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Abstract

Micromechanical tests are reliable tools to study the failure mechanisms in composites reinforced with continuous fibers. This paper presents an overview of various analytical models developed to study the pullout (push-back) behavior of a fiber embedded in a matrix block to characterize the fiber/matrix interfacial adhesion. Two approaches can be distinguished: one based on a maximum stress criterion (shear lag) and the other based on fracture mechanics. This article gives an overview of the analytical models reported in the literature to measure the shear strength and critical fracture energy at the interface, the parameters influencing these properties, the geometry of the model, embedded length of the fiber, fiber diameter and loading conditions (opening width between the knife-edges for example), including components (fiber, matrix, interface), manufacturing route and the resulting defects.

Key Words: Interface; pull-out; interfacial shear strength; micro-indentation; damage.

Contents

1   Introduction

Fiber composite technology is based on taking advantage of the high strength and high stiffness of fibers, which are combined with matrix materials of similar/dissimilar natures in various ways, creating inevitable interfaces. In fiber composites, both the fiber and the matrix retain their original physical and chemical identities, yet together they produce a combination of mechanical properties that cannot be achieved with either of the constituents acting alone, due to the presence of an interface between these two constituents **[1]**. The study of the mechanical behavior of composite materials often boils down to two basic constituents, the matrix and the reinforcement. While there is an abundant literature on composites, studies on the influence of the interface or the interphase are much sparser. Since the 1970s and in the last few years alone, fewer than 30% of published articles have dealt with interfaces while only 2% concern the interphase (**Fig.1**). The growing number of uses for fiber reinforced composites (FRCs) in many
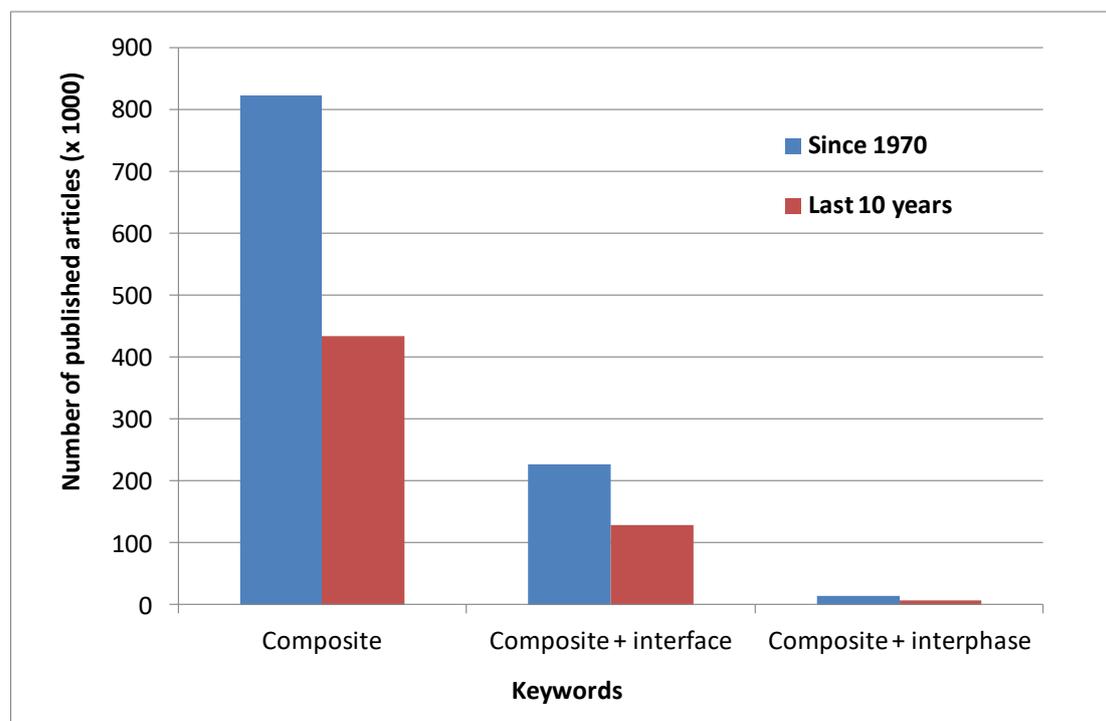
Fig.1. Number of publications on composites and interfaces / interphase since 1970.

3

engineering applications has made the issue of interface (or more properly termed, interphase (Drzal et al., 1983) [2]) a major focus of interest in the design and manufacture of composite components. A classic definition of the interface in fiber composites is a surface formed by a common boundary of reinforcing fiber and matrix that is in contact with and maintains the bond in between for the transfer of loads. It has physical and mechanical properties that are unique from those of the fiber or the matrix. The notion of interface or interphase remains relatively vague, as the interfacial zone does not exist in itself but is created during the implementation of the composite. Therefore, it appears very difficult to assign mechanical properties to it.

In contrast, the interphase is the geometrical surface of the classic fiber-matrix contact as well as the region of finite volume extending therefrom, wherein the chemical, physical and mechanical properties vary either continuously or in a stepwise manner between those of the bulk fiber and matrix material [3]. In other words, the interphase exists from some point in the fiber through the actual interface into the matrix, embracing all the volume altered during the consolidation or fabrication process from the original fiber and matrix materials. Therefore, the earlier definition of Metcalfe (1974) [4] for interface can be used for interphase as well: "An interface is the region of significantly changed chemical composition that constitutes the bond between the matrix and reinforcement". **Fig.2** schematically illustrates the concept of the interphase according to Drzal et al. (1983) [2]. Also shown in **Fig.2** are the various processing conditions that are imposed on the interphase to allow chemical reactions to take place and volumetric changes and residual stresses to be generated. However, for analytical purposes in micromechanics the interface is still conveniently considered to be infinitely thin and the properties of the mating fiber and matrix are isotropic and homogeneous.

Fig.2. Schematic illustration of the components of the three-dimensional interphase between fiber and matrix [2].

The study and application of composite materials are a truly interdisciplinary endeavor that has been enriched by contributions from chemistry, physics, materials science, mechanics and manufacturing engineering. The understanding of the interface (or interpha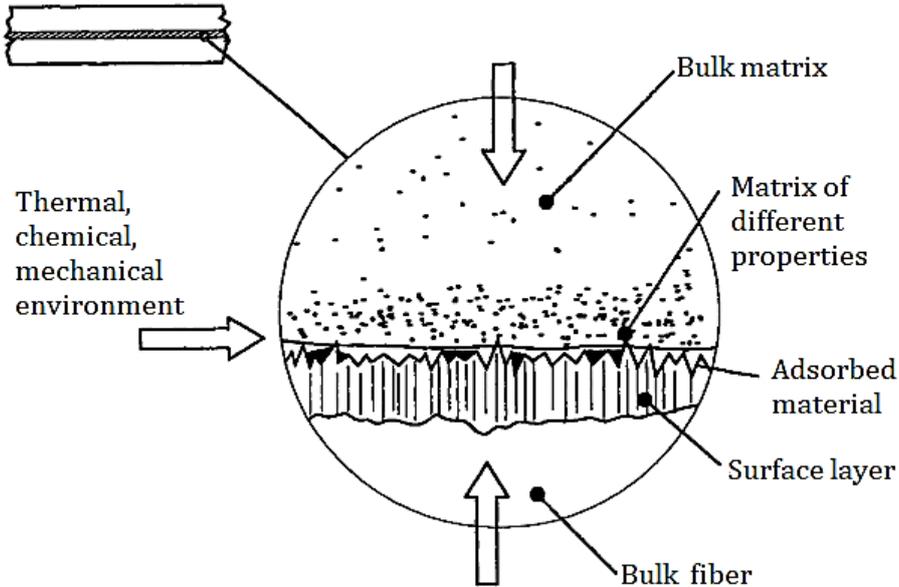se) in composites is the central point of this interdisciplinary effort, the proof that interfaces are critical to composite properties. From the early development of composite materials of various nature, the optimization of the interface has been of major importance. Even more important, the ideas linking the properties of composites to the interface structure are still emerging. Given a combination of fiber and matrix, it is desirable that the testing method will provide a reproducible and reliable means of not only measuring the interface adhesion but also allowing the failure mode at the interface region to be studied. One important requirement of these tests, whether the microcomposite tests or the bulk composite tests, is that the mechanics model developed for data reduction must be consistent with the actual failure mechanisms. But more often than not, particular failure is assumed to have taken place without confirmation in experiments. This practice not only makes the interface properties obtained doubtful, but it also degrades the whole value of the test method. However, all of these tests can hardly be regarded as providing absolute values for these interface properties even after more than 30 years of development of these testing techniques, this may also explain why there is an extremely large data scatter in the test results for apparently the same materials tested in different laboratories. Efforts are being continued to improve the quality and accuracy of experimental data and to develop better mechanics models underpinning these testing methods. The issue of understanding the composition and properties of interfaces in fiber composite materials is still evolving despite the fact that there have been a great number of works devoted to research in this field. Part of the reason for this evolution is the interdisciplinary nature of the subject. These works have provided a centralized forum not only to discuss and identify the important problems of the subject, but also to disseminate important research results from various sources. They are thus leading the scattered research and development efforts in a sensible direction, as well as helping to make significant contributions toward the improvement of our fundamental understanding of interfaces in polymer, metal and ceramic matrices composites.

It is well known that the properties of an interface are governed largely by the chemical/morphological nature and physical/thermodynamic compatibility between the two constituents and most often limit the overall performance of the bulk composite **[5-9]**. There is now a considerable amount of evidential data regarding the influences of interfaces on fracture toughness in both transverse and interlaminar fractures, and strength and stiffness of fiber composites in various failure modes and loading configurations **[10,11]**, although the relationship between documented material properties and the actual performances of composites is still in question. It follows therefore that a thorough knowledge of the microstructure-property relationship at the interface region is an essential key to the successful design and proper use of composite materials. Further, the interface properties are becoming gradually accepted as design and process variables to be tailored for particular end applications **[12]**. Although there is no simple quantitative relation known for interface optimization of a given combination of fiber and matrix, various chemical-physical and thermodynamic-mechanical principles along with previous experience

are invaluable sources of information to design the interface qualitatively. A number of potential solutions have been suggested to improve specific properties of the composites, particularly the interface bond quality for efficient stress transfer and the fracture resistance/damage tolerance of inherently brittle composites without sacrificing other important mechanical properties. This paper is concerned mainly with interfaces in advanced composites made from high performance fibers, such as glass, carbon, and matrix materials polymer. To control the interface properly and thereby to provide the composite with improved mechanical performance and structural integrity, it is essential to understand the mechanisms of adhesion which are specific to each fiber/matrix system, and the physico-chemical characterization of the interface with regard to the origin of adhesion.

The characterization of an interface is a challenging problem. To characterize the influence of interface on the load bearing capacity of composites, a number of experimental techniques, such as pull-out/ micro-droplet, compression test (Slice test), push-out (or indentation), microbond or fragmentation tests are commonly performed **[13-22]**. These tests have a variety of specimen geometries and scales involved. In these tests, the bond quality at the fiber-matrix interface is measured in terms of the interface fracture toughness, G_{ic}, or the interface shear (bond) strength (IFSS), τ_i, for the bonded interface; and the interface frictional strength (IFS), τ_{fr} , which is a function of the coefficient of friction, μ, and residual fiber clamping stress, q_0, for the debonded interface. Therefore, these tests are considered to provide direct measurements of interface properties relative to the test methods based on bulk composite specimens. Microcomposite tests have been used successfully to compare composites containing fibers with different prior surface treatment and to distinguish the interface-related failure mechanisms. Theoretical analysis of interfacial debonding has received significant attention especially for the fiber pull-out test. The condition of interface debonding has been defined by two distinct approaches: the shear strength criterion and the fracture mechanics approach. In the shear strength criterion, when the interface shear stress (IFSS) reaches the interface shear bond strength, τ_i, debonding occurs. In the fracture mechanics approach, extension of a debond crack requires the potential energy release rate of the composite constituents to reach a critical value, the interface fracture toughness, G_{ic}. In these two debond criteria, both τ_i and G_{ic} are assumed to be material constants, the characteristic interface properties to be determined in experiments.

One of the most important phenomena in FRCs for applications to load bearing primary structures is the stress transfer between the fiber and the matrix across the interphase/interface. When composites are subjected to various loading conditions, the efficiency of load transfer across the interface plays an important role in overall performance of the composites **[23, 24].** However, these zones (interface / interphase) play a leading role, as shown by Drzal 1986 **[25]** and Piggott 2004 **[26]**, since the interface and / or interphase ensure the transmission of the forces between the relatively soft matrix and the stiffer reinforcement. Consequently, the contribution of the reinforcement on the mechanical properties of the composite is directly related to the quality of the interfacial zone **[10]**. Kim et al. **[27, 28]** showed that a thorough understanding of the interfacial zone is considered as one of the criteria for composite design. From the stress-transfer mechanics viewpoint, theoretical analyses dealing with the stress state at the interface region are vital to understanding how and to what extent the interface

properties influence the mechanical performance and fracture behavior of the composites. Since the early pioneering work by Cox (1952) and Rosen (1964) **[29,30]**, a number of models have been developed to predict the response of composite materials in terms of thermo-mechanical properties and microfailure mechanisms under various loading conditions and different environmental situations. These range from simplified physical models such as the Kelly-Tyson model (1965) **[31]** to numerical solutions of stress and strain fields in the composite constituents based on rigorous finite element (FE) analyses. The fiber fragmentation test has a significant analogy with practical composites containing aligned short fibers when subjected to uniaxial tension along the fiber direction as it exhibits the fundamental damage modes that are present in the multiple fiber composites in service.

The central theme of this work is to propose a review of the different analytical models developed to study the pull-out (push back) behavior of a fiber embedded in a matrix block to characterize fiber / matrix interfacial adhesion. The available analytical models used to measure the shear strength and the critical fracture energy at the interface is described. The parameters influencing these properties, the geometry of the models, the embedding length of the fiber, the fiber diameter and the loading conditions (opening width between the knife-edges for example), including components (fiber, matrix, and interface), manufacturing route and the resulting defects are discussed in detail, all the models that are presented in this paper consider the material as a homogeneous structure, elastic, linear, that the radial effects are negligible (no radial dependence), that the strains and stresses imposed by the fiber under the application of the load F are fully accommodated within the interphase, of low thickness, the surrounding matrix is not disturbed.

2   Theories of adhesion and types of bonding

The physico-chemical aspect of composite interfaces is a difficult subject and our understanding of this feature is still far from complete. The nature or origin of the bonding between the fiber and matrix is discussed in terms of the theories of adhesion with associated mechanisms of bonding. The nature of bonding is not only dependent on the atomic arrangement, molecular conformation and chemical constitution of the fiber and matrix, but also on the morphological properties of the fiber and the diffusivity of elements in each constituent. It follows therefore that the interface is specific to each fiber-matrix system **[10]**. Proper characterization of composite interfaces, whether it is for chemical, physical or mechanical properties, is extremely difficult because most interfaces with which we are concerned are buried inside the material. Furthermore, the microscopic and often nanoscopic nature of interfaces in most useful advanced fiber composites requires the characterization and measurement techniques to be of ultrahigh magnification and resolution for sensible and accurate solutions. In addition, experiments have to be carried out in a well-controlled environment using sophisticated testing conditions (e.g. in a high vacuum chamber). There are many difficulties often encountered in the physico-chemical analyses of surfaces.

Adhesion in general can be attributed to mechanisms including, but not restricted to, adsorption and wetting, electrostatic attraction, chemical bonding, reaction bonding, and exchange reaction bonding **[12]**, which are schematically shown in Fig. 3 and discussed in the following sections. In addition to the major mechanisms, hydrogen bonding, van der Waals forces and other low energy forces may also be involved. All these

mechanisms take place at the interface region either in isolation, or, most likely, in combination to produce the final bond. Reviews on these major mechanisms can be found in many references including **[23, 32-37]** for polymer matrix composites; Metcalfe (1974) **[4]** for metal matrix composites (MMCs); and Naslain (1993) [38] for ceramic matrix composites (CMCs). More, mechanisms and mechanics modeling of interfaces in cementitious composites have received a lot of attention **[39, 40]**.
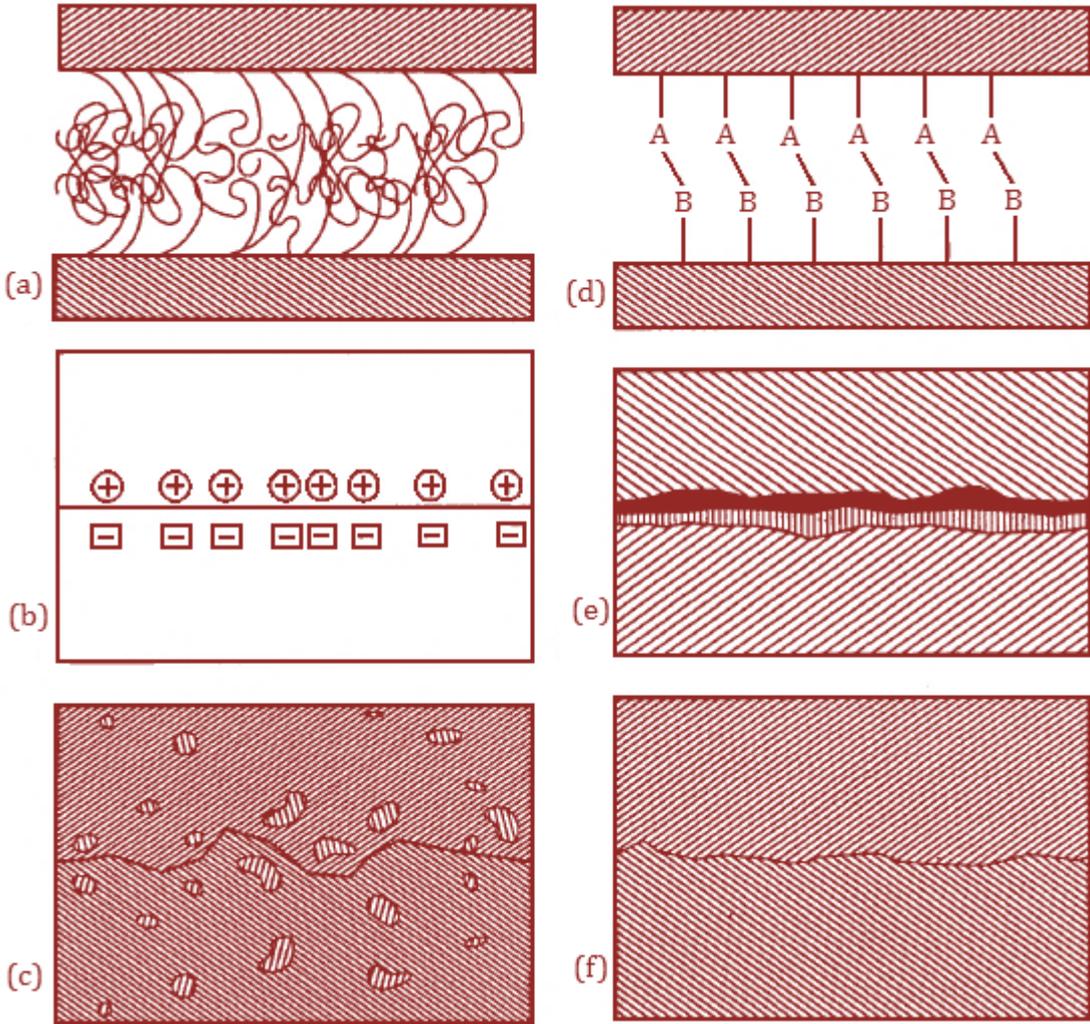
Fig. 3. Interface bonds formed (a) by molecular entanglement; (b) by electrostatic attraction; (c) by interdiffusion of elements; (d) by chemical reaction between groups A on one surface and groups B on the other surface; (e) by chemical reaction following forming of a new compound(s), particularly in MMCs; (f) by mechanical interlocking **[23]**.

2.1 Adsorption and wetting

Good wetting of fibers by matrix material during the impregnation stages of fabrication is a prerequisite to proper consolidation of composites, particularly for composites based on polymer resins and molten metals. It is well understood that physical adsorption of gas molecules to solid surfaces is ascribed to the attraction arising from the quantum mechanical effect due to the valence electrons present in the constituents as a free gas. The physical attraction between electrically neutral bodies is best described by the

wetting of solid surfaces by liquids. Bonding due to wetting involves very short-range interactions of electrons on an atomic scale which develop only when the atoms of the constituents approach within a few atomic diameters or are in contact with each other.

The determination of the thermodynamic characteristics of fiber surfaces is important as they play an important role in the adhesion process. Correct wetting of fibers by matrix resins is a necessary but not sufficient condition for good interface quality [41]. Improving wetting increases the reversible adhesion energy and reduces the number of defects in the interface region.

Many studies have examined the relationship between fiber/matrix interface strength, measured using micro-mechanics tests, and the reversible adhesion energy. This energy is measured by wetting studies [21, 42–44], or by inverse gas chromatography [45–50].

The work of adhesion WA, is a concept first introduced by Harkins [51]. In a simple system in which a liquid (L) adheres to a solid (S), the reversible work of adhesion is defined by (**Eq.1**):

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \qquad \text{(Eq.1)}$$

W$_A$ represents a physical bond resulting from highly localized intermolecular dispersion forces. It is equal to the sum of the surface free energies of the liquid,γ_1, and the solid, γ_2, less the interfacial free energy, γ_{12} . It follows that **Eq.1** can be related to a model of a liquid drop on a solid shown in **Fig.4**. Resolution of forces in the horizontal direction at the point A where the three phases are in contact yields Young's equation.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \qquad \text{(Eq.2)}$$

Where γ_{SV}, γ_{SL} and γ_{LV} are the surface free energies of the solid-vapor, solid-liquid and liquid-vapor interfaces, respectively, and θ is the contact angle. Liquids that form contact angles greater and less than 90° are respectively called 'non-wetting' and 'wetting'. If the liquid does not form a droplet, i.e. θ=0° it is termed 'spreading' and the relationship given by **Eq.2** becomes invalid. In this case, the equilibrium is expressed by an inequality

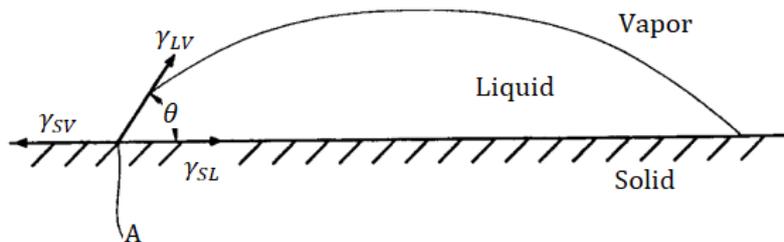$$\gamma_{SV} - \gamma_{SL} > \gamma_{LV} \qquad \text{(Eq.3)}$$

Fig.4. Contact angle, θ, and surface energies, γ_{LV} , γ_{SL} and γ_{SV} , for a liquid drop on a solid surface.

The surface energy of a solid (i.e. reinforcement in composites), γ_{SV}, must be greater than that of a liquid (i.e. matrix resin), γ_{LV}, for proper wetting to take place. Thus, glass and carbon fibers can be readily wetted by thermoset resins like epoxy and polyester resins at room temperature unless the viscosity of the resin is too high **[36]**, and by some thermoplastic resins (e.g. Nylon 6.6, PET, PMMA and PS). In contrast, it is difficult to wet polyethylene fibers (of surface energy approximately 31 mJ/m²) with any of these resins unless the fibers are surface treated. For the same reason, carbon fibers are often coated with Ti-B **[52]** using a chemical vapor deposition process to allow wetting by an aluminum matrix. Combining **Eqs. 1** and **2** yields the familiar Young-Dupre equation (**Eq.4**) :

$$W_A = \gamma_{LV}(1 + \cos\theta) \qquad\qquad\qquad\qquad (Eq.4)$$

The values of WA reflect directly the significance of energetics between the liquid and solid phases, i.e. the higher the work of adhesion the stronger the interactions. WA can be determined in experiments by measuring the surface energy of the liquid, γ_{LV}, and the contact angle, θ.

Although the discussion of wettability presented above has focused on the thermodynamics between the fiber surface and the liquid resin, real composite systems consist of an extremely large number of small diameter fibers embedded in a matrix. Adding to the issue of proper wetting of fiber surfaces by the resin, a key to creating good adhesion at the fiber-matrix interface is infiltration of the resin into the fiber tow during the fabrication process.

The relationship between the reversible energy of adhesion and the shear strength of the fibre/matrix interface has been studied by several authors **[47, 48, 53, 54]** who show that an increase in the work of adhesion is observed to result in an increase in shear strength.

Nardin and Schultz **[47]** proposed a pressure of adhesion concept for composite materials. After examination of a large number of polymer/fibre combinations they suggested that the reversible energy of adhesion, measured by inverse gas chromatography, could be related to the interfacial shear stress measured by fragmentation tests, by the linear expression (**Eq.5**):

$$\tau = \left(\frac{E_m}{E_f}\right)^{1/2} \frac{W_A}{\delta} \qquad\qquad\qquad\qquad (Eq.5)$$

with E_m Young's modulus of the matrix, E_f Young's modulus of the fibres, W_A reversible adhesion energy, δ is a distance independent of the system studied and equal to about 0.5 nm. It corresponds to the intermolecular distance, at equilibrium, between the centres of the molecules involved in interactions such as Van der Waals bonds.

In this approach the load transfer between fibre and matrix is considered to be perfectly linear elastic.

Pisanova and Mäder **[48]** studied the liaisons between different matrix resins and glass fibres, treated and untreated. The fibre treatment with coupling agents resulted in an improvement of the fibre/matrix adhesion which correlated well with the reversible adhesion energy.

2.2 Interdiffusion

A bond between two surfaces may be formed by the interdiffusion of atoms or molecules across the interface. A fundamental feature of the interdiffusion mechanism is that there must exist a thermodynamic equilibrium between the two constituents. The bond strength in polymer matrix composites will depend on the amount of molecular entanglement, the number of molecules involved and the strength of the bonding between the molecules. Interdiffusion may be promoted by the presence of solvents and the amount of diffusion will depend on the molecular conformation, the constituents involved, and the ease of molecular motion. For example, bonding between glass fibers and polymer resins through silane coupling agents by a process other than chemical bonding can be explained by interdiffusion and the interpenetrating network (IPN) formation in the interface region **[55-57]**, as illustrated in **Fig. 5.** A thin layer of epoxy matrix revealed on the fracture surface of the carbon fiber by using a scanning Auger microscope **[58]** is concrete evidence of interdiffusion.

The interface region thus formed has a substantial thickness, and its chemical, physical and mechanical properties are different from those of either the bulk fiber and the matrix (i.e., the interphase as opposed to the interface of zero thickness). The interphase is found to be significantly softer than the bulk matrix material in polymer matrix composites **[59, 60]**. For example, the average modulus of the interphase of a thickness of approximately 500 nm formed between a single carbon fiber and epoxy matrix is about one-quarter of that in the bulk matrix. However, the presence of a stiff fiber mitigates the effect of a soft interphase, increasing the effective modulus of the interphase beyond that of the bulk matrix in close vicinity of the fiber **[59-62]**.
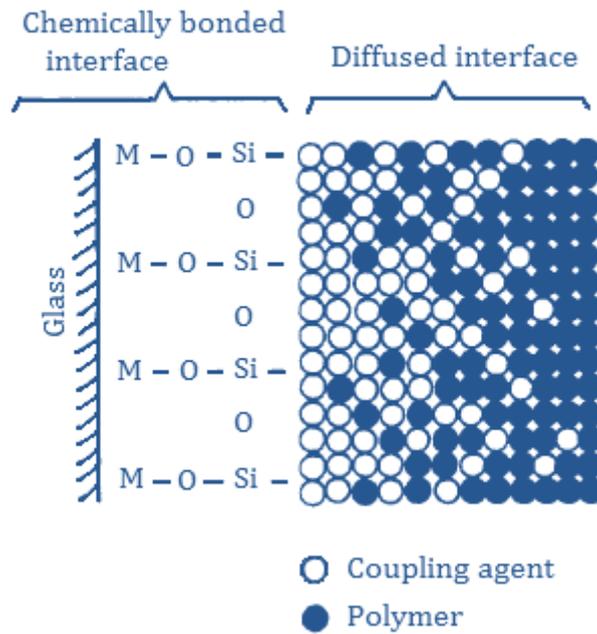
Fig. 5. A schematic model for interdiffusion and IPN in a silane-treated glass fiber-polymer matrix composite **[23]**.

In MMCs (Metal Matrix Composites), interdiffusion also plays an important role in promoting reaction between elements of each constituent at the interface region. The special type of interdiffusion that takes place in conjunction with chemical reaction in MMCs is called an exchange reaction. However, interdif- fusion in MMCs may not be always beneficial because undesirable compounds are often formed, particularly when the oxide films present on the fibers are completely disrupted under extremely high temperature and pressure in a solid state process **[4]**. To prevent or at least reduce the interaction, it is necessary to apply an effective diffusion barrier in the form of a coating on the fiber, or alloying elements in the matrix. The selection of an appropriate diffusion barrier relies on a detailed knowledge of the nature of the interaction taking place at the interface region, which is specific to each fiber-matrix system.

2.3 Electrostatic attraction

A difference in electrostatic charge between constituents at the interface may contribute to the force of attraction bonding. The strength of the interface will depend on the charge density. Although this attraction is unlikely to make a major contribution to the final bond strength of the interface, it could be important when the fiber surface is treated with some coupling agent. This type of bonding will explain why silane finishes are especially effective for certain acidic or neutral reinforcements like glass, silica, and alumina, but are less effective with alkaline surfaces like magnesium, asbestos, and calcium carbonate **[55]**.

2.4 Chemical bonding

Chemical bonding is the oldest and best known of all bonding theories. Physical adsorption mechanisms depend on van der Waal forces or the acid-based interaction, while chemical bonding mechanism is based on the primary bond at the interface. A chemical reaction at the interface is of particular interest in the study of polymer matrix

composites because it offers a major explanation for the use of silane coupling agents on glass fibers embedded in thermoset and amorphous thermoplastic matrices. Surface oxidative treatments of carbon fibers have been known for many years to promote chemical bonding with many different polymer resins. Buxton and Baillie, 1995 **[63]** has shown that the adhesion is a two-part process: the first part is the removal of a weak layer of a graphitic-like structure from the fiber surface particularly at low levels of treatment; and the second part is chemical bonding at the acidic sites. However, much further work is still needed to verify this hypothesis.

In this mechanism of adhesion, a bond is formed between a chemical group on the fiber surface and another compatible chemical group in the matrix, the formation of which results from usual thermally activated chemical reactions. For example, a silane group in an aqueous solution of a silane coupling agent reacts with a hydroxyl group of the glass fiber surface, while a group like vinyl on the other end will react with the epoxide group in the matrix. The chemical compositions of the bulk fiber and of the surface for several widely used fiber systems. It is interesting to note that except for glass fibers, the chemical composition of the surface does not resemble that of the bulk fiber, and oxygen is common to all fiber surfaces.

2.5   Reaction bonding

Other than in polymer matrix composites, the chemical reaction between elements of constituents takes place in different ways. Reaction occurs to form a new compound(s) at the interface region in MMCs (metal matrix composites), particularly those manufactured by a molten metal infiltration process. Reaction involves transfer of atoms from one or both of the constituents to the reaction site near the interface and these transfer processes are diffusion controlled. Depending on the composite constituents, the atoms of the fiber surface diffuse through the reaction site, (for example, in the boron fiber-titanium matrix system, this causes a significant volume contraction due to void formation in the center of the fiber or at the fiber-compound interface **[64]**, or the matrix atoms diffuse through the reaction product. Continued reaction to form a new compound at the interface region is generally harmful to the mechanical properties of composites.

Special cases of reaction bonding include the exchange reaction bond and the oxide bond. The exchange reaction bond occurs when a second element in the constituents begins to exchange lattice sites with the elements in the reaction product in thermodynamic equilibrium **[65]**. A good example of an exchange reaction is one that takes place between a titanium-aluminum alloy with boron fibers. The boride compound is initially formed at the interface region in an early stage of the process composed ofiboth elements. This is followed by an exchange reaction between the titanium in the matrix and the aluminum in the boride. The exchange reaction causes the composition of the matrix adjacent to the compound to suffer a loss of titanium, which is now embedded in the compound. This eventually slows down the overall reaction rate.

The oxide bond occurs between the oxide films present in the matching surfaces of fiber and matrix. The reaction bond makes a major contribution to the final bond strength of the interface for some MMCs, depending on the fiber-matrix combination (which determines the diffusivity of elements from one constituent to another) and the processing conditions (particularly temperature and exposure time).

In general, in most CMCs (ceramic matrix composites), chemical reaction hardly occurs between fiber (or whisker) and matrix. However, an extremely thin amorphous film can be formed, originating from the oxide present on the fiber surface, due to the limited fiber/matrix reaction, e.g., between alumina whisker and zirconia matrix **[66]**, or resulting from the decomposition of the metastable SiC fibers in SiC matrix **[38]**. The reaction compound thereby formed normally has a low fracture energy and is soft compared to the fiber or matrix. It acts as a compliant layer for the relaxation of residual thermal stresses and promotes longitudinal splitting along the fiber length.

2.6 Mechanical bonding

Mechanical bonds involve solely mechanical interlocking at the fiber surface. Mechanical anchoring promoted by surface oxidation treatments, which produce a large number of pits, corrugations and large surface area of the carbon fiber, is known to be a significant mechanism of bonding in carbon fiber-polymer matrix composites. The strength of this type of interface is unlikely to be very high in transverse tension unless there are a large number of re-entrant angles on the fiber surface, but the strength in longitudinal shear may be significant depending on the degree of roughness.

In addition to the simple geometrical aspects of mechanical bonding, there are many different types of internal stresses present in composite materials that arise from shrinkage of the matrix material and the differential thermal expansion between fiber and matrix upon cooling from the processing temperature. Among these stresses, the residual clamping stress acting normal to the fiber direction renders a synergistic benefit on top of the mechanical anchoring. These mechanisms provide major bonding at the interface of many CMCs (ceramic matrix composites) and play a decisive role in controlling their fracture resistance and R-curve behavior.

The next part of the review is dedicated to composites based on organic matrix reinforced by fibers. So, all the models presented thereafter refer to fiber and thermosetting resin.

3 The influence of the interface/interphase on the macroscopic behavior of the material

The results concerning the influence of the interface on the mechanical properties of a composite come either from mathematical studies (numerical or analytical) or experimental data. Mathematical models take into account the interface properties

(modulus, thickness) and analyze the effects of their variation on macroscopical properties of the composite. Experimental works consist in testing composites with interfaces that are variable in nature and/or thickness. In both cases, this influence is strongly conditioned by the direction of the load compared to the reinforcement. A simple way to highlight this is to apply the law of mixtures for the two analytical models of Reuss and Voigt **[67, 68]** which correspond to morphology patterns of multiphase material in series and in parallel respectively. **Fig.6 (a)** shows an association in series (example: transverse tension) expressed by **Eq.6,** and **Fig.6 (b)** an association in parallel (example: longitudinal tension), **Eq.7**.
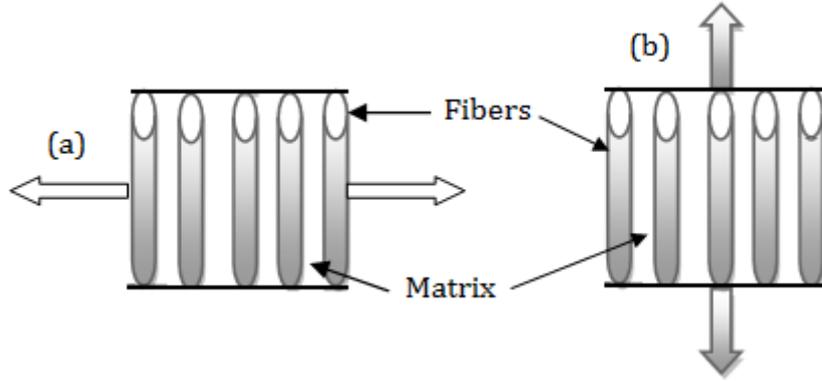
Fig.6. Models of association

$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{V_m}{E_m} + \frac{V_i}{E_i}$$ (Eq.6)

$$E_c = E_f V_f + E_m V_m + E_i V_i$$ (Eq.7)

Where V_f, E_f, V_m, E_m and E_i, V_i, are respectively the volume fractions and moduli of the reinforcement, the matrix, and the interphase.

Association (a) can be regarded as the case of a transverse load of a UD composite material. The effective modulus of the composite, E_c, can be calculated by the **Eq.6**. In case (b), the load is applied in the direction of fibers and effective modulus E_c is given by the **Eq.7**. In case (a), if the term V_f/E_f is negligible compared to V_m/E_m (high reinforcement fiber modulus compared to that of the matrix), term V_i/E_i in this case must be taken into account. It can become important in the case; for example, of an elastomer interphase whose modulus can be 100 times lower than that of the matrix (the volume fraction of the interphase V_i may approach 10% of that of the matrix). In this case the interphase has a marked effect on the behavior of the composite. In general, this effect is pronounced for all loads that involve the matrix, such as transverse tension in which the fibers are not loaded **[69, 70]**, shear tests **[71]**, toughness tests **[72, 73]**, or tensile tests on loaded polymers. Many studies emphasize the specific effect of the size of the interphase **[74-77]**, which presents an optimum with respect to the properties of the composite. It has also been found experimentally that an interfacial module that is too weak directly affects the module of the composite **[74]**. As shown Wu et al. (2000) **[78], t**he thickness of the interphase region ranges from 100 to 200 nm for carbon fiber-epoxy composites. However, the interphase thickness and properties depend on local changes in chemical and physical processes such as crystallization and crosslinking in the vicinity of the fiber.

For instance, for S-glass epoxy composites, interphase thickness varies from 10 to 1000 nm [60]. The interphase is either compliant or brittle depending upon the composite system. For S-glass epoxy and graphite-epoxy composites, the interphase is much more compliant than the matrix [60]. On the other hand, the interphase is stiffer than the matrix material for some uncoated carbon-epoxy composites or for glass fiber/polyester composites [79]. Micrographic image analysis of the interphase region suggests that the interphase has a gradient in material properties such that it matches the properties of the fiber and the matrix at the boundaries [60]. The relative stiffness of the interphase region also depends on the thickness of the interphase layer. A thicker interlayer means a stiffer interphase whereas a thin interlayer exhibits a softer behavior [79].

Case (a), association in series, shows the impact of the interface on the fracture properties. Among the three elements (fiber, matrix, and interface), it is the weakest link (the one with the lowest strength) which will initiate the fracture. As Ivens et al. (1993) pointed out [80], below a certain threshold (related to the fracture strength of the matrix), the interface is the limiting parameter (the weak point) which controls the fracture behavior of the composite. In case (b), an association in parallel, the effect of the interface is less obvious: in equation (7), the $E_f.V_f$ term dominates and the contribution of the interface is negligible, even compared to that of the matrix. Its effect on the modulus of the composite is then quasi-non-existent, as shown by experimental work [81, 82]. In order to understand this influence, it is necessary to analyze the fracture processes occurring in composites before the final failure and the role played by the interface in this process.

4   Rupture process in a composite: role of the interface

The interface is the element which conditions the degree of synergy of the fiber/matrix bonding [83], and which ensures the load transfer. Its role is crucial during the propagation of cracks in composites because in this case one of the components no longer bears its share of the applied load, which is transmitted to the rest of the material through the interface [84-86]. If we first consider the effect of fiber rupture, shown in **Fig.7**, the local normal constraint at the point of rupture is null, the shear stress at the fiber/matrix interface is maximum, and at a distance x = δ_f the fiber is fully reloaded whereas the shear stress r falls to zero.
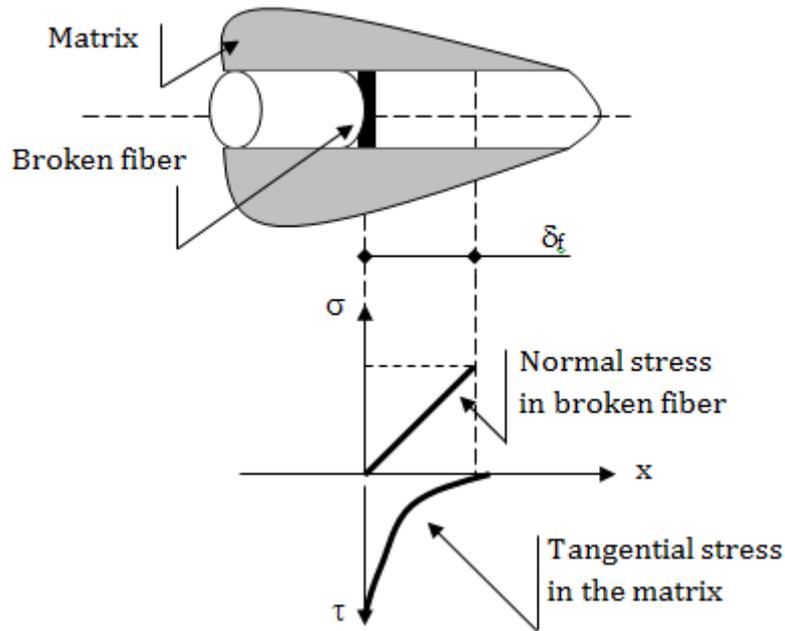
Fig.7. Mechanisms of load transfer by shearing of the matrix **[87]**.

Let us now consider the rupture process following a crack initiated by a fiber break in a UD composite. In the case of a strong interface, a fiber break can induce the creation of a brittle rupture facies, and the break will in all likelihood be sudden. In the case of a weak interface, in contrast, a fiber break causes interfacial cracking (more or less extensive depending on the quality of the interface). If the interface is sufficiently resistant, this phenomenon can be enough to dissipate the elastic energy released by the breaking of the fiber and to distribute the constraints over a sufficiently large zone for the cracking to be locally stopped. If the interface is too weak, interfacial separation is so extensive that the broken fiber no longer contributes to the strength of the composite. This case is less favorable than the previous one because the overload experienced by the remainder of the composite is higher (but less localized) **[7, 23, 77, 88-90]**. **Fig. 8** is a representation of the probable rupture processes following a fiber break in a UD composite according to the quality of the fiber /matrix interface. Case (a) presents a weak interface: interfacial debonding can occur. This failure mode is sought after in structures in service. Case (b) presents a material with a strong interface: as the crack cannot be projected at the level of the interface, the kinetics of the breakdown will spread to all the fibers, giving a brittle break **[91]**.

Fig.8. Damage in a UD composite **[91]**.

5 Methods of investigation

A number of experimental and theoretical methods developed to assess the quality of the interface bond are summarized. The study of the interface / interphase involves the use of methods capable of delivering information on the links that connect it in the composite to the fiber and the matrix. This can be studied on several levels: either by approaches that can be described as indirect, consisting of macroscopic mechanical tests 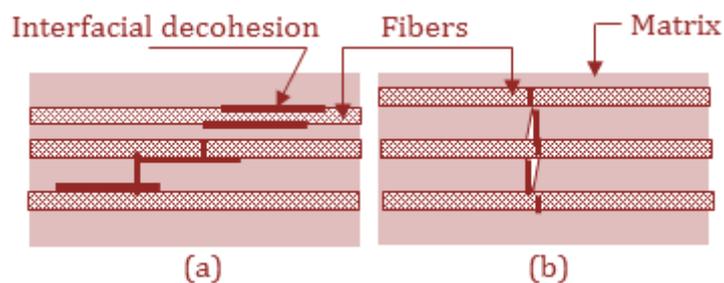**[7, 77, 92-101]** on industrial composites, or by more direct approaches, among which physicochemical tests [**102-107**] as well as "ad hoc" micromechanical tests **[21, 41,75-77, 92, 108-116]**. As there can be no question of giving an exhaustive list of all the methods of analysis, this paper will just mention those that seem the most significant.

5.1 Mechanical tests on composites

Mechanical tests are often used as indicators of the quality of the interfaces in composites. They nevertheless constitute indirect methods because they take several parameters into account, among which the one related to the interface is not necessarily the most important. They can only lead to a qualitative assessment of materials of the same kind, in which the rupture process involves the interface in the same way **[98-100]**. Defining a parameter that is intrinsic to the interface requires very precise knowledge of the respective contributions of the fiber and the matrix (the effects of which generally dominate), but also of the effects of defects in the material. Take the case of shear tests, which give access to the interlaminar shear strength (ILSS) of the composite. Several authors have shown that this value is often considered representative and highly sensitive to the quality of the interfacial zone **[92, 108, 117-119]**, and the fiber / matrix interface plays a role in controlling the toughness to interlaminar fracture. This is true, but shear tests also characterize interfaces generated by the implementation of the material, particularly interply interfaces. A comparison of diverse materials in terms of their fiber / matrix interface is possible only for composites with defects that are equivalent and do not mask the influence of this type of interface: in this type of test, rupture is highly dependent on how crucial the defects are (as example: porosity, misalignment of fibers): if there is a critical defect of implementation in the material, its ILSS will be limited, even if it has a very good interfacial strength. The ILSS is mainly conditioned by the weak point of the material.

The mechanical tests that seem most suited to highlighting the interface effect are matrix tests, transverse tests, off-axis tensile tests, bending fatigue tests to characterize the fiber / matrix interface, the off-axis bending test to study intra-plies or inter-wicks, toughness tests and above all shear tests (Iosipescu, short beam shear test, cube test, interlaminar (ISD),…).

Bending tests along the fiber axis, due to the curvature and the stress state imposed on the sample, can also be used to apply greater force to the matrix and interfaces than for example longitudinal tensile tests. The case of compression tests is different because although they are sensitive to the influence of the interface **[11, 81]**, the complexity of the phenomena involved makes them particularly difficult to interpret.

5.2 Physico-chemical techniques

Composite interfaces exist in a variety of forms of differing materials. The three-dimensional nature of the interfacial zone led researchers to try to "see" the interface **[120]**. A convenient way to characterize composite interfaces embedded within the bulk

material is to analyze the surfaces of the composite constituents before they are combined together, or the surfaces created by fracture. Surface layers represent only a small portion of the total volume of bulk material. The structure and composition of the local surface often differ from the bulk material, yet they can provide critical information in predicting the overall properties and performance. The basic unknown parameters in physico-chemical surface analysis are the chemical composition, depth, purity and the distribution of specific constituents and their atomic/microscopic structures, which constitute the interfaces. Many factors such as process variables, contaminants, surface treatments and exposure to environmental conditions must be considered in the analysis.

When a solid surface is irradiated with a beam of photons, electrons or ions, species are generated in various combinations. An analytical method for surface characterization consists of using a particular type of probe beam and detecting a particular type of generated species. In spectroscopy, the intensity or efficiency of the phenomenon of species generation is studied as a function of the energy of the species generated at a constant probe beam energy, or vice versa. Most spectroscopic techniques are capable of analyzing surface composition, and some also allow an estimation of the chemical state of the atoms. However, it may be difficult to isolate the contributions of each surface layer of the material being probed to these properties. Since most surface analysis techniques probe only the top dozen atomic layers, it is important not to contaminate this region. For this reason and particularly to reduce gas adsorption, a vacuum always has to be used in conjunction with these techniques. The emergence of ultrahigh vacuum systems of less than 10^{-6} Pa, due to rapid technological advances in recent years, has accelerated the development of sophisticated techniques utilizing electrons, atoms and ions. Amongst the currently available characterization techniques, the most useful ones for composite interfaces are: infrared (IR) and Fourier transform infrared (FTIR) spectroscopy, laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), solid state nuclear magnetic resonance (NMR) spectroscopy, wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) and the measurement of the contact angle. The use of spectroscopic methods to characterize the chemical composition of the interface has been discussed in some articles **[23, 102, 121, 122]**. These methods enable a chemical analysis of superficial layers (a few nanometers thick) to be carried out. They are applicable to the analysis of sizing on naked fibers, or even of debonded fibers, to identify (and quantify) the functional groups or to trace the concentration profiles of a given species. Each technique has its own complexity, definite applications and limitations **[23, 123]** for the in situ analysis of real composites. Often the information sought cannot be provided by a single technique. This has resulted in the design of equipment that utilizes two or more techniques and obtains different sets of data from the same surface of the sample (e.g. ISS/SIMS two-in-one and XPS/AES/SIMS three-in-one equipment). Adamson (1982) **[37]**, Lee (1989) **[124]**, Castle and Watts (1988) **[125]** and Ishida (1994) **[126]** have presented excellent reviews of most of these techniques, with Ishida (1994) being particulalry informative for characterization of composite materials.

In addition to surface analytical techniques, microscopy **[98-100]**, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can help determine the interphase thickness when it is clearly differentiated from the matrix. They allow observing the contact between phases at the atomic scale **[127]** and visualize porosity or potential phase separations. Highly detailed studies on the internal structure and surface of carbon fiber have been conducted with TEM. However, SEM which has

lower resolution has led to very fruitful applications in fractographic analysis (fracture surface analysis) to determine failure modes of composites subjected to mechanical stress **[71, 128]**. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM), also provide invaluable information regarding the surface morphology, physico-chemical interaction at the fiber-matrix interface region, surface depth profile and concentration of elements.

In fact, the interlayer between the fiber and the matrix is inhomogeneous, with a smooth transition of mechanical properties. At this scale, it becomes extremely difficult to conduct measurements, although the properties of interphases can be determined through molecular dynamics simulations. However, researchers have demonstrated the use of SIEM (Speckle Interferometry with Electron Microscopy) to measure the elastic properties of interphases **[129]**. The application of atomic force microscopy (AFM) to the study of the interphase is also a promising field of investigation. For example, Mai et al. (1998) **[130]** in force modulation mode showed that the variation in the fiber properties with respect to the matrix differed depending on whether the fiber is sized or not. It is thus possible to distinguish a linear gradient in the case of a sized fiber, whereas constant interphase properties are observed for untreated fibers. Joliff et al. **[131, 132]** characterized the interphase of a UD composite (glass/epoxy), first in terms of molecular mobility by micro-thermal analysis and then in terms of mechanical properties by force measurements with AFM. The measurements showed an increase in elastic modulus and in glass transition temperature around each fiber. Optical microscopy revealed considerable heterogeneity of fiber distribution inside the matrix with many contacts between fibers. A realistic microstructure including the interphase size (defined by µTA) and fiber distribution was therefore used to model the composite accurately.

5.3   Micromechanical testing

Micromechanical tests, unlike all the previous tests, are tests that were specially designed to determine the characteristics of fiber / matrix interfaces, in particular their strength or toughness, and to establish the fundamental features of load transfer and interfacial break. Most of these tests are performed on model composites (monofilament), i.e. on samples whose geometry is generally specific to each test, and which contain only one fiber surrounded by resin. It should be pointed out, however, that these tests are generally difficult to perform and limited to a small number of specialized research laboratories. The main tests include micro-indentation, fragmentation, debonding (better known as pull-out), of which a derived form is the 'micro-droplet' test, and compression **[13, 119]** (**Fig.9**).
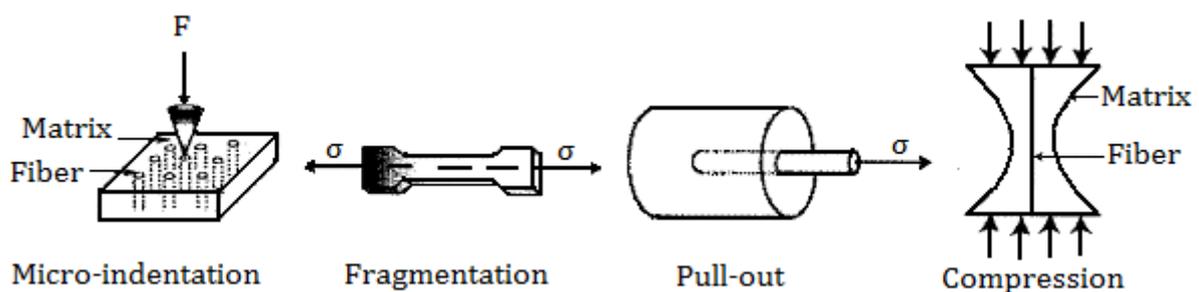

Fig.9. Examples of micromechanical tests used to characterize the fiber/matrix interface.

The micro-indentation test, proposed by Mandell et al. **[18]**, measures the debonding force in situ on real composites. This method at present comprises a fully automated measuring and data acquisition process **[133]**. It requires the polishing of composite samples with fibers perpendicular to the surface and consists in pressing the extremity of a fiber by means of an indenture until fiber debonding. This test can be applied to real composites, which avoids the often difficult manufacturing of a model composite and also guarantees the representativeness of the tested interface; in model composites (monofilament), the interface obtained can differ from that of real composites because of the conditions of implementation and the absence of surrounding fibers. The advantages of the indentation technique are that:

- it can be applied by using a polished face of a standard UD composite,
- it does not depend on the fiber break properties because the fiber is tested in compression.

Two types of samples can be used, either thick or thin samples. Thick samples are generally easy to produce, but the fiber is compressed during the test, which requires a strong force compared with the necessary sliding strength. Moreover, it is difficult to determine the length of the separated part of the fiber and as a result, calculating the interfacial pressures requires additional hypotheses. With thin samples, in contrast, it is easy to determine the parameters of the interface. However, the preparation of specimens containing fibers of small diameter remains the most difficult step. With thin samples, the test is named "push-up" or "push-down" **[134]**.

The most widely used micromechanical test is the fragmentation test **[135-137]** developed by Kelly and Tyson **[31]** and applied by Fraser et al. **[138, 139]** to composites with an organic matrix. The method consists in subjecting a specimen to a monofilament tensile test along the fiber axis. Continuous application of the force leads to breakage of the fiber in several places. The fragmentation process continues throughout the test until a certain critical fragment length is reached, L_C, that no longer allows the transfer of load by shear to generate tension constraints equal to the fiber strength. This technique is relatively simple to implement but has the disadvantage that it can only be used with strongly deformable matrices, which is rarely the case of commercial resins **[140]**. In the case of glass / epoxy systems, matrix cracking problems and the lack of interfacial debonding have for example been observed **[141]**, including in cases of pre-deformation of the fiber, which precludes any calculation of the load transfer capacity defined by Kelly and Tyson. This test is effective for determining the shear strength of the fiber / matrix interface especially when the interface is strong.

The pull-out method is the simplest test. It is the oldest test, but also the one that has been developed and improved the most in recent years. The test consists in extracting a fiber from a block **[142]**, a disk or a droplet of resin **[143]**. This technique presents several advantages, among which the possibility of taking into account friction phenomena following debonding and of determining the corresponding rupture energies or both phases (debonding and friction). Conversely, the downside is not only the great complexity of analyzing the results but especially the experimental difficulties of manufacturing, handling and loading the samples. The failure rate reaches over 75% according to Piggott **[142]**.

Lastly, the compression method was developed by Mooney and Mc Garry **[144]** based on microcomposites to measure the bond strength of glass fibers with

transparent polymer matrices, then Broutman **[145]**. This method consists in applying a compressive load to the parallelepipedic specimen or dumbbell to determine the compressive stress σ_c at which the onset of debonding is discerned. This test compresses both the fibers and the matrix by interposing a metal plate usually made of aluminum between the composite surface and the elements of the compression machine. The sample's geometry or the difference in the Poisson ratio between fiber and matrix and in their stiffness generates shear stress or tension at the interface. Interfacial debonding is detected either in the necking region **[146]** or at the ends of the fiber and propagates on a critical length L_c at a constant speed which then increases abruptly and initiates during loading. If the fibers are stiffer than the matrix, the deformation of the matrix is greater during the displacement of the transom. The fibers protrude from the matrix and leave footprints on the metallic plate which is assumed to be perfectly plastic **[147]**. The depth of these footprints corresponds to the maximum displacement of the fibers during the loading of the composite, and their residual displacement is measured directly on the composite.

The single fiber compression test has not been as popular as other microcomposite tests because of the problems associated with specimen preparation and visual detection of the onset of interfacial debonding. To be able to obtain accurate reproducible results, the fibers have to be accurately aligned. With time, this test method became obsolete, but it has provided a sound basis for further development of other testing techniques using similar single fiber microcomposite geometry.

5.4   Theoretical models: bibliographic contributions

Experimental evaluation of interfacial properties in fiber reinforced composites using fiber pull-out tests has been investigated by several researches **[148-153]**. However, analytical/numerical modeling of fiber pull-out (push-back) tests has gained popularity subsequent to experimental testing due to cost and time saving advantages. Several theoretical models have been developed to predict the load-displacement behavior of fiber pull-out test and the inherent interfacial properties **[154-158]**. Generally, these solutions are obtained by adopting a few simplistic assumptions. One of the commonly employed assumptions is the state of plane-strain **[29]** in the assembly in order to relate radial and shear stresses in the equilibrium equations. For example, **[154, 159-162]** published a series of papers on different aspects of fiber pull-out/push-out problems, adopting plane-strain conditions. However, the plane-strain assumption is not a good approximation for perfectly bonded interfaces where the load transfer length is very small (only a few fiber radii) (Hsueh, 1991). Another such simplification is to ignore the radial dependence of axial stresses, either in the fiber or matrix, or in both **[29, 159-161]**, which is justifiable only when embedded fibers are sufficiently long. Owing to the mathematically involved nature of this boundary value problem, a few investigators have chosen to impose boundary conditions in an approximate sense. For instance, Hsueh (1990, 1991) **[154, 159-161]** developed an analytical solution based on shear-lag theory. In this model, shear stress in the matrix region was assumed to be inversely proportional to the radial distance. Consequently, a stress free boundary condition was satisfied only in a limited sense which is appropriate only for problems where the outer radius of the matrix is considerably large compared to the fiber radius. Nairn (1997) **[163]** showed that the shear-lag analysis is best suited for composites with high fiber to matrix stiffness

ratio. Moreover, a shear-lag analysis predicts inaccurate results for composites with low fiber volume fractions. However, the total energy prediction through shear-lag analysis is reasonably accurate and therefore shear-lag theory has been utilized to study fracture mechanics of embedded fibers **[164]**.

A simple model to predict the ultimate tensile strength of fiber-reinforced composites when the failure is governed by fiber debonding has proposed by Stang and Shah **[155]**. Gao et al. **[156]** have studied the fiber/matrix debonding problem using a simple shear lag model, which includes friction at a debonded interface and Poisson contraction of the fiber. The authors have observed interfacial friction to have a significant effect on the debonding behavior. Further, the load–displacement relationship has been modeled in terms of interface toughness and frictional parameters of the interface. Hsueh **[154]** analyzed the nonlinear dependence of stresses required to debond the fiber/matrix interface and for fiber pull-out as a function of embedded fiber length for a fiber-reinforced composite. The roles of residual clamping stresses at the interface, and Poisson contraction of the fiber, have been taken into consideration. Kerans and Parthasarathy **[158]** have developed fiber pull-out and pushout models to predict the load–displacement behavior in terms of the fiber/matrix interface parameters. The authors have found residual axial strain in the fiber to have a significant effect on fiber debonding and also included fiber surface topography in their model. The authors have suggested a methodology to extract interface parameters from experimental data.

To develop tractable models, many researchers have modeled the interphase region as a homogeneous material **[165-169]**. However, a few studies considered the inhomogeneous nature of interphase adopting a stair-case variation of material properties across the thickness of the interphase layer **[170, 171]**. Alternatively, a few investigators proposed an effective interphase model (EIM) and uniform replacement model (URM) to replace the fiber and the surrounding interphase by an effective homogeneous fiber in order to convert a three-phase composite into a two-phase composite **[172]**. For mathematical convenience and to better describe the variation of properties within the interphase region, several researchers treated the interphase as an inhomogeneous material by smoothly varying the material properties as a function of radius. Usually in such models, the material properties are graded by adopting an empirical law **[173-178]**. Since, it is rather difficult to arrive at an explicit closed form 3D solution for such problems; many researchers have adopted numerical methods, particularly FE analysis **[176, 179, 180]**. Most of the analytical studies that exist in the literature do not account for the anisotropy of fibers. Nevertheless, **Wu et al. (2000) [78]** presented a generic solution that is valid for both isotropic and transversely isotropic materials for a two-phase fiber-reinforced composite.

6   Fiber / Matrix Interface

The mechanical performance and durability of composite materials are mainly governed by three factors: the strength and stiffness of the fibers; the strength and chemical stability of the matrix; the nature of the bond between the fibers and the matrix. While there is an abundant literature **[108, 181-183]** on general data and calculation methods according to the type of fiber and resin, the structure of the ply stack and rate of reinforcement, few studies have investigated the influence of the fiber/matrix interface on the behavior of the composite or characterized it. The absence of quantitative data means that the result of the so-called safety coefficients (or even ignorance coefficients)

has to be weighted. These coefficients are often very high, with the economic consequences which that engenders. Several studies have been conducted to observe the influence of the interface depending on the method of characterization, so as to specify the sensitivity of each technique to changes in the interfacial zone and clarify the role of the latter on the fracture behavior of composites by comparing the results of the mechanical properties of the micromechanical tests and the macroscopic tests.

For example, Keusch et al. **[92, 108]** used different tests (micromechanical and macro-mechanical) on UD composites (glass / epoxy) in order to compare the surface treatment of glass fibers. The composites used differed in the interface only, as it is of vital importance that all other parameters be kept constant for differences in behavior to be attributed to interfacial phenomena alone. The fiber / matrix bonding was characterized by determining the interfacial shear strength by a debonding (pull-out) test, the interlaminar shear strength by a compression shear test and short bending, and the transverse tensile strength of UD laminates. The results showed that the type of sizing has an influence on these properties, that the surface treatment of glass fiber has a pronounced effect, and that the use of an amino-silane as coupling agent improved all the properties measured.

Mäder et al. **[53]** studied the relations between surface, interphase and the final properties of composites with diverse surface treatments on various composites (glass/epoxy and carbon/epoxy). The characteristics of the carbon fiber surface and the surface of the treated glass were variously determined by contact angle measurements, using a capillary penetration technique and zeta potential measures. Micromechanical tests were applied to the model composites to establish the interphase properties (interfacial shear strength) with pull-out tests, fiber fragmentation and the mechanical properties of composites with the transverse tensile strength and interlaminar shear.

Herrera-Franco et al. **[118]** compared, for an epoxy matrix and carbon fibers with different surface treatments, the micromechanical properties (using fragmentation tests, microdroplet debonding, and micro-indentation) to macroscopic properties obtained from tensile tests on ± 45° specimens, Iosipescu shear tests and short beam shear tests. Among the different methods used on a single fiber to determine the interfacial shear strength, the fragmentation technique is more sensitive to changes in the fiber / matrix bonding that are due to the surface treatment effect or finishing, if the composite properties need to be predicted. Experimental results also suggest that it is possible to establish a correlation between the interfacial shear strength and the acoustic response of a laminate when subjected to localized heating. Samples with weaker interphases give stronger AE (Acoustic Emission) signals than those with a strong interfacial bond. A global thermal analysis is necessary to fully characterize this behavior of fiber-reinforced composites. In the various tests available on laminates, the Iosipescu shear test seems to be the most appropriate for determining the interfacial shear strength. Given that the interlaminar shear strength determined by the SBS (short beam shear) test method follows the same trends as the interfacial shear strength, it can be said that this technique is suitable for use as a screening tool to assess the strength of the fiber-matrix bond in a laminate. Even if micromechanical tests produce an interfacial shear strength value that is very similar to the composite values, the use of single-fiber measures should be avoided until further research is completed to predict composite properties.

Kessler et al. **[184]** showed that for glass/epoxy material with various surface treatments, the quality of the interface has a strong influence on the distribution of the damage during the impact. The matrix and the interface determine crack initiation by

loading in flexure, tension and shear and the subsequent development of delamination. To optimize material performance, it is important to establish how the microscopic properties (wetting, fiber / matrix bonding) are correlated with the behavior of the composite **[184]**.

The results from all these studies show that when the shear strength of the fiber/matrix interface is improved there is a corresponding improvement in the macroscopic composite properties. However, the improvement in macroscopic properties is rarely directly proportional to the improvement in microscopic properties. This underlines the complexity of this type of study, as parameters such as residual stresses and the development of interphase zones are difficult to control, but also shows that improved performance is attainable in this material **[119, 185].**

The analysis of different studies shows that the optimal interface is not the one with the highest characteristics. Furthermore, each fiber/matrix system considered has its own values of optimal interfacial properties, which are related to the properties of the fiber and the matrix. Lastly, for a given system, there is not a unique optimal interface; the study of every property of the composite (for example ILSS, fatigue behavior, fracture property) can lead to the definition of a different optimal interface each time.

7   Load transfer between the fiber and the matrix

The interface is where an important mechanism takes place, as the transfer of load between fiber and matrix within a composite material **[110]**. This transfer of load is fully dependent on the mechanical response of the contact zone between the fiber and the matrix, i.e. the interface or interphase. When composites are subjected to various loading conditions, the efficiency of the load transfer across the interface plays an important role in the overall performance of the composite **[23]**. It is this transmission of load that allows the composite to fulfil its mechanical function. Load transfer processes can be described with simplified micromechanical models considering, for example, an RVE (Representative Volume Element) consisting of a fiber embedded in a matrix cylinder to which a tensile stress is applied. The profile of the tensile stress in the fiber and that of the shear at the interface can be theoretically determined from the elastic equilibrium equations. From these data, it is possible to evaluate the stress-strain curve of the composite.

Depending on the assumed behavior of the interface, various responses can be simulated. In this paper, two pioneering models are presented, those of Cox (1952) **[29]** and of Kelly-Tyson (1964) **[84]**. In the Cox model, the link between fiber and matrix is assumed to be perfect and the mechanical behavior of these constituents is elastic. On the contrary, the Kelly-Tyson model was developed initially for materials with a metallic matrix in which the mechanisms of plasticity are activated in the vicinity of the fiber ends. Another model applicable to composites with polymer matrices that combines the approaches of Cox and Kelly-Tyson is the mixed model **[186]**, which adopts the Cox hypothesis in the central part of the fiber, i.e. that the fiber is subject to an elastic load until debonding of the interface, and in the part where debonding occurs, it adopts Kelly's assumption, i.e. constant shear.

7.1   Cox model, elastic load transfer

We consider an RVE consisting of a fiber radius fragment embedded in a matrix cylinder having a radius R set by the fiber volume fraction, V_f, and the hypotheses made on the fiber arrangement. This RVE is subjected at its extremities to a tensile strain ε_l.

Only the axial components of the stresses generated in the fiber and the matrix are considered. It is, therefore, a one-dimensional approach in which the axial stress in a given section of the fiber is also assumed to be uniform. In this model, the fiber and the matrix are assumed to be perfectly elastic and the fiber/matrix bond perfect. This model gives the stresses in the fiber and at the interface by **Eq.8** and **Eq.9** (profiles of the stresses are shown in **Fig.10**).

$$\sigma_f = E_f \varepsilon_l [1 - cosh(nx/r)/cosh(ns)] \qquad \text{(Eq.8)}$$

$$\tau_i = \frac{1}{2} n E_f \varepsilon_1 \, sinh(nx/r)/cosh(ns) \qquad \text{(Eq.9)}$$

where E_f is the Young modulus of the fiber, G_m shear modulus of the matrix, ε_1 is the applied strain, a, R, are respectively the radius of the fiber and the matrix, L is the fibre length, x is the variation of the length of the fiber, r variation of rate of the matrix , $s=L/a$ is the aspect ratio of the fiber, n is a constant calculated from **Eq.10**.

$$n^2 = \frac{2G_m}{E_f \, ln(R/a)} \qquad \text{(Eq.10)}$$
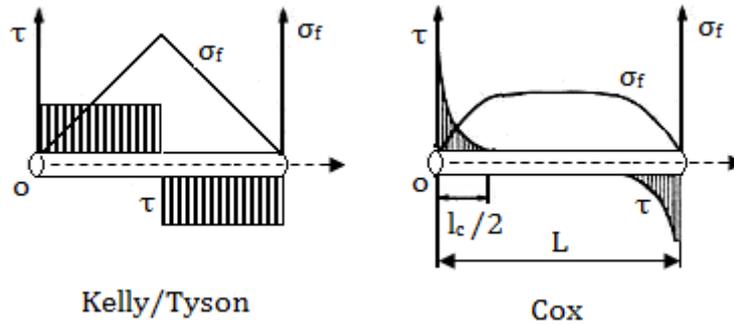
Fig.10. Profiles of the tensile stress in the fiber and shear at the interface from Kelly-Tyson and Cox models.

It can be seen that the development of shear stresses at the ends of the fiber fragment results in a progressive tensile loading of the fiber. Forces are therefore transferred from the matrix to the fiber.

7.2 Kelly-Tyson model

The Kelly-Tyson model was initially developed for materials with a metallic matrix in which the mechanisms of plasticity are activated in the vicinity of the fiber ends. The Cox model shows that the transfer of load leads to the development of interfacial shear stresses, the amplitude of which is maximum at the fiber ends. In practice, these concentrations of stress are limited by the plasticity threshold of the matrix or the sliding of the interface. Moreover, the elastic approach is no longer valid once the tensile stress in the matrix exceeds its elastic limit. These phenomena were initially demonstrated by Kelly et al. in the case of copper matrix composites reinforced by tungsten and molybdenum fibers. The very low yield strength of the matrix then leads, under tensile load, to the early and progressive development of a plastic deformation zone from the ends of the fiber.

To describe these processes, Kelly et al. **[84]** considered that the interfacial stress was constant at the fiber ends in the plastic zone. The elastic equilibrium of the fiber in this portion of the fiber is written by **Eq.11**:

$$\sigma_f = \frac{2\tau_i}{a}(L-x)$$ (Eq.11)

Where σ_f is the nominal tensile stress of the fiber, τ_i shear stress at the interface, a, is the radius of the fiber, L is the fiber length; x is the variation of the length of the fiber.

This relation also applies when the physical mechanism involved at the fiber ends corresponds to friction with constant stress. In this sense, the Kelly model can also be used for elastic matrix composites in which the reinforcement is achieved by sliding at the interface. The strain in the fiber cannot exceed the deformation of the composite, meaning that the stress σ_f increases linearly **Eq.11** from the end of the fiber, until the value $E_f \varepsilon_1$ if the fiber is long enough. The latter condition corresponds to the following criterion (**Eq.12**):

$$L_i \geq \frac{a E_f \varepsilon_l}{2\tau_i}$$ (Eq.12)

Where L_i is the so-called inefficient fiber length corresponding to the portion in which the tensile stress has not yet reached its maximum value: $\sigma_{fmax} = E_f \varepsilon_1$.

It is important to note that this model takes into account only the load transfer occurring in the plastic zone at the ends of the fiber. The effects of elastic load transfer in the central portion of the fiber are neglected $\tau_i = 0$. This approach is valid only if the plasticity threshold of the matrix (or the sliding threshold of the interface) is very low. In this case, plastic deformation (or slippage) occurs at the beginning of the loading, without an elastic load phase. The analysis usually adopted is that of Kelly and Tyson **[84]** which considers that the tensile stress in the fiber $\tau(x)$ increases linearly from the ends of the fragment (**Fig.10**).

7.3   Mixed model

In the Kelly model, elastic load transfer effects are totally neglected, which amounts to considering that the plastic deformation of the matrix, or the sliding of the interface, occurs at low strains. In reality, these processes often occur after a preliminary elastic loading phase that needs to be taken into account.

In the case of composites with a polymer matrix, the sliding of the interface occurs for a limit value of the interfacial shear stress τ_d, which corresponds physically to fiber/matrix debonding. In the debonded fiber zone, sliding processes depend on the value of the fiber / matrix friction coefficient and the radial stress applied to the fiber.

In such a situation, the corresponding value of interfacial shear τ_g is often less than the value of the debonding stress τ_d.

To account for these processes, we can consider an RVE in which:

- The central portion of the fiber is subjected to an elastic load; the value of interfacial shear is limited by the debonding stress τ_d. In this zone, exactly the same equations of elastic equilibrium as those introduced in the Cox model can be written.
- When $\tau_i > \tau_d$, sliding is considered to be at a constant stress τ_g. The load transfer in this zone is accomplished according to the hypotheses of the Kelly model. By solving the equilibrium equations with the appropriate boundary conditions, the stress-strain relationship can be calculated as follows by **Eq.13**.

$$\sigma_l = \left[V_f E_f + V_m E_m\right]\varepsilon_l - \frac{V_f}{s}\left[\frac{\left(E_f \varepsilon_l\right)^2 - \left(2\tau_d/n\right)^2}{4\tau_g} + \frac{2\tau_d}{n^2}\right]$$ (Eq.13)

Where V_f, E_f and V_m, E_m, are respectively the volume fractions and moduli of the reinforcement and the matrix, ε_l is the applied strain, $s = L/a$ is the aspect ratio of the fiber, n is a constant.

For low values of σ, the second term of the second member of **Eq.13** induces nonlinearity in the stress-strain relationship.

8 Principle and limitations of the debonding test (pull-out)

The debonding test (or pull-out test) is a micromechanical test used to characterize interfacial fiber / matrix bonding. It is considered to be the most advanced technique. It consists in conducting a tensile test on a monofilament partially embedded in resin and measuring the force required to extract the fiber from its matrix sheath. The debonding test was originally developed by Shiriajeva and Andreevskaya (1962) **[187]**, improved by Favre and Perrin (1972) **[188]**, Piggott et al. (1985) **[142]**, Hampe 1988 and Hampe et al. 1989 **[189, 190]**. There are several different pull-out configurations (**Fig.11**): the fiber may be embedded either in a microdroplet of resin or in a resin button or still, more typically, in a block of resin. In all cases, the resin is bonded to the lower part of the traction device.
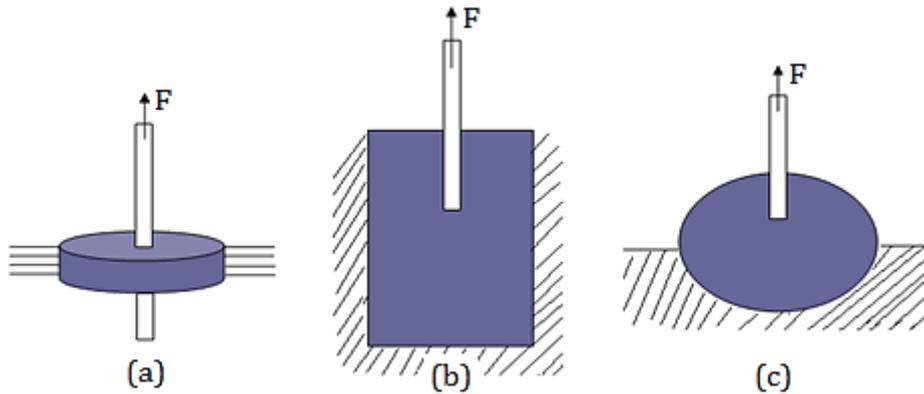
Fig.11. Different pull-out configurations: (a) Favre (b) Piggott (c) Hampe.

Fig.12 presents a typical curve obtained during the debonding test. It generally contains three typical zones **[191]**. The first part, $0 \le F \le F_d$, is linear and corresponds to an elastic solicitation of the whole: fiber, matrix, and interface. The force reaches its critical value at the point F_d at which the slope of the curve decreases and crack initiation occurs, related to the breakdown phenomenon at the interface. For the part, $F_d \le F \le F_{max}$, the fiber begins to pull out of the matrix by crack propagation, which explains the decrease in the slope to the point F_{max}. From this point on, all the part embedded in the matrix is extruded and complete debonding takes place. The only forces recorded from this moment on are friction forces between the fiber and the matrix. The interface quality is evaluated using

the interfacial strength (IFSS). This is calculated from the maximum debonding load, F_{max}, and the sample geometry.

Fig.12. Typical debonding curve: tensile **[110]**.

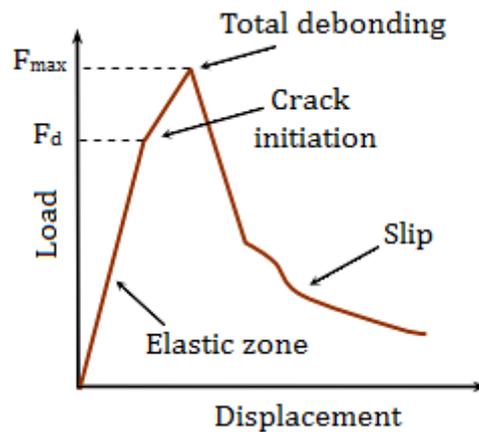The debonding load "F_d" is an important parameter of the test. The length of the embedded fiber is denoted L. In the case of systems with high interfacial adhesion, this length must be small enough for the strength necessary for debonding to remain lower than the tensile failure strength of the fiber **[97]**. The competition existing between these two phenomena can be demonstrated by a simple analysis. We can thus define the notion of critical embedding length; high adhesion systems require very low critical lengths (<100 μm) that are difficult to achieve in pull-out. For low embedding lengths, some studies have shown that in pull-out (in the case of configurations (a) and (c) only **Fig.11**), the force required to break the adhesion of the end of the fiber to the matrix was greater than the force necessary for debonding, making the test unusable. These disadvantages have led to the development of a variant of this test: the droplet test, which in addition to the easy implementation of samples, makes it possible to test systems with stronger adhesion (obtaining shorter embedded lengths).

The microdroplet test differs from that of debonding by the particular configuration of samples: here, the fiber is embedded in a micro-droplet of resin deposited on the monofilament before curing. With this technique, very low embedding lengths of 30 μm can be achieved, which is rarely possible in pull-out. The only limiting factor of the test is, in the case of a thermosetting resin, the initial viscosity of the resin which, if it is too high, prevents the deposition of small droplets. Lastly, the micro-droplet test, unlike pull-out, enables the relatively fast production of a large number of samples (as the implementation of the samples does not require specific mounting) **[97]**. **Fig. 13** shows the shape of the tensile curves obtained in the microdroplet test on glass/epoxy systems **[185]**. As in pull-out, these curves enable determination of the debonding load F_d. The main problem is then to relate this experimental quantity to a specific parameter in the interface: this is the subject of diverse modelings.
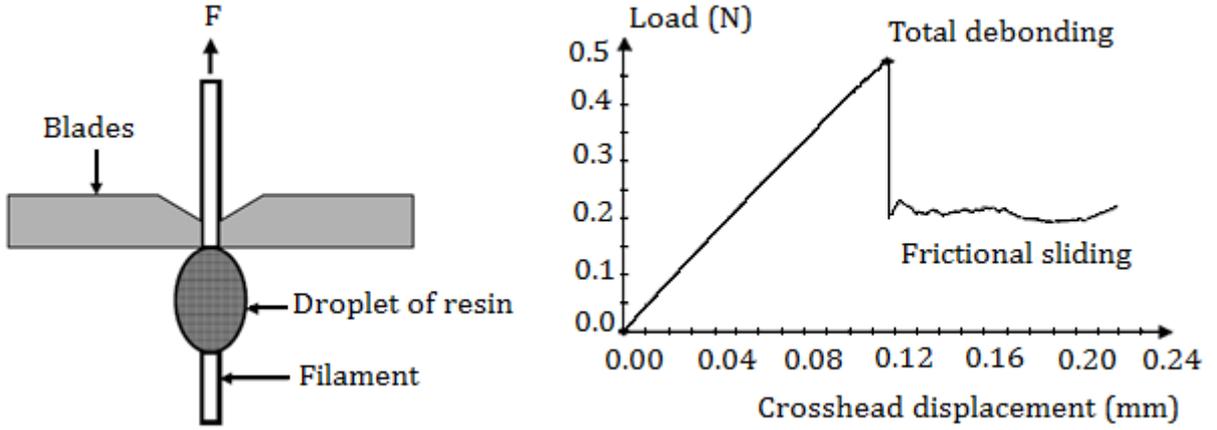
Fig.13. Schematic diagram of microdroplet test, typical debonding curve: tensile **[185]**.

- Notion of critical embedded length

Assumption: the interfacial shear strength at the fiber/matrix interface is homogeneous along the interface.

The equilibrium force on a fiber subjected to tension gives (**Eq.14**):

$$\pi r^2 \sigma = 2\pi r L \tau = F \tag{Eq.14}$$

Where r is the fiber radius, L is the embedded length, F is the tensile force applied to the fiber, σ the tensile stress in the fiber, and τ is the shear stress at the fiber / matrix interface.

For interfacial debonding τ_i to occur, the force F must be lower than the tensile failure strength of the fiber F_c such that τ_i gives (**Eq.15**):

$$\tau_i = \frac{F}{\delta_f} = \frac{F}{2\pi r L} \tag{Eq.15}$$

For interfacial debonding it is necessary that $F=F_d$ (**Eq.16**) (F_d debonding force)

$$\tau_d = \sigma_d = \frac{F_d}{2\pi r L} \tag{Eq.16}$$

Debonding without fiber failure occurs if (**Eq.17**):

$$F_f^R \geq F_d \text{ (Tensile strength of the fiber)} \tag{Eq.17}$$

This critical embedding length L_c is calculated by equations (**Eq.18**) and (**Eq.19**):

$$F_d = \sigma_d 2\pi r L_c \tag{Eq.18}$$

$$F_R^f = \sigma_R^f \pi r^2 \tag{Eq.19}$$

Inserting equations (**Eq.16**) and (**Eq.17**) into (**Eq.15**) gives (**Eq.20**):

$$L_c \leq \frac{\sigma_R^f}{2\sigma_d} r \tag{Eq.20}$$

With L_c the critical length.

For embedding values lower than L_c the pull out test can be performed.

For example for glass fiber E: $2r$=8µm, $\sigma_r = 3500 MPa$ and τ_i can be estimated as at least 50 MPa, hence L_c=140 µm.

9   Trends in the analytical pull-out test models developed

Few studies have been conducted so far on the micro-droplet test, which is a recent variant of the pull-out test. The numerous theories, however **[192-194]**, used in pull-out tests cannot be applied directly to the study of this test, since a simple comparison of test configurations (**Fig. 11** and **13**) shows that the boundary conditions imposed on the matrix and the fiber end are different. In general, in pull-out tests, the resin can be deformed more easily than in the micro-droplet test, especially in shear (as its stiffness is lower). Therefore, interpreting the microdroplet test requires specific modeling. As for micromechanical testing, one can distinguish two main approaches **[97, 191,195]**:

- A fracture mechanics approach, in which an energy balance at the moment of interfacial failure is established (energy criterion);
- A shear-lag type approach in which a balance of the stresses within the fiber/ micro-droplet system is established (maximum stress criterion).

Finite element analyses can be included in the latter type of approach.

9.1   Models using an energy criterion

The interest of this type of model was underlined in particular by Piggott. After having initially used a stress criterion in his early work, he chooses an energy criterion to interpret tests in which brittle fracture occurs, which is the case of glass or carbon/epoxy systems in particular, since sudden failure phenomena appear to be governed by an energy criterion resulting from the fracture mechanics, while the progressive failure process depends on a stress criterion **[193]**. The energy model developed by Piggott is well adapted to a classic pull-out configuration.

9.1.1   Piggott's model

The geometry used is that of pull-out **[196]**, in which a fiber of radius r has one end embedded on a length L in a resin cylinder with a radius R (**Fig.14**).
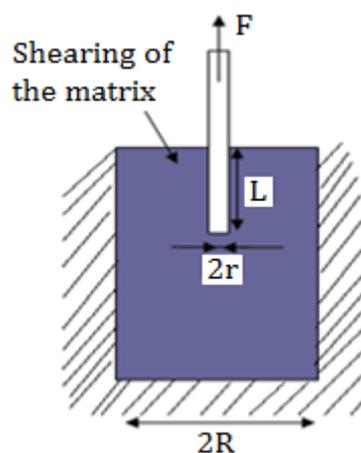

Fig.14. Test geometry used by Piggott.

Under the action of the tensile force, F, to which the fiber is subjected, the matrix is sheared. The fiber is abruptly debonded for a force F_c (**Eq.21**).

$$F_c = 2\pi r \sqrt{(E_f G_i r)} \sqrt{\left(\frac{nLth(nL/r)}{r}\right)}$$

(Eq.21)

With: $n^2 = \dfrac{2G_m}{E_f \ln\left(\dfrac{R}{r}\right)}$, E_f: the Young's modulus of the fiber, G_m: the shear modulus of the

matrix, G_i: the fracture energy of the interface and th: the hyperbolic tangent function .

It interesting to note that Piggott used this expression to criticize the results obtained with the microdroplet test **[152]** on a Kevlar/epoxy system, for which droplet lengths from 40 to 400µm were obtained.

9.1.2 Model of Penn and Chou

The geometry described by Penn and Chou **[197]** (**Fig.15**) is closer to that of the micro-droplet test.
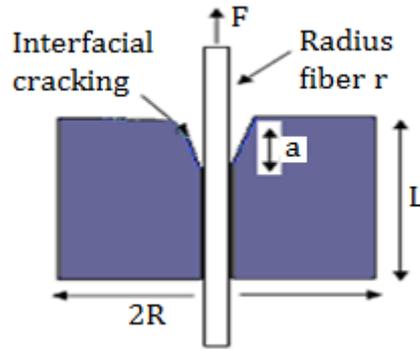
Fig.15. Model of Penn and Chou.

However, the presence of the blades that more or less embed the upper border of the matrix does not appear to be taken into account. The authors consider an initial interfacial crack size of length a. The energy equilibrium indicates that part of the stored elastic energy is released to allow breaking of the interface. This gives the expression of the debonding force F_c (**Eq.22**):

$$F_c = \frac{2\pi r \sqrt{(rE_f G_i)}}{\sqrt{\left(1 + \dfrac{1}{ch\left(ch\left(n\left(\dfrac{L-a}{r}\right)\right)\right)}\right)}}$$

(Eq.22)

with $n^2 = \dfrac{2G_m}{E_f \ln\left(\dfrac{R}{r}\right)}$ and ch: the hyperbolic cosinus function.

In the case where the crack length is negligible compared with the embedding length, $a \ll L$, this expression can be simplified to give **Eq.23**. This is particularly the case of samples for which Scanning Electron Microscopy observations have never revealed cracks.

$$F_c = \frac{2\pi r \sqrt{\left(r E_f G_i\right)}}{\sqrt{\left(1 + \dfrac{1}{ch\left(ch\left(\dfrac{nL}{r}\right)\right)}\right)}} \qquad \text{(Eq.23)}$$

This expression brings in the same parameters as that of Piggott, in particular as regards the parameter n, which is closely related to the shearing of the matrix sheath with a thickness R-r. When the embedding length "L" is sufficient, **Eq.23** has a simplified form $F_c = 2\pi r \sqrt{\left(r E_f G_i\right)}$ which cannot be used when the coated fiber lengths are too low.

9.1.3 Model of Palley and Stevans

The in-depth study of Palley and Stevans **[198]** considers a highly realistic test configuration (**Fig.16**). The droplet is represented by a cylinder of length L and diameter D. The model can take into account the possible spacing, h, of the two blades relative to the fiber. This spacing then causes, during the test, shearing of a matrix cylinder with a thickness h around the fiber; the matrix located below the blade is, in turn, compressed during the test. After the onset of interfacial cracking, friction between the separated fiber and the matrix is taken into account.
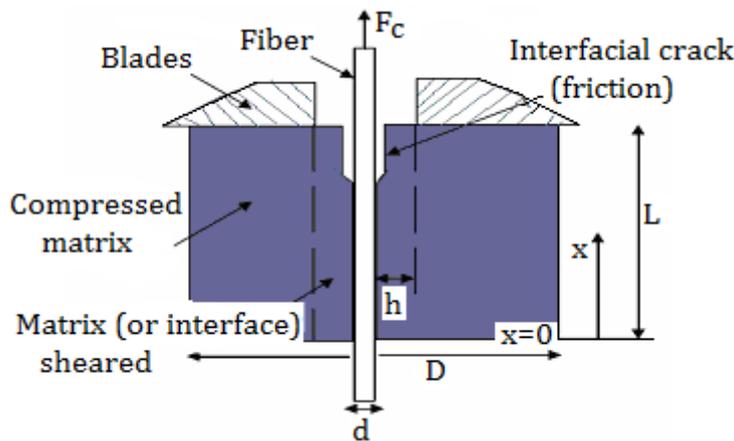
Fig.16. Definition of the geometry used by Palley and Stevans.

Palley and Stevans assume linear elasticity and consider the initiation and propagation of a cylindrical crack at the interface. Their energy balance equation leads to a rather complex expression of the debonding force, F_c, as a function in particular of the position of the crack front. This enables them to study the evolution of the strength during crack propagation.

The equation, which is complex but not restrictive, gives the debonding force and allows for numerical studies of sensitivity to various parameters such as the coefficient of interfacial friction and the thickness h of the sheared matrix. The latter parameter is considered to have only a minor influence on the result, and can therefore be neglected experimentally. This means that poor control of the positioning of blades should not, within limits at least, significantly impact the debonding force obtained, i.e. should not scatter the results.

The expression giving the debonding force F_c is then simplified by assuming first that the contribution of the shearing of the matrix cylinder is negligible, and second that the friction at the interface is very low. This leads to **Eq.24**:

$$F_c = 2\pi r \frac{\sqrt{(rE_f G_i)}}{\sqrt{\left(1 + \frac{E_f}{E_m\left(\frac{D^2}{d^2} - 1\right)}\right)}}$$

(Eq.24)

9.2 Models using a stress criterion

This group of models aims at estimating the profile of the stresses at the interface according to the applied load. Usually, it is postulated that debonding occurs when the maximum interfacial stress reaches the interfacial strength. This approach is simpler than the energy approach and often gives results that are closer to experimental reality.

9.2.1 Greszczuk analysis

Greszczuk's analysis, which is probably the oldest, has inspired many authors **[192,199, 200]** and is unquestionably the theory of reference for the interpretation of pull-out tests. The test geometry studied by Greszczuk is similar to that considered by Piggott (**Fig.14**), except that it introduces an interphase of thickness b_i and Coulomb modulus G_i, forming a sheath along the entire length of the fiber.

The assumptions made by Greszczuk when the model is axisymmetric, elastic, and linear, are: radial effects are negligible (no radial dependence); the strains and stresses imposed by the fiber on application of the load F are completely accommodated within the interphase that is assumed to be thin; the surrounding matrix is not disturbed. He obtains the expression of the stress profile along the interface. The shear stress is not constant along a fiber. The following formulation (**Eq.24**) estimates the value of the stress at a point of the fiber which is at a distance l with respect to an origin 0 (**Fig.17**).
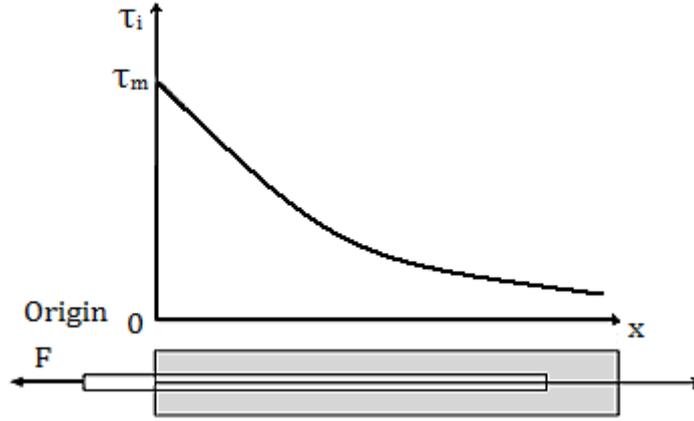
Fig.17. Shape of the interfacial shear stress curve as a function of distance from an origin (the pull-out method).

The fiber is embedded in the matrix at a depth L relative to the same origin; the shear stress is maximum at the point of emergence of the fiber and is:

$$\tau_i = \tau_m \frac{\alpha L}{th(\alpha L)} \qquad \text{(Eq.25)}$$

With $\quad \tau_m = \dfrac{F_d}{2\pi rL} \quad$ and $\quad \alpha^2 = \dfrac{2G_i}{b_i rE_f}$

This expression involves parameters that are specific to the interface, which limits the application of this model (in this form) since these quantities are generally unknown. To circumvent this difficulty, it is often assumed that $G_i = G_m$ and $b_i = r \ln (R/r)$ where R is the radius of the matrix surrounding the fiber, which leads to a new expression of α:

$$\alpha^2 = \frac{2G_m}{r^2 E_f \ln(R/r)} \qquad \text{(Eq.26)}$$

This expression is the most classical variant but other formulations can be found in the literature (the general formula giving τ_i remains unchanged). The problem of this type of model is to formulate precise hypotheses leading to the evolution of α.

Greszczuk's hypothesis, which posits that the deformations are fully accommodated by the interphase, is valid only if the deformation capacity of the interphase is much greater than that of the matrix (assumed to be rigid); in the opposite case, the calculation is incorrect and should take the contribution of the surrounding matrix into account.

9.2.2 Model of mean stress

The simplest hypothesis that can be formulated about the interfacial shear stress is, of course, that it remains constant throughout the fiber / matrix interface. This hypothesis is the one made by the mean stress model. The equilibrium of forces on the fiber gives (**Eq.27**):

$$F = 2\pi r L \tau_i \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(Eq.27)}$$

Where L is the embedded length, r is the fiber radius and τ_i is the interfacial shear strength. This formula gives an estimate of the mean shear stress; it is widely used for the microdroplet [201] and pull-out [188] tests and even in micro-indentation tests. Its simplicity allows rapid exploitation of the results. It is currently the most commonly used model for the interpretation of microdroplet test results.

9.2.3   Scheer and Nairn Analysis

Scheer and Nairn [201] consider the same type of geometry as Palley and Stevans, albeit with slightly different boundary conditions (**Fig.18**).
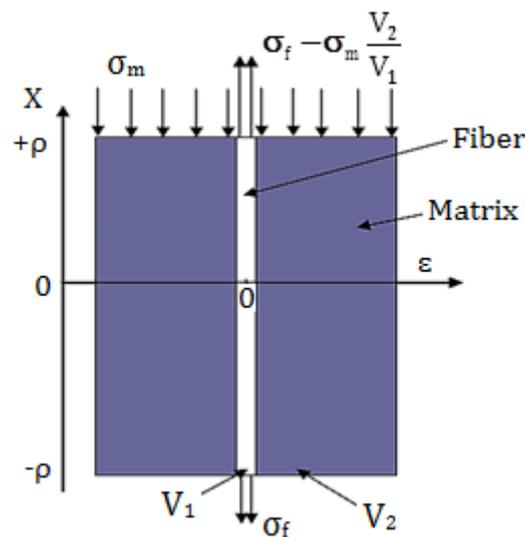
Fig.18. Geometry used by Scheer and Nairn.

The model is axisymmetric, elastic and linear; axial stresses in the fiber and the matrix are assumed to depend only on x (no radial dependence). Using a variational method, the most admissible stress field for the problem is sought. The general expressions obtained for the diverse internal stresses are complex and will not be described here, nor even exploited.

Scheer and Nairn plotted the stress profiles along the interface for the case of a microdroplet of epoxy resin on a carbon fiber. The embedded length chosen is ten times the fiber radius, which is a realistic experimental case. The major result which stands out from this study is the complex character of the stress state at the interface, which is as likely to break under the influence of the radial tensile stress as of the shear stress. Other authors [203] reach similar conclusions by modeling the pull-out test by finite elements. The interpretation of debonding in terms of failure then becomes much more difficult and it would perhaps be preferable to consider a mixed failure criterion. The microdroplet test may not provide the interfacial shear strength but rather the strength of the interface to a complex tensile / shear stress state.

9.2.4 Raman spectroscopy studies

Alongside the diverse mathematical models of micromechanical tests, an experimental technique to evaluate the deformations undergone during these tests has been developed over the last few years, namely infrared spectroscopy; at vibrational frequencies characteristic of the atomic groups of the material tested (Raman peaks). These frequencies are a function of the strength and length of interatomic bonds, and hence of the lattice strain. Raman spectroscopy gives a direct measurement of strains at a microscopic level (resolution of a few microns).

This technique has already been successfully coupled with micromechanical fragmentation tests **[204]** and pull out tests **[205, 206]**, allowing a direct visualization of the profile of global deformation applied to the specimen. We can go back to the profile of the interfacial shear stress, τ_i, by the classical expression of the equilibrium of forces on a fiber section (**Fig.19**) and by assuming the elasticity of the fiber, hence (**Eq.28**):

$$\tau_i = E_f \frac{r d\varepsilon}{2 dx} \tag{Eq.28}$$

Where ε is the axial strain in the fiber and E_f the Young's modulus.
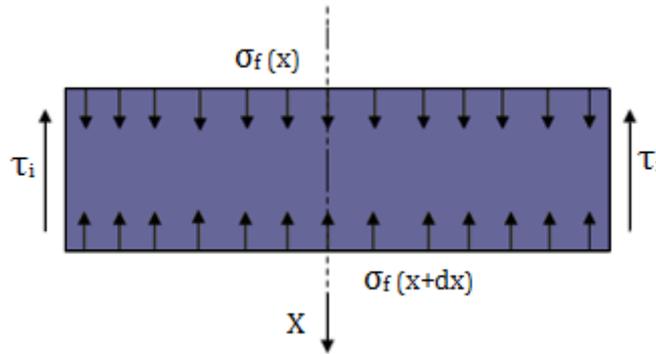
Fig.19. Equilibrium forces on a section of fiber

This technique to measure the deformations in situ has the advantage of limiting the number of hypotheses made to estimate the interfacial shear. Admittedly, any technique has its limitations and Raman spectroscopy can only be used to study the fibers situated on the surface of a composite, for a transparent matrix and for fibers having a sufficiently intense Raman signal. It can therefore be successfully applied to model composites such as those tested in pull-out and fragmentation tests. An application in micro-indentation tests is much more difficult to perform. This type of study still remains to be done on carbon/epoxy composites experimented in micro-droplet tests, where the presence of jaws can be an additional difficulty.

9.2.5 Large-Toumi Model

Large-Toumi **[97]** has developed an approach based on a stress criterion for a geometrical configuration that closely resembles the real test configuration (the micro-

droplet test, **Fig.11**). The model is on the same lines as that of Greszczuk (the same set of equations), but the geometry and the boundary conditions are adapted to the case of the droplet test. In this approach, the real test geometry can be modeled as indicated in **Fig.20**. The droplet is represented by a cylinder of length L, where L is not the embedding length, but the length of the droplet debonded from the fiber during the test (i.e., regardless of the residual meniscus). This value is obtained by a systematic visual inspection after each test. Given the elliptical shape of droplets and the relative position of the jaws, the diameter of the matrix cylinder in **Fig.14** is equal to the diameter of the droplet. This axisymmetric geometry is close to that considered by Palley and Stevans.
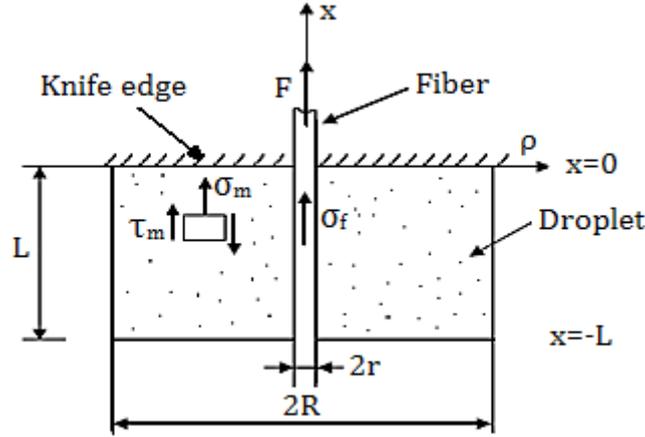
Fig. 20. Modeling the micro-droplet (B. Large-Toumi).

The indices "*m*" and "*f*" refer respectively to the matrix and the fiber, τ_i indicates the interfacial shear stress, that is $r = \rho$. It is assumed that the system is elastic and linear, with symmetry of revolution (no torsion). It is assumed that the axial stress in the matrix σ_m and in the fiber σ_f, do not depend on ρ and that radial effects are negligible. These effects include inflation of the matrix and contraction of the fiber due to the effects of the Poisson ratio; these two hypotheses are classical in analytical calculus (Greszczuk 1969, Piggott 1980).

Taking the boundary conditions into account, the expression of the stresses σ_f and σ_m can be formulated as follows (**Eq.29** and **30**):

$$\sigma_f = \frac{F[ch(\alpha(x+L))-1]}{\pi r^2 [ch(\alpha L)-1]} \qquad \text{(Eq.29)}$$

$$\sigma_m = \frac{-F[ch(\alpha(x+L))-1]}{\pi(R^2-r^2)[ch(\alpha L)-1]} \qquad \text{(Eq.30)}$$

When the applied force F reaches the debonding strength F_d, the maximum of the stress is the interfacial shear strength τ_i (**Eq.31**), therefore:

$$\tau_i(x) = \frac{-\alpha F}{2\pi r(ch(\alpha L)-1)} sh[\alpha(x+L)] \qquad \text{(Eq.31)}$$

With as before: $\alpha^2 = \dfrac{4G_m\left[\dfrac{r^2}{R^2}\left(\dfrac{E_f}{E_m}-1\right)+1\right]}{r^2 E_f\left[2Ln\left(\dfrac{R}{r}\right)-\left(1-\dfrac{r^2}{R^2}\right)\right]}$ $\qquad$ (Eq.32)

and sh: the hyperbolic sinus function

When R is greater than r, which is generally the case in pullout tests, the term α^2 can be simplified to **Eq.33** where we find the coefficient α initially introduced by Greszczuk (1969)

$$\alpha^2 = \frac{2G_m}{r^2 E_f Ln\left(\dfrac{R}{r}\right)} \qquad \text{(Eq.33)}$$

The expression τ_i obtained by the Large-Toumi model remains different from that obtained by Greszczuk $\tau_i = \dfrac{F_d}{2\pi rL}\dfrac{\alpha L}{th(\alpha L)}$, because of the particular boundary conditions of the droplet test.

9.2.6 The Zhang model

Zhang et al. **[191]** developed an analytical model to study the pull-out behavior of a continuous fiber-reinforced cementitious composite. This model is based on the analysis of the stress and displacement of the yarn combining continuity conditions. Zhang et al. studied the failure mechanism of continuous yarn reinforced cementitious composites (yarn embedded in a cement block). In this work, the failure mechanism was analyzed by dividing the pull-out curve into three phases: perfect bonding phase, debonding phase, and pure friction phase. When the uniaxial tensile force F applied on the free end of the yarn reaches a critical value F_c, debonding of the yarn begins to take place. This is the beginning of the second phase. The length of the debonding part increases as the applied force increases. When this length reaches the embedded length, the applied force reaches its maximum value F_{max}. This is the third phase which is pure friction between the yarn and the matrix. The level of applied force decreases greatly. These three phases are shown in **Fig.21**.
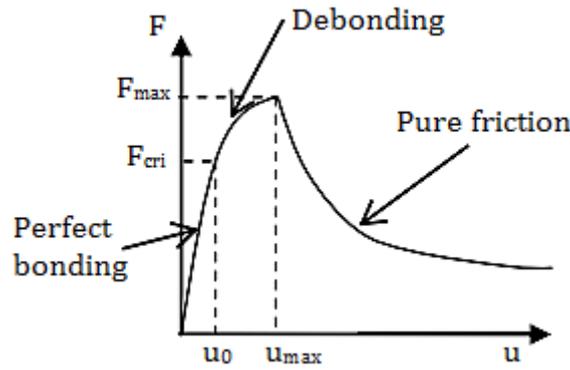
Fig.21. Pull-out curve **[191]**.

The following assumptions are made in this model:

- The matrix is considered as a rigid non-deformable body and only the displacement of the yarn in the matrix is studied;
- The multi-filament yarn is considered as a single fiber so there is no shear between filaments. Only the bond between multi-filament yarn and cementitious matrix is studied;
- The materials of the yarn and the matrix are respectively homogeneous, isotropic and linearly elastic;
- The shear stress τ at the interface between yarn and matrix increases proportionally to the displacement u of the yarn $\tau = k_1 u$ during the perfect bonding phase. It reaches its maximal value τ_{max} at the onset of the debonding phase and then it decreases proportionally to the displacement u of the yarn $\tau = k_2 u$ during the debonding phase. In the end, during the pure friction phase, it becomes constant τ_0 along all length of the yarn. **Fig.22** shows the shear stress versus displacement. k_1 and k_2 are the bond moduli corresponding respectively to the perfect bonding phase and the debonding phase. τ_{max} and τ_0 are bond parameters obtained from experimentation.

Fig.22. Shear stress versus displacement **[191]**.

The establishment of the relationship between the pull-out displacement u of a yarn and the pull-out force F is based on the analysis of the stress τ and displacement u of the yarn at the interface between yarn and matrix by considering different continuity conditions for each phase. A comparison of the analytical and experimental results showed that the

experimental results are in good agreement with those obtained according to the analytical model developed.

10 Microindentation test

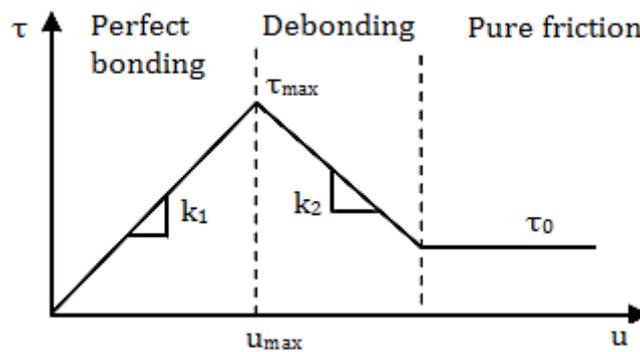The micro-indentation test is the closest to reality as it uses a finished product that integrates the manufacturing parameters of the material. This test is widely used to determine the two mechanical properties of the fiber-matrix interface, the friction coefficient and the residual radial stress according to Ye and Kaw [207], as it enables the debonding force to be measured in situ on real composites (mainly unidirectional). The success of the tests is also closely linked to the quality of polishing of the samples tested; unsuitable polishing can prevent the correct identification of fibers and cause their preliminary embrittlement. Based on the measure of the debonding stress σ_d, the interfacial shear strength τ_i, which is a rather complex function of σ_d, the elastic characteristics G_m of the matrix and E_f of the fiber, the diameter d of the fiber and the interfiber distance can then be deduced [98-100].

10.1 Modeling tests on organic matrix composites

In general, most of the models representing the behavior of organic matrix composites during micro-indentation tests take into account not only the difference in the elastic properties of the fibers and the matrix but also the interfiber distance. Obviously, as the interface is chemically bonded, the first goal is to characterize this adhesion, associated with the debonding force found experimentally. As in pull out tests, two approaches can be taken, one considering an energy failure criterion and the other one a maximum stress criterion. In micro-indentation tests, the latter criterion is the most widely used; even if certain authors [208] note that the interfacial toughness is doubtless the parameter that is intrinsic to debonding (this type of analysis would allow a better description of the dependence of the debonding force on the radius of the indented fiber). Due to the complexity of the stress states engendered (in particular because of the contact between the indenter and the fiber), many studies [209,210] use numerical methods, particularly finite element approaches. The push-through test, however, provides a very simple analysis.

10.1.1 Push-through test: mean stress analysis

The push-through test is to micro-indentation what the droplet test is to pull-out. The thinness of the samples used, coupled with the boundary conditions imposed on the fiber, mean that the interface can be stressed over its entire length, leading to complete debonding [211]. As in the droplet test, the test can be reasonably interpreted (in terms of the scatter of the results) by considering that the interfacial shear stress, τ, is constant (**Eq.34**), i.e.:

$$\tau = \frac{F_d}{2\pi r L} \tag{Eq.34}$$

Where F_d is the debonding force, r the radius of the fiber and L is the sample thickness. While this approach is extremely simple, it nonetheless requires very particular samples (between 80 and 1300 μm thickness for a glass/epoxy), which are very difficult to cut and

polish. The push-through test is, therefore, an interesting alternative that allows a simple analysis of the results, but that raises considerable experimental problems.

10.1.2 Classic configuration of the test: numerical studies

Numerical methods are very powerful and enable a large number of experimental parameters to be taken into account, such as those related to fiber loading. They are considered to give very good approximations of the fields of stress and strain within the composites tested. A detailed numerical study is that conducted by Mandell et al. [210] using the finite element method. This study has the enormous advantage of having been conducted and presented so that its results can be applied to highly diverse geometries and materials.

10.1.2.1 Finite element approach

The geometry used by Mandell 1986 [210] is represented in **Fig. 23**. The indented fiber of diameter D_f is surrounded by a thick matrix cylinder T_m, itself surrounded by a sheath of material possessing the average properties of the composite. The contact area between the punch and the fiber is characterized by its diameter D_σ, which is a fraction of the fiber diameter.
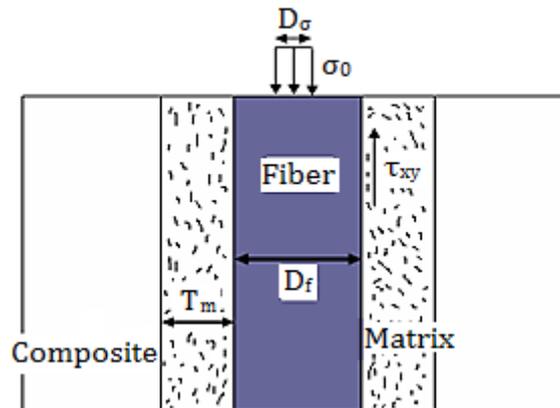
Fig.23. Geometry considered by Mandell 1986.

The authors conducted several sensitivity studies. Concerning the influence of the type of loading, they observed the influence of the diameter D_σ of the contact zone on the value of the ratio of the interfacial shear stress, τ_{xy} and on the medium stress applied to the fiber (**Eq.35**).

$$\sigma_m = \frac{4F}{\pi D_f^2} = \sigma_0 \frac{D_\sigma^2}{D_f^2}$$

(Eq.35)

Where F if the applied load, and σ_0, the stress at the summit of the fiber.

The authors assessed this effect in the case of a glass/epoxy material, and showed that while the location of the maximum shear stress along the interface depends on the extent

of the contact zone; its value is practically unchanged. This means that the real contact area can be neglected and that only the medium stress σ_m (**Eq.35**) needs to be taken into account.

10.1.2.2 *Boundary elements approach*

Chen and Young 1991 **[212]** used the same geometry and the same approach as the previous study; only the numerical method varied, as they proposed an integral method using not finite elements but boundary elements. This technique allows a better evaluation of interfacial stress fields, since the finite element method gives only an approximate solution (finite element stress values are calculated in fact not in the interface but on the mesh elements bordering it).

To conclude this part, it should be mentioned that numerical methods, although very efficient, require heavy investment, since they require the acquisition (or development) of a suitable calculation code, and perfect knowledge of the code in order to interpret the results critically (and detect, in particular, inadequacies in the code itself). Unfortunately, such studies are often reported in the literature as "black boxes": they deliver a lot of information, but the conditions in which the information was obtained are not made explicit (boundary conditions, geometric information, values of the constants used, etc.). Their validity is therefore difficult to assess.

10.1.3 Large-Toumi Model

In this model Large-Toumi et al. developed an analytical approach that is simpler to implement that in the numerical method, and which allows a more direct interpretation of the physical phenomena believed to take place during the tests **[97, 213]**. The model was based on the work of Piggott, 1980 (in turn influenced by previous work by Greszczuk, 1969), which already took into account the effect of inter-fiber distance but in a configuration of global tension of the composite specimen. Piggott's model was modified by introducing loading conditions and boundary conditions representative of the test conditions. They considered a perfect hexagonal arrangement of fibers and introduced the notion of an equivalent radius, R_{eq}, to reduce the initial geometry to an equivalent one (**Fig.24**) (The introduced geometry is an axisymmetric model formed of concentric cylinders).
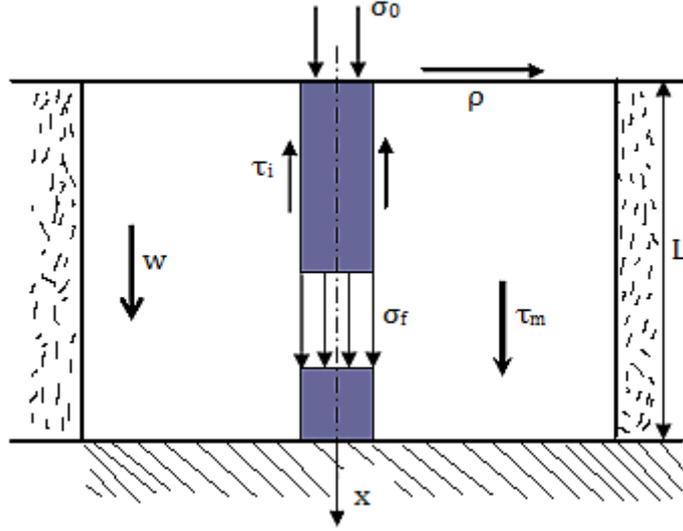
Fig.24. Equivalent geometry (section)

The equivalent radius is defined by: $\pi R_{eq}^2 - \pi r^2 = A$

Where r is the fiber radius and A is the matrix area contained in the circle of radius R. It is assumed that the longitudinal displacement is zero at the "equivalent" fiber/matrix interface (at a distance R_{eq}) since tests showed that the bordering fibers did not move and that the interfaces were not damaged. Using Piggott's approach, this leads to the differential equation (**Eq.36**):

$$\frac{d^2\sigma_f}{dx^2} = \frac{n^2}{r^2}\sigma_f \qquad\qquad (Eq.36)$$

Where

$$n^2 = \frac{2G_m}{E_f Ln\left(\dfrac{R_{eq}}{r}\right)}$$

σ_f is the fiber longitudinal stress, E_f the fiber Young's modulus and G_m the matrix shear modulus. The solution is done from **Eq.37**.

$$\sigma_f = Bsh(nx/r) + Dch(nx/r) \qquad\qquad (Eq.37)$$

With sh and ch refer respectively to the sinus and cosinus hyperbolic function.

To write the boundary conditions, it is assumed first that σ_f is homogeneous on a section of fiber (even on the upper surface) and second that $L>>R$, where L is the thickness of the sample. We obtain at $x=0$, $\sigma_f = \sigma_0 = -F/\pi r^2$ and at $x=L$, $\sigma_f = 0$. Thus (**Eq.38**):

$$\sigma_f = -\sigma_0\left[ch\left(\frac{nx}{r}\right) - coth\left(\frac{nL}{r}\right)sh\left(\frac{nx}{r}\right)\right] \qquad\qquad (Eq.38)$$

If τ_i is the interfacial shear stress, then the equilibrium force on a fiber section leads to **Eq.39**.

$$\tau_i = -\frac{r}{2}\frac{d\sigma}{dx} \qquad \text{(Eq.39)}$$

This gives (**Eq.40**).

$$\tau_i = \frac{n\sigma_0}{2}\left[sh\left(\frac{nx}{r}\right) - coth\left(\frac{nL}{r}\right)ch\left(\frac{nx}{r}\right)\right] \qquad \text{(Eq.40)}$$

τ_i is maximum at $x=0$ and $\tau_{imax} = \frac{n\sigma_0}{2}coth\left(\frac{nL}{r}\right)$ and as $L/r \to \infty : \tau_{imax} = \frac{n\sigma_0}{2}$ (indeed, experimentally L=1cm and R=10µm).

Then, for $F=F_d$, $\tau_{imax} = \tau_i$, where τ_i is the interfacial shear strength (**Eq.41**); thus:

$$\tau_i = \frac{F_d}{2\pi r^2}\sqrt{\frac{2G_m}{E_f Ln\left(\frac{R_{eq}}{r}\right)}} \qquad \text{(Eq.41)}$$

Determination of R$_{eq}$:

The real neighborhood of a fiber is different from the idealized case: the nearest fibers are positioned at various distances and generally, they do not have the same diameter. The tests performed induce only a partial debonding of each indented fiber; this means that the model presented above can be applied. The equivalent radius, R_{eq}, is then defined (**Eq.42**):

$$\frac{\theta R_{eq}^2}{2} = \frac{\theta r^2}{2} + A_m \qquad \text{or by} \qquad \frac{\theta R_{eq}^2}{2} = \frac{\theta R^2}{2} - A_f \qquad \text{(Eq.42)}$$

A_m (resp. A_f) is the area of matrix (resp. of fiber) included in the sector of angle θ and radius R (**Fig.25**). A_f is approximated by (**Eq.43**):

$$A_f = \frac{(\pi - \theta)c^2}{2} + cR\left(1 - cos\left(\frac{\theta}{2}\right)\right) \qquad \text{(Eq.43)}$$

So :

$$R_{eq}^2 = R^2 + c^2 - \frac{2cR}{\theta}\left(1 - cos\left(\frac{\theta}{2}\right)\right) \qquad \text{where } \theta = 2Arc\,sin\left(\frac{c}{R}\right) \qquad \text{(Eq.44)}$$
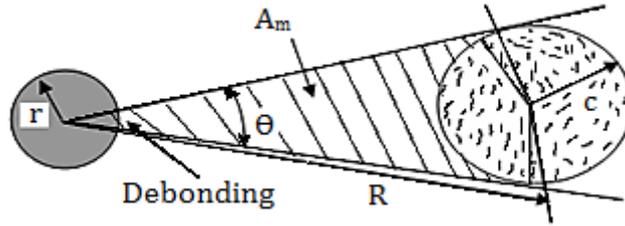
Fig.25. Local determination of the equivalent radius

11 Discussion: validity of different models

Frist of all, analytical models described in this review consider the matrix as a homogeneous structure with a well-defined interface. It is well known that a significant heterogeneous area can be presented at the vicinity of the fibers.

This assumption can be explained by the difficulty to characterize and analyze the vicinity of the fiber and the interphase area. Indeed, the experimental method micro/nanoscale limit the investigation of its areas at the initial state and during ageing. Due to a complex interaction between with chemical and physical phenomena, the mechanical behavior of the interphase can be highly modified (as example, local plasticity, local viscoelasticity....).

Moreover, the aim of the analytical representation is to proposed an approached solution of the real solution. In this case, the homogenous representation of the matrix can be proposed especially at the initial state. As example, Riano et al. **[214]** have shown that an error around 15% about the Young's modulus is calculated when the interphase is not taken into account in the numerical model. Similar results have been presented in the literature with the kinetic water diffusion **[132]** and stress at break **[215-217].**

11.1 Calculation of an interfacial characteristic

The results calculated with the various analytical models presented previously, which give the characteristic parameters of the interface, G_i the interfacial failure energy, and τ_i, the interfacial shear strength, are given in Table 1 for four materials were chosen to highlight the role of fiber / matrix interface. The materials have the same reinforcement fiber, T300-6K from Toray, and the same epoxy matrix, DGEBA/DDM, LY1808RF/HT972 from Ciba-Geigy, with a formulation very close to the system LY556/HT972).

The composite plates were made by stacking unidirectional layers (14 plies) and autoclave curing. Both cycles of curing are: A long said cycle containing a post-curing supposed to lead to a total crosslinking of network and an industrial cycle, said short, Says court, without post-curing, not that must produce that an incomplete crosslinking (slight sub-crosslinking). The sizings used for the manufacture of these materials are Toray Commercial sizings 4 and 5, with the sizing 5, which is the standard sizing T300 fibers, is an sizing compatible epoxy and polyester while the sizing 4 is only epoxy Compatible.

These four systems used in the analysis of different analytical models as well as the nomenclature used for designers are:

S: Standard- denotes the reference material, T300-6K-50B fiber (oxidized fiber, sizing 5) long cycle of curing;

SR: Under crosslinked- indicate the material in which the matrix has a density of weaker crosslinking, T300-6K-50B fiber (oxidized fiber, sizing 5) short curing cycle;

ENS: sizing- indicate the material for which the sizing has been modified, T300-6K-40D fiber (oxidized fiber, sizing 4) long cycle of curing;

NO: Oxidized No-indicate the material for which the fiber has not undergone a treatment of oxidation, T300-6K-59A fiber (unoxidized fiber, sizing 5) long cycle of curing.

Table 1: Evaluation G_i and τ_i by various models

Material	G_i (Piggott) J/m²	G_i (Penn) J/m²	G_i(Palley) J/m²	τ_i (Medium) MPa	τ_i (B.L .T) MPa
S (Reference system)	15±5 (36%)	21±10 (47%)	54±14 (27%)	72±8 (12%)	230±25 (11%)
SR (no oxidation)	15±4 (29%)	22±9 (39%)	51±12 (24%)	70±7 (10%)	215±21 (10%)
ENS (different sizing)	15,5±9 (58%)	22±16 (74%)	77±22 (28%)	78±10 (13%)	300±40 (13%)
NO (sub-crosslinking)	11±5 (49%)	15±9 (57%)	38±16 (42%)	60±11 (18%)	190±39 (20%)

It appears from the study of this table that:

- The NO material has, in all cases, a significant dispersion due to experimental scatter related to the material structure (in all likelihood, poorer homogeneity of the surface properties of unoxidized fibers);
- The energy models of Piggott and Penn lead to highly scattered results;
- The two models that evaluate the interfacial strength τ_i, lead to reasonable scatter, which may indicate a good description of the experimental results;
- In general, the orders of magnitude of the different values of τ_i (or G_i) obtained by the different models are not comparable; this partly explains the wide range of values that can be found in the literature concerning the same types of materials, in addition to problems associated with experimental techniques and the precise definition of the materials studied.

The study of the results shows that the models of Piggott and Penn do not reflect the real dependence of F_d (debonding force) on the droplet diameter. This is understandable,

given the test configurations chosen by the authors, which are relatively remote from the conditions imposed by the other models.

The models of Palley, mean stress and Large-Toumi take this dependence into account for the various materials. These three models are thus better adapted to the description of the tests, but in the range of the droplet diameters tested. However, this analysis does not really distinguish which of the three approaches is the most adequate.

11.2 Comparison of the different results

The interfacial failure energy values obtained by the model of Palley are the same order of magnitude as the results reported in the literature on carbon fiber composites (for example, G_i = 40 J/m^2, the value obtained by Piggott (1986) in pull out tests, the configuration the best adapted to Piggott's model), suggesting that the interfaces of the materials studied by Large-Toumi have a high failure energy for a carbon/epoxy composite (glass/epoxy having interfacial energies between 50 and 150 J/m^2). These values remain well below that measured on pure resin.

The gap between the interfacial strength estimated by the Large-Toumi and mean stress models assumes a constant stress profile along the interface, which is not absolutely unrealistic, (cf. the Raman spectroscopy studies or the finite element studies in pull out tests). The Large-Toumi model calculates the maximum of the shear stress, which is necessarily greater than τ_i (average) since:

$$\frac{1}{L}\int_{-L}^{0}\tau_i(B.L.T.)(x)dx = \frac{1}{L}\int_{-L}^{0}\frac{-F\alpha}{2\pi r[ch(\alpha L)-1]}sh[\alpha(x+L)]dx = \frac{-F[ch(\alpha(x+L))]_{-L}^{0}}{2\pi rL[ch(\alpha L)-1]} \qquad \text{(Eq.45)}$$

$$\frac{1}{L}\int_{-L}^{0}\tau_i(B.L.T.)(x)dx = \frac{-F}{2\pi rL} = \tau_i(average) \qquad \text{(Eq.46)}$$

The mean stress model simply evaluates the average value of the interfacial stress at the time of debonding, whereas the Large-Toumi model proposes an a priori evaluation that is more realistic of the interfacial strength.

Table 2 summarizes the results obtained in pull out tests or in droplet tests on carbon / epoxy composites. The classification is based on the type of modeling used since we saw that this had a significant impact on the magnitude of the results. It is difficult to make a global comparison of these results, however, because from one study to another not only the test configurations but also the materials and models used change.

Table 2: Synthesis of results obtained in droplet and pull out tests of carbon fiber / epoxy resin composites based on the type of modeling used.

Type of analysis	authors	Test Configuration	Material (fiber / resin) [1]	Fiber Type [2]	τ_i (MPa)
Average stress $\tau_i = F_d/2\pi rL$	Favre, Perrin (1972)	Pull-out	Courtauld HTS/epoxy HM/epoxy	HTS HM	57 5,5
	Piggott (1985)	Pull-out	Herculès AS1/epoxy	HM	56
	Herrera-Franco, Drzal (1992)	Droplet	Herculès AU4/828 AS4/828	HT N.O. O.	23 50
	Large-Toumi	Droplet	Toray T330-59/epoxy T330-50/epoxy	HT N.O. O.	60 72
Greszczuk [3] $\tau_i = \tau'\, \alpha L/th(\alpha L)$ **With** $\tau' = F_d/(2\pi rL)$	Barbier et al. (1989)	Pull-out	Courtauld XAU/5208 XAS/5208	HTS N.O. O.	88,5 125
	Désarmot, Sanchez (1984)	Pull-out	Courtauld HT/LY556 Toray T300/LY556	HT N.O. O. HT N.E. N.O. O.	20 70 50 60
	Guigon, Klinklin (1993)	Pull-out	Toray T300 /5208	HT N.E. N.O. O	133 150
Large-Toumi	Large-Toumi	Droplet	Toray T330-59/epoxy T330-50/epoxy	HT N.O. O.	190 230

[1] The resins used are epoxy resins, designated by their commercial name when known. LY556 and MY750 come from Ciba, 828 from Shell and 5208 from Narmco.
[2] The fibers are generally oxidized and sized unless otherwise stated; N.O.: unoxidized; N.E: unsized; HT and HTS: high strength fibers; HM: high modulus fiber;
[3] The expression of parameter α varies among the authors, but it still depends on the Young's modulus of the fiber, the matrix shear modulus, the fiber radius and the matrix radius.

If we look at all the results for a given method of calculation, the T300 (Toray) fiber / epoxy resin system has a high interfacial strength, as already noted by Favre and Perrin (1972), who were unable to test this system because its adhesion was too strong (leading to tensile failure of the filament). This system has a higher strength than that obtained with HTS fibers from Courtauld (XAU XAS). The same classification can be seen in the pullout tests of Désarmot and Sanchez (or Guigon and Barbier, who both used the same modeling). Désarmot and Sanchez tested unsized T300 fibers (T300 90A), which have lower adhesion properties than the fibers used in the study by Large-Toumi; the strengths obtained with unsized fibers (60MPa) are comparable to those of the Courtauld fibers (70 MPa).

The values obtained in the study by Désarmot and Sanchez contrast with those of Guigon on the one hand and Barbier on the other. The use of a different resin cannot explain such a discrepancy (a two- or three-fold difference, sets of values), which is probably due to the modeling used. The values obtained by Guigon on unsized T300 fiber can be considered as a lower bound compared to the material characteristics studied by Large-Toumi, which is not contradicted by the latter's results.

Note: In all which precedes, the authors did not evoke the phenomenon of plasticization some resin or interface, possible phenomenon seen the constraint levels undergone, this for two reasons, Firstly, the epoxy resin used is of brittle type, which makes this phenomenon very limited; secondly, the examination of the fracture facies in MEB indicates the existence of frank fractures in the level of the droplet, For which we do not distinguish a track of resin residual on the fiber: the facies are reflect of ruptures localized with the interface, without trace of plasticization.

Let us notice all the same that the hypotheses of linear elasticity formulated in most of the calculations (analytical and numerical) are likely limitative, even in the case of an epoxy resin; indeed, although his behavior can be considered elastic, it has marked non-linearity, in particular for deformations close to the fracture strain.

11.3 Interpretations

Whatever the model chosen, the classification of the materials S, SR, ENS and NO in terms of fracture energy or interfacial strength remains identical and can be summarized by:

$$NO \leq SR \leq S < ENS \qquad\qquad (Eq.47)$$

This classification is also highlighted in **Fig.26**, which also shows the scatter. The three models used thus propose the same relative assessment for the different materials; from this point of view, the average stress analysis is quite acceptable, and enables the various fiber resin systems to be compared. It should, however, be borne in mind that the τ_i parameter (average) delivered in such an approach is not the interfacial strength of the tested system, but only the average value of the shear stress at the time of failure; this value nevertheless enables a comparative analysis of materials.
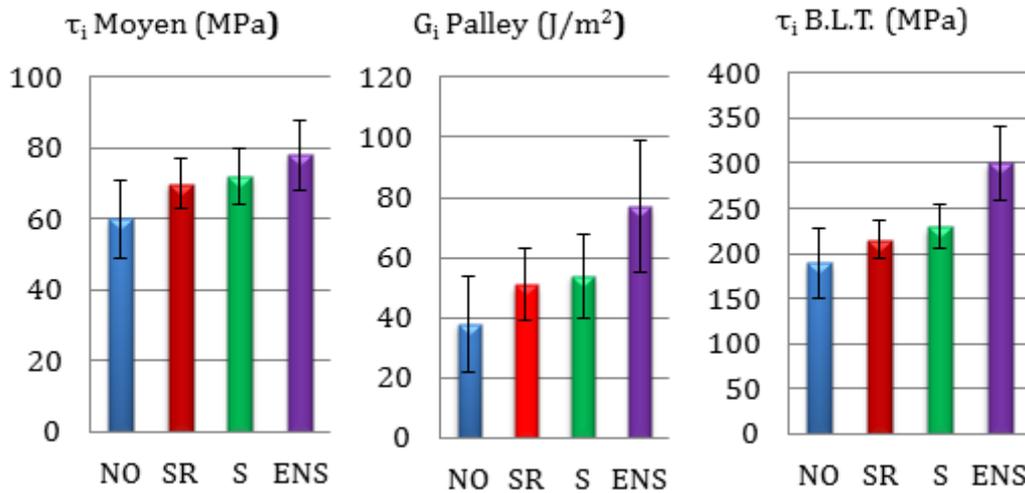
Fig.26. Value and dispersion of interfacial characteristics calculated by the models of mean stress, Palley and B.L.T.

The studies realized in the test of droplet proved that this test is a discriminating test, adapted to the characterization of the interface in carbon / epoxy systems. From a point of view material, these test there shown that:

- The industrial curing cycle used for the SR material leads to an interfacial resistance equivalent to that of a completely crosslinked material (material S);
- The epoxy-specific sizing (4) insures higher interfacial shear strength than the standard sizing (5);
- The oxidation treatment of the fibers increases the interfacial resistance and decreases the dispersions of the results (homogenization of the properties of the fibers by probable decrease in the number of surface defects).

The analysis of the different results obtained in the different studies showed that the optimal interface is not the one with the highest characteristics. Moreover, each system fiber/matrix considered has its own values of optimal interfacial properties, this one being related to the properties of the fiber and the matrix, at last, for a given system, there is not a single optimal interface; the study of each property of the composite (for example, ILSS, fatigue strength, property at rupture) can lead to the definition of an optimal interface each time.

12 Conclusion

An overview of some of the analytical models available to characterize the fiber/matrix interfacial area is proposed in this paper. Various analytical forms have been presented, but these forms differ from the boundary conditions applied and the presence of various factors that are not included in the analysis. We have seen that the complete modeling (i.e. taking into account radial effects and/or residual stresses as example) of this test is, from a mechanical point of view, a complex and as yet unresolved problem. Nevertheless, it appears that a simple approach that only evaluates an average shear stress at the interface

proves acceptable and representative of the quality of the fiber/matrix bond. We obtain thereby a good relative assessment of the interfacial properties. The pull-out (droplet) test, associated with this kind of modeling, then becomes a fairly easy to use and effective tool.

Of course, the problem of an absolute determination of the interfacial characteristics remains unsolved. Concerning the precise evaluation of the stress state during the test, Raman spectroscopy studies provide a wealth of information. The results of these tests may be considered as a reference, in particular for readjusting procedures addressed by the finite element method. Meanwhile, numerical studies (finite element or other approaches) should make it possible to investigate the influence of "loading parameters" (e.g., position and shapes of blades). These studies generally give access to very valuable information on the constraints and in particular on radial constraints, which Raman spectroscopy cannot do.

The real mastery of the pull-out (droplet) test thus necessarily involves a thorough mechanical analysis, combined with a good knowledge of the behavior of the tested material (plasticity, etc.). This is not specific to this test but highly characteristic of all micromechanical techniques, all of which tend to use simple assumptions. We now know that the stress state is a complex mixture of tensile and shear stress. In this case, what failure criterion should we choose? It appears necessary to introduce a more elaborate criterion than the criterion of a maximum stress fracture. The choice of an adapted criterion of break requires a study in oneself, both the possibilities are numerous and the fundamental problem. If a coupled criterion is considered, it can be noted that the apparent resistance in shear, evaluated by simpler models, can, depending on the state of the radial stresses, be remote enough away from its real value, in pull-out. A coupled criterion does not introduce any more one but at least two unknowns, who could be determined only by mastering at the same time the longitudinal and radial stresses, the latter depend on residual stresses of curing existing in the composite sample.

It is clear that any interpretation of the pull-out (droplet) test and of micromechanical tests in terms of absolute interfacial characteristics must take into account the effect of radial stresses. This doubtless limits the possibilities of analytical resolution and favors the use of numerical methods. Alongside this mathematical aspect, two crucial problems will then have to be addressed:

- Determination of the failure criterion;
- Knowledge of residual stresses in model composites and in real composites.

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