Reinforcing Efficiency of Carbon Nanotubes in Poly (vinyl alcohol) Composites

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By
Zhujuan Wang
School of Engineering and Materials Science
Queen Mary, University of London
Mile End Road, London, E1 4NS
Declaration

I declare that the work performed is entirely by myself during the course of my Ph.D. studies at the Queen Mary, University of London and has not been submitted for a degree at this or any other University.

Zhujuan Wang
I would like to thank all the people that helped me throughout my PhD study. First of all, I would like to thank Prof. Ton Peijs for giving me the opportunity to join his group in Queen Mary University of London. I enjoyed the cheerful and friendly atmosphere in our group, and I would like to thank Dr. Paola Ciselli, Dr Nattakan Soykeabkaew (Nancy), Chris Reynolds, Emiliano Bilotti, Hua Deng, Saharman Gea, and Rui Zhang for their encouragement and support.

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Abstract

In this work, the reinforcing efficiency of carbon nanotubes in Poly (vinyl alcohol) (PVA) composites has been studied. Homogeneous single-walled carbon nanotubes (SWNT) / PVA nanocomposite films were first prepared by a solution-casting method using DMSO as a solvent. The solution-cast films were drawn in the solid state to create uniaxial nanocomposites where polymer chains and the SWNTs are highly aligned. Mechanical properties studies show a remarkable increase in Young’s modulus and tensile strength with the addition of SWNTs. For example, the addition of only 1.0 wt.% of SWNTs led to an astonishing 200% increase in tensile strength. Micromechanical analysis showed that the nanotube contribution to the composite strength was as high as 88 GPa, which starts to exploit the extraordinary theoretical strength of the CNTs. This high reinforcing efficiency suggests that in current systems most of the prerequisites for obtaining highly efficient nanocomposites are fulfilled, i.e. (i) a high level of dispersion, (ii) good interfacial interaction, and finally (iii) a high level of alignment of the nanofillers. X-ray studies demonstrated that the observed improvements in mechanical properties were true reinforcing effects of the SWNTs and not the result of modification of the PVA matrix. We employed the same method to prepare PVA nanocomposite tapes filled with different types of carbon nanotubes. Mechanical tests suggested different reinforcing behaviour in composite tapes. Crystallinity studies and X-ray studies confirmed that polymer morphology had been changed by the addition of double-walled carbon nanotubes and multi-walled carbon nanotubes. It was found that the reinforcing efficiency is influenced by the structure of the tubes, modification of the polymer matrices induced by nanotubes and the interaction between the polymer and the tubes.
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Chapter 1

Introduction

1.1 Historical background on nanocomposites

Composites consist of two or more physically distinct different materials which are combined in a controlled way to achieve a mixture having more useful properties (to defined criteria) than any of the constituents on their own [1]. In other words, composites are combinations of materials which show tailored properties (mechanical, electrical, thermal and chemical properties). Composites are a very broad and important class of engineering materials and they are used in a wide variety of applications. In fact, natural biological materials such as wood, teeth and bone are often made up of two or more constituents. For example, wood is made up of fibrous chains of cellulose molecules in a matrix of lignin, while bone and teeth are both essentially matrix of a tough organic constituent called collagen [2].

There are different types of composites depending on the nature of the matrix. Metal matrix composites (MMCs), ceramic matrix composites (CMCs) and polymer matrix composites (PMCs) are most common composites. PMCs are very important commercial materials with a variety of applications. Intensive research activities
have been carried out in this field especially to enhance mechanical properties like higher strength and higher modulus. Since polymers normally have lower strength and modulus than common structured materials like metals and ceramics, high modulus fillers (fibres, platelets, particles, whiskers) have been included into polymers matrices to make composites. Fibre-reinforced plastics (FRP) can exhibit mechanical properties that vary significantly when measured in different directions. Fibres are the hard constituent in the composites and they may preferentially align in a particular direction. Fibres typically can have very high tensile strengths and Young’s modulus as shown from Table 1.1. Nowadays, carbon fibres and glass fibres are the most common fibres used in PMCs [2].

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Density $\rho$ (Mg m$^{-3}$)</th>
<th>Young’s modulus $E$ (GPa)</th>
<th>Tensile strength $\sigma$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>3.0</td>
<td>400</td>
<td>2.4</td>
</tr>
<tr>
<td>Boron</td>
<td>2.6</td>
<td>400</td>
<td>4.0</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.56</td>
<td>73</td>
<td>2.0</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.45</td>
<td>130</td>
<td>3.0</td>
</tr>
<tr>
<td>SiC whisker</td>
<td>3.2</td>
<td>450</td>
<td>5.5</td>
</tr>
<tr>
<td>Cellulose (flax)</td>
<td>1.4</td>
<td>80</td>
<td>1.5</td>
</tr>
<tr>
<td>Nicalon$^{\text{TM}}$</td>
<td>2.6</td>
<td>190</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Conventional composites are normally filled with micro-scale fillers, where enhanced mechanical properties are always combined with compromise. For example, these micrometer size fillers may act as stress concentration sites leading to embrittlement of the polymer. Nanocomposites open windows for optimizing
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unprecedented composites properties. Polymer nanocomposites are nano-scale filled polymer composites by definition, in which the filler is < 100 nm in at least one dimension [3]. The following properties have been shown to undergo significant improvements:

- Mechanical properties e.g. strength, modulus and toughness
- Thermal stability
- Flame retardancy
- Chemical resistance
- Electrical conductivity
- Optical clarity compared to conventionally filled polymers

The reason why nanocomposites arise significant interest in the scientific community is that the extremely small size of the fillers not only leads to unique properties themselves, but also attributes to unprecedented morphologies of the composites. For example, fillers and matrix are mixed at the nano-scale and the fillers are too small to act as stress concentrators when employed as reinforcing agent [4]. Besides, the addition of a few percentages of nanofillers will create a huge amount of filler-polymer interface, thus the matrix polymer can be considered as nano-scopically confined interfacial polymer [5]. Nanofillers restrict conformation of polymer chains and mobility, which might lead to changes in relaxation behaviour, free volume and thermal transitions like glass transition temperature, etc. For semi-crystalline polymers like poly (vinyl alcohol), polypropylene and polyethylene, nanofillers may even influence the degree of ordering and crystal packing, thus crystallinity or the micro-structure of the polymer will be altered. Nanocomposites offer opportunities of producing a new class of materials which would demonstrate their own structure - property relationship.
1.2 Discovery of carbon nanotubes

Carbon is one of the most abundant elements existing in nature. For centuries, diamond and graphite were considered to be the only two types of all carbon crystalline structure which naturally existed as allotropes. The discovery of $C_{60}$ by Kroto et al. in November 1985 [6], had an impact which extended way beyond the confines of academic chemical physics and marked the beginning of a new era in carbon science [6-7]. Like its name, this $C_{60}$ molecule contains 60 carbon atoms arranged in a spherical way, as in a soccer ball [8]. Several years later, Iijima of NEC laboratories in Japan, discovered carbon nanotubes which proved to be the most important fruit of this research [9]. Great attention has been attracted to this fascinating material which possesses extraordinary mechanical, electrical and thermal properties. One thing to note is that the carbon nanotubes observed by Iijima in 1991 [10] contained at least two concentric graphitic layers, which means they were multi-walled carbon nanotubes (MWNTs). The synthesis of the first single-walled carbon nanotubes (SWNTs) was reported two years later in 1993 by Iijima et al. [11] and Bethune et al. [12] independently. This proved to be an extremely important development, since SWNTs seem to have a seamless structure and possess the potential to be the ideal reinforcement filler for the next generation of high performance composites.
1.3 Carbon nanotube reinforced nanocomposites

Carbon nanotube reinforced nanocomposites are a relatively new type of composite material. It is expected that the classical compromise between properties and processing might be eliminated in these materials, since only low loadings of nanofiller are needed to reinforce the matrix. Furthermore, it is expected that nanocomposites might exhibit improved stiffness without sacrificing toughness [13]. However, the success of CNTs in polymer composites has been fairly limited and not yet leads to a wide range of commercial products. Figure 1.2 gives an example of the stress–strain curve for poly (ether ether ketone) (PEEK) / CNT composites [14] from recent literature, which clearly suggests limited reinforcing efficiency of CNTs even at high fraction of 15 wt.%. One reason being the difficulty in dispersing them in the
hosting matrix. This is not a trivial task, since the extremely large surface area that characterises nanotubes is responsible for their strong tendency to form agglomerates. In addition, the imperfect bonding between CNTs and polymer matrices to provide sufficient interfacial interaction and stress transfer compromises good mechanical properties of the composites. Finally, similar to macromolecules the excellent intrinsic mechanical properties of CNTs can only be completely exploited if uniaxial orientation is achieved.

![Stress-strain curves as a function of MWNTs loading at room temperature in carbon nanotubes / PEEK composites](image)

**Figure 1.2:** Stress–strain curves as a function of MWNTs loading at room temperature in carbon nanotubes / PEEK composites [14]

In this thesis, the results are described of the research into fabrication and characterization of carbon nanotube reinforced polymer nanocomposites. To be able to successfully produce the composites and to understand the reinforcing efficiency
of carbon nanotubes in the composites, the prerequisites for obtaining highly efficient nanocomposites need to be fulfilled i.e. (i) high level of dispersion, (ii) good interfacial interaction and finally (iii) a high level of alignment of the nanofillers. For this reason, most of the research has been focussed on oriented polymer fibres with aligned carbon nanotubes, followed by an investigation on the mechanical properties of the composites and the reinforcing efficiency of different types of carbon nanotubes.

The matrix polymer chosen to study is poly (vinyl alcohol) (PVA), because it is known from previous research that good levels of dispersion could be achieved in this system [15-18]. Moreover, PVA itself suggests considerable potential as high strength and high modulus polymer fibres, because it possesses intrinsically an extremely high crystal modulus of 250 GPa, comparable to polyethylene (PE), which theoretically can be approached when the chain is fully oriented or aligned. Previous research mainly reported studies on isotropic PVA / CNT films, however, only limited amount of literature is published on the incorporation of nanotubes in PVA fibres or oriented tapes. The aim of this research is to conduct a fundamental study on the properties of nanotube reinforced composites. This includes the mechanical characterization of nanocomposites on a meso- and nano-scale and studies on the reinforcing mechanism on a nanoscale. Carbon nanotubes combined with polymeric matrices will be used as model systems and the real potential of CNTs as reinforcing fibres in polymer composites will be investigated, with particular emphasis to oriented systems.
1.4 Outline of the thesis

In this thesis, several aspects of nanocomposite materials based on CNTs and poly (vinyl alcohol) will be discussed. Chapter 2 will introduce the materials employed in this study, including the different types of carbon nanotubes and polymer matrix PVA. Chapter 3 will present an overview on CNT / polymer composites. Processing procedure of the nanocomposites will be discussed with the emphasis on the preparation of oriented CNT / polymer nanocomposites. An extensive literature review on PVA / CNT composites and highlight on effective properties of CNTs in oriented nanocomposites will be introduced as well.

In Chapter 4, the preparation and characterization of the isotropic PVA / SWNT composite films will be discussed in detail. Dispersion condition, stress transfer efficiency as well as composite morphology will be investigated, and the mechanical properties will be assessed through micromechanical models. Chapter 5 will describe detailed characterization of the oriented PVA / SWNT tapes. Different techniques will be applied to understand the reinforcing mechanism of the SWNTs in this system. Attempts will be made to clarify whether the superior mechanical properties observed in nanocomposite tapes are true reinforcing effects from the SWNTs or affects that imagined from the modification of the polymer morphology through the addition of SWNTs.

In Chapter 6, comparative studies on the different reinforcing behaviours of different types of carbon nanotubes will be presented. Although improved mechanical properties were observed in all systems, different factors were found to attribute to the change. Finally, Chapter 7 will summarise the main conclusions from this research and an outlook is given regarding possible future research on this subject.
1.5 Reference


Chapter 2

Materials and backgrounds

2.1 Introduction

Before exploring the various aspects of carbon nanotubes (CNT) / polymer composites such as composite processing and characterization, we will provide some background information on the materials we used in this work. Carbon nanotubes can vary significantly depending on the type, purity, synthesis procedure and structure. First, we will briefly discuss the physical structure, production procedure and properties of carbon nanotubes. Secondly, a brief introduction to poly (vinyl alcohol) we used will be presented.

2.2 Carbon nanotubes

Carbon nanotubes can be visualized as graphite sheet rolled cylinders of covalently bonded carbon atoms, they are either capped by hemi-fullerenes or not. Carbon nanotubes exist as two types of structures: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Figure 2.1 shows the schematic pictures of different types of carbon nanotubes. MWNTs consist of several layers of
coaxially arranged graphite cylinder with interlayer distance of ~0.34 nm which is the interplane spacing of graphite. Double-walled carbon nanotubes (DWNTs) are a special case of MWNTs with only two concentric graphite cylinders. All these three types of carbon nanotubes will be investigated in our work.

![Figure 2.1](image)

**Figure 2.1**: Schematic illustration of different types of carbon nanotubes. (a) single-walled carbon nanotubes; (b) multi-walled carbon nanotubes [1]

### 2.2.1 Nanotube structure

The primary symmetry classification of a CNT divides them into achiral or chiral [2]. The two possible high symmetry structure known as ‘zig-zag’ and ‘armchair’ illustrated in Figure 2.2 are the only two cases of achiral nanotubes. However, it is believed that most nanotubes do not have these highly symmetric forms but have structures in which the hexagons are arranged helically around the tube axis. These structures are generally known as chiral, since they exist in two mirror related forms.
To simplify the structure of an individual carbon nanotube, a vector $C$ which joins two equivalent points on the original grapheme lattice is defined. In this case, the cylinder is produced by rolling up the sheet so that the end-points of the vector are superimposed (Figure 2.3). The chiral vector can be defined by the following equation:

$$\overline{C_h} = n\overline{a_1} + m\overline{a_2} \quad (2-1)$$

Where the integers $(n, m)$ are the lattice translation indices, in other words, the number of steps along the zig-zag carbon bonds of the hexagonal lattice, and $\overline{a_1}$ and $\overline{a_2}$ are the unit vectors. The chiral angle $\theta$ is the angle between the chiral vector $C_h$ with respect to the zigzag direction $(n, 0)$, where $\theta = 0^\circ$. The armchair nanotube axis is defined as the $\theta=30^\circ$ and the translation indices is $(n, n)$. All the other types of carbon nanotubes could be defined as a pair of indices $(n, m)$ where $n\neq m$ and
nanotube axis corresponds to $0 < \theta < 30^\circ$. The chiral vector also indicates the nanotube diameter since the inter-atomic spacing of the carbon atoms is known [4].

![Diagram of a hexagonal sheet of graphite being rolled to form a carbon nanotube](image)

**Figure 2.3**: Schematic illustration of how a hexagonal sheet of graphite is ‘rolled’ to form a carbon nanotube [5]

Although the chirality has a relatively small influence on the elastic stiffness, it plays a role in the nanotube plastic deformation under axial tension. When a lateral strain is applied to the tube axis, C-C bonds are broken, the neighbouring hexagons change into two pentagons and two heptagons, forming a pentagon-heptagon-heptagon-pentagon (5-7-7-5) defect as indicated by dashed lines in Figure 2.4 and is known as the Stone-Wales transformation. The Stone-Wales transformation effectively elongates the tube in the strain direction, releasing the excess strain energy [6].
Figure 2.4: Bond rotation in strained carbon nanotubes: (a) armchair tube under axial strain; rotating the bond “AB” by 90° forms a [5-7-7-5] defect (b) zigzag tube where the bond “EF” is responsible of the formation of the [5-7-7-5] defect [6]

2.2.2 Synthesis of carbon nanotubes

Carbon nanotubes can be produced through different ways and each technique has advantages and disadvantages. Though industry requires large-scale production of carbon nanotubes, impurity and uniformity remain big issues in the nanotube community. Arc-discharge, laser ablation and chemical vapour-growth deposition (CVD) are the most common manufacturing process method for carbon nanotubes. In the following paragraphs, the manufacturing process of carbon nanotubes will be
discussed; advantages as well as drawbacks of each process will be summarized.

**Arc-discharge**

MWNTs observed by Iijima *et al.* [7] were synthesized by electric-arc discharge technique. In 1992, large scale synthesis of MWNTs was reported by Ebbesen and Ajayan *et al.* [8]. For SWNTs, metal catalysts (e.g. Fe, Co, Ni) were found to be essential to assist the synthesis. A number of parameters have been carefully controlled to achieve high quality carbon nanotubes. The most important factor is the pressure of the helium in the evaporation chamber [8], the current [9] and the efficiency of cooling appear to be also very important [10]. A typical illustration of arc-discharge apparatus is shown in Figure 2.5. One thing to note is that the method requires high temperature, usually growth takes place at temperature estimated more than 5000 °C [11] and this leads to a high crystallinity of the materials. However, there is no real control over the dimension of the produced materials like diameter or length.

![Figure 2.5: Schematic illustration of arc-discharge technique for the production of fullerenes and nanotubes [10]](image-url)
**Laser ablation**

High power laser combined with a high temperature furnace offers an alternative way of producing carbon nanotubes. During a typical laser ablation experiment, high power laser is focused on a composite graphite target (in Ar atmosphere) inside a furnace at temperature near 1200 °C, where carbon nanotubes are then collected from Cu-cooled water trap [12]. For SWNTs using the laser ablation, it is also necessary to use metal catalyst, which will induce their growth. A typical experimental set-up is illustrated in Figure 2.6.

**Figure 2.6**: Schematic illustration of laser ablation technique for the production of nanotubes [13]

Both industry and academic society require large quantities of defect-free carbon nanotubes, the high cost of the arc discharge and laser ablation techniques makes the scale-up production hard. Besides the high cost, the products of these techniques normally contain impurities during the nanotubes synthesis like catalyst particles and amorphous carbon. This complicates purification techniques and applications, which leads to even higher cost towards industrialization.
CHAPTER 2. MATERIALS AND BACKGROUND

Chemical vapour-growth deposition (CVD)

Thermal decomposition or chemical vapour decomposition of hydrocarbons with the assistance of a catalyst has been used to make carbon fibres decades ago [14]. This method was employed by Yacaman et al. to produce MWNTs in 1993 [15]. This CVD technique has been subsequently improved and optimized. Generally, it includes catalyst-assisted decomposition of hydrocarbons, usually ethylene or acetylene, in a tube reactor at 550–750 °C and growth of carbon nanotubes over the catalyst upon cooling the system [16]. A typical experimental set up is illustrated in Figure 2.7. CVD method tends to produce fewer impurities and requires lower temperature for the nanotubes growth. This method seems to be easier to scale-up for industry use.

![Diagram of CVD process](image)

**Figure 2.7:** Schematic illustration of catalytic growth of carbon nanotubes. Hydrocarbon gas is decomposed in a quartz tube in a furnace at 550 – 750 °C over a transition metal catalyst (a CVD reactor) [16].

It is worth mentioning here that Smalley and his co-workers at Rice University have optimized the process to produce large quantities of single-walled carbon nanotubes
with remarkable purity. The so-called (high-pressure conversion of carbon monoxide) HiPco nanotubes have received considerable attention as the technology has been commercialized by Carbon Nanotechnologies Inc (Houston, TX) for large-scale production of high-purity single-walled carbon nanotubes [17].

The other unique aspect of CVD techniques is to synthesize aligned arrays of carbon nanotubes with controlled diameter and length. The synthesis of well-aligned, straight carbon nanotubes on a variety of substrates has been achieved by the use of plasma enhanced chemical vapour deposition (PECVD) [18, 19] or a microwave source [20]. Conventional CVD - produced carbon nanotubes are normally tangled and spaghetti-like, which could be produced at a larger quantity and lower cost than PECVD carbon nanotubes. However, there is less control over the parameters of the tubes like diameter, length and structure.

### 2.2.3 Properties of carbon nanotubes

#### Mechanical properties

Since the discovery of carbon nanotubes, their seamless cylindrical graphitic structure promises the superb mechanical properties and implies that nanotubes might be the ultimate fibres for strong, lightweight composite materials. To carry out mechanical characterization of polymer nanocomposites and study the reinforcing mechanism on a nano-scale, the mechanical properties of carbon nanotubes are crucial in this work. The most important modelling and experiments related to mechanical properties of carbon nanotubes will be reviewed in the following paragraphs.
Extensive theoretical predictions had been carried out in many groups, extraordinary mechanical performance from theoretical calculation showed that carbon nanotubes possess tensile modulus and strength as high as 1 TPa and 200 GPa respectively [21-24]. Early report from Ruoff and Lorents et al. [25] considered the case of defect-free nanotubes, both single-walled and multi-walled. By using the elastic moduli of graphite [26], which is 1060 GPa, the tensile stiffness for a SWNT with a wall thickness and diameter of 0.34 and 1 nm was calculated. The tensile strength of nanotubes was estimated by scaling the 20 GPa tensile strength of well-known Bacon’s graphite whiskers in the 1960s [27]. It is important to note that the Young’s modulus is directly related to the cohesion of the solid and therefore to the chemical bonding of the constituent atoms [28]. As for carbon nanotubes, the Young’s modulus is related to the sp$^2$ carbon-carbon bond strength and should equal to that of a graphite sheet if the diameter is not too small to distort the C - C bonds significantly.

Besides extensive theoretical modelling, experimental studies have also been carried out by many groups. Early research focused mainly on multi-walled nanotubes. Treacy et al. [29] first estimated the Young's modulus of isolated arc discharged multi-walled nanotubes by measuring, in the transmission electron microscope (TEM), the amplitude of their intrinsic thermal vibrations. The modulus calculated ranged from 0.41 - 4.15 TPa with an average of 1.8 ± 0.9 TPa for a number of nanotubes. However, the first direct measurement of arc - MWNTs was reported by Wong et al. in 1997 using atomic-force microscope (AFM) [30]. Individual and structurally isolated MWNTs were deposited on molybdenum disulfide (MoS$_2$) substrate, and pinned by deposition of a grid of square SiO pads as shown in Figure 2.8. The bending force was measured versus displacement along the unpinned lengths. The elastic modulus determined was 1.28 ± 0.59 TPa and the average bending strength measured was 14.2 ± 8.0 GPa. Salvetat et al. [31] also use AFM to
measure the elastic modulus of isolated MWNTs. Instead of applying a lateral force to tubes like Wong [30], they clamped the nanotubes to an ultrafiltration membrane and measured vertical deflection versus the force applied at the point midway along the length. In other words, nanotubes were treated as a beam that is clamped at each end and to measure elastic modulus. Three types of MWNTs were measured, 810 (+410 / -160) GPa of elastic modulus was measured for arc-MWNTs, while catalytic MWNTs ranged only from 10 to 50 GPa.

**Figure 2.8**: Overview of the approach used to probe mechanical properties of carbon nanotubes. (a) carbon nanotubes deposited on the substrate and pinned by square SiO pads; (b) Schematic of beam bending with an AFM tip and lateral force changes [30]

In 2000, Yu et al. [32] carried out the first tensile-loading experiment inside a scanning electron microscope (SEM) on individual MWNTs. The MWNTs broke in the outermost layer (sword-in-sheath failure), and the tensile strength of this layer ranged from 11 to 63 GPa. Analysis from stress-strain curves showed that the Young’s modulus (E) of the tubes ranged from 270 to 950 GPa. Figure 2.9 shows the SEM image of the tensile test. An individual MWNT was mounted between two opposing AFM tips with the lower soft cantilever used to determine the applied force.
and the top rigid AFM tip to apply tensile load to the MWNT. The MWNT section is covered by a square-shaped carbonaceous deposit.

![SEM image of the tensile test on an individual MWNT](image)

**Figure 2.9**: SEM image of the tensile test on an individual MWNT [32]

The measurement of SWNTs proved to be more challenging, since they tend to form bundles because of strong Van der Waal forces. It is almost impossible to measure individual single-walled tube as previously performed on MWNTs. Krishnan *et al.* [33] applied the technique of Treacy *et al.* [29] to measure Young’s modulus of isolated SWNTs. An average of 1.25 (-0.35 / +0.45) TPa modulus was found. However, the first measurements were carried out by Salvetat *et al.* [34] using AFM on arc-discharged SWNTs ropes. They determined both the elastic and the shear moduli for SWNT ropes, and an elastic modulus of about 1 TPa was calculated for small diameter and long ropes. However, low intertube shear stiffness dominated the flexural behaviour of the SWNTs ropes. Shear modulus decreases with the increase
of the diameter of the ropes, which shows nanotube slip within the bundle. Walters et al. [35] studied the elastic strain of pulsed laser vaporization grown SWNTs bundles using AFM. By assuming the elastic modulus to be 1.25 TPa, the result of maximum strain $5.8 \pm 0.9\%$ indicated a yield strength of $45 \pm 7$ GPa. Yu et al. [36] performed similar measurements on SWNTs ropes as well as MWNTs with moduli ranging from 0.32 to 1.47 TPa and strength between 13 to 52 GPa were observed.

Table 2.1 summarizes some of the mechanical properties of MWNTs (M) and SWNTs (S) calculated from various experiments in the literature. It is clear that carbon nanotubes exhibit extraordinary mechanical properties, though a gap still exists between the measured modulus, strength and theoretical predictions for ideal carbon nanotubes. It is important to note that the strength of a material is strictly linked with the structure defect and the imperfection of the materials. In other words, the mobility of dislocations and their ability to relax stress concentrations at the flow tip influence the strength and the breaking mechanism of the material [37]. Here, structure defects which exist on the shell of tube wall will lower the measured strength, and inhomogeneous diameter of the tubes also raise errors in the measurement.
### Table 2.1: Mechanical properties of carbon nanotubes from literature experimental data

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of CNT</th>
<th>Young’s modulus</th>
<th>Tensile strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct tensile test [38]</td>
<td>CVD – MWNT</td>
<td>0.45 ± 0.23</td>
<td>1.72 ± 0.64</td>
</tr>
<tr>
<td>[39]</td>
<td>CVD – MWNT</td>
<td>0.45</td>
<td>3.6</td>
</tr>
<tr>
<td>Nano-tensile test via AFM [40]</td>
<td>CVD – MWNT</td>
<td>-</td>
<td>17.4 – 259.7</td>
</tr>
<tr>
<td>[40]</td>
<td>Ws2 – MWNT</td>
<td>-</td>
<td>3.8 – 16.3</td>
</tr>
<tr>
<td>[36]</td>
<td>Arc – MWNT</td>
<td>0.27 – 0.95</td>
<td>11 – 63</td>
</tr>
<tr>
<td>laser evaporation-SWNT [36]</td>
<td></td>
<td>0.32 – 1.47</td>
<td>13 – 52</td>
</tr>
<tr>
<td>Tensile and bending test in a TEM [41]</td>
<td>Arc – MWNT</td>
<td>0.9</td>
<td>150</td>
</tr>
<tr>
<td>Micro–Raman spectroscopy [42]</td>
<td>Arc – MWNT</td>
<td>1.7 – 2.4</td>
<td>-</td>
</tr>
<tr>
<td>[42]</td>
<td>laser evaporation-SWNT</td>
<td>2.8 – 3.6</td>
<td>-</td>
</tr>
<tr>
<td>Amplitude of thermal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vibrating [29]</td>
<td>Arc – MWNT</td>
<td>1.8 ± 0.9</td>
<td>-</td>
</tr>
<tr>
<td>[43]</td>
<td>laser evaporation-SWNT</td>
<td>1.25 ± 0.45</td>
<td>-</td>
</tr>
<tr>
<td>direct tensile test with PVC [44]</td>
<td>CVD – SWNT</td>
<td>&lt;0.79</td>
<td>22.2 ± 2.2</td>
</tr>
<tr>
<td>Beam bending via</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFM [31]</td>
<td>CVD – MWNT</td>
<td>10 – 50</td>
<td>-</td>
</tr>
<tr>
<td>[31]</td>
<td>Arc – MWNT</td>
<td>810 ± 60</td>
<td>-</td>
</tr>
<tr>
<td>[34]</td>
<td>Arc – SWNT</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>[30]</td>
<td>Arc – MWNT</td>
<td>1.28 ± 0.59</td>
<td>(bending strength)</td>
</tr>
</tbody>
</table>
CHAPTER 2. MATERIALS AND BACKGROUNDS

Effective properties

To determine the elastic modulus of carbon nanotubes, an accurate definition of the nanotube cross-section area is of great importance. As mentioned previously, typically the hollow part of carbon nanotubes was not considered for the cross-section area, since it does not carry any load. For MWNTs, weak Van der Waals bonding between walls of the nanotubes implies that only the outer layer of the tube will carry almost the entire load from the tube – tube interphase. While for SWNTs, normally the calculation was performed on the assumption that only the perimeter SWNTs in the close-packed SWNT ropes carries the initial load. However, when carbon nanotubes are embedded to create nanocomposites, the modelling of composite elastic properties takes account of the whole volume fraction occupied by the nanotubes. Thus, the load carrying capability of the outer layer of the nanotube must be applied to the entire cross-section of the nanotube [45].

Figure 2.10: Schematic picture of (a) nanotube and (b) effective fibre used to model the elastic properties of a nanotube embedded in a composite [45]
Figure 2.10 shows the schematic picture of nanotube and effective fibre used to model the elastic properties of a nanotube embedded in a composite. Obviously, effective Young’s modulus as well as strength will be lower considering the entire cross-section of the nanotube carry the load rather than the outwall of MWNTs or the perimeter SWNTs in the close-packed SWNT ropes. Ciselli [46] calculated the effective Young’s modulus and tensile strength for SWNTs, DWNTs and MWNTs. Results are listed in Table 2.2 and Table 2.3. In the calculation, 1 TPa was used as the value for Young’s modulus, and 130 GPa as value for strength of various type of nanotubes. Indeed, effective properties of various types of carbon nanotubes reach lower bound values when only the external wall carries the load and upper bound values when all walls carry the load. For MWNTs, calculations are strongly dependent on the structure of the nanotubes and the interaction between the outermost and the internal layers. However, due to the small diameter of SWNTs, no significant change is observed for the calculation for SWNTs.

Table 2.2: Effective properties of various types of nanotubes, only the external wall carries the load (lower bound) [46].

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>d_e [nm]</th>
<th>E_eff [GPa]</th>
<th>σ_eff [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>1.4</td>
<td>971</td>
<td>126</td>
</tr>
<tr>
<td>DWNT</td>
<td>4.7</td>
<td>289</td>
<td>43</td>
</tr>
<tr>
<td>MWNT</td>
<td>15</td>
<td>91</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 2.3: Effective properties of various types of nanotubes, all walls carry the load (upper bound) [46].

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>$d_c$ [nm]</th>
<th>$E_{\text{eff}}$ [GPa]</th>
<th>$\sigma_{\text{eff}}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>1.4 nm</td>
<td>971 GPa</td>
<td>126 GPa</td>
</tr>
<tr>
<td>DWNT</td>
<td>4.7 nm</td>
<td>579 GPa</td>
<td>77 GPa</td>
</tr>
<tr>
<td>MWNT</td>
<td>15 nm</td>
<td>929 GPa</td>
<td>121 GPa</td>
</tr>
</tbody>
</table>

It is worth to note that the real advantage of CNT over other fibres such as carbon fibre is in tensile strength. In fact, the stiffest high modulus commercial carbon fibre Torayca M65J from Toray Industries (Japan) has a modulus of around 650 GPa compared to 971 GPa for SWNTs, while their strongest carbon fibre, T1000, has an ultimate tensile strength (UTS) of nearly 7 GPa. Clearly, when only the external wall of MWNTs carries the load, the effective strength of MWNTs is still twice the value of the strongest carbon fibre. As for SWNTs, their strength is nearly 20 times higher than that of the strongest carbon fibre. Because of their significant mechanical properties, SWNTs should be considered as ideal reinforcing filler for polymer nanocomposites.

**Vibration properties**

Raman spectroscopy is a widely used technique in materials science which involves the excitation of a sample with intense monochromatic light (typically laser light) followed by observations of the scattering of the incident radiation [47]. It is non-destructive and fast, the measurement could be performed over a range of temperature or pressures, above all, sample preparation is straightforward and relatively easy.
To illustrate the Raman effect, Figure 2.11 demonstrates the energy – level diagrams of Rayleigh scattering, Stokes Raman scattering, and anti-Stokes Raman scattering. When an incident beam encounters the sample, photons are absorbed by the material and scattered. The predominant amount of the scattered photons have exactly the same wavelength as the incident photons and are known as Rayleigh scatter, but a tiny portion (approximately 1 in 10^7) of the incident protons interact with the molecules in the way that the energy is either gained or lost. Stokes Raman scattering occurs when the photons lose energy from the vibrating molecules and spectrum shifts appear on the smaller energy sides of the incident laser energy. Anti – Stokes Ramans scattering appears on the bigger energy sides of the incident laser energy since the photons gain energy from the vibrating molecules. By measuring the intensity of the scattered light as a function of frequency downshift (losing energy) of the scattered light, Raman spectra is plotted [48].

![Energy-Level Diagrams](image)

**Figure 2.11**: The energy-level diagrams of Rayleigh scattering

Raman spectroscopy is one of the powerful tools to characterize carbon nanotubes. Figure 2.12 shows a typical Raman spectrum of single-walled carbon nanotubes [5].
CHAPTER 2. MATERIALS AND BACKGROUND

The most characteristic features are marked and summarized as follows: (1) the radial breathing mode (RBM) appearing at ~ 200 cm\(^{-1}\) for SWNTs is associated with the atomic vibration of the C atoms in the radial direction, as if the tube was breathing [49]; (2) The D band between 1250 and 1450 cm\(^{-1}\) is known to be disorder-induced (D: disorder); (3) The multi-peak feature around 1580 cm\(^{-1}\) provides a signature of carbon nanotubes and it is called tangential mode (G band) which corresponds to in-plane bond-stretching mode; (4) The G’ (often called D*) band between 2450 – 2650 cm\(^{-1}\) is the second – order overtone of D band.

Both theoretical and experimental work has shown that the frequency of the RBM is inversely proportional to the diameter of individual nanotubes [50]. Diameters of carbon nanotubes could be calculated through the relation

\[
\omega_{RBM}(d) = \frac{A}{d} + B
\]  

(2-2)

where the parameters A and B are determined experimentally. It is important to note that this relation is valid in a small range of size (1 nm < \(d_t\) < 2 nm), the intensity of the RBM feature is weak and is hard to observe for the large diameter tubes (\(d_t > 2\) nm) [49]. Temperature dependence [51] and effect of uniaxial strain deformation [52] upon the Raman radial breathing modes have been reported as well.
The SWNT G-band consists of multi-peaks due to the photon wave vector confinement along the SWNT circumference and due to symmetry-breaking effects associated with SWNT curvature. The two main components can be identified; one peaked at 1590 cm$^{-1}$ ($G^+$) and the other at about 1570 cm$^{-1}$ ($G'$). The $G^+$ feature is related to vibrations of carbon atoms along the nanotube axis, while the latter is associated with vibrations of carbon atoms along the circumferential direction of the SWNTs. This multi-peak could be used for diameter characterization, although the information provided is less accurate than the RBM mode. Figure 2.13 shows the schematic picture of the atomic vibration for the RBM and G band respectively.
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Figure 2.13: Schematic picture showing the atomic vibrations for (a) the RBM and (b) the G band.[49]

Most of the Raman studies focus on single-walled carbon nanotubes since characterization on multi-walled carbon nanotubes by Raman spectroscopy is not as straightforward as the SWNTs. Because of the large diameter of the outer tube for MWNTs, differences between carbon nanotubes and graphite in the Raman spectra are hard to distinguish [49].

Other properties

Carbon nanotubes are graphite sheets rolled into tubes, the nearly one dimensional structure because of their high aspect ratio combined with huge surface area from nano-size structure results not only in their outstanding mechanical properties, but also fascinating electronic properties, thermal properties and a whole range of promising applications. Carbon nanotubes are thermally stable up to 2800ºC in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [3]. Table 2.4
lists thermal conductivity and electrical conductivity of various engineering materials. Applications that exploit this behaviour of CNTs include making conductive composites; conductive coatings; electrostatic dissipation (ESD) or antistatic materials. Devices such as field-emission display [53], scanning probe microscopy tips [54] have been developed using carbon nanotubes.

### Table 2.4: Thermal conductivity and electrical conductivity of different engineering materials [55]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thermal conductivity (W / m.K)</th>
<th>Electrical conductivity (S / m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotubes</td>
<td>&gt;3000</td>
<td>$10^6$ – $10^7$</td>
</tr>
<tr>
<td>Copper</td>
<td>400</td>
<td>$6 \times 10^7$</td>
</tr>
<tr>
<td>Carbon fibre – Pitch</td>
<td>1000</td>
<td>2 – $8.5 \times 10^6$</td>
</tr>
<tr>
<td>Carbon fibre – PAN</td>
<td>8 - $10^5$</td>
<td>6.5 – $14 \times 10^6$</td>
</tr>
</tbody>
</table>

### 2.2.4 Carbon nanotubes in this work

Arc-discharge carbon nanotubes and catalytic carbon vapour deposition (CCVD) carbon nanotubes were used in this work. Arc-discharge grown nanotubes are known to exhibits the best graphitic structure. They are normally stiff and straight because of few defects in the structure. Single-walled carbon nanotubes we used were purchased from Carbolex labelled as AP-grade. These SWNTs consist of single-walled, closed-ended carbon nanotubes, which are made through arc-discharge method in specifically designed chambers. These carbon nanotubes have an average diameter of 1.4 nm and found in “ropes” which are typically ~20 nm in diameter or approximately 50 tubes per rope with lengths of 2–5 microns.
Impurities include approximately 35 wt.% of residual catalyst which is usually encapsulated in carbon shells. Some amorphous carbon may also be found on the outer surfaces of the ropes. The only post synthesis treatment of the nanotubes comes from the homogenization of the tubes directly from the chamber. The purity of Carbolex AP-grade SWNT is around 50 – 70 %.

Figure 2.14 shows a SEM image of a typical AP-Grade sample. The strand - like fibres in this image are "ropes" of parallel, individual single-walled carbon nanotubes (SWNT). Typical rope diameter: \(~ 20\) nm. Typical SWNT diameter: \(~ 1.4\) nm.

![SEM image of typical AP-Grade Carbolex Single-walled nanotubes](image)

**Figure 2.14:** SEM image of typical AP-Grade Carbolex Single-walled nanotubes

In addition to arc-discharged SWNTs from Carbolex, SWNTs, DWNTs and MWNTs from Nanocyl (Belgium) were also used in our study. These carbon nanotubes were produced via catalytic carbon vapour decomposition (CCVD) process and they exhibit various diameters and lengths. Figure 2.15a shows the typical SEM picture of catalytic grown MWNTs with average diameter of 10nm and lengths ranging from
0.1 to 10 µm. Nanotubes which exit the reactor are then purified to greater than 95 %
carbon. It is easy to observe that they are highly entangled and therefore difficult to
disperse in a polymer matrix to make CNT / polymer composites. The curvature in
these MWNTs indicates a great amount of defects in the structure.

![SEM images of carbon nanotubes](image)

**Figure 2.15**: SEM image of catalytic grown (a) Multi-walled; (b) Double-walled; (c)
Single-walled carbon nanotubes from Nanocyl (Belgium) [55]

Besides MWNTs, DWNTs used in our work are also produced via the CCVD
process. Nanotubes which exit the reactor are then purified to greater than 90 %
carbon. Figure 2.15b shows the SEM image of the DWNTs. Similar to MWNTs, they
are highly entangled and curly. DWNTs consist of only two graphite cylinders;
therefore exhibit an average diameter of around 4.7 nm and a length ranging from 1 to 10 µm. The CCVD-grown SWNTs shown in Figure 2.15c exhibit an average diameter of 2 nm and length of several microns. It is worth mentioning that functionalised MWNT were also used in this work, they are functionalized with -COOH groups from the MWNTs (Nanocyl) with less than 4 %. Table 2.5 summarizes different types of carbon nanotubes employed in our work.

<table>
<thead>
<tr>
<th>CNTs type</th>
<th>Diameter (nm)</th>
<th>Length (µm)</th>
<th>Purity (%)</th>
<th>-COOH functionalization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc-SWNTs</td>
<td>1.4 (single)</td>
<td>average</td>
<td>50-70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>~20 (bundle)</td>
<td>~1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CVD-SWNTs</td>
<td>2</td>
<td>several</td>
<td>&gt;80</td>
<td>_</td>
</tr>
<tr>
<td>CVD-MWNTs</td>
<td>10</td>
<td>0.1-10</td>
<td>&gt;95</td>
<td>_</td>
</tr>
<tr>
<td>CVD-MWNT-COOHs</td>
<td>10</td>
<td>0.1-10</td>
<td>&gt;95</td>
<td>&lt;4</td>
</tr>
<tr>
<td>CVD-DWNTs</td>
<td>4.7</td>
<td>1-10</td>
<td>&gt;90</td>
<td>_</td>
</tr>
</tbody>
</table>

It is important to point out that we noticed obvious differences between different batches of nanotubes produced by seemingly equivalent synthetic process. Therefore, we use the carbon nanotubes from the same batch and same grade of polymer throughout this study in order to be able to better compare results and clarify trends.
2.3 Poly (vinyl alcohol)

Poly (vinyl alcohol) (PVA) is a synthetic semi-crystalline polymer and unlike most polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer, vinyl alcohol, almost exclusively exists as the tautomeric form, acetaldehyde. PVA instead is prepared by the polymerization of vinyl acetate, followed by partial or complete catalysed hydrolysis to remove acetate groups. The degree of hydrolysis determines the number of acetate groups in polyvinyl alcohol and the principal grades of polyvinyl alcohol produced can be classified as fully hydrolyzed (97.5 – 99.5 percent degree of hydrolysis) and partially hydrolyzed (87 – 89 percent degree of hydrolysis). The physical characteristics of polyvinyl alcohol vary depending on the degree of polymerization, hydrolysis and distribution of hydroxyl groups.

PVA is very simple water soluble polymers from a structural point of view, it exhibits crystallinity as the -OH groups are small enough to fit into the lattice without disrupting it. Like many other hydrophilic polymers, it has found wide acceptance as a material for adhesive, hydrogel, membrane, and other applications [56-57]. In addition, PVA exhibits considerable potential as a material for high modulus, creep resistant films and fibres [58,59]. However these properties are dependent on humidity, in other words, more water leads to higher humidity. The water acts as a plasticiser and will reduce its tensile strength, but increase its elongation and tear strength. PVA has a melting temperature of 230°C and 180–190°C for the fully hydrolysed and partially hydrolysed grades. PVA also decomposes rapidly above 200°C, which means the melt temperature exceeds the degradation temperature for fully hydrolysed grades. Figure 2.16 shows the chemical structure of fully hydrolyzed and partially hydrolyzed poly (vinyl alcohol) grade.
In polymer materials high strength and stiffness can generally be achieved by orientation of polymer chains, creating unidirectional structures like films and fibres, thus high drawing is necessary to get high modulus and high-strength fibrous materials. However, the drawability of dried PVA films is affected by the structure and properties, and depends greatly on the molecular weight and the species of the solvents. For polymer like polyethylene (PE), orientation is relatively easy since only Van der Waals forces are present. In the case of PVA, strong intermolecular hydrogen bonds need to be broken and reformed during drawing, thus macromolecules orientation appears difficult. In addition, hydrogen bonds re-accumulate and restrain polymer chain extension, thus make the drawing process more difficult.

The first patent on PVA fibres goes back to 1931, when Herrmann *et al* [60] reported wet and dry spinning method for preparing PVA fibres. Later on, Sakurada and his collaborators [61] produced water-insoluble PVA fibres by wet spinning followed by formalisation of the fibre, which involves a treatment in formaline solution to create acetal bonds between adjacent hydroxyl groups. By applying the solution spinning
technology, the mechanical properties of the PVA fibres are normally several hundreds MPa tensile strength and about 10 GPa modulus. Since the gel spinning of ultra-high-molecular-weight polyethylene (UHMWPE) developed by Smith and Lemstra [62], many researchers have attempted to develop high-performance fibrous materials from other flexible semi-crystalline polymers including poly (vinyl alcohol) (PVA) [62-65]. Owing to the planar zigzag structure, the PVA crystal has a modulus in the chain direction as high as 250 GPa, comparable to PE [66]. However, as shown in Figure 2.17, the full potential of PVA has not been fully exploited yet, because as mentioned earlier it is difficult to achieve a high draw ratio. Typically the use of gel spinning technology allows reaching tensile strengths up to 2.5 GPa and Young’s modulus of 70 GPa [63].

Figure 2.17: Relationship between the crystal modulus and the maximum specimen modulus for various polymers [66].
In this work, PVA is purchased from Sigma-Aldrich and contains an average molecular weight ranging from 86,000 – 142,000 g/mol specified with a 99+ % degree of hydrolysation. All the samples are stored in a desiccator to keep PVA from absorbing water in the open environment. PVA films were first made from solution casting and film stretching in the solid state was performed at temperatures sufficient to allow molecular mobility (between $T_g$ and the melting temperature). The stiffness in the drawn direction related directly to the draw ratio $\lambda$ (ratio of final to initial length of the sample) [67].

### 2.4 Reference

CHAPTER 2. MATERIALS AND BACKGROUNDS


CHAPTER 2. MATERIALS AND BACKGROUNDs


CHAPTER 2. MATERIALS AND BACKGROUNDS


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Chapter 3

Carbon nanotube (CNT) / polymer composites

3.1 Introduction

In Chapter 2, materials and related background information in this work were introduced. Different types of carbon nanotubes will be employed as reinforcing fillers and semi-crystalline polymer PVA will be used as polymer matrix. Systematic characterization and result discussions on CNT / PVA composites will be presented in detail in the next chapters.

This chapter will introduce and discuss progress and challenges on various aspects of CNT / polymer composites. Due to their extraordinary mechanical, electrical and thermal properties, carbon nanotubes have attracted great enthusiasm among researchers and polymers filled with carbon nanotubes have been extensively exploited. Before exploiting the potential fantastic properties of CNT / polymer composites, there are some issues that have to be kept in mind. First, carbon nanotubes vary in chiralities, diameters, length, amount of impurities and defects from different preparations routes and they even vary in batches. With huge surface area, the possible strong interfacial interactions with polymer matrix suggest that
CHAPTER 3. CNT / POLYMER COMPOSITES

differences in carbon nanotubes might alter the final properties in composites. Thus, it is known to be difficult to carry out reproducible, well-controlled experiments, which makes it hard to compare results from different researchers [1]. Secondly, good CNT dispersion and efficient stress transfer from the matrix to the tubes is difficult to achieve. Fabrication of well-dispersed carbon nanotube / polymer composites is required in this field. Thirdly, due to the one-dimensional character of carbon nanotubes, oriented CNT / polymer composite fibres or tapes are of immense interest as such oriented nanocomposite systems would lead to a much better stress transfer efficiency of the nanotubes. In the first part of this chapter, a processing procedure for carbon nanotube / polymer composites will be discussed followed by the introduction of polymer and carbon nanotubes orientation. Finally, an extensive review on PVA / CNT composites and oriented CNT / polymer nanocomposite fibres in recent literature will be presented.

3.2 Processing of nanocomposites

Many efforts have been attempted to include carbon nanotubes into polymer matrices, though the properties of the final nanocomposites vary depending on the type of carbon nanotubes and polymer. Among processing routes which have been employed to make carbon nanotube / polymer composites, solution processing, melt mixing and in-situ polymerization are the most common ways. However, recently new techniques have proved to be working as well, such as latex technology [2], solid-state shear pulverization [3], etc. Though processing techniques differ intrinsically, the critical issues like uniform dispersion within the matrix and good carbon nanotube / polymer interfacial adhesion remain the same. In the following paragraphs, modification of carbon nanotubes and different processing routes of CNT / polymer composites will be reviewed, and the latest development in
processing routes will also be summarized.

3.2.1 Modification of Carbon nanotubes

Though carbon nanotubes are available commercially in the market, they differ between types even in batches because of their intrinsic morphology and physical properties are different. Despite their superb anisotropic properties, raw carbon nanotubes available are normally isotropic and contain some impurities which are not expected. Several steps are sometimes taken before carbon nanotubes are incorporated into the matrix: purification, exfoliation of carbon nanotubes and chemical functionalization. The following paragraphs will briefly mention common steps that are involved before processing composites.

Purification

As mentioned before, carbon nanotubes are always accompanied by impurities depending on the production method. Most production generates tubes with impurities like amorphous carbon, metal catalysts and fullerenes etc. Many methods have been applied to remove the by-products. Mechanical techniques like centrifugation [4], size exclusion chromatography [5] and filtration [5-7] have been applied successfully. Oxidation including acid oxidation and gas oxidation has been commonly employed to remove catalysts. Acid oxidation removes metal catalyst and amorphous carbon, but it will also form carboxylic acid groups at the tube ends and, possibly, form defects on the sidewalls. This may destroy intrinsic properties of carbon nanotubes. Gas phase oxidation is commonly used as the purification method for MWNTs as shown in Figure 3.1 [8, 9]. However, Dujardin et al. [8] suggested that gas-phase oxidation destroys the single-shell nanotubes before anything else in
the sample. Dillon et al. [10, 11] and Chiang et al. combined acid oxidation and gas oxidation to purify SWNTs, high purity of more than 98 % and 99.9 % had been achieved, respectively. Though purification could remove most of the impurities, the amount of materials that are lost during the process is still too much. Obviously, more rapid and efficient ways of purification are required.

Figure 3.1: TEM micrographs of as-synthesized carbon nanotubes (a) before purification; (b) after purification [8].
Exfoliation of carbon nanotubes

Because of strong Van der Waals forces between individual carbon nanotubes, they tend to form bundles. Deagglomeration for dispersing individual nanotubes is necessary before mixing with polymer matrix. Sonication of a CNT solution is the most common method, but severe sonication may damage tubes and make them shorter during the intense sonication [12, 13]. Polymer wrapping has been proposed as an alternative method to achieve good dispersion of carbon nanotubes without destroying their electrical properties [14] and this opens a door for biological relevant systems as well [15].

Chemical functionalization

Because of the perfect seamless structure of carbon nanotubes, they are not compatible to most of the polymer. Surface treatment is sometimes required to improve nanotube / polymer interface adhesion for processing as well as properties enhancement. Non-covalent functionalization and covalent functionalization are the two main approaches to functionalize carbon nanotubes. Surfactant and polymers are often employed in the non-covalent functionalization to overcome entanglement of carbon nanotube resulting from Van der Waals forces. The advantage of non-covalent functionalization is that the perfect structure of carbon nanotubes remains unaltered, thus mechanical and electrical properties of the tubes could be preserved. However, the drawback is that the interaction based on this functionalization is normally weak which leads to relatively low efficiency in stress transfer from matrix to nanotubes. In addition, the unwanted surfactants present and remain within the composites. For the covalent functionalization, functionalization has been carried out on sidewalls or defects of the nanotubes, reactions between functionalized tubes and polymer chains...
are followed. Many groups have performed these treatments to carbon nanotubes and good dispersion and property enhancement has been observed [16, 17]. However, chemical functionalization might result in a damaged structure of the carbon nanotubes, thus their fantastic electrical and mechanical properties may not be preserved. Of course, the competition between perfect dispersion and unaltered properties of carbon nanotubes always exist, as the most important issue is to obtain the optimum property for the final composites. Figure 3.2 illustrates four common types of functionalization on carbon nanotubes: oxidized carbon nanotubes, carbon nanotubes grafted with polymer, surfactant-assisted carbon nanotubes and polymer wrapped carbon nanotubes.

Figure 3.2: Functionalization of carbon nanotubes (1) oxidation; (2) polymer grafted; (3) surfactant-assisted; (4) polymer wrapped [18]
3.2.2 Solution processing

Solution processing is the most common method to prepare CNT / polymer composites. Though experimental details maybe different for individual polymers, basic route applies to all as simply illustrated in Figure 3.3. First, dispersion of carbon nanotubes in a proper solvent at room temperature or elevated temperature and a polymer solution is prepared at the same time. Then mixing the carbon nanotube suspension and polymer solution is performed. At last, careful control of the evaporation of solvent will be made and dry composite films will be left. One thing to note is that to disperse the pristine carbon nanotubes is difficult, thus agitation is required through the experiment. Commonly, agitation is provided by magnetic stirring, shear mixing, reflux, or, most frequently, ultrasonication. Sonication can be performed in two ways: mild sonication, in other words, sonication bath or high-power sonication using either tip or horn [19].

![Figure 3.3: A schematic procedure of solution processing of CNT / polymer composites](image-url)
3.2.3 Melt mixing

In addition to solution processing which is relatively easy for soluble polymers, melt mixing is also a common technological route to make composites, especially for thermoplastic. Thermoplastic polymers become soft when heated, amorphous polymers can be processed above the glass transition temperature ($T_g$) and semi-crystalline polymers can be melt and processed when heated above their melting temperature ($T_m$). Melt mixing is time efficient as well as simple, its ease of processing suits the increasing demand of large-scale production of CNT composites for industry application. The method is beneficial because they are free of solvents or contaminants, which are normally present in solution processing and in-situ polymerization [20].

In melt processing, high shear mixing is essential for nanofillers to be incorporated into the matrix, because their extremely large surface area leads to altered viscosity. Careful control over several parameters like shear mixing rate [21], mixing time and type of mixer [22] has to be taken to maintain good dispersion of tubes and produce homogenous CNT / polymer composites. Research has already shown that a high shear force may result in some breakage of CNTs [23] as well as unexpected polymer degradation [21]. Successful examples of melt mixing include MWNT / polypropylene [24], MWNT / polycarbonate [25] and MWNT / nylon 6 [26], etc.

3.2.4 In-situ polymerization

In-situ polymerization has been intensively investigated recently. In theory, polymers which could not be processed by melt processing and solution processing could be prepared by in-situ polymerization. The advantage of this method is that polymer
chains can be grafted on the carbon nanotubes on a molecular scale. This ensures better dispersion of carbon nanotubes and good interfacial adhesion between the polymer matrices and nanotubes. Using this technique, it is also possible to include higher nanotubes loading into the matrix while maintaining a relatively good dispersion. Results from different groups [27,28] show that uniform dispersion of CNTs can be achieved and significant enhancement of both mechanical and electrical properties has been observed.

### 3.2.5 Other methods

Regev et al. [2] developed a new approach to reinforce highly viscous polymer of basically any type by a network of individual or bundles of few SWNTs. Polystyrene latex nanoparticles in aqueous solution are mixed with SWNTs which have been exfoliated by surfactant. Percolation threshold was observed to be as low as 0.28 wt.%, and electron microscopy showed that good dispersion had been achieved. This simple method is promising and proved to be independent of polymer type. In another research, solid-state pulverization was applied to produce CNT / PP composites and good dispersion was achieved [3]. This pulverization process could be used alone or followed by melting process. It is advantageous that the cohesion between the nanotubes and the polymer matrix could be improved by mechanochemical effects and the number of defects and entanglement could be reduced to enhance dispersion quality. Moreover, Mamedov et al. [29] developed a layer-by-layer deposition technique to fabricate CNT composites. This technique prevented phase separation that normally happens during nanocomposites preparation. After subsequent cross linking, uniform dispersion was achieved. Composites with as much as 50 wt.% of SWNTs were prepared and exceptional
strong free-standing membrane showed great potential to be components for a variety of long-lifetime devices.

3.3 Alignment of carbon nanotubes

Carbon nanotubes are tubes with diameters in nanometer range and exhibit very high aspect ratio. They demonstrate intrinsic highly anisotropic physical and chemical properties that are attractive for future applications. However, carbon nanotubes tend to form bundles because of Van der Waals forces and it has always been difficult to disperse and align them. To realize their full potentials, well-aligned nanotubes are essential and fundamental to study. Nanotubes can be aligned through direct growth, by magnetic force, electric field, and by polymer flow introduced during mechanical stretching, melt fibre spinning, or spin casting. The following paragraphs will describe them.

Large-scale synthesis of aligned carbon nanotubes was reported by Li et al. in 1996. The aligned CNTs were achieved by chemical vapour deposition (CVD) of acetylene in nitrogen gas at temperatures above 700°C on mesoporous silica embedded with iron nanoparticles [30]. After that, Ren et al. successfully produced large arrays of aligned carbon nanotubes grown on nickel-coated glass below 660°C by plasma-enhanced chemical vapour deposition (PECVD). Figure 3.4 shows the SEM picture of aligned carbon nanotubes on the glass substrate [31]. Growth of aligned carbon nanotubes was reported by many other groups as well [32-35].
By applying electric field, carbon nanotubes could also be aligned. Carbon nanotubes dispersed in ethanol were aligned by an electric field by Bubka et al. [36]. Interestingly, electrospinning has recently been applied to align CNTs in composite fibres as well. Zhou et al. [37] reported polyethylene oxide (PEO) and polyvinyl alcohol (PVA) nanofibres containing MWNTs. Figure 3.5 clearly shows well oriented MWNTs in PEO nanofibres.

**Figure 3.4:** SEM picture of (a) array of aligned carbon nanotubes on glass substrate over large area; (b) enlarged view of (a) [30]
A high magnetic field is also an efficient and rather direct way to align carbon nanotubes. Much work has focused on aligning carbon nanotube magnetically, either by aligning nanotubes themselves [38] or nanotube / polymer composites [39]. Walters et al. [38] first produced macroscopic thin membranes with highly oriented SWNTs by using magnetic field. The thin membranes were produced by filtering suspended SWNTs segments out of the suspension and aligning them in high magnetic field. In Kimura et al. [39], high magnetic field was also employed to align MWNTs in the monomer solution, polymerization followed to form CNT / polymer composites. Set up for the preparation of nanocomposites is shown in Figure 3.6. Both electrical and mechanical properties were measured in the system, and showed that MWNTs were aligned parallel to the magnetic field inside the polymer composites. It is noted that this method has been mainly used to align nanotubes in low-viscosity suspensions based on the anisotropic magnetic susceptibility of
nanotubes. However, it is less promising in nanotube / polymer composites due to the higher viscosities of the polymer melts.

Figure 3.6: Set up for the preparation of MWNT / polymer composites inside a magnet where the polymerization is carried out [39]

Alternatively, polymer flow introduced orientation is rather simple and straight-forward. During mechanical stretching, melt fibre spinning, or spin casting, polymer molecules extend and orient along the stretching or flow direction and the frictional forces of the process align nanotubes within the polymer matrix. Among many mechanical methods used to align nanotubes in a polymer matrix, melt fibre spinning method exhibits the greatest degree of alignment and extensive work has been done in this area. PVA, poly (methyl methacrylate) (PMMA), poly (p-phenylene benzobisoxazole) (PBO), poly (acrylic-nitrile) (PAN) and polypropylene (PP) are some examples of matrix systems where CNTs have been well dispersed and aligned, and the oriented composite fibres with improved mechanical properties have been achieved [40-45]. Calculation on the orientation
degree of carbon nanotubes could be performed using Raman spectroscopy, and orientation of polymer chains could be measured by X-ray diffraction, etc.

### 3.4 Polymer Orientation

Highly oriented polymers have given tremendous stimulus to both basic polymer science and industrial developments in the period 1970s to the present. Much research has focused on achieving high strength and high modulus polymer via molecular orientation. The development of rigid chain polymer is the first method to produce very stiff and strong fibres, the polymers contain rigid rod units with chains containing bonds which are essentially colinear. Each chain has sufficient aspect ratio so that beyond certain solution concentration the chains pack into parallel arrays locally which could be spun and oriented in an elongational flow field [46]. Kevlar from Du Pont and Twaron from Teijin are examples of this type of fibres.

Typically, polymer chains crystallize in the form of thin lamella in which the chains are folded back and forth, with chains bridging the non-crystalline (amorphous) spaces between lamellar crystallites. The properties of the materials will depend on the efficiency of the load transfer across amorphous zones into crystalline zones. To explore the ultimate mechanical properties of the polymer, methods should be developed to transform folded-chain crystals into chain-extended structures.

First, chain extension in dilute solutions can be made permanent if extension is followed by crystallization. Early work from Zwijnenberg and Pennings [47, 48] introduced several set-ups to produce high stiffness and high modulus polyethylene fibres. A seed fibre was positioned between the inner and outer cylinder of a Couette flow configuration with a dilute solution of ultra high molecular weight polyethylene
(UHMWPE). The seed fibre was produced on the surface of the inner cylinder; fibre was produced by withdrawing the seed fibre. Shish-kebabs crystal structure was revealed in the produced fibre as shown in Figure 3.7. Gel spinning is another outstanding example of polymer orientation from solution. In this technique, polymer chains are disentangled in semi-dilute solution and typical shish kebab crystal morphology is obtained. The orientation of polymer chains is then performed by drawing in the semi-solid state (i.e. below the melting or dissolution temperature) [49]. It is worth to note that solvent in the processing is only to introduce a favourable disentangled structure or morphology for further ultradrawing, and the drawing is still possible after the removal of the solvent. A good example of gel spun polymer fibres is based on UHMW-PE, currently produced by DSM (Dyneema®) and its licensed Honeywell (Spectra®).

![Figure 3.7: Shish-kebab crystal structure [47, 48]](image)

Secondly, polymer orientation could be achieved by solid-state drawing. Solid-state
deformation is first employed to produce orientation in polymer by Ward and co-workers [50]. Usually the deformation is carried out at elevated temperature, above the $\alpha$-relaxation temperature but below the melting temperature. Draw ratio ($\lambda$) is defined as the ratio between the length after drawing and the original length, and is often used to measure the degree of orientation. By controlling the initial morphology, polymer molecular weight and drawing condition, high modulus and high strength fibres could be obtained.

3.5 CNT / PVA nanocomposites

As introduced in Chapter 2, PVA has been widely studied as matrix for carbon nanotube reinforced nanocomposites both in the form of isotropic films and oriented fibres. CNT / PVA composites have been fabricated mostly from solution since melt processing leads to severe thermal degradation of the polymer. The most common methods are gel spinning, solution casting and electrospinning. The processing procedure and properties of both isotropic and oriented CNT / PVA composites from literature will be briefly reviewed in the following paragraphs.

3.5.1 Isotropic CNT / PVA composite films

Since carbon nanotubes have been discovered, there is a growing demand of fabricating composite materials containing carbon nanotubes. Early work from Shaffer and Windle reported a successful route to produce large composite films with carbon nanotubes content up to 60 wt.%, based on solution processing [51]. High molecular weight PVA was used as matrix and chemical treated catalytically grown carbon nanotubes were employed as fillers. Mechanical properties were studied by a dynamic mechanical thermal analyzer (DMTA) and Krenchel’s expression for
short-fibre composites was applied to analyze the data. The best fit to the experiment data for the stiffness of the composites film was obtained by using an effective axial modulus of 150 MPa, which is far below the theoretical value. Intrinsic defect on the graphite walls of the carbon nanotubes and poor stress transfer from the out-layer to the inter-layer were suggested to be the possible reason for the low effective modulus [51].

Zhang et al. [52] prepared SWNT / PVA composite films with polyvinyl pyrrolidone (PVP) and sodium dodecyl sulphate (SDS) to assist the dispersion of the tubes. Significant improvement of mechanical properties was observed as shown in Figure 3.8, where nanocomposite films displayed both higher tensile strength and modulus than the pristine PVA and PVA / PVP/ SDS films. Moreover, the reinforcement was not due to the change in crystallinity since the nanocomposites crystallinity was even lower than the crystallinity of the pure polymer films.

![Figure 3.8: Stress-strain curve for SWNT / PVA films [52]](image-url)
In a series of publications, Cadek and Coleman et al. prepared and studied CNT / PVA composite films [53-55]. Significant improvement in modulus and tensile strength for composite films was reported. However, the study on the morphology of the polymer matrix showed that carbon nanotubes acted as nucleation agent and induced crystallization in the PVA (Figure 3.9). Their recent paper reported different types of CNTs for reinforcement of PVA films [56]. All types of carbon nanotubes contributed to the improvement of composite mechanical properties, however, it was suggested that in semi-crystalline polymer / nanotube systems, with non-covalent bonding between the filler and matrix, the formation of nanotube induced crystalline polymer domains is the dominant reinforcement mechanism and not stress transfer to the nanotube. This point is of crucial importance, since when carbon nanotubes alter the morphology of the polymer matrix and act as nucleation agent, it becomes very difficult to assess the real reinforcing efficiency of the fillers. Thus, caution should be taken into the effect of CNTs on the polymer morphology before evaluating the mechanical properties of the composites through micromechanical models, which will be discussed in detail in the following chapter.
PVA composite films with functionalized carbon nanotubes have also been intensively studied by many groups [57-59]. Lin et al. [57] employed SWNTs functionalized with low molecular weight PVA and enhancement of mechanical properties was observed. Liu et al. [16] used SWNTs with multiple surface hydroxyl groups, homogenous dispersion of the tubes in the PVA as well as strong adhesion between the tubes and the matrix attributed to the improvement of composites properties. In this study, the addition of functionalized SWNTs did not increase the crystallinity in the SWNT / PVA composite films.

Figure 3.9: (a) Stress-strain curve for MWNT / PVA film; (b) crystallinity versus volume fraction [55]
3.5.2 Oriented CNT / PVA composites

Due to the anisotropy of CNTs, oriented systems like fibres or tapes are of immense interests. In fact, the intrinsic mechanical properties of nanotubes are only exploited fully when loaded in the axial direction. PVA has been widely used as a matrix for carbon nanotubes reinforced composite films because of the good interfacial adhesion between the polymer and the nanotubes; however, there are only few studies on oriented CNT / PVA systems.

Dimethylsulfoxide (DMSO) is a very good solvent for PVA and many studies have been focused on the DMSO / water mixture solution for PVA gels [60-62]. Kumar et al. [63] successfully produced SWNT / PVA composite fibres via gel spinning. The gel spun PVA fibres normally have higher tensile strength and modulus than the traditional solution spun PVA fibres because of the induced crystallization and minimized chain entanglement during gel spinning [63]. In their studies, improved mechanical properties with the addition of SWNTs were observed, where tensile strength and modulus increased by 22 % and 39.8 % respectively at a loading of 3 wt.%.. Further WAXD measurement suggested that differences in crystallinity and crystal orientation are not the reasons for the improved mechanical performance of SWNT / PVA gel-spun fibre.

Solid-state drawing is another method to prepare oriented CNT / PVA composites. Matsuo et al. [64-66] have studied PVA gel film as well as PVA gel fibres extensively. Recently they performed some studies on MWNT / PVA composites prepared by gelation / crystallization from solution in DMSO and water mixtures [67]. Nanocomposite films and stretched tapes with draw ratio of 5 and 8 have been studied. The mechanical and electrical properties were improved significantly by
introducing MWNTs and VGCFs into the PVA matrix. The summary of mechanical properties is reproduced and plotted in Figure 3.10. It is interesting to note that both modulus and tensile strength increase with the draw ratio of the composites. However, the increasing rate of mechanical properties decrease after carbon nanotube loading reaches 3 wt%, mechanical properties even drop after 3 wt.% loading. We believe that the excess amount of carbon nanotubes disturbs the homogeneous dispersion of the tubes achieved at low weight fraction, thus leads to the poorer mechanical properties in the composites at higher content.
Another method to prepare CNT / PVA fibres from solution is electrospinning. It is a simple technique for producing micro- and nano- fibres of organic polymer and inorganic oxide materials [68]. So far, great process has been made in the fabrication of electrospun nanofibres. A schematic diagram to interpret electrospinning of polymer nanofibres is shown in Figure 3.11 [69]. In the electrospinning process, a high voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibres. Zhou et al. [37] prepared PVA and polyethylene oxide (PEO) nanofibres containing MWNTs by electrospinning methods. An attempt to calculate elastic modulus of the MWNTs was made, and it is found that the elastic modulus of

Figure 3.10: Summary of mechanical properties of CNT / PVA composites reproduced from [67]
MWNTs is in the order of 100 GPa. Recently, Young et al. [70] reported the deformation of individual SWNTs in electrospun PVA nanofibres using polarized Raman spectroscopy. Analysis showed that SWNTs have a high efficiency level with Young’s moduli of more than 800 GPa.

![Schematic picture of the electrospinning experiment setup from [69]](image)

**Figure 3.11**: Schematic picture of the electrospinning experiment setup from [69]

Despite the intrinsic rigidity and anisotropy, available forms of macroscopic CNTs are mainly powder from synthesis, suspension in solvents, or for SWNTs in thin mats, known as bucky paper [71]. In November of 2000, Poulin et al. [72] published a paper in Science on macroscopic fibres and ribbons of oriented carbon nanotubes. SWNTs were dispersed in sodium dodecyl sulphate (SDS) solutions, then the SWNT dispersion was injected through the flow of a PVA solution to form nanotubes mesh. Nanotube fibre was produced by washing the ribbons several times with pure water so that PVA and SDS desorb [73, 74]. A schematic of the experiment setup used to make macroscopic carbon nanotube fibres is shown in Figure 3.12. The produced nanotube fibres were very flexible, they could be bent and even knots could be made.
without fibres breaking. Mechanical measurement showed an elastic modulus around 9 to 15 GPa, which is already an order of magnitude higher than that of bucky paper [72]. Recently surfactant-free spinning of PVA carbon nanotube fibres [75] and treatment of spun composite fibres of SWNTs, MWNTs and PVA was reported [76]. Hot drawing was applied to then as spun fibres, higher crystallinity and degree of alignment was achieved in the treatment. This treatment significantly improved the energy absorption at low strain and the resistivity to moisture.

Figure 3.12: Schematic picture of the experiment setup to make macroscopic carbon nanotube fibres [72]

Super–tough fibres from single-walled carbon nanotubes was reported in Nature 2003 by Dalton et al. [77] By modifying the method reported by Poulin, they produced SWNTs fibres with lengths of up to 100 m, tensile strengths of 1.8 GPa and
a Young’s modulus of 80 GPa. Superb toughness was observed; the pre-drawn fibres match the energy absorption of spider silk up to the breaking strain of 30% and continue absorbing energy until they reach the energy of break (570 Jg\(^{-1}\)). Normalized to density, the strength and Young’s modulus of these fibres is over twice that of high performance steel wire and are over twenty times tougher [78]. The experiment setup used to make super-tough fibres is shown in Figure 3.13.

![Figure 3.13: Schematic picture of the experiment setup to prepare super-tough fibres from [77]](image)

It is worth noticing that PVA was washed out by water during the process for the macroscopic CNTs fibres [72], and for the super-tough SWNT fibres, they are composed of 60 wt.% by weight nanotubes and only 40 wt.% poly (vinyl alcohol). This means these types of PVA / CNT fibres are mainly composed of CNTs and there are obvious differences between these ropes and the conventional polymer / CNT composite fibres where the content of CNTs is normally below 10wt%.
3.6 Effective properties of CNTs in oriented nanocomposites

Now we consider the reinforcing efficiency of carbon nanotubes in the polymer matrices. Since extensive studies have been carried out on different matrices and different types of carbon nanotubes, we attempt to compare literature results by calculation of the effective contribution of the nanotubes to the composite properties using the ‘rule of mixture’ for uniaxial composites where it is assumed that the load transfer is perfectly transferred between the fibre and matrix [79].

\[
E_c = V_f E_f + (1-V_f) E_m
\]  \hspace{1cm} (3-1)

where \(E_c\), \(E_m\) and \(E_f\) are the Young’s modulus of the composite, matrix and the fibre, respectively, and \(V_f\) is the volume fraction of the fibre. For composites in which discontinuous fibres are not perfectly aligned, two parameters need to be incorporated in equation, the length efficiency factor, \(\eta_L\) and the orientation factor, \(\eta_o\) [79]

\[
E_c = \eta_L \eta_o V_f E_f + (1-V_f) E_m
\]  \hspace{1cm} (3-2)

The fibre length efficiency factor \(\eta_L\) can vary between 0 and 1. The orientation factor \(\eta_o\) is equal to 1 for fully aligned fibres. A similar equation can be formulated for strength;

\[
\sigma_c = \eta_L \eta_o V_f \sigma_f + (1-V_f) \sigma_m
\]  \hspace{1cm} (3-3)

Equations 2 and 3 can be used to evaluate the nanotube contributions to the
composite properties if the properties of the matrix, the composite and the nanotube volume fraction are known. As the composites are highly aligned we assume that all SWNTs are perfectly oriented with an orientation factor $\eta$ equal to 1. Hence, an effective nanotube modulus (or nanotube stress), which incorporates only the length efficiency of the nanotubes, given by equation 4 can be calculated.

$$E_{\text{eff}} = \eta L E_f$$  \hspace{1cm} (3-4)

Table 3.1 lists calculated effective modulis and strength from literature data. As mentioned previously, two types of nanocomposite fibres have been studied so far. The first category contains polymer composite fibres consisting of mainly or only of CNTs. When this type of calculation was applied to these high volume fraction CNT composite fibres, the super tough nanotube ropes containing around 60 % by weight of SWNTs are worth mentioning [77]. Although, the claimed fibre toughness which was greater than that of spider silk arose great excitement within the scientific community, the SWNT reinforcing efficiency is quite low with an effective Young’s modulus for the nanotubes of 147 GPa and a tensile stress as low as 3 GPa, being lower or comparable to the tensile strength of ordinary carbon fibres.
Table 3.1: Effective nanotube contributions to nanocomposite properties for the most important results reported in literature on uniaxially oriented films or fibres

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>Matrix</th>
<th>$E_{\text{eff}}$ [GPa]</th>
<th>$\sigma_{\text{eff}}$ [GPa]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>Pitch</td>
<td>1269</td>
<td>13</td>
<td>Andrews [80]</td>
</tr>
<tr>
<td>MWNT</td>
<td>UHMW-PE</td>
<td>868</td>
<td>4</td>
<td>Ruan [81]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PP</td>
<td>610</td>
<td>56</td>
<td>Kearns [82]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PBO</td>
<td>449</td>
<td>19</td>
<td>Kumar [83]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PVA</td>
<td>406</td>
<td>8</td>
<td>Zhang [63]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PA</td>
<td>153</td>
<td>36</td>
<td>Gao [84]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PAN</td>
<td>149</td>
<td>2</td>
<td>Sreekumar [85]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PAN</td>
<td>149</td>
<td>2</td>
<td>Chae [86]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PVA</td>
<td>147</td>
<td>3</td>
<td>Dalton [77]</td>
</tr>
<tr>
<td>MWNT</td>
<td>PP</td>
<td>134</td>
<td>5</td>
<td>Kumar [87]</td>
</tr>
<tr>
<td>MWNT</td>
<td>PAN</td>
<td>110</td>
<td>6</td>
<td>Chae [86]</td>
</tr>
<tr>
<td>DWNT</td>
<td>PAN</td>
<td>61</td>
<td>2</td>
<td>Chae [86]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PMMA</td>
<td>55</td>
<td>-</td>
<td>Haggenmuller [88]</td>
</tr>
<tr>
<td>MWNT</td>
<td>PC</td>
<td>48</td>
<td>-11</td>
<td>Poschke [89]</td>
</tr>
<tr>
<td>MWNT</td>
<td>PC</td>
<td>48</td>
<td>1</td>
<td>Fornes [90]</td>
</tr>
<tr>
<td>MWNT</td>
<td>PP</td>
<td>29</td>
<td>-</td>
<td>Andrews [23]</td>
</tr>
<tr>
<td>SWNT</td>
<td>PC</td>
<td>22</td>
<td>0</td>
<td>Fornes [90]</td>
</tr>
<tr>
<td>CNT</td>
<td>PA</td>
<td>18</td>
<td>-</td>
<td>Sandler [91]</td>
</tr>
<tr>
<td>CNT</td>
<td>PA</td>
<td>12</td>
<td>-</td>
<td>Sandler [91]</td>
</tr>
<tr>
<td>CNT</td>
<td>PA</td>
<td>4</td>
<td>-</td>
<td>Sandler [91]</td>
</tr>
</tbody>
</table>
The second category contains polymer fibres filled with relatively low CNT loading (up to 10 wt.%). The first report of nanocomposite fibres came from Andrews et al. [80], their studies on melt-spun SWNT-reinforced pitch-based carbon fibres showed significant improvement of mechanical properties. The tensile strength and modulus of a pitch based composite fibres with 5 wt.% of SWNTs exhibits an increase of 90 % and 150 % respectively, which result in a back-calculated nanotube effective Young’s modulus of around 1.3 TPa and stress of 13 GPa. Kumar et al. reported the synthesis and properties of SWNT / PBO fibres. [83] They performed in-situ polymerization in the presence of SWNTs before wet spinning of the fibres. With the addition of 10 wt.% of SWNTs, the modulus was increase from 138 GPa to 167 GPa, and the strength also increased from 2.6 GPa to 4.2 GPa, which was an impressive improvement as shown in Figure 3.14. In other studies, other polymer matrices have been used to make CNT / polymer fibres and promising increases in mechanical properties have been observed as well [81-86].

Figure 3.14: Typical stress-strain curve for PBO and PBO / SWNTs (90/10) fibres [28]
It is worthy to note that even though high effective Young’s modulus of CNTs (eg. Pitch, UHMW-PE, PP) has been achieved in some polymers, the calculated effective strength is far from theoretical strength values. In fact, the advantage of CNTs as reinforcing fillers lies especially in the extremely high tensile stress of nearly 150 GPa. Figure 3.15 illustrates the efficiency of carbon nanotubes from literature by plotting effective stress as a function of effective modulus from calculation obtained by analysing the data using Rule of Mixture. From this simple calculation, the contribution of the nanotubes to the composite both in modulus and strength can be shown. Figure 3.15 show that SWNTs demonstrate the highest reinforcing efficiency among all types of tubes.

![Figure 3.15: Effective strength versus effective modulus calculated from literature data](image-url)
3.7 Reference


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Chapter 4

Isotropic SWNT / PVA composite films

4.1 Introduction

In order to fully exploit the extraordinary theoretical mechanical properties of SWNTs in polymer composites such as tensile modulus of 1 TPa, tensile strength of 50 - 150 GPa, and failure strain of 5 - 10 % [1-5], a number of issues need to be addressed. A prerequisite for the effective reinforcement of polymer using nanofillers is a good dispersion of the nanofiller within the hosting matrix. In the case of SWNTs, exfoliation or debundling of the ropes is particularly challenging since the extremely large surface area that characterizes them is responsible for their strong tendency to form bundled agglomerates. In addition to that, good interfacial interaction and stress transfer between carbon nanotubes and polymer matrices is essential for good mechanical properties of the composites. Finally, the excellent intrinsic mechanical properties of CNTs can become ineffective in reinforcement through their random orientation in polymer composites. Similar to polymer molecules, much better efficiencies can be obtained if CNTs could be oriented.

In this chapter, solution-cast composite films from poly (vinyl alcohol) and SWNT
solutions will be prepared and fully characterized. In order to achieve high reinforcing efficiency, good dispersion of the carbon nanotubes and stress transfer efficiency from the polymer to the tubes is very important. Optical microscopy and UV-vis spectroscopy will be employed to study the dispersion condition of the tubes. The stress transfer efficiency in the composites will be investigated using Raman spectroscopy. Differential Scanning Calorimetry (DSC) will be applied to investigate the effect of SWNTs on polymer crystallinity as well as crystallization kinetics. The mechanical properties of these isotropic nanocomposite films will be measured by performing Dynamic Mechanical Thermal Analysis (DMTA) and assessed by using Cox-Krenchel micromechanical model for random short fibre composites.

4.2 Experimental

4.2.1 Materials

The poly (vinyl alcohol) (PVA) (Mw = 84,000 - 124,000 g / mol, 98 - 99 % hydrolysed) used in this investigation was purchased from Sigma-Aldrich and used as supplied. The SWNTs were purchased from Carbolex (Batch No CLAP8563). They are produced by arc-discharge method and the purity is around 70 %. The SWNTs were used without further purification. Dimethyl sulfoxide (DMSO) was purchased from Romil, and was used as solvent.

4.2.2 Composite preparation

Nanocomposite films were fabricated from solutions of SWNT / PVA. Poly (vinyl alcohol) was first dissolved in DMSO at 105°C and continuously stirred for 3 hours to give a 15 wt.% solution. The SWNTs were dispersed in DMSO followed by bath
and tip ultrasonication. An equal amount (50 g) of previously prepared PVA solution was gradually added into stirring CNT suspension. The SWNT concentration needed in the DMSO was calculated in order to obtain a loading of 1, 0.5 and 0.1 wt.% in the final composite. Mechanical stirring of the mixture was maintained for 1 hour to achieve good mixing. The composite solutions were cast into a polystyrene (PS) Petri dish and degassed in a vacuum oven. The films were dried at room temperature, peeled off from the PS dish and dried in a desiccator for at least a week before any further testing. Figure 4.1 shows the prepared composite films (from top to bottom: pure PVA film, 0.3 wt.% SWNT / PVA film and 1 wt.% SWNT / PVA film) which properties will be discussed in detail in the following chapters.

![Figure 4.1: Photograph of SWNT / PVA composite films.](image)

**Figure 4.1:** Photograph of SWNT / PVA composite films.
4.2.3 Composites characterization

**Optical microscopy**
Optical micrographs were obtained from an Olympus BX60F, fitted with a JVC color video camera, model KY-F55BE.

**UV-Vis Spectroscopy**
UV-Vis spectra were recorded by a Hitachi U-3000 spectrophotometer operating between 200 and 800 nm. For each experiment, 0.015 wt.% of SWNTs in DMSO was prepared and the solution was sonicated for the same time as during composite preparation. The SWNT solution was then mixed with viscous pure PVA / DMSO solution (15 wt.%), the amount of the latter was calculated to reach a certain weight ratio between PVA and SWNTs. Finally the mixture was diluted by DMSO, resulting in SWNT content of 0.0015 wt.% and UV spectra were recorded. Quartz cuvettes were employed and the pure DMSO was used as reference for measurement.

**Raman spectroscopy**
The Raman spectra were obtained on a Renishaw Raman Imaging Microscope System using a 50 × objective lenses and the excitation beam was from a 60 mW He-Ne laser (632.8 nm). The spectral resolution of the system is better than 1 cm⁻¹. A neutral grey filter was inserted in the path beam to reduce the laser power in order to avoid excessive heating and thus degradation of the sample. All the spectra were curve-fitted using Gaussian and/or Lorentzian routines and the G’ band positions and intensities were obtained. To study stress transfer efficiency in the composites, a rectangular strip was cut from the cast film and mounted on the elongation based strain rig shown in Figure 4.2. The rig was then placed on the microscope stage of the Raman spectrometer, positioned with the stretching direction parallel to the
polarisation direction. Five spectra were collected in the unstrained position along the length of specimen. The strain was then increased step-by-step by rotating the screw in ~ 0.06 % strain intervals before refocusing and taking other five spectra. By plotting the Raman wave number as a function of the applied strain, the band shift rate of the material was determined.

**Figure 4.2: Strain rig**

**Differential Scanning Calorimetry (DSC)**

Thermal properties of the SWNT / PVA films were examined by DSC in standard aluminium pans using a Mettler DSC 822e differential scanning calorimeter. The pure PVA and composite samples were simultaneously prepared in order to maintain the same thermal history. 7 mg were measured for all samples in the DSC and SWNT / PVA composite films with concentrations of 0.1 wt.% to 1 wt.% were measured. DSC measurements were done on two separate batches to assure the results were accurate. Two heating and two cooling had been performed and data had been collected. All crystallization and melting temperatures were determined by drawing asymptotic lines to the initial rise or drop in heat flow and determining the intersection with the baseline. PVA samples were heated from 25 °C at 10 °C per minute to 235 °C, held at this temperature for 1 minute, and then cooled at different cooling rate to room
temperature. 235 °C was above the end of the observed melting transition but was not above the equilibrium melting point.

Dynamic Mechanical Thermal Analysis (DMTA)

To check the mechanical properties of the composite films, DMTA was performed in a TA Instruments DMAQ800 machine fitted with a tensile testing head. Samples with dimensions of 20 mm length, 6 mm width and ~ 100 µm thickness were cut from the PVA / SWNT composite films and a gauge length of ~ 10 mm was used. The system was automatically cooled to 0 °C, and then heated at a rate of 5 °C per minute to 200 °C. A static force of 10 mN was applied to ensure that the sample was taut between the tensile grips. Strain control for applying the deforming load to the sample was selected, where a strain well within the linear region was kept constant during the test and the stress was measured by a force balance transducer or load cell.

4.3 Results and discussion

On account of the peculiar volume and interface effects, nano-structured materials can exhibit unusual and unexpected properties as compared to the same materials with larger size structures. Not only do carbon nanotubes have unique electrical properties, but also do they possess exceptional mechanical properties, which make these structures attractive as next generation reinforcing elements for composite materials. However, high reinforcing efficiency is still a great challenge for chemists and material scientists, since much work needs to be done to optimise the conditions required for the best dispersion of nanotubes as well as a good interfacial interaction.
4.3.1 Dispersion quality of composite solutions and films

Due to strong Van der Waals force, SWNTs tend to form bundles which would display significantly lower aspect ratios and inferior mechanical properties (due to slippage of individual nanotubes inside the bundles). To assess the dispersion quality, optical microscopy has been employed. Figure 4.3 shows the optical micrographs of the composite solutions at different stages of preparation. The sonication of SWNTs in DMSO is obviously not effective in producing a good degree of stable dispersion; instead it results in large agglomerates within minutes right after sonication. The mixture of SWNTs in DMSO showed a poor degree of dispersion (top left hand side). In fact, even though DMSO features all the characteristics to be a good solvent for carbon nanotubes, i.e. a high electron pair donicity ($\beta$) and low hydrogen bond parameter ($\alpha$), it is known to be in practice a mediocre solvent for CNTs [6]. However, dispersion quality improves with the addition of PVA solutions (from top to bottom, from left to right), and by mechanical stirring a homogenous composite solution is obtained. It is worth mentioning here that no further sonication is needed after PVA solution is added into the CNT suspension and the homogenous mixture is stable for months. High performance SWNT / PVA fibres extruded via solution (gel) spinning were reported in other groups [7]. DMSO / water were used as solvent, and the composite solution was subjected to further sonication and stirring for 12 h even after PVA was added. By adding viscous PVA solution, considerably less time is needed to obtain homogeneous and stable solution in our work.
UV-Vis spectroscopy has proved to be a useful tool to study the dispersion condition in CNT composite systems and has previously been employed to monitor the exfoliation process of SWNT bundles [8]. The value of absorbance in the range between 200-300 nm is proportional to the amount of isolated CNTs. One band centered at 265 nm is observed in the spectrum over the UV-Vis regions, which is typical for arc-discharge single-walled carbon nanotubes. To monitor the evolution of SWNT dispersion in DMSO solutions, pure PVA and SWNTs in DMSO are measured first and shown in Figure 4.4. No peak is observed in the measured area for
pure PVA, which assured that the peak we observe is from SWNTs alone.

![UV-Vis spectra of pure PVA and SWNTs in DMSO](image)

**Figure 4.4:** UV-Vis spectra of pure PVA and SWNTs in DMSO

Figure 4.5 plots the evolution of the UV-Vis spectra of SWNT / DMSO solutions as a function of weight ratio between PVA and SWNTs, it clearly shows the effect of PVA solution on the SWNTs debundling process within the system. It is obvious that with the addition of PVA solution, the intensity of the peak increases. In other words, the more PVA solution is added, the more exfoliated single carbon nanotubes appear in the solution, which is consistent with optical microscopy observation. UV-Vis studies clearly demonstrate that good degree of exfoliation of SWNT bundles has been achieved in the systems, leading to homogeneous composite materials.
Figure 4.5: Evolution of the UV-Vis spectra of SWNT / DMSO solutions as a function of weight ratio of PVA to SWNTs.

To further assess the evolution of the SWNT / DMSO solutions, the absorbance at several wavelengths as a function of the weight ratio of PVA to SWNTs is plotted as shown in Figure 4.6. It is obvious that the value of the absorbance reaches a plateau value after the weight ratio of PVA to SWNTs increases to around 2000. This levelling off which follows the initial increase in absorbance with the addition of PVA corresponds to the maximum achievable degree of exfoliation of SWNTs in the DMSO system.
Figure 4.6: Evolution of the value of the absorbance at different wavelengths for 0.0015 wt.% of SWNT solution as a function of weight ratio of PVA to SWNTs.

4.3.2 Raman studies – stress transfer

To achieve high reinforcing efficiency, load transfer from the matrix to the fillers is very important. There are three main mechanisms of load transfer from a matrix to filler [9]. The first is micromechanical interlocking; this could be difficult in nanotube composites due to their atomically smooth surface. The second is chemical bonding between the matrix and the filler. The third mechanism is weak Van der Waals bonding between the fibre and the matrix, which is the case in our study. In order to assess the reinforcing potential of carbon nanotubes as fillers, the issue of load transfer needs to be addressed.
It has been known for about two decades that the application of a mechanical strain to fibres such as carbon fibres or Kevlar results in a shift of the Raman band frequencies [9-12]. The reason is that when a strain is applied to a material, the interatomic distances change, and thus the vibrational frequencies of some of the normal modes change causing a Raman peak shift [9]. This phenomenon has been employed to evaluate strain distributions in fibre composites. Raman spectroscopy is also known to be a useful tool to study carbon nanotubes and CNT / polymer composites [9,11-17]. Mechanical response of carbon nanotubes under molecular and macroscopic pressure greatly interests researchers [12-16]. Raman D* band (also called G’ band) wave number shifts are observed when molecular pressure is applied by dispersing SWNTs in different liquids. Moreover, when macroscopic pressure was applied using diamond-anvil cell [15], the D* band peak shift was also observed. Since it was not possible to calibrate the Raman peak position with an applied strain as has been done with individual graphite fibres, it is clear that the larger the Raman peak shift, the larger is the strain carried by the nanotubes [9]. The D* peak position shifts to a higher wave number with compression and they shift to a lower wave number in tension indicating stress transfer from the matrix to the nanotubes and hence reinforcement by the nanotubes [16]. The D* band reflects a breathing vibration mode by which all atoms of a graphite sheet undergo in-plane movement. This type of study can provide information regarding both the matrix-nanotube load transfer efficiency and alignment of the nanotubes [17-18].

When plotting D* band position shift against the applied strain, the efficiency of stress transfer from the polymer matrix to carbon nanotubes is reflected by the slope of the plot. The larger the slope, the better the stress transfer from matrix to carbon nanotubes. It is worth noticing that the Raman laser spot size is several orders of magnitude larger than the size of nanotubes, thus the collected Raman spectrum is an
average response of nanotubes with different orientation degree. For a randomly distributed sample, the tubes in the stretching direction are under simple tension, while compression occurs for tubes in the direction transverse to the loading axis. Thus the more oriented the sample is, the more tubes are in the tension mode, thus exhibiting better stress transfer.

Figure 4.7: Typical Raman spectra of a drawn tape (a) unstretched and (b) under 1.0 % strain. The peak position shifts towards lower wavenumber

Figure 4.7 shows Raman spectra of a typical composite sample undergoing deformation. The position of the D* band for unstretched tape is 2633.1 cm\(^{-1}\). When the tape is stretched a band shift is observed. It is worth to note that during the tensile deformation of CNT / PVA composites, the applied tensile load not only provides the
tensile stress for elongation of the nanotubes but also the shear stress at the interface between the nanotubes and matrix. In theory, the strain in the nanotubes will equal that in the polymer matrix when there is good bonding between the nanotubes and matrix [19]. However, if the interfacial interaction between tube and polymer is poor, stress transfer efficiency between nanotubes and matrix becomes low resulting in the decrease of the rate of D* band shift with increasing tensile strain which reflects in a smaller slope in the Raman shift versus tensile strain plot.

Figure 4.8: Raman D* band shift as a function of the applied strain for SWNT / PVA composite films. The solid line is the linear fit of the data in the elastic region

Figure 4.8 shows the D* band shift for SWNT / PVA films as a function of applied strain, and a slope of -2.69 cm$^{-1}$/% is observed. The value of the slope is similar to
other PVA / SWNT systems reported [20, 21], which indicates that relatively good stress transfer has been achieved. In this system, linear dependence of the band shift is observed in the elastic region (up to about 1 % strain), which indicates that effective load transfer takes place during deformation. However, a non-linear dependence appears above the elastic region (> 1 % strain), which suggests possible slippage of nanotubes in the bundles or/and a debonding between nanotubes and polymer matrix occurs during tension or/and polymer yielding happens upon drawing [22].

Figure 4.9: Raman D* band shift as a function of the applied strain for PVA / SWNT / SDS composite films. The solid line is the linear fit of the data in the elastic region. [21]

A surfactant-assisted system was studied by Ciselli [21] and used here for
comparison purpose. Sodium dodecyl sulphate (SDS) was used as surfactant and the same PVA and SWNTs were employed as matrix and filler. A slope of -2.30 cm\(^{-1}\)/% for this system was observed from Raman stress transfer study as shown in Figure 4.9. The difference between the two slopes in the elastic region clearly showed that comparable stress transfer efficiency has been obtained for the SDS and DMSO systems. We should note that in SDS system, there are two competing factors, which contribute to the real stress transfer efficiency. Carbon nanotube bundles are well exfoliated and dispersed; however, they are surrounded by SDS molecules, which might reduce the interaction with the polymer chains. Compared to the SDS system, it is expected that a better interaction with SWNTs should be achieved in the DMSO system, since here no surfactant is present at the interface. Not surprisingly, for the DMSO system we found a slightly higher slope than in the SDS system. However, the nanotubes in the composite may not stay completely isolated but are often in the form of bundles or “ropes”. Stress transfer would therefore have to take place between adjacent nanotubes in bundles and the observed small difference in slope could be due to the breakdown of the interfaces between the nanotubes in the bundles. As a result, less individual carbon nanotubes get the chance to be in contact with the polymer chains, which decreases the efficiency of stress transfer.

It is possible to calculate the effective modulus values for the SWNTs from the dependence of the Raman band positions upon strain following the analysis of Cooper et al [17]. Recent study from Kannan et al [23] reported a D\(^*\) band shift up to 40 cm\(^{-1}\) for 1 % strain in electrospun PVA nanofibres, which is similar to that reported for the deformation of isolated nanotubes. Calculation indicates that the Young’s modulus of the SWNTs is at least 800 GPa. The same analysis is carried out in this system by assuming that the D\(^*\) band shifts in SWNTs have the same dependence upon modulus as those in carbon fibres where the calibration was done. Since the rate of band shift...
per unit strain was found to be proportional to the fibre modulus and \( -5 \text{ cm}^{-1} / \text{ GPa} \) was found and chosen to calibrate the Raman band shift for CNTs, results in our system with a shift rate of \( 2.69 \text{ cm}^{-1} / \% \) correspond to a modulus of only 53.8 GPa. However, the carbon nanotubes have a random distribution within the PVA films, which is different than the unidirectional alignment of the carbon fibres in calibration. Taking the orientation into account, an orientation factor \((2-D = 1/3, 3-D = 1/9)\) [17] is employed and the estimated effective modulus for SWNTs will be 161.4 GPa (2-D distribution) and 484.2 GPa (3-D distribution), respectively. The difference between the estimated and theoretical value could be attributed to the fact that some SWNTs may still in bundles and the dispersion or adhesion are not perfect in this case.

### 4.3.3 Thermal analysis

Since carbon nanotubes have been investigated as potential reinforcing filler for composites, significantly improved mechanical properties in polymer / nanotube composites have been observed [24-27]. However, to elucidate the reinforcing mechanism, many studies have focused on the effect of carbon nanotubes on polymer crystallization [28-30]. Coleman et al. [31] reported carbon nanotubes induced crystallinity nucleation in PVA films, and Probst et al. [32] studied the crystallization dynamics in SWNT / PVA composites. The results all suggested it might be the carbon nanotube-induced crystallinity that was responsible for the property increase observed in semi-crystalline PVA rather than the CNT reinforcement.

As already mentioned in previous chapters, it is very difficult to carry out crystallization studies on PVA, since the polymer degrades near its melting temperature and degradation lowers the crystallization temperature and the fractional crystallinity [32, 33]. Here the effect of degradation on the polymers will be
discussed first before describing the results of DSC experiments. Figure 4.10 compares the crystallization exotherms during the first and the second cooling scans at 10°C per minute. It is obvious that the crystallization temperature drops while the sample is cooled for the second time in all samples, and the difference between the two coolings is similar in composite films with different amount of tubes. The effect is attributed to degradation of the polymer during the slow cooling. It is worthy to note that the 1 wt.% sample, even at low cooling rate, shows only minor degradation for the polymer. We believe that higher cooling rates will lead to less degradation, thus the results will not be affected by the minor degradation caused by the addition of carbon nanotubes. Figure 4.11 shows the crystallization exotherms during the first and the second cooling scans at 30°C / min. It is clear that less degradation takes place at higher cooling rate, since no difference is observed between the two cooling exotherms.

![Figure 4.10: Crystallization exotherms during the first (solid line) and the second cooling scans.](image)

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**Figure 4.10:** Crystallization exotherms during the first (solid line) and the second cooling scans.
Figure 4.11: Crystallization exotherms during the first (solid line) and the second (dashed line) cooling scan at 10°C/min for composites films with different concentration of SWNTs.

Figure 4.12 shows the typical first and the second heating of the SWNT/PVA films. The broad curvature at around 100-120°C shown from the first heating step is attributed to the solvent DMSO and the water that is trapped in the film, thus in the second heating step the curvature is absent when the sample is reheated after cooling and solvent evaporates. The degree of crystallinity is calculated from the melting heat ($\Delta Q_m$) obtained from DSC measurement according to the following equation:
\[ X_c = \frac{\Delta Q_m}{\Delta H_o} \]  \hspace{1cm} (4-1)

Where \( \Delta H_o = 138.60 \text{ J/g} \) is the melt enthalpy of 100 % crystalline PVA [33]

**Figure 4.12**: DSC graph during the first (solid line) and the second (dash line) heating scan at 10°C/min for typical SWNT / PVA composite films

Table 4.1 lists DSC results of SWNT / PVA films with different concentration of SWNTs at cooling rate of 30°C/min. The melting temperature \( T_{m1} \) and \( T_{m2} \) from the first and the second heating are both listed and compared. It is worth to note that for heating, the first heating provides information on the crystallization that occurs when composite solutions dry to form composite film, while the second heating shows crystals formed from controlled cooling. In case of PVA, the first heating is very
important as the degradation effects in the first heating step might affect the second heating data. In our study, the upper temperature limit is 235°C in order to ensure the melting transition finishes and proper integration of the melt peak could be done. The DSC data from the second run could be used to assess the crystals formed during the controlled melt cooling so a comparison with solution cast crystallization could be made.

### Table 4.1: DSC measurement results

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ [°C]</th>
<th>$T_{m1}$ [°C]</th>
<th>$T_{m2}$ [°C]</th>
<th>$\Delta H$ [J/g]</th>
<th>$X_c$ [%]</th>
<th>$T_c$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td>55.2</td>
<td>216.4</td>
<td>212.04</td>
<td>44.6</td>
<td>32.2</td>
<td>180.9</td>
</tr>
<tr>
<td>0.1 wt.% SWNTs</td>
<td>54.8</td>
<td>215.8</td>
<td>211.07</td>
<td>42.7</td>
<td>30.8</td>
<td>180.0</td>
</tr>
<tr>
<td>0.3 wt.% SWNTs</td>
<td>56.1</td>
<td>215.5</td>
<td>211.68</td>
<td>43.2</td>
<td>31.3</td>
<td>180.7</td>
</tr>
<tr>
<td>0.5 wt.% SWNTs</td>
<td>56.4</td>
<td>214.4</td>
<td>210.06</td>
<td>46.0</td>
<td>33.4</td>
<td>181.7</td>
</tr>
<tr>
<td>1.0 wt.% SWNTs</td>
<td>55.4</td>
<td>216.6</td>
<td>212.79</td>
<td>40.1</td>
<td>29.2</td>
<td>183.4</td>
</tr>
</tbody>
</table>

The crystallinity was calculated from the second heating, the crystallization temperature was measured from the first cooling.

Comparing the first heating data with the second heating data, it is interesting to note a decrease in melting temperature upon second heating for all samples, which implies smaller crystals melt in the second run. The reason might be that the slow rate of crystallization during the solution casting process results in bigger size crystallites compared to relatively fast crystallization in the DSC chamber while cooling. DSC results also suggest no significant change to the PVA crystals upon the addition of SWNTs, since there is no remarkable change in glass transition temperature ($T_g$), and melting temperature ($T_m$). In order to compare the degree of crystallinity of all
nanocomposite, the total melting peak area has been evaluated, normalised to the fraction of polymer present. This approach leads to a roughly constant degree of crystallinity for all the composite films between 29–33%. Moreover, results from the cooling show only a small variation in the crystallization temperature \( T_c \) with each volume fraction of the SWNTs, thus implying that a well-defined crystal size is present irrespective of carbon nanotube loading.

To quantify the analysis of the non-isothermal crystallization data, the Ozawa method was applied [34]. Different cooling rates were employed to study the crystallization kinetics for the system. After cooling down to a certain temperature \( T \), the relative crystallinity function of temperature \( X(T) \) can be determined from the DSC crystallization curve using following equation:

\[
X(T) = \frac{A(T)}{A_{\text{total}}} \tag{4-2}
\]

Where \( A(T) \) is the partial area under the peak at temperature \( T \) and \( A_{\text{total}} \) is the total peak area.

\( X(T) \) can be represented as a function of cooling rate \( \theta \) as

\[
X(T) = 1 - \exp(-\frac{k_0}{\theta}) \tag{4-3}
\]

Where \( k_0 \) and \( m \) are parameters specific to a given crystallization condition, \( k_0 \) as the cooling function of the process and \( m \) as the Ozawa exponent. By plotting \( \ln(-\ln(1-X(T))) \) as a function of \( \ln(\theta) \) for a fixed temperature, a straight line should be
plotted. The $m$ could be determined from the negative value of the slope, and the $\ln(k_o)$ from the value of the $y$-intercept. The results of the analysis are shown in Table 4.2. It is obvious that the crystallization temperature ($T_c$) decreases with increasing of cooling rate in all systems. The reason is that when cooling at lower rate, crystals become refined by cooling and crystallize easier thus leading to higher crystallization temperature. The same trend is observed for the second cooling. As for samples at the same cooling rate, there are no remarkable differences in $T_c$ observed.

Table 4.2: Crystallization kinetics study results

<table>
<thead>
<tr>
<th>Cooling rate (°C / min)</th>
<th>PVA 0.1 wt.%</th>
<th>PVA 0.3 wt.%</th>
<th>PVA 0.5 wt.%</th>
<th>PVA 1 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>169.89</td>
<td>169.91</td>
<td>169.87</td>
<td>168.41</td>
</tr>
<tr>
<td>40</td>
<td>178.85</td>
<td>178.75</td>
<td>180.06</td>
<td>178.58</td>
</tr>
<tr>
<td>30</td>
<td>180.92</td>
<td>179.96</td>
<td>180.74</td>
<td>181.72</td>
</tr>
<tr>
<td>20</td>
<td>183.14</td>
<td>183.6</td>
<td>182.89</td>
<td>183.85</td>
</tr>
<tr>
<td>10</td>
<td>187.16</td>
<td>184.89</td>
<td>184.31</td>
<td>186.14</td>
</tr>
</tbody>
</table>

Table 4.3 shows the results from the Ozawa analysis, and both $K_o$ and $m$ are calculated. The degree of freedom for crystal growth, proportional to $m$ [35], increases with temperature. For nanocomposites, $m$ decreases with the addition of SWNTs and with the concentration of the SWNTs in the composites at certain temperature, implying that the SWNTs restrict the degree of freedom for crystal growth in the system. The extremely large surface area of SWNTs might attribute to it. Since $k_o$ is not only a function of the cooling rate but also a function of $m$, $K_o$ (i.e., $K_o = k_o^{1/m}$) is used. The calculated data also suggests that the crystallization growth rate ($K_o$) remains the same for the samples with and without nanotubes, which means
the SWNTs have no influence on the PVA crystallite growth. Figure 4.13 plots $\ln (-\ln (1-X(T)))$ as a function of $\ln (\theta)$ according to Ozawa theory for PVA and PVA/SWNT films at different fixed temperatures. The points are well fitted with straight line which confirms the validity of the Ozawa’s theory.

**Table 4.3:** Ozawa analysis results

<table>
<thead>
<tr>
<th></th>
<th>183°C</th>
<th>181°C</th>
<th>179°C</th>
<th>177°C</th>
<th>175°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>2.34</td>
<td>2.10</td>
<td>1.71</td>
<td>1.34</td>
<td>1.04</td>
</tr>
<tr>
<td>$K_o$ (1/sec)</td>
<td>16.46</td>
<td>20.61</td>
<td>25.07</td>
<td>31.03</td>
<td>40.36</td>
</tr>
<tr>
<td>0.1 wt.% SWNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>1.79</td>
<td>1.59</td>
<td>1.27</td>
<td>0.94</td>
<td>0.69</td>
</tr>
<tr>
<td>$K_o$ (1/sec)</td>
<td>16.48</td>
<td>20.19</td>
<td>24.57</td>
<td>31.37</td>
<td>43.98</td>
</tr>
<tr>
<td>0.5 wt.% SWNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>1.66</td>
<td>1.51</td>
<td>1.32</td>
<td>1.13</td>
<td>0.96</td>
</tr>
<tr>
<td>$K_o$ (1/sec)</td>
<td>17.23</td>
<td>21.19</td>
<td>25.33</td>
<td>30.53</td>
<td>37.53</td>
</tr>
</tbody>
</table>
CHAPTER 4. ISOTROPIC SWNT / PVA COMPOSITE FILMS

(a)

(b)
Figure 4.13: Plot of \( \ln[-\ln(1-X(T))] \) versus \( \ln Q \) (according to Ozawa’s theory) for (a) neat PVA, (b) 0.1 wt.% SWNT / PVA and (c) 0.5 wt.% SWNT / PVA. The straight lines confirm the validity of the Ozawa theory for the SWNT / PVA system.

The results of the crystallization analysis clearly indicate that the presence of SWNTs restricts the degree of freedom for PVA crystal growth in the composite films. However, no significant change of crystallinity and crystallization temperature has been observed, and calculation shows that the crystallization growth rate remains constant. We believe therefore that SWNTs do not act as nucleation agent in this system.
4.3.4 Mechanical properties

Since both good dispersion and good interfacial adhesion between the tubes and the polymer matrix have been confirmed in the previous investigation, it is expected that improved mechanical properties can be observed. Figure 4.14 plots the storage modulus of the composite films and the tan $\delta$ as a function of temperature, and Table 4.4 lists the storage modulus at room temperature ($25^\circ$C) and $T_g$ for SWNT / PVA composite films. It is clear that above $T_g$, there is no obvious difference in storage modulus for the materials, while below $T_g$, the CNTs have strong influence on the elastic properties of the polymer matrix. The tangent of the ratio of the complex to real modulus (tan $\delta$) is a measure of the damping and the peak in tan $\delta$ corresponds to the glass transition [35]. It is observed that the addition of the SWNTs changes the position of the peak where $T_g$ first decreases slightly with the addition of SWNTs and then increases with the amount of the SWNTs. The decreasing height of the peak is due to the reducing fraction of the polymer matrix, and the broadening behaviour of the tan $\delta$ spectrum is attributed to the fact that more polymer chains are restricted in the polymer / CNT interphase.
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Figure 4.14: DMA spectra of SWNT / PVA films (a) storage modulus against temperature, (b) tan δ against temperature
Table 4.4: Summary of the DMA measurement

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage Modulus @ 25 °C</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td>1701MPa</td>
<td>50.18</td>
</tr>
<tr>
<td>0.1 wt.% SWNTs</td>
<td>2213MPa</td>
<td>49.78</td>
</tr>
<tr>
<td>0.5 wt.% SWNTs</td>
<td>2637MPa</td>
<td>51.07</td>
</tr>
</tbody>
</table>

4.3.5 Micromechanical modelling

To quantify the reinforcing efficiency of the carbon nanotubes, Cox-Krenchel’s expression [36] for short-fibre composites is applied to calculate the effective modulus of the carbon nanotubes. This simple treatment of the elastic behaviour of aligned long-fibre composites is based on the premise that the “equal strain” condition is valid for loading along the fibre axis. The axial Young’s modulus of the composite can be written using the well-known rule of mixture.

$$E_c = V_f E_f + (1 - V_f) E_m$$  \hspace{1cm} (4-4)

where $E_m$ and $E_f$ are the Young’s modulus of the matrix and the fibre, respectively, and $V_f$ is the volume fraction of the fibre. For composites in which discontinuous fibres are not perfectly aligned, two parameters need to be incorporated in the equation, the length efficiency factor $\eta_L$ and the orientation factor $\eta_o$.

$$E = \eta_o \eta_L V_f E_f + (1 - V_f) E_m$$  \hspace{1cm} (4-5)

The fibre length efficiency factor $\eta_L$ can vary between 0 and 1. The orientation factor $\eta_o$ is equal to 1 for fully aligned fibres, 3/8 for random (in-plane) 2D orientation and
1/5 for random 3D orientation.

Figure 4.15: Plot of the storage modulus at room temperature as a function of the volume fraction of SWNTs in the composite films

Figure 4.15 plots the storage modulus at room temperature as a function of the volume fraction of the SWNTs. In the calculation, the orientation factor $\eta_o$ is chosen to be the theoretical random planar (2D) arrangement value of 3/8, as studies [37] showed that cast MWNT / PVA films tend to contract during film preparation, which resulting in preferential orientation of the nanotubes in the plane. SWNTs and PVA have the same density of 1300 kg / m$^3$, thus the weight fractions equal the volume fractions in our case. Calculations are made based on data from Table 4-4.

Since it is not possible to determine simultaneously both $E_f$ and $\eta_L$ [31], an effective
modulus given by \( E_{\text{eff}} = E_f \times \eta_L \) could be calculated. The experimental data were fitted with rule of mixture and the analysis gave an effective modulus of 503.7 GPa for SWNTs, while the theoretical value is as high as 1 TPa [1, 2]. The difference between the calculated effective modulus and the predicted theoretical value could be attributed to the existence of impurities in the batch as well as imperfection of dispersion of the tubes in the composites. If the 30 wt.% of impurities is taken into account, the effective modulus equals to 719.6 GPa.

By applying the Halpin-Tsai model, the aspect ratio \( l/d \) of the reinforcing nanotubes can be obtained if \( E_c, E_f, E_m \) and \( V_f \) are known. The Halpin-Tsai model [38] is a set of equations that is often used to calculate the stiffness of unidirectional short fibre reinforced materials. It allows the calculation of all elastic constants necessary to characterize the composite using the equation:

\[
\frac{M_c}{M_m} = \frac{(1 + \zeta \eta V_r)}{(1 - \eta V_r)} \tag{4-6}
\]

where

\[
\eta = \frac{\left( \frac{M_r}{M_m} - 1 \right)}{\left( \frac{M_r}{M_m} + \zeta \right)} \tag{4-7}
\]

in which \( M_c \) is the composite Young’s or shear modulus \( E_{11}, E_{33}, G_{12} \) or \( G_{13} \). \( M_r \) is the corresponding filler modulus \( E_r \) or \( G_r \), and \( M_m \) the corresponding matrix modulus \( E_m \) or \( G_m \). \( V_r \) is the volume fraction of the filler. \( \zeta \) is a factor that depends on the shape of
the filler particle and on the type of modulus to be calculated. For fibre reinforcement, it is advised to use the shape factors listed in Table 4.5, where $E_{11}$ and $E_{22}$ are longitudinal modulus and transverse modulus respectively and $l/d$ represents filler aspect ratio (length / diameter).

**Table 4.5: Summary of the shape factors in Halpin-Tsai model**

<table>
<thead>
<tr>
<th></th>
<th>$\zeta$ = $2 \frac{l}{d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{11}$</td>
<td>$\zeta = 2$</td>
</tr>
<tr>
<td>$E_{22}$ or $E_{33}$</td>
<td>$\zeta = 2$</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>$\zeta = \frac{1}{3 - 4 \nu m}$</td>
</tr>
<tr>
<td>$G_{13}$ or $G_{32}$</td>
<td>$\zeta = 1$</td>
</tr>
</tbody>
</table>

For composites containing randomly distributed fibres, the composite modulus can be calculated by the following equation

$$E_c = \frac{3}{8} E_{11} + \frac{5}{8} E_{22}$$

(4-8)

In this case for carbon nanotube reinforced polymer composite, the modulus could be calculated by the following equation:

$$E_c = E_m \left[ \frac{3}{8} \frac{1 + 2 \left( \frac{l}{d} \right) \eta_L V_f}{(1 - \eta_L V_f)} + \frac{5}{8} \frac{1 + 2 \eta_L V_f}{(1 - \eta_L V_f)} \right]$$

(4-9)

where
\[ \eta_L = \left( \frac{E_f}{E_m} \right)^{-1} \frac{1}{\left( \frac{E_f}{E_m} + 2 \frac{l}{d} \right)} \] (4-10)

and

\[ \eta_T = \left( \frac{E_f}{E_m} \right)^{-1} \frac{1}{\left( \frac{E_f}{E_m} + 2 \right)} \] (4-11)

To fit the experimental data to these equations, mass fractions are transformed to volume fractions as discussed before. In addition, \( E_f \) for SWNTs is taken to be 1 TPa in agreement with theoretical values [1, 2]. For the modulus of the polymer \( (E_m) \) and the composites \( (E_c) \), the data is taken from Table 4.4. The aspect ratio for carbon nanotubes is thus calculated from Equation 4-9 and is found to be 285. Considering the average nanotube length of our SWNTs is around 1 µm, an average bundle diameter equal to 3.5 nm is calculated. This result confirms that the good, but not perfect level of dispersion obtained in the DMSO solution is maintained throughout the composite formation.

### 4.4 Conclusion

This Chapter described the preparation of homogeneous SWNT / PVA films by a solution casting method using DMSO as a solvent. The nanocomposite films showed good dispersion as evidenced by optical microscopy and UV-Vis studies. Raman spectroscopy studies showed that good stress transfer from the polymer to the reinforcing nanotubes had been achieved. The results of the crystallization analysis
showed no significant change of crystallinity and crystallization temperature, and further calculations showed that the crystal growth rate remained constant for all samples. It suggested that SWNTs did not show a nucleating effect on the PVA matrix. Mechanical properties of the films were measured and micromechanical model showed that a good reinforcing efficiency of carbon nanotubes had been achieved.

4.5 Reference


CHAPTE R 4. ISOTROPIC SWNT / PVA COMPOSITE FILMS


34. Ozawa, T., Kinetics of non-isothermal crystallization, Polymer 1971, 12, 150-158


38. Mallick, P. K., Fibre-Reinforced Composites, Vol. 83 Marcel Dekker, Columbus / Ohio, 1993
Chapter 5

Oriented SWNT / PVA composite tapes

5.1 Introduction

As discussed in Chapter 2, PVA exhibits considerable potential as a material for high modulus fibres and it has received a lot of attention as matrix for nanotube reinforced composite films. In fact, as already discussed in Chapter 3, three factors strongly affect the macroscopic properties of nanocomposites, i.e. (1) dispersion of the CNTs throughout the polymer matrix, (2) adhesion between the nanotubes and the matrix and finally (3) uniaxial orientation of the CNTs, to exploit the intrinsic anisotropy of the carbon nanotubes.

In this chapter, the isotropic SWNT / PVA composite films will be drawn in the solid-state at elevated temperature and uniaxial nanocomposite tapes will be prepared where both the polymer chains and the SWNTs are highly aligned. The mechanical properties will be investigated by tensile tests and different techniques will be applied to characterise the orientation of the carbon nanotubes and the polymer matrix, as well as the stress transfer efficiency from the polymer matrix to the nanotubes. The Cox-Krenchel model will be used to assess the contribution of
SWNTs to the composite properties. The importance of initial morphology and pre-orientation of polymer crystals in cast films will be explained and wide angle X-ray diffraction (WAXD) will be used to measure the degree of polymer orientation. A further analysis will be applied to check if the improved mechanical properties are the results of a changed initial morphology of the polymer matrix by the nanotubes or a real reinforcing effect from the carbon nanotubes. Finally, a second system will be presented for comparison reasons, where nanocomposites consist of the same matrix and nanotubes but with the use of surfactant to assist nanotube dispersion. The contribution of carbon nanotubes to the composites will be calculated and the study of polymer pre-orientation will be briefly presented as well.

5.2 Experimental

5.2.1 Composite preparation

SWNT / PVA tapes were prepared from the cast dried films as described in Chapter 4, solid state drawing at elevated temperature of 130 °C was applied. All the tapes were kept in a desiccator for at least one week before any further characterization.

5.2.2 Composite characterization

Tensile test

For oriented nanocomposite tapes, direct tensile tests were performed. The mechanical properties of the SWNT / PVA tapes were evaluated using an Instron 5586 at room temperature. The tape samples were rectangular with approximate planar dimensions of 25 mm × 5 mm × ~ 50 µm. For all samples at least five
specimens were measured, the results analysed and the mean and standard deviation calculated.

**Raman spectroscopy**

Raman spectra were recorded on a Renishaw Raman microscope system using a 50 × objective lenses and the excitation beam from a 60 mW HeNe laser (632.8 nm). The spectral resolution of the system is < 1 cm⁻¹. A neutral grey filter was inserted in the path beam to reduce the laser power in order to avoid excessive heating and thus degradation of the sample. For a typical SWNT orientation measurement, VV configuration was set where the incident laser polarization and the scattered light is parallel. A rotational stage was used to rotate the sample angle with respect to the electric vector of the polarized excitation. To ensure that the Raman intensity ratios in the measurements were not from local variations in the degree of SWNT orientation, several measurements were recorded for each angle after slight repositioning.

**Attenuated Total Reflection Infrared (ATR-IR) spectroscopy**

The dichroism measurements were done using the Biorad FTS6000 FTIR spectrometer with the UMA 500 IR microscope. The slide-on ATR crystal (Si) mounted on the objective of the microscope was used to collect the spectra. A wire grid polarizer was mounted in front of the mercury-cadmium-telluride (MCT) detector to obtain polarized radiation. The sample was mounted in both parallel and perpendicular configuration to obtain the spectra in the machine direction (MD) and transverse direction (TD).
Wide Angle X-ray Diffraction (WAXD)

Oxford Diffraction Xcalibur XP was run with a Mo-Kα source at -50 KV and 40 mA. X-ray scattering patterns were recorded by an Onyx charge-coupled device (CCD) detector at a distance of 65 mm for 300 s. The two-dimensional X-ray patterns were transformed into one-dimensional patterns by performing integration of the Azimuthal intensity.

5.3 Results and discussion

5.3.1 Mechanical properties

As a general trend, the Young’s modulus and tensile strength increase with increasing draw ratio of the polymer, whereas the strain at break shows the opposite trend. This behaviour is expected for semi-crystalline polymers undergoing molecular orientation [1]. Indeed, oriented PVA tapes show much higher mechanical properties compared to isotropic films. Typical stress-strain curves for SWNT reinforced PVA tapes are presented in Figure 5.1. Oriented nanocomposite tapes of draw ratio 5 with concentrations of 0.1 wt.% to 1 wt.% SWNTs are tested and mechanical properties are investigated. All results are summarized in the Table 5.1. It can be clearly seen that the addition of SWNTs leads to a significant increase in both Young’s modulus and ultimate tensile strength (UTS). It is observed that the addition of only 1 wt.% of SWNTs leads to a 40 %, 188 % and 161 % increase in corresponding Young’s modulus, UTS and toughness, respectively.

The strain at break of the nanocomposite tapes remains unaltered by the addition of SWNTs. This behaviour is typical of well dispersed nanocomposites as opposed to classic composites with fillers in the micrometer range [2]. In the latter case, the
addition of rigid fillers to a ductile polymer often increases its strength at the expense of ductility, since the fillers act as stress concentrators, and initiate defects which quickly become larger than the critical crack size that causes failure. Nanofillers are much smaller than the critical crack size for polymers and, if well-dispersed, they do not initiate failure. Thus, they provide simultaneous strengthening and toughening. In the present case, SWNTs are well-dispersed in the polymer matrix and, considering their high perfection, act as rigid, stiffening agent in the nanocomposites, providing a strengthening effect with no loss in the ductility.

Figure 5.1: Stress-strain curve for oriented SWNT / PVA tapes with a draw ratio of 5, showing a strong increase in tensile strength with the addition of minute amounts of SWNTs to the polymer
Table 5.1: Mechanical testing result summary for SWNT / PVA nanocomposite tapes of draw ratio 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus [GPa]</th>
<th>UTS [MPa]</th>
<th>Toughness [MPa]</th>
<th>Strain at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>13.7 ± 0.3</td>
<td>421 ± 82</td>
<td>45.7 ± 6.3</td>
<td>15.3 ± 1.7</td>
</tr>
<tr>
<td>PVA / 0.1 wt.% SWNTs</td>
<td>14.3 ± 0.2</td>
<td>609 ± 30</td>
<td>62.8 ± 8.7</td>
<td>17.0 ± 0.9</td>
</tr>
<tr>
<td>PVA / 0.5 wt.% SWNTs</td>
<td>14.9 ± 0.6</td>
<td>922 ± 56</td>
<td>92.4 ± 5.4</td>
<td>17.5 ± 2.5</td>
</tr>
<tr>
<td>PVA / 1.0 wt.% SWNTs</td>
<td>19.1 ± 1.0</td>
<td>1211 ± 38</td>
<td>119.4 ± 11.3</td>
<td>17.3 ± 1.9</td>
</tr>
</tbody>
</table>

It is worthy to note the extremely high value of tensile strength (1.2 GPa) that was achieved by the addition of only 1 wt.% of SWNTs. Dalton et al. [3] reported about super tough SWNT / PVA fibres, whose strength reached 1.8 GPa. However, in that study the amount of carbon nanotubes in the fibres was as high as 60 wt.% To calculate the real contribution of carbon nanotubes to the mechanical properties of the nanocomposite fibres is of great interest, as it reveals the true efficiency of the CNT in various systems and will be discussed in detail.

5.3.2 Carbon nanotube orientation

Polarization effects are very important for samples with aligned carbon nanotubes. In our studies, since carbon nanotubes are expected to be well oriented inside PVA matrices by solid-state drawing, Raman Spectroscopy is an ideal characterization technique to study the orientation of CNTs. It has been observed that the Raman
spectra intensity of the tangential mode G band (1500-1700 cm\(^{-1}\)) monotonically decreases with increasing the angle between the drawing direction and the polarization direction of the polarizer for SWNTs, and this phenomenon has been used to show the orientation effect [4,5]. Orientation of aligned double-walled and multi-walled carbon nanotubes has also been measured and studied [6,7]. Several groups have used polarized Raman spectroscopy to study the degree of carbon nanotube alignment in the polymer matrix [8,9] and the orientation function has been calculate. Figure 5.2 shows a typical Raman spectrum of an oriented SWNT / polymer composite, the intensity reaches the maximum when the sample is parallel to the polarization direction of the polarizer and minimum when it is perpendicular.

**Figure 5.2:** Typical Raman spectra of an oriented SWNT / polymer composite, each curve is the spectrum for the indicated tape orientation with respect to the incident polarization
In a typical measurement, it is observed that for scattered light analyzed parallel to the incident laser polarization (VV geometry) all SWNT Raman peaks experience dramatic decrease in intensity as the oriented sample is rotated from parallel to perpendicular position with respect to the incident polarization [5]. For the VV measurement geometry the Raman intensity is proportional to \( \cos^4 \theta \), and \( \theta \) is the angle between SWNTs axis and the polarization direction of the polarizer as shown in Figure 5.3. The total Raman intensity could be integrated by summing up contributions from carbon nanotubes at different angles. In this way, the intensity of a Raman peak could be written as

\[
I(\psi) = \int_{\psi - \pi/2}^{\psi + \pi/2} c F(\theta - \psi, \Delta) \cos^4 \theta d\theta
\]

(5-1)

where \( \psi \) is the angle between the drawing direction (fibre axis) and the incident polarization, \( F(\theta - \psi, \Delta) \) is a distribution function and the parameter \( \Delta \) describes the width of the distribution. The \( c \) is the parameter that gives the maximum intensity when \( \theta = 0 \). J. Hwang \textit{et al.} suggested a Lorentzian form as shown in Equation 2 to fit the data [5]. The degree of SWNT alignment is determined by measuring \( I(\psi) \) for a convenient Raman peak at several fibre angles and performing a fit to Equation 1 by adjusting \( c \) and \( \Delta \) to minimize the variance.

\[
F(\theta - \psi, \Delta) = \frac{\Delta/2\pi}{[(\theta - \psi)^2 - (\Delta/2)^2]}
\]

(5-2)

where \( \Delta \) is now the full width at half maximum (FWHM) of the distribution. This parameter indicates the degree of orientation where larger \( \Delta \) suggested lower sample orientation.
**Figure 5.3:** Sketch of reference frames and angles. Subscript $f$ is for fibre, subscript $t$ is for nanotubes [1]

**Figure 5.4:** Polarized Raman spectra of 1 wt.% SWNTs in PVA tape. Each curve is the spectrum for the indicated tape orientation with respect to the incident polarization
Figure 5.4 is a typical Raman spectrum of the drop in intensity observed when the tape is rotated from parallel position to perpendicular position for SWNT / PVA tape of draw ratio 2. Figure 5.5 shows the G-band ratio intensity (the intensity at the 0° normalized as 1) of the drawn SWNT / PVA tapes versus the angle between the polarized direction and the drawing direction, which is also supposed to be the SWNT alignment direction. Clearly, orientation of carbon nanotubes has been observed in the systems. The intensity of G band $I (\psi)$ at different fibre angles is recorded, and a fit to Equation 1 is performed by adjusting $c$ and $\Delta$ to minimize the variance based on a Lorentzian distribution. The FWHM is then calculated from Equation 1 and was found to be 57° for SWNT / PVA composite sample of draw ratio 2.

**Figure 5.5**: The plot of the relative Raman intensity as a function of the angle $\psi$ ($0 - \pi/2$) between the sample axis and the optical polarization axis for drawn tapes. Composite sample contains 1 wt.% SWNTs with draw ratio 2
To compare the different degree of alignment of SWNTs in the composite tapes with different draw ratio, the orientation function of several nanocomposite tapes has been measured and calculated. Figure 5.6 shows the Raman intensity as a function of the angle between the sample axis and the optical polarization axis for drawn tapes with 1 wt.% SWNTs at different draw ratio. The line of $\cos^4(\Psi)$ which is expected for the case when the SWNTs are perfectly aligned along the fibre axis has been plotted as well. It is clear that higher draw ratios lead to better alignment of SWNTs in the polymer matrix. FWHM calculated from the fitting for all the tapes as a function of the draw ratio for the drawn composites tapes is shown in Figure 5.7. At draw ratio of 5, SWNTs are already highly oriented within the polymer matrix, the FWHM is observed to be as low as 20°.
Figure 5.6: The plot of the Raman intensity as a function of the angle $\Psi$ ($0 - 90^\circ$) between the sample axis and the optical polarization axis for drawn nanocomposite tapes with 1 wt.% SWNTs at different draw ratio. The line with $\bigcirc$ are $\cos^4(\Psi)$, expected for the case when the SWNTs are perfectly aligned along the fibre axis.
Polymer orientation

It is well known that the mechanical properties of polymers are closely related to the molecular orientation of the macromolecules occurring under various polymer processing conditions. Upon solid-state drawing, the isotropic network of polymer chain segments becomes anisotropic, from coils to extended and oriented chains. Many experimental techniques have been applied to determine the orientation degree in polymers on a molecular scale. In this study, polarized attenuated total reflection–infrared (ATR-IR) and wide angle X-ray diffraction (WAXD) have been employed to investigate the polymer orientation. Attempts have been made to correlate the orientation behaviour to the mechanical properties.
**ATR-IR measurement**

Polarized infrared spectroscopy can be used to study molecular orientation in polymers [10]. Since absorption in the infrared region only takes place when there is a change in the dipole moment of the molecule during the normal vibration. There is a transition moment or so-called infrared transition dipole parallel, perpendicular, or at some angle $\alpha$ to the major axis of symmetry of the molecule for each of infrared-active vibrational modes (stretching, bending, twisting, rocking, or a combination of these). Infrared radiation is only absorbed if two conditions are satisfied: the frequency of the radiation must correspond to the frequency of one of the IR vibrations and there must be a component of the electric vector, $E$, of the incident radiation parallel to the corresponding transition moment. If polarized radiation is used, there will be a differential absorption depending on the mutual position of the electric vector and the preferred orientation (machine direction, MD) of the sample. This phenomenon is called infrared dichroism and the orientation of the polymer can be described in terms of the dichroic ratio $D$.

$$D = \frac{A_{//}}{A_\perp} \quad (5-3)$$

where $A_{//}$ and $A_\perp$ are the absorbance for radiation parallel and perpendicular to the MD, respectively.

For perfectly oriented materials, the angle $\Psi$ between the transition moment direction and the electric vector direction will equal the angle between transition moment and the chain axis of the polymer $\alpha$ and the dichroic ratio $D_\alpha$ can be calculated as
\[ D_o = 2\cot^2 \alpha \quad (5-4) \]

In a real polymer film or fibre, the molecules are only partially oriented. When a certain fraction \( f \) of the molecules is perfectly oriented, the segmental orientation averaged over all chains in a polymer network subjected to uniaxial stretching may be explained by

\[
 f = \langle p_2(\cos \theta) \rangle = \frac{3(\cos^2 \theta) - 1}{2} \quad (5-5)
\]

where \( \theta \) is the angle between the direction of the stretching and the local chain axis of the polymer.

The orientation function \( f \) can be correlated to the dichroic ratio by the expression

\[
 f = \frac{(D - 1) \cdot (D_o + 2)}{(D + 2) \cdot (D_o - 1)} \quad (5-6)
\]

These concepts were introduced by Hermans and \( f \) is often called Hermans’ dichroic function [10]. For perfect alignment (\( \theta = 0^\circ \)) \( f \) equals +1; for perfect perpendicular alignment (\( \theta = 90^\circ \)) \( f \) equals -1/2 and for random orientation \( f \) equals 0.

Since most polymer films or fibres are too thick to study using transmission infrared method, the ATR-IR measurement has been successfully employed to determine the orientation of polymers [11, 12]. The advantage of the method is that electric fields exist in all spatial orientation at the reflection interface in the rarer medium, which is in contact with the denser internal reflection element. This is in contradistinction to
transmission spectroscopy, in which electric fields exist only at right angles to the
direction of radiation propagation [12]. Thus ATR can be used to investigate
orientation in three dimensions in a surface layer.

Flournoy et al. [13] studied the molecular orientation of stretched polypropylene film
by applying polarized ATR-IR techniques. By means of this method it is possible to
study the orientation at the surface of a polymer film. Four possible configurations
between the polarization directions of the radiation and the sample axis were
introduced. The \( x \) axis is the axis of drawing, the \( y \) axis is perpendicular to the \( x \) axis,
and the \( z \) axis is orthogonal to \( x \) and \( y \).

When \( x \perp \) plane of incidence (transverse direction, TD)

\[
\ln R_{TEx} = -\alpha k_x \\
\ln R_{TMx} = -\beta k_y - \gamma k_z
\]

when \( x \parallel \) plane of incidence (machine direction, MD)

\[
\ln R_{TEy} = -\alpha k_y \\
\ln R_{TMy} = -\beta k_x - \gamma k_z
\]

where \( \alpha, \beta \) and \( \gamma \) are functions of the refractive indices of the sample and substrate
and the angle of incidence. The \( k \) is the absorption indice and TE and TM represent
the transverse electric and the transverse magnetic waves respectively. The dichroic
ratio in the \( x-y \) plane, \( k_x / k_y \) can be calculated from the reflectivity \( (R_x \) and \( R_y) \).
These values can be obtained by recording spectra using the TE wave while rotating the sample 0 and 90 degrees.

\[ \text{Figure 5.8: Sample configuration on microscope stage (1) transverse direction; (2) machine direction (parallel to sample loading direction)} \]

In Figure 5.9 the ATR-IR spectra recorded with TE polarized radiation and the sample in the MD and TD direction (Figure 5.8) are shown for the stretched PVA tape. The dichroic difference spectrum (TD spectrum – MD spectrum) clearly shows the distinct bands which indicate parallel or perpendicular orientation. The assignment of the IR absorption bands in PVA is given in Table 5.2. The band at 1141 cm\(^{-1}\) is assigned to a C-C vibration in the crystalline phase [14], while bands at 1235 cm\(^{-1}\) and 917 cm\(^{-1}\) are assigned to the amorphous or a mixed (amorphous and crystalline) phase [15].
Figure 5.9: The ATR-IR spectra recorded with TE polarised radiation. The spectrum in the MD and TD direction and the dichroic difference spectrum (TD spectrum – MD spectrum)
Table 5.2: The assignment of different bands for poly (vinyl alcohol) [16]

<table>
<thead>
<tr>
<th>wave number [cm(^{-1})]</th>
<th>Phase</th>
<th>Assignment</th>
<th>Transition moment angle [°]</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1445</td>
<td>CH bending</td>
<td></td>
<td></td>
<td>(\perp)</td>
</tr>
<tr>
<td>1235</td>
<td>A,C</td>
<td>CH wagging or CH(_2) wagging</td>
<td>0</td>
<td>(\parallel)</td>
</tr>
<tr>
<td>1141</td>
<td>C</td>
<td>CC-O</td>
<td>81-83</td>
<td>(\perp)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>stretching,</td>
<td>out-of-phase</td>
<td></td>
</tr>
<tr>
<td>1081</td>
<td></td>
<td>CC-O</td>
<td></td>
<td>(\perp)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>stretching,</td>
<td>out-of-phase</td>
<td></td>
</tr>
<tr>
<td>917</td>
<td>A,C</td>
<td>Asymmetric</td>
<td>71</td>
<td>(\parallel)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH2 stretching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>847</td>
<td></td>
<td>CC-O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>stretching,</td>
<td>out-of-phase</td>
<td></td>
</tr>
</tbody>
</table>

From the absorbance of the various bands, the dichroic ratio is calculated. To do this the band cluster between 1150 and 950 cm\(^{-1}\) has been deconvoluted using the curve fitting module of Grams software (Galactic Inc.). The orientation function calculated from dichroic ratios of three different bands are given in Table 5.3.
Table 5.3: The calculated orientation function of three different bands of PVA tapes with different draw ratio.

<table>
<thead>
<tr>
<th>Draw ratio</th>
<th>0 wt.%</th>
<th>0.1 wt.%</th>
<th>0.3 wt.%</th>
<th>0.5 wt.%</th>
<th>1 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.24</td>
<td>0.35</td>
<td>0.34</td>
<td>0.27</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>0.54</td>
<td>0.60</td>
<td>0.59</td>
<td>0.71</td>
<td>0.63</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.71</td>
<td>0.63</td>
<td>0.74</td>
<td>0.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orientation function at 1143 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orientation function at 1237 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

Figure 5.10 plots the calculated dichroic ratio and Hermans’ orientation factor as a function of draw ratio of SWNT / PVA composite tapes at wavenumber of 917, 1143 and 1237 cm\(^{-1}\) respectively. It is clear that no significant change can be noticed on the degree of PVA molecular orientation between the pure polymer and composite tapes in both amorphous and crystalline phase. The orientation function increases with the draw ratio of the composite tape, which clearly indicates that solid-state stretching results in the alignment of PVA chains.
Figure 5.10: Dichroic ratios and Hermans’ factor as a function of draw ratio for the (a) 917, (b) 1143 and (c) 1237 cm$^{-1}$ absorption bands for oriented PVA and SWNT / PVA tapes
**X-ray diffraction measurement**

WAXD has been employed to monitor the orientation process of the drawn PVA tapes. Figure 5.11 shows the schematic illustration of the WAXD measurement and the 2D wide angle X-ray images of the as-prepared PVA and SWNT / PVA nanocomposite tapes at different draw ratios. Each of the patterns is individually optimised in contrast and brightness. The so-called the Debye-Scherrer rings are observed for film samples ($\lambda = 1$) which clearly indicate that crystallites are randomly oriented in the polymeric films. Upon drawing, the alignment of the crystallites with respect to the solid-drawing direction is revealed as evident by the pattern change from rings into arcs when the tapes are further stretched. As the crystallites orient more perfectly with the solid-state drawing, the Debye-Scherrer arc will get shorter as clearly shown in Figure 5.11.
### CHAPTER 5. ORIENTED SWNT / PVA COMPOSITE TAPES

<table>
<thead>
<tr>
<th></th>
<th>$\lambda = 1$</th>
<th>$\lambda = 2$</th>
<th>$\lambda = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>0.1wt% SWNTs</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>0.3wt% SWNTs</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
<tr>
<td>0.5wt% SWNTs</td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
</tbody>
</table>
CHAPTER 5. ORIENTED SWNT / PVA COMPOSITE TAPES

1.0wt% SWNTs

Figure 5.11: (a) Schematic of the WAXD measurement and (b) WAXD patterns of PVA and SWNT / PVA nanocomposites at different draw ratio

A quantitative measurement of crystallite orientation with respect to the drawing direction could be obtained from Azimuthal scans of the diffraction rings, where the arcs appear as peaks [17]. Here, 2D intensity data is integrated along the $2\theta$ axis and Figure 5.12 plots the integrated X-ray intensity as a function of the Azimuthal angle for PVA and 0.1 wt.% SWNT / PVA tapes with draw ratio of 1, 2 and 5, respectively. The background intensity is subtracted for all samples and the $0^\circ$ represents the equatorial direction. It is observed that unstretched films show isotropic behaviour of polymer chains which could be determined from the constant diffraction intensity over the whole angle range in all films. When films are stretched under solid-state condition, the intensity increases and the peak becomes sharper, which indicates that the drawing leads to higher degree of orientation of the polymer chains in both samples.
Figure 5.12: Integrated X-ray intensity (integrated along the $2\theta$ axis) versus the azimuth angle for (a) PVA sample and (b) PVA/0.1 wt.% SWNTs samples. Solid line is the fit to the data by Gauss functions. Composite tape draw ratio=5\textcircled{$\bullet$}; draw ratio=2\textcircled{$\bigcirc$}; draw ratio = 1
CHAPTER 5. ORIENTED SWNT / PVA COMPOSITE TAPES

Assuming a uniaxial Gaussian distribution, the Azimuthal peaks are fitted with a Gaussian curve and the widely accepted Hermans’ orientation factor could be calculated for both the drawn PVA and SWNT / PVA tapes. The crystal orientation function $f_c$ is calculated from the Hermans’ orientation equation, which has been introduced previously.

\[
f_c = \langle p_2(\cos \phi) \rangle = \frac{\langle \cos^2 \phi \rangle - 1}{2} \tag{5-11}
\]

Where $\langle \cos^2 \phi \rangle$ is calculated using the following equation

\[
\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \tag{5-12}
\]

where $\phi$ is the Azimuthal angle, at 90° corresponds to the draw direction, and $\phi = 0°$ corresponds to the transverse direction of the tapes.

Figure 5.13 shows the calculated Hermans’ orientation factor obtained from WAXD experiments perpendicular to the tape surface (see Fig. 5.11a) for composite tapes with draw ratio 2 and 5 at different SWNT weight fraction from 0.1 to 1 wt.%. As there are no major differences between the different samples, this confirms that the PVA matrix in the composite tapes and in the pure PVA tapes possess the same degree of molecular orientation at a given macroscopic draw ratio. For lower draw ratio 2 ($\lambda = 2$), the Hermans’ factor even goes down slightly with the addition of SWNTs. When the tapes are further stretched to a draw ratio of 5, where all the tensile tests are carried out, the Hermans’ factor remains constant for all tapes. It is worth to note that similar degrees of polymer orientation among all tested samples
guarantee a valid comparison of mechanical properties at a certain draw ratio for the stretched tapes. In other words, true reinforcement of the fillers could only be determined when mechanical properties are compared under conditions where the polymer orientation is the same. It is interesting to note that Hermans’ factor of PVA polymer chain at draw ratio of 2 is already around 0.7. Since the values of the Hermans’ factor range from 0 to 1, representing completely random and perfectly parallel orientation, the results indicate that solid-state drawing of dried films significantly aligns the polymer chains even at low draw ratio.

![Hermans’ factor as a function of weight fraction of SWNTs at the draw ratio of 2 and 5](image)

**Figure 5.13:** Hermans’ factor as a function of weight fraction of SWNTs at the draw ratio of 2 and 5
5.3.4 Stress transfer efficiency

Good interfacial interaction and stress transfer between carbon nanotubes and polymer matrices is essential for good mechanical properties of the composites. In this work, the stress transfer efficiency from the polymer matrix to SWNTs in the oriented tapes is studied using the elongation based strain rig under Raman spectroscopy microscopy as mentioned before in the previous chapter. Since the laser spot size in the Raman spectroscopy setup is around 1-5 µm, and nanotube diameters are only several nanometres in size, the Raman signal is averaged over nanotubes in all directions. It is worth to note that for isotropic samples that are under simple tension, only the carbon nanotubes that are oriented along the loading direction are under tension, while others which lie in the perpendicular direction are under compression because of simple Poisson’s contraction [18]. On the other hand, when oriented samples are under tension, most of the carbon nanotubes will experience tension, which would lead to a maximized Raman shift.

Figure 5.14 plots the Raman shift as a function of strain for oriented 0.1 wt.% SWNT / PVA tapes with different draw ratio. It is obvious that higher draw ratio leads to a higher slope which suggests that more carbon nanotubes are under stress after the drawing of the tapes. Figure 5.15 plots the Raman shift against strain for SWNT / PVA tapes with different concentrations to check the influence of the content of carbon nanotubes on stress transfer efficiency. The results clearly show that for the range of concentrations studied in this work, the stress transfer efficiency is independent of concentration of carbon nanotubes.
Figure 5.14: The Raman shift as a function of strain for SWNT / PVA tapes with different draw ratio. Solid line represents linear fit to the data.

Figure 5.15: The Raman shift as a function of strain for oriented SWNT / PVA tapes with different concentration of carbon nanotubes.
5.3.5 Micromechanical modelling

To evaluate the contribution of SWNTs to the composite mechanical properties, the Cox – Krenchel model is applied as discussed in detail in Chapter 2. Figure 5.16 shows the Young’s modulus and ultimate tensile strength (UTS) as a function of the vol. % of SWNTs. The effective contribution of the nanotubes to the composite properties, given by $E_{\text{eff}} = \eta L E_f$, can be calculated if the properties of the matrix, the composite and the nanotube volume fraction are known. As the composites are highly aligned we assume that all SWNTs are perfectly oriented with an orientation factor $\eta_o$ equals to 1. This analysis gives an average effective nanotube modulus of $\sim 600$ GPa for all SWNT / PVA tapes investigated. The same treatment is carried out for the composite strength and results in average effective nanotube strength of 88 GPa.
Comparing the data presented in Table 3.1 in Chapter 3 with the effective nanotube properties calculated for the current SWNT / PVA tapes of an $E_{\text{eff}}$ of 600 GPa and a $\sigma_{\text{eff}}$ of 88 GPa, calculation suggests that the nanotubes in our system show remarkable reinforcing effects. It should be noted that these values, although high, are still rather conservative estimates for the actual properties of the SWNTs as in the case of a discontinuous fibre composite, the effective properties need to be corrected for the length efficiency factor $\eta_L$, in addition, the purity of the nanotubes is only around 70% which means that the actual nanotube volume fraction is lower than assumed for the calculations. All of these effects would lead to higher effective nanotube properties (Young’s modulus of 857 GPa and tensile stress of 125 GPa) in
the composites. In fact, the stress carried by the nanotubes is so high that these composites for the first time start to exploit the exceptional high theoretical strength of nanotubes (100-150 GPa). For a comparison, as mentioned earlier similar calculations on super tough SWNT / PVA fibres reported by Dalton et al. [3] shows that the contribution of the nanotubes to the composite strength is only about 3 GPa, as the amount of CNTs in the fibre is as high as 60 wt.%. Figure 5.17 plots calculated nanotube contribution to nanocomposite fibre stiffness and strength, including data from literature as well as data obtained in our study. It is obvious that a very high reinforcing efficiency has been achieved and the effective tensile stress and modulus are close to the theoretical value. The reason of the gap between experimental and theoretical value might be the imperfection of the carbon nanotubes as well as the orientation.

![Figure 5.17: Calculated effective tensile stress and Young’s modulus of the carbon nanotubes from literature. • represents data in our work](image-url)
5.3.6 Pre-orientation study

As a first evaluation of composite reinforcement, the micromechanical calculation is very useful. However this simple treatment might be misleading for oriented semi-crystalline polymers such as PVA. In fact, in these systems the degree of molecular orientation plays a central role in the macroscopic mechanical behaviour. A high degree of polymer chain orientation is crucial to produce high performance polymers. The simplest parameter that can be used to describe molecular orientation is the draw ratio and a linear relation exists between Young’s modulus and draw ratio $\lambda$ [19]. However, if the polymers are prepared using different processing routes, i.e. casting vs spinning, or if the polymers are filled with various fillers, the comparison of mechanical properties of fibres with the same draw ratio might be erroneous. The reason is that the processing route or the fillers might change the pre-orientation condition in the polymer, thus similar macroscopic draw ratios can correspond to different degrees of molecular orientation in the modified polymers [20]. The same can be said for nanocomposites, where the presence of the filler might influence crystal morphology and/or orientation. This means that the nanocomposite and its reference material, i.e. the pure polymer matrix, can possess different morphologies even if they have the same draw ratio, hence the micromechanical calculation cannot be applied using the unfilled polymer data for the matrix composite.

It was previously shown that solution-cast polymer films were not truly isotropic. Smith et al. [21,22] showed in their papers on ultra high molecular weight polyethylene (UHMWPE) gel film that upon film drying, lamellar crystals in the gel tend to orient preferentially with the chain perpendicular to the surface of the polymer film. After removal of the solvent, the gels consisted of partially oriented conglomerates of lamellae with some preferential orientation. Figure 5.18 illustrates
the typical film casting procedure and crystal growth mechanism where preferential orientation of crystals is obvious. WAXD patterns of dried PE gel film from Figure 5.19 clearly confirm the proposed crystal growth mechanism where the polymer chains are already packed anisotropically along the direction (in plane) of the film thickness (B direction), while the polymer chains are distributed randomly (out of plane) in the surface (A direction).

**Figure 5.18:** Typical gel film casting procedure and crystal growth mechanism.
Later work by van Aerle [23] et al. explained the reason for the preferred orientation observed in cast dried film and also from single crystal mats obtained by filtering of a suspension of single crystals or by sedimentation [24-26]. In the case of single crystals mats, the combination of gravity and flow effects during the filtering causes the preferred orientation. For the cast dried film, the drying procedure causes the preferred orientation. It was pointed out that no preferred orientation was observed from the extracted gel films and in the unconstrained dried films. While for the constrained dried films where shrinking of the sample was attempted to avoid, preferred orientation was introduced. This means that it is the shrinking forces and not the gravity effects are responsible for the pre-orientation.

This preferential orientation clearly affects the structure development during the drawing process. In fact, the lamellar crystals need to be rotated in the direction of
stretching before being unfolded. To illustrate the drawing of the dried films, Figure 5.20 shows the possible deformation model for drawing from dried film (draw ratio = 1) to oriented tapes. It is clearly that the films are preferentially oriented even without drawing and the direction is perpendicular to the drawing direction. When the films are drawn, the folded crystal lamella has to ‘flip’ 90° to the drawing direction. Then upon further drawing, the microfibrils are stretched and slide within folded lamella until all the polymer chains are oriented in an ideal condition [27].

![Figure 5.20](image)

**Figure 5.20**: The schematic illustration of deformation model for drawing from dried film (draw ratio = 1) to oriented tapes. The drawing direction is shown. The symbols represent the polymer crystal lamella.

It is obvious from the schematic illustration that pre-orientation of the crystals has negative effects on the drawing since they have to overcome the ‘flip’. In other words, pre-orientation results in a lower degree of molecular orientation at the same macroscopic draw ratio for tapes obtained by solid-state drawing of solution-cast films as compared to fibres obtained by a spinning process, where no preferential orientation is present. Only if the total draw ratio, which takes pre-orientation into account, is considered, the properties of fibres and tapes obtained from different processing routes can be compared. The total draw ratio is given by the following equation:
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\[ \lambda_{\text{total}} = \lambda_{\text{pre}} \cdot \frac{L_{\text{final}}}{L_0} \]  

(5-13)

where \( \lambda_{\text{pre}} \) accounts for the preferential orientation and is referred to as pre-orientation. \( L_{\text{final}}, L_0 \) represents the final and the original length of the sample and \( L_{\text{final}} / L_0 \) is the macroscopic draw ratio.

Another way of comparing fibres or tapes obtained by different processing procedures could be by plotting tensile strength as a function of Young’s modulus as illustrated in Figure 5.21. Since the total draw ratio is strongly influenced by the pre-orientation condition of the polymer crystals, it might be misleading to plot the macroscopic draw ratio as a function of either \( E \) or \( \sigma \). Here, Young’s modulus is an indicator of molecular orientation, and a master curve can be obtained, which describes the true behaviour of the polymer, irrespective of processing parameters. Since carbon nanotubes are known to nucleate crystallization [28, 29] and may have an effect on the orientation of crystals [30]. By plotting measured composite properties onto the PVA master curve, it can be seen whether the data falls on the same master curve or not. If so, it is very likely that the improved mechanical properties are merely a result of the altered polymer morphology by the nanotubes. However, if the composite properties data deviates from the polymer master curve, it would indicate a true reinforcing effect from the filler into the polymer matrix.
Chapter 4 presented the crystallization studies on SWNT / PVA composite films, and concluded that SWNTs do not act as nucleation agents; further X–ray measurement on drawn nanocomposite tapes suggested the PVA matrix in the composite tapes and in the pure PVA tapes possess the same degree of molecular orientation at a given macroscopic draw ratio. Turning to nanocomposite again, attention should be paid to the effect of the nanofiller on the initial crystal morphology and/or pre-orientation.

In our work, all samples were not processed through extracting solvent but dried
under room temperature; it is likely that preferred orientation occurs in these dried films. The fillers might change the crystal morphology and the pre-orientation condition, which results in a different degree of molecular orientation in the initial state. It is important to make sure whether the unfilled polymer data can be used as the matrix in the calculation, in other words, the influence of the fillers on the matrix morphology has to be investigated. It is possible that the improved mechanical properties are simply attributed to the filler-induced alteration of morphology such as crystallinity, orientation, *etc*.

In order to clarify the reinforcing mechanism, all the composite films with SWNTs at various concentrations are measured, and diffraction patterns are taken from the out-of-plane as well as from in-plane. The same WAXD set up has been used and measurements are carried out as described before. The WAXD patterns of nanocomposite films are collected in the A and B positions as illustrated in Figure 5.22.

![Figure 5.22: Schematic illustration of the two positions where the WAXD patterns were recorded on SWNT / PVA films](image)

Figure 5.23 shows the WAXD patterns of dried SWNT / PVA composite films with different concentration of SWNTs recorded from the out-of-plane and in-plane,
respectively. The WAXD patterns recorded from the out-of plane (A position) show fully isotropic rings, which indicate random distribution of polymer crystals in the surface. However, the patterns measured from the in-plane (B position) show that there is a preferred orientation present as indicated by the arrows.

<table>
<thead>
<tr>
<th></th>
<th>A position</th>
<th>B position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>0.1wt% SWNTs</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>0.3wt% SWNTs</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 5.23: WAXD patterns of dried SWNT / PVA composite films with different concentration of SWNTs recorded from (a) out-of-plane and (b) from in-plane respectively.

Since it is difficult to distinguish the degree of pre-orientation in the composite films directly from the WAXD patterns, it is important to quantify the orientation function. Azimuthal angle as a function of the intensity is plotted and orientation function is calculated for all the carbon nanotube systems. Figure 5.24 plots the Azimuthal angle versus the intensity from the WAXD pattern for nanocomposite films. From these measurements it can be concluded that some clear pre-orientation exists in both PVA and SWNT / PVA samples before drawing as isotropic behaviour would have resulted in a constant diffraction intensity over the whole angle range. The results also show that the addition of SWNTs does not affect the amount of pre-orientation. It can therefore be assumed that upon subsequent solid state drawing, similar
macroscopic draw ratios will induce similar degrees of molecular orientation in both the pure PVA and SWNT / PVA tapes. Figure 5.25 shows the calculated Hermans’ orientation factor obtained from WAXD in-plane measurements (see Figure 5.22b) of both films and drawn tapes of draw ratio 5. As there are no major differences between the different samples in both cases, this confirms that the PVA matrix in the composite tapes and in the pure PVA tapes possesses the same degree of molecular orientation at initial stage as well as at draw ratio of 5. Hence, the improved mechanical properties as described are truly the result of nanotube reinforcement and cannot be ascribed to a different molecular orientation of the polymer matrix. For this reason, the micromechanical model can be applied using the unfilled polymer data as a reference for the composite matrix (film and drawn tapes) and the analysis presented previously was correct.
CHAPTER 5. ORIENTED SWNT / PVA COMPOSITE TAPES

(b)

Figure 5.24: Azimuthal angle as a function of intensity from WAXD pattern. (a) pure PVA films; (b) nanocomposite films with 0.1 wt.% SWNTs
Figure 5.25: Calculated Hermans’ factor obtained from WAXD in-plane measurements of (a) nanocomposite film; (b) nanocomposite tape of draw ratio 5
By plotting a PVA master curve, nanocomposites data is compared and plotted as shown in Figure 5.26. High modulus data for pure gel-spun PVA (black square) are taken from the work by Schellekens and Bastiaansen [31] where they used a type of PVA with similar molecular weight. It can be clearly seen that SWNT composites data deviates from the PVA master curve, indicating a true reinforcement of SWNTs in PVA matrix.

**Figure 5.26**: Mastercurve of PVA. Summary of mechanical properties of PVA at different draw ratio obtained with various processing routes showing the true behaviour of PVA. High modulus data for pure PVA (black square) are taken from the work by Schellekens and Bastiaansen [31] where they used a PVA with similar molecular weight.
5.3.7 Surfactant-assisted system

A surfactant-assisted system has been studied by Ciselli et al. [1] and some of the results are reported here for comparison. In this system, Sodium dodecyl sulphate (SDS) was employed to assist the dispersion of SWNTs, the same matrix and the same batch of carbon nanotubes were used in sample preparation. Oriented composite tapes were prepared through solution process and drawn at solid-state as well. Homogenous dispersion has been achieved as shown in Figure 5.27. Details on characterization of the tapes have been described [1].
The mechanical properties were measured by tensile tests. Figure 5.28 shows the stress-strain curve of the composite tapes. Significant improvement of the mechanical properties was observed. However, the addition of SDS decreases both modulus and the ultimate tensile strength (UTS) of the PVA matrix, while the elongation at break is increased, indicating that SDS molecules act as plasticiser. The use of both nanotubes and dispersing agent increases both Young’s modulus and UTS, while the elongation at break is maintained at a similar level as for PVA / SDS tapes. The same calculation used for our system was applied here as well for modulus and tensile strength. The analysis gave a very high effective modulus of 1.12 TPa and an effective stress of 45 GPa respectively. If the loss of nanotubes during the centrifugation step is taken into account, an even more exceptionally high value of 1.68 TPa modulus and 67.5 GPa of stress was obtained.
Chapter 5. Oriented SWNT / PVA Composite Tapes

Figure 5.28: Stress-strain curves of PVA and PVA / SWNT nanocomposite tapes at draw ratio of 4. [1]

It is not hard to notice that the strength is maximized by the nanotubes in our work, while Young’s modulus seems to be most affected by nanotubes in SDS systems similar to the previously reported work. WAXD measurement on the pre-orientation of the cast films was carried out and Figure 5.29 shows the Hermans’ orientation factor as calculated for all the films. It is clear that in the case of water / SDS system here, the addition of nanotubes decreases the pre-orientation, resulting in different drawing behaviour. This means that the molecular orientation of the polymer in the oriented pure PVA tape and in the nanocomposite is not the same, even though they have been drawn to the same macroscopic draw ratio.
**Figure 5.29:** Calculated Hermans’ orientation factor as a function of SWNT loading, indicating that the degree of pre-orientation in the cast SDS / PVA nanocomposite films decreases by adding SWNTs. [1]

Again the mechanical properties data is plotted on the PVA master curve in Figure 5.30, and this system clearly shows that all the data falls on the curve for PVA. Since no deviation from the PVA trend has been observed with the addition of SWNTs, it shows convincingly that here the improvement of composite properties is not a true reinforcing effect by the carbon nanotubes.
CHAPTER 5. ORIENTED SWNT / PVA COMPOSITE TAPES

5.4 Conclusion

This Chapter described the preparation of homogeneous SWNT / PVA nanocomposite tapes by a solid state drawing. The solution-cast films were drawn at elevated temperature to create uniaxial nanocomposites, where optimal reinforcing efficiency of nanotubes was expected. The mechanical properties of these materials had been investigated and showed a remarkable increase in Young’s modulus and tensile strength with the addition of only a small amount of SWNTs. For example, the addition of only 1.0 wt.% of SWNTs led to a 200 % increase in tensile strength. Micromechanical analysis showed that the nanotube contribution to the composite strength was as high as 88 GPa, which is very high when compared to other data.
reported in literature, and begins to exploit the theoretical strength of nanotubes. This high reinforcing efficiency suggested that in current systems most of the prerequisites for obtaining highly efficient nanocomposites had been fulfilled i.e. (i) high level of dispersion, (ii) good interfacial interaction and finally (iii) a high level of alignment of the nanofillers. X-ray studies on nanocomposite films demonstrated that pre-orientation of PVA crystals exist, but the addition of SWNTs did not change the initial morphology of the polymer matrix. A further analysis using a so-called PVA master curve confirmed the effect of SWNTs on the polymer morphology. By plotting UTS as a function of Young’s modulus, composites data was observed to deviate positively from the pure PVA master curve. Therefore, it was confirmed that the observed improvements in mechanical properties were true reinforcing effects of the SWNTs and not the result of some kind of modification of the PVA matrix.

A second system was presented for comparison reasons, where nanocomposites consisted of the same matrix and nanotubes but with the use of surfactant to assist carbon nanotube dispersion. Though significant mechanical property improvement had been observed from mechanical tests, X-ray studies suggested that it was the result of a changed initial morphology of the polymer matrix rather than a real reinforcing effect from the carbon nanotubes.

As a final remark, it is worth noticing that the interaction between the SWNTs and the PVA matrix are mainly by Van der Waals forces and even though the improvement in mechanical properties is already impressive as compared to the results found in literature, there might still be space for further improvement if the interfacial bonding between matrix and nanotubes is improved by the use of appropriate functional groups on the surface of the nanotubes.
5.5 References

20. Personal communication with Prof. Paul Smith.


Chapter 6

Comparison of reinforcing efficiency of different types of carbon nanotubes

6.1 Introduction

Carbon nanotubes can be either single-walled or multi-walled structures and both have been used as promising reinforcing fillers in polymer composites. Multi-walled carbon nanotubes (MWNTs) are basically concentric single-walled tubes with Van der Waals forces between the walls. Single-walled nanotubes (SWNTs), in theory at least, are more desirable for creating high-performance nanocomposites as the poor intra-tube wall interactions in MWNTs can result in minimal load transfer between the layers of the nanotubes and may lead to intra-tube slippage and a telescopic failure mode [1]. In fact, when multiwalled carbon nanotubes are embedded in a polymer to create a composite material, effective stress-transfer may be potentially only achieved through its outer wall. Moreover, when considering the effective properties of CNTs in polymer composites the entire cross-sectional area of the nanotubes must be taken into consideration, hence compromising the effective properties for MWNTs (see Table 2.3 and Table 2.4). In reality, however, often less impressive differences in reinforcing are found between SWNTs and MWNTs when
CHAPTER 6. REINFORCING EFFICIENCY OF DIFFERENT TYPES OF CNTS

they are employed in polymer composites [2]. The main reason for this is that in many studies bundled SWNTs remain throughout processing, which would display reduced mechanical properties and poor stress transfer as compared to isolated SWNTs. On the other hand, MWNTs are in general easier to disperse and their better dispersion often makes up for their intrinsically lower mechanical properties.

In this chapter, an attempt to explore the different reinforcing behaviours of different types of carbon nanotubes will be made. Three types of CCVD-grown carbon nanotubes (SWNTs, DWNTs, MWNTs) from Nanocyl (Belgium) will be incorporated into poly (vinyl alcohol) (PVA) matrices to prepare CNT / PVA composites. Solid state drawing will also been applied to fabricate oriented nanocomposite tapes. Mechanical properties of both isotropic films and oriented tapes will be investigated. To further understand the reinforcing mechanism, the structure of the nanotubes will be compared using Raman spectroscopy, the interface between tubes and the polymer will be studied using DMA. The effect of different carbon nanotubes on the crystallinity of polymer matrix will be analysed using differential scanning calorimetry (DSC). Possible fracture mechanisms for nanocomposite tapes containing SWNTs and MWNTs will be proposed to explain the difference in reinforcing efficiency between different tubes as well. To check the influence of carbon nanotubes on the initial polymer morphology, WAXD will be applied to assess the difference in nanocomposite filled with different types of tubes. Finally, CCVD-grown MWNTs with –COOH functional groups will be incorporated into PVA matrix to study the effect of nanotube surface functionalization on the mechanical properties of the composites.
6.2 Experimental

6.2.1 Materials

The polymer matrix used in this investigation was similar to that used in previous chapters. Poly (vinyl alcohol) (PVA) (Mw = 84,000 - 124,000 g / mol, 98 - 99 % hydrolysed) was purchased from Sigma-Aldrich and used as supplied. In addition to the Carbolex SWNTs (a-SWNT) produced by arc-discharge method, CCVD-grown CNTs (c-SWNT, c-DWNT, c-MWNT, c-fMWNT) from Nanocyl were employed in this Chapter. Details on different types of nanotubes had been introduced in Chapter 2. All types of nanotubes were used without further purification. Dimethyl sulfoxide (DMSO) was purchased from Romil, and was used as solvent.

6.2.2 Composite preparation

Nanocomposite films with Nanocyl CCVD-grown carbon nanotubes were prepared through solution cast method described in Chapter 4. Nanocomposite tapes were fabricated from cast films by solid state drawing at elevated temperature of 130°C.

To achieve optimum dispersion, PVA gels with c-fMWNT were prepared by crystallization from semi-dilute solutions in the DMSO and water (H₂O) mixtures. The DMSO / H₂O composition was set to be 70:30 (vol/vol) to assure the high drawability of PVA film as reported by Cha et al. [3]. PVA was first dissolved in DMSO and water solution at 105 °C and continuously stirred for 3 hours. Dispersion of c-fMWNT in DMSO was achieved using ultrasonication bath for one hour while ice was maintained in the bath to prevent excessive heat. The nanotube concentration
needed in DMSO was calculated in order to obtain a loading of 0.1, 0.5 and 1 wt.% in the final composite. The c-fMWNT suspension was gradually added into previously prepared PVA solution while stirring. Stirring of the mixture was maintained for 1 hour to achieve good mixing, the final concentration of PVA solution was 7.5 wt.% The homogenised mixture was then maintained in the hot bath for an hour to degas before the solution was poured into a metal plate. The metal plate was placed in a freezer at -20 °C for 20 hours, generating a gel. The gel was then immersed in water for a week to extract the solvent, dried films were obtained at room temperature. Oriented tapes were prepared under the same condition as described at 130 °C in the oven.

6.2.3 Composite characterisation

Dynamic Mechanical Analysis (DMA)
The experiments were carried out in a TA Instruments DMA Q800 machine fitted with a tensile testing head as described in the previous chapter. The system was automatically cooled to 0 °C, and then heated at a rate of 5 °C to 200 °C. All the test parameters are the same for all composite films. A static force of 10 mN was applied to ensure that the sample was taut between the tensile grips. Strain control for applying the deforming load to the sample was selected, where strain was kept constant well within the elastic region during the test and the stress was measured by a force transducer or load cell.

Tensile test
Tensile tests were carried out using an Instron 5586 at room temperature and the mechanical properties of the CNT / PVA tapes were evaluated. The tape samples were rectangular with approximate planar dimension of 25 mm × 5 mm × ~ 50 µm.
For all samples at least five specimens were measured, the results analysed and the mean and standard deviation calculated.

**Raman spectroscopy**
Raman spectra of different types of carbon nanotubes were recorded on a Renishaw Raman microscope system using a 50 × objective lenses and the excitation beam from a 60mW HeNe laser (632.8 nm). The spectral resolution of the system is < 1 cm⁻¹. Carbon nanotubes were first dispersed in DMSO using an ultrasonication tip, and then the CNT suspension was cast on glass slides and dried for Raman measurement.

**Differential scanning calorimetry (DSC)**
DSC measurements were carried out in standard aluminium pans using a Mettler DSC 822e differential scanning calorimeter. The PVA and composite samples were simultaneously prepared in order to maintain the same thermal history. 7 mg were measured for all samples in the DSC and nanocomposite films with different types of CNTs and concentration were measured. All crystallization and melting temperatures were determined by drawing asymptotic lines to the initial rise or drop in heat flow and determining the intersection with the baseline. To erase thermal history, all the film samples were heated from 0°C up to 250°C at 40°C per minute, held at that temperature for 1 minute, and then cooled at 40°C per minute to 0°C. After 1 minute equilibration time, the samples were reheated to 250°C and then cooled again. The endothermic data was taken from the second heating stage.

**Wide Angle X-ray Diffraction (WAXD)**
Oxford Diffraction Xcalibur XP was runned with a Mo-Kα source at -50 KV and 40 mA. X-ray scattering pattern were recorded by an Onyx CCD detector at a distance
of 65 mm for 300 s. The two-dimensional X-ray patterns were transformed into one-dimensional patterns by integrating the Azimuthal intensity.

6.3 Results and discussion

6.3.1 DMA

To check the reinforcing efficiency of different types of CNTs in PVA matrices, mechanical properties of both the isotropic composites films and the drawn tapes were measured. Preliminary DMA measurements were performed on isotropic nanocomposite films. In order to compare the contribution of different carbon nanotubes, the storage modulus at room temperature (25 °C) is plotted as a function of CNT volume fraction. Figure 6.1 clearly shows the trend for all types of carbon nanotubes. Obviously, the a-SWNTs demonstrate a remarkable 30.1 % increase of the storage modulus from 1701 MPa for pure PVA films to 2213 MPa with only 0.1 wt.% SWNTs. Compared to a-SWNTs, the CCVD-grown CNTs only display a moderate reinforcement in the isotropic films.
Figure 6.1: A comparison of the storage modulus at room temperature for different types of isotropic carbon nanotube / PVA films at different volume fractions

The effective modulus $E_{\text{eff}} = \eta_L E_f$ is again calculated for all the tubes as described in Chapter 3. The volume fraction of CNTs in each film is calculated from the mass fraction using densities, where $\rho = 1300$ kg / m$^3$ for both PVA and SWNTs, $\rho = 1500$ kg / m$^3$ for DWNTs and $\rho = 2150$ kg / m$^3$ for all MWNTs. Calculated results are listed in Table 6.1. The analysis gives a reasonably high effective modulus for all the CNTs ranging from around 400 GPa to 500 GPa.
Table 6.1: Calculated effective modulus for different types of carbon nanotubes

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Effective modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-SWNTs</td>
<td>503.7</td>
</tr>
<tr>
<td>c-SWNTs</td>
<td>470.2</td>
</tr>
<tr>
<td>c-DWNTs</td>
<td>379.9</td>
</tr>
<tr>
<td>c-MWNTs</td>
<td>398.3</td>
</tr>
</tbody>
</table>

Due to the one-dimensional character of CNTs, oriented fibres or tapes are of immense interest. It is expected that oriented nanocomposite systems would lead to a much better reinforcing efficiency of the carbon nanotubes if good stress transfer as well as orientation of the tubes have been achieved. DMA measurements were performed on oriented composite tapes as well. Figure 6.2 shows the storage modulus at room temperature from DMA as a function of the volume fraction of different carbon nanotubes for drawn composite tapes. Similar to the isotropic composite films, the storage modulus increases with the addition of the carbon nanotubes at low content of 0.1 wt.%. However, further addition of carbon nanotubes leads to a drop in storage modulus for some of the CCVD-grown carbon nanotubes, while c-DWNTs and a-SWNTs show different behaviour in that the storage modulus increases for all concentrations. The reason might be that excess tubes are not well aligned to efficiently reinforce the polymer matrix, instead tubes may aggregate and stay entangled, which leads to the decrease of the mechanical properties in the drawn tapes above a certain nanotube content. It should be noted that the draw ratio of the CCVD-CNT composite tapes was 4, while the a-SWNT films were drawn to draw ratio 5 to ensure homogenous tapes. This difference in draw ratio explains the higher storage modulus in a-SWNT system in Figure 6.2.
6.3.2 Tensile testing

DMA measurements showed that CNTs improve the storage modulus at all volume fractions in isotropic films, while some CNTs suggested a drop in modulus above a certain volume fraction in oriented tapes. The different behaviours in oriented systems need some further investigation. Therefore, direct tensile tests are carried out on oriented CNT / PVA tapes. Figure 6.3 shows the typical stress-strain curves for drawn PVA tapes with different types of carbon nanotubes. It is obvious that different carbon nanotubes demonstrate their unique mechanical reinforcing behaviour. Figure

Figure 6.2: A comparison of the storage modulus at room temperature for different types of oriented carbon nanotube / PVA tapes at different volume fractions
CHAPTER 6. REINFORCING EFFICIENCY OF DIFFERENT TYPES OF CNTS

6.4 plots the tensile strength, Young’s modulus, the strain at break and toughness calculated from tensile tests for different carbon nanotubes.
Figure 6.3: Stress-strain curve for (a) a-SWNT / PVA tapes, (b) c-SWNT / PVA tapes, (c) c-DWNT / PVA tapes, (d) c-MWNT / PVA tapes.
CHAPTER 6. REINFORCING EFFICIENCY OF DIFFERENT TYPES OF CNTS

It is obvious that the CCVD-grown nanotubes do not show significant reinforcing effect in PVA matrices. It is interesting to note the difference between a-SWNTs and c-MWNTs. The a-SWNTs do not influence the ultimate strain at break, but have significant effect on the Young’s modulus and the tensile strength. However, c-MWNTs do not influence the Young’s modulus and the ultimate tensile strength, but have a great effect on the strain at break.

The unaltered stiffness and strength might be explained by considering that MWNTs display intrinsic lower mechanical properties as compared to SWNTs. Experimental
and theoretical studies showed that the effective modulus for MWNTs is in the range of 10-500 GPa [4] as opposed to 1 TPa [5,6] for SWNTs, because of their bigger cross-sectional area (see Table 2.2 and 2.3). In addition, the MWNTs used in this study were grown at lower temperatures as compared to a-SWNTs (CCVD versus arc-discharge process), which makes the difference even bigger. Furthermore, MWNTs exhibit a so-called intrinsic ‘waviness’ as a result of their structural defects. These defects to the nanotube structure are expected to reduce significantly the mechanical properties of nanotubes. Indeed, finite element analysis of this issue has shown that the effective nanotube modulus decreases dramatically for such curved nanotubes [7,8]. These considerations can explain the unaltered stiffness and strength, but they cannot account for the dramatic increase of strain at break and the toughness.

Since c-MWNTs contain a high density of superficial defects, tensile stress can initiate fracture of the external layer, followed by inter-wall sliding. The telescopic failure mechanism of MWNTs could be an important energy absorbing mechanism that could lead to the observed toughening effect. However, if the load is not successfully transferred to the tubes, as suggested by the small contribution to the composite modulus and ultimate strength, probably because of the low aspect ratio in combination with weak interaction between the tube and the matrix, telescopic failure is unlikely to happen. This may lead us to another possible mechanism to explain the improved toughness, i.e. interfacial debonding. In fact, if the interaction between the polymer and the CNT is weak, then CNT debonding occurs. As nanofibres, MWNTs possess an extremely huge surface area, which means that interfacial debonding can give an important contribution to toughening of the composite.
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Figure 6.5 shows the schematic cartoon of the possible fracture mechanisms for nanocomposite tapes containing SWNTs and MWNTs. Because of the good interaction between SWNTs and the polymer matrix, as indicated by the improved modulus and tensile strength, SWNTs might be covered by a layer of polymer. In contrast, if load has been successfully transferred to the outer wall of the tubes, MWNTs will present telescopic failure where inter-wall sliding is likely to happen. Moreover, if the interaction between the polymer and the CNT is weak and stress transfer efficiency is low as might be in our case, it may lead us to another possible fracture mechanism, i.e. interfacial debonding. Figure 6.6 presents all the possible fracture mechanism of carbon nanotubes in matrix depending on the types of carbon nanotubes and polymers, as well as the interface interaction between the two.

Figure 6.5: Schematic drawings showing the possible fracture mechanisms for nanocomposite tapes containing SWNTs and MWNTs.
Figure 6.6: Schematic description of possible fracture mechanism of CNTs (a) initial state, (b) pull-out caused by debonding in case of weak interfacial adhesion, (c) rupture of CNT indicates strong interfacial adhesion, (d) telescopic pull-out of the outer layer, (e) bridging and partial debonding of the interface [9]

As a particular type of MWNTs, the intermediate structure of DWNTs is reflected in their reinforcing efficiency in Figure 6.3. The Young’s modulus, UTS and strain at break increase moderately. It is important to point out that 0.1 wt.% seems to give the optimum reinforcement in all CCVD-grown tubes. This threshold above which the mechanical properties drop could be attributed to the excess of nanotubes in the polymer matrix. In our sample preparation, since no surfactant or chemical functionalization was employed, the excess of nanotubes might lead to poorer dispersion in the polymer matrix. Though dispersion has been optimised in sample preparation, CCVD-grown carbon nanotubes are more difficult to disperse because of their intrinsic highly entangled and curly characteristic, poorer dispersion above 0.1 wt.% compromises the reinforcing efficiency significantly.

Effective modulus $E_{\text{eff}} = \eta_L E_f$ and effective strength $\sigma_{\text{eff}} = \eta_L \sigma_f$ of different carbon
nanotubes are calculated for oriented nanocomposite tapes. Table 6.2 lists the calculated results. Obviously, c-SWNTs and c-MWNTs suggest negative reinforcement, and a-SWNTs and c-DWNTs show positive reinforcement. It is important to note that all the calculations are based on the assumption that the polymer matrix morphologies are not changed with the addition of the filler.

### Table 6.2

<table>
<thead>
<tr>
<th>CNT type</th>
<th>$E_{eff}$ (GPa)</th>
<th>$\sigma_{eff}$ (GPa)</th>
</tr>
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<tr>
<td>a-SWNTs</td>
<td>600</td>
<td>88</td>
</tr>
<tr>
<td>c-SWNTs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c-DWNTs</td>
<td>220</td>
<td>34</td>
</tr>
<tr>
<td>c-MWNTs</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

#### 6.3.3 Raman spectroscopy studies

It has been clearly shown in the previous paragraphs that different types of carbon nanotubes demonstrate different reinforcing behaviours. There are many factors that might influence the reinforcing behaviour including dispersion condition of the tubes in the matrix, polymer / carbon nanotube interactions, different degree of orientation in the carbon nanotubes, as well as the different intrinsic structures of carbon nanotubes themselves. In this part, Raman spectroscopy is employed to study the differences in the structure of the carbon nanotubes. This study will give further insight in the mechanical property results. Figure 6.7 shows the Raman spectrum of different types of carbon nanotubes used in our study and the detailed physical structure differences of these carbon nanotubes are listed in Table 6.3.
Figure 6.7: Raman spectrum of different types of carbon nanotubes studied in this work

Table 6.3: Physical properties of different types of carbon nanotubes in this work

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>Diameter [nm]</th>
<th>Length</th>
<th>No of layers</th>
<th>l/d</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
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<tr>
<td>a-SWNTs</td>
<td>1.4</td>
<td>~1 µm</td>
<td>1</td>
<td>700-1800</td>
<td>0.219</td>
</tr>
<tr>
<td>a-SWNT bundles</td>
<td>20</td>
<td>~1 µm</td>
<td>1</td>
<td>100-250</td>
<td>0.219</td>
</tr>
<tr>
<td>c-SWNTs</td>
<td>2</td>
<td>several µm</td>
<td>1</td>
<td>500-5000</td>
<td>0.242</td>
</tr>
<tr>
<td>c-DWNTs</td>
<td>4.7</td>
<td>1-10 µm</td>
<td>2</td>
<td>200-2100</td>
<td>0.119</td>
</tr>
<tr>
<td>c-fMWNT</td>
<td>10</td>
<td>0.1-10 µm</td>
<td>10</td>
<td>10-1000</td>
<td>1.4</td>
</tr>
<tr>
<td>c-MWNTs</td>
<td>10</td>
<td>0.1-10 µm</td>
<td>10</td>
<td>10-1000</td>
<td>1.61</td>
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</tbody>
</table>
As mentioned in previous chapters, the typical graphitic peaks can clearly be seen in the Raman spectrum, the so-called graphite band \((G)\) band) and the defect band \((D)\) band) which originates from the disorder of the graphite structure. The \(\frac{D}{G}\) intensity ratio is frequently used to assess the degree of crystallinity in carbon samples [10]. A lower ratio suggests fewer defects in the crystal structure. The Raman spectrum clearly shows the difference in crystallinity between different types of carbon nanotubes used in this study. It is obvious from Table 6.3 that the a-SWNTs along with c-SWNTs and c-DWNTs display lower \(\frac{D}{G}\) ratio than the c-MWNTs, which indicate fewer defects in the tubes and much higher crystallinity. The difference in crystallinity could be one factor that attribute to the difference in reinforcing behaviours among the different types of carbon nanotubes. However, lower aspect ratio and waviness could be another reason as well since CCVD-grown carbon nanotubes are normally entangled and not straight.

6.3.4 Interface studies

Successful composites rely on controlling how the stress is transferred from the matrix to the high strength fibre components. Since different carbon nanotubes display different reinforcing behaviours, a study of stress transfer between carbon nanotubes and the polymer is necessary. In this part, DMA was applied; this type of study can provide information regarding the interphase between poly (vinyl alcohol) and different types of carbon nanotubes.

When filler is incorporated into a polymeric matrix, the polymer has to wet the filler surface to achieve a continuous phase between both. DMA can provide information
for the interphase properties of the composite as indicated by the change in glass transition temperature ($T_g$) and the value of dynamic modulus [11].

According to the early work by Souma et al. [12], the nature of the filler-polymer interactions in the composites can be determined by plotting a parameter $D^*$ against filler volume fraction.

$$D^* = \frac{D}{D_o} = \frac{E_c - E_{c'}}{E_p - E_{p'}}$$

(6-1)

where $D$ and $D_o$ are the difference in modulus between glassy state and rubbery state for composites and unfilled polymer, respectively. The typical graph of $D^*$ against the filler volume fraction shows three regions as illustrated in Figure 6.8:

A. The ideal case, where slip or restraint does not exist on the interphase between filler and matrix. The theoretical curve is connected between 1 of $\frac{D}{D_o}$ and 1 of $V_f$.

B. The filler and the polymer interact in such a way that the polymer chains slip among themselves, whose overall effect resembles that of internal plasticization [11].

C. The filler restrain the movement of the polymer chains in the interphase; strong filler-polymer interaction exists.
In order to investigate the nature of carbon nanotube-polymer interaction, the parameter $D^*$ was calculated and analysed for all our systems. Figure 6.9 plots the calculated $D^*$ against volume fractions for different carbon nanotubes from DMA measurements. Results clearly indicate that a ‘soft’ mesophase with good surface adhesion properties to the filler exist in CCVD-grown CNTs and a-SWNT / PVA systems. The type of filler-polymer interaction belonged to the second group B where the polymer chains slip among themselves in the interphase. However, a ‘strong’ mesophase seems to exist for c-fMWNT / PVA composites. This is not hard to understand since c-fMWNT could possibly form hydrogen bonds with the –OH groups in the PVA matrix, where the tubes might restrict the mobility of the polymer chains, and a strong interaction between the two could happen.
Lipatov theories [13] pointed out that when boundary layers have a $T_g$ lower than the matrix, a ‘soft’ mesophase with elastic properties is built up around the filler, which leads to a drop in the $T_g$ of the composites. In our case, both DSC and DMA measurements confirm that $T_g$ drops upon the addition of CCVD-grown CNTs and a-SWNTs at very low concentration as 0.1 wt.%, and then $T_g$ gradually increases with the addition of more carbon nanotubes. The reason is that the internal plasticization effect of the filler-polymer interaction leads to a $T_g$ drop, and the increasing surface area of nano-filler in the system restraints the free volume of polymer chains, which leads to a $T_g$ increase at higher concentration of carbon nanotubes. However, a ‘strong’ mesophase with strong interaction between the filler

**Figure 6.9**: Variation of $D^*$ as a function of the filler volume fraction for the composite films studied with different types of carbon nanotubes.
and the matrice exists in the c-fMWNT system, where $D^*$ was observed to be below the ideal case and $T_g$ increases with the addition of the carbon nanotubes.

Figure 6.10: Plot of tan δ as a function of temperature from DMA measurement. (a). a-SWNTs; (b) c-SWNTs; (c) c-DWNTs; (d) c-MWNTs; (e) c-f MWNT. Solid line
represents pure PVA films; dash line represents 0.1 wt.% CNT / PVA films

Figure 6.10 (a)-(e) plots the tan $\delta$ as a function of temperature from DMA measurement on different types of carbon nanotube / PVA composite films. It is clear that $T_g$ drops for all the system except in the c-fMWNT system where $T_g$ increases.

### 6.3.5 Crystallinity studies

Since PVA is semi-crystalline polymer, it is vital to investigate the influence of carbon nanotubes on the crystallization of the polymer matrix. DSC measurements were performed for all types of carbon nanotube / PVA composite films. All the isotropic film samples were heated from 0°C up to 250°C at 40°C per minute, held at that temperature for 1 minute, and then cooled at 40°C per minute to 0°C. After 1 minute equilibration time, the samples were reheated to 250°C and then cooled again. Since no significant change was observed between the 1st and the 2nd cooling scans, it was assumed that 250°C gave an acceptable level of degradation for all the types of carbon nanotubes.

In our study, the upper temperature limit is 250 °C in order to ensure the melting transition is finished and a proper integration of the melt peak can be performed for all samples. The DSC data from the second run could be used to assess the crystals formed during the controlled cooling so that a comparison to solution cast phase crystallization could be made.

Figure 6.11 plots the observed glass transition temperatures as a function of weight fraction of carbon nanotubes in nanocomposite film. $T_g$ of all composite films drops when 0.1 wt.% of nanotubes are added. This observation confirms the conclusion
from DMA measurement where the carbon nanotubes formed a ‘soft’ interphase and the interphase characteristics resulted in the decrease in \( T_g \). With more nanotubes are added into the polymer matrix, \( T_g \) show no significant change for most type of tubes except for c-DWNTs which suggest an increase of \( T_g \) with higher concentration of CNTs.

![Graph showing glass transition temperature as a function of weight fraction of different types of carbon nanotubes measured by DSC](image)

**Figure 6.11**: The glass transition temperature as a function of weight fraction of different types of carbon nanotubes measured by DSC

To assess the influence of carbon nanotubes on the crystallization of PVA, the crystallization temperature as well as the crystallinity determined from the first melting and the second melting are plotted as a function of the weight fraction of carbon nanotubes. Figure 6.12 clearly shows that the crystallization temperature
increases with the addition of all the CCVD-grown carbon nanotubes, and it increases with the amount of tubes in the composite films. Results suggest that the addition of CCVD-CNTs induces the formation of nuclei and crystals start to grow at higher temperature, indicating nucleation effects by the tubes. However, the addition of a-SWNTs does not seem to change the $T_c$ of the composite.

![Graph showing the crystallization temperature as a function of weight fraction of different types of carbon nanotubes measured by DSC](image)

**Figure 6.12:** The crystallization temperature as a function of weight fraction of different types of carbon nanotubes measured by DSC.

The crystallinity as a function of weight fraction of different types of carbon nanotubes determined from the first and second heating is also plotted in Figure 6.13 and Figure 6.14, respectively. From the first heating, crystallinity shows no significant change for the different concentrations of all types of CNTs except for the
c-SWNTs. The addition of c-SWNTs obviously leads to a drop in crystallinity at 0.1 wt.%, and gradually increases with the CNT loading. A similar trend was observed in the second heating process where the crystallinity drops slightly at 0.1 wt.% and increase with higher concentrations. The observed drop in crystallinity for c-SWNTs could be one of the reasons that only a moderate increase in mechanical properties was observed in DMA and tensile test measurements on nanocomposites described previously. It is interesting to note that the crystallinity calculated from the first heating is around 3 to 5 percent higher than from the second heating. The reason might be that the slow solvent evaporation ensures the crystals grow more refined, while crystals may not have enough time to grow when samples are cooled rapidly from the melt in the DSC pan.

![Crystallinity vs CNT wt.%](image)

**Figure 6.13:** The crystallinity as a function of weight fraction of different types of carbon nanotubes determined from DSC first heating
Figure 6.14: The crystallinity as a function of weight fraction of different types of carbon nanotubes determined from DSC second heating

From the DSC measurements, it can be suggested that the influence of carbon nanotubes on the crystallization of polymer matrix could result in different reinforcing efficiencies in the nanocomposites. In our case, c-DWNTs and c-MWNTs acted as nucleation agents, however, c-SWNTs induced significant decrease in the polymer crystallinity. As for a-SWNTs, no remarkable change of polymer matrix crystallization was observed. Different influences from different types of carbon nanotubes will result in different composite morphology, thus lead to different reinforcing efficiency in the final nanocomposites.
6.3.6 Pre-orientation study

To assess the initial morphology of PVA matrix with different types of carbon nanotubes, WAXD measurements were carried out using the same set up as described in Chapter 5. All the isotropic composite films with different types of carbon nanotubes at various concentrations were measured from the surface (out-of-plane) as well as from the side (in-plane) of the films.

Figure 6.15 shows the cross-sectional diffraction patterns of cast films of pure PVA, 0.1 wt.% a-SWNTs, 0.1 wt.% c-MWNTs and 0.1 wt.% c-DWNTs respectively. The WAXD patterns recorded from the surface (out-of-plane) show fully isotropic rings, which indicate a random distribution of polymer crystals in the out-of-plane. However, the patterns measured from the side (i.e. in the plane of the films) show that there is a preferred orientation present which is indicated by the arrows in each graph. These patterns confirm that pre-orientation exists in nanocomposite with all types of carbon nanotube as well as pure PVA films.
CHAPTER 6. REINFORCING EFFICIENCY OF DIFFERENT TYPES OF CNTS

Figure 6.15: Cross-sectional X-ray diffraction patterns of dried films. (a) pure PVA; (b) 0.1 wt.% a-SWNTs; (c) 0.1 wt.% c-MWNTs; (d) 0.1 wt.% c-DWNTs. Film surface is vertical, arrows indicate pre-orientation

Since it is difficult to distinguish the degree of pre-orientation in the composite films, it is important to quantify the orientation function. Figure 6.16 shows the calculated Hermans’ orientation factor for all composite films. It is clear that composite films with CCVD-grown carbon nanotubes and a-SWNTs display similar degrees of pre-orientation, and the orientation function stays constant with some carbon nanotubes except for c-MWNTs and c-SWNTs where Hermans’ factor increases with higher nanotube concentration. Since higher pre-orientation suggests a stronger negative effect before drawing, this could be the reason for the extremely low mechanical reinforcing efficiency observed in the tensile tests. Since c-MWNTs and c-SWNTs made the films less isotropic, it is more difficult to ‘filp’ the crystal in the drawing direction. In other words, the molecular orientation degree of the polymer chains will be less at the same macroscopic draw ratio in the composites compared to the pure PVA tapes.
CHAPTER 6. REINFORCING EFFICIENCY OF DIFFERENT TYPES OF CNTS

Figure 6.16: Pre-orientation of dried composite films with different types of carbon nanotubes. Plot of orientation function as a function of weight percentage of the carbon nanotubes.

By plotting the tensile strength as a function of Young’s modulus at different draw ratios, a master curve can be obtained, which has been described in the previous chapter. If the carbon nanotubes only change the morphology of the polymer matrix without any real reinforcing effect, the composites data should fall on the same curve as the pure polymer. However, a true reinforcement would be observed if the composites data falls above the pure polymer matrix curve as been shown in the a-SWNTs reinforced PVA tapes (see Figure 5.26). Figure 6.17 plots the master curve
for all types of carbon nanotubes studied in our study. It is clear that with the exception of the a-SWNTs which were already discussed in the previous chapter, all the other types of tubes still fall on the PVA master curve. This suggests that it is likely that the addition of the nanotubes changes merely the morphology of the polymer matrix instead of truly reinforcing the polymer. In other words, any nucleate agent could be employed to achieve the same results.

**Figure 6.17**: Plot of tensile strength as a function of Young’s modulus for CNT / PVA studied in this work. High modulus data for pure PVA (black square) are taken from the work by Schellekens and Bastiaansen [14] where they used a PVA with similar molecular weight.
6.3.7 The effect of nanotube surface functionalization on composite properties

Up till now, the interaction between the CNTs and polymer matrix in our studies mainly arises from electrostatic and Van der Waals forces, and even though the improvement in the composite mechanical properties is already impressive as compared to the results found in literature, there might be still some room for further improvement if the interfacial bonding between matrix and nanotubes is improved by the use of appropriate functional groups on the surface of the nanotubes. Wagner et al. performed pull-out experiments on individual carbon nanotubes embedded in a polymer matrix to calculate the interfacial shear strength of the tubes. The computer simulation showed that the interfacial adhesion to the polymer could be enhanced by chemical functionalisation of the nanotube surface [15,16]. To check the influence of functional groups on mechanical properties of CNT / PVA composites, c-fMWNTs were employed for the preparation of the samples for mechanical studies. Since these nanotubes contain –COOH groups and are partially water-soluble as PVA, homogeneous nanotube dispersion is feasible. Moreover, hydrogen bonding between the tubes and PVA is potentially possible and tends to improve interfacial bonding between the matrix and the tubes, thus enhancing the nanotube efficiency and the nanocomposite mechanical properties.

Tensile tests were performed on the nanocomposite tapes of draw ratio 5. Typical stress-strain curves for the c-fMWNT / PVA tapes are presented in Figure 6.18, and Table 6.4 lists the detail of mechanical properties of the tapes. It is obvious that the addition of functionalised nanotubes significantly improves the mechanical properties of PVA tapes. The Young’s modulus, tensile strength as well as the strain at break clearly increases in this system. Following the addition of only 0.5 wt.% of
nanotubes, the Young’s modulus and tensile strength of the composite tapes increases by 59 % and 72 % compared to the pure PVA tapes. It seems that c-fMWNTs demonstrate the highest reinforcing efficiency among all types of CCVD-tubes.

![Graph](image_url)

**Figure 6.18**: The tensile stress–strain curve for c-fMWNT / PVA tapes at draw ratio 5.
Table 6.4: Mechanical properties of c-fMWNT / PVA tapes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus [GPa]</th>
<th>UTS [MPa]</th>
<th>Toughness [MPa]</th>
<th>Strain at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>18.8 ± 0.7</td>
<td>627.5 ± 2.8</td>
<td>17.2 ± 10</td>
<td>5.5 ± 1.6</td>
</tr>
<tr>
<td>0.1 wt.% c-fMWNTs</td>
<td>23.7 ± 0.4</td>
<td>857.7 ± 10</td>
<td>49.6 ± 2.5</td>
<td>9.3 ± 0.2</td>
</tr>
<tr>
<td>0.5 wt.% c-fMWNTs</td>
<td>31.0 ± 1.6</td>
<td>997.1 ± 56</td>
<td>74.5 ± 8.8</td>
<td>11.2 ± 0.4</td>
</tr>
</tbody>
</table>

However, to understand the reinforcing mechanism in this system, further measurements were carried out as for other types of carbon nanotubes. Raman spectroscopy studies on the structure of c-fMWNTs clearly showed that these tubes displayed the least perfect structure and lowest crystallinity as well as aspect ratio, which compromised their potential reinforcing efficiency. However, interface analysis by DMA from Figure 6.9 indicated that the c-fMWNTs formed a ‘strong’ mesophase with strong interaction between the filler and the matrices and clearly the addition of the c-fMWNTs increased the \( T_g \) of the composite films. This strong interaction between the tube and the polymer benefits the reinforcement. An insight into the pre-orientation condition on the composite films is clearly helpful. WAXD studies show that pre-orientation exists in the dried composite films as shown in Figure 6.19. Further calculation of Hermans’ orientation orientation factor obviously confirms that the addition of the tubes does not change the degree of orientation the polymer crystals. (Figure 6.20)
Some conclusion could be drawn from these results. First, homogeneous dispersion of the functionalised nanotubes clearly demonstrated a positive effect on mechanical properties of the composite tapes. Secondly, the poor structure of the tubes themselves compromised the reinforcing efficiency. However, stronger interaction with the PVA matrix resulted in high stress transfer efficiency between the nanotube-PVA interfaces. Thirdly, the functionalised nanotubes did not change the initial morphology of the polymer matrix.
Since PVA is a semi-crystalline polymer, its mechanical properties strongly depend on the crystallinity of the polymer. Previous discussion has shown that some types of carbon nanotubes act as nucleation agent in the matrix rather than reinforcing fillers. Here, DSC is applied again on the nanocomposite films with various amounts of functionalised nanotubes. Results from the measurements are plotted in Figure 6.21. It is obvious that functionalised nanotubes induce crystallization in polymer matrix and act as nucleation agent. Strong interaction between the fillers and the polymer indeed results in an increase of \( T_g \). Crystallization temperature is observed to increase with the addition of the tubes and crystallinity calculated from both the first and the second heating apparently increases as well.
As plotted in Figure 6.17, composite mechanical data falls on the PVA master curve and indicates that significant mechanical properties improvement results from a change in the polymer morphology rather than a true reinforcing effect by the nanotubes. In this case, it is surprising that c-fMWNT demonstrated no influence on pre-orientation of the polymer crystals, the observed improvement of tensile modulus and strength can only be attributed to the change of crystallinity in the PVA matrix.

**Figure 6.21**: Parameter from DSC measurement (a) \(T_g\); (b) \(T_c\); (c) crystallinity from first heating; (d) crystallinity from the second heating
6.4 Conclusion

In this chapter, four types of CCVD-grown carbon nanotubes (c-SWNTs, c-DWNTs, c-MWNTs, c-fMWNTs) from Nanocyl (Belgium) were incorporated into PVA matrices. Homogeneous oriented nanocomposite tapes were produced and their mechanical properties were investigated. While all nanotubes contributed to property improvement, different types of nanotubes played a different role in reinforcing the PVA matrix. Because of the high degree of structure perfection, SWNTs act as real reinforcing elements with a maximum influence on the Young’s modulus and ultimate tensile strength, while MWNTs lead to a maximum increase of strain at break.

To investigate the reinforcing mechanism of different types of carbon nanotubes, different techniques were employed. In the case of c-SWNTs and c-DWNTs, Raman spectroscopy studies showed that these tubes displayed few defects and high crystallinity. However, DSC studies showed that the addition of c-SWNTs increased the $T_c$ but dramatically decreased the crystallinity of PVA matrix. Further WAXD results showed that the tubes also changed the initial morphology in the polymer films. These results explained the poor mechanical properties that were observed from the tensile testing. The addition of c-DWNTs had different effects on the polymer matrix, though they act as nucleation agents in the composites, the pre-orientation degree of the isotropic films was not altered by the addition of c-DWNTs. Only moderate improvement in mechanical properties was observed in the composites tapes. For c-MWNTs, Raman studies showed that these tubes possess a less perfect structure, and that they act as nucleation agent in the composite with the tubes changing the initial morphology of the polymer matrix. Results explained well the low reinforcing efficiency observed in the composites.
To study the influence of nanotube surface functionalization on the final properties of the composites, MWNTs with –COOH functional groups were incorporated into the PVA matrix. Significant mechanical property improvement was observed, where both Young’s modulus and UTS were increased. However, a deeper analysis showed that surprisingly c-fMWNTs did not change the pre-orientation degree of the polymer matrix, they acted as nucleation agents in the composites which contribute to the improvement of mechanical properties. DMA studies showed that a good interfacial adhesion exist in these systems which also contribute to good mechanical properties.

It is important to note that when employing carbon nanotubes as reinforcing fillers in a polymer matrix, many factors have to be considered. As discussed, a good degree of dispersion, a good interaction between the tubes and the matrix as well as a high degree of orientation in the tubes are vital in preparing highly efficient nanocomposites. However, the effect of nanotubes on the morphology of the matrix should not be neglected. All the systems studied in this work, only a-SWNTs suggested a true reinforcing effect to the composites rather than a change in mechanical properties due to a change in morphology or orientation of the polymer. Moreover, calculations using micromechanical models showed that only in the case of a-SWNT nanotubes the theoretical properties had been well exploited in the nanocomposite.
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6.5 Reference

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Chapter 7

Conclusion and future work

7.1 Conclusion

In this thesis, the reinforcing efficiency of carbon nanotubes in Poly (vinyl alcohol) composites has been explored. Homogenous PVA / carbon nanotube (CNT) composites have been prepared and the factors affecting the macroscopic properties of CNT polymer composites have been identified as (i) homogeneous dispersion of the CNTs throughout the polymer matrix, (ii) good interfacial interaction and stress transfer between the filler and matrix, and (iii) a high level of alignment of the nanofillers.

The potential of CNTs as reinforcing nanofibres in PVA has first been investigated with emphasis on oriented PVA / single-walled carbon nanotubes (SWNT) tapes that were prepared by a mild processing route, involving the use of dimethyl sulfoxide (DMSO) as a solvent. Composite films with homogeneously dispersed SWNTs were cast from solution and drawn into oriented tapes using solid state drawing. Wide Angle X-ray Diffraction (WAXD) and Infrared spectroscopy (IR) measurements suggested that both polymer chains and SWNTs were highly oriented upon drawing.
The mechanical properties of these materials have been investigated as a function of draw ratio and also of SWNT concentration. The addition of CNTs to the PVA matrix resulted in a remarkable increase in mechanical properties as compared to the reference polymer fibres or tapes. In particular, it is worth to note that the addition of 1.0 wt.% SWNTs tripled the ultimate tensile strength of the nanocomposite tapes from around 400 MPa to 1200 MPa. When the data was evaluated using rule of mixtures type of relationships, assuming that the increase in tensile strength (~ 800 MPa) was due to the addition of 1.0 wt.% SWNTs, a nanotube stress contribution $\sigma_{\text{NT}}$ of 88 GPa can be calculated for these composites. This extraordinary high value indicates a reinforcing efficiency that starts to fully exploit the theoretical strength (100-150 GPa) of the nanotubes. Also the contribution of the nanotube to the stiffness was very high for the PVA / DMSO based tapes with an $E_{\text{NT}}$ value of around 600 GPa. Another system where SWNTs were dispersed in water with the aid of a surfactant (SDS) was compared [1]. The nanocomposite films exhibited also a high degree of dispersion, as well as good stress transfer from the polymer matrix to the reinforcing nanotubes. The calculated stiffness contribution $E_{\text{NT}}$ was even higher at 1.12 TPa for the SDS / water system, while here a value of 45-70 GPa for $\sigma_{\text{NT}}$ was calculated.

For a first evaluation of the mechanical properties of the nanocomposites, the classic micromechanical models are very useful. However, care should be taken when using pure matrix data to evaluate the composite data in order to get the reinforcing effect of the CNTs. It can not simply be assumed that the morphology of the polymer is the same in the pure polymer and in the composite. Such an assumption can lead to errors, especially in the case of semi-crystalline polymers, where the addition of the nanofillers may have an effect on the crystal morphology and/or orientation. If these effects are present, they are amplified during the drawing process and the micromechanical model cannot be applied using the unfilled polymer properties for
the composite matrix. For all these considerations, a deeper analysis of the nanocomposite morphology needs to be undertaken. In our case the X-ray data for the PVA / SDS / water system showed that the addition of SWNTs did indeed alter the initial morphology of the polymer and a simple rule of mixture analysis using the pure PVA data for the composite matrix is therefore invalid. However, no effect of SWNTs on the polymer morphology was found for the PVA / DMSO system and it could therefore be concluded that for this system the enhanced mechanical properties were a true result of nanotube reinforcement.

In the last part of the thesis, different reinforcing behaviours have been observed on different types of carbon nanotubes in PVA / CNT composite tapes. To clarify the reinforcing mechanism, special attention has been paid to assess the effect of carbon nanotubes on polymer matrix morphology (e.g. crystallization, orientation). It was found that the different reinforcing behaviours could, to some extent, be attributed to the fact that carbon nanotubes differ in their intrinsic physical properties (crystallinity, waviness, etc), and some types of tubes induced changes in the initial morphology of the polymer matrix (crystallization or orientation). However, the enhanced mechanical properties from arc-discharge SWNTs can be fully ascribed to the true reinforcement of nanotubes within the PVA matrix, because these types of tubes did not nucleate the PVA crystals nor changed the polymer initial orientation.
CHAPTER 7. CONCLUSION AND FUTURE WORK

7.2 Future work

It has been shown in this thesis that SWNTs demonstrated significant reinforcing efficiency in PVA matrix, especially in oriented systems where both nanotubes and polymer are oriented. Micromechanical calculations suggested highly effective properties of CNTs that starts to explore the theoretical strength of carbon nanotubes. However, because of the relatively low draw ratio ($\lambda = 5$) employed, the highest strength reported for these nanocomposite fibres or tapes incorporating 1.0 wt.% SWNTs is still only around 1200 MPa, which is almost half that of a pure gel-spun PVA fibre [2] of higher draw ratio ($\lambda = 20$). In future work it would therefore be interesting to assess the reinforcement potential of SWNTs in these ultra-drawn high strength polymer fibres.

It is known that depending on whether the matrix or the fibre has the lower strain to failure, the composites failure stress can be identified differently [3]. Here, it is assumed that both fibre and matrix experience the same strain and they behave elastically and fail in a brittle manner.

In the case where the matrix has the higher failure strain ($\varepsilon_m > \varepsilon_f$), the composite failure stress depends on the volume fraction of the fibres ($V_f$). Take a PVA tape of draw ratio 5 (Young’s modulus = 13.7 GPa, tensile strength = 0.42 GPa and 16 % strain at break) as an example, and the theoretical mechanical properties of SWNTs (Young’s modulus = 971 GPa, tensile strength = 126 GPa and 13 % strain at break) are chosen as reported in the thesis of Ciselli [1]. Figure 7.1 shows the representative stress-strain curve of PVA tapes and SWNTs.
CHAPTER 7. CONCLUSION AND FUTURE WORK

**Figure 7.1**: Stress-strain curve of low draw ratio PVA tapes ($\lambda = 5$) and SWNTs

When composites with low $V_f$ of SWNTs are loaded, SWNTs will break first at a strain of $\varepsilon_f$. However, the extra load placed on the matrix after fracture of the CNTs is not sufficient to fracture the composites. It is often assumed that in this case only the matrix will bear the load when the fibre fracture is complete and failure occurs at the applied stress of $\sigma^*$[3].

$$\sigma^* = (1-V_f) \sigma_m$$  \hspace{1cm} (7-1)

When the $V_f$ is large, the load transferred to the matrix when fibres break is very large, and the composites will fracture instantaneously when the fibres fracture, and
\[
\sigma^* = (1-V_f) \sigma'_m + V_f \sigma_f
\]  

(7-2)

Where \(\sigma'_m\) is the matrix stress at fibre breakage. Figure 7.2 plots the variation of the composite failure stress as a function of \(V_f\) for low draw ratio PVA / SWNT nanocomposite tapes. In principle, there is a critical volume fraction \(V_c\) below which the small amount of fibres are ineffective in raising the composite failure stress, and \(\sigma^*\) falls below the unreinforced matrix. The \(V_c\) can be calculated as

\[
V_c = \frac{\sigma_m - \sigma'_m}{\sigma_f + \sigma_m - \sigma_m}
\]  

(7-3)

Calculation from Figure 7.2 clearly shows that the critical volume fraction \(V_c\) equals to 0.008 vol. %. This value is very small, which implies that any realistic addition of CNTs contributes to the tensile strength of the composites and the composite fails when the failure stress of SWNTs has been reached for most \(V_f\).
Figure 7.2: Variation of the composite failure stress as a function of $V_f$ for low draw ratio PVA / SWNT nanocomposite tapes

However, in the case where the fibre has a higher failure strain ($\varepsilon_m < \varepsilon_f$), two different composite failure stresses occur depending on $V_f$. Here, we consider a high performance PVA fibre of $\lambda = 20$ [2] (Young’s modulus = 70 GPa, tensile strength = 2.3 GPa and strain at break 4.2%) and theoretical mechanical properties of SWNTs (Young’s modulus = 971 GPa, tensile strength = 126 GPa and 13 % strain at break) are chosen. Figure 7.3 shows the representative stress-strain curve of ultra drawn PVA tapes and SWNTs.
When composites with a low $V_f$ of SWNTs are under stress, the PVA matrix breaks first at a strain of $\varepsilon_m$. However, the extra load transferred to the fibres is so large that it is sufficient to fracture the composites. Here the $V_f$ is small and the fibres are not able to support the load and as a result they break.

$$\sigma^* = (1-V_f) \sigma_m + V_f \sigma'_f$$  \hspace{1cm} (7-4)$$

Where $\sigma'_f$ is the fibre stress at the onset of polymer matrix failure.

**Figure 7.3**: Stress-strain curve of high draw ratio PVA tapes and SWNTs
When the $V_f$ is large, the PVA matrix only takes a small part of load, because $E_f \gg E_m$. Thus the load transferred to the fibres when the matrix breaks is so small that the composites will not fracture when the matrix break. Assuming that load is all transferred to the fibres, the composites will only break when the applied load increase until the failure stress of the fibres is reached, and

$$\sigma^* = V_f \sigma_f$$  \hspace{1cm} (7-5)$$

Figure 7.4 plots the variation of the composite failure stress as a function of $V_f$ for high draw ratio PVA / SWNT nanocomposite tapes. As mentioned before also here there is a critical volume fraction $V_c$ below which the composite fails when the matrix fails, while above $V_c$ the composite fails when the failure stress of SWNTs is reached. This $V_c$ can be calculated as

$$V_c = \frac{\sigma_m}{\sigma_f - \sigma_f + \sigma_m}$$  \hspace{1cm} (7-6)$$

Figure 7.4 shows the critical volume fraction $V_c$ equals 2.6 vol. %, indicating at least 2.6 vol. % of SWNTs are needed to fully explore the potential of SWNT strength provided that SWNTs have been homogenously dispersed, fully aligned and with good stress transfer efficiency. These results suggest that it is possible to exploit the reinforcing potential of SWNTs in ultra-high drawn high strength PVA fibres but only with higher CNT loading, since only moderate increase in UTS will be observed below the critical volume fraction. For example, to make a fibre stronger than 7 GPa which is the strongest carbon fibre (Toray T1000) now at the market, 5.5 vol.% of SWNTs will be needed according to Figure 7.4. However, it is worth to note that the
task of homogenous dispersion of SWNTs at such high volume fractions is very demanding. It will only until the optimisation of dispersion of carbon nanotubes, ultimate orientation of carbon nanotubes and good interaction between the polymer and the CNTs have been achieved that high performance PVA nanocomposite fibres be produced.

![Graph](image)

**Figure 7.4**: Variation of the composite failure stress as a function of $V_f$ for high draw ratio PVA / SWNT nanocomposite tapes
7.3 Reference