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Advanced Treatments of Aramid Fibers for Composite Laminates

Mikko Kanerva

Abstract

Aramid fibers form an important group of fibers for composite applications. These applications range through light-weight shell structures, protective structures in ballistic applications such as helmets and various shields, protective clothing, and car tires, for instance. For structural applications, the composites of aramid fibers and high performance resins must form integral and strong parts. Therefore, the fiber-matrix interface places a significant role. Numerous surface treatments and fiber modifications have been applied over the years to adjust aramid fibers. On the way to improve and optimize these interfaces, various test methods have been applied. The recent studies apply microtesting, e.g., in the form of microdroplet tests. Furthermore, the material properties of the resin, fiber, and interface are used to create numerical models. However, the current challenge is to collect statistically reliable data as well as the necessary parameters to validate the simulations on different length scales.

Keywords: aramid, fiber, interface, finite element analysis, microdroplet

1. Introduction

Aramid fibers are a group of tough and strong fibers. The uniting feature of aramid fibers is the synthetic, polymeric base of the fibers. This polymeric base contains essentially a repeating structure of benzene rings connected by amide bonds and interchain hydrogen bonds, and the vast group of these polymers and especially the spun fibers are commonly called aramid fibers. Historically, the commercial fibers were established after discovering the so-called lyotropic liquid crystalline aramids. The first successful spinning trials were run by a famous chemist S. Kwolek while working for the company DuPont. Nowadays, commercial trade names of Kevlar[®], Twaron[®], and Technora[®], are well known, provided by different manufacturers.

2. Applications

Aramid fibers have an inherent yellowish color that often is a sign of well-known applications of these fibers. Aramid fibers are good in light-weight applications because the density of the fibers is relatively low, in the order of 1.35–1.5 g/cm³. Naturally, the stiffness (modulus) and strength of the fibers finally determine the applications for optimum designs. Indeed, aramid fibers are commercially provided with a range of stiffness and ultimate strength. The fibers that

have the highest stiffness are common in structures where the design is dictated by deformation. Various secondary and tertiary structures in aircraft are typical, such as jet engine cowlings, leading edges of wings, and tail planes. It should be noted that it is rather a common tradition to apply fabrics of aramid fibers in combination with other reinforcements such as carbon and glass fiber-based fabrics in laminate lay-ups. If seen important, aramid fibers with Young's modulus matching that of glass fibers can be used. Modulus-matched designs can decrease the amount of internal stresses in composite structures, so that the durability is increased.

The fact is that aramid fibers are tough, and they can extensively absorb energy in different dynamic loading conditions. Indeed, aramid fibers are applied in structures where a high level of energy absorption is required. These fibers are superior to glass and carbon rivals that cannot meet the requirements in shielding constructions. This is typically the critical requirement when a structure is expected to be damaged by an impact during operation. Thus, a damaged structure is considered from the point of view of damage tolerance or damage resistance.

Clearly, aramid fibers are an optimum raw material option for ballistic applications—the examples of products range from composite helmets to protective shields and vests against ammunition. Importantly, by selecting aramid fibers with a lower stiffness, they can well be used in systems with elastomeric bimerals. The combination with rubbery polymers refers to shielding applications, such as flame- and cut-resistant clothing and gloves. Due to the very high toughness, various kinds of belts and ropes with fiber reinforcement have been developed using aramid fibers for industry and automotive machinery—in these elastomer-fiber applications, glass and carbon fibers are not an option. In car tires, aramid fiber reinforcements form the load-carrying structure of the most high-quality tires.

There are many applications for aramid fibers where they are not much visible. Chopped fiber form is typical reinforcement in clutch plates and brake pads. For the most requiring suburban locations, aramid fiber particles are used as the reinforcing component in cement and road surfacing. Most beautifully, sailboat sails are an application where all the features of aramid fibers are in operation at their full extent: maximum strength, stiffness, and ductility.

After all, it should be remembered that there are other design requirements than the mechanical allowables. Actually, the other requirements can be governing the product development. These requirements on the fiber level can refer to electrical conductivity, especially personalized esthetics, antibacterial activity, and extensive vibration damping. In the event of aramid fibers applied in the system, additional modification of the fibers or their surfaces must be accomplished.

3. Surface characteristics and fiber treatments

Surfaces of aramid fibers can be modified due to various reasons, and the enhancement of the adhesion to composites' matrix resins is not the least emphasized reason. The challenge with the surfaces of aramid fibers is twofold:

- I. The adhesion in general between aramid fibers and various polymers is poor [1, 2].
- II. The subsurface structure in aramid fibers can lead it to peeling off [3, 4].

The first of the above challenges is of primary importance because the latter one results only in the event of appropriate adhesion.

Therefore, many of the studies concerned with the poor adhesion had the target of improving the adhesion. As a starting point, due to the chemistry of the aramid polymer, the fiber surfaces are highly inert and do not dissolve in almost any practical solvent. Besides, as is typical for spun fibers, the surfaces of the fibers are smooth.

For aramid fibers, the fundamental theories forming the basis of understanding adhesion include [5, 6]:

- I. weak atomic interaction, i.e., the van der Waals forces between surfaces;
- II. intermediate atomic forces, i.e., ionic and hydrogen bonds;
- III. primary, metallic, and covalent bonds;
- IV. electrostatic forces; and
- V. mechanical interlocking (cohesive resistance).

The formation of the fiber-resin interface is largely affected by the polarity and total surface energy of the fiber surface. Thus, the addition of polar groups has been suggested as a viable solution to increase adhesion. Various oxidation treatments [1] form the basic methodology to modify fiber surfaces, and these procedures cover: (1) gaseous oxidation treatments; (2) solution oxidation treatments; and (3) electrochemical or electrolytic oxidation treatments. These treatments merely modify the fiber surface morphology and might give a change in the surface energy and chemistry as well. In addition to the oxidation treatments, plasma treatments have been applied to aramid fibers. Brown and Mathys [7] applied ammonia and oxygen plasma treatments and reported enhanced performance of laminates, in terms of interlaminar shear strength. Shaker et al. [8] applied radio-frequency (R-F) plasma to modify aramid fibers and reached improved laminate properties.

The application of surface modifications, to allow mechanical interlocking, has been introduced by Lee-Sullivan et al. [9], Palola et al. [10], and Wu et al. [11]. Naturally, the modification of surface roughness also affects the surface chemistry of the fibers. Lin [12] studied the use of bromination and metalation to modify surface roughness and chemistry. Very often effective and strong surface treatments lead to deterioration and lower strength and stiffness of the fibers, although macroscopic laminate properties of a composite might remain on an acceptable level or even on a high level [12].

In detail, the fiber-matrix interface, as a definition, is not entirely a black-and-white plane. Already due to the physical boundary set by the fiber and molecular orientation at the surface, an intermediate phase (interphase) forms with macromolecular polymer resins. Engineering of this interphase, and even its removal, has been reported [13, 14]. The typical surface treatments by solutions, namely sizings of aramid fibers are applications of emulsified solutions, e.g., solutions doped with ethylene oxide and propylene oxide chain fractions on fibers or bundles. Sizings based on aqueous epoxy-piperazine solutions were studied by de Lange et al. [13], and they reported improved adhesion in terms of bundle pull-out force. The identification of an interphase via X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering tends to be difficult due to common elemental species, such as those represented by nitrogen and oxygen bands, detected in the fibers and anticipated interphases. A fiber finish or sizing often includes oily low-molecular weight components, which might lead to a wider interphase formation but eventually, for overly large concentration, lower adhesion [15].

Many of the studies of surface treatments anticipated that the treatments did not result in covalent bonds between the fiber surface and the matrix polymers [15, 16]. Only few works reported the potential of covalent bonds [7, 17].

The optimization of surface treatments is important to gain the desired macroscopic behavior in specific composite laminates. Naturally, the recipe of an optimum treatment depends on the targeted laminate behavior. Due to the typical applications of aramid fibers and their reinforcements, impact tests are frequently used in the evaluation of the interface performance on a laminate scale. Impact resistance and impact damage are complex phenomena. Good interfacial adhesion does not necessarily lead to desired impact performance [8, 17]. Within impact, frictional sliding along layer and fiber (inter)faces plays a role in energy absorption and might be hindered by a high level of adhesion. When a surface treatment is tailored for a macroscopic performance, it is advantageous that secondary properties remain unchanged, while the primary properties are improved [18]. Moreover, the performance under effects of harsh operation environments should remain acceptable [18, 19].

It was mentioned that high enough adhesion can lead to shattering of the aramid surfaces upon loading due to the internal structure of aramid fibers. Kanerva et al. [18] applied a diamond-like carbon (DLC) coating to form a nanoscale protective surface structure and also to gain high adhesion between the fibers and an epoxy matrix. The high adhesion related to DLC-coated aramid fibers and matrix polymers was also established by Devlin et al. (US Patent 6432537) [20] for short fibers. The latest research of modifying aramid fibers has been targeted to improve the internal structure of aramid fibers in order to prevent the fiber's cohesive damage at high interfacial loads [4].

4. Aramid fiber-matrix interfaces and tests

To understand the influence and nature of a modification on adhesion, the interface between fibers and matrix must be probed. Because most of the interest in surface modifications is founded on the targets by mechanical performance, the mechanical testing of the fiber-matrix bond is surveyed in the following.

Whenever a single filament or a bundle of fibers is analyzed, the samples or test specimens are small. Consequently, the load introduction and sensor configuration must be arranged in a highly sophisticated way. Currently, there are several test methods to study fiber-matrix interfaces:

- the micro-droplet method, e.g., [21];
- the single-fiber fragmentation method, e.g., [22];
- the pull-out method, e.g., [23];
- the fiber push-out method, e.g., [24]; and
- the fiber bundle pull-out method, e.g., [10].

The mechanical testing of fiber-matrix interfaces is not standardized, and therefore, the methodology among the current literature is not in harmony. The devices, specimen preparation, statistical significance, and the theory of data analysis vary in different reports and publications.

Due to the challenges of surfaces of aramid fibers, the tests of fiber-matrix interfaces are much used. The main presumption behind different test methods of interfaces is that the breakage of the interfacial bond occurs in a brittle manner. Also, it is typical to estimate that only shear load is subjected to the interface during testing. Then, the basic form of “interfacial strength” is denoted by interfacial shear strength (IFSS):

$$IFSS = \frac{F_{crit}}{A_{emb}} \quad (1)$$

where F_{crit} represents the peak value of the shear force observed during a test, and A_{emb} is the area carrying the load, i.e., the embedded fiber area. Eq. (1) is rather useful when the microdroplet method is used because the embedded area is relatively easy to determine. However, several corrections to the calculation of IFSS have been formulated when testing droplets bonded on carbon, aramid, glass, and natural fibers. Synthetic fibers, especially aramid fibers, are typically considered smooth or nearly smooth with only minor roughness that could result in sheer mechanical interlocking. Thus, the presumption of brittle failure of the interface ought to be justified.

The main deficiency related to interface tests is the lack of statistical significance and, consequently, reliability. For example, many of the works done using the microdroplet method are covering a low number of fiber-droplet samples and a low amount of variation in the droplet configuration per aramid fiber sample [25]. Also, the localized plastic deformation occurring in the droplet has an effect on the interfacial loading but is seldomly accounted for yet it can be detected easily in the microscopy images of the tested droplets, as shown in **Figure 1**.

A specific note related to aramid fibers is the role of friction between individual fibers and bundles in a fabric or preform structure. For certain ballistic applications, the amount of resin in the final product is low or entirely omitted, and then, the behavior of the aramid fiber-based reinforcement is governed by friction [26].

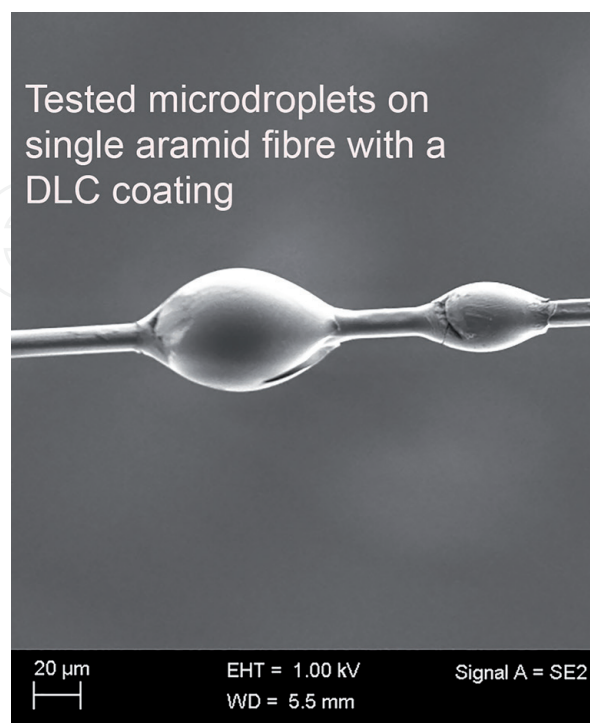


Figure 1.
An example of fiber-matrix droplets that have been tested using the microdroplet method [18].

In the end, the macroscopic behavior of a fibrous composite system is important. This means that the role of the interface and its strength should be known on the laminate level of length scales. Unfortunately, the exact relationship extending up from the single-filament behavior and up to the homogenized laminate level is lacking in the scientific literature. Several models exist to input interfacial effects while modeling bulk elasticity or strength [27]. To envisage the way that the combination of aramid fibers and matrix works, the well-known Halpin-Tsai model can be used as an example. For fibers, the model distinguishes between the effects of a particulate (“Greek symbol capital Phi” volume fraction) in its longitudinal direction and the effects in the transverse direction; these two directions are noted, by subindices L and T , here. Then, for the longitudinal direction, the model reads:

$$\frac{E_L}{E_m} = \frac{1 + \frac{l}{r} \eta_L \varphi}{1 - \eta_L \varphi} \quad (2)$$

where

$$\eta_L = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \frac{l}{r}} \quad (3)$$

and where l is the fibrous particles’ length, r is the diameter, and E refers to Young’s modulus of the individual components. The individual components are the matrix (m) polymer and the fibers (f). For the transverse direction, the model reads:

$$\frac{E_T}{E_m} = \frac{1 + 2 \eta_T \varphi}{1 - \eta_T \varphi} \quad (4)$$

where

$$\eta_T = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + 2} \quad (5)$$

By combining the longitudinal and transverse effects, the model yields the composite’s stiffness (modulus) in a system of randomly oriented fibers:

$$E_c = a E_L + (1 - a) E_T \quad (6)$$

where a is a parameter that could be considered a function of the interface, orientation, or a shape factor. The a -parameter can be a constant value or a function of other external factors [28]. However, there is no universal model to implement interfacial effects specific to aramid fibers by the parameter.

For advanced composites, where the fibers are continuous, the above format of Halpin-Tsai equations cannot be used (l goes toward infinity in Eqs. 2 and 3). In this case, the bulk composite properties are entirely anisotropic, and the elastic constants, for example, must be determined for each of the three directions individually [2]. In these formulations, the so-called Halpin-Tsai parameters can be thought to represent the interfacial effects on the laminate’s transverse and shear properties. Various studies have applied these equations to account for multiscale interfacial effects in composites (see, e.g., [29]).

5. Numerical predictions and finite element modeling

The experimental analysis of advanced composites is lacking the length scale of a representative bundle level. This is probably due to the practical challenges by small scale and due to the large variation, in size, of a representative bundle

or bundle-bundle cross-over point. However, the numerical simulations can be harnessed with models on different length scales. Models of a single-length scale as well as multiscale routines are excellent tools to survey various effects on composite properties.

To model an interface, its volume in finite element (FE) models is commonly estimated to be zero, i.e., interface is a two-dimensional object or contact formulation. As a first estimate, this type of an interface can be estimated to behave in a brittle manner for aramid fibers, so that linear elastic fracture mechanics (LEFMs) are applicable in addition to shear stress analysis. The power in the LEFM for interfaces is that a fracture toughness (G_i) in terms of a strain energy release rate can be used to describe the “strength” of an interface. With this type of a fracture parameter, the simulation results are somewhat less element mesh-dependent.

As noted, the plastic deformation of matrix around fibers affects interfacial breakage. To allow research of these effects, the models must be analyzed beyond LEFM. FE analysis with a homogenized interface model has been applied for models with a single fiber [30–32].

When plastic deformation at the interfacial region is considered, the fracture energy over the fiber surface (A_{emb}) divides into two parts upon fracture:

$$G_p = \frac{dW_p}{dA_{emb}} \quad (7)$$

and

$$G_e = \frac{dW_e}{dA_{emb}} \quad (8)$$

where the subindex p refers to plastic energy dissipation at interface, and the subindex e refers to the elastic strain energy release rate (ERR). In detail, the fracture toughness values can be related to the critical levels of energy release rate of damage onset (e.g., G_c) or propagation. In the applications of plastic dissipation at an interface, the common interface modeling method is the cohesive zone model (CZM). CZM refers to a mechanical model where the traction (τ) at the interface is defined as a function of the separation (δ) between the originally bonded bodies, i.e., fiber and matrix. As an example, a bilinear traction-separation law can be formulated as follows:

$$\tau = \begin{cases} K\delta & \delta \leq a_0 \\ \frac{a_1 - \delta}{a_1 - a_0} \tau_0 & \text{for } a_0 \leq \delta \leq a_1 \\ 0 & \delta \geq a_1 \end{cases} \quad (9)$$

In Eq. (9), the below notations are used:

$$a_0 = \frac{\tau_0}{K} \quad (10)$$

and

$$a_1 = \frac{2G_c}{\tau_0}. \quad (11)$$

It can be seen that the simple bilinear formulation leads to two strength-related parameters: fracture toughness (G_c) and the critical traction (τ_0) related to the onset criterion of damage. Additionally, the numerical computation requires a definite value for the interfacial stiffness (K). Due to the strong relation to the computational procedures, the definition of K is vague from the point of view of material interfaces—several theories for CZM applications have been presented (see, e.g., [33]).

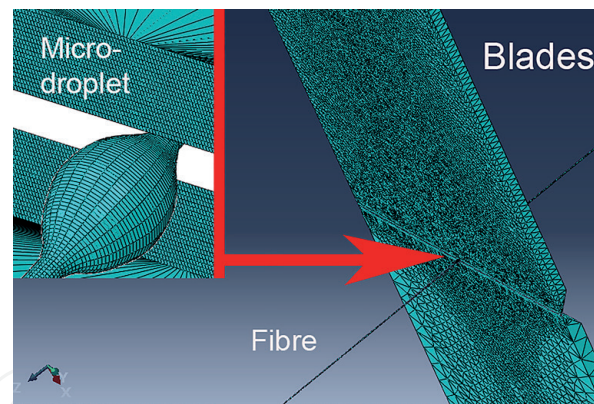


Figure 2.
An example of a 3D model simulating the microdroplet testing.

The power of numerical procedures allows to expand the analysis and consider exact three-dimensional models. Evidently, the parameters of the interface will have to be defined in the three-dimensional system. For example, the damage onset will require a fracture criterion, and the fracture toughness will have to be applied via an interaction function.

For aramid fiber composites, an FE analysis was reported by Kanerva et al. [18] with a full 3D representation (see **Figure 2**). For the DLC-coated aramid fibers, values of 22.2 MPa and 500 J/m² were determined for the case-specific critical traction and interfacial fracture toughness, respectively.

It is clear that the current numerical modeling techniques and computational capacities can offer efficient tools to study fiber-matrix interactions in composites with aramid fibers. However, the multiplicity of parameters currently leads to overlapping fitting procedures. Thus, the solutions are not typically unitary to the simulation case in question. There is an urgent need to improve the microtest methods in order to gain more experimental output and data to validate the numerical models. There are very recent works in the current literature that target to improvements in the test systems to enhance statistical significance, data rate, and accurate output from the microtests [34, 35].

In future, it will be possible to accurately account for plastic deformation, residual stresses, and a multistage fracture process in the simulations of fiber-matrix interfaces. This will be an important step toward analyses of fatigue and environmental effects on interfaces in composites with aramid fibers.

6. Conclusions

Aramid fibers have been modified and optimized for various applications ever since they were established. Around three decades, academic researchers have focused on trial-and-error type experiments to improve the surface characteristics in the sense that feedback based on laminate testing was behind burdensome and expensive testing efforts. After millennia, the microlength scale testing of fiber-matrix interfaces has improved, and more information about the interfacial performance is available. Meanwhile, the numerical analysis of interfaces has gained increasing amounts of attention. Efficient and valid numerical simulations could save time and resources in the optimization of surface treatments of aramid fibers for specific applications. However, there are still challenges in the validation of numerical models because the experimental output does not provide for necessary parameters and statistical certainty.

Conflict of interest

The author confirms no conflicts of interest.

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