BREAKING ADVANCED FIBER DEVELOPMENT PARADIGM: CONTINUOUS SUPERNANOFIBERS WITH LOW CRYSTALLINITY

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Classical manufacturing techniques of advanced polymer fibers rely on a combination of high polymer crystallinity and high degree of macromolecular alignment to achieve superior mechanical properties. As a consequence, advanced polymer fibers such as Kevlar and Spectra possess extraordinary strength, but low strains to failure and toughness. The strength/toughness trade-off is typical in engineering materials. Achieving simultaneously high strength and toughness is highly desirable for safety critical applications. It has long been believed that nanotechnology can produce the next breakthrough in advanced fibers and composites [1,2]. However, the research to date has focused mainly on discrete nanoparticles, such as carbon nanotubes and graphene. These nanomaterials have not yet produced a structural supernanocomposite defined in [2,3] as a nanocomposite with properties exceeding those of the current advanced composites. Continuous nanofibers (NFs), produced by electrospinning, are an emerging class of nanomaterials with unique properties that have gained attention for structural and functional applications [1,2]. While electrospun nanofibers have already found application in structural composites [2], until recently they have been considered weak.

Recent analysis of electrospun polyacrylonitrile (PAN) nanofibers in the ultrafine (100-250 nm) diameter range showed extraordinary simultaneous size effects in strength, modulus, and toughness.[4] Finest nanofilaments exhibited strength two orders of magnitude higher than that of thick NFs. The maximum recorded strength values approached those of advanced structural fibers. At the same time, toughness exhibited three orders of magnitude difference between the thick and ultrafine NFs, and maximum toughness values surpassed those of advanced fibers by more than an order of magnitude.

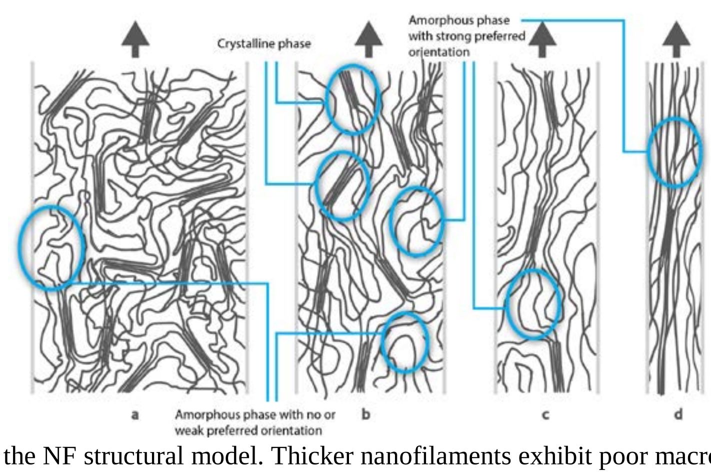

Figure 1: Schematic of the NF structural model. Thicker nanofilaments exhibit poor macromolecular alignment and higher crystallinity, while ultrafine NFs possess high degree of preferred orientation coupled with low crystallinity.

Structural investigations confirmed that this unique and highly desirable mechanical behavior may be due to high degree of macromolecular alignment coupled with low crystallinity (see Figure 1 for a schematic representation of the model). This structural explanation was supported by comparison of mechanical properties for as-spun and annealed NFs (where NF crystallinity was increased through the annealing process).

Here, we demonstrate that it is possible to control NF mechanical properties by changing nanomanufacturing parameters. Reduction in crystallinity of nanofibers achieved through changes in the solvent (Fig. 2a-b) resulted in significant increases in strain to failure and toughness (Fig. 2c-d).

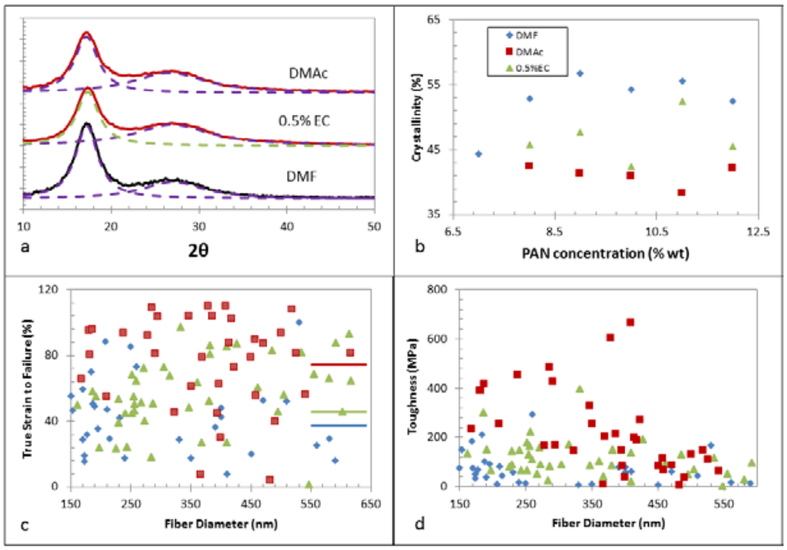

Figure 2: Crystallinity and mechanical properties of NFs in the 150-600nm diameter range. (a) XRD spectra for random mats electrospun from a 10% PAN solution for the different NF families; (b) XRD crystallinity obtained for the different NF families electrospun from different PAN solution concentrations; (c) True Strain to Failure (lines to the right correspond to the average values for the different NF families); (d) Toughness.

The change of the solvent system also resulted in improvements in NF strength and modulus that were attributed to improved polymer chain alignment as a result of increased drawability. The latter was confirmed through reduced average NF diameter (see Fig. 3a). A new quantitative indicator of macromolecular alignment developed and measured for individual nanofibers for the first time using polarized Raman spectroscopy correlated well with NF moduli (Fig. 3b). These results indicate the potential for further improvement in NF mechanical properties and strong prospects for economic upscaling of the nanomanufacturing process. Positive correlation between various mechanical properties was also demonstrated (Fig. 4). Different correlation slopes observed for different manufacturing conditions enable NF optimization and tailoring for specific applications.

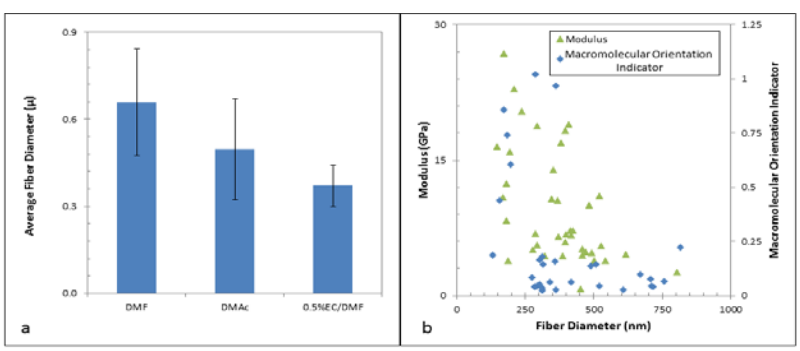

Figure 3: (a) comparison of average fiber diameter for the different nanofiber families spun from 10 wt% solutions (the error bars represent the standard deviation); (b) Comparison between the size effects in NF modulus and the macromolecular alignment indicator.

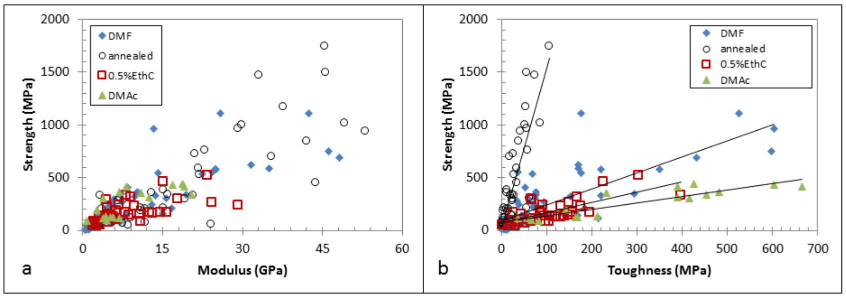

Figure 4: Correlations of mechanical properties of continuous NFs: (a) Strength/modulus and (b) strength/toughness correlations for different nanofiber families.

Reported dramatic simultaneous improvements in mechanical properties of NFs can lead to inexpensive, simultaneously strong and tough structures for safety critical applications. The proposed structural explanation of the unique NF mechanical behavior challenges the prevailing paradigm in advanced fiber development and calls for low polymer crystallinity coupled with high macromolecular alignment. Similar effects may be observed in continuous carbon nanofibers [5,6,7]. If confirmed, these effects can lead to entirely new class of advanced fibers and composites with superhigh toughness in addition to ultrahigh strength.

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