



Review

Electrospun nanofiber: Emerging reinforcing filler in polymer matrix composite materials

Guolong Wang^{a,b}, Demei Yu^{a,*}, Ajit D. Kelkar^b, Lifeng Zhang^{b,*}^a Department of Chemistry, School of Science, State Key Laboratory of Electrical Insulation and Power Equipments, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China^b Joint School of Nanoscience and Nanoengineering, North Carolina Agricultural and Technical State University, Greensboro, NC 27401, USA

ARTICLE INFO

Article history:

Received 23 March 2017

Accepted 3 August 2017

Available online 8 August 2017

Keywords:

Electrospinning

Nanofibers

Reinforcing

Polymer matrix composite

Mechanical property

ABSTRACT

The rapidly developing technique of electrospinning has gained surging research interest since the 1990s due to its capability of yielding continuous fibers with diameters down to the nanometer scale. Despite enormous efforts devoted to explore applications of electrospun nanofibers, such as separation, catalysis, nanoelectronics, sensors, energy conversion/storage, and biomedical utilization, there are limited attempts to employ these nanofibers for reinforcement in polymer composites. Electrospun nanofibers, however, possess comprehensive advantages not typically shared by other nanoscale composite fillers/reinforcing agents, such as continuity, diverse material choice, controlled diameter/structure, possible alignment/assembly, mass production capability and so forth. Therefore electrospun nanofibers have great potential as promising reinforcement fillers for next-generation polymer composites. This is a comprehensive and state-of-the-art review of the latest advances made in development of electrospun nanofiber reinforced polymer composite materials with intention to stimulate interests in both academia and industry.

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* Corresponding authors.

E-mail addresses: dmyu@mail.xjtu.edu.cn (D. Yu), lzhang@ncat.edu (L. Zhang).

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1. Introduction

1.1. Nanofiller for polymer composite

A polymer composite is a multi-phase material in which reinforcing fillers are integrated with a polymer matrix, resulting in synergistic mechanical properties that cannot be achieved from either component alone [1]. As the most used polymer composite material, fiber reinforced polymer (FRP) composite materials comprise lightweight polymer resins and high strength/modulus fibers, such as glass, carbon and aramid fibers with diameters from a few to tens of micrometers. The “Light and Strong” characteristic of FRP composite makes it very popular in our daily life as engineering materials for automobile, aerospace, sports utilities, construction, etc.

With widespread interest in nanomaterials, research on nanometer scale fillers for polymer nanocomposite materials has attracted growing attention along with a rising market [2–5]. According to Transparency Market Research, it is expected that the market value of PNC in 2018 will be 3.5–5 times higher than that in 2010. Generally a PNC is a polymer based composite material in which at least one phase has one, two or three dimensions in the nanometer scale. More commonly it refers to a bulk polymer matrix with solid nanofillers dispersed therein. In this review, PNC is referred to the broader meaning. Compared to conventional polymer composites with micrometer scale fillers, PNCs have demonstrated substantial mechanical property enhancements at much lower filler loading, facilitating reduced specific weight and simplifying processing [6]. Moreover due to nanometer size feature and concomitant ultra-high specific surface area of the dispersed nanofillers, PNCs possess unique properties typically not shared by their conventional counterparts, and has shown bright prospect in developing high-performance and lightweight composite materials with inherent processability [7].

The history of PNCs may be traced back to exfoliated layered silicate filled elastomer polymers in the 1950s [8]. Nonetheless PNCs did not attract significant attention from both academia and industry until 35 years later researchers from Toyota Central R&D Labs, in collaboration with Ube Industries, reported a new polymer composite material consisting of nylon-6 with nano-scale platelets of montmorillonite [9,10], a naturally occurring silicate clay. A very low loading of nanoscale platelets of montmorillonite resulted in significant enhancement of both thermal and mechanical properties of the resultant PNC. This nylon 6/clay composite material was subsequently used for passenger cars because of its heat resistance and dimensional stability. The early research interest in PNCs was largely based on naturally occurring clay and layered silicates fillers (e.g., montmorillonite and saponite), perhaps because their intercalation chemistry had long been known. These layered silicate fillers may be easily dispersed in various monomers/polymers in form of nano-layers after sufficient intercalation and/or exfoliation. Undoubtedly PNCs with layered silicates, particularly those with exfoliated structures, presented significant improvement in modulus and strength [11,12].

The rapidly developing nanotechnology enabled other kinds of nanofillers beyond the layered silicates for reinforcing purpose, e.g., nanoparticles, nanotubes, and nanosheets [13]. Among these emerging nanofillers, nanoparticles garnered considerable

attention first, because they are easily available by sol-gel processing or microemulsion methods in the laboratory, as well as by attrition or pyrolysis methods in industry. For example, silica (SiO_2) nanoparticles have been in the spotlight for long time due to remarkable mechanical enhancement of the resultant PNCs including tensile/flexural/impact properties, hardness, and fracture toughness [2]. Subsequently discovery of carbon nanotubes (CNTs) via arc evaporation by Iijima in 1991 offered an ideal nanofiller for PNCs [14]. It was revealed that CNTs provided the larger modulus enhancement in polymer matrices at fixed loading compared to silicate clays and nanoceramic particles [15]. This is ascribed to CNTs’ large aspect ratio, high mechanical strength, and high stiffness. The most recent research upsurge in the field of PNCs came following the first production of graphene in lab in 2003. Graphene is a monolayer of sp^2 -hybridized carbon atoms arranged in a two-dimensional lattice but shows similar high strength as CNTs. It was found that graphene even showed greater reinforcing potential than CNT in PNCs [4]. For example, tensile strength of neat epoxy resin was enhanced by 40% with 0.1 ± 0.002 wt.% graphene platelets while merely 11% and 14% improvements were observed with single-walled CNTs and multi-walled CNTs, respectively [16]. These attractive findings also stimulated revival of interest in exploiting other layered nanofillers such as exfoliated graphite and graphene nanosheets (few-layer platelets or monolayer carbon sheets with heteroatoms and topological defects) for PNCs [17].

1.2. Electrospinning

The top-down nanomanufacturing technique of electrospinning provides an universal approach to conveniently prepare polymeric, ceramic, and carbonaceous fibers with typical diameters from a few tens to a few hundreds nanometers (commonly termed as “electrospun nanofibers”) [18,19]. Unlike conventional fiber spinning techniques such as dry-spinning, wet-spinning or melt spinning driven by mechanical force, electrospinning is driven by electrical force and follows a “bending (or whipping) instability” thinning mechanism. This unique thinning mechanism enables approximately two to three orders of magnitude thinner fibers than either natural or conventionally spun fibers. Compared to most other 1D nanomaterials that are made from bottom-up methods such as nanotubes, nanowires, and nanorods, electrospun nanofibers are collected intrinsically in the form of a nonwoven mat and usually require no further purification. Electrospun nanofibers are inexpensive, continuous, and relatively easy to align, assemble, and process in applications. It is noteworthy that electrospinning is currently the simplest and most cost-effective method to produce a variety of long and continuous nanofibers and it does have scalability for mass production. Although there are several other techniques that can also produce fibers at nanometer scale from high-volume production techniques, such as melt fibrillation and gas jet, to highly precise techniques, such as nanolithography and self-assembly, their practicability is limited in consideration of restricted material range, possible fiber assembly, cost, and production rate [20]. In the recent decade, electrospinning and its unique nanofiber product have been developing at a breakneck speed. Enormous efforts around the globe have been undertaken to explore all possible applications of electrospun nanofibers. With their distinct small size and concomitant ultra-high specific surface area, electro-

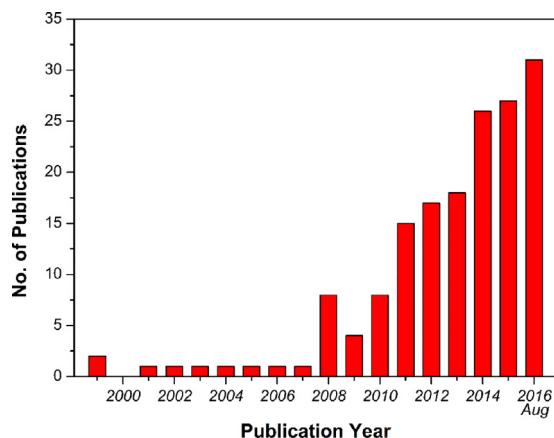


Fig. 1. Annual scientific publications that are related to electrospun nanofiber reinforced polymer composites since this term was introduced in 1999 (Data analysis of publications was based on Google Scholar search results as of August 2016).

spun nanofibers have seen a wide range of applications including filtration, catalysis, sensor, electronic and optical device, energy conversion and storage and biomedical uses [21–25].

1.3. Overview of research on electrospun nanofiber reinforced polymer composite materials

Despite the great success of electrospun nanofibers including those with multiple components (termed as electrospun composite nanofibers) in many applications, limited research outcome has been reported in developing electrospun nanofiber reinforced polymer composite. As a new member of fiber family, potential application of electrospun nanofibers in PNCs can never be neglected from the point of view of designing novel advanced FRP composite materials. The first published review that partially addressed the topic of electrospun nanofiber reinforced polymer composite was given by Huang et al. in 2003 [26]. Another two reviews that involved in this topic appeared in 2005 and 2009 by Chronakis [27] and Teo et al. [28], respectively. In all of these reviews, little space was reserved for mechanical reinforcement due to scant research outcome at that time. A detailed review of electrospun nanofibers for enhancing structural performance of composite materials was published by Zucchelli et al. [29] in 2011, which covered research outcome in this area through early 2010. It is noteworthy that the reviews mentioned in the preceding were concerned with electrospun polymer nanofibers as reinforcing fillers in PNCs. Two additional reviews appeared subsequently regarding the application of electrospun nanofibers in PNCs, with specific emphasis in damage self-healing and dental regeneration, respectively, where electrospun carbon and SiO_2 nanofibers for toughening/reinforcing purpose are discussed [30,31].

It has been a few years since the last comprehensive review, and considerable achievements of electrospun nanofibers for composite reinforcement has been seen in that period (Fig. 1). In particular, glass, ceramic, and carbon nanofibers from electrospinning have been applied in reinforcing PNCs. Although overall use of electrospun nanofibers for reinforcing purpose is still in its infancy, it is meaningful to summarize current research advances so as to broaden the scope of polymer composite research, and stimulate more academic and industrial interest towards advanced FRP composite materials. Herein we aim at a comprehensive and state-of-the-art review on reinforcing applications of electrospun nanofibers in polymer matrix composite materials during past six years with an opening analysis of electrospun nanofibers' potential for reinforcing purpose and a closing discussion of current challenges and perspectives. Our goal is to demonstrate an objective

and complete picture of current research endeavors that have been dedicated to development of advanced polymer matrix composite materials that reinforced with electrospun nanofibers.

2. Potential of electrospun nanofibers for reinforcement

Prior to considering the potential of electrospun nanofibers for reinforcement in composites, it should be noted that key issues for production of high performance conventional FRP composite material include (1) high strength and high stiffness fibers with respect to polymer matrix; (2) large aspect ratio of fibers; (3) homogeneous dispersion and embedding of fibers in polymer matrix; (4) strong interfacial interaction between fibers and polymer matrix. The potential of electrospun nanofibers for reinforcement in PNCs lies in following realistic aspects that go along with the these key issues.

The unique thinning mechanism of electrospinning delivers intrinsic opportunity for macromolecular alignment in the resulting nanofibers. When exposed to an electric field, a droplet of polymer solution for electrospinning (called the “spin dope”) at the tip of spinneret deforms from the shape caused by surface tension alone and forms a Taylor cone [32]. As the applied electrical force on the droplet of spin dope overcomes the forces from surface tension and viscoelasticity, a polymer solution jet ejects from the tip of the Taylor cone and electrospinning begins. The solution jet then follows a bending, winding, and spiraling path in three dimensions, thinning with the increasing loop circumference. This thinning mechanism represents a “bending (or whipping) instability” [33–36]. Typically the bending instability is able to elongate an electrospinning jet more than 10,000 times in 50 milliseconds or less with concurrent fiber thinning. This enables an extremely large stretching rate (up to $1000,000 \text{ s}^{-1}$) of macromolecular chains in the jet and closely aligns them along the nanofiber axes [36,37]. Such an enormous drawing rate is not accessible by other spinning techniques. In the meantime, over 99% of the solvent in the electrospinning jet can be removed during or shortly after the bending instability due to the large specific surface area. Thus, orientation of macromolecular chains is likely retained in the final electrospun nanofibers, and electrospun polymer nanofibers have the potential to become high-strength fibers considering their drawn structure in the process of electrospinning.

The “size effect” gives electrospun nanofibers another advantage over their conventional micrometer counterpart. It is believed that mechanical strength of fiber tends to increase with decreasing diameter [38]. A further explanation is that there probably is a lower degree of defects on and/or inside the fiber with fiber diameter reduction [39]. This definitely endows electrospun nanofiber with a large potential of higher strength since it has been repeatedly demonstrated that amount, size, and distribution of structural defect directly determine mechanical strength of fibers.

The concomitant huge specific surface area of electrospun nanofibers results in enormous interfacial area between nanofibers and polymer matrix and therefore leads to substantial improvement of fiber-matrix interfacial interactions. Complex architectures from electrospinning such as hollow nanofibers [40] can further increase corresponding specific surface area.

Electrospinning offers versatility of fiber functionalization and material combination such as polymer solution blending prior to spinning, post-spinning surface functionalization, and core-shell electrospinning setup for core–shell nanofibers [41–43]. Appropriate surface-functionalized nanofibers or core/shell nanofibers are of great importance for reinforcement because it helps to improve both dispersion of nanofibers in a polymer matrix and corresponding interfacial interactions to promote efficient load transfer from polymer matrix to nanofiber fillers. Development of elec-

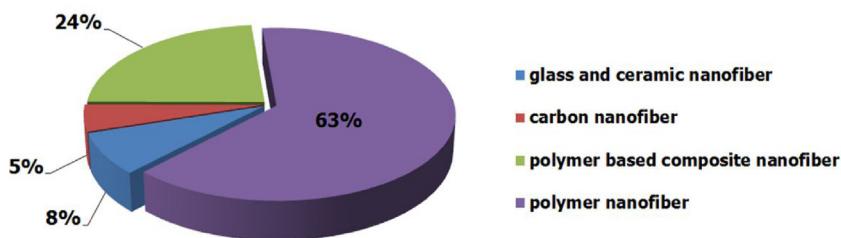


Fig. 2. Distribution of scientific publications that are related to electrospun nanofiber reinforced polymer composites based on type of nanofibers since 2010 (Data analysis of publications was based on Google Scholar search results, as of August 2016).

trospinning also generates nanofibers with multi-functionality for advanced PNCs, e.g., self-healing agent can be integrated with core-shell nanofibers with 3D microvascular structure for engineered PNCs with high structural reliability and long service life [44–48].

Electrospun nanofibers are long and continuous. If well-distributed in matrix, they may present fewer fiber edges and thus fewer stress concentration points in the polymer composite compared to shorter nanofillers. Both the efficient load transfer from polymer matrix to nanofiber filler and the reduced stress concentration points will benefit mechanical performance of electrospun nanofiber reinforced PNCs. In the meantime, nanofibers with large aspect ratio are expected to form 3-D geometrical percolation at low loading due to more efficient network formation [49], and demonstrate unusual reinforcing effect with small weight increase [50].

Electrospun nanofibers are normally collected as nonwoven mat with inherent 3-D connectivity, providing a potential 3-D skeleton for structural laminate composites. Nonwoven nanofiber mats may be easily placed in resin rich interlayers between reinforcing plies prior to laminate production. This can avoid nanofiller dispersion in the matrix resin and resultant tremendous viscosity increase in processing, which is problematic for all infusion applications such as resin transfer molding.

Recent studies have revealed that glass (SiO_2) and ceramic (e.g., TiO_2 and TiC) nanofibers with diameters of a few hundreds of nanometers may be prepared through electrospinning a spin dope containing a glass or ceramic precursor, followed by pyrolysis or carbothermal reduction at elevated temperature [51–54]. It is worth noting that glass and ceramics possess much higher mechanical strength and modulus than polymers and thus glass and ceramic nanofibers from electrospinning are better candidates for nanofiber reinforced PNCs.

Last but not least, technical development of electrospinning in recent years enabled scale-up production of nanofibers [55–57]. Electrospun nanofiber production capacity has increased from gram scale to kilogram scale. Substantial industrial attention have been attracted especially from traditional composite companies, which is undoubtedly a strong impetus for research and development of electrospun nanofiber reinforced PNCs.

3. Frontier research in the field of electrospun nanofiber reinforced polymer composite

Just as the widely produced polymer fibers relied on conventional mechanically driven spinning techniques, polymer nanofibers have been developed first through electrospinning. Consequently polymer nanofibers are the first type of electrospun nanofiber for reinforcement purpose in PNCs. Since the pioneer work of Kim and Reneker employing polybenzimidazole (PBI) nanofibers (ca. 300 nm diameter) to reinforce epoxy and rubber matrices in 1999 [58], attempts of electrospun polymer nanofibers for reinforcing purpose have accumulated significant encouraging results as indicated by early reviews [26–29]. A survey of open pub-

lications related to electrospun nanofiber reinforced PNCs since the review of Zucchelli et al. [29] is given in Fig. 2, where the distribution of these publications is organized based on nanofiber type. The data clearly reveal that polymeric nanofibers currently receive the major research attention for electrospun nanofiber reinforcement in PNCs, with increasing interest in polymer based composite nanofibers, as well as glass, ceramic, and carbon nanofibers. In the following sections, research advances in electrospun nanofiber reinforced PNCs are reviewed based on type of nanofibers. Potential applications of these electrospun nanofiber reinforced PNCs are also highlighted in this review, including structural material, biomedical and dental materials, and etc.

3.1. Polymer nanocomposite (PNC)

3.1.1. Polymer nanofiber reinforced PNC

It is well known that the mechanical performance of FRP composite material critically depends on the mechanical property of the fiber, its uniform dispersion in the polymer matrix, and strong interfacial bonding between the fibers and the surrounding matrix. To get high performance polymer nanofiber reinforced PNCs, correspondingly, most recent efforts have been devoted to enhancing these characteristics. The following section consists of a variety of factors that have been explored to make stronger/tougher polymer nanofiber reinforced PNCs in recent years.

3.1.1.1. Nanofiber parameter. Parameters of electrospun polymer nanofibers such as size, aspect ratio, alignment, loading, structure and post-treatment play an important role in performance of final PNCs.

3.1.1.1.1. Size. As emphasized in the preceding “size effect” is one of the greatest potentials of electrospun nanofibers for reinforcing purpose. A typical “size effect” was presented by Kowalczyk et al. [59], in which size reduction effect of cellulose nanofibers on mechanical properties of a polylactide (PLA) composite was evaluated by comparing cellulose nanofibers from electrospinning (200–300 nm) with cellulose standard fibers from classical dry-wet spinning (10–17 μm). The nanofibers outperformed the standard fibers at the same loading for reinforcement in storage modulus and yield strength of the PNC. Unlike natural fibers, such as hemp fibers, the electrospun cellulose nanofibers did not enhance nucleation and crystallization of the PLA matrix, with the resultant decrease of toughness. To investigate the size dependence of nanofibers on the reinforcing effect, Tang et al. embedded two kinds of electrospun cellulose nanofibers (diameters: 520 and 250 nm, respectively) into PLA matrix via a solution impregnation approach [60]. They showed that there was no interfacial debonding and fiber pullout on cross-sectional surface of the 250 nm fiber-reinforced composites, whereas these features dominated the cross-sectional morphology of the 520 nm fiber-reinforced composites (Fig. 3), suggesting a better interfacial interaction of the thinner fiber based composites. Given the same chemical structure of the counterparts, it was definitely the significant higher surface/contact area

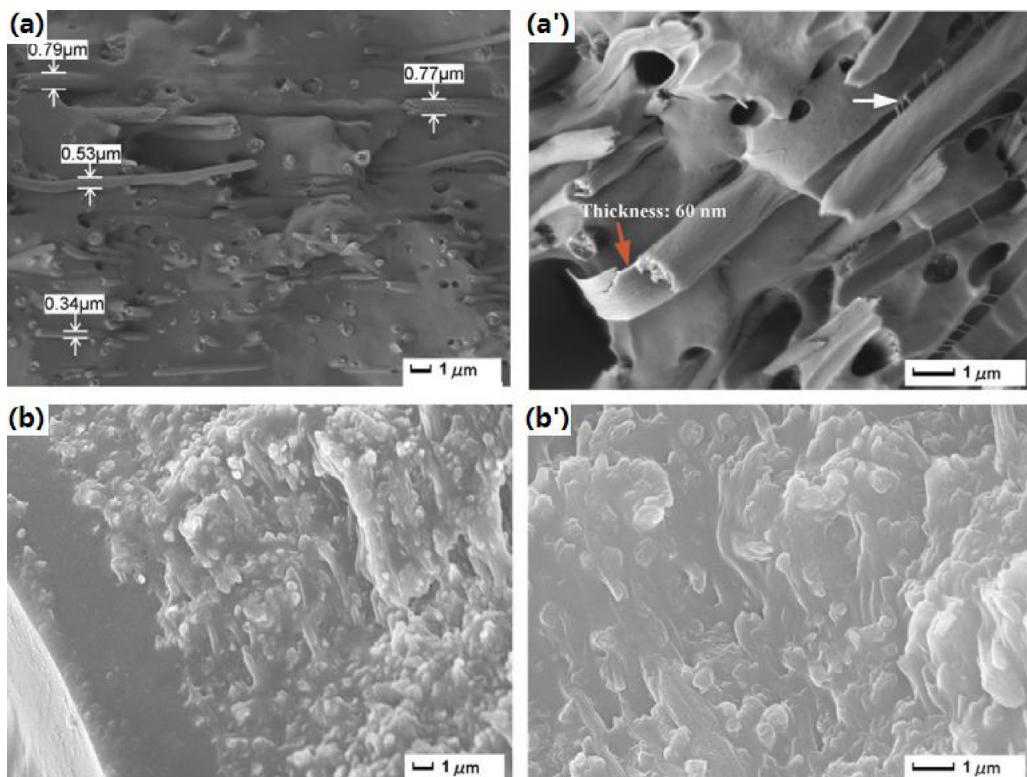


Fig. 3. Cross-sectional SEM images of electrospun cellulose nanofiber mats (CNM) reinforced PVA composite films with 20 wt.% loading: (a) thick-CNM/PVA and (b) thin-CNM/PVA. a' and b' are the corresponding images at higher magnification. [60], Copyright 2011. Reproduced with permission from Elsevier Ltd.

due to fiber diameter reduction that generated stronger interfacial adhesion (i.e., via hydrogen bonding) in the thinner nanofiber reinforced composite. Consequently, incorporation of 40 wt.% 250 nm nanofibers increased Young's modulus of the composite by 23% and improved stiffness at 160 °C by 25% compared to the counterpart. Later, Cai and coworkers discussed such size-dependent behavior based on electrospun PAN nanofibers (150 nm and 300 nm) [61]. It was found that nearly in all studied weight percentages the finer nanofiber based polyacrylamide gel composite outperformed the coarse nanofiber filled one in mechanical performance at the same filler loading. The better reinforcing/toughening effectiveness of the finer nanofibers could be ascribed to its diameter dependence in mechanical properties [62]. Particularly finer nanofibers may also promise higher light transmittance in PNCs. Benefit of such “size effect” of electrospun nanofibers on reinforcing PNCs was also discussed in non-polymer electrospun nanofibers [63].

Based on recent research results, “size effect” of electrospun nanofibers undoubtedly contributed to mechanical performance of PNCs. The “size effect” enabled not only higher strength/modulus [64] of nanofibers at smaller size but also stronger fiber-matrix interfacial interaction with decreasing fiber diameter, which together ensured effective load transfer from polymer matrix to nanofiber fillers and led to higher reinforcing/toughening effect.

3.1.1.1.2. Aspect ratio. The geometrical aspect ratio of a fiber is defined as ratio of its length to diameter. Higher aspect ratio fillers could generate better reinforcing effect due to formation of more efficient network in composite [49] and better stress transfer from the polymer matrix to the filler therefrom [65,66]. Many theoretical and experimental studies have shown that both Young's modulus and yield stress of composite materials increased with the increase of aspect ratio of reinforcing fillers [67–71].

Nanofibers from electrospinning possess exceedingly high aspect ratio and promise huge potential as reinforcement. Directly using electrospun nanofiber nonwoven mat as reinforce-

ing agent could be a simple but effective concept to obtain PNCs with improved mechanical performance. Possible reinforcing/toughening mechanism of these electrospun nanofiber nonwoven mat is creation of geometrical skeleton inside polymer matrix. Such inherently connected nanofibrous skeleton structure could strengthen/stiffen polymer matrix [72] while toughen the matrix by “fiber bridging” [73], “fiber necking” (plastic failure) [60], crack deflection and pinning effects [74,75], and etc. In practice, however, this concept suffers intrinsic limitation for scale-up because such long and continuous electrospun nanofibers in the form of nonwoven mat are very hard to be properly dispersed in solution or in melt due to strong entanglement. Improper dispersion of electrospun nanofibers seriously deteriorates their reinforcing effect and restricts their maximum loading. In this context, shortening of long electrospun nanofibers seems to be a compromising solution. The use of short electrospun nanofibers not only promotes dispersion of nanofibers in polymer matrix and eases composite processing (i.e., short nanofiber based composites can be processed via traditional liquid formulation molding such as injection, compression, and emerging 3D printing technology for complex shapes) but also provides opportunity to directly mix predetermined amount of nanofibers with matrix polymer either in solution or in melt.

Jiang et al. suggested a simple way through which long and continuous electrospun polymer nanofibers were cut into short ones by rotation blade [76,77]. It was found that addition of small amount (3.5 wt.%) of short electrospun nylon-6 nanofibers (ca. ~200 nm diameter and tens to hundreds micrometers in length) led to drastic enhancement in mechanical properties of thermoplastic polyurethane (TPU) matrix, i.e., 185% increase in Young's modulus without decrease of elongation at break [76]. This result was really exciting compared to ~82% improvement in Young's modulus of the TPU matrix reinforced by long and continuous electrospun nylon-6 nanofiber nonwoven at similar loading. It was also

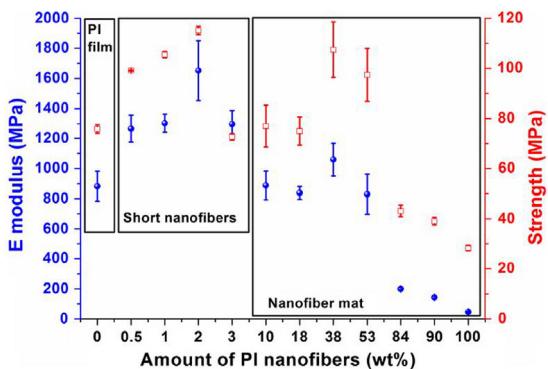


Fig. 4. Comparison of modulus (●) and strength (□) of pure polyimide (PI) film and PI composite film with reinforcement from short PI nanofibers and as-electrospun PI nanofibrous mat, respectively. [77]. Copyright 2013. Reproduced with permission from Elsevier Ltd.

shown that integration of only 2 wt.% short electrospun polyimide (PI) nanofibers increased tensile strength and modulus of PI composite film by 53% and 87%, respectively, with respect to neat PI film [77]. To achieve equivalent mechanical properties, as much as 38 wt.% continuous PI nanofibrous mat was required in a counterpart PI composite film (Fig. 4). Difficulty of wetting PI nanofibers in the latter case was an obvious disadvantage. It is difficult for polymer solution or melt to flow through densely packed electrospun nanofiber nonwoven mat and result in inhomogeneous dispersion of filler, poor interface and voids, which may bring about poor load transfer and more stress-concentration sites in PNCs and eventually lead to mechanical performance below expectation.

Similarly short electrospun PI nanofibers was explored to reinforce poly(vinylidene fluoride) (PVDF) matrix, where a homogeneous dispersion of nanofibers in matrix was fulfilled at quite high filler loading (up to 50 wt.%) along with a remarkable enhancement in tensile strength (by 743%) and tensile modulus (by 449%) [78]. In another research by Peijs et al. [79], short electrospun PLA nanofibers (diameter: 625 nm, length: 50–700 μm) as well as PLA nanofiber mats were used as reinforcing agents for poly(trimethylene carbonate) (PTMC) and both demonstrated excellent reinforcing effect. Interestingly, the nanofiber mats filled composites were stiffer and stronger than the short nanofiber filled composites but showed significantly reduced ductility and toughness. This research not merely provided a positive example that electrospun nanofiber with higher aspect ratio showed higher reinforcing effect, but also revealed that short PLA nanofibers could bring overall mechanical improvement of PTMC without compromising the ductility.

It is noteworthy that short electrospun nanofibers only improve mechanical properties of PNCs under the condition of optimum dispersion; otherwise PNCs would be weakened because nanofiber edges may serve as sites of stress concentration and possibly become crack initiators. Furthermore the fiber-cutting techniques, e.g., ultrasonication, mechanical stirring [79], UV-cutting [80], cryogenic-cutting [81], direct electrospinning [82] and specific electrospinning setup [83], need to be carefully selected with consideration of nanofiber material, nanofiber morphology after cutting [79], and mechanical properties of resultant composites. Once nanofiber' dispersion is addressed, mechanical improvement of PNCs also depends on strength of nanofibers, microstructure of composites, fiber/matrix interfacial adhesion, and etc. For example, even shortened PMMA nanofibers were well-dispersed in epoxy matrix, poor fiber/matrix adhesion and presence of porosity resulted in deterioration in mechanical properties of the resultant composites [84]. Up to date exploration of short electrospun polymer nanofibers for reinforcement in PNCs is still at early stage.

3.1.1.1.3. Alignment. Intrinsically nanofibers from electrospinning deposit randomly on collector and form a nonwoven nanofibrous mat. If special set-ups are employed, such as rotational cylinder collector [85] and electro-manipulated auxiliary electrode [86], electrospun nanofibers can be collected into aligned form with a variety of alignment angles and ratios by adjusting rotational speed of cylinder collectors and electrical field. According to some classical reinforcing/toughening mechanisms like fiber bridging, nanofibers that align along with force loading direction are expected to improve mechanical performance of matrix most efficiently because they impart additional strength/modulus through their own mechanical properties or absorb energy during fracture in a "full-on" manner. Aligned electrospun nanofibers, therefore, are likely to be more efficient than randomly orientated ones for reinforcing purpose.

Research endeavors have been devoted to evaluate effect of nanofiber alignment on mechanical performance of resultant PNCs. Wu et al. employed randomly organized and uniaxially aligned polyacrylonitrile (PAN) nanofibers to reinforce poly(methyl methacrylate) (PMMA) composites film by solution impregnation technique [87]. Tensile strength and Young's modulus of the composite film incorporating 16 wt.% aligned PAN nanofibers were 40% and 30% more than those of the composite film loading with the same amount of randomly organized fibers, respectively. Chen et al. employed two types of PI nanofiber mats, which were composed of randomly overlaid PI nanofibers and highly aligned PI nanofibers (Fig. 5), respectively, as skeletal framework to reinforce PA6 matrix through melt infiltration [85]. It is revealed that mechanical properties of resultant PA6/PI PNC were strongly dependent on alignment of PI nanofibers. In particular, the PNC containing 50 wt.% highly aligned PI nanofibers showed an amazing enhancement of tensile strength by 700% and modulus by 500% along the longitudinal direction compared to neat PA6. The PA6/PI PNC containing 50 wt.% randomly overlaid nanofibers had a relatively low but isotropic enhancement in tensile strength and modulus (both by ~270%) as compared to neat PA6. Another work by Liao et al. indicated that aligned cellulose nanofiber mats (a-CNM) were more efficient than randomly oriented ones (r-CNM) in reinforcing epoxy resin film [88]. Specifically mechanical strength and Young's modulus of the epoxy composite film containing 20 wt.% aligned nanofibers increased by 71% and 61%, respectively, compared to the epoxy composite film containing the same amount of randomly oriented nanofibers. Unlike fiber diameter and interfacial adhesion, alignment of reinforcing fibers, interestingly, had a minor impact on light transmittance of the composite films, which is another benefit of aligned nanofibers. In some specific cases, a simultaneous improvement in stiffness and ductility was achieved by employing aligned nanofibers [73], which is a departure from what is commonly observed in PNCs that modulus increase occurs at the expense of elongation at break [89].

To further reveal benefit from nanofiber alignment, effects of alignment ratio and alignment angle are also investigated recently. Çökeliler and coworkers manipulated the electric field and obtained two types of electrospun nanofibers with different ratios of alignment and alignment angle [86]. They found composites that embedded both types of aligned nanofibers along loading direction showed higher flexural strength, modulus and toughness than those of random fiber filled composites, and the composites containing nanofibers with higher alignment ratio and angle exhibited better mechanical performance. Nevertheless, since two types of aligned nanofibers used had very different diameters (ca. 155 nm and 317 nm), the effect, if any, of nanofiber alignment ratio and angle may be questioned. Change of force loading direction is equivalent to a change of nanofiber alignment angle, but is more straightforward in practice. Cai et al. reported that aligned PAN nanofibers stiffened polyacrylamide gel composite in both of

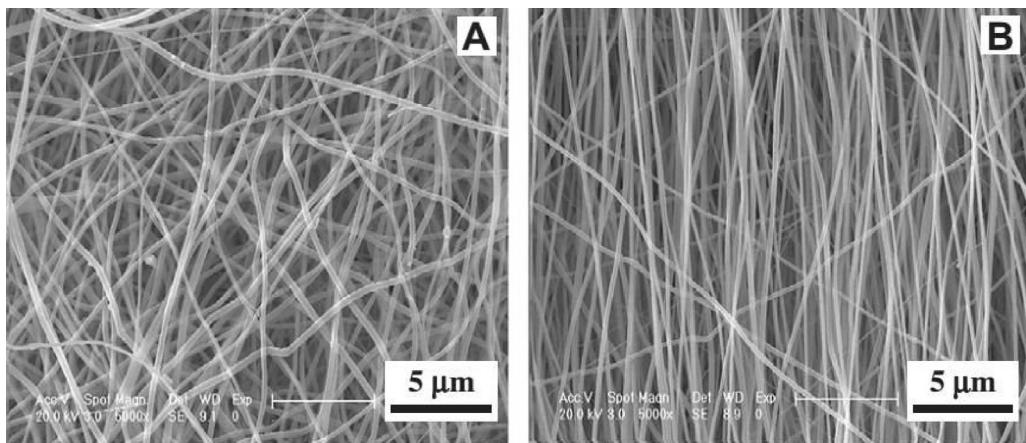


Fig. 5. Representative SEM images of electrospun mats consisting of randomly overlaid PI nanofibers (A) and highly aligned PI nanofibers (B). [85], Copyright 2011. Reproduced with permission from Elsevier Ltd.

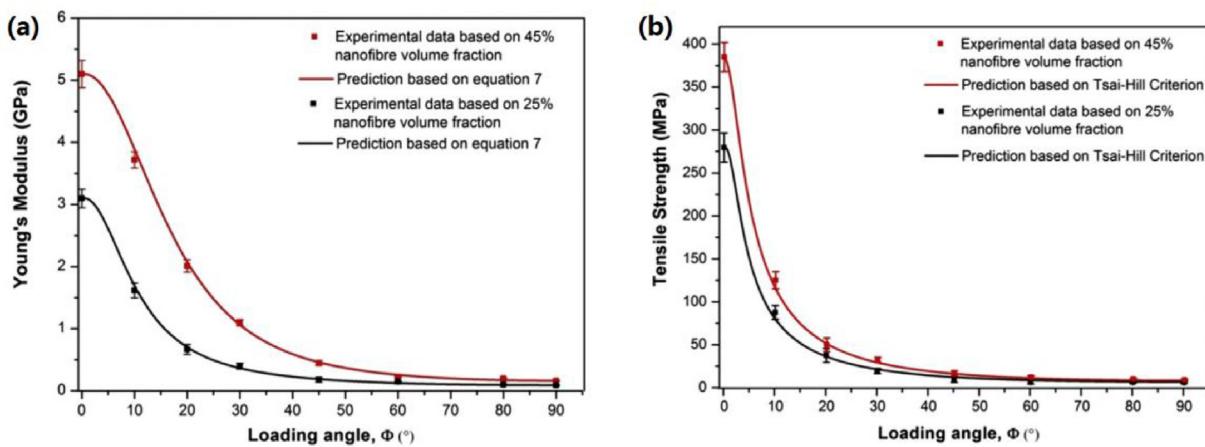


Fig. 6. Young's modulus (a) and tensile strength (b) vs. loading angles of aligned co-polyimide nanofiber reinforced composite at two fiber volume fractions. [91], Copyright 2015. Reproduced with permission from Elsevier Ltd.

orthogonal force loading directions and the stiffness of composite was higher along fiber direction [61]. Li et al. reported that aligned PA-6 nanofibers was able to reinforce PMMA and optical and mechanical properties of the resultant PNC were dependent on alignment degree of nanofibers [90]. Ullas et al. studied effects of fiber orientation on compressive and flexural properties of an epoxy syntactic foams embedded with electrospun nylon nanofibers [74]. Placement of 0.25 vol.% nylon nanofibers normal to loading direction caused remarkable improvement in flexural strength and strain of the resultant composite by 75% and 62%, respectively, in comparison to neat epoxy foam, but just 7% enhancement in compressive strength. However, there was no observable improvement in flexural strength when the nanofibers were randomly dispersed or placed parallel to the loading direction. Possible mechanism of flexural property improvement was attributed to crack deflection. Peijs et al. investigated mechanical properties of a thermoplastic elastomer reinforced by aligned co-polyimide nanofibers [91]. Particularly exciting is the reinforcing/stiffening effect of aligned nanofibers increased with decreasing loading angles (Fig. 6). The Young's modulus and strength data fitted well with theoretical model at two nanofiber volume fractions (45 vol.% and 25 vol.%).

These positive results demonstrated that aligned electrospun nanofibers are a better choice in reinforcing PNCs than randomly orientated ones. Given the merit of aligned electrospun nanofibers, the resultant PNCs are expected to be mechanically anisotropic. To take full advantage of alignment for isotropic composites, potential

strategies are developing multidirectional fibers for reinforcement as well as weaved fabrics on the basis of aligned electrospun nanofibers.

3.1.1.4. Loading. Considering electrospun nanofibers' potential of higher strength, it is expected that mechanical properties of these electrospun nanofiber reinforced PNCs increase with nanofiber loading. However, nanofibers intrinsically form agglomerates, especially at high loading level, to reduce their surface energy due to their ultra-high specific surface area. The resultant agglomerates act as defect sites rather than reinforcements in PNCs, leading to degradation in overall mechanical properties. An optimum loading level is therefore preferred for electrospun nanofibers in PNCs [92].

In the research of Gabr et al. [93], electrospun cellulose nanofibers (250 nm diameter) demonstrated their capability to gradually and simultaneously improve stiffness and fracture toughness of epoxy resin at low loading level up to 0.1 wt%. A higher loading of electrospun cellulose nanofibers at 0.3 wt% started to degrade mechanical properties of the epoxy based PNC. Neppalli et al. incorporated electrospun nylon-6 nanofibers in PLA matrix and revealed that tensile modulus of the resultant PNC increased three fold and 50%, respectively, at fiber loading of 1.5 and 2.5 wt% with respect to PLA matrices [94]. Lu et al. investigated reinforcement of electrospun nylon-66 nanofibre mats in high density polyethylene (HDPE) based PNC through melt impregnation [95]. The tensile strength, modulus and toughness of the PNC increased

with nanofiber content up to 0.26 wt.%. Nonetheless the improvement in mechanical properties became inconspicuous with higher nanofiber content. Dong and coworkers [96] evaluated mechanical and thermal properties of electrospun PLA nanofiber reinforced epoxy composites at fiber loadings of 3, 5, and 10 wt.%. In their study, 5 wt.% fiber loading was regarded as the optimum loading, at which 50.8% and 31.6% increment in flexural modulus and strength were achieved, respectively, along with considerably increased Tg. A recent work by Cai et al. [61] suggested that modulus and strength of PAN nanofiber reinforced polyacrylamide gel composites increased with nanofiber content within the surveyed range (up to 1.04 wt.%), but toughness of the PNC reached maximum value at 0.56 wt.% loading. Thus the optimum PAN nanofiber loading was likely to be 0.56 wt.% for strong and tough gel-composites.

Compared to long continuous nanofibers, optimum loading level of shortened ones is usually higher since short nanofibers are less prone to agglomeration at the same loading. Shen et al. found that short PI nanofibers could improve tensile strength and modulus of PVDF composites by increasing nanofiber fraction from 10 wt.% to 50 wt.% [78]. The research by Peijs et al. revealed that incorporation of 30 wt.% short PLA nanofibers led to higher mechanical enhancement of PTMC composite than that of 5 wt.% filled composite except elongation at break [97]. However, there are a few contradicting results though. For example, Jiang et al. found short PI nanofibers had a much lower optimum loading level (2 wt.%) than PI continuous nanofiber mats (38 wt.%) for PI matrix [77] while Tang et al. found that cellulose continuous nanofiber mats exhibited both high strength and modulus at a quite high optimized loading of 40 wt.% [60]. These observations indicate that the optimum loading of electrospun nanofibers in PNCs is actually influenced by multiple factors, e.g., aspect ratio, strength contrast between nanofiber and matrix, nanofiber-matrix interfacial adhesion (stress transfer), and microstructure inside composites, rather than solely by nanofibers' dispersion in matrix. A further revelation on reinforcing/toughening mechanisms such as nucleating ability of electrospun nanofibers [98] and critical particle-particle distance [99] is also highly desirable for better understanding optimum loading of electrospun nanofibers in practical design of PNCs.

3.1.1.5. Structure. With the development of co-electrospinning techniques, electrospun nanofibers with special structures such as hollow and core-shell structures have been produced to prepare PNCs. Antoine investigated mechanical and optical properties of PMMA composite films containing PAN hollow nanofiber [100]. Incorporation of 5 wt.% hollow nanofibers had little effect on optical transmittance, but significantly increased Young's modulus and tensile strength of the resultant composite films by 50% and 58%, respectively. Zanjani et al. demonstrated that mechanical properties of epoxy based PNC can be significantly improved by double-walled hollow nanofibers made through triaxial electrospinning [101]. The PMMA/polyacrylamide (PAAm) double walled hollow fibers and polystyrene (PS)/PAAm double walled hollow fibers both showed reinforcing effect in corresponding PNCs. The PMMA/PAAm hollow fibers outperform the PS/PAAm counterpart due to better interfacial compatibility between PMMA shell and epoxy matrix. One potential benefit of hollow-structured nanofibers is their specific strength (strength to weight ratio), although it has not yet been demonstrated in electrospun nanofiber reinforced PNCs.

Instead of utilizing nanofibers with special structure as the reinforcer in composite materials, Wang et al. [102] investigated the strategy directly using core-shell nanofibers to construct transparent composite film by hot pressing. Specifically, PA-6 core-PMMA shell composite nanofiber mats (fiber diameter: 270–2800 nm) as well as pure PMMA and PA-6 nanofiber mats (fiber diameter: 100–390 nm) were fabricated by coaxial-electrospinning and single phase electrospinning. Two transparent composite films

were fabricated by hot pressing multilayers of PA6/PMMA core-shell composite nanofiber mats and interlaced pure PA-6 and pure PMMA nanofiber mats, respectively, under the condition of same PA-6 nanofiber content. The results revealed that the composite film from core-shell nanofibers exhibited not only higher tensile strength and modulus (increment by 20%) but also better light transparency with respect to the counterpart from interlaced pure PA-6 and pure PMMA nanofiber mats. The better performance of the core-shell nanofiber based composite was ascribed to better interface between nanofiber and matrices, lower voids content, and more uniform distribution of nanofibers.

3.1.1.6. Post-treatment. Although electrospun nanofibers have the potential to become high strength fibers due to the unique thinning mechanism (bending instability) in electrospinning, the chaotic trajectory of electrospinning jet makes it difficult to form ordered and/or aligned assemblies of the electrospun nanofibers. In addition the macromolecular chains in nanofibers, especially with a trace solvent content, may relax to some extent after depositing on the collector. Post-drawing treatment on electrospun nanofibers has attracted attention in PNC research because it is just like what is done to conventional fibers in the current fiber industry. Post-drawing of electrospun nanofibers may further reduce fiber diameters while improve their degree of crystallinity [103,104] and degree of orientation (particularly for those random oriented nanofiber mats), which significantly influence mechanical properties of nanofibers. Sun et al. electrospun PAN/PMMA bicomponent DMF solution and acquired partially aligned PAN (core)/PMMA (shell) nanofiber membrane on a high-speed rotating drum roller [105]. The nanofiber membrane was stretched along fiber alignment direction for 5 min in a 120 °C oven. This post-drawing resulted in thinner and even better aligned bicomponent nanofibers. After being drawn to 200% of original length, tensile strength and modulus of the nanofiber membrane significantly increased by 673.4% and 875.3%, respectively. At 0.6 wt.% loading, the post-drawn nanofibrous membrane reinforced Bis-GMA/TEDGMA dental resin showed 13.6%, 5.3% and 30.4% increase in flexural strength, flexural modulus and work of fracture, respectively, compared to untreated nanofibrous membrane.

3.1.1.7. Combined nanofiber parameters. Reinforcing PNCs with electrospun nanofibers involves a number of issues. The six parameters of electrospun nanofibers mentioned in the preceding may operate together toward a high performance PNC. Consequently, most recent research regarding electrospun nanofiber reinforced PNCs has investigated coincident multiple parameters of electrospun nanofibers.

For example, in addition to fiber alignment study, Wu et al. also studied the effect of nanofiber loading on their PAN nanofiber reinforced PMMA PNC [87]. Tensile strength and Young's moduli of the PNC films increased with nanofiber content up to 16 wt.% no matter what nanofibers were used: aligned or randomly organized. In Chen's research [85], with the proportion increase up to 50 wt.% both aligned and randomly overlaid electrospun PI nanofibers led to steady increase of tensile strength and modulus of the PA6 PNC. However, with 100 wt.% electrospun PI nanofibers the corresponding PA6 PNC exhibited lower mechanical properties. Similarly the electrospun cellulose nanofiber mat reinforced epoxy composite films developed by Liao et al. [88] showed consistent mechanical property increase with nanofibers content, whether the nanofibers were aligned or not aligned (Fig. 7). In the hollow nanofiber study by Zanjani et al. [101], higher enhancement in flexural modulus of the PNC was observed with finer fibers. When the content of PMMA/PAAm double walled hollow nanofibers was fixed at 0.2 wt.%, decrease of the PMMA/PAAm nanofiber size from 500 nm to 100 nm increased the PNC's modulus from 1.44 ± 0.02 GPa to 1.72 ± 0.03 GPa. Meanwhile, the PNC's modulus increased from

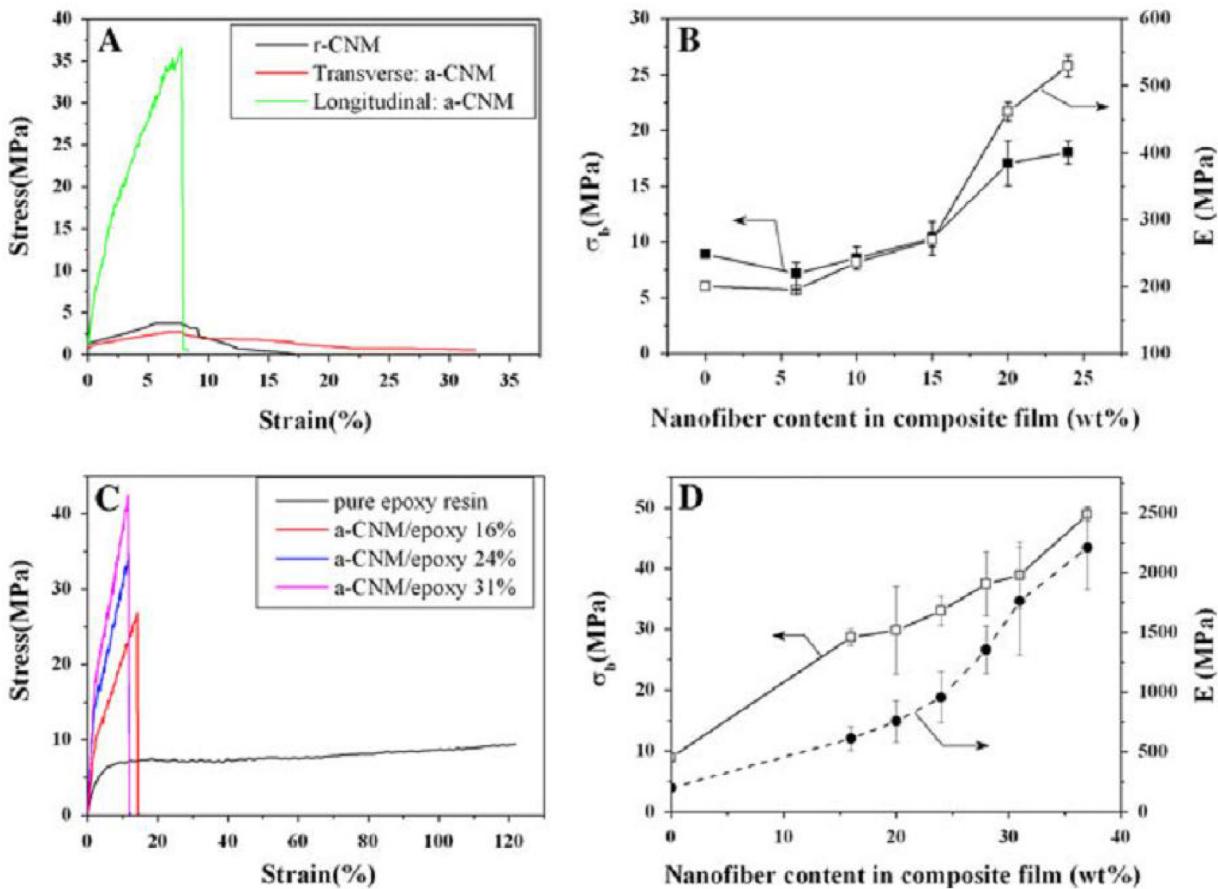


Fig. 7. (A) Typical stress-strain curves of cellulose nanofiber mats (CNM): aligned (a-CNM) and randomly oriented (r-CNM); (B) mechanical strength and Young's moduli of r-CNM/epoxy composite films as a function of fiber content; (C) typical stress-strain curves of a-CNM/epoxy composite films; (D) mechanical strength and Young's moduli of a-CNM/epoxy composite films as a function of fiber content. [88]. Copyright 2011. Reproduced with permission from Springer Science + Business Media.

1.38 ± 0.02 GPa to 1.63 ± 0.02 GPa by increasing the content of PS/PAAm hollow nanofibers from 0.2 wt.% to 2 wt.%. For post-drawn PAN/PMMA nanofibers from the research of Sun et al. [105], the mechanical properties of the PNC kept rising with the increase of nanofiber content from 0 to 1.2 wt.%. With 1.2 wt.% of the post-drawn nanofibers, corresponding flexural strength, flexural modulus and work of fracture increased by 51.6%, 64.3%, and 152%, respectively.

In most instances, the results from these combined parameter studies are in agreement with those seen from individual parameters. Since most reported research involves more than one nanofiber parameter, there will be no separated discussion on individual nanofiber parameters in the following sections.

3.1.1.2. Nanofiber-polymer matrix interfacial interaction. Electrospun nanofibers intrinsically have higher interfacial area in PNC than their micrometer scale counterpart from conventional fiber industry. This is a great benefit from electrospun nanofibers, but it is not enough in most cases for high performance composite materials. As indicated from studies of conventional FRP composites, strong interfacial interaction between nanofiber and polymer matrix is crucial for high performance PNCs.

Interfacial interaction between electrospun nanofiber and polymer matrix has been investigated in quite a few research papers. For example, Tang et al. compared mechanical properties of poly (vinyl alcohol) (PVA) composite films reinforced by cellulose acetate nanofibrous mats with hydrophobic surface (CANM) or cellulose nanofibrous mats with hydrophilic surface (CNM) [60]. The results indicated that nanofiber surface property had significant influence

on the composites' mechanical properties, with CNM demonstrating a better reinforcing effect than CANM. For a nanofiber content of 40 wt.%, Young's moduli of the PVA composite films with CANM and CNM were 1.1 GPa and 3.2 GPa, respectively, 4.8 and 14 times greater than that of neat PVA film. CNM showed better reinforcing effect due to better interfacial adhesion from its good wettability in the PVA matrix, as well as hydrogen bonding between hydroxyl groups on the CNM nanofiber surface and in the PVA matrix. Mechanical properties of the composite film decreased sharply at large nanofiber loading (> 40 wt.%), a result of the formation of fiber bundles that are subject to fiber slippage and separation. In another research from the same group, Liao et al. investigated how surface properties of electrospun nanofibers affected fiber-matrix interface and mechanical properties of resultant epoxy based PNC films [106]. Specifically, three electrospun nanofibrous mats, cellulose acetate (CA), polyurethane (PU), and cellulose acetate/polyurethane (CAPU), were fabricated aiming at nanofibers with different surface property. It was shown that the rough topography and polar hydroxyl groups on CA nanofiber surface resulted in strong CA/epoxy interfacial adhesion, yielding outstanding mechanical properties of the PNC film, whereas the smooth surface of PU nanofibers led to a weak interfacial adhesion and a low reinforcing effect. The mechanical properties of CAPU/epoxy PNC film fell between those of CA/epoxy and PU/epoxy PNC films. Stone and coworkers developed an all-organic stimuli-responsive PNC film reinforced by electrospun PVA nanofibers [107]. They used a rubbery 1:1 ethylene oxide/epichlorohydrin copolymer (EO-EPI) as matrix and introduced 4 wt.% PVA nanofiber mat into the matrix. The PNC film showed an increase of tensile

storage modulus by 2 orders of magnitude with respect to the neat film. This may be a result from hydrogen bond formation between alcohol groups of PVA nanofibers and ether functional groups of EO-EPI copolymer matrix. Intriguingly such reinforcing effect was negated upon exposure of the composite film to water as PVA nanofibers could plasticize and no longer provide mechanical reinforcement. This research demonstrated new potential of electrospun nanofibers for strengthening stimuli-responsive composites.

3.1.1.2.1. Compatibility between electrospun nanofiber and polymer matrix. Overall, the importance of interfacial interaction between electrospun nanofiber filler and polymer matrix has been recognized by PNC research. Considerable effort has been devoted to improve interfacial interaction in electrospun nanofiber reinforced PNCs by physically or chemically increasing compatibility between nanofibers and polymer matrix.

In order to improve compatibility between certain nanofiber and polymer matrix, the following approaches have been explored in recent years.

(1) Blending

Introducing appropriate components in electrospun nanofibers by blending can improve compatibility between the nanofibers and polymer matrix. In the research of Chen et al. [108], electrospun polylactide (PLA) nanofibers were electrospun to thin poly (ϵ -caprolactone) (PCL) sheets and then integrated into PCL matrix through multi-sheet thermal pressing for reinforcement. The PLA nanofiber reinforced PCL PNC exhibited higher tensile strength and modulus than those of neat PCL and even PCL/PLA blend. Furthermore introducing 10 wt.% PCL to PLA nanofibers through bicomponent electrospinning resulted in ~2 times increase of tensile modulus of the PNC compared to the control PNC with neat PLA nanofibers. Introduction of minor PCL to PLA nanofibers could improve nanofiber-matrix affinity and enhance interfacial adhesion through mutual fusion between the PCL phase on nanofiber surface and the PCL matrix. However, excessive PCL in PLA/PCL nanofibers resulted in decrease of both tensile strength and modulus due to degraded strength of the PLA/PCL nanofibers. In the experimental range, strength of the PNC increased with the bicomponent nanofiber content.

(2) Core-shell structure

Core-shell type electrospun nanofibers have shown their effectiveness in reinforcing PNCs by introducing a nanofiber shell that is compatible with the polymer matrix [105,109]. In a recent research of Cheng et al. [110], PAN core-PMMA shell nanofibers containing NaF were prepared by coaxial-electrospinning and used as reinforcing agent for bis-GMA/TEGDMA dental resin. Owing to the compatibility between the PMMA shell and the resin matrix, such PAN-PMMA core-shell nanofibers led to enhancement in flexural strength and modulus of the resultant composite compared to PAN nanofibers. It was also found that the reinforcing effect of the core-shell nanofibers varied with PMMA shell thickness and that thinner shells promised an improved reinforcing effect. The PMMA/PAAm double walled hollow fibers developed by Zanjani et al. exhibited better reinforcing effect in epoxy PNC than PS/PAAm double walled hollow fibers because of good compatibility between PMMA shell and epoxy matrix [101]. As depicted in Fig. 8, PMMA chains in outer shell of the PMMA/PAAm hollow nanofibers can be partially dissolved and then interpenetrate into epoxy matrix. Enhanced entanglement of PMMA chains with cross-linked epoxy network led to improved load transfer between electrospun nanofibers and epoxy matrix.

(3) Graft copolymer

Graft copolymers have been repeatedly demonstrated as compatibilizers in polymer blend materials. Electrospun graft copolymer nanofibers can thus serve as efficient reinforcing agent

in PNCs due to compatibility improvement with corresponding polymer matrix.

Poly(dimethyl siloxane) (PDMS) is a weak material and usually filled with high level particulate fillers to improve its mechanical properties. Swart et al. synthesized a graft copolymer nanofiber filler, poly(methyl methacrylate)-graft-poly(dimethyl siloxane) (PMMA-g-PDMS), through electrospinning and employed it to reinforce PDMS matrix using a layer-by-layer liquid impregnation method and subsequent thermal curing [111]. The PMMA-g-PDMS nanofibers showed enhanced compatibility with silicone matrix as well as excellent dispersion throughout the matrix, yielding a remarkable reinforcing effect. The PNC with PMMA-g-PDMS nanofibers containing 3.9 mol% grafted PDMS was both stronger and stiffer than the unfilled PDMS matrix along with a greater extensibility and toughness. Specifically, the corresponding strength, extensibility, toughness, and stiffness increased by 276%, 171%, 1164%, and 1137%, respectively. Likewise, Bayley et al. prepared electrospun polyacrylonitrile-graft-poly(dimethyl siloxane) (PAN-g-PDMS) nanofibrous mat and used it to reinforce PDMS (silicone) matrix [112]. PAN does not have a strong attractive interaction with silicone matrix due to their chemical structure difference. Experimental results revealed that the PDMS part in PAN-g-PDMS could provide compatibility between the reinforcing nanofibers and silicone matrix. Compared to the unfilled silicone, non-woven PAN-g-PDMS nanofiber mat filled silicone composite proved to be superior in terms of extensibility (4.7-fold increase) and toughness (31-fold increase) while aligned PAN-g-PDMS nanofiber mat filled silicone composite exhibited dramatically larger stiffness (11-fold increase).

3.1.1.2.2. Nanofiber surface modification. To improve nanofiber filler-polymer matrix interfacial interaction, most research work relied on non-covalent interaction such as hydrogen bonding and van der Waals force between chosen matrix and as-prepared nanofiber fillers. Considering that covalent bond is far stronger than non-covalent bond, a promising new concept is to tailor nanofiber surface and introduce chemical reaction between nanofiber surface and polymer matrix so that the resultant PNCs could substantially benefit from stronger interfacial bonding. As the first attempt of this concept, Özden et al. electrospun poly(styrene-co-glycidyl methacrylate) (P(St-co-GMA)) copolymer followed by spraying ethylenediamine (EDA, supplementary cross-linking agent) on nanofiber surface. This surface functionalized copolymer nanofiber P(St-co-GMA)/EDA was employed as reinforcing agent for epoxy [113]. Owing to the epoxide ring-rich surface from GMA part, such P(St-co-GMA)/EDA nanofibers was capable of being self-crosslinked as well as bonding with the epoxy matrix through interfacial reactions. Consequently, incorporation of 2 wt.% P(St-co-GMA)/EDA nanofibers led to remarkably improved storage modulus of the resultant composite, about 10 and 2.5 times higher than that of neat and P(St-co-GMA) nanofiber-reinforced epoxy, respectively, even above the glass transition temperature of polystyrene. Guo and coworkers prepared a core-shell type nanofiber with rubbery styrene-butadiene-styrene (SBS) block copolymer as core and PAN as hard shell via co-axial electrospinning and used it to improve toughness of epoxy resin [114]. The surface of the nanofibers was further aminated by reacting PAN shell with diethylenetriamine to improve interfacial interaction between the nanofibers and epoxy matrix. Such surface-modified nanofibers showed higher toughening effect than control fillers including aminated PAN powder and aminated PAN nanofibers, as evidenced by Charpy impact energy (Fig. 9). Incorporation of 4 wt.% aminated SBS/PAN core-shell nanofibers increased the Charpy impact energy of corresponding epoxy PNC by 150% in comparison with that of neat epoxy resin. The high impact resistance was attributed to SBS rubbery core of the nanofibers that could absorb and dissipate impact energy as well as covalent bonding

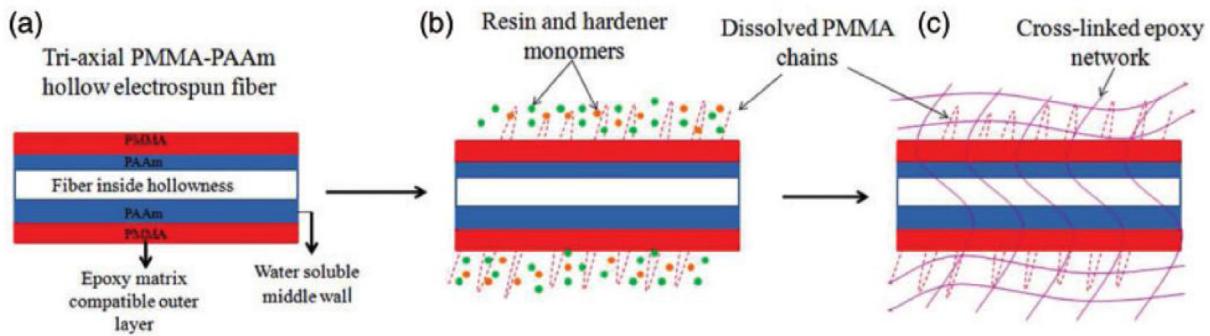


Fig. 8. Schematic representation of interpenetrating polymer network structure in PMMA/PAAm double walled hollow nanofiber reinforced epoxy composite: (a) PMMA/PAAm double walled triaxial hollow fiber; (b) partial dissolution of PMMA shell into epoxy resin and hardener system; (c) partial interpenetrating polymer network structure. [101]. Copyright 2015. Reproduced with permission from SAGE Publications.

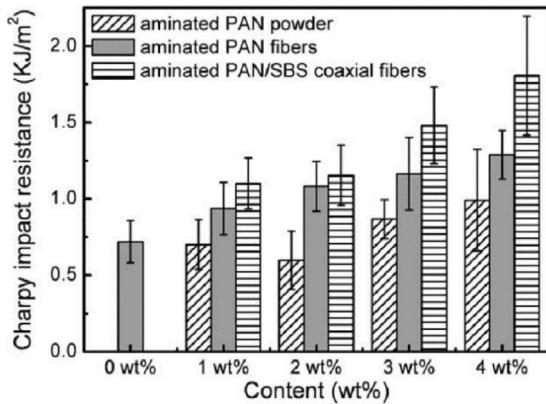


Fig. 9. Effect of aminated SBS/PAN core-shell nanofibers, aminated PAN nanofibers and aminated PAN powder on Charpy impact strength of corresponding filler reinforced epoxy composite. [114]. Copyright 2014. Reproduced with permission from John Wiley & Sons Inc.

between aminated nanofiber and epoxy matrix that brought about effective load transfer from the epoxy matrix to the nanofiber filler. Oh et al. [115] developed a meta-aramid/epoxy core-shell electrospun nanofiber to reinforce an epoxy adhesive. The low molecular weight epoxy shell is capable of covalently bonding nanofibers and matrix. Although to date there are only few research efforts aiming at introduction of covalent bonding between electrospun polymer nanofiber filler and polymer matrix, more examples are available in electrospun glass, ceramic or carbon nanofiber based PNCs where surface of electrospun nanofiber is tailored and chemical reaction is introduced between nanofiber surface and polymer matrix, as shown in following sections.

3.1.1.3. Composite processing. It is well known that processing influences morphological characteristics of PNCs, such as interfacial features, filler dispersion and orientation in matrix [116,117], which in turn affects the PNC mechanical performance. Fabrication of electrospun nanofiber reinforced PNCs is done mainly by impregnating electrospun nanofibrous mat with the polymer matrix through solution impregnation/casting or hot pressing. Although electrospun nanofibers are indeed effective in reinforcing PNCs, electrospun nanofiber based PNCs that are prepared via solution casting or hot pressing often suffer from poor nanofiber impregnation and fail to create a coherent interface for effective reinforcement. That motivates research interest in optimizing manufacturing process of electrospun nanofiber reinforced PNCs.

Stachewicz et al. optimized viscosity of polymer matrix solution for complete coverage of porous electrospun nanofibrous strips in a typical solution impregnation process based on Washburn theory

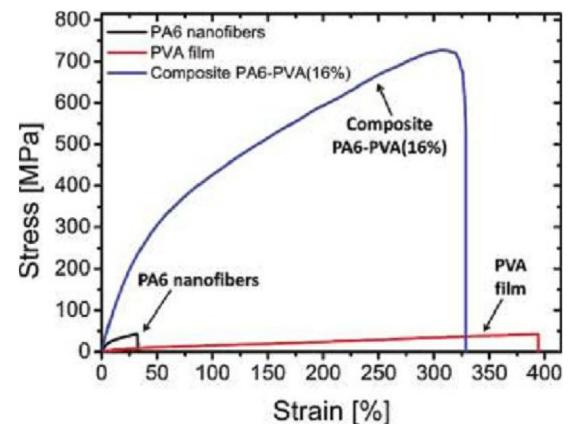


Fig. 10. Tensile stress-strain curves of electrospun nylon-6 nanofiber mat, PVA film, and nylon-6 nanofiber mat reinforced PVA composite prepared from 16 wt.% PVA solution. [118]. Copyright 2012. Reproduced with permission from the American Chemical Society.

[118]. This idea arose from the consideration that improper viscosity could lead to poor solution impregnation within electrospun nanofiber mat, resulting in voids in the final PNC. These voids may bring about poor load transfer and more stress-concentration sites in PNC under external loading, and eventually cause poor mechanical performance. Void-free nylon-6 nanofiber mat reinforced PVA PNC was obtained from a 16 wt.% PVA solution and the highest failure stress was observed therefrom (Fig. 10).

Two different wetting methods, i.e., dip coating (method 1) and liquid pass-through (method 2), were used by Jiang et al. to impregnate nylon-6 electrospun nanofiber mats within a melamine-formaldehyde (MF) matrix, followed by hot-press process [119]. It was found that wetting of nylon-6 nanofibers by passing through a solution of MF resin (method 2) was more effective than the immersion procedure (method 1). The resultant composite nanofibers from method 2 showed a core-shell morphology and the entire nylon-6 nanofibrous mat was completely wetted without cracks. A significant improvement in mechanical properties was observed. In another project, Jiang et al. developed a novel fabrication method that consisted of consecutive solution casting, electrospinning, and film stacking for a layer-by-layer fabrication of nylon-6 nanofiber reinforced thermoplastic polyurethane (TPU) composite films [120]. Unlike the composite fabrication approach mentioned above in which as-prepared dry nanofibrous mats were immersed in a matrix, in this case nylon-6 nanofibers (ca. 150–300 nm diameter) were directly electrospun onto wet TPU/DMF solution layer on a glass slide in a layer-by-layer way. A better distribution and wetting of reinforcing nanofibers

within TPU matrix was achieved and thereby a coherent interface between nanofiber and matrix was formed. Thus a remarkable reinforcement in the mechanical performance of TPU was observed. For example, introducing 1.7 wt.% nylon-6 nanofibers through this layer-by-layer way could double tensile strength, Young's modulus, and toughness of the PNC at one time.

Based on a similar layer-by-layer concept, Jang et al. developed a technique to fabricate 3D nanofiber-reinforced alginate hydrogel composites [121]. A coaxial electrospinning apparatus was employed to generate ethanol-treated PCL nanofibers and evenly deposit them on a thin layer of alginate/CaCO₃ mixture solution on collector. The mixture solution was reapplied and this process was repeated in a layer-by-layer manner until the desired nanofiber content was reached (Fig. 11). Finally a crosslinking initiator was added and a tight gel network was created. Enhanced compatibility between the nanofiber reinforcing agent and the hydrogel matrix through this layer-by-layer processing led to great improvement in compressive strength (up to 221%) and stiffness (up to 434%) of the final hydrogel composite compared to those of pure hydrogel, respectively. This innovative PNC processing technique not only satisfied nanofibers/hydrogel matrix interfacial interaction but also achieved high processing efficiency.

Karimi et al. employed a hybrid electrospinning-electrospraying approach to fabricate uniaxially aligned PVA nanofiber reinforced epoxy composites [73,122]. In this process, an aligned PVA nanofiber mat was initially prepared using a proprietary gap spinning and field control method. Epoxy/harderner mixture was electrosprayed onto the PVA nanofiber mat followed by vacuum consolidation. Such novel hybrid processing could increase fiber-matrix interfacial contact area and thereby led to an enhanced interfacial adhesion. This was confirmed by morphology of fracture surface from corresponding composite films. The composite from hybrid electrospin/spray processing showed more indistinct epoxy/fiber interface and rougher fracture surface when compared with the composite from liquid impregnation. The novel composite processing approach, hybrid electrospinning-electrospraying, promises mechanical improvement of resultant composite. For example, incorporation of 0.13 vol.% aligned PVA nanofiber mat resulted in enhancement in tensile strength of the composite by 472% and 695% compared to the liquid impregnated composite and unreinforced matrix, respectively. In addition, such hybrid electrospinning-electrospraying approach has great potential for scale-up and automated processing. This is particularly exciting in the context that electrospun nanofiber mat seems to be incompatible with large scale conventional liquid formulation molding.

Electrospun polymer nanofibers have not only been used as reinforcing/toughening agent in PNCs but also they have been employed as skeleton to develop smart materials with self-healing [30] or shape memory [123,124] functionalities. Core-shell electrospun nanofibers can be embedded into polymer matrix as a novel carrier of self-healing agent and their fibrous network structure provides an efficient conduit for healing processes. Self-healing PNCs hardly exhibit statical mechanical enhancement [125] and a decrease of mechanical strength [126] is even observed in many cases, but their mechanical performance under fatigue loading or damaging condition is indeed improved considerably when compared to neat polymers [125,127–130], promising higher structural reliability and longer service life.

3.1.2. Polymer based composite nanofiber reinforced PNC

As indicated earlier in this review, the mechanical performance of FRP composites critically depends on the mechanical property of fiber fillers. Polymers, however, is not a very strong material. Incorporation of stronger nanoscale fillers into electrospun polymer nanofibers has been carried out to boost their mechanical strength [131–134]. A variety of nanofillers such as carbon nanofibers

(CNFs), graphene, nano TiO₂, nano clays, and carbon nanotube (CNTs) have been included in electrospun polymer nanofibers in the quest for better reinforcement in PNCs.

Zhang and coworkers integrated vapor-grown carbon nanofibers (VGCNF) with polyetherketone cardo (PEK-C) nanofibers through bicomponent electrospinning [135]. The PEK-C/VGCNF composite nanofibers were used to toughen and reinforce a triglycidyl amino phenol epoxy resin. Strong and tough PNC was acquired with addition of 5 wt.% PEK-C/VGCNF nanofibers to the epoxy matrix. Compared to PEK-C powder and PEK-C nanofibers, only PEK-C/VGCNF composite nanofibers demonstrated a synergistic effect on the mechanical properties of the reinforced epoxy PNC, i.e., considerable increases in flexural strength, toughness and hardness were observed without noticeable loss in elastic modulus. Similar results are reported with CNF/PVA nanofibers [136].

Li et al. used graphene-incorporated electrospun nylon-6 nanofibers (Gr/nylon-6) as reinforcing agent for PMMA based transparent PNCs [137]. They first used a facile self-blending co-electrospinning setup shown schematically in Fig. 12A to produce hybrid Gr/nylon-6 + PMMA as-electrospun nanofiber mats. The hybrid nanofibrous mats were cut into pieces and stacked layer-by-layer followed by hot press molding to melt electrospun PMMA fibers and make PMMA based PNC film (Fig. 12B). This method can address not only aggregation issues of graphene in composite nanofibers but also poor dispersion of nanofibers throughout polymer matrix. The resulting Gr/nylon-6 nanofiber reinforced PMMA PNC exhibited a remarkable enhancement in overall mechanical properties at Gr loading of only 0.01 wt.%, i.e., nearly 56%, 113% and 250%, respectively, improvement in tensile strength, Young's modulus, and fracture toughness were achieved. Sisti et al. embedded electrospun PLA/graphene composite nanofibers containing 1.3 wt.% of graphene as reinforcing agent in poly(butylene succinate) (PBS) matrix through hot press molding [75]. Experimental results showed that incorporation of 0.8 wt.% the composite nanofibers could increase tensile strength and elongation at break of the obtained composite by 27% and 47%, respectively, when compared to PBS matrix. These improvements were only 16% and 26%, respectively, for PLA nanofiber reinforced composites. Based on fracture surface analysis, presence of nanofiber mats caused crack-stop and crack-deviation, which contributed to toughening effect.

Neppalli et al. used electrospun PS/TiO₂ nanoparticle composite nanofibers to reinforce a biodegradable poly (butylene succinate-co-adipate) (PBSA) composite [138]. The PS/TiO₂ composite nanofibers demonstrated tunable potential in reinforcing PBSA. The TiO₂ nanoparticles could alter crystallization kinetics of the PBSA matrix and affect interfacial adhesion between the composite nanofibers and the matrix. With addition of 1.5 wt.% PS/TiO₂ (95:5 wt.%) composite nanofibers, the reinforced PBSA PNC demonstrated higher Young modulus (542 MPa) and lower brittleness (4.9×10^9 Pa⁻¹) than those of neat PS nanofiber reinforced counterpart, which were 345 MPa and 9.0×10^9 Pa⁻¹, respectively. Marega et al. investigated the reinforcing effect of electrospun polyhydroxybutyrate (PHB) nanofibers containing two different nano clays, i.e., cationic Cloisite (CL) and anionic Perkalite (PK) [139]. It was found that PHB/CL nanofiber reinforced PCL composites exhibited higher modulus, tensile strength and strain at break than those of PHB/PK nanofiber filled ones as well as those of the PCL matrix.

Aside from the aforementioned nanofillers, carbon nanotubes (CNTs) have drawn a good deal of research interests in strengthening electrospun polymer nanofibers. This is mainly because incorporation of CNTs into electrospun polymer nanofibers dramatically increases their tensile strength [132]. To date a variety of factors have been investigated, including CNT content in composite nanofibers [112,140–142], proportion of composite nanofibers in polymer matrix [143–145], orientation of composite nanofiber

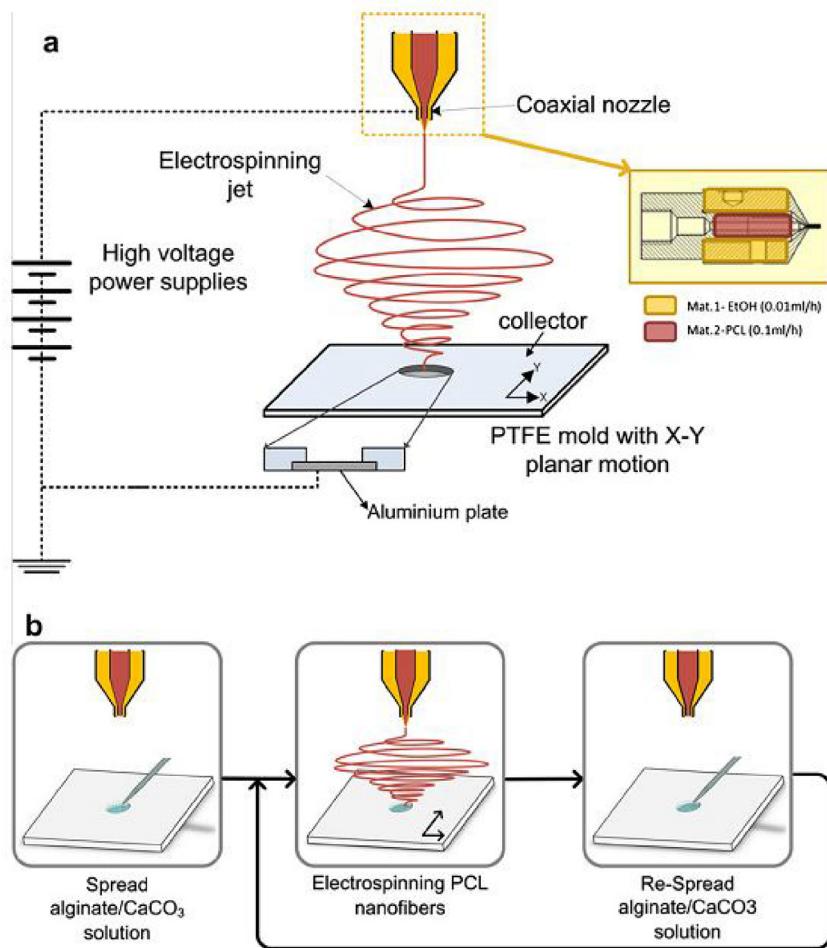


Fig. 11. Schematic illustration of the electrospinning system equipped with coaxial nozzle (a) and fabrication process of the PCL nanofiber reinforced alginate hydrogel composites (b). [121]. Copyright 2012. Reproduced with permission from Elsevier Ltd.

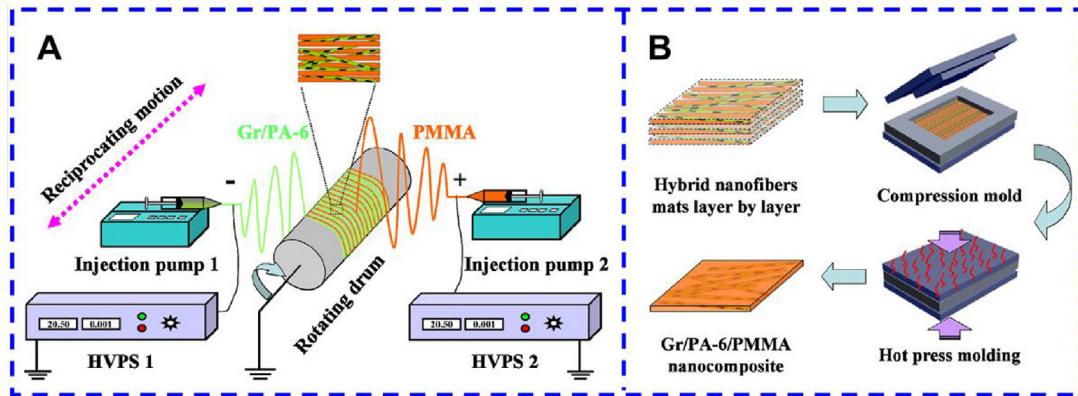


Fig. 12. Schematic diagram of preparation of hybrid Gr/PA-6 + PMMA nanofibrous mats via self-blending co-electrospinning (A) and fabrication of transparent PMMA-based composite reinforced with aligned electrospun Gr/PA-6 nanofibers through hot press molding (B). [137]. Copyright 2013. Reproduced with permission from Elsevier Ltd.

[112,146], as well as interfacial chemistry [147], on mechanical properties of the resultant PNCs.

The tensile properties of recently available CNT-containing polymer composite nanofiber reinforced PNCs are summarized in Table 1, along with those of neat polymer nanofiber filled PNCs as well as corresponding neat polymer matrices. Integration of CNTs in electrospun polymer nanofibers definitely enables better reinforcing effect in resultant PNCs and nanofiber alignment could further enhance their reinforcing performance in PNCs. Generally speak-

ing tensile strength and Young's modulus of corresponding PNCs increase with CNT content at low CNT loading level in nanofibers. At high CNT loading level, however, the reinforcing effect of CNT declined due to agglomeration of CNTs. In addition, electrospun polymer nanofibers containing both multi-walled CNTs (MWCNT) and nano-diamond (ND) particles demonstrated positive reinforcing effect [148]. ND/MWCNT/poly(azo-pyridine)/polyamide composite nanofibers showed higher reinforcing effect than those

Table 1

Tensile properties of electrospun polymer/CNTs composite nanofiber reinforced polymer composites.

Matrix	Reinforcing Nanofibers	Fiber Orientation	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)	Ref.
Silicone	None	–	0.3 ± 0.17	31 ± 17	47 ± 4 ($\times 10^{-6}$)	[112]
	PAN-g-PDMS ^a	Random	1.7 ± 0.06	137 ± 18	190 ± 14 ($\times 10^{-6}$)	
		Aligned	2.9 ± 0.58	13 ± 4	758 ± 19 ($\times 10^{-6}$)	
	8 wt.% CNT in PAN-g-PDMS ^a	Random	3.4 ± 0.32	127 ± 17	322 ± 9 ($\times 10^{-6}$)	
		Aligned	3.3 ± 0.77	23 ± 3	510 ± 13 ($\times 10^{-6}$)	
	16 wt.% CNT in PAN-g-PDMS ^a	Random	1.4 ± 0.27	29 ± 1	602 ± 1 ($\times 10^{-6}$)	
		Aligned	1.0 ± 0.23	10 ± 1	815 ± 20 ($\times 10^{-6}$)	
	32 wt.% CNT in PAN-g-PDMS ^a	Random	1.3 ± 0.14	45 ± 1	328 ± 1 ($\times 10^{-6}$)	
		Aligned	1.6 ± 0.46	17 ± 3	395 ± 1 ($\times 10^{-6}$)	
	0.1 wt.% CNT in PU	Random	12.7 ± 2	710 ± 40	4.2 ± 1.3 ($\times 10^{-3}$)	
Silicone	None	–	3.9 ± 0.7	2063 ± 518	0.29 ± 0.11 ($\times 10^{-3}$)	[149]
	Polyurethane (PU)	Random	10.5 ± 1.2	700 ± 50	3.7 ± 1.1 ($\times 10^{-3}$)	
	1 wt.% CNT in PI	Aligned	174.1 ± 10.4	57.2 ± 9.6	1.31 ± 0.12	
	2 wt.% CNT in PI	Aligned	176.5 ± 10.2	79.3 ± 8.6	1.23 ± 0.013	
	3.5 wt.% CNT in PI	Aligned	210.4 ± 14.6	80.8 ± 9.4	1.26 ± 0.13	
	5 wt.% CNT in PI	Aligned	169.2 ± 15.1	56.4 ± 10.3	1.34 ± 0.15	
Polyimide (PI)	None	–	88.4 ± 17.6	39.3 ± 9.2	1.29 ± 0.15	[141]
	PI	Aligned	174.1 ± 10.4	57.2 ± 9.6	1.31 ± 0.12	
	1 wt.% CNT in PI	Aligned	176.5 ± 10.2	79.3 ± 8.6	1.23 ± 0.013	
	3.5 wt.% CNT in PI	Aligned	210.4 ± 14.6	80.8 ± 9.4	1.26 ± 0.13	
Epoxy	None	–	52.1 ± 1.8	2.1 ± 0.32	3.38 ± 0.05	[142]
	Thermoplastic polyurethane (TPU)	Random	56.6 ± 2.7	3.02 ± 0.12	3.0 ± 0.75	
	1 wt.% CNT in TPU	Random	62.2 ± 2.3	2.8 ± 0.55	3.26 ± 0.09	
	3 wt.% CNT in TPU	Random	67.3 ± 1.9	2.5 ± 0.22	3.53 ± 0.08	
Epoxy	PAPBI/CNT-PA ^b	Aligned	347.9	28.1	16.6	[145]
	1 wt.% in PNC	Aligned	349.4	28.8	18.9	
	PAPBI/CNT-PA	Aligned	351.1	29.1	20.2	
	2 wt.% in PNC	Aligned	349.7	30.5	22.3	
	PAPBI/CNT-PA/PANI ^b	Aligned	352.3	31.6	24.2	
	1 wt.% in PNC	Aligned	366.8	32.7	27.6	
	PAPBI/CNT-PA/PANI	Aligned	346	27.6	12.8	
	2 wt.% in PNC	Aligned	349	27.9	13.9	
	PAPBI/CNT ^c	Aligned	354	28.1	14.7	
PAPBI	3 wt.% in PNC	Aligned	361	28.3	16.2	[143]
	PAPBI/CNT ^c	Aligned	374	28.5	19.9	
	1 wt.% in PNC	Aligned	393	28.9	20.2	
	PAPBI/CNT ^c	Aligned	417	29.3	22.1	
	2 wt.% in PNC	Aligned	346	1.6	0.5	
	3 wt.% in PNC	Aligned	42.1	4.1	8	
PMMA	None	–	33.8	3.9	9	[144]
	CNT-PTA-Si-Ti ^d	Aligned	42.9	3.7	11	
	0.1 wt.% in PNC	Aligned	43.9	3.6	15	
	CNT-PTA-Si-Ti ^d	Aligned	44.5	27.8	18.2	
	0.2 wt.% in PNC	Aligned	228.2	28.7	18.3	
	CNT-PTA-Si-Ti ^d	Aligned	236.7	28.3	18.6	
	0.5 wt.% in PNC	Aligned	245.9	29.4	19.3	
	CNT-PTA-Si-Ti ^d	Aligned	270.6	31.7	18.8	
	1 wt.% in PNC	Aligned	289.1	32.1	19.5	
PANPI ^e	PANPI/CNT ^c	Aligned	304.6	34.3	20.9	[150]
	1 wt.% in PNC	Aligned	212.2	27.8	18.2	
	PANPI 1 wt.% in PNC	Aligned	228.2	28.7	18.3	
	PANPI 2 wt.% in PNC	Aligned	236.7	28.3	18.6	
	PANPI 3 wt.% in PNC	Aligned	245.9	29.4	19.3	
	PANPI/CNT ^c	Aligned	270.6	31.7	18.8	

^a PDMS content in PAN-g-PDMS copolymer nanofiber is 16.3 wt.%.^b PAPBI: poly(azo-pyridine-benzophenone-imide); CNT-PA: polyamide-grafted-carbon nanotube; PANI: polyaniline; for PAPBI/CNT-PA, PAPBI: CNT-PA = 5: 1 (weight); for PAPBI/CNT-PA/PANI, PAPBI: CNT-PA: PANI = 5: 1 (weight).^c CNT content in composite nanofibers: 5 wt.%.^d CNT-PTA-Si-Ti: poly(thiophene amide)-silica-titania-grafted CNT; CNT-Si-Ti: PTA = 1: 5 (weight).^e PANPI: poly(azo-naphthyl-imide).

without ND particles in a bisphenol A diglycidyl ether (DGEBA) matrix.

A new concept was practiced recently to get better reinforcing effect from electrospun polymer based composite nanofibers. This concept is to create composites nanofibers with highly rough surface through additional nanofiber architecture. For example, Meng et al. designed an innovative thorn-like micro-/nanofibers consisting of polyarylene ether nitriles (PEN) "stems" and iron phthalocyanine (FePc) "thorns" (Fig. 13), to reinforce and toughen epoxy resin [151,152]. The hierarchical thorn-like nanostructure enhanced fiber/matrix interfacial contact area and strengthened physical-interlocking at nanofiber/matrix interface [153,154]. Specifically, a mixture solution containing PEN and FePc was prepared and then electrospun into fiber with PEN (core)-FePc (shell) structure due to viscosity difference of the two components. After heat treatment (140 °C – 230 °C), the FePc shell could self-assemble into thorns-like structure with controllable thorn length. Owing to these "thorns" on the nanofiber surface, such micro-/nanofibers could interlock and entangle with surrounding matrix when they were integrated into epoxy resin, resulting in a strong interfacial adhesion between the composite nanofibers and the epoxy matrix. For the epoxy resin with 4 wt.% thorn-like nanofibers, its flexural strength and modulus increased by 36% and 28%, respectively, compared to the neat epoxy resin, which are significantly higher than the case without thorn structure.

3.1.3. Glass/ceramic nanofiber reinforced PNC

Electrospinning is a versatile technique that has manufacturing capacity beyond polymer nanofibers. Our recent studies have revealed that glass (SiO_2) and ceramic (e.g., TiO_2 , ZnO , and TiC) nanofibers with diameters of a few hundreds of nanometers can be prepared through electrospinning a spin dope containing glass/ceramic precursor followed by sol-gel processing and subsequent pyrolysis or carbothermal reduction at elevated temperature [51,53,54,155]. Other ceramic nanofibers through electrospinning including Al_2O_3 , BN, SnO_2 , have also been reported [156–158]. So far these inorganic electrospun nanofibers have been developed with primary goal to explore their electronic, energy, and/or catalytic applications [159]. A noteworthy fact is that these inorganic nanofibers may possess outstanding mechanical properties like their bulk counterparts and therefore may be employed to make high performance electrospun nanofiber reinforced PNCs [160]. Very limited research endeavors, however, have been devoted to electrospun glass or ceramic nanofiber reinforced PNCs.

Among various electrospun inorganic nanofibers, glass (amorphous SiO_2) nanofibers are of particular interest as reinforcing filler in PNCs. There are several reasons: (1) precursors of SiO_2 (such as tetraethyl orthosilicate, TEOS) are well-studied and readily available; (2) the chemical inertness of SiO_2 renders resultant PNCs being useful in a variety of applications like dental and biomedical uses; (3) since SiO_2 has higher tensile strength and modulus than most polymers both in bulk and nanoscale, it is possible to produce a PNC with even higher strength and stiffness, e.g., glass nanowire with diameter of 100 nm has a tensile strength of 21 GPa and elastic modulus of 76.6 GPa [161,162]. Particularly glass nanofiber/nanowire can even show ductile feature, which is highly desirable for developing tougher PNCs [163,164]. Fong et al. dedicated their effort to reinforce Bis-GMA/TEGDMA dental composites with electrospun glass nanofibers (EGNFs) [165]. EGNFs were not only able to reinforce the dental composite but also help to reach translucent appearance of the dental composite, important for aesthetic purpose. In their study, EGNFs with diameters of approximately 500 nm were prepared through electrospinning a solution composed of TEOS (SiO_2 precursor) and poly (vinyl pyrrolidone) (PVP, a carrying polymer for good nanofiber formation) followed by pyrolysis at high temperature (800 °C). The continuous EGNFs were

subjected to ultrasonic vibration and converted to short glass fibers with the overall fiber morphology being retained. Prior to incorporating them into dental resin, EGNFs were also surface-silanized in order to improve nanofiber-matrix interfacial adhesion. Their results indicated that 7.5 wt.% substitution of conventional dental filler, i.e., glass powder, with EGNFs in Bis-GMA/TEGDMA dental composite brought about considerable improvement in flexural strength, modulus, and work of fracture by as much as 44%, 29%, and 66%, respectively. Likewise Cai et al. [166] incorporated shortened and surface-silanized EGNFs (diameter: 300–500 nm, length: 5–10 μm , amount: 5 or 10 wt.%) into Bis-GMA/TEGDMA dental composite containing SiO_2 microparticles (60 wt.%). Owing to high aspect ratio, well-dispersed EGNFs could overlap with one another and form a 3-D geometrical percolation structure at high fraction. It was such 3-D nanofiber network that acted as a stiff skeleton in the dental composite and improved its overall performance including 36% and 164% increase in flexural strength and modulus, respectively, as well as decreased polymerization shrinkage and improved wear resistance.

Fong and Zhang also extended the reinforcing role of short EGNFs (Fig. 14) to epoxy resin (SC-15A) [63]. Effects of EGNFs' surface modification by two types of silane coupling agents with respective amine and epoxy end groups as well as mass fraction of EGNFs in PNCs on overall mechanical properties of corresponding epoxy PNCs were carefully studied. It was found that EGNFs (ca. 400 nm diameter) remarkably outperformed conventional glass microfibers (ca. 10 μm diameter) in both tensile and impact tests and yielded simultaneous enhancement in strength, stiffness, and toughness of the epoxy based PNCs at small mass fractions of 0.5 wt.% and 1 wt.%. Tensile strength, Young's modulus, work of fracture, and impact strength of the EGNF reinforced epoxy composite were increased by up to 40%, 201%, 67%, and 363%, respectively. Saline treatment played an important role in mechanical performance improvement. EGNFs with epoxy end groups had better toughening effect while the one with amine end groups exhibited better reinforcing effect. To further explicate the merit of EGNFs as brilliant reinforcing/toughening agent, in a more recent research, Zhang and coworkers conducted a side-by-side direct comparison of nanoscale glass filler reinforced epoxy composites on the basis of EGNFs (with diameter of ~300 nm and length about a few tens of μm) and glass nanoparticles (GNPs, with diameter of ~20 nm) [167]. Within the surveyed filler loading scope (≤ 0.5 wt.%), EGNFs outperformed GNPs in terms of reinforcing and toughening effect. Surface functionalization brought in further mechanical improvement. Incorporation of 0.5 wt.% amino-functionalized EGNFs simultaneously increased tensile strength, elongation at break, and work of fracture of the resultant epoxy PNC by ~20%, ~20%, and ~50%, respectively, along with negligible change of Young's modulus. Given the much lower specific surface area of EGNFs than that of GNPs, the better performance of EGNFs was ascribed to larger aspect ratio (shape factor) that aroused "fiber bridging" mechanism as well as crack deflection, not shared by GNPs counterparts. It is noteworthy that Zhang et al. verified that there was no pseudo percolation in their EGNF reinforced PNC due to ultra-low filler loading, which is less than the critical volume fraction even for the case of pseudo percolation [72]. This result differs from that obtained by Cai and coworkers [166], where mechanical percolation occurs at high filler loading. The reinforcing/toughening mechanisms of EGNFs in PNCs, however, remain to be further understood in order to take full advantages of EGNFs in designing next-generation PNC materials.

In another study, Qin et al. prepared two other types of electrospun ceramic nanofibers, i.e., ZrO_2 nanofibers as well as ZrO_2 nanofibers with surface attached amorphous SiO_2 nanoparticles ($\text{SiO}_2@\text{ZrO}_2$) [168,169], through an electrospinning and/or an following sol-gel processing route. The obtained ZrO_2 nanofibers and

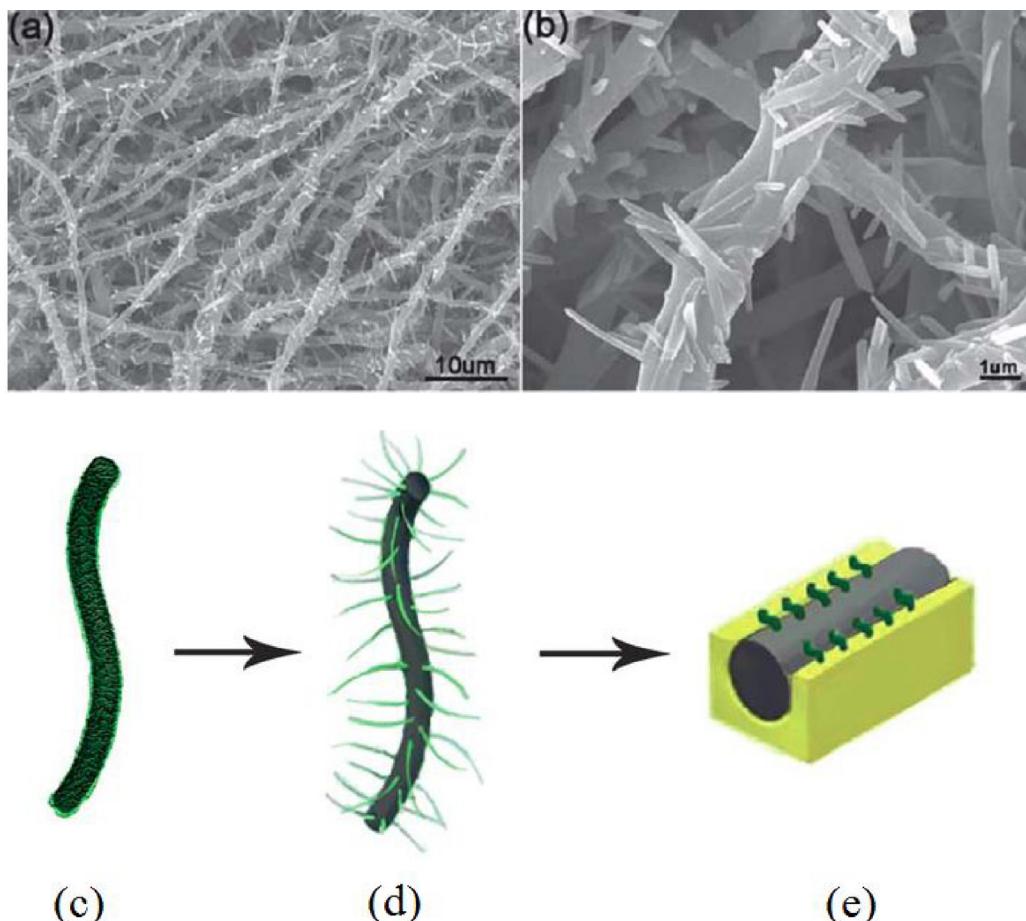


Fig. 13. PEN/FePc thorn-like composite micro-/nanofibers (treated at 180 °C for 4 h). Top: SEM images at low (a) and high (b) magnification; Bottom: Schematic representation of PEN/FePc micro-/nanofiber without treatment (c); thorn-like micro-/nanofibers (d); “thorns” interlocking surrounding epoxy resin (e). [151]. Copyright 2011. Reproduced with permission from the Royal Society of Chemistry.

$\text{SiO}_2@\text{ZrO}_2$ composite nanofibers were subsequently integrated into cyanate ester resin (CE, 2,2'-Bis(4-cyanatophenyl) isopropylidene) to make CE based PNC. The $\text{SiO}_2@\text{ZrO}_2$ reinforced CE PNC exhibited much higher storage moduli and glass transition temperature than ZrO_2 nanofiber reinforced CE PNC. This is a result from better interfacial adhesion between $\text{SiO}_2@\text{ZrO}_2$ and CE matrix caused by unique structure of $\text{SiO}_2@\text{ZrO}_2$ nanofibers. Specifically SiO_2 nanoparticles on ZrO_2 nanofiber surface provided physical interlocking between the matrix and $\text{SiO}_2@\text{ZrO}_2$ nanofibers while active –OH groups on surface of SiO_2 nanoparticles also brought chemical bonding with CE matrix. This was evidenced by SEM images of cross-section of ZrO_2/CE PNC and $\text{SiO}_2@\text{ZrO}_2/\text{CE}$ PNC (Fig. 15). In ZrO_2/CE PNC, there were some interspace between CE matrix and ZrO_2 nanofibers; meanwhile some ZrO_2 fibers were pulled-out from CE matrix and showed smooth surface, clearly suggesting lack of interfacial adhesion. This phenomenon did not appear in $\text{SiO}_2@\text{ZrO}_2/\text{CE}$ PNC. On the contrary, $\text{SiO}_2@\text{ZrO}_2$ nanofibers were closely surrounded by CE resin, indicating good interfacial adhesion.

3.1.4. Carbon nanofiber reinforced PNC

Carbon fiber possesses the highest specific strength and modulus among all reinforcing fibrous materials and therefore has been long used in FRP composite for a wide range of applications such as aircraft, vehicles, sports utilities, and so forth. The mechanical performance of carbon FRP composite is largely determined by strength and modulus of the reinforcing carbon fiber

inside. Although theoretical tensile strength of carbon fiber is over 180 GPa, the strongest carbon fiber that is produced today has a tensile strength of merely ~7 GPa (T1000®). It has been well demonstrated that the mechanical strength of carbon fiber increases with decrease of its diameter. The corresponding mechanism may vary, but is usually attributed to improvement in carbon structure and orientation, especially the reduction in quantity of defects as fiber size decreases. Industrial development in past decades has reduced diameter of carbon fiber to ~5 μm (T1000®), leading to remarkable improvement in its tensile strength. Nevertheless conventional spinning techniques in current fiber industry are generally not able to produce carbon precursor fibers with diameters that are orders of magnitude smaller than 10 μm, restricting further fiber size reduction. Undoubtedly electrospinning opens a door to make significantly smaller carbon fibers and thereby has great potential in developing carbon fibers with superior mechanical performance.

Similar to conventional carbon fiber production, polyacrylonitrile (PAN) is the most often used precursor polymer for carbon nanofibers from electrospinning. Electrospun PAN nanofibers are first stabilized under tension through a controlled heating procedure normally in air between 200 and 300 °C to convert PAN to a ladder compound, which stabilizes and enables these fibers to undergo further processing at higher temperature. Stabilized PAN nanofibers are subsequently converted to carbon nanofibers in a process of carbonization that involves heat treatment in an inert atmosphere up to 1500 °C. During this process, almost all elements

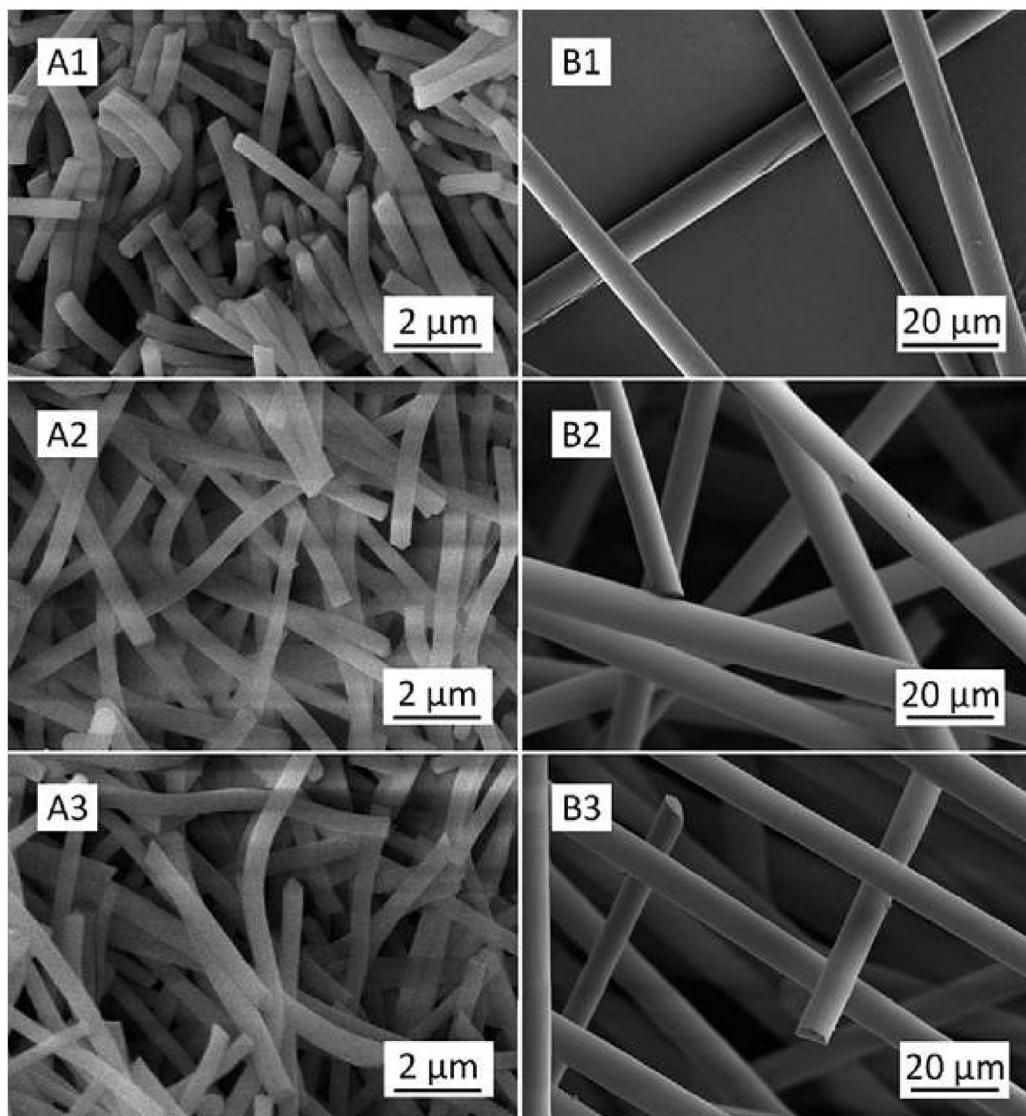


Fig. 14. SEM images showing representative morphologies of EGNFs after ultrasonication (A) and glass microfibers after being cut from glass wool (B): (1) untreated fibers, (2) epoxide-functionalized fibers, and (3) amine-functionalized fibers. [63]. Copyright 2011. Reproduced with permission from John Wiley & Sons Inc.

other than carbon are eliminated in the form of gas byproducts and a graphite-like structure is generated. The carbon nanofibers that are produced from electrospinning typically have diameters between 100 nm and 500 nm.

Current endeavor toward high-performance electrospun carbon nanofiber (ECNF) reinforced PNCs is very limited due to the fact that carbon nanofibers from electrospun PAN currently do not possess the anticipated high mechanical strength [170]. Most research regarding ECNFs is therefore restricted to functional applications such as energy storage and conversion, catalysis, sensor, adsorption, and biomedical applications based on their high specific surface area, great electrical conductivity, and good biocompatibility [23]. Nonetheless, developing strong ECNFs remains as a point of research interest. A series of studies have been done to improve mechanical properties of ECNFs by investigating thermo-chemical reaction and corresponding structural conversion of electrospun PAN nanofibers in the process of oxidative stabilization [171,172] as well as PAN nanofiber alignment [173–175], graphitization [176], and post-spinning stretching [177–179].

A couple of recent reports demonstrated potential of ECNFs as reinforcing agent in PNCs. The mechanical performance of ECNF reinforced epoxy PNCs were evaluated by Fong and co-workers

[180]. Long and continuous ECNFs from PAN precursor were cut to short fibers with diameters of ~200 nm and lengths of ~15 μm and applied in PNCs. Such shortened ECNFs were surface-functionalized with hexanediamine (HDA) in order to improve interfacial adhesion between the nanofibers and epoxy matrix. For comparison, vapor growth carbon nanofibers (VGCNFs) and graphite carbon nanofibers (GCNFs) were also investigated following the same surface-functionalization procedure. Results revealed that incorporation of a small amount of ECNFs (up to 0.5 wt.%) could lead to considerable enhancement in mechanical properties of epoxy resin. For example, incorporation of 0.5 wt.% HDA functionalized ECNFs led to 10%, 14.6%, and 43.7% increase in flexural strength, elastic modulus, and work of fracture of epoxy resin, respectively. Overall ECNFs showed similar reinforcing effect as VGCNFs but better performance than GCNFs. Given the advantage of low cost, ECNFs are more promising as reinforcing agent with respect to VGCNFs and GCNFs. Hou and coworkers also employed shorten ECNFs from PAN precursor as reinforcing agent [181]. In their research, ECNFs with diameter of 300–400 nm and length about 3–7 μm were found to be well-dispersed in PI matrix even at 5 wt.% loading level. The resultant PNC with 1 wt.% ECNFs exhibited significant enhancement in tensile strength and modulus by 30% and 101%, respectively,

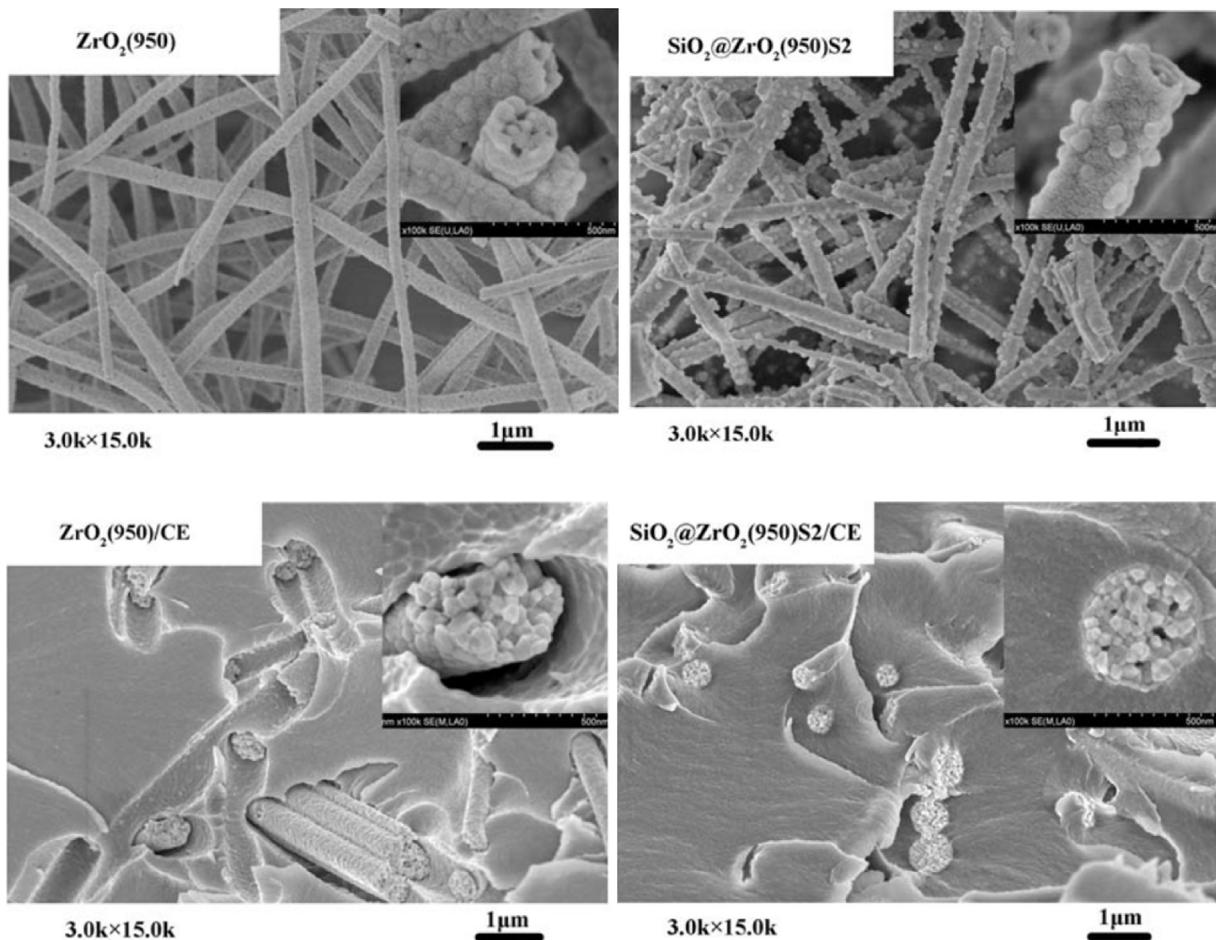


Fig. 15. SEM image of ZrO₂ and SiO₂@ZrO₂ nanofibers (top) and cross-sections of ZrO₂/CE and SiO₂@ZrO₂/CE PNCs (bottom). “950” in label stands for calcination temperature of 950 °C for making ZrO₂ nanofibers; “S2” in label stands for TEOS adding rate of 3.5 mL/min in sol-gel processing step. [169]. Copyright 2013. Reproduced with permission from SAGE Publications.

along with slightly reduced toughness. In addition to PAN-derived ECNFs, Tian et al. recently employed electrospun poly(amic acid) nanofibers as precursor to make ECNFs [182]. The ECNFs were incorporated into a PI matrix by conventional solution casting method following a 3-step route including ultrasonic dispersion, in-situ polymerization and subsequent thermal imidization. The resultant ECNF reinforced PI PNC film demonstrated significant improvement in mechanical properties due to well-dispersed carbon nanofibers and satisfying interfacial adhesion.

As depicted earlier, one of the unique feature of electrospinning is the ease of fiber functionalization, which promises the chance of making ECNFs beyond reinforcing fillers. In the work of Cai et al., a hybridized ECNF-containing calcium phosphate nanoparticles (ECNFs/CaP) were fabricated as osteo-compatible nanofillers in epoxy resin targeting for a bone repairing application [97]. The incorporated CaP nanoparticles endow ECNFs not only with rough surfaces that improve nanofiber-matrix interfacial adhesion through mechanical interlocking mechanism, but also with satisfying calcium and phosphate ion release behavior that are essential for bone remodeling. Such ECNFs/CaP was found to be more effective in improving flexural strength and modulus of the resultant epoxy PNC compared to pristine ECNFs. This is a typical example of multi-functional ECNFs as filler to develop PNCs with multi-functionality towards practical applications. It is worth noting that ECNFs also possess high electrical conductivity and thus can bring superior electrical, dielectric and thermal performance to PNCs besides mechanical improvement [181], which are criti-

cal for applications such as aircraft fuselage, energy storage and electronic packaging.

Based on the preceding discussions regarding electrospun nanofibers and their applications in PNCs, we can conclude that: first, electrospun nanofibers are highly potential reinforcing/toughening agents for polymer bulk matrix; second, the reinforcing/toughening effect of electrospun nanofibers is complicated in practice and depends on a variety of parameters that cover size, structure, composition, orientation, loading level of nanofibers, surface chemistry and morphology, and fiber/matrix interfacial adhesions; third, reinforcing/toughening mechanisms of electrospun nanofibers are proposed and may include fiber bridging, fiber necking, fiber pull-out/debonding, crack pinning and deflection, mechanical percolation or a combination of some of these, most of which are consistent with classical FRP theory but mechanical percolation should be further investigated.

3.2. Polymer composite laminate

In practice of FRP composite for high performance and structural applications, FRP layers are assembled together to make composite laminate to provide as-needed engineering properties. Among all manufacturing processes of composite laminates, preps that consist of a combination of partially cured resin matrix and fiber reinforcing filler in either unidirectional or fabric form are usually prepared and used for laminate mass-production. In composite laminates, fiber fabrics dominate in-plane mechan-

ical properties that are typically high enough for applications, whereas resin matrices dominate out-of-plane mechanical properties, e.g., interlaminar shear strength and delamination toughness, that are significantly lower than in-plane properties. Therefore delamination is the most important failure mode in composite laminate owing to the ply-by-ply nature of such materials. Delamination is dangerous because failure starts and proceeds beneath the composite surface and thus is usually invisible from outside, especially for opaque composite materials. To mitigate the problem, additional reinforcing agents have been incorporated particularly between neighboring laminas within the composite for the purpose of improving out-of-plane properties.

Recently nanoscale fillers such as carbon nanotubes and nano clay have attracted a lot of attention due to their capabilities of considerably improving out-of-plane properties of composite laminates [183–185]. Undoubtedly electrospun nanofibers have similar reinforcing potential in composite laminate materials. Research in the area of electrospun nanofiber reinforced PNCs has accumulated significant encouraging results that may be transferred to enhance mechanical properties of composite laminate. In addition to their advantage as reinforcing filler in polymer matrix, electrospun nanofibers may be deposited onto any substrates. This allows for convenient nanofiber deposition at interface, which can be merged into conventional manufacturing process of composite laminate (Fig. 16) [45]. Electrospun nanofibers are of great practical importance in composite laminate because a small amount of nanofibers are sufficient to implement reinforcement and thus addition of nanofibers will not increase either the weight or the thickness of the composite laminate material. A great deal of research effort has been invested in this field to meet the current demand of industrial applications. Similarly, research advances in electrospun nanofiber reinforced composite laminate are reviewed based on nanofiber type.

3.2.1. Polymer nanofiber reinforced polymer composite laminate

Pioneer work of polymer nanofiber reinforced composite laminate leads to a consensus that introducing electrospun polymer nanofibers to the interlaminar region of composite laminate is effective to enhance its interlaminar fracture toughness (ILFT), strength, and delamination resistance [29]. Recent research outcome further confirmed this nanofiber-enabled interlaminar enhancement as well as its resultant improvement in other mechanical properties such as load bearing strength, impact and damage tolerance, and so forth. For example, Khalil and coworkers deposited electrospun PAN nanofibers on woven carbon fabric and fabricated nanofiber modified carbon fabric/epoxy laminate [186]. Such pin-joined carbon fiber reinforced polymer laminate demonstrated 18.9% improvement in load bearing strength as well as 20.9% and 55.9% improvement in flexural modulus and flexural strength, respectively, due to delayed in-plane bending damage and delamination caused by the presence of the nanofiber mats. Saghafi et al. placed electrospun PVDF or PCL nanofiber layers in between neighbor glass fiber/epoxy preprints and evaluated their toughening effect on the resultant composite laminate [187,188]. It is found that the PVDF nanofiber layers increased absorbed energy under impact loading while the PCL nanofiber layers reduced the damaged area of the laminate after low-velocity-impact test, although both showed negligible toughening effect.

Delamination in composite laminate is normally investigated by testing ILFT of the composite in various modes of failure depending on loading conditions, including opening mode (Mode I), in-plane shearing mode (Mode II) and tearing mode (Mode III) [189]. Since ILFT can be expressed by a critical energy release rates G_C , there are three different values of G_C for those three modes, denoted G_{IC} , G_{IIC} , and G_{IIIc} , respectively. Each G_C value reflects ILFT of a laminate composite to some content. Electrospun polymer nanofibers

actually showed contradicting effect on the delamination of composite laminate based on reported ILFT. Interleaving a specific type of polymer nanofibers into a composite laminate will not always output the same toughening effect [190]. A typical example is that some research results revealed that interleaving polyamide (PA) nanofibers brought considerably high improvement in ILFT [191–195], whereas in other cases minor to no improvement was observed [196–198]. A few factors of electrospun polymer nanofibers including nanofiber morphology, structure and placement, and their effects on interlaminar strengthening/toughening have been explored by recent research and is discussed in the following sections.

3.2.1.1. Morphology of nanofiber mat. The principal merit of electrospun nanofiber mats is their nanofibrous morphology that comes with tremendous specific surface area and high porosity. It has been demonstrated that interleaving nanofibers in composite laminate outperformed their micro-fiber counterparts in improving interfacial interaction between strengthening fabrics and epoxy matrix [199]. Magniez et al. [200] showed that PVDF electrospun nanofiber mat was more effective than PVDF film in interlaminar toughening of carbon fiber/epoxy laminate because the porous nature of the nanofiber mat allowed epoxy resin to penetrate into the mat and therefore resulted in excellent integration of PVDF phase with epoxy matrix for a toughening effect. For comparison, the counterpart film hindered resin flow and caused poor integration of the two phases. Likewise, Clerck et al. found that porous PCL structures (i.e., electrospun nanofibers, microfibers, and microspheres) were more suitable candidates than non-porous structures (i.e., PCL films or spray-coated primary reinforcing microfibers) for interlaminar toughening in glass fiber/epoxy laminate [201]. Electrospun nanofibers impressively exhibited an overall better performance among these porous structures. Electrospun nanofibers can be longer and/or stronger than their conventional counterparts, such as micro-scaled fibers and those nanofibers prepared by other methods. In this regard, electrospun nanofibers are expected to be an ideal interlaminar toughening candidate since longer fibers [202] and stronger fibers [203] are favorable for higher interlaminar toughening effect.

It is noteworthy that interlaminar toughening in composite laminate is rather complicated and influenced by many factors. Therefore, whether such benefit from nanofibrous morphology takes effect or not varies from case to case. For example, Hamer et al. revealed that electrospun Nylon 66 nanofiber mats (fiber diameter: 500 nm) caused a significant increase in G_{IC} of a carbon/epoxy laminate, but was outperformed by commercial CEREX® spunbonded Nylon 66 microfiber mats (fiber diameter: 20 μm) [204]. This was ascribed to nonuniform thickness and mass per surface area or areal weight distribution of the electrospun nanofiber mats therein. The G_{IC} improvement achieved for the nanofiber mats may be interpreted by plastic zone yielding near the crack tip of nanofibers due to their high specific surface area whereas bridging seems to dominate for microfiber mats. It is also noteworthy that increase of laminate ILFT can still be achieved [205,206] even though nanofibers lose their shape during curing, i.e., the nanofibrous morphology no longer exists in laminates after curing process. The toughening effect, however, is still related to nanofibrous morphology as a result from favorable structure in laminate caused by the original nanofibrous morphology [207].

In the following section, morphological parameters that have been explored in recent years are summarized.

3.2.1.1.1. Nanofiber diameter. Toughening of composite laminate can benefit from smaller diameter nanofibers. Zhang and coworkers investigated the influence of nanofiber diameter on the mechanical response of electrospun PEK-C nanofiber interleaved carbon fiber/epoxy laminates [208]. Three types of nanofibers were

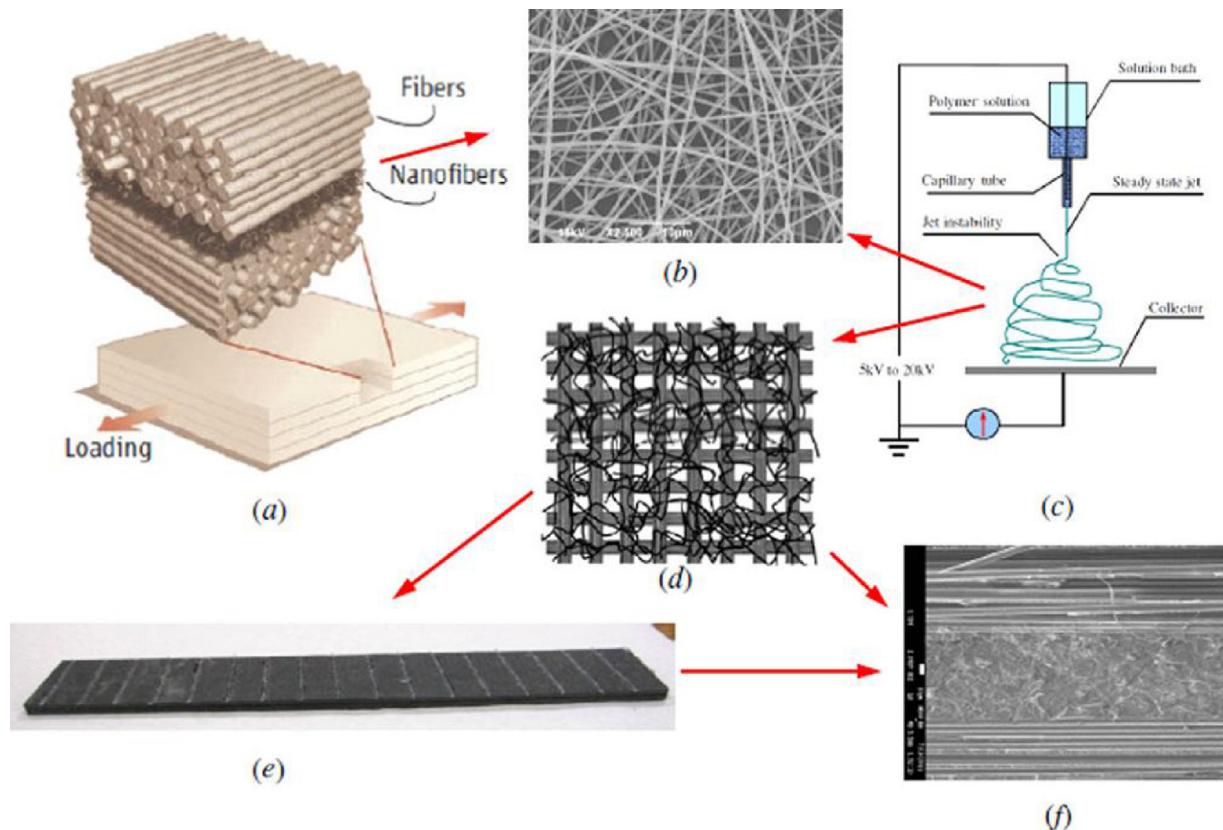


Fig. 16. Polymer composites laminate reinforced with electrospun nanofibers in interlaminar region: (a) schematic diagram of polymer composite laminate reinforced at multiple scale (conventional fibers plus nanofibers); (b) nonwoven electrospun nanofibers; (c) schematic setup of electrospinning; (d) schematic woven fabric coated with nonwoven electrospun nanofibers; (e) picture of multi-scale reinforced polymer composite laminate (produced by wet layup followed by VARTM); (f) SEM image of a nanofiber reinforced interlayer. [45]. Copyright 2012. Reproduced with permission from John Wiley & Sons Inc.

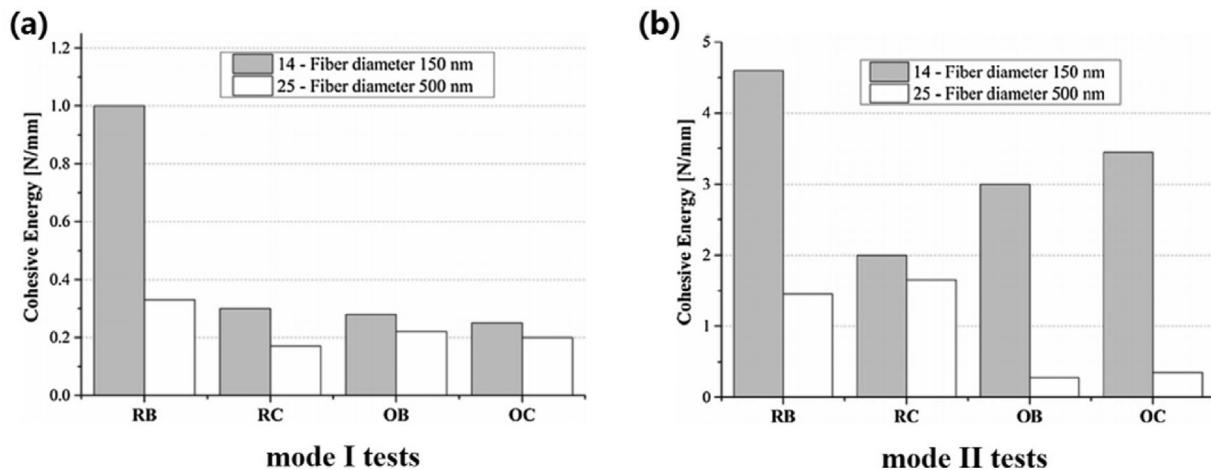


Fig. 17. Numerical cohesive energy of Mode I and Mode II tests of carbon/epoxy composite laminate interleaved by nylon 66 nanofibril mats with different diameters. The letters "R" and "O" represents random and oriented nanofibers, and the letters "B" and "C" represents nanofibril mat thickness of 25 and 50 μm , respectively. [210]. Copyright 2015. Reproduced with permission from Elsevier Ltd.

employed with diameters of 450 nm, 750 nm, and 950 nm, respectively, and corresponding results showed that finer nanofiber stabilized crack propagation during Mode I delamination and assisted with maintaining mechanical performance under flexure loading. Subsequently, Zhang et al. also employed electrospun PCL nanofibers with different diameters (103 nm, 125 nm and 210 nm) and a bead-on-string morphology as interlaminar toughening agent [209]. Similar to their previous work, larger fiber diameter showed less stable crack propagation at the same load-

ing level of nanofibers. The laminate with 125 nm PCL nanofibers exhibited the best toughening results as well as the best flexural property. Later, Palazzetti et al. conducted a comprehensive research project to investigate influence of morphological parameters of electrospun nylon 66 nanofibers on mechanical properties of a 20-ply woven carbon fiber/epoxy laminate with nanofiber sheet being placed between the 10th and 11th ply [198] followed by a numerical simulation using cohesive zone modeling [210]. In terms of Mode I loading (by the standardized double cantilever beam

(DCB) test), it was obvious that the smaller diameter of nanofiber was, the better laminate response was (Fig. 17). Smaller diameter nanofibers showed higher cohesive energy and led to higher energy absorption capability at the interface. This fully confirms a higher improvement in interfacial adhesion for smaller diameter nanofibers due to larger interfacial area. As for Mode II loading (by the standardized end notch flexure test, termed as ENF test), the dependence on fiber diameter was not as clear as that for the Mode I test, but smaller fiber diameter did result in higher cohesive energy according to ENF simulation. This probably because Mode I failure depends more on peel forces, while Mode II is dominated by shear forces, and other parameters such as thickness and orientation of the nanofiber mats played a role in Mode II test.

3.2.1.1.2. Thickness of nanofiber layer. The thickness of nanofiber layer is another important parameter determining interlaminar toughness. Zhang et al. reported that increasing thickness of PEK-C nanofiber interlayer from 40 μm to 105 μm led to enhanced Mode I delamination fracture toughness, but reduced flexure strength [208]. Likewise Mode I ILFT of a glass fiber/epoxy laminate was found to increase with thickness of PCL nanofiber interlayer [211]. Palazzetti et al. attempted to compare the interlaminar toughening effect of PA6,6 nanofiber mats with different thickness (25 μm and 50 μm) [198,210]. A thinner layer outperformed thicker one for DCB tests by reducing number of voids and strengthening the interface. In ENF test, however, no clear thickness dependence was concluded based on both experimental and numerical test. Later, Daelemans and coworkers conducted a more conclusive investigation on thickness dependence of nanofiber mats based on a system of carbon fiber/epoxy composite laminate interleaved with electrospun PA nanofibers [194]. It was found that thicker PA 6,9 nanofiber mats with areal density of 18 g/m² led to higher ILFT than the thinner one with areal density of 3 g/m² (the thickness of nanofiber mats increases with their areal density [193]) under both Mode I and Mode II loading conditions. The main interlaminar toughening mechanism was ascribed to bridging of cracks by PA nanofibers. With increasing thickness of nanofiber mats, larger amount of bridging nanofibers were generated and larger amounts of energy was correspondingly absorbed, leading to a higher Mode I and Mode II ILFT. More recently, Daelemans et al. further investigated thickness dependence through a multiscale analysis of nanofiber mat (PCL and PA6, respectively) interleaved epoxy laminates [190]. Interlayer thickness of the interleaved composite laminates increased linearly with nanofibrous veil areal density (Fig. 18a). Under Mode I loading, the thicker the PCL nanofiber mat was, the less the amount of interlaminar crossings. An optimum G_{IC} increase was achieved at intermediate interlaminar thickness. As for PA6 interleaved laminates, excessive peeling of PA6 nanofibers in interlaminar crossings due to poor interfacial adhesion led to a slight improvement in G_{IC} independent of fiber layer thickness (Fig. 18b). Under Mode II loadings, the amount of interlaminar crossings was much less affected, and thickness dependence of interlaminar toughening effect was clearly observed for both PCL and PA6 nanofiber mats (Fig. 18c).

As shown above, there are discrepancies in the reported results. These discrepancies are probably related to the toughening (micro) mechanism that dominates in nanofiber interleaved laminates. Generally thickness of nanofiber mat affects interlaminar toughening by changing loading level, porosity, and adherence of nanofiber mat on primary reinforcement (i.e., carbon or glass fabrics). Higher porosity of the mat can lead to higher permeability, then enable polymer resin to flow through the plies more easily, and eventually results in better adhesion between the two layers in favor of interlaminar toughening [198]. Since there might be decrease in porosity or easy separation of nanofiber mat from primary reinforcing fabric with increasing thickness of nanofiber mat, an optimum thickness

of interleaving nanofiber mat [199,212,213] and discrepancies in thickness effect [214] are both observed. The thickness range used by different researchers are about 20 μm to 150 μm, or the average areal density (mass per unit surface area) of the fiber layer was about 0.7 g/m² to 45 g/m². These results are hardly comparable due to the complicated interlaminar toughening mechanisms. Each specific laminate system may have its own appropriate morphological parameters of electrospun nanofibers such as an optimized thickness.

3.2.1.1.3. Orientation of nanofiber. Nanofiber orientation requires equal attention in interlaminar toughening of composite laminates. This mainly because nanofiber bridging, the main toughening mechanism, is dependent on a good load transfer to the nanofibers [194], while nanofiber orientation affects such load transfer. Palazzetti et al. have revealed that random nanofibers were more preferable than oriented ones under Mode I loading whereas aligned nanofibers seemed to be more suitable than random ones under Mode II loading [198]. Better Mode I interlaminar performance of random nanofibers was attributed to their higher porosity with respect to aligned ones and a better adhesion between adjacent fabric plies is expected. Daelemans et al. depicted a strong effect of nanofiber orientation on toughening mechanism during Mode II crack propagation [215]. The Mode II ILFT of PA6,9 nanofiber interleaved carbon fiber/epoxy prepreg laminate increased by ~50%, 75%, and ~100%, respectively, when the nanofibers were parallel (PAR), transverse (TRANS), and random (RNDM) to the crack growth direction as compared to virgin laminate without nanofibers. According to fractographic analysis, the nanofiber interleaved laminate showed two distinct failures as observed in another report [190] including interlaminar failure Type A (similar to the virgin laminate), and interlaminar failure Type B (failure at points where crack passes from one side of the nanofiber interlayer to the other). The different fracture behaviors were attributed to nanofiber bridging zones, which develop mainly in Type A failure regions for PAR interleaved laminates and mainly in Type B failure regions for TRANS interleaved laminates. RNDM interleaved laminates could develop nanofiber bridging zones in both failure regions and thus showed the highest improvement in Mode II ILFT (Fig. 19). The toughening effectiveness of randomly oriented nanofibers is highly favorable for practical applications because of uncertain crack growth direction in practice as well as ease of processing.

3.2.1.2. Chemical structure. Chemical structure of polymer nanofibers has great influence on mechanical properties of corresponding composite laminate due to varied compatibility/adhesion between nanofiber and matrix [216]. Hence research efforts have been devoted to utilize nanofibers with specific chemical structure to enhance their compatibility and adhesion strength with polymer matrix in composite laminates. Magniez et al. investigated interlaminar toughening of carbon fiber/epoxy composite laminate by depositing a ~20 μm thick layer of electrospun poly(hydroxyether of bisphenol A) (phenoxy, 0.5–2 wt.%) nanofibers onto Torey G83C plies [217]. Phenoxy has a similar chemical structure to the diglycidyl ether of bisphenol-A (DGEBA) epoxy matrix (Fig. 20). Owing to the conformability in structure, phenoxy could diffuse through the epoxy matrix to form a semi-interpenetrating network, endowing the epoxy interlayer with a nodular morphology. It was such special morphology that contributed to improvement of fracture toughness in Mode I (opening failure) and Mode II (in-plane shear failure) by up to 150% and 30%, respectively. Bilge et al. electrospun an epoxy compatible copolymer, poly(styrene-co-glycidyl methacrylate) (Poly (St-co-GMA)), directly onto a carbon fiber/epoxy prepreg layer and investigated its effect on mechanical properties of a 6-ply laminate hosting 5 interlaminar nanofiber layers [218].

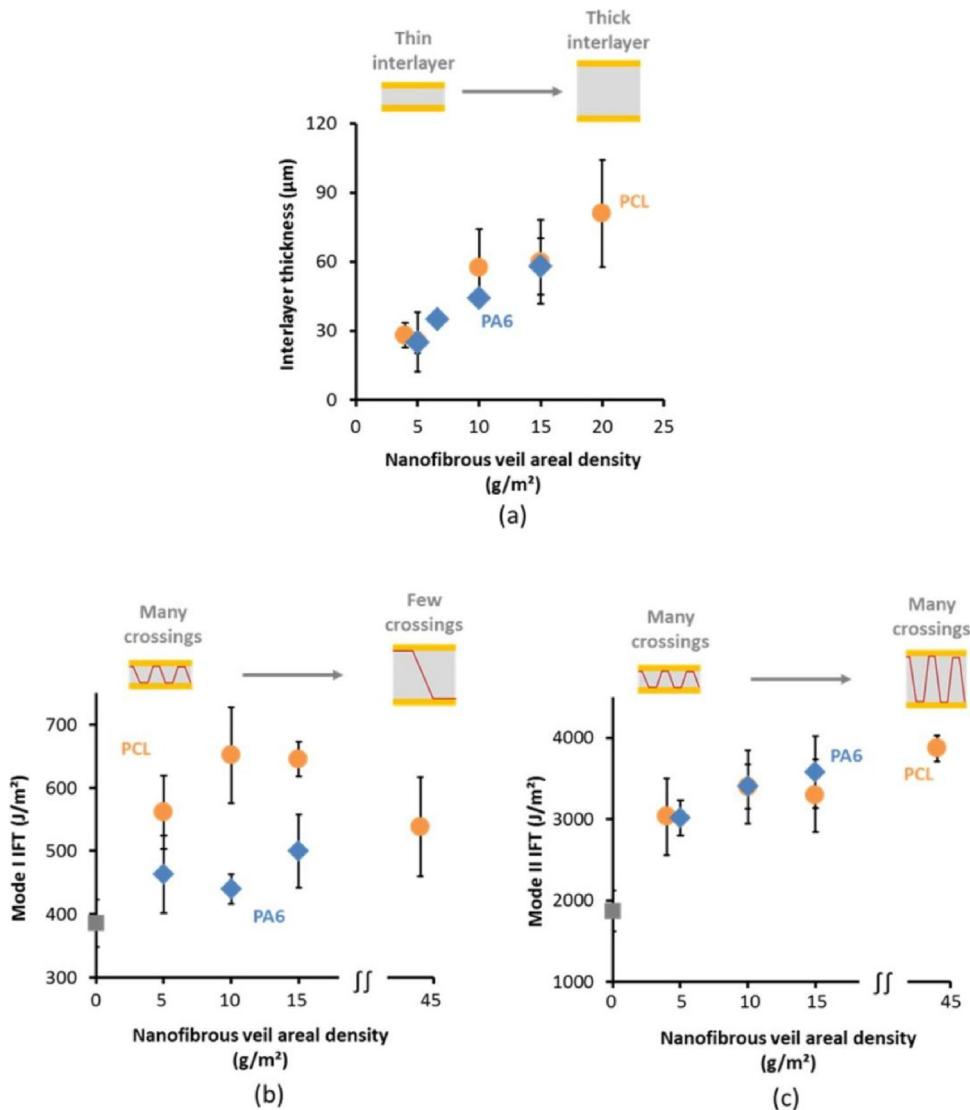


Fig. 18. (a) The linear increase of interlayer thickness of PA6 and PCL interleaved composite laminates with areal density of nanofibrous veil; (b) The Mode I interlaminar fracture toughness of PCL or PA6 interleaved laminates; (c) The Mode II interlaminar fracture toughness increases with increasing veil density. [190], Copyright 2016. Reproduced with permission from the American Chemical Society.

Uni-axial tensile test of the laminate showed increase in tensile strength by up to 18% with almost no weight penalty. That is also a successful demonstration that electrospun nanofiber interlayers may improve in-plane strength of composite laminate. Recently Daelemans et al. compared ILFT of PA6 and PCL interleaved composites with the same interleaving method, nanofiber mat areal density, and ply architecture [190]. Under Mode I loading condition, PCL nanofibers showed an extraordinary increase in G_{IC} whereas PA6 nanofibers hardly had any effect on G_{IC} . The analysis revealed that PA6 nanofibers only had fairly weak van der Waals forces with the epoxy matrix while PCL nanofibers formed mechanical interlocking with surrounding epoxy matrix at molecular level due to diffusion of PCL in epoxy.

In addition to satisfy compatibility/adhesion between nanofiber and matrix for interlaminar toughening, polymer nanofibers need to be tough, possess high shear strength, and/or exhibit plastic deformation capacity [193]. The chemical structure of polymer nanofibers determines their physical properties and thus significantly influences their toughening effect. Beckermann and Pickering et al. [193] studied the toughening effects of five types of electrospun polymer nanofiber interlayers, including polyamide

66, polyvinyl butyral (PVB), PCL, polyethersulfone (PES), and polyamide-imide (PAI), which represent nanofibers with a wide range of mechanical and physical properties, on Mode I and Mode II ILFT of a carbon fiber/epoxy composite laminate. It was anticipated that ductile polymer nanofibers with high elongation-to-break (e.g., nylon66 and PVB) performed better than those with low elongation-to-break (e.g., PES, PAI) in Mode I testing, because high elongation-to-break nanofibers could induce plastic deformation while those with low elongation-to-break could not. In terms of Mode II loading where failure results from a combination of shear and tensile micro-crack growth, nanofibers with higher tensile strength (e.g., nylon66, PES, and PAI) would better bridge/resist the opening of micro-crack in interlayer and thus showed better toughening. Results showed that 4.5 g/m² nylon 66 nanofiber mat provided the best fracture toughness with 156% increase in Mode I and 69% increase in Mode II, which is linked to compatibility of nylon 66 with epoxy resin as well as high intrinsic toughness, strength and ductility of the polymer.

Other parameters that are associated with polymer chemical structure, such as polymer molecular weight, solubility, melting point and polymorphic behavior, can also influence interlaminar

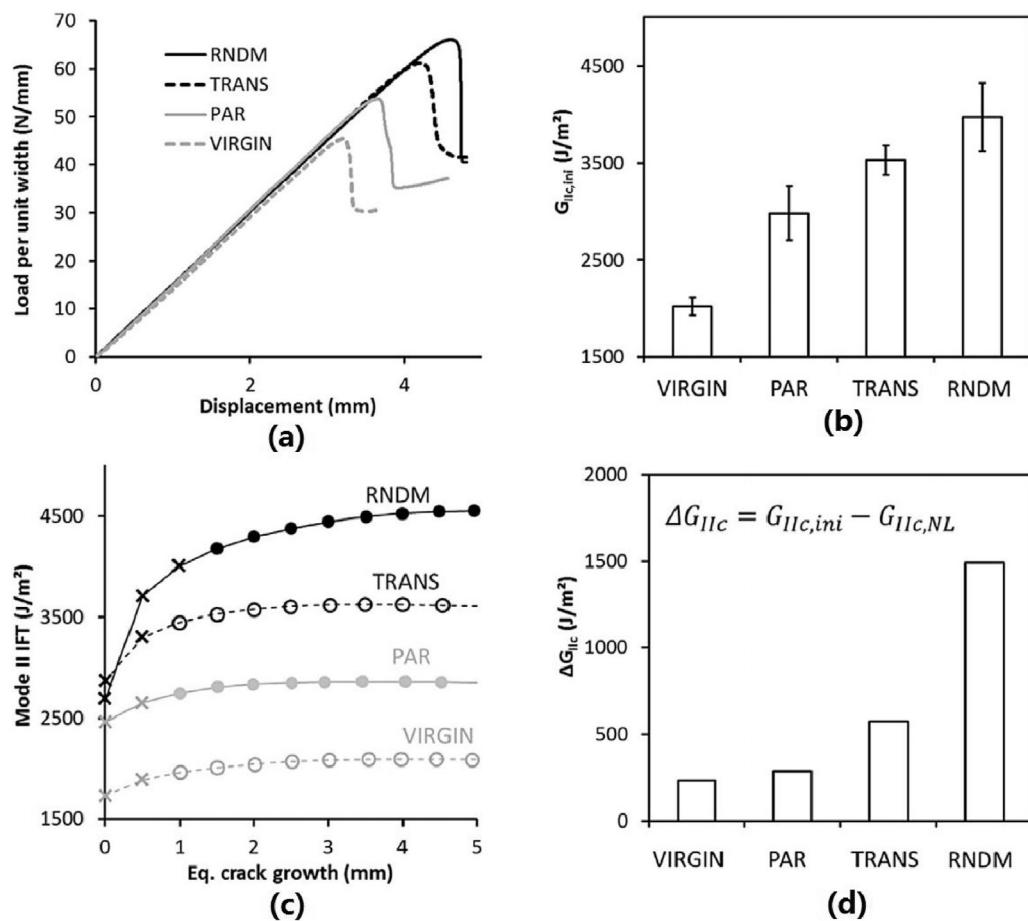


Fig. 19. Typical load-displacement curves (a) and resultant initiation fracture toughness ($G_{IIC,ini}$) values (b) for the four different configurations; Typical R-curves (c) and ΔG_{IIC} values for each configuration revealing the effect of nanofiber orientation on the fracture behavior. [215]. Copyright 2015. Reproduced with permission from Elsevier Ltd.

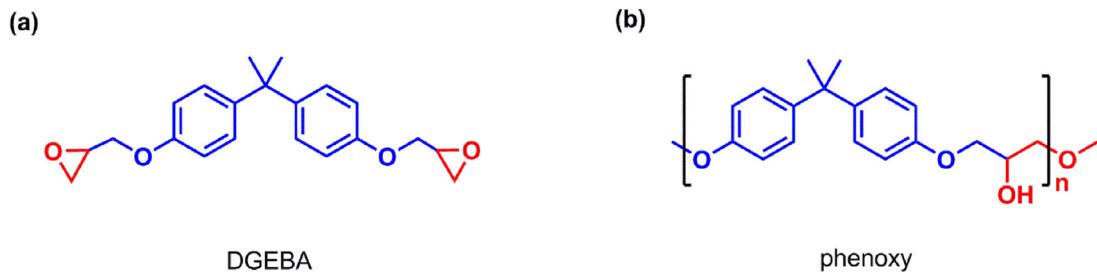


Fig. 20. Chemical structure of (a) diglycidyl ether of bisphenol-A (DGEBA) and (b) poly(hydroxyether of bisphenol A) (phenoxy).

toughening effect of nanofibers. Magniez et al. [200], investigated interlaminar toughening effect of electrospun PVDF nanofiber mat in a carbon fiber reinforced composite laminate. Therein the curing temperature (150°C) was below the melting point of PVDF ($165\text{--}170^\circ\text{C}$), thus PVDF nanofibers largely maintained their nanofibrous morphology in the final laminate. Inclusion of high or low molecular weight PVDF ($M_n = 250,000$ or $70,000\text{--}80,000$) nanofiber mats resulted in different level of plastic deformation at crack tip, which directly translated to a different increase in Mode II ILFT of the laminates by 53% and 57%, respectively. PVDF crystallized primarily in its β phase but with co-existing α phase. It was also suggested by this research that higher content of ductile α phase PVDF crystalline may improve the Mode I ILFT of the laminate. In another research, the effect of PVDF nanofibers on Mode I ILFT of resultant laminate increased from -20% to 0% by increasing the curing temperature from 150°C to 175°C , which is

over the melting point of PVDF [200,209]. It is indicated that PVDF nanofibers become more effective when they melt after cure. Subsequent research [205,206] revealed that incorporation of PVDF nanofiber mat in a 14-ply carbon fabric/epoxy laminate cured at temperatures over the melting point of PVDF (up to 190°C) indeed significantly improved Mode I ILFT of the laminate because the melted PVDF nanofibers induced plastic deformation of the epoxy matrix and absorbed more energy during crack propagation. In the case of PCL nanofibers, a combination of their solubility, melting behavior, ductile nature as well as manufacturing affects their toughening effect. For example, Zhang et al. revealed that PCL nanofibers formed relatively uniform particulate phase separation with epoxy matrix due to their favorable melting characteristic and solubility in epoxy during the manufacturing of carbon fiber/epoxy composite laminate [209]. Such ductile thermoplastic-rich particulate microphases [208,209] resisted crack growth intermittently

during crack propagation and contributed to enhanced ILFT. By contrast, no interlaminar toughening effect was observed if PCL nanofibers totally melted and dissolved into epoxy during the curing process, neither restraining their nanofiber morphology nor forming ductile microphases [193].

Results from different studies also created a question that whether it is possible to use mixed multi-type nanofibers to take advantage of each type of nanofibers. Saghafi et al. placed electrospun nylon 66, PCL, and nylon 66/PCL mixed nanofibrous mats in respective mid-plane of 16-ply unidirectional glass fiber/epoxy prepreg laminates and investigated their effects on mode I and mode II energy release rate of the laminates [195]. Results indicated that nylon 66 was only effective in mode II fracture toughness with 68% enhancement while PCL showed almost the same enhancement (~25%) in both mode I and mode II toughness. The mixed nylon 66/PCL nanofiber mat could use the capability of both types of nanofibers and yielded 21% and 56% increase in modes I and II toughness, respectively, which are in between the results of individual nylon 66 and PCL nanofiber mats. Similar results were obtained in another study of the same group [196].

From a broader perspective, any difference of interleaving nanofibers induced by polymer chemical structure, such as moisture take-up [194,199], may affect mechanical response of resultant composite laminate to some extent, thus no additional examples of the scattered research are reviewed herein. In summary, the chemical structure of electrospun polymer nanofibers has a profound influence on their interlaminar toughening effect either by changing nanofiber/matrix interfacial interaction or determining specific physical property of nanofibers. However, it is difficult so far to derive a universal guideline to identify what kind of chemical structure of polymer is most likely to affect ILFT since the same interleaving polymer nanofibers may perform quite differently under Mode I and Mode II loadings [200] or in different laminate systems.

3.2.1.3. Placement of nanofiber layer. Most of the research described in the preceding placed a layer of nanofiber mat in mid-plane of the composite laminate [192,193,195,204,206,208,215,220] mainly because crack is supposed to propagate between mid-layers of the laminate under certain modes of failure, such as Mode I [196]. For example, electrospun nanofibrous nylon 66 random mat was used as interlayer in glass fiber/epoxy laminate [192]. Ten plies of glass fiber/epoxy preprints were stacked and one layer of nanofiber mat was interleaved in mid-plane of the laminate. A Teflon sheet was placed in the mid-plane interface to induce initial delamination. DCB and ENF results indicated that use of electrospun nanofiber mat was able to increase corresponding laminate's initial energy release rates G_{IC} and G_{IIC} by 62% and 109%, respectively. Similarly Filippo et al. [219] and Alessi et al. [221] studied delamination behavior of carbon fiber/epoxy composite laminates with electrospun nylon 66 nanofiber mat that was placed in mid-plane interface and revealed a significant improvement in Mode I fracture toughness and interlaminar shear strength by 50% and 30%, respectively. The experimental behavior of electrospun nanofiber interleaved laminate matched well with a bilinear damage law due to crack bridging and crack propagation-inhibiting effect caused by electrospun nanofibers, whereas the original laminate complied with a simple linear damage law based on a numerical analysis [222].

Recently, the position of a nanofiber layer in a composite laminate has attracted attention. Palazzetti et al. investigated the effects of electrospun nylon 66 nanofiber interlayer on static and dynamic properties of carbon fiber/epoxy composite laminate, including stiffness, harmonic frequencies, and damping, before and after low velocity impact test [223]. Electrospun nylon nanofiber layers were placed at specific interfaces of a ten-layer woven carbon

fiber/epoxy preprints in order to understand the best position of nanofiber layer in composite laminate (Fig. 21). SEM images revealed that nanofibers still linked to the two layers that they were inserted in between when the polymer matrix was broken, increasing the damage tolerance of the laminate. In most cases, a symmetric configuration (Nano1 in Fig. 21) outperformed non-symmetric configurations (Nano2 in Fig. 21).

Instead of interleaving nanofiber layer into mid-plane or some certain planes of laminate, Akangah and coworkers interleaved a quasi-isotropic [0/45/90/-45]_{2S} carbon fabric/epoxy laminate with a single layer of nylon 66 nanofiber mat placed in every interlayer of two neighboring plies [224]. It was reported that the interleaved nylon 66 nanofiber mat increased threshold impact force of the composite laminate by about 60%, along with a reduced impact damage growth rate. Shivakumar and coworkers studied the influence of nylon 66 nanofiber interlayers on the low velocity impact damage resistance and tolerance of a 24-ply aerospace grade carbon fiber/epoxy laminate [225]. The interleaved laminate was made by placing a layer of nylon 66 electrospun nanofibers (0.27% of ply weight) between adjacent carbon prepreg plies as well as on top and bottom surface of the laminate. The results indicated that the nylon 66 nanofibrous interlayers had great potential to improve the impact damage resistance and tolerance of the laminate. Specifically, the nanofibrous interlayers increased the laminate's threshold impact force, threshold impact energy, and residual compression strength after impact by ~12%, 33%, and ~10%, respectively. Similar mechanical improvement of laminate from interleaving electrospun nanofibers at all of the interlayers were reported by other researchers [186,190].

Methods to integrate electrospun nanofibers within composite laminate have been investigated. Nanofiber mats may be either manually placed between laminate plies [226] or directly deposited onto woven fabrics/prepregs in the process of electrospinning [208]. Schoenmaker et al. compared two ways to integrate electrospun nylon 6 nanofiber interlayers within a glass fiber/epoxy composite laminate [214]. The nanofiber interlayers were incorporated into the laminate as (1) stand-alone layers between any two adjacent glass fabrics and (2) direct-spun layers on glass fabrics. Neither method showed negative effect on epoxy resin impregnation, and both methods improved mechanical characteristics of the laminate. In tensile and shear tests the laminate prepared by direct-spun nanofiber layers outperformed the counterpart produced using stand-alone nanofiber layers. Optical microscopic images showed that there were many more cracks in the laminate with stand-alone nylon 6 interlayers than in the one with direct-spun nylon 6 interlayers at a stress of 40 MPa. Clerck et al. studied three different interleaving configurations of PCL nanofiber mats in a glass fiber/epoxy composite laminate [211]. These configurations included SLD (a single layer of nanofibers directly electrospun onto one side of each glass fabric ply), DLD (one layer of nanofibers directly electrospun onto both sides of each glass fabric ply), and IL (one stand-alone layer of electrospun nanofiber mat inserted in between every two adjacent glass fabric plies). Compared to the original laminate, interleaving PCL nanofiber mats improved Mold I ILFT of the laminates under all three configurations. The DLD configuration is superior over the other two configurations because delamination crack therein propagated, at least partially, through the toughened interlayer. A 100% improvement in initiation ILFT was observed by interleaving PCL nanofiber mat under DLD configuration at 20 g/m². Molnar et al. electrospun PAN nanofibers directly onto unidirectional (UD) and woven carbon fabrics using a needleless electrospinning technology (Nanospider™) and produced epoxy based composite laminate through a hand layup method [227]. Experimental results demonstrated that the presence of nanofibers could effectively increase impact strength of the laminate without compromising its in-plane strength. The

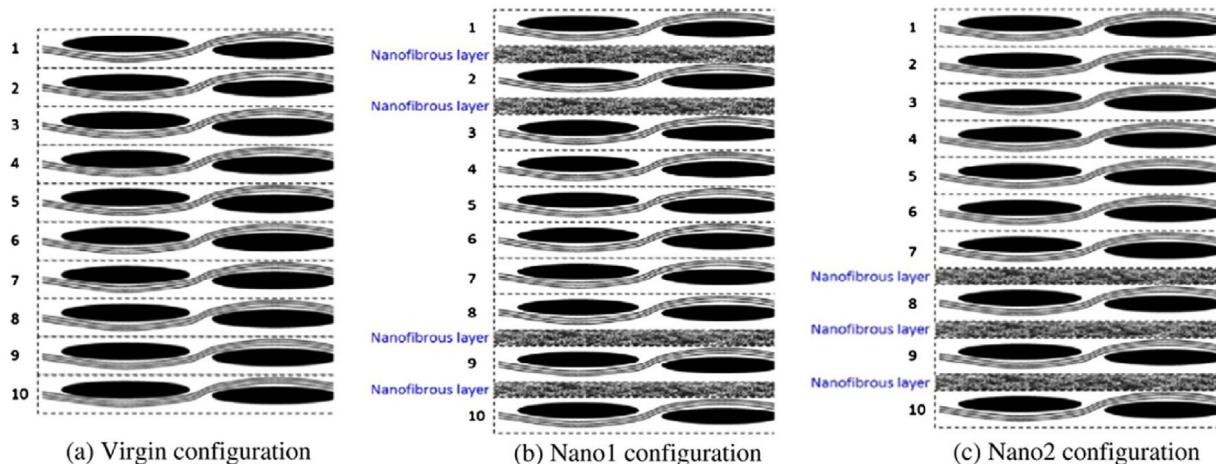


Fig. 21. Configurations of electrospun nanofibrous mat interleaved composite laminates: (a) Virgin configuration: no nanofibrous mat; (b) Nano1 configuration (symmetric): nanofibrous mats were placed into the two uppermost and the two lowest interfaces of the laminate; (c) Nano2 configuration (non-symmetric): nanofibrous mats were placed only in three lowest interfaces. [223]. Copyright 2013. Reproduced with permission from Elsevier Ltd.

improvement may be explained by good load distribution and transfer through the nanofibers to carbon fibers. The common fact is that direct-spun nanofiber layers may result in direct contact between the deposited nanofibers and the laminate fabrics, which may further facilitate transfer of load to laminate fabrics, the primary reinforcing agent in the laminate [211,214]. Nevertheless, one should also be careful about a possible drawback of the direct-spinning manner, i.e., damaging interaction may occur between electrospinning solvent and prepreg material.

As depicted previously, electrospun nanofibers may also be dispersed into epoxy matrix, forming a nano-epoxy. Based on this concept, Manh et al. directly mixed electrospun silk fibroin nanofibers into epoxy resin using a homogenizer, and then the obtained mixture was manually integrated with 10 layers of plain-woven carbon fabric to prepare composite laminate [228]. Results revealed that Mode II ILFT of the laminate increased with increasing nanofiber content and reached 30% improvement at the maximum nanofiber loading of 0.1 wt%. This was ascribed to improved adhesion between carbon fabric and epoxy matrix due to the incorporation of silk fibroin nanofibers. Despite the potential of significant ILFT improvement, this concept may conceal some unique features of electrospun nanofibers, such as compatibility with conventional manufacturing process of composite laminate without bringing increase in resin viscosity that other types of toughening agents usually do.

Based on the research related to placement of nanofiber layer in composite laminate, in general, interleaving nanofiber layer into mid-plane, in a symmetrical configuration, in every interlayer, or in matrix improves the laminate's ILFT.

All research results from polymer nanofiber reinforced polymer composite laminate so far highlighted appropriate use of electrospun polymer nanofiber interlayer in composite laminates for toughening purpose and provided useful information to understand toughening mechanism, which is necessary for designing next generation composite materials. Interlaminar toughening effect in practice is usually a result of several micromechanisms and may vary under certain conditions such as fracture mechanics and delamination path in interlaminar region, configurations of composite laminate (either woven or unidirectional), chemical/mechanical/morphological features, loading level, interleaving methods and positions, or a combination of some of these. Therefore, further systematic studies are needed with the aim to fully understand interlaminar toughening mechanism and evoke full benefit of electrospun polymer nanofibers.

3.2.2. Polymer based composite nanofiber reinforced polymer composite laminate

As shown in the preceding, reinforcement effectiveness of electrospun nanofibers in PNCs is greatly enhanced by integrating stronger nanoscale fillers. Unlike the literature on bulk PNCs, there are only few reports on polymer based composite nanofibers for strengthening/toughening composite laminates. Current reports only involve multi-walled carbon nanotubes (MWCNTs).

Bilge et al. integrated MWCNTs into electrospun P(St-co-GMA) nanofibers and the nanofibrous mat was used as an interlayer reinforcing material for conventional carbon fiber/epoxy preprints [229]. P(St-co-GMA) demonstrated excellent capability to incorporate MWCNTs as well as compatibility with epoxy resin. Compared to the laminates without nanofibrous interlayers, the laminate with P(St-co-GMA) nanofiber interlayers exhibited up to 17% increase in flexural strength and modulus. Introduction of 1 wt.% MWCNTs, based on weight of the copolymer nanofibers, further improved the laminate's flexural strength and modulus by up to 21% and 29%, respectively. The presence of P(St-co-GMA) interlayers at pre-crack tip increased corresponding mode II ILFT G_{IIC} by 55%. A further G_{IIC} improvement by up to 70% was observed with incorporation of MWCNTs, suggesting a MWCNT-derived toughening. All these mechanical improvements were achieved with a very low weight penalty (0.2%). Subagia et al. electrospun PU nanofibers with 1, 3, 5 wt.% MWCNTs (based on the weight of PU) onto basalt fiber layers and prepared a 12-ply basalt fiber/epoxy composite laminate with two nanofibrous mats interleaved between the 4th and 5th ply and between the 8th and 9th ply, respectively [230]. Improved tensile and flexural properties were observed when PU/MWCNTs nanofibrous mats were integrated within the multi-scale basalt fiber-epoxy laminate. Tensile strength, tensile modulus, flexural strength, and stiffness of the laminate increased with increase of MWCNTs content in PU nanofibers. The largest increase in tensile strength and flexural strength, by 13% and 17.3%, respectively, occurred when a surfactant, Triton-X, was introduced to assist in dispersing MWCNTs in the spinning solution. The property increase was attributed to homogeneous dispersion of MWCNTs in PU nanofibers and their high specific surface area.

Li et al. integrated MWCNTs-EP (MWCNTs with epoxy functional groups) with polysulfone (PSF) in solution, and directly electrospun partially aligned PSF/MWCNTs-EP nanofibers onto carbon fiber/epoxy preprints in a direction perpendicular to the carbon fibers [231]. A composite laminate was subsequently prepared using the nanofiber-modified preprints. The orientation of the

composite nanofibers along collecting direction improved with increasing loading of MWCNTs-EP [232]. Compared to the laminate with neat PSF nanofibers, the laminate with PSF/MWCNTs-EP composite nanofibers demonstrated gradually increasing flexural strength and modulus with increase of MWCNTs-EP loading. The flexural strength and modulus was increased by 13.3% and 22.8%, respectively, at 20 wt.% MWCNTs-EP loading with respect to PSF. Compared to the laminate without nanofibers, mode II ILFT G_{IIC} of the laminate with nanofibers increased slightly as MWCNTs-EP loading was low (< 5 wt.%). The G_{IIC} reached the maximum value at 10 wt.% MWCNTs-EP loading, which increased by 48.4% compared to that of the laminate with neat PSF nanofibers. The simultaneous reinforcement and toughening was attributed to chemical interfacial interaction between MWCNTs-EP and epoxy matrix as well as MWCNTs-EP alignment. Hamer et al. [203] prepared a carbon fiber/epoxy laminate interleaved with MWCNT reinforced electro-spun Nylon 66 nanofiber mat. Remarkably enhanced ILFT under both Mode I and Mode II loading was observed when compared with either non-interleaved laminate or the one interleaved with neat Nylon 66 nanofiber mat. On the basis of test data and fractographic study of post-test specimen surfaces, mechanism for such ILFT increase was proposed as (1) the nanofiber mat interlayer increased resistance to crack propagation and therefore improved G_{IC} and G_{IIC} ; (2) incorporation of the MWCNT stiffened nanofibers and facilitated plastic zone generation near crack tip under both Mode I and Mode II loading; (3) bridging mechanism and crack pinning mechanism of MWCNT reinforced nanofiber mat were enhanced compared to those of the neat nanofiber mats.

These results indicated the potential of MWCNT reinforced electro-spun polymer nanofiber mats for improving G_{IC} and/or G_{IIC} of composites laminate. More research is expected in the future for polymer based composite nanofibers to strengthen/toughen polymer composite laminate.

3.2.3. Non-polymer nanofiber reinforced polymer composite laminate

Likewise there are only a few reports on non-polymer nanofiber strengthened/toughened composite laminate materials. Glass (SiO_2) and carbon nanofibers are currently two major non-polymer nanofibers for reinforcing purpose in polymer composite laminate.

3.2.3.1. Glass nanofibers. Tetraethyl orthosilicate, TEOS, is a well-known precursor for glass. Kelkar et al. incorporated electro-spun TEOS nanofiber layer into mid-plane of 10-ply glass fabric/epoxy laminates [233]. Incorporation of a small amount of TEOS nanofiber (0.5 wt.%) led to a small reduction in Mode I ILFT (G_{IC}) by about 5% compared to the original laminate. When TEOS nanofibers were sintered at 600 °C for 6 h prior to use [234,235], a 15% increase in interlaminar shear strength was observed for the laminate that was interleaved with 0.6 wt.% the nanofiber mat. In addition, three point bending test results demonstrated that interleaving TEOS nanofiber mat had a potential in enhancing delamination strength and damage tolerance of the composite laminates. Fong et al. explored electro-spun glass nanofibers (EGNFs) as reinforcing agent in composite laminate [199]. Short EGNFs were dispersed into epoxy resin to form a homogeneous nano-epoxy resin and then used, instead of neat resin, to fabricate glass fabric/epoxy composite laminate. According to fracture surface of three-point bending specimen, interfacial bonding between glass fabrics and epoxy resin was improved by application of EGNFs and resistance to crack growth was increased. Overall mechanical properties, particularly out-of-plane mechanical properties, of the multi-scale (micro- and nano-) glass fiber reinforced laminate were substantially improved. At loading level of 0.25 wt.%, EGNFs improved interlaminar shear strength, flexural strength, impact absorption

energy, and tensile strength of the laminate by 35.3%, 86.2%, 35.4%, and 69.4%, respectively. Once their mass fraction exceeded 0.5 wt.%, EGNFs tended to form agglomerates in the laminate and consequently led to a lower mechanical performance. For comparison, chopped glass microfibers were also employed to develop a laminate following the same procedure. Such laminate showed some improvement in mechanical performance with respect to original laminate, but not as much as that using glass nanofibers. The flexibility of EGNFs may be adjusted by varying the pyrolysis procedure. Flexibility of EGNFs suggests different levels of structural defects and thus may affect EGNFs' reinforcing effect in composite laminate. Fong and coworkers [202] recently developed a mechanically flexible glass nanofiber mat by optimizing pyrolysis conditions and procedures and then investigated interlaminar toughening effect in composite laminate under two configurations: (1) short EGNFs in the matrix; and (2) EGNF mats in every interlayer. Laminate samples containing six layers of conventional glass fabrics, with or without EGNFs reinforcement, were fabricated by vacuum assisted resin transfer molding (VARTM, Fig. 22). Incorporation of EGNFs into glass fabric/epoxy laminate led to substantial improvements in out-of-plane mechanical properties and the EGNF mats outperformed short EGNFs. Continuous nanofiber network in the EGNF mats was believed to have better load distribution in the interlaminar region and thus contributed to higher values of interlaminar shear strength and flexural strength of the resultant laminates.

Motivated by the fact that functionalization of interlaminar toughening agents may lead to significant improvement in Mode I fracture behavior of composite [233], Kelkar and coworkers investigated effect of silane-treated EGNF mats on Mode I delamination behavior of EGNF mats-interleaved glass fabric/epoxy laminate [236]. Two silane treatment methods, namely liquid phase deposition (LPD) and vapor phase deposition (VPD), were employed. Results showed that instead of an expected improvement, silane treatment gave no increase (VPD) or even decrease (LPD) in Mode I ILFT of EGNF-mats interleaved laminates. The decrease was attributed to insufficient wetting of nanofiber mat because the LPD caused loss in porosity of nanofiber mats. Although VPD seems to be a more appropriate choice, further investigation and optimization are needed in order to realize promising benefit of silane-treated EGNFs on ILFT of composite laminates.

3.2.3.2. Carbon nanofibers. Electrospun carbon nanofibers (ECNFs) have demonstrated their potential for reinforcing composite laminate. Fong et al. fabricated hybrid multi-scale composite laminate consisting of six layers of conventional T300® carbon fabrics with five layers of ECNF mats sitting in between adjacent carbon fabric layers through VARTM [237]. Evaluation of resultant composite laminate showed that its interlaminar shear strength increased by up to 86% while its flexural strength and work of fracture improved by 11% and 21%, respectively, compared to those of counterpart laminate without ECNFs. The reinforcement mechanism was believed to be similar as EGNFs: improved interfacial bonding between carbon fabric and epoxy resin by application of ECNFs and increase of resistance to crack growth. Dhakate et al. prepared a carbon fabric laminate with semi-aligned ECNF layers interleaved between adjacent carbon fabric pre-creeps by a compression molding technique [238]. ECNF interlayers at 1.1 wt.% loading level improved bending strength, modulus and interlaminar shear strength by 175%, 200% and 190%, respectively. The mechanical improvement was ascribed to the suppressed crack propagation through interlaminar region since the interleaving nanofiber layers with high surface area improved interfacial adhesion.

Instead of sandwiching ECNFs mats between carbon fabric laminates, Fong et al. directly electrospun PAN nanofibers onto T300 carbon fiber fabrics followed by stabilization and carbonization

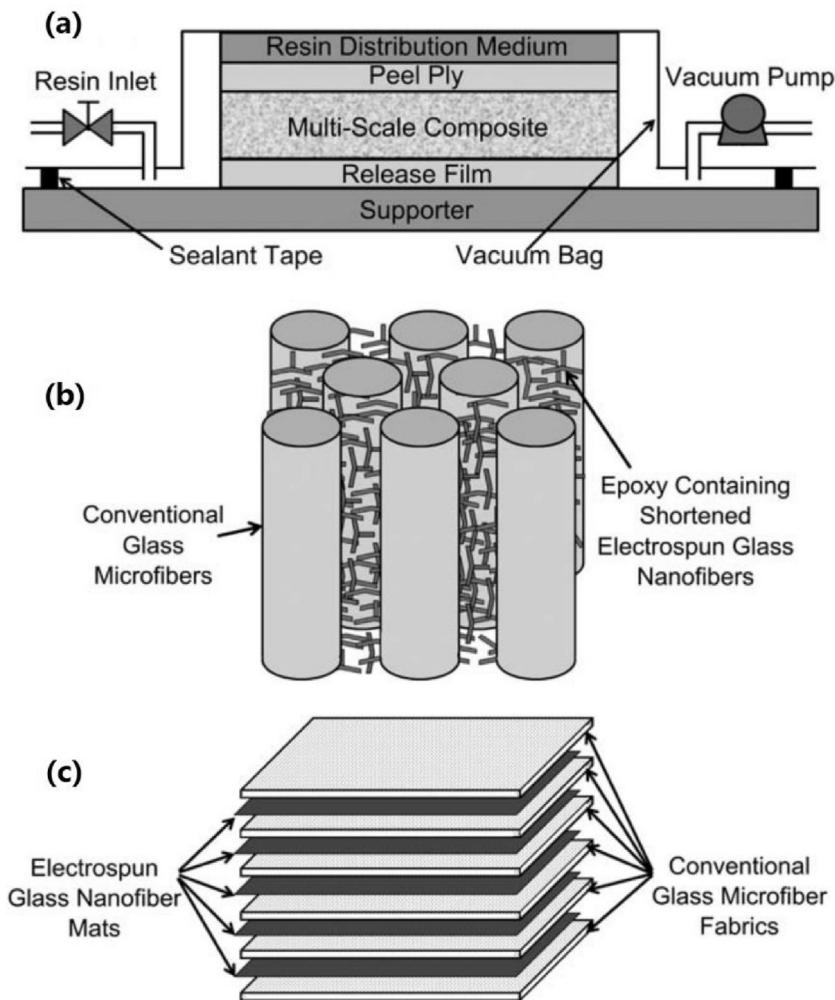


Fig. 22. Schematic representation of the VARTM process (a), the hybrid multi-scale composites developed from glass microfiber fabrics and nano-epoxy resin containing short electrospun glass nanofibers (b), and the hybrid multi-scale composites fabricated from six layers of conventional GF fabrics and five layers of EGNF-mats (c). [202], Copyright 2015. Reproduced with permission from John Wiley & Sons Inc.

to convert PAN nanofibers to ECNFs [213]. Generally speaking, increase of collecting time of electrospun PAN nanofibers would increase the volume fraction of ECNFs in composite laminate, but would also result in easy separation of ECNF nanofibrous mats from carbon fabrics, restraining reinforcement. With an optimal time (10 min) to collect electrospun PAN nanofibers, the resultant ECNF/carbon fiber/epoxy composite laminate demonstrated respective improvement in flexural strength, work of fracture, interlaminar shear strength, and elastic modulus by 23.5%, 47.3%, 221.1%, and 105.0% compared to the control laminate without ECNFs (Fig. 23). Such improvement was attributed to high mechanical strength of ECNFs as well as stronger interfacial bonding strength between the multi-scale carbon fiber fabrics and epoxy resin.

Overall the toughening/strengthening effect of interleaved electrospun nanofibers in composite laminates is complicated and likely to be influenced by a variety of factors at different level: the intrinsic properties of nanofibers; the interfacial area available for bonding (related to fiber diameters and areal density); the interaction strength between nanofibers and polymer matrix (related to compatibility, mechanical interlocking, and adhesion); the loading level and orientation of nanofibers; the interleaving methods and positions of nanofibers in laminates; configurations of laminate composite (either woven or unidirectional). To date, the involved toughening mechanisms cover fiber bridging,

debonding, crack propagation inhibition and deflection, plastic deformation, matrix yielding and etc. It has to be pointed out that compared to polymer nanofiber reinforced polymer composite laminate, current research effort on polymer composite laminates that are reinforced by polymer based composite nanofibers and non-polymer nanofibers is very limited. In-depth study on reinforcing/toughening mechanism in electrospun nanofiber reinforced polymer composite laminate and a general guideline for designing an efficient nanofiber-reinforced laminate system is urgently demanded.

4. Current research challenges and perspectives

To date, electrospun nanofibers have demonstrated outstanding potential in enhancing mechanical properties of polymer matrix composite materials including tensile strength, Young's modulus, work of fracture, and impact strength for polymer nanocomposites as well as delamination and impact resistance, flexural strength, damping, and fatigue for polymer composite laminates. Nevertheless there are challenges to overcome to take full advantage of electrospun nanofibers for reinforcement in polymer matrix composites. These research challenges are addressed in the following sections.

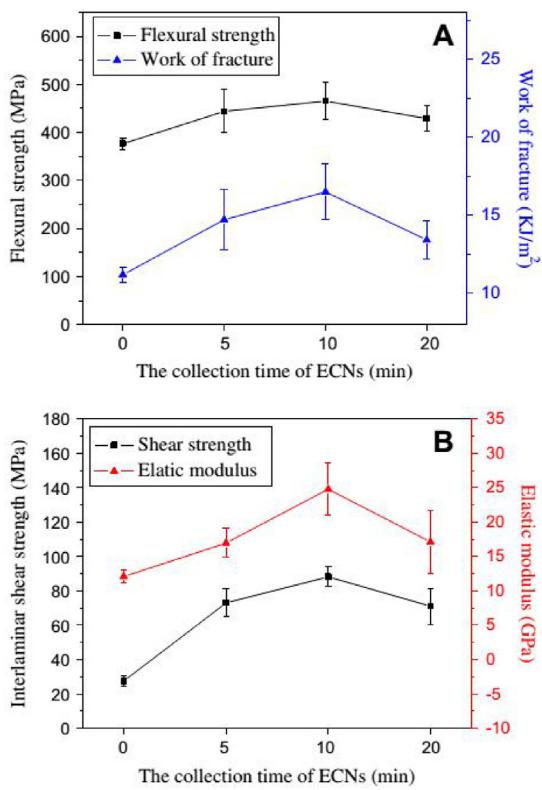


Fig. 23. Mechanical properties (A: flexural strength and work of fracture; B: interlaminar shear strength and elastic modulus) of epoxy composite laminates reinforced with multi-scale carbon fibers (electrospun carbon nanofiber mat/T300 carbon fabrics); collecting time of electrospun PAN precursor nanofibers on the carbon fabrics was set at 5 min, 10 min, and 20 min, respectively. 0 collecting time stands for the control laminate with T300 carbon fabrics. ECN stands for electrospun carbon nanofibers. [213]. Copyright 2012. Reproduced with permission from Elsevier Ltd.

4.1. High strength electrospun nanofiber

At present neither electrospun nanofibers with expected high strength and modulus available, nor is the mechanical behavior of single electrospun nanofiber well understood. It is well known that strength and modulus of reinforcing fibers are primary factors to determine mechanical performance of resultant polymer composite materials. However, most electrospun nanofibers typically possess tensile strength < 0.3 GPa and Young's modulus < 3 GPa while commercial high-performance fibers for reinforcing purpose show typical tensile strength of 3–4 GPa and modulus of 100–300 GPa [64]. Among all types of electrospun nanofibers, carbon nanofibers have demonstrated the greatest promise so far for reinforcement in polymer composites. Based on electrospun PAN precursor nanofibers, Young's modulus of carbon nanofibers reached 191 ± 58 GPa upon carbonization at 1700°C and tensile strength of carbon nanofibers achieved 3.52 ± 0.64 GPa upon carbonization at 1400°C, as indicated in recent research [239]. Such improvement was attributed to increase of crystallites in carbon nanofibers as well as smooth surface morphology. Obviously, the strength of electrospun carbon nanofibers, however, is still far below its theoretical value and even lower than that of high performance carbon fibers from conventional carbon fiber industry. More research effort is needed to further improve the strength of individual electrospun nanofibers, for example, by aligning, drawing, and annealing as done in the conventional fiber industry [178,179]. More importantly, research focus should move from polymer based nanofibers to stronger non-polymer nanofibers such as glass, ceramic, and carbon nanofibers to further improve

reinforcing effect of electrospun nanofibers in polymer composite materials.

4.2. Single nanofiber mechanical test

Another challenge in the field of electrospun nanofiber reinforced polymer composite is the lack of strength and modulus data of single electrospun nanofiber due to the limitations of precise micro-mechanic devices to directly measure mechanical property of single nanofiber. In recent years, some techniques have emerged to investigate mechanical property of single electrospun nanofiber through either AFM and/or microelectromechanical (MEMS) based nanoscale testing platforms [38,62,132,240–243], or through modeling tensile behavior of electrospun nanofibrous mat [244]. These research attempts have revealed some interesting properties of electrospun nanofibers. For example, individual electrospun PAN nanofiber showed dramatic increase in toughness along with increase in strength with decreasing diameter [245]. Specifically, as the diameter of PAN single nanofiber reduced from 2.8 μm to ~ 100 nm, its elastic modulus, true strength, and toughness simultaneously increased from 0.36 to 48 GPa, from 15 to 1750 MPa, and from 0.25 to 605 MPa (MJ/m^3), respectively. Even though the mechanical behavior of polymer single electrospun nanofiber has been partially revealed, more work is required especially to learn about mechanical behavior of non-polymer single electrospun nanofiber including glass, ceramic and carbon single electrospun nanofibers. Accordingly sophisticated and precise instrument that can handle and measure single nanofiber should be developed. Furthermore it is urgent to understand structure-property relationship of electrospun nanofibers and its influence on mechanical properties of resultant reinforced polymer composite materials. Modeling work should be established based on mechanical data when they become available to predict stiffness and strength of electrospun nanofiber reinforced polymer composites. Research outcome from single nanofiber mechanical test may overturn decades-old paradigm of high performance fiber development in fiber industry and will have broad impact on fiber and composite science and technology.

4.3. Nanofiber alignment and scale up

Unlike fibers from conventional fiber industry, electrospun nanofibers intrinsically deposit onto collector in the form of non-woven mat and lack alignment control. According to the success of conventional FRP composite materials, it should be noted that a strong polymer composite goes beyond random dispersion of nanofibers. Therefore nanofiber alignment during both electrospinning and composite fabrication is necessary. Numerous attempts have been taken to improve order and/or alignment of electrospun polymer nanofibers and to prepare aligned polymer nanofiber bundles or yarns [174]. The nanofiber bundles or yarns acquired, however, are relatively short with poor yield. Furthermore, the aligned nanofiber bundles or yarns in these reports showed only limited improvement in their mechanical properties [178]. Control of nanofiber orientation in the polymer matrix is also of great importance for mechanical enhancement of composite materials. Nonetheless a well-oriented and well-controlled electrospun nanofibrous yarn or mat for effectively reinforcing polymer matrix composite is still unavailable. Furthermore all the research reviewed herein is limited to lab-scale. Despite some industrial endeavor for mass-production of electrospun nanofiber nonwovens such as Elmarco Nanospider equipment, large-scale strong nanofiber production with controllable alignment of nanofibers is urgently needed.

4.4. Nanofiber design

In spite of their ultra-high specific surface area, electrospun nanofibers mostly show limited interfacial strength when dispersed in a polymer matrix due to absence of sufficient bonding between the nanofibers and polymer matrix. This leads to poor load transfer from polymer matrix to reinforcing nanofibers and degrades the mechanical performance of the resultant polymer composite. In order to fully realize the reinforcing potential of electrospun nanofibers, proper nanofiber design need to be addressed to achieve good interfacial interaction in the nanofiber reinforced polymer composite materials. As presented in this review, some research efforts have already been carried out to deal with this issue by multi-component blending or functionalizing electrospun nanofiber surface through either chemical or physical approaches. However, how to efficiently functionalize nanofiber surface while maintaining their uniform and individual dispersion in polymer matrix is still under investigation. Co-axial electrospinning may be a good alternative to nanofiber surface modification. This method benefitted from the development of electrospinning apparatus and has been proved to be very simple and effective to get electrospun nanofibers with desired core-shell or hollow structures. Nonetheless the productivity of co-axial electrospinning became a bottleneck for large-scale core-shell nanofiber production and composite application. Novel approaches that can efficiently produce surface-functionalized electrospun nanofibers are always welcome.

4.5. Nanocomposite processing

The processing of electrospun nanofiber reinforced polymer composites is still in its infancy. Significant issues remain to be solved regarding fiber dispersion, orientation, processing efficiency, cost, scale-up, and more importantly the performance of the resultant nanocomposites. For chopped electrospun nanofibers with limited aspect ratio (ca. tens to hundreds), the ability to disperse these nanofibers into polymer matrix is likely to be the most critical processing parameter for regulating properties. Several processing approaches for 1D nanofillers (i.e., solution mixing or in-situ polymerization) have been proved to be effective to achieve homogenous nanofiller dispersion at laboratory scale, but whether these methods can be safely, consistently and cost-effectively up-scaled is still pending. As for continuous and long nanofibers, their position, orientation and pattern are essential to enhance mechanical property of the resultant composite as revealed by conventional fiber-reinforced polymer composites. However, corresponding composite processing can be rather challenging owing to the difficulty in manipulating nano-scaled fibers. The main processing method so far is to impregnate electrospun nanofibers either in the form of random or oriented mats with polymer matrix through solution/melt impregnation. Aside from issues of scale-up and cost-effectiveness, this method suffers poor nanofiber impregnation and insufficient fiber arrangement occasionally. Therefore, novel processing techniques for electrospun nanofiber reinforced polymer composites that deal not only with nanofiber production, alignment and impregnation, but also with high versatility, efficiency and yield will be advantageous to a wider range of practical applications. Interdisciplinary technological convergence may breed such novel processing technique in the future. For example, Spackman et al. recently presented a perfect example wherein a 3D printing technology has been developed to combine deposition of either aligned or random nanofiber mat with conventional inkjet-based printing of ultraviolet (UV) curable polymers [246–248]. This multi-material additive manufacturing technique enables processing of electrospun nanofiber reinforced polymer composites with

characteristic length-scales in the tens of millimeters range along with significantly improved mechanical properties.

5. Conclusions

Advantages of electrospun nanofibers open up great possibilities for reinforcing purpose in polymer matrix composite materials. This review summarizes research advances in electrospun nanofiber reinforced polymer nanocomposites as well as polymer composite laminates in past five years. Modern concepts and general approaches are systematically described. Generally speaking, structure and mass fraction of the nanofibers, dispersion and orientation of the nanofibers in polymer matrix, and interfacial interaction between the nanofibers and polymer matrix are three critical issues to fabricate high-performance electrospun nanofiber reinforced polymer composites. Among all kinds of electrospun nanofibers that are involved in reinforcing polymer composites, polymer based nanofibers have received the most research interest to date because they were first developed and relatively mature for application. Although glass, ceramic, and carbon nanofibers have not been extensively studied for the purpose of reinforcement in polymer matrix composites, these non-polymer electrospun nanofibers have already demonstrated great potential for further research. In short, electrospun nanofibers especially glass, ceramic and carbon nanofibers are emerging reinforcing fillers in polymer matrix composites. These materials are young but promising for reinforcing purpose and deserve much more attention. It is envisioned that electrospun nanofiber reinforced polymer matrix composites are going to be important components in the family of fiber reinforced polymer composite materials.

Acknowledgments

The authors would thank the supports from International Scientific and Technological Cooperation and Exchange Program of Shaanxi Province, China, project No. 2015KW-016; the academic exchange program between North Carolina A&T State University and Xi'an Jiaotong University; and the State of North Carolina.

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