



Preparation of aramid nanofiber and its application in polymer reinforcement: A review

Bo Zhang^{a,b}, Wencai Wang^{a,b,*}, Ming Tian^{a,b,*}, Nanying Ning^{a,c}, Liqun Zhang^{a,c}

^a Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

^b Key Laboratory of carbon fiber and functional polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China

^c State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

In recent years, aramid nanofibers (ANFs) have been widely used in polymer reinforcement and toughening fields, due to their large specific surface area, high aspect ratio and retaining the excellent strength, modulus and high temperature resistance of aramid micron fibers (AMFs). It is considered that ANFs have excellent reinforcement effects for polymer composites and much attention has been focused on them. ANFs have excellent water dispersibility, which provides convenience for their reinforced polymers. ANF-reinforced polymers could also impart excellent properties such as high temperature resistance, flame retardancy, and tear resistance. Therefore, it is necessary to find a simple and efficient preparation method of ANFs. However, there is almost no literature review on the research progress of the fabrication of ANFs and ANF-reinforced polymer composites. This article reviews the recent research progress of the preparation of ANFs and the advantages and disadvantages of different preparation methods, and presents the applications in reinforcing various polymer matrices such as epoxy, rubber and composites. Finally, we proposed our own opinions on the issues of ANF-reinforced polymers.

1. Introduction

Based on the unique nano-effects, nanomaterials often exhibit physical or chemical properties not possessed by conventional macromaterials, and have developed rapidly in various scientific and industrial fields [1,2]. Nanomaterials have unique surface and interface characteristics, so they have an excellent reinforcement effect on the polymer matrix [3]. In the past decade, aramid nanofibers (ANFs) have been extensively studied due to their excellent properties, such as large specific surface area, high aspect ratio and retaining the excellent strength, modulus and high temperature resistance of aramid micron fibers (AMFs). ANFs have the advantages of excellent comprehensive properties of AMFs and nano-effects of high-performance polymer nanofibers, and become a novel nanoscale building block that can effectively solve the problem of chemical inertness, low reactivity and smooth surface of AMFs. ANFs have broad application prospects in the fields of polymer reinforcement [4], battery separators [5], adsorption filtration [6], electrical insulation [7], supercapacitor electrodes [8].

Polymer nanofibers have a variety of preparation methods, including hot-stretching [9], templated synthesis [10], self-assembly

polymerization [11], phase separation [12], and electrospinning [13,14], of which electrospinning is the most widely used method [15]. AMFs with excellent toughness and strength have been widely used as a reinforcement material for advanced composite materials [16]. However, the inherent hydrogen bonds between molecular chains will cause the controlled nanofiber preparation process of aramid fiber to be difficult to achieve. Since Kotov et al. [17] first reported the preparation of ANFs from an alkaline solution of dimethyl sulfoxide (DMSO) in 2011. ANFs have attracted more and more scientific attention in many research fields [18]. The long preparation period, low efficiency, complicated steps and high preparation costs are the problems in the current preparation process of ANFs. Therefore, it is of great significance to find a simple, effective and low-cost ANFs preparation technology for its industrial application. In addition, researches for the preparation of ANFs, made from AMFs with the potential to reduce the use of conventional nanomaterials, are also related to the increased interest of material researchers and industries in the development of new ANF-reinforced materials.

In this article, we summarize the recent research progress of the preparation of ANFs and the advantages and disadvantages of different

* Corresponding authors at: Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, PR China.

E-mail addresses: wangw@mail.buct.edu.cn (W. Wang), tianm@mail.buct.edu.cn (M. Tian).

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preparation methods, and presents the applications in reinforcing various polymer matrices such as epoxy, rubber and composites. The use of ANFs as reinforcement in nanocomposites has become a popular research topic. In addition, we analyzed the problems and challenges encountered in the preparation of ANF-reinforced polymers. Finally, we proposed our own opinions on the issues of ANF-reinforced polymers. This is a comprehensive review of the recent advances made in development of ANF-reinforced polymer composites with intention to stimulate interests in both academia and industry.

2. Preparation methods of ANFs

Aramid fibers combine high mechanical properties, thermal and chemical stability with low density, attributed to its regular molecular chain structure and hydrogen bonds between molecular chains, which also poses a lot of challenges for the preparation of ANFs. However, Kotov et al. [17] first reported the preparation of ANFs from an alkaline solution of DMSO in 2011. Since then, the preparation of ANFs and their reinforcement of polymers have been extensively studied. There are mainly four methods for preparing ANFs, including top-down electrospinning [19], mechanical disintegration [20], deprotonation [17], and bottom-up polymerization induced self-assembly [21]. It is important to mention that since the published papers have deeply investigated the preparation approaches of ANFs, the present review gives a brief summary on the said topic in this section.

2.1. Electrospinning

Electrospinning is a highly versatile technology to fabricate polymer nanofibers with remarkable high aspect ratio and high porosity properties [22,23]. Electrospinning is cost-effective and simple in preparing polymer nanofibers with controllable nanostructures for the industrial applications. However, it is very challenging to prepare ANFs by electrospinning. For the preparation of *meta*-ANFs (m-ANFs), researchers usually dissolve m-ANFs in a solution of N, N-dimethylacetamide (DMAc) and lithium chloride (LiCl) or calcium chloride (CaCl₂), and then conduct electrospinning by adjusting the spinning parameters, such as voltage and flow rate [19,23–29]. The m-ANFs prepared by electrospinning exhibit relatively low mechanical strength and poor chemical stability due to the use of dipolar aprotic solvents and salts. Kim et al. [26] discussed a new microwave method to fabricate high strength electrospinning m-ANFs mats which showed 2.8-fold increase in the tensile strength compared with an untreated m-ANFs mat. After electrospinning of m-ANFs, Pan et al. [27] conducted hot-stretching to m-ANFs to improve its mechanical properties. Compared with the untreated m-ANFs mats, the tensile strength and modulus of the hot-stretched mats exhibit the maximum increase by 50% and 196%, respectively. Kwak et al. [28–30] post-treated the m-ANFs by salt removal and heat treatment to enhance mechanical properties and chemical stability. The sequential post-treatment induced the reintegrating of intermolecular hydrogen bonds between the molecular chains. Thus, the post-treated m-ANFs mats exhibit enhanced mechanical properties and chemical stabilities. In general, researchers have tried to conduct different post treatments in the formulation of m-ANFs to strength the mechanical properties and chemical stabilities.

Due to the regular structure of the *para*-aramid fiber molecular chains and the existence of intermolecular hydrogen bonds, it is very difficult to dissolve it in general solvents which makes the electrospinning of *para*-ANFs (p-ANFs) a great challenge. Peijs et al. [31] conducted electrospinning of p-ANFs with diameters between 275 nm and 15 μ m from anisotropic concentrated sulfuric acid (H₂SO₄)/*para*-aramid fiber solutions, although the electrospinning process was difficult to control. However, this method involves the use of concentrated sulfuric acid and high voltage, which could easily cause corrosion to the equipment and do harm to the environment. Two novel hydride-based (NaH and KH) procedures were used to prepare various N-

functionalized p-ANFs on a multigram scale, reported by Trexler et al. [32]. The high-performance properties of AMFs are retained during the transformation of fibers to the nanoscale. In addition, Trexler et al. [33] also reported a new type of Cl-substituted p-ANFs, that is, through the introduction of chlorine atoms, *para*-aramid fibers could be dissolved in DMAc/LiCl solutions for electrospinning. Jiang et al. [34] conducted electrospinning of aramid fiber (1314) to study its adsorption properties. Through the above researches, it can be concluded that the p-ANFs are more difficult to be prepared due to the existence of hydrogen bonds between molecular chains. This is very unfavorable for practical applications.

2.2. Mechanically assisted preparation

The ANFs prepared by mechanical assistance usually do not destroy the chemical structures, and could maintain the original excellent mechanical properties, high temperature resistance and chemical stability of AMFs. Ifuku et al. [20] prepared p-ANFs consisted of *para*-crystallite by a mechanical treatment of *para*-aramid fibers with the existence of NaOH. It was easily disintegrated into nanofibers, which have large surface-to-volume ratios and efficient mechanical properties, with the help of electrostatic repulsive force. The average Young's modulus, tensile strength, and strain of p-ANFs sheet fabricated by filtration followed by hot-pressing at 100 °C were 2.0 GPa, 26.8 MPa, and 1.5%, respectively. These mechanical properties are strongly affected by the preparation process. Recently, Parker et al. [35] has studied a method of preparing nanofibers by centrifugal force, called immersion rotary jet-spinning (iRJS), which avoids the usage of high voltage. Using this method, p-ANFs with a diameter of 500–1000 nm were successfully prepared and showed satisfactory mechanical properties. However, due to the use of complex equipment and low production efficiency, the industrial application of this method is severely limited.

2.3. Deprotonation and its improvement

Kotov et al. [17] first reported the preparation of ANFs, with a diameter of 3–30 nm and up to 10 μ m in length, from an alkaline solution of DMSO in 2011, which is called deprotonation. The prepared ANFs display promising mechanical properties and thermal stability as well as high aspect ratio, which make them a new nanoscale building block. Compared with the above-mentioned two methods, the deprotonation method does not require expensive equipment and complicated steps, and only needs to be stirred at room temperature. Arruda et al. [36] used commercial *para*-aramid yarns immersing in KOH/DMSO solutions to make stable dispersions of ANFs. ANFs were then hydrolyzed using phosphoric acid (PA) and were crosslinked by glutaraldehyde (GA). After that, the ANFs formed into macroscopic thin films by vacuum-assisted filtration. However, there are some difficulties related to the fabrication of ANFs through deprotonation, such as the time-consuming process (about 7 days) and low preparation efficiency. A facile and direct monomer-to-ANFs synthesis via an as-prepared intermediate low-molecular-weight poly (p-phenylene terephthalamide) without requiring the fiber spinning process was described by Hwang et al. [37]. This method requires only 15 h to prepare ANFs, which is very short compared to the original deprotonation method (about 7 days). Yang et al. [38] introduced fibrillation, ultrasonication and proton donor into the deprotonation process to shorten the preparation time of ANFs and improve the preparation efficiency. In particular, the preparation process of ANFs can be completed in only 4 h after adding the proton donor. This is very beneficial for industrial application, but the preparation process of AMFs cannot be avoided, which is high energy-consuming and environmentally unfriendly. Despite the easy processing of this methodology, its multi-step procedure makes it a time-consuming technique, limiting its efficiency for large-scale production.

In addition, there are researches on the preparation of ANFs with

different types of aramid fibers and proton donors. Zhang et al. [39] investigated the different ANFs and ANF films derived from the typical aramid yarns, chopped fiber, pulp fiber and fibril fiber, respectively. The results showed that the ANFs films made from chopped fiber exhibited excellent thermal stability and mechanical properties with ultimate strength of 103.41 MPa and stiffness of 4.70 GPa. Huang et al. [40] presented a facile fabrication of ANFs membrane formed by different proton donors (water or ethanol) via a simple vacuum-assisted suction method. The ANFs membrane assisted by water (203.92 MPa) display higher tensile strength compared with the membrane assisted by ethanol (141.34 MPa), since ethanol is a weaker proton donor. Vilatela et al. [41] provided new ideas for preparing ANFs, that is introducing oligo-(1,6-pyrene terephthalamide, oPyrTA) as an oligoamide model for Kevlar, then preparing nanofibers by deprotonation. Although the advantages of the deprotonation method include mild reaction conditions, no need of expensive equipment, and simple operation steps, its long preparation cycle and low preparation efficiency seem to be the main problems limiting its industrial application.

2.4. Polymerization induced self-assembly

All the aforementioned three methods need to prepare aramid fiber in advance, and then post-treat aramid fiber to prepare ANFs, which is complicated, time-consuming and cost-ineffective. Tuo et al. [21] proposed a new method for preparing p-ANFs by direct polycondensation, which introduced methoxy polyethylene glycol (mPEG) as the interfacial tailoring agent as well as the dispersant. The addition of mPEG is crucial to the formation of ANFs. The molecular formula and surface morphology of ANFs are shown in Fig. 1. The as-prepared ANFs exhibit superior dispersibility in solvents such as water or ethanol, and have a high aspect ratio and excellent thermal stability. The polymerization induced self-assembly method has the advantages of simple steps, high preparation efficiency, and no need of complicated equipment, which is

very suitable for large-scale production.

There are also exist methods for preparing ANFs with different structures. Li et al. [42] designed a fully rigid, discotic-shaped aromatic aramid molecule which can spontaneously self-assemble into nanofiber. Yoshioka et al. [43,44] used a precipitation polymerization method to prepare aromatic polyamide nanofibers with trifluoromethyl (CF_3) groups, which were polymerized by 4, 4-diphenyldicarbonyl chloride and 2, 2-bis(trifluoromethyl) benzidine in a dioxane solution containing water. The morphology of the aromatic polyamide nanofibers could be varied obviously by changing the composition of the reaction solution. The as-prepared aromatic polyamide nanofibers exhibited excellent thermal stability and chemical resistance. After that, Yoshioka [45] also conducted annealing treatment for aromatic polyamide nanofibers to investigate the structural changes. After annealing, the intermolecular hydrogen bonding and crystallinity of aromatic polyamide nanofibers increased, but the surface morphology remained unchanged. The nanofibers prepared by these methods are very unfavorable for industrial application.

We summarize the advantages and disadvantages of different preparation methods of ANFs, as displayed in Table 1. Polymerization induced self-assembly method can avoid the preparation process of AMFs, which is cost-effective, high efficiency and easy to be large-scale prepared. Moreover, the as-prepared ANFs show promising mechanical properties and water dispersibility, which is very beneficial to be used in polymer reinforcement. The effective reinforcements in mechanical properties of various polymers by ANFs have been discussed in the following sections.

3. Applications in polymer reinforcement

ANF has large specific surface area, high aspect ratio, excellent mechanical properties, favorable chemical stability and thermal stability, which makes it have a superior reinforcement for polymers.

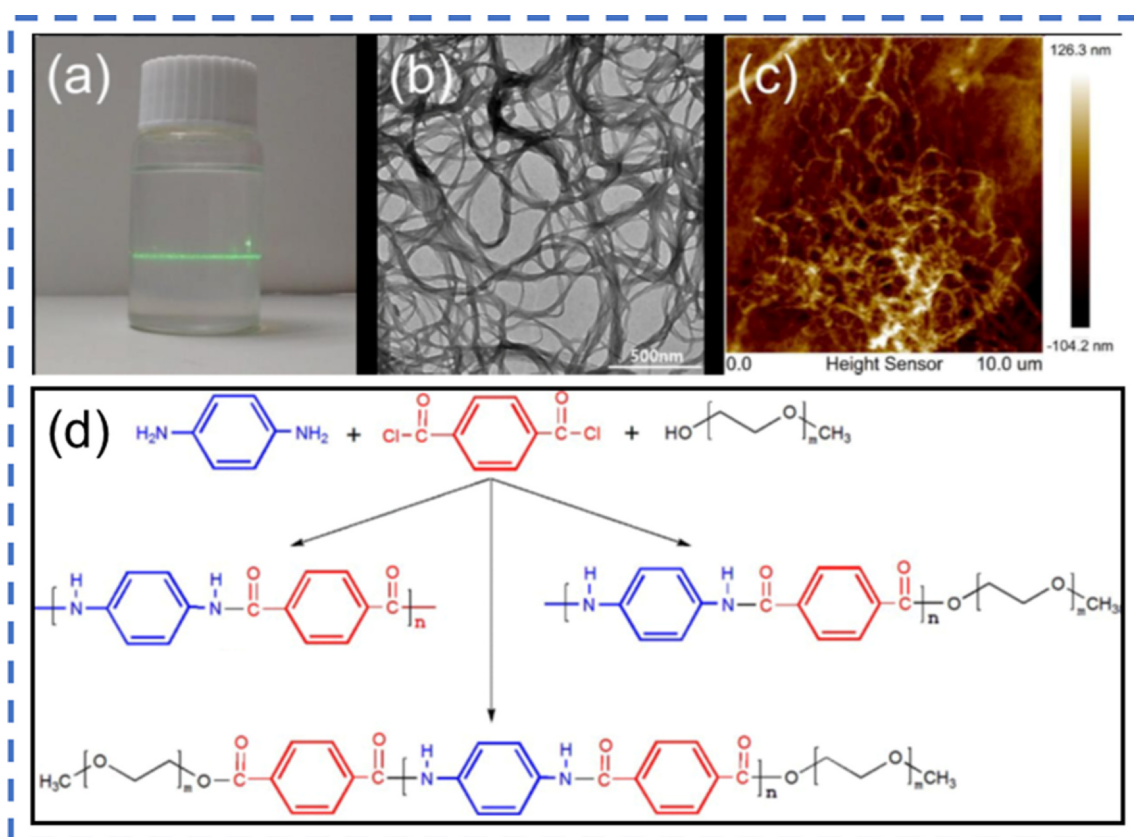
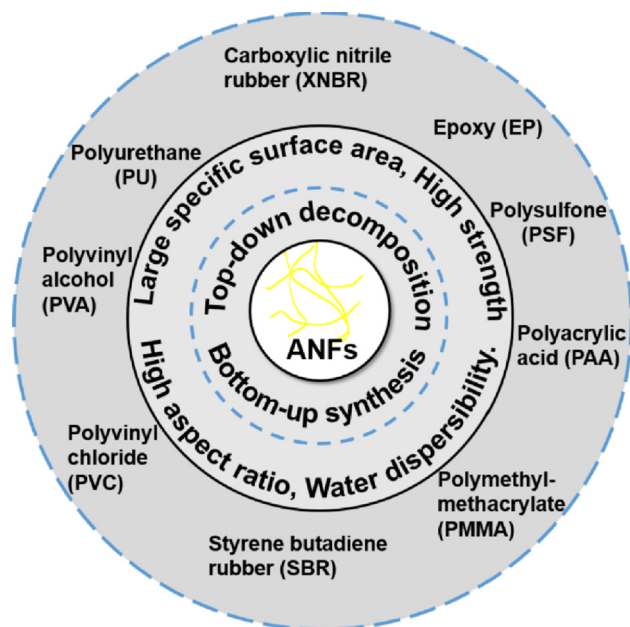


Fig. 1. (a) Tyndall effect of PPTA nanofiber colloid; surface morphology of ANFs (b) TEM; (c) AFM; (d) molecular structures of ANFs [21].

Table 1

The advantages and disadvantages of different preparation methods of ANFs.

Preparation method	Advantages	Disadvantages	Time (h)
Electrospinning	<ul style="list-style-type: none"> Continuous spinning 	<ul style="list-style-type: none"> Complicated steps Corrosion equipment High cost 	<ul style="list-style-type: none"> ~24
Mechanical disintegration	<ul style="list-style-type: none"> Excellent performance 	<ul style="list-style-type: none"> High energy consumption Requirements for equipment 	<ul style="list-style-type: none"> ~24
Deprotonation	<ul style="list-style-type: none"> Simple steps Mild conditions 	<ul style="list-style-type: none"> Long preparation cycle Low efficiency 	<ul style="list-style-type: none"> ~168
Polymerization induced self-assembly	<ul style="list-style-type: none"> No need of AMFs Simple steps High efficiency 	<ul style="list-style-type: none"> None 	<ul style="list-style-type: none"> N/A

**Scheme 1.** Schematic diagram of the types of ANFs reinforced polymers.

Compared with the smooth surface and chemical inertness of AMFs [46,47], ANFs could be combined with the polymer matrix through a variety of interactions, such as hydrogen bonding, π - π stacking and chemical interaction. In this section, we present the applications of ANFs in reinforcing various polymer matrices such as epoxy, rubber and composites, as shown in Scheme 1.

3.1. ANFs reinforced rubber matrix

It is necessary to use nanomaterials to reinforce rubber materials, because the mechanical strength of most pure rubber is generally low [48]. Jia et al. [49] developed a method to obtain water-dispersible Kevlar nanofibers (KNF) by modifying KNF with epichlorohydrin (m-KNF). Furthermore, m-KNFs were added to the rubber matrix by latex co-coagulation method to prepare styrene-butadiene rubber (SBR)/m-KNFs nanocomposites. The results show that m-KNFs have an excellent reinforcement effect on SBR through π - π stacking. The tensile strength of SBR filled with 7 phr (parts per hundred rubber) m-KNFs is increased by 576% compared with those of neat SBR. Fig. 2 is the schematic diagram of the interaction between m-KNFs and SBR and typical stress-strain curves of SBR/m-KNFs nanocomposites. In addition, Jia et al. [50] incorporated water-dispersible hydrolyzed Kevlar nanofibers (hANFs) into carboxylated acrylonitrile butadiene rubber (XNBR) by a latex co-coagulation method for the first time. The hANFs were prepared by acid-assisted hydrothermal treatments of Kevlar nanofibers (ANFs). The tensile strength of XNBR filled with 7 phr hKNFs is

increased by 236% compared with those of pure XNBR. Moreover, Jia et al. [51] also incorporated m-KNFs into the compound of XNBR/SBR through a facile latex co-coagulation method to improve its compatibility and mechanical properties. The results show that the compatibility and tensile strength of XNBR/SBR have been improved, as displayed in Fig. 3. The above researches prove that the water-dispersible ANFs have an excellent reinforcement effect on the rubber matrix with different polarities, but the formation of the filler network and the interfacial interaction between the filler and the rubber have not been studied.

3.2. ANFs reinforced resin matrix

The nanofillers used in polymer nanocomposites typically lead to improve the stress transfer efficiency between the polymer matrix and fillers, thus increasing the overall performance of the nanocomposites [52,53]. Sodano et al. [54] prepared glycidyl ether silane coupling agent modified ANFs and investigated their reinforcement effect on the mechanical properties of epoxy resin. The results show that the Young's modulus and tensile strength of the nanocomposites reinforced with 1 wt% epoxy-functionalized ANFs (EANFs) increased by 16.8% and 14.0%, respectively, as shown in Fig. 4(a). Sodano et al. [55] also discussed a simple and effective method to prepare isolated ANFs, and used them to reinforce epoxy resin to obtain nanocomposites with outstanding elastic modulus and fracture toughness, as shown in Fig. 4(b). Iijima et al. [56] deposited silver nanoparticles uniformly on the surface of ANFs to prepare functionalized ANFs and combine them with epoxy resin to prepare transparent nanocomposites. In addition, Kim et al. [57–59] used m-ANFs reinforced epoxy resin to reduce the thermal expansion coefficient and improve the adhesion strength.

Moreover, through the combination of direct blending, layer-by-layer (LBL) assembly and copolymerization, ANFs have a promising reinforcement effect on a variety of thermoplastic materials. Hwang et al. [37] prepared nanoscale ANFs to enhance the mechanical properties of thermoplastic polyurethane (TPU). That is, at an ANFs content of only 0.04% by weight, a 1.5-fold increase in TPU toughness and a maximum ultimate tensile strength of 84 MPa are achieved. Tang et al. [60] employed ANFs to reinforce waterborne polyurethanes (WPU) using LBL assembly and vacuum assisted flocculation (VAF) method, which obtained a composite film of record-high modulus of 5.275 GPa and ultimate strength of 98.02 MPa, as shown in Fig. 5(a). Zhang et al. [61] demonstrated for the first time that ANFs can be used as desirable building blocks to endow the LBL assembled GO@PU nanocomposites with excellent mechanical properties. Wang et al. [62] have successfully prepared ANFs through the deprotonation process of AMFs in DMSO with KOH and used a simple solution casting approach to fabricated poly (vinyl alcohol) (PVA)/ANFs nanocomposite films (as can be seen in Fig. 5b) with both excellent strength and toughness which were 79.2% and 148.8% higher than that of pure PVA, respectively. Peng et al. [63] prepared molecular composites comprising poly (p-sulphophenylene terephthalamide) (sPPTA) and flexible-chain PVA with

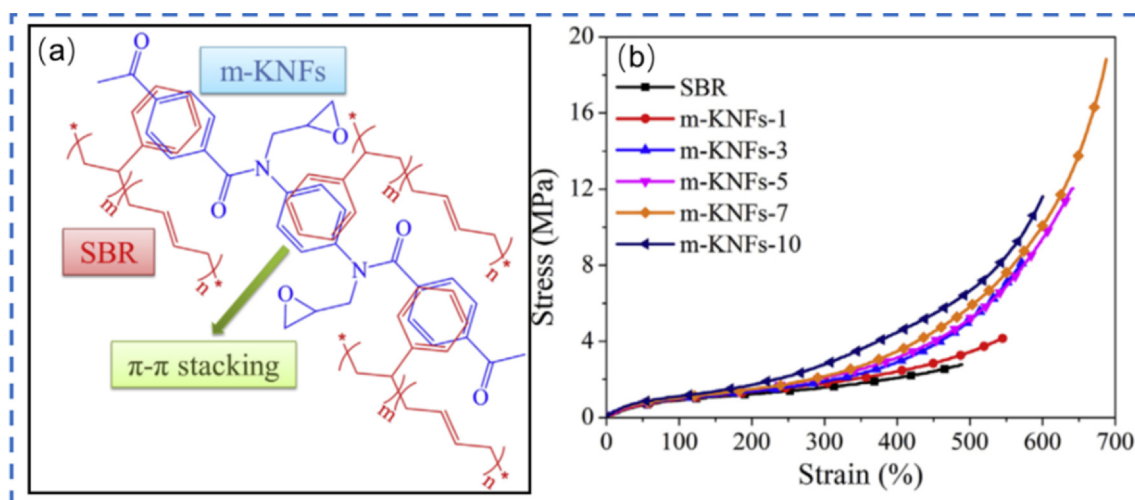


Fig. 2. (a) Schematic diagram of interaction between m-KNFs and SBR and (b) typical stress-strain curves of SBR/m-KNFs nanocomposites [49].

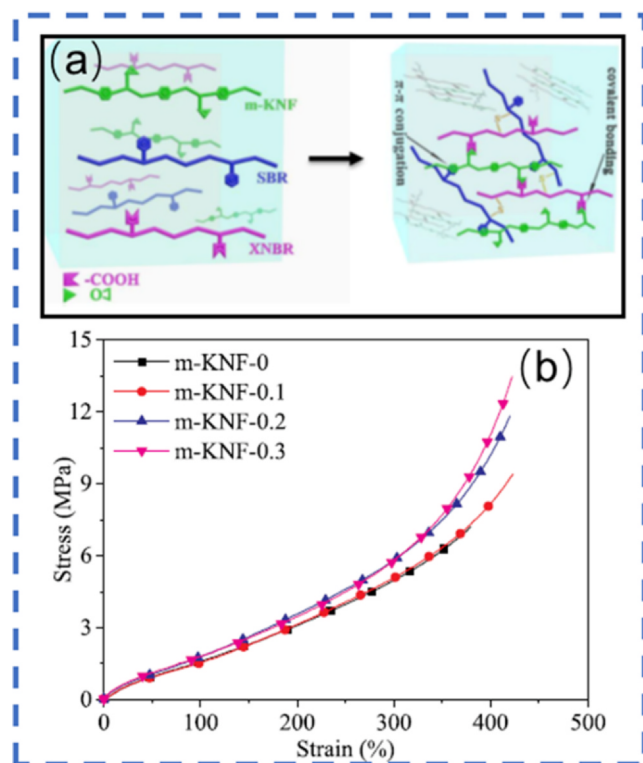


Fig. 3. (a) Schematic of the compatibility of m-KNFs in the XNBR/SBR blend and (b) typical stress-strain curves of XNBR/SBR/m-KNFs blends [51].

excellent reinforcement effect by a green and easy-to-scale-up water casting method, as displayed in Fig. 5c. Moreover, Kotov et al. [64] reported the preparation of ANF-reinforced polyacrylic-acid thin films using vacuum-assisted flocculation with high transparency. The above polymer matrix contains functional groups such as hydroxyl, carboxyl and amino groups, all of which could form intermolecular hydrogen bonds with ANFs to obtain excellent reinforcement effects. Therefore, further investigations are required to improve the reinforcement effect through the utilization of the surface modification of ANFs in non-polar or weakly polar polymer system to enhance the mechanical and other properties of the prepared materials.

There are also reports of some ANFs reinforcing other resin matrix. For example, Sun et al. [65] prepared ANFs derivatized with non-polar alkyl groups including ethyl, octyl and dodecyl groups to reinforce

polyvinyl chloride (PVC) with weak polarity. The results demonstrate that the alkyl-derivatized aramid nanomaterials (R-ANMs) improved the Young's modulus, toughness and yield strength of the PVC films. Fig. 6(a) is the schematic illustration of the fabrication process of R-ANMs/PVC films. Hwang et al. [66] fabricated an interactive ANF-reinforced polysulfone (PSU) nanocomposites via *in situ* nucleophilic aromatic substitution (SNAr) polymerization, which exhibited unprecedented reinforcement, in which PSU-I-0.15 exhibited a 1.6-fold increased UTS (79 MPa) and a 3.4-fold increased toughness (16 MJ m^{-3}) compared to those of neat PSU. Fig. 6(b) is the schematic illustration of the nanocomposite preparation by *in situ* and blending methods. Cheng et al. [67] incorporated hydrophilic ANFs into the PSU matrix by bulk blending to improve the filtration performance of the nanocomposite membranes. In addition, Shi et al. [68,69] used aramid fiber oligomers or ANFs to modify graphene under π - π stacking to prepare hybrid materials for enhancing the mechanical properties of poly (methyl methacrylate) (PMMA). And the hybrid materials showed outstanding reinforcement effect for PMMA. Sodano et al. [70] prepared ANF-reinforced thermoplastic nanocomposites and the results showed that the performance of the nanocomposite is highly dependent on the chemical structure which is similar with the ANF's, indicating that amide-amide hydrogen bonding plays a decisive role in mechanical properties. The above results indicate that ANFs have promising reinforcement effects on a multitude of resins, but the reinforcement mechanism needs to be further studied. Therefore, how to further strengthen the interactions between nanofillers and the matrix is of great significance in ANF-reinforced polymers.

3.3. ANFs reinforced cellulose

Cellulose is the most abundant natural polymer fibers on earth [71,72]. However, the strength of the cellulose membrane decreases significantly under wet or water conditions. It is an effective strategy to combine cellulose with ANFs to strength the performance of cellulose. Kim et al. [73] successfully prepared electrospinning *meta*-aramid/cellulose acetate and *meta*-aramid/cellulose composite nanofibers which show enhanced thermal mechanical properties. Yang et al. [74] investigated the differences of mechanical properties, the retention of wet strength (RWS), optical property, UV shielding, wettability and thermal stability of cellulose and ANFs. The results indicate that ANFs and paper have excellent comprehensive properties. Because ANFs are sensitive to ultraviolet (UV) irradiation, Luo et al. [75] discussed the evolution of structure and performance of ANF films under UV irradiation. Huang et al. [76] fabricated the ANFs/bacterial cellulose nanocomposite membranes with different loadings of ANFs via a facile

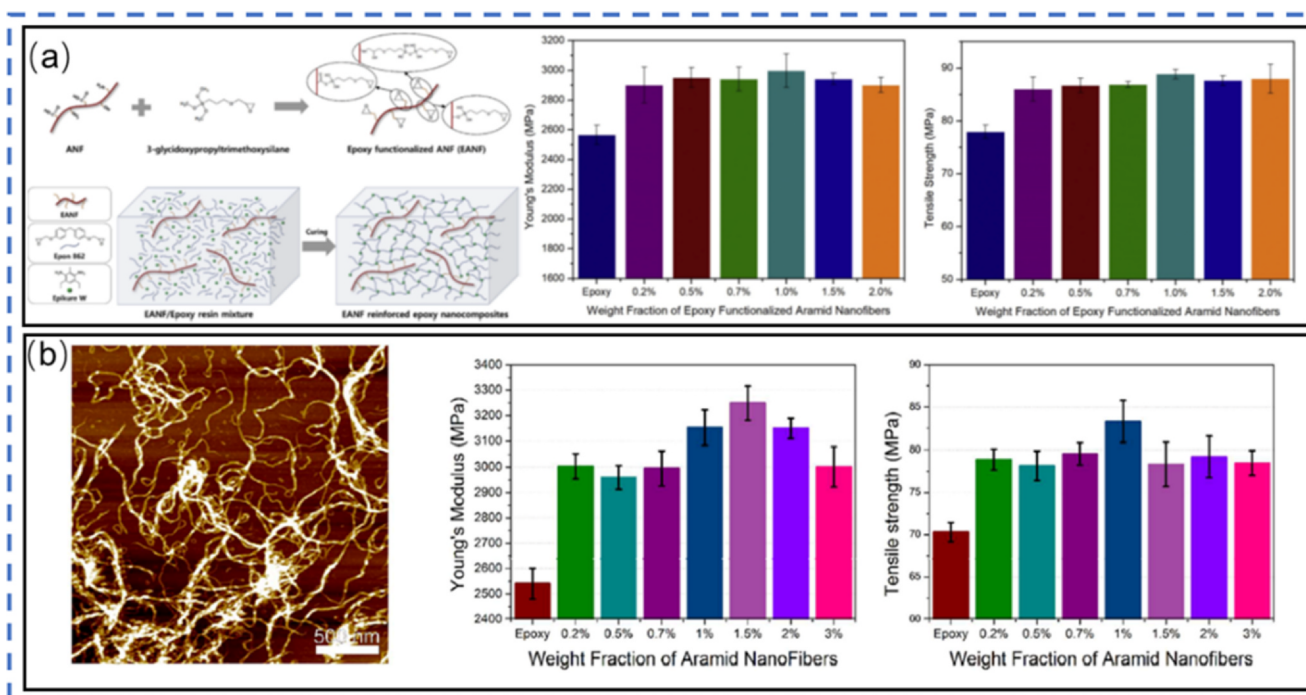


Fig. 4. (a) Schematic diagram of epoxy modified ANFs added to epoxy and comparison of mechanical properties [54] and (b) Mechanical properties of separated ANF reinforced epoxy nanocomposites with different weight fractions [55].

and simple vacuum assisted flocculation route, which maintain excellent transparency and flexibility. In addition, Zhang et al. [77] prepared ANFs-functionalized nanofibrillated cellulose (NFC) composite film which showed excellent UV shielding performance due to the incorporation of ANFs. It should be noted that researchers have tried to develop the combination of cellulose with ANFs to overcome the shortcomings of pure cellulose. The above reports prove that the addition of ANFs can effectively improve the mechanical properties and UV shielding performance of cellulose membranes. How to better combine ANFs and cellulose to prepare high performance and multiple functional films is one of the future research directions.

3.4. ANFs reinforced composite interface

The excellent specific strength and stiffness, thermal stability and high modulus make carbon fiber, aramid fiber and glass fiber suitable for advanced engineering material used in aerospace, transportation and military fields. Interfacial adhesion between the fiber and matrix in high performance fiber reinforced composites is a critical factor for their mechanical performance in structural applications [78]. However, due to the smooth and chemically inert surface, carbon fiber, aramid fiber and glass fiber have poor interfacial adhesion to the matrix, and usually require surface modification to improve the interfacial adhesion. The interfacial strength of fiber reinforced polymer composites can be significantly improved by introducing different nanomaterials

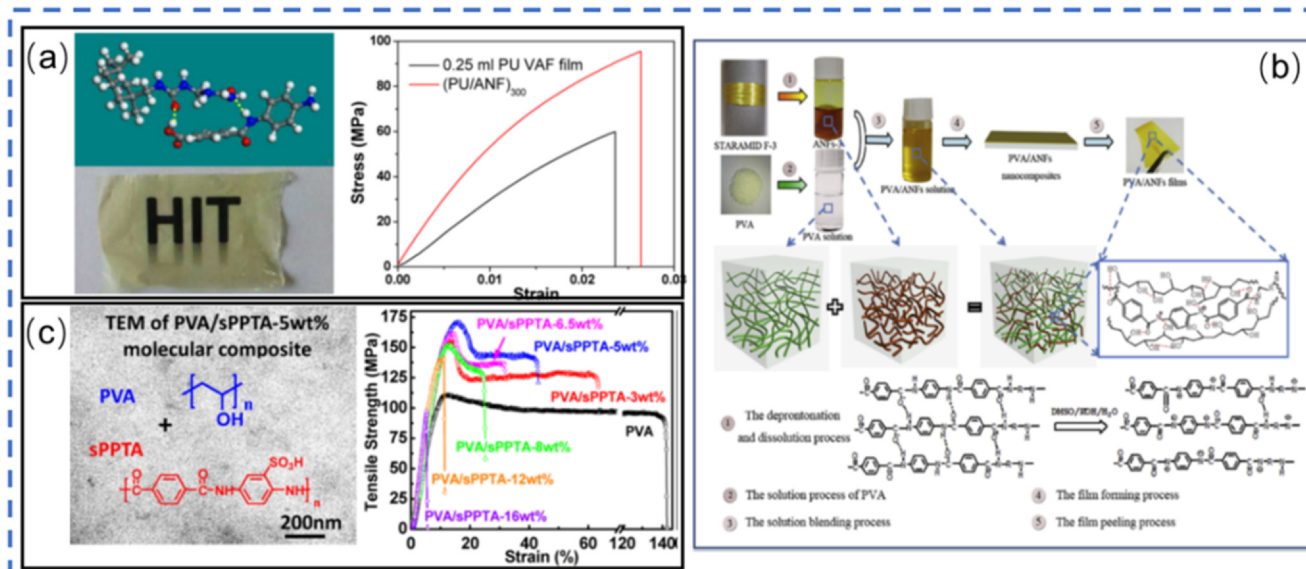


Fig. 5. (a) Schematic diagram of molecular structure, optical image and stress – strain curves of composite film, [60] (b) Schematic illustration of interactions for PVA and ANFs via a simple solution casting method [62] and (c) Typical stress – strain curves of PVA/sPPTA composites with various sPPTA contents [63].

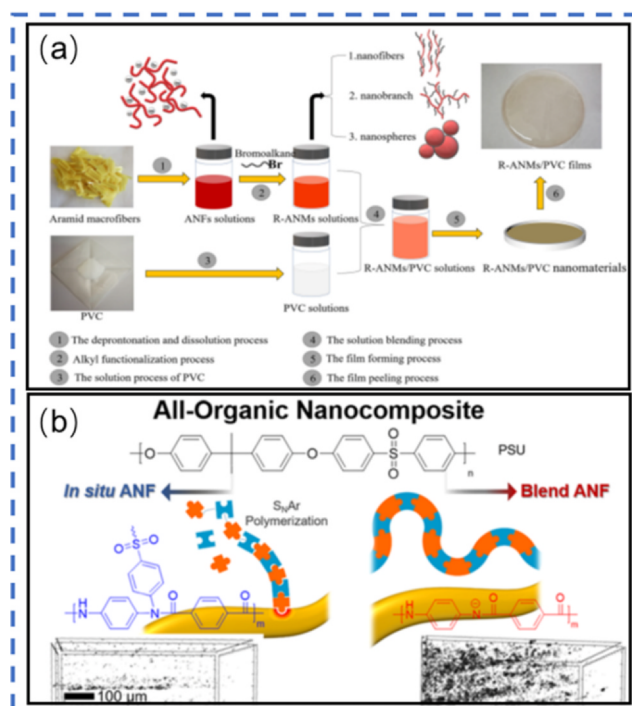


Fig. 6. (a) Schematic illustration of the fabrication process of R-ANMs/PVC films [65] and (b) Schematic illustration of the nanocomposite preparation by *in situ* and blending methods [66].

on fiber surface to construct surface nanostructures, such as carbon nanotubes [79–82], graphene oxide [83,84], zinc oxide [85,86], nanoclay [87], and metal–organic frameworks [88].

ANFs can also adsorb onto the surface of macroscale fibers to enhance the interfacial properties through mechanical interlocking and/or chemical bonding with the matrix. Sodano et al. [89] employed ANFs to effectively reinforce both epoxy matrix properties as well as the interfacial adhesion, which leads to improved interlaminar shear strength and fracture toughness, as displayed in Fig. 7(a), (with a maximum increase of interlaminar shear strength at 43% for 2 wt% ANFs). Sodano et al. [90,91] also investigated the deposition of ANFs on the surface of aramid fiber and glass fiber to improve the interfacial adhesion, which provides a simple and cost-effective method for constructing nanostructures on the fiber surface. Bahrami et al. [92] investigated the low-velocity impact response of aramid/epoxy laminates containing nano-interlayers. The results demonstrate that the incorporation of nanofibers makes composites able to absorb significantly higher impact energy in comparison with laminates without any nanofibers. Lee et al. [93] conducted an anodic electrophoretic deposition to facilitate the large-scale uniform coating of ANFs onto carbon fibers to enhance the interfacial properties between carbon fibers and epoxy matrix. It can be seen from Fig. 7(b) that with the deposition of ANFs, the surface free energy and interfacial shear strength of carbon fibers gradually increased, which proves that the introduction of ANFs can effectively improve the interfacial properties between carbon fibers and the matrix. Peng et al. [94] synthesized functionalized ANFs (fANFs) through polymerization induced self-assembly to reinforce and toughen the epoxy resin and multiscale carbon fiber/epoxy composites. The flexural strength, interlaminar shear strength, total energy dissipation and flexural strain at break of the multi-scale composites are increased by ~57%, ~38%, ~65% and ~71%, respectively. Moreover, Kim et al. [95] presented a novel LBL assembly for the surface modification of glass fiber to enhance the interfacial properties of glass fiber/epoxy composites through the combination of solution-processable graphene oxide (GO) and ANFs. The surface free energy and interfacial shear strength were improved by 23.6% and 39.2%, respectively, compared

with those of the bare glass fiber, as can be seen in Fig. 8. Researchers have also studied the *in situ* growth of ANFs on the fiber surface to enhance the interfacial adhesion between the fiber and the resin [96]. The above researches show that the surface construction of ANF nanostructures can effectively improve the interfacial adhesion properties between high performance fibers and the matrix, which provides new insights into the surface modification of fibers. However, how to improve the chemical bonding and mechanical interlocking of the ANFs at the fiber–matrix interface to achieve higher interfacial shear strength is worthy of further study.

4. Conclusions and outlooks

In summary, we review the recent research progress of the preparation of ANFs and the advantages and disadvantages of different preparation methods, and present the applications in reinforcing various polymer matrices such as epoxy, rubber and composites. Compared with the smooth, chemically inert surface of the aramid fiber and the unsatisfactory composite reinforcement effect, ANFs can be combined with the polymer matrix through hydrogen bonding, π - π stacking, chemical bonding and mechanical interlocking to achieve excellent reinforcement effect and have greatly enriched the applications of high-performance fiber materials. However, there are still some problems in the large-scale preparation of ANFs: 1) the preparation of ANFs from the top-down methods cannot avoid the preparation of AMFs, which is energy-consuming, environmentally unfriendly and cost-ineffective; 2) deprotonation and electrospinning methods for preparing ANFs have the problem of using a lot of solvents, which is harmful to the environment and workers; 3) the long preparation cycle and low efficiency of the deprotonation method are also serious shortcomings. In general, the ANFs prepared by polymerization induced self-assembly are most likely to achieve large-scale fabrication. Therefore, how to prepare high-quality ANFs efficiently is one of the focuses of future research.

ANF has high specific surface area, large aspect ratio, excellent mechanical properties and thermal stability, which makes it have an outstanding reinforcement for polymers. ANF reinforced polymer composites and their interfaces have been preliminary investigated. However, there are still some problems worth investigating:

- 1) For rubber nanocomposites, the dispersion of ANFs and the interfacial interaction between ANFs and rubber need to be further studied, which is of great significance for the enhancement and load transfer efficiency between ANFs and rubber. Moreover, the utilisation of latex co-coagulation method is very promising for preparing ANF-reinforced rubber composites, since ANFs have good water dispersibility.
- 2) ANFs have an outstanding reinforcement effect for polar resin matrix, but for non-polar or weakly polar resin matrix, further surface modification is required. Therefore, it is necessary to explore new and effective surface modification methods of ANFs. The enhancement of high temperature resistance and flame retardancy brought by ANF for resin matrix also need to be further studied.
- 3) ANFs play an indispensable role in the construction of nanostructures on the surface of high-performance fibers. However, there are few reports on the stress transfer mechanism and quantitative characterization of the interface between the fiber and the matrix. The interface thickness and interface modulus gradient changes of the ANF-reinforced composite is worth investigating, which is of great significance for practical applications.
- 4) Mathematics and computer-related software should be fully utilized to dynamically simulate the dispersion process of ANFs in the polymer matrix, and mathematical models should be established and optimized to explore the enhancement mechanism and used to guide experimental design.

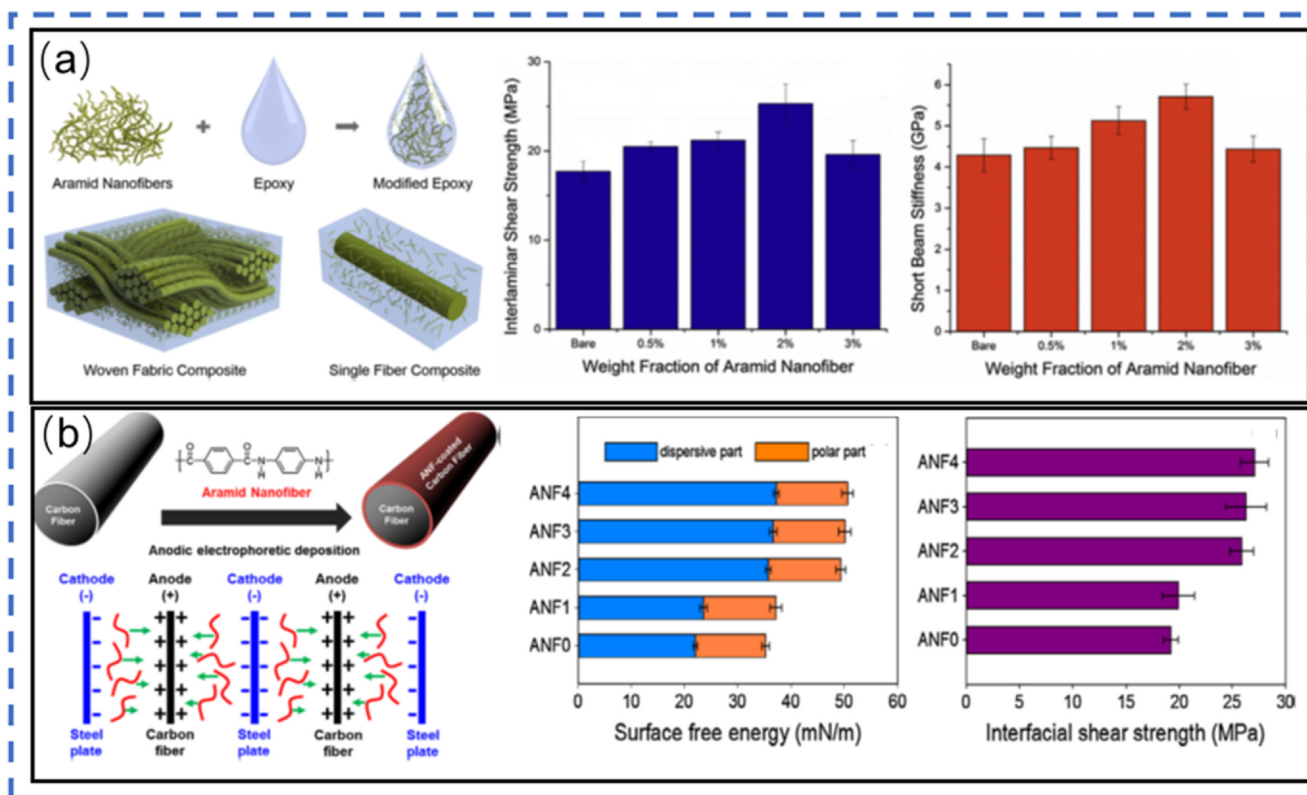


Fig. 7. (a) Schematic of modified fiber reinforced polymer composite and the incorporation of ANFs and the comparison of interlaminar shear strength [89] and (b) Schematic illustration of coating of ANFs on carbon fiber surfaces by anodic electrophoretic deposition and the comparison of different properties [93].

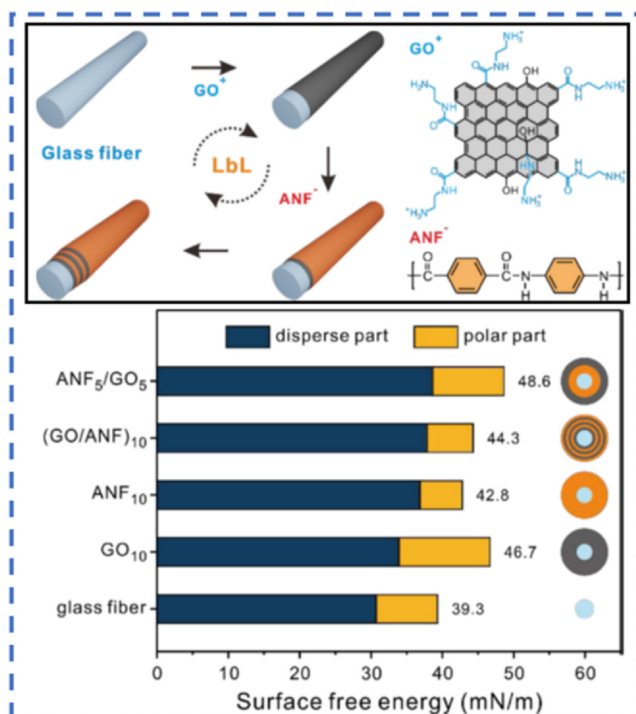


Fig. 8. Schematic of the preparation of a positively charged GO and negatively charged ANF multilayer coating on a glass fiber and surface free energy [95].

We anticipate that these difficulties can be solved by conducting lots of experiments. Thus, we believe that the present review may deliver an in-depth information about the recent experimental findings of ANFs, which help the scientific society to develop new generations of ANF-

reinforced polymer nanocomposites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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