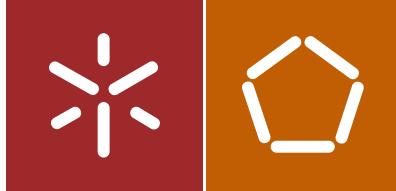




Universidade do Minho
Escola de Engenharia

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Structure-property relationships
in polymer nanocomposites



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Structure-property relationships in polymer nanocomposites

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Ciência e Engenharia de Polímeros e Compósitos

Trabalho efectuado sob a orientação do
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STATEMENT OF INTEGRITY

I hereby declare having conducted my thesis with integrity. I confirm that I have not used plagiarism or any form of falsification of results in the process of the thesis elaboration.

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¹<http://www.contactproject.eu/>

Abstract

Carbon nanotubes/ carbon nanofibres (CNTs/CNFs) are considered to be among the most promising reinforcements for improving the mechanical properties of polymers while at the same time offering enhanced electrical and thermal conductivity. Because of their exceptionally high aspect ratio and high surface area in combination with a low density, already small volume fractions can potentially transfer their superior properties to a polymer matrix. However when used as reinforcements in polymeric composites, phenomena at the nano- and micro-scales, such as agglomerations, waviness/curliness, surface defects or imperfect bonding between the reinforcement and the polymer, can dramatically decrease the composite properties. The main objective of this work is to understand and to analyse how microstructural effects influence the overall composite behaviour on the macroscale in order to enable the full potential of these materials and to establish guidelines for the design of materials that meet specific requirements for the mechanical performance.

Dependent on the polymer system, different processing techniques based on high shear mixing were applied to enhance the dispersion of nanoparticles in the polymer system. It was shown that the elastic moduli of polymers reinforced with CNTs/CNFs do not increase linearly for high volume fractions. The reasons for this behaviour were investigated by means of modelling approaches together with data analysis using different microscopy techniques. Information about the dispersion and distribution of nanotubes was obtained using optical light microscopy (OLM), whereas transmission electron microscopy (TEM) was used for direct observations and information about their spatial geometry and orientation. Probability distribution functions for agglomeration, length, curliness and orientation were determined for CNT reinforced nanocomposites and used as input parameters for the developed models.

Preliminary studies were conducted to compare analytical models with Finite Element (FE) simulations, for modelling polymers reinforced with nanofillers of simplified geometries. They were aimed at investigating the influence of structural characteristics, such as curvature, orientation and dispersion of reinforcements, as well as of different FEs and boundary conditions on the effective elastic stiffness tensors.

Based on the obtained findings a two-step homogenisation method was developed. In the first step, curved nanotubes were uniformly distributed in cube-shaped volume elements using Monte-Carlo simulations according to the prior experimentally obtained

probability distribution functions of orientation and curvature parameters. The mechanical properties of these volume elements with three-dimensional (3D) spatial oriented nanostructures were evaluated by an Eshelby based analytical model and periodic homogenisation using the FE code ABAQUS. The nanoreinforcements were treated as curved hollow cylindrical structures perfectly bonded with the polymer matrix. In the FE method inclusions were incorporated into the polymer matrix using an embedded element technique. In the second homogenisation step the composite was considered as a two-phase material consisting of agglomerates in an isotropic medium made of the polymer matrix with perfectly dispersed curved nanostructures. Information about the number and sizes of agglomerates was obtained from OLM analyses. A Mori-Tanaka model was used to calculate the effective elastic properties of the resulting composite.

The obtained Young's moduli of polymeric nanocomposites were validated with experimental results, showing that the proposed technique may provide an attractive combination of accuracy, computational costs and flexibility for modelling arbitrary nanocomposites.

Resumo

Considera-se que os nanotubos de carbono/nanofibras de carbono (CNTs/CNFs) estão entre os reforços mais promissores para melhorar as propriedades mecânicas dos polímeros, oferecendo também uma condutividade elétrica e térmica melhorada. Devido à sua razão de aspeto e área de superfície excecionalmente elevadas em combinação com uma baixa densidade, mesmo pequenas frações volumétricas podem potencialmente transferir as suas propriedades superiores para uma matriz polimérica. Contudo, quando usados como reforços em compósitos poliméricos, fenómenos à nano e microescala, tais como aglomerações, ondulação/curvas, defeitos de superfície ou uma ligação imperfeita entre o reforço e o polímero, podem diminuir drasticamente as propriedades do compósito. O principal objetivo deste trabalho é compreender e analisar como é que efeitos microestruturais influenciam o comportamento global do composto à macroescala de modo a possibilitar o pleno potencial destes materiais e estabelecer diretrizes para a conceção de materiais que cumpram os requisitos específicos para o desempenho mecânico.

Dependendo do sistema polimérico, diferentes técnicas de processamento baseadas na mistura de alto cisalhamento foram aplicadas para melhorar a dispersão de nanopartículas no sistema polimérico. Foi demonstrado que o módulo de elasticidade dos polímeros reforçados com CNTs/CNFs não aumenta linearmente para frações volumétricas elevadas. Os motivos para este comportamento foram investigados através de abordagens de modelação e da análise de dados com diferentes técnicas de microscopia. A informação sobre a dispersão e distribuição dos nanotubos foi obtida através de microscopia ótica, ao passo que para efetuar observações diretas e obter informação sobre a geometria e orientação espacial dos nanotubos se utilizou a microscopia eletrónica de transmissão (TEM). Funções de distribuição de probabilidade para a aglomeração, comprimento, ondulação/curvas e orientação foram determinadas para diferentes nanocompósitos e utilizadas como parâmetros de entrada para os modelos desenvolvidos.

Foram efetuados estudos preliminares para comparar modelos analíticos com simulações de Elementos Finitos (FE), para modelar polímeros reforçados com nanopartículas de geometrias simplificadas. Procurou-se investigar a influência de características estruturais como a curvatura, orientação e dispersão dos reforços, bem como de diferentes FEs e condições de contorno, sobre os tensores de rigidez elástica efetiva.

Com base nas descobertas obtidas, foi desenvolvido um método de homogeneização de duas fases. Na primeira fase, nanotubos curvados foram uniformemente distribuídos

em elementos de volume em forma de cubo utilizando simulações de Monte Carlo de acordo com as funções de distribuição de probabilidade dos parâmetros de orientação e curvatura obtidas experimentalmente. As propriedades mecânicas destes elementos de volume com nanoestruturas tridimensionalmente orientadas foram avaliadas através de um modelo analítico baseado no modelo de Eshelby e da homogeneização periódica com o código FE ABAQUS. Os nanoreforços foram tratados como estruturas cilíndricas ocas e curvadas perfeitamente ligadas com matriz polimérica. No método FE foram incorporadas inclusões na matriz polimérica utilizando uma técnica de embedded element. Na segunda fase de homogeneização o compósito foi considerado como um material bifásico composto por aglomerados num meio isotrópico feito da matriz polimérica com nanoestruturas curvas perfeitamente dispersas. Informação sobre o número e o tamanho dos aglomerados foi obtida a partir de análises de OLM. Um modelo Mori-Tanaka foi utilizado para calcular as propriedades elásticas efetivas do compósito resultante.

Os módulos de Young de nanocompósitos poliméricos obtidos foram validados com resultados experimentais, demonstrando que a técnica proposta pode proporcionar uma atraente combinação de precisão, custos computacionais e flexibilidade para a modelação de nanocompósitos arbitrários.

Nomenclature

Acronyms

2D	Two-Dimensional
3D	Three-Dimensional
AFM	Atomistic Force Microscopy
BPA	BisPhenol A
CNF	Carbon NanoFibre
CNT	Carbon NanoTube
CVD	Carbon Vapour Deposition
DC	Direct Current
DoF	Degree of Freedom
DST	Domain Superposition Technique
EE	Embedded Element
FE	Finite Element
FEM	Finite Element Method
FESEM	Field Emission Scanning Electron Microscopy
GNP	Graphite NanoPlatelets
HF	High Frequency
KUBC	Kinematically Uniform Boundary Conditions
LAND	Length Analysis by Nanotube Diffusion
LDF	Length Distribution Function
MD	Molecular Dynamics

MFA	Mean Field Approach
MPC	Multi-Point Constraint
MUBC	Mixed Uniform Boundary Conditions
MWNT	Multi-Walled carbon NanoTubes
ODF	Orientation Distribution Function
OLM	Optical Light Microscope/ Microscopy
PA6	PolyAmide-6
PBC	Periodicity Boundary Conditions
PC	PolyCarboante
PMA	Periodic Microfield Approach
PMUBC	Periodicity compatible Mixed Uniform Boundary Conditions
PP	PolyPropylene
RVE	Representative Volume Element
SEM	Scanning Electron Microscopy
SUBC	Statically Uniform Boundary Conditions
SVE	Statistical Volume Element
SWNT	Single-Walled carbon NanoTubes
TEM	Transmission Electron Microscope/ Microscopy
UHMWPE	UltraHigh Molecular Weight PolyEthylene
VGCNFs	Vapour Grown Carbon NanoFibres
XRD	X-Ray Diffraction
Coordinate Systems	
X, Y, Z	global coordinate system with direction X indicating the longitudinal orientation/ injection flow
x_1, x_2, x_3	local coordinate system with direction 1 indicating the inclusion axis
1,2,3	global coordinate system with direction 1 indicating the longitudinal orientation
Greek Symbols	

α	angle between Y-axis and nanotube projection onto YZ-plane
$\Delta^k \xi$	constant distance vector between pairs of opposite surfaces
$\Lambda(L^*)$	effective length distribution function
$\langle \sigma \rangle$	volume average stress
$\langle \sigma \rangle_p$	phase average strain
$\langle \varepsilon \rangle$	volume average strain
$\langle \varepsilon \rangle_p$	phase average stress
ν_m	Poisson's ratio of matrix
Ω	homogenisation volume element
ϕ	angle between X-axis and nanotube projection onto XY-plane
$\Phi(E_r^*)$	effective length distribution function
$\Psi(\phi, \theta)$	orientation distribution function
ρ	density
σ^0	constant stress tensor
σ_r	stress state in reinforcement
θ	angle between nanotube director and Z-axis
ε_τ	transformation strain in homogenous inclusions
ε_c	uniform strain in constrained inclusion
ε_t	eigenstrains in inhomogenous inclusions
C_m	elasticity tensor of matrix
C_r	elasticity tensor of reinforcement
Roman Symbols	
A	amplitude of the sine
a	radius of the helix
A_r^{NI}	non-interacting inhomogeneity strain concentration tensor
a_1	start radius
a_2	end radius

A_{cell}	cross-sectional area of the unit cell transverse to the nanotube axis
a_{XY}	radius of projection onto XY-plane
a_{YZ}	radius of projection onto YZ-plane
C	stiffness tensor
C^{app}	apparent stiffness tensor
C^{eff}	effective stiffness tensor
c_r	concentration of the reinforcement
$c_r^{2nd-step}$	volume fraction of agglomerations during second homogenisation step
E^a	effective Young's modulus of agglomeration
E_r^*	Young's modulus of straight inclusion
H	wave length of the sine
h	pitch/ length of cubic volume element
h_{XY}	projection of spiral pitch onto XY-plane
h_{YZ}	projection of spiral pitch onto YZ-plane
I	rank four unit tensor/ identity tensor
L^*	effective length of nanotube
L_{CNT}	length of nanotube
L_s	length of spiral
m	matrix
P	Eshelby tensor
r	reinforcement
R_{CNT}	outer radius of nanotube
r_{CNT}	inner radius of nanotube
S	compliance matrix
S^{app}	apparent compliance tensor
S^{eff}	effective compliance tensor

T	transformation matrix of strain tensor
u	displacement vector
u_1	displacement along the first DoF
v	volume of a segment
W	rotation matrix between engineering strain and strain tensor
w	waviness/curviness parameter
a	radius
d	diameter
h	pitch/ side length of cube
l	length/ length of segment
N	number of particles/ number of segments
R	distance between nanotube end points
S	surface area
t	thickness

Contents

1	Introduction	1
1.1	Background and motivation	1
1.2	Objectives	3
1.3	Outline of the thesis	4
2	Literature review	5
2.1	Carbon nanotubes/Carbon nanofibres	5
2.1.1	Carbon nanotubes	5
2.1.2	Carbon nanofibres	6
2.1.3	Synthesis of CNT and CNF	6
2.1.4	Mechanical properties of CNTs/CNFs	8
2.2	Nanocomposites	10
2.2.1	Functionalization	13
2.2.2	CNTs/CNFs composites processing methods	15
2.3	Characterisation	20
2.4	Modelling	25
2.4.1	Mean Field Approach	27
2.4.2	Periodic Microfield and Windowing Approaches	30
3	Experimental methods	33
3.1	Composite manufacturing	34
3.1.1	Thermoset matrix	34
3.1.2	Thermoplastic matrix	34
3.2	Microscopic characterisation	35
3.3	OLM	35
3.4	TEM	38
3.5	Tensile testing	40
3.6	Flexural testing	40
4	Modelling	43
4.1	Preliminary studies	43
4.1.1	Influence of waviness and curliness on mechanical properties	43

4.1.2	Influence of curviness and segment number per CNT on mechanical properties	54
4.1.3	Influence of FE modelling techniques on mechanical properties	57
4.2	Real arbitrary composites	62
5	Results and discussion	69
5.1	Experimental characterisation	69
5.1.1	OLM	69
5.1.2	TEM	75
5.1.3	Tensile testing	82
5.1.4	Flexural testing	84
5.2	Modelling	85
5.2.1	Influence of waviness and curliness on mechanical properties	85
5.2.2	Influence of curviness and segment number per CNT on mechanical properties	91
5.2.3	Influence of FE modelling techniques on mechanical properties	91
5.2.4	Real arbitrary composites	102
6	Conclusions	113
6.1	Experimental characterisation	113
6.2	Modelling	115
6.2.1	Influence of waviness and curliness on mechanical properties	115
6.2.2	Influence of concentration and segment number per CNT on mechanical properties	115
6.2.3	Influence of FE modelling techniques on mechanical properties	116
6.3	Real arbitrary composites	117
6.4	Recommendations for future work	118
6.5	Publications	119
	Bibliography	121
A	Analytical modelling	137
A.1	General approaches for linear elasticity	137
A.2	Dilute Eshelby model	139
A.3	Mori-Tanaka model	140
B	Orientation averaging	142

List of Figures

Figure 2.1:	TEM images of different CNTs: SWNTs (a) and MWNTs with 5, 2 and 7 layers (b) [1]	6
Figure 2.2:	High Resolution TEM Image showing the stacked-cup structure of a Pyrograf III CNF	7
Figure 2.3:	Scanning electron microscopy (SEM) image of entangled MWNT (©CONTACT)	8
Figure 2.4:	TEM images of the as-prepared arc-grown SWNTs (a) and the purified SWNTs (b)	9
Figure 2.5:	Esterification of nanotube-bound carboxylic acids [2]	14
Figure 2.6:	Calendaring (or three roll mill) machine used for particle dispersion in a polymer matrix (Polymer Department, University of Minho)	16
Figure 2.7:	OLM images of 0.05wt% CNTs in epoxy after: shearing with $100s^{-1}$ for 1 min (a), sonicating for 10 minutes (b) [3]	17
Figure 2.8:	Nanocomposite structure development after processing at different gap settings: $50\mu m$ (a), $20\mu m$ (b), $10\mu m$ (c), $5\mu m$ (d) [4]	18
Figure 2.10:	In-line and off-line electrical conductivities of injection moulded parts with 2wt% of CNTs in PC [5]	20
Figure 2.9:	Orientation of CNTs in an injection moulded (2 wt% of CNTs in PC) sample at $2\mu m$ (a) and at $43\mu m$ (b) from the surface [6]	20
Figure 2.11:	Orientation angle as a function of the shear rate [7]	23
Figure 2.12:	Characterisation of MWNT orientation state in TEM image [8]	24
Figure 2.13:	Evaluation of nanotube waviness: TEM image of CNTs (a) [9] and distribution of waviness parameters for highlighted nanotubes (b) [10]	24
Figure 2.14:	Clustered microstructures: bad distribution (a) and good distribution (b) [11]	24
Figure 2.16:	Histograms representing “no” (a), ”intermediate” (b) and “perfect” (c) dispersion in CNF/polymer composites [12]	25
Figure 2.15:	OLM images of masterbatches (a) as well as dispersion index and agglomerate number (b) [13]	25

Figure 3.1:	Schematic depiction of the relationship between pixel colour and local volume fraction	35
Figure 3.2:	Examples of grey scale histograms of CNT/PC specimens: 1wt% with a threshold of 136 (a) and 7wt% with a threshold of 65 (b)	37
Figure 3.3:	Micrograph of CNT/PC specimens with 2wt% (a) and corresponding binarised image (b)	37
Figure 3.4:	Reconstruction of agglomerates in two-phase composite: projection onto 2D plane (a) and depiction in 3D space (b)	37
Figure 3.5:	Examples of directors (grey) and centrelines (blue) of nanotubes in a tensile specimen with 2wt% CNT: projection onto XY-plane (a) and projection onto YZ-plane (b)	39
Figure 3.6:	Coordinate system and definitions of angles α , ϕ and θ	39
Figure 4.1:	Representations for sinusoidally (a) and helically (b) curved nanotubes	45
Figure 4.2:	Coordinate system of inhomogeneities and definitions of angles θ and ϕ	46
Figure 4.3:	Notation of the faces (North, South, East, West, Top, Bottom) of a volume element [14]	51
Figure 4.4:	Sinusoidal (a) and helical (b) inclusions meshed with solid elements	52
Figure 4.5:	MD model of nanotube of sinusoidal shape [15]	53
Figure 4.6:	MD model of nanotube of helical shape [15]	54
Figure 4.7:	CNT represented as sequence of straight, joined segments	55
Figure 4.8:	Number of segments per CNT as function of the volume fraction	57
Figure 4.9:	Sinusoidal fibre meshed with solid elements (“full model”)	61
Figure 4.10:	Volume element containing a simulated population of nanotubes at 0.5wt% (a) and close-up of nanotubes discretised with shell elements (b)	66
Figure 4.11:	Substitution of curved nanotube with ellipsoidal inclusion	67
Figure 5.1:	OLM micrographs and grey scale histograms of CNT/PC samples with different weight fractions: 0.5wt% (a,b), 1.0wt% (c,d), 3.0wt% (e,f) and 7.0wt% (g,h)	71
Figure 5.2:	OLM micrographs and grey scale histograms of CNF/PC samples with different weight fractions: 0.5wt% (a,b), 1.0wt% (c,d), 3.0wt% (e,f) and 7.0wt% (g,h)	72
Figure 5.3:	OLM micrographs and grey scale histograms of CNF/epoxy samples with different weight fractions: 0.1wt% (a,b), 0.5wt% (c,d), 1.5wt% (e,f) and 3.0wt% (g,h)	73
Figure 5.4:	Calculated widths of OLM histograms: CNT/PC (a), CNF/PC (b) and CNF/epoxy (c)	74

Figure 5.5:	OLM micrographs and binarised micrographs of CNT/PC samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h) .	75
Figure 5.6:	OLM micrographs and binarised micrograph of CNF/PC samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h) .	76
Figure 5.7:	OLM micrographs and binarised micrograph of CNF/epoxy samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h) .	77
Figure 5.8:	OLM micrographs with smaller magnification of CNF/PC samples with different weight fractions: 0.5wt% (a), 1.0wt% (b), 3.0wt% (c) and 5.0wt% (d)	78
Figure 5.9:	TEM images of PC reinforced with CNTs at three different wt%: Sections with 1wt% along (a) and perpendicular to the flow direction (b), sections with 2wt% along (c) and perpendicular to the flow direction (d), sections with 5wt% along (e) and perpendicular to the flow direction (f)	79
Figure 5.10:	Measured and fitted distributions of the orientation angles ϕ and α for PC reinforced with three different wt% of CNTs: Sections with 1wt% along (a) and perpendicular to the flow direction (b), sections with 2wt% along (c) and perpendicular to the flow direction (d), sections with 5wt% along (e) and perpendicular to the flow direction (f)	80
Figure 5.11:	Normalisation coefficient and standard deviations of normal distributions approximating the orientation distributions of nanotubes in the XY-plane according to Equation 5.1 plotted as functions of the concentration of nanotubes	81
Figure 5.12:	Superimposed TEM images of nanocomposites with CNT concentrations of 1wt% (a) and 2wt% (b)	82
Figure 5.13:	Distributions of pitches h and radii a of the spiral's projections onto the XY- and YZ-planes: h_{XY} (a), h_{YZ} (b), a_{XY} (c) and a_{YZ} (d)	83
Figure 5.14:	Simulated distributions of nanotubes in a slice with the dimensions $2 \times 2 \times 0.1 \mu\text{m}$ and a weight fraction of 1%: XY-plane (a) and YZ-plane (b)	83
Figure 5.15:	Young's moduli of PC/CNT and PC/CNF samples with different wt%	84
Figure 5.16:	Flexural modulus of CNF/epoxy samples with different wt% . .	84
Figure 5.17:	Elastic moduli in the X -direction (a) and in the Y -direction (b) predicted for PC reinforced with aligned CNT as functions of the fibre orientation angles ϕ and θ	85
Figure 5.18:	Elastic moduli predicted for composites reinforced with wavy nanotubes	87

Figure 5.19: Elastic moduli predicted for composites reinforced with helical nanotubes	88
Figure 5.20: Influence of FE model on the longitudinal shear moduli of composites reinforced with a square array of helical inhomogeneities using PMUBC	88
Figure 5.21: Comparison of MD results with FE predictions and analytical solutions for the longitudinal Young's modulus of composites reinforced by curvy CNTs	90
Figure 5.22: Predicted elastic moduli in the dilute case (Young's moduli in main directions (E_{11} (a), E_{22} (b), E_{33} (c)) and shear moduli (G_{12} (d), G_{13} (e), G_{23} (f)) as functions of the curliness parameter	92
Figure 5.23: Predicted elastic moduli for CNT/PC composites (Young's moduli in main directions (E_{11} (a), E_{22} (b), E_{33} (c)) and shear moduli (G_{12} (d), G_{13} (e), G_{23} (f)) as functions of the CNT weight fraction	93
Figure 5.24: Predicted and measured elastic moduli for CNT/PC composites	94
Figure 5.25: Wavy hollow sine-like tubes with a outer fibre radius of $R_{CNT}=0.16$, meshed with solid (a-b), beam (c-d) and shell (e-f) elements. a,c and e present longitudinal displacements and b,d and f distributions of the longitudinal normal stress component, a cut being made with an $x=\text{constant}$ plane in the middle of the tube. The deformation scale factor is set to 500.	96
Figure 5.26: Distribution of axial normal stress in detail of longitudinal section of arrangement of 16 tubes, $w=0.125$: 3D full solid model (a), embedded beam elements (b), embedded shell elements (c) and embedded solid elements (d)	97
Figure 5.27: Longitudinal elastic modulus predicted for fibres with different waviness: $w=0.0$ (a), $w=0.08$ (b), $w=0.125$ (c) and $w=0.2$ (d)	98
Figure 5.28: Relative difference in the predicted Youngs's moduli between the conventional 3D solid model, the embedded shell (E_{11} (a), E_{22} (c), E_{33} (e)) and the embedded solid models (E_{11} (b), E_{22} (d), E_{33} (f)), respectively	100
Figure 5.29: Relative difference in the predicted shear moduli between the conventional 3D solid model, the embedded shell (G_{12} (a), G_{13} (c), G_{23} (e)) and the embedded solid models (G_{12} (b), G_{13} (d), G_{23} (f)), respectively	101
Figure 5.30: SVEs of CNT reinforced PC with different concentrations: 0.5wt% (a), 1.0wt% (b), 2.0wt% (c), 3.0wt% (d) and 5.0wt% (e)	104
Figure 5.31: Normalised effective longitudinal Young's moduli computed by FEM in the 1st homogenisation step	105
Figure 5.32: Normalised effective transverse moduli (b) and shear moduli (c) computed by FEM in the 1st homogenisation step	105

Figure 5.36: Normalised effective longitudinal (a) and transverse (b) Young's moduli computed by analytical micromechanics in the 1st homogenisation step (averaged over Λ, Ψ distribution functions) and compared with finite beam/shell element models	106
Figure 5.33: Orientation distributions for different weight fractions of ellipsoidal inclusions: COS (a), 0.5wt% (b), 1.0wt% (c), 2.0wt% (d), 3.0wt% (e) and 5.0wt% (f)	107
Figure 5.34: Effective length distributions for different weight fractions of ellipsoidal inclusions: 0.5wt% (a), 1.0wt% (b), 2.0wt% (c), 3.0wt% (d) and 5.0wt% (e)	108
Figure 5.35: Normalised effective longitudinal (a) and transverse (b) Young's moduli computed by analytical micromechanics in the 1st homogenisation step	108
Figure 5.38: Normalised effective longitudinal Young's moduli computed by analytical micromechanics in the 1st homogenisation step (averaged over Λ, Ψ, Φ distribution functions) and compared with finite beam/shell element models	109
Figure 5.37: Effective reinforcing Young's modulus of straight ellipsoidal inclusions representing the curved nanotubes	109
Figure 5.39: Normalised effective longitudinal Young's moduli computed by analytical micromechanics in the 2nd homogenisation step (averaged over Λ, Ψ, Φ distribution functions) and finite beam/shell element models with and without dispersion analysis	111
Figure B.1: Coordinate system of inhomogeneities and definitions of angles θ and ϕ	143

List of Tables

Table 1.1:	Dimensions and corresponding number of particles in composites for different reinforcements	3
Table 2.1:	On-axis mechanical properties of CNTs and CNFs	11
Table 2.2:	Structure-property relationships for CNT/CNF polymeric composites [16]	28
Table 3.1:	Reconstruction of spiral geometries (blue) from their projections (red)	40
Table 4.1:	Material properties used for calculations	48
Table 4.2:	Dimensions of volume elements and inhomogeneities	48
Table 4.3:	Matrices of boundary vectors for the load cases “Tensile 1” and “Shear 13”	51
Table 4.4:	Mesh parameters and number of segments per CNT versus volume fraction	55
Table 4.5:	Material properties used for simulations	58
Table 4.6:	Values of volume fraction c_r and waviness parameter w covered in the present study for wavy fibres ($R_{CNT}=0.04$)	61
Table 4.7:	Values of volume fraction c_r for straight nanotubes with different outer radii	61
Table 4.8:	Material parameters used in periodic homogenisation	66
Table 4.9:	Input data to calculate properties of agglomerations	68
Table 5.1:	Radii of agglomerates for different weight fractions	76
Table 5.2:	Percentages of agglomerated CNTs and effective volume fractions	77
Table 5.3:	Normalisation coefficients and standard deviation of normal distributions approximating the orientation distributions of nanotubes for different concentrations of nanotubes	81
Table 5.4:	Relative errors for sine-like inhomogeneities (with respect to FEM_PBC results)	89
Table 5.5:	Relative errors for sine-like inhomogeneities (with respect to FEM_PBC results)	89

Table 5.6:	Comparison of the stiffness of single, free, sine-like tubes ($w = 0.125$) of different radii, meshed with different types of element	95
Table 5.7:	Relative difference in the predicted six elastic moduli between conventional 3D solid model and embedded beam model	100
Table 5.8:	Correction by volume fraction. Relative difference in longitudinal Young's modulus between embedded beam/shell/solid models and conventional full 3D solid model	102
Table 5.9:	Corrected weight and volume fractions for different concentrations	103
Table 5.10:	Effective properties of CNT/PC composite by FEM in the 2nd homogenisation step (integration of dispersion analysis into FEM)	111
Table 5.11:	Effective properties of CNT/PC composite by analytical micromechanics in the 2nd homogenisation step (integration of dispersion analysis into analytical model)	111

Chapter 1

Introduction

1.1 Background and motivation

CNTs and CNFs, with an electrical conductivity comparable to that of copper [17,18] and a Young's modulus several times greater than the one of steel [19–23], enable the creation of materials with superb characteristics. Incorporating the right amount of nanoparticles into a polymer matrix can lead to increased stiffness, strength and toughness as well as increased electrical and thermal transport properties of the polymer, while most of the polymer's other beneficial properties remain the same. Typically 1–3wt% of these nanoparticles provide a major enhancement in the physical properties of the composite [1]. This is of large interest in different high-performance applications in the fields of automotive, aerospace, biomedical, marine and civil engineering, as well as packaging and sports. The commercial potential is huge, but only a fraction of the possible applications have reached the market.

Due to the difficulties associated with the dispersion of nanoparticles during processing and poor interfacial interaction with the polymer matrix, the full potential of CNTs/CNFs and other nanoparticles as reinforcements has not been fulfilled. However, the nature of dispersion problem for rod like nanoparticles is rather different from that of other conventional fillers, such as spherical particles or carbon fibres. Because of the combination of a small diameter in nanometer scale with high aspect ratio (>1000) there is a significant increase in the surface area and decrease in the distance between particles [24].

In order to address the potential of these materials and their applications the Marie Curie Initial Training Network CONTACT for the tailored supply-chain development of CNT filled composites with improved mechanical and electrical properties, funded by the European Community's Seventh Framework Programme (FP7-PEOPLE-ITN-2008-238363, <http://www.contactproject.eu/>) was initiated, as part of which the present research was performed. In this CONTACT network, 15 early-stage researchers and three experienced researchers worked for a total of 576 months on individual projects, hosted by ten partners (academic and industry) from seven different countries. The technical

aim was to improve the mechanical and electrical properties of CNT filled polymer composites for applications in construction, wind turbine blades, electrically conducting parts and electrodes for redox flow batteries. This was achieved by optimising the CNT synthesis and dispersion, the processing of CNT compounds, modelling and characterisation of CNT and CNT composites. This PhD thesis covers the modelling development and optimisation of modelling techniques aiming at developing the tools necessary for accurate prediction of the bulk properties of CNT polymer compounds.

Table 1.1 compares the average dimensions (d denotes the diameter, l the length and t the thickness), the density ρ , the number of particles N corresponding to a uniform filler volume fraction of 0.1% in a composite of 1.0 mm³ cube as well as the surface area S of commonly used fillers including Al_2O_3 particles, CNFs, graphite nanoplatelets (GNP) and CNTs. Because there are large differences in dimension and geometry of these four different types of reinforcements, the number of fillers contained and total surface area for a given filler volume fraction will also vary markedly [1]. A large surface area of fillers means that there is significant interface or interphase area for stress transfer between the nanoparticles and the polymer that leads to improved composite properties. On the other hand due to the size and geometry effects it can be seen that a uniform distribution of nano-scale fillers such as GNPs and CNTs is far more complicated to obtain than with microscale particles. Considering electrostatic interaction and the van der Waals force between nano particles, the real distribution of nanoscale fillers is an even more challenging task. It has been shown that bundles and agglomerates result in decreased mechanical and electrical properties of composites as compared with theoretical predictions for composites with perfectly dispersed nanoparticles [25, 26].

Additional investigations of the composites' structure at the nanoscale by TEM showed that CNTs tend to have strongly curved shapes. This may be due to high aspect ratios, the associated low bending stiffness and to surface defects that are introduced during the synthesis of CNTs. For example multi-walled carbon nanotubes (MWNT) produced by carbon vapour deposition (CVD), a relatively cheap way for large-scale production of nanotubes, have structural disorders and defects, and as a result the nanotubes show wavy and curly shapes [21, 27].

In other words, in theory increased concentrations and high aspect ratios of fillers should result in high mechanical/electrical properties but in practice, due to dispersion problems, non-perfect adhesion between polymer and particles, non-uniform orientation or curved geometries, the final properties show a high deviation from the theoretical estimates. To analyse experimentally the influence of each of these parameters on the composite properties is complex, time consuming and an expensive task. Future development and optimisation of processing techniques will therefore benefit from a strong coupling with mathematical models as an important and useful tool for understanding the behaviour of nanocomposite materials. In order to obtain a precise description of composite properties accurate, detailed models, which take into account the volume fraction, dispersion quality, aspect ratio, orientation, waviness/curliness as well as the

Table 1.1: Dimensions and corresponding number of particles in composites for different reinforcements

Filler	Average dimension	ρ [g/cm ³]	N	S
Al_2O_3 particle	d = 100 μ m	4.0	1.9	πd^2
CNF	d = 5 μ m d = 200 μ m	2.25	255	$\pi dl + \frac{\pi d^2}{2}$
GNP	l = 45 μ m (square) t = 7.5 nm	2.2	6.58 E ⁴	$4l^2 + 2lt$
CNT	d = 12 nm l = 20 μ m	1.8	4.42 E ⁸	$\pi dl + \frac{\pi d^2}{2}$

adhesion with polymers, have to be established.

Molecular dynamics (MD) and ab-initio methods can give accurate results and describe phenomena at the nanoscale, but they are very expensive computationally. Mostly these modelling techniques focus on single-walled nanotubes (SWNT) and assume defect-free surfaces or a small number of point-like defects such as vacancies or Stone-Wales defects. In contrast, analytical micromechanical models can give low-cost but coarser approximations. Based on mean field approximations they can be applied to simulate the macroscopic behaviour of composite materials. When such analytical solutions cannot be obtained easily or more detailed information is required on the meso- or macroscales, then FE-based homogenisation can be applied. Due to the very high aspect ratios of nanotubes, approximating their geometry with continuum solid elements is rather computationally expensive. Alternatively, CNT can be modelled as beam or shell elements that are linked to the solid elements describing the matrix via embedded element techniques [28,29], providing an attractive combination of accuracy and computational costs.

1.2 Objectives

The main research objectives of this work are aimed at understanding the relationships between processing induced morphological characteristics and the mechanical properties of nanocomposites. This is achieved by developing methodologies for quantifying the level of dispersion, orientation and curliness of nanofillers based on microscopy analyses. The study focuses on the prediction of the effective properties of nanocomposites. The reliability of the proposed numerical and analytical approaches is verified with experimental results. Specific objectives of the present research are:

1. Develop and validate reliable methods for the structure and morphology character-

isation: quantification of dispersion, distribution, orientation and waviness/curliness of nanoparticles in the resin system.

2. Assessing efficient analytical and numerical continuum-level modelling approaches, that may be used for studying the mechanical response of composites reinforced with arbitrarily curved CNTs at various levels of concentration.
3. Investigating the influence of dispersion, distribution, interface, orientation, waviness/curliness, aspect ratio of nanoparticles on the mechanical properties using the developed models.

1.3 Outline of the thesis

The thesis is structured in five main parts:

- I Literature review
- II Experiments
- III Characterisation
- IV Modelling
- V Results and discussion
- VI Closure

In-depth discussion about CNTs, CNFs and CNT/CNF reinforced polymers is provided in Chapter 2. It contains a state of the art review of existing processing methods of polymer nanocomposites, their morphology characterisation and different modelling techniques at different length scales. Chapter 3 focuses on the processing of nanocomposites, the main challenges of dispersing nanofillers in thermosets/thermoplastics, as well as the characterisation of the morphology, such as qualification and quantification of the dispersion/ distribution, orientation and waviness/curliness of CNTs/CNFs. The chapter further comprises the mechanical testing of nanocomposites. It is followed by Chapter 4 which describes and relates different modelling techniques. Comparisons between numerical approaches and analytical micromechanical models for modelling polymers reinforced with CNT/CNF are presented. Preliminary studies (Section 4.1) were conducted to analyse the waviness of fibres, described by sinusoidal and helical models. A deduced modelling approach is applied to composites reinforced by arbitrarily, 3D curved CNT and described in Section 4.2. Each section or subsection in Chapter 4 has been written as a self-contained unit and has been published in scientific journals and proceedings. In Chapter 5 the results obtained are presented and discussed. Chapter 6 summarises this work and gives recommendations for further research, which will facilitate the development of accurate models of the behaviour of CNT/CNF reinforced polymers.

Chapter 2

Literature review

2.1 Carbon nanotubes/Carbon nanofibres

After decades of intense research carbon nanostructures continue to be the focus of the composite community for the development of new material with improved mechanical, electrical, thermal, transport, barrier properties. Carbon nanotubes and carbon nanofibres are the most prominent among them due to their unique properties [30–32]. By 2004 there were 54 producers of nanotubes and nanofibres with an outcome of 65 tons per year. In 2010, available data for only 13 out of 96 worldwide companies producing CNTs indicates a combined production of 2050 tons per year [33]. The rapid increase in the number of companies shows on the one hand that the industry gained precision control over nanoscale processes and on the other hand that there is a dynamically growing market. Key applications for CNTs/CNFs materials are in sporting equipment (golf shafts, bicycle frames, hockey sticks, tennis rackets), electronic devices (flat screen panels, transistors, memory chips, super capacitors), energy storage devices (lithium ion batteries, thin-film solar cells, hydrogen fuel cells), automotive (fuel lines and filters, electrostatic paints for mirror housing), as well as in food, military and medical applications [34–36].

One of the main differences between CNTs and CNFs is the price, which varies depending on the production method. The cost of CNTs is an order-of-magnitude higher than for CNFs². Additional surface treatments of CNTs for functionalization and purification increase their costs. But in general, CNTs and CNFs have many similarities in terms of their syntheses, final properties and applications. Therefore, in this work modelling of these carbon based rod-like hollow nanostructures will be conducted in the same way.

2.1.1 Carbon nanotubes

Carbon nanotubes are carbon nanomaterials of rolled-up graphene monolayers. Depending on the process SWNT or MWNT can be obtained. A SWNT is rolled up from

² www.pyrographproducts.com

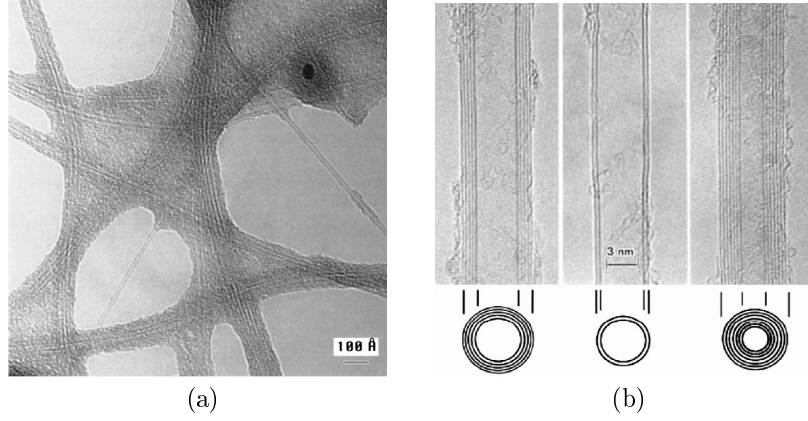


Figure 2.1: TEM images of different CNTs: SWNTs (a) and MWNTs with 5, 2 and 7 layers (b) [1]

a single graphene layer, whereas a MWNT from two or several concentric cylindrical shells of graphene monolayers kept together by van der Waals forces (Figure 2.1) [1]. Depending on the sheet direction about which the graphite layer is rolling to form the nanotube cylinder, nanotubes can exhibit either metallic or semiconductive behaviour. Because of the nearly 1D electronic structure, metallic SWNTs and MWNTs show ballistic conductivity along the nanotube length, enabling them to carry high currents without heating-up [37]. This make them perfect candidates as fillers in polymers to create an electrically conductive nanocomposite [38]. Depending on the polymer matrix, conductivities of 0.01 to 0.1 S/cm can be obtained for 1% of volume fraction [39]. Besides the improvement of the electrical conductivity at extremely low nanotube contents, nanotubes can be excellent material for reinforcing polymers and improving their mechanical properties [25, 40–42].

2.1.2 Carbon nanofibres

Carbon nanofibres belong to the same class of material as nanotubes with the difference that they have curved graphite layers nested to resemble stacked cups around the hollow core, as shown in Figure 2.2³. Because graphene layers are not oriented along the fibre axis CNF have a higher chemical reactivity and electron transport across their sidewalls compared to CNT which is important for their functionalization and electrochemical applications.

2.1.3 Synthesis of CNT and CNF

Different techniques have been developed to produce CNT and CNF. Among the most prominent are electric arc discharge and catalytic growth. The arc discharge method has previously been developed for the production of fullerene and is based on the generation of an electrical arc between two graphite electrodes. In a direct current (DC)

³http://apsci.com/?page_id=19

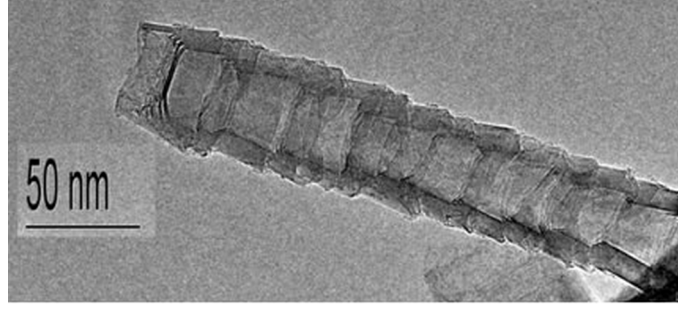


Figure 2.2: High Resolution TEM Image showing the stacked-cup structure of a Pyrograf III CNF

electric arc discharge, usually employed to generate CNTs, only the cathode accumulates the carbon product. In a produced plasma carbon is vaporised from the anode, deposited at the cathode and collected as so-called soot material, that can exceed 30% of the total product [43,44]. To generate CNFs, Pacheco et al. [45] proposed a glow-arc High Frequency (HF) discharge. It changes the electric field across the electrodes as well as the temperature in the gap and provides the energy and dynamics necessary for the dissociation of carbon coming from an hydrocarbon gas and from graphite electrodes to form CNFs. The catalytic growth of CNTs/CNFs is an alternative to the high-temperature arc discharge technique and is currently the most promising route for the large-scale production of nanostructures [46]. The main idea is the catalytic decomposition of a hydrocarbon (natural gas, propane, acetylene, etc.) over catalyst particles, such as Fe, Ni, or other metal catalysts introduced onto a substrate [47]. By setting up the synthesis parameters, such as the length, the diameter, and in case of CNTs also the number of walls, the chiral vectors can be controlled which govern the mechanical and electrical properties [48, 49]. For instance, Meysami et al. [48] showed that the properties of MWNTs can be tuned by modifying the composition of the precursor and thus the total mass of the synthesised nanotubes can be improved by more than 60%. Tibbets et al. [49] showed that by adjusting the feedstock compositions and furnace operating conditions in the syntheses of CNFs, different thickness of vapor deposited carbon can be produced. It was also shown that a heat treatment with temperatures above 1500°C will recrystallise the vapour-deposited carbon exterior layer on the conical interior planes decreasing its mechanical and electrical properties in the longitudinal direction. The diameter of a CNT/CNF is controlled by the size of the metal particle from which it starts growing and the length of the fillers has an approximately linear dependence on the reaction time. On the other hand, spending extra seconds within the decomposing hydrocarbon atmosphere a layer of vapour-deposited carbon both thickens the individual fibres and joins them together in big bunches. Strong entanglement of CVD grown nanotubes and nanofibres is one of the disadvantages of this method compared to the arc-grown CNTs/CNFs, as it is quite difficult to break dense agglomerates during dispersion processes (Figure 2.3) [24].

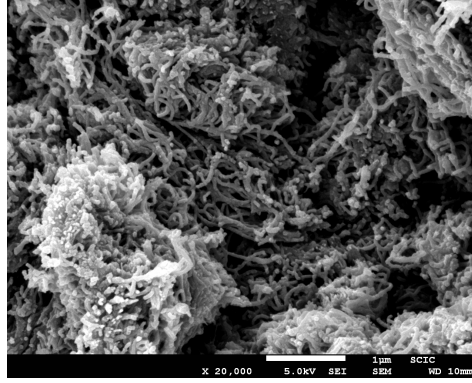


Figure 2.3: Scanning electron microscopy (SEM) image of entangled MWNT (©CONTACT)

Both the CVD and arc discharge method produce amorphous graphitic nanoparticles next to pure CNTs and CNFs (Figure 2.4) [47]. Additionally CVD grown CNTs/CNFs have catalyst residues that should be removed. The impurity content can significantly affect mechanical, thermo-mechanical and electrical properties of the resulting composites [50]. Different purification methods exist, including chemical oxidation, physical separation, and combinations of chemical and physical techniques to obtain CNTs/CNFs with the desired purity [24]. The oxidation technique is based on the idea that carbonaceous impurities are oxidised at a faster rate than CNTs/CNFs, and that the metallic impurities are dissolved by acids [51]. The disadvantage of the oxidative technique is that it always influences the structure. For instance, due to the oxidation involved in the purification of CNTs, the caps can be opened or totally disappear, which influences their electrical and mechanical properties. The physical-based purification methods are based on the difference in aspect ratio, physical size, solubility, gravity, magnetism, etc. of CNTs/CNFs and impurities. Filtration, chromatography, electrophoresis and high temperature annealing have been extensively investigated [52–54]. A common advantage of these methods is that they don't require oxidation and therefore prevent surface from damage. However physical methods are always complicated, time consuming and less effective. The biggest advantage of the oxidation method is that during the treatment functional groups, mainly carboxylic, are formed on the surface, which can be used for further chemical functionalization with multifunctional amines. In Section 2.2 the influence of the functionalization on the dispersion and the mechanical performance of composites will be discussed.

2.1.4 Mechanical properties of CNTs/CNFs

Due to the graphitic structure, CNTs and CNFs have the potential to have very high mechanical properties by analogy with graphite (in-plane modulus of graphite is known to be 1.30 GPa and the tensile strength, estimated from the properties of C-C bonds is 130 GPa [55]). Generally CNFs show lower mechanical properties than CNTs and one of the reasons is the stacking angle of the graphitic walls of CNFs. But because nanofibres

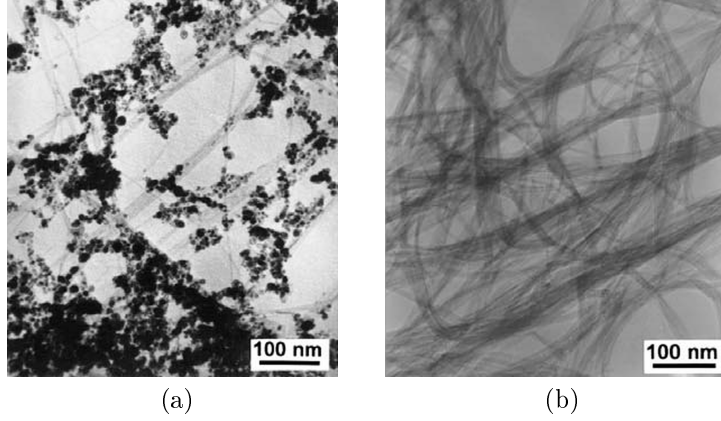


Figure 2.4: TEM images of the as-prepared arc-grown SWNTs (a) and the purified SWNTs (b)

and nanotubes are very sensitive to the aspect ratio and the degree of graphitisation, the tensile modulus and strength of some types of nanofibres can be as high as of CNTs.

Before reliable experimental measurements of nanotubes were established, mechanical properties of nanotubes were studied using computer simulations. In 1993 Overney et al. [56] calculated the rigidity of carbon tubules consisting of 100, 200, and 400 atoms, using an empirical Keating Hamiltonian with parameters determined from *ab initio* local density calculations. The calculated Young's modulus was 1500 GPa. Lu [20] investigated the elastic modulus of a nanotube using the empirical lattice dynamics model. The atomic interactions were approximated by a sum of pair-wise harmonic potentials between atoms. It was shown that the Young's modulus of nanotubes with a radius of the out-most layer greater than 1 nm was close to 1 TPa independent of the nanotube type and diameter. Different results were obtained by Treacy et al. [57] in 1996 as the first actual mechanical measurement. For the arc-grown nanotubes with a length between 1.1 μm and 1.5 μm Young's moduli were found in the range between 0.40 GPa and 4.15 GPa for different outer and inner diameters. The modulus of isolated nanotubes was estimated in TEM by measuring the amplitude of their intrinsic thermal vibrations. Poncharal et al. [58] introduced a technique that is based on electromechanical resonant vibrations of nanotubes in situ in a TEM. Analyses of static and dynamic mechanical deflections induced in cantilevered arc-grown MWNT gave elastic bending moduli in a range from 100 GPa up to 1000 GPa. The results indicate that the elastic modulus is a function of the diameter that decreases sharply with increasing diameter (from 8 nm to 40 nm).

The first technique allowing a direct measurement of the mechanical properties of individual nanotubes was based on the Atomic Force Microscopy (AFM). Salvétat et al. [21] carried out measurements on CVD MWNTs using AFM in a contact mode, which allows to measure the deflection of samples as a function of the applied force. Young's moduli were found to fall into the range of 10-50 GPa when evaluated from

beam theory with the cross sections of beams accounting for the inner and outer radius of the nanotube. Xie et al. [59] designed for the direct measurement of the Young’s properties of CNT ropes a special “stress-strain puller” and obtained an average Young’s modulus for CVD nanotubes of 450 GPa . The authors stated that uncertainty of the real sample cross-section may result in an error of 20% for the Young’s modulus. The highest value obtained for the tensile strength of MWNT was 63 GPa [55,60], which is an order of magnitude higher compared to the strongest CNFs. Yu et al. [60] measured the stress-strain response and strength-at-failure of arc-grown MWNTs under tensile loading. Individual nanotubes were picked up and then attached at each end of a section length onto the opposite tips of AFM cantilever probes. Each nanotube section was then stress-loaded and observed in situ in the SEM. Measuring mechanical properties of SWNT is a more challenging task due to their cross-section. Lourie and Wagner [61] used Micro-Raman spectroscopy to monitor the cooling-induced compressive deformation of CNTs embedded in an epoxy matrix. The Young’s modulus of SWNTs and MWNTs were derived from a concentric cylinder model for thermal stresses. Salvetat et al. [22], Li et al. [19], Yu et al. [62] directly measured the Young’s modulus and tensile strength of SWNT nanotube ropes. The individual nanotube’s properties can be derived knowing the density packing of the ropes.

Regarding CNF, Jacobsen et al. [63] studied the elastic properties of individual vapour grown CNF (VGCNFs) using the low-strain, vibrating-reed technique. The average Young’s modulus was found to be 680 GPa, which exceeds values found by high-strain and static-pulling methods [18]. Ozkan et al. [64] tested VGCNF by means of Microelectromechanical systems tools. It was shown that the Young’s modulus of high temperature heat-treated and oxidised VGCNF is 245 GPa, while as-fabricated fibres have 180 GPa. On the contrary the mechanical strength of the CNF decreased due to the heat-treatment by 15–20%. A summary of mechanical properties for CNT and CNF presented in literature is listed in Table 2.1.

2.2 Nanocomposites

CNTs/CNFs with their high modulus, tensile strength, strain to fracture, excellent damping characteristics are used to produce lightweight structural composites with high elastic modulus as well as high tensile and compressive strength [30, 31, 49, 66]. Along with good mechanical properties CNTs/CNFs have unique electrical [67–69] and thermal conductivities [70], opto-electronic properties, which can be explored to develop multi-functional composites as conducting plastics, thermal conductors, conductive adhesions, thermal interface materials, chemical sensors, energy storage devices, etc. [1, 26, 71]. Battisti [72] showed that catalytically-grown CNTs dispersed in an polyester matrix reduce the percolation threshold to below 0.026wt% and increase the overall

Table 2.1: On-axis mechanical properties of CNTs and CNFs

Material type		Tensile modulus [GPa]	Tensile strength [GPa]
SWNT	CVD	790 [19]	7.5-22.2 [19]
	Laser ablation	320-1470 [62], 1002-1330 [65], 2825-3577 [61]	13-52 [62]
	Arc-discharge	1000 [22]	50 [55]
MWNT	CVD	10-50 [21], 300 [55], 450 [59]	3.6 [59], 10 [55]
	Laser ablation	1700-2400 [61]	
	Arc-discharge	270-950 [60], 810 [21], 400 - 4150 [57]	11-63 [60]
CNF	CVD	180 [64], 200-300 [18], 680 [63]	2.90 [64], 5 [18]

conductivity. An electrical percolation threshold below 0.1% was observed for CNTs in vinyl ester [73]. Group of Sandeler investigated the influence of CNTs on the electrical, thermal [74, 75] and optical properties [76]. Regarding mechanical properties, the full promise of CNTs/CNFs as a reinforcement has not been achieved yet, but existing experimental observations are quite optimistic. Ruan et al. [77] reported an increase of 150% in strain energy density, 140% in ductility and up to 25% in tensile strength when 1wt% of MWNT were added to an Ultrahigh molecular weight polyethylene (UHMWPE). They attributed the above observations to the chain mobility enhancement in UHMWPE induced by the MWNTs. Liu et al. [78] prepared MWNTs/polyamide-6 (PA6) nanocomposites with different MWNTs concentrations using the simple melt-compounding approach. Compared with neat PA6, the elastic modulus of the composite and the yield strength were improved by about 214% and 162%, respectively, when incorporating only 2wt% of MWNTs. Dalton et al. [79] spun 100-metre-long CNT composite fibres to produce supercapacitors that are suitable for being woven to textiles. The resulting composite fibres contain 60% by weight of MWNT and are 20 times tougher than steel wires. This toughness results from a combination of high strength (1.8 GPa) and high strain to failure.

However, the measured mechanical properties of CNT composites are often found far below their theoretically predicted potentials. Chang et al. [80] analysed mechanical properties and the structure of SWNT/polypropylene (PP) composites at different concentrations. They increased the Young's modulus of the composite ~ 3 times by adding 1wt% of SWNT compared to the neat polymer. At the same time, an increasing SWNT concentration did not lead to further matrix enhancements and the achieved performance of the composite is significantly less than it was theoretically predicted. Thus, there is a need to understand the principals controlling the behaviour of CNT/CNF assemblies in order to enable the full potential of these materials and create marketable products [49, 81]. Because of the high aspect ratio and high surface energy (due to nanoscale diameters), CNT/CNF tend to agglomerate, leading to inhomogeneous dispersion. The presence of agglomerated nanotubes dramatically decreases the nanocomposite properties, especially the mechanical ones [25, 26]. Another reason that is affecting the composite properties is the weak interfacial interaction between CNTs/CNFs and the polymer. The interfacial area in CNT/CNF reinforced nanocomposites is extremely large due to the high aspect ratio of the CNTs/CNFs and therefore plays an even more important role in the ultimate performance of the composite. Schadler et al. [82] studied the load transfer in MWNT/epoxy composites in both tension and compression. It was found that the load transfer to the nanotubes in the composite is high in compression and rather poor in tension. One of the reasons is that during the load transfer to a MWNT, only the outer layers are stressed in tension whereas all the layers respond in compression. Song et al. [83] studied the rheological, mechanical, electrical and thermal properties of CVD MWNT reinforced epoxy. In regard to the mechanical properties it has been reported that the load transfer from the polymer to the

CNTs is not large enough to break the CNTs under tensile loading. Instead of breaking, the nanotubes were frequently pulled out due to the weak van der Waals forces acting between individual graphene shells in the MWNTs, which resulted in slipping between the shells. This phenomenon was observed by field emission scanning electron microscopy (FESEM). In contrast Wagner et al. [84] showed the evidence of strong bonding between polymer and nanotubes. Nanotubes containing thin polymeric films were analysed under tensile stresses and single nanotube fragmentation was observed. The stress transfer efficiency was at least one order of magnitude larger compared with conventional fibre-based composites.

2.2.1 Functionalization

To enable perfect interfacial bonding between CNTs/CNFs and polymer, there are several surface modification treatments. The main approaches for the modification of CNTs/CNFs can be grouped into two categories [85]:

1. The covalent attachment of chemical groups through reactions onto the π -conjugated skeletons.
2. The non-covalent adsorption or wrapping of various functional molecules.

Moreover, for CNTs there is in addition the endohedral filling of their inner empty cavity that improves the bonding with the polymer [85]. Oxidation treatments are perhaps the most used methods in covalent functionalization [86]. The incorporation of oxygen-containing functionalities onto the graphitic surface can enhance the interfacial adhesion between CNTs/CNFs and polymer. As a result, the unique mechanical and electrical properties can be transferred from CNTs/CNFs to the polymer. The most synthetically useful group activated during oxidation is carboxylic acid [85]. The research group of Sun et al. [87] studied two different reaction conditions to attach poly(ethyleneimine) chains to activate nanotubes. In the first one, the free carboxylic acid functions were converted to acyl chlorides and in the second, to get a soluble functionalized material, oxidized nanotubes were directly heated in the polymer melt. Both methods were effective functionalization methods and the polymer-attached MWNTs were found to be soluble in many common organic solvents and in-water. Hill et al. [2] functionalized CNTs with a polystyrene copolymer. The functionalization reaction conditions were designed to attach poly(styrene-co-p-(4-(4'-vinylphenyl)-3-oxabutanol)) polymers to CNTs via the esterification of the nanotube-bound carboxylic acids (see Figure 2.5). The obtained polymer-attached CNTs were soluble in common organic solvents.

Lakshminarayanan et al. [88] proposed an oxidation of VGCNFs with nitric acid that leads to a threefold increase in surface oxygen functionality within 10 min. No damage to the fibres was observed even after 10 h or more in 69-70% HNO₃ at 115°C, which is important for the further use as polymer reinforcement. Zhu et al. [89] introduced functional amine terminated groups via silanization to the surface of CNFs,

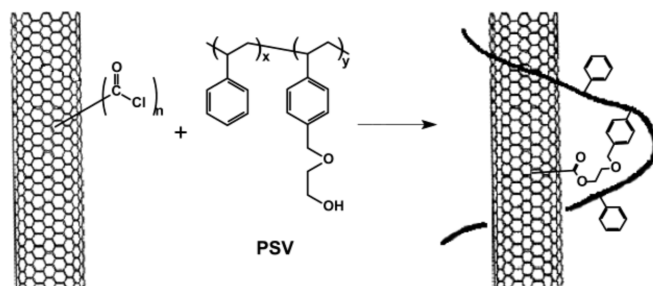


Figure 2.5: Esterification of nanotube-bound carboxylic acids [2]

which in situ react with epoxy monomers. The influence of particle concentration and surface treatment on the complex viscosity, storage modulus and loss modulus was investigated. The tensile strength and elongation-to-break of 0.1wt% functionalized-CNF/epoxy nanocomposites were found to be 12.6% and 25.4% higher than those of the 0.1%wt as-produced CNF/epoxy nanocomposites. The group of Schulte et al. [90] oxidised arc-grown MWNTs with a mixture of sulphuric and nitric acid in order to remove impurities and thereafter functionalized them with multi-functional amines. The amino-functionalized nanotubes were dispersed in an epoxy resin. TEM investigations gave evidence for an improved interfacial interaction between the functionalized nanotubes and the matrix. Good dispersion of CNTs due to the presence of carboxylic acid groups was reported. Fiedler et al. [91] used shear mixing to disperse amino-functionalized double-walled CNTs and as-produced double-walled CNTs in epoxy. For the addition of 0.3wt% the fracture toughness of the neat matrix increased up to 45% with the use of amino-functionalized CNTs, and up to 30% with as-produced CNTs. Spitalsky [92] studied a different oxidation technique and its influence on the mechanical and electrical properties. It was found that the strong oxidative treatment applied to the nanotube lead to the two-fold increase in the flexural modulus and a decrease of DC conductivity by two orders of magnitude. Therefore a mild oxidative treatment such as that provided by NH_4OH/H_2O_2 was proposed to achieve a combined improvement of both modulus and DC conductivity.

Non-covalent functionalization methods, such as the use of surfactants, are particularly attractive because it offers the possibility of attaching chemical handles without damaging the graphitic structure of CNTs/CNFs. Surfactants are amphiphilic molecules possessing both polar and apolar properties. This nature makes them adsorbed at the interface between two immiscible phases reducing the surface tension. Moore et al. [93] made a comparative analysis of different surfactants on the suspendability of CNTs. Islam et al. [94] used sodium dodecylbenzene sulfonate to solubilize high weight fraction SWNT in water and around 60% of the SWNT bundles were exfoliated into single tubes. Surfactant-assisted processing of tubes can be also used to improve dispersion and interfacial bonding of CNTs with the polymer. Gong et al. [95] studied thermomechanical properties of a CNT/epoxy composite with the presence of nonionic

surfactant (polyoxyethylene 8 lauryl). It was reported that with the surfactants as the wetting agent the addition of only 1wt% CNTs led to a 30% increase of the elastic modulus and a shift of the glass transition temperature from 63°C to 88°C. Geng et al. [96] treated CNTs with a nonionic surfactant Triton X-100. The enhanced interfacial interactions after treatment gave rise to an improved dispersion and wetting of CNTs in epoxy, improving the impact fracture toughness, flexural strength and modulus of the nanocomposite. However, the treatment with surfactants reduced the conductive properties of the CNT/polymer composite due to the decreased contact between CNTs.

2.2.2 CNTs/CNFs composites processing methods

As mentioned in section 2.2.1, surface treatment is primarily used to improve the interfacial interaction between CNTs/CNFs and a matrix as well as the CNT/CNF dispersion within the matrix enhancing the mechanical properties of the composite. However, surface functionalization may damage the graphitic structure of CNTs/CNFs reducing the intrinsic properties of CNTs/CNFs in the final composites. Moreover, CNTs/CNFs treated by different surfactants may decrease the contact between them, decreasing the final conductive properties of the composite. Thus depending on the application, especially for an electric conductive composite where good contact between individual CNTs/CNFs and an effective conducting path is important, surface treatment for CNTs/CNFs is not desirable [71].

There are several processing methods based on high speed mixing to achieve good dispersion of non-functionalized CNTs/CNFs in polymers [1]. In addition, external forces introduced during processing affect the CNT/CNF orientation influencing both mechanical and electrical properties of the nanocomposite. Control of the alignment of CNTs/CNFs towards the pre-determined direction is an important issue for the design of these composites. For example, good dispersion of nanotubes and their alignment would result in a significant improvement of the mechanical material strength but electrical conductivity would be lost due to the absence of the percolation threshold. On the other hand randomly oriented and badly dispersed CNTs/CNFs will not enhance mechanical properties, but conductivity may increase due to the percolation path. Therefore existing dispersion methods as well as stabilisation concepts for low viscosity liquids, such as thermosets, and for high viscosity thermoplastics should be optimised for the desired level of dispersion and orientation of nanofillers [97,98].

Ultrasonication

Ultrasonication is a cavitation method based on applying ultrasound energy to disperse CNTs and CNFs into low viscous liquids, such as water, acetone and ethanol. As most polymers are either in a solid or viscous liquid state they need to be dissolved or diluted before. The most commonly used equipments are the ultrasound bath and the ultrasound probe. The use of an ultrasound horn, also known as a sonicator, is

the preferred method as it has a lower frequency, 23 kHz, compared to the ultrasound bath with 40-50 kHz [1]. Low frequencies produce large bubbles, which release high energies when collapsing and hence lead to the increased dispersion capability. The cavitation process can be so energetic, that CNTs/CNFs can be seriously damaged. Lu et al. [99] showed on electron micrographs that sonicated nanotubes had a very high concentration of defects due to bending and buckling. With the increased duration of the sonication the increased disorders in the carbon structures were observed, leading to the formation of amorphous carbon. Additionally to the induced graphitisation of the graphite structure, filaments can break during ultrasonication decreasing the composite mechanical properties. Also taking into account technical difficulties related to the long time degassing after the cavitation process, this approach is not amenable to high volume rate productions and thus is limited in scalability.

Calendering approach

The application of mini-calendar to disperse CNTs/CNFs is a very promising approach to obtain a good level of dispersion. It utilises three adjacent cylinders rotating at different velocities to impart high shear stresses, commonly known as three roll mills and shown in Figure 2.6. Because of the narrow gap between the rollers, of only a few μm and different angular velocities the process uniformly shears the entire volume of the material.



Figure 2.6: Calendaring (or three roll mill) machine used for particle dispersion in a polymer matrix (Polymer Department, University of Minho)

Gojny et al. [40] dispersed CNTs in a thermoset resin using a three roll mill and a horn sonicator. The quality of dispersion was investigated by TEM and the calendar approach was found to be more efficient for dispersing CNTs. Schulz et al. [3] reached the same conclusion, when studying the dispersion state of CNT/epoxy suspensions prepared by different mixing techniques (Figure 2.7).

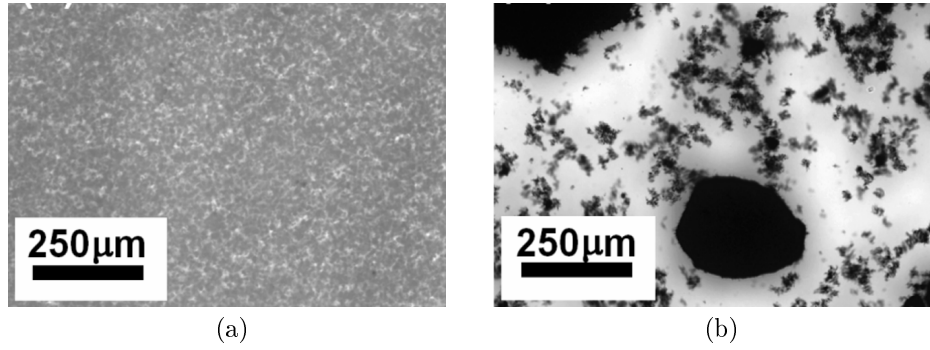


Figure 2.7: OLM images of 0.05wt% CNTs in epoxy after: shearing with $100s^{-1}$ for 1 min (a), sonicating for 10 minutes (b) [3]

Thostenson et al. [4] performed a series of experiments under different processing conditions. Figure 2.8 shows the progressive development of the dispersion quality during the calendaring process. Because as-produced CNTs/CNFs are usually highly agglomerated it is recommended that the mixture is first processed at a larger gap and then subsequently passed-through the mill at progressively smaller gap settings. A major advantage of this method is that it does not require solvents and allows efficient manufacturing of larger amounts of nanocomposites.

Melt processing

Melt mixing is a cost efficient and effective route to produce CNT/CNF reinforced thermoplastic composites. It is a continuous process that does not involve the use of extraneous ingredients like solvents. When carried out in a twin-screw extruder this process offers numerous advantages over other melt processing methods including:

1. Possibility to a large-scale production
2. A short residence time at elevated temperatures
3. A high reproducibility
4. Intensive mixing (dispersive or distributive mixing)
5. High throughput rates

The most used extruder for the production of thermoplastic based nanocomposites consist of two intermeshing, co-rotating screws mounted on splined shafts in a closed barrel⁴. Closely intermeshing and co-rotating screw elements along the entire processing section provide continuous helical material transport and ensure self-wiping characteristics. Together with high hydrodynamic shear forces optimum compounding results in terms of dispersion and distribution can be achieved.

⁴<http://www.kraussmaffeiberstorff.com>

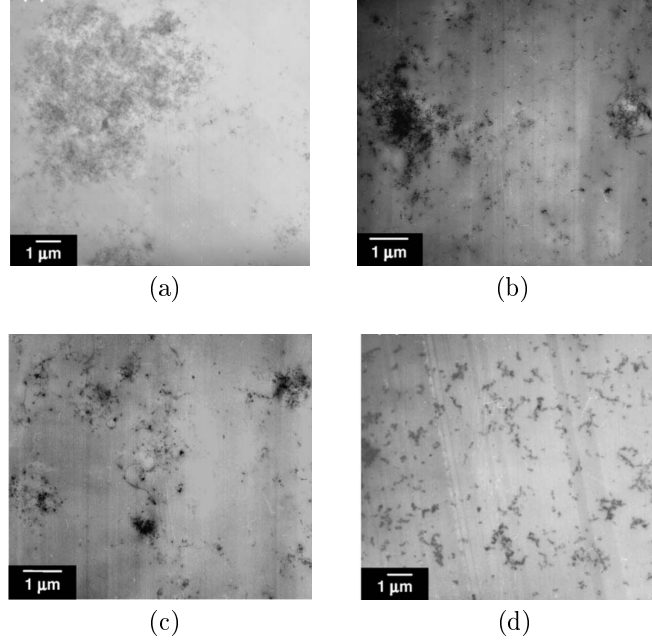


Figure 2.8: Nanocomposite structure development after processing at different gap settings: $50\mu\text{m}$ (a), $20\mu\text{m}$ (b), $10\mu\text{m}$ (c), $5\mu\text{m}$ (d) [4]

The processing parameters, such as the feeding rate, sequence of feeding, temperature, the screw configuration, the screw speed determine the dispersion and distribution of CNTs/CNFs and their ultimate aspect ratio. High shear levels involved significantly improve dispersion but simultaneously lead to a significant break-up of the fibres [100]. In order to optimise the composite's performance it is necessary to understand how all processing variables influence the nanocomposite's morphology and consequently its properties. Villmow and co-workers [101] studied the influence of different screw configurations, temperature profiles and screw rotations on the dispersion of CNTs in polycaprolactone. It was found that the rotational speed had the highest influence on the dispersion of CNTs. An increase in the rotational speed from 100 to 500 rpm led to a decrease of the agglomeration area fraction by about 70%.

Injection moulding

To produce large numbers of complex 3D parts made of thermosets or thermoplastics reinforced with CNT/CNFs, injection moulding would be the most efficient route. The raw material is injected into a mould which shapes the polymer into the desired shape under high pressure. Thermoplastics are more suitable for injection moulding due to their ability to soften and flow upon heating.

During injection moulding the polymer melt is subjected to shear and elongation forces, which depend on the feeding and injection speeds used. These forces strongly influence the morphological structure, the dispersion, distribution and orientation, thus the CNT network and consequently the mechanical as well as electrical conductiv-

ity [102–105]. Injection moulded parts present a skin-core structure as a result of the processing conditions (see Figure 2.9). The skin-core structure determines particularly the electrical surface and volume (bulk) resistivity. With increasing amounts of CNTs the electrical surface/volume resistivity reduces [106–111]. According to Villmow et al. [112] are the injection speed and the melt temperature the most effective process parameters which determine the conductivity of injection moulded polymeric parts reinforced with CNTs. Electrical conductivity does not necessarily imply a well dispersed CNT structure [113]. Agglomerated and dispersed CNTs can form conductive percolating networks. Electrical conductivities of CNT networks in loosely agglomerated networks are often higher than in dispersed parts [114, 115]. On the contrary, well dispersed and distributed CNTs are ideal for improving the mechanical properties.

The skin-core structure originates from high shear and rapid solidification of the polymer at the mould surface. The shear flow is strongest near the mould surface, while it is negligible at the mould centre [114–116]. The structural differences between the skin and core result in variations of the electrical volume resistivity within the part. CNTs and polymer molecules in the skin layer are more oriented [6, 112, 116, 117]. A light orientation of CNTs increases the electrical conductivity, whereas a strong orientation reduces the electrical conductivity due to the reducing percolation density [118, 119]. Thus, the skin of a part generally has a higher electrical resistivity than the core as a result of the reduced percolation caused by shear. The orientation and the agglomerations of CNTs in the skin are affected by melt temperature, injection speed and mould temperature [112]. A low shear rate promotes agglomeration whereas a high shear rate facilitates the dispersion of CNTs [115, 120–123] and leads to reduced electrical conductivities [5, 114, 115, 124]. A low injection speed implies a thicker frozen skin layer when the hot melted polymer comes in contact with the cold mould surface [117]. With increasing injection speed the shear flow increases, CNTs close to the mould surface are more aligned and the surface resistivity increases [108, 125, 126]. On the contrary, the electrical volume resistivity decreases with increasing injection speed [126]. Agglomerates break under shear or tensile stress when the applied stress is greater than the agglomerate strength [120, 127]. Therefore, the length of CNTs is dependent on the agglomerate strength and the amount of entanglements. A higher melt temperature increases the mobility of the polymer chains. Hence, the viscosity of the polymer is reduced which facilitates to dissipate the alignment enforced by the polymer flow and reconstruct a CNT network [115, 120, 124, 125]. With higher melt temperatures the electrical resistivity of the part is reduced (Figure 2.10) [5, 124]. This effect is the same for both amorphous and semi-crystalline polymeric matrices. In experiments by Tiusanen [128] it was shown that a melt temperature below the polymers decomposition temperature results in the maximum volume conductivity.

In summary, a low injection speed and a high melt temperature result in a low electrical resistivity. However, the best dispersion is obtained at low melt temperatures with shear stresses high enough to break the agglomerates and a melt viscosity low

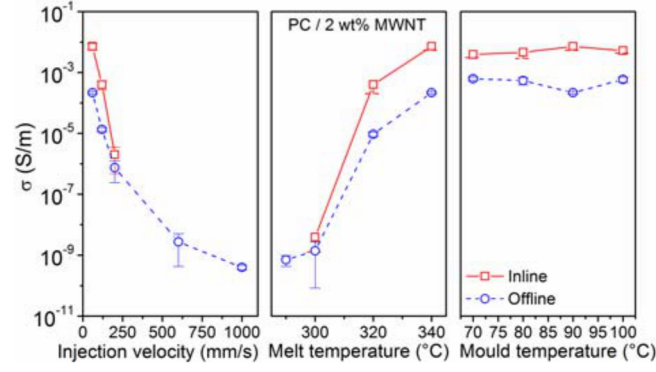


Figure 2.10: In-line and off-line electrical conductivities of injection moulded parts with 2wt% of CNTs in PC [5]

enough to wet the agglomerates and reduce the agglomerate strength [120, 125, 127].

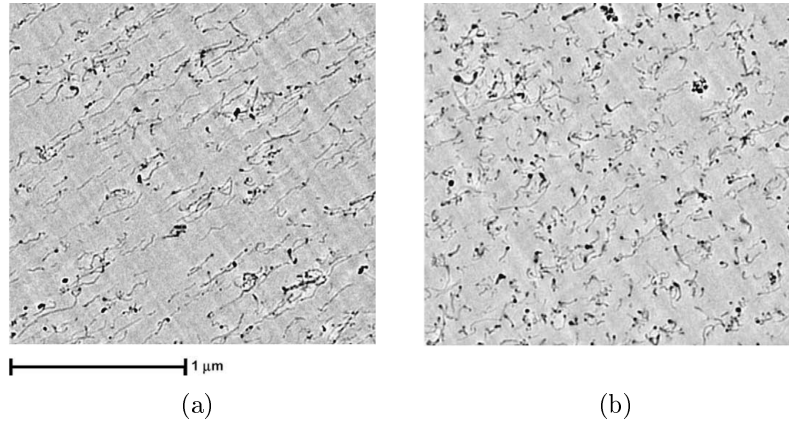


Figure 2.9: Orientation of CNTs in an injection moulded (2 wt% of CNTs in PC) sample at $2\mu\text{m}$ (a) and at $43\mu\text{m}$ (b) from the surface [6]

2.3 Characterisation

A variety of direct and indirect techniques exist to verify the efficiency of the production method in terms of dispersion of CNTs/CNFs in polymeric matrices and to characterise the orientation, aspect ratio, geometry (curviness) of the nanoreinforcements. The most commonly used are AFM, TEM, SEM, OLM, X-ray diffraction (XRD), Raman spectroscopy and polarised light diffraction. Direct length measurements of CNTs/CNFs with microscopy techniques is a challenging task, since a large number of CNTs/CNFs are separated during the specimen preparation with a microtome. Streit et al. [129] proposed a new technique called “length analysis by nanotube diffusion” (LAND) for measuring the length distribution of dispersed SWNT samples by analysing diffusional motions of many individual nanotubes in parallel. The method is based on tracking

the translational trajectories of individual nanotubes at different locations, computing the corresponding diffusion coefficients and converting those values to nanotube lengths. Computed distributions were validated by conventional AFM analysis of the same samples. Regarding the orientation characterisation several techniques commonly used to study the polymer crystallite orientation, such as XRD and polarised Raman spectroscopy, were applied to characterise the nanotube alignment [130,131]. Wood et al. [132] showed the difference between the Raman shifts of longitudinally and transversely aligned CNT-based composites. Hobbie et al. [7] measured the orientation of MWNTs in sheared semidilute surfactant-stabilised water suspensions using small-angle polarised light scattering and optical microscopy. Figure 2.11 shows the orientation angle inferred from the light scattering data as a function of the shear rate.

Although XRD, Raman spectroscopy and polarised light diffraction can qualify the CNT/CNF orientation angles in the sample, they provide only indirect results which are difficult to validate or calibrate with direct measurements. For a direct characterisation of the orientation and the curved geometry of CNTs/CNFs direct microscopy techniques on nano-/microscales has to be utilised.

Fan and co-workers [8] mixed functionalized CNTs in vinyl ester resin. The combination of ultrasonication and mechanical stirring was applied to disperse nanotubes. The produced suspension was forced to flow into micro- and nanochannels formed by glass fibres in a hexagonal arrangement within a fibre tow. TEM was employed to investigate the effect of shear forces on the nanotube alignment. The cured composites were sliced with a microtome at various locations. Due to the high resolution, a direct observation of nanotubes was possible allowing to measure the orientation angle of the nanotubes. Each nanotube, or more correctly each part of a nanotube observed on a TEM image, was characterised by a unit vector placed in the average direction of its length (Figure 2.12). In case of large curvatures, nanotubes were represented with several direction vectors. The distribution of orientation angles of these vectors provided a probability distribution function. The second moments of this probability distribution functions were calculated for all TEM images, representing the orientation state of the suspension at different locations. The degree of MWNT alignment was found to increase with increasing shear.

Curvature of CNTs/CNFs is another very critical parameter that has to be quantified and taken into account when modelling and designing a composite. Several researchers showed that the curved shape of CNTs/CNFs can dramatically decrease the effective elastic composite modulus [10,133–135], but up to this day there is no effective and reliable method to quantify the curved geometries of CNTs/CNFs. Motivated by micrographs Fisher [10] proposed that nanotubes take sine-like geometries and thus a distribution of wavelengths could be extracted from TEM images (Figures 2.13). The proposed method may not reflect the real CNT/CNF geometry as TEM micrographs show only projections of CNTs/CNFs in the sectional plane. Looking to a SEM image of CNTs (Figure 2.3) nanotubes are arbitrary curved in space, presenting a mixture

of helical, sine-like and twisted geometries. The term waviness refers from now on to a curved geometry in the 2D space, such as a sine shape, whereas curliness relates to arbitrary geometries in the 3D space.

Electronic microscopy methods are often the first choice to obtain dispersion quality in nanocomposites. Luo and Koo [136] measured the free-path spacing between CNTs/CNFs from the randomly taken representative TEM images. The dispersion parameter was defined as the probability of the free-path distance distribution in the range of $0.9\bar{\mu} - 1.1\bar{\mu}$, where $\bar{\mu}$ is the mean spacing. MWNTs showed much lower dispersion compared to CNFs. Kim and co-workers [137] proposed three different techniques to assess the dispersion and distribution of nanoparticles in polymers: the TEM particle density, Morisita's index and the skewness-quadrat method. The TEM particle density was calculated as a ratio between the number of particles in each quarter of each of the TEM picture and the average number of particles in each sample. It is a simple method to quantify the dispersion, which does not provide any information about the distribution of nanoparticles. The Morisita's index developed from a statistical background considers the variation of the spatial distribution, counting single nanoparticles and aggregates as single points, thus losing information about dispersion. The quadrat method was found to be the most appropriate to estimate the effects of dispersion and distribution. The measured area was divided into small cells of equal size, called quadrats, and the number of particles in each quadrat was counted, thus providing information about dispersion and the spatial arrangement of the particles in a sample. Bakshi et al. [138] distinguished dispersion and distribution of nanotubes as well, applying two different techniques for the quantification. The first method based on SEM image analyses of the size of CNT clusters was proposed for the dispersion. And the second method based on the distances between nearest neighbours (obtained by constructing the Delaunay triangulation of the centres of the nanotubes) was proposed for the distribution. The estimated local volume fraction of CNT reinforcements at different sample locations was investigated for the effect on the localised mechanical properties. The results were compared with experimental data obtained by nanoindentation testing. A schematic image of the difference between dispersion and distribution is presented in Figure 2.14. The dispersion factor, defined as the ratio of the number of particles that are placed in clusters to the number that are placed at random coordinates within the remaining area, is about the same for both images. But the distribution, the spatial arrangement of particles and clusters, is very different. Although these two effects are dependent on each other, it is important to identify them individually. Depending on the processing equipment and different sets of conditions nanotubes could be all separated from each other having a good dispersion, but when grouped on the skin/edges of the part the mechanical and electrical properties are decreased.

On the one hand electronic microscopes have very high resolutions allowing direct visualisation of particles, on the other hand only a very small and specific selected area of the bulk composite can be analysed. To characterise larger areas for the dispersion

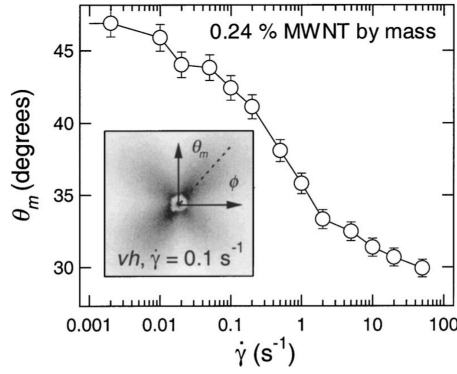


Figure 2.11: Orientation angle as a function of the shear rate [7]

quality several quantitative methods based on the OLM technique were described in the literature [66, 139]. Villmow et al. [13] proposed a method based on transmitted light microscopy to quantify the state of dispersion. A dispersion index was defined as the correlation between the agglomerate area, the total investigated area, the volume fraction of nanotubes and the density of CNT agglomerates. Area and number of agglomerates were calculated for different sections, neglecting those agglomerates with diameters smaller than $5 \mu\text{m}$ (Figure 2.15).

Another method for quantifying the morphology is based on grey scale analysis. A method that uses hundreds of optical micrographs taken of a sample in combination with the histograms of pixels plotted for each micrograph. The shape of a histogram or the variance of the pixel distribution quantitatively characterises the dispersion of a nanocomposite (Figure 2.16). The analysis of variances of histograms from all taken micrographs gives information about the spatial distribution of nanoparticles.

The methods described above for the characterisation of orientation, curviness, dispersion and distribution of CNTs/CNFs allow setting up synthetic volume elements that satisfactorily describe nanocomposites filled with CNTs/CNFs.

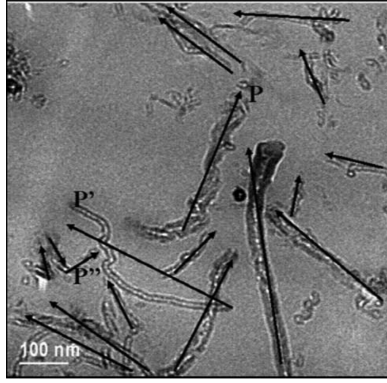


Figure 2.12: Characterisation of MWNT orientation state in TEM image [8]

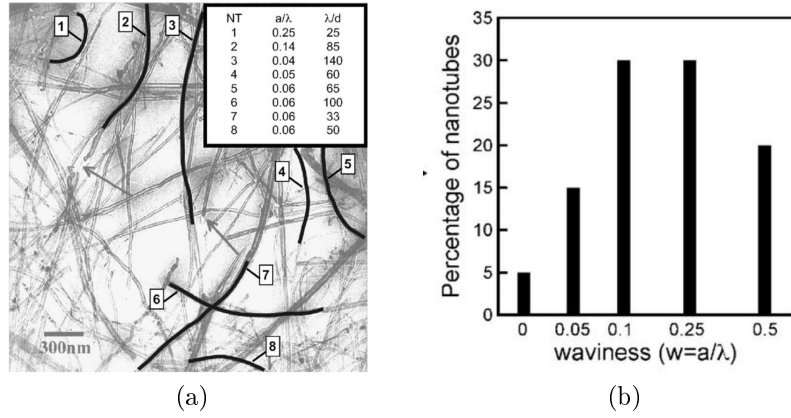


Figure 2.13: Evaluation of nanotube waviness: TEM image of CNTs (a) [9] and distribution of waviness parameters for highlighted nanotubes (b) [10]

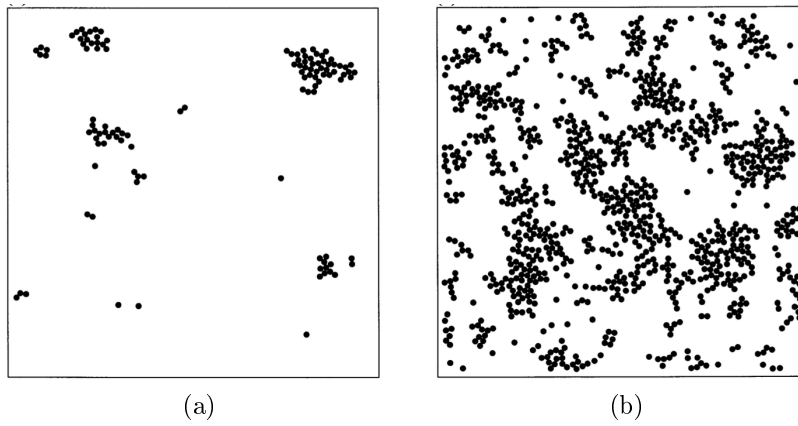


Figure 2.14: Clustered microstructures: bad distribution (a) and good distribution (b) [11]

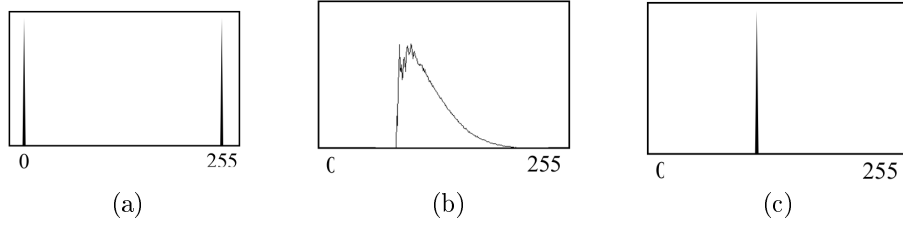


Figure 2.16: Histograms representing “no” (a), “intermediate” (b) and “perfect” (c) dispersion in CNF/polymer composites [12]

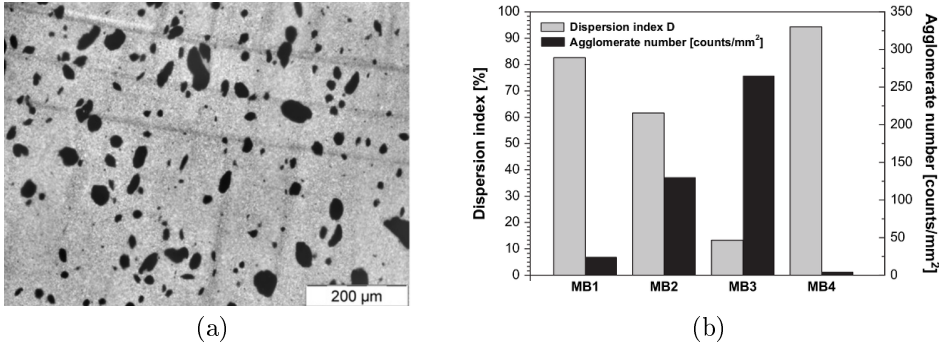


Figure 2.15: OLM images of masterbatches (a) as well as dispersion index and agglomerate number (b) [13]

2.4 Modelling

To apply modelling and computer simulations for the design and optimisation of a nanostructured material, it is necessary to consider structure-property relationships. A list of a few principal relationships dependent on different length scales, as mainly outlined by Gates and Hinkley [16], is given in Table 2.2. Molecular mechanics, molecular dynamics, coarse-grained and Monte-Carlo simulations can give accurate results and describe phenomena on the atomistic and molecular level. In coarse-grain models molecular chains are represented as simpler bead-spring models. Nevertheless they do preserve many of the important aspects of the chemical structure allowing the simulation of material behaviour above the nanoscale with less CPU time. With respect to CNT/polymer modelling, most of the above approaches focus on SWNTs and assume defect-free surfaces or a small number of point-like defects such as vacancies or Stone-Wales defects. To model the macroscopic behaviour the discrete atomistic and molecular structure is substituted with a continuum structure that obey several fundamental laws [16]. The continuum method relates the deformation of a continuous

medium to the external forces acting on the medium and the resulting internal stress and strain. A necessary and sufficient condition for equilibrium is that the virtual work done by a sum of external and internal forces vanish for any virtual displacement. With an appropriate linking between computational chemistry and solid mechanics Odegard et al. [140, 141] replaced discrete molecular structures with equivalent-continuum models, therefore representing the nanoscale interactions between polymer and nanoparticles and at the same time determining continuum effective properties for the composite. A review of similar methodologies applicable to a hierarchical approach for modelling the macroscopic behaviour of nanostructured materials can be found in [142].

Any continuum model for mechanical properties replaces the multi-phase composite material with a homogeneous continuum. An estimation of the properties of that continuum involves the averaging of the phase properties. For a sufficiently large volume element Ω of an inhomogeneous material, which contains no significant gradients of composition and shows no significant variations in the applied loads, homogenisation relations take the form of volume averages of some variable $f(x)$ [143].

$$\langle f \rangle = \frac{1}{\Omega} \int_{\Omega} f(x) d\Omega \quad (2.1)$$

Ideally, a homogenisation volume element Ω of sufficient size can be a proper representative volume element (RVE). It must be large enough to contain all information necessary for describing the behaviour of the composite, which should be independent of the actual position and orientation of the RVE and/or of the boundary conditions applied to it. On the other hand, the RVE is required to be sufficiently small for the statistical representation of the microgeometry and it is necessary that the influence of macroscopic gradients is negligible. A proper RVE and a suitable averaging technique lead to the volume average stress and strain in the composite.

$$\begin{aligned} \langle \sigma \rangle &= \frac{1}{\Omega} \int_{\Omega} \sigma(x) d\Omega \\ \langle \varepsilon \rangle &= \frac{1}{\Omega} \int_{\Omega} \varepsilon(x) d\Omega \end{aligned} \quad (2.2)$$

The basic concepts of the continuum micromechanics can be found in [143], where modelling approaches are divided into two groups. The first group of models describes the microgeometries of inhomogeneous materials on the basis of statistical information. The most commonly used approaches are:

- Mean Field Approaches (MFAs): The microfields within each constituent of an

inhomogeneous material are approximated by their phase averages $\langle \varepsilon \rangle_p$ and $\langle \sigma \rangle_p$,

$$\begin{aligned}\langle \sigma \rangle_p &= \frac{1}{\Omega_p} \int_{\Omega_p} \sigma(x) d\Omega \\ \langle \varepsilon \rangle_p &= \frac{1}{\Omega_p} \int_{\Omega_p} \varepsilon(x) d\Omega\end{aligned}\tag{2.3}$$

leading to the average stress and strains defined as

$$\begin{aligned}\langle \sigma \rangle &= \frac{\sum_p \Omega_p \langle \sigma \rangle_p}{\sum_k \Omega_k} \\ \langle \varepsilon \rangle &= \frac{\sum_p \Omega_p \langle \varepsilon \rangle_p}{\sum_k \Omega_k}\end{aligned}\tag{2.4}$$

where p denotes a given phase of the material and Ω_p is the volume occupied by this phase. Volume fraction, inhomogeneity aspect ratio distribution, orientation, etc. enter the homogenisation via statistical descriptors. MFA methods typically assume some idealised statistics of the phase arrangement at the microscale and in the literature are referred to as “noninteracting approximation”.

The second group of models is based on studying discrete microstructures and counts for the interaction between inhomogeneities:

- Periodic Microfield Approaches (PMAs) or Unit Cell methods: It is a periodic homogenisation scheme, in which the inhomogeneous material is approximated by an infinitely extended material model with a periodic phase arrangement. PMA can give detailed information on the local stress and strain fields within a given unit cell but they tend to be computationally expensive.
- Windowing approaches: Rectangular or hexahedral subregions of a given phase arrangement is subjected to homogeneous strain and stress boundary conditions to estimate lower and upper bounds for the overall mechanical behaviour of the material.

2.4.1 Mean Field Approach

This section focuses on the two-phase material presented by polymer with embedded rigid prolate inclusions of constant aspect ratio. The bonding between inclusions and matrix is assumed to be perfect. The material behaviour of both reinforcement and matrix is taken to be linear (thermo)elastic, with small strains and temperature changes. Over the past three decades many micromechanics approaches were developed for the evaluation of the overall elastic properties of such heterogeneous materials. Special

Table 2.2: Structure-property relationships for CNT/CNF polymeric composites [16]

	Structure			Properties	
	Nano	Micro	Meso	Macro	
Inter-molecular interaction		Molecular weight	Volume fraction	Strength	
Bond rotation		Cross-link density	Orientation	Modulus	
Bond angle		Crystallinity	Dispersion	Glass transition temperature	
Bond strength		Particle/polymer interaction	Distribution	Coefficient of thermal expansion	
Chemical sequence			Curviness	Viscosity	
Diameter				Toughness	
Length				Dielectric density	
Aspect ratio				Conductivity	
Chirality				Plasticity	

attention in the literature is given to the effective field methods of the Mori-Tanaka type [144]. These approaches are based on Eshelby equivalent inclusion theory [145]. Eshelby showed that the eigenstrain applied to an elastic homogeneous ellipsoidal inclusion in an infinite matrix results in uniform stress and strain states in the constrained inclusion. Following Mura's [146] definition: eigenstrain is the nonelastic strain such as, thermal expansion, phase transformation, initial strains, plastic and misfit strain. On the basis of this theory Eshelby described the stress and strain fields in inhomogeneous inclusions that are embedded in a matrix, which have different properties than the inclusion. He replaced an actual perfectly bonded inhomogeneous inclusion, which is subjected to a given unconstrained eigenstrain with a "equivalent" homogeneous inclusion subjected to a "equivalent" eigenstrain. This equivalent eigenstrain must be chosen in such a way that the inhomogeneous inclusion and the equivalent homogeneous inclusion attain the same stress state and the same constrained strain.

$$\sigma_r = C_r [\varepsilon_c - \varepsilon_t] = C_m [\varepsilon_c - \varepsilon_\tau] \quad (2.5)$$

Here $\varepsilon_c - \varepsilon_t$ and $\varepsilon_c - \varepsilon_\tau$ are the elastic strains in the inhomogeneity and the equivalent homogeneous inclusion, respectively. σ_r is the stress state in the inclusion (reinforcement), C_r and C_m are the reinforcement and matrix elasticity tensors, ε_c is the uniform strain in the constrained inclusion, ε_τ and ε_t are eigenstrains in homogeneous (equivalent) and inhomogeneous inclusions, correspondingly.

In 1984 Tandon and Weng [147] derived analytical equations to calculate five independent constants of a material filled with aligned general spheroidal particles. In 1987 Benveniste [148] computed the effective elasticity tensors of composites based on a reconsideration and reformulation of the Mori-Tanaka's theory. An inclusion phase consisted of aligned and randomly oriented ellipsoidal particles. A review of different micromechanical models for the stiffness of aligned short-fibre composites, including the dilute model based on Eshelby's equivalent inclusion, the self-consistent model for finite-length fibres and Mori-Tanaka type models can be found in [149]. Odegard [150] applied Mori-Tanaka type models to study the stiffness of SWNT reinforced polymer composites, averaging the elasticity tensors over various nanotube orientations. Such an approach counts for an idealised case of CNT/CNF reinforced polymers, when particles are uniformly dispersed, aligned and perfectly bonded with the matrix. In reality the averaging process must account not only for the orientation of a phase, but also for the dispersion and curviness of the inclusions.

Spanos et. al [151] proposed a two-step homogenisation method for determining mechanical properties of polymers reinforced with SWNTs. First, the local material properties were determined in each FE model using the Mori-Tanaka method taking into account volume fraction, aspect ratio, shape and orientation of the inhomogeneities. Second, the obtained information was incorporated into a Monte Carlo FE method which accounts for the effect of the non-uniform dispersion and distribution of SWNTs in

the matrix. Hsiao and Daniel [152] introduced an analytical procedure for modelling the effect of wavy fibres, dividing them into infinitesimally thin slices. For the compliance matrix of each slice, he used the simple rule of mixture. The same approach can be used for elasticity/compliance tensors being calculated with mean field methods. Shao et al. [153] studied the effect of the waviness of CNTs and the interfacial debonding between nanotubes and the matrix on the effective moduli. The curved fibre was replaced by one straight fibre along the chord and two other straight fibres in the perpendicular direction. Shi et al. [27] considered CNTs as a helical fibre sliced into segments and the properties were integrated along the length of the nanotube. The elasticity tensor was expressed in Hill's notations [154]. Such simplified analytical procedures can be applied to inclusions of arbitrary shape but due to the significant simplification the accuracy of the predicted properties is limited.

Mean field micromechanical models provide the ability to assess the key factors, e.g. volume fraction, orientation, diameter and length distributions, controlling the effective elastic behaviour. But accounting for the twisted, complicated tangled and clustered geometries of the reinforcements is a difficult issue for these modelling approaches.

2.4.2 Periodic Microfield and Windowing Approaches

PMAAs aim at modelling inhomogeneous materials that have periodic microstructures. Infinite periodic phase arrangement which is represented by a periodically repeating unit cell is analysed under the action of far field mechanical loads or uniform temperature fields. A big variation of unit cells exist, ranging from simple periodic arrays of single inclusions to volume elements containing complex arrangements of inhomogeneities. For some simple unit cells as well as for linear behaviour analytical solutions can be derived. Slepyan et al. [155] studied the effective elastic properties of composites consisting of helical inclusions in an elastic matrix using the superposition of fundamental solutions for a homogeneous elastic space (matrix without fibres) together with the constitutive and equilibrium equations for the rods. This work is limited to inhomogeneities of regular shapes and cannot be extended to arbitrary geometries. For more complex phase geometries FE-based homogenisation models are among the most appropriate tools to study the macroscopic mechanical properties of periodic inhomogeneous materials [156, 157]. In periodic microfield analysis three major types of boundary conditions or their combination must be used (periodicity, symmetry and antisymmetry) irrespective of the numerical method employed for solving the equilibrium equations [143].

When applying such boundary conditions is impossible or the volume element is non-periodic, windowing methods should be applied to estimate the macroscopic properties of inhomogeneous materials. Depending on the applied boundary conditions either lower or upper bounds for the overall mechanical behaviour of the material can be estimated. Macroscopically homogeneous stress boundary conditions (statically uniform boundary conditions (SUBC)) lead to lower estimates, whereas macroscopically homogeneous strain

boundary conditions (kinematically uniform boundary conditions (KUBC) lead to upper estimates for the overall elastic tensors of a given volume element. Thus the results of windowing analyses are referred to as apparent (rather than effective) properties. Different combinations of SUBC and KUBC, called mixed uniform boundary conditions (MUBC), result in different estimates for the apparent macroscopic tensors. Pahr and Zysset [14] found a specific set of MUBC applied to the volume element with orthotropic phase arrangement which resulted in the same predictions for the macroscopic elasticity tensor as obtained with periodic homogenisation. Accordingly, they have been referred to as periodicity compatible mixed uniform boundary conditions (PMUBC). It was shown in [158], that PMUBC can be an appropriate tool for estimating the macroscopic elasticity and thermal expansion tensors of periodic and non-periodic volume elements. The biggest advantage of periodic microfield and windowing approaches is that they can estimate macroscopic material properties for unit cells with complex arrangements of inhomogeneities.

Garnich and Karami [159] presented a model of a unit cell containing a wavy fibre subjected to periodic boundary conditions (PBC). The elastic constants of the composite were determined for a range of amplitude-to-wavelength ratios. Bradshaw and Fisher [10, 133] proposed a semi-analytical model combining the FE method (FEM) and analytical micromechanics to examine the influence of CNT's waviness on the reinforcing capabilities of CNTs, being modelled as isotropic cylinders of sinusoidal shape. Symmetry boundary conditions were applied to the RVE containing a single wavy fibre. Schmidt and Tserpes modelled nanotubes as straight, hollow cylinders with transversely isotropic material properties in [160] and with orthotropic properties in [161], in order to elucidate the influence of the interface stiffness and thickness on the effective elastic properties. PBC have been applied to the RVE using constraint equations in opposite faces. Additional parameters such as anisotropy, hollowness of nanotubes, effects of their interface with the matrix as well as dispersion, orientation and aspect ratio distributions can lead to more accurate results for the elastic properties of polymeric composites reinforced with curved CNTs. To the present day, accounting for the complex 3D arrangements of CNTs/CNFs, evident in TEM/SEM images, remains an unsolved issue.

The geometric complexity of volume meshes for CNT/CNF reinforced polymers taxes standard approaches to FEM-based micromechanical models, in which all phase regions are discretised by volume elements and the meshes of the phase boundary surfaces being identical in matrix and reinforcement. Detailed models obtained this way are expensive in terms of computational resources and manpower. Accordingly, simplified procedures are of considerable practical interest. One such approach showing considerable potential are superposition techniques in which matrix and reinforcements are discretised independently and tied together by suitable constraint equations to make up the full model. Embedding options are typically available in major FE codes, e.g. for modelling rebars. Jiang et al. [162] introduced the domain superposition technique

(DST) for simplifying the discretisation of 3D models of woven fabric composites. In the DST the phase regions are meshed separately, the inhomogeneity mesh is embedded in the matrix mesh, and the two meshes are linked by suitable coupling equations. To counteract effects of the geometric overlapping between the inhomogeneities and the matrix, the material properties used for the latter are chosen as the excess stiffness of the fibres compared to the matrix. This concept has been extended to nonlinear matrix behaviour [163], whereas Biragani and Hallett [164] reported employing such a technique for evaluating the full stiffness tensors of weaves. Tabatabaei et al. [28] used a DST-like method that applies the “embedded element” (EE) constraints available in the FE package ABAQUS to the mesoscopic FEM analysis of fibre reinforced composites. A quantitative assessment of the differences in the stress fields and macroscopic stiffness tensors predicted by the full and EE models was presented and good correlation was reported for several case studies: a single cylindrical carbon fibre, irregularly distributed unidirectional carbon fibres, a single crimped yarn with carbon fibres as filaments inside a polymeric matrix, and a 5H satin reinforced composite. Their approach, in which both matrix and fibres are modelled by volume elements, appears to be also applicable to arbitrarily curved CNTs. However, meshing thousands of nanotubes of high aspect ratio with 3D solid elements and coupling them with the matrix tends to constitute a rather complex task [165].

Methods that use beam elements for studying the mechanical responses of CNT based composites can significantly reduce computational cost. Gorski [166] combined beam elements for representing straight or sinusoidally curved, parallel nanotubes with a matrix described by a boundary element method. The resulting two-dimensional (2D) models required no embedding. Harper et al. [29,167] applied beam elements embedded into a matrix to investigate volume elements of composites reinforced with discontinuous straight CNFs, also in a 2D space. Johnson [168] modelled arrays of vertically aligned CNTs, being meshed with linear or quadratic shell elements. In a convergence study of the Young’s modulus, quadratic eight-node elements showed the most consistent behaviour upon increasing the numbers of nodes and elements. Ghasemi et al. [169] investigated the influence of discretisation and approximation errors on the macroscopic behaviour for one type of shell elements.

Chapter 3

Experimental methods

As explained before in Section 2.2, to attain the best utilisation of nanoreinforcements and their properties for composite materials, CNT/CNF must be uniformly dispersed within a polymer matrix. There are several processing methods to disperse nanoreinforcements in polymers dependent on its chemical type, such as: high speed mixing, high-energy sonication, solution-evaporation processing, surfactant-assisted processing through formation of a colloidal intermediate, with or without functionalisation of the CNT/CNF as well as extrusion compounding. Most of these approaches are limited in their scalability, and not amenable to high volumes and high rate productions.

In this study, different CNT and CNF reinforced polymeric composites were produced using a thermosetting epoxy matrix as well as a thermoplastic polymer matrix. The thermoplastic specimens were manufactured by Promolding B.V.⁵, a partner company within the framework of the CONTACT project. The CNF reinforced thermoset matrix was produced by means of a calendaring approach introduced by Gojny [40], commonly known as three roll mill. This machine utilises for mixing high shear stresses created by three adjacent horizontal cylinders, rotating in opposite direction and at different velocities. Because all of the mixture must pass the narrow gap between the rotating cylinders the process uniformly shears the entire volume of the material. Advantages of roll mill machines are that high viscosity mixtures can be milled, and that it is a solvent free and scalable manufacturing process.

Basis for the analytical and numerical modelling approaches presented in the Chapter 4 is a detailed analysis of the microstructure of the CNF/CNT reinforced composites. Microscopy is up to date the most common technique to estimate the quality, quantify the level of dispersion and to observe directly the percolation networks of CNFs and CNTs in composite materials [138]. Different microscopy techniques, namely OLM and TEM, were used to obtain the necessary input for modelling as the information is dependent on the respective length scale.

⁵Jyri Tiisanen, Promolding B.V., The Netherlands

3.1 Composite manufacturing

3.1.1 Thermoset matrix

Samples made of an epoxy matrix (HEXION EPIKOTE 04908) were produced using 0.1, 0.5, 1.5 and 3.0wt% of the CNF Pyrograph III TM, PR-19-LHT-XT supplied by Applied Sciences Inc., Cedarville, Ohio. A commercially available laboratory scale three roll mill (EXAKT 80E), consisting of three chrome-plated hardened steel rolls with a diameter of 80 mm, was used to disperse the CNFs in the liquid epoxy matrix. The mismatch between the angular velocity of adjacent rolls was fixed. The centre roll rotates three times faster than the feed roll and the apron roll (speed is set to 250 rpm) rotates three times faster than the centre roll. As the initial agglomerates were quite large the CNF/epoxy mixture was processed at a gap of 50 μm . Thereafter, the gap was progressively decreased to 30, 20, 10 and 5 μm . At each gap setting the entire volume passed at least 3 times the three roll mill or until a segregation of agglomerates in the feed area could not be observed. At the minimum setting of 5 μm the mixture the three roll mill 10 times.

The different samples were heated up to 50°C in an oven to reduce their viscosity and mixed with the curing agent (Ethacure 100 Curative) using a ratio of 26.4/100. The curing agent was mechanically mixed by means of a clamp-mounted mixer propeller with a hydrofoil propeller at 500 rpm for 5 min. Subsequently, the mixed samples were degassed in a vacuum oven at an absolute pressure of 20 mbar for 10 min. An open silicone mould was used to form rectangular bars with a length of 60 mm, a width of 10 mm and a thickness of 2 mm. After an initial cure at room temperature for 48 h, a post cure cycle of 4 h at 70°C and 6 h at 80°C was employed.

3.1.2 Thermoplastic matrix

Masterbatches are commercially available for a variety of polymers, including polycarbonate (PC), polypropylene, polyamide, polyethylene, and polyether ether ketone. Each masterbatch uses tailored-shear extrusion based on a dispersion analysis to achieve the best performance for each application. A PC masterbatch with Pyrograf-III CNF supplied by Applied Science Inc. was used to injection mould tensile test specimens with 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0wt%. Additionally, PC samples filled with MWNTs (Nanocyl NC7000 produced by CVD) were prepared by the masterbatch dilution method. A PC based masterbatch (PC1501) with 15 wt% of CNTs was diluted with neat PC (Lexan 123R). The dilution was performed with a twin-screw extruder Nanjing Giant SHJ-30, with a screw diameter of 30.5 mm and length diameter ratio of 40:1. A low barrel temperature of 260°C, a screw rotation speed of 590 l/min and a throughput of 11 kg/h was employed to obtain the raw material used to feed the injection moulding machine. The extruded strand was quenched in a water bath and chopped to pellets.

The specimens studied were injection moulded with an ENGEL ES 330/80 HLS.

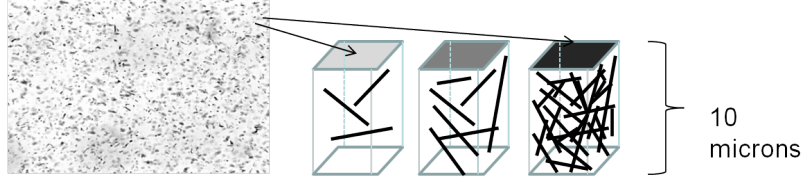


Figure 3.1: Schematic depiction of the relationship between pixel colour and local volume fraction

As aforementioned in Section 2.2.2, a low injection speed and a high melt temperature result in a low electrical resistivity. The thermoplastic specimens were manufactured by Promolding B.V. with the objective to obtain a high electrical conductivity. Therefore, the injection moulding process conditions for producing the specimens were: an injection speed of 10 mm/s, a melt temperature of 300°C, a holding pressure of 450 bar and a time of 8 s, the back pressure was 22 bar, the screw rotation speed 240 1/min, and the cooling time 30 s. One complete cycle in the applied process took 49 s. The actual mould temperature was measured to be 90°C, the cooling medium used was water. The injection speed of 10 mm/s corresponds to a volume flow rate of 9.62 cm³/s and a flow velocity of 241 mm/s at the centre of a part with a cross-section of 10 mm x 4 mm. The holding and back pressure values given above were the specific pressure values induced by the retractable screw head on the polymer melt.

3.2 Microscopic characterisation

3.3 OLM

All prepared composite samples were analysed on the microscale using OLM to quantify the level of dispersion of the nanoparticles. Slices with a thickness of 10 μm for the CNF/epoxy and 5 μm for the CNT/PC were cut using a microtome (Leitz 1401) with glass knives. The thickness of CNF/PC samples was 10 μm as thinner slices broke constantly in pieces. Optical micrographs (1280 x 1024 pixels, total resolution 1 pixel=0.132 μm) were taken with a OLM Olympus BH2 with a 50x magnification and a digital Leica camera DFC 280 with a 1.67x magnification. The sliced samples were partitioned on average into 15 columns and 10 rows, resulting in 150 micrographs per sample.

Although OLM doesn't allow a characterisation of individual nanoparticles due to the scale size their spatial arrangement, the dispersion and distribution, can be determined [13, 66, 139, 170, 171]. The level of grey in the obtained micrographs can be correlated with the quality of dispersion, as each pixel gives information about the amount of CNT/CNF contained in it. Two methods are generally used to obtain an estimate of the level of dispersion. The first utilises the shape of grey scale distribution histograms by calculating a ratio of the variance/mean of the grey scale values [170].

The narrower the grey scale distribution, the smaller is the variance and the better the level of dispersion. This method provides quantitative information about the distribution of the local volume fraction, which can be implemented as input data for modelling. One way to implement the obtained information is to relate the pixel colour with the local volume fraction as depicted in Figure 3.1. The other method makes use of geometric properties such as the number and area of darker pixels, which are related to agglomerated nanoparticles. Hence, a dispersion index, defined as the correlation between agglomerated area to total investigated area and volume fraction, can be calculated. Villmow et al. [13] and Leblanc et al. [172] showed that in this way the level of dispersion can be estimated and statistically quantified at the microscale.

Moreover, due to differences related to variations of the exposure time for different concentrations, external light, effects of the microtome's knives, absolute values cannot be obtained. Therefore, to investigate the influence of dispersion a binarising method is proposed to calculate the area distributions of agglomerates that are clearly seen on the images. The rest of the grey background is assumed to be uniform. For this purpose a threshold level, which is a normalised intensity value in the range $[0, 1]$, was computed to convert the grey scale images into binary images (see Figure 3.2).

The resulting black and white image replaces all pixels in the input image having a grey value greater than the threshold with the value 1 (white) and replaces all other pixels with the value 0 (black). The latter, which corresponds to the left tail in the histograms, are taken to represent the agglomerates (Figure 3.3).

All agglomerates with a diameter less than the length of a CNF/CNT were filtered out. Thereafter, the number and the area of all agglomerates were calculated using the open source program ImageJ. The volume fraction of the agglomerated nanotubes can be estimated from the ratio of the agglomerates' surface area to the total area of the image [173]. Assuming that agglomerates have spherical shapes and are completely packed with nanotubes, a reference values for the most negative case due to agglomerates is obtained. Hence, the 3D microstructure representing a two-phase composite can be reconstructed (see Figure 3.4), in which the reinforcement phase consists of agglomerates and the matrix is an isotropic medium made of polymer and perfectly dispersed nanotubes.

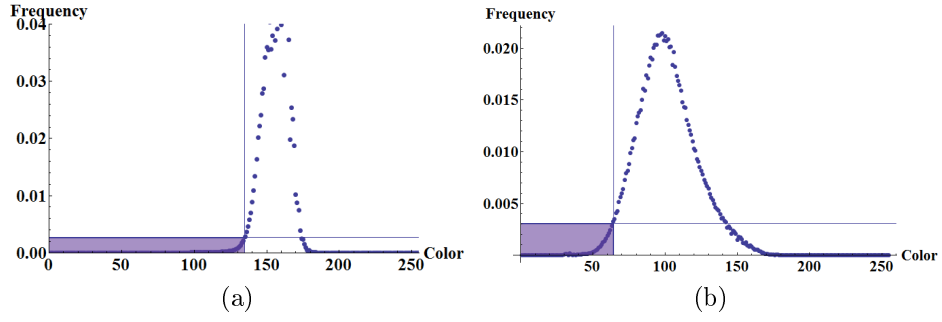


Figure 3.2: Examples of grey scale histograms of CNT/PC specimens: 1wt% with a threshold of 136 (a) and 7wt% with a threshold of 65 (b)

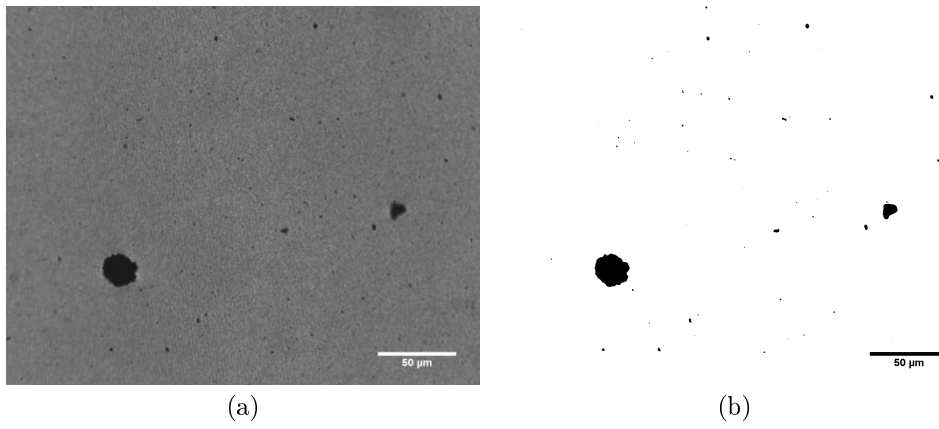


Figure 3.3: Micrograph of CNT/PC specimens with 2wt% (a) and corresponding binarised image (b)

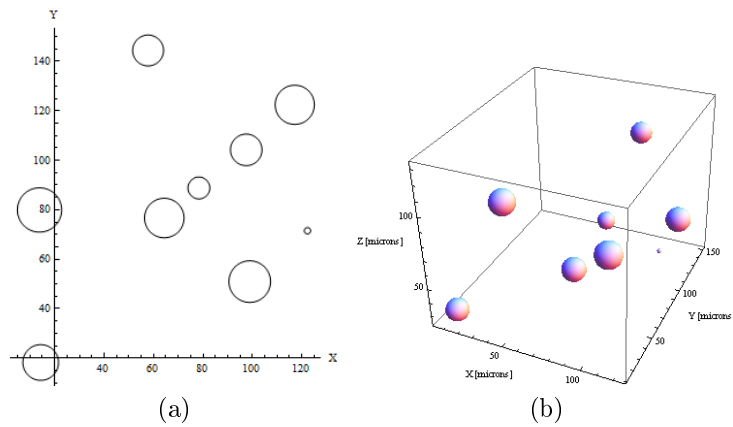


Figure 3.4: Reconstruction of agglomerates in two-phase composite: projection onto 2D plane (a) and depiction in 3D space (b)

3.4 TEM

Furthermore, in order to analyse the aforementioned CNT filled PC samples on the nanoscale and to obtain information about the orientations and 3D curved geometries of the MWNTs TEM was performed⁶. The tensile test specimens of dog-bone shape were sectioned in the centre of the narrow part in the longitudinal (along the injection flow) and in the transverse (perpendicular to the injection flow) directions in slices of 100 nm using an ultramicrotome (Leica ultracut UCT) with a diamond knife. A calibration was performed to obtain a relationship between “nm” and “pixel”.

As outlined in Section 2.3, Fan et al. [8] employed TEM to characterise the orientation of a nanotube by a unit vector placed in the average direction of its length. In this way probability distribution functions of the orientation angle could be obtained. Due to the length scale of TEM images only parts of a CNT reinforced composite can be analysed. The thickness of a sliced sample and thus the visible length and geometry is only a fraction of its actual length and shape. However, the orientation and curviness distributions are sufficient to model CNTs in the 3D space. In order to investigate the influence of the nanotubes’ 3D curved geometries and orientations on the effective mechanical properties a methodology was developed to numerically reconstruct the morphological characteristics. The following definitions and assumptions were used:

1. The geometry of each nanotube can be described by a number of spiral-shaped segments of different pitch and radius that are joined together continuously to make up the tube’s centreline.
2. TEM images of slices along the flow and normal directions show projections of the nanotubes onto the XY- and YZ-planes, respectively (see Figure 3.5(a) and (b)). The X-direction is the main direction of the injection flow, the Y-direction is the in-plane transverse direction and the Z-direction corresponds to the out-plane-direction.
3. Each curve segment in the XY- and YZ-planes can be treated as a projection of a spiral of one pitch, which is a part of an entire nanotube.
4. The “director line” of a projected nanotube is defined as a line between its end points, passing through the centre of mass (see Figure 3.5 and Table 3.1).
5. The maximum distance between the projections of points of curves in the XY- and YZ-planes onto the director defines the projections of pitches: h_{XY} and h_{YZ} for a given spiral segment. Here h_{XY} is the projection of the spiral’s pitch onto the XY-plane and h_{YZ} is the projection of the spiral’s pitch onto the YZ-plane.

⁶Experiments performed at the Research Institute for Technical Physics and Materials Science, Hungarian Academy of Science, Budapest, by Bernadeth Kiss-Pataki, a colleague in the CONTACT project

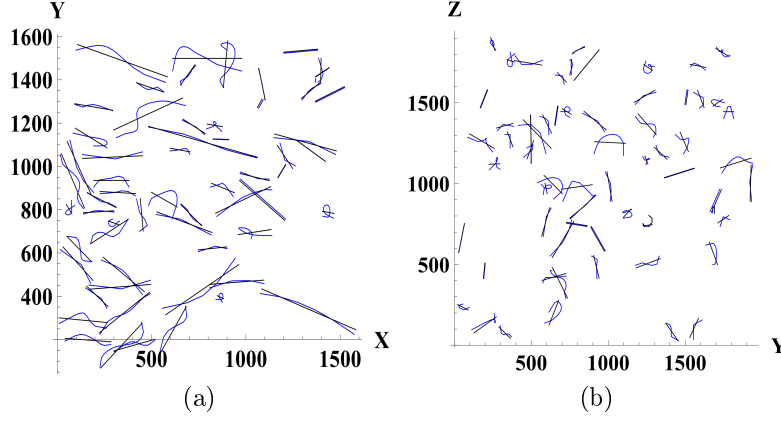


Figure 3.5: Examples of directors (grey) and centrelines (blue) of nanotubes in a tensile specimen with 2wt% CNT: projection onto XY-plane (a) and projection onto YZ-plane (b)

6. The radius is the maximum distance between the director and the points on the spiral, where a_{XY} is the radius of the projection of the spiral segment onto the XY-plane and a_{YZ} is the radius of the projection onto the YZ-plane.
7. The total spiral radius a is the maximum of the radii a_{XY} and a_{YZ} .
8. The direction of the director in the XY- and YZ-planes defines the orientation of each projected nanotube, described by the angle θ , see Equation 3.1 and Figure 3.6. ϕ is the angle between the X-axis and the nanotube projection onto the XY-plane, whereas α is the angle between the Y-axis and the nanotube projection onto the YZ-plane.
9. If $\theta \in [45^\circ, 135^\circ]$ then $h = \frac{h_{XY}}{\sin \theta}$ and if $\theta \in [0^\circ, 45^\circ] \cup [135^\circ, 180^\circ]$ then $h = \frac{h_{YZ}}{\cos \theta}$.

$$\theta = \arcsin \frac{h_{XY}}{\sqrt{h_{XY}^2 + (h_{YZ} \sin \alpha)^2}} \quad (3.1)$$

To verify the aforementioned definitions and assumptions, several spiral geometries of known pitch, radius and orientation were projected onto the XY- and YZ-planes, and h_{XY} , h_{YZ} as well as a_{XY} , a_{YZ} were calculated. The main pitch and radii were reproduced, according to items (7) and (9) in the above list. Minor differences between the input data and the calculated results were found, as shown in Table 3.1.

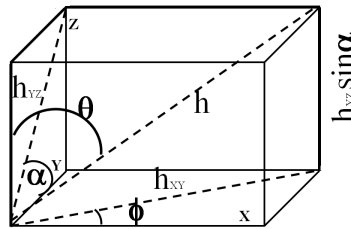
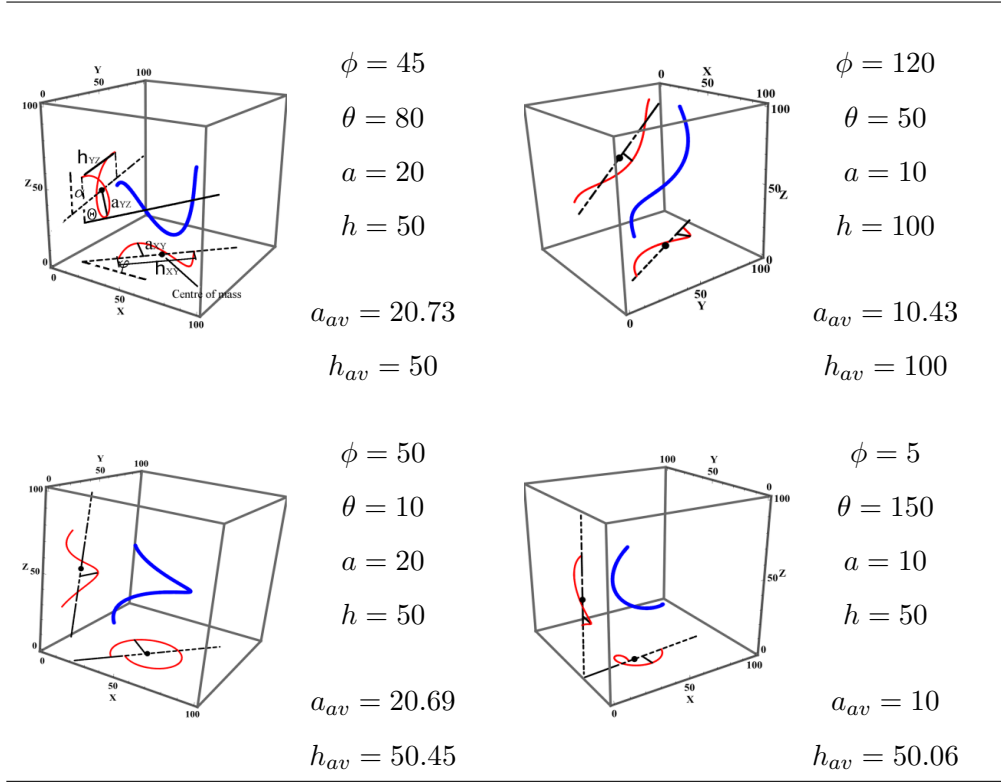


Figure 3.6: Coordinate system and definitions of angles α , ϕ and θ

Table 3.1: Reconstruction of spiral geometries (blue) from their projections (red)



3.5 Tensile testing

Quasi-static tensile testing was performed to obtain validation data for the analytical and numerical models. A displacement-controlled universal testing machine (Zwick/Roell Z005) capable of loading 5 kN was used. The cross-head loading rate was held constant at 2 mm/min following the ASTM D 638 - 03 test method [174]. The dog bone shape of the specimens and their dimensions were defined by the respective manufacturing process, and were measured prior to testing. The measured test data were used to calculate the longitudinal modulus of elasticity as well as the ultimate tensile strength and strain.

3.6 Flexural testing

Three-point bending tests were performed according to the ISO standard 178 [175] to analyse the influence of different weight fractions on the flexural behaviour of CNF/epoxy

nanocomposites. The INSTRON 4505 testing machine was used together with a 50 kN load cell. Standard dimensions, a specimen width of 10 mm and a length of 80 mm, were used. Four weight fractions with five specimens in each case were loaded at a test speed of 2 mm/min until failure occurred. Stress-strain details were taken to determine the maximum flexural load, the flexural stress as well as the flexural modulus.

Chapter 4

Modelling

The following chapter presents and explains various analytical and numerical modelling approaches conducted in this thesis work. CNF/CNT can show straight or curved shapes, CNT can be either single-walled or multi-walled, both nanoparticles can have different radii and lengths, and may have a wide range of orientation and spatial distributions in the matrix. All these factors complicate simulations of the effective mechanical responses of CNF/CNT reinforced composites. The concepts of statistical and representative volume elements allow investigating these parameters one by one or in groups by choosing appropriate unit cells. In Section 4.1 simplified geometries were created first and analysed to assess the influence of different geometric parameters and the capabilities of different numerical techniques for predicting the effective elastic stiffness tensor. In Section 4.2 arbitrary composites, based on distribution functions obtained from experiments, are analytically and numerically studied.

Beforehand it is important to note that the volume fraction, also called concentration in this thesis, of any phase is defined as

$$c_p = \frac{\Omega_p}{\sum_k \Omega_k} \quad (4.1)$$

where k and p are indices which represent all the phases as well as Ω_k and Ω_p which denote volumes related to phases k and p , respectively. For the special case of matrix-reinforcement topologies with only one type of inclusion the subscript r refers to the reinforcement, and the subscript m to the matrix, which are related to each other as $c_m = 1 - c_r$.

4.1 Preliminary studies

4.1.1 Influence of waviness and curliness on mechanical properties

Microscopy analyses of the composites' structure at the nanoscale showed that CNT tend to have strongly curved shapes. This may be due to high aspect ratios, the as-

sociated low bending stiffness, and to surface defects that are introduced during the synthesis of carbon nanotubes. To improve the understanding of the behaviour of such fibrous reinforcements, it is essential to develop models taking into account wavy and curly fibre geometries. Molecular dynamics and *ab initio* methods can give accurate results and describe phenomena at the nanoscale, but they are very computationally expensive. In contrast, analytical micromechanical models can give low-cost but coarser approximations. Based on mean field approximations they can be applied to simulate the macroscopic behaviour of composite materials. When such analytical solutions cannot be obtained easily or more detailed information is required on the meso- or macroscales, then FE-based homogenisation can be applied. Due to the very high aspect ratios of nanotubes, approximating their geometry with continuum solid elements is rather computationally expensive. Alternatively, CNT can be modelled as beam elements that are linked to the solid elements describing the matrix via the embedded element technique [29, 167], providing an attractive combination of accuracy and computational costs. Spanos and Esteva [134] used beam elements embedded into matrix to study the influence of entangled and non-straight fibres on the effective elastic and thermal properties of polymer nanocomposites. The RVE contained fibres presented as sequences of segments joint together. Their approach is based on generating random microstructures by Monte Carlo simulation and computing the effective properties depending on the microstructural parameters. The problem was solved in a 2D space.

In this Section⁷ parametric studies were employed to relate different fibre geometries in nanocomposites and investigate the influence of CNT curviness in the framework of analytical and numerical continuum micromechanics. For validation of the proposed approaches, normalised predictions of the effective elastic modulus were compared with MD simulations. Only the effect of the nanotubes' curviness was investigated in detail, but the analysis can be further extended to hollow nanotubes with anisotropic properties and with interphases or imperfect interfaces. For numerical simulations this can be achieved, e.g. by introducing extra layers with appropriate properties around the fibres, and in analytical models by substituting curved, hollow inclusions with solid cylindrical inhomogeneities having effective properties.

Analytical model

The relation between the average and the local behaviour is a well-known problem in micromechanics of composites. Continuum models for the mechanical properties of multi-phase composite materials replace the latter by homogeneous reference media. The present work was concerned with the case of two-phase materials, viz. polymers with embedded, stiff, curved, cylindrical inhomogeneities of some given aspect ratio. Therefore, the reinforcement phase typically introduces macroscopic anisotropy, which

⁷Section is reproduced with adaptations from "A.Y. Matveeva, S.V. Pyrlin, M.M.D. Ramos, H.J. Böhm and F.W.J. van Hattum. Influence of waviness and curliness of fibres on mechanical properties of composites. Computational Materials Science, 87:1 - 11, 2014"

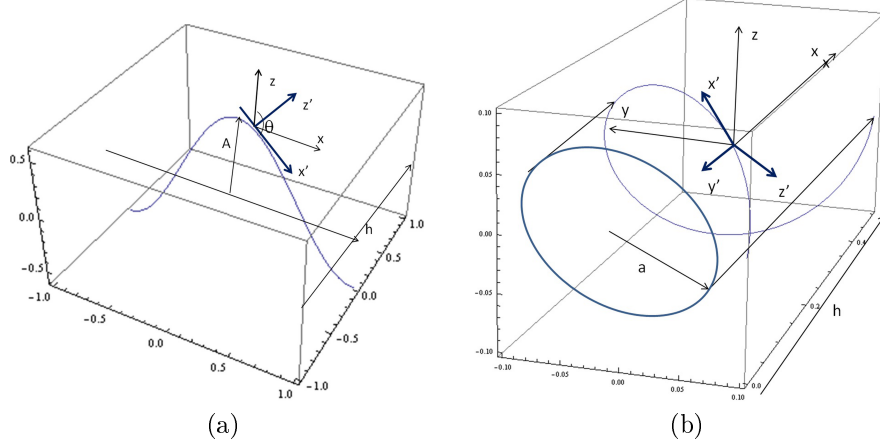


Figure 4.1: Representations for sinusoidally (a) and helically (b) curved nanotubes

means that averaging processes must account for the complex geometry of that phase. Following the analytical approach proposed by Hsiao and Daniel [152] the effect of CNT waviness was investigated using a micromechanical framework based on Eshelby's theory of equivalent inclusions [145] and on the Mori-Tanaka theorem of average stresses in the matrix [144]. The analytical model is described in detail in Appendix A. Two idealised types of curviness for the nanotubes were considered, 2D sinusoidal (Equation 4.2) and 3D helical shapes (Equation 4.3) as shown in Figure 4.1. Both microstructures were assumed to be periodic, so that it was sufficient to consider only one period for studying their macroscopic stiffness.

$$\begin{cases} x = t \\ y = 0 \\ z = A \cos \frac{2\pi t}{H} \end{cases}, t \in [-1, 1] \quad (4.2)$$

$$\begin{cases} x = \frac{ht}{2\pi} \\ y = a \sin t \\ z = a \cos t \end{cases}, t \in [0, 2\pi] \quad (4.3)$$

Here A stands for the amplitude of the sine, H for the wave length of the sine, a is the radius of the helix and h is its pitch. A waviness parameter, defined as $w = A/H$ for sinusoidal inhomogeneities and as $w = a/h$ for spirals, was used for comparing 2D and 3D curved fibre geometries.

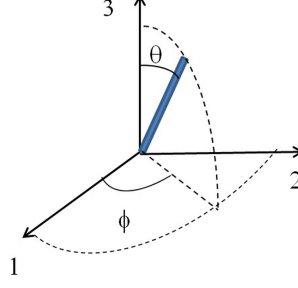


Figure 4.2: Coordinate system of inhomogeneities and definitions of angles θ and ϕ

The inhomogeneities were divided into segments of large aspect ratio, each segment being characterised in space by two angles, as presented in Figure 4.2. The elastic tensor was calculated for each segment in the local coordinate system (i.e. with an orientation tangential to the segment), then the coordinate transformations to the global system were applied, and finally orientational averaging was carried out by integrating over all orientations occurring along the path of the fibre, resulting in the macroscopic stiffness.

In the local coordinate system the effective elasticity tensor of a dilute composite can be written as [148]

$$C = C_m + c_r (C_r - C_m) A_r^{NI} \quad (4.4)$$

with

$$A_r^{NI} = (I + P S_m (C_r - C_m))^{-1} \quad (4.5)$$

Here A_r^{NI} is the non-interacting (or dilute) inhomogeneity strain concentration tensor, P is the Eshelby tensor related to the geometry of the inclusion, I is the rank four unit tensor, C is the elasticity tensor, S is the compliance tensor, c_r is the volume fraction of the reinforcement, and the subscripts r and m refer to the reinforcement and matrix phases, respectively. This approximation of the effective elasticity tensor is only valid for small concentrations of inhomogeneities. For the low fibre volume fractions considered here, non-interacting (Eshelby) solutions are essentially identical to the Mori-Tanaka results actually shown. The components of the Eshelby tensor were given, e.g. by Mura [146] for different inclusion geometries. For an infinitely long circular cylinder ($r/a_3 \rightarrow 0$) its components are

$$\begin{aligned} P_{2222} = P_{3333} &= \frac{5-4\nu_m}{8(1-\nu_m)} & P_{2121} = P_{3131} &= \frac{1}{4} \\ P_{2233} = P_{3322} &= \frac{4\nu_m-1}{8(1-\nu_m)} & P_{2323} &= \frac{3-4\nu_m}{8(1-\nu_m)} \\ P_{2211} = P_{3311} &= \frac{\nu_m}{2(1-\nu_m)} & P_{1111} = P_{1122} = P_{1133} &= 0 \end{aligned} \quad (4.6)$$

where ν_m denotes the Poisson's ratio of the matrix.

A_r^{NI} and C are the dilute inhomogeneity strain concentrator and the stiffness tensor in the local coordinate system, respectively. To obtain the stiffness tensor in the global coordinate system it is necessary to average the properties over the angles θ and ϕ , which can be expressed in a parametric way through the parameter t as

$$\iint_{\Delta} \bullet d\phi(t) d\theta(t) \rightarrow \int_t \bullet dt \quad (4.7)$$

where Δ is the range of the angles ϕ and θ , respectively. For spiral and wavy inclusions the parametric equations take the forms according to Equation 4.8 and 4.9, respectively.

$$\begin{cases} t \in [0, 2\pi] \\ \theta = \arccos \frac{-w \sin t 2\pi}{\sqrt{1+4\pi^2 w^2}} \\ \phi = \arcsin \frac{w \cos t 2\pi}{\sin \theta \sqrt{1+4\pi^2 w^2}} \end{cases} \quad (4.8)$$

$$\begin{cases} t \in [-1, 1] \\ \theta = \arccot \cot -A\pi \sin \pi t \\ \phi = 0 \end{cases} \quad (4.9)$$

The orientational average of the elasticity tensor $\langle C(t) \rangle$ can be evaluated as

$$\langle C(t) \rangle = \int_t \bar{C}(t) dt \quad (4.10)$$

Here $\bar{C}(t)$ is the transformed stiffness tensor in the global coordinate system $\{X, Y, Z\}$ defined as

$$\bar{C} = [T] C [T^*]^{-1} \quad (4.11)$$

where $[T^*] = [W] [T] [W]^{-1}$ is the rotation matrix of the engineering strain components with $[W]$ being the transformation matrix between the engineering strain and strain tensor, and $[T]$ is the rotation matrix. In this model wavy and helical fibres were described by unconnected fibre segments having orientation distributions equivalent to that of the actual reinforcement. The main advantage of this analytical approach is that it enables a fast approximation of the full elasticity tensor of heterogeneous materials with arbitrarily reinforcement shapes, while the experimental measurement of the full multi-axial responses is a complicated task.

The selection of input data for the material properties of nanotubes is an open question. As explained in Section 2.1.4, according to experimental investigations of MWNT produced by CVD their Young's modulus can range from 10 GPa to 450 GPa, depending on the presence of defects and the nanotubes' aspect ratio. The Young's moduli and Poisson's coefficients of the reinforcement described as isotropic solid and

Table 4.1: Material properties used for calculations

Constituent	E	ν
	[GPa]	
$c_r = 0.01\%$, aspect ratio=infinite		
MWNT	300	0.3
Matrix	2.4	0.3

Table 4.2: Dimensions of volume elements and inhomogeneities

Curviness parameter	Sinusoidal inclusion			Helical inclusion		
w	A	H	r	a	h	r
0.05	0.1		0.0354	0.1	2	
0.062	0.125		0.0351	0.125	2	
0.08	0.16	2	0.0347	0.169	2.1	0.0356
0.093	0.187		0.0344	0.2	2.14	
0.125	0.25		0.0335	0.28	2.24	
0.2	0.4		0.0314	0.5	2.5	

the matrix phase used for the calculations are presented in Table 4.1.

FE-based homogenisation

FE models were used for numerically computing the effective elastic stiffness tensors of composites reinforced with aligned, sinusoidal and spiral nanotubes. The aspect ratio of the inclusions was set to infinity as nanotubes are known for their high aspect ratio (≥ 100). This approximation also allows relatively small volume elements to be used. It was assumed that the nanotubes have a solid circular cross-section, which is perpendicular to their centreline and follows a sinusoidal or helical curve. This representation of the nanotubes introduced symmetries that support using periodic models, the volume element containing a single wave of a sinusoidal inhomogeneity or a single pitch of a helical inhomogeneity. The size of the volume element and the radius of the inhomogeneity were chosen such that the volume fraction is equal to 0.1% (see Table 4.2). Since micromechanical models of this type do not have an absolute length scale, actual units of length do not play a role. The FE code ABAQUS/Standard and the associated pre-processor ABAQUS/CAE were used.

Two types of FE were employed for representing CNTs: beam elements and 3D solid elements. The former type of model makes use of an embedded element technique [29, 167], a structured volume mesh being used for the matrix to which the degrees of freedom (DoF) of the beams are connected by suitable constraint equations. Compared to unit cells using continuum elements for both constituents, this technique markedly reduces the effort in pre-processing. However, it is subject to limitations in describing the interactions of the constituents under transverse loading and in correctly representing phase volume fractions, the beam elements being overlaid on the solids in the model. Therefore, the present work explored some of these issues for the regime of low volume fractions. In addition, different sets of boundary conditions were considered to account for the periodicity of the structure.

The volume averages of the strains and stresses of a suitable volume element of a heterogeneous material are denoted as $\langle \varepsilon \rangle$ and $\langle \sigma \rangle$. The elastic compliance and stiffness tensors, S and C , are then given by the relations

$$\langle \varepsilon \rangle = S^{app} \langle \sigma \rangle \quad (4.12)$$

$$\langle \sigma \rangle = C^{app} \langle \varepsilon \rangle \quad (4.13)$$

Here S^{app} and C^{app} are the apparent elastic tensors, which approach the effective compliance and stiffness tensors, S^{eff} and C^{eff} , as the volume element approaches a RVE. Accordingly, depending on the geometry of the volume element and on the boundary conditions applied to it, “apparent” or “effective” overall stiffness tensors can be computed.

In 1963 Hill [176] showed that if the stress and strain fields, σ and ε , of an elastic, inhomogeneous material satisfy the relation

$$\langle \sigma : \varepsilon \rangle = \langle \sigma \rangle : \langle \varepsilon \rangle \quad (4.14)$$

the necessary and sufficient conditions are fulfilled for the equivalence between the energetically and mechanically defined properties of elastic materials. Equation 4.14 is satisfied by four different types of boundary conditions [14, 158]:

1. Homogeneous displacement boundary conditions (Dirichlet, kinematic),

$$u(x) |_{\partial V} = \varepsilon^0 x, \nabla x \in \partial V \quad (4.15)$$

2. Homogeneous traction boundary conditions (Neumann, static),

$$t(x) |_{\partial V} = \sigma^0 n, \nabla x \in \partial V \quad (4.16)$$

3. Orthogonal mixed displacement-traction boundary conditions,

$$\left(t(x) - \sigma^0 n\right) \left(u(x) - \varepsilon^0 x\right) = 0, \nabla x \in \partial V \quad (4.17)$$

4. Periodicity boundary conditions.

Here σ^0 and ε^0 are constant stress and strain tensors prescribed a priori on the volume element, ∂V is the element's boundary, and t , u , n , x are the traction, displacement, normal and position vectors, respectively.

Hazanov and Huet [177] proved that the effective elasticity tensor as well as apparent elasticity tensors based on mixed BC always lie between the apparent elasticity tensors computed with uniform static and kinematic boundary conditions. Pahr and Zysset [14] proposed a specific set of uniform mixed boundary conditions and showed that - for periodic microgeometries of orthotropic or higher elastic symmetry - it gives rise to apparent elastic tensors that correspond to results obtained with PBC. Therefore, PBC and PMUBC were additionally compared for composites reinforced by aligned wavy and helical CNT.

PBC can be applied in FE analyses by subjecting pairs of homologous nodes, which occupy corresponding positions ξ on pairs of opposite faces of the volume element, to constraint conditions of the type

$${}^{k^+}u(\xi) - {}^{k^-}u(\xi) = \varepsilon^0 \Delta^k \xi \quad (4.18)$$

Here u is the displacement vector, ε^0 is a constant strain tensor describing the macroscopic behaviour of the volume element, and $\Delta^k \xi$ is a constant distance vector between pairs of opposite surfaces k^+ and k^- . Subjecting the volume elements shown in Figure 4.4 to PBC allows for periodic square arrangements of the sinusoidally or helically curved CNTs.

Referring to Figure 4.3 and to Figure 4.4, the directions 1, 2 and 3 correspond to the longitudinal and transverse directions of the arrangements, respectively. The periodic volume elements (or unit cells) are cubes with the side length h and contain a single period of a sine-shaped or a single pitch of a helical inhomogeneity, see Figure 4.4. For a periodic homogenisation node SWB, see Figure 4.3, is locked, nodes SEB, NWB and SWT function as “master nodes” controlling the macroscopic displacements of the East, North and Top faces, respectively, and the boundary conditions of the other surface nodes follow Equation 4.18, ensuring that opposite faces of the unit cells deform in a compatible way. Loading by normal stresses was implemented by applying normal concentrated forces in the 1-, 2- and 3-directions to the master nodes SEB, NWB and SWT. In addition, three simple shear load cases were set up by subjecting the master nodes to suitable tangential concentrated forces. For each of the above load cases the volume averaged stress components were linked to the prescribed concentrated forces via the appropriate cross-sectional areas of the unit cell. Results were obtained in the form

of the displacements of the master nodes, which in combination with the edge lengths of the unit cell allow extracting the volume averaged strain components. Detailed relations between master node forces/displacements and volume average stresses/strains are given in [178].

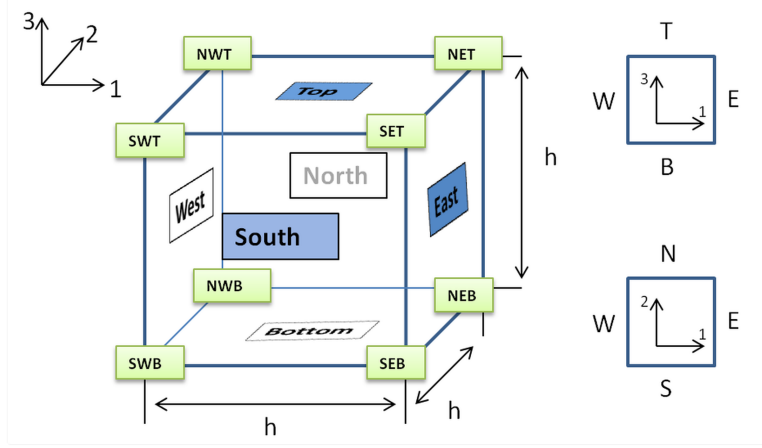


Figure 4.3: Notation of the faces (North, South, East, West, Top, Bottom) of a volume element [14]

When PMUBC are used six analogous linearly independent load cases were applied via “boundary vectors”, two examples of which are listed in Table 4.3. For a complete listing of boundary vectors and an in-depth discussion see Pahr and Zysset [14]. For this type of analysis the phase averaged stress components were evaluated from volume weighted sums of the appropriate integration point values. PMUBC have the advantages of being capable of handling non-periodic face arrangements and of not being based on compatible meshes on opposite faces of periodic unit cells, which greatly facilitates the meshing of volume elements, as nodes on opposite faces are not required to use homologous meshes. PBC, however, allow linear perturbation analysis to be used in ABAQUS/Standard, so that the FE system matrix must be inverted only once for the six load cases.

Table 4.3: Matrices of boundary vectors for the load cases “Tensile 1” and “Shear 13”

Tensile 1				Shear 13		
	East	North	Top	East	North	Top
e_1	$u_1 \neq 0$	$t_1 = 0$	$t_1 = 0$	$t_1 = 0$	$t_1 = 0$	$u_1 \neq 0$
e_2	$t_2 = 0$	$u_2 \neq 0$	$t_2 = 0$	$u_2 = 0$	$u_2 = 0$	$u_2 = 0$
e_3	$t_3 = 0$	$t_3 = 0$	$u_3 \neq 0$	$u_3 \neq 0$	$t_3 = 0$	$t_3 = 0$

In the models describing the CNTs with solid elements, matrix and nanotubes were discretised by meshes using 20-node brick elements with quadratic shape functions (C3D20), as they are known to be the best elements for linear elastic calculations [179]. The CNTs were modelled as solid cylinders (see Figure 4.4). In the models describing the nanotubes via three-node Timoshenko beam elements (B32), the matrix is discretised by structured, regular meshes using C3D20 as well. The beam elements of the nanotubes were linked to the matrix mesh by multi-point constraints (MPC) [29, 167]. Since beams are structural elements with rotational degrees of freedom, appropriate constraints have to be applied to these DoF in implementing PBC. Also, provision must be made for explicitly accounting for the beams' contributions in numerical volume averaging. Furthermore, it is worth noting that in this type of model the elements describing CNT and matrix are physically overlaid on each other, introducing an approximation in terms of the phase volumes into the models. The resulting errors are minor at low volume fractions considered here, but must be explicitly accounted for at elevated fibre contents.

The solutions of the above six linearly independent load cases, obtained either using PBC or PMUBC, provide six pairs of phase averaged stress and strain tensors. These allow setting up 36 equations, from which the 36 elastic constants making up the macroscopic elasticity tensor can be obtained. The ILSB in-house software MedTool was used, on the one hand, for generating the boundary conditions and load cases and, on the other hand, for extracting the elastic tensors.

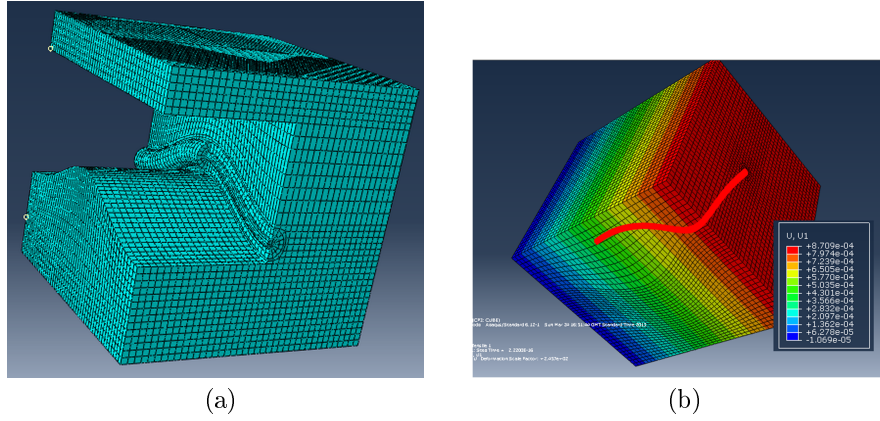


Figure 4.4: Sinusoidal (a) and helical (b) inclusions meshed with solid elements

Molecular dynamics modelling

To investigate the effects of curved nanotubes on the composites' mechanical properties via molecular dynamics, CNTs in the shape of sine-like waves (Figure 4.5) or helices

(Figure 4.6) of different curvature were embedded in a polymer matrix.⁸ In all cases a 13.2 nm long section of a (9,0) CNT (diameter ~ 0.7 nm) was used. The PC matrix was modelled by some 50-300 Bisphenol A (BPA) PC molecules and 5-60 BPA blocks in length, resulting in a CNT volume fraction of approximately 0.4%. The overall number of atoms in the model was kept at some 50 000 due to computational limitations.

Composite models were prepared by random allocation of initial polymer molecules in a sparse box, which was reduced during the MD simulation of the evolution of the polymer chains at $T \sim 500$ K in the course of $\sim 1\text{-}3 \times 10^6$ time steps (1 time step ~ 0.2 ps) under PBCs until the experimentally observed PC density of 1.2 g/cm^3 was reached [180], followed by box relaxation. A DREIDING force field [181] was used to describe interatomic forces. Simulations were conducted using the LAMMPS MD package [182]. After initial “sample preparation” each sample was subjected to simulated expansion and contraction in each direction at an effective rate of 2% per 105 time steps. After collecting the strain-stress data fitting with linear relations was used for extracting the elastic constants. For pure polycarbonate a Young’s modulus of 2.33 ± 0.13 GPa was obtained, which is in good agreement with typical experimental values of 2.1-2.4 GPa [180]. For single straight carbon nanotubes the Young’s modulus along the tube axis was evaluated as 2 TPa, which is within the range of experimentally observed values [183].

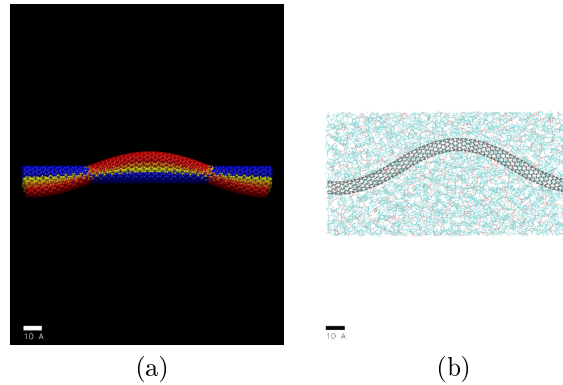


Figure 4.5: MD model of nanotube of sinusoidal shape [15]

⁸Simulations performed at the Physics Department, University of Minho by Sergey Pyrlin, colleague in the CONTACT project

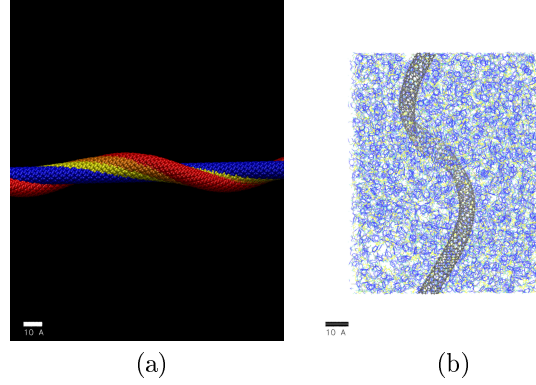


Figure 4.6: MD model of nanotube of helical shape [15]

4.1.2 Influence of curviness and segment number per CNT on mechanical properties⁹

Even though the use of beam elements, as proposed in Section 4.1.1, significantly reduces computational time compared to solid elements for RVEs with high concentrations of nanotubes the number of elements can be a limiting factor. Therefore, in the next step a semi-analytical model, described in the following Section, was proposed, which combines FE-based models and the analytical micromechanical Mori-Tanaka method. It is assumed that a higher volume fraction can be related to a more distinct curviness and thus to a higher number of segments per CNT which affects the concentration tensors and the overall mechanical behaviour. Consequently, in the first step single CNTs with different, increasing segment numbers, corresponding to increasing volume fractions, were modelled and their concentration tensors were calculated. In the second step the numerically computed stress/strain concentrations tensors were implemented in the Mori-Tanaka model, described in detail in Appendix A.3, to calculate the final stiffness matrix. In order to validate this semi-analytical method the aforementioned beam element procedure was used to model the arbitrarily curved CNT reinforced polymeric composites.

Numerical models

3D finite beam-element models of arbitrarily curved nanotubes were created to compute numerically the effective elastic stiffness tensors of the composite. Using Monte Carlo simulations nanotubes with concentrations from 0.5% up to 7% by weight fraction were distributed in a cube-shaped volume element as sequences of segments joined together at randomly chosen angles. The number of tubes for each concentration was kept constant at 500, the size of the RVE being adapted to achieve the required volume fractions. The aspect ratio of the reinforcement was set to 166, a value corresponding to MWNT with

⁹Section is reproduced with adaptations from “A.Y. Matveeva, H.J. Böhm and F.W.J. van Hattum. Semianalytical stiffness tensor approximation for polymers reinforced with curved nanotubes. Proceedings of Composites week @ Leuven and TEXCOMP-11 Conference, 2013”

Table 4.4: Mesh parameters and number of segments per CNT versus volume fraction

w	w_r	c_r	RVE length	No. of seeds	No. of segments
		[%]		per cube edge	per CNT
1	0.5	0.29	282	48	2
2	1	0.57	225	38	3
3	2	1.15	178	30	5
4	3	1.74	155	26	7
5	5	2.92	130	22	9
6	7	4.12	116	20	12

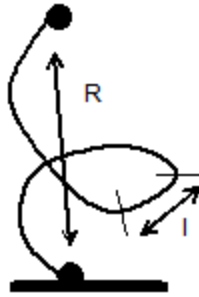


Figure 4.7: CNT represented as sequence of straight, joined segments

a length of $1.5 \mu\text{m}$ and a diameter of 9 nm . Since micromechanical models of this type do not have an absolute length scale, actual units of length do not play a role. The matrix was discretised by structured, regular meshes using C3D20 brick elements. The nanotubes were meshed with B32 beam elements and were embedded into the matrix using MPC. The FE code ABAQUS/Standard and the preprocessor ABAQUS/CAE were used. A mesh size of 5 units was employed for all cases in order to reduce the influence of mesh size on the results' trends. In Table 4.4, the numbers of seeds per edge of the RVE size are given for different sizes of the RVE. The number of solid elements increases with the cube of the latter parameter.

The last column in Table 4.4 relates to the number of segments per nanotube. Flexible nanotubes with random kinks can be regarded as chains of almost straight segments, and the average number of segments N per nanotube (or the effective length of segments l) can serve for characterising the “waviness”, see Figure 4.7.

To relate the average number of segments per nanotube with the CNTs' volume fraction, we can apply the statistical apparatus developed for flexible polymer chains in

solutions, from which it follows that the length of a “straight” segment decreases (and the number of segments per nanotube grows) with the volume available for chain shrinking (corresponding to growth of the CNT volume fraction). The number of straight segments and length of segments are described by the following relations, the same as it was for ideal polymer coils [184].

$$c_r < \frac{Nv}{l^3 N^{\frac{3}{2}}} \quad (4.19)$$

$$R = lN^{\frac{1}{2}} \quad (4.20)$$

R is the distance between the end points of the nanotube, l and N stand for the length and the number of segments, respectively, and v is the volume of a segment. As these formulas were developed for ideal coils, these values are overestimated for stiff inclusions. It is believed, however, that the trend of the number of segments versus concentration is captured correctly, and values are normalised by assuming that at extremely dilute concentrations nanotubes are straight. The resulting numbers of segments per nanotube for different volume fractions, which form the basis of the Monte Carlo simulations, are presented in Figure 4.8. Even though this input data is not very straightforward, it was considered to be good enough for the purpose of comparing different calculation methods.

After creating the RVE, a set of six linearly independent load cases (three tensile and three shear) was applied to it using a specific set of orthogonal PMUBC [14] of the type

$$\left\{ (t(x) - \sigma^0 n) (u(x) - \varepsilon^0 x) = 0 \quad , \nabla x \in \partial \right. \quad (4.21)$$

for obtaining the full stiffness tensors. In Equation 4.21 σ^0 and ε^0 are homogeneous stress and strain tensors prescribed to the RVE, ∂V represents the surface of the RVE, and t , u , n , x are the traction, displacement, normal and position vectors, respectively. In [158] it was shown that for macroscopically orthotropic, inhomogeneous materials such PMUBC give the same results as PBC. To solve for the effective modulus of the cell the total reaction forces on the faces of the RVE were computed. Dividing the obtained values by the surface area of the corresponding cube faces, six normal and shear stress components were obtained for each load case. Together with the prescribed strains they allow a system of 36 equations to be set up, from which the 36 coefficients of the effective elasticity matrix can be determined.

Semi-analytical model

Unit cells describing CNTs embedded in a matrix with a small volume fraction of 0.1% were studied, the corresponding dilute elasticity tensors being evaluated numerically using the methodology described above. In addition, the strain concentration tensor of the dilute inhomogeneities A^{dil} was evaluated, which relates the average inclusion

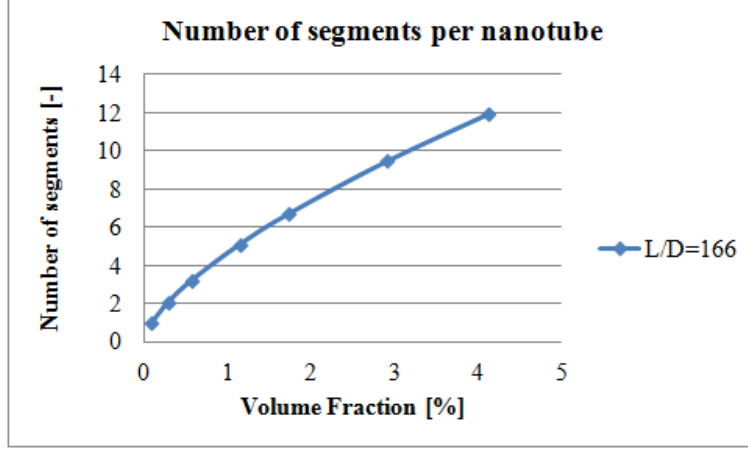


Figure 4.8: Number of segments per CNT as function of the volume fraction

strain to the applied far field strain [133]. Because the CNT were described by beam elements this cannot be done by calculating phase averages of the strain tensor and general relations holding for mean field methods [149] are resorted as

$$C = C_m + c_r (C_r - C_m) A^{dil} \quad (4.22)$$

Here C is the dilute effective elasticity tensor, C_r and C_m are the elasticity tensors of inhomogeneities and matrix, respectively, and c_r stands for the inhomogeneity volume fraction, which in the present case is equal to 0.1%. Previous studies (Section 4.1.1 and 5.2.1) of continuous fibres of sinusoidal and helical shapes based on continuum solid elements showed that the differences between analytically and numerically evaluated strain concentration tensors are only minor.

In the next step, the computed dilute strain concentration tensor was used as input for a Mori-Tanaka model to calculate the effective elastic tensors of polymers reinforced with curved nanotubes at non-dilute volume fraction, using the Mori-Tanaka relationship

$$C = C_m + c_r (C_r - C_m) A^{dil} \left[(1 - c_r) I + c_r A^{dil} \right]^{-1} \quad (4.23)$$

which accounts for the interactions between different CNTs in a collective way [149]. In Equation 4.23 I denotes the identity tensor. The advantage of the proposed hybrid micromechanical modelling technique is that it can be applied to any material microstructure with any reinforcement concentration at low computational cost.

4.1.3 Influence of FE modelling techniques on mechanical properties

In the following Section¹⁰ different superposition techniques were used to model periodic arrangements of hollow MWNTs embedded in a polymeric matrix and evaluate their

¹⁰Section is reproduced with adaptations from “A.Y. Matveeva, H.J. Böhm, G. Kravchenko and F.W.J. van Hattum. Investigation of the embedded element technique for modelling wavy CNT composites. CMC Computers, Materials & Continua, vol.42, no.1, pp.1-23, 2014”

Table 4.5: Material properties used for simulations

Constituent	E	ν
	[GPa]	
hollow MWNT	400	0.3
Matrix	2.4	0.3

influence on the mechanical properties. Unit cells containing one CNT or a square arrangement of CNTs were modelled and appropriate boundary conditions applied. The nanotubes are assumed to show a ratio of 2 between the outer and inner diameters and an infinite length (for comparison, amino-modified MWNTs-NH₂ were found to have an outside diameter of 8-15 nm, an inside diameter of 3-5 nm and an average length¹¹ of 50 nm). Following Equation 4.2 nanotubes were represented as sine-like fibres of various amplitudes. Several configurations were considered, which are characterised by different values of the waviness parameter, the radii of the CNT and the reinforcement volume fraction. Different ways of discretising CNT and matrix were compared in each case in order to elucidate trade-offs and identify approaches suitable for modelling composites reinforced by curved fibres at good accuracy and low cost.

The first case study consisted of single, wavy, hollow nanotubes without matrix material, which were subjected to tensile loading. The aim was to analyse the influence of different values of slenderness of the tubes on models utilizing beam, shell, and solid elements. Since the models of this type do not have an absolute length scale, actual units of length do not play a role. The waviness parameter was maintained at a value of 0.125, the wavelength being 2 length units, as stated in Equation 4.2, and the amplitude 0.25 units. Outer radii of 0.08, 0.12, 0.16 and 0.2 units were used for varying the tubes' slenderness, the inner radii taking half these values. Material properties of the reinforcement and matrix phase used in the simulations, such as the Young's moduli and Poisson's coefficients, are listed in Table 4.5.

The models of the second case study were wavy, hollow nanotubes embedded in matrix material, the cube-shaped volume elements having an edge length of two units, which also equals the wavelength of the tubes' curviness. Constant outer and inner radii, $R_{CNT}=0.04$ and $r_{CNT}=0.02$, were considered, the amplitude of the sine being varied to give waviness parameters of 0.08, 0.125, 0.2. For the superposition models the nanotubes were meshed with solid, shell and beam elements and multi-point constraints were used to embed the reinforcements in the matrix. In addition, conventional, "full" 3D solid models were created for providing reference solutions. Different fibre volume

¹¹<http://www.nanoamor-europe.com/nanomaterials/carbon-nanotubes-nanofibers/carbon-nanofibers-special-cnts/amino-modified-mwnts/mwnt-nh2-1562yjf.html>

fractions were obtained by changing the number of nanotubes within the unit cell, 1, 2, 4 or 16 nanotubes being arranged evenly in a square pattern, see Table 4.6. For straight nanotubes ($w = 0.0$), different volume fractions were obtained by changing radii of nanotubes, see Table 4.7. The reinforcement volume fraction was evaluated as

$$c_r = \frac{\pi N R_{CNT}^2}{A_{cell}} \quad (4.24)$$

where N is the number of nanotubes in the unit cell and A_{cell} stands for the cross-sectional area of the unit cell transverse to the nanotube axis. In actual nanocomposites, the polymer matrix does not penetrate the CNTs and an interphase layer is present. The thickness of this interphase layer may be approximated by half the equilibrium van der Waals separation distance between CNT and matrix, and subsumed into the fibre volume, compare Han and Elliot [185]. Such a model would require adapting the nanotubes' stiffness to include interphase contributions and was not used in the present work.

The material parameters used for the simulations are presented in Table 4.5. The approach of assigning material parameters corresponding to the difference between the elasticity tensors of nanotubes and matrix as proposed by Jiang et al. [162, 163] was not followed in the present work because its consistent extension to the bending and torsion stiffness associated with the rotational degrees of freedom of beam and shell elements does not appear feasible. Detailed discussions of experimental findings as well as theoretical and computational models for the mechanical properties of carbon nanotubes can be found in [186]. A wide range of Young's moduli have been reported for different types of CNTs, which is partly due to the presence of dislocations, voids, point defects, etc. Young's moduli obtained by experimental investigations of MWNT produced by the CVD method varied from 10 GPa to 450 GPa for ordered and disordered multi-walled carbon nanotubes [21, 59]. A value of $E_r = 400$ GPa was chosen for describing the material behaviour of MWNTs modelled as isotropic hollow tubes. In future work anisotropic properties of CNT may be used, e.g. by following the approach of Papanikos et al. [187], who evaluated the equivalent properties of beams by relating the tensile, bending and torsional stiffness with the chiral number of nanotubes.

The FE code ABAQUS/Standard and the associated pre-processor ABAQUS/CAE were used for numerically computing the effective elastic properties for the two case studies described above. The nanotubes in the first case study were modelled as hollow wavy tubes of fixed wavelength and amplitude but different radii, beam, shell and solid elements being used to discretise them. Three-node Timoshenko beam elements (B32) and Mindlin-Reissner thick shell elements with quadratic interpolation (S8R) were chosen to handle transverse shear flexibility, the outer surface of the nanotubes being used as the reference surface in the latter case. Both shells and beams carry transverse loads by bending or shearing action; the main difference in their behaviours being due to the shells' better capabilities of modelling changes in tube cross section.

Similar to the continuum models in Section 4.1.1 C3D20 brick elements were chosen for the solid models.

The single sine-like hollow nanotubes investigated in the first case study were solely loaded in their longitudinal X-direction and fixed on one end by suitable boundary conditions: For fibres meshed with beam elements, all translational DoF of the node on the “back face” ($X=0$) and the translational DoF in the Z-direction of the node on the “front face” ($X=H$) were fixed, while the rotational DoF of all nodes remained free. For fibres meshed with shell and solid elements the translational DoF in the X-direction of all nodes on the “back face” were fixed, node $(0.,0.,0.)$ is completely fixed and node $(0.,0.,D_{CNT})$ is not allowed to move in the Y-direction. The translational DoF in the longitudinal X-direction of all nodes on the “front face” are constrained to the corresponding DoF of node $(H, 0., 0.)$, which is loaded in the longitudinal X-direction. Here H stands for the wave length of the sine and D_{CNT} for the diameter of the nanotube. Additionally, node $(H, 0., 0.)$ is fixed in the Y- and Z-directions. The rotational DoFs of the shell elements remained free. With such boundary conditions the fibres were prevented from twisting and the cross-section was allowed to change. The results for wavy tubes ($w=0.125$) of different radii were evaluated in terms of the longitudinal stiffness k , which takes the form

$$k = \frac{F}{u_1} \quad (4.25)$$

where F is the force applied to the body and u_1 is the computed displacement along the first DoF.

In the second case study infinitely long, hollow, wavy tubes perfectly bonded within a matrix material were modelled by unit cells containing one wavelength of the fibres, see Figure 4.9. In the “full” 3D FE model, where both fibres and matrix were described by solid elements, C3D20 elements were used wherever possible and 15-node quadratic triangular prism elements (C3D15) were inserted where required by the automatic hexahedral mesher. For the superposition models the regular, structured mesh of 20-node hexahedra was again employed for the matrix. Beam, shell or solid elements were used for independently meshing the nanotubes, which were then embedded in the matrix “host” mesh. The translational DoFs of the embedded nodes were constrained to the interpolated values of the corresponding DoFs of the appropriate host elements, whereas the rotational DoFs of the beam and shell elements are not constrained by the embedding.

The representation of the nanotubes introduced symmetries that support the use of periodic models. For the purpose of determining the composite’s effective stiffness tensor, PBC as described in Section 4.1.1 were applied. For a periodic homogenisation using the method of macroscopic degrees of freedom [188], the macroscopic displacement field within the unit cell was completely defined by the displacements of characteristic vertices with the described master node concept. Loading was implemented by applying

Table 4.6: Values of volume fraction c_r and waviness parameter w covered in the present study for wavy fibres ($R_{CNT}=0.04$)

No. of CNTs in unit cell	$w=0.08$	$w=0.125$	$w=0.2$
	[%]		
1	0.13	0.14	0.16
4	0.53	0.57	0.66
9	1.19	1.28	1.49
16	2.13	2.29	2.65

Table 4.7: Values of volume fraction c_r for straight nanotubes with different outer radii

R_{CNT}	$w=0.0$
	[%]
0.08	0.5
0.12	1.13
0.2	3.14

normal concentrated forces in the 1-, 2- and 3-directions to the master nodes SEB, NWB and SWT in Figure 4.3 and by subjecting the master nodes to suitable tangential concentrated forces. The macroscopic elasticity tensor was obtained using the ILSB in-house software MedTool.

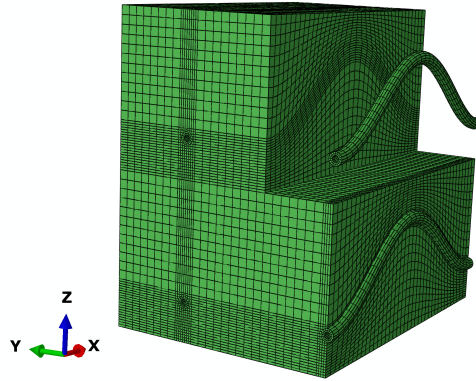


Figure 4.9: Sinusoidal fibre meshed with solid elements (“full model”)

4.2 Real arbitrary composites

In this Section¹² a two-step homogenisation method is described for studying the influence of curvature, orientation and dispersion of the reinforcements in arbitrary composites. In the first step, curved nanotubes were uniformly distributed in cube-shaped volume elements using Monte Carlo simulations according to prior obtained distributions of orientation and curvature parameters. The mechanical properties of these volume elements were evaluated by periodic homogenisation using FE analyses. In the second homogenisation step the composite was considered as a two-phase material consisting of agglomerates of CNTs in an isotropic medium made up of the polymer matrix and dispersed nanotubes. A Mori-Tanaka model was used to analytically calculate the effective elastic properties of the resulting composite.

Acceptance-rejection method

In order to describe the elastic behaviour of well-dispersed CNTs/CNFs in a polymer matrix SVEs were set up, the geometries of the nanotubes in them being randomly generated by means of a Monte Carlo process. Distribution functions of morphological characteristics were obtained fulfilling the definitions and assumptions listed in Section 3.4. The experimentally obtained angles α , ϕ and θ of nanotube directors were used to calculate the orientation distribution function according (ODF) to the procedure described in Appendix B (see Figure 5.10). A waviness distribution function was derived using the obtained pitches and radii from the TEM images (see Figure 5.13). Consequently, CNTs were uniformly distributed in a cubic volume element based on these orientation and waviness density distributions and the thus obtained models were incorporated into ABAQUS. The shape of each nanotube was described by a spatially curved centreline, modelled as a sequence of spiral segments sharing a common director line. The length of the nanotubes L_{CNT} was fixed and thus defined the number of spirals.

Within this approach an acceptance-rejection sampling method was used to generate the starting point $\{x_A, y_A, z_A\}$ of a given spiral, its starting and end radii a_1 , a_2 , the pitch h and the orientation angles of the centreline ϕ , θ , being based on the corresponding distribution functions. The acceptance-rejection sampling method is used as follows

1. Sample a point from the pertinent distribution.
2. If the randomly generated value is greater than the probability of the sampled value according to the desired distribution, return to step 1.

¹²Section is reproduced with adaptations from “A.Y. Matveeva, S.V. Pyrlin, B. Kiss-Pataki, J. Tiusanen, F. Regel, M.M.D. Ramos, F.W.J. van Hattum and H.J. Böhm. 3D microstructure reconstruction and stiffness prediction of CNT filled injection moulded polymer composite parts. To be submitted in Journal Composites Science and Technology”

Knowing the orientation of the director line, the starting point of the nanotube as well as the pitch and radius of its first spiral segment the geometrical parameters of a nanotube can be calculated as follows. First, the rotation matrix pertinent to the angle θ and the unit vector of the nanotubes' director $u = \{u_x, u_y, u_z\}$, where $u_x^2 + u_y^2 + u_z^2 = 1$, is established as

$$R_{\{u_x, u_y, u_z\}}(\theta) = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \quad (4.26)$$

with

$$\begin{aligned} R_{11} &= \cos \theta + u_x^2(1 - \cos \theta) & R_{12} &= u_x u_y(1 - \cos \theta) - u_z \sin \theta \\ R_{13} &= u_x u_z(1 - \cos \theta) + u_y \sin \theta & R_{21} &= u_y u_x(1 - \cos \theta) + u_z \sin \theta \\ R_{22} &= \cos \theta + u_y^2(1 - \cos \theta) & R_{23} &= u_y u_z(1 - \cos \theta) - u_x \sin \theta \\ R_{31} &= u_z u_x(1 - \cos \theta) - u_y \sin \theta & R_{32} &= u_z u_y(1 - \cos \theta) + u_x \sin \theta \\ R_{33} &= \cos \theta + u_z^2(1 - \cos \theta) \end{aligned}$$

Consequently the unit-directional vector of the spiral is obtained with (4.27)

$$\begin{cases} \vec{j}_1 = R_{\vec{k}}(\phi) \vec{j} \\ \vec{i}_1 = R_{\vec{j}_1}(\theta - \frac{\pi}{2}) R_{\vec{k}}(\phi) \vec{i} \\ \vec{k}_1 = R_{\vec{j}_1}(\theta - \frac{\pi}{2}) \vec{k} \end{cases} \quad (4.27)$$

The spiral geometry in the local coordinate system is defined as

$$\begin{cases} x_1 = \frac{ht}{2\pi} \\ x_2 = (a_1 + \frac{t(a_2 - a_1)}{2\pi}) \cos t \\ x_3 = (a_1 + \frac{t(a_2 - a_1)}{2\pi}) \sin t \end{cases}, t \in [0, 2\pi] \quad (4.28)$$

and from this the coordinates of a spiral in the global coordinate system can be calculated with Equation (4.29) as

$$\{X, Y, Z\} = \{x_A, y_A, z_A\} + x_1 \vec{i}_1 + x_2 \vec{j}_1 + x_3 \vec{k}_1 \quad (4.29)$$

The length of a spiral is defined as

$$L_s = \int_0^{2\pi} \sqrt{\left(\frac{dx_1}{dt}\right)^2 + \left(\frac{dx_2}{dt}\right)^2 + \left(\frac{dx_3}{dt}\right)^2} dt \quad (4.30)$$

with

$$\begin{cases} \frac{dx_1}{dt} = \frac{h}{2\pi} \\ \frac{dx_2}{dt} = \frac{(a_2-a_1)\cos t}{2\pi} - (a_1 + \frac{t(a_2-a_1)}{2\pi})\sin t \\ \frac{dx_3}{dt} = \frac{(a_2-a_1)\sin t}{2\pi} - (a_1 + \frac{t(a_2-a_1)}{2\pi})\cos t \end{cases} \quad (4.31)$$

and t in the range $[0, 2\pi]$. Substituting (4.31) into (4.30), the length of a spiral with non-constant radii is

$$L_s = (\frac{a_2 - a_1}{2\pi})^2 t^2 + \frac{2a_1(a_2 - a_1)t}{2\pi} + a_1^2 + \frac{h^2}{4\pi^2} + (\frac{a_2 - a_1}{2\pi})^2, t \in [0, 2\pi] \quad (4.32)$$

Once the first pitch has been obtained and plotted, it is assumed that the radius a_1 of the next pitch is equal to the radius a_2 of the previous pitch, ensuring the continuity of the nanotube. The second radius a_2 and the pitch of the second spiral are chosen from the distribution of pitches. Consequently, each nanotube has a predefined orientation according to the ODF of the director lines and its complex 3D curved shape is characterised by the distribution functions of pitches and radii obtained for the spirals.

Each cube-shaped SVE with a side length of $1 \mu\text{m}$ contains CNTs with a fixed length of $1.5 \mu\text{m}$. Different volume fractions from 0.5% to 5% by weight were achieved by increasing the number of nanotubes per volume element and taking into account their finite diameter, which is equal to 9 nm. If, in the course of the Monte Carlo simulation, parts of a tube's centreline fell outside the cube, it was translated to the opposite face of the cube resulting in periodic volume elements.

First homogenisation step: FEM-based periodic homogenisation

The FE code ABAQUS/Standard and the associated pre-processor, ABAQUS/CAE, were used for numerically estimating the effective elastic properties of SVEs generated by the approach described above. To obtain shell models of the nanotubes, which were used in most analysis, cylindrical surfaces were extended from the spatially curved centre lines. A Python script was written that creates a datum plane perpendicular to the first segment of each tube at its starting point. A circle with a radius of $4.5 \mu\text{m}$ (corresponding to the radius of a nanotube) was drawn in this datum plane with its centre in the starting point of the nanotube. To create the surface this circle was swept along the centreline, without keeping it normal to the centreline. In order to avoid unphysical intersections of nanotube surfaces and to enable sweeping of the nanotubes the previously generated coordinates of the centrelines were adjusted using the MD package LAMMPS. This was done by approximating the nanotubes as coarse grained bead-spring models that were then relaxed in LAMMPS using a soft (cosine-shaped)

potential with the following parameters

$$\begin{cases} U_{nb}(r) = A \left(1 + \cos \pi \frac{r}{r_c}\right), r < r_c \\ U_b(r) = K_b (r - r_0)^2 \\ U_a(r) = K_a (\theta - \theta_0)^2 \end{cases} \quad (4.33)$$

where U_{nb} signifies the non-bonded interactions, U_b the bonded interactions and U_a the angle interactions, d denotes the nanotube diameter equal to 9.5 nm as well as the beads' diameter, A was equal to 1000 kcal/mole, $r_c=1.5d$, $K_b=1$ kcal/mole, $r_0=d$, K_s was equal to 1000 kcal/mole and $\theta_0=180$.

To prevent the models from moving too far from their initial positions under large initial forces additional harmonic bonds of 20 kcal/mole were applied between initial and current position of each bead. The proposed set of parameters allowed relaxing the curved shapes of the CNTs without introducing large displacements and keeping the nanotubes sufficiently smooth so that a mesh could be applied to their surfaces for 3D FE modelling. In order to keep the numerical effort at a manageable level superposition models were used, in which the FEs describing the nanotubes, in the present case shell or beam elements, were overlaid on the solid elements describing the polymer matrix based on aforementioned preliminary studies.

The superposition models employed a regular, structured mesh of 8-node hexahedral solid elements for the polymer matrix. Beam and shell elements were used for independently meshing the nanotubes. B32 elements with a thick pipe crosssection, an outer radius of 4.5 μm and a wall thickness of 3.5 μm (corresponding to 10 graphen layers with 0.34 nm distance between them) were used when the nanotubes were modelled as beams. For the shell models S8R elements were chosen, so transverse shear stiffness could be handled appropriately. These elements were given a thickness of 3.5 μm , offset from their outer surface. The beam or shell elements were then embedded into the "host" mesh describing the matrix. The translational DoF of the embedded nodes were constrained to the interpolated values of the corresponding DoF of the appropriate host elements, whereas the rotational DoF of the beam and shell elements were not constrained by embedding. An example of a volume element containing a simulated population of nanotubes at 0.5wt% with a close-up of nanotubes discretised with shell elements is presented in Figure 4.10. The ILSB in-house code MedTool was used for applying PBC and for determining the elastic tensors of the composite. The employed material parameters are listed in Table 4.8.

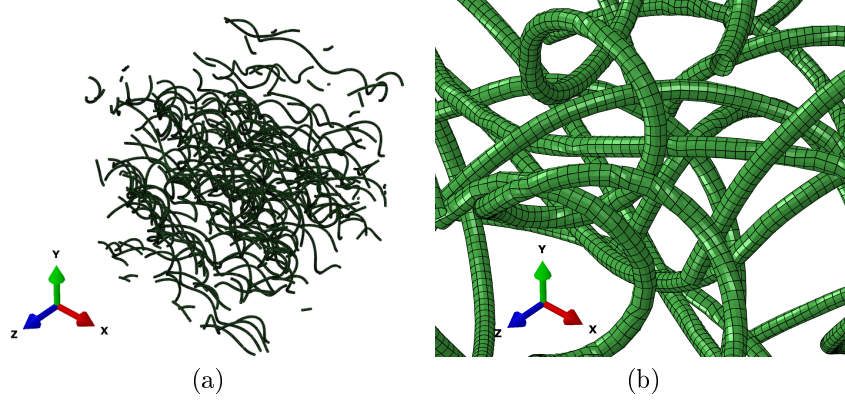


Figure 4.10: Volume element containing a simulated population of nanotubes at 0.5wt% (a) and close-up of nanotubes discretised with shell elements (b)

Table 4.8: Material parameters used in periodic homogenisation

Constituent	E	ν
	[GPa]	
hollow MWNT	450	
solid MWNT	427	0.3
Matrix	3.0	

First homogenisation step: Analytical micromechanics

To estimate analytically effective Young's moduli of systems with curved preoriented nanoinclusions of different concentrations, curved CNTs can be substituted by ellipsoidal inclusions with corrected effective lengths and corrected Young's moduli, as depicted in Figure 4.11. To estimate the length of ellipsoidal inclusions, all segments of curved CNTs were projected on the centreline. The distance between endpoints corresponds to the effective length of nanotubes, L^* . For all modelled SVEs, created according to the procedure described in Section 4.2, length distributions, for different concentrations are presented in Figure 5.34 in Chapter 5. The averaging over length and orientation distributions of the stiffness tensors was incorporated into the Mori-Tanaka model and is presented in Figure 5.36 (Chapter 5).

Additionally the composite stiffness must be averaged over the inclusion's elastic modulus which depends on the inclusion shape. Six different types of inclusions were numerically analysed for its elasticity constants (Figure 4.4):

1. 2D sinusoidal shape with three different amplitudes
2. 3D helix shape, with two different radii

Inclusions were assumed to be solid elements with circular cross-section and infinite length perfectly embedded into the polymer. PBCs were applied on the RVE which has



Figure 4.11: Substitution of curved nanotube with ellipsoidal inclusion

a size chosen to be big enough to reduce the influence of its length on the results. Six different load cases (three tensile and three shear) were applied in order to obtain full stiffness tensors (Section 4.1.1). In this study inclusions were assumed to be isotropic so only one load case is needed to determine the effective Young's modulus of the composite. Knowing the modulus of the composite E the modulus of straight inclusions E_r^* , which represents curved inclusions, can be determined by reverting the simple rule of mixture as follows

$$E_r^* = (E - E_m c_r) / c_r \quad (4.34)$$

Distribution of Young's moduli were calculated for five different curviness cases. Finally, the overall composite effective properties were averaged over the ODF, $\Psi(\phi, \theta)$, the effective length distribution function (LDF), $\Lambda(L^*)$ and the inclusion's Young's modulus distribution function $\Phi(E_r^*)$

$$\langle C \rangle = \int \int \int \int C(\phi, \theta, L^*, E_r^*) \Psi(\phi, \theta) \Lambda(L^*) \Phi(E_r^*) d\phi d\theta dL^* dE_r^* \quad (4.35)$$

Second homogenisation step: Analytical micromechanics

In order to investigate the influence of the CNT dispersion the composite was represented in the next step as a two-phase material: an isotropic medium in which spherical agglomerates were embedded. This isotropic medium resembled a polymer reinforced by perfectly dispersed nanotubes, homogenised using the aforementioned FE method. Collective interactions between the inhomogeneities were introduced by a Mori-Tanaka concentration tensor [144, 149] defined as

$$A_r^{MT} = A_r^{NI} \left((1 - c_r^{2nd-step}) I + c_r^{2nd-step} A_r^{NI} \right)^{-1} \quad (4.36)$$

where $c_r^{2nd-step}$ denotes the volume fraction of spherical inclusions during second homogenisation step, which is equal to agglomeration's volume fraction, see Equation A.21. The final effective properties of the composite was calculated using the effective elasticity tensor in Equation A.9. Agglomerated inclusions were considered as embedded stiff spheres of different radii, as shown in Figure 3.4. Size and volume fraction of the

Table 4.9: Input data to calculate properties of agglomerations

Parameter	Value	Description
c_a	0.25	Density of agglomerates
E_m	3.0 GPa	Young's modulus of polymer
E_r^*	353.5 GPa	Average Young's modulus of inclusions from Φ
l^*	1.1 μm	Average length from Λ
Ψ	random	Orientation distribution function

agglomerates were taken from the OLM analyses described in Section 3.3. An open question is the density of the agglomerates, which was investigated in several studies in the literature. In [120] the packing density was defined as 0.25. For Nanocyl NC7000 nanotubes the degree of dispersion was reported to be in the range of 0.07 and 0.25, depending on the processing conditions [66]. Thus the determination of a dispersion factor introduces a high uncertainty. In this study a density of 0.25 was used and the Young's modulus of an agglomerate could be derived using the Mori-Tanaka model with the input data from Table 4.9. Using this data the effective Young's modulus of agglomerates E^a is computed as 21420 MPa, which is further used in the second homogenisation step.

Chapter 5

Results and discussion

The following chapter presents the results of experimental, analytical and numerical analyses explained and conducted in this thesis. Briefly summarised, it comprises microscopy analyses to obtain details about the dispersion and orientation of the nanoparticles. Moreover, mechanical tests under tensile and flexural loading were performed, as outlined in Chapter 3, to reveal the mechanical behaviour of CNT/CNF reinforced polymeric composites. Numerical and analytical modelling approaches described in Chapter 4 were used to predict elastic properties of nanotube reinforced polymers. Preliminary studies were conducted to evaluate the influence of nanoparticle geometries and boundary conditions in order to define a numerical model, which was used subsequently to predict the mechanical behaviour of arbitrary CNT reinforced polymeric composites.

5.1 Experimental characterisation

5.1.1 OLM

OLM was employed to analyse the level of dispersion, which is generally understood as a ratio between uniformly distributed and agglomerated nanofillers. Figure 5.1, 5.2 and 5.3 present micrographs and grey scale distributions obtained for CNT/PC, CNF/PC and CNF/epoxy samples with different weight fractions, respectively. From Figure 5.4 it can be seen that with increasing concentrations the width of histograms increases showing that the level of dispersion decreases. Moreover it can be seen that the grey scale distributions shift with increasing concentration from the right to the left, which means that the range of colours grows dark influenced by either the concentration or the exposure time. It has to be noted that the exposure time was fixed for all micrographs of one sample. Figure 5.4(b) presents the calculated widths of histograms for CNF/PC samples. It can be seen that the width is increasing for small concentrations. However, with increasing weight fraction the width decreases. As aforementioned, CNF reinforced samples could only be cut in 10 μm thick slices which could be explained by the length difference between CNT and CNF. Therefore the micrographs are too dark and the range of greys is reduced, which complicates and even renders grey scale analyses impossible.

In the next step the binarising method was used to determine the area distributions of agglomerates. In the micrographs of CNT/PC samples agglomerates are clearly visible as circular inclusions as shown in Figure 5.5. However, in binarised micrographs of CNF reinforced polymers it is difficult to distinguish agglomerated from dispersed nanofillers as shown in Figure 5.6 and 5.7. For this reason the samples were analysed with a 5x smaller magnification (microscope 10x, camera 1.67x). Figure 5.8 presents micrographs of CNF reinforced PC samples with a smaller magnification. On the one hand for small concentrations agglomerates become clearly visible. On the other hand for higher concentrations only a uniform grey image can be observed, thus it does not facilitate a dispersion analysis. It can be summarised that the thinner the slice the better is the contrast between dispersed and agglomerated nanoparticles, and thus the easier and better are dispersion analyses.

Exemplarily the dispersion analysis described in the following was employed for CNT/PC composites. The degree of dispersion can be defined as the percentage of nanoparticles that are agglomerated. The number and the area of all agglomerates were determined using the open source program ImageJ. It was assumed that agglomerates have spherical shapes and are densely packed with nanotubes, consequently radii and volumes could be calculated. The degree of dispersion strongly depends on the packing density of nanoparticles within the agglomerates, which is difficult to measure experimentally and cannot be determined by means of OLM or TEM. Although the density assumption does not correspond to reality it gives at least reference values for the worst case effect due to agglomerates. From Table 5.1 it can be seen that the maximum radius of an agglomerate rises with increasing weight fraction. However, the calculated mean radii are similar indicating that rather the number of agglomerated CNTs increases. The calculated volumes were related to the volume of one nanotube to obtain the number of CNT in all agglomerates. Hence, the percentages of agglomerated CNTs can be obtained and is listed in Table 5.2. The percentages were used to calculate effective concentrations which correspond to the volume fractions of perfectly dispersed nanotubes. These values were used in the first homogenisation step of the presented modelling approach in Section 4.2. Radius distribution functions and the ratio of agglomerated volume to the total volume, which was defined as agglomeration's volume fraction, were implemented in the second homogenisation step.

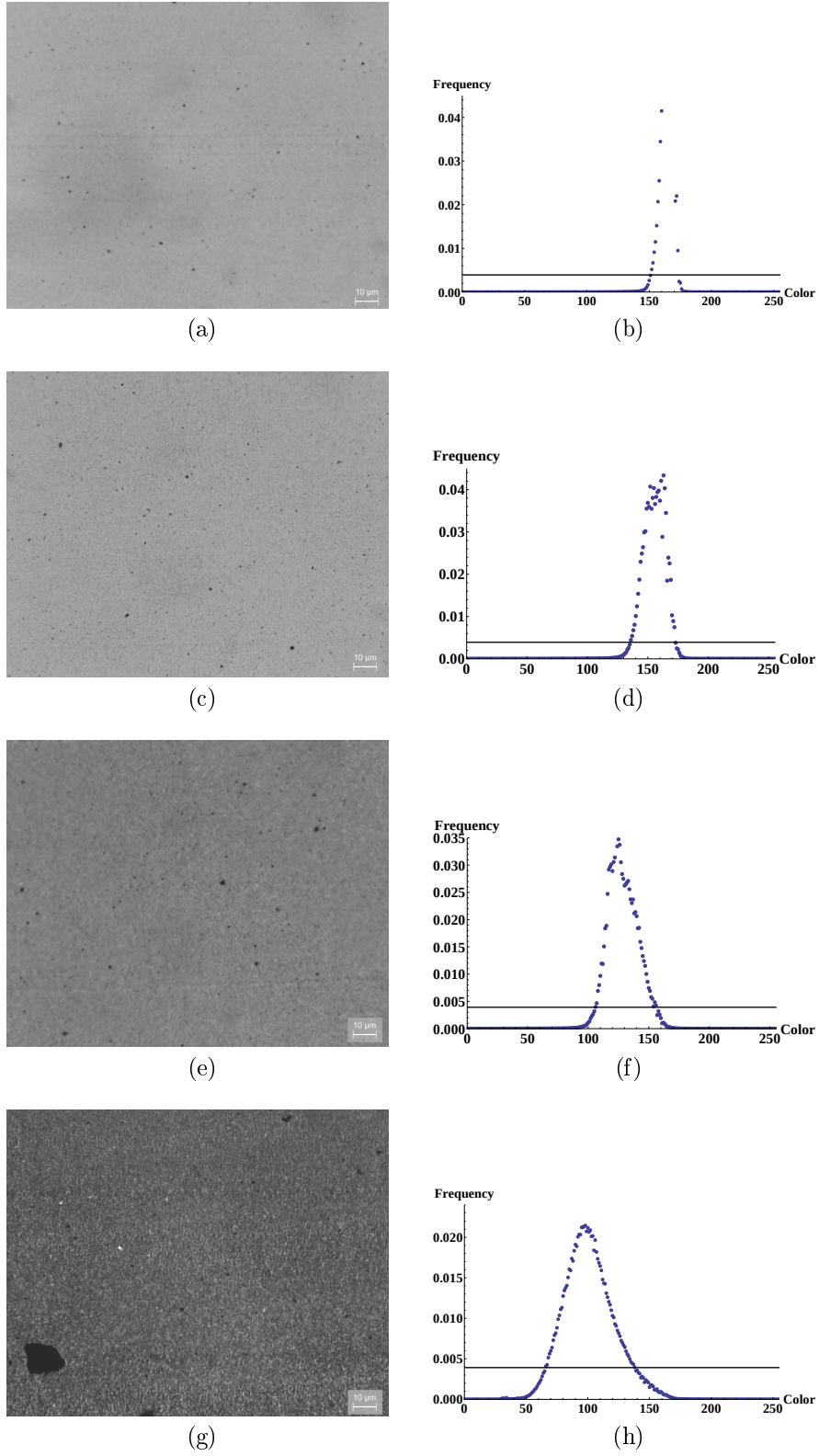


Figure 5.1: OLM micrographs and grey scale histograms of CNT/PC samples with different weight fractions: 0.5wt% (a,b), 1.0wt% (c,d), 3.0wt% (e,f) and 7.0wt% (g,h)

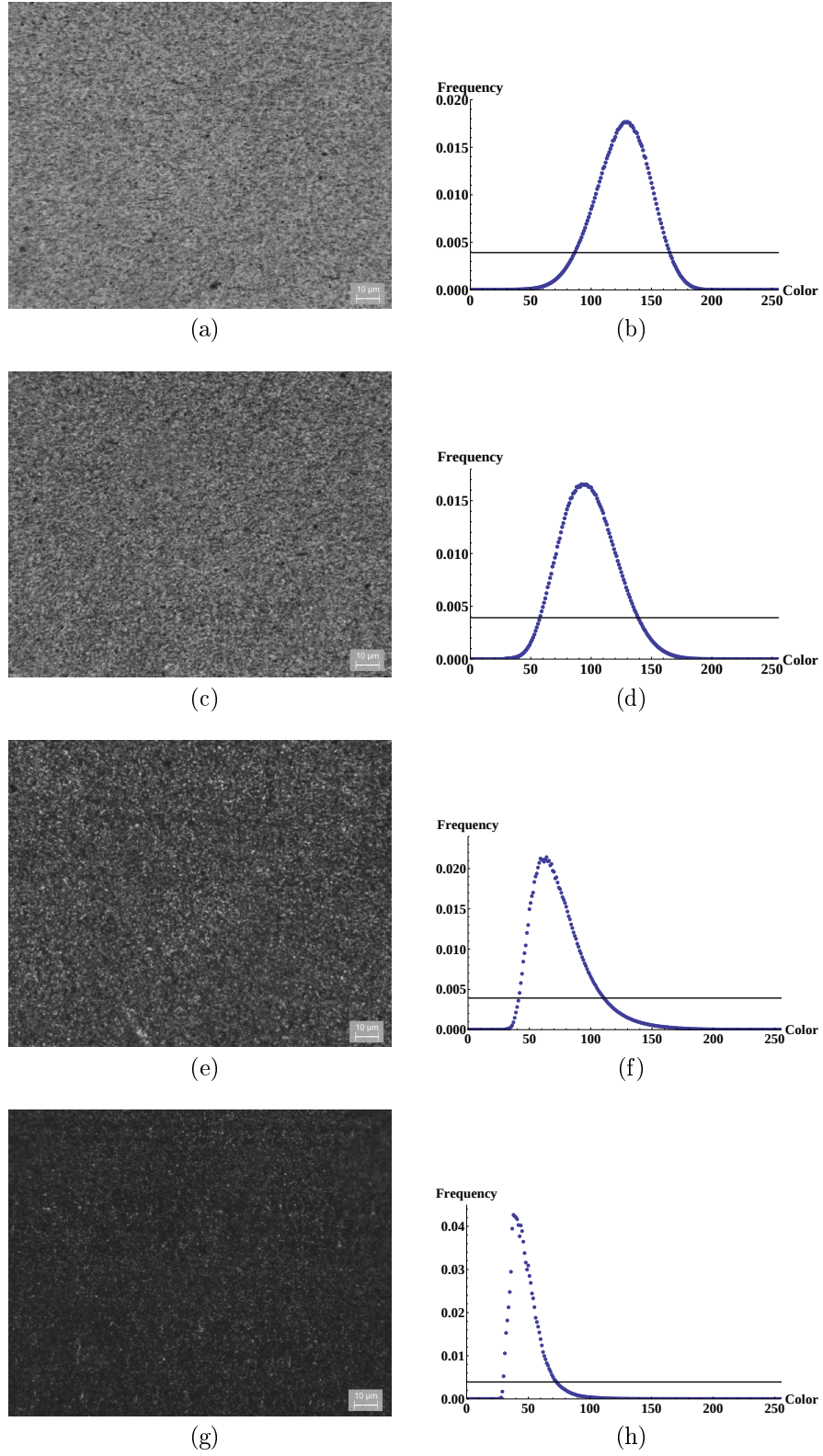
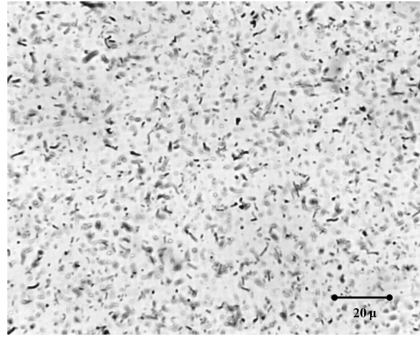
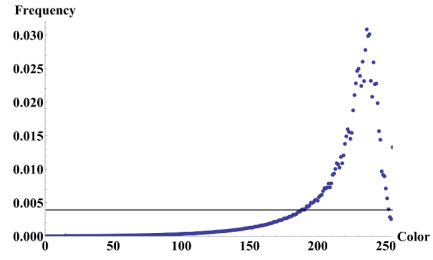


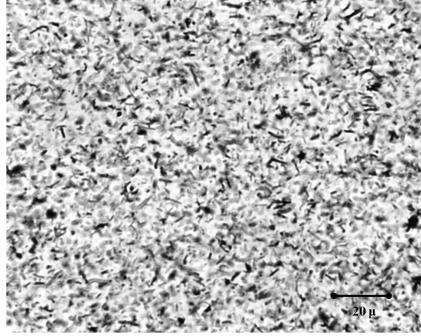
Figure 5.2: OLM micrographs and grey scale histograms of CNF/PC samples with different weight fractions: 0.5wt% (a,b), 1.0wt% (c,d), 3.0wt% (e,f) and 7.0wt% (g,h)



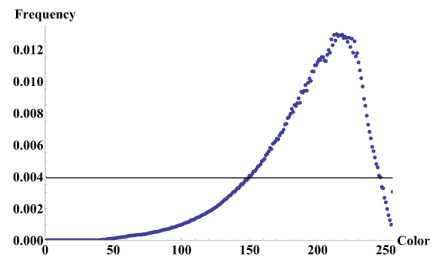
(a)



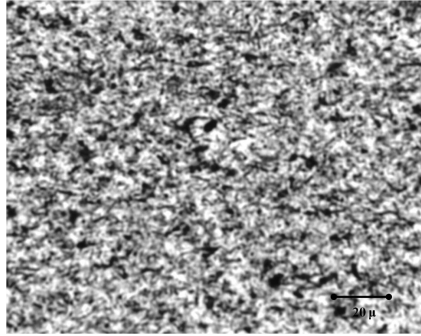
(b)



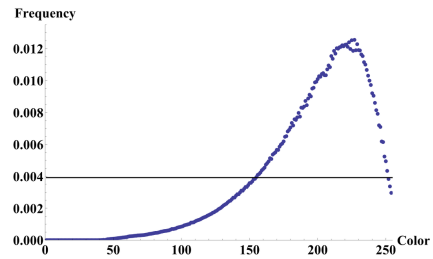
(c)



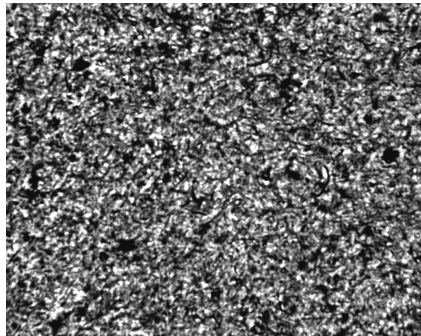
(d)



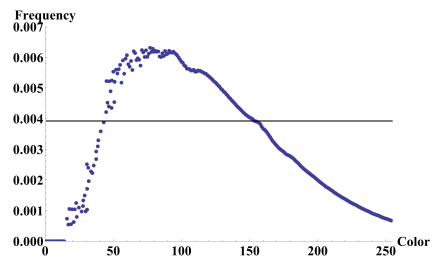
(e)



(f)

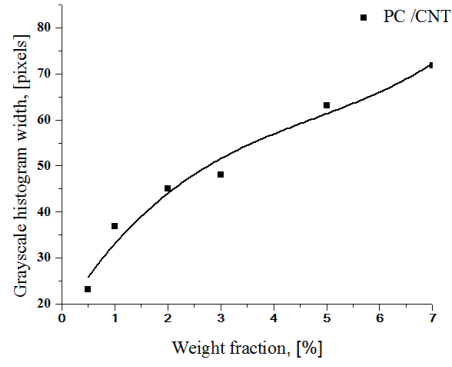


(g)

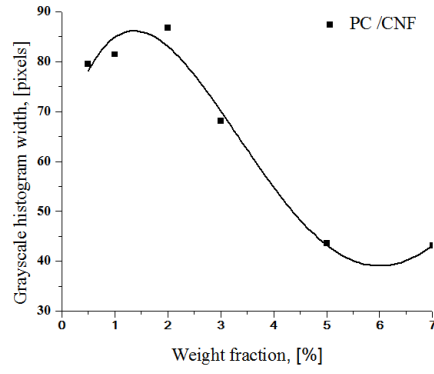


(h)

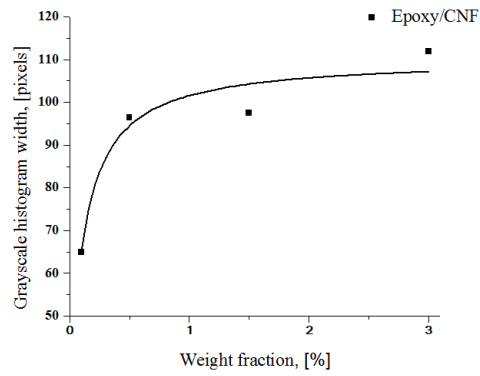
Figure 5.3: OLM micrographs and grey scale histograms of CNF/epoxy samples with different weight fractions: 0.1wt% (a,b), 0.5wt% (c,d), 1.5wt% (e,f) and 3.0wt% (g,h)



(a)



(b)



(c)

Figure 5.4: Calculated widths of OLM histograms: CNT/PC (a), CNF/PC (b) and CNF/epoxy (c)

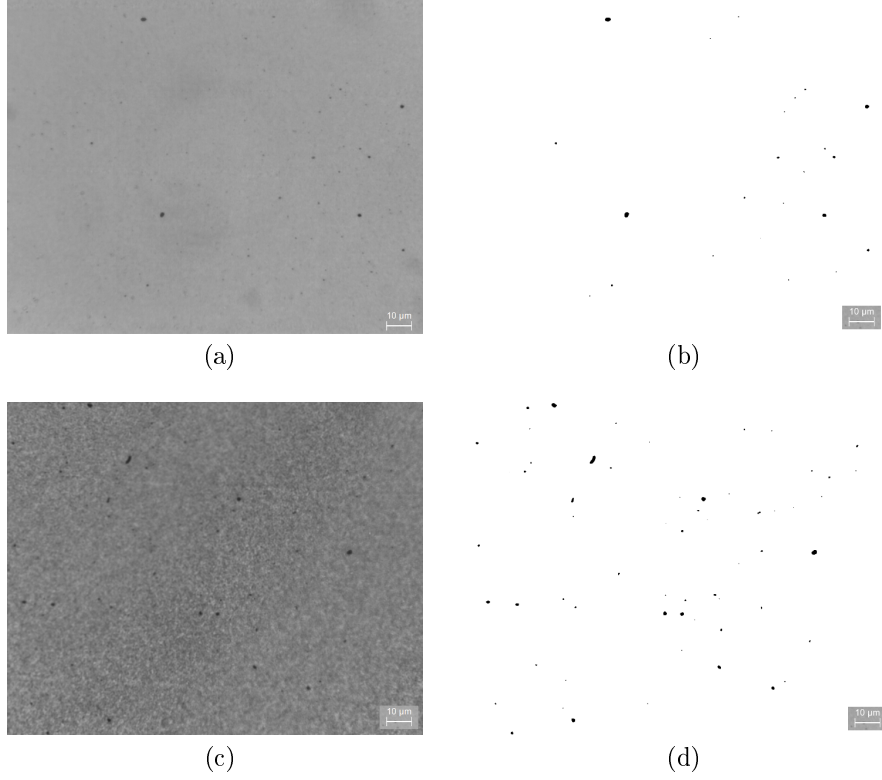


Figure 5.5: OLM micrographs and binarised micrographs of CNT/PC samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h)

5.1.2 TEM

Figure 5.9 presents TEM images obtained for slices of CNT/PC samples cut along the injection flow and perpendicular to the flow direction. It can be seen that CNTs tend to have arbitrarily curved shapes and that CNTs in samples with small nanotube concentrations (weight fractions up to 2%) have a preferred orientation along the injection flow.

Orientation

From Figure 5.10 it can be seen, that the distributions of the orientation angles in the XY-plane, ϕ , along the flow direction are narrower for concentrations of 1wt% and 2wt% compared to 5wt%, whereas the distributions of the angles in the YZ-plane, α ,

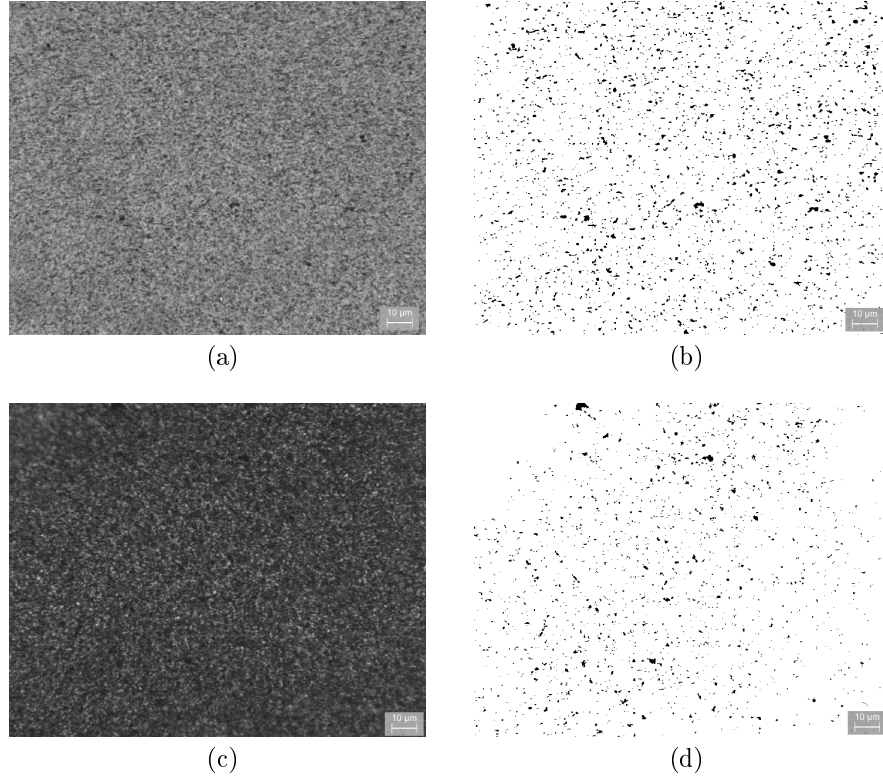


Figure 5.6: OLM micrographs and binarised micrograph of CNF/PC samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h)

Table 5.1: Radii of agglomerates for different weight fractions

w_r	Mean	STD	Max
[μm]			
0.5	0.55	0.31	1.87
1.0	0.47	0.34	6.45
2.0	0.48	0.36	9.92
3.0	0.58	0.43	7.33
5.0	0.49	0.48	18.98

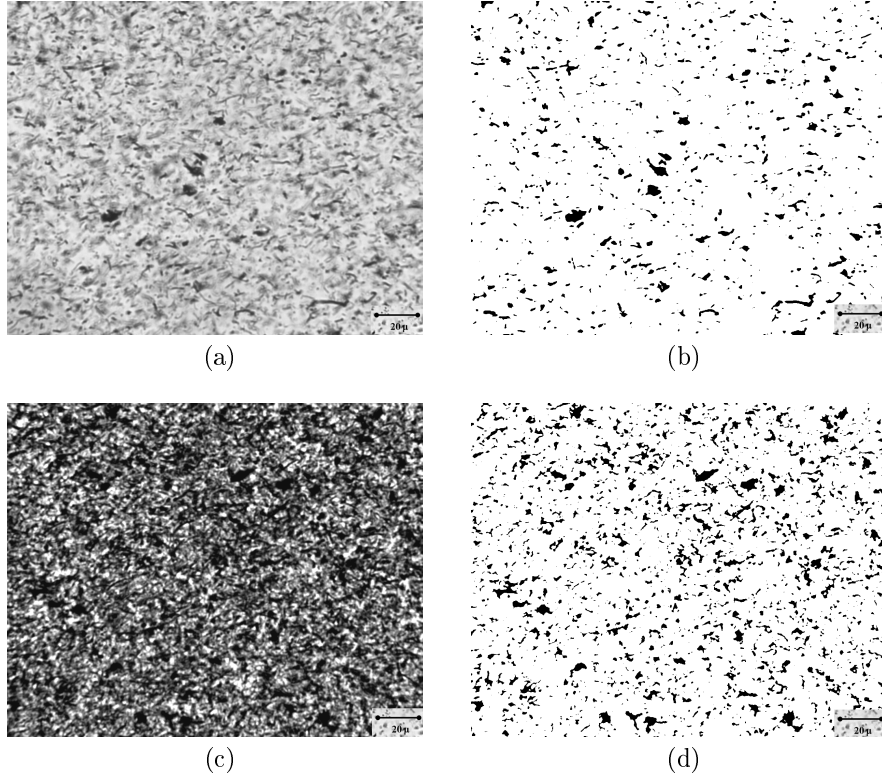


Figure 5.7: OLM micrographs and binarised micrograph of CNF/epoxy samples with different weight fractions: 0.5wt% (a,b) and 3.0wt% (g,h)

Table 5.2: Percentages of agglomerated CNTs and effective volume fractions

w_r	c_r	CNT in agglomerates	Effective c_r
[%]			
0.5	0.29	3.82	0.27
1.0	0.57	1.83	0.56
2.0	1.15	1.46	1.13
3.0	1.74	1.3	1.71
5.0	2.92	15.65	2.46

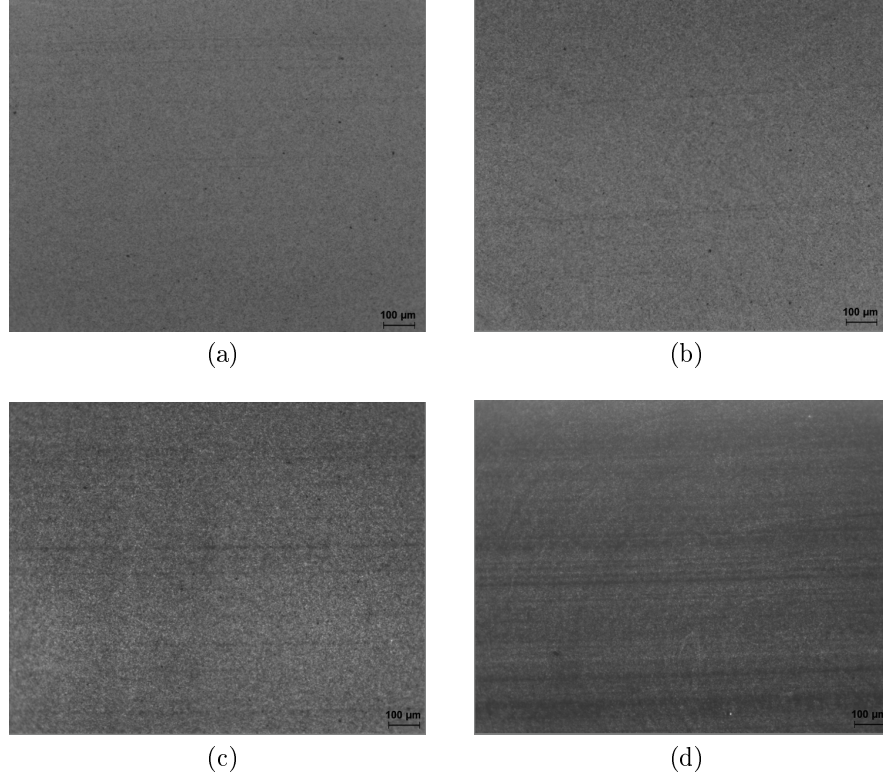


Figure 5.8: OLM micrographs with smaller magnification of CNF/PC samples with different weight fractions: 0.5wt% (a), 1.0wt% (b), 3.0wt% (c) and 5.0wt% (d)

perpendicular to the injection flow show large standard deviations for all concentrations. TEM images are available only for samples with 1wt%, 2wt% and 5wt%, whereas experimental data are available for samples with concentrations of 0.5wt%, 1wt%, 2wt%, 3wt% and 5wt%. Therefore, orientation distribution functions for the missing concentrations were estimated. The existing distributions of the angles in the XY- and YZ-planes, respectively, were approximated with normal distributions according to

$$y = Ae^{-0.5(\frac{x-x_c}{w})^2} \quad (5.1)$$

where A is a normalising coefficient and w is the standard deviation. Measured orientations and their approximation according to Equation 5.1 are shown in Figure 5.10.

Fits for the normalised coefficient A and the standard deviation w , obtained from the measured orientations, using the assumption of a linear dependence on the weight fraction of nanotubes are presented in Figure 5.11 and Table 5.3. It can be seen that the orientation is changing with increasing concentrations from an aligned to a more random orientation.

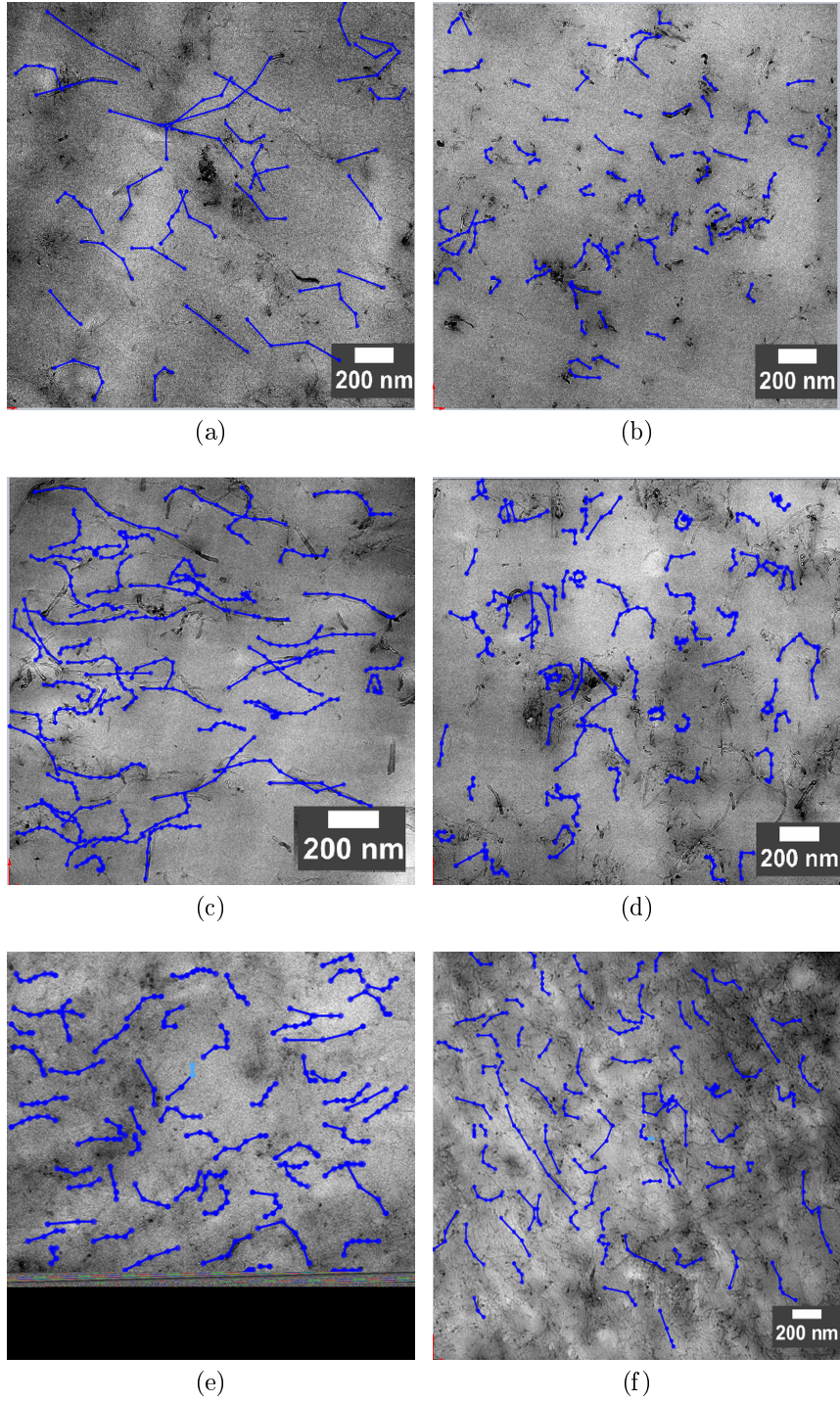


Figure 5.9: TEM images of PC reinforced with CNTs at three different wt%: Sections with 1wt% along (a) and perpendicular to the flow direction (b), sections with 2wt% along (c) and perpendicular to the flow direction (d), sections with 5wt% along (e) and perpendicular to the flow direction (f)

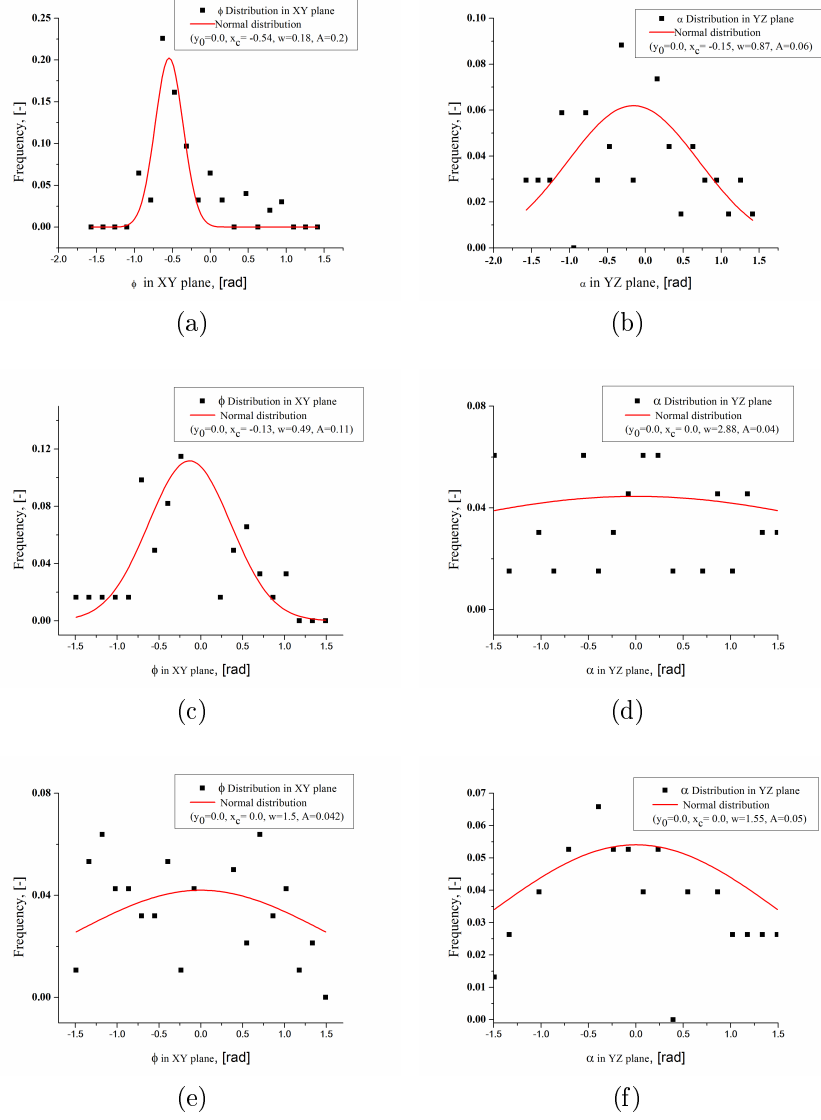


Figure 5.10: Measured and fitted distributions of the orientation angles ϕ and α for PC reinforced with three different wt% of CNTs: Sections with 1wt% along (a) and perpendicular to the flow direction (b), sections with 2wt% along (c) and perpendicular to the flow direction (d), sections with 5wt% along (e) and perpendicular to the flow direction (f)

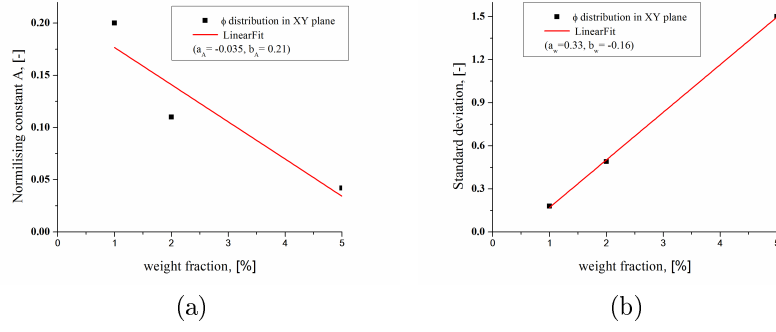


Figure 5.11: Normalisation coefficient and standard deviations of normal distributions approximating the orientation distributions of nanotubes in the XY-plane according to Equation 5.1 plotted as functions of the concentration of nanotubes

Table 5.3: Normalisation coefficients and standard deviation of normal distributions approximating the orientation distributions of nanotubes for different concentrations of nanotubes

w_r [%]	ϕ distribution in XY-plane		α distribution in YZ-plane	
	A	w	A	w
0.5%	0.195	0.005	0.05	1.766
1%	0.175	0.17	0.05	1.766
2%	0.14	0.5	0.05	1.766
3%	0.105	0.83	0.05	1.766
4%	0.07	1.16	0.05	1.766
5%	0.035	1.49	0.05	1.766

Curved geometries

The curved shapes are assumed to be a physical characteristic of the nanotubes and to be independent of their concentration. Single nanotubes can be clearly distinguished on TEM images of samples with small concentrations (1wt% and 2wt%), which were taken to evaluate the distributions of the pitches and radii of the spirals. To obtain the average distribution between samples of 1wt% and 2wt% TEM images were superimposed, see Figure 5.12.

The extracted distributions of the pitches and radii were approximated with log-normal distributions. Figure 5.13 shows the distributions of pitches and radii obtained from the TEM images together with their approximation according to Equation 5.2.

$$y = \frac{A}{\sqrt{2\pi}wx} e^{\frac{-(\ln \frac{x}{x_c})^2}{2w^2}} \quad (5.2)$$

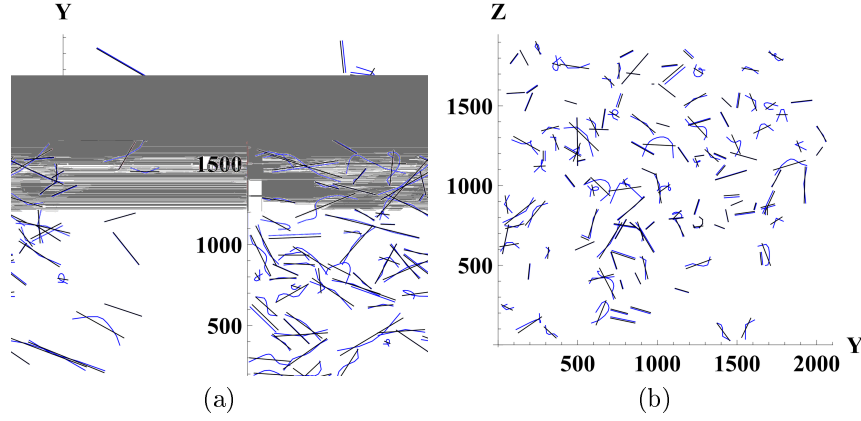


Figure 5.12: Superimposed TEM images of nanocomposites with CNT concentrations of 1wt% (a) and 2wt% (b)

To assess the methodology proposed in Section 4.2, cube-shaped volume elements of a side length of $2\text{ }\mu\text{m}$ were generated, each of which contains nanotubes of a fixed length equal to $1.5\text{ }\mu\text{m}$. Pitches, radii and orientations of the centrelines of the nanotubes were chosen by Monte-Carlo algorithms using the above distribution functions. Thin slices with a thickness of 100 nm , similar to the thickness used for the TEM images, were extracted at the centres of the XY- and YZ-planes of the simulated volume elements, see Figure 5.14. Obviously identical shapes to the ones obtained by microscopy, see Figure 5.9(a) and (b), could not be obtained, but similarities between the two sets of plots are clearly evident.

5.1.3 Tensile testing

The injected PC/CNT and PC/CNF samples were tested on a displacement-controlled universal testing machine to determine their Young's moduli. Ten specimens were tested for each series. Moduli of elasticity were calculated according to the ASTM standard D638-03 [174] and are presented in Figure 5.15. The Young's modulus of CNF reinforced PC increases nearly linearly with increasing weight fraction. On the contrary CNT reinforced PC presents a different behaviour. A plateau can be clearly seen for weight fractions higher than 4%, thereafter the modulus increases only moderately. As seen from OLM micrographs dispersion cannot be used for explaining the observed behaviour. Other important structural factors are curviness and orientation. It is assumed that CNF are compared to CNT straighter due to their higher aspect ratio and diameters. Moreover, it can be seen in Figure 5.11 that the orientation in CNT/PC samples is changing with increasing concentrations from an aligned to a more random orientation. Detailed analyses of the CNF/PC samples were not performed within the framework of the CONTACT project. Therefore, information about the orientation and curviness

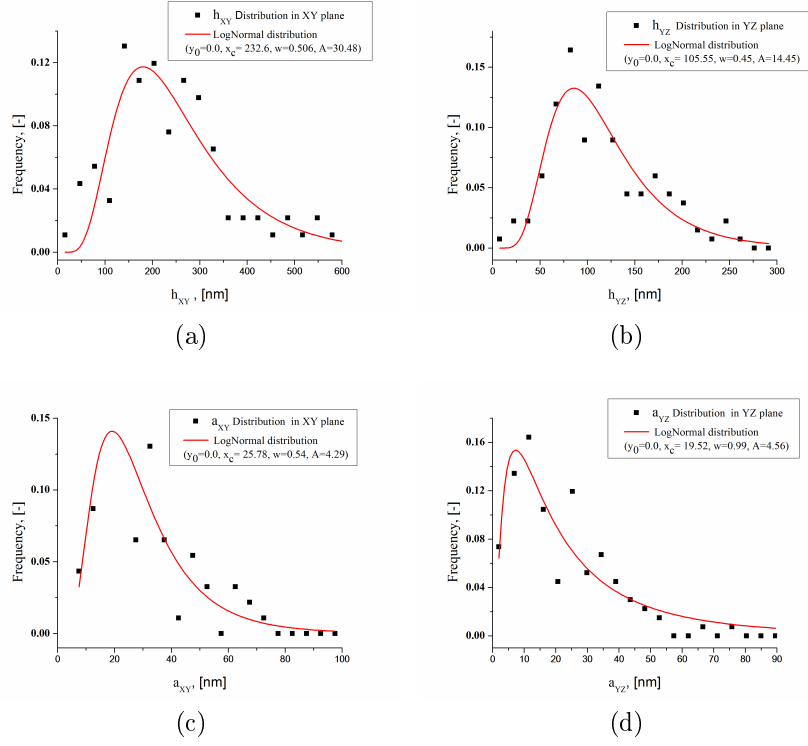


Figure 5.13: Distributions of pitches h and radii a of the spiral's projections onto the XY- and YZ-planes: h_{XY} (a), h_{YZ} (b), a_{XY} (c) and a_{YZ} (d)

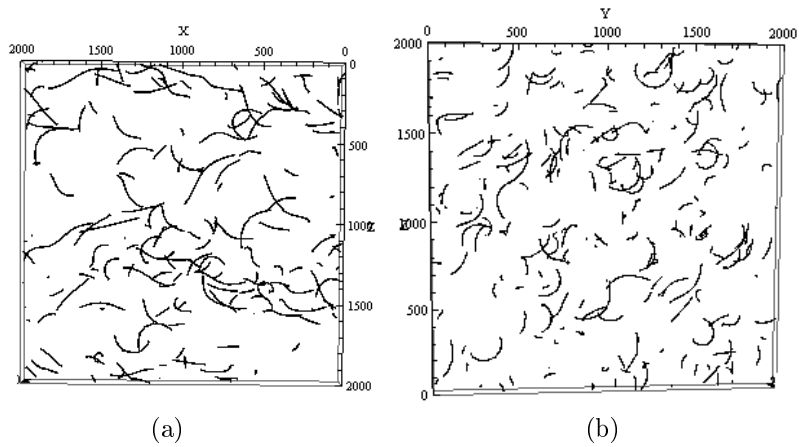


Figure 5.14: Simulated distributions of nanotubes in a slice with the dimensions $2 \times 2 \times 0.1 \mu\text{m}$ and a weight fraction of 1%: XY-plane (a) and YZ-plane (b)

are missing. However, due to the obtained results a detailed analysis of the orientation and curviness of CNF reinforced polymers has to be performed in future studies.

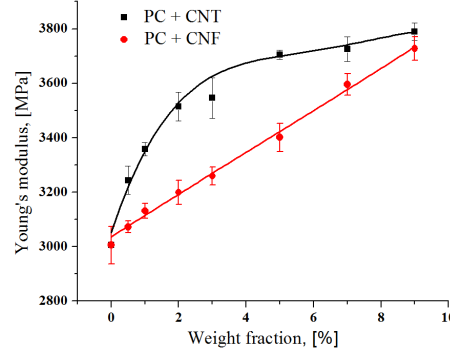


Figure 5.15: Young's moduli of PC/CNT and PC/CNF samples with different wt%

5.1.4 Flexural testing

CNF/epoxy composites were tested to examine the influence of different weight fractions on their flexural properties. On the contrary to the tensile results the flexural modulus only increases linearly for small concentrations up to 1.5wt%. The observed mechanical behaviour is rather similar to the tensile behaviour of CNT/PC. It was seen in Figure 5.4(a) and (c) that the widths of histograms increased for both samples with increasing concentrations. Thus it is concluded that the mechanical properties of CNF and CNT reinforced polymers are influenced by an interaction of dispersion, orientation and curviness.

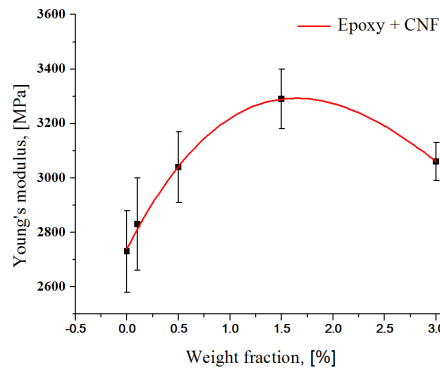


Figure 5.16: Flexural modulus of CNF/epoxy samples with different wt%

5.2 Modelling

5.2.1 Influence of waviness and curliness on mechanical properties

Analytical model

The longitudinal and transverse Young's moduli evaluated from Equation 4.11 are shown in Figure 5.17 as functions of ϕ and θ . It can be seen that, with increasing θ and with the planar angle ϕ approaching π , the modulus in the Y -direction reaches its maximum, whereas the stiffness in the X -direction is markedly reduced. This helps explaining the results presented below for the elastic moduli of helical and sinusoidal inclusions for different curviness parameters.

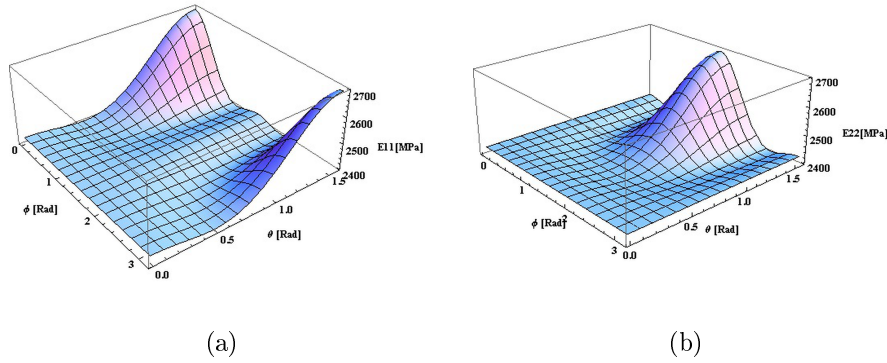


Figure 5.17: Elastic moduli in the X -direction (a) and in the Y -direction (b) predicted for PC reinforced with aligned CNT as functions of the fibre orientation angles ϕ and θ

FE vs. analytical results

Figure 5.18 and Figure 5.19 present comparisons between predictions obtained with FE-based models and the analytical model. The identifiers "FEM_PBC" and "FEM_PMUBC" indicate models that combine solid elements for describing the fibres with PBC and PMUBC, respectively. Similarly, "FEM_Beam_PBC" and "FEM_Beam_PMUBC" stand for models in which beam elements are used for describing the fibres subjected the above types of boundary conditions. The analytically predicted macroscopic behaviour is orthotropic for the wavy fibres and transversally isotropic for the helical ones. The numerical models using PBC, which describe square arrangements of fibres, predict tetragonal elastic symmetry in the latter case, the deviation from transverse isotropy being very small. The PMUBC give rise to orthotropic behaviour in both cases, see the discussion below. E_{11} stands for the longitudinal macroscopic Young's modulus and E_{22} as well as E_{33} are the transverse macroscopic Young's moduli. G_{12} and G_{13} denote the longitudinal and G_{23} the transverse macroscopic shear moduli of the composite.

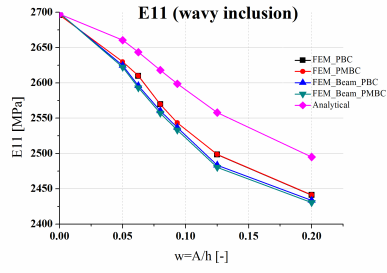
The amplitudes of the sine waves A and a are normalized with respect to the length of the volume element h and thus the wavelength of the “perturbation”. Figure 5.18 shows plots of the six macroscopic elastic moduli as functions of the normalized amplitude predicted for composites reinforced by wavy nanotubes having the shape of sine waves in the 13-plane, and Figure 5.19 shows analogous results for reinforcing with helical fibres.

Generally, the agreement between the different predictions for each of the composites’ six macroscopic moduli is satisfactory. The highest relative errors with respect to FE predictions combining PBC with inhomogeneities modelled with solid elements are presented in Table 5.4 and Table 5.5, the latter models introducing the least approximations for the configurations considered here. For both sinusoidal and helical inhomogeneities the analytical results and the numerical predictions using beam elements for describing the fibres give upper and lower estimates, respectively, for the macroscopic elastic moduli. Softer responses may be obtained with the analytical approach by using Eshelby tensors pertaining to spheroids of some appropriately chosen finite length, a path not followed here. As expected, the longitudinal Young’s moduli decrease with increasing curviness parameter w . The transverse Young’s moduli, with the exception of E_{22} in the case of wavy fibres (i.e. the modulus describing the behaviour normal to the plane of the sine waves), however, show a more complex behaviour with a minimum at approximately $w = 0.1$. No comparable effect is evident in the longitudinal or transverse shear responses. For the configurations considered here, the longitudinal Young’s moduli obtained with models discretising the fibres with continuum and beam elements, respectively, differ by 0.6% at most.

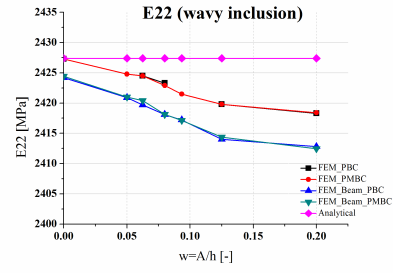
A detailed look at the results obtained for helical fibres, Figure 5.20, shows small, but consistent differences between predictions obtained with PBC and PMUBC, respectively, for the case of helical inhomogeneities. Whereas the former resulted in approximately transversally isotropic behaviour, the mixed uniform boundary conditions gave rise to minor differences in the predicted longitudinal shear moduli in the 12- and 13-planes, making the elastic symmetry orthotropic.

Comparison between continuum model and MD predictions

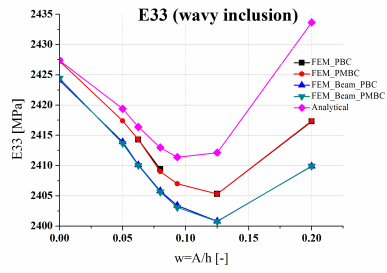
Comparisons between results obtained with FE as well as analytical continuum models and with molecular dynamics simulations are presented in Figure 5.21. The continuum



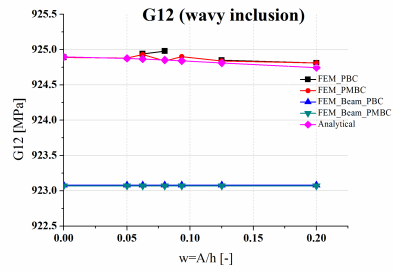
(a)



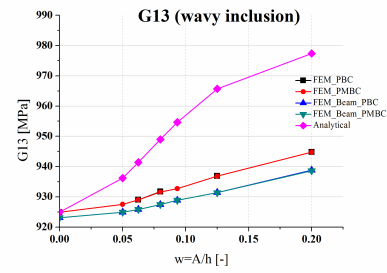
(b)



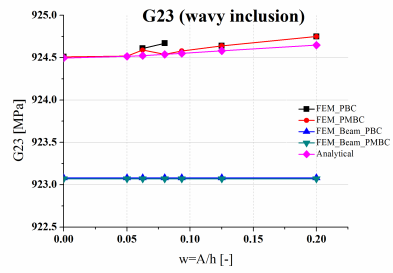
(c)



(d)



(e)



(f)

Figure 5.18: Elastic moduli predicted for composites reinforced with wavy nanotubes

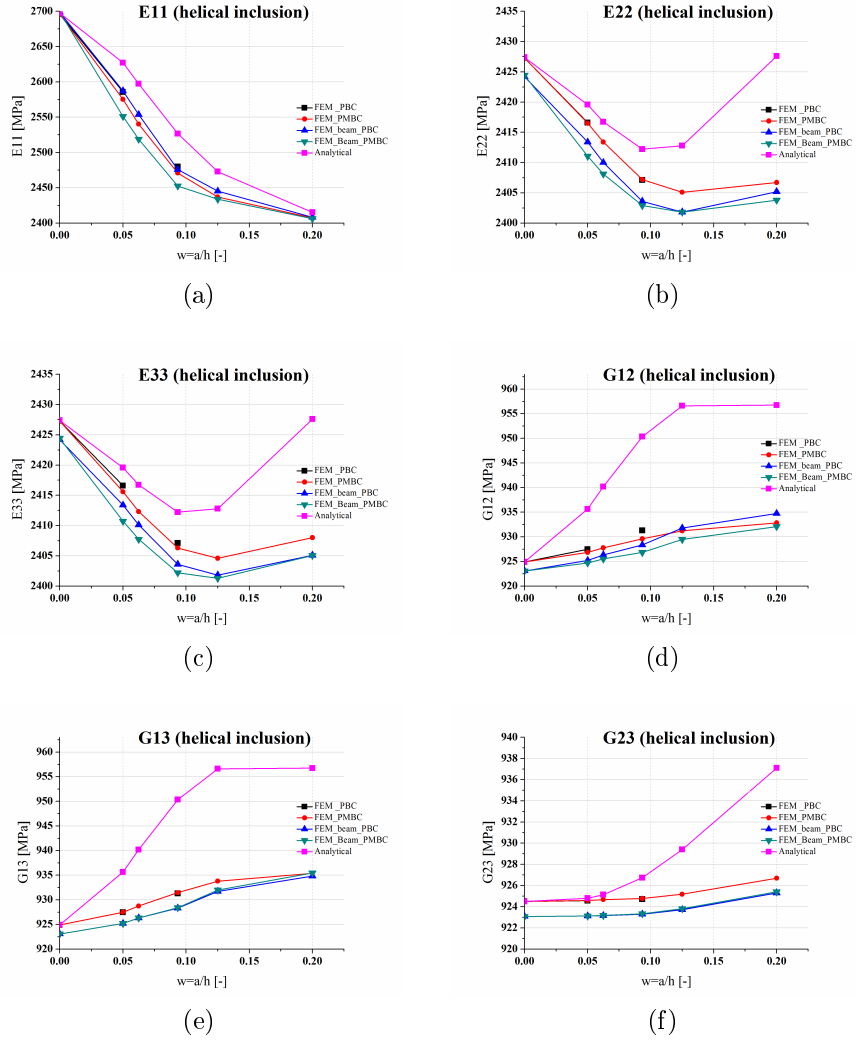


Figure 5.19: Elastic moduli predicted for composites reinforced with helical nanotubes

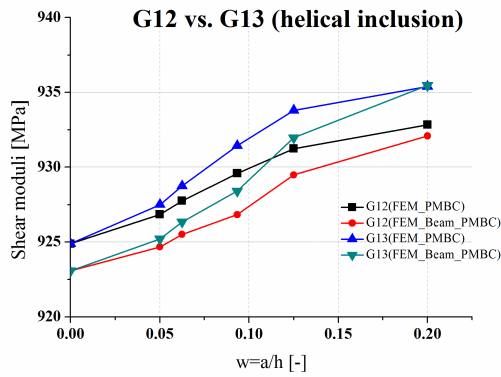


Figure 5.20: Influence of FE model on the longitudinal shear moduli of composites reinforced with a square array of helical inhomogeneities using PMUBC

Table 5.4: Relative errors for sine-like inhomogeneities (with respect to FEM_PBC results)

	FEM			Analytical
	3D_PMUBC	Beam_PBC	Beam_PMUBC	
	[%]			
E_{11}	0.011	0.600	0.725	2.381
E_{22}	0.017	0.240	0.241	0.376
E_{33}	0.017	0.306	0.306	0.677
G_{12}	0.015	0.205	0.206	0.014
G_{13}	0.016	0.633	0.654	3.451
G_{23}	0.014	0.181	0.182	0.014
Average	0.015	0.361	0.386	1.152
Dispersion	0.002	0.200	0.240	1.430

Table 5.5: Relative errors for sine-like inhomogeneities (with respect to FEM_PBC results)

	FEM			Analytical
	3D_PMUBC	Beam_PBC	Beam_PMUBC	
	[%]			
E_{11}	0.406	0.161	1.341	1.887
E_{22}	0.004	0.145	0.230	0.213
E_{33}	0.041	0.145	0.244	0.213
G_{12}	0.185	0.317	0.480	2.045
G_{13}	0.015	0.321	0.310	2.045
G_{23}	0.007	0.157	0.156	0.218
Average	0.110	0.208	0.460	1.103
Dispersion	0.161	0.086	0.445	0.975

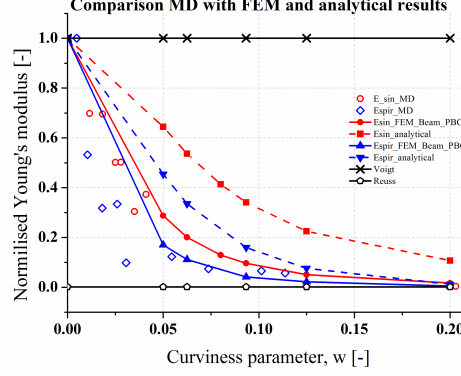


Figure 5.21: Comparison of MD results with FE predictions and analytical solutions for the longitudinal Young’s modulus of composites reinforced by curvy CNTs

models in this section use a Young’s modulus of SWNT of 2 TPa, in correspondence with the stiffness obtained by molecular dynamics. As in both FEM and analytical micromechanics the nanotubes were modelled as having a solid, circular cross-section as well as infinite length, whereas in MD they were treated as hollow tubes of monoatomic thickness and finite length, the results in Figure 5.21 were normalised with respect to the effective longitudinal stiffness of a composite reinforced by straight, aligned fibres E_c^* in order to focus on the effects of the reinforcements’ curvature according to

$$E^{norm} = \frac{E_c - E_m}{E_c^* - E_m} \quad (5.3)$$

Here, E_c is the effective longitudinal Young’s modulus computed for composites with curved nanotubes. E_{sin-MD} and $E_{spir-MD}$ denote the MD-predictions for the normalised longitudinal Young’s modulus of PC reinforced with sine-like and helical CNT, respectively. Due to the good agreement between results obtained with PBC and PMUBC, only the latter were used for comparison, the pertinent predictions being denoted as $E_{sin-FEM-Beam}$ and $E_{spir-FEM-Beam}$ in Figure 5.21. $E_{sin-analytical}$ as well as $E_{spir-analytical}$ indicate results obtained from the analytical Mori-Tanaka estimates. In addition, the well-known Voigt and Reuss bounds [189] for the Young’s modulus are given, which pertain to all composites considered here, but are very slack.

A fairly good agreement between the FE and MD results can be seen, with the latter tending to predict more compliant longitudinal elastic behaviour; the analytical estimates give noticeably higher longitudinal stiffness. Whereas the continuum models are based on the assumption of homogeneous matrix behaviour, the MD models include deviations from the bulk behaviour of the matrix in the immediate vicinity of the nanotubes. Such “interphase effects” can be expected to account for some of the differences between the FE and MD results and they may be introduced into continuum models, e.g. by the provision of an interphase region differing in stiffness from the matrix [190]. All models show a tendency for helical inhomogeneities to be more deleterious

to the composite's macroscopic longitudinal Young's modulus than are sine-like, wavy reinforcements of the same curviness parameter. For nanotubes of very pronounced curviness, the loss in longitudinal stiffness at elevated curviness levels is predicted to be very marked, indeed.

5.2.2 Influence of curviness and segment number per CNT on mechanical properties

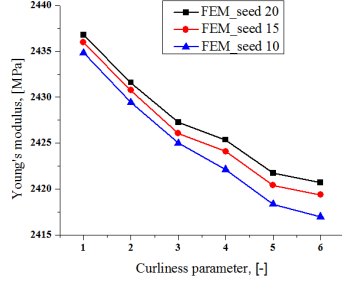
Results for different waviness parameters are presented in Figure 5.22, the curliness parameters corresponding to the data given in Table 4.4. The convergence of the results with respect to mesh size was also investigated, the seed number per cube edge being reduced from 20 to 10. A minor difference of approximately 0.05% between the results was observed, see Figure 5.22.

Results for the corresponding effective elastic moduli are presented in Figure 5.23 as functions of the CNT weight fraction and compared with results from the semi-analytical model.

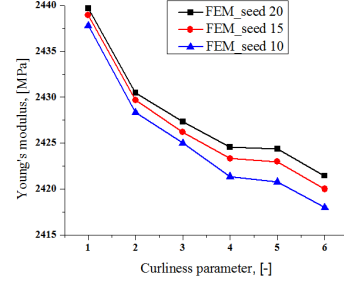
For the validation of the proposed models, injection moulded parts were made from pre-melt-compounded PC filled with different CNT concentrations up to 7wt% (see section 3.1.2 in chapter 3). The parts were made with constant injection moulding process parameters and were tested for tensile strength and Young's modulus. It can be seen that the numerically computed Young's moduli give similar trend as the experimentally evaluated ones. Part of the difference in the results may be due to the use of beam elements for describing the CNT. As it was shown in Section 5.2.1, beam elements tend to give lower estimates for the elastic constants than solid continuum elements. The number of straight segments to be used for modelling curved nanotubes is not yet fully resolved, either.

5.2.3 Influence of FE modelling techniques on mechanical properties

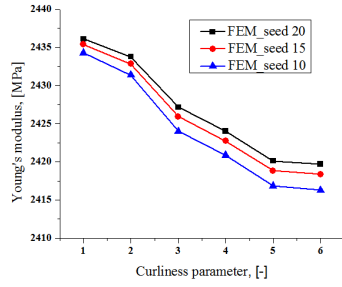
The effects of discretisation by different element types on the axial displacements u_1 and the longitudinal stiffness k_1 of free nanotubes are presented in Table 5.6. Keeping the wavelength as well as the amplitude, and thus the waviness parameter ($w=0.125$), of the sine fixed while varying the radii of the nanotubes, these results probe interactions between the slenderness of the fibres and the different discretisations. The applied force F was 4 N. Displacements are given in units of length and stiffness in units of N per unit of length. The wavelength of the sine equals 2 length units, and the error pertains to the axial stiffness, see Equation 5.4. As expected the stiffness increases markedly with



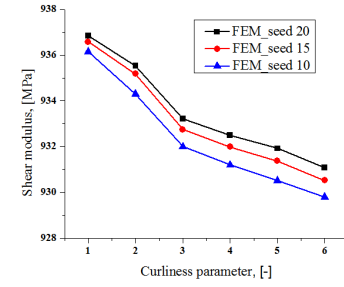
(a)



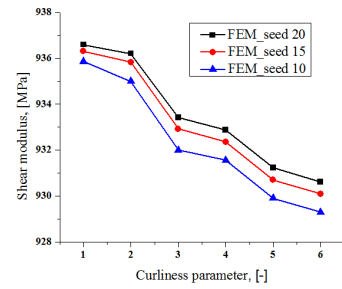
(b)



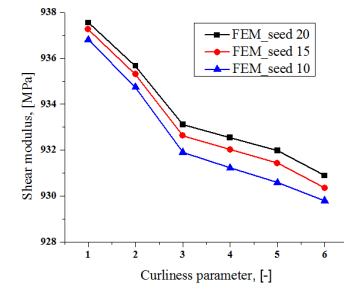
(c)



(d)

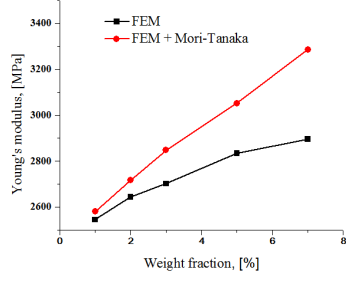


(e)

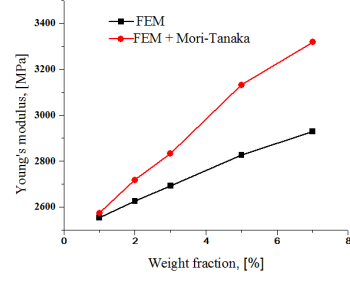


(f)

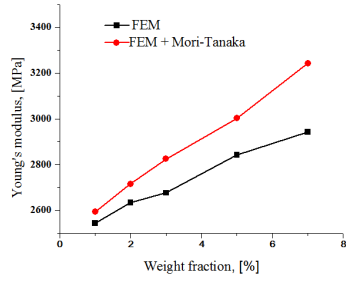
Figure 5.22: Predicted elastic moduli in the dilute case (Young's moduli in main directions (E_{11} (a), E_{22} (b), E_{33} (c)) and shear moduli (G_{12} (d), G_{13} (e), G_{23} (f)) as functions of the curliness parameter



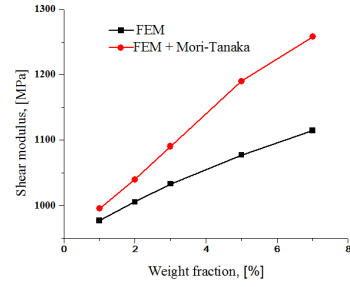
(a)



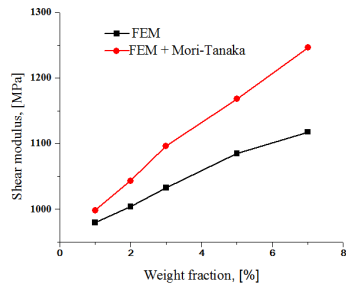
(b)



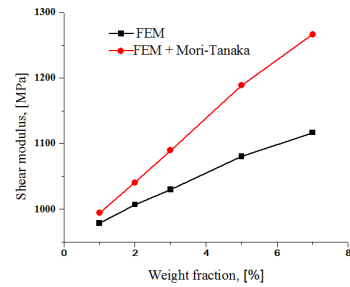
(c)



(d)



(e)



(f)

Figure 5.23: Predicted elastic moduli for CNT/PC composites (Young's moduli in main directions (E_{11} (a), E_{22} (b), E_{33} (c)) and shear moduli (G_{12} (d), G_{13} (e), G_{23} (f)) as functions of the CNT weight fraction

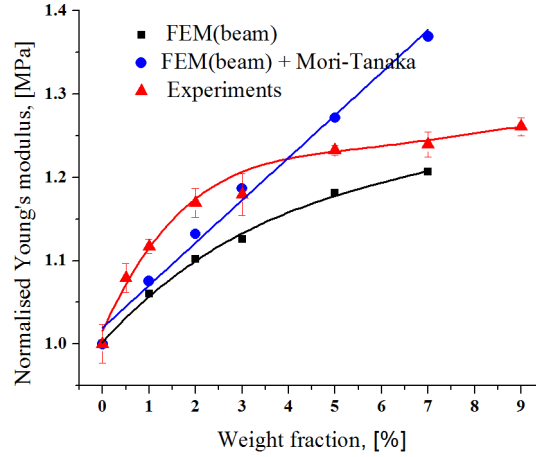


Figure 5.24: Predicted and measured elastic moduli for CNT/PC composites

an increasing CNT radius. To assess the efficiency of the different mesh element types, the relative error in stiffness with reference to solid elements was evaluated, which is defined as

$$error = \frac{k_1^{beam,shell} - k_1^{solid}}{k_1^{solid}} \quad (5.4)$$

Compared to the full solid model, both beam and shell models overestimate the axial stiffness for the lower fibre radii considered and underestimate it for the higher radii. The tendency is for the beam models to do better for more slender tubes, and for the shell models for large fibre diameters. One of the reasons for this behaviour lies in the response of the cross sections. Figure 5.25 presents comparisons between displacements and stress states obtained with solid, beam and shell-models, respectively, pertaining to an outer fibre radius of $R_{CNT}=0.16$. Ovalisation of the tubes' cross section is evident for the solid and shell models, but is not included in the beam elements' formulation. This leads to a higher stiffness of the latter models for the case considered.

With decreasing tube radii, the influence of changes to the cross section decreases and the stiffness of the beam model approaches that of the solid model. The shell model, however, is clearly too stiff in this regime. For the simulations in the second case study, a small outer radius is used, $R_{CNT}=0.04$, for a unit cell length of 2 units.

In the following the results assessed with different types of mesh element being constrained to the matrix using the embedded element technique. Figure 5.26 presents comparisons between stress profiles obtained with unit cells containing 4x4 tubes of waviness parameter $w=0.125$ in a regular, square arrangement for four different models (one 3D solid full model and three models with beam, shell and solid elements embedded

Table 5.6: Comparison of the stiffness of single, free, sine-like tubes ($w = 0.125$) of different radii, meshed with different types of element

	Solid elements	Beam elements	Shell elements	Relative error		Relative error
				Beam vs. Shell	Shell vs. Solid	
[%]						
$R_{CNT}=0.08$	$u_1=2.49$ E-2	$u_1=2.47$ E-2	$u_1=2.48$ E-2	0.80		9.02
$r_{CNT}=0.04$	$k_1=160.64$	$k_1=161.94$	$k_1=175.13$			
$R_{CNT}=0.12$	$u_1=5.46$ E-3	$u_1=5.52$ E-3	$u_1=5.28$ E-3	-1.09		3.40
$r_{CNT}=0.06$	$k_1=732.60$	$k_1=724.63$	$k_1=757.57$			
$R_{CNT}=0.16$	$u_1=1.93$ E-3	$u_1=2.03$ E-3	$u_1=1.96$ E-3	-5.03		-1.55
$r_{CNT}=0.08$	$k_1=2074.04$	$k_1=1969.54$	$k_1=2041.85$			
$R_{CNT}=0.20$	$u_1=8.99$ E-4	$u_1=9.81$ E-4	$u_1=9.39$ E-4	-8.28		-4.16
$r_{CNT}=0.01$	$k_1=4444.59$	$k_1=4076.31$	$k_1=4259.85$			

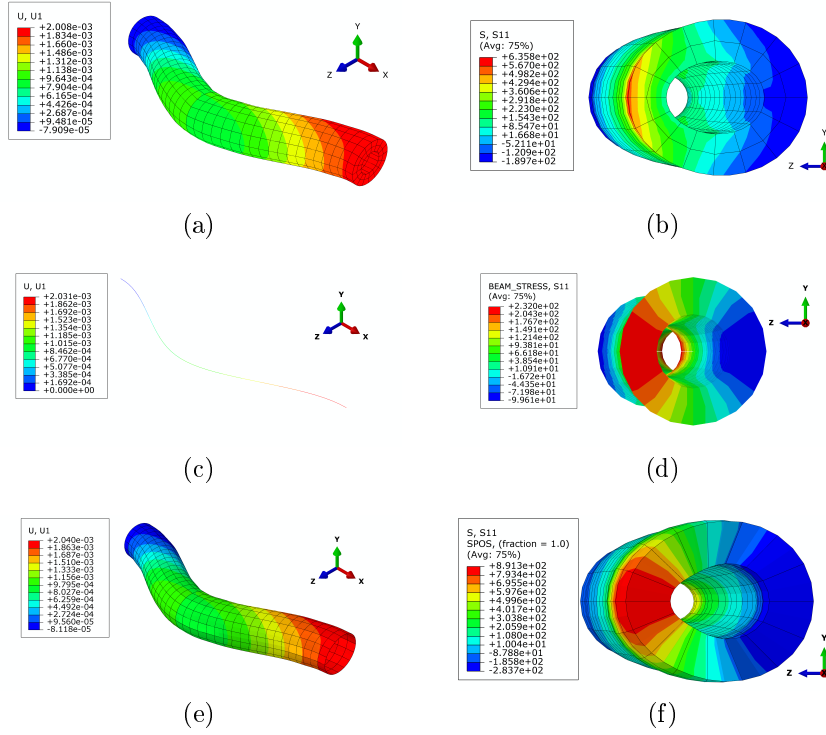


Figure 5.25: Wavy hollow sine-like tubes with a outer fibre radius of $R_{CNT}=0.16$, meshed with solid (a-b), beam (c-d) and shell (e-f) elements. a,c and e present longitudinal displacements and b,d and f distributions of the longitudinal normal stress component, a cut being made with an $x=\text{constant}$ plane in the middle of the tube. The deformation scale factor is set to 500.

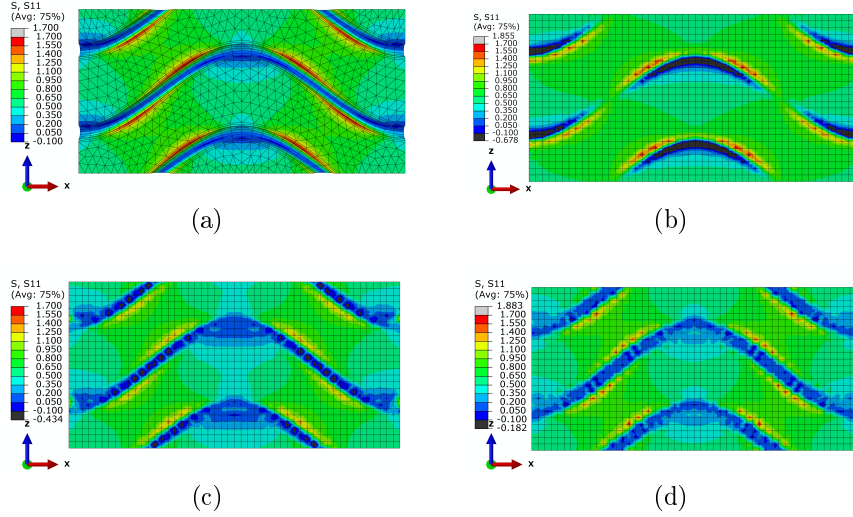


Figure 5.26: Distribution of axial normal stress in detail of longitudinal section of arrangement of 16 tubes, $w=0.125$: 3D full solid model (a), embedded beam elements (b), embedded shell elements (c) and embedded solid elements (d)

in the matrix). A part of a longitudinal section of the unit cell, measuring 2×1 length units, is shown.

Generally, the embedding technique captures the stress distribution quite well, though for the model using embedded beams the compressive axial stresses are considerably more strongly concentrated, with small regions showing elevated negative values of σ_{11} . This is due to the 1D nature of the beam elements, which do not have proper volume and interact with a smaller number of elements in the matrix. The stress distributions predicted by the embedding models using solid and shell elements are quite similar, differences being apparent mainly in the regions of maximum curvature of the tubes. Quantitative comparisons of the Young's moduli obtained for models with different waviness parameters are presented in Figure 5.27. The identifiers "EmbBeam", "EmbShell", "EmbSolid" indicate models that use the embedding technique in superimposing matrix and tube meshes, the latter using beam, shell and solid elements, respectively. "Solid" refers to the conventional 3D full solid model. Different fibre volume fractions were obtained by changing the number of nanotubes within the unit cell for wavy fibres with $R_{CNT}=0.04$ (Table 4.6) and by changing the radius for straight fibres (Table 4.7). For straight nanotubes ($w=0.0$), the linear dependence between volume fraction and axial Young's modulus is evident and the models give fairly similar results. For the non-zero waviness parameters, the axial Young's moduli obtained with the superposition method tend to underestimate the results obtained with the full 3D solid model, but are much more efficient in terms of computational and modelling effort. For all cases, the beam models show the softest behaviour, whereas the shell models are considerably closer to the embedded solid models. For waviness parameters of $w=0.125$ and $w=0.2$ the

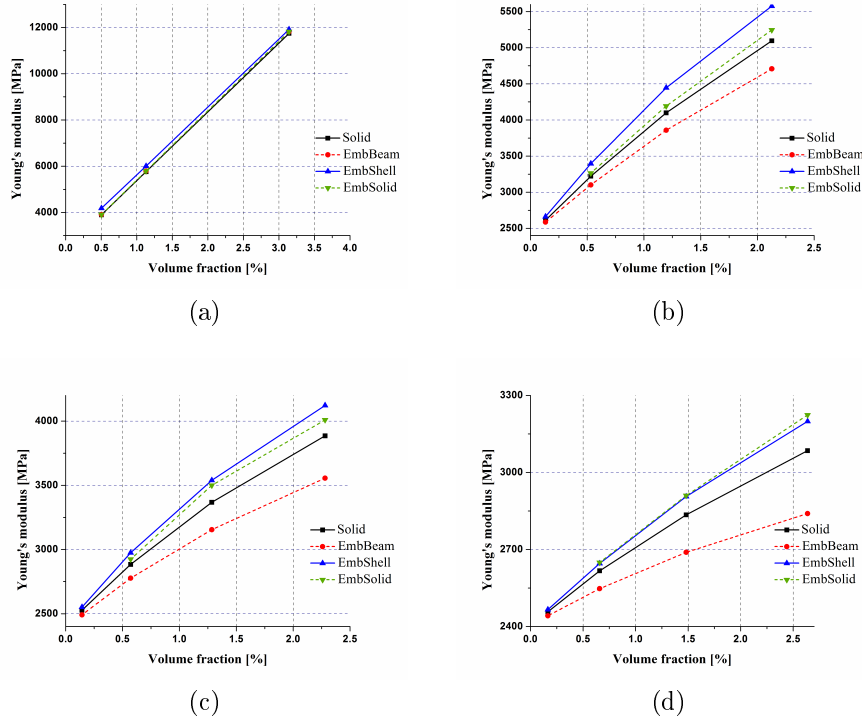


Figure 5.27: Longitudinal elastic modulus predicted for fibres with different waviness: $w = 0.0$ (a), $w = 0.08$ (b), $w = 0.125$ (c) and $w = 0.2$ (d)

embedded shell predictions give better agreement with the full 3D model results than do the ones generated with the embedded solid model. As expected, waviness can be seen to reduce the effective longitudinal elastic modulus. At a reinforcement volume fraction of 2% a waviness parameter of $w = 0.2$ is predicted to give rise to a reduction of the Young's modulus from 8 GPa to 2.8 GPa, which corresponds to a loss of 65% in stiffness.

In terms of the longitudinal Young's modulus, the responses generated with embedded solid and, especially, the embedded shell models in Figure 5.27 are promising. When comparing these results with the ones obtained in first case study of the free CNTs, a much more favourable behaviour of the shell models is evident. This appears to be due to cancelling out of errors from the discretisation of the CNT and from the embedding procedure.

Since the periodic homogenisation approach can provide full elastic tensors rather than just the longitudinal Young's modulus, the influence of the discretisation strategy on the other effective elastic constants can also be assessed. When realistic geometries with twisted and tangled CNTs are considered, of course, the interactions between fibres and matrix must be described sufficiently well for all local loading conditions, translating into a requirement for good quality approximations for all moduli. Figure 5.28

and 5.29 shows plots of the relative error in six of the nine elastic moduli relevant to macroscopically orthotropic behaviour. The data is given as functions of the reinforcement volume fraction and the waviness parameters, the fibres having the shape of sine waves in the XZ-plane. E_{11} stands for the longitudinal macroscopic Young's modulus, E_{22} as well as E_{33} for the transverse macroscopic Young's moduli, G_{12} and G_{13} for the longitudinal and G_{23} for the transverse macroscopic shear moduli of the composite.

Errors in excess of 5% can be seen to occur for the axial Young's modulus E_{11} predicted by the embedded shell models for small waviness parameters and for the longitudinal shear modulus in the plane of waviness G_{13} for both solid and shell embedded models at high waviness parameters. In the case of the transverse Young's modulus E_{22} which describes the response normal to the plane of waviness, the errors of both models approach 4%, with the embedded shells being superior for small waviness parameters. For the other moduli the embedded shell approach gives errors of less than 2% and shows a more favourable behaviour than the embedded solid models. For the whole range of waviness and concentration the beam models show much softer behaviour for all elastic moduli. As example, the relative differences in the predicted six elastic moduli between the conventional 3D solid model and the embedded beam model are shown in Table 5.7.

The embedding technique is subject to limitations in correctly representing phase volume fractions and total solid volume, the shell and solid elements describing the nanotubes being overlaid on the solids making up the matrix. Thus, corrections by volume fraction must be considered. As mentioned before, this can be achieved for straight nanotubes by assigning the difference between the elasticity tensors of reinforcement and matrix to the latter, compare [162, 163]. For beam and shell models describing more complex nanotube geometries fibre bending plays an appreciable role. However, this approach requires verification, which is outside the scope of the present contribution. Table 5.8 shows that overlaying the volumes of matrix and reinforcement does influence the predicted macroscopic moduli. The results labelled "EmbShell model with corrected volume" were obtained by removing the equivalent volume of the nanotubes from the matrix, followed by superimposing the fibre mesh and connecting it to the matrix with standard embedding constraints provided by ABAQUS. The positive sign in the relative difference means that embedded models give stiffer responses than the conventional model. The volume-corrected shell models, of course, are mainly useful for comparisons because their use negates most of the advantages in terms of modelling effort that led to studying embedded models in the first place. The relative difference between the embedded and the conventional solid model for a c_r of 0.1653% could not be obtained due to numerical difficulties.

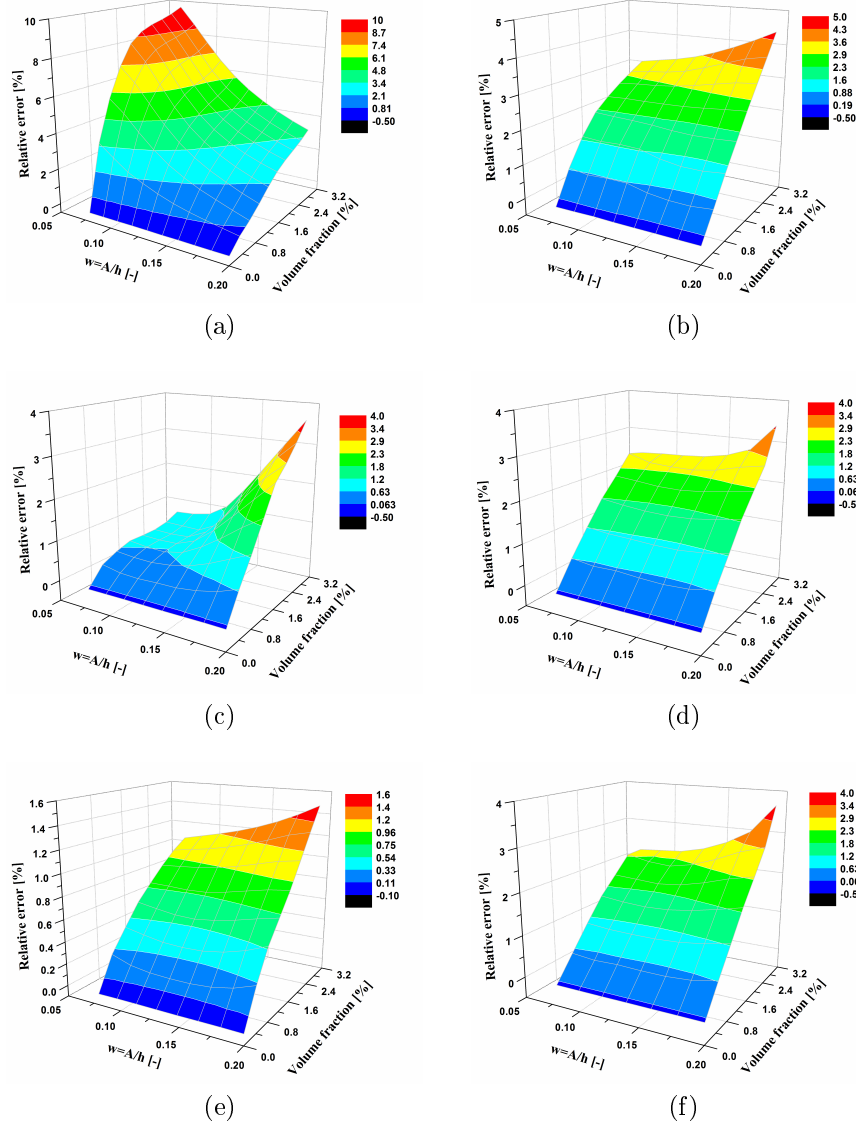


Figure 5.28: Relative difference in the predicted Young's moduli between the conventional 3D solid model, the embedded shell (E_{11} (a), E_{22} (c), E_{33} (e)) and the embedded solid models (E_{11} (b), E_{22} (d), E_{33} (f)), respectively

Table 5.7: Relative difference in the predicted six elastic moduli between conventional 3D solid model and embedded beam model

	E_{11}	E_{22}	E_{33}	G_{23}	G_{13}	G_{12}
$w = 0.2, N = 16, c_r = 2.65\%$						
[%]						
Relative error	-7.94	-4.63	-5.90	-4.49	-13.00	-4.69

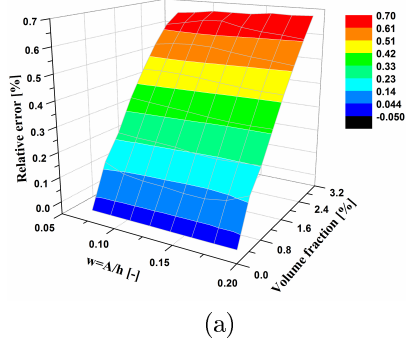
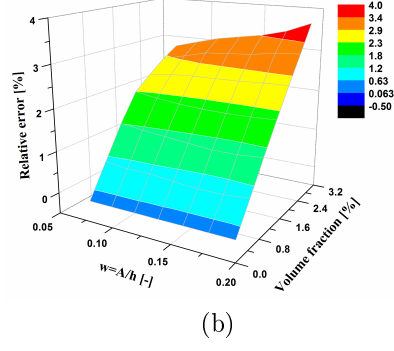
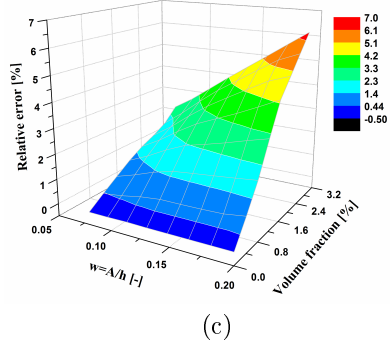
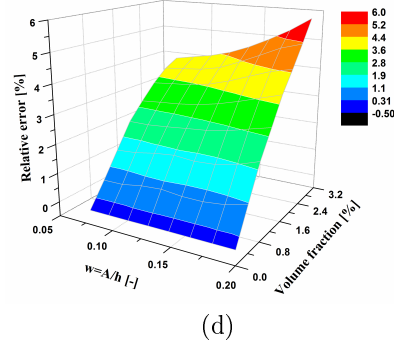
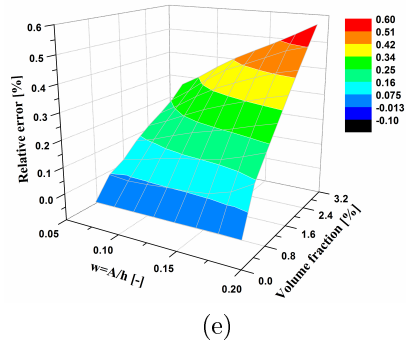
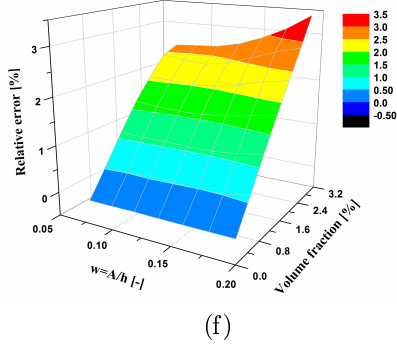


Figure 5.29: Relative difference in the predicted shear moduli between the conventional 3D solid model, the embedded shell (G_{12} (a), G_{13} (c), G_{23} (e)) and the embedded solid models (G_{12} (b), G_{13} (d), G_{23} (f)), respectively

Table 5.8: Correction by volume fraction. Relative difference in longitudinal Young's modulus between embedded beam/shell/solid models and conventional full 3D solid model

c_r [%]	EmbShell with corrected volume vs. Solid	EmbShell vs. Solid	EmbSolid vs. Solid	EmbBeam vs. Solid
0.1653	0.2116	0.3662	-	-0.6918
0.6578	0.6954	1.0852	1.2380	-2.4798
1.4822	1.7038	2.5257	2.6562	-4.7339
2.6369	2.3598	3.6921	4.5089	-7.5559

5.2.4 Real arbitrary composites

First homogenisation step: FEM-based periodic homogenisation

In the first step, curved CNTs were uniformly distributed in cube-shaped volume elements using Monte Carlo simulations according to experimentally obtained distributions of orientation and curvature parameters. The distributions obtained for spiral pitches and radii (Figure 5.13) as well as the orientations of the directors of the nanotubes (Figure 5.10) were used to create cube-shaped volume elements with different concentrations of nanotubes ranging from 0.5wt% to 5wt%. The obtained SVEs for different concentrations are presented in Figure 5.30. As aforementioned in Section 4.2, if parts of nanotubes fell outside the cube, it was translated to the opposite face of the cube. Furthermore, the length of a CNT was fixed to $1.5 \mu\text{m}$. Due to the random creation of segments, it occurred that the total length of a nanotube could be bigger. Consequently segments were eliminated and corrected weight as well as volume fractions were calculated, as presented in Table 5.9.

Five FE models based on the SVEs were created, with different, but statistically equivalent arrangements of nanotubes, for each concentration. The mechanical properties of these volume elements were evaluated by periodic homogenisation and averages over the obtained sets of data were determined. In addition, beam and shell discretisation schemes for the nanotubes were compared. The FEM results for Young's moduli in longitudinal and transverse directions and shear moduli are presented in Figure 5.31 and Figure 5.32, respectively. Values are normalised with respect to Young's modulus of the matrix ($E_m = 3 \text{ GPa}$, PC). The difference between beam and shell elements for all elastic constants, longitudinal and transverse Young's moduli as well as shear moduli, is of the order of 25% for a concentration of 1.53%. The maximum standard deviation for a set of five models was found to be 77 MPa (normalised value is 0.026), in

Table 5.9: Corrected weight and volume fractions for different concentrations

w_r	c_r	Distributed c_r
[%]		
0.5	0.29	0.26
1.0	0.57	0.51
2.0	1.15	1.03
3.0	1.74	1.54
5.0	2.92	2.64

case of shell elements and a concentration of 1.53%, which corresponds to about 1.82% of the corresponding averaged value.

First homogenisation step: Analytical micromechanics

The SVEs used in the FEM simulations were further analysed to analytically estimate the effective Young's moduli. Curved inclusions were substituted by straight ellipsoidal inclusions. Therefore, corrected orientation and effective length distributions for ellipsoidal inclusions were calculated and are shown in Figure 5.33 and 5.34, respectively. The change from an aligned to a more random orientation when increasing the concentration is clearly visible in Figure 5.33. As the waviness parameter and thus pitches as well as radii were kept constant, the effective length in models with different weight fractions is about the same, which can be seen from Figure 5.34.

The obtained analytical results of longitudinal and transverse Young's moduli averaged over effective length distributions and orientation distributions are presented in Figure 5.35. The moduli are additionally compared with analytical results obtained using Mori-Tanaka models for randomly oriented ellipsoidal inclusions as well as straight and aligned particles, respectively. It can be seen that moduli decrease for higher concentrations as the orientation changes from an aligned to a random state. To compare and validate the analytical and FE models with experimental data the results were additionally plotted in Figure 5.36(a) and 5.36(b). It can be seen that the proposed analytical model allows for capturing the trend for longitudinal as well as transverse moduli.

Inclusions were assumed to be straight elements with circular cross-section. In order to obtain the Young's modulus, which represents an arbitrarily curved CNT,

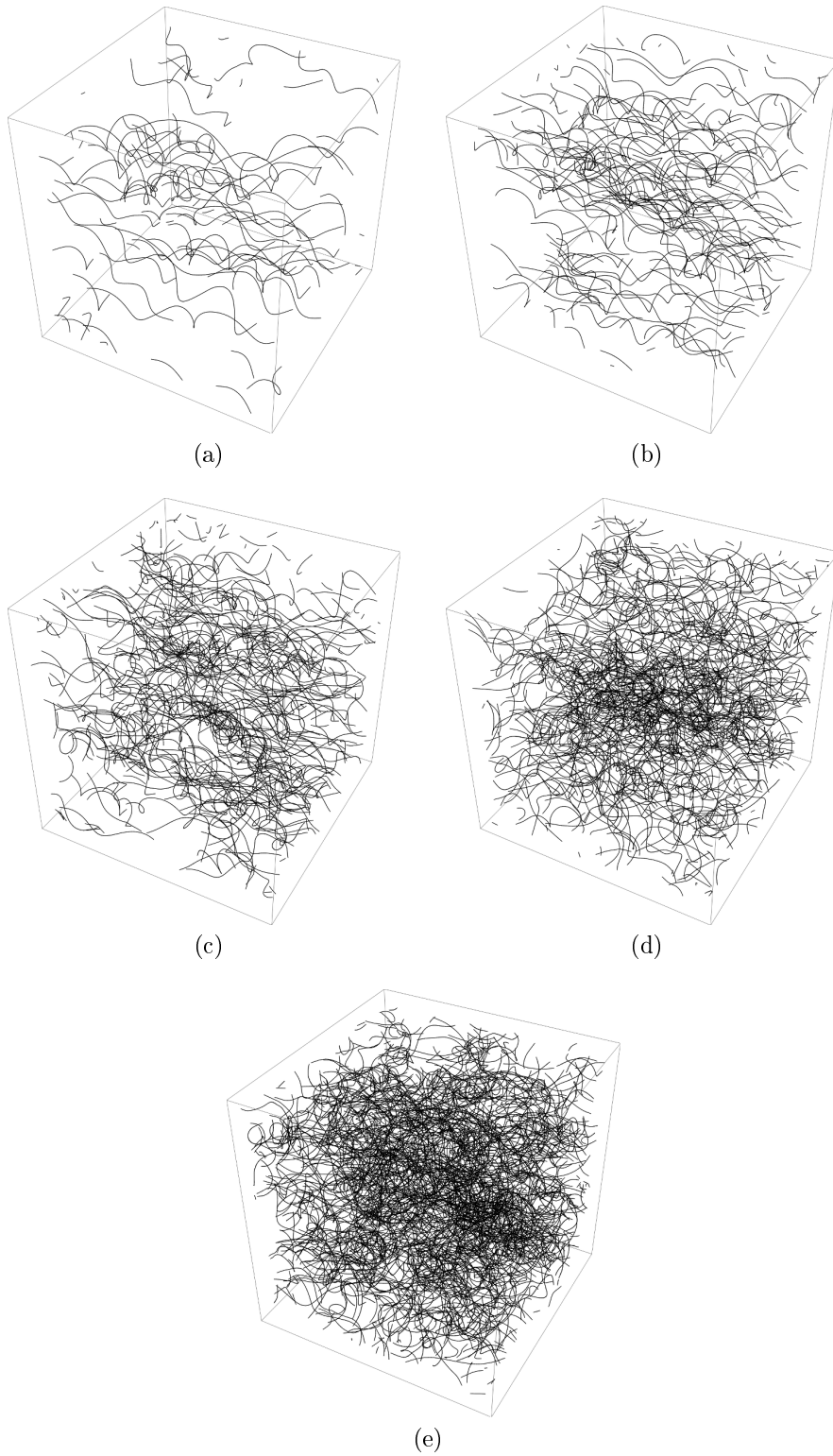


Figure 5.30: SVEs of CNT reinforced PC with different concentrations: 0.5wt% (a), 1.0wt% (b), 2.0wt% (c), 3.0wt% (d) and 5.0wt% (e)

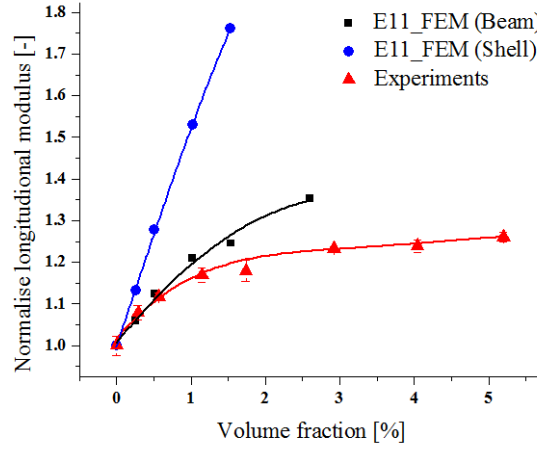


Figure 5.31: Normalised effective longitudinal Young's moduli computed by FEM in the 1st homogenisation step

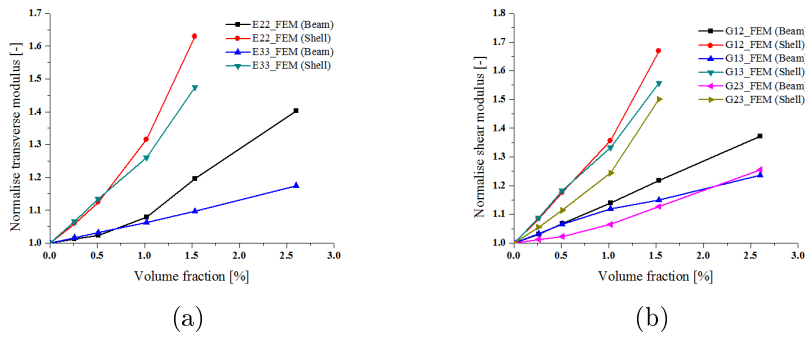


Figure 5.32: Normalised effective transverse moduli (b) and shear moduli (c) computed by FEM in the 1st homogenisation step

distributions of Young's moduli were calculated for five different curviness cases. Figure 5.37 presents the distribution of averaged inclusion's moduli, which was further used for analytical modelling. In the first analytical step the Young's modulus for straight CNT with solid cross-section was assumed to be 427 GPa (Table 4.8). However, from Figure 5.37 it can be seen that modulus of straight inclusions, representing curved CNT, is reduced to a value of about 350 GPa. Hence, Figure 5.38 presents the normalised longitudinal Young's modulus computed by analytical micromechanics and averaged over the ODF, the effective LDF as well as the inclusion's Young's modulus distribution function. It can be seen that with increasing concentration the overall longitudinal Young's modulus is further reduced.

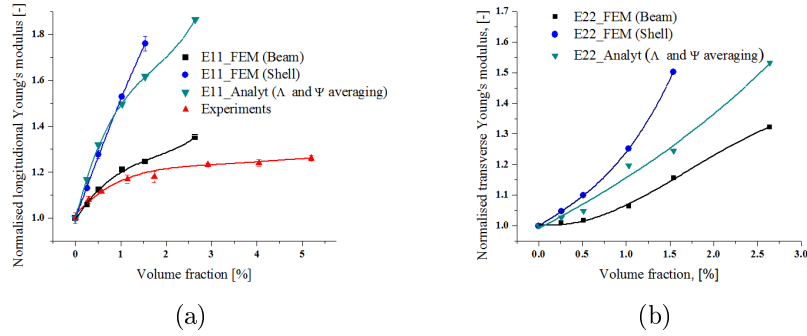


Figure 5.36: Normalised effective longitudinal (a) and transverse (b) Young's moduli computed by analytical micromechanics in the 1st homogenisation step (averaged over Λ , Ψ distribution functions) and compared with finite beam/shell element models

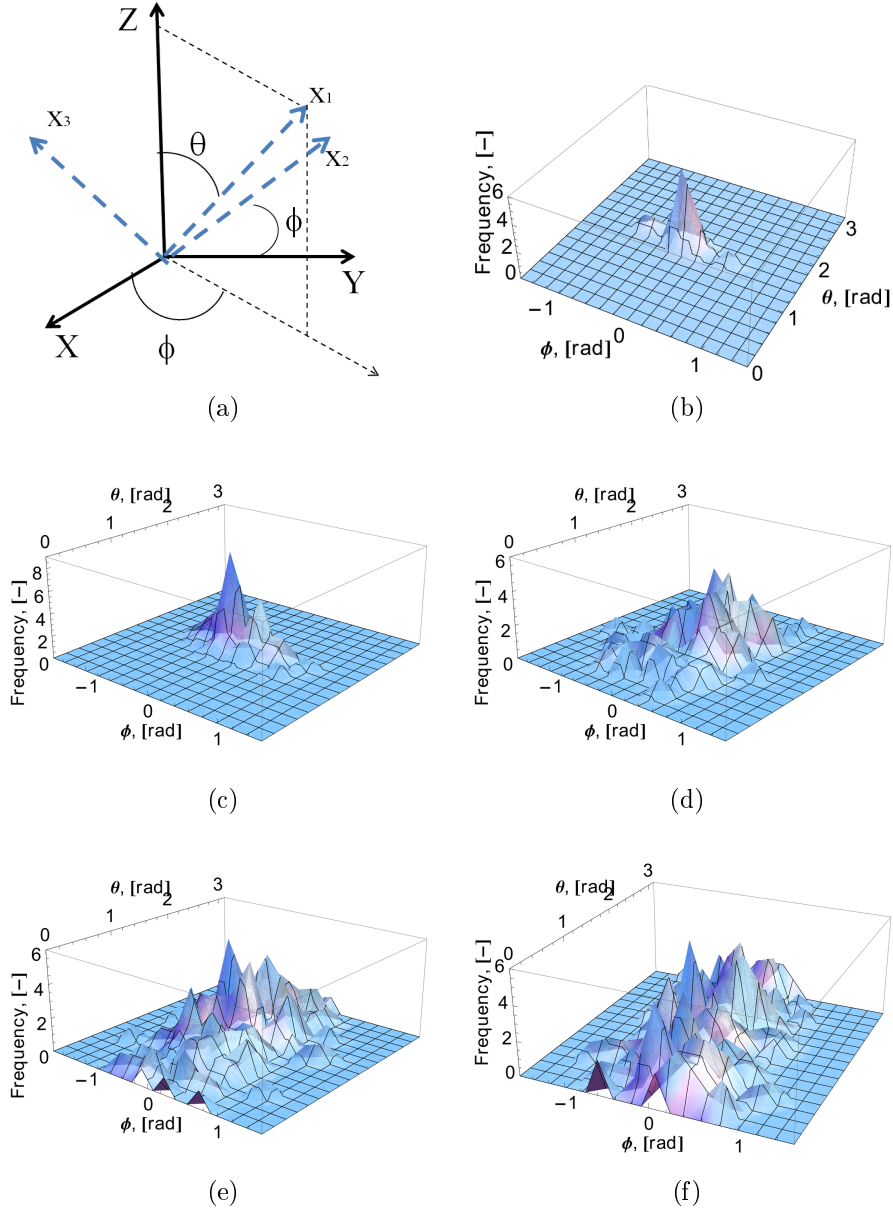


Figure 5.33: Orientation distributions for different weight fractions of ellipsoidal inclusions: COS (a), 0.5wt% (b), 1.0wt% (c), 2.0wt% (d), 3.0wt% (e) and 5.0wt% (f)

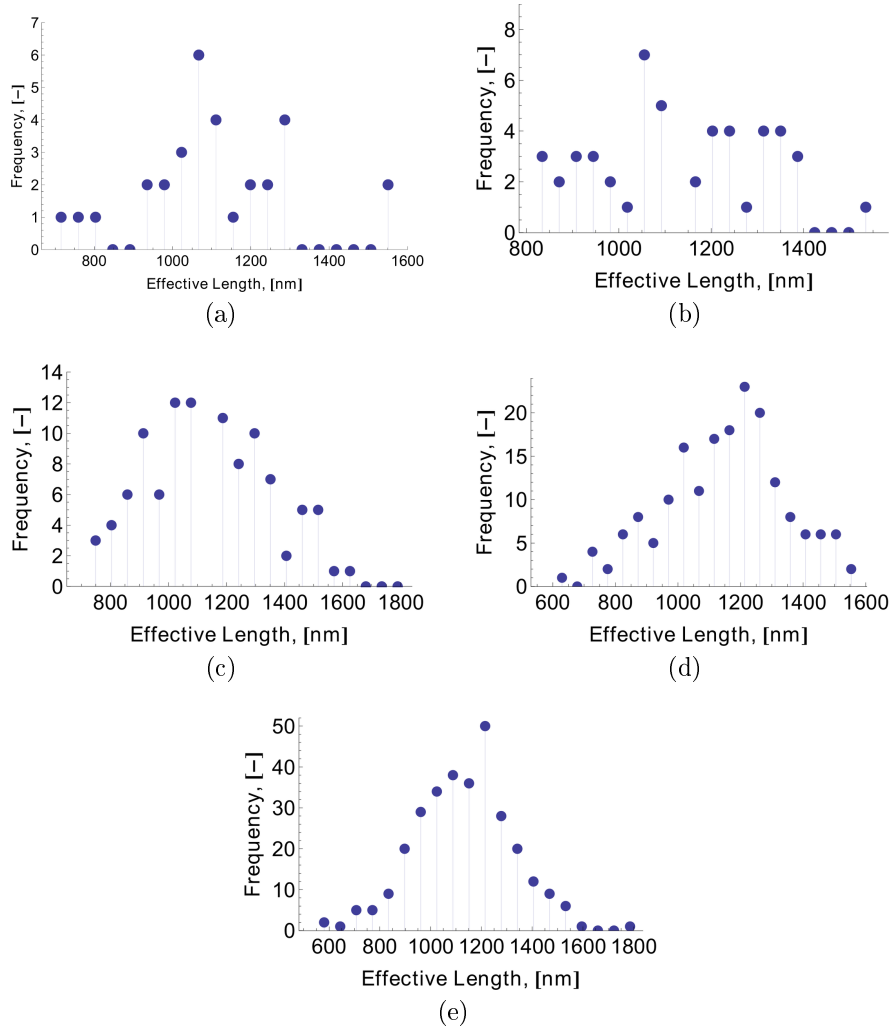


Figure 5.34: Effective length distributions for different weight fractions of ellipsoidal inclusions: 0.5wt% (a), 1.0wt% (b), 2.0wt% (c), 3.0wt% (d) and 5.0wt% (e)

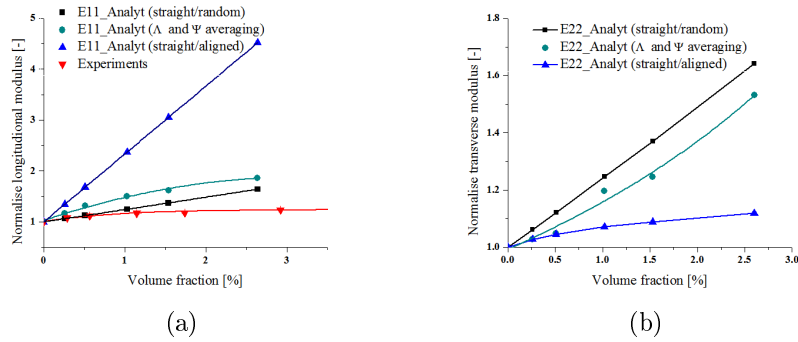


Figure 5.35: Normalised effective longitudinal (a) and transverse (b) Young's moduli computed by analytical micromechanics in the 1st homogenisation step

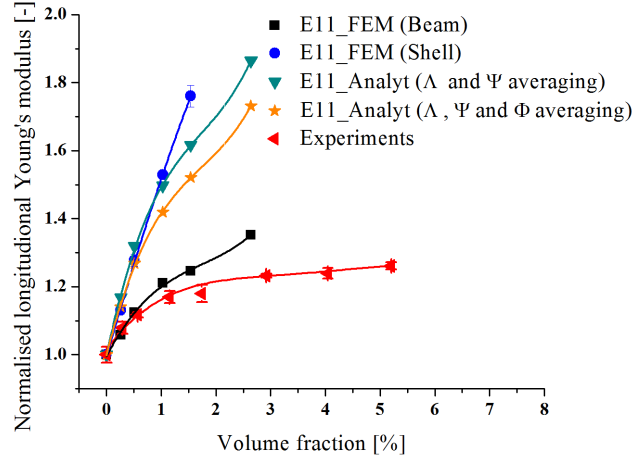


Figure 5.38: Normalised effective longitudinal Young's moduli computed by analytical micromechanics in the 1st homogenisation step (averaged over Λ, Ψ, Φ distribution functions) and compared with finite beam/shell element models

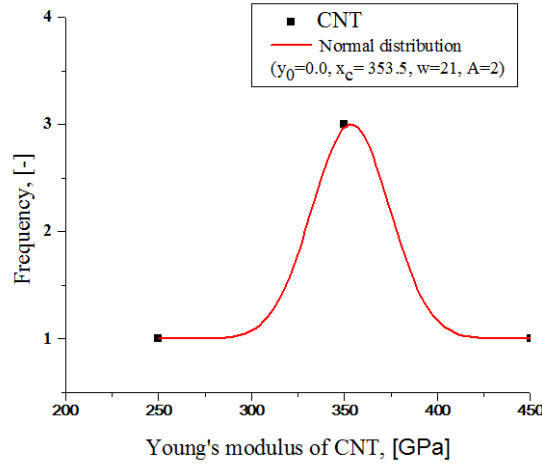


Figure 5.37: Effective reinforcing Young's modulus of straight ellipsoidal inclusions representing the curved nanotubes

Second homogenisation step: Analytical micromechanics

In the second homogenisation step the effect of dispersion was integrated into the numerical and analytical calculation of the effective Young's modulus. Analyses in the first homogenisation were performed for c_r of 0.29, 0.57, 1.15, 1.74 and 2.92%. In order to evaluate the effective Young's modulus for perfectly dispersed nanotubes E_{FEM}^{disp} the normalised effective longitudinal Young's modulus computed by the finite beam element

model shown in Figure 5.38 was approximated with a cubic polynomial (Equation 5.5) using corrected concentrations for perfectly dispersed nanotubes c_r^{disp} . The Young's modulus of the neat polymer matrix was 3.0 GPa.

$$y = 0.995 + 0.315x - 0.136x^2 + 0.026x^3 \quad (5.5)$$

To compute the Young's modulus for nanocomposites with spherical embedded inclusions E_{FEM}^{sphere} the previously obtained modulus E_{FEM}^{disp} and the concentration of agglomerated nanotubes c_r^{sphere} was utilised to represent the isotropic medium in the Mori-Tanaka modelling approach. Although this isotropic representation is just an approximation due to the orientation of the nanotubes. Moreover, the effective Young's modulus analytically computed and averaged over Λ, Ψ, Φ distribution functions was recalculated for the corrected concentrations c_r^{disp} . The obtained modulus E_{analyt}^{disp} was used, similar to the aforementioned procedure, as input for the isotropic medium in the Mori-Tanaka model to calculate the effective modulus for a nanocomposite with spherical agglomerations E_{analyt}^{sphere} . The obtained results were compared with results for the perfectly dispersed nanotubes calculated in the first homogenisation step and are presented in Tables 5.10 and 5.11, respectively. w_r denotes the weight fraction of CNTs in the polymer, c_r is the CNT volume fraction, $E_{11}^{FEM/Beam}$ the longitudinal Young's modulus computed by FEM in the 1st homogenisation step with beam elements for curved pre-oriented nanotubes, E_{11}^{analyt} the longitudinal Young's modulus computed by analytical micromechanics in the 1st homogenisation step for curved pre-oriented nanotubes and E^a is the Young's modulus of agglomerates (computed in Section 4.2).

It can be seen in Figure 5.39 that the modulus decreases in the second homogenisation step for increasing concentrations and increasing amount of agglomerations seen in OLM micrographs. The difference between results computed for perfectly dispersed and agglomerated nanotubes is less than 0.5% for almost all cases. However, the difference for the composite with a concentration of 2.92% is up to 6.6% for the analytical model and 4.3% for the FE model using beam elements. The difference between the finite beam element model with integrated dispersion analysis and experimental results for longitudinal Young's moduli is 8.17% for a volume fraction of 2.92%. Considering the complicated microstructure and the random morphological characteristics for nanocomposites a good agreement between experimental and modelling results was obtained.

Table 5.10: Effective properties of CNT/PC composite by FEM in the 2nd homogenisation step (integration of dispersion analysis into FEM)

w_r	c_r	$E_{11}^{FEM/Beam}$	c_r^{disp}	E_{FEM}^{disp}	E^a	c_r^{sphere}	E_{FEM}^{sphere}
	[%]	[MPa]	[%]	[MPa]		[%]	[MPa]
0.5	0.29	3232.23	0.27	3217.51		0.02	3218.47
1	0.57	3411.43	0.56	3405.84		0.01	3406.34
2	1.15	3657.12	1.13	3650.74	21420	0.02	3651.79
3	1.74	3811.54	1.71	3804.52		0.03	3806.13
5	2.92	4214.89	2.46	4008.77		0.46	4034.37

Table 5.11: Effective properties of CNT/PC composite by analytical micromechanics in the 2nd homogenisation step (integration of dispersion analysis into analytical model)

w_r	c_r	E_{11}^{analyt}	c_r^{disp}	E_{analyt}^{disp}	E^a	c_r^{sphere}	E_{analyt}^{sphere}
	[%]	[MPa]	[%]	[MPa]		[%]	[MPa]
0.5	0.29	3549.2	0.27	3512.58		0.02	3513.6
1	0.57	3907.44	0.56	3891.72		0.01	3892.26
2	1.15	4412.27	1.13	4387.73	21420	0.02	4388.9
3	1.74	4774.65	1.71	4744.14		0.03	4745.97
5	2.92	5442.5	2.46	5052.85		0.46	5081.94

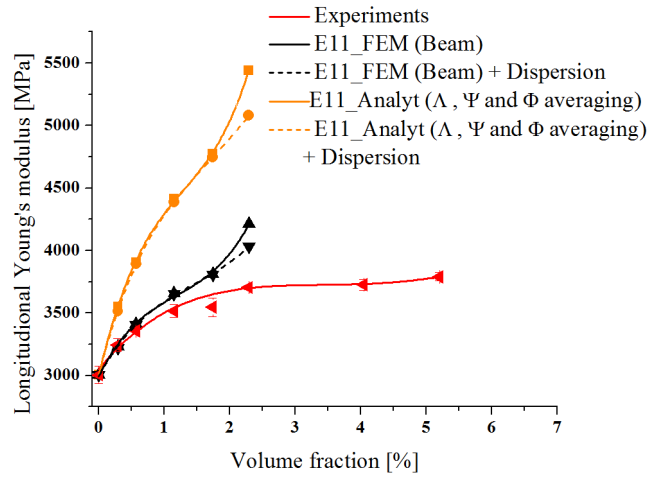


Figure 5.39: Normalised effective longitudinal Young's moduli computed by analytical micromechanics in the 2nd homogenisation step (averaged over Λ, Ψ, Φ distribution functions) and finite beam/shell element models with and without dispersion analysis

Chapter 6

Conclusions

Carbon nanotubes/ carbon nanofibres (CNTs/CNFs) allow for improving mechanical properties of polymers and offer additionally enhanced electrical and thermal conductivity. Due to difficulties associated with processing induced morphological characteristics, such as the dispersion and orientation, the full potential of CNTs/CNFs as reinforcements in polymeric matrices for structural parts has been limited. The research work presented in this thesis aimed at understanding the relationships between processing induced morphological characteristics and the mechanical properties of nanocomposites. Methodologies were developed for quantifying the level of dispersion, orientation and curliness of nanofillers. The obtained data was implemented in analytical and numerical modelling approaches for the prediction of effective properties. The reliability of the proposed numerical and analytical approaches was verified with experimental results. The aim of this chapter is to discuss findings of the presented studies, to highlight significant conclusions and to give recommendations for future work.

6.1 Experimental characterisation

Different processing techniques and polymer matrices were used to produce composites reinforced with different concentrations of CNTs/CNFs. OLM was employed to analyse the level of dispersion by means of grey scale distributions. Additionally, a binarising method was used to determine the area distributions of agglomerates. It was shown that both the calendaring approach and melt processing/ injection moulding can be used to obtain a good level of dispersion of nanoparticles in polymeric materials. However, with increasing concentrations the width of histograms increases showing that the level of dispersion decreases. In micrographs of CNT/PC samples agglomerates are clearly visible as circular inclusions. On the contrary, in binarised micrographs of CNF reinforced polymers it is difficult to distinguish agglomerated from dispersed nanofillers. Due to difficulties during sample slicing, CNF reinforced samples could only be cut in 10 μm thick slices resulting in dark micrographs with reduced ranges of greys, which complicate and even render grey scale analyses impossible. It was concluded that the thinner

the slice the better is the contrast between dispersed and agglomerated nanoparticles, and thus the easier and better are dispersion analyses.

Orientation as well as curviness distributions are sufficient to model nanoreinforcements in the 3D space. Therefore, TEM was performed to analyse the CNT filled PC samples on the nanoscale and to obtain information about the orientations and 3D curved geometries of MWNTs. It can be seen that CNTs tend to have arbitrarily curved shapes and that CNTs in samples with small nanotube concentrations (weight fractions up to 2%) have a preferred orientation along the injection flow. Moreover, it could be seen that the orientation is changing with increasing concentrations from an aligned to a more random orientation. In order to investigate the influence of the nanotubes' 3D curved geometries and orientations on the effective mechanical properties by means of numerical models a methodology was developed to numerically reconstruct the morphological characteristics. The obtained distribution functions of orientation, pitches and radii were employed in a Monte Carlo scheme to choose random pitches, radii and orientations of CNT centrelines in order to generate cube-shaped volume elements. Thereafter, thin slices with a thickness of 100 nm, similar to the thickness used for the TEM images, were extracted at the centres of the XY- and YZ-planes. Although identical shapes to the ones seen in samples obtained by microscopy could not be obtained, similarities between the two sets of plots were clearly evident.

Tensile experiments were performed to serve as validation data for the presented analytical and numerical modelling approaches. Three point bending tests at quasi-static rates of loading were used to determine differences between tensile and flexural behaviour. The Young's modulus of CNF reinforced PC increased nearly linearly with increasing weight fraction. On the contrary CNT reinforced PC presented a linear increase in stiffness for weight fractions smaller than 4%, thereafter the modulus reached a plateau and increased only moderately. As seen from OLM micrographs dispersion could not be used for explaining the observed behaviour. However, TEM images showed that the orientation in CNT/PC samples was changing with increasing concentrations from an aligned to a more random orientation.

In contrast to the tensile results the flexural modulus of CNF/epoxy samples only increased linearly for small concentrations up to 1.5wt%. The observed mechanical behaviour was similar to the tensile behaviour of CNT/PC. Moreover, it was seen that the widths of histograms increased with increasing concentrations. Thus it was concluded that the mechanical properties of CNF and CNT reinforced polymers are influenced by an interaction of dispersion, orientation and curviness.

6.2 Modelling

6.2.1 Influence of waviness and curliness on mechanical properties

The comparisons of different methods for assessing the effects of nanotube waviness and curliness on macroscopic elastic behaviour of CNT reinforced polymers indicated that FE models using beam elements for discretising nanotubes and employing PMUBC show a very attractive combination of relatively low computational requirements and good accuracy, provided the CNT volume fraction is low. The much cheaper Mori-Tanaka-based analytical model, which introduced strong assumptions on the description of the fibre geometries, provided similar trends for the elastic constants compared to the results obtained with FE models, but had a clear tendency towards overestimating the moduli.

The results demonstrated that the curviness of nanotubes reduces the effective longitudinal modulus of the composite. The degree of loss in longitudinal stiffness depends on the ratio of the sinusoidal amplitude or helical radius to the period of the waviness or the pitch of spirals. Furthermore, it was shown that with respect to this parameter the effects of helical CNTs are more marked than those of wavy ones.

6.2.2 Influence of concentration and segment number per CNT on mechanical properties

Taking into account the complex geometry of CNTs a hybrid FE-micromechanical model and a fully numerical model were proposed for calculating the effective elastic tensors of composites filled with different concentrations of CNTs. The nanotubes were embedded into the matrix as beam elements using a MPC technique available in the FE-code ABAQUS. Curliness was presented by modelling the CNTs in a cube as sequences of segments joined together at randomly chosen angles using Monte Carlo simulations. The number of segments per CNT was chosen according to the statistical apparatus developed for flexible polymer chains in solution. For the semi-analytical method the dilute stiffness tensor was calculated first by the FE method, followed by an analytical extraction of the phase averaged strain concentration tensor using the mean field formalism. The dilute strain concentration tensor was incorporated into Mori-Tanaka models in order to calculate the effective elastic tensors of composites with different volume fractions of randomly oriented inclusions. The second approach was based on numerically evaluating the effective elasticity tensor of RVEs containing CNTs at concentrations ranging from 0.5 to 7% by weight fraction. The specific PMUBC were used in both approaches. Comparison with experimental results showed that the fully numerical results follow the trend of the experimental data better, though the effective moduli were considerably lower. The main strength of the proposed methods was that they are capable of taking into account arbitrary curliness of CNTs. Using a statistical apparatus and Monte Carlos simulations it was shown that with increasing concentrations of CNTs the curviness is increased, however the mechanical properties are not

enhanced.

6.2.3 Influence of FE modelling techniques on mechanical properties

The performance of composites reinforced by CNT depends strongly on the geometric parameters of the nanotubes, including aspect ratio, waviness, orientation, spatial distribution plus many other factors. Existing quantum mechanical and molecular dynamics methods have only limited applicability to analysing this issue, mainly because the volume elements to be studied are relatively big. The objective of the present work is assessing efficient numerical continuum-level modelling procedures that may be used for studying the mechanical responses of composites reinforced with arbitrarily curved nanotubes at various levels of concentration. Due to computational requirements and difficulties in meshing, the use of conventional full 3D solid models, in which reinforcement and matrix are meshed compatibly with volume elements, is a challenging task. A superposition model was employed for describing CNTs, which were meshed using beam, shell and solid elements, and embedding into polymer matrices. CNTs were modelled as sine-like hollow tubes or shells with predefined thickness.

At first beam and shell element models of curved tubes without a matrix were compared to solid models in order to study the influence of the fibre radius of individual CNTs on the choice of element type. It was observed that the predictions for the longitudinal stiffness of single nanotubes in the absence of a matrix are sensitive to the discretisation. In a second step CNTs were meshed independently with beam, shell or solid elements and embedded into a matrix by linking the translational degrees of freedom. Unit cells were subjected to six linearly independent load cases to evaluate the effective elastic tensor. Results were compared with calculations obtained with conventional 3D full solid models. For all models the effective Young's and shear moduli increased markedly with increasing reinforcement concentration and decrease with increased CNT waviness.

The relative difference in the Young's and shear moduli between conventional full solid models and embedded beam/shell/solid models was largest for the beam models, resulting in a much more compliant macroscopic behaviour. In addition, embedded beam models lacked accuracy in describing the mechanical responses in the transverse directions and under shear loading, especially for increased concentrations. Shell and solid elements were found promising for modelling the effective properties of composites reinforced by CNTs as they tend to give reasonable values for all considered moduli when compared with the corresponding 3D full models. Overall, embedded shell and embedded solid models exhibit a slightly stiffer longitudinal modulus than the conventional 3D solid model. The accuracy of the simulations depends, on the one hand, on the modelling technique used and, on the other hand, on the material properties chosen for the constituents as well as on the phase geometries. In terms of geometry the analysis is a considerable advance with regard to other available models, but the material

properties contain a big amount of guesstimates. Since the shells were shown to be considerably closer to the full solid model in the studies of reinforcements without matrix there is a pretty high probability that errors in the material data are cancelled out to a larger degree by errors in the beam model than by errors in the shell models. An interesting fact was that, upon increasing the nanotube waviness, the embedded shell model gave more accurate results for the longitudinal elastic modulus compared with embedded solid models. In addition, the embedded shell models gave better results than the embedded solid models for the transverse Young's and shear moduli independently of waviness or volume fraction.

Hence it was concluded that for the purpose of modelling arbitrarily curved CNTs, especially when they exhibit strong curvature and have a wide range of orientations, the embedded technique using shell elements appears to be a promising approach to reducing computational effort.

6.3 Real arbitrary composites

In order to model arbitrary CNT reinforced polymeric composites and account for the influence of morphological effects, such as the curvature, dispersion and orientation, a two-step homogenisation method was proposed. In the first step, different concentrations of curved nanotubes ranging from 0.5wt% to 5wt% were uniformly distributed in cube-shaped volume elements using Monte Carlo simulations according to experimentally obtained distributions of orientation and curvature parameters as well as distributions for spiral pitches and radii. FE models based on these SVEs were created, using beam as well as shell elements, with different, but statistically equivalent arrangements of nanotubes, for each concentration. The mechanical properties of five volume elements were evaluated by periodic homogenisation and averages over the obtained sets of data were determined. The difference between beam and shell elements for all elastic constants, longitudinal and transverse Young's moduli as well as shear moduli, for example, is of the order of 25% for a concentration of 1.53%. Moreover, a Mori-Tanaka model was used to analytically calculate the effective elastic properties of the resulting composite. The curved inclusions in the SVEs were substituted by ellipsoidal inclusions with reduced lengths and Young's moduli. From the results of longitudinal and transverse Young's moduli averaged over effective length distributions and orientation distributions it can be concluded that moduli decrease for higher concentrations as the orientation changes from an aligned to a random state. A comparison of analytical, FE models and experimental data showed that the proposed analytical model allows for capturing the trend for longitudinal as well as transverse moduli. Moreover, it could be seen that modulus of straight inclusions, representing curved CNT, takes a reduced values of about 350 GPa. Hence, it was shown that the overall analytically obtained Young's modulus, averaged over the orientation distribution function, the effective length distribution function as well as the inclusion's Young's modulus distribution function, were

further reduced with increasing concentration.

In the second homogenisation step the effect of dispersion was integrated into the numerical and analytical calculation of the effective Young's modulus. The composite was considered as a two-phase material consisting of agglomerates of CNTs in an isotropic medium made up of the polymer matrix and dispersed nanotubes. Longitudinal moduli accounting for spherical agglomerations were approximated based on the normalised effective Young's moduli computed by the finite beam element model as well as on the averaged analytical model. It was shown that the modulus decreases in the second homogenisation step for increasing concentrations and increasing amount of agglomerations. The difference between results computed for perfectly dispersed and agglomerated nanotubes is less than 0.5% for almost all cases. However, the difference for the composite with a concentration of 2.92% is up to 6.6% for the analytical model and 4.3% for the FE model using beam elements. The difference between the finite beam element model with integrated dispersion analysis and experimental results for longitudinal Young's moduli is 8.17% for a volume fraction of 2.92%. Considering the complicated microstructure and the random morphological characteristics for nanocomposites it was concluded that a good agreement between experimental and modelling results was obtained. Moreover it was shown that, similar to the conclusion taken from the experimental characterisation, the mechanical properties of CNT reinforced polymers are influenced by an interaction of dispersion, orientation and curviness.

6.4 Recommendations for future work

Upon reaching the current development further research topics have inevitably revealed their importance. For this reason recommendations for future studies are listed below.

Experimental characterisation

- More elaborated experimental analyses to reveal testing errors and obtain sound validation data for modelling approaches.
- TEM analyses of CNF reinforced polymeric matrices to obtain information about orientation and curviness on the nanoscale.
- Development of reliable experimental approach to quantify the level of dispersion in samples with low and high concentrations of nanoreinforcements.

Modelling

- To improve the analysis of dispersion effects on the mechanical properties a more detailed study has to be performed using better presentations of real material systems, such as FE models using a representative medium with randomly dis-

persed and agglomerated nanotubes. In this way the influence of the density of agglomerates as well as their number and size can be analysed in detail.

- Integration of interface between nanotubes and polymer as well as anisotropy of nanoreinforcements.

6.5 Publications

The research presented in this thesis has resulted in a number of contributions in the field of nanocomposite modelling, which have been published as oral communications and peer-reviewed publications as listed in reverse chronological order below.

- Anna Y. Matveeva, Helmut J. Böhm, Gregory Kravchenko, Ferrie W.J. van Hattum. Investigation of the embedded element technique for modelling wavy CNT composites. CMC Computers, Materials & Continua, vol.42, no.1, pp.1-23, 2014
- Anna Y. Matveeva, Sergey V. Pyrlin, Marta M.D. Ramos, Helmut J. Böhm, Ferrie W.J. van Hattum. Influence of waviness and curliness of fibres on mechanical properties of composites, Computational Materials Science, 87C, pp. 1-11, 2014
- Anna Y. Matveeva, Helmut J. Böhm, Ferrie W.J. van Hattum. Semianalytical stiffness tensor approximation for polymers reinforced with curved nanotubes, Proceedings of Composite Week at Leuven and TexComp-11 conference, Leuven, Belgium, 2013
- Anna Y. Matveeva, Jyri M. Tiusanen, Sergey V. Pyrlin, Ferrie W.J. Van Hattum. Investigation of the mechanical properties of injection moulded CNT reinforced thermoplastic polymer parts, Proceedings of SAMPE 2013 Conference and Exhibition, Long Beach, USA, 2013
- Matveeva, A.Y., Van Hattum, F.W.J., Pyrlin, S.V., Orientation and dispersion influences on elastic properties of CNT/CNF polymer nanocomposites, Proceedings of SAMPE Tech 2012 Conference and Exhibition, North Charleston, USA, 2012
- Anna Y. Matveeva, Ferrie W.J. van Hattum. Structure-property relationship in polymer nanocomposites, Proceedings of ECCM15 - 15th European Conference on Composite Materials, Venice, Italy, 2012
- Anna Y. Matveeva, Ferrie W.J. van Hattum. Relations between quantification of CNT dispersion and micromechanical prediction of mechanical properties of CNT/polymer composites, Proceedings of Mechanics of Nano, Micro and Macro Composite Structures, Politecnico di Torino, Italy, 2012
- Anna Y. Matveeva, Ferrie W.J. van Hattum. Orientation and dispersion influences on elastic properties of CNT/CNF polymer nanocomposites, IV Annual Meeting I3N, Quiaios, Portugal, 2012

- Anna Y. Matveeva, Ferrie W.J. van Hattum. Structure-property relationship in CNT composites, III Annual Meeting I3N, Fatima, Portugal, 2011

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Appendix A

Analytical modelling

A.1 General approaches for linear elasticity

The aim of the following micromechanical models is to predict the average elastic properties of a nanocomposite. Various modelling approaches have been established in dependence on the volume fraction of CNT/CNF, their geometry as well as interactions between single reinforcements.

As aforementioned in Section 2.4 of Chapter 2, microfields within each constituent of an inhomogeneous material can be approximated by their phase averages. Assuming perfect bonding between the phases, the constitutive equations for the reinforcement and matrix are

$$\langle \sigma \rangle_p = C_p \langle \varepsilon \rangle_p \quad (\text{A.1})$$

$$\langle \varepsilon \rangle_p = S_p \langle \sigma \rangle_p \quad (\text{A.2})$$

where p represents either the matrix, m , or the reinforcement, r . C_p and S_p denote the phase elasticity and compliance tensors, respectively, and $\langle \sigma \rangle_p$ and $\langle \varepsilon \rangle_p$ are phase averaged stress and strain tensors defined by Equation 2.3 in Section 2.4. The relationships between the fibre, matrix and overall averages can be derived with Equation 2.4 in Section 2.4.

$$\langle \sigma \rangle = c_r \langle \sigma \rangle_r + c_m \langle \sigma \rangle_m \quad (\text{A.3})$$

$$\langle \varepsilon \rangle = c_r \langle \varepsilon \rangle_r + c_m \langle \varepsilon \rangle_m \quad (\text{A.4})$$

The effective composite elastic tensors, the elasticity tensor C and the compliance

tensor S can be defined as the relations between homogenised strains and stresses.

$$\begin{aligned}\langle \varepsilon \rangle &= S \langle \sigma \rangle \\ \langle \sigma \rangle &= C \langle \varepsilon \rangle\end{aligned}\tag{A.5}$$

An important related concept, first introduced by Hill [176], is based on the ratios between the average reinforcement strain (or stress) and the corresponding average in the composite

$$\begin{aligned}\langle \varepsilon \rangle_p &= A_p \langle \varepsilon \rangle \\ \langle \sigma \rangle_p &= B_p \langle \sigma \rangle\end{aligned}\tag{A.6}$$

where A_p and B_p are fourth-order phase strain-concentration and stress-concentration tensors, respectively. Implementing Equations A.3 and A.4 in Equation A.6, the strain and stress concentration tensors fulfil the following relations

$$\begin{aligned}c_r A_r + c_m A_m &= I \\ c_r B_r + c_m B_m &= I\end{aligned}\tag{A.7}$$

where I denotes the identity tensor. Combining Equations A.3, A.4, A.5 and A.6, the effective stiffness and compliance tensors can be obtained from the phase properties as

$$\begin{aligned}C &= c_r C_r A_r + c_m C_m A_m \\ S &= c_r S_r B_r + c_m S_m B_m\end{aligned}\tag{A.8}$$

When A_r , A_m , B_r , B_m are derived, the elastic properties of the composite are completely defined through C_r , C_m and S_r , S_m . Explicit expressions for the elastic tensors can be derived by inserting Equations A.7 into Equation A.8.

$$\begin{aligned}C &= C_m + c_r (C_r - C_m) A_r \\ S &= S_m + c_r (S_r - S_m) S_r\end{aligned}\tag{A.9}$$

From Equation A.9 it is evident that it is sufficient to compute one elastic phase concentration tensor in order to describe the full elastic behaviour of a two-phase inhomogeneous material. In the literature exist different approaches allowing the phase concentration tensors to be obtained by means of the phase elastic tensors [143]. A combination of the models based on Eshelby's equivalent inclusion methods and Mori-Tanaka's concept of "average stress" [144] in the matrix is proposed to be utilised to predict the elastic properties of an arbitrary nanoparticle reinforced composite. With small modifications it can be used for any type of reinforcements, such as spheres, fibres

or platelets.

A.2 Dilute Eshelby model

As aforementioned in Section 2.4.1, Eshelby's model is based on the concept of replacing an actual perfectly bonded ellipsoidal inhomogeneous inclusion with the stiffness C_r by an "equivalent" homogeneous inclusion with the stiffness C_m subjected to an "equivalent" eigenstrain ε_τ . This equivalent eigenstrain applied to a homogeneous (equivalent) inclusion must be chosen in such a way that the inhomogeneous inclusion and the equivalent homogeneous inclusion attain the same stress state and the same constrained strain ε_c .

$$\varepsilon_c = P\varepsilon_\tau \quad (\text{A.10})$$

where P denotes the Eshelby tensor. The concept of the equivalent homogeneous inclusion can be extended to a case where a uniform mechanical strain ε_0 or external stress σ_0 is applied to a perfectly bonded inhomogeneous elastic inclusion in an infinite matrix. Equation 2.5 in Section 2.4.1 (Chapter 2) can be rewritten as

$$\sigma_r = C_r [\varepsilon_0 + \varepsilon_c] = C_m [\varepsilon_0 + \varepsilon_c - \varepsilon_\tau] \quad (\text{A.11})$$

Implementing Equation A.10 in Equation A.11 leads to the relationship

$$\sigma_r = C_r [\varepsilon_0 + P\varepsilon_\tau] = C_m (\varepsilon_0 + [P - I]\varepsilon_\tau) \quad (\text{A.12})$$

Thus, the equivalent eigenstrain can be expressed through the applied uniform mechanical strain ε_0 as

$$[(C_r - C_m)P + C_m]\varepsilon_\tau = (C_m - C_r)\varepsilon_0 \quad (\text{A.13})$$

Inverting Equation A.10 to $\varepsilon_\tau = P^{-1}\varepsilon_c$ and implementing the strain in the reinforcement defined as $\varepsilon_r = \varepsilon_0 + \varepsilon_c$ in Equation A.13, the strain in the inhomogeneity can be expressed through the uniform mechanical strain in an infinite matrix as

$$\varepsilon_0 = [I + PS_m(C_r - C_m)]\varepsilon_r \quad (\text{A.14})$$

Because the strain in the inhomogeneity is homogeneous $\varepsilon_r = \langle \varepsilon \rangle_r$ and for a dilute composite the average strain is identical to the strain applied at infinity $\langle \varepsilon \rangle = \varepsilon_0$ the strain concentration tensor for dilute inhomogeneities can be expressed as

$$A_r^{NI} = (I + PS_r(C_r - C_m))^{-1} \quad (\text{A.15})$$

Here A_r^{NI} is called Eshelby's non-interacting (dilute) inhomogeneity strain concentration tensor. The Eshelby tensor P depends only on the material properties of the matrix and on the aspect ratio of the inclusions. Exemplarily, the Eshelby tensor of spheroidal

inclusions embedded in an isotropic matrix can be expressed as [146]

$$g = \frac{a_{ld}}{(a_{ld}^2 - 1)^{\frac{3}{2}}} \left\{ a_{ld}(a_{ld}^2 - 1)^{\frac{1}{2}} - \cosh^{-1} a_{ld} \right\} \quad (\text{A.16})$$

$$\begin{aligned} P_{1111} &= \frac{1}{2(1-\nu_m)} \left\{ 1 - 2\nu_m + \frac{3a_{ld}^2 - 1}{a_{ld}^2 - 1} - g \left[1 - 2\nu_m + \frac{3a_{ld}^2}{a_{ld}^2 - 1} \right] \right\} \\ P_{2222} &= \frac{3}{8(1-\nu_m)} \left(\frac{a_{ld}^2}{a_{ld}^2 - 1} \right) + \frac{1}{4(1-\nu_m)} g \left[1 - 2\nu_m - \frac{9}{4(a_{ld}^2 - 1)} \right] \\ P_{2233} &= \frac{1}{4(1-\nu_m)} \left\{ \frac{a_{ld}^2}{2(a_{ld}^2 - 1)} - g \left[1 - 2\nu_m + \frac{3}{4(a_{ld}^2 - 1)} \right] \right\} \\ P_{2211} &= -\frac{1}{2(1-\nu_m)} \frac{a_{ld}^2}{a_{ld}^2 - 1} + \frac{1}{4(1-\nu_m)} g \left[-(1 - 2\nu_m) + \frac{3a_{ld}^2}{a_{ld}^2 - 1} \right] \\ P_{1122} &= -\frac{1}{2(1-\nu_m)} \left[1 - 2\nu_m + \frac{1}{a_{ld}^2 - 1} \right] + \frac{1}{2(1-\nu_m)} g \left[1 - 2\nu_m + \frac{3}{2(a_{ld}^2 - 1)} \right] \\ P_{2323} &= \frac{1}{4(1-\nu_m)} \left\{ \frac{a_{ld}^2}{2(a_{ld}^2 - 1)} + g \left[1 - 2\nu_m - \frac{3}{4(a_{ld}^2 - 1)} \right] \right\} \\ P_{1212} &= \frac{1}{4(1-\nu_m)} \left\{ 1 - 2\nu_m - \frac{a_{ld}^2 + 1}{a_{ld}^2 - 1} - \frac{g}{2} \left[1 - 2\nu_m - \frac{3(a_{ld}^2 + 1)}{a_{ld}^2 - 1} \right] \right\} \end{aligned} \quad (\text{A.17})$$

where a_{ld} denotes the aspect ratio and ν_m is Poisson's coefficient of the matrix.

To predict the composite stiffness, Eshelby's non-interacting inhomogeneity strain concentration tensor defined in Equation A.15 is implemented in Equation A.9 as

$$C = C_m + c_r (C_r - C_m) A_r^{NI} \quad (\text{A.18})$$

Hence Eshelby's solution according to Equation A.18 is derived for a single inclusion embedded into an infinite matrix. From Equation A.15 it can be seen that Eshelby's strain concentration tensor does not depend on the volume fraction, resulting in a linear increase of the composite elastic properties. In order to avoid overestimations this model should be applied only to composites with very small concentrations.

A.3 Mori-Tanaka model

In order to calculate properties for non-dilute composites, it is necessary to modify Eshelby's model and to introduce interactions between particles. The concept of effective fields in composites is based on the approximation of stresses acting on an inhomogeneity, which may be viewed as a superposition of the applied far field stress and the fluctuation stresses caused by the presence of other inhomogeneities using an appropriate matrix stress. Effective field theories of this type are generally referred to as Mori-Tanaka's methods [144] for calculating the average internal stresses in the matrix containing homogeneous inclusions with transformation strains. Benveniste [148] applied Mori-Tanaka's approach to compute the effective properties of composites.

Suppose that the matrix is reinforced with a certain type of particles, and that for a single inclusion in an infinite matrix the dilute strain concentration tensor A^{NI} is

known. Moreover, Mori-Tanaka's assumption is that, when many identical particles are introduced in the composite the macroscopic strain $\langle \varepsilon \rangle$ and stress $\langle \sigma \rangle$ are substituted by the phase averaged matrix strain and stress $\langle \varepsilon \rangle_m$ and $\langle \sigma \rangle_m$, respectively. Thus, each particle "sees" a far-field strain equal to the average strain in the matrix. The new strain and stress concentration tensors are denoted as A_r^{NI} and B_r^{NI} , respectively.

$$\begin{aligned}\langle \varepsilon \rangle_r &= A_r^{NI} \langle \varepsilon \rangle_m \\ \langle \sigma \rangle_r &= B_r^{NI} \langle \sigma \rangle_m\end{aligned}\tag{A.19}$$

Inserting Equation A.19 in Equations A.3 and A.4 leads to the expression

$$\begin{aligned}\langle \varepsilon \rangle &= \left(A_r^{NI} \right)^{-1} \left[(1 - c_r) I + c_r A_r^{NI} \right] \langle \varepsilon \rangle_r \\ \langle \sigma \rangle &= \left(B_r^{NI} \right)^{-1} \left[(1 - c_r) I + c_r B_r^{NI} \right] \langle \sigma \rangle_r\end{aligned}\tag{A.20}$$

Consequently, Mori-Tanaka's strain and stress concentration tensors for the reinforcements can be written in terms of the dilute concentration tensors as

$$\begin{aligned}A_r^{MT} &= A_r^{NI} [(1 - c_r) I + c_r A_r^{NI}]^{-1} \\ B_r^{MT} &= B_r^{NI} [(1 - c_r) I + c_r B_r^{NI}]^{-1}\end{aligned}\tag{A.21}$$

Similar expressions can be obtained for the matrix. By implementing Equation A.21 together with Equation A.15 in Equation A.9 the elastic properties of a nanoparticle reinforced composite can be predicted with a Mori-Tanaka model.

Appendix B

Orientation averaging

The most general description of a fibre orientation state can be obtained by means of a probability orientation distribution function $\Psi(\theta, \phi)$, where θ and ϕ denote the fibre orientation angles (Figure B.1). $\vec{P} = \{p_1, p_2, p_3\}$ is a unit directional vector of the fibre, therefore $\sum_i p_i^2 = 1$.

$$\begin{cases} p_1 = \sin \theta \cos \phi \\ p_2 = \sin \theta \sin \phi \\ p_3 = \cos \theta \end{cases} \quad (\text{B.1})$$

The set of all possible directions of $\vec{P}$ corresponds to a unit sphere

$$\oint d\vec{P} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \sin \theta d\theta d\phi \quad (\text{B.2})$$

The orientation probability function $\Psi(\theta, \phi)$ must satisfy certain physical conditions:

1. First, a fibre oriented at any angle (θ, ϕ) is indistinguishable from a fibre oriented at the angles $(\pi - \theta, \pi + \phi)$, therefore Ψ must be periodic $\Psi(\theta, \phi) = \Psi(\pi - \theta, \pi + \phi)$.
2. Ψ must be normalised, since every fibre has its own orientation.

$$\oint \Psi(\vec{P}) d\vec{P} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \Psi(\theta, \phi) \sin \theta d\theta d\phi = 1 \quad (\text{B.3})$$

Consider some tensor property $U(\vec{P})$ (e.g. stiffness, compliance, stress concentration, stress concentration tensors) of second order, associated with a unidirectional microstructure aligned in the direction of $\vec{P}$. U must be transversely isotropic with $\vec{P}$ as its axis of symmetry. The orientation average of U is denoted by $\langle U \rangle$ which is defined as

$$\langle U \rangle = \oint U(\vec{P}) \Psi(\vec{P}) d\vec{P} \quad (\text{B.4})$$

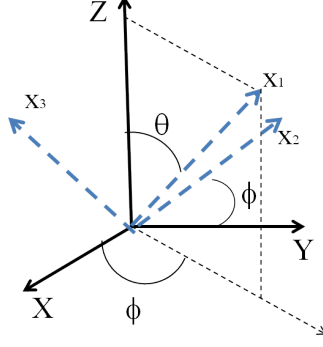


Figure B.1: Coordinate system of inhomogeneities and definitions of angles θ and ϕ

U is known in the local coordinate system x_1, x_2, x_3 , where the inclusions are aligned along x_1 . To calculate $U(\vec{P})$ for an arbitrary orientation of vector P in the global coordinate system X, Y, Z , the local coordinates have to be transformed. In general, the rotation matrix pertinent to the angle θ and the unit vector of the nanotubes' director $u = \{u_x, u_y, u_z\}$, where $u_x^2 + u_y^2 + u_z^2 = 1$, is established as

$$R_{\{u_x, u_y, u_z\}}(\theta) = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \quad (\text{B.5})$$

with

$$\begin{aligned} R_{11} &= \cos \theta + u_x^2(1 - \cos \theta) \\ R_{12} &= u_x u_y(1 - \cos \theta) - u_z \sin \theta \\ R_{13} &= u_x u_z(1 - \cos \theta) + u_y \sin \theta \\ R_{21} &= u_y u_x(1 - \cos \theta) + u_z \sin \theta \\ R_{22} &= \cos \theta + u_y^2(1 - \cos \theta) \\ R_{23} &= u_y u_z(1 - \cos \theta) - u_x \sin \theta \\ R_{31} &= u_z u_x(1 - \cos \theta) - u_y \sin \theta \\ R_{32} &= u_z u_y(1 - \cos \theta) + u_x \sin \theta \\ R_{33} &= \cos \theta + u_z^2(1 - \cos \theta) \end{aligned}$$

In order to transform the global coordinate system into the local coordinate system (Figure B.1), two successive rotations have to be performed. First the global coordinate system is rotated by an angle ϕ around the Z -axis. This rotation around the Z -axis

can be presented by

$$R_Z(\phi) = \begin{bmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (\text{B.6})$$

The second rotation is performed by an angle θ around the Y -axis. Thus, the final transformed coordinate system is

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = R_{x_2}(\theta - \frac{\pi}{2}) R_Z(\phi) \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (\text{B.7})$$

In order to transform local coordinates to the global coordinate system the transformation matrix must be inverted. The complete transformation matrix between global and local coordinate systems is denoted as $[\Omega]$ with the components $w_{ij}, i, j = 1, 2, 3$

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = [\Omega] \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \quad (\text{B.8})$$

The elements of vectors u_i and second rank tensors U_{ij} given in the local coordinate system x_1, x_2, x_3 can be transformed to the global coordinate system X, Y, Z in the following way

$$\begin{aligned} u_i &= w_{ij} u'_j \\ U_{ij} &= w_{ik} w_{jl} U'_{kl} \end{aligned} \quad (\text{B.9})$$

Or in a matrix form

$$[U] = [T][U'][T^T] \quad (\text{B.10})$$

where the rotation transformation matrix T is expressed through the components w_{ij} , $i, j = 1, 2, 3$ of the matrix Ω

$$[T] = \begin{bmatrix} l_1^2 & l_2^2 & l_3^2 & 2l_2l_3 & 2l_1l_3 & 2l_1l_2 \\ m_1^2 & m_2^2 & m_3^2 & 2m_2m_3 & 2m_1m_3 & 2m_1m_2 \\ n_1^2 & n_2^2 & n_3^2 & 2n_2n_3 & 2n_1n_3 & 2n_1n_2 \\ m_1n_1 & m_2n_2 & m_3n_3 & m_2n_3 + m_3n_2 & m_1n_3 + m_3n_1 & m_1n_2 + m_2n_1 \\ l_1n_1 & l_2n_2 & l_3n_3 & l_2n_3 + l_3n_2 & l_1n_3 + l_3n_1 & l_1n_2 + l_2n_1 \\ l_1m_1 & l_2m_2 & l_3m_3 & l_2m_3 + l_3m_2 & l_1m_3 + l_3m_1 & l_1m_2 + l_2m_1 \end{bmatrix} \quad (\text{B.11})$$

in which l , m and n are defined as

$$\begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{bmatrix} = \begin{bmatrix} w_{11} & w_{12} & w_{13} \\ w_{21} & w_{22} & w_{23} \\ w_{31} & w_{32} & w_{33} \end{bmatrix} \quad (\text{B.12})$$

For second rank tensors in matrix form weighted averaging as described by the ODF can be expressed as

$$\langle U \rangle = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} T(\theta, \phi) U'(\theta, \phi) T^{-1}(\theta, \phi) \Psi(\theta, \phi) \sin \theta d\theta d\phi \quad (\text{B.13})$$

Within the framework of the proposed Mori-Tanaka model Equation B.13 needs to be employed to average stiffness, compliance, strain concentration, stress concentration tensors. One must be very careful in translating tensors into matrices and applying Equation B.13. Errors can come from the difference between engineering strain and tensor strain

$$\epsilon = [W]\varepsilon \quad (\text{B.14})$$

Here ϵ is the engineering strain and $[W]$ is the transformation matrix

$$[W] = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{bmatrix} \quad (\text{B.15})$$

which depends on each type of matrix. The correct transformation rules has to be applied in Equation B.13. It can be shown that the elasticity, compliance, strain concentration and stress concentration tensors need to be transformed into the global coordinate system as follows

$$\begin{aligned} [C(\theta, \phi)] &= [T(\theta, \phi)][C'(\theta, \phi)][T^*(\theta, \phi)]^{-1} = [T(\theta, \phi)][C'(\theta, \phi)][T(\theta, \phi)]^T \\ [S(\theta, \phi)] &= [T^*(\theta, \phi)][S'(\theta, \phi)][T(\theta, \phi)]^{-1} = [T^*(\theta, \phi)][S'(\theta, \phi)][T^*(\theta, \phi)]^T \\ [A(\theta, \phi)] &= [T^*(\theta, \phi)][A'(\theta, \phi)][T^*(\theta, \phi)]^{-1} = [T^*(\theta, \phi)][A'(\theta, \phi)][T(\theta, \phi)]^T \\ [B(\theta, \phi)] &= [T(\theta, \phi)][B'(\theta, \phi)][T(\theta, \phi)]^{-1} = [T(\theta, \phi)][B'(\theta, \phi)][T^*(\theta, \phi)]^T \end{aligned} \quad (\text{B.16})$$

with

$$[T^*(\theta, \phi)] = [W][T(\theta, \phi)][W]^{-1} \quad (\text{B.17})$$