Advanced Structured Materials

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Additive Manufacturing Hybrid Processes for Composites Systems

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Advanced Structured Materials

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João P. T. Pereira · Luis Miguel Oliveira
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Preface

This book is centred on the emergent technology of additive manufacturing (AM) and its application beyond the state of the art in fibre reinforcement thermoplastics (F RTP). It includes the development of a hybrid and integrated process that combines, into a single-step platform, additive and subtractive operations and allows CAD-to-Part productions with freeform shapes using long or continuous F RTP. Moreover, it addresses the following engineering issues:

- Design rules for hybrid additive manufacturing (hAM).
- Thermoplastics compounds for AM processing appropriate to high temperature and strength applications.
- Advanced extrusion heads and process concepts for AM of F RTP.
- Hybridization strategies regarding AM specifications (supports, slicing, filling, etc.) and material in-process properties (rheology, interfacial adhesion, layer consolidation, etc.).
- Software ecosystem for hAM design, pre-processing, process planning, emulating and multi-axis processing.
- Three-dimensional path generator for hAM based on a multi-objective optimization algorithm that matches the recent curved adaptive slicing method with a new transversal scheme.
- hAM parameters real-time monitoring and closed-loop control.
- Multi-parametric nondestructive testing (NDT) tool customized for F RTP AM parts.
- Sustainable manufacturing process validated by advanced LCA/LCC models.

Development of a constitutive model to predict the elasto-plastic behaviour of 3D-Printed thermoplastics using a meshless formulation. Covering the whole value chain, this next-generation technology is presented starting with part design, simulation and materials composition; then going through transformation stages; and finishing with the product evaluation and end-of-life studies.

Additive manufacturing (AM) is one of the most promising manufacturing technologies nowadays. Aeronautics and aerospace surrendered to the advantages of AM. The sale of AM professional industrial equipment increased regularly and is

expected the worldwide turnover on AM to quadruple between 2015 and 2020. Numbers are even more impressive for metal additive manufacturing showing the higher growth rates within the different available additive technologies.

Similarly, the composite materials industry assists a movement of great progression and penetration into new sectors, exploring the main advantages of high performance allied to lightweight designs. In order to reduce the labour intensive and manual operations typically associated with composite fabrication and to satisfy the needs for flexible automated composite processes, research is committed in investigating the feasibility of highly automated, integrated and reproductive processes based in principles such as extrusion, automated tape placement or automated fibre placement.

Several scientific initiatives are known to intent the implementation of composite manufacturing processes through AM, but these attempts collide with a number of shortcomings that limit their usability. Identified issues are related to the layer-by-layer approach of AM without reinforcements between layers (composites anisotropy that decreases through-thickness properties), the use of short fibres, the high roughness low-quality surface finishing, the added complexity of algorithms and motion paths. The poor performance of raw materials when directly used in AM processes without appropriate properties optimization and the dependence on experimental equipment based on available commercial machines (mainly SLS and FDM) without proper design for the processes to be implemented is also an important issue.

Still, there are insufficient or no exploration of certain required scientific fields starting by the balancing of properties when composing raw materials for AM processes. The fabrication of the fibre-reinforced composite filaments or laminates is required as a pre-step before AM processing, necessitating the need for materials to be composed and developed. A fibre-reinforced thermoplastic raw material for AM proposes should present an adequate rheological profile (viscosity), compatibility with the heat sources (softening/melting temperature ranges) and suitable mechanical behaviour in terms of ductility and flexibility avoiding brittleness. Using long or continuous fibres instead of short fibres is difficult to incorporate into processing and additional processing functions have to be merged like the fibre cutting systems.

The purpose of this book is to walk through the challenging scientific route to develop an advanced hybrid additive manufacturing process beyond the state of the art, which enables the lightweight design and manufacture of fibre-reinforced thermoplastics products under ecological friendly conditions.

The research developments presented in this book include a high potential manufacture process, the additive manufacturing hybridized with subtractive technologies and an innovative product and high-performance composite parts produced without moulds and with tailored properties. Both process and products hold a high potential of, in future, converting into tradable goods fostering the industry in particular and the economy in general.

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Acronyms

3D	Three Dimensions
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
AR	Aramid fibre
ASTM	American Society for Testing and Materials
ATC	Automatic trajectory control
ATRP	Atom transfer radical polymerization
BiCGStab	Bi-conjugated gradient stabilized
CAD	Computer-aided design
CAM	Computer-aided manufacturing
CBAM	Composite-based additive manufacturing
CCD	Charge-coupled device
CFD	Computational fluid dynamics
cFR	Continuous fibre reinforced
CFRP	Carbon fibre-reinforced polymer
cFRTP	Continuous fibre-reinforced thermoplastics
CIRP	College International pour la Recherche en Productique
CLFDM	Curved Layered Fused Deposition Modelling
CMOS	Complementary metal-oxide semiconductor
CNC	Computer numeric control
CNT	Carbon nanotube
DCB	Double cantilever beam
DED	Direct energy deposition
DFM	Design for manufacturing
DfMA	Design for additive manufacturing
DIC	Diagonal incomplete-Cholesky
DILU	Diagonal incomplete-LU
DIY	Do-it-yourself
DMA	Dynamic mechanical analysis
DMD	Direct metal deposition

DOE	Design of experiments
DSC	Differential scanning calorimetry
EBM	Electron beam melting
EC	Eddy current
EHS	Experimental hybrid system
EM	Electromagnetism-like
EPDs	Environmental report declarations
ER	Experimental rig
ERS	Experimental rig system
FBG	Fibre Bragg gratings
FDM	Fused deposition modelling
FEA	Finite element analysis
FEM	Finite element modelling
FFF	Fused filament fabrication
FGM	Functionally graded materials
FP	Fabry–Perot
FRTP	Fibre-reinforced thermoplastics
G-Code	G-code protocol (ISO/DIN 66025 standard)
GnP	Graphene nanoplatelets
GS	Granty speed
HVAC	Heating, ventilation and air conditioning
IPC	Institute of Polymers and Composites
IR	Infrared
ISO	International Organization for Standardization
L/C-FRTP	Long and continuous fibre-reinforced thermoplastics
LC	Life cycle
LCA	Life cycle assessment
LCC	Life cycle cost
LENS	Laser Engineering Net Shape
LM	Layer-by-layer manufacturing
LMD	Laser metal deposition
MAT	Medial axis transformation
MEMS	Microelectromechanical system
MFG	Multi-functional and graded features
MFI	Melt Flow Index
MIP	Mathematical integer programming
MIT	Massachusetts Institute of Technology
MMC	Metal matrix composites
MOPSO	Multi-objective particle swarm optimization
MQ	Multi-quadric
MT	Magnetic particle testing
MWCNT	Multi-walled carbon nanotube
NASA	National Aeronautics and Space Administration
NDT	Nondestructive testing
NiTi	Nitinol

NPV	Net present value
NSGA-II	Non-dominated sorting genetic algorithm
OCT	Optical coherent tomography
OEM	Original equipment manufacturer
OM	Origami mechanism
PA	Polyamide
PA 12	Polyamide 12
PA 66	Polyamide 66
PAEK	Polyaryletherketone
PAI	Polyamide-imide
PBF	Powder bed fusion
PC	Polycarbonate
PCG	Pre-conditioned conjugate gradient
PCL	Polycaprolactone
PCR	Product Category Rules
PDMS	Poly (dimethylsiloxane)
PE	Polyester
PEEK	Polyetheretherketone
PEI	Polyetherimide
PEKK	Poly Ether Ketone Ketone
PES	Polyethersulphone
PI	Polyimide
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
POF	Polymeric optical fibres
PPPA	Phenylphosphonic acid
PPS	Polyphenylene sulphide
PPSU	Polyphenylsulphone
PS	Polystyrene
PT	Penetrant testing
PTFE	Polytetrafluorethylene
PVC	Polyvinyl chloride
R&D	Research and development
RA	Raster angle
RBF	Radial basis function
RP	Rapid prototype
RPIM	Radial point interpolation method
RTM	Resin transfer moulding
RVE	Representative volume element
SAFE	Semi-analytical finite element method
sCF	Short carbon fibres
sCFPA12	Short carbon fibre polyamide 12
SEM	Scanning electron microscopy
SETAC	Society for Environmental Toxicology and Chemistry
sFRTP	Short fibre-reinforced thermoplastics

SHS	Selective heat sintering
SLA	Stereolithography (Chap. 2)
S-LCA	Social life cycle assessment
SLE	Selective laser erosion
SLM	Selective laser melting
SLS	Selective laser sintering
SMA	Shape memory alloys
SMP	Shape memory polymers
SROI	Social return on investment
STL	Stereolithography (Chap. 1)
STL	Standard Tessellation Language (Chap. 2)
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
TO	Topology optimization
TPO	Thermoplastic olefin
TW	Welding time
UAV	Unmanned aerial vehicle
UD	Unidirectional
UNEP	United Nations Environmental Programme
US	Ultrasound
UT	Ultrasonic tests
UTS	Ultimate tensile strength
VE	Vinylester
WLF	Williams–Landel–Ferry
Xc	Degree of crystallinity

Symbols and Units

ρ	Density
γ'	Shear rate
$\emptyset$	Diameter
$\varphi_j(\mathbf{x}_I)$	Interpolations functions (Chap. 6)
$\varphi^T(\mathbf{x}_I) = \{\varphi_1(\mathbf{x}_I), \varphi_2(\mathbf{x}_I), \dots, \varphi_n(\mathbf{x}_I)\}$	Interpolation function calculated at the interest point
σ	Stress tensor (Chap. 6)
$\sigma_Y _{\text{tensile}}, \sigma_Y _{\text{comp}}$	Yield stresses of the same material when subjected to tensile or compression loads, respectively (Chap. 6)
ε	Strain tensor (Chap. 6)
$\delta\varepsilon$	Virtual strain tensor (Chap. 6)
δu	Virtual displacement (Chap. 6)
$d\lambda$	Plastic strain multiplier (Chap. 6)
$d\varepsilon^e$	Infinitesimal elastic strain increments (Chap. 6)
$d\varepsilon^p$	Infinitesimal plastic strain increments (Chap. 6)
$d\sigma$	Stress increment (Chap. 6)
σ_{Y0}	Initial yield stress (Chap. 6)
λ	Relaxation time
τ	Deviatoric stress tensor
$\square$	E-step values
∇	Gradient
Ω	Domain (Chap. 6)
Γ	Boundary (Chap. 6)
$\mathbf{a}$	Normal vector (Chap. 6)
$a_i(\mathbf{x}_I), b_j(\mathbf{x}_I)$	Non-constant coefficients of $R_i(\mathbf{x}_I)$ and $p_j(\mathbf{x}_I)$, the polynomial basis, respectively, with m being the basis monomial number (Chap. 6)

a_T	Shift factor
A	Hardening parameter (Chap. 6)
$\mathbf{b}$	Body forces per unit volume (Chap. 6)
$\mathbf{B}$	Deformation matrix (Chap. 6)
BT	Building time
c, p	Shape parameters (Chap. 6)
c_1	WLF parameter
c_2	WLF parameter
cm	Centimetre
c_p	Heat capacity
$^{\circ}\text{C}$	Degree Celsius
$^{\circ}\text{C}/\text{min}$	Degree Celsius per minute
$\mathbf{D}_{\text{ep}}$	Elasto-plastic constitutive matrix given (Chap. 6)
ΔH_f^0	Standard enthalpy of formation
ΔH_m	Melting enthalpy
$\Delta \lambda_{\text{FBG}}$	FBG wavelength shift
$\Delta \lambda_{\text{FP}}$	FP wavelength shift
$\Delta \varepsilon$	Strain shift
ΔT	Temperature shift
Δt	Periods of time
f	Frequency
F, G and H	Material constants and characterize the anisotropy (Chap. 6)
g/10 min	Gram per ten minutes
$\mathbf{G}$	Matrix (Chap. 6)
G'	Storage modulus
G''	Loss modulus
GPa	Gigapascal
h	Hour
h	Convection coefficient
H'	Proportionality parameter used to update the yield stress based on strain hardening (Chap. 6)
$\mathbf{H}$	Blocks of diagonal matrixes, $\mathbf{H}^j$, containing the shape function of each node j of a given ‘influence domain’, with $\mathbf{H}^j = \varphi_j(\mathbf{x}_1)\mathbf{I}$ (Chap. 6)
H_c	Enthalpy of combustion
Hz	Hertz
i	Node calculated at the interest point $\mathbf{x}_1$ (Chap. 6)
I	Period

<i>I</i>	Identity matrix with dimension $[d \times d]$, where d is the number of degrees of freedom of the analysed problem (Chap. 6)
J	Joule
J/g	Joule per gram
<i>k</i>	Thermal conductivity
$k_{\text{FBG}\epsilon}$	Strain sensitivity
k_{FBGT}	Temperature sensitivity
kg	Kilogram
kg/h	Kilogram per hour
kN	Kilonewton
K_0	Initial stiffness calculated using the elastic constitutive matrix, <i>D</i> (Chap. 6)
<i>L</i>	Differential operator (Chap. 6)
L_0	Length of filament at the pre-set extruder speed
L_{arb}	Arbitrary Length
L_{real}	Real Length
L_{ref}	Reference mark on the filament
L_{rem}	Remaining Length
μm	Micrometre
<i>m</i>	Mass
m	Metre
m/min	Metre per minute
mg	Milligram
mL/min	Millilitre per minute
mm	Millimetre
mm/s	Millimetre per second
$\dot{M}_i$	Throughput
MPa	Megapascal
<i>n</i>	Power law exponent
<i>n</i>	Number of nodes within the ‘influence domain’ of x_1 (Chap. 6)
η^*	Complex viscosity
η_∞	Viscosity at the lower Newtonian plateau
η_0	Viscosity at the upper Newtonian plateau
N	Newton
<i>p</i>	Pressure
<i>P</i>	Polynomial matrix (Chap. 6)
Pa	Pascal
Pa s	Pascal second
<i>R</i>	Matrix (Chap. 6)
Ra	Surface roughness measure
$R_i(x_1)$	Radial basis function RBF (Chap. 6)
rpm	Revolution per minute

s	Second
SA	Support area measure
SE	Staircase effect measure
SA	Adapted support area measure
SE	Adapted staircase effect measure
t	Time
$\bar{t}$	Traction forces acting on the natural boundary Γ_1 (Chap. 6)
t_1, t_2	Initial and final time (Chap. 6)
T	Temperature
T_0	Reference temperature
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
u	Velocity vector
$\mathbf{u}$	Displacement field (Chap. 6)
$\mathbf{u}$	Kinematically admissible displacement field (Chap. 6)
u_i	Value of the field variable in the node i and $\varphi_i(\mathbf{x}_1)$ (Chap. 6)
$\dot{\mathbf{u}}$	Velocity (Chap. 6)
$\mathbf{u}(\mathbf{x}_1) = \sum_{i=1}^n \varphi_i(\mathbf{x}_1) \mathbf{u}_i$	Interpolation functions, being n the number of nodes inside the ‘influence domain’ of the interest point $\mathbf{x}_1$ (Chap. 6)
v_{ext}	Pre-set extruder speed
V	Volt
$\mathbf{x}_1$	Integration point (Chap. 6)
$\mathbf{x}_I, \mathbf{x}_J$	Interest points containing the same number of nodes (sixteen), but a different radius ($r_I \neq r_J$) (Chap. 6)
W	Relative water content
W/g	Watt per gram
W/m K	Watt per metre Kelvin

Chapter 3

New Material Concepts

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Abstract This chapter focuses on new compositions of thermoplastic matrices and reinforcements to process by fused deposition modelling (FDM). The available materials for this additive manufacturing (AM) technique are generally limited to PLA—polylactic acid, ABS—acrylonitrile butadiene styrene and PA—polyamide (NYLON®) with temperature gradients and mechanical behaviours that are not suited for high-performance applications, such as aeronautics and automotive sector. In this work, an intensive research was made in order to evaluate mechanical, thermal and rheological properties considered important for 3D printing of commercial filaments. Results aided in the selection of high-performance reinforced materials for AM. Advanced polymers, such as PEEK—polyether ether ketone and PA66—polyamide 66, were the matrices chosen to produce high service nanocomposite formulations, each with varying amounts of multi-wall carbon nanotubes (MWCNTs). The resulting feedstock materials were characterized using the same techniques as the commercial filaments. Preliminary tests with printed parts of these composites were made in pursuance of their optimal printing parameters to undergo an experimental hybrid system (EHS).

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3.1 Introduction

Fused deposition modelling (FDM) is the most used additive manufacturing technology [1–3]. During the process, a filament of material is fed into a heated liquefier where it is melted and pushed through a print nozzle. This nozzle moves by a gantry in the horizontal *x-y* plane resulting in the material deposition on a build surface. The most important material properties to be studied, assessed, controlled and monitored to allow printing FDM parts with the desired and required quality are viscosity [4, 5], crystallinity [6–8], thermal conductivity [9, 10], dimensional stability (ASTM D1204) [8, 11], mechanical properties [12–14] and heat resistance (ASTM D5499-94(2013)) [15]. Figure 3.1 summarizes those parameters.

3.2 Material Concepts and Composition

3.2.1 Characterization of Commercial Filaments

Different grades of PLA, ABS and PA12 were chosen as experimental filaments to evaluate the required material properties to be printed by FDM. Therefore, PLA basic (white), PLA Smartfil (white) and PLA/FC Protopasta filaments were purchased from Filament2Print S. L. (Coruña, Spain). PLA Premium (white), ABS Pro

Fig. 3.1 General FDM specifications overview. Adapted from Mohamed et al. [16]

(white) and PA12 (clear) filaments obtained from DOWIRE (Portugal). The melting and crystallization behaviour of the blends and nanocomposites were studied under nitrogen atmosphere, by DSC at a heating rate of 10 °C/min. TGA was used to measure the weight loss of a sample as a function of temperature, under air and nitrogen atmosphere, using a heating rate of 10 °C/min and temperature range of 60–700 °C. Measurements of the diameters were carried out on all the materials in order to evaluate the diameter's uniformity along their length. For that, sections of the different filaments were measured at each 20 cm. The melt flow index and density were measured by using MFI Daventest equipment, according to ISO 1133 at processing temperatures indicated by the suppliers. Rheological measurements were carried out on a TA Instruments AR-G2, a stress-controlled rheometer with parallel-plate geometry with a diameter of 25 mm. Filaments were granulated, and the resulting granules were formed into discs with a diameter 25 mm and thickness of 1 mm by hot pressing, using a Moore press. The measurements were performed in the linear viscoelastic region with dynamic oscillatory mode under nitrogen atmosphere, at 210 °C (PLAs), 250 °C (ABS) and 275 °C (PA12). Frequency scans were taken at the frequency range between 0, 1 and 100 Hz. Tensile testing was applied to each filament with an INSTRON 5969 equipment without extensometers, at 23 °C with a crosshead speed of 50 mm/s, according to ASTM D638-1. A 5 kN of load cell and a 45 mm of gauge length were used. E-modulus, tensile strength and elongation at break were evaluated from the stress–strain data.

3.2.1.1 Differential Scanning Calorimetry

DSC analysis was performed in order to analyse the thermal differences between different PLA filaments (both neat and with carbon fibre reinforcement) and other different commercial materials, in the interest of assessing the main thermal peaks and crystallinity. The thermograms (second heating) for comparison between all materials are presented in Figs. 3.2 and 3.3.

Fig. 3.2 DSC thermograms PLA Basic filaments, PLA Smartfil, PLA Premium and carbon fibre-reinforced PLA

Fig. 3.3 DSC thermograms of PLA Smartfil, ABS and polyamide 12

As a semi-crystalline polymer, PLA's thermogram consists of glass transition, crystallization exotherm and melting endotherm peaks, as seen in Fig. 3.2—left. PLA samples do not crystallize during cooling; instead, they crystallize during heating, as indicated by the exothermal peak in the heating portion of the DSC thermograms. The degree of crystallinity (X_c) is calculated by $X_c = H_c / \Delta H_f^0$, being $\Delta H_f^0 = 93$ J/g. Regarding the thermogram that compares PLA Smartfil with PLA reinforced with carbon fibre (Fig. 3.2—right), we can state that the T_g is 60.6 °C, meaning that the existence of reinforcement slightly raised the T_g of its raw material. As opposed to the T_g , melting temperature slightly decreases relatively to the neat PLA. However, the differences between both materials are not meaningful.

Figure 3.3 presents the DSC thermogram, which displays the distinction between different materials, namely PLA, ABS and Polyamide 12. ABS's thermogram exhibits the T_g at 74.9 °C. There is no presence of any other exotherm or endotherm peaks since ABS is an amorphous polymer. In contrast, polyamide possesses glass transition, crystallization exotherm and melting endotherm peaks in its thermogram. From all the results, we can conclude that the crystallinity of the materials is between 10 and 35%. Table 3.1 shows all these obtained values and all are in agreement with the values reported in the literature.

3.2.1.2 Thermographic Analysis

All polymeric filaments were characterized by thermogravimetric analysis since this technique allows us to determine thermal stability and to quantify the amount of reinforcement. Figure 3.4 shows that the decomposition process is very similar for all three PLAs. Only one degradation step is observed in the 348–355 °C range, and the total weight loss was approximately 99% for all of them. In terms of the PLA/FC composite's TGA curve, it also shows a single degradation step at 350 °C with a mass low of 84.7%, meaning that the remaining mass corresponds to the reinforcement's amount ($\approx 15\%$).

Table 3.1 Values of glass transition, melting temperature, melting enthalpy, crystallization temperature and degree of crystallinity of PLAs, carbon fibre-reinforced PLA, ABS and polyamide 12 commercial filaments

	PLA Basic	PLA Smartfill	PLA Premium	PLA/FC	ABS	Polyamide 12
T_g (°C)	60.2 ± 1.4	61.7 ± 0.3	59.5 ± 0.4	60.6 ± 1.8	74.9 ± 3.6	134.5 ± 0.4
T_m (°C)	150.0 ± 0.7	151.6 ± 1.3	151.8 ± 0.1	150.9 ± 0.2	–	245.7 ± 0.1
ΔH_m (J/g)	34.2 ± 2.0	19.7 ± 0.2	27.3 ± 0.1	19.4 ± 0.2	–	21.7 ± 1.8
T_c (°C)	107.2 ± 0.5	115.8 ± 6.2	119.1 ± 0.1	116.3 ± 4.7	–	173.7 ± 0.1
X_c (%)	36.8 ± 2.2	21.2 ± 0.2	29.3 ± 0.1	20.9 ± 0.2	–	10.4 ± 0.9

Fig. 3.4 TGA curves of PLA Smartfil and PLA with carbon fibre composite filaments

The degradation temperatures for ABS occur at 419 and at 453 °C for polyamide 12. The total weight loss is about 93.3 and 99.4%, in the same order, as shown in Fig. 3.5.

Comparing all three different polymeric materials, we can say that polyamide 12 has better thermal stability, followed by ABS. The mentioned values of degradation temperatures and total weight loss are detailed below in Table 3.2.

3.2.1.3 Dimensional Range

A dimensional measurement was pursued, aiming the evaluation of the variability of filament diameter. According to the suppliers, the diameters should be between 2.85 ± 0.10 mm, and, in Fig. 3.6, it is possible to confirm that all the filaments are within

Fig. 3.5 TGA comparison curves between the different material filaments, PLA Smartfil, ABS and polyamide 12

Table 3.2 Values of total weight loss and degradation temperatures for all the filaments

	PLA Basic	PLA Smartfil	PLA Premium	PLA/FC	ABS	Polyamide 12
Total weight loss (%)	98.5	99.2	98.9	84.7	93.3	99.4
Degradation temperature (°C)	355	348	353	350	419	453

Fig. 3.6 Dimensional tolerance analysis of the diameter of all filaments

those values. Nevertheless, it is noteworthy that PLA Smartfil, PLA/FC composite and ABS show more uniform diameters, as we can state from Table 3.3.

Table 3.3 Values of main and standard deviation of the filament diameters

PLA Basic	2.83 ± 0.06
PLA Smartfil	2.79 ± 0.01
PLA Premium	2.80 ± 0.03
PLA/FC	2.81 ± 0.01
ABS	2.81 ± 0.01
Polyamide 12	2.78 ± 0.02

Fig. 3.7 Melt flow index analysis of all the filaments, at their processing temperature

3.2.1.4 Melt Flow Index

The variation of melt flow index of all the materials is illustrated in Fig. 3.7. Comparing PLAs, PLA Premium has higher MFI than the others, even than that of reinforced PLA. Correlating the distinct materials, the most fluid appears to be ABS, while polyamide 12 is the less fluid. The values of melt flow index range between 15 and 25 g/10 min.

3.2.1.5 Parallel-Plate Rheometry

Viscosity is also an important factor in the transformation of the materials. Therefore, dynamic oscillatory shear measurements were performed to investigate the response of the materials to the dynamic shearing. Figure 3.8 shows the complex viscosity (η^*) of PLAs, CF-reinforced PLA, ABS and polyamide 12 as a function of frequency (f) in Hz. The complex viscosity of PLAs, PLA/CF composite and polyamide 12 melt show only a small frequency dependence, revealing a Newtonian plateau at low

Fig. 3.8 Complex viscosity versus frequency curves of all filaments

frequency. It can also be observed that viscosity for all filaments decreased with the increase in frequency, which is called shear thinning. All pure PLA, reinforced PLA and polyamide 12 exhibit a weak shear thinning effect, while ABS shows a significant strong shear thinning behaviour. Compared to PLA Smartfil (neat polymer), the viscosity of PLA/FC nanocomposites was raised notoriously. The increase in viscosity is a usual phenomenon for filler-reinforced polymers since there is an interaction between the carbon fibre and PLA hindering the movement of PLA chains. Then, polyamide 12 is the most viscous polymer after the composite.

Figure 3.9 demonstrates the storage modulus (G') and loss modulus (G'') of the PLAs, carbon fibre PLA composite, ABS and polyamide 12 as a function of frequency at their molten state. Such as the complex viscosity, PLA/FC showed an increase in G' and G'' when compared to neat PLA (PLA Smartfil). A greater G' meant a more elastic structure, which implies the restriction of polymer chain movement due to the carbon fibre filler. ABS, polyamide and PLA/FC present the highest modulus at low frequencies indicating that they are capable of storing more energy than the others store. At high frequencies, PLA/FC followed by polyamide 12 and PLA Smartfil shows the best storage modulus, comparing to the others.

Fig. 3.9 G' (left) and G'' (right) versus angular frequency for all materials

3.2.1.6 Tensile Tests

Tensile testing was performed to measure the tensile properties of all commercial filaments. Figure 3.10 shows representative stress/strain curves from each material, showing strains up to specimen fracture, with a zoom up.

All the filaments showed distinctive ductile behaviour, with the occurrence of necking, especially polyamide 12, with the exception of PLA/FC which exhibited the nature of brittle fracture due to the fibre’s reinforcement. Furthermore, tensile strength, elongation at break and tensile modulus were obtained from the stress/strain curves and presented in Figs. 3.11 and 3.12.

As shown in Fig. 3.11 (left), PLA Basic has the highest yield tensile strength, followed by polyamide 12, both displaying values above 50 MPa. In contrast, PLA/FC is the weakest, as we can see by the tensile strength values of around 25 MPa. The

Fig. 3.10 Representative tensile curves obtained for the different material filaments

Fig. 3.11 Mean and standard deviation values of yield tensile strength (left) and elongation at break (right) for all the filaments

Fig. 3.12 Mean and standard deviation values of tensile modulus

elongation, exhibited in Fig. 3.11 (right), of PLA reinforced with carbon fibre is very limited ($\approx 4\%$). Particularly, the elongation decreased almost half the value of its neat PLA (PLA Smartfil: $\approx 7\%$). Furthermore, ABS and polyamide 12 showed significant elongation under tension, notably polyamide 12 since it reached nearly 315% of deformation. Contrarily, as it is possible to observe in Fig. 3.12, ABS and polyamide 12 show the lowest tensile modulus, around 1.3 GPa and 0.8 GPa, respectively, in comparison with the values for PLAs (between 1.7 and 2 GPa). However, the main surprise here was PLA/FC, on behalf of its low tensile modulus (around 0.8 GPa). This value reveals that the addition of carbon fibre to PLA did not improve its mechanical properties.

3.2.2 Summary of Main Results

Considering all the obtained results for the commercial filaments, it is possible to state that to produce our own formulations, the materials must have the following working windows:

- Viscosity at shear rates of $100\text{--}200\text{ s}^{-1}$ between 150 and 600 Pa s. This shear rate range was chosen since it corresponds to the typical shear rate in the nozzle region for FDM [17].
- Crystallinity between 10 and 35%.
- Carbon fibre content around 15% (m/m).
- Melt flow index between 15 and 25 g/10 min.
- Dimensional ranges of the filaments within ± 0.1 mm.
- Thermal conductivity between 75 and 150×10^{-3} W/m K.

Table 3.4 Selected materials for composite filament processing

Grade	T_g (°C)	Viscosity (Pa s) @shear rate 100–200 s ⁻¹	Thermal conductivity (W/m K)	Manufacturer
Zytel E42A NC010	70	500–510 (290 °C)	160×10^{-3}	DuPont
Victrix PEEK 450G	143	350	–	BASF

Therefore, the selected materials (PA66 and PEEK) are presented in Table 3.4.

3.3 Reinforcements Impregnation

3.3.1 Development of PEEK and PA66 Formulations

As previously stated, the purchased grade of PA66 granules was Zytel E42A NC010 from Biesterfeld Ibérica S.L.U. (Barcelona, Spain), with a working temperature between 275 and 295 °C. High-performance PEEK granules (grade Victrix 450G) were obtained from Policomplex, S. L. (Valencia, Spain), which requires temperatures around 355–375 °C to be processed. Multi-wall carbon nanotubes (MWCNTs or simply CNTs), selected to be the reinforcement material, were purchased from Nanocyl S.A. (Belgium) with the reference NC7000TM.

3.3.2 Filaments Processing

An extrusion line of monofilaments, composed by a Coperion ZSK 26 Mc double screw extruder (Fig. 3.13) and accessory equipment, produced PEEK composites with 2 and 4% carbon nanotubes. Because of excessive hydrolysis of the thermoplastic matrix, we were only able to, successfully, produce PA66 composites with 4% CNTs. This percentage of fillers enabled sufficient viscosity for the consolidation of the composite and winding into filament.

In order to obtain the composites, a configuration of screws was selected aiming a good dispersion and distribution of the reinforcements in the thermoplastic matrix. Each screw is composed by kneading blocks that aid in the dispersion and distribution of the CNTs. PEEK granules were previously dried in a Piovani dehumidifier at 150 °C during 4 h, whereas PA66 granules were dried at a temperature of 90 °C during 6 h, in order to remove excess humidity, to avoid degradation of the material. After drying, the granules were introduced in a gravimetric feeder and CNTs in a volumetric feeder. Since the density of the material depends on the type and amount of the incorporated reinforcement, both feeders were calibrated in pursuance of assuring the desired flow rate. The extrusion started by feeding the granules from a hopper and CNT

Fig. 3.13 Coperion double screw extruder with kneading blocks

reinforcements from a lateral entrance into the extruder. Figure 3.14 illustrates the heating and feeding zones of the extruder.

The filaments came out from two separate 2 mm diameter orifices located at the front of the extrusion die, and they naturally cooled by air. Thereafter, a set of rollers at a constant speed allowed the stretching of the filaments and their advance along the extrusion line. Figure 3.15 shows the composite filaments being produced by the extrusion die and a 1 kg spool of extruded PEEK filament.

The extrusion processing conditions, such as flow rate, temperatures and screw speed are presented in Table 3.5.

Fig. 3.14 Illustration of the heating and feeding zones of the Coperion extruder

Fig. 3.15 Upstream view of filament extrusion process (left) and spool of extruded PEEK filament

Table 3.5 Processing conditions for the extrusion of the composite filaments

Composite filaments	Flow rate (kg/h)	Cylinder and die temperature (°C)	Screw speed (rpm)
PEEK	3	300-370-370-370-370-370-370-365	180
PA66	3	260-280-285-285-285-285-280-275-270	180

3.4 Material Concepts Validation

3.4.1 Characterization of PEEK and PA66 Formulations

Having established, earlier, a range of values of all the most important properties for 3D printing and machining for commercial filaments, a selection of materials consisting of PEEK, PA66 and carbon nanotubes was made in order to produce nanocomposite filaments with improved performance characteristics. PEEK and PA66 nanocomposite filaments, with different quantities of carbon nanotube reinforcement (PEEK/2% CNTs, PEEK/4% CNTs and PA66/4% CNTs), as well as their optimal processing parameters were studied to find the best formulation for the objectives established regarding additive manufacturing, taking into consideration all of their characterized properties. The melt and crystallization behaviour of neat PEEK and CNT reinforced PEEK and PA66 filaments were studied under nitrogen atmosphere by DSC 200 F3 Maia Netzsch, using 3–6 mg sample sealed into aluminium pans. The temperature was raised from 0 to 450 °C at a heating rate of 10 °C/min for PEEK composites, whereas for PA66 composite, the temperature was raised from 0 to 300 °C at the same heating rate. Second heating similar to the first was then performed in order to erase the thermal history. The melting thermogram was recorded from the second heating. Subsequently to the second heating, the temperature was decreased at a cooling rate of 10 °C/min for PEEK composites and at

40 °C/min for PA66 composite (this increase was an attempt to hinder the crystallization of the polyamide matrix). The crystallinity percentage was calculated by using ΔH_f^0 PEEK = 130 J/g and ΔH_f^0 PA66 = 160 J/g [18, 19]. TGA measurements have been performed on TA Q500 of TA Instruments, under air at a flow rate of 60 mL/min and nitrogen at a flow rate of 40 mL/min. Heating rate was of 10 °C/min in a temperature range of 60–900 °C for PEEK composites and 60–700 °C for PA66 composite. Measurements of the diameters were carried out at each 20 cm on all the materials in order to evaluate the diameter's uniformity along their length. MFI Göttfert MI-3 determined melt flow index and density. After an established time, the material was forced through a capillary by means of the application of 10 kg. PEEK and PEEK composites were tested at 360 °C, while PA66 composite was tested at 285 °C, according to supplier data. The granules were first dried, respectively, at 150 °C for 3 h and 90 °C for 6 h. Tensile testing was applied to each filament with an INSTRON 5969 equipment without extensometers, at 23 °C with a crosshead speed of 5 mm/min, according to ASTM D638-1. A 5 kN load cell and a 45 mm gauge length were used. E-modulus, tensile strength and elongation at break were evaluated from the stress–strain data. The determination of the amount of water absorbed by the samples was pursued according to ASTM D570. Granulated filament pieces with constant dimensions and weights were immersed in 15 ml falcon tubes filled with distilled water at 23 °C during 15 min, 1 h, 2 h, 4 h, 18 h, 24 h, 48 h, 7 days, 14 days and 21 days. These time points were sufficient to establish a saturated state. At the specific time, five specimens of each composite were removed from the water, patted dry with a piece of laboratory paper and then weighed. The relative water content, W , was determined as the percentage increase in weight, m , at different times, t .

$$W = \frac{m_{\text{wet}}(t) - m_{\text{dry}}}{m_{\text{dry}}} \cdot 100 \quad (1)$$

DMA performed on a TT DMA (Triton Technology Ltd.) measured the storage modulus, loss modulus and $\tan\delta$. Filament sections were cut and tested in tension mode at a clamp distance of 15 mm. During the scans, the specimens were heated up to 200 °C at 2 °C/min, at a 1 Hz frequency, 0.05 N initial dynamic force and strain amplitude of 67 μm . Electrical conductivity was measured in 1 cm between electrodes, -10 to 10 V, at 23 °C. Finally, SEM analysis was done on samples submerged in liquid nitrogen before applying a 2 mm layer of platinum.

3.4.1.1 Differential Scanning Calorimetry

The assessment of the main thermal peaks and crystallinity of PEEK formulations was possible by using DSC analysis. This analysis was also conducted to understand the influence of different amounts of carbon nanotubes in the thermal history. The thermograms (second heating) for comparison between PEEK formulations are presented in Fig. 3.16.

Fig. 3.16 DSC thermograms of PEEK and PEEK composite filaments with 2 and 4% of CNTs

Observing the PEEK formulation is possible to identify the existence of glass transition, crystallization exotherm and melting endotherm peaks. Firstly, we can state that the existence of CNT filler slightly decreased the T_g and ΔH_m but increased the T_m of its thermoplastic matrix. As usual, PEEK and PEEK composites crystallize during cooling, as indicated by the exothermal peaks in the cooling portion. In summary, there is a slight increase of crystallization temperature values when the percentage of nanotubes is raised. However, the increase of nanotube content lowered the degree of crystallinity. The obtained values are noted in Table 3.6, and all are in agreement with the values reported in the literature.

Regarding the PA66 formulation thermogram in Fig. 3.17 and comparing it to neat PA66, one could notice the very high crystallization degree of its matrix since the T_g (which relates to the amorphous region of the polymer) is barely visible. Although melt temperatures were similar, the crystallization temperature increased significantly with the added nanotubes, which narrowed the gradient window between T_c and T_m , as seen in Table 3.7.

Table 3.6 Values of glass transition, melting temperature, melting enthalpy, crystallization temperature and crystallinity degree of PEEK and PEEK/CNTs filaments

	PEEK	PEEK/CNT 2%	PEEK/CNT 4%
T_g (°C)	149.9 ± 2.6	146.5 ± 5.1	147.3 ± 1.3
T_m (°C)	340.8 ± 0.1	342.5 ± 0.1	342.2 ± 0.1
ΔH_m (J/g)	58.5 ± 0	57.1 ± 1.8	51.4 ± 4.2
T_c (°C)	287.0 ± 0.3	293.5 ± 0.4	293.8 ± 0.6
X_c (%)	45.0 ± 0	44.0 ± 1.4	39.6 ± 3.3

Fig. 3.17 DSC thermograms of PA66 and PA66 composite filament with 4% of CNTs

Table 3.7 Values of glass transition, melting temperature, melting enthalpy, crystallization temperature and crystallinity degree of PA66 and PA66/MWCNT 4% filament

	PA66 granules	PA66/MWCNT 4%
T_m (°C)	263.0 ± 0.3	265.6 ± 0.2
ΔH_m (J/g)	45.9 ± 0.4	71.9 ± 3.7
T_c (°C)	189.6 ± 0.7	223.5 ± 1.2
X_c (%)	18.0 ± 0.2	28.2 ± 1.5

3.4.1.2 Thermogravimetric Analysis

Thermogravimetric analysis was used to determine thermal stability and to quantify the amount of reinforcement in the PEEK formulations. Figure 3.18 exhibits the results for neat PEEK and its formulations with 2 and 4% CNTs. The degradation thermogram clearly indicates that the weight loss of PEEK and PEEK formulations is a one-step process, which starts at around 510 °C and exhibits the maximum rate at 900 °C. The weight loss, according to Ellis, Naffakh, Marco & Hendra [20], involves decarboxylation, decarbonylation and dehydration processes, resulting in the formation of phenol groups, carbon dioxide and water. The medium residual

Fig. 3.18 Thermogravimetric curves of PEEK, PEEK/2% and PEEK/CNT 4% composites

Table 3.8 Total weight loss and degradation temperature values obtained from TGA analysis for PEEK and PEEK composites

	PEEK	PEEK/CNT 2%	PEEK/CNT 4%
Total weight loss (%)	52.2 ± 1.9	47.0 ± 0.1	46.3 ± 1.7
Degradation temperature (°C)	594.1 ± 3.2	579.6 ± 2.0	575.4 ± 0.8

amount at 900 °C is about 47.0, 52.2 and 46.3% of the initial weight for PEEK, PEEK/CNT 2% and PEEK/CNT 4%, respectively, due to the remaining ether and aromatic structures as well as CNTs of PEEK composites in the residue. Therefore, the CNT amount for each composite was not possible to guarantee by TGA analysis. Degradation temperatures were observed at around 594.1, 579.6 and 575.4 °C for the aforementioned sequence. Total weight loss and degradation temperature values for each sample are stated in Table 3.8.

PA66/MWCNT 4% TGA results in Fig. 3.19 show a total weight loss of 92.9%, which is inferior to an average weight loss of 95.5% described in the literature for

Fig. 3.19 Thermogravimetric curves of PA66/MWCNT 4% composites

Table 3.9 Total weight loss and degradation temperature values of PA66/MWCNT 4%

	PA66/MWCNT 4%
Total weight loss (%)	92.7 $\pm$ 0.2
Degradation temperature (°C)	430.9 $\pm$ 0.1

neat PA66 [21], revealing the presence of nanotubes. In addition, the degradation temperature increased to 430.9 °C. Table 3.9 presents those values.

3.4.1.3 Dimensional Range

The diameter of our own produced composite filaments and its uniformity is an important parameter. Thus, the diameter was evaluated by a dimensional measurement. The diameter target was 1.75 mm, and by Fig. 3.20 and Table 3.10, we can state that both PEEK composite filaments are relatively uniform and within the desired value.

Similar results were obtained for the PA66 composite filament with 4% CNTs that is also within targeted range, with a 1.72 mm diameter, seen in Fig. 3.21 and Table 3.11.

Fig. 3.20 Dimensional tolerance analysis of PEEK composites**Table 3.10** Mean and standard deviation values of dimensional tolerance analysis

	Diameter (mm)
PEEK/CNT 2%	1.70 $\pm$ 0.07
PEEK/CNT 4%	1.73 $\pm$ 0.06

Fig. 3.21 Dimensional tolerance analysis of PA66/MWCNT 4%

Table 3.11 Mean and standard deviation values of dimensional tolerance analysis

	Diameter (mm)
PEEK/CNT 4%	1.72 ± 0.09

3.4.1.4
Melt Flow Index

Melt flow index values of PEEK and PEEK composites are presented in Fig. 3.22, along with mean and standard deviation. As expected, the presence of the CNT reinforcement significantly decreases the MFI, from approximately 23 to 10 or 3.5 g/10 min, with the increase of CNT. Consequently, viscosity of neat PEEK increased by the addition of CNT.

The results of melt flow index for PA66 granules and PA66/MWCNT 4% filament subjected to the same processing conditions are 28.6 g/10 min and 9.3 g/10 min,

Fig. 3.22 MFI mean and standard deviation values of PEEK and PEEK/CNT composites

Fig. 3.23 MFI mean and standard deviation values of PA66 and PA66/MWCNT 4%

respectively. This also shows a significant drop in fluidity of the polyamide matrix with the increase of nanotube filler, as can be seen in Fig. 3.23.

3.4.1.5 Parallel-Plate Rheometry

Due to limitations in the heating capacity of our rheometer that reaches a maximum temperature of 300 °C, dynamic oscillatory shear measurements could only be performed for neat PA66 and PA66/MWCNT 4%. Figure 3.24 illustrates the complex viscosity (η^*) of these materials as a function of frequency (f) in Hz. The response of the neat material to the dynamic shearing shows very small frequency dependence represented by weak shear thinning, while the viscosity of the composite material shows strong shear thinning behaviour as it decreases substantially with the increase in frequency. Again, these results exhibit the augmented viscosity of the composite material due to nanotube filler content.

Fig. 3.24 Complex viscosity versus frequency curves of PA66 and PA66/MWCNT 4% filaments

3.4.1.6 Tensile Tests

PEEK composite specimens were subjected to tensile testing in order to obtain their elastic modulus, yield tensile strength and elongation at break. Representative stress/strain curves for each composite are shown in Fig. 3.25 from which is possible to see the strain of the specimens until fracture. Both composites exhibit elastic and plastic behaviour, with the occurrence of necking, and thus, they are ductile composites.

As shown in Fig. 3.26, PEEK/CNT 4% is somewhat stronger than PEEK/CNT 2% since it can take more stress until yield, with tensile strengths at levels of 106.2 MPa

Fig. 3.25 Representative tensile curves obtained for PEEK/CNT 2% and PEEK/CNT 4% composite filaments

Fig. 3.26 Yield tensile strength (left), elongation at break (middle) and tensile modulus (right) values (mean and standard deviation) of the PEEK composite filaments

in comparison with the 98.8 MPa of the PEEK/CNT 2%. On the contrary, elongation under tension is lesser for the PEEK composite with the highest CNT amount (around 29%), while the composite with 2% of CNT can reach up to approximately 36%. In addition, the tensile modulus of PEEK/CNT 4% is higher than the PEEK/CNT 2% (around 2.9 GPa and 2.6 GPa, respectively). There is evidence to support that the incorporation of CNTs in PEEK matrix improved its mechanical properties since it is possible to perceive that 4% of CNTs provide greater improvement to PEEK matrix than only 2% of CNTs.

In Fig. 3.27, PA66/MWCNT 4% also shows ductile behaviour with neck formation, almost doubling the strain to fracture. Yield tensile strength reaches a value of 70.1 MPa, while elongation at break is 68.1%, making the composite material stronger and more able of supporting dimensional change without fracture, compared to literature values of neat PA66 with 52 MPa and 50%, as seen in Fig. 3.28.

Fig. 3.27 Representative tensile curves obtained for PA66/MWCNT 4% composite filament

Fig. 3.28 Yield tensile strength (left) and elongation at break (right) values (mean and standard deviation) of the PA66/MWCNT 4% composite filament

Fig. 3.29 Water absorption of PEEK/CNT 2% and PEEK/CNT 4% during specific time instants

3.4.1.7 Water Absorption

Figure 3.29 compiles the saturated water contents of PEEK composite specimens. PEEK consists of strong polar groups, which benefit the bonding of water molecules to its surface, by hydrogen bridges. In general, PEEK composites do not absorb much water; the maximum value of water absorption is around 4 wt% after 21 days. Literature only reported values lower than 0.5 wt%, which can be related to the only made timepoint of 24 h. Comparing both composites, the one with higher amount of CNT absorbs more water than the one with lower content, but the differences are not significant.

On the other hand, given that polyamide is a highly higroscopic thermoplastic matrix, there was increased moisture intake registered for PA66 and PA66/MWCNT 4%. After 21 days, there was more than 8 wt% of water absorption, as shown in Fig. 3.30.

3.4.1.8 Dynamic Mechanical Analysis

Figure 3.31 shows the viscoelastic properties of the PEEK nanocomposites, such as storage modulus and loss tangent evolution with temperature, while applying an oscillating force to the materials. For both specimens, the temperature was raised from room temperature to 200 °C, and not higher, since temperatures above this value were not advisable because of equipment limitations. Nonetheless, it is possible to observe in the DMA graph that increasing the CNT content also increases the storage modulus as the material becomes stiffer due to enhanced interactions between the matrix and reinforcement. $\tan \delta$ is the ratio of the loss component to the storage component of the modulus, and it helps determine the damping properties of the material. When the CNT content increases from 2 to 4%, a reduction in the peak height occurs which

Fig. 3.30 Water absorption of PA66 granules and PA66/MWCNT 4% during specific time instants

Fig. 3.31 DMA curves of PEEK/CNT 2% and PEEK/CNT 4% during heating

translates into a decrease in damping capacity. This occurrence was expected because of the restricted polymer chain mobility during the glass transition that is caused by higher filler loading [22].

A comparison between neat PA66 and PA66/MWCNT 4% was not able to be made since we could not produce a suitable neat PA66 filament for testing. Nonetheless, we can infer from the graph in Fig. 3.32 that there is a noticeable thermomechanical transition at 53.7 °C that seems to be representative of the material's T_g (a feature that we were previously not able to detect during DSC testing).

Fig. 3.32 DMA curves of PA66/MWCNT 4% during heating

Fig. 3.33 Electrical conductivity of PEEK and PA66 composite filaments

3.4.1.9 Electrical Conductivity

Certain composite materials can effectively conduct electric impulses through their thermoplastic matrices, depending on type and concentration of filler. In Fig. 3.33, it is shown that PEEK/MWCNT 4% is the most conductive of the three analysed nanocomposite filaments since it possesses the lowest resistivity, and the reported values are in accordance with the literature.

3.4.1.10 Scanning Electron Microscopy

Cross sections of prepared samples of PEEK/MWCNT 2% and PEEK/MWCNT 4% were analysed qualitatively using SEM at $\times 1000$ and $\times 100,000$ magnification (Fig. 3.34). On inspection of the images, we are able to verify an overall good dispersion of fillers. It is more evident in the case of the 2% composite, where a ≈ 24 nanotube agglomerate μm is visible compared to the ≈ 53 μm agglomerate of the 4%

Fig. 3.34 SEM images of PEEK/MWCNT 2% (left) and PEEK/MWCNT 4% (right) with $\times 1000$ magnification (above) and $\times 100,000$ magnification (below)

composite, both at $\times 1000$ magnification. At $\times 100,000$ magnification, we can see the interface between the carbon nanotubes (bright spots) and the polymer matrix. Samples seem to exhibit good adhesion with low occurrence of fibre “pull-out”, particularly in the case of PEEK/MWCNT 4%.

In Fig. 3.35, the PA66/MWCNT 4% sample SEM image shows irregular surface morphology of the cross section, which corresponds to fracture zones. At the top right of the $\times 1000$ magnification, we can verify a small nanotube agglomerate of only a few micrometres, indicating that this composite has also a good dispersion of fillers. Upon close inspection (at $\times 100,000$), we can see similar interface adhesion to the aforementioned PEEK composites.

3.4.2 Summary of Main Results

- PEEK composites present a slight increase of crystallization and melt temperature values when the percentage of nanotubes is higher. On the other hand, the increase of nanotube content lowers the enthalpy of melt and consequently the degree of crystallinity. Nanotubes highly increase the value of T_c in PA66, which makes for narrow temperature gradients when comes to printing the material, since this value is closer to T_m .
- The degradation of PEEK and PA66 formulations happens in a one-step process, which for PEEK starts at around 510 °C and finishes at 900 °C and for PA66 starts at 430 °C and finishes at 700 °C. However, the CNT amount present in

Fig. 3.35 SEM images of PA66/MWCNT 4% with $\times 1000$ magnification (above) and with $\times 100,000$ magnifications (below)

each PEEK composite was not possible to guarantee by TGA analysis since the medium residual amount at $900\text{ }^{\circ}\text{C}$ was around 50% for all the specimens, due to the remaining ether, aromatic structures as well as CNTs.

- The diameter target for the feedstock filaments was 1.75 mm, and the obtained diameters for all were within the desired value.
- Viscosity of neat PEEK and neat PA66 increased by the addition of CNTs, and thus, PEEK/CNT 4% is the most viscous filament. In addition, all the filaments are ductile.
- In contrast to commercial materials (PLA, PLA/FC, ABS and PA12), our formulations (mainly PEEK composites) have shown better properties, considering that the tensile strength values were between 25 and 55 MPa, and elongation at

break values ranged between 5 and 15% (except when compared to the 315% of polyamide 12). Furthermore, PEEK composite filaments also exhibited much higher tensile modulus compared to commercial materials (commercial materials presented values around 0.7–2 GPa).

- The water absorption of PEEK composites was not so significant since it only reached 4 wt% after 21 days immersed in water. Although, in the case of PA66 composites, there was high moisture intake recorded at 8%.
- PEEK/MWCNT 4% proved to be the most conductive of the produced composite filaments.
- The increase of nanotube reinforcement content in PEEK enhanced the thermo-mechanical stability of the material at higher temperatures.
- PEEK and PA66 composites showed overall good dispersion of fillers and interfacial adhesion.

3.4.3 Formulation Processing Requirements for AM

All the characterization tests applied to the produced PEEK and PA66 formulations were of paramount importance for estimating its response during and after printing, such as layer rebate and part shrinkage. The obtained information led to a suitable approach of geometrical allowances and process parameters. For instance, some polymers and/or dense part geometries require raft or skirt structures for expanding the contact surface of the first layers plus the use of heating printing bed/chamber in order to avoid detachment or warping problems. Furthermore, the printing process of PEEK parts is studied in this milestone considering relevant aspects that can be adjusted by means of one proposed design of experiments (DOE) such as the printing temperatures, printing speeds and the layer infill scheme/strategy, which determine the material packing level and/or interlayer strength. This experimental work consisted in a broad search for the best printing parameters to successfully print PEEK's formulations by AM manufacturing, taking into account the most important printing parameters.

3.4.3.1 Selected Material

The extensive printing process was only performed to PEEK/CNTs 4% due to the fact that, of all the characterized composite filaments, it was the one that yielded the best results. This filament, as previously described, was produced using high-performance PEEK granules (grade Victrex 450G) and multi-wall carbon nanotubes (NC7000TM) in an extrusion line of monofilaments, composed by a Coperion ZSK 26 Mc double screw extruder. The diameter of this filament is of 1.73 ± 0.06 mm with a melting temperature at around 342.2 °C, glass transition temperature at 147.3 °C

and crystallization temperature at 293.8 °C. Its degradation starts at around 510 °C, and its MFI is 3.5 g/10 min.

3.4.3.2 Preliminary Tests

Before the main printing process based in the aforementioned DoE, some preliminary tests were pursued in order to diminish the quantity of printing parameters to consider in the DoE. The following tables summarize all the elaborated work. Table 3.12 lists the parameters at the beginning, without changing the speeds, height and width of the lines and just altering the printing temperature.

The result of this initial test was for the first approach (printing at 400 °C) an incomplete printing and for the second one (printing at 410 °C) a printing with low quality. However, 410 °C was the selected printing temperature to carry out the next preliminary tests. Printed line dimensions were changed once the obtained results were weak for different temperatures at low printing speeds. Therefore, the second preliminary test involved the change in height and width of the line. Two approaches were tested as seen in Table 3.13.

Table 3.12 Printing parameters for the first preliminary test, evaluating two different printing temperatures

	mm		°C		mm/s
Layer height	0.2	Printing temperature	400	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.2	Chamber temperature	100	Initial layer speed	5
	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.2	Chamber temperature	100	Initial layer speed	5

Table 3.13 Printing parameters for the second preliminary test, with different initial layer heights

	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.3	Bed temperature	160	Travel speed	15
Line width	0.4	Chamber temperature	100	Initial layer speed	5
	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.4	Chamber temperature	100	Initial layer speed	5

Table 3.14 Printing parameters for the third preliminary test, with evident different chamber temperatures

	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.4	Chamber temperature	100	Initial layer speed	5
	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.4	Chamber temperature	120	Initial layer speed	5
	mm		°C		mm/s
Layer height	0.2	Printing temperature	410	Gantry speed	10
Initial layer height	0.2	Bed temperature	160	Travel speed	15
Line width	0.4	Chamber temperature	130	Initial layer speed	5

For the first approach with an initial layer height of 0.3, the result was poor adhesion of the first layer to the bed and between the layers. Concerning the second one, the printing improved, but the dogbone specimens presented some warpage, and thus, this approach was chosen to carry out the next tests. Usually, the width of the line must be at least 1.2 times greater than the height. In the last preliminary test, the closed chamber temperature was modified in order to find the best temperature with no signs of warpage. Consequently, Table 3.14 exhibits the printing parameters.

It was seen that at a chamber temperature of 100 °C, the specimens warped, whereas at 130 °C, there was no printing but rather the formation of a tangle due to the curling of the filament at the exit of the nozzle. Hence, it was established that 120 °C was the best closed-chamber temperature.

3.4.3.3 Printing Process

Typical dogbone models were designed by means of *Solidworks software*, according to ISO 527-2 type 1BA. The planning to print these dogbone samples was made by recurrence to one design of experiments (D.O.E.), resulting in eight different experiments, using printing parameters such as printing temperature (Printing T.—A), bed temperature (Bed T.—B), the printing speed (gantry speed—C) and the infill. The resultant DOE to test dogbone printed parts is summarized in Table 3.15.

From the preliminary printing tests, values for other printing parameters were specified and further used in the experiments of the aforementioned DOE. Table 3.16 states these values.

The set of all these printing specifications were defined in the .*stl* file obtained from CAD software, *Solidworks*, by using *Cura* software, with the purpose to slice dogbone parts into layers according to the corresponding specifications and creating

Table 3.15 Design of experiments to print PEEK/CNT 4% dogbone specimens testing different printing and bed temperatures, as well as gantry speeds

EXP.	Printing T. (A)	Bed T. (B)	Gantry speed (C)
1	400	130	10
2	400	130	15
3	400	160	10
4	400	160	15
5	410	130	10
6	410	130	15
7	410	160	10
8	410	160	15

Table 3.16 Additional important printing parameters

Printing parameter	
Layer height (mm)	0.2
Initial layer height (mm)	0.2
Line width (mm)	0.4
Environment temperature (°C)	120
Raster angle	−45°/45°
Initial layer speed (mm/s)	5
Travel speed (mm/s)	15–20
Brim width (mm)	3

a .gcode file, which will be read by the printer. A batch of at least five sequentially printed samples of all the eight experiments for both specimens was printed in an FDM machine Apium P155 printer with a nozzle of 0.4 mm. In addition to all of the printing specifications, Kapton® tape was applied to the bed support as well as hairspray before the printing started, aiming the strengthening of the adhesion between the first layer and the bed, consequently reducing warping. The visual quality of two printed dogbone specimens at 400 °C and 410 °C are exhibited in Fig. 3.36a and b.

After printing all of the experiments from the DOE, it was able to infer that the ones realized at a printing temperature of 400 °C (such as Exps. 1, 2, 3 and 4) were impossible to finish printing, mainly due to poor adhesion between the layers or due to the curling of the filament around the nozzle, creating a tangle. Regarding experiments 5, 6, 7 and 8, which were printed at 410 °C, resulted in a successful printing of specimens. Therefore, for these experiments, the infill density was also tested, namely densities of 50, 98 and 100%.

Fig. 3.36 Pictures taken to two representative dogbone specimens **a** printed at 400 °C; **b** printed at 410 °C

3.4.4 Materials for Optical Fibre Sensors

Optical fibre sensors are a very well-established technology for real-time monitoring of composite structures. The fibres chosen for this work are composed by fused silica, due to their low cost, good mechanical properties and the wavelength range, which is compatible to the available equipment [23]. Optical fibre sensors are very well suited to be embedded in different matrix materials such as PEEK and PA. With such sensors, it is possible to evaluate the structure condition in real time, during process or for health monitoring, by measuring the parameters of interest, such as strain and temperature. One of the sensing configurations that will be employed is the fibre Bragg grating (FBG), whose scheme is shown in Fig. 3.37 (left). Typically, it consists of a short segment of a single-mode optical fibre (with a length of a few millimetres) with a photo-induced periodically modulated index of refraction along the fibre core [24]. A network of FBGs can be established in a single optical fibre, by writing several structures in series, with a minimum separation of ~ 1 cm. Therefore, several locations can be monitored at the same time, using only one fibre. The second configuration investigated is the Fabry–Perot (FP) cavity, whose schematic design is shown in Fig. 3.37 (right). It consists of a small section of a hollow-core fibre (e.g. as a silica tube or a hollow-core photonic crystal fibre) spliced between two sections of single-mode optical fibres (SMF). However, this is an interferometric configuration, so the number of FP cavities that can be multiplexed in a single optical fibre is very limited due to its complexity.

Typically, FBGs can withstand maximum strain variations of 2% and temperatures up to 400 °C [23]. Above this temperature, the signal begins to degrade until it is completely erased. Regarding the Fabry–Perot cavities, they can operate until 0.5%

Fig. 3.37 Schematic of an FBG sensor (left) and a Fabry–Perot sensor (right)

strain [25] and with temperatures up to 1000 °C [26]. The optical fibre sensors integration in polymeric materials can be done during the manufacturing process. In this case, the fibre becomes fully embedded in the material, thus presenting a more accurate response towards strain and temperature. However, effects of adhesion with the surrounding materials, high temperature/pressure or optical fibre damage during the manufacturing must be considered. An alternative solution to these issues is the creation of channels in the structure for posterior sensors introduction though the sensors response can become less reliable.

3.4.5 *Materials for Nitinol Fibre Reinforcement*

Advances in the area of FDM have allowed the development of interconnects and components, such as bulk wire and mesh, shape memory fibre/tape, optical and piezoelectric fibres, able of being embedded in 3D printed structures, by submerging the wire/mesh into the thermoplastic. Systems embedding multifunctional material can be already found in some publications [27–29]. Main challenges identified for AM of thermoplastics with embedded SMA fibres include the changing transformation characteristics of NiTi wires as a result of the processing temperature of the thermoplastic (melting point of PEEK $\approx$ 340 °C). For this reason, incorporation of NiTi wires in a thermoplastic matrix has been limited to heat treatments at 300 and 350 °C. Special attention is required for the relation between the actuating temperature of the NiTi wire and the glass transition temperature (T_g) of the polymer matrix. On this respect, a lower melting point material will present a lower T_g (e.g. 47 °C for Nylon). As the actuation force in SMA is resulting from the reverse transformation (martensite to austenite), it is very important that the NiTi wire is fully austenitic below T_g of the thermoplastic matrix [30]. A home-made equipment (Fig. 3.38) has been used to perform the localized heat treatments along the wires. The wires studied were heat treated at 300 °C and 350 °C for 10 and 30 min. The equipment (Fig. 3.38) has a sliding contact system with two electrodes to drive/inject an electrical current in the specimen. The material between the two electrodes is heat treated by Joule effect (Patrick Inácio, Telmo Santos; UNIDEMI, FCT/UNL).

In the framework of the FIBR3D project, functionally graded shape memory alloy (NiTi) wires (0.4 mm diameter) have been studied, including thermal, mechanical, thermomechanical and structural characterization [31].

Transformation temperatures of the different segments of the heat-treated wires have been determined by DSC using a 204 F1 Phoenix from Netzsch. Thermal cycles from -150 °C to $+150$ °C with heating/cooling rate of 10 K/min were used. TMA has been performed using a PT 1600 from Linseis. Only the samples from interior part of the wires were tested in a temperature range from -10 to 60 °C, using a heating/cooling rate of 1 K/min. The tests were run in three-point bending, using a support span of 9 mm and an actuation force following a triangular waveform (frequency 0.01 Hz); the force was ranging from 100 mN and different maximum forces

Fig. 3.38 Experimental prototype to allow localized heat treatments along a wire or strip

(from 1000 to 4500 mN), in order to accommodate the different deformation characteristics of the austenite (higher temperature range) and R-phase (lower temperature range). The maximum deflection of the wires ranged from 400 μm to 1 mm, according to the heat treatment. The tensile tests were performed in a Shimadzu NG50KN, using a 500 N load cell. All tests consisted of three cycles, run with a crosshead speed of 1 mm/min and maximum stroke of 6% of the gauge length. For each heat treatment condition, two different gauge lengths have been tested: (i) 32 mm gauge length, where the tensile test is representative of the total length of the localized heat treatment; (ii) 44 mm gauge length, where the tensile test is representative of the “composite” behaviour of the heat-treated segment (32 mm long). SR-XRD experiments on the localized heat-treated wire were performed in transmission mode, at beamline P07 High Energy Materials Science (HEMS) of Petra III/DESY, using a wavelength of 0.124 $\text{\AA}$ (100 keV); a beam spot $1000 \times 500 \mu\text{m}^2$ was used to scan the wire along its length and a 2D detector Perkin–Elmer was placed at 1.65 m from the sample. The raw 2D images were treated using Fit2D program in order to calculate the individual XRD patterns by integration from 0 to 360° [32].

3.4.5.1 Transformation Temperatures Versus Heat Treatment

The heating parameters required to obtain a maximum temperature of 300 or 350 °C at the central region of the wire were determined, and the repeatability of the localized heat treatments has been checked through DSC results. Figure 3.39 shows the DSC results for: (i) as-received wire and (ii) the internal segment of two different wires heat treated at 350 °C for 10 min. The very small differences between the two different heat-treated wires (heat treatments more than 2 months apart) in terms of

Fig. 3.39 Reproducibility check of the localized heat treatment (350 °C, 10 min) on two different wires (blue and red curves) separated by more than two months (black curve: as-received material)

transformation temperatures and peak areas are negligible, allowing us to state that the localized heat treatments may be considered reproducible with the equipment used.

The transformation temperatures of the internal and external segments of the heat-treated wires are presented in Fig. 3.40. They are designated by A, R and M, respectively, for austenite (B2 structure), R-phase (trigonal structure), martensite (B19' structure) and the subscripts “s”, “f” and “p”, respectively, for start, peak and finish. The analysis of this data shows that, for all cases here studied, during cooling: (i) the temperature range for the A → R transformation for the heat-treated segments

Fig. 3.40 Transformation temperatures of the wires with different heat treatment conditions

was always above 0 °C, compared to the as-received ($R_f = -15.5$ °C); also, the peak temperature R_p is always above 20 °C, except for the external segment heat treated at 300 °C for 10 min; (ii) the transformations $A \rightarrow R$ (R_s) are always starting at higher temperature compared to the as-received condition; (iii) the transformations $R \rightarrow M$ (M_s) are kept constant for heat treatments at 300 °C (both for 10 and 30 min duration) but are higher for 350 °C treatments (both for 10 and 30 min duration) compared to the as-received condition; (iv) the highest transformation temperatures for $A \rightarrow R$ (R_s) were reached for the heat treatments at 300 °C (10 and 30 min duration), compared to 350 °C. On heating, only the external segments heat treated at 300 °C had A_s temperatures below the corresponding as-received condition. A_f temperatures for all segments in all conditions were always higher than for as-received wire. Increasing the heat treatment duration from 10 to 30 min always increased the transformation temperatures, except for the external segments heat treated at 300 °C.

3.4.5.2 Tensile Tests

The tensile tests on the wires at the different conditions (as-received and heat treated) are presented in Fig. 3.41. Also, the values of the upper stress plateau at 2.5 and 5.5% strain are plotted (Fig. 3.42) as a function of the condition for the two gauge lengths (32 and 44 mm). For all tests, a continuous decrease of the upper and lower stress plateaus is observed, as well as, for each test, a continuous decrease of the non-recovered deformation after each cycle. For all heat-treated wires, during loading, there is a two-step plateau for the gauge length 44 mm, while, for the 32 mm gauge length, only a slight increase of the plateau stress is observed beyond $\approx 5\%$ strain. For each heat treatment condition, the first step of the loading branch of the 44 mm

Fig. 3.41 Three consecutive cycles during tensile testing of samples as-received (a) and with different conditions of heat treatment: b 300 °C/10 min, c 300 °C/30 min, d 350 °C/10 min, e 350 °C/30 min; blue curve: 32 mm gauge length; red curve: 44 mm gauge length

Fig. 3.42 Mechanical characteristics as a function of the heat treatment for the 32 mm gauge length (local heat treated) and 44 mm gauge length (local heat treated + non-heat-treated edges): **a** Peak value of the stress-induced martensite; **b** Stress value for the lower plateau (2.5% strain) and higher plateau (5.5% strain)

gauge length is very close to that of the beginning of the plateau of the corresponding 32 mm gauge length. The second step of the loading branch of the 44 mm gauge length samples reached 450–500 MPa, very close to the stress level of the plateau for the as-received sample (475–500 MPa). Comparing the values of the stress at 2.5 and 5.5% strain, representatives, respectively, of the beginning and end part of the stress-induced martensite (SIM) plateau, the stress increment is observed to range between 40 and 60 MPa for the 32 mm gauge length, while it ranges from 70 to 180 MPa for the 44 mm gauge length.

3.4.5.3 In Situ Analysis During Load/Unload Tensile Testing

The in situ SR-XRD tests were used to follow the structural changes along the wires with different heat treating conditions, as illustrated in Fig. 3.43 for the localized heat treatment at 300 °C for 10 min, during a full load/unload superelastic cycle.

3.4.5.4 Thermomechanical Analysis

The TMA tests, as seen in Fig. 3.44, show a general trend of the amplitude of the deflection of the wires that stays constant at the highest temperature range (above 50 °C) where the austenite is stable. With decreasing temperature, this deflection amplitude starts increasing up to a maximum that occurs very close to the R_p (peak temperature of the $A \rightarrow R$ transformation) of the corresponding wire: ≈ 35 °C for the wire heat treated at 300 °C for 30 min and ≈ 25 °C for all the remaining heat-treated conditions.

Fig. 3.43 XRD patterns along the full gauge length (44 mm) of the heat-treated wire (local heat treatment at 300 °C for 10 min of the 32 mm central part of the wire)

Fig. 3.44 Maximum amplitude displacement of the wires with different heat treatment conditions during three-point bending tests at different temperatures (TMA tests)

3.4.5.5 Summary of Characterization of Nitinol Fibre Reinforcement

- The functional gradient caused by Joule effect heat treatment along the wire has been clearly put in evidence;
- It was observed that localized heat treatment (300 °C for 10 min) increased the austenitic finish temperature;

- The SIM transformation can be characterized by in situ SXRD analyses under load–unload tensile test. The transitional R-phase is firstly stress-induced from about 0.7% of strain prior to the B19' martensitic phase. At 2.4% strain, B19' peaks are observed. Both phase transformations are reversible during load/unload.

3.5 Conclusions

An extensive analysis was conducted in terms of evaluating the mechanical, thermal and rheological properties that are most relevant for 3D printing of commercial filaments. The obtained characterization results aided in the selection of PA66 and PEEK grades as matrices for the production of high performance formulations reinforced with MWCNTs. Composite filaments of PEEK with 2 and 4% carbon nanotubes, as well as PA66 with 4% CNTs, were successfully produced in a double screw extrusion line. These were studied with the same characterization techniques as the commercial filaments. The following conclusions can be drawn based on this research:

- Working windows of viscosity, crystallinity, filler content, MFI, dimensional range and thermal conductivity are established for commercial 3D printing filaments.
- The produced composite filaments have better overall properties, such as higher crystallization, viscosity, tensile strength and modulus, in addition to enhanced electrical conductivity and thermomechanical stability.
- PEEK/CNTs 4% is the composite filament that presents the best property results and therefore was subjected to an experimental printing process for AM requirements.
- To successfully print parts with the aforementioned reinforced PEEK filament, the optimal printing temperature is 410 °C, and bed temperature is 160 °C. There is mostly no visible warping at an initial layer speed of 5 mm/s, printing speed of 10 mm/s and a raster angle of $-45^{\circ}/45^{\circ}$, as well as other important tabled printing parameters.
- The role of optical fibres on the strain and temperature monitoring during processing and in service was demonstrated by their incorporation during additive manufacturing of nitinol-reinforced polymer matrix composites.
- The nitinol fibres were successfully heat treated to give rise to a functionally graded response.
- The chosen temperature range for the heat treatment (300–400 °C) combines the interest on the analysis of structural changes occurring during the process of additive fabrication, as well as the analysis of the functional characteristics resulting from different ageing treatment.
- The structural changes occurring in functionally graded wires during tensile loading/unloading (at room temperature) were analysed by in situ XRD.

- The thermomechanical response of nitinol wires was analysed in the temperature range -10 to 60 °C as a basis for understanding the in-service functional response of the nitinol fibres.

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