





Review

Development in Additive Methods in Aramid Fiber Surface Modification to Increase Fiber-Matrix Adhesion: A Review

Sarianna Palola ^{1,*} , Jyrki Vuorinen ¹ , Jacques W. M. Noordermeer ²  and Essi Sarlin ¹ 

¹ Engineering Materials Science, Tampere University, P.O. Box 589, 33014 Tampere, Finland; jyrki.vuorinen@tuni.fi (J.V.); essi.sarlin@tuni.fi (E.S.)

² Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands; j.w.m.noordermeer@utwente.nl

* Correspondence: sarianna.palola@tuni.fi

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Abstract: This review article highlights and summarizes the recent developments in the field of surface modification methods for aramid fibers. Special focus is on methods that create a multifunctional fiber surface by incorporating nanostructures and enabling mechanical interlocking. To give a complete picture of adhesion promotion with aramids, the specific questions related to the challenges in aramid-matrix bonding are also shortly presented. The main discussion of the surface modification approaches is divided into sections according to how material is added to the fiber surface; (1) coating, (2) grafting and (3) growing. To provide a comprehensive view of the most recent developments in the field, other methods with similar outcomes, are also shortly reviewed. To conclude, future trends and insights are discussed.

Keywords: aramid fiber; surface modification; mechanical interlocking; nanostructures; adhesion; multifunctional fiber surface

1. Introduction

Aramids are a group of wholly aromatic polyamides. They are synthetic fibers with high elastic modulus, high tensile strength, low density, high resistance to abrasion and excellent chemical stability [1,2]. Since their discovery in the 1960s they have gained footage as a material for fiber reinforced composites in demanding applications ranging from automotive tyres to aerospace structures and structural applications [3–7]. Aramid fibers are used in composites as continuous filaments, fiber bundles and tows, short cut fibers, pulp, fabric, powder and paper depending on the application. However, the chemical structure of aramid fibers limits their use due to difficulties with matrix adhesion. Adhesion is critical in composite applications as it influences the functionality and durability of the composite structure as a whole. For this reason, industrial scale surface treatment methods [8–10] have been developed to overcome the issues with adhesion in aramid fiber composites. However, the currently used surface treatment methods have some disadvantages. Firstly, they render the aramid fibers compatible with only one type of matrix material. Secondly, they can influence the mechanical properties of the fibers negatively. Thirdly, the effect of the treatment may wear off with time. In addition, the chemicals used in the surface treatments are highly harmful and carcinogenic. Due to these factors and especially due to stringent environmental regulations and health guidelines there is high demand for new innovations in the field of aramid fiber surface treatments.

Very interesting progress has been made in this field by introducing hierarchical structures and multifunctionality to the fiber surface. The hierarchical structures and increased surface roughness introduce mechanical interlocking between the fiber and the matrix creating a strong interphase [11–14].

This type of interphase is not dependent on the chemical compatibility of the materials but has benefits from a frictional bond, which has a significant advantage. Another benefit of this approach is that the structures created on to the fiber surface can be considered permanent and therefore, the surface treatment can withstand longer storage times. Additionally, added multifunctionality opens the field for new innovations, such as dynamic sensing and failure analysis [15–18]. These kinds of approaches have great potential to solve the issues related to the surface treatment methods used at the moment. Hence, there is high activity within the field to develop new surface treatments for aramid fibers. Our feeling is that mechanical interlocking which utilizes the frictional bond is a very much rising trend in the field of aramid reinforced composites.

This review highlights the recent developments in the field of surface treatments for aramid fibers that enhance adhesion by creating a multifunctional fiber surface combined with mechanical interlocking of the fiber and matrix. In this context, a multifunctional surface is considered to be a surface that offers other benefits or properties besides adhesion promotion to the surface. For example, by incorporating nanoscale texture to the fiber surface, mechanical interlocking between the fiber and matrix can be achieved. The main focus is on methods that aim to increase adhesion in fiber reinforced composite structures by material addition. Thus, all surface treatment methods for aramid fibers will not be discussed. These include, for example, methods to decrease adhesion for the benefit of specific applications, methods suitable only for aramid pulp, paper on nanofibers [19–21] or methods to create hierarchical structures by material removal. The scope of the discussion is in the most recent developments in the field (21st century), and hence, some older, although widely used chemical methods, such as resorcinol formaldehyde latex (RFL) coatings for rubber application, are not discussed in detail. In addition, methods that aim to purely address other issues than adhesion related to aramid fibers, such as Atomic Layer Deposition (ALD) coating to improve Ultra Violet (UV) resistance [22], will be omitted.

In the following sections, state of the art surface modification methods are reviewed and discussed in more detail. First, some basic principles of aramid reinforced composites are presented and the reasons behind the need for surface treatment explained. The phenomenon behind multifunctional surfaces and mechanical interlocking is explained to highlight the benefits of using hierarchical structures to increase adhesion. The discussion is then divided into sections according to the main method of how changes are introduced to the surface and the appearance of the modified surface. First, methods that add a substantial layer or a coating of material onto the fiber surface are discussed. Silane coupling with aramid fibers is presented also in this section, as it can be considered as a uniform coating even though at the molecular level the method of attaching the silane to the surface is grafting. Second, methods that focus on grafting nanofibers, nanoparticles or polymers to the fiber surface are reviewed. Third, methods that grow nanotubes, -rods or -particles on to the fibers are investigated. The last section presents some other novel approaches that enable mechanical interlocking and create multifunctional fiber surfaces to highlight the fact that material addition is not the only way to create hierarchy at the fiber surface.

2. Structure and Adhesion in Aramid Reinforced Composites

A composite structure is defined as a combination of two or more materials that together constitute to better properties than the materials on their own would [23]. The main components of the structure are a matrix material and a reinforcing material. Key tasks of the matrix are to hold the reinforcement in place, give the composite its shape and to transmit loads to the reinforcement. The reinforcing material, on the other hand, is responsible for the load carrying capacity of the composite structure. Aramid fibers are a highly desirable reinforcement material for composite structures due to their ductility and high fracture toughness, excellent thermal properties as well as the ability to transfer mechanical loads efficiently along their molecular structure [24].

To gain full use of the mechanical strength of the reinforcement and structural stability of the matrix, the matrix and the reinforcement need to be joined together [25]. This is referred to as adhesion.

An adhesive bond is formed at the interfacial region between the reinforcing fiber and matrix, which is the region defined by the physical boundaries of the two materials [26]. The adhesive bond can be physico-chemical or frictional [27] depending on the properties of the reinforcing material and the matrix as well as their compatibility. Frictional bonds, such as in mechanical interlocking of the reinforcement and matrix, are often considered to be less important in polymer composites, even though they provide some very specific advantages due to the lack of need for chemical compatibility.

Adhesion is one of the main factors that influences the properties of the interphase [28]. The main functionality of the interphase is to transfer loads from matrix to the reinforcement and poor adhesion at the interface may cause catastrophic failure of the composite piece as a whole. On the other hand, too strong bonding at the interface is hardly ever beneficial as it can compromise the long-term effectiveness of the composite [28,29]. For example, in ballistic or other impact protection applications a low level of adhesion is used to maximize energy absorption and dissipation in to the composite structure to prevent catastrophic failure during impact [30]. Thus, it is critical to optimize the interfacial properties of any composite structure to fit the matrix and reinforcing materials as well as the intended application.

2.1. Structure of Aramid Fiber

When considering the interface between aramid fibers and polymeric matrix, most effort is usually aimed at increasing the interfacial adhesion, as stated above. This is because the chemical structure of aramid fibers is such that they adhere poorly by nature. Aramid fibers consist of highly oriented polymer chains with aromatic rings, as seen in Figure 1, that constitute a highly crystalline structure [31–33]. In the direction of the polymer chains, strong covalent bonds link each molecule creating highly oriented macromolecules. These macromolecules form the fibrillar structure of aramid fibers [24], which in turn accounts for the excellent mechanical properties of the fiber, such as high tensile strength and elastic modulus. However, perpendicular to the polymer chains covalent bonding does not occur. The macromolecules are linked together with weak hydrogen bonds and/or van der Waals forces. Thus, the fiber fibrillates easily in abrasion. The outmost surface of the fiber is very smooth and chemically inert. There are no side groups at the fiber surface, that would enable strong bonding with the surrounding environment [32]. Hence, without any surface treatment, it is impossible to form a strong interphase between the matrix and the aramid fibers that is needed to create a strong and durable composite structure.

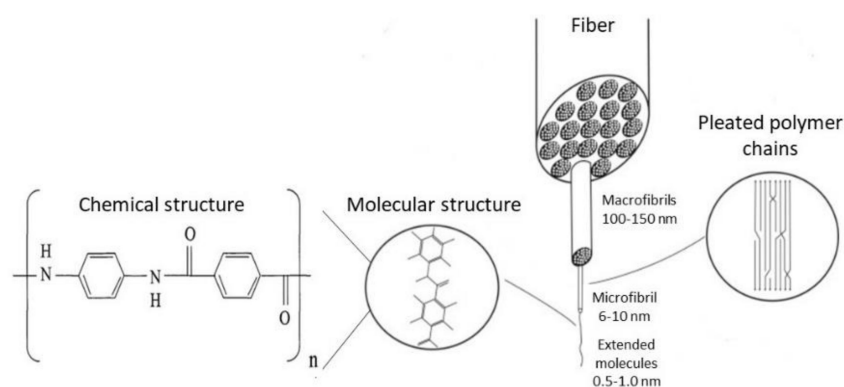


Figure 1. Chemical and fibrillar structure of para-aramid fiber, adapted from [24]. Reprinted with permission from ref. [24]. Copyright 2008 Elsevier.

Another aspect that should be considered when it comes to surface modification of aramid fibers, is their unique skin/core structure [34]. The core of the fiber has a highly crystalline pleated structure, created during the initial melt spinning process [24,35], which gives the fibers their characteristic elastic properties. The skin, or the outer layer, of the fiber is considered non-crystalline. This causes the typical failure mode in interfacial shear tests to be delamination with some fibrillation, which highlights

the complexity of any surface modification process when it comes to aramid fibers. This issue can be overcome by increasing cross-linking in the core phase of the fiber. This causes the failure mode to change from delamination towards debonding between the fiber surface and matrix, which in turn, increases compressive strength of the fiber and adhesion between the fiber and matrix [36,37]. Similar effect can be obtained by incorporating a carbon nanotube (CNT) network into the aramid fiber structure during manufacturing [38].

2.2. Chemical and Physical Bonding of Aramid

To achieve a strong enough adhesion with the matrix, a variety of surface treatments have been developed that are specifically designed for aramid fibers. Depending on the final application of the composite product, different surface treatment methods are used. Commonly used methods include coating with a coupling agent or a finish formulation [39,40]. These aim to create chemical bonding with the matrix. Other commonly used methods include plasma treatment [41,42] and chemical activation of the fiber surface [43]. In plasma treatment, the aramid fiber surface is bombarded with high energy plasma, which increases the surface energy of the fibers and enhances wetting [42]. The treatment creates a physical bond [26,44] (Figure 2a) between the matrix and fibers by increasing hydrogen bonds and other weak attractive forces, such as van der Waals forces, at the fiber surface. The treatment also increases the surface area of the fiber due to surface roughening caused by a sputtering effect but not to an extent where it could be considered as the sole reason for an increase in adhesion [45]. However, often the issue with this method is that the effect of the treatment decreases with time [42,45]. Research and development in this field on aramid fibers is ongoing [46–48], so new approaches should be expected.

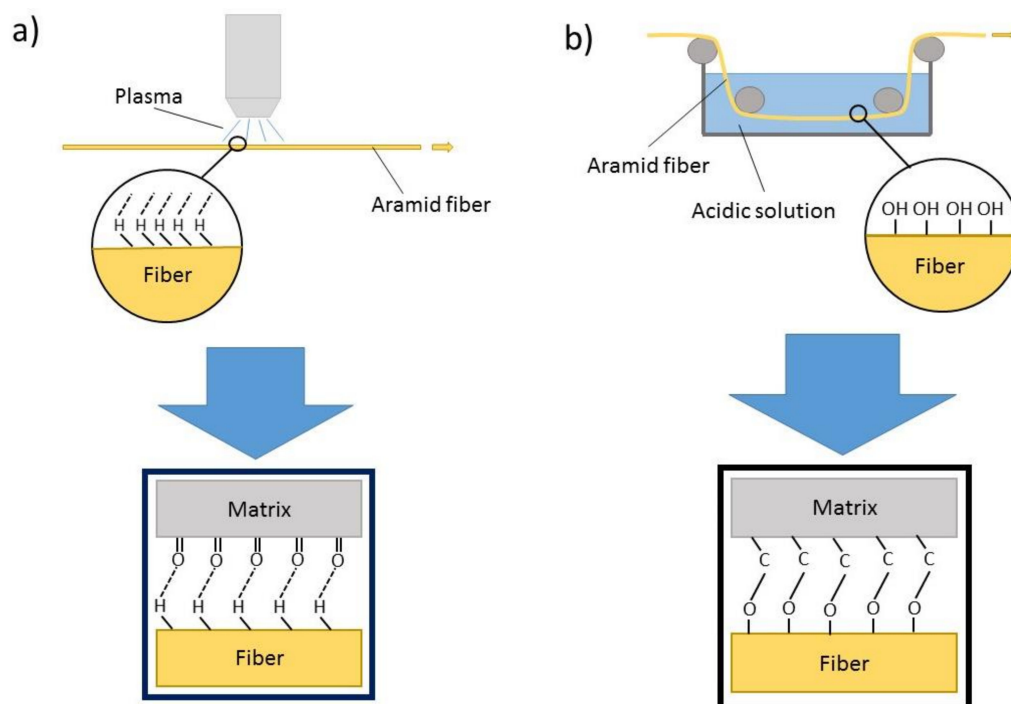


Figure 2. Schematic presentation of (a) physical and (b) chemical adhesion between fiber and matrix.

As a contrast to physical bonding, the chemical surface activation methods aim to attach reactive side groups, such as amine or carboxylic groups, on to the fiber surface to create a strong chemical bond [26,49,50] (Figure 2b) between the matrix and the fibers. Primary amines are often used to achieve this as they are also found in epoxy, which is a widely used matrix material. Due to the treatment, the adjacent reactive groups on the fiber surface and in the matrix create a chemical bond between the fibers and epoxy [51]. However, the surface activation process is typically an acidic surface treatment.

The oxidative nature of the acids is often too harsh for aramid fibers causing degradation of the fiber surface and core, thus having a negative impact on the tensile properties of the treated fibers [43]. This is because the addition of the carboxylic or hydroxyl groups on to the main polymer chain happens by chain scission.

In the rubber industry, the most commonly used method for adhesion promotion is the resorcinol formaldehyde latex coating (RFL) [52,53]. In this method, a two-component coating is applied typically to aramid cord or woven fabric. A pretreatment of an epoxy-amine coating [53,54] or polyurethane, is often applied to the fibers to enhance the coating process and to help the RFL-coating to adhere to the fibers. The coating is composed of a resorcinol part, which attaches the coating to the aramid, and a latex part, which chemically bonds with the rubber matrix. However, the limitation of this method is that it is suitable for rubber matrices only. In addition to this, formaldehyde used in the process, is regarded potentially carcinogenic and highly harmful [55,56]. According to the rising worldwide trends in eco-friendly manufacturing and production, it is considered beneficial to limit the use of formaldehyde.

2.3. Mechanical Bonding with Multifunctional Fibers

In the previous paragraph, physical and chemical bonding methods were discussed briefly but mechanical/frictional bonding can also be used to create a strong interface. In mechanical bonding or interlocking, the two adjacent surfaces interlock with each other by protrusions or cavities on the surfaces [57] as can be seen in Figure 3. This enhances the stress transfer between the fibers and matrix [58]. Although a mechanical bond is not as strong as a chemical bond [57], it has some clear advantages especially with aramid fibers, where it is difficult to create a chemical bond between the fiber and matrix. The main benefit of mechanical bonding is that it is not specific to just one matrix material. This makes the bonding mechanism more versatile as it can be used in a variety of applications. This is why a significant amount of research [59–63], is currently directed towards adhesion promotion methods that would create a mechanical bond between the reinforcing fibers and the matrix material. Mechanical bonding can be introduced into the reinforcing elements by material removal also. Common problem with material removal, however, is that it often affects the mechanical properties of the fibers negatively.

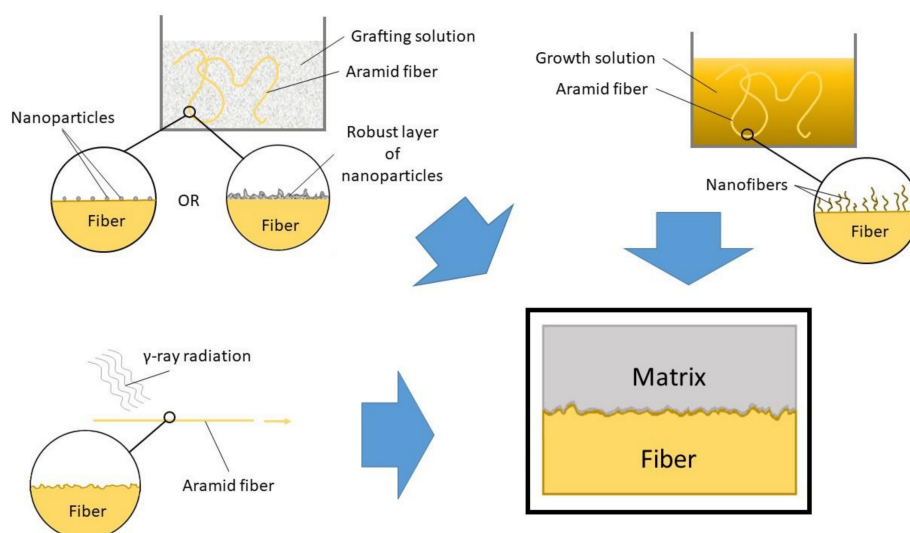


Figure 3. Schematic presentation of different methods to create mechanical bond between fiber surface and matrix.

Mechanical bonding or interlocking between the reinforcing component and matrix material can also be induced by creating hierarchical structures on the fiber surface or by increasing the surface roughness of the fiber. Hierarchical structures are structures that have additional smaller length

dimensions within the composite [64]. Typically, one of the length dimensions is in the nanoscale. A good example of a naturally occurring hierarchical composite structure is nacre [65], where hard aragonite particles are interconnected with each other by soft proteins, creating a unique hardness and toughness combination. Synthetic hierarchical structures can be created by various methods [60,66,67] and recently more and more research has been directed towards using hierarchical structures as a way to increase adhesion between reinforcing components and matrix material in composites structures [59–63,68]. With these kinds of structures new combinations of properties can be introduced into the composite, creating a multifunctional fiber surface. Such properties can be, for example, better strength and fracture toughness combination [69], increased adhesion combined with enhanced electrical conductivity [18] or real-time damage sensing [70,71].

3. Novel Coating Methods

In this section, novel coating methods that aim to increase adhesion and introduce mechanical interlocking with the matrix and aramid fibers will be discussed. The term coating in this case refers to methods that add a substantial amount of material as a uniform or semi-uniform layer on to the fiber surface. Surface coupling with silanes will be presented here as well even though at molecular level the mechanism is grafting. This is because the silane forms a thick uniform coating-like layer onto the fiber surface. The silane coupling is a well-established method for glass fibers [72,73] and natural fibers [74] but new approaches on applying the method with aramid fibers have recently come to light, as seen in Section 3.3. In addition to adhesion promotion, other new coating methods for aramid fibers have been developed as well, such as SiO₂ grafting to improve thermal stability [75] and iron coordination to enhance UV-resistance and adhesion simultaneously [76].

3.1. Multifunctional Hybrid Coatings

Hybrid materials are becoming more common in the industry at the moment. By definition they are materials that include two moieties blended on molecular scale [77] to create a new type of materials or desired combination of properties in an existing material. A good example of this is the luminescent high performance poly(m-phenyleneisophthalamide) (MPIA) fiber created by Miguel-Ortega et al. [78] that could be used as luminescent color converter (LUCO) in lighting applications. Hybrid materials occur in nature also and, for example, Wang et al. [79] took inspiration from mussels on their ethylene glycol diglycidyl ether (EDGE) hybrid coating for aramid fibers. They created the coating by first immersing the fibers in a polycatechol and polyamine solution (PCPA) for one hour under UV irradiation and continued by adding EDGE into the solution. With this very efficient method they were able to increase the adhesion force of the fibers by 86% [79] in a rubber matrix compared to untreated fibers. The fiber surface roughness increased significantly due to the grafted EDGE on the fiber surface but the increase in adhesion force was achieved due to the abundant epoxy groups of EDGE, making it possible to form covalent bonding with the rubber matrix. This makes the approach a possible candidate for replacing the suspected carcinogenic RFL treatment that is at the moment used with rubber matrices. Tensile strength of the treated fibers decreased slightly, as can be expected, due to the effect of UV radiation but the effect was very minimal as PCPA acted as a free-radical scavenger protecting the fibers.

A very efficient hybrid coating for aramid fibers was also introduced by Chen et al. [63]. They designed a method where the aramid fibers are first surface activated with phosphoric acid solution and then dip-coated with a liquid shape memory polyurethane (SMPU) and SiO₂ hybrid solution and dried. The hybrid coating created a “pizza-like” structure on the fiber surface (shown in Figure 4a), which increased the interfacial shear strength by 45% [63] compared to just activated fibers. This is a clear indication that the interfacial adhesion between the fibers and matrix has been greatly improved due to increased surface roughness of the fiber. Another positive impact of the coating method was an increase in tensile strength of the treated aramid fibers by 6% [63]. This is significant as some of the

traditional surface treatment methods decrease the tensile strength of the fibers, making the fibers not suitable for structural components anymore.

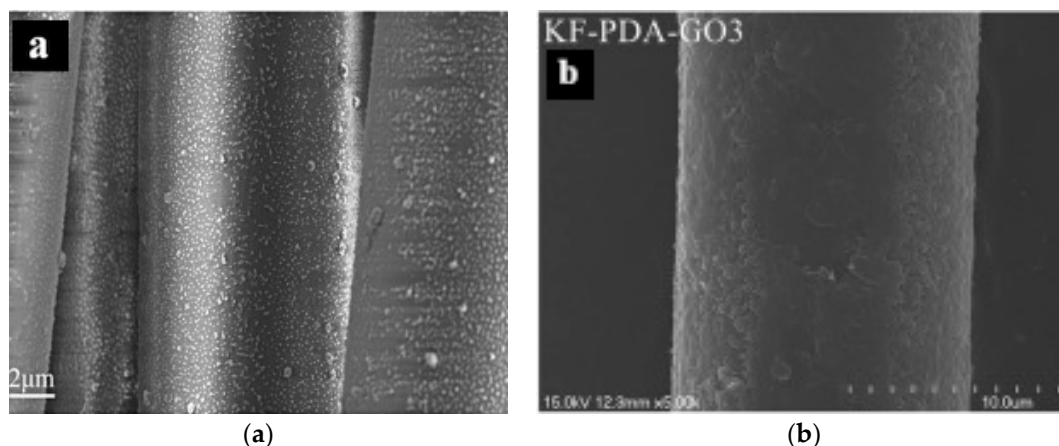


Figure 4. The appearance of (a) pizza-like shape memory polyurethane (SMPU)/SiO₂ hybrid coating [63] and (b) polydopamine-graphene oxide (GO) hybrid coating [80]. Reprinted with permission from ref. [63,80]. Copyright 2014 & 2017 Elsevier.

Another kind of aramid hybrid structure was created by Hussain et al. [62] by using graphene oxide (GO). They reported that a higher level of mechanical interlocking at the nanofiller matrix interface can be achieved with GO than carbon nanotubes. This is highly beneficial as GO is more affordable than carbon nanotubes and thus, more suitable for full scale industrial use. In this study p-phenylene terephthalamide (PPTA) fiber produced without the manufacturing related surface sizing, was coated with a functional primer of allylamine-octadiene with plasma co-polymerization. To create GO deposits on the functionalized fiber surface, the fibers were immersed in graphite oxide suspension baths. This resulted in uniform coverage of the fiber surface with graphene sheets and an increase of 7.8% in breaking strength of the fibers due to the fact that the graphene sheets covered up possible defects in the fiber surface, helped with the load distribution and made a positive strength contribution. In addition, a significant increase in the InterFacial Shear Strength (IFSS) in an epoxy matrix of the treated fibers was noted with a maximum increase of approximately 44% [62]. They studied the process parameters of the coating process and it was noticed that an alkaline graphite oxide suspension bath in the surface treatment process produced better results with respect to IFSS, breaking strength and chemical bonding of the graphene sheets with the fiber.

A unique feature of GO is, that it is able to act as an UV absorber. Zhu et al. [80] have taken the full advantage of this by creating a polydopamine-GO hybrid coating for PPTA fibers, presented in Figure 4b. They used a two-step process by first soaking and oscillating the PPTA fibers in dopamine solution for 24 h and then transferring them into a GO solution at set temperature for 10 h. As a result, they managed to produce a hybrid aramid fiber with significantly improved UV resistance, surface activity, mechanical resistance and thermal properties [80]. By using polydopamine as the “activating” pretreatment they were able to eliminate the use of a harsh acidic treatment in the process, which would have deteriorated the mechanical properties of the fibers.

Another approach to increasing surface activity and UV-resistance simultaneously was introduced by Zhou et al. [81] with a layer-by-layer coating mechanism. They created the structure by alternatively dipping PPTA fibers in SiO₂ and positively charged layered double hydroxyl nanosheets (LDH-NS) suspension. They noticed that by increasing the number of added layers, the tensile strength of the fibers increased also due to repair of surface flaws present in the original fibers. Even though they did not study changes in the adhesion of the treated fibers, an increase can be expected as a water droplet test revealed increased wetting due to increased surface activity and surface roughness [81].

Patterson et al. [82] noticed a similar trend with their ZnO nanoparticle sizing. By creating an even ZnO coating by a dip coating process onto aramid fibers, they were able to simultaneously improve the UV-resistance and IFSS of the fibers. Eventhough, the IFSS increased by 18.9% [82], the tensile strength and modulus of the fibers decreased slightly also. The exact value of decrease was not stated.

3.2. Polymeric Coatings

Not much of research has been aimed at developing purely polymeric coatings for adhesion promotion of aramid fibers. This is undoubtedly due to the surface chemistry of aramid fibers but also a may be result of the need for multifunctional fiber surfaces, which could not be achieved solely with polymeric materials. However, Zhang et al. [83,84] have demonstrated that this can be done. In their first attempt [84], they did not use a traditional dip-coating method but rather a more complex method of polymerizing the coating directly onto the fiber surface. Typically, in this way better adhesion can be obtained between the coating and the substrate. First, they grafted γ -methacryloxypropyltrimethoxysilane (MPS) and γ -glycidloxypropyltrimethoxysilane (GPTMS) on to a PPTA fiber surface as a pretreatment. This was followed by a co-hydrolysis and condensation reaction of the two to create hyperbranched polysiloxane (HPSI) directly onto the PPTA fiber surface [84]. Wettability and UV resistance was increased with this method.

Zhang et al. [83] achieved similar results also with a different process path. By using a strong acidic pretreatment and then adding the pretreated PPTA fibers to an already polymerized solution of HPSI and NaOH, the HPSI was grafted directly onto the fiber surface. They successfully created a method to increase UV-resistance and surface properties of the fibers simultaneously. Surface free energy and wettability of the fibers increased due to the epoxy and Si-OH-groups on the fiber surface of the coating, which is highly beneficial from an adhesion point of view. Interestingly, they have not studied the effect of the surface treatment on adhesion with actual adhesion tests. Due to the fact that the coating had abundant epoxy reactive groups on the surface, an increased surface energy and roughened surface structure, as can be seen in Figure 5, it can be expected to adhere well to an epoxy matrix at least.

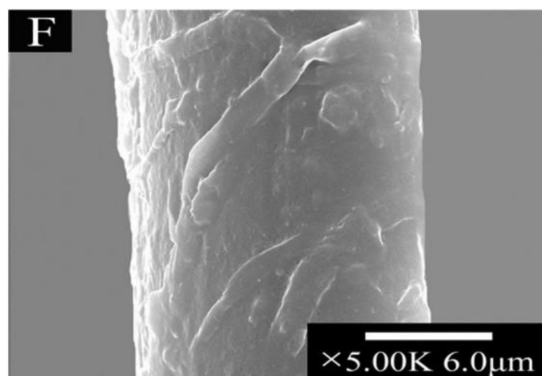


Figure 5. Hyperbranched polysiloxane (HPSI) coated aramid fiber [83]. Reprinted with permission from [83]. Copyright 2014 Elsevier.

Zhang et al. [83] came across another interesting factor, namely the effect on tensile strength. They used a very harsh acidic bath as pretreatment method for the coating process, which caused a 5–10% decrease in tensile strength, when compared to pristine PPTA fibers. However, after the coating process the tensile strength had improved to an even slightly higher level than that of untreated fibers. This indicates that even though acidic treatments are considered detrimental to the tensile properties of the fibers, such treatment can be used as a pretreatment when combined with a suitable surface treatment process. A similar trend has been observed with other novel surface treatment methods [59,81] as well.

In contrast to the above mentioned approaches, Cheng et al. [85] have approached the subject from the point of view of preserving the mechanical integrity of the fibers. They grafted polyethyleneimine (PEI) to poly-p-phenylene-benzimidazole-terephthalamide (PBIA) fibers with the aid of Fe^{3+} coordination. The significance of this method is that during the processing neither chain scission nor bond breakage occurs. Thus, the mechanical properties of the fibers are not affected, which was confirmed with tensile tests. In addition to this, the IFSS increased by 47% [85] in an epoxy matrix compared to untreated fibers due to increased wetting and the chemical affinity of the epoxy groups with PEI.

3.3. Surface Coupling with Silanes

Silane coupling agents are widely used in composite structures to increase adhesion with chemical and physical coupling. Silane coupling can be used on a macroscopic level in composite-composite adhesion [49], as well as on a smaller scale in reinforcement-matrix adhesion [86]. Especially in fiber reinforced composites silane coupling is often used with glass fibers [72,73] and natural fibers [74,87]. The most widely used organofunctional silane coupling agent is γ -MPS, as it can effectively form strong chemical bonds between inorganic reinforcement and an organic matrix. Zhang et al. [83] used this method successfully as a pretreatment for an adhesion promotion coating for aramid, as seen in the previous section.

Recently, the application of silane coupling agents as a primary surface treatment also for aramid fibers has been implemented. Some of the first ones to explore this route were Ai et al. [88] on PPTA fibers. They used γ -chloropropyltrimethoxysilane. In their approach, PPTA fibers were first soaked in a dimethylsulfoxide (DMSO) and sodium hydride solution at elevated temperature and then transferred into a DMSO and γ -chloropropyltrimethoxysilane solution under nitrogen atmosphere. The fibers were let to react in the silane solution for several hours to achieve a uniform coverage. As a result, an increase of 57% in interlaminar shear strength (ILSS) was observed as well as a ten-fold increase in surface area of the fibers [88]. The improved adhesion is partly due to the introduction of polar groups on to the fiber surface, which can react with epoxy groups, and partly due to the increased surface roughness, which enables mechanical interlocking with the matrix. This is significant as it highlights the fact that a combination of different adhesion mechanisms can effectively be utilized to increase the overall adhesion. On the other hand, Ai et al. did not investigate the effect of the treatment onto mechanical properties of the fibers, which causes some reason for concern.

Another approach was made by Sa et al. [89] with MPIA alias meta-aramid fibers and a combination of polydopamine (PDA) and a silane coupling agent. They created a novel “one step” process where the fibers were first functionalized in PDA and tris(hydroxymethyl aminomethane) solution and then γ -(2,3-epoxypropoxy)propyltrimethoxysilane (KH560), which is an epoxy functionalized silane, was added into the same solution. With this method, they were able to increase the amount of epoxy groups on the fiber surface that could react with a rubber matrix, which lead to an increase of 63% in IFSS [89]. The significance of the research is that the method is non-toxic and gentler, compared to acidic treatments. This is a major advantage in today's eco-friendly objectives. In addition, dopamine is typically considered a universal adhesive, which indicates that this method may be applicable to other chemically inert fibers, such carbon fiber or polyethylene fibers, as well.

Wang et al. [90] continued developing this approach further with slightly varied process parameters. They used PPTA fibers, catechol/polyamine (CPA) that was polymerized to PCPA to functionalize the fibers and γ -glycidyloxypropyltrimethoxysilane (GPTMS) as the silane. This way they were able to increase the IFSS of aramid fibers in rubber matrix by 16% compared to the previous approach [89], which in total means that the IFSS increased by 84% [90] compared to untreated aramid fibers. In addition to the important advantage of increased adhesion strength, the cost-efficiency of CPA compared to PDA is also a factor to consider. When looking to replace an existing industrial method, production costs are something that have a high impact on the applicability of the new next-generation surface treatment methods.

In a further study Cheng et al. [91] combined the chemical bonding abilities of silane coupling agent and mechanical bonding through increased surface roughness. First, they created a rough SiO_2 layer onto PBIA fiber through sol-gel process. Second, they used condensation reaction between 3-aminopropyltriethoxysilane and vinyltrimethoxysilan to form high concentration of NH_2 and $\text{C}=\text{C}$ groups onto the fiber surface. With this treatment combination the PBIA fibers can form strong chemical bonds with matrix material with varying polarity contributing to a clear increase in IFSS. For example, with natural rubber and epoxy the IFSS increased by 117% and 43%, respectively, compared to untreated PBIA fibers [91]. Additional benefit of the method is that it is able to preserve the mechanical integrity of the fibers, because the main grafting reactions happen at the benzimidazole's side chains and not through chain scission or bond cleavage of the main polymer chain. All of these aforementioned methods for aramid fibers are intriguingly similar to the RFL treatment used to bond aramid to rubber. The results indicate that perhaps a non-toxic and environmental approach can be found that could replace RFL in the future.

4. Creating Hierarchical Structures

The main function of hierarchical structures on reinforcing fibers is to add another level of reinforcement to the structure. This way the strengthening effect is expanded to work as transverse reinforcement. The focus of this section is on methods that create hierarchical structures by grafting or growing material onto the fiber surface in a non-uniform or un-coating-like fashion. This is done to highlight the difference in deposition methods and how they affect the chemical bonding of the deposited matter when compared to traditional coatings.

The discussion is divided into methods that use grafting and methods that use growing as the main method to introduce substance to the fiber surface, as they are fundamentally two opposite approaches towards surface modification. Different types of materials can be grafted or grown onto surfaces, such as carbon nanotubes (CNT), aramid nanofibers (ANF) or nanoparticles.

4.1. Grafting onto the Fiber Surface

In grafting, a chemical bond needs to be introduced in between the grafted material and substrate to ensure the grafted material stays on the substrate. This is usually done by first activating both the grafted material and the substrate with, for example, an acidic treatment. The problem is, however, that it poses a threat to the mechanical integrity of the materials. On the other hand, in some cases this can be prevented as seen in the following paragraphs.

4.1.1. Nanotubes and Nanofibers

CNTs are nanoscale tubular structures that have superior mechanical, optical, electrical and thermal properties [92]. They are used in composite structures to create ultimately lighter and stronger hybrid structures with, for example, added electrical functionality. Similarly, ANFs are nanoscale structures with excellent solvent resistance and mechanical properties [93]. They are created by dissolving bulk PPTA fibers into a solution of dimethyl sulfoxide (DMSO) and potassium hydroxide (KOH). This splits the long polymer chains of the PPTA into nanoscale polymers with similar crystal structure as the bulk fiber [94,95]. Currently, the most frequently used method to attach CNTs or ANFs onto aramid fibers is grafting them onto the fiber surface.

The first attempts to attach CNTs to aramid fibers included swelling the fibers in a solution of N-methylpyrrolide with carbon nanotubes [96]. This way a certain amount of nanotubes would attach themselves to the fiber surface. The effect was not permanent, however, as most of the CNTs were washed away by rinsing the sample [96]. This is a clear example of what an important role the interface between the CNTs and aramid fiber surface plays. With the right kind of surface activation of the aramid fiber and of the CNTs, a strong chemical bonding can be achieved between the nanotubes and aramid fiber. Chen et al. [59] devised a method to graft carbon nanotubes onto PPTA fibers where pendant amine groups were first introduced to the fiber surface by immersing in a solution of

hexamethylene diisocyanate and 1,4-diazabi-cyclo [2,2,2] octane (DABCO). The actual grafting of the nanotubes was done in N-methylpyrrolidone (NMP) solution with functionalized multiwalled carbon nanotubes (MWCNT) with the aid of ultrasonic treatment. They noticed that although the amination treatment actually damages the fibers, the carbon nanotube grafting compensates the damage and overall the tensile strength of the fibers increased by 12% [59]. A similar trend was observed with CNT grafted carbon fibers [97]. It was also noticed that the nanotubes were actually chemically bonded with the fiber surface rather than just deposited on to the surface. This can be considered to be due to the successful amination treatment of the fibers, which introduced pendant amine groups onto the fiber surface, that could readily react with the oxidized CNTs. This kind of surface treatment procedure increased the interlaminar shear strength (ILSS) of a bismaleimides (BMI) resin composite by 30%. The study also showed that the carbon nanotubes on the fiber surface were more effective in increasing adhesion than amine groups created in the amination process [59]. This is quite significant as it shows that a combination of a mechanical and chemical bond can be stronger together than just chemical bonding. The bonding mechanism should be considered as a combination of the two as the CNTs grafted on to the fiber surface create their own chemical bonds with the matrix in addition to mechanically locking the fibers in place.

Research towards CNT-aramid hybrid fibers has increased recently and very promising results have been achieved. For example, Rodriguez-Uicab [61] and his colleagues demonstrated that CNTs can be deposited onto chemically modified and as-received PPTA fibers from chloroform solution with the aid of ultrasound. They used two types of chemical treatments to modify the fiber surface prior to the CNT deposition to find out how the chemical treatment affects the outcome of the CNT deposition process. Acids used were a combination of nitric and sulfuric acid as well as chlorosulfonic acid. Both of the treatments were expected to modify the amorphous regions of the fiber surface by either opening the amide bonds at the surface or by adding sulfonic groups to the aromatic rings in the structure. These changes would again help the CNTs to attach themselves to the fiber surface. Quite unexpectedly the study revealed that the as-received fibers, which had no acid treatment prior to CNT grafting, showed the best results. When repeating the experiment with chlorosulfonic acid, they noticed that a significantly more consistent coverage with the CNTs could be achieved, as seen in Figure 6. This highlights the fact that the interfacial properties of the fibers are highly complex. Another study supporting this was done by De Lange et al. [39] with epoxy-amine coating. They noticed that a small amount of surface sizing or oily finish on the aramid fiber surface enhanced the formation of an even coating layer.

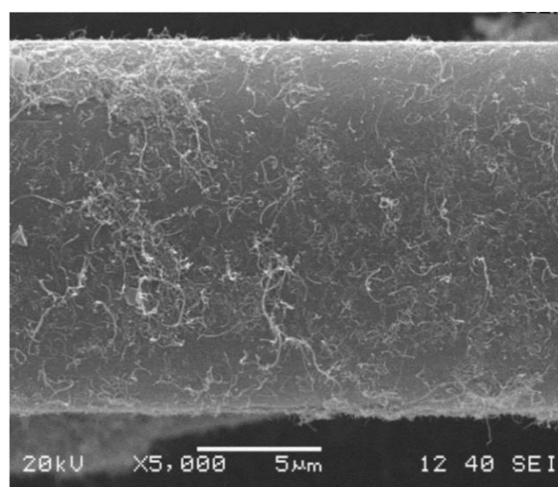


Figure 6. p-phenylene terephthalamide (PPTA) fiber with carbon nanotubes (CNTs) attached on to the surface [61]. Reprinted with permission from ref. [61]. Copyright 2016 Elsevier.

Although, Rodriguez-Uicab et al. [61] achieved promising results with the chlorosulfonic acid treatment, they came at the expense of tensile strength [61]. Fiber tensile tests revealed that the tensile strength of the chlorosulfonic acid and nitric+sulfuric acid treated aramid fibers decreased by 5.1% and 27%, respectively. This is due to the oxidating effect of the acids, which has been reported previously [43]. The decrease in the tensile properties is quite significant, which means that the acid treatments used in this study are not suitable for fibers to be used in structural composites. On the other hand, the fibers which were treated in the as-received state may be a very good candidate for such applications. However, no tensile strength measurements were reported on the CNT grafted fibers, so it is impossible to know for certain if the tensile properties have remained the same during the CNT deposition process. Another positive outcome of this method was reported to be an increased electrical conductivity [61].

The grafting of CNTs onto aramid fibers, was taken to another level by Lv et al. [98] with their direct fluorination scheme. They used direct fluorination as a pretreatment to create active spots for copolymerization of AA and divinylbenzene (DVB) onto PBIA fiber surface. This created an abundance of covalently bonded -COOH groups to the surface. The -COOH functionalized fibers were then subjected to a condensation reaction with amine-functionalized CNTs, which led to a high amount of CNTs to be grafted onto the fiber surface. This treatment increased the surface energy and roughness of the PBIA fiber, as seen in Figure 7. Due to the changes in the surface chemistry and morphology, the IFSS in epoxy increased by 69% compared to untreated fibers [98].

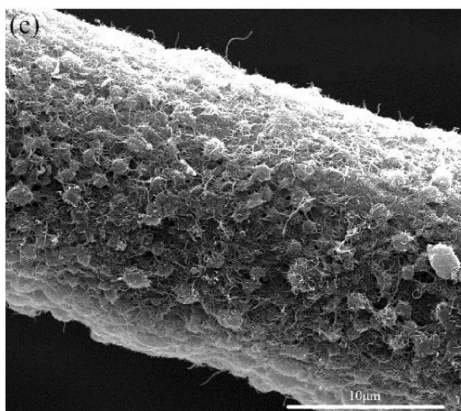


Figure 7. Poly-p-phenylene-benzimidazole-terephthalamide (PBIA) fiber with CNTs attached to the surface [98]. Reprinted with permission from ref. [98]. Copyright 2020 Elsevier.

They also noticed that the increase in the surface energy, due to the AA-DVB copolymer, was a more effective way to increase IFSS than mechanical bonding caused by the CNTs in epoxy. This is in line with the common understanding of bonding mechanisms; with strong chemical bonding, such as covalent bonding, between filler and matrix a strong interphase can be formed. Remarkably, tensile properties of the fibers remained in their original level even after the surface treatments.

Nasser et al. [99] achieved similar results with ANF grafted aramid fibers as seen in Figure 8. They used a solution of KOH and DMSO with dissolved PPTA fibers to treat unidirectional PPTA tape. With a simple dip-coating process they were able to increase IFSS in epoxy by 70% [99], compared to as-received aramid fibers, while preserving the mechanical properties of the treated fibers. What is notable, is that the ANFs are adsorbed onto the aramid surface. Which means that the bonding with the fiber occurs through physisorption and hydrogen bonding, so-called weak bonds, and still the increase in IFSS is notable.

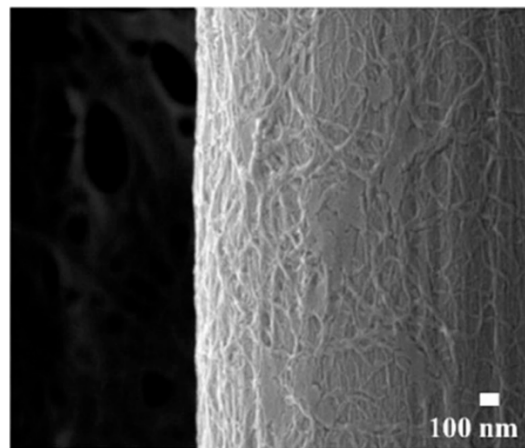


Figure 8. A network of aramid nanofibers (ANFs) grafted PPTA fibers [99]. Reprinted with permission from ref. [99]. Copyright 2019 Elsevier.

4.1.2. Inorganic Nanoparticles

Nanoparticles are small nanoscale particles ranging typically from 1 to 100 nm in size. They can be of any material inorganic as well as organic. For example, Hwang and his team [100] used ceramic nanoparticles, namely zinc oxide, to increase interyarn friction between fiber tows in woven PPTA fabric. The nanoparticles were deposited onto the fabric by dipping the fabric in colloidal solution containing zinc oxide nanoparticles and annealing the fabric at 150 °C for 10 min. Annealing was used to enhance adhesion between the nanoparticles and the fiber surface. By repeating the dipping and annealing process several times they were able to create a uniform coverage of the nanoparticles onto the fabric surface. A tow pull-out test was used to determine the influence of the nanoparticles to interyarn friction and it revealed a ~230% increase in pull-out energy and ~190% increase in peak load when compared to untreated fabric [100]. Although, actual adhesion testing was not performed the results indicate that an increase in adhesion should be anticipated, as the higher interyarn friction shows increased frictional/mechanical bonding in between the fibers. Similar behavior could be expected to occur in a traditional matrix material also. In addition, ZnO nanoparticles can be effectively used to protect aramid fibers from UV-radiation [82,101].

4.1.3. Polymer Particles

Polymers can also be grafted as nanosized particles. This way perhaps compatibility between the fibers and matrix may be achieved more naturally. Xing et al. [68] used a process called mutual irradiation grafting, where high energy gamma rays were used together with reactive polymers to create an embellished surface to aramid fiber-3. They used diethanolamine (DEA) and epichlorohydrin (ECH) as grafting media and were able to create nodules and pits on the fiber surface. The best result was obtained with ECH, as the aramid fiber surface has more affinity towards the functional groups in ECH when excited with gamma rays. The increased surface area and wettability of the fiber surface contributed to a 31% and 25% increase in IFSS and ILSS, respectively, when compared to untreated aramid fibers [68]. However, this method has a slight negative impact on the tensile strength of the fibers due to the nature of high energy radiation. It was studied that the tensile strength decreased 1.3% with DEA grafting and 2.6% with ECH [68]. This is a very small decrease but it may have an impact in certain applications. On the other hand, the advantage of the mutual irradiation grafting is its versatility. It can be carried out at any temperature, with any grafting media and without any separate catalysts.

Wang et al. [102] also addressed this issue by studying the effect of process time on the mechanical integrity of the treated fibers. They grafted polymeric nanoparticles onto aramid fibers by vapor phase deposition to introduce the polymer onto the fiber surface. They used plasma induced vapor

phase graft polymerization (PIVPGP) to create a coating of acrylic acid (AA) onto PPTA fiber surface. Plasma treatment of aramid fibers is not a novel technique and it has some major drawbacks, as stated earlier, but by using the plasma to polymerize a coating onto the fiber surface significantly improved results can be obtained. The process was initiated by subjecting the fibers to plasma to achieve surface activation of the fibers and then adding acrylic acid gas to the reaction chamber, which induced the polymerization reaction. In this way, the surface roughness of the PPTA fibers increased tremendously as AA polymerized on to the fiber surface as particles. An increase in wettability of the fibers was observed due to abundant polar groups at the fiber surface. These two factors increased the interfacial shear strength of the fibers in an epoxy matrix by 122% [102] compared to untreated fibers. The authors investigated the effect of the treatment on the tensile strength of the fibers and concluded that it had no significant impact on the tensile strength, when less than 15-min treatment time was used. Longer treatment times lead to a decreased tensile strength. This is because at the shorter treatment times the plasma had time to react only with the surface layer of the fiber and it is known that the main load carrying capabilities of aramid fibers are due to the crystal structure of the core [103]. Thus, by influencing only the surface no great change is expected to occur. With the longer treatment time, however, the plasma had time to affect the core material as well, which caused a decrease in tensile properties.

Another approach to grafting AA to aramid surface was created by Xu et al. [104]. Instead of PIVPGP they used electron beam (EB) to activate the PPTA fiber prior to AA polymerization. With this method, abundant carboxylic groups could be introduced onto the fiber surface. Even though the exact effect on adhesion was not studied, an increase should be expected in an epoxy matrix at least due to the added -COOH groups and increased surface roughness created by the nodules of poly(acrylic acid) (PAA) polymerized onto the surface. The effect on tensile properties was also not covered, which is of concern as the EB irradiation releases free radicals from the fibers. No apparent change in the appearance of the fibers after the irradiation could be observed, but no conclusions should be drawn from that.

4.2. Growing onto the Fiber Surface

As opposed to grafting material onto a substrate, by growing it, no pretreatment is needed to the material that is grown onto the surface. This in a way simplifies the process. However, inducing the growth process on chemically inert aramid fiber surface is a complicated issue. To ensure adequate bonding between the substrate and the grown material, the substrate is typically activated in a similar fashion as with grafting processes described in the previous section. This, naturally, may cause similar issues with preserving mechanical integrity, as was the case with grafting. Regardless of this, progress has been made in this field as well. In this section the growth of CNTs, ZnO nanowires and nanoparticles onto aramid fibers will be discussed. The significance of growing, for example, CNTs, onto aramid is that another dimension of multifunctionality, besides enhanced adhesion, can be added to the fibers.

4.2.1. Carbon Nanotubes

CNTs have already been successfully grown on to carbon fibers [97,105,106] and glass fibers [107] to improve interfacial adhesion, tensile and strength properties of composites. Now the first research results are presented that this can be done with aramid fibers as well [60]. First study in to the actual growing of CNTs onto an aramid fiber surface, was introduced by Hazarika et al. very recently [60]. They used microwaves to grow CNTs to pretreated PPTA fabric from ferrocene particles. Ferrocene and graphite can be used to create CNTs under microwave radiation as reported by Bajpai et al. [108]. As graphite heats up rapidly due to the microwave radiation it diffuses the heat to ferrocene. Due to the intense heat, ferrocene decomposes into atomic iron, which further condenses and agglomerates to iron nanoparticles. These particles act as the starting point for the CNT growth. Carbon atoms from graphite diffuse into the iron nanoparticles and once the saturation point is reached, the nanotube starts

to grow [108]. Hazarika's approach used this phenomenon to grow CNTs straight on the aramid fabric. Instead of graphite, however, they used a conductive polypyrrole/graphite oxide coating. Ferrocene was introduced onto the fabric surface by immersion in a ferrocene/toluene solution for 15 min in a sonication bath. The fabric was then subjected to microwave radiation to induce the growth of CNTs. Further analysis of the CNTs revealed that they were MWCNTs. This method increased the in-plane shear strength of the CNT decorated PPTA fabric in unsaturated polyester resin (PES) matrix by 81% [60]. In addition, the tensile strength and modulus of the composite was reported to increase by 105% and 126%, respectively [60] compared to untreated fabric. Effect of the treatment on tensile properties of the individual fibers in the fabric was not investigated. Although, it has been studied [109] that microwave radiation in itself does not affect tensile properties of aramid fibers, it is not necessarily the case here as the polymerization process of the polypyrrole/GO coating is oxidative. In addition to the increased adhesion properties, the conductivity of the PPTA fabric increased significantly.

The research towards creating CNT-aramid hybrid fibers has increased recently. The fact that some of the methods were able to increase the tensile strength of the fibers, is very encouraging. By incorporating CNTs onto aramid fibers, a unique combination of mechanical and chemical bonding as well as conductivity can be created, that offer new ways to utilize aramids in high performance applications. In addition, by being able to grow CNTs with other methods than the traditional chemical vapor deposition (CVD) opens new possibilities for cost efficient and environmentally friendly manufacturing.

4.2.2. Zinc Oxide Nanowires

Zinc oxide nanowires are small inorganic hairs or bristles that are used, for example in solar cells and semiconductors [110]. They are a high-interest material because they are inexpensive to manufacture and their unique, almost 1-dimensional, structure is anticipated to be the solution for some of the next generation high-tech applications, such as LED lights and lasers [110]. Research [51,100,111] has shown that ZnO nanowires can also be used in a similar fashion as carbon nanotubes to modify the fiber-matrix interface in hybrid polymer composite structures. The nanowires can be grown onto the aramid fiber surface to increase mechanical interlocking between the aramid fiber and polymer matrix. In an earlier study Ehlert et al. [51] devised a method that enabled chemical bonding of the grown zinc oxide nanowires with the PPTA fiber surface. Their study revealed that by cleaving a portion of the polymer chains on the surface of PPTA fibers by ion exchange, a carboxylic acid group can be created on the surface. The carboxylic acid forms a strong chemical bond with the zinc oxide nanowire, as it is grown onto the fiber surface in a preheated growth solution. This kind of surface treatment led to a 51% increase in the interfacial strength in an epoxy matrix [51] compared to untreated fibers. Without the ion exchange functionalization process the zinc oxide nanowires did not adhere strongly to the PPTA fiber surface and were easily removed from large areas simultaneously. It was also noted, that the surface treatment process did not affect the tensile properties of the PPTA fibers negatively. In fact, tensile strength even increased slightly due to the removal of the weaker outer layer of the fiber.

More recently, Hwang et al. [100,112] have also utilised zinc oxide (ZnO) nanowires to increase surface roughness of fibers in PPTA fabric. In their study PPTA fabric was used to study how interyarn friction can be increased by ZnO nanowires on the fabric surface. The nanowires were introduced to the surface by a two-stage process: (1) the fabric was soaked in a colloidal suspension of ZnO nanoparticles and annealed at 150 °C; (2) the fabric was placed in a hydrothermal growth solution at 86 °C. The soaking and annealing step was repeated several times to make sure that the fabric was completely covered with the ZnO nanoparticles that would act as nucleation sites for the nanowires. An aramid fiber with a ZnO nanowire covered surface is presented in Figure 9a. It is clear from the image that a very dense and uniform coverage of the fiber surface with the ZnO nanowires was achieved. A tow pull-out test was used to determine the sliding friction between tows and to find out how the ZnO nanowires affect the results. A tow pull-out test was used as it measures the required force to free a fiber bundle or two from the fabric as the sum of the frictional forces from all intersecting

points of the yarns [100,112]. The fabric with the ZnO nanowires revealed a 2200% increase in pull-out energy and 990% increase in peak load [100]. In both cases, the particles or wires were breaking off during the pull-out and the debris gathered at each tow. This contributed to the need for additional force for the pull-out process.

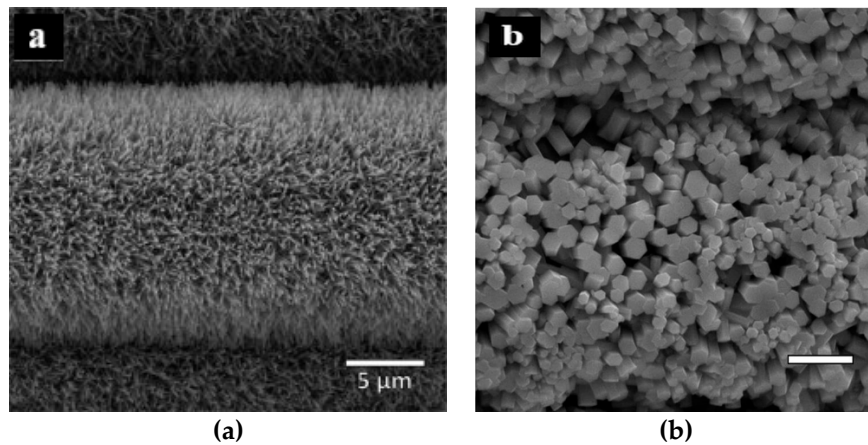


Figure 9. Zinc oxide nanowires (a) with high aspect ratio [100] and (b) with low aspect ratio (scale bar 3 µm) [112] that have been hydrothermally grown on to a PPTA fiber surface. Reprinted with permission from ref. [100,112]. Copyright 2015 Elsevier.

In a further study of the ZnO nanowires Hwang et al. [112] continued to research the morphology of the nanowires as the previous study indicated that the shape and size of the ZnO nanowires may influence the behavior of the composite during pull-out. To find the optimum parameters for the zinc oxide nanowire growth is critical for aramid fabrics used in ballistic applications. In these applications the interyarn friction should not be too high as it may cause a premature rupture in the fabric at impact [113,114]. They grew nanowires with four different morphologies on to the aramid fibers, by controlling the length and diameter of the nanowires. The study revealed that the highest peak load and pull-out energy was achieved with nanowires with the lowest aspect ratio, as presented in Figure 9b. Lowest values were noted with the nanowires with the highest aspect ratios. However, even the lowest values for peak load and pull-out energy were higher than the values achieved with a polymer coated PPTA fabric tested similarly [115]. In addition to this, it was noticed that the lower nanowire aspect ratios showed increasing amounts of aramid fiber fibrillation during the tow-pullout tests. This suggests a better ability to dissipate energy during the test. Additionally, in this study, the pile up of broken nanowires acted as additional strengthening to increase the pull-out force of tows. This was very clear especially in the low and medium aspect ratio nanowires, whereas with high aspect ratio nanowires the mechanical interlocking dominated the behavior [112]. From this it could be deduced that high aspect ratio nanowire arrays would be more suited for aramid fibers used as bundles or single filaments rather than as fabrics.

A similar conclusion was reached by Hazarika et al. [111] who studied this phenomenon by growing zinc oxide nanowires to aramid fabric with different seed cycles. They concluded that less but longer nanowire arrays are more beneficial to the impact properties of the fabric [111]. Malakooti et al. [116] further validated this finding in their study on the role of the ZnO nanowires upon impact. They concluded that the reason why ZnO nanowires on aramid fabric increase impact resistance is, that they enhance interyarn friction and favorably limit yarn mobility; thus, increasing the energy dissipation of an impacted projectile. Total or too high limitation of the yarn mobility would decrease the energy dissipation [117].

As noticed in the studies presented above, the brittle nature of ZnO nanowires makes them more suitable for ballistic applications where optimization of the interfacial adhesion is critical. At the point of impact too low adhesion prevents stress transfer from the matrix to the fibers, where it

could be dissipated, and a too strong adhesive bond would cause brittle fracture of the fiber and matrix, which would lead to catastrophic failure of the composite [113,114]. Perhaps very short almost nanoparticle like ZnO nanowires could be better suited for softer structural applications, such as tires and hoses, with ductile matrix material. Combining these properties to the piezoelectric and semiconductive properties of the ZnO nanowires, multifunctional fibers could be created, for example, with embedded sensing abilities. In any case, very promising results can be achieved by using ZnO nanowires as hierarchical structures on aramid fibers.

4.2.3. Nanoparticles

In addition to grafting, nanoparticles can also be grown onto the fiber surface. Wang et al. [118] successfully used titanium oxide (TiO_2) nanoparticles to increase the interfacial adhesion of PPTA fibers. The PPTA fibers were washed and functionalized in NaOH and HCl solutions prior to the TiO_2 deposition process. The TiO_2 nanoparticles were grown onto the fiber surface in a growth solution of tetrabutyl titanate and acetic acid at 120 °C for 5 h. The resulting fibers, in Figure 10, showed an even coverage of the TiO_2 nanoparticles, which subsequently lead to better wetting and to a 67% increase in interfacial shear strength in an epoxy matrix [118].

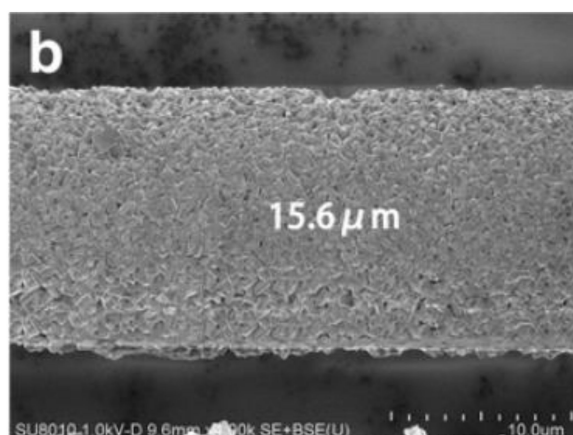


Figure 10. TiO_2 nanoparticle covered PPTA fiber surface [118]. Reprinted with permission from ref. [118]. Copyright 2016 Elsevier.

Wang et al. [118] also noticed that by decreasing the nanoparticle size, a better interfacial adhesion could be obtained. This is because smaller particles offer larger surface area that is in contact with the matrix. In addition to increased interfacial adhesion, the UV resistance of the fibers increased as well. The even coverage of TiO_2 nanoparticles absorbed UV-radiation readily protecting the fiber. However, this method caused a slight decrease of 4% in the tensile strength of the PPTA fibers, due to the hydrothermal ageing that the fibers were subjected to during the TiO_2 growth process. Thus, this method is not suited for applications where tensile properties of the fibers are critical. It has been shown [101,119,120] that TiO_2 particles are very effective in UV protection of aramid fibers even though not many focus on the effect of the treatment on adhesion properties.

In another study, nanoparticles were introduced to the PPTA fiber surface by microwave irradiation. With a simple and fast microwave assisted process Palola et al. [109] were able to create carbon based nanodeposits from ferrocene and graphite onto a PPTA fiber bundle, thus increasing the bundle pull-out force by 259% in rubber compared to untreated fiber. The force-displacement curves revealed that the increase was solely due to mechanical interlocking of the fibers with the matrix. In addition, the treatment had no negative impact on tensile properties of the fiber filaments.

The significance of the processes, where increase in interfacial adhesion can be created with nanoparticles is, that it highlights the effect of mechanical bonding. Friction between the fibers and matrix increases greatly even though the protrusions are of nanoscale. In addition, as the nanoparticles

are very small and not as protruding as nanowires or CNTs, further processing and storage may be simpler.

5. Other Methods to Introduce Functionality to the Surface

In the previous sections, methods have been discussed that can be used to create hierarchical structures to aramid fiber surfaces by adding material, either as a full coating or as nanofibers and particles. In contrast, the discussion in this section is focused on methods that aim to modify the fiber surface to induce mechanical interlocking by some other means, such as direct fluorination and high energy irradiation, where no material is added to the surface.

Direct fluorination is a process, in which elemental fluorine gas is introduced onto the material surface. It is an exothermic process, where only a thin layer of the material surface is affected [121]. With direct fluorination material surface properties, such as wetting and surface morphology [98,122,123], can be improved. It has been shown [124], that at low partial pressure ($F_p \leq 10$ kPa) during direct fluorination fluorine reacts with amine groups in aramid fibers. Whereas, with increasing F_p , the reaction is more favorable with benzene rings, as is an addition reaction. Low F_p has little impact on the surface morphology of aramid but with increasing F_p , the surface acquires a roughened appearance and tensile strength decreases [124]. In addition, increasing the process temperature enhances this behavior [122]. Cheng et al. [123] studied the chain cleavage during the fluorination process of PBIA. They noticed that the chain cleavage products, Figure 11, remain on the fiber surface after the fluorination process but they are not chemically bonded to the surface. Regardless of this, their presence contributes to an increased IFSS and enhanced wetting. This is an example of the importance of chemical bonding of the deposited substrate. Mechanical bonding cannot occur, as the surface protrusions are not strongly attached to the fiber. Increase in adhesion in this case is due to abundant polar groups on the surface.

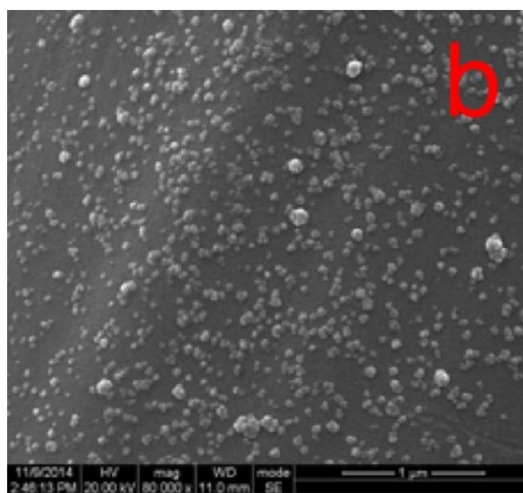


Figure 11. Chain cleavage products on PBIA fiber surface after direct fluorination [123]. Reprinted with permission from ref. [123]. Copyright 2016 Elsevier.

In a further study, Cheng et al. [125] noticed that the degree of fluorination influences the surface morphology and the amount of polar side groups at the fiber surface. By increasing the degree of fluorination, the surface roughness also increases up to a certain point until etching of the surface becomes predominant and the surface becomes smooth again. An increase of 39% in adhesion in an epoxy matrix was achieved. On the other hand, by introducing silanes to the fiber surface after the fluorination they were able to achieve an even greater increase of 46.7% [126] in the adhesion strength compared to untreated fibers, with no influence on tensile strength.

High-energy radiation is widely used in the polymer and healthcare industry to modify material properties with ionizing radiation. For example, crosslinking of rubbers and curing of composites [127],

surface modification of different materials, molecule size alteration in polymers and sterilization of disposable plastic instruments are some of the most common uses for high-energy radiation [128]. Two of the most used radiation sources within the industry are gamma ray (γ -ray) and electron-beam.

In most recent studies, γ -ray radiation is used with aramid fibers. In an earlier study Zhang et al. [129] studied the effects of Co60 γ -ray radiation on the interfacial bonding of aramid with epoxy. They noticed that the composition of the gas atmosphere influences the adhesion properties of the fibers. By using N_2 , an increase of 18% in ILSS in epoxy could be achieved compared to untreated fibers. When using air, the increase was only 16%. The greater increase in adhesion when using N_2 is due to increased surface roughness and formation of polar functional groups on the surface. As with all surface treatments that modify the fiber surface by altering the crystal structure of the fiber, the integrity of the fiber tensile properties is a concern. However, with an irradiation dose of 600 kGy, the tensile strength of the fibers remained similar to the untreated fibers.

Zhang et al. [130] continued to investigate the effect of the irradiation medium by irradiating Armos fibers in different concentrations of phenol-formaldehyde (PH) and ethanol solutions. With this approach, they were able to increase the ILSS by 25% in an epoxy matrix compared to untreated fibers [130]. Similar to the previous study, the increased adhesion was partly due to polar oxygen containing functional groups, that were introduced on to the fiber surface, but also due to increased surface roughness, which enabled mechanical interlocking of the fibers and matrix. However, the appearance of the fibers between the two experiments varied significantly. With N_2 and air as the irradiation medium, deep grooves were formed on the fibers, whereas with the PH and ethanol solution grooves were replaced by domes and hills.

Xing et al. [131] came to similar conclusions in their study of γ -ray irradiation of domestic aramid fiber-12 (DAF12). They also used several radiation doses, ranging between 30–1000 kGy, from a Co^{60} radiation source and concluded that by increasing the radiation dose to a certain degree the surface roughness of the fibers increased creating grooves and dents on the fiber surface. The increase in topography was caused by etching of the fiber surface as the high energy radiation excited the molecules at the fibers surface and enabled ionization of the surface. As with the above-mentioned research, they noted that etching and oxidation of the surface due to the high energy radiation also has an impact on the tensile properties of the fibers. Thus, they concluded that an irradiation dose of 400 kGy is optimum when trying to increase the adhesion properties of DAF12 [131].

In a very recent study, Xie et al. [132] combined chemical treatment and γ -ray irradiation, in a similar manner as Zhang et al. did [130], but with a distinct difference to introduce $-NH_2$ functional groups on to the surface. The significance of this is that the $-NH_2$ groups can actively take part in the curing process of epoxy. This was achieved by first irradiating the fibers in 1,4-dichlorobutane with a 400 kGy radiation dose and then soaking them in a solution of ammonia and alcohol. They were able to increase IFSS by 40% compared to untreated fibers but simultaneously the tensile strength of the fibers decreased slightly due to alkaline hydrolysis. Alkaline hydrolysis occurs during the ammonification process and damages the fiber surface. On the other hand, benefit of the γ -ray treatment is that it is already an industrially used bulk method. This means that it may be easier to upscale these surface treatment methods. Additionally, lasers are an industrially available high energy source that can be used for surface modification quite easily. Nasser et al. [133] created graphene microfibers with a CO_2 laser onto para-aramid fiber tapes. This increased their interlaminar properties in epoxy while maintaining mechanical properties.

In addition to radiation, fluorination and amination, cryogenic treatment can also be used to modify the aramid fiber surface, as Xu et al. [134] have shown. They used two different types of cryogenic treatment; a temperature program controlled method (TPCM) which is a low cooling rate process and a quenching method which is a rapid cooling rate process. With the two processes, they were able to increase the IFSS of PPTA fibers in epoxy by 19% and 6%, respectively, compared to untreated fibers due to increased surface roughness of the fibers [134]. This indicates that mechanical interlocking of the fibers and matrix is the main mechanism behind the increased IFSS. Residual compression stresses

in the process increased the abrasion resistance and tensile strength of the fibers due to a more compact core structure and stronger interactions between individual fibrils.

6. Summary and Future Insights

In this review several aspects of adhesion promotion methods which take advantage of mechanical interlocking for aramid fibers in composite structures have been discussed. All of the methods presented in the review are summarized in Appendix A, while a concise summary of the surface treatment types is presented below in Table 1. Forming strong adhesive bonds with aramid is difficult due to its chemical structure and smooth surface. Being a high-performance fiber with immense potential, a lot of research has been conducted to solve this problem with different kinds of surface treatments. The creation of multifunctional fibers, which combine mechanical interlocking and chemical bonding between the fibers and matrix is the most current trend in the field at the moment. Multifunctional aramid fibers open the field for new innovations, such as in-situ sensing of damages with CNT and ZnO covered aramid fibers.

Table 1. Concise summary of the surface treatment types discussed in this review.

| Type of Method | | Increase in IFSS [%] | Change in Mechanical Strength [%] | Reference |
|----------------|------------------|----------------------|-----------------------------------|---------------|
| Coating | Hybrid coating | 19 ... 47 | 0 ... 6 | [62,63,82,85] |
| | Silane coupling | 63 ... 166 | 0 | [90,91,98] |
| Grafting | Nanotubes/fibers | 70 | 0 | [98,99] |
| Growing | Nanoparticles | 31 ... 122 | −3 ... −1 | [68,102] |
| | Nanowires | 51 | 0 | [51] |
| | Nanoparticles | 67 | −4 | [118] |

As to the recent highlights in the field of mechanically bonding aramid, several clear benefits over traditional methods are seen from the results. By introducing protrusions and grooves on to the fiber surface, the surface area of the fiber can be increased significantly. This allows larger contact area with the matrix and thus stronger bonding. In addition, the studies reported increased the wettability of the surface by introduction of polar functional groups at the fiber surface, thus creating a combination of mechanical and chemical bonding between the fibers and matrix. Another point to consider is that when the surface of the aramid fiber is roughened, it reduces stress concentrations at the interface, which might act as starting points for delamination. Other benefits reported in the studies are, for example, increased electrical conductivity, UV-resistance and thermal stability achieved by the creation of a multifunctional fiber surface. In addition, the impact resistance of aramid fiber composites can be improved and tailored with ZnO nanowires and nanoparticles.

There were some key problems that repeatedly surfaced in the studies. A re-occurring issue is the negative effect on tensile properties of the fibers. Most of the surface treatments aiming to create hierarchical structures on to the fiber surface need a pretreatment of the fibers, which may be an acidic or high energy irradiation treatment. This evokes the old problem of oxidizing the fiber surface and causing chain scission, which impacts the tensile properties of the fibers. On the other hand, in some cases the surface treated fibers demonstrated an increase in tensile properties due to the repairing effect of the treatments. This is encouraging contrast to the other results.

Another challenge that could be observed is the difficulty of upscaling the methods to industrial scale, as most of the methods presented are of laboratory scale. In addition, production costs may hinder the industrial utilization prospects. However, some of the methods, such as γ -ray irradiation, are already industrially used methods and as such, cost effective. In addition to this, enhanced results were achieved in some cases by simplifying and eliminating processing steps [79,89] of the surface treatments.

As seen by the prominent results, new and innovative surface treatments have been developed that can be viable and highly successful alternatives to replacing some of the older and environmentally harmful methods in the future. An example of this is the silane coupling, which is an excellent candidate to replace RFL treatment because of the non-toxic and environmentally friendly nature of the method. Aramid fibers have attracted an increasing amount of attention due to their excellent properties and new aramid based composite materials have been developed, such as aramid nanofibers [135,136], aramid wrapped CNTs [137,138] and a combination of aramid nanofiber and CNT composites [139].

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Appendix A

Table A1. A summary of the methods to improve adhesion of aramid fibers by introducing hierarchical structures to the fiber surface as well as their key benefits and challenges.

| Method | Outcome of the Method | Increase of Adhesion [%] | Matrix Used | Adhesion Evaluation | Other Benefits of the Surface Treatment | Effect on Tensile Strength of Fibers [%] | Reference |
|---------------------------------------------------------------------|-------------------------------------------------------|--------------------------|-------------|-------------------------|-----------------------------------------------------------------------------------------|------------------------------------------|-----------|
| Multiphase coating process | Uniform coating with nano-protrusions | 45 | SMPU | IFSS | | +5.7 | [63] |
| Immersion in graphite oxide suspension | Uniform coverage with graphene sheets | 44 | EP | IFSS | | | [62] |
| Immersion in MWCNT solution and sonication | MWCNTs on the fiber surface | 30 | BMI | ILSS | | +12 | [59] |
| Zinc oxide nanowire growth | ZnO nanowires on the fiber surface | 51 | EP | IFSS | | ±0 | [51] |
| Plasma induced vapor phase graft polymerization of acrylic acid | Poly(acrylic acid) nanoparticle covered fiber surface | 122 | EP | IFSS | | ±0 | [102] |
| Low temperature hydrothermal growth of titanium oxide nanoparticles | Titanium dioxide nanoparticle cover surface | 67 | EP | IFSS | | −4 | [118] |
| High energy gamma ray irradiation | Highly increased surface roughness | 45 | EP | IFSS | | N/A | [131] |
| Irradiation grafting of DEA/ECH to aramid fiber surface | DEA/ECH embellished fiber surface | 31/25 | EP | IFSS/ILSS | | −1.3–2.6 | [68] |
| Deposition of oxidized CNTs onto aramid fibers via sonication | CNT covered hybrid fibers | N/A | N/A | N/A | electrical conductivity | −5.1–27 | [61] |
| Growth of CNTs onto Kevlar fabric via microwave irradiation | Fabric surface covered with iron decorated CNTs | 81 | PES | in-plane shear strength | electrical conductivity, increased impact resistance, strength and modulus of composite | N/A | [60] |
| HPSi grafting onto aramid fibers surface | HPSi covered fiber surface | N/A | N/A | N/A | improved UV-resistance, increased thermal stability and flame retardancy | + | [83] |

Table A1. Cont.

| Method | Outcome of the Method | Increase of Adhesion [%] | Matrix Used | Adhesion Evaluation | Other Benefits of the Surface Treatment | Effect on Tensile Strength of Fibers [%] | Reference |
|-------------------------------------------------------------|-------------------------------------------------------------------|--------------------------|-------------|---------------------|----------------------------------------------------------------------------------------|------------------------------------------|-----------|
| A two-step process to create polydopamine GO coated fibers | two layered structure of polydopamine and GO sheets | N/A | N/A | N/A | improved UV-resistance, thermal stability, surface activity, mechanical properties | +3.8–8.2 | [80] |
| UV assisted PCPA deposition and EDGE grafting | Increased surface roughness with PCPA and EDGE, and epoxy groups | 85.6 | rubber | Pull-out test | | - | [79] |
| A green layer-by-layer self-assembly technique | Layered coating structure or SiO ₂ and LDH-NS | N/A | N/A | N/A | Improved surface activity, thermal resistance, mechanical properties and UV resistance | +12 | [81] |
| Grafting γ -chloropropyltrimethoxysilane onto Kevlar | Introduction of polar groups and roughened fiber surface | 57 | EP | ILSS | Increased wetting | N/A | [88] |
| “one step” process of silane grafting with PDA | Uniform layer of grated silane on the fiber surface | 62.5 | rubber | IFSS | | N/A | [89] |
| Silane (GPTMS) grafting with PCPA | Uniform coating of GPTMS on the fiber surface | 83.3 | rubber | IFSS | | N/A | [90] |
| ZnO nanoparticle sizing via dip coating | ZnO decorated fiber surface | 18.9 | EP | IFSS | Improved UV resistance | very minimal decrease | [82] |
| Grafting of PEI through Fe ³⁺ coordination | Surface embellished with PEI | 47 | EP | IFSS | | ±0 | [85] |
| EB induced grafting of AA | Roughened fiber surface with nodules of PAA | N/A | N/A | N/A | Improved surface activity, COOH added to the surface | N/A | [104] |
| Cryogenic treatment of Kevlar | Increased surface roughness | 5.7–19 | EP | IFSS | Abrasion resistance increased | +24.9 | [134] |
| Direct fluorination of PBIA fibers | Changes in the surface morphology and polar groups at the surface | 39 | EP | Pull-out strength | | N/A | [125] |

Table A1. Cont.

| Method | Outcome of the Method | Increase of Adhesion [%] | Matrix Used | Adhesion Evaluation | Other Benefits of the Surface Treatment | Effect on Tensile Strength of Fibers [%] | Reference |
|---------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------|-------------------|--------------------------|-------------------------------------------------------------------|------------------------------------------|-----------|
| Direct fluorination and silane grafting of PBIA fibers | Silane grafted onto the fiber surface | 46.7 | EP | IFSS | | ±0 | [126] |
| γ-ray radiation of Armos fiber in N ₂ | Increased surface roughness, introduction of polar oxygen containing groups | 17.7 | EP | ILSS | Increased wetting | ±0 | [129] |
| γ-ray grafting of Armos fiber in PF/ethanol | Increased surface roughness and polar groups | 25.4 | EP | ILSS | Increased wetting | N/A | [130] |
| γ-ray irradiation and ammonification | Increased surface roughness and –NH ₂ groups at the surface | 40.55 | EP | IFSS | | –0.3 | [132] |
| Microwave assisted surface treatment | Nanodeposit covered PPTA fiber bundle | 259 | rubber | Modified bundle pull-out | | ±0 | [109] |
| Grafting of CNTs onto PBIA fibers via direct fluorination | CNT and AA+DVB copolymer covered fiber surface | 69.1 | EP | IFSS | Increases electric conductivity and surface energy | ±0 | [98] |
| Grafting ANFs onto PPTA tape | ANF covered fiber surface | 70.27 | EP | IFSS | Increased short beam shear strength by 25.6% | ±0 | [99] |
| Grafting SiO ₂ and silane coupling agents to PBIA fibers | Increased surface roughness and ability to chemically bond with different type of matrixes | 117/166/43 | NR/ BMI/ EP | IFSS | ability to chemically bond with matrixes in a wide polarity range | ±0 | [91] |

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