summarizes the processing parameters for quasi-carbonization process used in this work.

Measurements. The tensile properties for all the fabric specimens were measured using a universal testing machine (UTM-4467, Instron). Measurements for the breaking strength and modulus of woven fabric were performed according to the raveled strip method based upon KS K 0520, as shown in Figure 3. The fabric specimen of 120 mm $\times$ 35 mm was raveled out from both sides of the specimen

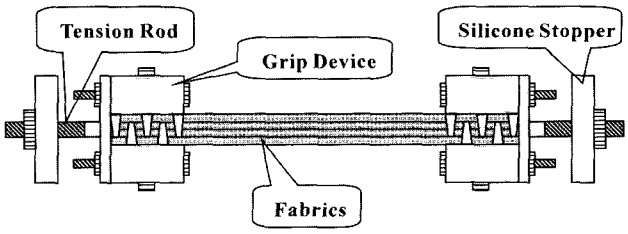

Figure 1. A schematic assembly of spun yarn woven fabrics gripped with tension devices.

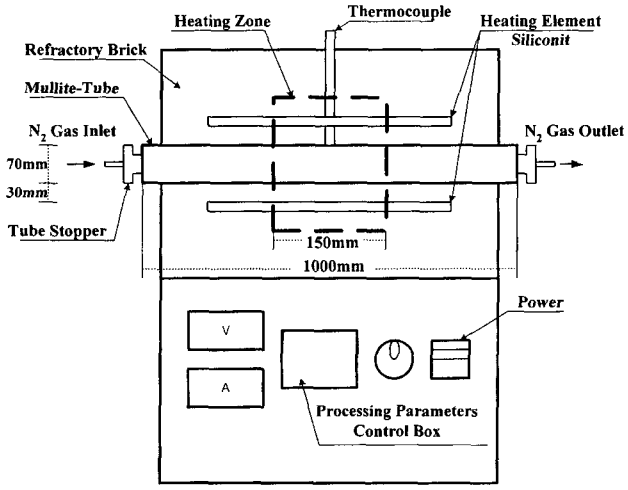

Figure 2. A schematic layout of the tube-type Siliconit carbonization furnace used for quasi-carbonization processes in this work.

to be 120 mm$\times$ 25 mm in size. The crosshead speed was 30 cm/mm. A load cell of 100 kg was used. To calculate the breaking strength and modulus, the average thickness of the measuring fabric was determined from a number of spots in a specimen using a micrometer. A scanning electron microscope (Hitachi S-2400) was used to observe the texture pattern of quasi-carbon fabrics before and after applying different tensions.

Table I. A Summary of the Processing Parameters for Quasi-Carbonization

Processing Parameters	Variables
Tension	0 kg_f, 4 kg_f, 12 kg_f, 33 kg_f
Final HTT	1,000 °C, 1,100 °C, 1,200 °C
Heating Rate	30 °C/h, 60 °C/h, 100 °C/h
Heating Step (Up to Final HTT)	One-step: 600 °C, 800 °C, 1100 °C Two-step: 600 °C and 800 °C, 600 °C and 1,100 °C, 800 °C and 1,100 °C Three-step: 600 °C, 800 °C, and 1,100 °C
Holding Time at Each Step	30 min, 60 min, 90 min, 120 min
Cooling Rate	60 °C/h, 100 °C/h, Natural cooling
Purging Gas Purity	99.9% N_2, 99.999% N_2

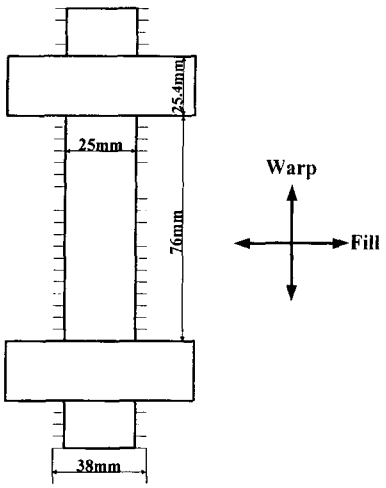

Figure 3. An illustration of the specimen used to measure the breaking strength and modulus of woven fabric by a raveled strip method.

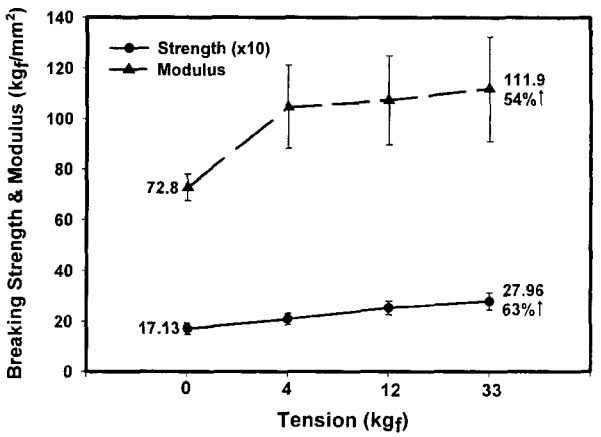

Figure 4. The effect of applied tension on the breaking strength and modulus of spun type quasi-carbon fabrics. Other processing conditions; final HTT 1,200 °C, 60 °C/h, no heating step, no holding at HTT, natural cooling, and 99.999% N_2.

Results and Discussion

Effect of Applied Tension. The tension was continuously applied from the outside of the furnace during each quasi-carbonization process, using the devices illustrated in Figure 1. The degree of the applied tension has been quantitatively evaluated by converting the numerical values of the longitudinal extension of the gripped fabrics into the corresponding force measured with an attachment of tension devices including the fabrics by means of a tensile test machine. As seen in Figure 4, with increasing tension the breaking strength is linearly enhanced while the modulus is largely enhanced with about 44% from 0 to 4 kg_f tension and then is slightly increased about an additional 10% from 4 to 33 kg_f. Use of the tension of 33 kg_f increases the breaking strength of quasi-carbon fabric by 63% and the modulus by 54% in comparison with the result without tension. This means that the alignment and preferred orientation of crystalline fibers are primarily attained by the initially applied tension up to 4 kg_f and then the tension-induced alignment effect is gradually reduced with increasing tension. The formation of well-aligned fiber structure with the assistance of tension may contribute to gradually increasing the breaking strength and modulus of quasi-carbon fabric. It was found that there was no fiber damage by the tension applied in this work.

It has been found that the areal density of the spun yarn fabric is obviously increased with increasing tension, as seen in Figure 5. In the figure, "free state" designates that spun OXI-PAN fabrics are freely placed in the furnace and quasi-carbonized without using a tension grip device and applied tension. "Tension 0 kg_f state" designates that spun OXI-PAN fabrics are firmly gripped with tension grip devices but no tension from the outside of the furnace is applied during quasi-carbonization process. "Tension 12 and 33 kg_f states" indicate that each tension is continuously applied by screwing up a stainless steel rod from the outside of the furnace through quasi-carbonization process. With a close inspection of Figure 5, the tension effect is visually clear. The number of yarn tows per unit area is relatively increased with increasing the applied tension and the longitudinal width of each tow becomes narrow along the applying tension direction (top ↔ bottom) in each figure. It is also observed that the tows located in the fill direction are come out to view at higher applied tensions((c) and (d)), which are not seen in (a) and (b). No disentanglement between the staple yarns due to applied tension was observed after completion of each carbonization process.

Effect of Final Heat-Treatment Temperature. Figure 6 shows the effect of final HTT on the breaking strength and modulus of spun type quasi-carbon fabrics prepared in the presence of different tensions. The increasing behavior of the breaking strength and modulus is similar with the result described in Figure 4. The higher the tension applied the greater the breaking strength and modulus at each final HTT. It is also found that the higher the final HTT the greater the breaking strength and modulus. The breaking strength of quasi-carbon fabric heat-treated at 1,200 °C is increased about 37% higher than that heat-treated at 1,000 °C in the presence of 33 kg_f tension. The modulus change is relatively higher in the temperature range of 1,000 ~1,100 °C in the presence of 12 kg_f tension (Figure 6(a)) and higher in the temperature range of 1,100~1,200 °C in the presence of 33 kg_f tension (Figure 6(b)). In the presence of 12 kg_f tension, the modulus of quasi-carbon fabric heat-treated at 1,200 °C is increased about 30% higher than that at 1,000 °C while in the presence of 33 kg_f tension it is increased about 8%. Based on the explanation given in Figure 4 in terms of tension-induced fiber alignment, the presence of the lower applied tension of 12 kg_f increases the modulus

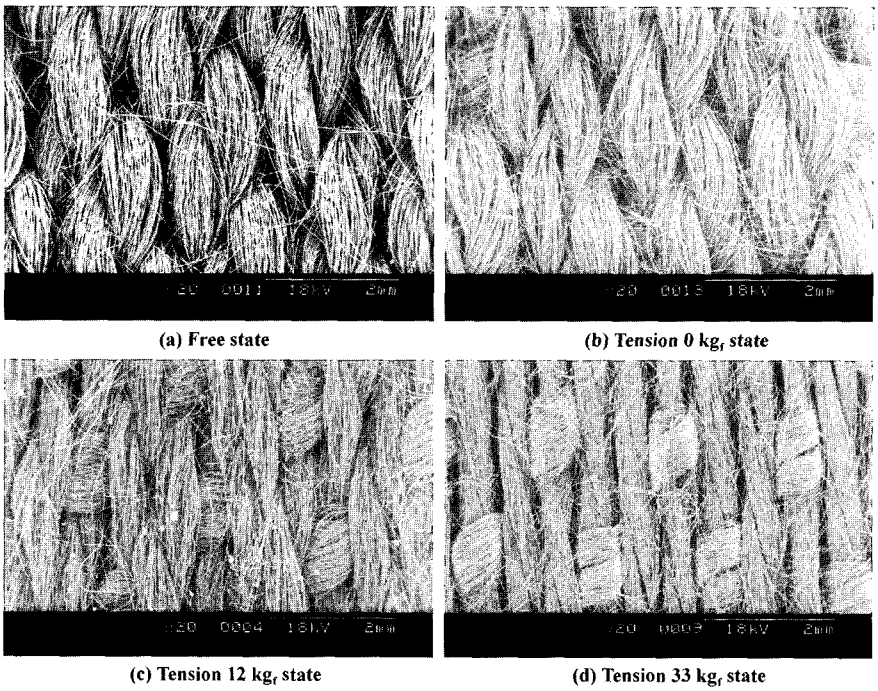

Figure 5. Scanning electron microphotographs (× 20) showing the texture pattern of spun yarn type quasi-carbon fabrics in the presence of different tensions. Final HTT: 1,200 °C, heating rate: 60 °C/h, and 99.999% N_2.

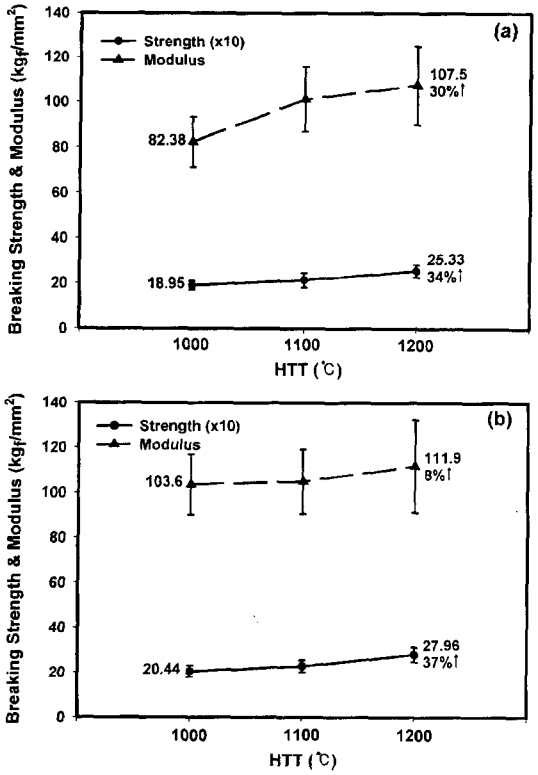

Figure 6. Effect of final HTT on the breaking strength and modulus of quasi-carbon fabrics. (a) tension 12 kg_f ; (b) tension 33 kg_f. Other processing conditions: 60 °C/h, no heating step, no holding at HTT, natural cooling, and 99.999% N_2.

more effectively than that of 33 kg_f. Therefore, it may be concluded that the final HTT at lower tension more importantly contributes to enhancing the modulus of quasi-carbon fabric. An increase of the breaking strength and modulus with increasing final HTT can be explained by that the aromatic structure develops with a greater extent and the graphene layers with turbostratic structure in more ordered pattern can be formed at higher final HTT.

Effect of Heating Rate. The results shown in Figure 7 indicate that the slower the heating rate from 100 to 30 °C/h up to the final HTT the higher the breaking strength and modulus obtained. Also, the heating rate more influences the modulus than the breaking strength of quasi-carbon fabric. The modulus and strength at the heating rate of 30 °C/h is increased about 23~25% and 8~13%, respectively, depending upon the applied tension, compared with those at 100 °C/h. With varying heating rate the higher values of the breaking strength and modulus are obtained with the presence of higher tension even though the improvement of the breaking strength and modulus is greater with the lower tension of 12 kg_f (Figure 7(a)) than with the higher tension of 33 kg_f (Figure 7(b)). The fabrics are exposed to the heat-treatment condition for a longer period of time at lower heating rate. Such a processing condition can provide more thermally stable structure to the resulting fabrics. It is suggested that slow heating rate is likely more desirable than fast one to have better tensile properties of quasi-carbon fabric. However, appropriate heating rate should be chosen considering of the

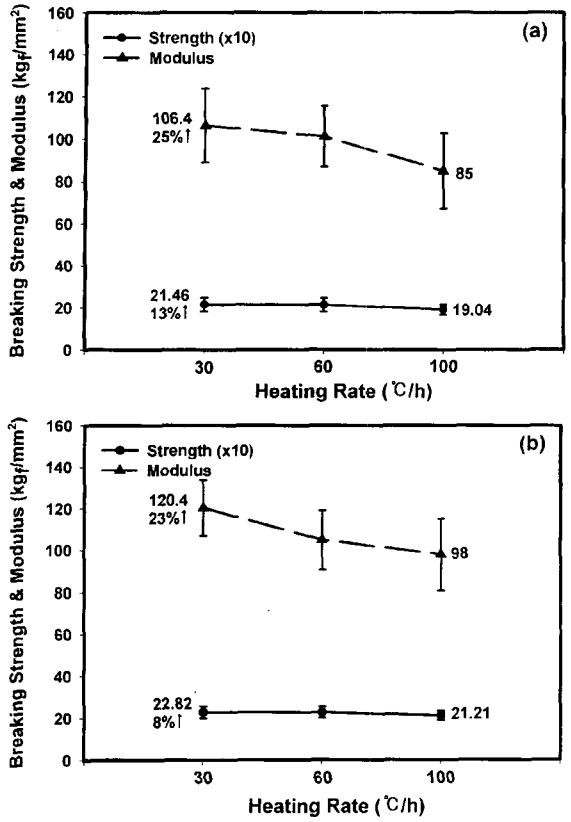

Figure 7. Effect of heating rate on the breaking strength and modulus of quasi-carbon fabrics. (a) tension 12 kg_f; (b) tension 33 kg_f. Other processing conditions: final HTT 1,100 °C, no heating step, no holding at HTT, natural cooling, and 99.999% N_2.

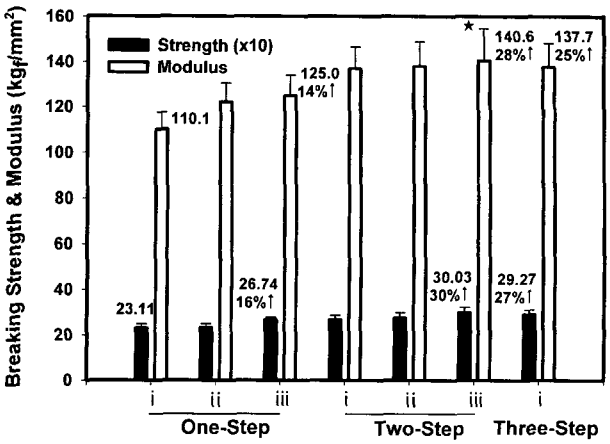

Figure 8. Effect of heating step on the breaking strength and modulus of quasi-carbon fabrics in the presence of 33 kg_f tension. Other processing conditions: final HTT 1,100 °C, 60 °C/h, 60 min holding at each step, natural cooling, and 99.999% N_2. One-Step; (i) 600 °C, (ii) 800 °C, (iii) 1,100 °C. Two-Step; (i) 600 and 800 °C, (ii) 600 and 1,100 °C, (iii) 800 and 1,100 °C. Three-Step; (i) 600, 800 and 1,100 °C.

balance of processing time and cost. In addition, combining the results obtained from Figures 4-7, it is noted that the breaking strength and modulus are improved with a large extent in the presence of lower applied tension, that the apparent breaking strength and modulus become greater with increasing the applied tension, and that the applied tension more significantly contributes to the final HTT effect than to the heating rate effect.

Effect of Heating Step. Figure 8 shows the effect of heating step on the breaking strength and modulus of spun-yarn quasi-carbon fabric in the presence of 33 kg_f tension. During carbonization process, the most profound chemical changes including the evaporation of volatile gases and the alteration of chemical structure occur around 800 °C. It has been known that most of volatile gases involved in the stabilized PAN fiber, for example, NH_3, H_2O, CO, CO_2, CH_4, begin to evaporate around 600 °C but N_2 gases are removed beyond 800 °C.[5] Therefore, in this work, heating steps at 600, 800, and 1,100 °C have been chosen considering of possible chemical changes involved. As seen in Figure 8, in one-step processes (non-stop processes to final HTT), quasi-carbon fabrics processed at higher temperature give better breaking strength and modulus than those at lower temperature. This is because denitrogenation takes place with high population at higher HTT holding for 60 min. As a result, the thermally stable aromatic structure with ordered crystalline alignment is more developed during quasi-carbonization at higher temperature. From the result of the heating step effect, it can be noted that two-step or three-step process for quasi-carbonization is more desirable for improving the tensile properties than one-step process, showing an enhancement of 25~30% in the breaking strength and modulus. The highest values of the strength and modulus are obtained in the case of two-step (iii) quasi-carbonization process. However, there is no significant difference between two-step and three-step processes.

Effect of Holding Time. Figure 9 represents the effect of holding (or dwell) time (30, 60, and 90 min) at each heating step up to 1,100 °C on the mechanical properties. The highest values were obtained in the conditions of 800 and 1,100 °C (two-step (h)) and 600, 800 and 1,100 °C (three-step (i)) for 90 min holding at each step. The lowest values were obtained at 600 and 1,100 °C (two-step (a)) for 30 min holding at each step. In this experiment, one-step process has been excluded based upon the result of the heating step effect. The breaking strengths in the cases of (h) and (i) are increased by 24% and the modulus by 9% in comparison with the result in the case of (a). Combining the results from other processing parameters, it may be said that the holding time further improves the tensile properties of quasi-carbon fabric but other parameters like tension, final HTT, and heating rate are more effective. The result also suggests that an extended period of holding time at final HTT may further improve the properties. The heat-treatment for an extended period of holding time provides enough time to develop the order of

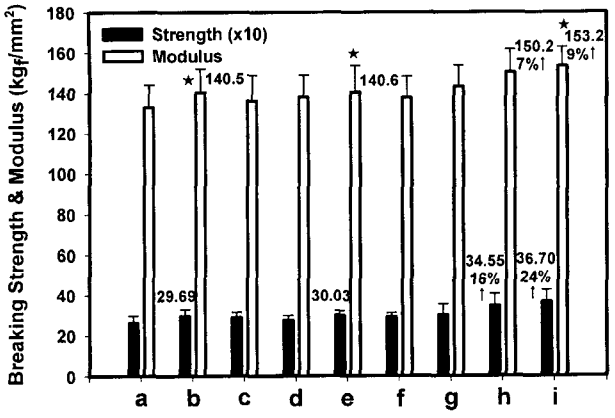

Figure 9. Effect of holding time on the breaking strength and modulus of quasi-carbon fabrics in the presence of 33 kg_f tension. Other processing conditions: final HTT 1,100 °C, 60 °C/h, natural cooling, and 99.999% N_2. 30 min holding at each step: (a) 600 and 1,100 °C, (b) 800 and 1,100 °C, (c) 600, 800 and 1,100 °C; 60 min holding at each step: (d) 600 and 1,100 °C, (e) 800 and 1,100 °C, (f) 600, 800 and 1,100 °C; 90 min holding at each step: (g) 600 and 1,100 °C, (h) 800 and 1,100 °C, (i) 600, 800 and 1,100 °C.

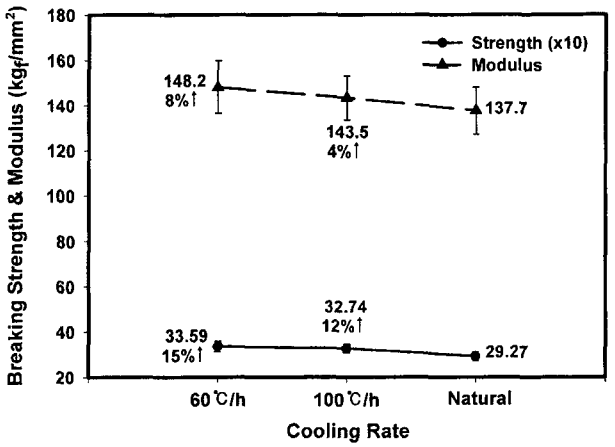

Figure 10. Effect of cooling rate on the breaking strength and modulus of quasi-carbon fabrics in the presence of 33 kg_f tension. Other processing conditions: final HTT 1,100 °C and 99.999% N_2.

basal plane and the aromatic structure with rigid chains. It may result in an additional increase of the breaking strength and modulus. However, excessive holding time may cause the deterioration of the strength due to microstructural defects formed on the fiber surface.

Effect of Cooling Rate. As can be seen in Figure 10, the slow cooling rate of the furnace after quasi-carbonization process is more desirable for improving the breaking strength and modulus of quasi-carbon fabric in the presence of tension. During natural cooling, the mold temperature dramatically falls down to about 400~500 °C. This quenching may inhibit the additional growth of crystalline structure. The result indicates that the breaking strength and modulus of quasi-carbon fabric are increased about 15% and 8%, respectively, compared with those by natural cooling.

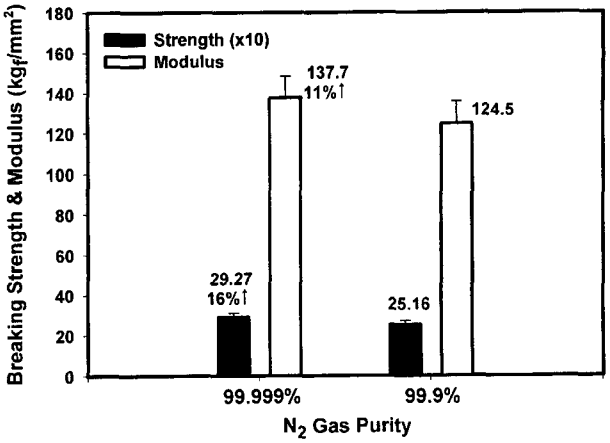

Figure 11. Effect of purging gas purity on the breaking strength and modulus of quasi-carbon fabrics in the presence of 33 kg_f tension. Other processing conditions: final HTT 1,100 °C, 60 °C/h, and natural cooling.

Effect of Purging Gas Purity. Figure 11 presents that the inert gas purity purging into the carbonization furnace may also influence the breaking strength and modulus of quasi-carbon fabrics. The nitrogen gas of 99.9% purity is a grade for general purpose of use. The 99.999% nitrogen gas is of high purity and far more expensive. It is obvious that the higher purity of purging gas provides the better tensile properties of quasi-carbon fabrics. The nitrogen gas of lower purity may cause undesirable microstructural defects on the fiber surface at the early stage of quasi-carbonization process between 600 ~ 1,000 °C, at which low molecular weight compounds are removed vitally. The reactivity of dehydrogenation and/or denitrogenation may also be reduced prior to transformation to ordered aromatic structure. The less developed crystal structure may be formed with an inert gas of low purity at this heat-treatment stage. However, practically one should consider of both cost and performance effects together.

Conclusions

The breaking strength and modulus of quasi-carbon fabric significantly depend on the presence and absence of applied tension during quasi-carbonization process. The higher the tension applied the greater the tensile properties. The breaking strength of quasi-carbon fabric heat-treated at 1,200 °C is increased about 37% higher than that heat-treated at 1,000 °C. The slower the heating rate from 100 to 30 °C/h up to the final HTT the higher the breaking strength and modulus

obtained. Multiple heating steps at 600, 800, and 1,100 °C during quasi-carbonization process are more desirable for improving the breaking strength and modulus than one-step heating. The longer holding time (90 ~ 120 min) at the intermediate (800 °C) and final (1,100 or 1,200 °C) HTT significantly increases the tensile properties of quasi-carbon fabrics. The slower the cooling rate the better the breaking strength and modulus of quasi-carbon fabric. The higher purity of purging gas provides the greater breaking strength and modulus of quasi-carbon fabric. The results inform that optimal conditions of applied tension, final HTT, heating rate, and heating step during quasi-carbonization process are more important than other processing parameters (holding time, cooling rate, and gas purity) for improving the breaking strength and modulus of quasi-carbon fabrics. It is also noted that, in practice, best processing conditions for quasi-carbonization should be determined considering of the balance of processing time, cost, and performance together. From this study, it is convinced that the well-determined processing parameters of quasi-carbonization are required for improving the mechanical properties not only of resulting quasi-carbon fibers with a yarn texture but also of related composite materials.

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