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Note

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The synergetic effect of phenolic anchoring and multi-walled carbon nanotubes on the yarn pull-out force of *para*-aramid fabrics at high speed

Jinsil Cheon[1], Byung Il Yoon[2], and Donghwan Cho[1,♠]

[1]Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 39177, Korea
[2]DACC Carbon, Co., Ltd, Jeonju, Jeonbuk 54853, Korea

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♠Corresponding Author
E-mail: dcho@kumoh.ac.kr
Tel: +82-54-478-7688

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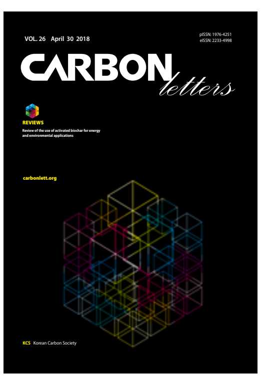

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para-Aramid fiber has well-oriented molecular chains and a structure with a large number of microfibrils. As a result, it has an excellent tensile strength and modulus and impact resistance [1]. Accordingly, a typical *para*-aramid fiber Kevlar® has been predominantly used as an anti-bulletproof material since 1971 when it was first developed by Du Pont Co. [2,3]. Once *para*-aramid fibers are used as a reinforcement in polymer resins, the resulting composites exhibit high mechanical properties compared to the composites with other organic reinforcements [4,5]. However, uses of *para*-aramid fibers or fabrics are somewhat limited due to their high cost. Therefore, it would be very desirable if an increase of the mechanical properties and a weight reduction of the resulting materials could be attained with a reduced amount of *para*-aramid fibers or fabrics.

Because *para*-aramid fabric is exposed to an external load, the yarns existing in the warp and weft directions could be slipped off by the applied force, which is high or fast enough to influence the individual yarns in the fabric. As a result, the fabric may be deformed without breakage of the individual fiber filaments which consist of yarn [6-8]. That is, the yarns in the warp and weft directions of the fabric can be pulled out upon deformation. It would be nice if one can measure the variation of the mechanical resistance to the applied force, in particular, under the yarn pull-out condition at high speed. The result obtained from the yarn pull-out testing at high speed may be useful for understanding not only the tensile or breaking properties of aramid fabrics but also the pseudo-anti-bulletproof resistance of relevant materials of interest [6,9].

Carbon nanotubes (CNT) have, in general, an aspect ratio higher than 100 and exhibit excellent mechanical properties and thermal and electrical conductivities along with the longitudinal direction [10,11]. It is not easy to successfully disperse them into a polymer resin without any surface modifications or without using any dispersing agents. Accordingly, dispersing CNTs into a polymer matrix as a filler has been a challenging issue in relevant polymer composites [12]. To date, there have been a number of studies on polymer composites with increased mechanical and thermal properties obtained by the assistance of dispersed CNTs [13-16]. It could be possible that CNT nano-particles can be firmly attached by applying a highly diluted thermosetting resin to the fiber surfaces, which is, for the first time, referred to as the anchoring effect of CNTs on the fibers in the present work. Consequently, the objectives of the present study were to prepare *para*-aramid fabrics containing multi-walled carbon nanotubes (MWCNT) of various concentrations in the absence and presence of phenolic anchoring on the fiber surfaces and also to investigate the synergetic effect of the phenolic anchoring and the MWCNT on the force-displacement curve of the *para*-aramid fabrics using yarn pull-out testing at a high speed of 800 mm/min.

para-Aramid fabrics (HERACRON®, HT840) with a plain weave pattern, which were manufactured by KOLON Co., Korea, were used in this work. The fiber yarns in the warp and weft directions are of 840 denier, and their fabric densities are 26.7 counts/in. The areal density is 200 g/cm^2. The *para*-aramid fabrics were used 'as-received' without further treatment. Multi-walled carbon nanotubes (MWCNT, CVD-CM95), which were manufactured by a chemical vapor deposition (CVD) method, were purchased from HANWHA Chemical

Co., Korea and were used as a filler without further purification. Methanol with a purity of 99.95% was purchased from Daejung Chemicals and Metals, Co., Korea and used to disperse the MWCNT. Resole-type phenolic resin (KRD-HM2), which was manufactured from KOLON Industries, Co., Korea, was used as an anchoring agent for physically attaching the MWCNT particles on the aramid fiber surfaces, and the 'as-received' resin contained a solid content of 60% with 40% methanol as the diluent. The resin concentrations in the MWCNT/methanol mixture were 0, 0.05, 0.1, and 0.3 wt%. The MWCNT concentrations in the methanol solution were 0, 0.05, 0.1, 0.2, and 0.3 wt%. Each MWCNT/phenolic/methanol solution was sufficiently mixed with a magnetic stirrer and then uniformly dispersed with an ultrasonic process prior to the anchoring step according to the scheduled concentrations. The ultrasonic process was carried out with a frequency of 40 kHz at 50~60℃ for 1 hour with an ultrasonic apparatus (Model Power Sonic 420, 600 W, HWASHIN Co, Korea).

The *para*-aramid fabrics were cut to 150 × 550 mm in size. The MWCNT/phenolic/methanol mixtures prepared according to each MWCNT or phenolic concentration were incorporated into the individual *para*-aramid fabrics by soaking the fabrics in each mixture and also by ultrasonicating the mixture with the fabrics for 10 h. The fabrics treated with the mixture were cured at 80℃ for 10 min. in a convection oven. During curing, the methanol therein was completely removed. A fabric without the phenolic anchoring step was also prepared for comparison.

High-speed yarn pull-out tests were performed with the fabrics with a universal testing machine (UTM) as follows. The *para*-aramid fabrics used were cut to 150 × 50 mm in size. Each fabric was sandwiched in between two identical fabric specimen fixtures made with the carbon fabric/epoxy composite frames and then firmly fixed with multiple mechanical clamps shown in Fig. 1. The warp and weft yarns in a piece of fabric 150 × 50 mm were removed by cutting out them with a scissor leaving behind a small portion (50 mm long) of a single yarn in the specimen shown in Fig. 1C, and then, the single yarn was gripped firmly with the UTM grips. A load cell of 5 kN was used. A high crosshead speed of 800 mm/min was used throughout the work. Ten specimens for each sample were used for the high-speed yarn pull-out testing, and the force-displacement curves for individual specimens were obtained.

To inspect the distribution of the MWCNT anchored on the fiber filament surfaces consisting of the yarns, a field-emission scanning electron microscope (JSM-6500F, JEOL, Japan) was used. Each yarn was coated with platinum (Pt) for 5 min. with a sputtering method.

Fig. 2(A) shows the yarn pull-out forces as functions of the phenolic concentration and displacement with varying MWCNT concentrations for the 'as-received' *para*-aramid fabric (curve a) and the fabrics (curves b and c) coated with the dilute phenolic resin in the absence of the MWCNT. It was clearly observed that the load required for pulling out a single yarn in the fabric at a high pull-out speed was remarkably increased by about 6.6 times from 9.1 to 59.8 N with an increasing phenolic concentration up to 0.3 wt% compared to that of the 'as-received' *para*-aramid fabric. Moreover, the slope of the curve became higher with the increasing concentration due to the increased

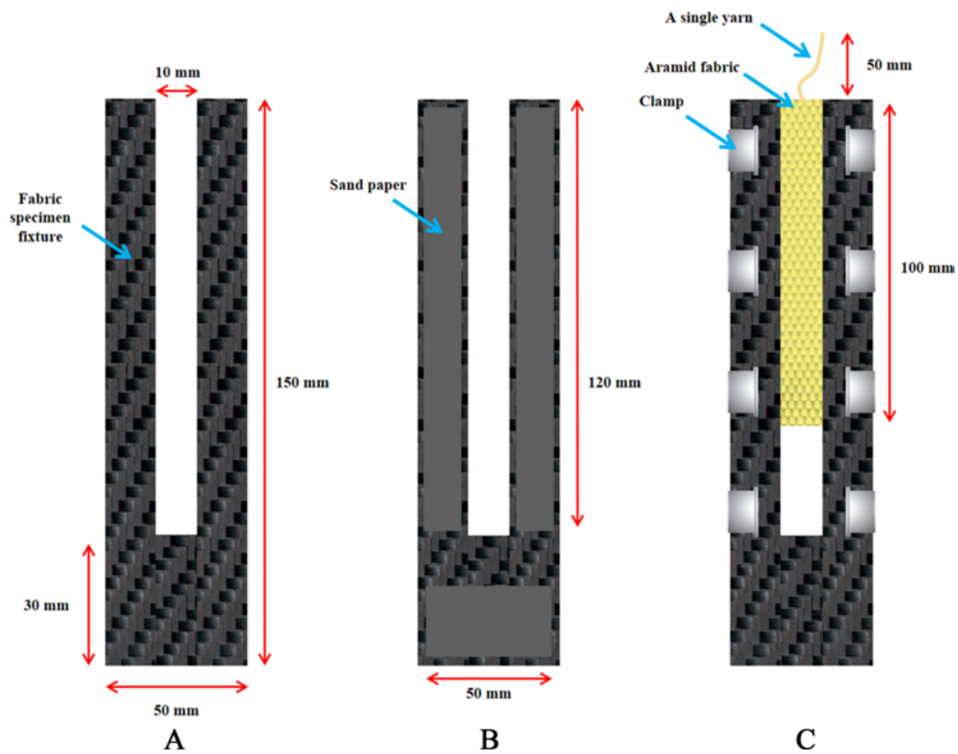

Fig. 1. Tailor-made device for single yarn pull-out testing of the *para*-aramid fabric, including a fabric specimen fixture made with carbon/epoxy composite frames, clamps, and a single yarn (A: the fixture-outside, B: the fixture-inside, C: the fixed fabric including a single yarn and clamps).

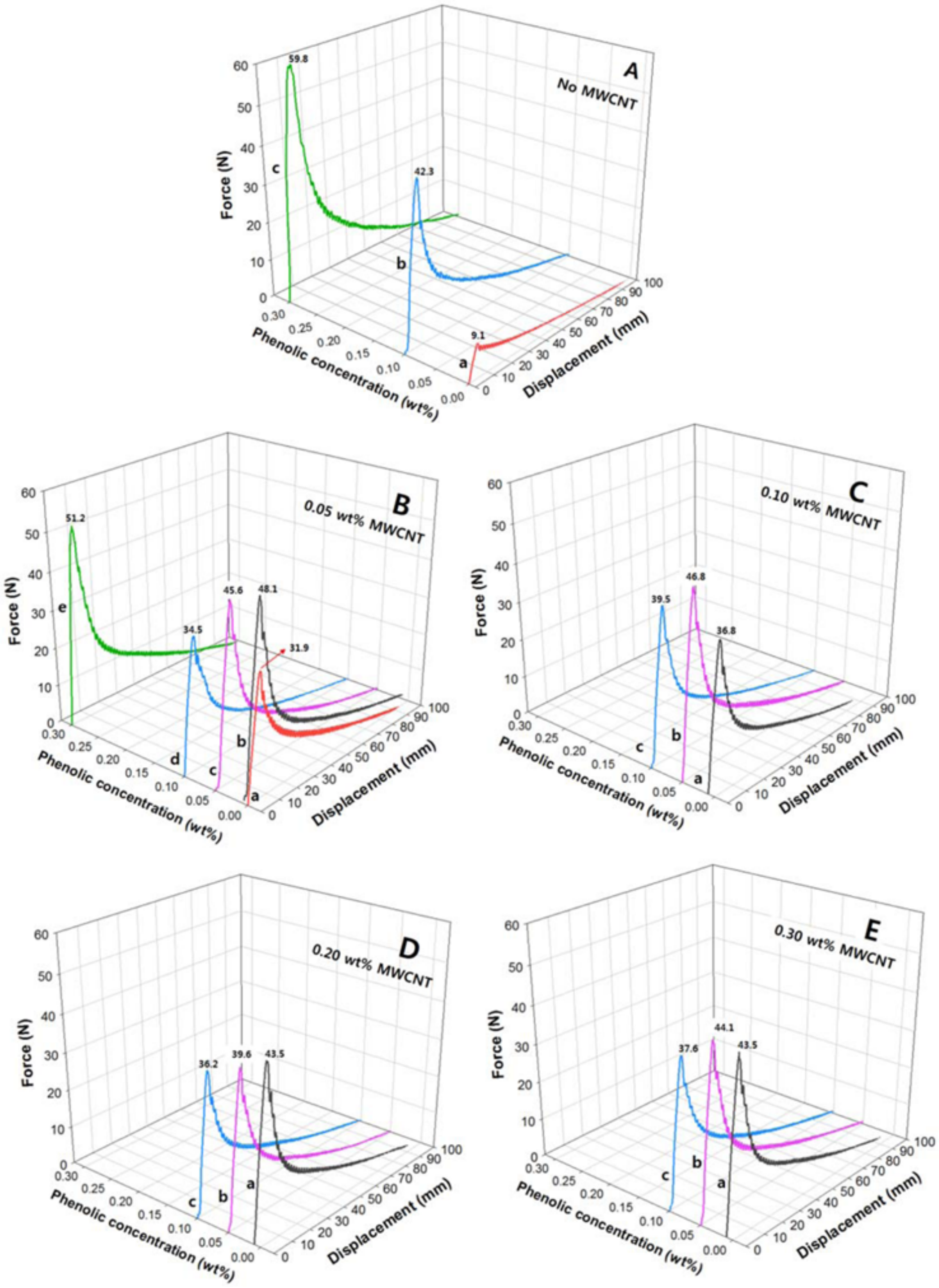

Fig. 2. Representative curves showing the yarn pull-out forces as functions of phenolic concentration and displacement with varying the MWCNT concentration.

stiffness of the aramid fabric by the phenolic coating. It seemed that the use of a phenolic concentration of about 0.3 wt% was high enough to decrease the flexibility of both the aramid yarn and the fabric. The addition of even a small amount of MWCNT resulted in an increase in the resin viscosity and the aggregation of the MWCNT particles. It made the infiltration of the MWCNT into the individual fiber filaments more difficult during the fabric treatment. It was found that the coating with 0.3% phenolic resin made the aramid fabric too stiff to handle. Therefore, it would not be desirable for potential anti-bulletproof applications. Accordingly, it was noticed that the fabric coated with 0.3 wt% phenolic resin is not appropriate for incorporating the MWCNT into it.

Fig. 2 (B to E) also shows the force-displacement curves measured for the *para*-aramid fabrics containing the MWCNT anchored on the fiber surfaces with a diluted phenolic resin in the range of 0 to 0.3 wt%. The MWCNT concentrations are 0.05(B), 0.1(C), 0.2(D) and 0.3 wt%(E). As seen in Fig. 2(B), the force (curve d, 51.2 N) measured for the fabric with the 0.3 wt% phenolic resin and 0.05 wt% MWCNT was

Table 1. A summary of the forces required for pulling out single yarns in *para*-aramid fabric at 800 mm/min with varying phenolic and MWCNT concentrations

Single Yarn Pull-out Forces at High Speed (N)					
MWCNT Concentration (wt%)	Phenolic Concentration (wt%)				
	0	0.01	0.05	0.10	0.30
0	9.0 (±0.1)	-	-	42.0 (±0.9)	59.9 (±1.9)
0.05	31.5 (±0.4)	48.0 (±0.8)	45.0 (±0.5)	34.5 (±0.4)	50.8 (±0.8)
0.10	-	37.0 (±0.8)	46.6 (±0.3)	39.5 (±0.6)	-
0.20	-	43.9 (±0.8)	39.7 (±0.6)	36.3 (±0.7)	-
0.30	-	43.4 (±0.6)	44.2 (±0.7)	37.7 (±0.6)	-

the highest, whereas that (curve a, 31.9 N) with 0.05 wt% MWCNT without the phenolic anchoring was lowest. As described earlier, the fabric (curve d) coated with the 3 wt% phenolic resin was stiffer than that with the phenolic resins at a lower concentration, and also, the maximum force value (curve d, 51.2 N) was lower than that (curve c of Fig. 2A, 59.8 N) in the absence of the MWCNT due probably to the dispersion problem into the resin at a relatively high concentration. Accordingly, the phenolic coating at 0.3 wt% was excluded in the following experimental procedures. With the exception of the 0.3 wt% phenolic coating, the fabric (curve c of Fig. 2B) with the 0.05 wt% phenolic and 0.05 wt% MWCNT exhibited the highest force (45.6 N) and a relatively low slope (less stiff) among the force-displacement curves shown in Fig. 2B. In Fig. 2C, at 0.1 wt% MWCNT, the highest force (46.8 N) at the curve peak was found with the fabric (curve b) containing the 0.05 wt% phenolic resin, whereas the lowest (36.8 N) was with the fabric (curve a) containing the 0.01 wt% phenolic resin. In the case of the 0.2 wt% MWCNT in Fig. 2D, the highest force (43.5 N) was with the fabric (curve c) containing the 0.1 wt% phenolic resin. On the other hand, in the case of the 0.3 wt% MWCNT in Fig. 2E, the highest force (44.1 N) was obtained with the fabric (curve b) containing the 0.05 wt% phenolic resin. The result indicates that the highest load is with the *para*-aramid fabric anchored with the 0.05 wt% phenolic resin containing the 0.3 wt% MWCNT (curve e of Fig. 2B).

Table 1 summarizes the effect of the phenolic and MWCNT concentrations on the average force required for pulling-out a single yarn from the *para*-aramid fabric at high speed (800 mm/min). The average forces (N) were obtained from 10 specimens per sample. The result shows that the force required for pulling out a single yarn from the *para*-aramid fabric was markedly higher in all the cases (31.5 to 59.9 N) with the anchored phenolic and with the incorporated MWCNT than in the case (9.0 N) without the phenolic resin and MWCNT. The result indicates that with the exception of the cases at 0.3 wt% phenolic resin, the highest force (48 N) required for pulling out a single yarn from the aramid fabric under the high-speed pulling-out test condition was achieved with both the lowest phenolic (0.01 wt%) and MWCNT (0.05 wt%) concentrations in the present work. The pull-out force with only 0.05 wt% MWCNT was about 350% higher that of the 'as-received' *para*-aramid fabric without both

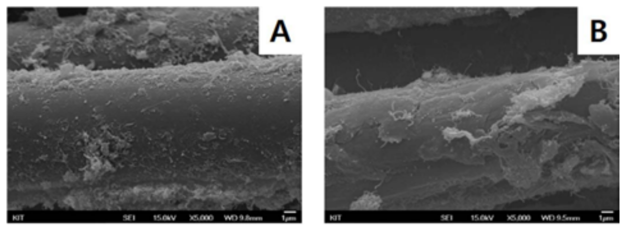

Fig. 3. SEM images (×5000) of the individual fiber surfaces of the *para*-aramid fabric with 0.05 wt% MWCNT anchored by 0.01 wt% (A) and 0.1 wt% (B) phenolic resins, respectively.

phenolic anchoring and MWCNT. The force with the 0.01 wt% phenolic anchoring and 0.05 wt% MWCNT was about 530% higher than that of the 'as-received' fabric and about 53% higher than that with the 0.05 wt% MWCNT only.

When increasing the phenolic concentration at a fixed concentration of MWCNT at 0.05 wt%, the pull-out force decreased to 34.5 N with the 0.1 wt% phenolic resin with the exception of the 0.3 wt% phenolic resin because of the increased fabric stiffness as described above. With the 0.01 wt% phenolic resin, the force decreased to 37 N at 0.1 wt% MWCNT and increased to 43~44 N when increasing the MWCNT to 0.2 and 0.3 wt%. One possible explanation is that in the mixture of the 0.01 wt% phenolic and 0.1 wt% MWCNT, aggregation may be the most pronounced on the fiber surfaces. However, in the cases of the 0.2 and 0.3 wt% MWCNT, the particles remaining (or being scattered) even after aggregation may contribute, to some extent, to an increase of the pull-out force. In the case of the 0.05 wt% phenolic anchoring, the highest force (46.6 N) was found at 0.1 wt% MWCN. The force decreased at 0.2 wt% MWCNT and then increased at 0.3 wt% MWCNT which was similarly the case for the 0.01 wt% phenolic anchoring. In the case of the 0.1 wt% phenolic, the forces obtained with varying MWCNT concentrations were lower than the highest forces with 0.0 and 0.005 wt% phenolic. It was found that the use of phenolic resin of 0.1 wt% or higher with the addition of MWCNT may cause either the aggregation of the MWCNT particles or an increase in the fabric stiffness.

Consequently, it is noted that the synergetic effect of the phenolic anchoring and MWCNT incorporation on the enhancement of the single yarn pull-out force in *para*-aramid fabric is most profound in the presence of 0.05 wt% MWCNT with 0.01 wt% phenolic anchoring. By increasing the phenolic concentration more, the MWCNT can be accommodated in the mixture, but lowering of the pull-out force should be considered.

Fig. 3 shows the SEM images for the fiber filaments in the *para*-aramid fabric containing 0.05 wt% MWCNT at different phenolic concentrations observed prior to the yarn pull-out testing. At 0.01 wt% phenolic resin (A), it is clear that the MWCNT particles are distributed in the fiber surface with an increased surface roughness. It could be expected that frictional resistance [17] between the individual fibers or yarns in the fabric may have a role in increasing the force for pulling out a single fiber or yarn. It may be mentioned that it somewhat contributes to increasing the frictional forces between the inter-filaments and also between the warp yarn and the weft yarn in the fabric. As a result, the force required for pulling out individual yarns at high speed would be increased as well. As seen in Fig. 3B, although the phenolic concentration was increased 10 times from 0.01 to 0.1 wt%, some MWCNT aggregation on the fiber surface was found showing clustering of the MWCNT particles. Such a carbon cluster may alleviate to some extent the effectiveness of the increased frictional force between the inter-filaments resulting in a decreased force required to pull out a single yarn. These images support quantitatively that the yarn pull-out force at high speed is increased in the case of the 0.01 wt% phenolic anchoring whereas it is somewhat lessened in the case of the 0.1 wt% presented in Table 1.

In conclusion, both phenolic anchoring and MWCNT incorporation at low concentrations provide a synergetic effect on enhancing the force required for pulling out individual single yarns in the *para*-aramid fabric at high speed (800 mm/min). The result reveals that the pull-out force was highest when 0.05 wt% MWCNT was anchored on the fiber surface by 0.01 wt% phenolic resin. In that case, the pull-out force was about 530% higher than that of the 'as-received' fabric without both phenolic anchoring and MWCNT, and it was further improved by about 53% by incorporating 0.05 wt% MWCNT into the phenolic resin. In the present study, 0.3 wt% or higher phenolic resin would not be appropriate to use due to possible MWCNC aggregation and less fabric flexibility even though the pull-out force was highly increased compared to that of the 'as-received' *para*-aramid fabric. The pull-out force was considerably increased with the incorporation of 0.05 wt% MWCNT between the individual filaments of the yarns comprising the fabric and further effectively increased by anchoring the MWCNT particles on the fiber surfaces with the assistance of a cured phenolic resin at a very low concentration. Such a high-speed yarn pull-out phenomenon and primary result of this study may trigger a fundamental understanding of the role of phenolic anchoring and carbon nanotubes in potential anti-bulletproofing materials consisting of multiple *para*-aramid fabrics, which are normally performed even with extremely high speeds.

Conflict of Interest

There are no potential conflicts of interest relevant to this article.

Acknowledgements

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