UNIVERSIDAD POLITÉCNICA DE MADRID

Escuela Técnica Superior de Ingenieros de Caminos,
Canales y Puertos

MICROSTRUCTURE-PROPERTIES RELATIONS FOR HIERARCHICALLY STRUCTURED CNT FIBRES

TESIS DOCTORAL

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Ingeniero Técnico Aeronáutico

Master en Ciencia e Ingeniería de Materiales

2018

Departamento de Ciencia de Materiales

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2018

"In order to improve the mind,
we ought less to learn,
than to contemplate"
René Descartes

Con todo cariño, a mis padres

Acknowledgements

First of all, I would like to express my sincere gratitude to my supervisors Juan José Vilatela and Álvaro Ridruejo. Thanks for all those evenings talking about high quality science. I have learnt a lot about you both personally and professionally. All the synchrotron experiments carried out in this work have been developed in the NCD beamline from ALBA synchrotron in Barcelona. This is why I would like to thank to all the personal staff from this center, specially, Dr. Marc Malfois, Dr. Christina S. Kamma-Lorger and Dr. Eduardo Solano. Moreover, some results of this thesis were obtained during a stay in the NanoHAC group from Imperial College of London. This is why I would like to thank Prof. Milo Shaffer and all the group for their supportive help. In this regard, I really appreciate the guide of Dr. Noelia Rubio during this time. This stay was completely funded by a Cost Action grant. Furthermore, all this research work has been funded by the Ministerio de Educación y Ciencia from the Spanish government and by means of an ERC grant through the STEM project.

I would like to thank also to all the members of the Multifunctional Nanocomposites Group for their continuous support during all this long time: 6 years since I started my Final Project Degree. I need to remark all the tremendous effort carried out in the synthesis of CNT fibres by Dr. Víctor Reguero, Dr. Belén Alemán, Dr. Laura Cabana, Dr. María Vila and Mr. Xaquín Rodiles. Furthermore, it has been very important the supportive help received by Dr. Cleis Santos and Dr. María Vila during the redaction of this thesis. In addition, the personal support of Dr. Alicia Moya, Dr. Víctor Reguero and Mr. Alfonso Monreal in the hardest moments of this thesis have been quite encouraging for me. Regarding the personal staff of IMDEA it is necessary to highlight the tremendous labour carried out by the technicians, specially remarkable has been the help received by Dr. José Sánchez during the development of in-situ mechanical measurements. Furthermore, SEM and TEM pictures that appear in this thesis have been taken by Dr. Miguel Castillo. Moreover, I express my sincere gratitude for the help received by persons which were not involved in my research group and, event

thought, they spent their time trying to solve very important problems treated in this thesis. In this regard, I would like to thank very specially to Eva Andrés and Gustavo Esteban for their help on the numerical calculations carried out in this work and Luis Carlo Herrera for their help during the development of experiments. I consider you not only my colleagues but my friends too.

En el plano personal, me gustaría expresarme en mi lengua materna para así poder reflejar con mis palabras mi más sincero agradecimiento. Primero, a mis compañeros de piso, que siempre han sabido sacarme una sonrisa cuando estaba cansado o deprimido. Especialmente a Juan Fernández, Jesus Tendero, Natalia Sánchez, y Luis de la Fuente a los que considero ya parte de mi vida. A los villacañeros, los aeronáuticos y los imdeanos, que siempre tienen tiempo para una cerveza y una buena conversación. A mi familia, por supuesto, nadie como los Toribio saben insuflarte ánimo y alegría cuando ya no te queda ganas de nada. Especialmente relevantes han sido mis padres, quienes con su duro trabajo y su bien hacer han sabido salir adelante en los momentos más difíciles. A mi padre Justo, por su templanza y saber estar en los peores momentos y a mi madre Juani, por su alegría y ánimo constantes: gracias, ojalá algún día podáis estar tan orgullosos de mi como yo lo estoy de vosotros. Por último, pero no por ello menos importante, a mi hermana Ángela; quien con su coraje, independencia e inteligencia es un referente a seguir para mí y un constante apoyo. A todos ellos: gracias por ayudarme.

Resumen

Uno de los retos más importantes dentro del mundo de los nanotubos de carbono consiste en la transferencia de sus incomparables propiedades mecánicas de la escala nano a la escala macroscópica. En este sentido, el ensamblaje de nanotubos en forma de fibra busca sacar partido del carácter anisótropo de los tubos. De esta manera, cabría esperar que dicha transferencia de propiedades sería altamente eficiente. Sin embargo, el ensamblaje de nanotubos en una estructura macroscópica da lugar a morfologías jerárquicas altamente complicadas. Así, el comportamiento final de la fibra de nanotubos es el resultado de muchas variables actuando simultáneamente a diferentes escalas. Este es el hecho que convierte la caracterización de fibras de nanotubos de carbono en un verdadero reto.

En este sentido, la investigación llevada a cabo a lo largo de esta tesis busca establecer los mecanismos físicos que se encuentran detrás del comportamiento mecánico de la fibra y, de esta manera, desarrollar un modelo propio. Con este fin, se ha establecido un paralelismo entre la fibra de nanotubos y fibras poliméricas y de carbono. Así, la fibra se asemeja a una red de madejas de nanotubos distribuidos a lo largo del eje de la fibra siguiendo una función de distribución de orientaciones. De esta manera, las propiedades mecánicas de la fibra están fuertemente influenciadas por el grado de alineamiento de esta y, por tanto, este parámetro necesita ser muy bien caracterizado mediante el uso de técnicas sofisticadas como la espectroscopía Raman o la difracción de rayos-x. De esta manera, el alineamiento inducido durante el ensayo mecánico de la fibra puede ser seguido a través de ensayos in-situ.

Finalmente, las fibras han sido fabricadas siguiendo un proceso CVD modificado. Como consecuencia, estas muestras poseen un fuerte comportamiento elastoplástico. Éste, ha sido explicado en base a un decaimiento progresivo de la resistencia al alineamiento por parte de la fibra. De acuerdo a los ensayos de difracción de rayos x llevados a cabo in-situ, este decaimiento sigue una función de distribución de Weibull. De esta manera, el alineamiento

de los tubos aparece como el elemento fundamental a la hora de explicar el comportamiento mecánico de la fibra. Así, toda la energía utilizada en estirla es directamente empleada en alinear los nanotubos dentro de ella. De acuerdo a este análisis, hemos sido capaces de estimar de manera bastante ajustada el esfuerzo máximo cortante entre los tubos de la fibra.

Abstract

One of the most exciting challenges in the field of carbon nanotubes (CNTs) is the transference of their outstanding mechanical properties to the macroscale. In this regard, one of the most successful approaches have consisted on their assembly in the shape of a fibre. Thus, their inherent anisotropic behaviour can be fully exploited. However, the arrangement of nanotubes in a macroscopic fibre leads to a complex morphology based on the existence of hierarchical levels. Therefore, the final behaviour is the result of the confluence of many variables coming from different scales. This is the reason why the characterization of CNT fibres in terms of morphological features appears as a challenging task.

In this research work we have been focused on establishing the physical mechanisms that lie behind the mechanical behaviour of CNT fibres and to develop a proper model in this regard. For this purpose, CNT fibres have been compared with polymer and carbon fibres. Accordingly, they have been idealized as an assembly of fibril-like CNT bundles oriented along the fibre's axis according to an orientation distribution function (ODF). Hence, the final mechanical properties are strongly dependent of the degree of alignment of bundles and, therefore, this parameter needs to be properly measured. For this purpose, synchrotron source x-ray scattering plus Raman spectroscopy have been used. Thus, changes on the orientation induced by tensile stretching can be monitored by means of in-situ mechanical experiments.

Finally, CNT fibres fabricated in this work have been made by a modified CVD process. These samples behave according to a strong elastoplastic behavior which has been explained in terms of a progressive decaying shear modulus. In this regard, in-situ SAXS/WAXS measurements have confirmed a Weibull type distribution function. This fact has pointed out to the alignment as the key parameter in terms of explaining the mechanical behaviour of CNT fibres. Thus, all the energy used to stretch the fibre is, in turn, used on the mechanical alignment of nanotubes along the axis. Accordingly, we have been able to estimate quite

accurately the maximum strength reached by a CNT bundle just before fail under shear.

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Chapter 1

Introduction

The production of macroscopic fibres made of carbon nanotubes (CNTs) wants to efficiently exploit their outstanding physical properties. This fact can be explained in terms of the high anisotropy of the tubes. Thus, their alignment along a certain direction promotes the transference of properties from the nano- to the macro-scale. However, the morphology revealed by CNT fibres is far of being formed by the arrangement of nanotubes perfectly aligned and closely parallel one to each other. Instead, a complex hierarchical structure is obtained. Thus, nanotubes are arranged into close packed bundles which, in turn, are disposed along an anisotropic network. Therefore, the final behaviour of the fibre results from the confluence of many variables spanning from nanotube properties to the alignment of CNT bundles. This fact becomes the characterization of physical properties in terms of morphological features in a very challenging task. In this regard, one of the most interesting topics to research about has been focused on establishing a clear structure-property relationship in terms of mechanical properties. Thus, despite some qualitative relationships have been already established in this regard, there is a clear lack of quantitative characterization methods. These are necessary in order to develop a mechanical model which compiles all the physical mechanisms that lie behind the mechanical behaviour of CNT fibres. In Chapter 2 we discuss in detail the current status in the study of mechanical properties of CNT fibres and the approaches followed in terms of modelling their mechanical properties.

In order to carry out this research work, we have produced our own CNT fibres following a CVD route. These samples have been mechanically tested and characterized through techniques such as Raman or X-ray scattering. In this regard, all the details about synthesis conditions, characterization techniques and experimental details of experiments have been

explained in Chapter 3.

It is well-known that the alignment of nanotubes play a major role on the mechanical properties of CNT fibres. Therefore, a proper measurement of this parameter is necessary. For this purpose, Chapter 4 is focused on the measurement of the orientation distribution function (ODF) of nanotubes by means of X-ray scattering and Raman spectroscopy. Thus, in order to carry out this research work, CNT fibres winded at different rates and, consequently, with different degrees of alignment have been used. Accordingly, X-ray measurements were carried out in synchrotron facilities involving both wide-angle and small-angle x-ray scattering or, shortly, WAXS and SAXS. The differences between both techniques are related with the type of scattering involved and the scale at which this takes place. However, in both cases, the anisotropy on the arrangement of the tubes leads to an anisotropic signal which is proportional to the ODF. On the other hand, Raman technique is based on the relative change on intensity using a polarized configuration. The resonant behaviour of nanotubes make of Raman a highly suitable technique. However, in contrast to SAXS or WAXS, these measurements are not direct and the degree of alignment is obtained from applying a polarized Raman theory. Thus, both techniques are compared each other in order to prove the validity of Raman for measuring the alignment of CNT fibres.

CNT fibres studied in this thesis are obtained by drawing a floating CNT aerogel from the top part of a vertical CVD furnace. It has been reported that samples made in this way show a strong elastoplastic behaviour. Thus, we can study separately the effect that elastic and plastic stretching has on the morphology of CNT fibres. Accordingly, an analytical model which relates the elastic properties of CNT fibres with their degree of alignment is presented in Chapter 5. This, in turn, is based on a classical model originally developed for polymer and carbon fibres. According to it, a fibre can be thought as the assembly of well-aligned fibril-like elements which can be axially strained or shear aligned towards the fibre's axis. As a result, the stiffness shown by a fibre is directly related with the alignment of structural elements along its axis. This has been experimentally determined by means of a statistical study of mechanical properties of CNT fibres with an ODF previously determined in Chapter 4. Moreover, this model establishes a relationship between micromechanical parameters and macroscopic properties and, therefore, it constitutes an excellent characterization method. Thus, some important conclusions regarding the arrangement of nanotubes have been obtained in this way. Finally, the effect that the elastic stretching of CNT fibres has on the

molecular level has been studied by in-situ Raman experiments.

On the other hand, Chapter 6 treats about the effect that plastic stretching has on the morphology of CNT fibres. In contrast to the previous chapter, the theory of polymer fibres has been proved to be highly inaccurate in terms of modelling the plastic deformation of CNT fibres. Therefore, in-situ SAXS/WAXS tensile tests have been carried out with the aim of monitoring the mechanical alignment of CNT fibres. As a result, the resistance of the fibres to be aligned decays progressively with the stress according to a Weibull type distribution. This fact has been directly related with the elastoplastic behaviour of CNT fibres. Indeed, in-situ Raman experiments have confirmed the same tendency. Finally, according to this Weibull analysis, we have been able to estimate pretty accurately the maximum shear strength among nanotubes. Moreover, some morphological features such as the overlap length has been firstly estimated using this method.

Concluding remarks involving the effect of the different morphological features on the final mechanical behaviour of CNT fibres is presented in Chapter 7. This section also includes the future work regarding the study of mechanical properties of CNT fibres and the experiments that need to be carried out in this regard. Finally, appendices A, B and C compile all the mathematical development that is not directly included in the thesis.

Chapter 2

Literature review

2.1 Carbon nanotubes

Since their discovery in 1991, [56] carbon nanotubes have been potential candidates to develop high performance nanomaterials. Both their excellent axial properties and their low weight have become them in exceptional nanobuilding blocks to fabricate macroscopic assemblies. However, the transference of their outstanding physical properties from nanotubes to the macroscopic scale has been shown highly inefficient. In this regard, one of the most promising challenges to maximize this transference of properties have consisted on assembling the tubes very parallel one to each other in the shape of a fibre. This way, we can take advantage of the inherent anisotropy of the tubes. This strategy is consistent with basic principles for making high-performance fibres, the properties of which depends on the alignment of extended molecules along the fibre's axis.

2.1.1 Structure

A carbon nanotube can be thought as a graphene layer rolled up into a seamless cylinder. Accordingly, the surface of the tube is made of carbon atoms each joined to three neighbours by strong sp^2 -hybridized σ bonds. However, a different structure can be obtained depending on the direction at which the graphene sheet is rolled. In this regard, a chiral vector ($\vec{C}_h$) is defined according to the schematic picture shown in Figure 2.1. Thus, based on the graphene primitive lattice vectors $\vec{a}_1$ and $\vec{a}_2$, the chiral vector is expressed as $\vec{C}_h = n \vec{a}_1 + m \vec{a}_2$ [117].

Hence, each lattice point can be expressed in terms of the coordinates (n,m) which defines the chirality of a tube. Similarly, the chirality can be also expressed as an angle (θ) defined in terms of (n,m) as:

$$\theta = \arctan\left(-\frac{\sqrt{3}m}{2n+m}\right) \quad (2.1)$$

Fig. 2.1 Illustration of a graphene sheet with unitary vector $\vec{a}_1$ and $\vec{a}_2$. The chirality of a nanotube is associated to a chiral vector $\vec{C}_h$ or the chiral angle θ which define the rolling direction of the graphene sheet. An armchair and a zig-zag configuration have been plotted over the original schematic obtained from ref [117].

In terms of the chirality there are three types of tube structures termed armchair, zig-zag and chiral. Thus, when $(n, m) = (2p, -p)$ for p an integer, the chiral angle is $\theta = 30^\circ$ and the tube is classified as armchair; however, when $(n, m) = (p, 0)$ the chiral angle is $\theta = 0^\circ$ and the tube shows a zig-zag architecture. These two configurations have been depicted in Figure 2.1. The rest of nanotubes with angles within the range $(0^\circ, 30^\circ)$ are called chiral. The diameter of the tubes (d_t) are related to the chirality by the following expression

$$d_t = \frac{a \sqrt{m^2 + mn + n^2}}{\pi} \quad (2.2)$$

where $a = 1.42 \times \sqrt{3} \text{ \AA}$ is lattice constant in graphene.

Furthermore, in terms of the number of layers we can distinguish between single-wall(SWNT) and multi-wall nanotubes (MWNT). In this regard, graphitic layers are separated each other by a minimum distance of $\sim 0.34\text{nm}$ in a crystalline arrangement of graphene sheets [87]. However, this distance increases for a turbostratic stacking of graphitic layers. Thus, the diameter of the tubes ranges from 1 to 100 nm and their length can be in the order of cm [48], giving as a result extremely high aspect ratios $10^4 \sim 10^6$. Nonetheless, this can be even much higher taking into account recent research works in which half a meter nanotubes have been synthesized [161].

2.1.2 Mechanical properties

Hence, both the strength of the C-C bonds and the honeycomb lattice provide outstanding properties to nanotubes. This is why their mechanical properties are theoretically similar to those shown by graphene sheets [147]. However, the biggest difficulty in terms of measuring tensile properties of nanotubes is the definition of an effective cross-section. Thus, despite one may argue that the thickness of a graphene sheet defines the load bearing area for a nanotube, we must take into account that tubes can be made of several layers which interact each other by means of Van der Waals forces [117]. Thus, in order to avoid this difficulty, an easier way to proceed has been by means of normalizing tensile properties with respect to the mass per unit length of the nanotube, which is equivalent to use specific properties; that is, properties divided by the material's volumetric density, usually expressed as its specific gravity (SG).

Table 2.1 shows the experimental values of specific strength and specific stiffness corresponding to different types of nanotubes and bundles. For the calculus of specific properties, the areal density of a graphene layer has been used: $(0.75 \text{ mg}/\text{m}^2)$. Here, it can be easily observed how values corresponding to a bundle of SWNT or a MWNT lie below mechanical properties of graphene. However, there is a big scattering among these values. Thus, whereas the ultralong SWNT from ref [161] reaches a tensile strength comparable to that shown by a single graphene layer, tensile properties decrease dramatically in the rest of the cases. The reason of this fact might come from the poor stress transference among nanotube layers. Thus, while they are tensile stretched, nanotubes show a significant gradient in terms of

bearing load. Indeed, the outer layer is overstressed whereas the inner layers barely bear any load. An evidence of this fact is found on the fracture surface revealed by nanotubes tensile tested. In this regard, Figure 2.2 shows a TEM picture of the fracture of a MWNT where a typical "sword-in-sheath" failure can be observed. This failure mechanism consists on the breakage of the outer layers and subsequent sliding of inner layers. Thus, on the one side of the fracture there are 18 sheets whereas only 15 of them have been counted at the other side. Therefore, calculus of tensile properties considering only the outer layers provide more reasonable values. This is the case of MWNTs from ref [101] in which the number of broken layers was determined by TEM pictures of the fracture surface. However, the rest of the cases have considered all CNT walls and, consequently, values are far below those shown by graphene. Finally, the highest strength and the highest stiffness ever measured for a nanotube is around $\sigma_b = 54.4 \text{ GPa}/SG = 120 \text{ GPa}$ [161] and $E = 300 \text{ GPa}/SG = 1105 \text{ GPa}$ [101], respectively. Both of them are very close to physical properties of a single graphene layer. Therefore, these are the reference values to consider in order to fabricate high performance CNT-based materials.

Table 2.1 Specific strength and stiffness of CNTs and graphene

	Strength (GPa/SG)	Stiffness (GPa/SG)	Comments	Ref.
DWNT bundle	0.7	47	-	[37]
SWNT bundle	5.0	170	-	[152]
MWNT	1.4	31	-	[153]
MWNT	20	300	breakage of the outermost layer	[101]
Ultralong SWNT	54.4	-	-	[161]
Graphene	56	453	-	[73]

Fig. 2.2 (left) TEM image of a sword-in-sheath fracture morphology corresponding to a MWNT. (right) Intensity profiles corresponding to the paths B and C through which we can observe the number of layers present at each side of the fracture.[101]

2.2 Challenge in forming macroscopic ensembles from individual nanotubes

Accordingly, it seems obvious that one of the main goals in the field of carbon nanotubes would consist on the transference of their outstanding mechanical properties to the macroscopic scale. This way, a light material with far superior mechanical properties than any other high performance fibre would be obtained. To fulfil this aim, the most logical approach to follow is the synthesis of ultralong CNTs. However, the length of nanotubes is very limited by the synthesis process. In this regard, the synthesis of half a meter long nanotubes carried out by Zang et al. [161] encourage us to follow this strategy. Nonetheless, so far, this is an exceptional result in the broad world of CNT synthesis and it remains discarded from the current strategies to follow.

Over the past decade, considerable attention has been directed toward the post-processing of nanotube suspensions and/or nanotube–polymer blends [121]. The exceptionally high

aspect ratio of nanotubes together with their high surface area become them in exceptional candidates to act as nanofillers. Indeed, theoretically, a fully transference of properties from nanotubes to the macroscopic CNT-composite is expected assuming a continuous network of CNTs into the polymer matrix [17]. However, experiments have demonstrated the huge inefficiency of this method. Thus, for instance, one of the best achievements in the field of polymer-nanotube composites was reported by Coleman et al [16] for a PVA-nanotube composite. As a result, tensile strength and stiffness of the nanocomposite increased from the original values $E = 1.92 \text{ GPa}$ and $\sigma = 81 \text{ MPa}$ corresponding to the polymer matrix to $E = 7.04 \text{ GPa}$ and $\sigma = 348 \text{ MPa}$ for a 0.6 vol% MWNT-PVA composite. Nonetheless, these values were obtained for nanotubes previously doped in order to increase the strength of the polymer-nanotube interface. Generally, values obtained are considerably lower. Thus, one of the first studies carried out in this field reported an increase on tensile stiffness from $E = 6 \text{ GPa}$ to $E = 12 \text{ GPa}$ for a 60 wt% MWNT-PVA composite. [123]

The inefficient behaviour of these systems can be explained in terms of their strong limitations. Thus, the tensile strength of polymer-CNT composites is strongly determined by the polymer-nanotube interface. Indeed, the introduction of highly stiff elements in a soft matrix promotes a decohesive fracture between them [17]. In this regard, Figure 2.3 a) shows a TEM picture of the crack propagation in a MWNT-PS composite. Here, it can be easily observed how both sides of the crack are bridged by nanotubes which are continuously pulled out from the polymer matrix. Furthermore, nanotubes tend to aggregate themselves driven by Van der Waals forces. This way, highly anisotropic nanofillers become in microscopic aggregates and, consequently, the aspect ratio diminishes dramatically. As an example, Figure 2.3 b) shows an optical micrograph of a 1 wt% MWNT-PC melt in which aggregates of several hundreds of microns can be observed. Due to this fact, the stress transference between the matrix and aggregated particles decreases dramatically and, therefore, mechanical properties too.

Fig. 2.3 a) In-situ TEM observation of crack propagation in MWNT-PS thin films. The MWNTs tend to align and bridge the crack wake then break and/or pull out of the matrix. [17] b) Optical micrograph of polycarbonate melt compound with 1 wt% MWNT. The aggregation of nanotubes form big agglomerates which reach values in the order of $\sim 100\mu\text{m}$. [65]

Another approach in order to fabricate macroscopic CNT-based materials have consisted on the direct production of CNT assemblies. In these materials, nanotubes act as nanobuilding blocks into a macroscopic structure. Thus, due to they are attracted by Van der Waals forces, nanotube assemblies are very limited by these relatively weak interactions. This fact points to some similarities between macroscopic assemblies and polymer nanotube composites. Indeed, we can thought on CNT assemblies as a kind of composite in which the role of the matrix in terms of stress transference is played by electrostatic interactions among tubes. However, in these assemblies we have a more direct control over the arrangement of nanotubes. Thus, we can vary the orientation and the configuration of them in order to obtain CNT arrays (3D), CNT films (2D) or CNT fibres (1D). Among these configurations, it seems obvious that the assembly of nanotubes in the shape of a fibre takes advantage of the inherent anisotropy of the tubes and, therefore, it provides a much better mechanical behaviour. However, we must not think on these macroscopic assemblies as the perfect arrangement of nanotubes perfectly parallel one to each other. Instead, they show a much more complex morphology and, as a result, the transference of properties from individual nanotubes is negatively affected. In this regard, the main goal of this thesis consists on guessing the physical mechanisms which lie behind the mechanical behaviour of CNT fibres

and, therefore, establish clear structure-property relationships.

2.3 Characterization of Carbon Nanotube fibres in terms of the fabrication method

In order to assemble nanotubes in the shape of a macroscopic fibre, three main approaches have been followed:

- The **wet-spinning process** consists on winding CNTs which have been previously dispersed in a solution. Thus, Figure 2.4 a) shows a schematic of the process followed to this aim. According to it, nanotubes are previously dispersed by means of using superacids [26] or ethylene-glycol [162]. Then, this solution is injected into a coagulation bath and continuously spun as a CNT fibre [33]. The structure of the fibre obtained is reminiscent of the crystalline arrangement of nanotubes in the liquid phase. Thus, nanotubes are highly oriented and densely packed into the fibre such as it can be easily observed by SEM pictures in Figure 2.4 a). On the other hand, this method needs of highly purified nanotubes in order to disperse them in the liquid state [129]. Moreover, the use of superacids usually leads to shorten the tubes.

An alternative approach of this method consists on substituting the coagulation bath by a polymer solution, giving as a result a CNT/polymer fibre [23, 22, 132]. This last case; however, does not provide a pure CNT fibre but a composite. The polymer can be removed afterwards by means of a thermal treatment but a highly brittle material is obtained as a result [132].

- **Spinning from CNT forests.** Macroscopic fibres can be obtained by means of drawing nanotubes from a CNT forest. Due to Van der Waals forces among them, the tubes remain joined during the drawing process [160]. This step is usually followed by an induced twisting which improves the interaction among nanotubes and deliver a more dense material. This procedure can be easily observed in the picture from Figure 2.4 b) where it appears both the method of drawing from a CNT array and a SEM picture of the dense fibre obtained. Therefore, the properties and the morphology of these materials depend on both the types of the tubes forming the CNT forest and the degree

of twisting induced afterwards.

- The **direct spinning process** is a continuous fabrication method which involves both the synthesis and the alignment of CNT fibres. Thus, a CNT aerogel is formed by a CVD reaction at the top zone of a vertical furnace from which it can be mechanically drawn and rolled onto a rotating spool such as Figure 2.4 c) depicts schematically. The chemical reaction carried out is based on the decomposition of carbon sources at a extremely high temperature (1250°C). Thus, in an atmosphere highly saturated by carbon, CNTs grow in the presence of both a reducing hydrogen atmosphere and iron catalyst particles [77]. The action of Van der Waals forces lead nanotubes to form an aerogel able to be drawn. This step is usually followed by a densification process which consists on bringing in contact the fibre with liquid. Thus, by capillary forces, a significant reduction in density and cross-section is produced. This fact can be explained in terms of the huge porosity revealed by the fibre. Indeed, values of specific surface area as high as $260 \text{ m}^2/\text{g}$ have been measured for this type of samples [155]. This is shown in Figure 2.4 c) where the presence of impurities onto the graphitic surface can be also noticed. The origin of these impurities can be found on the synthesis process and the use of iron based catalyst particles [111].

Moreover, in spite of being a continuous process, the synthesis and the alignment steps are physically separated each other. In this regard, it has been demonstrated that the morphology of nanotubes are basically tuned by the chemical CVD reaction taking place at the top of the furnace [111]. On the other hand, the degree of alignment of nanotubes along the fibre's axis varies with the winding rate [3]. Finally, Km of fibre per day can be produced by means of this manufacturing technique [111]. This fact becomes this method in the most suitable one in order to fabricate CNT fibres at an industrial level.

Fig. 2.4 a) Schematic of the wet-spinning process for spinning CNT fibres [162] and a view of both lateral and cross-section of a solution spun fibre [49] b) Spinning from a CNT array and a SEM image of an as-spun fibre [41] c) Schematic illustration of the direct spinning process and a SEM picture of the porous structure revealed by the fibre [135]

Table 2.2 compiles relevant mechanical properties of CNT fibres according to the literature. Here, all the entries have been classified in terms of the fabrication method used in each case. Moreover, some important features regarding nanotube characteristics or the gauge length of the sample tested have been also reported. Thus, the first thing to remark from the table corresponds to both the highest strength and stiffness ever reached by a CNT fibre. It was measured for a 1mm length fibre fabricated by the direct spinning method. Due to the fact that the length of the tubes resulted from this process rounds the mm length, it seems obvious that this strongly improved behaviour was due to some nanotubes were directly stretched. However, the values here reported are far below those measured for an individual CNT $\sigma_b = 120 \text{ GPa}$ and $E = 1105 \text{ GPa}$. This fact reveals that another morphological features

regarding the assembly of nanotubes weakens the fibre. This study also shows the dramatic decrease of mechanical properties when a standard 20 mm fibre was tested instead. Furthermore, mechanical properties of fibres fabricated by the direct spinning method have been shown very sensitive to changes on the alignment. Thus, Aleman et al [3] have reported a significant increase on both tensile strength and stiffness by means of varying the winding rate. This was explained as an increase on the alignment of nanotubes, such as it was confirmed by x-ray measurements. Moreover, as it has just been said, the versatility of this method enables the change of the type of tubes by means of modifying the chemical reaction into the tubular furnace. In this regard, mechanical properties improve in the case of aligned SWNT-fibres respect to fibres mainly made of FWNTs. However, despite this improvement was significant regarding the modulus of aligned samples $E_{\text{SWNT}} = 67 \text{ GPa}$ and $E_{\text{FWNT}} = 50 \text{ GPa}$, there was no such improvement in the tensile strength $\sigma_{b\text{SWNT}} = \sigma_{b\text{FWNT}} = 1.5 \text{ GPa}$. Indeed, this fact constitutes a simple example about the problem of guessing how much contribute each morphological feature to the final properties of the fibre.

On the other hand, the wet-spinning method always deliver a fibre extremely aligned. However, depending on the solvent used to disperse the tubes, the length of nanotubes are significantly shortened or not. In this regard, the sulphuric acid has been proven to shorten the tubes until reaching submicrometrical lengths [6]. As a result, extremely low strengths have been reached $\sigma_b = 0.2 \text{ GPa}$. However, the stiffness shown by these fibres is considerably high $E = 120 \text{ GPa}$. In this regard, it has been proved that the use of chlorosulfonic acid does not disturb the geometry of the tubes which remains unaffected along the process [7]. This way, fibres obtained in this way reach considerably higher values of strength $\sigma_b = 1.3 - 2.4 \text{ GPa}$ but the modulus remains in the same order of those fibre spun from a sulphuric acid-CNT solution $E = 150 - 207 \text{ GPa}$. This fact reveals both the main role of alignment in terms of making stiff fibres and the huge effect that the nanotubes length has on the tensile strength.

Finally, comparing fibres obtained from arrays of nanotubes, we have been able to observe a clear dependence of mechanical properties with the type of tubes. In general terms, it has been shown that mechanical properties are improved by means of drawing longer nanotubes. Moreover, for 1 mm long tubes, the strength and stiffness of a DWNT fibre are significantly improved respect to a MWNT fibre. Thus, whereas a MWNT fibre shows strengths and stiffnesses in the range of $0.2 - 0.5 \text{ GPa}$ and $6 - 38 \text{ GPa}$ [163], respectively, a DWNT fibre shows values in the range $1.35 - 3.3 \text{ GPa}$ and $100 - 263 \text{ GPa}$ [165]. This fact points to long

few-wall CNTs as the best candidates in order to make both stronger and stiffer CNT fibres by this method. Therefore, a direct relationship between mechanical properties and nanotubes' aspect ratio should be expected. However, this relationship is not completely fulfilled for all MWNT fibres. This may be explained as a different twisting effect in each CNT fibre.

Table 2.2 Compilation of strength and stiffness values of CNT fibres in terms of the fabrication process used. All the entries have been classified in terms of nanotube characteristics such as the type of the tube, length, diameter and, consequently, aspect ratio (length/diameter). In all the cases it also appears the gauge length used plus comments about some relevant parameters of the morphology of the fibre. * Original values were expressed with specific units (GPa/SG) and they have been multiplied by the theoretical specific gravity of a bundle: 1.8. ^c estimated in ref [6]

	CNT characteristics				Comments	Mechanical Properties		Gauge length (mm)	Ref.
	type	Length (μm)	Diameter (nm)	Aspect ratio (L/d)		Modulus (E) (GPa)	Strength (σ_b) (GPa)		
DIRECT SPINNING METHOD	DWNT	-	5-10	-	collapsed structure low-winding rate	117*	2.2*	-	[89]
					collapsed structure extreme-winding rate	288*	4*		
	DWNT	1000	4-10	$1.50 \cdot 10^5$	long yarn	90*	1.8*	20	[71]
					short yarn	630*	16*	1	
	SWNT	1000	-	-	unaligned filament	28*	0.3*	20	[3]
					aligned filament	67*	1.5*		
	FWNT	1000	-	-	unaligned filament	10*	0.5*	20	[3]
					aligned filament	50*	1.5*		
	SWNT	-	-	-	-	30*	1.46*	-	[88]
	MWNT					10*	0.28*		
WET SPINNING METHOD	SWNT	0.5	$\sim 1^c$	~ 500	Sulfuric acid dispersion coagulated in water	120	0.116	-	[33]
	DWNT	~ 5	2-6	1250	Chlorosulfonic acid dispersion	150	1.3	20	[7]
	DWNT	-	-	4400	coagulated in water	207	2.4	20	[129]
SPINNING FROM CNT FORESTS	MWNT	100	10	10^4	twisted	5-30	0.15-0.46	10	[160]
	MWNT	2000	40	$5.0 \cdot 10^4$	twisted	51.1	0.77	10	[41]
	MWNT	1000	10	$1.0 \cdot 10^4$	twisted	6-38	0.2-0.5	10	[163]
	DWNT	1000	7	$1.50 \cdot 10^5$	twisted	100-263	1.35-3.3	10	[165]

Table 2.2 characterizes manufacturing methods in terms of important mechanical features such as the strength and the stiffness of CNT fibres. Nonetheless, Figure 2.5 shows the tensile curve shown by characteristic CNT fibres fabricated according to the manufacturing techniques described above. Here, it can be easily observed that a solution-spun fibre is stretched almost linearly until failure. The case here plotted corresponds to a sample made from a chlorosulfonic acid solution and, consequently, a high strength has been reached. In this regard, data corresponding to a fibre made from a CNT-sulphuric acid solution has not

been found in the literature. However, it is expected that the stress would increase following the same trend but breaking at $\sigma_b = 0.18 \text{ GPa/SG}$ [33]. Regarding the fibre spun from a CNT forest, two curves appear representing the behaviour of the fibre just as-spun and after being twisted. Accordingly, the twisted fibre is slightly more linear than the fibre just spun. However, although a significant improvement of mechanical properties is produced by twisting, this is counterbalanced by an increase of density. Thus, due to all the curves have been plotted in specific terms, twisted and untwisted fibres reach a similar strength. Finally, a home-made fibre fabricated by the direct spinning method has been plotted. It seems obvious the huge difference existent with the rest of fibres in terms of plastic stretching. Indeed, this fibre is strained 4 times more than the rest of the samples. Moreover, it shows both a high stress and stiffness which are in the range of those shown by the wet-spun fibre. Nonetheless, a huge energy is plastically dissipated during this process. In this regard, it seems obvious the huge potential of this manufacturing method in order to fabricate high-performance fibres. Structure-property relationships of CNT fibres made by this method is the main subject of this thesis.

Fig. 2.5 Comparison of mechanical properties of CNT fibres fabricated by different manufacturing processes: a solution spun fibre [49], a fibre just spun from a CNT forest and after being twisted [41] and a home-made fibre fabricated by the direct spinning method.

2.4 The hierarchical structure of CNT fibres and its role on the mechanical behaviour

As it has just been reported, fabrication methods determine the mechanical behaviour of CNT fibres. This can be explained in terms of the fact that each technique provides a different way in which nanotubes are aggregated. Thus, a clear structure-property relationship is elucidated. However, the morphology resulted of assembling nanotubes in a macroscopic material is quite complex and, therefore, the study of physical properties in terms of specific morphological features appears quite complicated. Instead, many variables play a certain role on the physical behaviour of CNT fibres and the main challenge consists on guessing how much contribute each one.

Indeed, CNT fibres show a hierarchical structure. The term hierarchical makes reference to the relationship between structural features in the fibre spanning from the nano- to the macroscopic scale. Thus, Figure 2.6 depicts schematically the hierarchical levels shown by a CNT fibre: nanotube-, bundle- and network-level. Obviously, individual nanotubes constitute the basic building elements into the fibre. However, these do not appear as single elements but closely arranged forming CNT bundles. Scaling up, bundles appear entangled in a highly anisotropic network which constitutes the macroscopic fibre.

Fig. 2.6 Scheme of the hierarchical structure of a CNT fibre in which the three hierarchical levels shown (network, bundle and nanotube) are clearly depicted and distinguished by using also SEM and TEM pictures.

Therefore, the mechanical behaviour of CNT fibres is expected to be determined by the confluence of many parameters from different hierarchical levels. Identifying such parameters and determining their contribution to bulk properties either experimentally or by modelling of CNT fibres has been a challenging task in the field studies. Previous work, largely through optimisation of fibre tensile properties has established some basic relations between structure and tensile properties. Thus:

- **CNT-aspect ratio**

At nanotube scale, Tsentalovich et al.[129] have recently demonstrated that the aspect ratio (length/diameter) of nanotubes and the tensile strength of the corresponding CNT fibre are directly related. For this purpose, CNT fibres based on high purity nanotubes were synthesized by the wet-spinning method. As a result, highly aligned CNT fibres with a Herman's orientation parameter of $\langle P_2(\cos\beta) \rangle = 0.966$ were obtained. Due

to this fact, the single parameter to be changed was related to the length and number of layers of the tubes. Accordingly, Figure 2.7 a) shows the fitted relationship established between tensile strength and CNT aspect ratio. For this study, CNT samples provided by seven different supplier were used. However, no significant effect of polydispersity can be observed in the graph. Instead, tensile strength increases quite accurately following a straight line with a slope of 0.9 regardless of even the type of the tubes: single-wall (SWNT) or double-wall (DWNT) nanotubes. This fact goes closely in agreement with a friction dominated failure which establishes that tensile strength and aspect ratio are related by a power law of 1 [6, 146]. This fact is graphically depicted in Figure 2.7 b) where it appears the theoretical dependence of the fibre strength normalized by the individual nanotube strength with the aspect ratio. According to this model, three main forces are involved on maintaining a bundle integrity: intrinsic nanotube strength, capillary forces (energy necessary to create a new surface) and internanotube friction. Depending on the aspect ratio, Figure 2.7 b) clearly identifies the regions at which failure is dominated by each one of these three forces. Thus, at low aspect ratios, failure is dominated by capillary forces and at the intermediate region this is due to friction among nanotubes. Therefore, for fibres perfectly aligned, tensile strength increases with CNT-aspect ratio according to a power law relationship.

Fig. 2.7 a) CNT fibre tensile strength versus aspect ratio for fibres made from SWNTs and DWNTs from different manufacturers[129] b) Tensile strength of a perfectly aligned bundle of CNTs as a function of aspect ratio. Three regions can be distinguished. The first is dominated by capillary forces and is independent of aspect ratio. The intermediate region is dominated by internanotube friction and tensile strength is linearly proportional to CNT aspect ratio (slope of 1 in a log–log plot). In the final region (at higher aspect ratios), bundle tensile strength coincides with the strength of a single CNT. [6]

Thus, it is well-known that longer nanotubes means fewer tube-ends per unit length, which are regarded as defects [165]. On the other hand, regarding CNT diameter, few-walled CNTs with large diameters lead to fibres with higher tensile properties [88, 58]. The explanation to this fact can be found on the lower energy necessary to flatten or even collapse nanotubes with fewer walls and large diameters which, increases the contact area and, therefore, the intertube load transfer [134]. Figure 2.8 shows a TEM picture of a bundle made of few-wall nanotubes collapsed which resemble more to graphene layers stacked [89]. This highly collapsed structure may explain that single-wall and few-wall nanotubes follow the same trend line in Figure 2.7 a).

Fig. 2.8 TEM image of a bundle revealing the collapsed structure of DWNTs in the fibre.[89]

- **Shear strength**

Due to the friction dominated failure, the shear strength between CNT walls is an important parameter to be characterized. Thus, Table 2.3 shows the reported values of shear strength either measured or calculated by frictional sliding of CNTs, graphite or CNTs on graphite. This comparison wants to offer an overall perspective about the frictional behaviour shown by nanotubes comparing to graphite. It is well-known that graphite can be easily exfoliated and, therefore, one may expect that nanotubes would behave in a similar way. However, values reported in the table reflect enormous differences between the shear strength shown by a graphite crystal and nanotubes sliding each other. There is an open debate about the origin of this disagreement. Some

authors claim that the most of the friction between nanotubes comes from the effect of the ends of the tubes and the presence of defects [99]. On the other hand, calculations made using molecular dynamics have found much higher values for shear strength between nanotubes than those measured for graphite [75, 38, 164, 107, 19]. However, these studies always assume a perfect crystalline arrangement of nanotubes whereas the turbostratic assembly of them implies almost no energy to slide one on each other [119].

Firstly, we must distinguish between static and dynamic friction. Some authors have calculated the friction between nanotubes during sliding which, by definition, is a dynamic friction [154, 66]. These values are much lower than those corresponding to the static friction which is the real cause of failure of CNT bundles. Accordingly, values of shear strength are in the range of 0.9-69 MPa. It has been shown that the shear strength is very dependent of the chirality. In this regard, Wei et al.[144] reports 30 MPa for an armchair configuration and the double for a zig-zag tube. Moreover, collapsed nanotubes need 8 times higher strength to be pulled out from a bundle [164]. To this variability it must be added that associated to the experiment itself. In this regard, it has been demonstrated that the value of shear strength varies with the contact length [125, 144, 138]. Thus, some authors have been successfully used the shear-lag model to calculate the stress [144, 38] . Nonetheless, others have simply divided the force by the area. This fact makes clear that the measurement of the shear strength must be standardized in order to compare values. Nevertheless, the range of 0.9-69 MPa, despite it is quite wide, is pretty far below the tensile strength of 120 GPa of individual nanotubes [161]. Therefore, the sliding between nanotubes is a strong limiting factor regarding the mechanical behaviour of CNT fibres.

Table 2.3 Shear strengths of graphite and CNTs

Material	Experiment	Shear stress (MPa)	Observations	Ref.
single crystal graphite	mechanical shear	0.029	static friction	[124]
MWNT on graphite	tube rolling and sliding	2	static friction	[34]
MWNTs	Intertube sliding	0.08	dynamic friction	[154]
MWNTs	Intertube sliding	0.04	dynamic friction	[66]
MWNTs	Intertube sliding	2.0-69.0	static friction	[125]
MWNTs	Intertube sliding	30.0-60.0	static friction (shear-lag)	[144]
SWNTs and MWNTs	Intertube sliding	4	indirect measurement by AFM	[10]
bundle of SWNTs	molecular dynamics	37	static friction	[19]
bundle of SWNTs	molecular dynamics	0.9	static friction	[107]
bundle of SWNTs	molecular dynamics	6.1-49	static friction	[164]
bundle of SWNTs	molecular dynamics	0.9	static friction (shear-lag)	[38]
SWNTs	molecular dynamics	5-35	static friction	[75]

• Bundle aggregation

Mechanically speaking, CNT bundles are strongly limited by relatively weak shear interactions among nanotubes. In fact, they behave similarly to MWNTs and their layers. Indeed, they fail according to a sword-in-sheath failure mechanism since nanotubes slide one to each other under tension [37]. These similarities reveal the inefficient load sharing among CNTs into a bundle. An strategy to overcome this non-collaborative action of all nanotube walls has consisted on cross-linking them. Thus, Filleter et al. [37] have reported an increase of mechanical properties for DWNT bundles exposed to a TEM electron beam. This can be explained in terms of the fact that electronic irradiation leads to the formation of some defects which, in turn, results in covalent bonding between adjacent CNT walls [127]. This cross-linking phenomena leads to a more collaborative behaviour among graphitic sheets into CNT bundles and, consequently, a better mechanical performance. An evidence of this behaviour can be easily observed in Figure 2.9 where it appears both the "sword-in-sheath" fracture revealed by a lightly irradiated DWNT bundle (Figure 2.9 a)) and the completely fractured surface of a highly irradiated DWNT bundle (Figure 2.9 b)). However, it can

be also observed that a highly dose leads to a significant loss of crystallinity. Indeed, mechanical improvement shows a maximum in terms of the radiation dose [101]. However, the same cross-linking strategy has been shown quite inefficient for CNT fibres. This has been done following different routes such as the electronic radiation and the functionalization with ozone [85, 55]. However, no significant change on the tensile strength has been measured.

Fig. 2.9 Breakage of a DWNT bundle tensile tested by in-situ TEM lightly (a) and a highly b) crossly linked. [37]

• Density

Twisting has been proved to have a positive effect on the mechanical properties of CNT fibres drawn from CNT arrays. The reason of the enhancement has been surely attributed to the higher density of twisted yarns. Thus, the distance between CNTs is smaller and, consequently, Van der Waals interaction enhances significantly [41]. Nonetheless, this improvement has not been measured for CNT fibres manufactured by the direct spinning process. For these fibres, the imperfect packing of bundles reveal a huge porosity and values of surface area as high as $260 \text{ m}^2/\text{g}$ [155]. Therefore, one may think that a better mechanical performance can be achieved by densifying this highly porous structure. For this purpose, CNT yarns are brought in contact with a drop of liquid and pore sizes are significantly reduced due to capillary forces. As a result, an increase on density by ~ 120 has been estimated [3]. However, Aleman et al. [3] have reported that densification does not provide a closer arrangement of nanotubes. Moreover, minor differences in the mechanical behaviour shown before and after densification were observed. Hence, it seems that the relevant points of inter-

action from the network are previously fixed during the synthesis; that is, in the aerogel.

- **Orientation**

On the other hand, fibres have been shown really sensitive to the effect of alignment which leads them to increase both stiffness and strength [3]. However, not in the same extent, due to strength is more dependent of variables at nanotube scale while orientation plays the main role when it treats of stiffness [7]. In this regard, it has been proved that the Young's modulus does not show any relationship with the aspect ratio as tensile strength does [6, 134]. In fact, one of the higher modulus ever reported for a CNT fibre ($E = 120 \text{ GPa}$) was obtained for a solution-spun fibre with extremely short tubes [33]. The reason of this fact was found on the shortening effect that the sulphuric acid has on the tubes [6]. In contrast, short tubes are superaligned in this structure such as confirms both SEM images and X-ray results. This evidence has been confirmed with latter solution-spun fibres made with chlorosulfonic acid instead of sulphuric acid. This solvent has been proven not to shorten the tubes [7, 129]. Thus, the results reveal that the stiffness remain in the same order whereas the strength increases considerably (Table 2.2). This fact reveals the main role of orientation on the Young's modulus of CNT fibres. Therefore, a deep study involving the measurement and quantification of orientation needs to be carried out.

2.5 Strategies for modelling mechanical properties of CNT fibres

In order to fully describe the mechanical behaviour of CNT fibres, several mechanical models have been developed in the last decade. However, the number of publications in this regard do not reach by far the extensive literature available about the characterization of CNT-based materials. The reason of this may be found on the multiple variables which affect to the overall mechanical behaviour of a CNT fibre. In this regard, we have already summarized the effect that the different hierarchical levels have on the mechanical properties of CNT fibres. Due to this fact, it results quite difficult to extract qualitative structure-property relations because that implies decoupling various interlinked features, such as CNT orientation, composition, length and association in crystals.

Nonetheless, Vilatela et al. [134] proposed a simple analytical model based on the yarn-like properties of CNT fibres. According to it, the axial strength of CNT fibres can be calculated in terms of the fundamental mechanical properties of the constituent CNTs. This model consists on assuming that the fibre is built by rigid rods assembled perfectly parallel one to each other. Thus, the failure is reached at a critical shear stress because fibrous elements slide out each other. A graphical schematic of the model can be observed in Figure 2.10. Thus, this model for yarn failure reflects the fibrillar nature of the fracture [135]. Accordingly, the tensile strength depends on the contact length between nanotubes, the shear strength among them and the contact area, leading to an expression such as follows

$$\sigma = \frac{1}{6} \Omega_1 \Omega_2 \tau_f L \quad (2.3)$$

where σ is the specific stress in N/tex (GPa/SG); Ω_1 is the fraction of the total number of graphene layers on the outside of the fibrous element; Ω_2 is the fraction of the surface of the outer graphene wall(s) of the element in contact with neighboring elements; τ_f is the interfacial shear strength; L is the mean length of the fibrous elements and the numerical prefactor of $1/6$ has the units of m^2/Kg . The predicted strength given by the model, when it is parameterized in terms of the individual nanotubes being the basic fibrous elements, is 3.5 N/tex , which is comparable to a CNT bundle intrinsic strength of 5 N/tex [71].

Fig. 2.10 Simple model of the fibre as a collection of fibrous elements [134]

In spite of its simplicity, this model allows to capture some important features regarding the morphology of CNTs. Thus, by means of $\Omega_1 \Omega_2$ we are able to quantify the effect that polygonization or collapsing of nanotube walls have in terms of contact area. Moreover, the contact length effect is also involved in this expression. This fact agrees with the positive

effect that the aspect ratio has on the tensile strength of CNT fibres. Thus, few-wall nanotubes with high diameters can be easily collapsed and, therefore, deliver a high tensile strength according to equation 2.3.

In a similar way, Wei et al.[143] developed a model which can be considered an improved version of the previous one. Similarly, the yarn is modelled as an assembly of rigid rods representing CNT bundles. However, in this case, the hierarchical structure of CNT fibres is considered. Thus, Figure 2.11 shows that the macroscopic yarn is formed by the assembly of rigid CNT bundles which, in turn, are made of 1-D elements arranged closely parallel one to each other, such as nanotubes into a bundle. Thus, equipped with a Weibull distribution to take into account the probability of tensile fracture of CNT bundles, a Monte Carlo based model has been developed. Accordingly, when a bundle reaches the predicted strength, it directly breaks and the load is redistributed among remaining bundles. Finally, upper bounds on CNT yarn mechanical properties fits with experimental values.

Fig. 2.11 Schematics of the hierarchical structure used to predict mechanical properties of CNT fibres by means of a Monte Carlo model. [143]

It seems obvious that among the main limitations of the models are that they do not take into account the orientation of nanotubes. Instead, CNT bundles are arranged perfectly parallel one to each other and, therefore, they are only focused on the shear interaction between fibrous elements. However, it has been reported that the alignment of nanotubes play an important role on real fibres. Therefore, it seems obvious that there is a strong need in terms of developing a new mechanical model able to involve the effect of alignment into it.

2.6 Relationship between structure and mechanical properties in high-performance fibres and their similarities with CNT fibres

As it has been compiled by previous mechanical models, the arrangement of stiff nanotubes by relatively weak electrostatic forces makes of the interface the weakest element to fail under tension. This fact is confirmed by the fibrillar fracture of CNT fibres which, as it can be easily observed in the SEM picture from Figure 2.12 a), reveals the progressive decohesion of CNT bundles. This mode of fracture dominated by the interface is very well-known in high performance fibres. Indeed, SEM image from Figure 2.12 b) shows the fibrillar fracture of a Kevlar fibre under tension. In this regard, the similarities between CNT fibres and high performance fibres are far beyond the fracture mechanism. Thus, carbon nanotubes in many ways resemble a rigid conjugated polymer. Indeed, both nanotubes and polymers are macromolecules consisting of long chains of a repeating molecular unit. In addition, in both cases high aspect ratios and long persistence lengths are expected. Regarding the aspect ratio, there is no doubt about the strongly 1D shape of nanotubes since their length is $\sim 10^4$ or $\sim 10^6$ times higher than their diameter. Fluorescence visualization of individual SWNTs in aqueous suspensions revealed that the persistence length of SWNTs ranges from 32 to 174 μm [32, 31], even higher than theoretical estimates of $\sim 26 \mu\text{m}$ based on in-plane rigidity [72]. Comparing to rigid polymer chains such as PPTA (Kevlar) (30 nm) or PBO (60-120 nm) [44], the persistence length of individual nanotubes is extremely long. Therefore, one may expect that the arrangement of CNTs would resemble the structure of polymer chains into the fibre

Fig. 2.12 Fibrillar fracture of a) CNT-yarn[135] and b) kevlar fibre [120]

Indeed, Figure 2.13 shows a comparative picture between the structure of polymer (Figure 2.13 a)) and CNT fibres (Figure 2.13 b)). According to it, polymer chains tend to align themselves towards the fibre's axis. However, due to their finite length, they can not be perfectly stacked one parallel to each other. Instead, the structure reveals some voids and a certain misalignment. This schematic agrees with the illustrative model about the morphology of a CNT fibre (Figure 2.13 b). According to it, the structure of a CNT fibre can be thought as the assembly of long fibril-like bundles along the fibre's axis.

Fig. 2.13 a) A single-phase structural model for a polymer fibre [94] b) Schematic illustration of the morphology revealed by CNT fibres due to the imperfect packing of long CNT bundles (courtesy of B. Mas)

All these similarities seem to point out to a certain parallelism in terms of structure-property relationships. Thus, the role of alignment has been shown quite important regarding mechanical properties of CNT fibres. However, current models do not compile the effect of orientation. In contrast, this relationship is very well-known in the field of high performance fibres. In fact, it is strongly reported that, for fibres below the glass transition temperature, the chain alignment is the dominant structural parameter [95, 97, 141]. In this regard, Figure 2.14 a) shows how varies the tensile behaviour of PET fibres with the draw ratio. Here, it is clearly observed how the material becomes stronger and stiffer as the draw ratio increases. This fact has been associated to a higher alignment of the polymer chains and, therefore, a better use of their superior axial properties. This dependence of mechanical properties with alignment has been also reported for CNT fibres. Thus, Figure 2.14 b) shows the results of a research work developed for our group in which the stress-strain curves of several CNT fibres have been plotted. These samples were winded at different rates and made of different types of nanotubes. Here, the same hardening effect with the orientation previously reported for polymer yarns has been observed. The degree of alignment was measured by x-ray scattering techniques.

Fig. 2.14 a) Stress-strain curves of PET fibres obtained at different draw ratios [96] b) Stress-strain curves for highly and poorly oriented CNT fibers made of SWCNTs or MWCNTs [3]

Northolt et al. [94] developed a mechanical model which relates the tensile properties of high performance fibres with their alignment. According to it, fibres are thought as the arrangement of crystalline domains oriented an angle Θ with the fibre's axis. These domains act as structural bodies which can be strained along the fibre's axis by means of both tensile stretching and rotation. This is graphically explained in Figure 2.15 a) where it can be observed the contribution of both extensions to the axial strain. According to it, elements are stretched along the chain segment and, as a result, they pass of an initial length "a" to a new strained length "b". In addition, the element is aligned by shear rotation towards the fibre axis which leads to a lower angle θ and, consequently, to an axial length "c". Thus, the mechanical behaviour of these crystalline domains is completely characterized by their tensile stiffness (e_c) and shear modulus (g). However, these domains show different geometries depending on the way in which their constituents are arranged. Thus, for rigid rod polymer fibres, Figure 2.15 b) shows a schematic of the morphology shown in this case. Accordingly, rigid polymer chains are arranged closely parallel one to each other forming long cylindrical microfibrils. On the other hand, carbon fibres constitute an special case in the field of high-performance fibres. Thus, in contrast to polymer fibres which are based on long polymer chains, the morphology of a carbon fibre is characterized by the arrangement of graphene layers preferentially oriented along the fibre axis, such as Figure 2.15 c) schematically depicts. Therefore, elements proper from a CF are basically 2D crystals because they consists on graphene layers stacked whereas those obtained by the arrangement of polymer chains have a 1D shape. This fact has a strong influence regarding the interaction among constituents. Thus, polymer chains interact point by point by electrostatic interactions

along all the microfibril length whereas surface interactions take place among graphitic layers in a 2D crystal. Therefore, mechanical parameters are defined along the axis direction for rigid rod polymer fibres and, on the other hand, these are defined from the c-axis stacking direction for carbon fibres which, by definition, is normal to the axis.

Fig. 2.15 a) Schematic illustration of a deformed rectangular domain; in the lower part of the picture, the two contributions to the fibre strain are depicted. The projection length of the undeformed chain segment is equal to "a", the projection length of the elongated segment is equal to "b", and the projection length of the elongated and rotated segment is equal to "c". [94] b) Structural model of a PBO fibre [68] c) Structural model of the internal structure of a carbon fibre. [9]

Finally, according to the uniform stress model (USM), a series arrangement of identical crystalline domains are subjected to the same stress of the fibre [94]. Therefore, the stiffness or Young's modulus of the fibre is related to the degree of alignment of these crystalline domains and the mechanical parameter e_c and g from single crystalline domains. Thus, in the case of polymer fibres, the compliance ($1/E_f$) of polymer fibres is defined as follows

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle \sin^2 \phi \rangle_E}{2g} \quad (2.4)$$

where $\langle \sin^2 \phi \rangle_E$ is an orientation parameter function defined from the fibre's axis [94]. This model have been successfully applied to rigid rod polymer fibres such as Kevlar [97] or PBO [67]. The graph shown in Figure 2.16 a) reveals the accurate fitting to this relationship of experimental data obtained for a a PBO fibre. On the other hand, the USM for carbon fibres is expressed as follows

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle \cos^2 \varphi \rangle}{g} \quad (2.5)$$

where $\langle \cos^2 \varphi \rangle$ is defined using the stacking c-axis direction as a reference and, therefore, considering the angle φ which is complementary to ϕ ; that is, $\varphi = 90^\circ - \phi$ [98]. In this regard, Figure 2.16 b) shows the accurate fitting of experimental data obtained for a rayon based carbon fibre to this linear relationship. Finally, it seems obvious that in order to apply the USM for CNT fibres it becomes necessary to quantify the alignment of nanotubes according to the corresponding orientation parameter.

Fig. 2.16 a) Fitting of experimental data obtained for a PBO fibre to the expression 2.4 [67] b) Fitting of experimental data obtained for a rayon-based carbon fibre to the expression 2.5 [98]

2.7 Summary and objectives

In this chapter we have summarized the clear disagreement existent between CNT fibres and individual CNTs in terms of mechanical behaviour. The reason of this can be found on the arrangement of nanotubes forming a complex hierarchical structure. Thus, the overall mechanical behaviour of CNT fibres is the result of the confluence of many parameters coming from all the hierarchical levels into the structure. This fact makes very difficult to decouple all the variables which affect to a certain mechanical performance and, this way, establish a close relationship between the structure and the properties of CNT fibres.

Nonetheless, based on the extensive literature existent we have been able to summarize the effect that different structural parameters have on the mechanical properties of CNT fibres. Thus, nanotubes fail through their interface by shear. Accordingly, it has been shown that the tensile strength of CNT fibres is positively affected by the aspect ratio of nanotubes. Therefore, long few-layer tubes with a large diameter are desirable in order to reach the best mechanical performance. Nonetheless, in terms of tensile stiffness the morphology of the tubes are not very significant. In contrast, the alignment of them play the main role in this regard.

Current mechanical models for CNT fibres are mainly focused on their fibrillar fracture. Thus, fibres are thought as an assembly of rigid rods perfectly parallel each other. This way,

the stress transference among these fibrils takes place through the interface which is also the weakest point regarding failure. Among these models we must remark the existence of a simple analytical model which delivers a specific stress of $3.5\text{GPa}/SG$ as the characteristic strength of a CNT bundle. This is the primitive version of a more refined model based on a Monte-Carlo simulation which allows a more complicated failure mechanism. However, none of the existent models considers the orientation as the key parameter which it actually is.

Due to this fact, there is a strong need of an analytical model able to explain the mechanical behaviour of CNT fibres based on a solid experimental support. This must include the effect of orientation. In this regard, similarities between CNT fibres and high performance fibres lead us to think on the well-known mechanical models used for these last. According to them, the mechanical behaviour is strongly dependent of certain orientation parameters. Therefore, in order to apply these classical models in CNT fibres, the alignment of nanotubes must be properly measured. For this purpose, characterization techniques such as synchrotron source x-ray scattering or Raman spectroscopy have been used. Moreover, by means of these techniques we have been able to monitor the evolution of the structure during tensile stretching of CNT fibres and, this way, a wide perspective about the evolution of certain morphological features has been obtained.

Chapter 3

Experimental techniques

Specific details of the instruments, experimental parameters and techniques used in the empirical results referred to in this thesis are discussed here.

3.1 Synthesis and spinning parameters

CNT fibres were synthesized by the direct spinning method whereby an aerogel of CNTs is directly drawn out from the gas phase during growth by floating catalyst chemical vapor deposition (CVD) [77]. Two sets of fibres were produced, with differences in their constituent CNTs. In both cases ferrocene was used as iron catalyst source and Hydrogen as carrier gas. The reaction was carried out at 1250 ° C in a vertical tubular furnace reactor. Along all this thesis, fibres will be characterized in terms of the main morphology of the tubes. This characteristic is controlled by the composition of the chemical reaction which takes place at the furnace. Thus, fibres of few-layer MWNTs were synthesized using butanol as carbon source and adjusting the promotor (sulphur) and catalyst (ferrocene) content accordingly (97.7 : 1.5 : 0.8) to produce CNTs with the desired number of layers [111]. Fibres of collapsed DWNTs were produced using toluene as carbon precursor with a reactant concentration of (96.3 : 1.3 : 2.4). The type of CNT was determined by Raman spectroscopy and HRTEM. For each sample set, the degree of CNT orientation in the fibre was varied by changing the rate at which the fibres were drawn out of the reactor [3], equivalent to the winding rate. Samples were collected onto a spool cutted in a way which allows that the fibre would be free standing. Thus, single filament samples can be easily manipulated directly from the spool. All samples were densified with acetone after spinning and left to dry overnight. Densification produces

a reduction in cross section by a factor >50. The fibre samples in this work were produced by Dr. Víctor Reguero, Dr. Belén Alemán and Mr. Xaquín Rodiles from the MNG group.

3.2 Linear density measurement

The measurement of linear density is quite important in terms of normalizing mechanical properties. For this purpose, two different approaches have been followed:

- The **vibroscopic method** is based on the dependence of the natural frequency of a material with its mass. Accordingly, prior to tensile tests, the linear density of 20 mm samples was determined using a Textechno Favimat tensile testing machine. This was done by means of measuring the resonance frequency through the use of ultrasonic sounds. By means of this way, the linear density ρ can be calculated using the following expression

$$\rho = \frac{T}{4l^2 f^2} \quad (3.1)$$

where T is the tension applied to the fibre, l its length and f its frequency of oscillation. [43]

- The **gravimetric method** consists on collecting fibre on a spool at a constant rate. Therefore, the total length of fibre collected can be simply calculated as $length = winding\ rate \times time$. Finally, the sample mass is measured using a precision balance and the linear density corresponds to the ratio $mass/length$.

Both methods have been used interchangeably during this thesis. It seems obvious that the gravimetric method is much easier to carry out. However, by means of this way there is a clear loss in terms of statistical variation which is recovered by the vibroscopic method. Indeed, linear density of each sample tested is measured in this way. This is why, in general terms, mechanical properties measured by Textechno Favimat were normalized using the linear density provided by the vibroscopic method whereas in-situ experiments used the linear density measured through the gravimetric process.

3.3 X-ray scattering

X-ray scattering is a widely used technique for probing the structure of various materials. Due to x-ray photons have a wavelength of around $1\text{\AA}$, being comparable to the inter-atomic distance, it is intrinsically an excellent source for obtaining information on the arrangement of atoms within a material. Moreover, x-rays penetrate through the sample and, therefore, provide structural information of all the irradiated volume. This technique is based on the elastic scattering of X-rays due to the interaction with electrons. Thus, the intensity of scattered x-rays is directly related to electron density fluctuations within the material.[115]

In transmission, x-ray scattering can be outlined according to the illustration depicted in Figure 3.1. Here, it can be easily observed the incident and scattered x-ray photons characterized by their corresponding wavevectors, $\vec{K}_i$ and $\vec{K}_s$. Due to the elastic nature of the phenomenon, the modulus of the vector remains unchanged because there has not been any loss of energy in the process. However, the photon scattered changes its direction forming an angle 2θ with respect to the incident vector. The difference between both vectors is expressed in terms of a reciprocal wavevector $\vec{q}$ whose magnitude is mathematically expressed as

$$q = 2K\sin\theta = \frac{4\pi}{\lambda}\sin\theta \quad (3.2)$$

where λ corresponds to the incident wavelength.

Fig. 3.1 Schematic of the scattering process of an x-ray in transmission mode

This vector is related to the morphology of the sample according to the Bragg's law. This physical law establishes the dependence of the interplanar distance in a crystalline arrangement d and the scattering angle θ in the following way

$$n\lambda = 2d\sin\theta \quad (3.3)$$

where λ is the x-ray wavelength and n is an integer [115]. Assuming $n = 1$, which is the most common case, the reciprocal wavevector can be expressed as

$$q = \frac{2\pi}{d} \quad (3.4)$$

Therefore, x-ray scattering and the reciprocal space are tightly linked by means of q . Accordingly, at higher scattering angles and, consequently, higher reciprocal wavevectors, the information comes from smaller distances and viceversa. In this regard, we distinguish between wide-angle and small-angle x-ray scattering or, in other words, WAXS and SAXS. Figure 3.2 shows an illustration where appears schematically depicted the beamline where experiments were carried out. Here, it can be observed that the WAXS detector is very tilted respect to the sample because of the high scattering angles involve in this measurement. As a result, information coming from distances in the range of Å is obtained. Moreover, x-rays are diffracted in a cone shape and, therefore, a partial pattern is obtained due to the rectangular shape of the detector. On the other hand, SAXS detector is placed at the end of a large vacuum tube of around 6 or 7 meters length depending of the set-up used. The reason of this long path can be found on the low scattering angle shown by x-rays. Therefore, they can be barely distinguished from the unscattered transmitted beam unless the detector would be placed pretty far from the sample. Distances in a wide range spanning from the nano to the mesorange are observed by means of this technique. Furthermore, the long distance besides the small scattering angles allows that this planar detector provides an overall pattern.

Fig. 3.2 Schematic of the set-up used in synchrotron facilities.

All the results here presented were obtained at the Noncrystalline diffraction (NCD) beamline at ALBA Synchrotron. The radiation provided by the beamline is characterized by a wavelength $\lambda = 1\text{\AA}$. However, for the duration of this thesis there have been two different configurations in terms of the type of measurements carried out:

- **standard beamline** The radiation wavelength was $1\text{\AA}$ and the spot size at the focal plane of approximately $100\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$. The distance from the sample to the WAXS detector was around 174 mm and it increases up to 7500 mm when it treats of the SAXS detector. Detector sizes were $85 \times 255\text{ mm}^2$ and $168.7 \times 179.4\text{ mm}^2$ for WAXS and SAXS, respectively. A minimum exposure time of 5 min has been used in all the experiments.
- **microfocus-assisted measurement** The use of a microfocus allows to reduce significantly the spot size. By means of this device the original x-ray beam coming from the synchrotron line is strongly focused and it reaches a diameter of $\sim 10\text{ }\mu\text{m}$. However, the transmitted x-rays show a higher divergence. This is the reason why the SAXS detector is approximated 1 m to the sample whereas WAXS detector does not change its original position. In both configurations data were analysed with the software Dawn[36].

3.4 Raman spectroscopy

Raman is a spectroscopic technique which has achieved a strong relevance in the characterization of carbon nanotubes and graphene based materials. It is based on the scattering of light from a material previously excited by means of a laser. This is classically explained in terms of the polarizability of the material. In this regard, the incident electric field disturbs the electronic charge distribution of all the molecules irradiated by laser light and thereby induces them dipole moments. As a result, the material shows a macroscopic polarization which acts as the source for a secondary electric field irradiated by the molecules. Thus, the induced dipole moment ($\vec{\mu}$) depends on the electric field of the incident light $\vec{E}$ in the following way

$$\vec{\mu} = \underline{\underline{\alpha}} \vec{E} \quad (3.5)$$

where $\underline{\underline{\alpha}}$ is the polarizability tensor of the material. [27]

Regarding nanotubes, Raman scattering involves a resonantly enhanced process. This is due to the fact that the excitation wavelength falls within the optical transitions between Van Hove singularities [110]. Thus, when the incident monochromatic light interacts with nanotubes, electrons promote to an excited level which rapidly leave emitting a photon. If the electrons come back to the initial state, the energy of the incident laser (E_L) fits to the energy separation between two electronic states (ΔE) and there is no loss of energy in the process (Rayleigh scattering, Figure 3.3b)). However, when there is inelastic scattering, electrons in an excited state leave to a vibrational state different to the initial one emitting or absorbing a phonon of energy $\hbar\omega$. Thus, we can talk about Stokes or anti-Stokes Raman scattering depending on whether the scattered light shows lower or higher energy than the incident Raman laser. In this regard, the difference in frequency between the initial and final states (ω) is commonly referred as Raman shift. These different Raman processes appear schematically depicted in Figure 3.3. Nonetheless, in this thesis we are only interested in Stokes scattering since it is the most common Raman scattering studied in the field of carbon nanotubes

Fig. 3.3 Schematic illustration about the different Raman scattering processes using the resonant approach: Stokes, Rayleigh and Anti-Stokes.

Figure 3.4 shows a typical Raman spectra corresponding to a CNT-based material. Here, we should distinguish between first-order and second-order peaks. The difference between both types of peaks is the number of scattering events involved in each case. Accordingly, the following peaks can be assigned:

Fig. 3.4 Raman spectra of a SWNT fibre in which it appears clearly depicted the characteristic peaks associated to CNT-based materials. Courtesy of Dr. Belén Alemán.

- **First-order peaks** A first-order transition follows the schematic shown in Figure 3.4a) where, as a result of the inelastic scattering, a phonon with an energy $E_v = \hbar\omega$ is emitted. The main characteristic of these peaks is that they do not shift when the power of the incident light is changed [29]. Moreover, due to the nature of this transition and taking into account that this is a resonant process, the scattered intensity appears related to the polarizability tensor in the following way

$$I \propto (\vec{e}_s \underline{\alpha} \vec{e}_i)^2 \quad (3.6)$$

where $\vec{e}_i$ and $\vec{e}_s$ are the unit polarization vectors of the incident and analyzed polarizations [42]. This dependence of the polarization of light constitutes the basics of current Raman theories to measure orientation in CNT-based materials. In this field we find two peaks from the Raman spectra:

- **Radial Breathing Mode (RBM)** peaks are typically found in the range of $70 - 400 \text{ cm}^{-1}$. They are associated with the expansion/contraction of nanotubes along the radial direction. This is why the energy of vibration increases with the number of walls and, therefore, these peaks are only observed for SWNT or few-wall nanotubes (FWNT). Moreover, it is well-known that Raman behaviour shown by these modes are strongly dependent of the geometry of the tube. Thus, for a SWNT, the frequency at which these peaks appear is inversely dependent of the diameter of the tube (d) according to the following relationship $\omega = \frac{a}{d} + b$ in which a and b are experimentally determined parameters. [86]
- **G peak** is observed around 1580 cm^{-1} . It is associated to tangential vibrations and, therefore, it involves the direct stretching of $sp^2 - sp^2$ bonds into the tubes. The shape shown by this peak is very dependent of the type and geometry of the tube. Thus, for SWNTs the peak can be deconvoluted in two peaks: G^+ is at $\omega \sim 1582 \text{ cm}^{-1}$ and G^- peak at $\omega \sim 1570 \text{ cm}^{-1}$. In this regard, G^- is very dependent of the geometry of the tubes whereas G^+ is barely affected. As the number of layers increase, both peaks tend to converge to a single symmetric peak.[29]
- **Second-order peaks** Second-order transitions involve both a more complicated schematic picture than that shown in Figure 3.4a) and a highly complex mathematical treatment

of the scattered intensity. Moreover, they show a power dispersive behaviour and, therefore, Raman peaks shift with the laser excitation energy.[29]

- **D peak** appears at $\sim 1320\text{cm}^{-1}$. This peak is associated to impurities in the form of sp^3 bonds and poor graphitisation. Indeed, the ratio (I_D/I_G) is widely used as a standard measurement of the impurity shown by a graphitic material. Thus, the lower this ratio, the higher is the quality of nanotubes in this regard. [29]
- **2D peak** appears in the range of 2650 to 2700 cm^{-1} . It is an overtone of the D peak, although it is not directly related to poor graphitisation in the material in the same way. However, it is strongly reported that it shows a variable shape associated to the interaction between stacked graphene layers and by the termination of layers [145, 35].

3.4.1 Orientation measurement by Raman

One of the most important topics in this thesis involves the measurement of the alignment of nanotubes into the fibre structure. In this regard, a method based on the variation of Raman G-peak intensity while the fibre rotates has been developed and, for this purpose, an special set-up has been used. This new set-up consists on a rotating disk mounted onto the standard holder of a Renishaw inVia microRaman spectrometer. This special set-up can be observed in Figure 3.5 where it is shown both the rotating holder used to carry out the measurements (left) and one image of the fibre rotated an angle Φ (right). Thus, the experiment consists on rotating the fibre from 0° to 90° and to obtain two Raman spectra at different polarization systems for each $\Delta\Phi = 10^\circ$. The difference in polarization consists on making that both the incident and scattered light would be polarized along the direction in which $\Phi = 0^\circ$ or, in contrast, crossly polarized. Thus, calling vertical(V) to the direction of $\Phi = 0^\circ$ and horizontal (H) to its normal, the two configurations used are termed as VV or VH in the case of parallel and crossly polarized light.

Fig. 3.5 (left) Set-up used for rotating the CNT fibre under Raman exposure. (right) Optical micrograph of a CNT fibre rotated an angle ϕ

This study was made in collaboration with NanoHAC group from Imperial College of London thanks to the funding of a CostAction grant. Here, the experiments were carried out with a laser light of $\lambda = 633\text{nm}$ at a 10 % of power during 10 s of fibre exposure. However, due to the difficulty of the experiments, there was not enough time to carry out all of them during the time of the stay. This is why the study was completed in IMDEA Materials Institute. Here, a laser light of $\lambda = 533\text{nm}$ was used and the power of the light was reduced to a 5% while the fibre was exposed during 10s. Due to relative intensities are involved in these measurements and first-order peaks do not shift with the incident wavelength we can compare all the measurements interchangeably. The magnification used in all the cases was $50\times$.

3.5 Mechanical tests

3.5.1 Standard measurements

Mechanical properties of the different fibre samples were determined using a Textechno Favimat tensile testing machine. Thus, a single filament was positioned vertically and clamped by two rubber grips by means of an adjustable-force spring. The gauge length used was 20 mm and the tensile test was carried out at a rate of 2 mm/min. A minimum of 10 samples per batch were tested in order to develop an statistical study of mechanical properties.

Specific stress was calculated as the maximum force reached by a sample normalized by its linear density. This is expressed in N/tex in which $tex = (g/Km)$. This is a very well-known unit of linear density measurement widely used in the industry of textiles and yarns. Finally, N/tex is equivalent to the stress expressed in GPa divided by the specific gravity of the material (GPa/SG). This way, the problem of determining the effective cross-section of a porous material is avoided.

Regarding stiffness, the method followed is a bit more complicated because the definition of this parameter implies a linear stress-strain relationship. However, according to Figure 3.6 a) in which the first derivative of a stress-strain curve has been plotted, there is no a constant region and, consequently, a linear regime in the original curve. Nonetheless, it can be easily observed that there is a point at which the rate of decreasing of stress speeds up or, in other words, stress starts to increase much slower. In this regard, we can thought on this as a yield point which differentiate the elastic from the plastic region. Indeed, as 3.6 b) reveals, the region delimited by this point fits pretty accurately to a straight line with a fitting parameter of $R^2 = 0.997$. However, it seems obvious that this is an approximation and the real behaviour is further complex. This fact will be treated in more detail in Chapter 6 where plasticity of CNT fibres is studied. Until then, this has been the procedure used to calculate stiffness of CNT fibres.

Fig. 3.6 Determination of yield point from the first derivative of the stress-strain curve a) and its corresponding value from stress-strain graph b).

Furthermore, in the elastic region from Figure 3.6a) there is a peak centred at about 0.06% strain. This peak is associated to the effect of waviness on stretching CNT fibres. In this

regard, due to very low effort necessary to straight wavy elements into the fibre, a characteristic “knee” appears on its tensile behaviour [50]. This corresponds to a maximum in the first derivative as that shown in the graph. However, in this case, the maximum appears close to 0 and no significant knee can be seen at first glance on stress-strain graph. This fact reveals that the effect of waviness is simply negligible and, therefore, this variable will not be considered for studying mechanical properties of CNT fibres.

3.5.2 In-situ mechanical tests

For the duration of this thesis, in-situ tensile tests have been developed with the aim of monitoring morphological changes into the structure of the fibre while this is mechanically stretched. For this purpose, CNT fibres were subjected to the action of both Raman and X-rays during tensile tests. These measurements were carried out by a Kammrath und Weiss miniaturized tensile stage. This device is shown in Figure 3.7 where it can be easily observed all the machinery of the system. In this regard, the original load cell of the machine was replaced by a load cell Honeywell model 31 because of the extremely accurateness of this device. Moreover, the strain was controlled with a system of gears which were calibrated to move at $2\text{ }\mu\text{m/s}$. Finally, all these devices were controlled using a home-made software created entirely by Dr. José Sánchez.

In order to test CNT fibres, these were placed onto a frame made of paperboard such as that shown in the onset from Figure 3.7. This was done by sticking the end points of the fibre to the frame using an epoxy glue. This way, the rest of the sample remains free standing and it can be tested by simply cutting the lateral parts of the frame which, in turn, is mechanically clamped to the tensile testing machine such as it appears in Figure 3.7. Thus, single filaments of 15 mm were tested in this way.

Fig. 3.7 Tensile testing device used for in-situ mechanical measurements and the paperboard frame designed for testing CNT fibres.

With the aim of measuring morphological features of a CNT fibre during mechanical testing we have followed a stepwise method. According to it, the fibre is not mechanically strained while it is irradiated by x-rays or Raman laser and, therefore, there is no any dynamic effect to take into account during the exposure time. In contrast, the experiment can be thought as a series of quasi-static points associated to a certain stress and strain. In this regard, Figure 3.8 a) shows the results given by the load cell during a tensile test. Here it can be easily observed the different steps followed along the test. Firstly, the fibre is pre-stretched at a high force to be unloaded just after this and, finally, develop the stepwise tensile test. However, a stress relaxation happens just after all loading steps. This may be associated to the viscoelastic behaviour shown by CNT fibres which has been simply ignored in this research work[136]. Thus, the procedure followed in this regard appears schematically depicted in Figure 3.8 b). Here, it can be observed how the force tends to a constant force with the time which has been termed as force* and at which both x-ray scattering and Raman measurement were developed. This way, all the measurements were carried out at a constant force with an error

of $\pm 0.7\text{mN}$ associated to sensitivity of the load cell.

Fig. 3.8 a) Force measured by the load cell during an in-situ mechanical experiment. Here it can be easily observed the strong viscoelasticity shown by CNT fibres. b) Relaxation effect after loading a CNT fibre. Force decays exponentially towards a constant value $Force^*$ at steps of 0.7mN .

Figure 3.9 shows the results of an in-situ mechanical test. As in the standard case, the force is normalized by the linear density and the stress is expressed as GPa/SG . The strain is obtained by means of the extension L as $\text{strain}(\%) = (L - L_0/L_0) \times 100$ where $L_0 = 15\text{mm}$. The reason why the fibre must be pre-stretched comes from the need of separating the elastic from the plastic contribution during the experiment. Thus, due to this is not known a priori, we took advantage of the cyclic behaviour shown by CNT fibres. Accordingly, the fibre is firstly strained until some plasticity starts to appear (onset of the figure). After this, the fibre is completely unloaded and a certain hysteresis appears as a result of the energy dissipated in the process. Due to this fact, the fibre is strained back an extension of ϵ_b such as it appears in Figure 3.9. Thus, when the fibre is stretched again, we assure that the elastic region would be mainly limited to this strain ϵ_b and just after this the fibre would be plastically strained.

Fig. 3.9 Force-strain behaviour during an in-situ mechanical measurement. Firstly, the fibre is prestrained until some plasticity is reached (onset). After that, the fibres is unloaded and strained back a value ϵ_b to be stretched again according to a stepwise method. Thus, the fibre is linearly stretched in the range delimited by ϵ_b and it is plastically strained afterwards.

As it has been said, in-situ mechanical measurements are focused on developing tensile tests of CNT fibres while these are monitored by Raman or x-rays. Regarding x-rays, the experimental conditions have been described in section 3.3 for the two configurations available. Thus, during the thesis we will remark which system has been followed in each case. Regarding Raman it must be remarked that this study was completely carried out in the IMDEA Materials institute. In this case, the magnification was reduced to $20\times$ which is equivalent to a spot size of $1.6\ \mu\text{m}$. This data was obtained by directly calibrating the Raman microscopy. This reduce of magnification was done in order to increase the area of measurement and to assure that the information comes always from the same region. Thus, according to Figure 3.9, the maximum strain reached by the fibre is $\sim 5\%$. Assuming that the strain is

uniform along all the fibre, the increase of the area respect to the initial illuminated region ($A_0 = \pi(1.6/2)^2$) can be approximated as an ellipse as ($A = \pi(1.6/2)((1.6/2) \cdot (1 + 0.05))$). Thus, the area out of focus because of stretching is calculated as $((A - A_0)/A_0 \approx 0.055)$. This is a pretty tiny difference and we can consider that information always comes from the same region during test. Moreover, a laser light of $\lambda = 533nm$ at a 5 % of power was used during 10 s of fibre exposure.

3.6 Electron microscopy

For this thesis, CNT fibres were imaged using both a FIB-FEG SEM Helios NanoLab 600i (FEI) and a LEO Gemini 1525 FEG SEM (Carl Zeiss) working with typical acceleration voltages of 10 kV and 5 kV, respectively. The transmission electron microscope instrument used was a Talos F200X FEI operating at 20kV. All the images shown in the thesis were taken by Dr. Miguel Castillo from IMDEA Materials Institute and Mrs. Sandy Fisher from the NanoHAC group in Imperial College.

Fibre diameter was determined by image analysis of SEM pictures using ImageJ software.

Chapter 4

Orientation analysis of CNT fibres through SAXS/WAXS and Raman spectroscopy

It is well known that the orientation of nanotubes in macroscopic assemblies has a strong influence on their bulk physical properties. In the context of mechanical properties, a higher CNT alignment has been identified as a key factor to obtain both a high tensile strength and stiffness [71, 3, 140, 15, 79]. Moreover, nanotube assemblies have also shown significant improvements in terms of electrical [52] and thermal conductivities [45, 52] with orientation.

In this regard, x-ray diffraction is a widely used technique in the field of polymer fibres to measure, among other morphological features, the alignment [115]. The first part of this chapter is focused on developing a method based on WAXS and SAXS techniques to measure the alignment of CNT yarns. Moreover, a proper quantification of the alignment of these fibres in terms of orientation parameters is presented.

On the other hand, the second part is focused on determining the alignment of CNT fibres by means of polarized Raman spectroscopy. This method is based on the relative change on the intensity of G peak while the fibre rotates. Thus, this variation is strongly dependent of the alignment of highly anisotropic nanotubes along the fibre's axis. In this regard, we discuss about the suitability of this technique for the specific case of CNT fibres.

Hence, the content of this chapter is mainly focused on comparing both techniques. For this purpose, CNT yarns with a different degree of alignment have been characterized by both methods and the results are analysed and compared. In this regard, the samples analysed were wound at different rates leading to a wide range of orientation distributions.

4.1 The hierarchical structure of the CNT fibre shown by wide-angle (WAXS) and small-angle x-ray spectroscopy (SAXS)

Due to the hierarchical structure of the fibre, the use of a technique which provides morphological information from different range scales seems pretty convenient. This is the case of x-ray scattering since it allows to separate the contribution of each scale in terms of the scattering angle θ . In this regard, we must distinguish between wide-angle and small-angle scattering. However, when it treats of x-ray patterns, it is much more convenient to use the reciprocal wavevector $q = \frac{4\pi \sin(\theta)}{\lambda}$ where λ corresponds to the incident x-ray wavelength. This parameter, in turn, is related to real sizes (d) as $q = \frac{2\pi}{d}$, according to Bragg's law (see section 3.3 for more details). Consequently, SAXS is associated to real sizes in the range of several tens of nanometres whereas WAXS provides information coming from scattering elements below 1 nm size.

Taking this into account, Figure 4.1 shows a schematic comparative between both WAXS and SAXS and the different hierarchical levels of the fibre associated to each technique. Thus, SAXS have been compared with the microstructure of the fibre which has been shown by a SEM picture. This is due to the fact that SAXS reflection comes from the mesoporous revealed by the fibre due to imperfect packing of CNT bundles. Thus, the huge difference on electronic density between carbon and air leads to scatter highly collimated x-rays from the incident beam. As a result, a highly anisotropic reflection is obtained. This anisotropy is explained in terms of the preferential alignment of scattering elements along the fibre's axis. This effect has been widely reported for SAXS studies of fibrillar materials such as polymer or carbon fibres [47, 104, 28, 108]. On the other hand, WAXS has been compared with a TEM image in which an individual tube is represented. The reason is found on the fact that WAXS patterns are characterized by diffraction rings associated to atomic scale crystalline domains. In this case, it must be remarked the existence of a highly anisotropic signal which

has been associated to the 002 peak. This corresponds to the separation of graphitic nanotube walls and, therefore, it is strongly dependent on the alignment of the tubes along the fibre's axis.

Fig. 4.1 Comparative between the hierarchical structure of a CNT fibre and x-ray based techniques WAXS and SAXS. The highly porous microstructure revealed by the fibre is directly shown by a SEM picture which leads to SAXS scattering. Crystalline arrangement of nanotubes can be observed by means of WAXS in which the 002 signal is associated to the separation of graphitic walls on nanotubes such as it has been schematically depicted on a picture of an individual tube obtained by TEM. TEM picture was a courtesy of Dr. Víctor Reguero.

Hence, by means of x-ray scattering an overall perspective about the fibre structure can be obtained. However, WAXS and SAXS are based on different but related physical mechanisms such as scattering and diffraction. In this regard, diffraction implies necessarily scattering but the same does not happen in the inverse direction. This fact makes of WAXS an inherent less sensitive method than SAXS. Moreover, the fact that SAXS comes from the porous structure of the fibre is a huge advantage for a material such as the CNT fibre which poses a surface area as high as $260 \text{ m}^2/\text{g}$ [155]. On the other hand, WAXS is based on diffraction rings

whereas SAXS shows a continuous reflection. This fact increases the difficulty regarding the interpretation of SAXS patterns. Finally, it has been observed that both WAXS and SAXS are very sensitive to the effect of the alignment of the fibre which would allow us to quantify orientation of nanotubes along the fibre's axis.

4.2 WAXS analysis of CNT fibres: orientation of nanotubes along the fibre's axis

X-ray diffraction provides multiple information about the morphology of any material, including orientation. Due to this fact WAXS patterns of CNT fibres must be carefully analyzed. The main purpose wanted by means of this analysis is to provide both qualitative and quantitative information about the alignment of nanotubes. Therefore, in order to fulfil this aim, the morphology of the fibre needs to be firstly analysed through its corresponding diffraction pattern. This way, we can distinguish the signal associated to the arrangement of nanotubes and measure its anisotropy.

4.2.1 Basic constituents of CNT fibres: radial integration

In order to obtain information about the existence of crystalline or sufficient regular domains into the fibre's structure, a radial integration of the WAXS pattern has been developed. Figure 4.2 a) shows a schematic representation of this procedure according to which scattered signal is integrated along the q -range. As a result, Figure 4.2 b) shows the corresponding graph in which diffraction peaks provide information about the crystallinity of the different constituents into the fibre structure. Here, it can be clearly observed the highest intense 002 peak previously mentioned and its corresponding double order 004 peak. Moreover, a peak corresponding to the 100 peak associated to intralayer crystallinity in nanotube walls appear overlapped with peaks corresponding to iron based nanoparticles impurities coming from the synthesis process. This has been previously reported for other CNT fibres synthesized following a CVD route such as that followed in this work [111, 25]. This phenomena supposes a great problem regarding the characterization of crystalline domains into the fibre structure because the decoupling of all these effects remain unsolved. Therefore, the use of

the 100 peak in order to analyse the structure of the fibre, including orientation, is not possible.

Fig. 4.2 a) schematic representation of the radial integration of a WAXS pattern from a CNT fibre & b) diffraction peaks obtained by radial integration in terms of q where the 002 peak has been highlighted in the onset of the figure.

Nonetheless, the use of the 002 peak to analyse orientation of nanotubes has been widely reported [25, 7, 5]. The fact that this reflection is produced by the stacking of graphitic planes makes it suitable, not only for the study of CNT assemblies, but also for the rest of carbon based materials, such as carbon fibres [100]. According to the onset from Figure 4.2 b), the 002 peak appears at 18.4 nm^{-1} , in agreement with a turbostratic arrangement of CNT layers [89, 70]. Moreover, it can be easily noticed that the peak shows an asymmetric shape. This is due to the presence of two kinds of populations in terms of graphite stacking. Firstly, the presence of MWNTs in the fibre contributes to the diffraction pattern because of the interwall separation. Secondly, the distance between nanotubes' outer walls highly aggregated into bundles leads also to x-ray diffraction [112]. However, no difference can be established between both signals in terms of orientation analysis. This is due to the fact that nanotubes are closely parallel one to each other in bundles and, therefore, the same orientation distribution is expected in both cases.

4.2.2 Azimuthal distribution of the 002 peak to compute the alignment of nanotubes

Hence, the orientation analysis can be computed by means of integrating azimuthally the 002 peak according to Figure 4.3 a). The result appears in Figure 4.3 b) where experimental results have been forced to fit to two different curves. Firstly, following the method already used for high performance fibres such as PBO [24] or PpTA [93], the azimuthal profile is first fitted to a Lorentz-IV function.

$$I(\beta) = \frac{I_{\max}(\beta)}{(1 + (\sqrt[n]{2} - 1)(\frac{\beta}{\gamma})^2)^n} + I_0, \quad n = 4 \quad (4.1)$$

where $\gamma = FWHM/2$ and I_0 corresponds to the background intensity. However, it can be clearly observed that the fitted curve obtained underestimates the weight of tails in the distribution. Using, instead, a simple Lorentzian function ($n=1$ in equation 4.1), leads to a better fit. The main difference between both functions is that the fourth power in the Lorentz-IV forces it to converge faster than Lorentz's. This fact points out to a system intrinsically more misaligned than high performance fibres.

Fig. 4.3 a) schematic representation of the azimuthal integration carried out over the 002 signal from WAXS pattern of a CNT fibre & b) results of azimuthal integration fitted to both Lorentz and Lorentz-IV functions.

Another important characteristic to take into account is the origin of the background intensity. This is due to the presence of randomly oriented graphitic elements into the fibre. Despite this contribution can come from nanotubes themselves, this possibility is highly unlikely because of the manufacturing process. Thus, direct spinning of nanotubes from the CVD furnace leads nanotubes to align themselves highly parallel one to each other. In contrast, there is no any reason why graphitic impurities grown onto the surface of the fibre had to be aligned towards any preferential direction. Therefore, an isotropic diffraction ring associated to these impurities would be expected. Consequently, the procedure to measure orientation needs necessarily of removing this constant intensity. This will have important consequences on quantifying orientation but, so far, only the FWHM of the azimuthal profile would be used to characterize the alignment of the fibre.

4.3 Dependence of WAXS and SAXS sensitivity with the structure of CNT fibres

So far, it can be said that the problem of measuring orientation of CNT fibres has been solved. Thus, by means of WAXS analysis, the azimuthal distribution of CNTs along the fibre's axis can be obtained. However, according to Figure 4.4, the sensitivity of this technique is quite poor. In comparison, SAXS provides an azimuthal profile almost 10 times greater, even with a time of exposure 6 times lower. It must be remarked that azimuthal profiles in SAXS are developed around a complete circumference whereas those obtained by WAXS are delimited by the size of the detector. This way, WAXS detector delivers a partial pattern whereas the small scattering angles involved in SAXS allows an overall pattern (see section 3.3 for more details about WAXS and SAXS detectors). Anyhow, the differences in intensity are due to different physical phenomena involved in each case. Therefore, different morphological information is obtained as a result. Thus, the low intense signal from WAXS is an evidence of the lack of crystallinity of the fibre structure. This fact agrees with previous WAXS analysis which pointed out to the turbostratic arrangement of the tubes. In contrast, SAXS is directly related to the surface area revealed by the fibre. Due to values of surface area as high as $260 \text{ m}^2/\text{g}$ has been measured for CNT fibres [155], SAXS becomes a more suitable technique than WAXS in terms of sensitivity.

Fig. 4.4 Comparison of azimuthal profiles obtained by WAXS and SAXS for a single filament CNT fibre exposed to the action of x-rays during 1800s and 300 s respectively.

On the other hand, SAXS is based on a continuous reflection and, therefore, it involves a wide range of scattering lengths in terms of the reciprocal wavevector ($q = \frac{2\pi}{d}$), where d are real sizes. In the case of Figure 4.4, the azimuthal integration has been developed over the whole q -range. In contrast, the azimuthal profile obtained by WAXS corresponds to a well-defined diffraction ring. In this regard, there is no any obvious relationship between the anisotropy shown by the 002 peak from WAXS and that corresponding to SAXS reflection. This is why a direct comparison between WAXS and SAXS has become necessary in order to define the proper way of measuring alignment by SAXS.

4.4 Orientation of CNT fibres by SAXS: the FF peak

In terms of all we have explained so far, the main problem regarding SAXS scattering comes directly from the interpretation of results. Thus, the continuous anisotropic reflection

observed in SAXS patterns does not reveal, at first sight, the existence of any peak through which a clear relationship between the real and the reciprocal space could be established. Nonetheless, this analysis must be done in terms of the radial integration of SAXS patterns, carried out according to the schematic picture shown in Figure 4.5 a). The results obtained appear graphically depicted in Figure 4.5 b). Firstly, it must be mentioned that at very low q -values, intensity remains constant. This region has been classically called as Guinier region and it is strongly dependent of the radius of gyration (R_g) of particles into the system [115]. However, the expression which enables the measurement of this parameter has been developed for dilute solutions. This fact supposes a great problem for a highly aggregated system such as the CNT fibre. After this initial region, intensity decreases according to a power law behaviour. A recent work published by this group points to a fractal-like scattering as the origin of this behaviour [156]. Despite all this information can be used to extract important morphological features from CNT fibres; the Form-Factor peak must be highlighted in terms of orientation measurement. This small peak or hump appears in Figure 4.5 at the q range $(0.7 - 0.8)nm^{-1}$ which, in turn, corresponds to distances ~ 9 nm. However, this peak can appear shifted depending on the diameter of nanotubes [57]. Its appearance has been previously observed on another CNT-based materials and it is strongly related to the resemblance of nanotubes to hollow cylinders. Thus, the scattering produced by the difference on electronic densities between the air from the core and the carbon-based skin of the tube leads to the appearance of this peak [137]. As a result, it contains multiple information about the morphology of nanotubes and, more importantly, it has been widely used to measure the orientation of CNT forests [137, 83, 148, 130, 13].

Fig. 4.5 a) Typical SAXS pattern from a CNT fibre oriented vertically. It is depicted the equatorial area over which the radial integration has been carried out. b) Results of radial integration where important regions regarding scattering behaviour of CNT fibres are distinguished.

In order to know if it would be also useful to measure the orientation of nanotubes in CNT fibres, an azimuthal integration has been carried out at the FF peak. This procedure is graphically depicted in Figure 4.6 where it can be clearly observed the position of the FF peak in the SAXS pattern. The result is directly compared to the azimuthal profile obtained by WAXS. As a result, the same Lorentzian distributions are followed in both cases. Nevertheless, in the case of SAXS, the curve seems to be slightly asymmetric with respect to the almost perfect distribution obtained by WAXS. The reason might come from the fact that the FF peak in the SAXS pattern is relatively weak. With the aim of comparing them, azimuthal distributions have been plotted using relative, instead of absolute intensities. However, SAXS signal is actually 25 times weaker than WAXS. In fact, it can not be distinguished at first sight from the SAXS pattern. Therefore, SAXS measurements are very sensitive to the presence of reflections which, taking into account that SAXS detector is placed around 6 meters far from the sample, are almost impossible to avoid.

Fig. 4.6 a) Schematic picture about the development of an azimuthal integration at the FF region from a SAXS pattern. b) Azimuthal integrations obtained by means of both WAXS and SAXS analysis of a CNT fibre.

Once it has been proved the perfect correspondence between the FF peak from SAXS and the 002 diffraction signal from WAXS in terms of alignment, it can be said that the problem of measuring orientation of CNT fibres has been completely solved. However, the low sensitivity of WAXS has made necessary the use of multiple filaments in order to have a signal strong enough. Thus, for instance, results shown in Figure 4.6 corresponds to a fibre made of 100 filaments. However, this method has important disadvantages in terms of modelling mechanical properties of CNT fibres, which is the final goal of this thesis. Thus, mechanically speaking, the sample analysed would behave more as a tow than a fibre. Therefore, mechanical properties have been always refereed to single filaments. Moreover, multiple filament fibres show always a considerably higher misalignment than single filaments since they are basically mats of fibres. Therefore, the perfect correspondence between x-ray measurements of multifilament fibres and mechanical properties from single filaments is highly unlikely. This is why orientation measurements must be obtained for single filaments and, in this case, important differences regarding SAXS and WAXS have been found.

4.5 From multiple-to single-filament samples. A method to estimate the alignment of CNT fibres by SAXS

The measurement of single filaments supposes the irradiation of a fibre of around $\approx 10\mu\text{m}$ diameter with an x-ray beam which is 5 times greater. This fact has necessarily a direct impact on x-ray scattering. However, this effect differs depending if we are talking about WAXS or SAXS. Thus, whereas WAXS signal is so low that it can barely be measured, the high sensitivity of SAXS provides a clear pattern. However, SAXS patterns obtained for single filaments are quite different to those previously measured for multiple filaments. In this regard, Figure 4.7 shows the results of two SAXS patterns corresponding to a CNT fibre made of 100 filaments and a single filament sample. For comparison purposes, two radial integrations along an equatorial and a meridional sector have been obtained in each case, following the schematic picture which appears in the onset of both graphs. At first sight, by means of simply having a look to SAXS patterns, the loss of intensity from multifilament to single filament samples is quite obvious. This is graphically depicted in Figure 4.7 b), where it can be easily observed how equatorial and meridional profiles of a single filament decreases progressively until they reach a flat plateau. This fact points out to a clear loss of anisotropy when single filaments are measured. Thus, on the other hand, Figure 4.7 a) shows how the anisotropy of the equatorial reflection remains until the limits of SAXS detector when a multifilament fibre is measured. Here, the FF peak can be easily observed whereas this simply disappears when single filaments are measured. This fact avoids any orientation measurement of single filaments by SAXS; at least, by means of the azimuthal integration at the FF peak.

The reason of this loss of anisotropy can be found on the decreasing behaviour of SAXS scattering with q . In this regard, it may differ the slope followed, but this would be always negative. Accordingly, scattering events are less probable as we move on q . Therefore, any reduction on scattering probability such as that associated to a decrease on the number of filaments would have a higher effect at high q values. As a result, both equatorial and meridional profiles reach a flat plateau which fits to the isotropic background and, consequently, any azimuthal integration at high q values would deliver a constant intensity. Therefore, any orientation measurement which involves single filaments would need either estimating this parameter in terms of the available q -range or modifying standard synchrotron facilities using a special microfocus device.

Fig. 4.7 Radial and equatorial profiles measured for SAXS patterns corresponding to a sample made of 100 filaments a) and one filament b).

4.5.1 Evolution of the FWHM with q . Failure of classical models

Due to the orientation measurement of single filament fibres has been shown clearly hampered because of the loss of anisotropy in SAXS, we are going to study how azimuthal profiles vary with the reciprocal wavenumber q . In this regard, Figure 4.8 shows the results obtained in two samples consisting of 100 and a single filament, respectively. As it could be expected, in the case of the multifilament fibre, the FWHM obtained by both WAXS and SAXS fits accurately at the position of the FF peak. Moreover, as it could be also expected, the results corresponding to a single filament fibre does not reach the position of the FF peak because of the loss of anisotropy. Nonetheless, it can be easily observed that the same tendency seems to be followed in both cases. This is characterized by the presence of a maximum from which azimuthal profiles tend to get narrower up to reach the same value of FWHM at both high and low q values. According to the multifilament sample, these values are pretty close to those obtained at the FF peak. In this regard, Table 4.1 shows the specific case of the fibre made of 100 filaments. Here, an error in terms of the FWHM below 1 ($^\circ$) has been found. This fact would allow us to measure the orientation of a single filament sample simply evaluating the azimuthal profile at the low q -range. However, this approximation can not be made yet because it has not been confirmed for the case of a single filament sample. For this purpose, the azimuthal profile at the FF peak must be obtained. However, this would

not be ever possible without modifying the standard synchrotron facilities.

Fig. 4.8 Evolution of the FWHM shown by azimuthal distributions with the reciprocal wavenumber (q). Two SAXS patterns corresponding to a CNT fibre made of 100 filaments and a single filament fibre have been analyzed.

According to the reciprocal wavenumber ($q = \frac{2\pi}{d}$), orientation values obtained at a low q -range are associated to real sizes around 100nm and, therefore, reveal the alignment of the mesoporous structure from the fibre. Hence, the fact that orientation measurements at low- q values fit to the FWHM of the distribution at the FF peak points to a perfect correspondence between the porous structure of the fibre and nanotubes themselves in terms of alignment. This can be explained as a consequence of the preferential arrangement of nanotubes parallel to the fibre's axis. Thus, voids formed by the imperfect stacking of CNT bundles show highly eccentric shapes and, consequently, the orientation distribution of pores into the fibre would fit quite well with that shown by nanotubes forming bundles. In this regard, the existence of 1-D voids is characteristic of fibrillar materials which, as it has been already mentioned, show an equatorial streak similar to that shown by CNT fibres in SAXS [47, 28, 108]. In this regard, the theory of SAXS scattering from fibrillar microstructures predicts a corrected FWHM from orientation measurements. According to this theory, azimuthal profiles show

a broadening effect with q which, for Lorentzian type distributions, fulfils the following expression

$$q * FWHM_{obs} = \frac{2\pi}{L_3} + FWHM^* q, \quad (4.2)$$

where L_3 represents the average pore length into the fibre structure and $FWHM_{obs}$ and $FWHM^*$ are the full width at half maximum directly measured from azimuth distributions and its correspondence after correction [105]. Thus, by means of this way, the width shown by azimuthal profiles can be easily predicted by fitting the FWHM to equation 4.2. Hence, in order to guess if this relationship is fulfilled in this case, Figure 4.9 depicts values of the FWHM from Figure 4.8 multiplied by its corresponding value of q . However, the linear relationship that it would be expected according to equation 4.2 does not appear. Instead, two linear regimes can be distinguished in the case of the fibre made of 100 filaments. In the first region, fitting cuts y-axis at negative values which, according to equation 4.2, means that L_3 is negative which, in fact, does not have any physical meaning. In the second region, the slope does not show any agreement with WAXS. Moreover, in the case of single filaments, the second linear regime is not even observed because of the narrower q -range. Instead, a single linear relationship with a negative L_3 has been found. Accordingly, it can be claimed that the classical theory of SAXS scattering from fibres is not followed for CNT fibres; at least, regarding orientation measurement. On the other hand, taking into account the complex hierarchical structure revealed by CNT fibres, this conclusion seems reasonable. Thus, in terms of x-ray scattering, the structure of CNT fibres can not be simplified as simply fibrillar.

Fig. 4.9 Evolution of the parameter $q \cdot \text{FWHM}$ with the reciprocal wavenumber (q) for two CNT fibres made of 100 filaments and 1 filament. Results have been fitted to equation 4.2 at different linear regions in order to test the validity of the classical model developed for SAXS of fibrillar materials.

4.5.2 Microfocus assisted SAXS/WAXS of single filament samples

As it has just been mentioned, the big problem involving x-ray scattering from single filament fibres is the lack of intensity. This is the reason why microfocus assisted measurements have been carried out. By means of this set-up, the original beam coming from the synchrotron beamline is focused and its cross-section is considerably reduced. Thus, in this research work, the x-ray beam reaches sizes in the order of fibres' diameter values ($\approx 10\mu\text{m}$). This way, the number of x-ray photons interacting with CNTs is maximized and, consequently, x-ray scattering increases dramatically. This effect can be clearly observed in the graph from Figure 4.10. Here, two radial profiles obtained from WAXS analysis of a single filament sample have been shown in terms of the set-up used: with and without microfocus. According to it, diffraction peaks can be barely distinguished in the absence of microfocus. Regardless of the highly time of exposure used (50 minutes). In contrast, the use of microfocus leads to the appearance of well defined peaks by only exposing the filament for 125 seconds. Consequently, orientation measurements of single filaments can be carried out by WAXS analysis.

Fig. 4.10 Radial integration of a WAXS pattern measured for a single filament using standard and microfocus assisted synchrotron facilities. The time of exposure changes from 50 minutes to 125 seconds respectively.

Regarding SAXS, the characteristic loss of anisotropy previously reported is not shown any more. On the contrary, according to Figure 4.11, the radial profile measured for a single filament fits quite well with the SAXS behaviour shown by a 100 filaments fibre. However, some differences can be noticed between curves obtained with and without microfocus. In this regard, apart from the fact that some discontinuities appear in the curve when the microfocus is employed, which is simply due to the use of a different detector; the q range appears also significantly narrowed in this case. This is explained by the divergence that the use of a microfocus produces on the scattered x-ray beam. This fact led to approach the SAXS detector to the sample and, in some cases, to increase the beamstopper size. As a result, the q -range is significantly narrowed at both high and low q values. In spite of this fact, the FF peak can be easily distinguished in the case of a single filament. Moreover, its position remains fixed in the range $(0.07 - 0.08)nm^{-1}$.

Fig. 4.11 Radial profiles obtained for two samples made of one and 100 filaments measured with and without microfocus, respectively.

On the other hand, important differences can be found in the evolution of alignment with q . In this regard, Figure 4.12 shows the results corresponding to two single filaments measured with and without microfocus. According to this figure, curves differ greatly one from each other at low q values. Thus, when the microfocus is used, the width of azimuthal distributions increases as we move towards lower q values. This fact contrasts to the case of the filament measured without microfocus which, as it was previously reported, shows a decreasing tendency. On the other hand, both curves tend to follow the same decreasing behaviour as q increases. In fact, it has been shown that the FWHM decreases with q according to a power-law expression¹. Therefore, there is a clear disagreement between values of orientation at low and high q values when the microfocus is used. Consequently, no relationship can be established between the microstructure of the fibre and nanotubes in terms of their alignment; as it was previously done for multiple filament fibre. However, in this case, the disagreement comes from the use of the microfocus and not from the morphology of the fibre itself. The reason of this instrumental broadening at low q -values remains unclear and it might be studied in the near future.

¹For simplicity it has been plotted the x-axis as logarithmic. This way any power-law relationship is represented as a line shape.

Fig. 4.12 Evolution of the FWHM with the reciprocal wavevector (q) for CNT fibres measured by SAXS with and without microfocus. It has been shown that at high q values the width decays according to a power-law relationship.

Anyhow, the use of microfocus has allowed to measure orientation of single filaments at the FF peak. In this regard, results from Table 4.1 shows a great accurateness between WAXS and SAXS measurements obtained in this way. Moreover, it has been also shown that the FWHM decreases until the FF peak position following a power-law expression with q . This fact has been also observed when filaments were measured without microfocus. However, in this last case, orientation measurements do not reach the position of the FF peak because of the loss of anisotropy. This is the reason why orientation values for a CNT fibre can be estimated by means of fitting existent results to a power-law equation and to evaluate the fitted curve at the FF peak position. This can be done for all those results which follow a decreasing tendency; that is, after the characteristic maximum shown by all samples measured without microfocus. This procedure is pretty useful since it allows to estimate the value of orientation at the FF peak in the cases in which this can not be directly obtained; these are, when single filaments have been measured by standard synchrotron facilities. This way, it becomes unnecessary the use of a microfocus set-up which is quite convenient due to the intrinsic difficulties which imply using it. Among others, it must be remarked the fact that it takes much more time to hit the fibre with the beam because of its pretty small cross-section. This fact make microfocus assisted measurements a very time consuming process. Moreover, this special facility has

not been always available during this thesis. In fact, most of the measurement here reported have been carried out using standard synchrotron facilities.

4.5.3 Correspondence between SAXS from low q -values and the tendency predicted orientation at the FF peak. An alignment dependent method

Finally, according to everything reported in this section, the orientation measurement of single filaments by SAXS consists on integrating azimuthally the SAXS pattern at the range which fits to the FF peak. However, this is not possible unless microfocus would be used. Thus, in order to estimate the orientation of CNT fibres by means of standard synchrotron facilities, this might be calculated by fitting measured orientation values to a power-law expression. This way, as it has been carefully explained in section 4.5.2, the FWHM at the FF peak can be estimated. Furthermore, in section 4.5.1 we have reported that orientation values at low q -values are close to those shown at the FF peak for multifilament samples. This fact was associated to a perfect correspondence between the alignment of the porous structure and CNTs themselves. Due to the use of microfocus implies an intrinsic azimuthal broadening at low q -values, this relationship has not been possible to be established for single filaments. In order to do this, values of orientation at low q values have been compared with those estimated by its corresponding fitting.

In this regard, Table 4.1 compiles orientation measurement of different CNT fibres in terms of the FWHM of their azimuthal profiles. All the samples here reported have been fabricated in-house following the direct spinning method. Thus, maintaining fixed the chemical composition at the hot zone in the vertical furnace, orientation of CNT fibres can vary by means of changing the winding rate. Thus, due to the chemical reaction controls the morphology of the tubes forming the fibre, all the fibres here have been distinguished in terms of the rate at which they have been wound to and the main characteristics of the tubes forming part of the fibre. In addition, both the number of filaments in the fibre and the technique followed to measure them (microfocus and standard facilities) appear clearly specified. Thus, according to the results, it can be firstly observed the excellent agreement between WAXS and SAXS measurements for multifilament samples as well as when the microfocus has been used. These measurements were carried out at the FF peak from SAXS patterns. However, orientation values have been also evaluated at low q -values. The range chosen in this regard

$(0.07 - 0.08)nm^{-1}$ corresponds to the lowest common q-range in all the experiments carried out, except in some cases in which the range appears clearly indicated. According to these measurements, we confirm the huge disagreement between low q-values and the FF peak when the microfocus is used.

Table 4.1 Results obtained from SAXS and WAXS measurement techniques in terms of the FWHM of the distribution. Regarding SAXS it may be differentiated between those values obtained directly from integration of the SAXS pattern (measured) and those estimated by means of fitting existent measurements (prediction). Moreover, regarding those measured, orientation has been able to be measured at the FF peak and at a low q-range $(0.07 - 0.08)nm^{-1}$ depending on the measurement technique. (*) Range of measurement in SAXS pattern: $(0.11 - 0.15)nm^{-1}$

			WAXS	SAXS (measured)		SAXS (prediction)
			FWHM (°)	FWHM (°) (FF peak)	FWHM (°) ($0.07 - 0.08$) (nm^{-1})	FWHM (°)
winding rate (m/min)						
Few-wall MWNTs (100 filaments)	standard beamline	10	25.5	25.2	26.12	-
		10	11.17	11.03	18.94*	-
Collapsed DWNTs (1 filament)	Batch a (microfocus)	20	10.03	-	-	-
		30	9.15	8.8	17.72	-
		40	9.83	9.89	18.42	-
		20	-	-	21.9	22.8
	Batch b (standard beamline)	30	-	-	16.3	18.2
		40	-	-	10.1	10.9
Few-wall MWNTs (1 filament)	standard beamline	4	-	-	14.66	15.3
		8	-	-	15.74	15.4
		12	-	-	10.0	10.8
		16	-	-	8.5	7.7
SWNTs (1 filament)	standard beamline	3	-	-	47.2	31.76
		12	-	-	10.1	9.9

Regarding single filaments measured by standard synchrotron facilities, which are the most of them, the value of orientation obtained at low-q values is directly compared with the value of FWHM estimated. According to the results from the Table 4.1, in almost all the cases, both orientation values can be compared each other. However, the case of the SWNT fibre winded at 3 m/min must be remarked. In this specific case, the difference between both values differs

a 50%. However, in the rest of the cases, the error does not reach a 10%. Thus, with the aim of explaining this disagreement, Figure 4.13 shows the evolution of the FWHM of azimuthal profiles with q for different samples reported in Table 4.1. Here, it can be easily observed that the SWNT-fibre which shows a huge disagreement between the predicted and the measured value of SAXS shows a behaviour which differs greatly respect to the rest of the curves. Thus, this sample does not follow the typical tendency previously reported and it does not possess a maximum. Instead, a continuum power-law decaying behaviour is shown all along the q -range. The explanation to this atypical behaviour is precisely the higher misalignment with respect to the rest of the samples. This fact fits with the fabrication process followed in this case since the fibre was winded at a very low rate. Accordingly, the effect of waviness in the microstructure can be very important and, as a consequence, the microstructure would show a more misaligned structure than that followed by nanotubes themselves. On the other hand, Figure 4.13 reveals that the rest of the samples here depicted follow the expected behaviour based on which the approximation method presented in section 4.5.1 has been developed. Thus, the FWHM obtained at low q -values is similar to that predicted by the power-law expression at high q -values. Nonetheless, comparing both values, a maximum difference in terms of the FWHM of a 10% have been found. However, the alignment of any sample can not be quantified by means of the width of its azimuthal profile. Instead, highly complex orientation parameters must be used and, as it will be shown in the following section, differences in these parameters tend to decrease with respect to the case of the FWHM.

Fig. 4.13 Evolution of the FWHM against q for different CNT fibres. Results of orientation from samples here depicted appear compile in table in terms of the main morphology of the nanotubes forming the fibre and the rate at which fibres have been winded. The decreasing part regarding the FWHM of distributions have been fitted to a power-law expression (dashed line).

4.6 Comparison of WAXS/SAXS analysis in terms of orientation parameters

In the previous section it has been extensively talked about orientation measurement by means of WAXS and SAXS. For this purpose, we have used the FWHM showed by the azimuthal profiles. This has been done due to the scattered intensity is proportional to the number of scattering elements into the fibre [115]. Therefore, regarding orientation, the intensity is proportional to the polar distribution of nanotubes which is expressed as $\rho(\beta)$ (see appendix A.1 for more details). Accordingly, $\rho(\beta)$ can be directly obtained from $I(\beta)$ as

$$\rho(\beta) = \frac{I'(\beta)}{\int_0^\pi I'(\beta) \sin(\beta) d\beta},^{23} \quad (4.3)$$

being the FWHM shown by the distribution $I(\beta)$ an excellent way to quantify the well alignment of nanotubes along the fibre's axis.

However, despite it is widely used when dealing with distributions, the direct comparison of the FWHM only offers a qualitative information about orientation. Instead, a proper quantification of the orientation of nanotubes is needed with the aim of analysing the role that this parameter plays on the final mechanical properties of the fibre. Thus, the orientation distribution function (ODF) of a fibre can be expressed as a series of even Legendre polynomials as follows

$$f(\beta) = \sum_{i=0}^{\infty} \frac{2i+1}{2} \langle P_i(\cos\beta) \rangle P_i(\cos\beta), \quad (4.4)$$

where $P_i(\cos\beta)$ is the Legendre polynomial of degree i and $\langle P_i(\cos\beta) \rangle$ is its average value (see appendix A.3 for a table of even Legendre's polynomial functions)[131]. This is why $\langle P_i(\cos\beta) \rangle$ are defined as orientation order parameters.

A special mention needs to be made when we consider the second order parameter ($\langle P_2(\cos\beta) \rangle$), also known as Herman's parameter. In agreement with the literature, this is presented as the standard orientation parameter for measuring the alignment on CNT assemblies [84, 137, 133]. According to this, there are three reference values: 1, when nanotubes are perfectly aligned along the axis; 0, when they are randomly oriented and -0.5 when they are perfectly aligned in the direction perpendicular to the axis. However, as it is pointed out by equation 4.4, this parameter is simply one of those involved in an infinite series of even polynomial functions. This is why the quantification of the alignment in terms of this single value leads to a clear inaccuracy. Nonetheless, due to the convergent behaviour of the series, orientation parameters tend to 0 as their order increase. Accordingly, a compromise must be reached in terms of the number of orientation parameters necessary to accurately quantify

² $I'(\beta) = I(\beta) - I_0$ according to equation 4.1

³The range of integration according to the theory is between 0 and π . Nevertheless, a Lorentzian function centered at 0 approximates $I(\beta)$ between 0 and $\pi/2$. However, the result can be obtained assuming the symmetry of the function respect to $\pi/2$. See appendix A.2 for more information about the procedure followed. These assumptions will be used along this thesis and the range of integration can change from $[0, \pi/2]$ to $[0, \pi]$ indistinctly.

the alignment of nanotubes.

To this aim, the ODF measured by WAXS/SAXS analysis has been compared to that calculated by means of the orientation parameters. For this purpose we have distinguished between the experimental and the estimated ODF. In this regard, the average of Legendre polynomials can be defined from $\rho(\beta)$ as follows (see appendix A.2 for the mathematical deduction)

$$\langle P_i(\cos\beta) \rangle = \frac{\int_0^\pi P_i(\cos\beta) \rho(\beta) d\beta}{\int_0^\pi P_i(\cos\beta) d\beta} = \frac{\int_0^{\pi/2} P_i(\cos\beta) I'(\beta) \sin(\beta) d\beta}{\int_0^{\pi/2} I'(\beta) \sin(\beta) d\beta}, \quad (4.5)$$

On the other hand, the experimental ODF can be also directly obtained from $\rho(\beta)$ based on the assumption that the orientation of nanotubes depends exclusively on β (see appendix A.1 for more details). Thus,

$$f(\beta) = \frac{1}{4\pi^2} \rho(\beta) = \frac{1}{4\pi^2} \frac{I'(\beta)}{\int_0^\pi I'(\beta) \sin(\beta) d\beta}, \quad (4.6)$$

Therefore, based on the maximum entropy formalism, it has been estimated an ODF in terms of the orientation parameters obtained from WAXS/SAXS measurements (see appendix A.4 for an explanation of the method used in terms of the maximum entropy formalism). In this regard, Figure 4.14 shows a comparative picture in which an hypothetical ODF is estimated by the maximum entropy formalism in terms of the orientation parameters used to define it. Figure 4.14 a) depicts a highly aligned sample, whereas Figure 4.14 b) corresponds to a poorly aligned one. A clear difference can be seen in both cases: whereas for the best aligned sample a 20th order has been necessary in order to reach an accuracy of $R^2 = 0.98$, for the most misaligned sample, we only need a sixth order approximation to reach the same accuracy. Therefore, the number of orientation parameters necessary to measure the alignment depends on the degree of alignment itself. This fact proves the limitation of approximating the actual ODF with a reduced number of parameters.

Fig. 4.14 Fitting between the experimental ODF of an hypothetical sample and its estimation in terms of the number of orientation parameters used. For this purpose, it has been used two hypothetical cases in which it is supposed an oriented FWHM=9.5°(a)) and a misaligned FWHM=32°(b)) CNT fibre. By means of this way it is shown how the distributions obtained by the maximum entropy formalism (dashed line) and the experimental ODF (solid line) tends to fit one to each other with the increasing order of Legendre's polynomials, varying the order in terms of the alignment of the sample.

Nevertheless, due to its importance according to the literature, $\langle P_2(\cos\beta) \rangle$ has been used for comparison purposes. Thus, values of FWHM from Table 4.1 have been used to calculate Herman's Orientation parameters by means of combining equations 4.1 and 4.5 and the results have been compiled in Table 4.2. Here, it can be easily observed that some features are shared by both the FWHM and $\langle P_2(\cos\beta) \rangle$. Thus, orientation measurements evaluated by WAXS and SAXS at the FF peak position fit perfectly one to each other. This was possible when multifilaments were used ;or well, when single filaments were subjected to microfocus assisted synchrotron measurements. Nonetheless, in this last case, the value of $\langle P_2(\cos\beta) \rangle$ reveals a much more misaligned sample when azimuthal profiles are evaluated at low q-values in SAXS. This has been already reported to be an instrumental induced broadening associated to the use of microfocus. However, when single filaments are measured without this optical device, the two parameters obtained by SAXS analysis fit almost perfectly one to each other except in the case of the SWNT-fibre winded at 3 m/min. This special case was already discussed in section 4.5.3 and it was shown that the difference in this regard was due to an intrinsic misalignment of the fibre. However, whereas the difference in terms of the FWHM was of a 50%, this is significantly reduced up to a 20% in terms of $\langle P_2(\cos\beta) \rangle$. This fact is repeated with the rest of the samples. Thus, the maximum error in terms of the FWHM (10%) is significantly reduced up to reach a maximum difference of a 2% in terms of $\langle P_2(\cos\beta) \rangle$.

This fact supposes an almost perfect agreement between both SAXS based techniques which, in fact, is the prove that orientation measurements at low q -values fit almost perfectly with the predicted alignment of nanotubes. This, in turn, supposes that the measurement of alignment in terms of $\langle P_2(\cos\beta) \rangle$ can be done by means of both techniques. However, evaluating this parameter at low q -values is much easier and less-time consuming than predicting it by fitting to a power-law decaying behaviour.

Table 4.2 Results obtained from SAXS and WAXS measurement techniques in terms of $\langle P_2(\cos\beta) \rangle$. Calculus have been made based on values of FWHM reported in Table 4.1. (*) Range of measurement in SAXS pattern: $(0.11 - 0.15)nm^{-1}$

			WAXS	SAXS (measured)		SAXS (prediction)	
			winding rate (m/min)	$\langle P_2(\cos\beta) \rangle$	$\langle P_2(\cos\beta) \rangle$ (FF peak)	$\langle P_2(\cos\beta) \rangle$ (0.07 – 0.08) (nm^{-1})	$\langle P_2(\cos\beta) \rangle$
Collapsed DWNTs (100 filaments)	standard beamline	10	0.48	0.49	0.48	-	
		10	0.61	0.62	0.54*	-	
Few-layer MWNTs (1 filament)	Batch a (microfocus)	20	0.63	-	-	-	
		30	0.64	0.64	0.55	-	
		40	0.63	0.63	0.54	-	
		20	-	-	0.51	0.50	
	Batch b (standard beamline)	30	-	-	0.56	0.55	
		40	-	-	0.63	0.62	
Collapsed DWNTs (1 filament)	standard beamline	4	-	-	0.58	0.57	
		8	-	-	0.57	0.57	
		12	-	-	0.63	0.62	
		16	-	-	0.65	0.66	
SWNTs (1 filament)	standard beamline	3	-	-	0.36	0.44	
		12	-	-	0.63	0.63	

Finally, once it has been measured, results of alignment reported in Table 4.2 allow us to reach some conclusions. Firstly, as Alemán et al. [3] pointed out, the alignment of CNT fibres increases with the winding rate. However, it has been shown that this variation is not greatly reproducible. Thus, for the same manufacturing process, orientation parameters of CNT fibres winded at the same rate vary significantly in terms of the batch used. In this regard, a difference of up to a 20 % has been shown for a CNT fibre winded at 20 m/min if we compare batch a) and b). Moreover, using these two batches as a reference, a different sensitivity of the process to the winding rate can be easily observed. Thus, whereas in the

batch a) only a small 5% of increasing is observed if the winding rate increases from 10 m/min to 40 m/min, this difference reaches a 20 % if we compare samples obtained at 20 m/min and 40 m/min from the batch b). This fact seems to point out to problems on the manufacturing process in the case of the batch a); however, due to these samples have been used to measure orientation by means of SAXS, WAXS and Raman, these would be really important for comparison purposes.

On the other hand, observing values of orientation parameters obtained, these are pretty far of those reported for high-performance fibres such as Kevlar ($\langle P_2(\cos\beta) \rangle = 0.976$ [93]) or PBO-AS ($\langle P_2(\cos\beta) \rangle = 0.972$ [24]). This fact seems to confirm what was already proved in section 4.2.2: the inherent misalignment of the system under study. In this regard, Vilatela et al. [133] reported a value of $\langle P_2(\cos\beta) \rangle = 0.66$ for a CNT fibre fabricated also by means of the direct spinning method. This value agrees with those showed from our samples; in fact, it is only a 3% higher than our most oriented fibre. This can be explained as a direct consequence of the Lorentzian shape distribution, because orientation parameters are negatively affected by the large weight of the tail ends of the curve. In contrast, we can find in the literature examples of superaligned CNT fibres. In these cases, orientation values in the order of high performance fibres have been obtained. In this sense, Behabtu et al. has reported values for CNT fibres as high as $\langle P_2(\cos\beta) \rangle = 0.986$ [7]. This is explained in terms of the Gaussian distribution function employed in this case. Thus, the sample is much more oriented despite its azimuthal profile shows an FWHM in the order of the values reported here ($\approx 9.5^\circ$). In order to find a physical explanation to this disagreement, it must be said that the superalignment of CNT fibres has been achieved by means of slow spinning from an acid solution of CNTs. We are of the opinion that the reason of the inherent misalignment showed by CNT fibres come directly from the direct spinning process and, more concretely, from the synthesis process. Thus, in this step both very complicated synthesis processes and a complex state of aggregation are taking place simultaneously [3]. This fact gives as a result the formation of a CNT aerogel which, up to our knowledge, remain unknown in terms of its physical properties. Therefore, according to the results shown in this chapter, the alignment of CNT fibres is mostly determined by the synthesis conditions and the role that the winding rate play has been overestimated. This conclusion supposes a dramatic change on the perspective through which the alignment problem has been usually faced. At the same time, this fact supposes a very challenging and exciting future work which involve a proper characterization of the CNT aerogel during a floating CVD reaction.

4.7 Comparative study between WAXS/SAXS and polarized Raman spectroscopy. Failure of the classical theory

As it has been shown along this chapter, the use of x-rays to measure the alignment of CNT fibres supposes many advantages. Thus, apart from the fact that the orientation distribution is directly obtained, this technique is also convenient in terms of resolution, depth of penetration and, above all, multi-scale information. However, WAXS and SAXS measurements on individual filaments requires the use of synchrotron facilities.

This is why a great effort is currently doing in developing methods to measure orientation through more standard techniques. Literature shows examples characterizing the alignment of CNT based materials by means of polarized Raman spectroscopy [78, 39]. This section deals with a comparison of ODFs determined by Raman using the established method, and those directly calculated from x-ray scattering.

In this regard, polarized Raman spectroscopy has been widely used to measure orientation of CNT based materials [78, 103, 39, 11]. For this purpose, a generalized criteria has been classically established. Thus, according to Figure 4.15 a) the fibre rotates an angle Φ from the vertical (V) to the horizontal (H) direction. This axis system define the directions at which both incident and scattered light is polarized. Thus, the nomenclature followed regarding Raman intensity is expressed as I^{is} where the superscripts i and s makes reference to the incident and scattered light, respectively. Thus, I^{VV} corresponds to when both incident and scattered light are polarized vertically. On the other hand, when the scattered light crosses polarized, it would be indicated as I^{VH} .

Accordingly, if a fibre is rotated, Raman intensity would vary with the rotation angle Φ in a way which would be dependent on the degree of alignment of the fibre. As an example, Figure 4.15 b) shows the dramatic decrease on Raman G peak when the fibre is rotated 90° in a VV polarization. At 90° , the fibre's axis is oriented normal to the polarization of the laser, and because nanotubes in this CNT fibre are mainly aligned towards the fibre's axis, these would be mainly excited perpendicular to their own axis. Therefore, due to the strong anisotropy of the tubes, scattering is significantly reduced as a result. In contrast, if the sample had consisted on CNTs randomly oriented, there should not have been any

reduction on Raman intensity. Hence, the ratio $I^{VV}(\Phi = 0^\circ)/I^{VV}(\Phi = 90^\circ)$ or, alternatively, $I^{VV}(\Phi = 0^\circ)/I^{VH}(\Phi = 0^\circ)$ provides a relative measurement of the degree of alignment of CNT-based materials. However, all the information extracted through this ratio is simply qualitative unless polarized Raman theory is used.

Fig. 4.15 a) Schematic illustration of the axis system of polarization and the definition of the rotation angle Φ formed by a CNT fibre & b) Comparison of the G peak shown by a CNT fibre placed at $\Phi = 0^\circ$ and $\Phi = 90^\circ$.

In this regard, the theory of polarized Raman used is based on the assumption that a nanotube behaves as a perfect uniaxial dipole which resonates under the Raman laser [78]. This phenomena is called antenna effect and can be described by classical electromagnetic theory. Thus, the dependence of Raman intensity with the rotation angle Φ depends on the polarization configuration used as follows

$$I^{VV}(\Phi) \propto (\cos^4\Phi - \frac{6}{7}\cos^2\Phi + \frac{3}{35}) \langle P_4(\cos\beta) \rangle + (\frac{6}{7}\cos^2\Phi - \frac{2}{7}) \langle P_2(\cos\beta) \rangle + \frac{1}{5} \quad (4.7)$$

$$I^{VH}(\Phi) \propto (-\cos^4\Phi + \cos^2\Phi - \frac{4}{35}) \langle P_4(\cos\beta) \rangle + \frac{1}{21} \langle P_2(\cos\beta) \rangle + \frac{1}{15} \quad (4.8)$$

where both expressions contain the orientation parameters $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$.

Therefore, from experimental data on the variation of intensity as a CNT fibre is rotated provides the second and the fourth order average of Legendre's polynomial. This way orientation can be indirectly measured by means of following the evolution of the G peak during the rotation of the fibre. The choice of the G peak is because often it is the most intense first-order peak from Raman spectroscopy of CNT based materials. Peaks such as D or 2D are associated to second-order transitions, which can not be explained by the classical electromagnetic theory used in this case.

Figure 4.16 shows an accurate fitting between experimental data points obtained by rotating a CNT fibre and expressions 4.7 and 4.8 corresponding to a VV and a VH polarization system. Here, it can be clearly observed how different is the evolution of the G peak depending of the optical configuration. Thus, whereas in a VV configuration Raman intensity decreases monotonically, it shows a maximum at 45° when the system follows a VH polarization. Despite both tendencies have been successfully predicted by the theory, the fact that expressions 4.7 and 4.8 imply proportionality and not equality makes necessary to normalize the intensity in order to calculate $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$. As a consequence, a numerical calculation needs to be carried out based on fitting parameters. For this purpose, only results obtained by means of a VV configuration can be considered since equation 4.8 corresponding to a VH polarization shows convergence problems (see appendix A.5 to see the details about the procedure). Finally, $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ are obtained by means of rotating the sample, following a method which hereafter will be refereed as standard.

Fig. 4.16 Results of the evolution of the G peak intensity with the rotation angle Φ and their corresponding fitting to equations 4.7 and 4.8 for VV and VH configurations respectively.

The term standard wants to differentiate this method respect to Liu's approximation. This last is presented in reference[78] and it is the most used method to calculate $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ by means of polarized Raman spectroscopy. This has been called approximation since it is not a theory by itself. Instead, it is based on equations 4.7 and 4.8 from the original theory of polarized Raman. Thus, these expressions constitute a system of equations with two unknown variables which correspond to the orientation parameters. Thus, becoming $\Phi = 0^\circ$ and $\Phi = 90^\circ$, the system can be easily solved leaving the following expressions

$$\langle P_2(\cos\beta) \rangle = \frac{3R_1 - 4R_2 + 3}{3R_1 + 8R_2 + 12}; R_1 = \frac{I^{VV}(\Phi = 0^\circ)}{I^{VH}(\Phi = 0^\circ)}; R_2 = \frac{I^{VV}(\Phi = 90^\circ)}{I^{VH}(\Phi = 90^\circ)} \quad (4.9)$$

$$\langle P_4(\cos\beta) \rangle = \frac{3(R_1 + R_2 - 6)}{3R_1 + 8R_2 + 12}; R_1 = \frac{I^{VV}(\Phi = 0^\circ)}{I^{VH}(\Phi = 0^\circ)}; R_2 = \frac{I^{VV}(\Phi = 90^\circ)}{I^{VH}(\Phi = 90^\circ)} \quad (4.10)$$

Hence, $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ can be directly obtained by means of simply measuring VV and VH Raman scattering at the two-end points of the angular distribution such as Figure 4.16 reveals. Thus, the procedure followed is considerably simplified and it would be only necessary to measure Raman spectroscopy at two angle positions, instead of rotating all the sample. Moreover, taking into account that $I^{VH}(\Phi = 90^\circ) = I^{VH}(\Phi = 0^\circ)$ and $I^{VV}(\Phi = 0^\circ) = I^{HH}(\Phi = 90^\circ)$, orientation parameters $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ can be calculated by simply obtaining Raman G peak at three polarization systems (VV, VH

and HH) without rotating the fibre. This fact leads to a much more less time consuming experiment which, moreover, allow us to obtain information about orientation from each point of the sample. Thus, orientation mapping has been carried out on CNT films using Liu's approach [11]. Accordingly, it seems logic that Liu's approximation would be used instead of the standard method.

Table 4.3 Comparison of orientation measurements $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ obtained by polarized Raman spectroscopy to those given by WAXS/SAXS analysis. Results from Raman have been obtained by means of the standard method and Liu's approximation.

		winding rate (m/min)					
		10	20	30	40	3	12
		Few-layer MWNTs				SWNTs	
$\langle P_2(\cos\beta) \rangle$	WAXS/SAXS	0.61	0.63	0.64	0.63	0.36	0.63
	Standard	0.23	0.27	0.26	0.23	0.33	0.23
	Liu	0.22	0.30	0.22	0.23	0.28	0.38
$\langle P_4(\cos\beta) \rangle$	WAXS/SAXS	0.40	0.41	0.43	0.42	0.11	0.41
	Standard	0.23	0.26	0.25	0.27	0.42	0.28
	Liu	0.02	0.10	-0.04	0.07	-0.01	0.28

Finally, with the aim of proving the validity of both the theory from the standard method and Liu's approximation; orientation parameters obtained by these techniques have been directly compared those calculated from WAXS/SAXS analysis. The results obtained have been compiled in Table 4.3 and, as it can be easily observed, none of the values obtained from any Raman technique fits to those measured by WAXS/SAXS. In fact, standard and Liu's method do not even fit each other. Thus, whereas in the case of $\langle P_2(\cos\beta) \rangle$ it can be argued that it exists a relative correspondence between values obtained from Raman, this is not the case for $\langle P_4(\cos\beta) \rangle$. In this regard, it is pretty remarkable the fact that $\langle P_4(\cos\beta) \rangle$ would be negative in some cases since this does not have any physical meaning. The reason of this disagreement is purely mathematical and it is based on a wrong assumption used by Liu and which does not apply in this case. Thus, according to Liu, scattering produced at both VV and VH configurations are equally proportional and, therefore, equations 4.7 and 4.8 can be directly divided. However, only in the case shown in Figure 4.16, intensity scattered in the VV configuration is 5 times higher than when the light is crossly polarized. Therefore, by means of applying Liu's approximation to our fibre we are establishing a wrong system of

equations based, of course, on wrong parameters. However, if we observe values given by the standard method, these do not improve in terms of approaching orientation parameters from WAXS/SAXS. Moreover, it has been shown that even using the standard method the most misaligned sample shows that $\langle P_4(\cos\beta) \rangle > \langle P_2(\cos\beta) \rangle$ which, again, does not have any physical meaning. Therefore, there is no discussion about it, the theory of polarized Raman fails when we apply it for CNT fibres.

4.8 Comparison and analysis of orientation measurements by Raman

Once it has been established the failure of Raman spectroscopy to measure orientation of CNT fibres, it seems reasonable to observe how this method works for other CNT-based materials. For this purpose, Table 4.4 compiles values of $\langle P_2(\cos\beta) \rangle$ for different CNT assemblies from the literature. Measurements here reported have been obtained by Raman and by diffraction of x-rays in some cases. A first sight confirms which have been already observed for home-made CNT fibres along this chapter. That is, the disagreement between both techniques. It is remarkable the case of the SWNT film shear aligned since, according to WAXS, it is extremely well-aligned. Nonetheless, Raman measurements reveal a much more misaligned structure. On the other hand, in the case of PvOH/SWNT fibre, the tendency is reversed. That is, Raman measurement is higher than that provided by WAXS. In this regard, attending to the results exposed in Table 4.4, it seems that Raman measurements are very dependent of some aspects regarding the morphology of the samples. Thus, we can establish some qualitative relationships.

- **CNT type** Both CNT assemblies and CNT-polymer composites which appear in the table are based on SWNTs. This is explained in terms of the fact that polarized Raman theory was exclusively developed for these type of nanotubes. This way, we assure that electronic transitions are based on well-defined Van Hove singularities and, therefore, the resonant behaviour of Raman scattering is guaranteed [128]. In this regard, the antenna behaviour seems to be an effect of the specific resonance conditions that are different for parallel and perpendicular directions and change with the photon energy [61]. Nonetheless, the antenna effect has been also measured for MWNTs using a laser wavelength of $\lambda = 514nm$ [159]. However, in this case, this behaviour is associated to

a highly anisotropic absorption of light which leads to suppress any Raman scattering perpendicular to the nanotube's axis. Anyhow, the main assumption of the Raman theory which is the antenna effect is fulfilled regardless of the type of nanotube used.

- **Light absorption** According to the table, the SWNT film shear aligned increases the orientation measurement by Raman taking into account the anisotropy of the sample in terms of light absorption. That is, the film absorbs much more light in the direction of preferential alignment than normal to it; therefore, this effect must be considered. However, despite the original value is significantly improved, this is still pretty far from the superalignment measured by WAXS analysis.
- **Aggregation** It seems that CNT assemblies show much more misaligned structures than nanocomposites. Despite a lower alignment could be expected for buckypapers, SWNT fibres and films should be highly aligned or, at least, not as poorly aligned as Raman measurements show. In the case of composite fibres, orientation values are much higher and even, in the case of PvOH, can be higher than the value provided by x-rays. In this regard, it must be pointed out that nanotubes in macroscopic assemblies are much more closely arranged into bundles than nanocomposites. Moreover, in the case of composites, it is completely ignored the effect of the polymeric matrix on the polarizability of nanotubes or CNT bundles. Therefore, according to these results, it seems that the basic antenna effect is not enough to explain the complex Raman behaviour of CNT-based materials which, at least, show a dependence of the type of arrangement.

Table 4.4 Comparison of $\langle P_2(\cos\beta) \rangle$ of different CNT-based materials according to different references from the literature. Values of $\langle P_2(\cos\beta) \rangle$ have been obtained by analysing a certain Raman peak. In some cases, the results have been obtained from WAXS analysis too. Basic information about processing conditions of different samples have been also compiled.* Value obtained after correction from anisotropic absorbance. ^L calculated using Liu's approximation. ^{Std} calculated using the Standard method.

	Processing conditions	$\langle P_2(\cos\beta) \rangle$ (Raman)	Raman peak	$\langle P_2(\cos\beta) \rangle$ (WAXS)	Ref.
SWNT film	Shear aligned films based on acid solutions of SWNTs	0.53^L (0.73)*	G peak	0.973	[49]
SWNT buckypaper	Buckypaper magnetically aligned with a 7T field	0.31^{Std}	G peak	-	[39]
SWNT buckypaper	Buckypaper magnetically aligned with a 26T field	0.37^{Std}	G peak	-	[39]
SWNT fibre	Spun from SWNT/DMF solution	0.40^{Std}	G peak	-	[42]
SWNT fibre	Spun from SWNT/DMF solution	0.41^{Std}	RBM	-	[42]
PMMA/SWNT film	Slowly spun composite of 1 wt.% SWNT in PMMA	0.70^{Std}	RBM	-	[54]
PMMA/SWNT film	Quickly spun composite of 1 wt.% SWNT in PMMA	0.89^{Std}	RBM	-	[54]
Highly strained PVA/SWNT film	Mechanically strained film made of 0.01 wt % of SWNTs in PVA	0.8^L	-	-	[157]
PVOH/SWNT fibre	10 KDa PvOH grafted SWNT	0.7^L	G peak	0.51	[74]

4.9 The depolarization effect on Raman scattering of CNT fibres

The one-dimensional nature of nanotubes plays an important role on the light-absorption properties [113, 139]. In the static limit, an electric field parallel to a nanotube axis does not induce any polarization. This can be explained by the high aspect ratio shown by nanotubes which implies that there would be a net charge only at the ends of the tubes. However, if the electric field would be applied in the perpendicular direction to the tube axis, an induced

polarization will reduce the effect of the external field [2]. This shape induced polarization leads to an anisotropic polarizability on light absorption. The essence of this fact is that in one-dimensional systems, such as in nanotubes, there is practically no absorption for polarizations perpendicular to the nanotubes axis [2, 8, 126].

This is why when nanotubes are assembled into macroscopic materials, it could be expected an anisotropy in terms of light absorption too. Thus, the absorption would be higher in the direction of preferential alignment than normal to it. Therefore, orientation measurements obtained by Raman spectroscopy can be corrected by a dichroic ratio Δ . This parameter is obtained from absorption measurements as $\frac{A_{\parallel}}{A_{\perp}}$, where $A_{\parallel}$ and $A_{\perp}$ is the absorbance parallel and perpendicular to the fibre's axis, respectively. In the case of CNT fibres, due to the high thickness ($\approx 10\mu m$), there is no any light transmission and, therefore, absorbance can not be directly measured on fibres. Instead, absorbance can be measured using a sample made of a few CNT layers on a glass substrate. Thus, the transmittance of light is assured. Nonetheless, this measurement has not been possible to be carried out for the duration of this thesis and it remains as a pending task for the future. Finally, equation 4.11 delivers the corrected Herman's orientation parameter in terms of the dichroic ratio Δ [158]

$$\langle P_2(\cos\beta) \rangle = \frac{6\Delta R_1 - 8R_2 + 3(1 + \Delta)}{6\Delta R_1 + 16R_2 + 12(1 + \Delta)}; R_1 = \frac{I^{VV}(\Phi = 0^\circ)}{I^{VH}(\Phi = 0^\circ)}; R_2 = \frac{I^{VV}(\Phi = 90^\circ)}{I^{VH}(\Phi = 90^\circ)} \quad (4.11)$$

According to this, Figure 4.17 shows the variation of $\langle P_2(\cos\beta) \rangle$ with the dichroic ratio Δ . This graph has been developed according to the experimental data obtained by one of the samples here studied (CNT fibre winded at 30 m/min from Table 4.3). Thus, the corresponding $\langle P_2(\cos\beta) \rangle$ measured by Liu's approximation (0.22) corresponds to a dichroic ratio $\Delta = 1$. Moreover, it has been also plotted the corresponding value of $\langle P_2(\cos\beta) \rangle$ obtained by WAXS analysis. According to this graph, a dichroic ratio $\Delta \approx 30$ is needed in order to explain the disagreement between WAXS and Raman. However, for a single nanotube, this ratio has been calculated to show a maximum around ~ 20 [1]. Obviously, this parameter tends to decrease dramatically for CNT assemblies. Thus, values around 1.15 [158] or 3.3 [49] have been measured for poorly and extremely well-aligned SWNT films, respectively. According to these results, it seems extremely unlikely that the anisotropy on light absorption would be the main reason of the disagreement between WAXS and Raman in terms of measuring orientation.

Fig. 4.17 Evolution of $\langle P_2(\cos\beta) \rangle$ with the dichroic ratio Δ according to equation 4.11. Experimental values corresponding to the sample wound at 30 m/min from Table 4.3 have been used. Accordingly, the value of $\langle P_2(\cos\beta) \rangle$ at $\Delta = 1$ fits to Liu's approximation. The value measured by WAXS appears for comparison purposes.

4.10 Raman scattering of CNTs from a non-resonant approach

It has been strongly reported that the orientation measurement by Raman is based on the antenna effect. This behaviour, in turn, is linked to the existence of Van Hove singularities in SWNTs. Thus, the incident laser light falls within a certain electronic transition leading to a resonant behaviour[128]. However, when this strong 1-D resonant behaviour is diminished, it is unknown how Raman scattering is affected. For this purpose, based on a theoretical study which uses the non-resonant bond polarization theory, the polarized Raman behaviour of an hypothetical (10,10) nanotube has been calculated. Furthermore, we present a small literature review regarding the failure of the antenna effect on Raman measurements of CNTs and CNT bundles.

4.10.1 Raman G peak of an armchair (10,10) nanotube

The G peak is associated to high frequency tangential modes of vibration and, therefore, it necessarily implies directly stretching of strong $sp^2 - sp^2$ carbon bonds [113]. According to the theory of Raman of nanotubes, due to both the folding of the graphite Brillouin zone and the nanotube curvature, the G band in nanotubes contains several modes with different symmetries [109]. Specifically, this peak involves the action of 6 phonon modes which are represented in terms of its symmetry as two A (A_{1g}), two double degenerate E1 (E_{1g}) and two double degenerate E2 (E_{2g}) modes. For each symmetry mode, the atomic vibrations can be along the tube axis direction, or along the circumferential direction. However, in the zigzag and armchair tubes, because of the high symmetry, only three of the six peaks can be seen in a Raman spectrum [64, 118, 62]. On the other hand, for general chiral tubes, the direction of atomic vibrations is no longer parallel or perpendicular to the C-C bonds, but rather depends on the chiral angle. [64, 62]

In order to get deeper into the study of the modes of vibration, we have used the armchair configuration as a reference. This has been done because of both vibration modes are highly simplified in this way and the only theoretical study available in this regard is based on a (10, 10) nanotube [118]. In this regard, according to the theory of Raman, the G peak is due to overlapping of 3 similar frequency modes of vibration. This appears schematically depicted in Figure 4.18 where it can be observed the relative movements of carbon atoms associated to each symmetry. According to it, the A_{1g} mode corresponds to a nodeless optical vibration in which atoms vibrate oppositely one facing each other along the circumferential direction. On the other hand, the E_{1g} mode implies also out-of-phase atomic vibrations but along the axis of the tube. Moreover, it shows 2 nodes which appear clearly depicted in the figure as red atoms. The third case corresponds to the E_{2g} symmetry which is a 4 node optical phonon in which atoms vibrate also along the circumference of the tube [117]. However, we must take into account that this configuration is only valid for armchair nanotubes. Thus, the movement of carbon atoms changes with the chiral angle, leading them to move in the opposite direction when nanotubes show a zig-zag architecture instead of armchair; that is, axial becomes circumferential and viceversa [128].

Fig. 4.18 Scheme of the 3 modes of vibration involved by the G peak from Raman spectroscopy in terms of the relative movement of carbon atoms. These are termed based on the group theory as A_{1g} , E_{1g} and E_{2g} .

Hence, for each symmetry mode schematically depicted in Figure 4.18, Saito et al [118] have calculated the polarized Raman scattering of an hypothetical (10,10) nanotube while it rotates. The schematic followed in this case agrees with the one depicted in Figure 4.15 a) for a CNT fibre but using a single nanotube instead. Figure 4.19 shows the results expressed in arbitrary units due to the intensity have been normalized such as $I^{VV}/I^{VV}(0^\circ)$. The evolution of each vibration mode delivers a very different behaviour. Due to the G peak is the result of overlapping the peaks corresponding to each frequency mode, the total scattering can be approximated as the sum of all of them $I_{\text{TOTAL}} \approx I_{A_{1g}} + I_{E_{1g}} + I_{E_{2g}}$. The corresponding curve has been plotted together with the behaviour predicted by the antenna effect $I_{\text{antenna effect}} \propto \cos^4 \Phi$ [42]. As it can be easily observed, the difference between both curves is quite clear. One of the most remarkable differences in this regard is the behaviour shown at 90° which, according to the antenna effect does not provide any scattering whereas it does using the non-resonant approach.

Fig. 4.19 Raman intensity of the phonon modes A_{1g} , E_{1g} and E_{2g} corresponding to a (10,10) nanotube. Data have been calculated for a VV polarization system in ref [118]. The total scattering has been obtained as the sum of all the scattering curves and it has been plotted together with the corresponding curve predicted by the antenna effect.

This fact points out to a more complicated Raman behaviour than that predicted by the antenna effect. In this regard, the total intensity can be calculated as

$$I \sim \sum_n |\vec{e}_s \cdot \alpha_{=n} \cdot \vec{e}_i|^2 \quad (4.12)$$

where $\alpha_{=n}$ corresponds to the polarizability tensor associated to the n^{th} phonon and $\vec{e}_i$ and $\vec{e}_s$ are the incident and scattered polarization vector, respectively. [42] In order to calculate the Raman response associated to a (10,10) nanotube and according to Figure 4.19, the effect of E_{2g} can be considered negligible in comparison with E_{1g} and A_{1g} . Therefore, for simplicity purposes, the total scattering behaviour has been associated to two polarizability tensors such as

$$\alpha_{=A_{1g}} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{bmatrix} \quad \alpha_{=E_{1g}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & p \\ 0 & p & 0 \end{bmatrix} \quad (4.13)$$

which fits with the symmetry associated to the A_{1g} and E_{1g} phonon mode, respectively. Thus, the diagonal terms a and c corresponds to the radial and axial polarizabilities associated to the A_{1g} symmetry. One special case of this symmetry mode comes when c is much higher than a and, therefore, the tube mainly behaves as an axial dipole such as the antenna effect assumes. However, we must also take into account the significant effect of the E_{1g} mode which implies an out of diagonal p term. Indeed, in the specific case of a (10,10) tube, the polarizability tensors in relative units leave as follows (see appendix A.6 for the demonstration)

$$\alpha_{=A_{1g}} = \begin{bmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \alpha_{=E_{1g}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}/2 \\ 0 & \sqrt{2}/2 & 0 \end{bmatrix} \quad (4.14)$$

where it can be easily observed that both a and p are not negligible at all and, therefore, Raman scattering is far from behaving as an antenna as it is commonly assumed.

4.10.2 Raman measurements of CNTs and CNT bundles. Failure of the antenna effect

Table 4.5 compiles some of the research works which imply polarization Raman scattering of individual nanotubes and CNT bundles. Here, it appears the ratio I^{VV}/I^{VH} measured in each case. According to the antenna effect, such as it has been just explained, the ratio 1 : 0 should be expected in all the cases. However, this has happened only when individual nanotubes or ropes of a few nanotubes have been measured. In contrast, when nanotubes appear highly aggregated in well-aligned ropes or arrays, there is intensity at cross-polarized (VH) Raman scattering. Accordingly, it seems obvious that the aggregation of nanotubes has an important effect on Raman scattering of CNT-based materials.

Table 4.5 Ratio I^{VV}/I^{VH} for individual nanotubes and bundled CNT assemblies obtained from the literature.

	I^{VV}/I^{VH} (G peak)	Ref.
Individual SWNTs	1:0	[63]
Ropes of a few SWNTs	1:0	[30]
Rope of SWNTs	1:0.20	[60]
Individual MWNT	1:0	[159]
Aligned array of MWNTs	1:0.39	[109]

Indeed, some authors point that the aggregation of nanotubes leads to the disappearance of Van Hove singularities which, in turn, are strongly associated to the 1-D behaviour of nanotubes [82]. Thus, the antenna effect which is strongly linked to the existence of well-defined electronic transitions is clearly affected. In this regard, previous measurements carried out with MWNTs have pointed out to the anisotropic light absorption as another reason for the antenna behaviour. However, as it has been developed in section 4.9, the depolarization effect is discarded as a plausible reason in this regard. Thus, a dichroic ratio as high as $\Delta \approx 30$ would be necessary in order to explain the big gap between Raman orientation measurement and that obtained by WAXS analysis. Instead, the non-resonant Raman scattering of a (10,10) nanotube has shown a much more complicated behaviour. Indeed, the Raman response is no longer due to an uniaxial vibration of the tubes but to a combined action of different phonon modes. In this regard, we are of the opinion that for strong aggregated systems such as the CNT fibre the theory needs to be revised in terms of the antenna effect assumption. For this purpose, it has become necessary the development of a fundamental research work in order to analyse the Raman response given by CNT bundles. One may expect that the aggregation would lead to the appearance of A_{1g} and E_{1g} modes and, therefore, polarizability tensors such as those appearing in equation 4.14. However, values obtained in the previous section involves the theoretical response of an armchair (10,10) nanotube. Therefore, it seems reasonable to think that the values obtained for a CNT bundle formed by the arrangement of tubes with different chiralities and diameters do not fit with those given by the theory. Nonetheless, these can be used as reference values in future experimental works involving

the effect of aggregation on Raman polarized behaviour of CNT bundles.

4.11 Summary

This chapter has been a comparative study between x-ray based techniques and Raman spectroscopy to measure orientation. The study has been focused on CNT fibres because, obviously, it is the material about this thesis treats about. However, the most of the conclusions here summarized can be extrapolated to the rest of macroscopic assemblies of CNTs, as well as CNT based composites.

Regarding the use of WAXS and SAXS to measure orientation of single filaments, the use of microfocus has been shown necessary in the first case and highly desirable in the second. Otherwise, multiple filaments fibres must be used. Nonetheless, orientation measurements of single filaments can be approximated by means of SAXS if microfocus is not available. The error in these cases is below 2% in terms of the Herman's orientation parameter ($\langle P_2(\cos\beta) \rangle$). In any case, it has been demonstrated the direct relationship existent between the anisotropy of the 002 diffraction signal from WAXS and that shown by the FF peak from SAXS. A Lorentzian type azimuthal distribution is followed in both cases. Thus, as a consequence of the high weight that end tails has on this type of distributions, an inherent misalignment comes associated to the structure of the fibre. This has been finally confirmed due to the highest $\langle P_2(\cos\beta) \rangle$ measured in this work has been 0.64, which differs significantly from the $\langle P_2(\cos\beta) \rangle = 0.986$ reported for a superaligned CNT fibre[7].

Comparing results given by x-ray scattering from CNT fibres to those obtained by polarized Raman spectroscopy it has been demonstrated that this last technique fails in this regard. The reason of this comes probably from the basics of the Raman theory, according to which orientation measurement depends on the antenna effect. However, this behaviour has been demonstrated to fail for aggregated systems. This can be explained in terms of a loss of resonant 1-D scattering behaviour. Indeed, the theoretical Raman scattering of a (10,10) nanotube calculated according to a non-resonant approach points to this fact. This is why a fundamental study which involves the behaviour of CNT bundles to Raman polarized spectroscopy should be carried out in the near future.

Regarding the manufacturing process, it has been firstly quantified the effect that winding rate has on the alignment of CNTs along the fibre's axis. The results differ depending on the parameters from the process. Moreover, even though we maintain the same parameters, a clear disagreement between different batches has been measured. Thus, whereas in the batch b) it has been shown that $\langle P_2(\cos\beta) \rangle$ increases a 20% when the winding rate passes from 20 to 40 m/min, this increase does not even reach 5% in the batch a). This fact has been associated to changes carried out on the furnace when the batch b) was manufactured. Nevertheless, it clearly points out to the need of developing a control of alignment with the manufacturing process since, as it will be explained in the next chapter, the Young's modulus shown by CNT fibres is mainly determined by their alignment.

Chapter 5

Tensile stiffness of Carbon nanotube fibres described by the Uniform Stress Model (USM)

This chapter presents a model to describe the elastic properties of macroscopic fibres of carbon nanotubes (CNTs). The core idea is to treat them as a network of CNT bundles with a tensile stiffness dependent on their alignment in terms of an orientation distribution function. This enables prediction of the tensile modulus with good agreement with experimental data for fibres produced in-house with different constituent CNTs and for different draw ratios.

The parameters extracted from the model are the shear modulus and the Young's modulus of CNT bundles. These are high compared with values for single-crystal graphite and short individual CNTs. Applying this model to different CNT fibres provides mechanical parameters of the microstructure based on the bulk tensile mechanical behaviour.

5.1 The elastoplastic mechanical behaviour of CNT fibres

Firstly, in order to develop a model to explain the mechanical behavior of CNT fibres, this last must be deeply analysed. To this aim, Figure 5.1 shows a schematic stress-strain graph in which it can be observed a classical elastoplastic mechanical behaviour. According to it, the fibre starts to stretch elastically; that is, the work necessary to deform it is stored in

terms of elastic energy and, therefore, the fibre shows a linear relationship between stress and strain. As the fibre is continuously strained, it starts to deform plastically at some point. This plasticity comes from the action of energy dissipative mechanisms and, therefore, the line shape starts to curve gradually from the initial straight line.

Fig. 5.1 Elastoplastic mechanical behaviour of a CNT fibre during tensile test.

Hence, this mechanical performance is mainly characterized by four different parameters: the Young's modulus (E), ultimate strength (σ_b)(and strain ϵ_b), fracture energy and yield point (σ_y).

The evolution of the elastoplastic behaviour from CNT fibres can be easily observed by means of a cycling test. Thus, Figure 5.2 shows the characteristic lineshape of a CNT fibre subjected to loading-unloading cycles. This graph has been obtained from reference[136]. According to it, the fibre shows an elastic and a plastic deformation after each cycle. These are related to the energy stored and dissipated during the process. Moreover, an increase in Young's modulus is observed with the number of cycles. This hardening effect is also characteristic of highly crystalline polymer fibres such as Kevlar [97] and it is associated to an ordering of fibrils induced by mechanical stretching. This fact points out to a certain parallelism

between CNT fibres and high performance fibres. Note, however, that high-performance fibres deform mainly elastically [4]. Deformation that can be thus related to the macroscopic behaviour of CNT fibres. Raman is a powerful technique that can provide information on molecular structure. The elongation of carbon bonds due to mechanical stretching lowers their vibrational frequencies. Hence, the shift of characteristic Raman modes can be used to monitor the contribution of nanotubes to the bulk tensile behaviour of CNT fibres. In particular, the 2D peak is typically used, as it shows the highest sensitivity to stress [20].

Fig. 5.2 Cyclic tensile behaviour of a CNT fibre. Graph obtained from reference[136]

In-situ mechanical tests monitored by Raman were carried out on individual CNT fibres (see section 3.5.2 for details about experimental conditions). Figure 5.3 shows a plot of the position of the 2D peak against the strain of the fibre. This curve appears together with the corresponding stress-strain curve followed by the fibre during tensile testing. Thus, according to it, the 2D peak shifts linearly to lower wavenumbers while the fibre is elastically stretched. This region is characterized by the slope $\frac{\Delta Pos_{2D}}{\Delta \epsilon}$ obtained from linear fitting of data points. In contrast, it barely changes its position when the plastic region has been reached. Thus, it can be established that the elastic region of the deformation of a CNT fibre corresponds almost exclusively to elastic deformation of CNTs. However, when plasticity comes, they do not

bear much more load. In fact, according to the graph all the strain shown by the fibre does not suppose any increase in the load state of nanotubes and, consequently, all the mechanical energy is completely dissipated. Since individual nanotubes under tensile stress show an almost perfect elastic behaviour [37], plasticity in the fibre clearly must arise from sliding of elements past each other.

Fig. 5.3 Position of Raman 2D peak with strain plotted together with the corresponding tensile behaviour of the fibre.

5.2 CNT bundles as basic load-bearing elements: the uniform stress model

In the previous section it has been explained that CNTs act as load bearing elements while the fibre is elastically stretched. However, they can not be treated as individual elements because of their stacking into close-packed bundles which, actually, can be thought as the basic structural elements into the fibre. Thus, structurally, in spite of their complex morphology, CNT fibres are mainly fibrillar due to the imperfect packing of CNT bundles. In fact, they show a yarn-like behaviour [135]. Therefore, they can be compared to high-performance fibres such as Kevlar or, obviously, carbon fibres (CF). In all these cases, fibres are described

as a network of crystallites which bear all the load the fibre is being subjected to. In this regard, we can make a direct comparison between these crystalline domains and the CNT bundles. These similarities point to the use of the uniform stress model (USM) to describe the properties of CNT fibres. This model assumes that a fibre is formed by the parallel array of identical fibrils which, in turn, are the result of assembling structural elements in series all along the fibril's length. As a result, the stress is uniformly shared among all their constituents which show a different behaviour depending on the orientation angle β . In this regard, Figure 5.4 shows the state of stresses of a schematic structural body in terms of the orientation angle β . Accordingly, the original stress along the fibre's axis (σ_f) is divided into an axial ($\sigma_f \cos^2\beta$), a normal ($\sigma_f \sin^2\beta$) and a shear contribution ($\sigma_f \cos\beta \sin\beta$).

Fig. 5.4 Illustration of the state of stresses for a structural elements into the fibre according to the uniform stress model.

Hence, the application of this model requires of a proper definition of these basic elements. Obviously, this fact is strongly dependent of the morphology shown by the material itself. Thus, whereas in polymer fibres these bodies are built by the crystalline arrangement of rigid polymer chains [14], carbon fibres (CF) show crystalline domains made by stacking of graphene sheets[98]. The difference in terms of geometry is significant because it passes of being a highly anisotropic body to become a 2-D crystal. In the case of CNT fibres, the proper definition of these elements constitutes a very delicate matter. On the one hand, we can not talk about crystalline structures because of the turbostratic arrangement of nanotubes (section 4.2.1). On the other hand, nanotubes are strong 1D materials. Nonetheless, CNTs tend to polygonize when they approach each other [116]. In fact, they can even collapse, resembling to graphene layers stacked. In this regard, Figure 5.5 shows a TEM picture taken

by one in-house fibre in which a bundle of completely flattened CNTs can be clearly observed. Obviously, the mechanical response associated to it would be dominated by Van der Waals interactions among graphite sheets, as in the case of CF. This way, a clear parallelism between CNT bundles and graphite crystalline domains is established. This fact supposes a great difference with respect to the case of anisotropic polymer chains to which nanotubes have been classically compared with. These comparisons have been usually done in terms of the high aspect ratio shown by both polymer rigid rods and CNTs. However, polymer chains are assembled by means of point by point interactions through relatively strong electrostatic forces, such as hydrogen bonds in the case of Kevlar [4] or PBO [14, 4]. In contrast, CNTs interact one to each other through graphitic surfaces.

Fig. 5.5 TEM picture of a CNT bundle corresponding to an in-house CNT fibre where a highly collapsed structure can be shown. Courtesy of Dr. Víctor Reguero.

Thus, based on the USM, Figure 5.6 shows schematically the contribution of a CNT bundle to the macroscopic fibre stretching. Firstly, CNT bundles are axially stretched and, consequently, nanotubes themselves. The second contribution is related to the misalignment of the bundle respect to the fibre's axis, initially represented as β_0 . Thus, the shear interactions between nanotubes induce an alignment of them leading to a new lower angle. However, due to this structure is associated to nanotubes stacked, the complementary angle ϕ has been used instead of β . The effect of normal strength has been considered negligible due to the well-alignment of the bundle.

Fig. 5.6 Schematic representation of the contribution of CNT bundles to the macroscopic fibre stretching: axial stretching and shear alignment.

Thus, the Young's modulus (E) of a well-aligned CNT fibre can be mathematically expressed such as [98]

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle \cos^2 \phi_0 \rangle}{g} \quad (5.1)$$

where $\langle \cos^2 \phi_0 \rangle$ represents the degree of alignment of the fibre in the unloaded state (see appendix B.1 for more information about the calculus of this parameter) and e_c and g corresponds, respectively, to the axial stiffness and the shear modulus shown by a CNT bundle.

5.3 The well-alignment criteria in the mechanical properties of CNT fibres

Finally, a mathematical expression has been obtained to explain the elastic behaviour of CNT fibres in terms of the Young's modulus of the fibre (E_f) or, best said, the compliance ($1/E_f$). However, it has been greatly specified that this model is only valid for well-aligned fibres. Nonetheless, it has not been clearly defined how much aligned must be a sample to be explained by the USM. In this regard, the uniform stress model as originally developed by Northolt and Ruland for carbon fibres was proposed to apply when $\langle \cos^2 \phi_0 \rangle \gg \langle \cos^4 \phi_0 \rangle$ [98]. Similarly, the elastic unwrinkling model developed by

Ruland [40] can lead to describe CFs by means of equation 5.1 when $\langle \sin\phi_0 \rangle \approx 1$.

Table 5.1 Evaluation of the different orientation parameter values $\langle P_2(\cos\beta) \rangle$, $\langle \cos^2\phi_0 \rangle$, $\langle \sin\phi_0 \rangle$ and $\langle \cos^4\phi_0 \rangle$ for different CNT fibres in terms of the major morphology of nanotubes and the winding rate. The Young's modulus of CNT fibres (E_f) and the ultimate tensile strength (σ_b) have been also compiled for modelling purposes.

	winding rate (m/min)	$\langle P_2(\cos\beta) \rangle$	$\langle \cos^2\phi_0 \rangle$ ($\times 10^{-2}$)	$\langle \sin\phi_0 \rangle$	$\langle \cos^4\phi_0 \rangle$ ($\times 10^{-2}$)	E_f (GPa/SG)	σ_b (GPa/SG)
Collapsed DWNTs	4	0.58	8.89	0.91	2.1	44 ± 9	1.0 ± 0.2
	8	0.57	9.7	0.90	2.3	32 ± 7	1.1 ± 0.1
	12	0.63	7.46	0.93	1.7	56 ± 8	1.3 ± 0.2
	16	0.65	5.42	0.95	1.1	31 ± 7	1.7 ± 0.3
Few-layer MWNTs	20	0.51	11.58	0.88	2.8	33 ± 8	0.7 ± 0.1
	30	0.56	10.08	0.90	2.4	38 ± 8	0.8 ± 0.1
	40	0.63	6.37	0.94	1.3	64 ± 16	1.1 ± 0.2

As the present study, a range of fibres with different degrees of alignment but nominally identical composition are prepared. In the case of CNT fibres, Table 5.1 shows different orientation parameters corresponding to different samples tested mechanically. According to it, $\langle \cos^4\phi_0 \rangle$ is at least a 76% lower than $\langle \cos^2\phi_0 \rangle$. Similarly, in the case of $\langle \sin\phi \rangle$ the lowest value correspond to 0.88. Despite these values are not equal, it establishes a clear tendency according to which both Northolt and Ruland's conditions are mostly fulfilled and, therefore, equation 5.1 should be valid. However, the sensitivity of mechanical properties to these conditions is simply unknown. In the case of CF, it has been shown that the compliance ($1/E_f$) remains linear to $\langle \cos^2\phi_0 \rangle$ values up to $\langle \cos^2\phi_0 \rangle < 0.16$ [94]. This fact makes that the condition of well alignment would be intrinsically linked to the corresponding fitting of the uniform stress model in the case of CNT fibres. In this regard, with the aim of offering a more intuitive parameter to compare alignment, $\langle P_2(\cos\beta) \rangle$ has been obtained in each case by means of using equation B.2.

5.4 The uniform stress model applied to CNT fibres

According to values compiled in Table 5.1, Figure 5.7 shows the fibre compliance ($1/E_f$) against $\langle \cos^2\phi_0 \rangle$ in order to confirm the behaviour predicted by equation 5.1. To this graph it has been added two TEM pictures showing the main morphology of CNTs forming the

structure of each fibre. Thus, despite the morphology differs greatly one respect to each other, experimental data of both samples exhibit the same linear relationship with the orientation parameter $\langle \cos^2 \phi_0 \rangle$. This is in excellent agreement with equation 5.1 and support the use of the uniform stress transfer model for oriented fibres. From this fitting, some interesting features about the mechanical properties of CNT fibres can be extracted.

Fig. 5.7 (left) Fitting of the uniform stress model to the experimental results reported for CNT fibres in Table 5.1. (right) TEM pictures showing the different types of CNTs that each CNT fibre here studied is mainly made of (courtesy of Dr. Víctor Reguero).

- Assuming a CNT fibre specific gravity of 1.8, values for $e_c \approx 540$ GPa are obtained. The CNT bundle stiffness value e_c is close to the in-plane Young's modulus of graphite ($E=1020 \pm 30$ GPa)[87] and in the range of experimental values for individual CNTs and bundles [102, 152]. Considering the spread in the fibre stiffness values, the agreement is remarkable.
- From the slope of the linear fitting it can be found that $g=8.1 \pm 1.8$ GPa. This value is above the theoretical shear modulus of single-crystal graphite ($G_{\text{graphite}}=4.6$ GPa) [91]. However, compared to CF, it can be considered a conservative value. Thus, Figure 5.8 modified from reference [94] shows values of shear modulus which ranges from 5 to 33 GPa corresponding to different carbon fibres. This spread is directly related to the crystallographic arrangement of graphite planes in the polycrystalline structure

of the fibre. Thus, an increase in $d(002)$ means an increase in the average distance between graphite layers stacked. This has been mostly associated to an increase in the concentration of crystallite defects corresponding to sp^3 - sp^3 covalent bonds between graphitic layers [94]. This is why graphite ensembles show a more rigid response under the same shear stress when $d(002)$ increases. Another explanation is given by Johnson et al. [59], according to which carbon fibres show a "ribbon-like" structure and, therefore, a network of undulating planes in which a three-dimensional interlinking is realized through twisted planes. Independently of the model chosen, the limit can be found in a perfect graphite crystal; that is, pure graphite, as it is clearly shown in the graph.

Due to this fact, a further study involving crystalline arrangement of nanotubes needs to be developed. In this regard, despite it has been extensively said that nanotubes are turbostratically assembled, there should be crystalline domains into CNT bundles. These last structures correspond to regions delimited by coherence lengths into which non defective crystalline areas are shown. In the case of carbon fibres they are easily defined by means of two crystallites sizes L_a and L_c perpendicular and parallel to c-axis respectively. These are easily obtained by means of WAXS measurements. However, it has been shown that CNT fibres made in-house show diffraction peaks corresponding to iron catalyst particles which overlap all the possible information about crystalline arrangement of CNT bundles (section 4.2.1). This is why another alternatives such as Raman are being currently studied in this regard. Following this method, a characteristic L_a value of about 2 μm were found for CNT fibres manufactured by means of the direct spinning process [12]. This is very surprising taking into account that nanotubes synthesized using this process are mm long [3]. Therefore, it seems that more than length of nanotubes, the main variable to consider in terms of mechanical properties should be the size of crystalline domains. However, fibres analysed by means of this method were submitted to an unknown purification process which could be affecting to the crystalline structure itself. Moreover, this is a very preliminary study about measuring crystalline domains by Raman. In fact, this measurement considers that crystals are delimited by the end of the tubes. However, the length of a crystalline domains is a coherence size which delimits the region into which a perfect crystalline structure can be found. Therefore, the more graphitic the material would be, the higher would be the length of the crystal. Thus, for instance, in highly purified pitch based CF this size has been measured by WAXS and it is around 60 nm [98]. This is the reason why we expect that L_a would be even much lower for CNT fibres than 2 μm . This fact becomes necessary the development of a research work about the crystallographic arrangement of nanotubes.

- Finally, fitting parameter values suppose a measurement of which has been already strongly reported in the literature. The Young's modulus of CNT fibres is mainly determined by the orientation effect. The high axial stiffness shown by CNT bundles (e_c) lead them to be mainly strained by shear driven by the shear modulus g . This is why the overall response from the macroscopic system is very sensitive to the misalignment of CNT bundles according to equation 5.1.

Moreover, a very important conclusion can be extracted from the graph. CNT fibres follow the same straight line regardless of the major morphology of nanotubes. This is very surprising due to it seems to go against the literature. Thus, many research works have reported that the load bore by a nanotube is basically carried out by the outer shell which, in fact, explains the "sword-in-sheath" failure mechanism[153]. Therefore, different relationships between fibre compliance ($1/E_f$) and orientation parameter $\langle \cos^2\phi_0 \rangle$ should be expected depending on the type of nanotubes the fibre is made of. However, the behaviour here shown seems to point out that CNT bundles behave more as monolithic hard elements in which all graphitic layers contribute equally to the mechanical behaviour of the fibre.

The explanation to this disagreement could be found on the highly collapsed structure shown by CNT bundles in this work. In this regard, Vilatela et al. [134] already pointed out to this effect as one of the causes of a higher strength in CNT bundles. Accordingly, nanotube layers completely flattened allows a better shear interaction among them. Therefore, it seems that an increase on the number of walls when nanotubes are highly collapsed means also an increase on the number of graphite layers bearing the load. However, if the number of walls increases excessively, nanotubes would not collapse and, therefore, intertube share loading would be significantly reduced. This evidence elucidates a compromise in terms of mechanical properties which can be easily shown in the fact that the highest strength ever reached by a CNT fibre correspond to those mainly made out of either double wall or few wall nanotubes [7, 106, 71, 166].

Finally, according to this study, it would be established that the well alignment criteria for the case of CNT fibres is fulfilled when $\langle \cos^2\phi_0 \rangle < 0.12$ or $\langle P_2(\cos\beta_0) \rangle > 0.49$. In the light of these results, the conclusion made in section 4.2.2 about the inherent misalignment of CNT fibres from this work needs of being carefully redefined. Thus, despite comparing the literature the orientation parameter values obtained for CNT fibres are very low, in terms of mechanical properties these are high enough to apply the uniform stress model. This fact remarks the relativity of the alignment measurement and its dependence of the physical property it varies with. Of course, the well alignment criteria has been established in this case based on experimental results and, therefore, this threshold can be modified in future works and it can be even different for other CNT assemblies made by different processes.

5.5 Comparison of results with the literature

In order to demonstrate the validity of the model, Figure 5.9 shows a comparative graph in which the results obtained from this work and its corresponding fitting to the uniform stress model are plotted together with literature data (see appendix B.2 for a discussion of the literature data). At first sight it can be easily observed that literature data fits asymmetrically to the linear relationship corresponding to the uniform stress model from this work. Thus, at lower $\langle \cos^2 \phi_0 \rangle$ the agreement is quite remarkable whereas the misfitting increases at medium-high ranges of this parameter. This fact seems to point to the lack of alignment as the main reason of this disagreement. However, it is really notable that the misfitting takes place for fibres submitted to post processing methods which directly affects either orientation or mechanical measurement.

Fig. 5.9 Compliance (E_f^{-1}) of CNT fibres plotted against the orientation parameter $\langle \cos^2 \phi_0 \rangle$ for both in-house fibres and data obtained from the literature. These last correspond to both single [133, 129, 7] and multifilament samples[45].

Thus, as it has been explained in Chapter 4, it is usual for x-ray measurements to use multifilament samples in order to increase dramatically the intensity of diffraction at the expense of a decrease on alignment measurement. This has been the approach followed by Gspann et al [45] whose values have been classified as "multifilament" in the graph from Figure 5.9. On the other hand, the Young's modulus was measured using single filament fibres. As a result, specific mechanical properties improve significantly with respect to multifilament fibres. As an example, in this work, CNT fibres mainly made of few-layer MWNTs and wound at 20 m/min suffer a decrease on stiffness from 33 GPa/SG to 8.5 GPa/SG depending if they are made of one or 20 filaments, respectively [122]. This difference in the methodology used by Gspann can be justified in terms of easily obtaining a qualitative relationship between orientation and mechanical properties. However, in this work, the correspondence between these parameters do not follow the uniform stress model.

Conclusively, results here reported seems to confirm which have been said along all the chapter; that is, equation 5.1 and, therefore, the uniform stress model is followed when both uniform stress condition and well-alignment criteria are fulfilled. This is the case of extremely well aligned single CNT fibres, which fit perfectly to the linear relationship from the graph. This fact allows to definitively claim that, when it treats of elastic properties, it is the alignment which plays the dominant role. This is why the improvement of mechanical properties needs necessarily of enhancing the alignment from the samples obtained which, in turn, implies to affect directly on the synthesis process. However, as it has been discussed in section 4.6, the effect that the direct spinning method has on orientation has been overestimated in previous works.

5.6 The use of in-situ Raman spectroscopy to measure elastic properties of CNT fibres

As it has been previously explained, the shift of the 2D Raman peak is directly related to the stretching of CNTs into the fibre. Accordingly, any change on the position of the 2D peak to lower wavenumbers corresponds to an increase on the stress state of individual nanotubes (σ_r) such as

$$|dPos_{2D}| \propto d\sigma_r \quad (5.2)$$

In this regard, it must be taking into account the finite size of the tubes. Therefore, during mechanical stretching, multiple CNT based elements act all along the gauge length. According to the USM, it has been assumed that nanotubes are disposed according to a series model. Due to only elastic properties are considered in this section, CNT bundles can be thought as spring elements. This way, a CNT fibre can be considered as a network of springs disposed all along the gauge length such as Figure 5.10 depicts. Thus, any increase on the strength applied to the overall system (σ_f) has associated an strain (ϵ_f) according to which it is defined the Young's modulus as ($E_f = \frac{\sigma_f}{\epsilon_f}$). Due to strings are connected in series, each string is subjected to the same stress σ_f , such as the USM assumes. Therefore, by means of substituting $\sigma_r = \sigma_f$ in equation 5.2, we obtain the following expression

$$\frac{|\Delta Pos2D|}{\Delta \epsilon_f} \propto \frac{\sigma_f}{\epsilon_f} = E_f \quad (5.3)$$

Fig. 5.10 Scheme of a network of spring elements disposed according to a series model.

This relationship points to an uniform stress distribution among load bearing nanotubes during elastic stretching. This assumption was successfully fulfilled according to the USM. However, results shown in Figure 5.11 reveals a slightly shift in this regard. Here, the evolution of Raman 2D peak shift per 1% of strain have been plotted in terms of the Young's modulus. This has been done for different CNT fibres and CNT films measured in this work and compiled from the literature. In addition, results corresponding to carbon fibres have been also included. This has been done in order to compare both graphene based fibres because it is well-known that CF fit accurately the criteria of uniform stress and, therefore, follows the equation 5.3. Accordingly, a linear relationship with a slope of $5 \text{ (cm}^{-1}/1\%) / \text{GPa}$ is followed in the case of CF. However, values obtained are pretty far of a single graphene layer which shows a Raman shift of 60 cm^{-1} per 1% strain [151]. Nonetheless, a 1TPa

stiffness would be also expected in this last case. According to the USM, this disagreement comes from the misalignment of graphite crystallites respect to the fibre's axis. Thus, for a fibre perfectly aligned $\langle \cos^2 \phi_0 \rangle = 0$, the Raman shift would be close to that shown by a single graphene layer. According to Figure 5.11 and considering the large error bars associated to CF, the linear relationship obtained by Copper et al. in ref [18] seems to point to this fact. However, regarding CNT fibres, we can not say that they follow this behaviour. Firstly, values obtained are far below those measured for CF. Moreover, there is a significant scattering among the few data points available in the literature (onset from Figure 5.10). This is why data points corresponding to CNT fibres have been fitted to another linear relationship. However, nothing can be assumed from this poorly fitted behaviour. Nonetheless, a previous research work involving individual CNTs points to a more complicated Raman behaviour than CF. Thus, a Raman shifts of 37.5 cm^{-1} per 1% strain has been reported when a SWNT is tensile tested [20]. This value is pretty far of that measured for a single graphene layer. Moreover, the results obtained for nanotubes show a high spread because of variables such as their chirality or diameter among others. Nevertheless, the USM has been successfully fitted in the previous sections of this chapter and it would remain considered in the absence of a clear Raman response which would point to another behaviour.

Fig. 5.11 Variation of Raman shift/tensile strain with the Young's modulus of CNT fibres, CNT films and carbon fibres (CF). Data corresponding to CNT fibres were both measured in this research and reported in references [133, 80, 76]. Data of CF are originally reported in [18]. The Raman shift for a single graphene layer is reported in ref [151].

The evolution of the 2D peak during tensile testing does not only involve a shift but also an asymmetrical broadening. This fact is depicted in Figure 5.12 where it appears the 2D peak for unstrained and maximum strained position. Each peak has been fitted to two Voigt functions. This is explained in terms of the asymmetry of the peak towards lower wavenumbers. The fact that this asymmetry appears in the unloaded state reveals the compositional nature of this behaviour. However, this asymmetric shape increases as the fibre is continuously strained. This effect has not been ever reported for individual nanotubes; however, it is commonly observed in CNT macrostructures [80] and composites[92] under axial loading. This is the reason why it has been commonly associated to an inhomogeneous state of stresses among load bearing nanotubes. Thus, plasticity in CNT-based materials comes from nanotube

bundles breaking during mechanical stretching. As a result, remaining nanotubes must bear the excess of the load. This fact leads the 2D peak to show a slightly smoother tail at lower wavenumbers due to the contribution of overstressed nanotubes.

Fig. 5.12 2D peak for unstrained and maximum strained CNT fibre during mechanical testing. Each peak has been fitted to two Voigt functions because of the assymetry of the peak.

A detailed analysis about the asymmetrical broadening of the 2D peak in a CNT fibre has been plotted in Figure 5.13 a). Here, the ratio of the FWHM at the left and at the right of the Raman position has been plotted together with the Raman peak shift. Thus, the left ratio is defined as $\frac{FWHM_{left}}{FWHM}$ and the right ratio as $\frac{FWHM_{right}}{FWHM}$, according to the schematic peak shown in Figure 5.13 b). The results reveal quite clearly that the asymmetry of the peak increases mainly during the elastic regime to remain almost fixed when the plasticity is reached. This fact supposes an argument against the idea that relates the asymmetry of the 2D peak to an inhomogeneous stress distribution due to the breakage of CNT bundles. Instead, the asymmetry increases while nanotubes are being elastically stretched. In this regard, Cui et al. monitored the Raman response of individual DWNTs and SWNTs embedded into a polymeric matrix [21]. Their results clearly demonstrates that the asymmetry of this peak appears when the tube show several graphitic layers. This fact is in agreement with graphite and graphene Raman spectra where the shape of the 2D peak has been shown to be very sensitive to the number of layers [81]. According to Cui et al., the 2D peak shown by a

DWNT can be deconvoluted in two peaks associated to the internal and the external layer. In this study, almost all the shift shown by the 2D peak is due to the action of the external layer. This has been associated to the poor stress transference between CNT walls which makes that the external layer bear all the load. However, in the case of CNT fibres, the results delivered by the USM points to a collaborative action of all nanotubes. Moreover, the tendency followed by DWNTs in ref [21] would deliver an asymmetry towards higher wavenumbers, in contrast to the results here shown.

Fig. 5.13 a) Evolution of the position of the 2D peak with tensile strain plotted together with the left and right ratio associated to the FWHM. b) Schematic peak which illustrate the separation of the FWHM by the position of the maximum.

Hence, some questions regarding the Raman response of a CNT fibre while it is stretched remain open. Thus, both Raman shift and the asymmetric broadening of the 2D peak involve the elastic region and, consequently, are due to direct stretching of nanotubes. However, there is nothing clear about the source of this behaviour. This is why a further study focused on establishing a clear relationship between Raman shift and Young's modulus is needed. Furthermore, a more fundamental research work which involves the source of the asymmetry of the 2D peak and the explanation of the asymmetrical broadening with the stress is also needed.

5.7 Summary

A model has been successfully developed for the elastic stretching of CNT fibres. According to it the CNT fibres can be thought as an array of well aligned CNT bundles which act as the basic load-bearing elements. These last contribute to the extension of the overall assembly by both axial stretching and rotation by shear. The results here shown point to the main role of alignment over the rest of features regarding the morphology of the fibre. However, this has been enclosed on the assumption of well alignment which has been established in terms of the experimental results as $\langle P_2(\cos\beta) \rangle > 0.49$.

By means of this model, a powerful characterization tool has been also obtained. Thus, by means of the fitting to the uniform stress model it has been predicted values for the Young's modulus and the shear modulus of $e_c \approx 540$ GPa and $g = 8.1 \pm 1.8$ GPa respectively. Despite the first value is in agreement with the literature, the shear modulus is found really high comparing to pure graphite. On the other hand, this parameter is in the order of those reported for carbon fibres which were explained in terms of the interlocking effect produced by defects and edges among graphitic planes following a wide distribution of inter layers spacing.

Finally, the stiffness shown by well aligned CNT assemblies can be predicted by simply measuring their orientation. Furthermore, the fact that the shear modulus and the Young's modulus of CNT bundles can be obtained through this model allows to develop characterization studies which involve the role of the interaction between nanotubes into bundles. Thus, quantitative studies about the role of functionalization and cross-linking among nanotubes can be done in a simple manner following this approach.

There are some questions about the Raman behaviour of CNT fibres during tensile stretching which remain open. These are related to the elastic stretching of nanotubes and its effect on both the asymmetrical broadening of the 2D peak and the relationship between Raman shift and Young's modulus. Due to the lack of research works in this field it has been not possible to solve these feature which need of a more fundamental research.

Chapter 6

Plasticity in CNT fibres: microstructural evolution and a novel Weibull-based mechanical model

In this chapter, the effect of plasticity on the morphology of CNT fibres has been studied. This has been done by means of in-situ SAXS/WAXS and Raman experiments. The results obtained have revealed a progressive failure of CNT bundles based on a Weibull distribution. This fact goes against the classical polymeric fibres theory which was used in order to explain elastic stretching of CNT fibres. Nonetheless, when plasticity is considered, another route must be followed. To this aim, the alignment of CNT bundles has been studied by means of modified stress-strain curves obtained by SAXS/WAXS and the 2D peak from Raman spectroscopy has directly revealed the progressive failure of CNT bundles. As a result, a novel mechanical model able to provide important micromechanical parameters has been developed.

6.1 The theory of polymeric fibres applied to tensile stretching of CNT fibres

So far, we have successfully applied the theory of carbon fibres to explain the mechanical behaviour of CNT fibres in the elastic regime. It must be remarked that this theory was originally developed for polymer fibres. Nonetheless, the different geometries of crystalline

domains in each case led to reformulate the expressions. However, the physical assumptions involved in each case are exactly the same. These are: tensile stress is uniformly shared among basic load-bearing elements which can be both axially stretched and shear aligned towards the fibre's axis. In the case of CNT fibres, the theory resulted of applying these assumptions have been fitted quite accurately to experimental results involving Young's modulus. Nonetheless, it is not clear how this model would fit when plasticity comes into consideration. In order to assess it, we will study the effect of plasticity on the morphology of polymer fibres and its relationship with CNT fibres.

6.1.1 The effect of plastic rotation on $\langle \cos^2 \phi_0 \rangle$

According to the USM, CNT bundles are aligned by shear forces towards the fibre's axis. This effect is compiled in equation 5.1 in terms of a shear modulus g . This parameter relates the shear stress and the angular deformation of CNT bundles. However, this relationship does not seem as obvious in terms of the tensile stress σ . In this regard, according to the continuum mechanics theory, Northolt [93] obtained the following expression

$$\langle \cos^2 \phi \rangle = \langle \cos^2 \phi_0 \rangle \exp(-\sigma/g); \quad (6.1)$$

where the alignment parameter $\langle \cos^2 \phi \rangle$ decreases exponentially with the stress applied driven by the shear modulus g . Regarding CNT fibres, this expression would describe the elastic rotation of CNT bundles. The importance of this equation arises from the fact that it is obtained by applying the equilibrium of forces to CNT bundles. Therefore, it can be used as long as we assume that the tensile stress of a CNT fibre is counterbalanced by internal stresses. Due to the fact that viscoelastic behaviour of CNT fibres is not studied in this thesis and, therefore, the effect of strain rate is not involved, we must assume that this condition is always fulfilled.

However, as it has just been mentioned, equation 6.1 is limited to the elastic stretching of CNT fibres. Therefore, in terms of plasticity, there is no reason why this relationship should be fulfilled. Nonetheless, regarding polymer fibres, in order to phenomenologically include the effect of plasticity on the alignment of the fibres, a new parameter g_v simply replaces shear modulus g [96]. As a result, equation 6.1 reads as follows

$$\langle \cos^2 \phi \rangle = \langle \cos^2 \phi_0 \rangle \exp(-\sigma/g_v) \quad (6.2)$$

Accordingly, equation 6.2 explains what is known as plastic rotation. Thus, the parameter g_v can be thought as a kind of secant modulus on shear which fulfils that $g_v = g$ for a perfect elastic behaviour. Therefore, the lower the value of g_v , the higher the plastic rotation and, consequently, the higher the importance of plasticity on the mechanical behaviour. Hence, it is always fulfilled that $g_v \leq g$. Moreover, it must be remarked that this parameter is not related to any specific plastic mechanism. This fact allows to use the same concept for fibres which show a highly complex plastic deformation such as PET [149] and almost pure elastic fibres such as PpTA (Kevlar ®) [96].

Thus, combining equation 5.1 which relates elastic properties and alignment in terms of $\langle \cos^2 \phi_0 \rangle$ and equation 6.2 which explains the evolution of alignment as a result of plastic rotation, we obtain a general expression such as this

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\langle \cos^2 \phi \rangle}{g} \exp(\sigma/g_v) \quad (6.3)$$

where $\langle \cos^2 \phi \rangle$ represents the alignment of nanotubes along all the tensile curve. This way, the alignment just before failure $\langle \cos^2 \phi_b \rangle$ can be obtained by means of this expression. This fact is extremely important due to a direct relationship between the final stress of a fibre (σ_b) and its Young's modulus (E_f) can be finally established using an appropriate failure criterion.

6.1.2 Relationship between ultimate stress and orientation: a fibrillar fracture model based on the Tsai-Hill criterion

In terms of failure mechanisms, it is a well-known fact that the weakness of the interface among nanotubes lead them to fail by shear. Scaling up to a highly entangled network such as the CNT fibre, this fact necessarily leads to a fibrillar fracture mechanism. Indeed, Figure 6.1 shows a SEM picture in which an extensive shear-induced decohesion between CNT bundles is observed in the fracture surface.

Fig. 6.1 SEM image of the fracture surface of a CNT fibre in which a fibrillar morphology is revealed.

This is the main reason why a CNT fibre can be compared with a fibre reinforced composite. Thus, a composite is made of reinforcing uniaxial elements assembled by a continuum matrix. Similarly, a CNT fibre can be thought as an assembly of stiff CNT-based elements embedded in a matrix of secondary bonds. Nonetheless, this comparison allows only a fibrillar type failure, which does not always happen in the case of composites. Instead, the failure mechanism in laminate composites depends on the fibre angle.

The Tsai-Hill model is a failure criterion classically applied to unidirectional composites [96]. According to it, the ultimate strength (σ_{comp}) reached by a composite varies with the fibre angle with respect to the load direction (θ) in the following way

$$\sigma_{\text{comp}} = \left[\frac{\cos^4 \theta}{\sigma_L^2} + \left(\frac{1}{\tau_b^2} - \frac{1}{\sigma_L^2} \right) \sin^2 \theta \cos^2 \theta + \frac{\sin^4 \theta}{\sigma_T^2} \right]^{-\frac{1}{2}} \quad (6.4)$$

where σ_L is the axial strength of the fibres, σ_T is the strength normal to the composite's symmetry axis and τ_b is the critical shear strength in a plane parallel to the fibres [53]. Therefore, the Tsai-Hill model constitutes a failure envelope which involves three different failure mechanisms in terms of the mechanical parameters σ_L , σ_T and τ_b .

Nonetheless, such a model can be easily applied to CNT fibres taking some concepts into consideration. Firstly, CNT fibres do not show a single orientation angle θ ; instead, nanotubes follow an orientation distribution function ($\Psi(\theta)$) (Chapter 4). This is why the average angle between the axial loading direction and load bearing elements $\langle \cos^2 \phi_b \rangle$ is obtained from the ODF at fracture ($\Psi(\phi_b)$), noting that $\phi = \frac{\pi}{2} - \theta$. Moreover, for highly aligned fibres the

transverse properties are negligible and the last term in 4 can be neglected. Finally, fibre tensile strength can be approximated by

$$\sigma_b \approx \left[\frac{\langle \sin^4 \phi_b \rangle}{\sigma_L^2} + \left(\frac{1}{\tau_b^2} - \frac{1}{\sigma_L^2} \right) \langle \cos^2 \phi_b \sin^2 \phi_b \rangle \right]^{-\frac{1}{2}} \quad (6.5)$$

where the trigonometric expressions used have been adapted to the complementary angle ϕ in terms of the equality $\sin \phi = \cos \theta$ and viceversa. This expression contains two unknown parameters: the critical axial CNT bundle strength (σ_L) and the critical shear strength (τ_b). In a macrocomposite the fibres are continuous and σ_L is simply the strength of fibres. But in the case of a CNT fibre visualised as a composite, its constituent CNTs are of finite length, which implies that load is transferred from one CNT bundle to another through shear. Shear stress arising at the end of an element can, upon exceeding a limiting stress τ_b , cause debonding from its nearest neighbours. σ_L is thus the maximum axial stress in the CNT bundle before shear failure. σ_L is clearly then dependent on the shear strength τ_b . In this regard, Yoon [150] derived an expression for polymer fibres of very long chains and failure in shear, which relates these two parameters with the crystallite elastic constants e_c and g . Applied to CNT fibres it leads to

$$\sigma_L = 1.14 \cdot \tau_b \cdot \sqrt{\frac{e_c}{g}}, \quad (6.6)$$

Implicit in the model discussed above is the view that CNT fibres are treated as a network of CNT bundles, corresponding to long crystalline domains. Failure occurs through shearing of CNT bundles, leading to fibrillar fracture before any CNT rupture occurs. The network is a continuum of crystalline domains and there is no reason to expect that all ends of CNTs in a domain match and hence that a bundle terminates abruptly. Instead, the 1-mm long CNTs can easily form part of several crystalline domains, very much in the same way polymer chains do.

6.1.3 Preliminary results. An explanation of the potential of plastic and failure criteria to explain the mechanical behaviour of CNT fibres

Hence, based on the theory of polymer fibres, CNT bundles are continuously aligned towards the fibre's axis by plastic rotation according to equation 6.2. This way, the fibre is continuously aligned until a critical degree of alignment is reached: $\langle \cos^2 \phi_b \rangle$. The modified Tsai-Hill failure criterion expressed in equation 6.5 establishes a direct relationship between alignment and ultimate stress σ_b . Thus, taking into account some trigonometric approximations, a single equation able to relate Young's modulus and ultimate strength can be obtained by means of combining equation 6.3 and 6.5 (see appendix C.1 for the mathematical deduction of the equation).

$$\frac{1}{E_f} = \frac{1}{e_c} + \frac{\exp(\frac{\sigma_b}{g_v})}{g} \cdot \frac{(3 \sigma_L^{-2} - \tau_b^{-2}) + \sqrt{(\tau_b^{-2} - 3 \sigma_L^{-2})^2 - 4 (4 \sigma_L^{-2} - 2 \tau_b^{-2}) (\sigma_L^{-2} - \sigma_b^{-2})}}{2 (4 \sigma_L^{-2} - 2 \tau_b^{-2})} \quad (6.7)$$

Equation 6.7 can be considered a relevant step forward in terms of modelling. Thus, this formula relates macroscopic properties (E_f , σ_b) with micromechanical parameters (σ_L , τ_b , e_c , g). Moreover, no orientation measurement is involved in it, even though the effect of alignment is implicit in the formula. Despite equation 6.7 might seem complicated at first sight, it can be analytically solved. This fact enables the calculus of micro-mechanical parameters such as τ_b or g_v using experimental results. For this purpose, the statistical study carried out from home-made CNT fibres and compiled in Table 5.1 (section 5.3) have been used. According to it, Figure 6.2 shows the tensile strength plotted against the Young's modulus of different CNT fibres. In this case, in contrast to what happened with elastic properties, it seems obvious that the morphology of the tubes plays an important role. In order to obtain a quantitative confirmation of this fact, both series of CNT fibres have been fitted to equation 6.7. Due to it is already known that $e_c \approx 540 \text{ GPa}$ and $g = 8.1 \pm 1.8 \text{ GPa}$ from section 5.3 and σ_L is related to τ_b by equation 6.6, τ_b and g_v are the free parameters to fit. According to Figure 6.2, equation 6.7 fits successfully in both cases and, considering 1.8 as specific gravity of the tubes, Table 6.1 compiles extensive micromechanical parameters derived from fitting.

Fig. 6.2 Graph of tensile strength against tensile stiffness for different CNT fibres in terms of the major morphology of the tubes. These home-made samples are part of the statistical mechanical study already shown in section 5.3 and compiled in Table 5.1. The modified Tsai-Hill based failure criterion which is expressed in equation 6.7 fits accurately in both cases (dashed-lines). This model enables to fit parameters τ_b and g_v which define maximum shear strength and shear stiffness of the CNT bundles, respectively.

Table 6.1 Parameters τ_b and g_v determined with the fibrillar model.

	τ_b (MPa)	g_v (GPa)	g_v/g	σ_L (GPa)
Collapsed DWNTs	450	2.1	0.26	5
Few-wall MWNTs	270	1.1	0.12	2.5

Results from Table 6.1 confirms some successes of the mechanical model. Firstly, the micromechanical parameters obtained are in agreement with macroscopic mechanical results. Thus, both τ_b and g_v are higher in the case of fibres mainly made by collapsed DWNTs which, in turn, show much better mechanical properties. Accordingly, collapsed tubes improve surface interactions and, therefore, the maximum shear stress increases as a result [134]. Moreover, the small values of g_v compared to $g = 8.1 \text{ GPa}$ reflects the importance that plasticity has on CNT fibres. In fact, this parameter barely reaches a 12 % of the shear modulus in the case of few-wall MWNTs. In order to offer a more intuitive point of view about mechanical properties, σ_L has been also presented in Table 6.1. As it has been already

mentioned, this is not a direct parameter and it is obtained from equation 6.6. Nonetheless, it offers a more intuitive perspective regarding mechanical properties. Thus, σ_L can be thought as the ultimate strength of a CNT fibre ideally aligned along the fibre's axis; that is, $\sigma_L = \sigma_b : \langle \cos^2 \phi \rangle \rightarrow 0$. Therefore, this parameter offers a direct idea about the potential of CNT fibres in terms of mechanical properties. Attending to this fact, it seems clear that by changing the morphology of the tubes and by achieving a more collapsed structure, the mechanical properties may double with respect to a slightly collapsed morphology.

So far, the comparison made has consisted on establishing the agreements between the values obtained and the morphology of the fibres. However, if the model wants to be confirmed, absolute values must be compared to experimental results. In this regard, τ_b appears as the most convenient parameter because it has been extensively measured and calculated in the literature. In Table 2.3 from section 2.4 a compilation about some of the most relevant research works carried out in this field has been presented. According to this, the lowest value here reported is 4 times greater than the highest value found in the literature; which corresponds to the value $\tau_b = 69 \text{ MPa}$ reported by Suekane et al. [125]. On the other hand, regarding polymeric fibres, values here obtained are in the range of some high performance materials such as PpTA (Kevlar) or PBO [96]. This seems to go against the clear disagreement existent between them in terms of failure and plastic behaviour. Thus, the fracture in polymer fibres is mainly brittle because the single source of plasticity comes from breaking interchain bonds. This fact commonly leads to a significant stress concentration and a rapid failure. Moreover, this molecular-scale fracture takes place in a single section of the fibre whereas in CNT fibres other morphology micromechanisms occur leading to a collaborative behaviour and additional plastic deformation. Thus, the importance of plasticity in CNT fibres is quite remarkable and, consequently, its fracture can not be considered as brittle. Therefore, the application of the Tsai-Hill model classically used as failure criteria for brittle composite laminates is on doubt. Moreover, as it will be shown in the following sections, SAXS/WAXS measurements deliver another behaviour for mechanical alignment than that pointed out by plastic rotation. These are the reasons why the theory of polymer fibres does not apply in terms of explaining plasticity on CNT fibres and, therefore, an specific model must be developed in this regard.

6.2 In-situ SAXS/WAXS of a CNT fibre tensile stretched.

The elastoplastic shear alignment of nanotubes

The already mentioned failure of the polymer fibres theory lead us to think that new morphological features are involved during tensile stretching of CNT fibres. Regarding orientation, by means of WAXS/SAXS technique we are able to monitor the evolution of the ODF while the fibre is strained. According to the USM, CNT bundles will align themselves towards the fibre's axis leading to a narrower ODF and, therefore, a smaller $\langle \cos^2 \phi \rangle$. In this regard, Northolt's expression for elastic rotation establishes an exponential decaying relationship during elastic stretching. According to it and considering low stresses we can group some terms into the original equation 6.1 in order to obtain the following expression

$$\frac{\langle \cos^2 \phi_0 \rangle}{\langle \cos^2 \phi \rangle} = \exp(\sigma/g) \approx 1 + \frac{\sigma}{g} \quad (6.8)$$

From where, it results trivial that

$$\sigma = g U \quad (6.9)$$

where $U = (\frac{\langle \cos^2 \phi_0 \rangle}{\langle \cos^2 \phi \rangle} - 1)$ has no units and can be considered as the strain due to alignment. That is, the strain along the fibre's axis only due to reorientation of nanotubes towards this axis. This way, it is not difficult to establish a direct comparison between equation 6.9 and Hooke's law for tensile tests.

Fig. 6.3 Graph of tensile strength against the alignment strain $U = \frac{\langle \cos^2 \phi_0 \rangle}{\langle \cos^2 \phi \rangle} - 1$. Orientation measurements have been carried out by means of both WAXS and SAXS. Due to the fibre started to be unfocused during the experiment, two type of measurements were carried out at two different positions separated $100\mu m$ one to each other along the fibre.

Accordingly, Figure 6.3 shows which has been called a shear alignment curve. Here, the stress of a CNT fibre during an in-situ tensile test is plotted against the strain by alignment U . With the aim of measuring this last parameter, both x-ray scattering techniques WAXS and SAXS were used. For this purpose, the use of microfocus was necessary. Thus, the procedure followed to this aim is explained in detail in Chapter 4. In this regard, the first feature to remark from the graph is the accurate agreement between WAXS and SAXS data points. Nonetheless, it is also worth mentioning the existence of two types of data points obtained at different positions placed $100\mu m$ far from each other. This was done because the fibre was out of focus during mechanical measurement due to a slightly displacement of it respect to the x-ray beam. In that moment the problem was solved moving horizontally the

holder of the tensile testing machine. According to Vilatela et al., there should not be any significant difference along the fibre length in terms of x-ray scattering [133] and, in fact, the results here shown seems to confirm this argument.

Moreover, Figure 6.3 reveals the existence of two regions regarding mechanical alignment. Firstly, stress increases linearly with U such as equation 6.9 predicts. Therefore, this region corresponds to the elastic rotation of CNT bundles. This seems logical because, as it was already said, Northolt's expression is based on the general theory of continuum mechanics and, therefore, it must be valid for any system which fulfils the USM. In this regard, the linear fitting developed in Figure 6.3 delivers a shear modulus $g = 3.3\text{GPa}$. This value is much below the reference value of $g = 8.1\text{GPa}$ obtained by applying the USM in section 5.4. The reasons of this fact are mostly likely related to the nature of the experiments carried out in each case. Thus, when the USM was applied, the Young's modulus was statistically obtained by means of standard tensile tests. On the other hand, the graph here presented is the result of testing a CNT fibre by means of a stepwise process. Thus, the fibre is strained until a certain strain or force value to be remained in that position while SAXS and WAXS measurements are carried out (see section 3.5.2 for all the experimental details). All these facts make that both cases are simply not comparable between them in terms of the values obtained. Furthermore, just after elastic rotation, the alignment rate increases dramatically without any significant increase on the stress. This behaviour differs greatly from the plastic rotation shown by polymer fibres. Instead, an elastoplastic mechanical alignment is followed.

This evidence implies a clear breakthrough in the study of relations between morphology and mechanical properties of CNT fibres. Thus, the elastoplastic tensile behaviour shown by CNT fibres is also observed in the alignment of nanotubes. Therefore, the physical mechanisms involved during tensile testing of a fibre have a direct effect on the reorientation of nanotubes. This fact allows us to study plasticity, as well as elasticity, by means of monitoring the alignment of nanotubes by tensile stretching such as Figure 6.3.

6.3 Analysis and characterization of the elastoplastic behaviour of CNT fibres by means of shear alignment curves

The previous section hints a clear evidence of the elastoplastic alignment of nanotubes inside CNT fibres. However, the experimental conditions to carry out this measurement were very exceptional. Thus, for instance, the use of microfocus was necessary. However, this feature has not been always available for the duration of this thesis. Instead, standard synchrotron facilities have been used in the most of the cases. However, counterintuitive as it may seem, this set-up provides better results in terms of analysis. The focus used is 5 times bigger than fibre's diameter ($\sim 10\mu m$). This way, results obtained corresponds to a larger integrated value than those obtained using microfocus which delivers a beam with a size comparable to the fibre's diameter. This is the reason why the fibre was out of focus during tensile stretching and the results from Figure 6.3 corresponds to two different positions along the fibre. Moreover, according to the low- q values approximation (section 4.5.3), orientation of well-aligned CNT fibres can be directly measured by SAXS analysis. Therefore, there is no need of WAXS in this regard. Hence, the elastoplastic alignment of CNT fibres can be analyzed by means of in-situ SAXS measurements only.

Fig. 6.4 Shear alignment curves obtained by in-situ SAXS mechanical tests of three CNT fibres wound at different rates. An increase of mechanical properties with the winding rate can be observed, including the elastic shear modulus (G_0).

In this regard, Figure 6.4 shows three curves corresponding to the shear alignment of nanotubes into CNT fibres in terms of their winding rate. These samples correspond to those already classified as few-wall MWNTs because of the main morphology of the tubes into the fibre's structure (see section 3.1 for the experimental conditions of synthesis). As a consequence of measuring a higher integrated volume, the results obtained are less sensitive to movements of the fibre during the experiment and, therefore, the curves are smoother than in the graph from Figure 6.3. As it can be easily observed, the mechanical behaviour regarding alignment improves with the winding rate. In this regard, it must be highlighted the increase of the elastic shear modulus; here denoted as G_0 . The use of the term elastic to define the shear modulus can be redundant since, by definition, the shear modulus always implies elasticity. However, in this chapter the concept of shear modulus is applied to the tangent modulus at each point along the curve. Thus, $G = \frac{d\sigma}{dU}$ for a continuous and differentiable curve. However, due to the fact that the tensile curve is the result of a stepwise experiment, the shear modulus is approximated as $G = \frac{\Delta\sigma}{\Delta U}$, such as in Figure 6.4. Thus, G_0 corresponds to the first derivative of the curve at $\sigma = 0$. The increase of G_0 values with the winding rate seems to go against the USM (section 5.2) which assumes that CNT bundles show the same shear modulus. However, we will see that a higher alignment implies also a change on the

morphology of the fibre in terms of the overlap length and, consequently, shear interaction between nanotubes.

6.3.1 The progressive sliding of CNT bundles in terms of a Weibull shear modulus distribution

Figure 6.5 shows a comparative graph where we have plotted together the shear alignment curve followed by both an ideal CNT bundle and a CNT fibre. According to the USM, a CNT bundle is tensile aligned toward the fibre's axis driven by the shear modulus G_0 . Finally, the bundle fails through the interface when a critical shear stress is reached. From this moment, nanotubes slide one to each other following a perfect plastic behaviour. That is, no extra energy is needed to stretch the bundle and, consequently, align it. As a result, a perfect elastoplastic shear alignment curve is obtained. However, this sharp transition is not observed in real shear alignment curves such as Figure 6.5 shows. Instead, a much smoother transition between the elastic and plastic region is observed. Indeed, the morphology of the fibre is quite complex and it involves a network of CNT bundles oriented according to a certain ODF. Therefore, it seems obvious that bundles into the fibre structure would not slide at the same stress all together but they would show a progressive failure. Thus, CNT bundles would slide with the increase of stresses and, consequently, the resistance of the fibre to be aligned would decrease leading to a lower shear modulus as a result. This way, the shear modulus appears as the physical parameter in which the contribution of all active elements in the alignment of CNT fibres is invalid.

Fig. 6.5 Shear alignment curve of a CNT fibre plotted together with the schematic behaviour shown by a single CNT bundle.

In this regard, according to the theoretical behaviour of a CNT bundle, a complete drop of the shear modulus occurs when plasticity is reached. It should be mentioned that plasticity does not imply mechanical failure. Nonetheless, in this region, all the work necessary to stretch the fibre is completely dissipated by nanotubes sliding. As a result, when a critical shear stress τ_b is reached and a CNT bundle enters in plasticity, the shear modulus drops from G_0 to zero. As we are working with axial stresses, σ_b is defined instead. These concepts are graphically represented in Figure 6.6 a) where it can be observed by the dashed line the ideal behaviour followed by a CNT bundle. Thus, the normalized tangent shear modulus G/G_0 drops from 1 to 0 at the critical stress σ_b . Nonetheless, this transition is less sharp when it corresponds to a CNT fibre. Indeed, data points have been successfully fitted to a Weibull type distribution function, such as Figure 6.6 a) depicts. Accordingly, the probability of not failure or success (P_s), where "failure" just means sliding of nanotubes, shows an exponential decaying behaviour with the stress σ such as

$$P_f = 1 - P_s = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_{0b}}\right)^m\right] \quad (6.10)$$

in which m is usually called "Weibull modulus or shape factor" and σ_{0b} is the scale factor for the bundle failure strength. [142].

Fig. 6.6 a) Normalized shear modulus of a CNT fibre in terms of the tensile stress. The experimental data have been successfully fitted to a Weibull distribution. The ideal behaviour of a single CNT bundle which starts to slide plastically at a sharp threshold σ_b has been also plotted as a dashed line. b) Weibull plot corresponding the experimental data from the left which fits accurately to a linear relationship. The slope of this fitting provides the Weibull modulus m .

Among all the parameters, the Weibull modulus is extremely important in order to characterize the strength distribution of the fibre. Thus, if the value of m is large, stresses even slightly below the normalising value σ_{0b} would lead to a low probability of failure. On the other hand, a low Weibull modulus would introduce much more uncertainty about the strength of a fibre. A limit example can be found on the ideal sharp behaviour of the CNT bundle from Figure 6.6 a). In this case, $m \rightarrow \infty$ due to the failure probability in this case is a Dirac δ function centred at the stress σ_b . In order to determine the value of the modulus from experimental results, Figure 6.6 b) shows the so called Weibull plot. In these graphs, experimental results which follow a Weibull type distribution can be successfully fitted to a linear relationship. This is explained attending to the following expression obtained by rearranging terms from equation 6.10

$$\text{Ln}\left[\text{Ln}\left(\frac{1}{P_s}\right)\right] = \text{Ln}(L) - \text{Ln}(L_0) + m \text{Ln}(\sigma) - m \text{Ln}(\sigma_0) \quad (6.11)$$

Accordingly, the slope of the straight line in a Weibull plot corresponds to the modulus m . In this regard, Figure 6.6 b) shows the accurate fitting of experimental results from the left to a straight line from which the slope m can be easily obtained. Thus, experimental results from Figure 6.6 a) have been directly fitted to equation 6.10 taking into account previously determined modulus and leaving σ_{0b} as a free parameter. This way, both Weibull parameters can be obtained from a shear alignment curve.

6.3.2 Characterization of the shear alignment of CNT fibres in terms of Weibull parameters

According to the previous section, some interesting features regarding mechanical properties of CNT fibres can be extracted by means of a Weibull analysis of the shear alignment curves. Thus, the behaviour shown by the three CNT fibres from Figure 6.4 can be studied. To this aim, the tangent shear modulus G/G_0 of each curve is evaluated. This parameter appears in terms of success probability (P_s) plotted against the stress in Figure 6.7 a). The experimental data from this graph follows a Weibull distribution where the modulus m is obtained from the Weibull plot analysis. This can be observed in Figure 6.7 b) where some important characteristics about the mechanical properties of CNT fibres can be easily observed. Thus, the slope increases with the winding rate for samples obtained at 20 and 30 m/min. This increase on the Weibull modulus is indicative of a higher collaborativeness among CNT bundles in terms of failure distribution. Thus, when $m \rightarrow \infty$ all bundles should fail at a single stress. However, the behaviour changes dramatically when we analyse the fibre winded at 40 m/min. In this case, two linear regions can be clearly distinguished. According to the graph, during the first part of the experiment CNT bundles start to fail until a certain stress region where there is an inflection point and $m \approx 0$. However, just after this, the slope starts to increase again up to fibre fracture.

Fig. 6.7 a) Normalized shear modulus of three CNT fibres tested by in-situ SAXS and their corresponding fitting to a Weibull distribution. b) Weibull plot corresponding the experimental data from the left and their fitting to linear relationships.

Table 6.2 Weibull parameters σ_{0b} and m obtained by in-situ SAXS mechanical experiments. The results are classified in terms of the rate at which CNT fibres have been wound.

winding rate m/min	m	σ_{0b} (GPa)
20	0.8	0.10
30	2.2	0.43
40	1.5	0.23
	1.8	1.4

Table 6.2 compiles the results of this analysis in terms of the two Weibull parameters σ_{0b} and m . As it was already mentioned, the Weibull modulus increases with the winding rate in the two first cases. Similarly, the scale factor σ_{0b} also does it. However, the tendency is not followed by the fibre wound at 40 m/min. In this case there are two different values of each parameter corresponding to each linear region in the Weibull plot¹. In this regard, this and previous studies have found that samples produced close to the maximum winding rate have more scattering in mechanical properties and tend to be more heterogeneous. We think that

¹To fit the curve from Figure 6.7 a) corresponding to the fibre wound at 40 m/min it has been used a two terms Weibull expression $P_s = A_1 * \exp(-(\sigma/\sigma_1)^{m1}) + A_2 * \exp(-(\sigma/\sigma_2)^{m2})$.

failure of the model for this particular sample is indeed because of local heterogeneities.

In order to compare the results obtained for CNT bundles by in-situ SAXS, Table 6.3 compiles some values from the literature. Here, different high-performance fibres have been included. In all these cases, tensile strengths have been accurately fitted to a Weibull type distribution. Regarding the Weibull modulus it can be easily observed that the highest value has been obtained for a CNT fibre. However, this fibre is different from those measured in this work because it shows a extremely high degree of alignment ($\langle P_2(\cos\beta) \rangle = 0.986$ [7]. Compared to others such as those from the family of carbon fibres or Kevlar, the difference is quite important. In this regard, it seems that the improvement on the alignment of CNT fibres has an extremely positive effect in terms of narrowing tensile strength distribution. On the other hand, both the lowest scale factor and Weibull modulus that we have found correspond to cellulose fibres. Cellulose is a semicrystalline material with small crystals microfibrils embedded in a disordered matrix [69]. In this regard, it seems obvious that the degree of collaborative loading among structural elements would be lower than highly crystalline materials such as carbon fibres or Kevlar. This is the reason why they show both low m and σ_{0b} values. In this work we have found values in the range of cellulose fibres which makes us an idea about the poor collaborative behaviour shown by CNT fibres. However, we must also take into account that different physical mechanisms are involved in each case. Thus, whereas Table 6.3 shows Weibull parameters corresponding to tensile properties of fibres, our analysis implies the progressive sliding of CNT bundles into the fibre structure. Therefore, we must be very careful in terms of making direct comparisons between both results. Nonetheless, in the light of these results, we can conclude that the alignment plays an important role in this regard. Thus, a narrower range of failure than high-performance fibres is reached by samples of CNT fibres with a degree of alignment comparable to the rest of the fibres. This fact is in agreement with a highly collaborative action of all resistive elements into the structure. Therefore, the low values found in this work must be related to the considerably lower alignment of our fibres compared to the rest of the samples .

Table 6.3 Weibull parameters σ_{0b} and m corresponding to the tensile failure distribution of high-performance fibres, cellulose fibres and CNT fibres.

	m	σ_{0b} (GPa)	Gauge length	Ref.
PAN-based carbon fibre AS4	6.5	3.9	20 mm	[51]
PAN-based high-modulus carbon fibre T300	5.5	3.2	30 mm	[114]
High modulus pitch based carbon fibre XN-90	5.0	3.2	25 mm	[90]
E-glass	4.1	1.9	20 mm	[51]
Kevlar KM2	6.5	4.0	20 mm	[51]
SiC	6.8	2.5	20 mm	[46]
Solution-spun CNT fibre	7.8-13.9	1.55-2.80	20 mm	[49]
Wood-based cellulose	1.26	0.18	2 mm	[69]
Cotton-based cellulose	1.77	0.56	2 mm	[69]

6.3.3 Characterization of micromechanical parameters based on the elastoplastic alignment of CNT fibres. An indirect measurement of the overlap length

Finally, it has been shown that alignment plays a very important role in terms of Weibull parameters. Thus, a higher alignment leads to a narrower failure distribution which, in turn, leads to a higher modulus m . Thus, in this work we have obtained that both Weibull parameters increase when the winding rate also increases from 20 to 30 m/min. The case becomes a bit more complicated in the case of 40 m/min. However, it seems that we have found a tendency. In this regard, Figure 6.8 a) introduces a schematic to illustrate how both a higher m and σ_{0b} is a natural consequence of a narrower ODF (i.e. lower $\langle \cos^2 \phi \rangle$). So far, it is a well-known fact that CNT bundles fail by shear at a certain shear stress τ_b which, in turn, corresponds to a tensile strength σ_y such as Figure 6.8 b) depicts. According to the

theory of continuum mechanics, both parameters are related with the misalignment angle through the function $f(\phi_y) = \sin\phi_y \cos\phi_y$. This function shows a maximum at 45° . However, the probability of finding a CNT bundle misaligned more than 45° is almost negligible. Therefore, the more misaligned the fibre, the lower the strength necessary to reach the critical shear stress τ_b and, consequently, the scale factor σ_{0b} would be also lower. This way, it can be easily related the effect of alignment with the failure distribution of CNT bundles.

Fig. 6.8 a) Schematic illustration of the state of stresses of a CNT bundle tensile tested at a stress σ_y in terms of its misalignment angle ϕ_y . b) Shear alignment curve where it can be observed how the scale factor from Weibull analysis σ_{0b} fits the yield point.

Taking this into account, a more detailed mechanical analysis can be done based on the scale factor σ_{0b} . According to the expression 6.10, this value simply represents the strength at which a CNT bundle has a failure probability of 63 %. However, regarding the shear alignment behaviour, it has been shown that the scale factor fits quite well to the yield point, σ_y . In this regard, Figure 6.8 b) shows the yield point corresponding to the experimental data and the scale factor according to Weibull analysis. This fact is not intuitive at all since almost a 63 % of the bundles have been failed at this point. In this regard, we must consider the statistical nature of the mechanical properties of CNT fibres. Accordingly, into the complex network which gives shape to the fibre, the energy is stored and dissipated during all the tensile test. Therefore, the macroscopic behaviour corresponds to the balance among all these internal processes from the microstructure. This is why the fibre starts to stretch plastically in a significant manner only when there is a strongly accumulated slippage which, according to the results here obtained, is around σ_{0b} .

Thus, the scale factor has been approximated to the yield point σ_y in each case. Due to this fact, we have assumed that all CNT bundles start to fail at σ_y and, therefore, stress is still uniformly shared among CNT bundles. Thus, the maximum tensile strength of CNT bundles before failing can be calculated as $\sigma_n = \sigma_y < \sin^2 \phi_y >$ and, similarly, the ultimate shear stress is $\tau_b = \sigma_y < |\sin \phi_y \cos \phi_y| >$. The orientation parameter functions have been obtained from SAXS ODF according to the method explained in section 4.6. All these mechanical parameters have been calculated for each sample here tested and they appear compiled in Table 6.4. It must be remarked that the absolute value have been used because $\sin \phi_y \cos \phi_y$ is an even function and, consequently, $< \sin \phi_y \cos \phi_y > = 0$. Both shear stress and tensile strength values agree more with literature results than those data already reported by the polymer fibres theory. In this regard, they are in the order of previous reported values in which a shear-lag based stress transference mechanism has been fulfilled [125, 144, 138]. Nonetheless, in another previous reports, the shear stress is simply defined as the total shear force divided by the whole area. Instead, according to the shear-lag model, the shear force is not constant along the overlap region but it shows a distribution type hiperbolic sine [53]. This could be the main reason why shear strength results show a significant scattering in the literature. Moreover, this also seems to be why shear interaction among nanotubes increase in terms of both the elastic shear modulus G_0 and the shear strength τ_b with the winding rate.

Table 6.4 Michromechanical parameters obtained from the Weibull analysis of shear alignment curves. Absolute values are obtained assuming a specific gravity of 1.8.

winding rate m/min	G_0 (GPa)	σ_y (GPa)	$\sigma_n = \sigma_y < \sin^2 \phi_y >$ (GPa)	$\tau_b = \sigma_y < \cos \phi_y \sin \phi_y >$ (MPa)	$\tilde{L}$ nm
20	5.6	0.14	0.13	22.4	19
30	16.0	0.34	0.32	40.8	25
40	18.4	0.29	0.27	40	22
		1.3	-	-	-

According to all the results here obtained, it seems that the stress transference mechanism follows a shear-lag model. This model is completely standardized in short-fibre composites[53] and it has been already applied on modelling mechanical properties of CNT fibres[143]. It explains the stress-transference between stiff fibre-like elements trough a weak interface. Based on it, Yoon et al. [150] obtained expression 6.6 which relates axial and shear strength for long polymer chains. Despite it was used in section 6.1.2, we did not get into further detail because we assumed a high overlap length between nanotubes. However, the shear-lag

model is a bit more complicated and considers that the interface fails at a critical shear stress τ_b according to the following expression

$$\sigma_n = \left(\frac{w_{\text{eff}}}{\pi d \delta} \right) \cdot \frac{2\tau_b}{\lambda} \tanh\left(\frac{\lambda \tilde{L}}{2}\right) \quad (6.12)$$

which relates the tensile strength σ_n with the overlap length $\tilde{L}$ in terms of the thickness of the interface δ , the outer diameter of nanotubes d , the effective contact width of two nanotubes w_{eff} and the parameter $\lambda = \sqrt{\frac{2*G_0}{e_c \delta}} \left(\frac{w_{\text{eff}}}{\pi d \delta} \right)$ [144].

We can then obtain the overlap length $\tilde{L}$ assuming that $\sigma_b \approx \sigma_n$. Thus, according to the USM, $e_c \approx 540 \text{ GPa}$. Regarding G_0 , it has been shown that this varies with the winding rate, such as it appears in Table 6.4. One may think that e_c could vary with orientation as the shear modulus does. Nonetheless, we must take into account that the Young's modulus e_c implies directly stretching CNTs. In this regard, the loss of crystallinity may have any affect on this value but it is not expected that a variation on the degree of alignment would affect to the mechanical properties in the axial direction. Moreover, according to TEM pictures we have been used a generic $d = 6 \text{ nm}$ and the thickness of the interface has been approximated to $\delta = 0.34 \text{ nm}$. Regarding the contact width, Suekane et al. [125] calculated this parameter for two DWNT with an outer diameter $d \approx 3 \text{ nm}$. Due to the lack of information in this regard, we have assumed that $w_{\text{eff}} \approx 1 \text{ nm}$ in agreement with this research work. Finally, calculations were very limited because of the hyperbolic tangent function. This is why another approximation has been made assuming the weakness of the interface and, consequently, the low value of λ . Due to this fact, equation 6.12 can be approximated to a linear function such as this

$$\sigma_n = \left(\frac{w_{\text{eff}}}{\pi d \delta} \right) \cdot \tau_b \tilde{L} \quad (6.13)$$

The results obtained using this approximation appear in Table 6.4. According to them, a significant increase of both the overlap length and the winding rate is produced. This fact is in line with the significant improvement in both mechanical strength and initial shear modulus G_0 . However, as it was said, it seems to go against the USM because this last considers the existence of a constant shear modulus $g = 8.1 \text{ GPa}$. Nonetheless, we must take into account that in this last case micromechanical parameters were obtained by means of standard tensile tests. Thus, due to the statistical nature of CNT fibres in terms of mechanical properties, it seems that the variation of the shear modulus remains below the error bars associated to this study. Nonetheless, we must emphasize the good approximation reached by the USM. In

fact, the value of g is in the order of the initial shear-modulus G_0 values measured in this section. Taking into account the simplicity of the USM model, this fact supposes a great success. However, it seems that a higher overlap length $\tilde{L}$ leads to increase both maximum strengths and elastic shear modulus G_0 .

In this regard, it seems that we can make a direct comparison between the overlap length $\tilde{L}$ and the crystallite size L_a defined in graphite based systems. This last value determines the size of graphite crystalline domains in the direction perpendicular to the c-axis[87]. This is classically obtained by means of WAXS in terms of the 100 peak [98]. However, as it was explained in section 4.2.1, diffraction rings coming out from the iron particles used in the synthesis process overlap with this peak. Therefore, there is no way to obtain the value of this parameter by means of x-ray diffraction. On the other hand, the overlap length $\tilde{L}$ defines the size between two end-points or defects within which two nanotubes interact each other. Accordingly, this can be thought as the length of a CNT bundle. Thus, in agreement with the estimation made here, the increase on both the elastic shear modulus G_0 and shear strength with the winding rate can be explained as an increase on the size of the bundles. However, this fact seems to go against the behaviour shown by carbon fibres. Thus, the tendency followed by carbon fibres, because their trend behaviour is the opposite. That is, a lower L_a means a more corrugated surface and, consequently, a higher shear modulus [98]. However, the shear-lag model predicts an increase on both the overlap length and the shear interaction. Therefore, due to the fact that we can not compare the overlap length and the crystalline size empirically, this step must be thought as a theoretical exercise about the hypothetical tendency the overlap length should follow according to the shear-lag model.

6.4 The elastoplastic behaviour of CNT fibres shown by in-situ Raman spectroscopy

So far, the progressive sliding of CNT fibres have been shown by means of SAXS and WAXS. At this point, we assume that there is nothing else to say about the difficulty of measuring morphological changes by x-ray scattering and, especially, if we use synchrotron radiation. Therefore, Raman appears again as a more suitable technique in order to measure these features. More precisely, the 2D peak can be thought as the spectroscopic image of the state of stresses bore by individual nanotubes. There has been a previous study about this peak

and its evolution during mechanical stretching of CNT fibres in section 5.6. Nonetheless, this was mainly focused on the elastic region and its effect on both the Raman shift of the peak and its asymmetric broadening. This is why the current study would left apart these items already discussed to be more focused on the total broadening of the 2D peak. In this regard, the evolution of the 2D peak in terms of both shape and Raman shift is directly related to the stretching of $sp^2 - sp^2$ bonds into nanotubes. Thus, the width shown by this peak might be related to the distribution of stresses among CNTs. This seems to go in agreement with Figure 6.9 which shows how the FWHM of the 2D peak increases with the strain as the stress does during a tensile test. This fibre corresponds to an already classical FWNTs fibre wound at 20 m/min (section 3.1). The similar behaviour of the FWHM and the tensile curve of a CNT fibre has been already reported [76, 133]. However, this relationship has not been carefully analysed in terms of the already well-known Weibull analysis.

Fig. 6.9 Evolution of the FWHM of the 2D peak with the strain plotted together with the tensile curve followed by the CNT fibre during testing.

Among all the conclusions reached in the previous section it must be remarked the accurate fitting existing between the elastoplastic alignment of CNT bundles and the mechanical behaviour of CNT fibres. This fact seems logical because the CNT bundles into the fibre would stop bearing more load as they progressively fail. Therefore, it could be expected that the tangent elastic modulus $E(\sigma) = \frac{d\sigma}{d\epsilon}$ shown by a CNT fibre would follow a failure distribution very similar to that followed by the shear modulus on a shear alignment curve.

In this regard, Figure 6.10 a) shows the evolution of the normalized elastic modulus E/E_0 with the tensile stress of the fibre. This has been calculated from available data points as $E = \frac{\Delta\sigma}{\Delta\epsilon}$ as it appears schematically in Figure 6.9. Moreover, Figure 6.10 a) also shows the normalized increase of the FWHM ($\Delta FWHM^*$) corresponding to the 2D peak. It can be clearly observed that the curves drawn by each data points are complementary to each other. This is, $\Delta FWHM^* + E/E_0 = 1$. In terms of probability, this fact means that whereas the elastic modulus follows a Weibull distribution in terms of probability of success (P_s), the increase of the FWHM corresponds to the probability of failure (P_f) (equation 6.10). This can be understood if we think that the progressive sliding of CNT bundles leads to a continuously less uniform stress distribution among nanotubes. As a result, the 2D peak broaden with the stress at the rate at which CNT bundles fail. In fact, according to the Weibull plot shown in Figure 6.10 b) it can be easily observed that both parameters follow exactly the same tendency. From the Weibull analysis carried out it has been obtained that $m = 4.3$ and $\sigma_{0b} = 0.62 \text{ GPa/SG}$. Despite these values seem to be a bit higher than those reported in section 6.3.2, it must be remarked that the results here shown do not correspond to any of the fibres tested in the previous section. In fact, it results that the fibre here reported shows a much better mechanical performance than any of those appearing in section 6.3.2. This fact has been unfortunately common for the duration of this thesis since CNT fibres made according to the same manufacturing conditions can show very different properties. The reason of this can be found on several technical problems associated to the tubular furnace which took place mainly in the last period of this thesis. This is why the mechanical properties show certain scattering depending on the batch used and, consequently, Weibull parameters can not be generalized in terms of manufacturing conditions. Nonetheless, the Weibull distribution is always fulfilled regardless of the mechanical properties of the fibre.

Fig. 6.10 a) Normalized FWHM of the 2D peak ($\Delta FWHM^*$) and tangent modulus E/E_0 against tensile stress of the fibre. Both data points have been fitted to a Weibull expression in terms of probability of failure (P_f) and probability of success (P_s), respectively. b) Weibull plot corresponding to data points plotted at the left. It must take into account that the Weibull plot always refers to P_s and, therefore, in terms of the FWHM it is plotted $P_s = 1 - \Delta FWHM^*$.

Weibull parameters have been proved to be really important in terms of calculating some important features regarding micromechanics. However, to this aim we need of measuring orientation during the tensile test. Therefore, until the problem of measuring orientation by Raman is solved, the use of SAXS or WAXS is necessary. There might be an alternative associated to the use of FFT-SEM pictures during in-situ SEM mechanical tests [11]. However, this technique is in a very preliminary step and it needs to be further studied. Instead, the most important conclusion regarding Figure 6.10 a) and b) arises from the fact that both the failure probability measured by Raman in terms of the FWHM and that corresponding to the tangent elastic modulus fits perfectly one to each other. This fact supposes a big step forward in terms of linking the microstructure and the macroscopic mechanical behaviour of a CNT fibre. Indeed, very important features can be extracted from the tensile curve by means of Weibull analysis.

6.5 The mechanical alignment of nanotubes as the source of the elastoplastic behaviour of CNT fibres

According to this research work, it seems pretty obvious that the alignment plays the main role in terms of mechanical properties. Indeed, the degree of alignment determines the

stiffness of a CNT fibre according to the USM (section 5.4), but also an oriented fibre shows a more collaborative behaviour and, consequently, higher Weibull parameters m and σ_{0b} . Moreover, preliminary results seems to link a better mechanical performance with a higher overlap length due to an increase of orientation. Finally, this point seems to be definitively clear when this study has just related the elastoplastic tensile behaviour of a CNT fibre and the mechanical alignment of nanotubes into it.

Fig. 6.11 Schematic model about the effect of mechanical alignment on the morphology of the fibre during a tensile test.

In this regard, Figure 6.11 shows a schematic model in order to explain the role of mechanical alignment on the tensile behaviour of a CNT fibre. For this purpose, a standard tensile curve has been used. Thus, in the unloaded state, the morphology of the fibre is characterized by imperfectly packed bundles. However, we have a continuous network in which bundles are interconnected among them. Thus, nanotubes can be part of several bundles and these bundles, in turn, can be made of several nanotubes along its length. This idea of continuous network was already contemplated in previous works involving SAXS scattering of CNT fibres [156]. Thus, once the fibre starts to stretch, the most misaligned bundles are the weakest elements

in terms of sliding. Accordingly bundles are continuously aligned towards the fibre's axis and, consequently, nanotubes are closer one to each other. This way, they can be attracted by Van der Waals forces creating new increasingly aligned bundles and, therefore, stiffer. In this regard, it requires much less energy to align nanotubes than stretching them and, therefore, almost all the energy used to stretch the fibre would be applied to align the tubes. This fact agrees with the USM and the main role that the shear alignment plays in terms of determining the elastic properties of CNT fibres (section 5.4). Accordingly, the physical mechanism which determines the tensile behaviour of CNT fibres is the mechanical alignment of nanotubes. In this regard, the ultimate strength would be reached when nanotubes were perfectly aligned. Nonetheless, if this is the case, one may expect that the final alignment just before failure would be very close to $\langle \cos^2 \phi \rangle = 0$ or $\langle P_2(\cos \beta) \rangle = 1$. However, we are pretty far of this case due to the maximum alignment reached in this work was for the fibre winded at 20 m/min which passes from $\langle \cos^2 \phi_0 \rangle = 0.071$ to $\langle \cos^2 \phi \rangle = 0.037$ just before failure which, equivalently, means that the fibre shows a $\langle P_2(\cos \beta_0) \rangle = 0.57$ and a $\langle P_2(\cos \beta) \rangle = 0.64$ before fracture. Nonetheless, close to the fracture point, shear alignment curves reveal that the shear modulus and, consequently, the stiffness of the fibre to be aligned is mainly 0. In this regard, we must consider that the alignment of nanotubes does not only imply a change on the orientation but also a change on the morphology in terms of contact area or contact length such as it has just explained. Accordingly, Weibull distribution encompasses both the failure of CNT bundles in terms of sliding of nanotubes but also the dynamic recombination of nanotubes during the process. Finally, the accumulated slippage gives as a result a morphology that can not be more aligned, reaches its maximum available sliding length in a certain section and, consequently, breaks. The explanation to this fact still remains unknown and it will be an important topic to be treated in future research works.

6.6 Summary

In contrast to the elastic properties, the theory of polymer fibres is not suitable to model plasticity in CNT fibres. Regarding this, it has been found that the concept of plastic rotation used for polymers is simply invalid in terms of explaining the shear alignment of CNT bundles. Instead, a more complex elastoplastic alignment has been observed by means of in-situ SAXS/WAXS mechanical experiments. Based on this behaviour it has been found that CNT bundle fails by sliding according to a Weibull distribution function. This has been guessed in terms of the tangent shear modulus which decreases exponentially as bundles

progressively fail.

Based on the Weibull parameters obtained from shear alignment curves and according to the dependence of mechanical properties with the alignment, a Weibull based mechanical model has been developed. According to it we have been able to estimate the maximum shear strength reached before nanotubes sliding (τ_b). Moreover, the overlap length between nanotubes have been also calculated assuming a shear-lag model. In fact, it has been shown that this length can be thought in terms of longitudinal bundle size. This way, mechanical properties dependent of the shear interaction among nanotubes would be strongly dependent of this parameter. In this regard, it has been shown an increase on both elastic shear modulus G_0 and the shear strength τ_b with this parameter.

Finally, the analysis of the FWHM of the 2D peak from Raman has revealed that this peak broadens according to the probability of failure of CNT bundles. Similar to the case of shear alignment curves, the tangent Young's modulus behaves according to a Weibull distribution too. The main point comes when both distributions are compared and they fit each other. Accordingly, the elastoplastic alignment of nanotubes has been proved to be the source of the mechanical behaviour of CNT fibres. In this regard, we have proposed a model which implies a dynamical changing morphology as the result of this mechanical alignment. However, it is not fully explained yet how these morphological features would affect to the shear alignment of the fibre and, consequently, to the Weibull analysis. Therefore, it has become necessary to carry out new measurements in a future work in which all these facts would be taken into account. Nonetheless, so far, we can conclude that the progressive sliding of nanotubes and all which implies govern the mechanical behaviour shown by CNT fibres.

Chapter 7

Conclusions and future work

The assembly of carbon nanotubes as a macroscopic fibre is intended to exploit their highly anisotropic behaviour. Nanotubes arrange themselves closely parallel one to each other and, as a result, the transference of properties from the nano- to the macro-scale should be optimized in this way. However, the real assembly of nanotubes as a macroscopic fibre has been shown to be quite more complex. Thus, a CNT fibre shows a hierarchical structure in which morphological features from different range scales are interrelated. Accordingly, nanotubes are arranged into close packed bundles because of Van der Waalls forces and these, in turn, are highly aligned along the fibre's axis. Therefore, the fibre obtained reveals a complex morphological system whose behaviour is very sensitive to many different variables spanning from nanotubes themselves to the highly anisotropic network formed by CNT bundles. Therefore, mechanical properties of CNT fibres are pretty far away from those corresponding to carbon nanotubes themselves. In this regard, using the tensile strength as a reference, a strength of $\sigma_b = 120GPa$ [161] has been measured for an individual nanotube whereas the maximum strength ever reached for a CNT fibre is of $\sigma_b = 16GPa$. [71]

Hence, the complex morphology of the fibre leads to a mechanical behaviour which results from the confluence of many variables from the different hierarchical levels. In this regard, assessing how much each variable affects the final behaviour of the fibre has been proved to be a daunting task in this field. Nonetheless, some qualitative relationships based on a wide experimental research work have been currently established. Regarding nanotubes themselves, the use of long few-wall tubes with large diameters promote the stress transference among them and, consequently, the final tensile strength of the fibre is significantly improved. Furthermore, the alignment of CNTs along the fibre's axis favoured the mechanical properties

too. In this regard, the stiffness has been proved to be mainly determined by the alignment of nanotubes. However, there is a lack of studies establishing quantitative relationships between morphological parameters and mechanical properties in terms of a complete mechanical model. This has been the main purpose of this thesis and in order to fulfil it, we have used CNT fibres synthesized by the direct spinning method. Both the versatility and the ability of this technique to produce continuously spun CNT fibre makes of this method the most suitable one to carry out this research work.

In this regard, the main conclusion to extract from this thesis is that the alignment of nanotubes plays a key role on the final mechanical behaviour of CNT fibres. Hence, regarding stiffness, we have been able to establish a direct relationship between the compliance ($1/E_f$) and the orientation parameter $\langle \cos^2 \phi_0 \rangle$ by means of applying the uniform stress model (USM). This has been proved to be valid for single filament samples with $\langle P_2(\cos \beta) \rangle > 0.49$. However, there is no reason why this would not be valid for multiple filament fibres. However, in this case, the real correspondence between WAXS and SAXS in terms of nanotube and CNT bundle alignment must be carefully studied. Furthermore, for the first time, we have proved that the mechanical alignment of CNT bundles during the tensile stretching of the fibre plays a fundamental role for its elastoplastic mechanical behaviour. Thus, CNT bundles slide with stress according to a Weibull distribution which is narrower as the winding rate increases. Accordingly, the alignment of nanotubes leads to a more collaborative system in which CNT bundles fail at a narrower range of stress and, therefore, higher Weibull parameters are obtained as a result. Nonetheless, despite this trend has been presented here for the first time, the next step in this regard seems to be the development of a more extensive work which involves more samples and a wider range of orientation.

Due to the prominent role of orientation, a research work involving the synthesis of CNT fibres has become necessary. In this thesis, the relative misalignment of the fibre has been established. Thus, according to WAXS and SAXS analysis, the ODF of CNT fibres fabricated by the direct spinning method follows a Lorentzian type function. The large weight that tail ends have on these type of distributions affect negatively the orientation parameters. Due to this fact, values quite far from those shown by high performance fibres are obtained for CNT fibres manufactured by this technique. In fact, neither the increase of the winding rate nor the mechanical alignment have been able to change this type of distribution. However, this inherent misalignment seems to have its source on the synthesis process. Thus, superaligned CNT fibres ($\langle P_2(\cos \beta) \rangle = 0.986$) with Gaussian-type ODF have been manufactured by

the wet-spinning method [7]. This fact makes very necessary to know what is the origin of this intrinsic misalignment which, in turn, implies a study of the aggregation of nanotubes in the gas phase.

In order to measure the orientation of CNT fibres, the use of SAXS and WAXS has proved to be the best approach so far. According to the approximation method presented here for well-oriented filaments, azimuthal integration of SAXS patterns at a low q -range delivers quite accurate orientation parameter values. This range fits with the most intense SAXS signal and, therefore, a much lower exposure time is needed to measure alignment. The use of a larger time of exposure in this work was due to the fact that, a priori, SAXS behaviour was completely unknown. Accordingly, in-situ SAXS experiments might be improved by means of replacing the stepwise method currently used with a continuous tensile test. This way, we will be able to study the morphological effects that lie behind the viscoelastic mechanical behaviour of CNT fibres. Nonetheless, Raman spectroscopy seems to be the best technique through which in-situ orientation measurements can be standardized in the field of CNT-based materials. However, this is an indirect method which is not suitable for systems with nanotubes highly aggregated in bundles such as the CNT fibre. In this regard, the main conclusion here reached is that polarized Raman measurement of CNT bundles is needed. This way, the polarizability tensor associated to this scattering element will be obtained. However, we are concerned about the difficulty of measuring individual CNT bundles. This is why we propose that highly aggregated CNT fibres would be measured instead. In this regard, the use of superaligned CNT fibres spun from an acid solution seems to be the best candidate. Thus, in a first approximation, we can assume perfect alignment of nanotubes and that the polarized Raman behaviour arises from the aggregation of the tubes.

Apart from the role of alignment, the use of the USM and Weibull analysis has delivered important conclusions. The USM allows to obtain micromechanical parameters from macroscopic measurements. Indeed, values of stiffness ($e_c \approx 540\text{GPa}$) and shear modulus ($g = 8.1\text{GPa}$) have been measured using this technique. Moreover, CNT fibres made from different types of nanotubes follow the same straight trendline which, in turn, points to the collaborative load bearing of all CNT walls in the fibre. This seems to contradict the literature in which is very well-established that the outer layers from a MWNT or external CNTs into a CNT bundle bear almost all the load. This assumption has been proved to be non accurate for few-wall nanotubes such as in the case of the fibre. One reason for this behaviour can be found on the collapse of CNTs, which directly leads to a uniformly shared load among CNT

walls. Furthermore, the analysis of shear alignment curves has provided values of maximum shear strength which agrees with shear-lag based experimental measurements. This fact points out to a new morphological parameter playing a relevant role on the mechanical behaviour of CNT fibres: the overlap length. This has been firstly estimated using values provided by in-situ SAXS measurements. However, the overlapping of the (100) peak with the iron from nanoparticles prevents the measurement of L_a . We conjecture that there is a direct relationship between both parameters since in both cases we are talking about a coherence length. However, there is no any experimental evidence in this regard. For this purpose, the purification of home-made CNT fibres can not be further postponed. This way, nanoparticles would be removed and, therefore, we would be able to finally compare the estimated values here presented with a direct measurement of L_a by WAXS analysis.

Therefore, it seems that mechanical properties would improve by means of both increasing the overlap length between nanotubes and aligning them along the fibre's axis. This is the same as saying that we want stronger CNT bundles and better aligned. However, we have already discussed the important role of the CNT aerogel regarding the Lorentzian ODF of nanotubes and the intrinsic misalignment associated to this type of distribution. In this regard, it seems that the overlap length is very affected also by this phenomenon. Indeed, it increases with the winding rate because of the better alignment of tubes along the fibre's axis. Therefore, it seems that a significant improvement on the orientation of nanotubes would lead also to an increase on the overlap length. This fact invites us to focus even more on further research of the synthesis process in order to find what is the ultimate reason of the Lorentzian distribution of nanotubes.

Weibull analysis is formulated in terms of normalized variations of the shear modulus. This analysis was carried out by means of shear alignment curves which, in turn, were obtained by in-situ SAXS. It has been also shown that Young's modulus of CNT fibres follows a Weibull type distribution. This behaviour has been confirmed by in-situ Raman spectroscopy. Therefore, the next step regarding Weibull-analysis will consist on establishing a relationship between both Weibull distributions. This way, a complete mechanical model which delivers the evolution of Young's modulus in terms of the mechanical alignment of CNT bundles would be obtained. In this regard, the USM relates the elastic modulus with the orientation parameter $\langle \cos^2\phi \rangle$ and the shear modulus g . Therefore, one may expect that the evolution of stiffness will be established in terms of a parameter related to mechanical alignment and another which involves the change of the shear modulus. The best experiment to develop this

task will be an in-situ Raman experiment in which both orientation and the evolution of the 2D peak will be followed simultaneously. However, this also requires solving the problem of measuring the alignment of CNT fibres by Raman spectroscopy. Moreover, there are some aspects regarding the 2D peak that have not been completely solved. For instance, it is well known that the total broadening of the peak is due to the stress distribution among nanotubes. However, it is still unknown which is the origin of the asymmetry of this peak and the role that the Raman shift plays. For this purpose, a complete study involving CNT fibres with different orientations and a different composition of nanotubes is needed. This way, a clear relationship between the Young's modulus and Raman shift can be established and we could also study the compositional origin of the 2D peak.

Finally, the mechanical model described in this thesis constitutes by itself a quite powerful characterization technique. Indeed, the USM delivers micromechanical parameters in terms of macroscopic properties. Moreover, Weibull analysis provides values such as the maximum shear strength between nanotubes. Consequently, one of the most critical and difficult features to characterize for CNT assemblies or CNT-polymer composites can be finally understood: the interface. Thus, this technique has important applications in studies involving functionalization in order to evaluate the quality of the new interface. In our case, we would be finally able to know the role of catalyst particles or amorphous carbon by removing it from the fibre and analysing the change of the interface. For alternative fabrication methods of CNT fibres, this model will allow us to measure the increase on shear strength by means of varying morphological features such as the aspect ratio, the alignment, the degrees of twisting and so on. Therefore, there are many future applications of this work, either for characterization techniques or as a mechanical model. However, the model must be particularized for each case. Hence, all the work carried out in this thesis constitutes the first step in the development of a general model valid for all CNT-based materials.

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Appendix A

A.1 Polar distribution and Orientation Distribution Function of CNT fibres

All the nanotubes into the fibre do not show the same orientation. Instead, a distribution of orientation exists. Thus, the probability of a CNT having an orientation between (α, β, γ) and $(\alpha + d\alpha, \beta + d\beta, \gamma + d\gamma)$ is called the orientation probability distribution function (ODF) $f(\alpha, \beta, \gamma)$. The orientation of a nanotube in terms of the Euler's angles α , β and γ appears schematically depicted in Figure A.1.

Fig. A.1 Position of a CNT in terms of the three Euler angles α , β and γ

Accordingly, the ODF fulfils that

$$\int_0^{2\pi} \int_0^\pi \int_0^{2\pi} f(\alpha, \beta, \gamma) \sin\beta \, d\alpha d\beta d\gamma = 1 \quad (\text{A.1})$$

In the specific case of CNT fibres, due to both the cylindrical shape of nanotubes and their preferential alignment along the Z-axis we can assume that the ODF remains unaffected for changes on γ and α respectively. Thus, the ODF is expressed in terms of β such as $f(\beta)$. Therefore, equation A.1 leaves as follows

$$4\pi^2 \int_0^\pi f(\beta) \sin\beta \, d\beta = 1 \quad (\text{A.2})$$

In this regard, an alternative distribution function has been proposed for the case of fibres or well-aligned samples. According to it, the Z-axis fits with the fibre's axis which is usually called as polar direction. Thus, considering the angle β as the single variable to consider, the polar distribution function is defined as

$$\int_0^\pi \rho(\beta) \sin\beta \, d\beta = 1 \quad (\text{A.3})$$

This last definition is more useful to work with and, moreover, it is very well related to the ODF according to the following expression

$$\rho(\beta) = 4\pi^2 f(\beta) \quad (\text{A.4})$$

A.2 Analysis of symmetric functions

Fitting of azimuthal profiles in the range $[0, \pi]$ has been necessary in order to calculate the orientation distribution of nanotubes. Accordingly, the symmetry of patterns lead to an azimuthal profile which is, in turn, symmetric respect to the angle $\pi/2$ or 90° . Thus, as it appears clearly depicted in Figure A.2, the azimuthal profile can be fitted to two Lorentzian profiles along all the angular range. These two peaks are almost identical but shifted π radians or 180° each other.

Fig. A.2 Azimuthal profile obtained from a SAXS pattern and its corresponding fitting to two Lorentzian functions centred at 0° and 180° .

Therefore, we must take advantage of the symmetry in order to calculate any integration. Thus, the integration of the azimuthal profile can be expressed as

$$\int_0^\pi (I(\beta) - I_0) \sin\beta \, d\beta = 2 \int_0^{\pi/2} (I(\beta) - I_0) \sin\beta \, d\beta \quad (\text{A.5})$$

which, in turn, allow us to use a single Lorentzian peak centred at 0° . Thus, for an hypothetical function $A(\beta)$, the average integrated value $\langle A(\beta) \rangle$ can be expressed as

$$\langle A(\beta) \rangle = \int_0^\pi A(\beta) \rho(\beta) \sin\beta \, d\beta = 2 \int_0^{\pi/2} A(\beta) \rho(\beta) \sin\beta \, d\beta = \frac{\int_0^{\pi/2} A(\beta) (I(\beta) - I_0) \sin\beta \, d\beta}{\int_0^{\pi/2} (I(\beta) - I_0) \sin\beta \, d\beta} \quad (\text{A.6})$$

A.3 Table of even Legendre's polynomials

Orientation is calculated using the average of even Legendre's polynomial functions. In this regard, Table A.1 compiles the first i^{th} order Legendre's polynomials ($P_i(\cos\beta)$) up to the 10th.

Table A.1 Table of even Legendre's polynomials

$P_0(\cos\beta)$	1
$P_2(\cos\beta)$	$1/2 (3\cos^2\beta - 1)$
$P_4(\cos\beta)$	$1/8 (35\cos^4\beta - 30\cos^2\beta + 3)$
$P_6(\cos\beta)$	$1/16 (231\cos^6\beta - 315\cos^4\beta + 105\cos^2\beta - 5)$
$P_8(\cos\beta)$	$1/128 (6435\cos^8\beta - 12012\cos^6\beta + 6930\cos^4\beta - 1260\cos^2\beta + 35)$
$P_{10}(\cos\beta)$	$1/256 (46189\cos^{10}\beta - 109395\cos^8\beta + 90090\cos^6\beta - 30030\cos^4\beta + 3465\cos^2\beta - 63)$

A.4 The maximum entropy formalism

In order to construct the ODF based on orientation parameters, the maximum entropy formalism is used. According to it, the widest ODF consistent with the measured orientation parameters will be used. For this purpose, the information entropy is maximized. In this regard, the information entropy is expressed as follows

$$S = -K \int_{\Omega} f(\Omega) \ln f(\Omega) d\Omega \quad (\text{A.7})$$

where $\Omega = (\alpha, \beta, \gamma)$ and K is a constant [131]. Finally, due to $f(\Omega) = f(\beta)$ for highly aligned samples such as the CNT fibre, the solution of maximizing the entropy leads to an expression for the ODF based on Legendre's polynomials. Accordingly, the ODF is expressed such as follows

$$f(\beta) = A \cdot \exp\left(-\sum_i \lambda_i P_i(\cos\beta)\right) \quad (\text{A.8})$$

where A and λ_i are calculated by solving a system of equations. Thus, in terms of the two orientation parameters $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$, the system leaves as follows

$$\begin{cases} \int_{\gamma=0}^{\gamma=2\pi} \int_{\alpha=0}^{\alpha=2\pi} \int_{\beta=0}^{\beta=\pi} f(\beta) \sin(\beta) d\beta d\alpha d\gamma = 1; \\ \int_{\gamma=0}^{\gamma=2\pi} \int_{\alpha=0}^{\alpha=2\pi} \int_{\beta=0}^{\beta=\pi} P_2(\cos\beta) f(\beta) \sin(\beta) d\beta d\alpha d\gamma = \langle P_2(\cos\beta) \rangle; \\ \int_{\gamma=0}^{\gamma=2\pi} \int_{\alpha=0}^{\alpha=2\pi} \int_{\beta=0}^{\beta=\pi} P_4(\cos\beta) f(\beta) \sin(\beta) d\beta d\alpha d\gamma = \langle P_4(\cos\beta) \rangle; \end{cases} \quad (\text{A.9})$$

The system is formed by three equations which depends of three unknown parameters A , λ_2 and λ_4 . The system has been solved numerically by means of the Netwon-Raphson method using the software Matlab 6.2. Thus, once the system has been solved, the ODF is expressed as

$$f(\beta) = A \cdot \exp(-(\lambda_2 P_2(\cos\beta) + \lambda_4 P_4(\cos\beta))) \quad (\text{A.10})$$

The procedure has been developed using two orientation parameters for simplicity purposes. The method followed would be exactly the same if the number of orientation parameters increases. In fact, we have calculated the ODF of a sample in terms of 20 orientation parameters.

A.5 Calculus of $\langle P_2(\cos\beta) \rangle$ and $\langle P_4(\cos\beta) \rangle$ by means of polarized Raman spectroscopy using the standard method

The expression 4.7 delivered by the Raman theory is based on a relationship of proportionality. Thus, in order to normalize the expression, the corresponding value at $\Phi = 0^\circ$ is used.

$$I^{VV}(\Phi = 0^\circ) \propto \frac{8}{35} \langle P_4(\cos\beta) \rangle + \frac{4}{7} \langle P_2(\cos\beta) \rangle + \frac{1}{5} \quad (\text{A.11})$$

Finally, once the expression is normalized, parameters can be recombined in order to obtain an equation such as follows

$$\frac{I^{VV}(\Phi)}{I^{VV}(0^\circ)} = a\cos^4\Phi + b\cos^2\Phi + c \quad (\text{A.12})$$

where

$$\begin{aligned} a &= \frac{\langle P_4(\cos\beta) \rangle}{\frac{8}{35} \langle P_4(\cos\beta) \rangle + \frac{4}{7} \langle P_2(\cos\beta) \rangle + \frac{1}{5}} \\ b &= \frac{\frac{6}{7}(\langle P_2(\cos\beta) \rangle - \langle P_4(\cos\beta) \rangle)}{\frac{8}{35} \langle P_4(\cos\beta) \rangle + \frac{4}{7} \langle P_2(\cos\beta) \rangle + \frac{1}{5}} \\ c &= \frac{\frac{3}{35} \langle P_4(\cos\beta) \rangle - \frac{2}{7} \langle P_2(\cos\beta) \rangle + \frac{1}{5}}{\frac{8}{35} \langle P_4(\cos\beta) \rangle + \frac{4}{7} \langle P_2(\cos\beta) \rangle + \frac{1}{5}} \end{aligned} \quad (\text{A.13})$$

Therefore, by means of fitting experimental data of $\frac{I^{VV}(\Phi)}{I^{VV}(0^\circ)}$ to the equation A.12 we obtain three fitting parameters a , b and c . For this purpose, the fitting must be forced to be 1 at 0° . This has been done in Origin software by means of imposing that $a + b + c = 1$. Finally, experimental data have been accurately fitted by the theory such as Figure A.3 reveals. Therefore, the corresponding values $\langle P_4(\cos\beta) \rangle$ and $\langle P_2(\cos\beta) \rangle$ can be obtained by means of solving two of the three equations described above.

Fig. A.3 Experimental data corresponding to the evolution of normalized intensity with the rotation angle fitted to equation A.12.

A.6 Calculus of polarizability tensors for an armchair (10,10) nanotube using the non-resonant approach

Based on the symmetries associated to A_{1g} and E_{1g} , some schematic polarizability tensor are associated to each phonon mode

$$\alpha_{=A_{1g}} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{bmatrix} \quad \alpha_{=E_{1g}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & p \\ 0 & p & 0 \end{bmatrix} \quad (\text{A.14})$$

These tensors are expressed in the axis system of the nanotube. However, the polarized Raman behaviour assumes the rotation of the tube according to the schematic shown in the onset from Figure A.4. In this Figure it also appears the contribution of each phonon mode A_{1g} and E_{1g} according to a VV configuration. These curves show some specific features that allow us to calculate the final polarizability tensors. However, for this purpose, we need to previously express these tensors in terms of the reference axis XYZ. This has been done in the following way

$$\alpha_{=xyz} = A^{-1} \alpha_{=} A \quad (\text{A.15})$$

where $\underline{A}$ is the matrix of rotation around the x axis

$$\underline{A} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\Phi & -\sin\Phi \\ 0 & \sin\Phi & \cos\Phi \end{bmatrix} \quad (\text{A.16})$$

Due to a VV configuration is used, $\vec{e}_i = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$ and $\vec{e}_s = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$. Therefore, the total intensity scattered for each phonon mode is calculated as follows

$$I = |\vec{e}_s \alpha_{\text{xyz}} \vec{e}_i|^2 \quad (\text{A.17})$$

leading to the following expressions

$$I_{A_{1g}}^{VV} \propto ((c-a)\cos^2\Phi + a)^2 \quad I_{E_{1g}}^{VV} \propto (p\cos 2\Phi)^2 \quad (\text{A.18})$$

Fig. A.4 Evolution of the relative Raman intensity associated to a A_{1g} and E_{1g} mode in a VV configuration. It has been also plotted the schematic followed for rotating an hypothetical (10,10) nanotube according to the research work from ref[118].

According to the Figure A.4, the curve corresponding to the A_{1g} mode is zero at an angle $\phi_{min} \approx 55^\circ$. Consequently, imposing this condition in the equation A.18, this is fulfilled only if $a = -\frac{1}{2}c$. Moreover, the expression A.18 corresponding to the E_{1g} phonon has a maximum at 45° at which scattered intensity is $I_{E_{1g}}^{VV}(45^\circ) = 0.5$. Accordingly, $p = \frac{\sqrt{2}}{2}c$. Therefore, due to all the calculus have been made in terms of the normalized intensity $\frac{I^{VV}}{I^{VV}(0^\circ)}$, it is fulfilled that $c = 1$. Finally, the tensors obtained for each symmetry mode leaves as follows

$$\alpha_{=A_{1g}} = \begin{bmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \alpha_{=E_{1g}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}/2 \\ 0 & \sqrt{2}/2 & 0 \end{bmatrix} \quad (\text{A.19})$$

Appendix B

B.1 The parameter $\langle \cos^2 \phi \rangle$ and its relationship with $\langle P_2(\cos \beta) \rangle$

Along all Chapter 4, orientation parameters have been always defined with respect to the azimuthal angle β . This angle has been defined respect to the equator in SAXS and WAXS patterns because it corresponds to the direction of maximum intensity and, therefore, the direction of maximum alignment. Hence, a clear parallelism between the equator and the fibre's axis can be established in order to define the ODF ($f(\beta)$). Accordingly, the probability of finding a nanotube between an angle β and $\beta + d\beta$ can be calculated as $4\pi^2 f(\beta) \sin \beta d\beta$. In this regard, it must be taking into account that this thesis is focused on modelling and characterizing mechanical properties of CNT fibres in terms of structural features such as orientation. However, nanotubes do not contribute individually to the overall behaviour of CNT fibres. Instead, they are strongly aggregated into bundles which would act as the basic load bearing elements. Therefore, the mechanical properties would be very much dependent of intertube interactions into bundles than uniaxial properties from nanotubes themselves. This is why the theory about mechanical behaviour of CNT fibres has been developed based on the direction of stacking of graphitic layers from nanotubes. This is called c-axis in clear reference to Bernal's work on graphite and, therefore, it is normal to the direction shown by the bundle's axis [87]. Thus, as Figure B.1 shows, the ODF obtained from WAXS/SAXS $f(\beta)$ has been shifted 90° to define the new orientation distribution $f(\phi)$ where $\phi = 90^\circ - \beta$. Accordingly, $4\pi^2 f(\phi) \sin \phi d\phi$ is the fraction of c-axis with angles between ϕ and $\phi + d\phi$.

Fig. B.1 Shifting of 90° from the ODF $f(\beta)$ centered at the fibre's axis to obtain the new ODF $f(\phi)$ corresponding to the c-axis.

Based on this new ODF ($f(\phi)$), the alignment of CNT fibres can be newly measured. In fact, in Chapter 5 is established that the Young's modulus of CNT fibres is strongly dependent of $\langle \cos^2 \phi \rangle$. This parameter may seem familiar due to the average of Legendre's polynomial are, in fact, a series of $\langle \cos^n \beta \rangle$. The definition in both cases is exactly the same since they correspond to the n^{th} moment of the orientation distribution function. However, the distribution function changes in each case. Thus, instead of being $f(\beta)$, $f(\phi)$ is used. This fact leaves the following expression

$$\langle \cos^2 \phi \rangle = 8\pi^2 \int_0^{\pi/2} \cos^2 \phi f(\phi) \sin \phi d\phi \quad (\text{B.1})$$

This parameter, despite very useful to model mechanical properties, is not intuitive at all. This is the reason why it would be pretty convenient to obtain a relationship which defines it in terms of another well-known orientation parameter. In fact, taking into account the second order of both parameters, it would much more convenient to establish a mathematical relationship with the Herman's orientation parameter ($\langle P_2(\cos \beta) \rangle$). This task has been shown pretty difficult in terms of their definition since it involves trigonometric functions into an integral expression such as equation B.1 reveals. Nevertheless, this relationship can be estimated by means of calculating both parameters for two Lorentzian functions centred

at 0° ($f(\beta)$) and 90° ($f(\phi)$), respectively. This has been done for different FWHM, some of them corresponding to the samples here studied. As a result, Figure B.2 shows that both parameters are strongly related each other. However, this relationship changes with the degree of alignment. Thus, for extremely well aligned samples, it can be clearly observed a rapid increase of the rate to reach the value $\langle P_2(\cos\beta) \rangle = 1$ when $\langle \cos^2\phi \rangle = 0$. This tendency is limited to a range of $\langle \cos^2\phi \rangle < 0.025$, above which an almost linear decaying behaviour is observed. In this regard, a linear relationship has been obtained by means of fitting both theoretical and experimental data points from the graph. This has resulted on the following expression

$$\langle P_2(\cos\beta) \rangle = -2.3 \langle \cos^2\phi \rangle + 0.73 \quad (\text{B.2})$$

We must not forget that this mathematical expression has been found assuming a Lorentzian distribution. However, as we have already reported, for superaligned CNT fibres it has been shown that a Gaussian distribution is obtained [7]. Therefore, it seems obvious that the relationship would be very different in this case and it would be very convenient to develop the same exercise here presented.

Fig. B.2 Evolution of the Herman's orientation parameter $\langle P_2(\cos\beta) \rangle$ with the new orientation parameter $\langle \cos^2\phi \rangle$ for both theoretical and experimental data points. This relationship has been obtained by means of assuming that the Lorentzian distribution is always fulfilled.

B.2 Information about literature data regarding compliance-orientation relationship

Table B.1 presents details of the composition of the samples analysed in this study, as well as of the method used to obtain the orientation density function (ODF) and, therefore, the parameter $\langle \cos^2\phi_0 \rangle$.

Table B.1 Information about data obtained from literature in Figure 5.9.

Ref	CNT type	Manufacturing method	Orientation measurement technique	Data analysis to obtain the ODF
Tsenlalovich [129]	High quality DWNTs	Wet spinning of a liquid crystalline suspension of CNTs	WAXS (single filament)	Gaussian fit of the 0 0 2 azimuthal profile
Behabtu [7]	High quality MWNTs	Wet spinning of a liquid crystalline suspension of CNTs	WAXS (single filament)	Gaussian fit of the 0 0 2 azimuthal profile
Vilatela [133]	Collapsed few-layer MWNTs	Direct spinning method	WAXS (single filament)	Lorentzian fit of the 0 0 2 azimuthal profile
Gspann [45]	Few-layer MWNTs	Direct spinning method	SAXS (Multifilament)	Calculated by fitting the azimuthal integration to a Lorentzian distribution
	MWNTs			
	SWNTs			

Appendix C

C.1 Mathematical derivation of the strength-stiffness equation

The uniform stress-model relates the Young's modulus to the initial orientation parameter of the crystallites $\langle \cos^2 \phi_0 \rangle$

$$\frac{1}{E} = \frac{1}{E_c} + \frac{\langle \cos^2 \phi_0 \rangle}{g} \quad (\text{C.1})$$

The Tsai-Hill model was used to derive a relationship between the tensile strength and the orientation parameter just before breakage $\langle \cos^2 \phi_b \rangle$, as follows

$$\sigma_b \approx \left[\frac{\langle \sin^4 \phi_b \rangle}{\sigma_L^2} + \left(\frac{1}{\tau_b^2} - \frac{1}{\sigma_L^2} \right) \langle \sin^2 \phi_b \cos^2 \phi_b \rangle \right]^{-\frac{1}{2}} \quad (\text{C.2})$$

For the well-aligned fibre, the following trigonometric approximations can be made

$$\langle \sin^4 \phi_b \rangle \approx 1 - 2 \langle \cos^2 \phi_b \rangle + 2 (\langle \cos^2 \phi_b \rangle)^2 \quad (\text{C.3})$$

$$\langle \sin^2 \phi_b \cos^2 \phi_b \rangle \approx \langle \cos^2 \phi_b \rangle - 2 (\langle \cos^2 \phi_b \rangle)^2 \quad (\text{C.4})$$

Equation C.2 can be reduced to a quadratic equation

$$(4 \sigma_L^{-2} - 2 \tau_b^{-2}) (\langle \cos^2 \phi_b \rangle)^2 + (\tau_b^{-2} - 3 \sigma_L^{-2}) \langle \cos^2 \phi_b \rangle + (\sigma_L^{-2} - \sigma_b^{-2}) \approx 0 \quad (C.5)$$

which can be solved to obtain the orientation parameter just before fibre failure

$$\langle \cos^2 \phi_b \rangle \approx \frac{(3 \sigma_L^{-2} - \tau_b^{-2}) + \sqrt{(\tau_b^{-2} - 3 \sigma_L^{-2})^2 - 4 (4 \sigma_L^{-2} - 2 \tau_b^{-2}) (\sigma_L^{-2} - \sigma_b^{-2})}}{2 (4 \sigma_L^{-2} - 2 \tau_b^{-2})} \quad (C.6)$$

In order to establish a relationship between the Young's modulus and the tensile strength it is necessary to relate the initial orientation parameter $\langle \cos^2 \phi_0 \rangle$ and the orientation parameter just before breakage $\langle \cos^2 \phi_b \rangle$. In this work they have been related assuming plastic rotation of nanotubes.

$$\langle \cos^2 \phi_b \rangle = \langle \cos^2 \phi_0 \rangle \exp\left(-\frac{\sigma_b}{g_v}\right) \quad (C.7)$$

Hence, equation C.1 can be expressed in terms of the final orientation parameter as

$$\frac{1}{E} = \frac{1}{e_c} + \frac{\exp\left(\frac{\sigma_b}{g_v}\right)}{g} \langle \cos^2 \phi_b \rangle \quad (C.8)$$

Combining equation C.6 & C.8 leads to

$$\frac{1}{E} = \frac{1}{e_c} + \frac{\exp\left(\frac{\sigma_b}{g_v}\right)}{g} \cdot \frac{(3 \sigma_L^{-2} - \tau_b^{-2}) + \sqrt{(\tau_b^{-2} - 3 \sigma_L^{-2})^2 - 4 (4 \sigma_L^{-2} - 2 \tau_b^{-2}) (\sigma_L^{-2} - \sigma_b^{-2})}}{2 (4 \sigma_L^{-2} - 2 \tau_b^{-2})} \quad (C.9)$$