Making polymer fibers strong and tough simultaneously

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It has long been a great challenge to prepare materials with integrated merits of high strength, high modulus, high toughness, and light weight for structural material applications (e.g., aircrafts, automobiles). High strength representing a good resistance to deformation usually requires the material have a rigid/hard molecular structure, whereas high toughness representing a good resistance to fracture typically originates from a soft/flexible molecular structure. Therefore, the trade-off between the rigid and flexible components in a molecule usually leads to an intrinsic conflict between high strength and high toughness [1]. It is more intuitively in the typical stress-strain curves, where the integrated area of a tensile curve can be calculated for the toughness. Apparently, the attainment of high toughness needs not only high strength but also high tensile strain. Carbon fibers composed of rigid molecular structures (conjugated carbon bonds) have very high strength and modulus, but they are brittle and have very poor toughness due to the limited tensile strain (less than 5%). On the contrary, flexible polymeric materials (with linear molecular chains) typically have high tensile strain and toughness but low strength owing to the soft chemical bonds. Even though some exceptions such as novel alloy steels possess both high strength and toughness (ductility) [2], their high density makes them inferior in specific strength. Now, Liao *et al.* [3] make a breakthrough in making polymer fibers with simultaneous high strength, high toughness, and light weight.

As we know, the dragline spider silks have very high strength and toughness, due to their unique structures, i.e., rigid β -sheet nanocrystals bonded by hydrogen bonds embedding in a semi-amorphous matrix, in protein-based fibers [4]. Therefore, learning from the nature, the mechanical properties of polymeric materials could be readily tuned through engineering molecular structure and crystallinity. For example, by adjusting the rigid

(aromatic groups) and flexible (linear bonds, such as ether bonds) components in polyimide (PI) molecules, PI fibrous membrane/belts with both high strength and toughness were achieved [5]. In addition, it has been reported that single nanofibers with very small diameters (less than 100 nm) prepared by electrospinning technique also showed high strength and high toughness simultaneously due to the high molecular chain orientation induced by electrospinning process [6]. However, the individual nanofibers cannot realize real-world applications, and they usually lose the high strength when twisted into bundles/yarns due to the defects. Herein, Liao *et al.* [3] reports a novel strategy—orienting the fibrils and interlinking the fibrils by reactive molecules—in promoting the strength and toughness of electrospun polyacrylonitrile (PAN) fibers, and multifibrillar yarns with notable mechanical properties (1236 $\pm$ 21 MPa in strength, 137 $\pm$ 21 J g⁻¹ in toughness) were prepared (Fig. 1a), thus paving the way for practical application.

They fabricated the highly strong and tough fibers (abbreviated as i-EASYs) by electrospinning commercial PAN copolymer (PAN-co-MA) with addition of an interconnecting molecule (poly(ethylene glycol) bisazide, PEG-BA), following by high temperature stretching and annealing. The amount of PEG-BA, stretching temperature, stretch ratio (SR), and annealing temperature and time were systematically studied. The optimal properties were achieved at 4 wt% of PEG-BA, stretching at 160°C with SR of 8, and annealing at 130°C for 4 h. Results revealed that the fibrils were aligned and the diameter was decreased under stretching (Fig. 1b, c), and the crystallinity was remarkably increased from ~56.9% (at no stretch) to ~92.4% (at SR 9). Even though the strength and modulus of the as-spun multifibrillar yarn could also be largely improved by only performing the stretching process without addition of interconnecting molecule

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Figure 1 Photograph, morphology, and structure of the reported strong and tough fibrous yarn. (a) Photograph of stretched yarns; (b, c) scanning electron microscopy images of stretched (at SR 8 at 160°C) and annealed (130°C for 4 h) yarns; (d) the chemical reaction between PAN and PEG-BA; (e) a model for the stress/strain behavior of yarns. Reproduced with permission from Ref. [3], Copyright 2019, American Association for the Advancement of Science.

PEG-BA, the toughness did not increase. The addition of PEG-BA and annealing under tension are critical processes that can not only further increase the strength but also promote the toughness significantly, due to the chemical reaction between PEG-BA and the PAN molecules (Fig. 1d). Overall, the enhancement in mechanical properties is synergistically attributed to the stretch-induced high fibril orientation, high crystallinity, and the interconnection of fibrils (Fig. 1).

In summary, the above work reports a novel strategy in breaking the conflict between high strength and high toughness of polymeric materials, and highly strong and tough electrospun PAN multifibrillar yarns were successfully made. Notably, the strategy, as they show, is not restricted to the present system, but could also be applied to other systems in which the yarns could be stretched to induce orientation of the fibrils and have reactive groups for interlinking. In addition, this work shines a bright

light on the practical application of electrospun fibrous materials in the future.

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