Functionalization of multi-walled carbon nanotubes for enhancement of thermomechanical properties of dielectric epoxies

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**FUNCTIONALIZATION OF MULTI-WALLED CARBON
NANOTUBES FOR ENHANCEMENT OF THERMO-
MECHANICAL PROPERTIES OF DIELECTRIC EPOXIES**

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SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

2010

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TABLE OF CONTENTS

	ACKNOWLEDGMENT	<i>i</i>
	TABLE OF CONTENTS	<i>ii</i>
	SUMMARY	<i>v</i>
	LIST OF FIGURES	<i>vii</i>
	LIST OF TABLES	<i>xiii</i>
	Table A: Definitions and acronyms	<i>xiv</i>
	Table B: Symbols	<i>xvi</i>
1	BACKGROUND OF THE THESIS	<i>1</i>
1.1	Introduction	<i>2</i>
1.2	Motivation	<i>4</i>
1.3	Objectives	<i>5</i>
1.4	Contribution of the Thesis	<i>6</i>
1.5	Organization of the Thesis	<i>8</i>
2	COMPOSITE MATERIALS	<i>9</i>
2.1	Introduction	<i>10</i>
2.2	Composition of composite materials	<i>10</i>
2.3	Homogenization of constituents	<i>14</i>
2.4	Properties of composite materials	<i>15</i>
2.5	Materials selection for the present study	<i>35</i>
2.6	Chemical properties of CNTs	<i>41</i>
2.7	Mechanical properties of CNTs	<i>42</i>
2.8	Thermal properties of CNTs	<i>57</i>
2.9	Conclusions	<i>63</i>

3	CHEMICAL TREATMENT OF CNT FILLERS	64
3.1	Introduction	65
3.2	Selection of CNT raw material	65
3.3	Chemical treatment of the CNTs	73
3.4	Experimental procedure	77
3.5	The proposed mechanism of reaction	83
3.6	Conclusions	88
4	CHARACTERIZATION OF CNT FILLERS	89
4.1	Introduction	90
4.2	Experimental analysis	90
4.3	FTIR analysis	97
4.4	TEM of functionalized CNTs	107
4.5	Conclusions	108
5	EPOXY COMPOSITE FABRICATION	109
5.1	Introduction	110
5.2	Mass preparation of CNT fillers	112
5.3	Composite fabrication	116
5.4	Optical and microscopic characterization	123
5.5	Discussion	133
5.6	Conclusions	134
6	MECHANICAL CHARACTERIZATION OF THE COMPOSITE MATERIAL	135
6.1	Introduction	136
6.2	Dynamic Mechanical Analysis	137

6.3	Discussion on experimental results	<i>147</i>
6.4	Finite element model of composite debonding	<i>153</i>
6.5	Conclusions	<i>157</i>
7	THERMAL AND ELECTRICAL CHARACTERIZATION OF THE COMPOSITE	<i>159</i>
7.1	Introduction	<i>160</i>
7.2	Thermal characterization	<i>160</i>
7.3	Electrical characterization	<i>166</i>
7.4	Conclusions	<i>170</i>
8	CONCLUSIONS AND FUTURE WORK	<i>171</i>
8.1	Conclusions	<i>172</i>
8.2	Future work	<i>173</i>
	Publications and patents	<i>174</i>
	References	<i>175</i>
	Annex A. Fundamentals of thermodynamics	<i>193</i>
	Annex B: Mechanical properties of materials	<i>200</i>

SUMMARY

This thesis consists of a feasibility study on the use of carbon nanotubes as fillers in epoxy resins. The study is oriented towards the fabrication of epoxy composites that are both mechanically robust and thermally conductive. The specificity of this work is to evaluate the effects of functionalizing the carbon nanotubes before insertion into the epoxy matrix. Among the different chemical routes explored, a method consisting of covalently bonding functional molecules on carbon nanotubes is selected.

During the chemical reaction, the bonded molecules contain epoxide rings which improve the chemical compatibility between the carbon nanotubes and epoxy resins. Moreover, the epoxide ring is believed to take part in the polymerization of the epoxy and thus create a strong link between the fillers and the matrix. This molecular link is expected to improve the interfacial mechanical and thermal transfer between the two materials.

Other than describing the chemical procedure, a thorough characterization of the treated carbon nanotubes is presented. Moreover, the fabrication process of composite materials made up of an epoxy matrix and the functionalized carbon nanotubes is described in details. Special attention is devoted to demonstrate the easiness and efficiency of the dispersion as a result of the chemical treatment that is applied to the carbon nanotubes.

The thermo-mechanical impact of the carbon nanotube covalent functionalization on the composites is evaluated with the help of various thermal and mechanical

characterization methods. The results tend to demonstrate the presence of an interphase between the bulk epoxy matrix and the carbon nanotube. This interphase is believed to consist of epoxy molecules whose arrangement around the carbon nanotubes is dependent on the resin pre-polymer physical characteristics. The interphase is thought to play a dominating role in the thermo-mechanical characteristics of the resulting composite.

LIST OF FIGURES

Fig. 2.1: Tensile stress applied on composite, perpendicular (a) and along (b) fiber orientation.

Fig. 2.2: Equal strain and equal stress conditions for two phase composite materials.

Fig. 2.3: Variation of shear stress along a fiber inside an expanding matrix.

Fig. 2.4: Equilibrium of forces between fiber and matrix.

Fig. 2.4: Variation of shear stress (a) and tensile stress (b) along the fiber.

Fig. 2.5: Saturation of interface shear stress (a) and tensile stress (b) at the tips of the fiber.

Fig. 2.6: Fibers inside a matrix tilted at an angle θ .

Fig. 2.7: Variation of the composite tensile strength with respect to the fiber angle.

Fig. 2.8: The molecular structure of graphene.

Fig. 2.9: The lattice structure of graphene in the k-space.

Fig. 2.10: Description of the crystal structure of the CNT as a wrapped graphene sheet.

Fig. 2.11: Variation of the density of CNTs.

Fig. 2.12: Quasi sp^2 hybridization state of the carbon atoms in CNTs.

Fig. 2.13: Graph of the Young's modulus of a single CNT as experimented by different research groups.

Fig. 2.14: Summary of mechanical properties of individual CNTs based on literature review.

Fig. 2.15: Evaluation of the tensile strength expected from hollow cylindrical fillers having a diameter of about 50 nm.

Fig. 2.16: Dependence between the interfacial shear yield strength of the nanotube and the critical length for different nanotube diameters.

Fig. 3.1: SEM of CNTs grown randomly.

Fig. 3.2: Magnification of Fig. 3.1 showing a dense mesh of CNTs.

Fig. 3.3: A sharp elbow bending of a CNT which indicates that it may be a defect site.

Fig. 3.4: A TEM picture showing that even smooth bends result in defect sites.

Fig. 3.5: A closer view of the TEM picture of Fig. 3.4 shows a discontinuity in the crystal lines indicating the occurrence of both a bending and a twisting of the CNT.

Fig. 3.6: TEM showing that some bending sites also result in a reduction in diameter of the CNT.

Fig. 3.7: TEM picture of a CNT tip showing damages resulting from an acid treatment.

Fig. 3.8: SEM of a bundle of CNTs which are vertically-align grown.

Fig. 3.9: Higher magnification picture showing a dense forest of rectilinear CNTs.

Fig. 3.10: Various covalent functionalization techniques reported by Burghard et al.

Fig. 3.11: A review of the strategies to covalently functionalize CNTs reported by Nakashima et al.

Fig. 3.12: Attack of the CNTs by n-butyllithium.

Fig. 3.13: Visible difference in dispersion of f-CNTs in solution: left = pure CNTs, right = f-CNTs.

Fig. 3.14: Break in double bond between two carbon atoms to favor the grafting of the butyl molecule.

Fig. 3.15: Reaction mechanism of the chemical attack of the CNTs.

Fig. 3.16: Nucleophilic substitution between carbanions on the CNT sidewall and epichlorohydrin molecules resulting in epoxy groups covalently bonded to the CNTs.

Fig. 3.17: Reaction mechanism of the nucleophilic substitution between epichlorohydrin and the lithiated CNT.

Fig. 4.1: Figure showing the Raman spectroscopy of functionalized MWNTs.

Fig. 4.2: Figure showing the thermo-gravimetric analysis of the f-CNTs.

Fig. 4.3: Figure showing the Differential Scanning Calorimeter analysis of f-CNTs.

Fig. 4.4: Sketch showing the grafting of functional molecules on the side wall and tips of CNTs.

Fig. 4.5: Broad FTIR spectrum of the f-CNTs between 400 cm^{-1} and 4000 cm^{-1} .

Fig. 4.6: High precision FTIR spectrum of the f-CNTs in the range of 800 cm^{-1} to 1800 cm^{-1} .

Fig. 4.7: First order derivative of the FTIR spectrum shown in Fig. 4.6.

Fig. 4.8: (a) Positions 1 and 2 are the locations of the binding sites for the functional molecules on the tip of the CNT (Half fullerene C_{30} molecule) (b) Cluster model of the functionalization of a C_{30} molecule.

Fig. 4.9: Sketch of a Stone-Wales defect site found on the side wall of a CNT.

Fig. 4.10: Optimized configurations of the 3 conformers created by grid scan technique for the functionalized half-fullerene.

Fig. 4.11: TEM images of f-CNTs.

Fig. 5.1: Chemical route followed by the CNTs using BuLi as initiator to graft epoxide branches on the sidewalls.

Fig. 5.2: 500 X optical microscope view of CNTs in solution: (a) f-CNTs, (b) pure CNTs.

Fig. 5.3: Samples of epoxy composite after curing presenting numerous pores. Sample (a) consists of EPON 828 stirred at 120 rpm and sample (b) is EPICOTE at 180 rpm.

Fig. 5.4: Viscosity measurements of the epoxy resin during stirring. The three samples are made up of EPICOTE 1006A. Sample (A) is the pure resin, sample (B) is the resin with 0.1 wt% f-CNTs and sample (C) is the resin with 0.2 wt % f-CNTs. The yellow bar represents the viscosity measurements made after 24 hrs of rest subsequent to the measurement in blue.

Fig. 5.5: SEM pictures of epoxy composite samples which are not cured completely.

Sample (a) is the trench view and sample (b) is the surface view of the composite.

Fig.5.6: Sketch of the experimental setup to introduce the hardener in the composite.

Fig. 5.7: Design of the aluminum mold to cure the epoxy composite.

Fig. 5.8: Curing profile of the composite.

Fig.5.9: Sample on the left contains 0.1 wt % of vertically aligned grown f-CNTs and on the right 0.1 wt % of randomly grown untreated CNTs.

Fig. 5.10: Samples of epoxy composite containing f-CNTs. (a) Same sample as the one in Fig. 5.9 left, but after surface polishing. (b) Selection of samples used for thermo-mechanical characterization.

Fig. 5.11: Room temperature fracture of composite samples made up of randomly grown CNT bundles dispersed in EPON 828 epoxy resin. (a) Non-functionalized. (b) Functionalized. (c) Magnification of (b). (d) Magnification of (c).

Fig. 5.12: Room temperature fracture of a composite sample made up of vertically aligned grown and functionalized CNTs dispersed in EPON 828 epoxy resin. (a) Surface of the fractured area. (b) Magnification of (a). (c) Magnification of (b). (d) Magnification of (c).

Fig. 5.13: Epoxy composite consisting of f-CNTs dispersed in EPICOTE 1006A epoxy resin. Sample elongated at 150°C. (a) Slit showing CNTs still linking the two sides of the matrix. (b) Single CNT under elongation having 4 different diameters. (c) and (d) Mode I fracturing at the failure zone showing the different deformation stages.

Fig. 5.14: Epoxy composite sample consisting of 5 wt % f-CNTs dispersed in EPON 828 epoxy resin after mild attack by hydrogen peroxide. (a) – (d) Analysis of different areas of the sample.

Fig. 5.15: Epoxy composite sample consisting of 7 wt % f-CNTs dispersed in EPICOTE 1006A epoxy resin. After curing, the sample undergoes mild chemical attack by hydrogen peroxide.

Fig. 5.16: 7 wt % f-CNTs dispersed in EPICOTE 1006A epoxy resin and attacked by hydrogen peroxide after curing. (b) is the magnification of (a).

Fig. 5.17: Epoxy composite sample after prolonged chemical attacked by hydrogen peroxide.

Fig. 5.18: f-CNTs tips (a) & (b) and bent sidewalls (c) & (d) adhering to the epoxy matrix.

Fig. 5.19: Pristine CNTs blended in EPON 828. (a) Dense pack of CNTs with some visible bundles. (b) Closer range showing a bundle on the bottom right.

Fig. 6.1: Experimental disposition of the sample under test.

Fig. 6.2: Storage modulus of epoxy composite samples made up of vertically-aligned grown, untreated CNTs dispersed in EPON 828.

Fig. 6.3: Storage modulus of epoxy composite samples made up of vertically-aligned grown f-CNTs dispersed in EPON 828.

Fig. 6.4: Storage modulus of epoxy composite samples made up of vertically-aligned grown f-CNTs dispersed in EPICOTE 1006A.

Fig. 6.5: Comparative efficiency of the different composites.

Fig. 6.6: Los modulus of epoxy composite samples made up of pristine CNTs in EPON 828.

Fig. 6.7: Los modulus of epoxy composite samples made up of f-CNTs in EPON 828.

Fig. 6.8: Los modulus of epoxy composite samples made up of pristine f-CNTs in EPICOTE 1006A.

Fig. 6.9: Possible organization of the epoxy pre-polymer molecules around the CNTs.

(a) Long pre-polymer strands. (b) Short pre-polymer strands.

Fig. 6.10: Model of a CNT inside an epoxy matrix with an interphase.

Fig. 6.11: CNT pull out from the interphase.

Fig. 6.12: Stress and displacement of an interphase having a good CNT adhesion.

Fig. 7.1: Specific heat capacity of the composite for different weight percentage of CNT addition.

Fig. 7.2: Isothermal change in specific heat capacity with respect to the f-CNT concentration. Measurements made at 100°C.

Fig. 7.3: Raman spectroscopy of pure epoxy polymer and f-CNT / epoxy composite.

Fig. 7.4: Electrical resistivity characterization of the epoxy composite samples.

Fig. 7.5: Comparative permittivity of epoxy composites containing pristine and functionalized MWNTs. A) Real permittivity. B) Imaginary permittivity.

Fig. A.1: Extensive and intensive parameters of a thermodynamic system.

Fig. B.1: Determination of the yield strength of a material.

Fig. B.2: Plastic flow of a material beyond the yield length.

Fig. B.3: Definition of the viscous flow of a material.

Fig. B.4. Graph showing the behavior of different viscous materials.

Fig. B.5: Graph showing behavior of time dependant viscous materials.

Fig. B.6: Two simple mechanical objects used to describe the elastic and viscous behavior.

Fig B.7: Maxwell element showing a spring and a dashpot in series.

Fig. B.8: Definition of the shear stress applied on a material.

Fig. B.9. Definition of the tensile stress applied on a material.

Fig.B.10: Definition of the isotropic compression applied on a material.

LIST OF TABLES

Table A: Definitions and acronyms.

Table B: Symbols.

Table 2.1: Main mechanical properties of the most common fillers.

Table 2.2: Literature review of the experimental measurements of the Young's Modulus of CNTs.

Table 3.1: Chemical reactions tested during this study. (Remarks in blue are good, in green are bad).

Table 3.2: Solvents tested for the reaction of CNTs with n-butyllithium.

Table 3.3: List of molecules tested for the substitution of lithium on the CNT wall.

Table 4.1: List of known IR resonant vibrations related to straight chain alkanes, epoxide rings and water molecules.

Table 4.2: Theoretical results of the covalently grafted bond states for different orientations.

Table 4.3: Vibrational modes comparison between experiment and theoretical work.

Table 5.1: The chemical reaction route.

Table 5.2: Physical properties of the epoxy resins.

Table 5.3: Properties of the two curing agents. Unless specified, the values correspond to measurements made at 25°C.

Table A: Definitions and acronyms

ACRONYM	DEFINITION
IC	Integrated Circuit
TSV	Through Silicon Via
3D	3 Dimensions
CNT	Carbon Nanotube
SWNT	Single Wall Nanotube
DWNT	Double Wall Nanotube
MWNT	Multi Wall Nanotube
FTIR	Fourier Transform Infra Red
T.S.	Tensile Strength
Tan δ	Loss tangent
MMC	Metallic Matrix Composite
CMC	Ceramic Matrix Composite
PMC	Polymer Matrix Composite
DGEBA	Di-Glycidyl Ether of Bisphenol A
AEP	N-Aminoethyl Piperazine
TETA	Triethylenetetramine
MD	Molecular Dynamics
CVD	Chemical Vapor Deposition
f-CNT	Functionalized CNTs
DMF	Dimethylformamide
BuLi	N-butyllithium
TGA	Thermo-gravimetric analysis
CTE	Coefficient of thermal expansion
TMA	Thermo-mechanical analysis
DMA	Dynamic Mechanical Analysis
DEA	Dielectric analysis
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope

PS	Polystyrene
GF	Geometry factor
SDS	Sodium dodecyl sulphate
RBM	Radial breathing mode
FEA	Finite element analysis
RVE	Representative volume element

Table B: Symbols

SYMBOL	MEANING
U	Internal energy
S	Entropy
T	Temperature
W	Work
Q	Heat energy
V	Volume
N	Number of particles
μ_c	Chemical potential
F	Free energy
H	Enthalpy
G	Free enthalpy (Gibbs enthalpy)
J	Grand potential
C_v	Heat capacity at constant volume
c_v	Specific C_v
C_p	Heat capacity at constant pressure
c_p	Specific C_p
α	Coefficient of thermal expansion
β_T	Isothermal compressibility
k_B	Boltzmann constant
σ	Tensile stress
ϵ	Tensile strain
σ_y	Yield Strength
γ	Shear strain
τ	Shear stress
η	Viscosity
$\dot{\gamma}$	Rate of change of γ
η_0	Time independent η
G	Hooke's modulus

F	Force
ω	Angular frequency
γ_0	Amplitude of strain
[]*	Complex notation
[]'	Real part
[]''	Imaginary part
T_g	Glass transition temperature
V_x	Volume fraction of x
μ	Coefficient of friction
l_c	Critical length
K	Thermal conductivity
ρ	Density
D	Thermal diffusivity

CHAPTER 1

BACKGROUND OF THE THESIS

1.1 Introduction

The quest for new materials is an important aspect in the development of new technologies and innovative structures. Materials performance is obviously an important feature in the design of a new device but, associated with it, the device reliability also plays a fundamental role towards its repeatability in performance and its sustainability in time. Thus, the materials resistance to changes in any properties playing a role in the device performance is a key parameter in the materials design. The common materials properties that must be monitored to prevent failure are changes in morphology and internal structure under the action of a force or under the action of heat and resistance to chemical attack, fracture and delamination.

A lot of effort is devoted to the invention of new high performance materials. However, now that the intrinsic properties of almost all chemical elements have been thoroughly explored and exploited on a macroscopic scale, the key to making higher performance materials is in the mixing of different components together. In doing so, one expects to take advantage of a remarkable property from each constituent so that the resulting composite mixture owes its enhanced properties to a unique combination of raw materials.

In today's nanotechnology era, materials properties at the nanometric scale open new doors to science and technology. Unexpected new properties follow from materials which are scaled down to nano-sizes. Moreover, for a given mass of a material, the total surface area of its corresponding nanoparticles produced is much larger than its micro counterpart. Therefore, even when small weight percentages of the material are involved, the random dispersion of the nano-sized particles already leads to the

formation of networks which interconnect various point of the bulk composite. The point above which this interconnection takes place, also called the percolation threshold, occurs at very low weight percentages for nanoparticles. If, in addition to that, the nanoparticles have a high aspect ratio, the percolation threshold can occur at even lower weight percentage [1]. Therefore, the amount of nanoparticle additive to be inserted in a composite to alter a property can be dramatically less [1, 2]. Thus, composite materials that are based on the addition of nano-sized fillers have the potential to be innovative.

However, this new technology is also accompanied with some difficulties. The major problems related to the use of nano-fillers are, first, to obtain a uniform dispersion of the particles and secondly, to interpret and apply properly the changes brought to the material. Such factors impinge on the performance and reliability of the composite [3]. For example, in an attempt to perform toxicological studies of nanoparticles, Powers et al. report the issues in properly characterizing the size, shape and state of dispersion of material samples due to the inability to determine the correct experimental protocols which can ensure that the tested samples are truly representative of the bulk material [4]. Indeed, they mention that size, shape and density variations have a big influence on the characterization results when nano-sized particles are involved. Another example of such issues can be found by reading the review paper of Wu et al. who report on the difficulties of producing fluids containing suspended solid nanoparticles [5]. The paper describes the critical complexities in properly characterizing some physical and chemical properties of the composite and the instability of the material due to effects such as evaporation and sedimentation.

1.2 Motivation

Nowadays, the main issues related to the packaging of integrated circuits (ICs) in the electronics industry are mainly mechanical and thermal. The current microprocessor chips available on the market have above a thousand times more processing power than those of a decade ago. Because of the high heat generated by the ICs, there are big issues concerning the mechanical mismatch and heat dissipation of the packages. Consequently, the current technology found in the packaging products does not meet up the criteria requested by the circuit designers yet. Heat dissipation is still considered to be one of the main bottle necks in the electronics technology. Therefore, at the present time, alternative solutions such as using multi-core processors are developed to get round these issues.

During the last decades, in the packaging of ICs, there has been a progressive shift of packaging materials towards polymers [6]. Organic polymeric materials have the advantages over other materials of being lighter, easily processed and readily available. Furthermore, when pure polymers exhibit limited properties, a simple alternative strategy is to incorporate fillers of various kinds in the original material so that the enhanced properties of the fabricated composite material can meet the expected specifications. For example, a key strategy to enhance the electrical and thermal properties of dielectric polymers is to add metal particles in it [7,8]. Both electrical and heat transport are thus ensured by the free flow of electrons resulting from the network of metal particles which is formed within the polymer matrix. One of the circumstances under which this strategy cannot be applied is when high thermal dispersion is required from a dielectric material. In such a case, special ceramics and glasses are still the preferential materials used [9].

Now that a novel technology called through silicon via (TSV) [10] has been developed to perforate a die of silicon to form vias, a new generation of ICs is currently being developed by stacking many dice on each other to form 3D structures. Due to the fact that such a technology does not require any wire bonding between the dice, the amount of dice to be bonded together can potentially be much bigger than currently stacked dice where not more than five dice are usually used. Furthermore, due to the absence of wires, all the dice can be of the same size and, when stacked on each other, only the lateral parts of each die is in contact with the packaging material. These closely packed structures will eventually raise even more thermo-mechanical issues due to the limited thermal evacuation paths available. Moreover, each die may have a different operating temperature if heat is not dissipated evenly. Thus, the ability of the packaging material to dissipate a maximum of heat uniformly will play a crucial role in the reliability of such devices.

1.3 Objectives

The first objective of this work is to explore the use of carbon nanotubes (CNTs) as fillers dispersed in packaging materials to improve its mechanical resistance and heat dissipation. The desired tasks of the CNT fillers are first to behave as heat carrying pipes which will drag out the heat from the circuits and, secondly, as a reinforcing network to enhance the mechanical strength of the polymer matrix.

Among the different types of filler used in composite materials, the only one having such a high aspect ratio combined with an exceptionally high thermal conductivity [11-22] and unique mechanical properties [23,24] is the CNT. However exploiting the unique marvelous properties of CNTs is not always an obvious task. What may appear

as an advantage at one time may turn out to be a major disadvantage in another circumstance. For instance, the chemical inertia of CNTs is a very interesting property which ensures that the material does not change or degrade with time. Conversely, this property soon becomes quite troublesome when the solubility and anchoring of the fillers in polymers are concerned.

The work reported in this thesis is about the development of a proper chemical treatment that can improve the fabrication process of CNT fillers in epoxy composites. Moreover, the same chemical treatment is expected to enhance both the mechanical and thermal behavior of CNTs in epoxy composites. The strategy is to develop a method where, by bonding molecules on the surface of the CNTs, its behavior can be altered, allowing it to be more chemically compatible with the polymer during homogenization and more thermo-mechanically efficient within the hosting matrix. Indeed, it is demonstrated that the behavior and properties of CNTs can be altered by covalently bonding molecules on its sidewalls and tips. Thus, uniform dispersion of the fillers is achieved and interfacial properties can be controlled.

1.4 Contribution of the thesis

The contribution of this thesis can be stated in a few points:

- A new chemical route is proposed for the treatment of CNTs. This chemical treatment involves the covalent bonding of functional molecules containing an epoxide ring on the sidewalls and tips of CNTs. It is a non-destructive method that neither alters the size of the CNTs nor generates amorphous carbon residues.

- An innovative strategy to characterize the functionalization of CNTs is demonstrated. The strategy, which consists of a combination of experimental characterizations together with a theoretical model, is used to confirm the occurrence of the covalent bonding between the functional molecules and the CNTs.
- A method is described to obtain a homogenous dispersion of the functionalized CNTs (f-CNTs) in the epoxy resin. Processing details related to the repeatability of the results are given. In addition, all the processing steps involved in the curing of the composite resin are studied and the impact of the presence of f-CNTs in the homogenization and curing are described.
- The provision of proof via a thorough mechanical and thermal characterization validating that functionalization can also improve the mechanical resistance and thermal dissipation of the original resin.
- The thermo-mechanical characterization of the resulting composite material also contributes to understand better:
 - the hybridization state of carbon at the covalent bonding sites,
 - the constituents and structures of CNT / matrix interphase layers,
 - the effects of covalent functionalization on the interphase layer,
 - the effects of interphase layers on the composite thermo-mechanical properties,
 - the effect of epoxy pre-polymer chain length on the mechanical properties of the composite.

1.5 Organization of the thesis

The thesis is divided into 8 chapters:

Chapter 1 describes the background of this thesis and the motivation in performing this study.

Chapter 2 consists of a general introduction about composite materials, followed by a thorough description of the materials used in this study and a review of all the research work done on CNTs in polymeric composite materials for mechanical and thermal improvement.

Chapter 3 explains the chemical treatment of CNTs.

Chapter 4 characterizes the narrowed down chemical treatment chosen for this study.

Chapter 5 describes how the composites are fabricated.

Chapter 6 is devoted to a mechanical characterization of the composite.

Chapter 7 focuses on the thermal characterization of the composite.

Chapter 8 concludes about the study and gives some ideas about further studies.

Two annexes are provided about general thermo-mechanical aspects of materials.

CHAPTER 2

COMPOSITE MATERIALS

2.1 Introduction

The focus of this chapter is to give a broad picture of the classification and purpose of the major components present in composite materials. Then, a detailed description of the essential principles that portray the thermal and mechanical properties of two-component composite materials is given. Finally, a review of the thermal and mechanical properties of individual CNTs and CNT based composite materials is presented. A few annexes relating some basic principles of thermodynamics and materials mechanics are provided at the end of the thesis for easy reference.

2.2 Composition of composite materials

The materials constituting a composite can be grouped into two sets, the matrix which is the main body of the composite and additives which are the various components that are incorporated in the matrix [25]. There is no standard denomination for materials with respect to the fraction of its constituting elements. For example, in conductive pastes, 80 % of the material is made up of a metal powder and the remaining 20 % is composed essentially of a binding polymer and a solvent. Nevertheless, the metal powder is still considered to be an additive and the polymer, the matrix. In such cases the definition of the matrix would rather be the binding material that holds additives together.

2.2.1 Matrix

The materials matrices that are commonly used to fabricate composites can be grouped into three main categories [25]:

- Metallic Matrix Composite (MMC)
- Ceramic Matrix Composite (CMC)

- Polymer Matrix Composite (PMC).

The existence of these categories is justified by the fact that each of them is used in very distinctive applications. Subsequently, every composite material is sub-classified into smaller groups based on the following properties:

- Efficient temperature range (Temperature interval within which the other properties do not vary too much)
- Mechanical properties (Strength, hardness...)
- Thermal properties (Conductivity, resistivity)
- Electrical properties (Conductivity, resistivity, charge retention...)
- Chemical properties (Resistance to wear, chemical inertness...)
- Cost of production

2.2.2 Additives

It is sometimes necessary to insert additives in a polymer to enhance some properties so that it can meet the requirements of a specific application. The different additives usually put in can be classified as follows [26]:

- Fillers
- Plasticizers
- Reinforcements
- Flame retardants
- Colorants
- Impact modifiers
- Others (processing aids, stabilizers, biocides, ..)

Plasticizers

Plasticizers are used to reduce the modulus of polymers by lowering its glass transition temperature, that is, to soften the polymers.

The Wood equation is often used to determine the change in glass transition temperature [26]:

$$T_g = \frac{T_{g_1} + (kT_{g_2} - T_{g_1})W_2}{1 - (1 - k)W_2} \quad (2.1)$$

Flame retardants

When polymers are exposed to a huge heat flux for a prolonged period, it will thermally degrade. When deprived from oxygen, thermal degradation is called pyrolysis but in the presence of oxygen it is called thermal-oxidative degradation. Flame retardants are inserted in polymers to prevent the combustion from occurring over a more extended harsh thermal band.

Colorants

Plastics can be colored by adding soluble dyes and pigments that are dispersed in the polymer during processing.

Impact modifiers

This process is usually performed by blending other polymers in the primary one in order to modify its glass transition temperature. The impact strength of brittle plastics such as polystyrene can be significantly improved by dispersing in it small particles of a rubbery phase polymer.

Fillers and reinforcements

The reasons for adding fillers in polymers are much diversified. The main reasons are as follows:

- reduce resin cost
- improve processability
- dissipate heat
- reduce mold shrinkage
- minimize electrostatic charging
- improve mechanical properties
 - o modulus
 - o tensile / tear strength
 - o abrasion resistance
 - o fatigue strength
- reduce the weight
- improve conductivity

The most common materials used as fillers are: wood flour, clay, talc, fly ash, sand, mica, glass beads, graphite, carbon black, aluminum flakes, carbon fibers, glass fibers, silica, etc. The amount of fillers added to a polymer usually ranges from about 20% to 80%.

2.3 Homogenization of the constituents

There are various factors which determine whether a specific polymer blend will be homogeneous or phase-separated. The main factors are the kinetics of the mixing process, the processing temperature, and the impact of any solvent or other additives.

Nevertheless, the major consideration in determining the miscibility of the two polymers comes from a thermodynamic point of view and it is governed by the Gibbs free enthalpy equation of state (*see annex A for details*):

$$\begin{aligned} G &= H - TS \\ \Rightarrow dG &= dH - SdT - TdS \end{aligned} \quad (2.2)$$

If the temperature is maintained constant, then the equation becomes:

$$dG = dH - TdS \quad (2.3)$$

Using the expression of Flory-Huggins for entropy change due to mixing:

$$dS = -k_B(n_1 \ln V_1 + n_2 \ln V_2) \quad (2.4)$$

where V_1 and V_2 are the volume fractions of the two components and n_1 and n_2 are the number of molecules of each component, we have a final expression:

$$dG = dH + k_B T (n_1 \ln V_1 + n_2 \ln V_2) \quad (2.5)$$

If ΔG is positive over the entire composition range at a given temperature, then the two polymers in the blend will separate into phases that are pure in either component, provided that a state of thermodynamic equilibrium has been reached. However, to obtain complete miscibility the Gibbs enthalpy must be negative and it must contain only one *extremum* minimum. Mathematically speaking, the conditions that must be reached to obtain such a thing are:

$$\blacksquare \quad \Delta G < 0 \quad (2.6)$$

$$\blacksquare \quad \left(\frac{\partial^2 \Delta G}{\partial V_2^2} \right)_{T,p} > 0 \quad (2.7)$$

2.4 Properties of composite materials

A composite material usually contains several additives that modify the original properties of the hosting matrix. However, to understand better the underlying science accounting for the alterations observed following the dispersion of one specific filler inside a matrix, it is wise to proceed stepwise. Since the context of this thesis is to study the implications of adding CNTs to epoxies, most of the materials descriptions are focused on dual composition composites only. First, the broad mechanical and thermal aspects of dual materials are addressed successively. Then, these aspects are investigated for CNTs in epoxies. For comparison, Table 2.1 summarizes the properties of traditional fillers used for mechanical reinforcement. *(A reminder of the various mechanical properties of materials is available in Annex B)*

Table 2.1: Main mechanical properties of the most common fillers [25, 26]

Fiber	Tensile Modulus (GPa)	Tensile strength (GPa)	Density g cm ⁻³
Boron	386	3.4 – 3.7	2.38 – 2.66
E-glass	72.4	3.45	2.55
S-glass	85.5	4.83	2.49
Graphite			
High modulus	483-517	1.86	1.97
High strength	234-255	2.83	1.77
Kevlar 49	138	2.76	1.44
Steel	407	4.14	7.81

2.4.1 Mechanical behavior of a dual composite material

For a dual material, it is essential to understand the mechanical properties of a heterogeneous composite material containing two components of the same geometry and orientation. The two components are noted as the material matrix (m), which is the weak constituent, and the material filler (f) which is the strong constituent (Fig. 2.1). Since orientation is involved, it is clear that the composite mechanical properties vary depending on the orientation of the work done on the material [27].

The stress experienced by each component in the situation of Fig. 2.1 (a) is the same and is equal to F/L^2 . However, in the configuration of Fig. 2.1 (b), both components

Fig. 2.1: Tensile stress applied on composite, perpendicular (a) and along (b) fiber orientation [27].

experience a different stress such that the total applied force, $\mathbf{F}$ is divided into two parts: $\mathbf{F}_m$, the force exerted on the matrix and $\mathbf{F}_f$, the force exerted on the filler. Thus, the stress borne by the matrix, for example is [27]:

$$\sigma_m = \frac{\vec{F}_m}{Nl_m L} \quad (2.8)$$

where N is the total number of blocks in the matrix component.

On the other hand, the strain occurring in each component of situation (b) is the same and is equal to dL/L , whereas the strain for each component in case (a) is different.

The strain experienced by the matrix for example is [27]:

$$\epsilon_m = \frac{dl_m}{l_m} \quad (2.9)$$

Thus, configuration (a) is called the equal stress condition and configuration (b) is called the equal strain condition.

In order to assess the effect of orientation on the overall mechanical performance of the material, the total composite modulus of each situation is calculated. The volume fraction of each component is [27]:

$$V_m = \frac{l_m}{l_m + l_f} \quad V_f = \frac{l_f}{l_m + l_f} . \quad (2.10)$$

2.4.1.1 Orientation effects on a dual composite material

2.4.1.1.1 Configuration (a): Equal stress condition

The total elongation of the composite is [27]:

$$dl_c = Ndl_m + Ndl_f \quad (2.11)$$

Thus, from Equation (2.9), the total strain is:

$$\begin{aligned} \varepsilon_c &= \frac{dl_c}{N(l_m + l_c)} \\ &= V_m \varepsilon_m + V_f \varepsilon_f \end{aligned} \quad (2.12)$$

If perfect elastic deformation is assumed, in an equal stress condition:

$$\varepsilon_m = \frac{\sigma}{E_m} \quad \varepsilon_f = \frac{\sigma}{E_f} \quad \varepsilon_c = \frac{\sigma}{E_c} \quad (2.13)$$

and:

$$\frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_f}{E_f} \quad (2.14)$$

Rearranging Equation 2.14:

$$E_c = \frac{E_m E_f}{(V_m E_f + V_f E_m)} \quad (2.15)$$

2.4.1.1.2 Configuration (b): Equal strain condition

In this configuration, as mentioned before, the total force exerted on the material has two components [27]:

$$\begin{aligned} F &= F_m + F_f \\ &= \sigma_m Nl_m L + \sigma_f Nl_f L \end{aligned} \quad (2.16)$$

The cross sectional area over which the force is applied is $NL(l_m + l_f)$. Thus, the composite stress is:

$$\begin{aligned}\sigma_c &= \frac{\sigma_m l_m}{l_m + l_f} + \frac{\sigma_f l_f}{l_m + l_f} \\ &= \sigma_m V_m + \sigma_f V_f\end{aligned}\tag{2.17}$$

Assuming that the two phases undergo elastic deformation, and taking into account that it is the equal strain condition:

$$\sigma_c = E_c \varepsilon \quad \sigma_m = E_m \varepsilon \quad \sigma_f = E_f \varepsilon\tag{2.18}$$

Substitution in the composite stress equation gives:

$$E_c = V_m E_m + V_f E_f\tag{2.19}$$

Equations 2.15 and 2.19 are the volume-fraction rules that are the lower limit and upper limit respectively of the modulus of any two-phase material. The same formulation also applies to the composite strength. The volume fraction rules are illustrated in Fig. 2.2. As mentioned before, the filler component is the one being the strong phase. Thus, the highest modulus is attained when the only constituent is the filler.

Fig. 2.2: Equal strain and equal stress conditions for two phase composite materials [27].

This development successfully describes the mechanical behavior of composite materials containing continuous fibers. However, as it is the case for this study, composite materials do not only exist in such a configuration. Thus, an introduction to the mechanical effects of discontinuous fibers in a composite material also has to be evoked. For simplicity, the case of aligned discontinuous fibers is first introduced and then uniformly dispersed discontinuous fibers are treated.

It is important to understand that in the case of discontinuous fibers, the force exerted on the composite material is not exerted directly on the fillers. Instead, the load is transferred from the composite matrix to the fillers by means of shear stresses along the fiber-matrix interface.

Fig. 2.3: Variation of shear stress along a fiber inside an expanding matrix.

When a material experiences a deformation under the action of a force, if there are no additional constraints, the change in dimensions will be the same for every unit square of that material. We can observe from Fig. 2.3 that, even though the expansion of each square of the matrix is the same, the relative displacement of the matrix with respect to the fiber increases along the $|x|$ direction.

Fig. 2.4: Equilibrium of forces between fiber and matrix [27].

Consequently, this means that the shear stress between the matrix and the filler is null at the centre of the fiber but maximum at its tips. This variation of shear stress has

evidently repercussions on the matrix to filler load transfer and, consequently, on the reinforcement effects of the fibers.

To build a relation between the deforming matrix and the fiber, a force balance at the filler-matrix interface is applied (Fig. 2.4) [27]:

Interfacial shear stress = fiber tensile stress

$$\tau_m(\pi d_f)dx = \left(\frac{\pi d_f^2}{4} \right) d\sigma_f \quad (2.20)$$

where σ_f is the local tensile stress carried by the fiber, τ_m the local shear stress, d_f the fiber diameter and x the distance from the fiber end. Thus, by rearranging this equation:

$$\frac{4\tau_m}{d_f} = \frac{d\sigma_f}{dx} \quad (2.21)$$

Assuming that the composite deforms elastically, the integration of this equation demonstrates that the shear stress is zero at the midpoint of the fiber and maximum at its tips (Fig 2.5 a). On the other hand, the tensile stress is maximum at the fiber midpoint and null at its tips (Fig 2.5 b) [27].

Fig. 2.5: (a) Variation of shear stress and (b) tensile stress along the fiber [27].

In fact, by executing an elastic analysis of the composite material under tensile stress, even for very small strains the magnitude of the shear stress occurring at the fiber tips interface is very big. Consequently, if the bonding between the matrix and the fiber is not strong, it readily delaminates. However, if the bonding is strong, the matrix undergoes local plastic shear. This phenomenon takes place even if the bulk matrix is still in its elastic regime with respect to the applied stress. By assuming that the matrix does not work harden, that is, it is perfectly plastic, then the shear stress at the fiber interface cannot not rise infinitely because the interfacial material cannot undergo any further shear deformation [27]. Thus, a preceding layer of the matrix which surrounds the interfacial layer starts to deform and so on and so forth. Under the action of the matrix strain, the shear stress along the fiber rises until it reaches the shear yield strength and, at this point, saturates (Fig 2.6 (a)). Assuming that the transition period occurs on a very short distance, the shear stress varies between two values along the fiber: the shear yield strength and zero. An interesting phenomenon to note at this point is that, if the fiber is longer than a minimum length, the maximum tensile stress

will be experienced at the fiber midpoint and in its neighboring areas (Fig 2.6 (b)). This maximum tensile stress corresponds to the one experienced during the equal strain condition. This implies that, even if the fibers are not continuous along the whole composite material length, as long as they exceed a minimum length, they will have the same reinforcing effect.

Fig. 2.6: Saturation of interface shear stress (a) and tensile stress (b) at the tips of the fiber [27].

To determine this critical length, l_c we state that, at $x = l_c/2$ the stress carried by the fiber is the one experienced during the equal strain condition, that is [27]:

$$\sigma_f(\epsilon_c) = E_f \epsilon_c \quad (2.22)$$

for an elastic fiber. In such a case:

$$2 \frac{\tau_{my} l_c}{d_f} = \sigma_f(\epsilon_c) = E_f \epsilon_c \quad (2.23)$$

By rearranging Equation 2.23:

$$\frac{l_c}{d_f} = \frac{\sigma_f(\epsilon_c)}{2\tau_{my}} \quad (2.24)$$

which is the minimum critical aspect ratio necessary for a fiber to have the same reinforcement ability as in the equal strain condition.

It should be noted that this equation is related to the elastic deformation of fibers which are tightly bonded to the matrix. In the case where such a bonding does not exist, as mentioned before, the fiber will be delaminated from the matrix. In such a case, the tensile stress is transferred to the fiber by frictional forces and the minimum critical aspect ratio is [27]:

$$\frac{l_c}{d_f} = \frac{\sigma_f(\epsilon_c)}{2\mu P} \quad (2.25)$$

where μ is the coefficient of friction and P is the internal pressure at the fiber-matrix interface. Values of μP are typically an order of magnitude less than $2 \tau_{my}$. Thus, the aspect ratio of the fibers should then be one order of magnitude bigger in the case where there is not a strong bonding between the fiber and the matrix. Thus, the reinforcement power of a fiber is much bigger in the non-delaminating case. Therefore, to obtain an optimal reinforcement the bonding between the matrix and the fiber must be good.

2.4.1.2 Fiber random orientation effects

The last aspect that has to be introduced is the description of the mechanical effects of non-aligned fibers in a composite matrix. If the angle θ between the direction of the load and the fiber varies, different effects result (Fig. 2.7).

Fig. 2.7: Fibers inside a matrix tilted at an angle θ [27].

The two extreme cases are when $\theta = 0^\circ$, in which case the maximum fiber strength is the one of the equal strain condition ($T.S._{Strain}$) and $\theta = 90^\circ$ where the maximum fiber strength is the one of the equal stress condition ($T.S._{Stress}$). For any angle in-between, the resulting effect will depend on the preponderance of the resolved force and on the angle on which it is acting. If the angle varies just a little bit around zero, then the cross sectional surface is $A_0/\cos\theta$ and the force is $F.\cos\theta$. Thus, the tensile strength of the composite is:

$$T.S._{Composite} = \frac{T.S._{Strain}}{\cos^2 \theta} \quad (2.26)$$

and the failure mechanism is that of the fiber longitudinal fracture. If the angle varies slightly around 90° , then the resolved force is $F \cdot \sin\theta$ and the area on which it is acting is $A_0/\sin\theta$. Thus, the tensile strength of the composite is:

$$T.S._{Composite} = \frac{T.S._{Strain}}{\sin^2 \theta} \quad (2.27)$$

and the failure mechanism is that of the transverse fracture of the matrix. In the region situated far from those two poles, the most dominant mode of failure is the matrix shear along the fiber. The shear force is $F \cdot \cos\theta$ and the area on which it acts is the matrix-fiber shear surface increased by a factor of $\sin\theta$. The resulting tensile strength of the composite is:

$$T.S._{Composite} = \frac{\tau_{my}}{\cos \theta \cdot \sin \theta} \quad (2.28)$$

Fig. 2.8 illustrates the different effects that take place in a composite material containing a fiber oriented at various angles. The solid line, corresponding to the minimum tensile strength for each angle, is the effective dominant failure mechanism that is most likely to happen at that angle.

Fig. 2.8: Variation of the composite tensile strength with respect to the fiber angle [27].

2.4.2 Thermal properties of a dual composite material

2.4.2.1 Key parameters in heat transfer

The study of the thermal properties of a material necessitates an understanding of a set of thermodynamics principles and how it relates to the material under examination. As far as heat energy transport in a dielectric material is concerned, the main factor that requires attention is the atomic vibrations and its interactions with neighboring atoms. The extent to which a singular atomic vibration can transfer its vibrational energy to a chain of successive atoms is called the mean free path and this principle was developed by Debye [28]. Further to that, Peierls developed the quantum theory of elastic waves by assimilating each vibrational mode as a quasi-particle, the phonon [29]. Still at the same atomic scale, the specific heat capacity of a material is defined as the sum of degrees of liberty of the atoms for all its vibrational modes. The set of vibrational modes present in a material is obviously temperature dependant because it

illustrates all the different ways in which atoms will move for a given amount of energy. The more energy is given to the material, the greater and the more intense will the vibrational modes be. Consequently, the specific heat capacity is also temperature dependant and it will increase with temperature. The mean free path of a phonon depends on its scattering with boundaries or defects and on its collision with other phonons. It is also temperature dependant but this time its tendency is to decrease with rising temperature because the vibrational modes become more populated and phonon-phonon couplings take place more often and thus limit the phonon ballistic trajectories. Based on these principles the thermal conductivity, k of a material can be defined as [30]:

$$k = \frac{1}{3} C_v \cdot v \cdot l \quad (2.29)$$

where C_v is the heat capacity per unit volume at constant volume, v is the speed of sound in the material and l is the mean free path of phonons in the latter.

From a macroscopic point of view, a system at equilibrium can be thermodynamically described using state functions (*see Annex A for details*). One such function is the internal energy, U which is defined as the sum of the kinetic energies of all the particles within the system. By expressing the internal energy of a system at equilibrium as a function of the temperature, T , the volume of the system, V and the number of particles contained inside the system, N , one can express the differential form of U as [31]:

$$dU = \left(\frac{\partial U}{\partial T} \right)_{V,N} dT + \left(\frac{\partial U}{\partial V} \right)_{T,N} dV + \left(\frac{\partial U}{\partial N} \right)_{T,V} dN \quad (2.30)$$

The heat capacity of the system at constant volume, C_v is defined by the first partial differential equation of Equation 2.30:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \left(\frac{\delta Q}{dT} \right)_{V,N} \quad (2.31)$$

where δQ is defined as a small change in heat energy of the system. However, it is sometimes inconvenient to measure heat capacity at constant volume for liquids and solids because the external pressure, p that must be applied to maintain the volume of the system constant may be quite high. Thus, a more accessible measurable quantity from a macroscopic point of view is the heat capacity at constant pressure, C_p which is defined by [31]:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{p,N} = \left(\frac{\delta Q}{dT} \right)_{p,N} \quad (2.32)$$

where H is the enthalpy of the system and is defined as $H = U + pV$. At this point it is essential to connect C_p and C_v to ensure that the system can further be described both macroscopically and at the molecular level. This is ensured by the Clapeyron relation [32]:

$$C_p - C_v = \frac{\alpha^2 TV}{\beta_T} \quad (2.33)$$

where α is the coefficient of thermal expansion and β_T is the isothermal compressibility of the material [32]:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (2.34)$$

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (2.35)$$

The thermal conductivity of a material is expressed macroscopically by [32]:

$$k = \rho c_p \mathbf{D} \quad (2.36)$$

where ρ is the density of the material, c_p is the specific heat capacity ($c_p = C_p/m$ where m is the mass) and $\mathbf{D}$, the thermal diffusivity which is another macroscopic quantity

used to describe the thermodynamic state of materials [33]. By comparing Equations (2.29) and (2.36) we observe that D is a dynamic quantity which expresses the speed at which thermal energy is transported in the material whereas the specific heat capacity is a static quantity which expresses the ability of a material to store thermal energy. Thermal diffusivity can be measured efficiently at different temperatures using the laser flash method [34, 35] and the heat capacity by a modulated differential scanning calorimeter [36]. If α and β are also known, a complete set of parameters are thus present to analyze in detail the responses of the material to a thermal exposure.

2.4.2.2 Thermal transport in hybrid crystalline / amorphous composites

The study of the transport mechanisms involved in particulate materials consisting of a matrix which is more frequently amorphous and fillers which are dispersed homogeneously across the matrix had already started to raise the interest of Lord Rayleigh [37] and Maxwell [38] at the end of the 19th century. Since then, a wide variety of different approaches have been explored to analyze both theoretically and experimentally these phenomena. A very consistent method to model the transport in such composite materials has been developed by Bruggeman [39] and treated quantitatively by Landauer [40]. The method, called the effective-medium approach, has been generalized by Stroud for fillers of arbitrary shapes, sizes and orientations [41]. Further to that, a few theoretical studies have been developed to analyze the effective thermal transport in various composite materials [42-46]. One study which attracts particular attention is the one of Benvensite and Miloh [47-49] where they take into account the thermal resistance which is responsible for a temperature discontinuity at the interface between the matrix and filler contact surface, in order to develop a theoretical model of the heat diffusion in a composite. This thermal

boundary resistance, also called the Kapitza resistance [50-52], is described in details by Swartz and Pohl [53]. In the model of Benvensite and Miloh, the Kapitza resistance is introduced by defining the interfacial matrix/filler boundary condition by [47]:

$$k_{matrix} \frac{\partial \phi^{matrix}}{\partial n} = k_{filler} \frac{\partial \phi^{filler}}{\partial n} = \beta (\phi^{matrix} - \phi^{filler}) \quad (2.37)$$

where k_{matrix} and k_{filler} are the thermal conductivities of the matrix and fillers respectively, ϕ represents the temperature field, n is the normal unit vector from the filler to the matrix and β is introduced as the skin constant. Consequently, the composite interfacial adiabatic situation occurs when $\beta \rightarrow 0$ and its isothermal situation occurs when $\beta \rightarrow \infty$. Conversely, any positive finite real value of β ($\beta \in \mathcal{R}^+$) describes the situation where there is a contact resistance between the matrix and fillers. Based on their simulation results they concluded that due to the Kapitza resistance, there is a non-negligible dependence between the size of the fillers and the effective thermal conductivity.

2.4.2.2 Filler size dependence

As the heat transfer efficiency is related to the contact surface area, it follows that the bigger a particle, the lower will be the contact resistance and thus, the more effective will be the contribution of that individual particle to the overall heat transfer. This implies that the use of very small size fillers is restricted by the contact surface area between each particle and its surrounding. Thus, nano-particles such as CNTs to be used as heat dissipation enhancement fillers are suitable only if the thermal interfacial resistance is reasonably low. On the other hand, it should also be pointed out that the trade off in using nano-fillers is that the sum of surface areas of all particles is much bigger than that of bigger size particles for an equivalent total mass. That is, for the

same material and an equal weight percentage addition, nano-size fillers have a bigger total surface area than, for example, micro-size fillers. Therefore, there is balance between the efficiency of an individual particle and the efficiency of the sum of all particles when size, quantity and surface area are concerned. Thus, a compromise has to be found between these parameters so that an appropriate configuration leads to an optimal repercussion on the heat dissipation.

2.4.2.3 Kapitza resistance between fillers and matrix

If the surface property of nano-particles is properly modified so that the contact resistance is reasonably reduced, the resulting contribution of such particles is expected to be drastically enhanced. So, besides the geometrical factors, the essential feature that has to be taken into account is the surface compatibility of the nano-particles so that the interfacial thermal conductance is optimal. A simulation based on the effective medium approach has been applied by Nan et al. to model the effective thermal conductivity of composite materials [54]. An important observation that has been drawn from their simulation results is that, depending on the importance of the interface resistance, the effective thermal conductivity of the composite may not necessary be within the bounds set by the individual thermal conductivities of the fillers and matrix. That is, high conductivity fillers can have a negative impact on the thermal transport leading to an effective thermal conductivity which is lower than that of the matrix if the contact resistance is high. In such a case the composite behaves like a material bearing voids. This model of Nan et al. indeed demonstrates that a key parameter in the improvement of the heat transport of a material by using fillers lies in the reduction of the interfacial contact resistance between the fillers and the matrix.

2.4.2.4 Mode of transport between matrix and fillers

An additional aspect of thermal transport in composite materials that must be gone through is the compatibility in thermal transport mechanism between the matrix and fillers. In the case where there is no percolation network of the fillers within the matrix, heat necessarily needs to be repetitively transferred from one material to another. In the case of dielectric materials where electron flow does not occur, the only mode of transport is through molecular vibration and electromagnetic radiation. Thus, heat diffusion within the matrix material plays a crucial role because it will govern the transport mechanism of the composite. Various studies have been devoted to the understanding of the thermal transport in amorphous materials. The first papers published were related to the temperature dependence of the thermal conductivity of inorganic materials such as glass which follow the inverse trend of crystalline materials [55-57]. It is reported that the reason why the thermal conductivity of crystalline materials decreases with rising temperature is because of the increase in phonon coupling which affects the mean free path of phonons. On the other hand, the short phonon mean free path of amorphous materials is not affected by phonon coupling and thus remains almost constant with rising temperature. However, amorphous materials do experience an increase in thermal conductivity with rising temperature but this is because of the contribution of another parameter in the thermal conductivity, namely the heat capacity alteration which increases with rising temperature and thus results in an improved thermal conductivity. Some work has also been reported on the heat transport in amorphous polymers [58-60]. It is pointed out that the phonon mean free path in amorphous materials is mainly governed by structural scattering which is a temperature independent factor. This explains why the mean free path is almost constant for every amorphous material [58]. Moreover, an

experiment in which the degree of crystallinity of a polymer is changed demonstrates the transition in mechanism between phonon coupling and phonon scattering and its effect on the mean free path and the thermal conductivity [60].

Based on this study, all the statements that have been mentioned about the dependence of the composite properties on interfacial effects justify the importance of devoting in-depth research work on the characterization of new materials when they are expected to be used as fillers in composites. Consequently, the core of this thesis is devoted to the study of the macroscopic impacts that CNTs have on a dual composite material with respect to interfacial modifications between the fillers and the matrix.

2.5 Materials selection for the present study

2.5.1 Composite matrix

The material matrix which is selected in this thesis is the epoxy and it belongs to the PMC category. The reason why this polymer is chosen is that epoxy resins occupy the most important place in the polymeric IC packaging industry. Besides its wide application in the IC packaging industry, it is also used as a structural material (aerospace, automotive...) or surface material to protect surfaces or repair damaged surfaces. The main characteristics of epoxies are:

- Solvent resistant (anticorrosion)
- Good rigidity and light weight
- Surface adhesion
- Water resistant.

Epoxy is a thermoset type of polymer which is usually made up of two parts: the resin and the curing agent. More specifically, the epoxy resins that are used for this research work are a Di-Glycidyl Ether of Bisphenol A (DGEBA) types of epoxy. They are the most widespread type of epoxy around the globe counting for 95 % of the world epoxy production [61]. The two sets epoxy resins and curing agents used in this thesis are EPON 828 and EPIKURE 3202 manufactured by Hexion Chemicals Inc. and EPICOTE 1006A Part A & B manufactured by Wee Tee Tong Chemicals Pte Ltd. During the curing phase, the polymerization process that takes place is called poly-addition and it occurs without any by-products. It consists of the oxirane ring opening of the resin and recombination with the amine groups. This reaction is exothermic and the total heat evolved during the complete polymerization process is constant and time independent. If the curing schedule is too rapid and the curing temperature high, due to the bad thermal conductivity of epoxies, heat is trapped inside the material and it gives rise to internal stresses. Thus, it is paramount to determine the proper curing protocol of the material [62].

The epoxy composites used in the IC packaging industry exist in a wide variety of grades where varying amounts of different additives are present in the matrix to suit specific purposes and meet diverse specifications. However, in this study, in order to assess properly the direct impact of adding CNTs to an epoxy, no other additives are used. The study consists essentially of adding treated CNTs to a pure epoxy resin.

2.5.2 Composite fillers

CNTs are undoubtedly among the most attracting candidates to bring a technological revolution in the area of materials science. Since the 70s, micrographs of CNTs are

seen in the thesis of Morinobu Endo from the laboratory Marcel Mathieu in Pau (France), under the supervision of Oberlin and published in an article in 1976 [63]. At that time they were referred to as hollow cores because they constitute the internal central core over which carbon layers are deposited to form vapor-grown carbon fibers. CNTs were not devoted much attention then, until Iijima made the detailed analysis of its structure in 1991 [64]. Consequently, that study has initiated intensive research on CNTs. As a result, the experiments that are carried out, unveil the outstanding properties of CNTs, putting them in the top list of almost every physical and mechanical properties such as thermal conductivity and elastic modulus for example. Before getting into details about CNTs, it is worth mentioning a few facts about graphite, which can be regarded as the basic constituent of the CNTs.

2.5.2.1 Structure of graphite

Graphite is a natural form of carbon. It is a black mineral which is opaque and has a density of 2.23 g/cm^3 . Graphite is a good electrical conductor and is classified as being a semi-metal, which means that it owns metallic properties but with a small amount of free electrical charges. This is due to the fact that the conductive band and the valence band have a very small overlapping. Moreover, graphite is also a good thermal conductor and its melting point is very high ($\sim 3500^\circ\text{C}$).

Fig. 2.9: The molecular structure of graphene.

Graphite is made up of flat mono-layers of graphene which has honeycomb hexagonal crystal structure (Fig. 2.9).

Fig. 2.10: The lattice structure of graphene in the k-space.

The unit cell of the crystal structure of graphene also referred to as the Wigner-Seitz zone in real space and the Brillouin zone in reciprocal space (k space) is made up of two carbon atoms are shown in Fig. 2.9 and 2.10 respectively. The distance between the two carbon atoms, d_{C-C} is of $1.42 \text{ \AA}$ and the distance between each unit cell, referred as the lattice constant, is $a = 2.46 \text{ \AA}$ in real space and is $4\pi / \sqrt{3}a$ in the

reciprocal space. The primitive and reciprocal primitive vectors are labeled respectively as (a_1, a_2) and (b_1, b_2) .

2.5.2.2 Structure of a carbon nanotube

In 1991, the CNT is identified as a tubular structure of carbon. A CNT consists of a graphene sheet that is rolled up and closed on itself. This leads to a hollow tube containing walls of hexagonally arranged carbon atoms. The sp^2 chemical bond imposes a locally flat hexagonal structure which is rolled over to form a tube (Fig. 2.11).

Fig. 2.11: Description of the crystal structure of the CNT as a wrapped graphene sheet.

A configuration containing only one wrapped graphene sheet is referred to as a single-walled nanotube (SWNT). However, a CNT may contain many tubes intertwined in one another and is then referred to as a multi-walled nanotube (MWNT). The interaction between the different walls or even two distinct CNTs is related to the interaction between the unhybridized p_z orbitals which form π bonds between neighboring carbon atoms. The diameter of the tube is in the order of the nanometer where as its length is in the order of the micrometer. Thus, the aspect ratio of CNTs are very high ($10^3 \rightarrow 10^6$).

Fig. 2.12: Variation of the density of CNTs.

The density of CNTs is represented in Fig. 2.12 and, as it can be seen, it depends on its diameter. There are three main different methods to synthesize CNTs. However, we can observe some common factors that are necessary to make this crystal growth feasible:

- A carbon source (Solid, liquid or gas)
- A heat source (~ 700°C)
- An inert atmosphere
- A catalyst

The high temperature is necessary to initiate the pyrolysis of the carbon source and the catalyst allows its recombination in nanotubes. The three methods which are the most widely used to grow CNT crystals are:

- The electric arc method [64]
- The laser ablation [65,66]
- Chemical vapor deposition [67,68]

2.6 Chemical properties of CNTs

As mentioned, the hybridization state of the carbon atoms is a quasi sp^2 configuration with the only difference that, because of the curvature of the nanotube, the hybridized orbitals are slightly slanted down towards the interior of the cylinder (Fig. 2.13). The consequence of this is that the unhybridized p orbital is deformed, resulting in an asymmetrical distribution of the electron density. The smaller the nanotube, the bigger

Fig. 2.13: Quasi sp^2 hybridization state of the carbon atoms in CNTs.

will be the corresponding deformation [69]. This characteristic has an effect on the chemical property of carbon nanotubes. Indeed, the smaller the CNT, the more reactive it will be. For example, SWNTs, which are usually smaller than MWNTs, are thus more chemically active. Nevertheless, the reactivity of any form of CNTs is so low that it is still considered as being an inert material. The positive effect of this chemical inertia is that it does not degrade with time. Thus, the length and lattice structure of CNTs are not affected so easily by low and medially reactive chemicals.

The chemical inertia of CNTs also has drawbacks. If, for example, a CNT is embedded in a material, the forces of attraction between the nanotube and the material will only be of van der Waals nature. There are no spontaneous reactions occurring that can bond the CNT to the surrounding material. Consequently, this will have a

negative effect on the mechanical properties of the material because of a poor load transfer.

Finally, the chemical properties of CNTs also limit its dispersion in solvents and in polymeric materials. CNTs tend to be entangled and to form bundles because of their high aspect ratio and their flat, graphene like walls. Thus, it is not easy to disperse the CNTs in a matrix to obtain a homogenous distribution of individual nanotubes. Commonly, the methods employed for composite fabrication only lead to the dispersion of bundles of CNTs. Consequently, besides the fact that this issue affects the materials uniformity, it also brings very fair enhancements in the material.

2.7 Mechanical properties of CNTs

2.7.1 Mechanical properties of individual CNTs

The mechanical properties of CNTs are subject of intense research. This research is justified by the foreboding based on the properties of diamond and carbon fibers which are already known for their exceptional mechanical properties and which are already widely used in that sense. During the last two decades more accurate measurements of the Young's Modulus of CNTs have been obtained (Fig 2.13). Consequently, it has been demonstrated by both experimental measurement and simulation that CNTs have the largest Young's Modulus as compared to any other material. Table 2.2 summarizes the main experiments which have been carried out to mechanically characterize individual CNTs.

Fig. 2.14: Graph of the Young's modulus of a single CNT as experimented by different research groups.

Table 2.2: Literature review of the experimental measurements of the Young's Modulus of CNTs.

Author (year)	Mechanical test	Type of CNTs	Young's Modulus (TPa)
Treacy et al. (1996) [70]	Tip thermal vibrational amplitude in TEM	Electric arc MWNTs Ø (5.6, 24.8) nm	0.4 – 4.15
Wong et al. (1997) [71]	AFM 2 points bending	Electric arc MWNTs Ø (26, 76) nm	1.28 ± 0.59
Krishnan et al. (1998) [72]	Tip thermal vibrational amplitude in TEM	Laser ablation SWNTs Ø (1.0, 1.5) nm	1.25 ± 0.45
Poncharal et al. (1999) [73]	Resonant frequency by electrostatic deflection in SEM	Electric arc MWNTs Ø (8, 40) nm	1 – 0.1
Salvetat et al. (1999) [74]	AFM 3 points bending	Electric arc MWNTs Ø (9.6, 20) nm	0.81 ± 0.41
Yu et al. (2000) [75]	Uniaxial traction by AFM in SEM	Electric arc MWNTs Ø (13, 36) nm	0.013 – 0.052
Demczyk et al. (2002) [76]	Uniaxial traction and bending by micro-machine in SEM	Electric arc MWNTs Ø (8, 12.5) nm	0.91 ± 0.18
Qi et al. (2003) [77]	Nano-indentation bending of MWNT mat	CVD MWNTs Ø (55, 104) nm	0.91 – 1.24

Based on the experimental and theoretical researches that had been done before 2003, it was commonly thought by the scientific community that CNTs only had a linear elastic regime, the limit of which would be fracture. However, in 2003, Bozovic et al demonstrate the plastic properties of SWNTs [78]. They even measure experimentally a deformation of up to 30 % on a SWNT under tensile stress.

Fig. 2.15: Summary of mechanical properties of individual CNTs based on literature review.

Fig. 2.15 shows a summary of the mechanical properties of CNTs that are determined experimentally and reported in the literature. Even though the interval for each property is wide, the range within it lays still makes this material to be of great interest as to what concerns its mechanical properties.

2.7.2 Mechanical properties of CNT composites

The development of epoxy composites containing carbon nanotubes as reinforcement fillers attracts a lot of attention in the scientific community. For example, Ci et al. report on the dependence between the epoxy matrix stiffness and the reinforcement role of CNTs [79] and conclude that homogeneously dispersed CNTs have a poor interface interaction in stiff matrices. Zhang et al. perform a thorough study on the CNT fillers size effects on the fatigue and creep behavior of epoxy composites [80-82]. They conclude that the best reinforcement effects are obtained with long, thin and well dispersed CNTs. Thostenson and Chou also study the degree of CNT dispersion resulting from the shear mixing induced by a calendaring approach and they demonstrate that they are able to obtain a homogeneous composite with an appreciable improvement in the fracture toughness and thermal conductivity with up to 5 % of CNTs fillers addition [83]. From these studies the main remark is that uniform dispersion of individual CNTs is a dominating factor in the fabrication of CNT based composites.

Various other interesting research works are carried out to develop epoxy composites using CNTs as mechanical reinforcement fillers [84-90]. The trend of all those studies is to use a physical method to debundle and untangle the CNTs while keeping the outer surface of the nanotubes intact. Sometimes an intermediate step is used and it consists of dispersing the CNTs in a solvent, adding the epoxy resin to it and finally evaporating the solvent. The general tendency is to use only a few wt % of CNTs based on the very high aspect ratio of the filler, its low percolation threshold and poor solubility. The limitations of these dispersion strategies used to insert CNTs in an epoxy matrix are, first, that there is no parameter to control the load transfer between

the matrix and the fillers and, second, such methods sometimes turn out to be incompatible with the already existing, well established industrial process flow. The ability to control the interface parameters between fillers and matrices is critical in the behavioral predictability of the resulting composite materials.

2.7.2.1 Static analysis: Surface energy

In the research context of this thesis, it is necessary to present a description of a CNT within a polymer matrix by taking into account the intrinsic properties of an individual nanotube within the material at different scales. To start with, it is important to understand the energy distribution at the surface of an individual nanotube and its dependence on various tube parameters such as the diameter and chirality. The surface energy of CNTs is the dominant attractive force that bonds it to a polymer matrix. Thus, in order to have a proper stress transfer from a mechanically weak polymer matrix to a network of strong nano-fillers, it is of major importance that the fillers have a high surface energy. The impact of weak interface interactions with traditional fibers such as glass fiber and carbon fiber is that the resulting composite will have low strength and stiffness, but high resistance to fracture. On the other hand, if the interaction is strong the composite will have high strength and stiffness, but it will be brittle [91]. However, it is not the case for CNTs because of its intrinsic tensile strength which makes it almost unbreakable. Thus, if the CNT to matrix interface is strong, the resulting composite should be strong, stiff and fracture resistant.

Dujardin et al. measure the critical surface tension of CNTs and estimate that for MWNTs, the upper limit is roughly within 100 to 200 mJ/m² [92], and it is within 40 to 80 mJ/m² for SWNTs [93]. However, they are not able to determine any diameter

dependence on the wettability of CNTs. Nuriel et al. demonstrate experimentally that the surface energies of carbon fibers ($\varnothing = 6.4 \mu\text{m}$), carbon nano-fibers ($\varnothing = 150 \text{ nm}$) and MWNTs ($\varnothing = 30 \text{ nm}$) are almost the same of around 45 mJ/m^2 [91]. By attaching an individual MWNT to the tip of an AFM, Barber et al. [94] are able to setup at a nanoscale an experiment to measure the wetting parameters necessary to determine the surface tension of the CNT using Owens and Wendt principles [95] and they report that the curved crystal structure of CNT modifies its wetting characteristics as compared to graphene. The liquids tested for wetting with the CNT are polydimethylsiloxane (PDMS), polyethylene-glycol, glycerol and water and it is observed that PDMS is the most wetting liquid based on a contact angle measurement of almost 0° . The discrepancy in surface energy reported in the literature brings to evidence that this parameter has to be controlled in order to obtain repeatability of results.

Neimark develops a theoretical model to show the dependence between the wetting properties of fibers and its curvature [96]. His model demonstrates that fibers having a diameter of less than 4.1 nm should have a contact angle $> 90^\circ$ meaning that they are non-wetting. Similarly, Werder et al. develop a theoretical molecular dynamics model which highlights that pristine SWNTs are non-wetting to water and they suggest that the wetting properties measured experimentally may be due to defects in the CNTs or impurities in the liquid [97]. Thus, based on these models, it appears that the surface energy should not only be controlled but also improved.

2.7.2.2 Dynamic analysis: Interfacial stress transfer

Using the notions described above, a basic theoretical evaluation can be done. The estimations are obtained from the Kelly-Tyson model which is based on the reasoning

that for the reinforcement to occur, the load applied on the matrix must be transferred to the fiber by means of shear forces [98, 99]. As illustrated in Fig. 2.6, along a fiber, the maximum shear forces are at the tips and are reduced to zero at the middle. Conversely, the tensile force distribution along the fiber is a maximum at the middle and zero at the tips. Assuming that no delamination occurs, by applying a force balance between the matrix shear force and the fiber tensile force for a hollow cylinder [27]:

$$\tau_m(x)(\pi d_f)dx = \left(\frac{\pi d_f^2}{4} - \frac{\pi(d_f - 2t_f)^2}{4} \right) d\sigma_f(x) \quad (2.38)$$

where $\tau_m(x)$ is the position specific matrix interfacial shear stress, $\sigma_f(x)$ is the position specific filler tensile stress, d_f is the diameter of the cylinder and t_f is the thickness of the tubular wall. This relation between shear force and tensile force is simplified to:

$$dx = \frac{t_f}{\tau_m(x)} \left(1 - \frac{t_f}{d_f} \right) d\sigma_f(x) \quad (2.39)$$

To exploit the full strength of a fiber, a force transfer corresponding to the maximum amount of tension that it can sustain must be applied to it. Thus, the position along that fiber where it experiences the biggest load must undergo the maximum tensile force that is, the tensile strength $(T.S.)_f$. Consequently, the optimal situation for this to occur should be when the greatest shear load transfer is applied, that is the shear yield strength, τ_{my} . If on top of that the size of the fiber is restrained to its minimum length, by integrating the differential equation (Equation 2.39) between $l_c/2$ and 0 for x , that is the middle of the fiber to its tip for a fiber which is at the critical length and between $(T.S.)_f$ and 0 for $\sigma_f(x)$, that is the tensile force from the tensile strength to 0, we obtain

the expression for l_c in its optimal reinforcement configuration corresponding to $(T.S.)_f$ at the middle of the nanotube and to τ_{my} at the tips:

$$l_c = \frac{2t_f}{\tau_{my}} \left(1 - \frac{t_f}{d_f} \right) (T.S.)_f \quad (2.40)$$

Here the variations in tensile stress and shear stress along the CNT are assumed to be linear. This assumption has negligible impact on the estimations because both the shear stress and the tensile stress are of the second order and proportional to each other [100]. Thus, in a force balance, the integration of the individual components along the fiber length leads to coefficients that almost cancel out each other.

Fig. 2.16: Evaluation of the tensile strength expected from hollow cylindrical fillers having a diameter of about 50 nm.

First, by varying the interfacial shear stress over a diameter distribution of (50 ± 20) nm, the target is to evaluate the corresponding tensile strength that should be guaranteed by an individual CNT (Fig. 2.16). The shaded area represents the window of tensile strengths for individual CNTs which have been published so far. This graph

is evaluated for CNTs having a constant l_c of 10 μm and a wall thickness of 0.34 nm [101]. However, it is also interesting to estimate how l_c varies with respect to the shear yield strength. Fig. 2.17 shows this variation for different fibers. For comparison, the graph also includes the l_c of a carbon fiber (CF). For the CNTs the $(T.S.)_f$ is set at 60 GPa [77] and for the CF 6 GPa. The graph shows that the magnitude of the mechanical reinforcement of a CNT strongly depends on the ability of the interface to transfer load from the matrix by shear stress. Indeed, the degree of the shear yield strength corresponds to the extent of the interfacial adhesion and it can be noted that its magnitude has a big impact on the minimum length necessary to take a given load (tensile strength of an individual CNT). If delamination occurs the interface stress transfer takes place by frictional force between the filler and the matrix. It is reported that the critical length in such a case is roughly 1 order of magnitude higher [27].

Consequently, it appears that in order to unveil the true potential of CNTs to be used as reinforcement fillers in epoxies, the adhesion between the nanotube and the polymer under an external force has to be determined. However, making such experimental measurements is not trivial for CNTs. Various studies tentatively devoted to the measurement of the interfacial strength between fibers and epoxies can be found in the literature [102-106]. Even though they are devoted to micro-sized fibers, they still provide very interesting information on the purely classical mechanical effects in fiber reinforcement phenomena.

Fig. 2.17: Dependence between the interfacial shear yield strength of the nanotube and the critical length for different nanotube diameters.

On a nanoscale basis however, the current volume of information available is not enough to draw a clear picture of the actual reinforcement effects occurring in nanocomposites. Different studies tend to contradict each other and the justifications made are not indisputable [107]. For example, experimental studies such as the one of Wong et al. tend to reveal that the adhesion is very high [108]. For demonstration, they fabricate two set of composites, one with CNTs and polystyrene (PS) and the other one with CNTs and epoxy. Simultaneously, they also do a simulation study which estimates that the shear stress at the CNT to epoxy interface is 138 MPa at 0 K. However, the experimental characterization does not reflect their theoretical expectations and this is justified by a bad dispersion of the fillers in the matrix.

Pulickel et al. published a thorough study on the failure analysis of CNT epoxy composites and CNT amorphous carbon composites using Raman spectroscopy and

conclude that the adhesion in-between nanotubes in a bundle is very weak and the adhesion between a nanotube and the polymer is not optimal if no treatment of the CNTs is done [109]. They suggest that strategies which create a bond between the fillers and the matrix should be considered to ensure an optimal load transfer. Cooper et al. develop an experimental technique to investigate the adhesion between CNTs and epoxies [110]. The study is devoted to individual MWNTs and SWNT ropes and it consists of a pull out technique of the CNTs using a modified scanning probe microscope that can record the variation in force exerted to expel the nanotubes from the matrix. Based on this experiment they are able to evaluate the CNT epoxy shear strength for different nanotube embedded lengths, and they find that the general trend of the results is that shear strength is inversely proportional to the embedded length. Kis et al. carry out an experiment to demonstrate that the adhesion between interpenetrated nanotubes of the same MWNT is very weak [111]. They report that the frictional forces between the tubes are near to zero. These experimental results tend to suggest that MWNTs may not be optimal as reinforcement fillers because all the stress transferred to the outermost nanotube only. Moreover, it also suggests that if the CNT concentration is too high, sliding within fillers will occur in the matrix. Thus, a reasonably low amount of CNT fillers should be used.

By using a modified approach of the Kelly-Tyson model [27], Wagner shows that SWNTs have good interfacial shear strength in polymers [112]. He also mentions that the shear strength is strongly dependant on the defect sites found on the walls of the nanotube. Moreover, he demonstrates that the shear strength depends greatly on the CNT diameter. In a theoretical study based on the Cox model [113], Xiao et al. address the distribution of the stress along a CNT under external loading [101], and

they demonstrate that for a minimum length of about 500 nm CNTs ($\phi = 2$ nm), a tensile stress distribution going from zero at the tips to a maximum at the middle. They also study the CNT diameter dependence on the stress transfer magnitude and determine that it is inversely proportional to the CNT diameter. Thus, these models show that the CNT diameters should be relatively big which corresponds to CNT diameters usually met with MWNTs. Therefore, based on literature review, the best compromise tends to be towards using MWNTs, even if the internal nanotubes are rather useless.

2.7.2.3 Ageing effects: Fracture & Debonding

Besides analyzing the predominant impact of CNT epoxy adhesion on load transfer and methods of optimizing this relationship, some emphasis should also be placed on the failure modes of the reinforcement fillers and on methods of reducing or preventing such occurrences. Resulting from the wide spread use of fibers in composite materials, several experimental studies are carried out aiming at understanding the failure modes of individual fibers in a composite matrix [114-116]. Using individual glass fibers and carbon fibers in an epoxy matrix, Kim et al. [117, 118] carry out an experimental study to understand the propagation mode of interface debonding and its impact on the fiber fracture. They notice from their analysis that, after fracture, the recoil of the fibers can take a few minutes to stabilize, pointing out the slow fiber response to varying loadings. Moreover, they also observe that the subsequent debondings occurring along a fractured fiber require more load to occur, which corresponds to the statement of Cooper et al. [110] about shear strength and embedded length. This phenomenon is explained in details by Pitkethly and Doble [119] as being related to tip length of a fiber over which most of the shear load is

transferred from the matrix. This length, called the ineffective length, is a region at the tips of the fiber where the tensile load is insignificant and the shear load is a maximum. The rest of the fiber length, however, takes most of the tensile load with almost no shear load. Thus, if during a fiber pull out the embedded fiber length is less or equal to the ineffective length, the shear load measured will be important.

In order to propose a tangible explanation for the experimental evidences, various theoretical models are developed to try to determine the stress transfer mechanism from the composite matrix to the fillers [120-124]. In a model that describes the shear distribution along fillers before and after failure, Tripathi et al. address the evolution in material properties under destructive external loading [125]. The particularity of the model is that it takes into account the matrix plasticity, debonding and frictional effects during the filler fracture. The model uses a modified variational method [126] to describe the debonding and fracture effects between a glass-fiber filler and an epoxy matrix. By considering the effects of having an imperfect interface, the predictions of the model are that the maximum shear stress is dislocated to an intermediate position which creates a variation in the distribution of the tensile stress. Furthermore, failure at the tip caused by either interface debonding or transverse matrix cracking creates a sharp reduction in stress transfer related to the diminished efficiency of frictional forces in transferring load. Thus, the overall tensile stress borne by the fiber is lessened implicating that its reinforcing effect is reduced and consequently, its fracture is less likely to occur.

In another study which also takes into account the propagation of the interfacial damages, Paipetis et al. [127] report the stress transfer variations of fibers during

fragmentation while considering simultaneously damaged and imperfect interfaces. Together with this analytical model, they also provide experimental data on individual fiber fractures obtained by Remote Laser Raman Microscopy which validates the theoretical model according to a good mapping between each other. The model introduces a new parameter, called the interface parameter, which successfully accounts for the different criteria and factors involved in interfacial stress transfer. Their study provides a better understanding of the propagation of the damage zone during recurring strain and the resulting failure mode. Moreover, they also point out the significant impact that the adhesion strength has on the debonding and fracture of the fillers.

2.7.2.4 Surface treatment of CNTs

In-depth studies related to the mechanical behavior of individual nano-fibers in composite materials exist in relatively small amount. Moreover, characterization techniques and experimental analysis together with relevant models that study the stress transfer, stress distribution, debonding propagation and fracture of individual nano-fibers inside composite matrices under external strain are scarce because they require complex setups. There are nevertheless a few conclusions that can be drawn based on the reported microscopic studies. The two key parameters affecting classical reinforcement efficiency and durability are the contact surface uniformity and the adhesion strength between the matrix and fillers. Thus, it can be assumed that the feasibility of using CNTs as fillers in epoxies rely at least on the ability of the epoxies to properly wrap the nanotube during polymerization and curing. After curing, epoxies are rigid and the molecules are arranged in a configuration where their potential energy is a minimum. This arrangement depends on the curing parameters

[128, 129] and does not necessarily correspond to a smooth curved wrapping of CNTs. Even if such irregular structures have negligible effects on contact area of micro-scale fillers, it may result in significant interfacial contact surface irregularities for nanotubes which are only a few tens of nanometers in diameter and a few microns in length. The consequence is that it may induce important interfacial voids that will affect the stress transfer to occur [130]. Moreover, during repeated extension and compression, the plastic deformation of the matrix may result in wavy or accordion structures, and this also affects the surface contact area and plays a determinant role in the progressive reduction of material strength. One essential point that should be considered about putting CNTs in polymers such as epoxies is that the filler is of the same dimensional order as the polymer strands. Thus, the effects related to this similarity in size should also be considered.

It is reported that a potential strategy to optimize interfacial stress transfer, make debonding more unlikely and fracture improbable, is to treat the CNTs so that the adhesion with the epoxy matrix is enhanced. One way to realize this approach is to covalently bond the nanotubes to the epoxy matrix. This approach is demonstrated for other polymer matrices such as poly (methyl methacrylate) (PMMA) [131]. Such a procedure is also introduced for epoxy matrices by Zhu et al [132] and Eitan et al. [133, 134]. However, besides the fact that these research groups demonstrate the merits of the strategy and report a more efficient CNT reinforcement, it can be noticed that the treatment strategy being used consists of bonding the CNT with the epoxy matrix during the primary dispersion stage even before the curing agent is added. Therefore, the industrial implementation and large scale compatibility with already existing processes of such techniques are rather unfeasible because materials suppliers

usually favor strategies where a bare monomer or pre-polymer is used as starting point and into which various additives are incorporated and homogenized by simple mixing in various proportions depending on the end application. If an intermediate step that alters any resin properties is introduced (Example: viscosity), it implies that the whole process flow has to be reviewed and adaptation to the new material properties have to be developed.

2.8 Thermal properties of CNTs

2.8.1 Thermal properties of individual CNTs

The information obtained from the theoretical investigations of heat transfer in CNTs shows great deviations. Using molecular dynamics (MD) simulation, Berber et al. [11] report a room temperature thermal conductivity of 6600 W/m K for (10, 10) SWNTs, while a much different value of 1600 W/m K is proposed by Osman et al. [12]. Applying the theory of force field, Che et al. [13] point out that the thermal conductivity of (10, 10) SWNTs is 2980 W/m K, differing much from the above results. Maruyama [14] performs non-equilibrium MD simulation and find that the thermal conductivity of SWNTs increases linearly with their length up to 0.5 mm. In his work, the thermal conductivity of a (10, 10) SWNT 200 nm long is calculated to be 375 W/m K at room temperature.

As for the experimental study, only a handful of experiments are conducted to measure the thermal conductivity of CNTs. Hone et al [15] measure the thermal conductivity of dense-packed SWNT ropes, and attain a value of 35 W/m K for an as-grown mat sample and only 2.3 W/m K for the sintered sample. It is worth noting that these experimental results differ significantly from the theoretical predictions (1600–

6600 W/m K). The thermal conductivity of parallel SWNTs is also measured [16] and a larger value of 218 W/m K is obtained, which is still much smaller than the theoretical predictions reviewed above. The thermal conductivity of C₆₀-filled SWNTs is measured to be 15 W/m K using the comparative method [16]. Recently, Shi et al.[17] measure the thermal and thermoelectric properties of one-dimensional nanostructures using a micro-fabricated device. They report thermal conductivities of 3 W/m K and 150 W/m K for SWCNT bundles of 148 and 10 nm diameters, respectively. For MWNTs, experiments conducted by Yi et al. [18], Xie et al. [19] and Lu et al. [20] lead to a thermal conductivity of only about 27 W/m K. Yang et al. [21] measure the thermal conductivity of aligned MWNT arrays to be 12–17 W/m K. They estimate the thermal conductivity of pure nanotubes to be 200 W/m K. However, Kim et al. [22] measure the thermal conductivity of an individual CNT to be over 3000 W/m K at room temperature. They also estimate the mean free path of phonons in the nanotube to be around 500 nm, comparable to the effective length of the tube (2.5 μ m) and conclude that the boundary scattering of phonons could substantially reduce the measured thermal conductivity.

There are some measurements done to investigate the chirality [135], length [136], diameter [137], temperature [138], impurity and functionalization dependence [139] on the thermal conductivity of CNTs. These studies point out that the thermal conductivity of SWNTs is chirality dependant because first, the portion of heat transported by free electron flow is affected in semi-conducting CNTs and secondly, due to the fact that the orientation of the crystal has an impact on the phonon modes, the thermal transport occurring by lattice vibration also varies from one chirality to another. The length of individual CNTs affects the thermal conductivity only due to

phonon scattering. Since the mean free path of the phonons is of the order of a few 100 nm meters, very long CNTs will have more phonon scattering as compared to short CNTs where the transport is almost ballistic. Thermal conductivity is reported to be the highest between 300 K and 400 K and then gradually falls on both sides of this interval. It is reported that covalent grafting of molecules behaves in the same way as lattice defects and thus reduce the thermal conductivity of the nanotube. However, it also improves the interfacial phonon transport between the CNTs and the matrix. Finally, it is also reported that the ratio of the thermal conductivity of CNTs are about 1:9 electron to phonon based [36]. This implies that if the outstanding thermal transport properties of CNTs are to be exploited, a method must be developed that will enable atomic vibrations to be transferred from the material matrix to the CNT and fro.

2.8.2 Thermal properties of CNT composites

Epoxy composites containing CNT fillers go through various kinds of thermal characterizations for diverse purposes. One of the first concerns is to determine the consequence of CNT incorporation on the curing parameters of the thermosetting composite. Puglia et al. [140, 141] do a thorough study of the cure kinetics of epoxy composites bearing various amounts of SWNTs and they report that it has a positive reducing impact on the heat of reaction, vitrification transition temperature [142] and curing time of the composite. This effect is attributed to the high conductivity of CNTs which spreads the heat energy more efficiently in the composite. The same kind of study is performed by Abdalla et al. but their focus is to determine how the surface treatment of CNTs affects the curing properties of the epoxy composite [143]. The study concludes that the functionalization of CNTs also alters the curing kinetics of

the composite in a way that is dependant on the functional molecule. Based on the same reasoning, calorimetric analysis is used by Kim et al. to investigate the CNT dispersion quality in a uniform network of individual nanotubes [144]. The study shows that there is indeed a correlation between the degree of dispersion and the heat of reaction.

Besides using thermal characterization as a tool to determine the change in curing properties of CNT/epoxy composites, Bryning et al. measure the thermal conductivity enhancement of SWNT fillers dispersed in an epoxy matrix processed according to two different methods [145]. The first method consists of using DMF which is a very good polar aprotic solvent for CNTs, and the other method consists of using aqueous suspensions of sodium dodecylbenzene sulfonate surfactant to disperse the CNTs before incorporation in the epoxy matrix. In both cases they observe enhancements in thermal conductivity but they report that the use of a surfactant induces a higher interface contact resistance than the use of a solvent. On the other hand, they mention that the use of a surfactant allows a greater amount of CNTs to be dispersed so that the overall enhancement finally turns out to be better. Biercuk et al. also report remarkable thermal conductivity enhancements in CNT loaded epoxies [146]. Their strategy also consists of dispersing the CNTs in DMF using ultrasonication followed by progressive addition of the epoxy resin. The issues however with the strategy are that the use of DMF, which is a very toxic mutagenic solvent, and the use of ultrasonication for 48 hours are two arguments that render the transfer of such technology to the industrial scale very unfeasible.

What can also be inferred from the studies present in the literature is that the uniform dispersion of the CNTs plays a major role in the thermal conductivity enhancement of

the composite. Moreover, a strategy to minimize the thermal contact resistance at the interface between the nanotube filler and the epoxy matrix is important to optimize heat transport. A model developed by Nan et al. aims at determining the effect of the Kapitza resistance on the overall thermal conductivity of the composite [147]. The model demonstrates that, even if CNTs have a very high thermal conductivity, the effective composite thermal conductivity remains primarily dictated by the Kapitza resistance. Yamamoto et al. [148, 149] develop a model to determine the nature of the thermal conductance along a nanotube. Based on their simulation results they conclude that the thermal transport across a CNT at room temperature occurs at 90% through phonons and that it is chirality independent. This result suggests that to enhance the effective thermal dissipation power of composites containing CNTs, the interfacial Kapitza resistance must be reduced by focusing on a strategy that would allow a more efficient transfer of phonons. Moreover, since the thermal transport in CNTs mostly relies on lattice vibration, if the metallic behavior of the nanotubes are reduced due to covalent functionalization, the CNT will still have outstanding heat transfer properties.

Huxtable et al. do measurements of Kapitza resistance at the CNT to surfactant interface for nanotubes uniformly dispersed in D₂O using sodium dodecyl sulphate (SDS) [150]. They measure that the thermal conductance at the CNT to surfactant interface is of $12 \text{ MWm}^{-2}\text{K}^{-1}$ indicative of a high contact resistance. They claim from their molecular dynamics simulations that the high Kapitza resistance originates from the vibrational constraint where by heat is transferred only by a small amount of low-frequency phonons and that all the high-frequency phonons have to undergo internal phonon-phonon coupling to be shifted to low-frequency modes so that they can go

through the interface. They further state that if the CNTs are linked by a covalent bond, then the high-frequency phonons may become strongly coupled to the surrounding of the nanotube, implying a good energy transfer both in the high and the low vibrational modes. Wang et al. do a comparative study involving pristine CNTs and acid treated CNTs [151], and based on the reasoning that short CNTs are easier to disperse, they use a physical method and a chemical method to shorten the nanotubes. They report that the mechanically chopped CNTs provide the better enhancement as compared to that from the uncut CNTs and the acid shortened CNTs. Their study is very indicative of the negative effect of extreme crystal disruptions in the CNT walls due to chemical attack. Liu and Fan, on the other hand, do comparative studies of the consequences between mild and strong chemical modifications of the CNT sidewalls on the effective thermal conductivity [152]. They report that mild chemical attack is beneficial to the overall heat transport because it leads to a covalent link between the fillers and matrix which brings each other closer and thus favors a better heat transfer. A theoretical study by Shenogin et al. using classical molecular dynamics leads to the conclusion that the covalent bonding between a nanotube and a polymer matrix consequently reduces the thermal boundary resistance [153]. On the other hand, the simulation results also reveal that bonded sites affect the intrinsic thermal conductivity of the CNT. Thus, if the CNTs do not contain too much bonded sites, the overall effect is dominated by a positive effective enhancement in thermal conductivity. Finally, concerning the electrical behavior of CNTs, it is reported by Skakalova et al. that some chemical treatments can enhance the electrical conductivity of the nanotube while others can reduce it [154].

2.9 Conclusions

The composition and properties of composite materials are described in details in this chapter. Moreover, CNTs are introduced as a potential new filler additive for composite materials. Various aspects of CNTs are described in relation to composite material fabrication and to its potential contribution to the improvement of the composite mechanical reinforcement and heat dispersion. In conclusion, the properties of CNTs that can be exploited are very promising. First, from a mechanical point of view, it has a tensile strength of roughly 60 GPa and a Young's Modulus of more than 1 TPa. Also, its thermal conductivity is estimated to be around $\kappa = 3000 \text{ W/mK}$. The combination of these properties can indeed be exploited in composites as reinforcing fillers and heat dissipaters. Thus, the resulting composite material offers very interesting properties. However, there remain two important issues that have to be over-come when using CNTs as a raw material for filler application: first, a suitable process must be developed for dispersing individual nanotubes uniformly in the matrix and second, good interfacial transfer between the CNTs and the epoxy matrix must be achieved. The research work that is presented in this thesis is a potential solution to these issues. Subsequently, the consequences of the proposed solution on the thermo-mechanical properties of the composite material are studied and the results of the study are used explain some fundamental phenomena which are still not very well understood about CNTs in composite materials.

CHAPTER 3

CHEMICAL TREATMENT OF CNT FILLERS

3.1 Introduction

Covalent functionalization opens new possibilities to the application of CNTs in composite material fabrication. The tailoring of fillers at the nano-scale is one area of material science which fits perfectly in the nanotechnology era. Thus, the ability to scale up this technology to an industrial level is another good demonstrator of the tremendous possibilities of nanotechnology. Among the various fields involving innovative composite materials, the specific area of IC packaging epoxy composites occupies a relatively important place. Based on the intrinsic CNT properties described in Chapter 2, it can be speculated that CNTs have the potential of being fillers of interest in composite materials. However, as also mentioned in that chapter, a few issues have to be overcome to make this application feasible. First, from a process point of view, a method must be developed to untangle and debundle the CNTs and disperse them homogeneously in the epoxy. Second, from a mechanical approach, the interfacial load transfer between the epoxy matrix and the CNTs must be improved. Finally, from a thermodynamic position, the heat transport through the dielectric composite must be enhanced. Thus, a coherent method must be developed to answer simultaneously for these issues. Moreover, the method should be scalable to an industrial level and compatible with the manufacturing process flow of epoxy based IC packaging composite materials. Consequently, a chemical treatment involving the bonding of functional molecules to the CNTs must be developed in the context of CNT dispersion in epoxy resins towards improved thermo-mechanical characteristics.

3.2 Selection of the CNT raw material

Starting from the origin of the material, the correct strategy that must be employed to grow the CNTs is the CVD aligned growth because other techniques result in low

quality CNTs that are entangled and require destructive efforts to un-mesh [155-157]. Indeed, it can be observed from the SEM in Fig. 3.1 that CNTs which are not produced by aligned growth are in the form of entangled balls. A closer view at these CNT balls show that the CNTs are densely packed and meshed-up (Fig. 3.2). An unknown material property which must be clarified is whether the curved shapes of the meshed CNTs occur naturally due to their flexibility or whether they result from lattice defects. The sharp bend that are observed in Fig. 3.3 may indicate that it is a defect site but it is difficult to draw any conclusion based on SEM pictures.

Fig. 3.1: SEM of CNTs grown randomly.

Fig. 3.2: Magnification of Fig. 3.1 showing a dense mesh of CNTs.

Fig. 3.3: A sharp elbow bending of a CNT which indicates that it may be a defect site.

Fig. 3.4: A TEM picture showing that even smooth bends result in defect sites.

Fig. 3.5: A closer view of the TEM picture of Fig. 3.4 shows a discontinuity in the crystal lines indicating the occurrence of both a bending and a twisting of the CNT.

Fig. 3.6: TEM showing that some bending sites also result in a reduction in diameter of the CNT.

The TEM characterization of the CNTs reveals further details on the integrity of the nanotube structure. The TEM in Fig. 3.4 shows that even very smooth bends contain defects. The defects appear in the form of pinches and recesses in the CNT walls. A magnification of Fig. 3.4 is displayed in Fig. 3.5. The picture shows parallel lines along the CNT length which are the CNT walls. At the bending site however, we observe a discontinuity in the lines suggesting both bending and twisting of the CNT with possible rupture point as indicated by the arrow. Moreover, as seen in Fig. 3.6 the bending of the CNT can also result in a diameter reduction of the nanotube. These defect sites are located on the randomly grown CNTs and contain numerous weak points. They will lead to tearing of CNTs during ultra-sonication or chemical attack during strong chemical reactions such as acid treatments [158]. The tip of the CNT shown in Fig. 3.7 is an example of a CNT that has been cut down or progressively

shortened from one tip as a result of the chemical attack during an acid treatment. What is observed on the picture is an extremely uneven tip bearing an open structure with graphene-like endings. It is improbable that this tip structure was formed during the CNT growth because as-grown CNT tips tend to be closed even if they are deformed. Thus, the more plausible origin of this tip structure is the acid treatment that was done on a sample of randomly grown CNTs for demonstration. Based on these facts, it is clear that the vertically-aligned growth of CNTs is a more appropriate technique for obtaining raw material of better quality.

When high quality vertically-aligned grown CNTs are used, entanglement and high defect site densities are two issues that are already eliminated. By high quality we mean CNTs which are grown using the correct temperature, pressure, gas and catalyst combination so that densely packed vertically aligned forests of CNTs are produced. Thus, the resulting raw material produced is in the form of bundles of aligned CNTs which are closely packed together. Fig. 3.8 shows the SEM of a sample of such high quality CNTs. The CNTs were grown in-house with a PECVD dedicated to this effect.

Fig. 3.7: TEM picture of a CNT tip showing damages resulting from an acid treatment.

Fig. 3.8: SEM of a bundle of CNTs which are vertically-align grown.

Fig. 3.9: Higher magnification picture showing a very dense forest of rectilinear CNTs.

A higher magnification of the CNTs shows that they are almost all perfectly rectilinear (Fig. 3.9). This is already a first indication of the good quality of the CNTs. To have a more accurate evaluation of the crystal quality of the CNTs, a Raman spectrometry is the relevant tool to be used and this characterization technique is described in more details in the next chapter. An important feature to be controlled about the CNTs is that the growth is uniform so that the diameter, length and average defect density are the same for the different samples of CNT produced. If the repeatability of these parameters cannot be ensured, it becomes difficult afterwards to make a good comparative assessment of the impact, on the composite material, of applying changes to the interfacial characteristics. Thus, any additional, step such as purification, which may incur changes in the length, diameter and average defect density of the CNTs should preferably be avoided. Unfortunately, high purity CNTs grown in-house could only be obtained in small samples. So, for the purpose of this

research where many tens of grams of CNTs were required, the CNT raw materials were out-sourced.

3.3 Chemical treatment of the CNTs

Using vertically-aligned grown CNTs, the next step consists of applying a procedure that results in a homogeneous dispersion of individual nanotubes into the epoxy matrix. Traditionally, to debundle CNTs, the solid powder is put in an aprotic, polar solvent such as dimethylformamide or n-methylpyrrolidone and sonicated for some hours [159-162]. However, the limit of this method is that both the fillers and solvent are added to the polymer and the solvent is then evaporated from the composite after thorough mixing. Most of the solvents that are adapted for CNT dispersion have high boiling points (Boiling point of dimethylformamide = 153 °C) and the thermal budget of pre-polymers including epoxy resins is quite restricted due to spontaneous polymerization risks. Moreover, by adsorption effects some residual solvent molecules are also retained in the composite resulting in alterations of the interfacial mechanical properties of the composite. Furthermore, the addition of solvents in the fabrication of IC packaging materials is restricted in the industry both for hazardous reasons and process compatibility issues.

By excluding the use of any solvent and targeting to add the CNTs in powder form to the epoxy resin, the most strategically sound method is to modify the chemical compatibility of the CNTs, i.e. to improve its solubility. Wrapping the CNT with a surfactant or with DNA strings improves the solubility but the presence of a solvent medium is still necessary. However, a particularly attracting method that is well renowned to modify the surface chemical properties of CNTs is the covalent bonding

of specific molecules on the outermost CNT wall. In such methods, the strong chemical bond between the CNT and the functional molecules preserves its integrity even if it is in a dry atmosphere. So, the covalent functionalization strategy is the most appropriate answer to powder form insertion of CNT fillers in epoxies.

Various chemical routes are reported in the literature for covalently bonding molecules on CNTs. Two excellent review papers devoted to the covalent functionalization of CNTs are the one of Burghard et al. [163] and Nakashima et al. [164]. Fig. 3.10 and Fig. 3.11 summarize the common chemical routes used to initiate reactive sites on the CNT sidewalls and tips.

Fig. 3.10: Covalent functionalization techniques reported by Burghard et al. [163]. (a) Addition reactions using pristine CNTs. (b) Nucleophilic substitution reactions using fluorinated CNTs.

Fig. 3.11: A review of the strategies to covalently functionalize CNTs reported by Nakashima et al. [164].

Fig. 3.10 (a) and 3.11 (b) show addition reactions that can occur on pristine CNT sidewalls. The correct choice of the organic molecule (R) can potentially functionalize the surface of the CNTs provided that it is chemically compatible with the reactants and remains unaffected during the reaction. Nevertheless, the functionalization process does not necessarily need to occur in one step. Fig. 3.10 (b) is an example of fluorinated CNTs (reaction marked with * in Fig. 3.10 (a)) which undergo a second chemical reaction to substitute the fluorine radicals with functional molecules. Another common technique is to functionalize acid-treated CNTs using traditional carboxylic acid chemical reactions (Fig. 3.11 (a) & (c)).

Among the various chemical routes that have already demonstrated the ability to overcome the relative chemical inertness of CNTs, four are explored in the course of this study. These reactions represent a first step which is necessary to create chemically reactive sites on the CNTs. The second step consists of finding the correct molecule to bond to the reactive sites to serve a specific function.

Table 3.1: Chemical reactions tested during this study. (Remarks in blue are good, in green are bad)

Functionalization method	Remarks
Acid treatment [165, 166]	<ul style="list-style-type: none"> • Reaction protocol extracted from the publications • Reaction rate is good • Process a relatively easy and can be done under ambient atmosphere • Separating the f-CNTs from the supernatant is relatively easy • CNTs are damaged and cut down into smaller pieces • Amorphous carbon is generated
Prato reaction [167-169]	<ul style="list-style-type: none"> • Reaction protocol extracted from the publications • Very slow reaction with a negligible yield on MWNTs
Strano reaction [170]	<ul style="list-style-type: none"> • Reaction protocol extracted from the publications • Unable to reproduce reaction on MWNTs
Lithiated alkyl [171-175]	<ul style="list-style-type: none"> • Reaction rate is good on MWNTs • Reaction does not alter the length of CNTs • Debundling of CNTs is facilitated with the help of electro-repulsion of the charged CNTs • Reaction can only be done under controlled atmosphere

Among the different chemical treatments available to initialize a covalent bond on the CNTs, the one that should be chosen must also help to debundle the CNTs during the reaction so that, while the CNTs are being functionalized, they are also dispersed at the same time. This technique thus enables the functionalization to be uniform along the CNTs without having parts of the sidewalls being masked due to the closely packed bundles. Table 3.1 summarizes the four chemical routes that are evaluated during this study. The chemical reaction that is chosen is the lithiated alkyl and the justification for this are mentioned in Table 3.1. The only disadvantage of this chemical treatment is that it has to be performed under controlled atmosphere. Otherwise, it is a very suitable method that results in the best yield due to the fact that no by-products resulting from damaged CNTs are produced. The following sections contain detailed descriptions of the chemical protocols that are conducted based on lithiated alkyl chemical attacks of the CNTs.

3.4 Experimental procedure

The CNTs used in the course of this study are MWNTs bought from Nanothinx Ltd. They are grown by a vertically-aligned PECVD with the characteristics:

Purity > 95 %

Diameter 30-50 nm

Length 5 – 15 μm

Amorphous carbon contents < 3 %.

The chemical reaction to initiate reactive sites on the CNT outermost wall is based on the preliminary work which has already been demonstrated using lithiated alkyls to covalently functionalize SWNTs and fullerenes [171-175]. To precisely reproduce

this chemical reaction, the first step is to determine the suitable solvent. The solvents that are evaluated for this reaction are listed in Table 3.2. Toluene and cyclohexane solvents are both inert to the lithiated alkyl. However, CNTs are slightly more soluble in toluene than in cyclohexane. Moreover, a polar aprotic solvent such as toluene favors the chemical reaction with lithiated alkyls and therefore results in a better yield of reaction [171]. Thus, toluene is the preferred solvent provided that its water amount is negligible. Indeed, an anhydrous medium is essential because the strong chemical reaction between lithiated alkyls and residual water contents has an impact on the yield of reaction and the chemical products [175].

Table 3.2: Solvents experimentally evaluated during this study for the reaction of CNTs with n-butyllithium.

Solvent	Remark
Dimethylformamide	Good solvent for CNTs but reacts with n-butyllithium
N-Methylpyrrolidone	Good solvent for CNTs but reacts with n-butyllithium
Toluene	Polar aprotic solvent. Relatively good CNT dispersion. Inert with n-butyllithium
Cyclohexane	Aprotic solvent. Relatively good CNT dispersion. Inert with n-butyllithium.
Dimethylsulfoxide	Good solvent for CNTs but reacts with n-butyllithium

First, the “as-grown” CNTs are mixed in anhydrous toluene in a closed vessel under argon atmosphere and stirred using a magnetic stirrer. After 2 hours of stirring, the lithiated alkyl, n-butyllithium (BuLi) is gradually added to the mixture and let to stir for 2 more hours (Fig. 3.12). The chemical attack of the BuLi molecules leads to charged CNTs that disperse naturally due to electro-repulsion in the solution. This

colloidal mixture is maintained under inert atmosphere during the reaction process, because at this point, the f-CNTs also react with atmospheric humidity. As shown in red on the right side of Fig. 3.12, when BuLi attacks a CNT, the butyl molecule is bonded on one carbon atom resulting in a negatively charged neighboring carbon atom which is in ionic equilibrium with the positively charged lithium ion. In the unfortunate presence of water, the lithium ion reacts with the OH^- ion to form LiOH and the hydrogen ion covalently bonds to the negatively charged carbon ion on the CNT surface. This chemical reaction must be avoided because the product of the reaction is very stable and complicates further functionalization reaction because hydrogen can hardly be substituted.

Fig. 3.12: Chemical attack of the CNTs by n-butyllithium in toluene solvent.

At this stage, another reactant must be added to the solution to stabilize the reaction because the f-CNTs are too reactive in this ionic form. For example, addition of these f-CNTs to an epoxy resin causes spontaneous polymerization of the epoxy. Moreover, the strategy at this point is to choose a functional molecule that will not only neutralize the ionic solution but also give a new property to the CNT. This concept of

functional molecule which has the purpose of bringing an additional characteristic to the material on which it is bonded is the core of this study. Halogeno-alkyls are the most favorable molecules to neutralize the solution because they result in a simple substitution reaction of the lithium ion and the enthalpies of reaction are high enough to promote the reaction and low enough to prevent the constituents from undergoing further chemical reactions [175]. Substitution reactions involving hydroxyl groups are, in principle, also feasible. However, a strong exothermic reaction can have a negative impact on the final product of the reaction because in some cases it can alter the functional molecules, as discussed below. Among the existing halogeno-alkyls, chloro-alkyls are the most adapted because the energy of formation of LiCl is the more appropriate as compared to the other halogeno salts of lithium. Thus, the functional molecule should contain a chloride termination provided that the molecule does not also contain another more reactive termination such as a hydroxide termination which is more reactive and thus, can be concurrent and destructive.

Table 3.3: List of molecules experimentally tested in the course of this thesis for the substitution of lithium on the CNT wall.

Reactant	Remark
Tetrachlorosilane followed by water	Violent reaction. Formation of HCl fumes. Solution turns grayish with the formation of SiO ₂ . CNTs appear to bond together if the amount of reactants are not properly dosed.
Epichlorohydrin	Reaction occurs. Details of the reaction below.
1-Propanol	Reaction occurs. Formation of LiOH byproduct in the form of white crystals. Reaction is very appropriate to verify the occurrence of the first step reaction and to evaluate the effect of surface non-uniformities on bundling.

Glycidol	Reaction occurs. Formation of a dense block of CNTs possibly bonded together. The viscosity of the product leads to the conclusion that the ring of the oxirane opens up due to a spontaneous polymerization.
Ammonium hydroxide	
Aniline	
Benzenethiol	
Chloromethylbenzene	
Methanol	
Ethanol	Reaction occurs. The products are suitable to improve the solubility of CNTs in various polymers and solvents.
Chlorobenzene	
Trityl chloride	
Silver chloride	
Silver nitrate	

The various chemicals which have been tested during the second step of the reaction are listed in Table 3.3. Although some reactions have failed to occur, a few have succeeded giving rise to interesting products. For example, CNTs functionalized with chloromethylbenzene display some improved solubility characteristics in aromatic solvents and in epoxy resins. Another interesting example is the one ammonium hydroxide where the solubility improvement of the f-CNTs is not as good as chloromethylbenzene but the product has the same characteristics of a curing agent precursor. It should be noted, that the same property was noticed while mixing commercially available amine functionalized CNTs. Even though, the polymerization rate is slow, after about two days the epoxy resin had completely hardened. This proscribes the use of some amine and amide functionalized CNTs because of the resulting short pot life of the resin.

The targeted product due to the reaction of glycidol and epichlorohydrin is f-CNTs bearing molecules that can take part in the polymerization process of the epoxy resin so that a strong covalent bond between the nanotubes and the epoxy matrix can help to improve the mechanical load transfer for the improved adhesion and to enhance the thermal dissipation resulting from a better phonon transport via molecular bridging. As mentioned in Table 3.3, the reaction with glycidol could not be controlled. The energy generated during the reaction causes the oxirane ring to open and the f-CNTs to bond to each other. This, spontaneous polymerization resulted in black blocks of CNTs being stuck together.

On the other hand, the attempts at chemically reacting epichlorohydrin with the lithiated ionic CNTs seem more encouraging because no apparent polymerization were noted. The solvent of the reaction turned pale-orange suggesting the creation of a byproduct and thus, indicating that a reaction has indeed occurred. No change in viscosity and no agglomeration of the CNTs are noted even after the pot is left untouched for a few hours. The f-CNTs remain dispersed in the vials leading to a uniformly black solution (Fig. 3.13).

Fig. 3.13: Visible difference in dispersion of f-CNTs in solution: left = pure CNTs, right = f-CNTs.

The apparent occurrence of the reaction with epichlorohydrin has led to further studies, first, to confirm and explain the chemical reaction and then, to evaluate the comparative impact of this molecule on CNTs dispersed in epoxies.

3.5 The proposed mechanism of the reaction

The functionalization of CNTs is carried out recurring to a liquid phase procedure, employing anhydrous toluene as reaction medium and BuLi as reactant. Even though the BuLi molecule is a lithiated butane molecule via pure covalent bonds, the huge difference in electronegativities between lithium (0.98) and carbon (2.55) [176, 177] accounts for a highly polarized bond which can be regarded as being quasi-ionic, and the ionic nature of the bond can be used to explain the extremely powerful organometallic nucleophilic behavior the butyl quasi-carbanion. Consequently, BuLi reacts with the CNTs by nucleophilic attack of the double bonds located in the CNT structure (Fig. 3.14). It is believed that the attack will occur preferentially at the defect sites of the lattice structure because the pure pristine hexagonal lattice is very stable and almost inert [171]. The defect sites are either the non hexagonal sites naturally found at the tips of the CNTs or the non-hexagonal fracture and bending sites found at the sidewalls which occur during the CNT growth.

Fig. 3.14: Break in double bond between two carbon atoms to favor the grafting of the butyl molecule.

The most feasible chemical mechanism is the nucleophilic addition of BuLi molecules on the CNT carbon atoms resulting in an electronic shift on the neighboring carbon atoms and formation of intermediate ionic species. During the nucleophilic attack, the butyl carbanion (Bu) covalently bonds to one of the two double-bonded carbon atoms by breaking the existing π bond (Fig 3.15). There is thus a negative charge shift on the neighboring carbon atom creating a carbanion on which the Li^+ ion stagnates to form a highly polarized covalent bond. In turn, the CNTs become very reactive nucleophilic agents because of the carbanion / Li quasi-ionic pairs.

Fig. 3.15: Proposed reaction mechanism of the chemical attack of the CNTs.

During the second chemical reaction, when epichlorohydrin is added to the mixture, the reactive sites readily undergo metathetic exchange reactions [178] with the halogenated molecules during which more stable lithium halides are formed and the remaining molecule containing the epoxide ring is bonded to the carbanion site found on the CNT (Fig. 3.16).

Fig. 3.16: Nucleophilic substitution between carbanions on the CNT sidewall and epichlorohydrin molecules resulting in epoxy groups covalently bonded to the CNTs.

The lithiated CNTs now behave as nucleophilic agents for the epichlorohydrin electrophiles. The nucleophile attacks the C-Cl bond in a S_N2 mechanism resulting in a substitution of the Cl ion. While the free Cl ion forms an ionic bond with the Li ion, the nucleophile covalently bonds to the CNT on the C atom which is next to the butyl bonded C atom (Fig. 3.17).

Fig. 3.17: Proposed reaction mechanism of the nucleophilic substitution between epichlorohydrin and the lithiated CNT.

It should be noted that, besides reacting with CNTs, BuLi also reacts with residual amorphous carbon present in the solution. Therefore, by using a controlled excess amount of BuLi, amorphous carbon can be removed from the solution during the

filtration process. Thus, this chemical procedure also avoids doing any lengthy pre-treatment of the as-grown CNTs.

It must be pointed out that reaction mechanisms cannot be proven. They are not used to prove that the chemical reaction occurs. The use of the reaction mechanism is to illustrate a possible mechanism of reaction. Usually, whenever the synthesis of a new chemical takes place, the inventor proposes a reaction mechanism based on some known chemical rules [179]. Then, the viability of the route is usually put to test the other way round in the sense that, if one does not agree with one mechanism, he or she must bring an experimental proof that it is wrong.

3.6 Conclusions

Various chemical routes are explored in view of treating CNT fillers for a better dispersion in polymers. A few chemical treatments are well adapted for a proper dispersion in epoxy resins due to an improved interfacial chemical compatibility. Among these, one seems particularly interesting not only as a good candidate for dispersion improvement but also to alter the thermo-mechanical interface between the CNT fillers and the epoxy matrix of the solid composite. The next chapter develops the experimental and theoretical proofs that this chemical reaction indeed occurs as predicted in the chemical reaction mechanism.

CHAPTER 4

CHARACTERIZATION OF CNT FILLERS

4.1 Introduction

Among the various chemical treatments that were evaluated for the functionalization of MWNTs, one which is of particular interest for its potential in epoxy reinforcement has been identified. As mentioned, the target is to evaluate the thermo-mechanical impact of having covalent bonds at the interface between the epoxy matrix and the CNT fillers. However, before doing this evaluation, it is necessary to devote some attention to the f-CNT fillers in order to confirm that the functional molecules described in the previous chapter are covalently grafted on the nanotube walls. Thus, several experiments are carried out on f-CNT samples, first to determine if the functional molecule is present in the samples and then to investigate whether this molecule is covalently bonded to the CNTs. Even if the two chemical reactions involved in this reaction are reported to be feasible [180-182], an experimental proof must be given to confirm this occurrence on CNTs.

4.2 Experimental analysis

Restricted to the sole characterization study of f-CNTs which is specific to this chapter, the concentrations of BuLi and epichlorohydrin used during the chemical treatment are 20 times higher than the concentrations used for the synthesis of the composite material. This is done so that the characterization is more measurable because very small proportions of functional molecules tend to be undetectable mainly during spectroscopic analysis. On the other hand, too high concentrations of covalently bonded functional molecules tend to alter negatively the intrinsic properties of CNTs. Thus, the f-CNTs produced for characterization are not optimal for composite fabrication.

Before making any structural analysis of the f-CNTs, a lot of care is devoted to clean the material to be tested after it has been produced by chemical reaction. Acetone is inert to the f-CNTs and is a very good solvent for a lot of organic chemicals. Moreover, it has a low boiling point which makes its evaporation from the sample easy. Thus, the f-CNTs are repeatedly added to acetone solvent and sonicated. Then, by ultra-centrifuging the mixture, the black sediment is extracted from the supernatant so that any non-reacted chemicals and by-products are filtered away due to their solubility in acetone. The f-CNTs are then dried in a vacuum oven at mild temperature to avoid altering the molecular structure.

A Renishaw RM 1000 Raman spectroscopy is used to make a comparative analysis between the pristine and f-CNTs. Among the various modes present in the Raman spectrum of CNTs, it is reported that, at around 1354 cm^{-1} , there is one peak relating the defects present in the lattice structure of the nanotubes [183, 184]. Any alteration in this, so called disordered mode (D-mode) peak would be a clear indication that there is indeed a covalent grafting of molecules on the CNT body because, once a molecule is covalently bonded to a carbon atom present in the CNT, its hybridization state would change from a quasi- sp^2 to quasi- sp^3 [185, 186]. Thus, this structural difference induces changes in the lattice vibration of the CNT in the same fashion as other defects would do. The spectrum obtained for the CNTs confirms this occurrence (Fig. 4.1). By normalizing the spectra obtained for non-functionalized CNTs and f-CNTs with respect to the Tangential mode (G-mode) [182], the change in D-mode peak size is assessed. The G/D ratio for pure CNTs is 1.8 and the one for f-CNTs is 1.1 showing a rather big raise in D-mode peak.

This observation also reveals that the chemical attack of the lithiated alkyl does not only occur on the defect sites as predicted in the literature [175], but takes place also at the on graphene-like pristine sites of the MWNT outermost wall. This is important because it implies that the reaction rate can thus be controlled by external parameters such as chemical concentration and temperature. These parameters are more easily monitored during f-CNT synthesis than the amount of defect sites are during CNT growth. This experiment reveals that the examined CNTs contain more defect sites. However, Raman spectroscopy cannot inform whether the functional molecule which attacked the CNTs, are still present in the sample under test.

Fig. 4.1: Figure showing the Raman spectroscopy of functionalized MWNTs.

Thus, using a TGA Q500 from TA Instruments, a comparative thermo-gravimetric analysis of the CNTs is also executed. Three identical runs are carried out and a mean curve calculated both for non-functionalized CNTs and f-CNTs. The protocol for the measurement is done in conformation with the NIST Recommended Practice Guide with a heating rate of 5°C/min in air until 800°C and an isothermal of 15 minutes at

that temperature. It can be observed from the graph (Fig. 4.2) that at lower temperatures there is a consequent change in weight for the f-CNTs indicative of the disintegration of the grafted molecules. Moreover, one can also notice that, at higher temperatures, there is also a bigger trend for f-CNTs to burn away as compared to pure CNTs. This observation is coherent with the fact that covalent functionalization induces defects in the CNT lattice and in doing so it makes the structure more susceptible to thermal degradation [187]. Indeed, a CNT structure bearing defect sites is more similar to amorphous carbon than to graphene sheets and it thus disintegrates more easily.

Fig. 4.2: Thermo-gravimetric analysis of pristine and f-CNTs.

Besides providing evidence about the presence of functional molecules, this TGA can also give a rough estimate about the number of bonding sites present on one CNT. Based on the average diameter (40 nm) and length (15 μm) of the MWNTs and an approximate density of 2.1 g/cm^3 , the average mass of a single MWNT is:

$$m_{MWNT} = 3.7 \times 10^{-15} \text{ g}$$

The mass of the combined butyl and oxirane functional molecules is:

$$m_f = 1.9 \times 10^{-22} \text{ g}$$

As shown in Fig. 4.2, the mass of functional molecules corresponds roughly to 15%.

Thus,

$$\frac{y \times m_f}{x \times m_{MWNT} + y \times m_f} = 0.15 \quad (4.1)$$

where x and y correspond the number of MWNTs and functional molecules respectively.

Therefore,

$$\frac{y}{x} = \frac{0.15}{0.85} \frac{m_{MWNT}}{m_f} \approx 3.4 \times 10^6 \quad (4.2)$$

As the functional molecules are only bonded to the outermost CNT wall, the number of bonding sites present at the surface must be determined. By calculating the average surface area of a MWNT and using the lattice constant of graphene (0.246 nm) we obtain an average of 1.5×10^7 pair of bonding sites. All the sites bearing functional molecules should, in principle, have a distorted surrounding. Thus, not only the functional molecules but also part of the CNT body should also be degraded at low temperature. Therefore, the 15% measured with the TGA include both the functional molecules and a fraction of the damaged CNT parts. This implies that at most $\frac{1}{4}$ of the surface carbon atoms are functionalized, half with butyl molecules and the other half with oxirane molecules. We can deduce that for the synthesis of the composite material a rough estimate of at most $\frac{1}{80}$ atoms are functionalized.

The use of a TGA is able to confirm that the functional molecules are present. However, it cannot predict if the oxirane ring is still intact or if it has been damaged during the chemical reaction. Thus, a comparative differential scanning calorimetric (DSC) analysis between pure CNTs and f-CNTs is carried out. Using a DSC-Q10 equipment from TA Instruments, the calorimetric properties of the CNTs are analyzed. The experiment is conducted using aluminium pans at a heating rate of 5°C/min. It is observed that for the f-CNTs sample there is an endotherm above 57°C (Fig. 4.3). This result is indicative of a change in state of the sample and most probably corresponds to the spontaneous oxirane ring opening and polymerization of the functional molecules bonded on the CNTs [188, 189].

Fig. 4.3: Figure showing the Differential Scanning Calorimeter analysis of f-CNTs.

The combination of a Raman spectroscopy, a TGA and a DSC are able to determine that the CNT graphene structure is altered and that the functional molecules are present in the sample but it is still undetermined whether these molecules are the one which are covalently bonded the CNTs. There are no known generic nondestructive

methods to make such a direct measurement. However, there are a few atypical cases where the study has been made possible. For example, Coleman et al. [190] develop a method to demonstrate the presence of covalent bonding. They graft thiolic functional molecules on the CNTs and disperse gold nanoparticles in a solution containing the f-CNTs. Then, using an atomic force microscope to scan a sample of the dispersed f-CNTs on a flat surface, they show CNTs decorated with nanoparticles. However, this method is only usable to demonstrate that covalent bonds indeed occur on CNTs. It is a destructive method that alters the chemical characteristics of the functional molecules and it is only compatible with the grafting of functional groups that can bond to nanoparticles which do not necessarily suit the targeted application.

Blake et al. [175] demonstrated that there is indeed a covalent bond between functional molecules and CNTs by grafting silicon and tin based molecules on the nanotubes and by looking for C-Si and C-Sn vibration modes in the Fourier Transform Infrared (FTIR) spectrum. Infrared spectroscopy is a crucial tool to characterize the structure of matter at the molecular scale. Based on the singular resonant vibrational modes of different branches or body parts of a molecule, one can reveal its constituting elements and its bonding arrangement. The reverse process is also exploited because a specific molecule possesses a unique infrared spectrograph equivalent to a finger print which can unveil its identity. FTIR spectroscopy analysis is a method based on the principle of infrared spectroscopy, and it has extended its area of application to the study of nano-scaled objects during the last decade. However, the application of FTIR in the characterization of functionalized nanoparticles can be difficult because it may not reveal the chemical bonds between the nanoparticles and the functional molecules based on a database of known

vibrational frequencies. This is because the chemical bond between the functionalized molecules and the nano-material is usually novel. The particularity of the molecules investigated by Blake et al. is that they contain silicon and tin atoms. C-Si and C-Sn vibrations occur in a very specific narrow range, almost independently of the remaining molecular structure, due to the relatively big difference in atomic masses of the two atoms. However, carbon to carbon bonds exist in a very wide range of wavenumbers due to the huge amount of existing organic molecules and their various configurations. Thus, such an affirmation cannot be done if purely carbon based functional molecules are grafted as it is the case in the present study. Thus, a strategy based on FTIR spectroscopy has been developed to provide evidence about the resonant vibrational information between the grafted molecules and the nano-sized particles.

4.3 FTIR analysis

In order to extend the applicability of FTIR to this study, a theoretical method must also be developed to derive the FTIR spectroscopy of the f-CNTs and compare it with the experimental results obtained. Thus, the method that is presented here is a combined experimental and theoretical FTIR analysis of f-CNTs to unveil the occurrence of a chemical covalent bond between functional molecules and CNTs. Pristine MWNTs show very weak resonant frequencies in the infrared spectrum in the 400 cm^{-1} to 4000 cm^{-1} range. However, once molecules are grafted on it, a differential infrared absorption response due to the functional sites is observed. The purpose of this work is to provide evidence that the observed differential response is not due to either adsorbed molecules, wrapping molecules or any other such kind of residual

particles which are not covalently bonded to the CNTs, but it is indeed due to the covalent bonding of the grafted molecules to the CNTs.

4.3.1 Experimental FTIR

As described in Chapter 3, during the chemical treatment, each functionalized site contains two branches, namely a butyl branch and an epoxide branch (Fig. 4.4).

Fig. 4.4: Sketch showing the grafting of functional molecules on the side wall and tips of CNTs.

Using a Perkin-Elmer System GX 2000 FTIR spectrometer, an extensive FTIR analysis is performed on f-CNT samples. The samples are prepared by taking a small amount of f-CNTs in powder form and mix it with potassium bromide (KBr) powder. KBr is the common transparent material used to trap nanoparticles for FTIR analysis because it has no resonant frequency in the interval investigated for organic molecules. The homogeneous powder is then compressed so that KBr vitrifies to result in a thin glassy semi-transparent disc with trapped particles. The discs are analyzed in the spectrometer under ambient conditions using different wavenumber resolutions. First,

a broad scan of the sample is performed from 400 cm^{-1} to 4000 cm^{-1} with a step of 4 cm^{-1} (Fig. 4.5). Among the various peaks present in the spectrum, several are already

Fig. 4.5: Broad FTIR spectrum of the f-CNTs between 400 cm^{-1} and 4000 cm^{-1} .

clearly identifiable as belonging to the functional molecules. For example, the peak at 830 cm^{-1} corresponds to a mono-substituted epoxide ring vibration. Peaks corresponding to the straight chain alkanes or branches of the epoxide molecules are also observed. The list of known wavenumber ranges obtained from FTIR databases [191] is listed in Table 4.1. As shown in Fig. 4.6, in order to obtain more detailed spectra of the sample, a higher precision FTIR analysis on a narrower range of 800 cm^{-1} to 1800 cm^{-1} is performed with a step of 0.1 cm^{-1} . Moreover, in order to distinguish between the overlapping peaks that are masked because of the convolution, a first order derivative of the spectrum is performed (Fig. 4.7). After deconvolution, the information collected in these spectra reveal peaks, such as the peaks at wavelengths of 1401 cm^{-1} and 1470 cm^{-1} , which are not identifiable in the database of the pure initial constituents.

Table 4.1: List of know IR resonant vibrations related to straight chain alkanes, epoxide rings and water molecules [191].

Wavenumber range (cm ⁻¹)	Deformation type	Fragment
445 – 825	Water	O-H out-of-plane bending vibration
455 – 455	Straight chain alkanes	C-C skeleton vibration
485 – 540	Straight chain alkanes	C-C skeleton vibration
805 – 880	Mono-substituted epoxide ring	Ring vibration
1060 - 1150	Saturated aliphatic esters	C-O asymmetric stretching
820 - 1140	Saturated aliphatic esters	C-O symmetric stretching
1370 - 1390	R – CH ₃	C-H symmetric deformation vibration
1440 – 1480	-CH ₂ -	C-H scissor vibration
1475 – 1500	Mono-substituted epoxide ring	CH ₂ deformation vibration
1595 – 1710	Water	O-H in-plane bending vibration
2865 - 2885	R-CH ₃	C-H symmetric stretching vibration
3000 - 3700	Water	O-H stretching vibration
3230 - 3550	Water	Intermolecular hydrogen bond

Fig. 4.6: High precision FTIR spectrum of the f-CNTs in the range of 800 cm^{-1} to 1800 cm^{-1} .

Fig. 4.7: Deconvolution of the spectrum shown in Fig. 4.6 between 1300 cm^{-1} and 1600 cm^{-1} .

4.3.2 Theoretical FTIR

In order to identify the significance of each peak, a model of the f-CNTs must be developed and the different vibrational modes of the designed macro-molecule must be compared to the experimental results. As CNTs are almost chemically inert, a chemical reaction is more likely to occur first on the reactive defect sites and then on the rest of the CNT walls. The most probable location to find grafted molecules on the CNTs is a place where defects naturally occur, that is, the tip of the CNTs. Besides the tips, there are also a few well-known structural defects that are regularly found on side walls. Therefore, the model that is developed consists of grafting molecules on both CNT tips and on lateral defect sites and the different vibrational modes of the resulting structure are then computed.

Fig. 4.8: (a) Positions 1 and 2 are the locations of the binding sites for the functional molecules on the tip of the CNT (Half fullerene C_{30} molecule) (b) Cluster model of the functionalization of a C_{30} molecule.

The first cluster model consists of half a fullerene (C_{30}) to which are attached a butyl molecule and an epoxide molecule placed on atomic sites where the most active binding regions are deemed to be located. Such locations are found at the junction

between pentagonal and hexagonal rings (Fig. 4.8). In order to avoid any geometry reconstruction at the hemi-spherical edge, the dangling bonds are saturated with hydrogen atoms. After performing a relaxation of the cluster, the Hessian matrix is calculated in order to evaluate the resonant vibrational frequencies of the molecular model [192]. The second model consists of a 7-5-5-7 Stone Wales defect site (Fig. 4.9) commonly found on the side wall of CNTs [193] on which the same molecules are grafted and the same procedures are performed.

Fig. 4.9: Sketch of a Stone-Wales defect site found on the side wall of a CNT.

The most stable configuration of the models is first investigated. For example, in the case of the functionalized half-fullerene, a study of the optimal arrangement of the molecule which is displayed in Fig. 4.8b is performed. Grid scan conformer search technique [194] is employed by fixing the half-fullerene and the butyl molecule while rotating the epoxide ring at three different angles with respect to the butyl molecule. The same procedure is then repeated for side-wall functionalization. Three configurations are created and geometrically optimized for each model. For example, the final configurations of the functionalized half-fullerene are shown in Fig. 4.10.

Fig. 4.10. Configurations of the 3 conformers created by grid scan technique for the functionalized half-fullerene.

The binding energy (B.E.) and the length (L) of the C-C bond linking the butyl molecule to the C₃₀ (C_{CNT}-C_{butyl}) and the epoxide molecule to the C₃₀ (C_{CNT}-C_{epoxide}) are summarized in Table 4.2. The values of B.E. are calculated based on the following equation:

$$\text{B.E.} = E(\text{C}_{30} + \text{butyl} + \text{epoxide}) - E(\text{C}_{30}) - E(\text{butyl}) - E(\text{epoxide}), \quad (4.3)$$

where $E(\text{C}_{30} + \text{butyl} + \text{epoxide})$, $E(\text{C}_{30})$, $E(\text{butyl})$ and $E(\text{epoxide})$ are the respective total energies of the indicated systems.

Table 4.2: Theoretical results of the covalently grafted bond states for different orientations.

Configuration	B.E. (eV) ^a	L (C _{CNT} -C _{butyl}) (Å) ^b	L (C _{CNT} -C _{epoxide}) (Å)
4.10a	2.58	1.685	1.836
4.10b	6.61	1.581	1.571
4.10c	6.47	1.577	1.577

^a Binding Energy (Absolute Value), ^b bond length, L.

The conformations 4.10b and 4.10c in Table 4.2 are very close to each other in both the B.E. and L. The carbon atom located at position 1 for these two configurations is distorted and a tetrahedral sp^3 hybridization contributing to the overall structural stability is formed. On the other hand, the same carbon atom in the configuration

4.10a remains at its original position, leading to an unstable arrangement with a B.E. of about 4 eV less than the two other conformations. Correspondingly, the calculated $L(C_{\text{CNT}}-C_{\text{epoxide}})$ in 4.10a is somewhat larger than 4.10b and 4.10c by about 0.26 Å and this also reflects a much weaker covalent bonding in that configuration as compared to those in the 4.10b and 4.10c arrangements. Therefore, to model the covalent functionalization of CNTs, the configuration 4.10b is chosen in order to determine the IR spectrum of the f-CNTs.

The vibrational spectrum of the f-CNTs are examined by means of cluster models with methods based on the density functional theory (DFT) within the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation functional [195]. The calculations are closed shell and are performed using the Dmol³ module of Materials Studio from Accelrys. The electronic wavefunctions are expanded in atom-centered basis functions defined on a dense numerical grid. The chosen basis set is double numerical plus d-polarization (DND). DND is an all-electron basis set composed of two numerical functions per valence orbital, supplemented with a polarization d-function on all the non-hydrogen atoms. Each basis function is restricted to a cut-off radius. A global real space cut-off is selected as the maximum value of the cut-offs specific for every element of the system. Real space cut-offs for atomic species are optimized by considering total energies of atoms. The chosen cut-off values lead to atomic energies with an accuracy of 0.1 eV/atom, allowing calculations without a significant loss of accuracy. The self consistent field (SCF) convergence has been tested and a convergence threshold less than 10^{-6} Ha has been evaluated to be satisfactory to achieve the structural optimization.

Table 4.3: Vibrational modes comparison between experiment and theoretical work.

Wavenumber (cm ⁻¹)		Fragment deformation	
Experimental	Theoretical		
489	493	Straight chain alkanes	C-C skeleton vibration
830	843	Epoxide Ring	Ring vibration
1401	1403	C _{CNT} -C _{Epoxide}	C-C stretching
1470	1475	C _{CNT} -C _{butyl}	C-C stretching
1504	1504	Epoxide Ring	CH ₂ bending

From the simulation of Dmol³, the harmonic wavenumbers obtained are listed in Table 4.3 together with the corresponding experimental results. In agreement with the theoretical results, the covalent bond formation of the epoxide molecule on C₃₀ is disclosed by the wavenumber 1403 cm⁻¹. Also, the covalent bond formation of butyl molecule on C₃₀ is attributed to the C_{CNT}-C_{butyl} stretch at around 1475 cm⁻¹. Besides these two crucial wavenumbers, the theoretical results are in agreement with the experimental vibrational frequencies of the functional molecules such as the ring oscillation and the alkyl stretching. However, there are still some peaks that are not identified such as the peaks which are found at 873 cm⁻¹, 1297 cm⁻¹, 1333 cm⁻¹ and 1358 cm⁻¹. It is believed that this is because the attachment of the molecules occurs on various defect sites bearing different molecular configurations and hence it is not feasible to unveil all of them using any method since it's impossible to know the molecular structure of all the grafted sites that actually exist. Moreover, the water content in the KBr powder has a masking effect on the peaks that would lie within the intervals of 445 cm⁻¹ to 825 cm⁻¹, 1550 cm⁻¹ to 1750 cm⁻¹ and 3000 cm⁻¹ to 3700 cm⁻¹ [196, 197].

4.4 TEM of functionalized CNTs

Visual inspection of the f-CNTs is not obvious because the functional molecules are very small. Moreover, it is difficult to make an objective assessment on what is seen. As shown in Fig. 4.11, TEM images reveal non-uniformities at the CNT surface. However, one cannot say for sure whether the bulbs consist of functional molecules or whether they are defect sites (Fig. 4.11 (a)). A close capture of another site shows a rather big object bonded to the CNT (Fig. 4.11 (b)). However, in this case also it is difficult to make any assumptions on the composition of the object. Therefore, the preferred visual technique is to analyze by SEM f-CNTs inside epoxy matrices. This technique is described in details in the next chapter.

Fig. 4.11: TEM images of f-CNTs.

4.5 Conclusions

The characterization results performed on the f-CNTs prove that there are indeed changes in the crystal structure of the CNTs after functionalization and that there are organic molecules present in the sample. From the DSC measurements, it appears that there is a change of state in the sample under test which strongly suggests the presence of an epoxide ring. The combination of these characterization results with an FTIR analysis constitutes an exhaustive study of the f-CNTs. Indeed, the use of an experimental FTIR analysis and a theoretical FTIR model successfully demonstrates nature of the bond between the functional molecules and the CNT. The identity of the molecular conformations present on the f-CNTs is effectively unveiled and the presence of covalent bonding between the grafted molecules and the CNTs proven. Now that there is no doubt about the efficiency of the chemical treatment of the CNTs, the objective, as described in the next chapters, is to fabricate epoxy composites and evaluate the impact on the thermo-mechanical properties of the material.

CHAPTER 5

EPOXY COMPOSITE FABRICATION

5.1 Introduction

Now that the CNTs are successfully treated, the objective is to determine its efficiency in improving the process fabrication and the impact of this functionalization on the mechanical resistance and thermal dissipation efficiency. Process plays an important role in the fabrication of a composite material. If the process is not feasible on large scale or if it involves procedures that are not permitted at an industrial level for safety or ecological reasons, no matter how efficient the composite material may be, there is no way for it to reach the market. As mentioned in Chapter 1, the objective of this work is to develop an efficient way to use CNTs as fillers in epoxy matrices for IC packaging. It should be noted that epoxy composites for IC packaging exist in different grades with a relatively big variety of additives incorporated in the epoxy matrix. Thus, if one filler imposes huge efforts and a lot of restrictions during the fabrication process, it is more likely to be phased out. Thus, the optimal target is to have ready to use additives that can be dispersed into the epoxy in a single step with of help of simple mechanical stirring without any incompatibility with other additives.

There is already a wide variety of methods developed to insert CNTs in various polymers [198-205] and more specifically in epoxies [23, 84, 86, 88-90, 132, 140, 206-208]. One of the main concerns is to overcome the bundling of the CNTs and ensure a homogeneous dispersion of individual CNTs. Therefore, most of methods reported in the literature consist of looking for a suitable solvent, a surface active agent or chemical treatment to disperse the CNTs. Then, the practice is to use this solution form of CNTs and mix it with the polymer or pre-polymer solution. Finally, both solvents (CNTs and polymer) are evaporated resulting in a uniform dispersion of

the CNTs in the polymer. From an industrial point of view, the issues that can be pointed out with such strategies are:

- The dispersion in the solvent and polymer is usually done using sonication and this is a method which is barely used on a large scale in the polymer industry. Moreover, as mentioned in the previous chapter, prolonged sonication has been proved to damage or even break the CNTs into smaller pieces.
- Because of the evaporation stage, only selective solvents which are chemically compatible with the components present in the composite material and which have a low boiling point as compared to the different components can be used.
- During evaporation, one cannot ensure that 100% of the solvent evaporates. Thus, the remaining solvent may have secondary effects such as acting as a plasticizer or may have unwanted consequences on one or some of the properties of the material.

These are among the reasons why a new strategy for CNT insertion in a polymer is developed in this thesis. As described in Chapter 3, the dispersion strategy for CNTs in epoxy resins is to covalently bond functional molecules containing epoxide rings.

In terms of composite material synthesis, the consequences are:

- Surface non-uniformities prevent CNTs from bundling
- Improved chemical compatibility between the CNT surface and the epoxy resins results in a higher degree of solubility between the two components

- The f-CNTs are in powder form and can be dispersed easily at any time during the composite material fabrication process as any other traditional fillers

5.2 Mass preparation of CNT fillers

The ability to develop chemical treatments dedicated to CNTs for demonstration purposes is one thing but the ability to do such treatments in big volumes adds a level of difficulty to the execution of the procedure. Indeed, the process repeatability and uniformity must be taken into account together with big quantity handling. Thus, based on the strategy demonstrated in the previous chapters, a chemical route is developed by considering the constraints linked to large volume treatments. A reliable characterization method that would give an estimation of the functionalization per CNT or even one that could measure the relative chemical reaction uniformity in f-CNT lots of a few grams could not be developed. The only experiment which is carried out is to do FTIR analysis of samples taken randomly in the bulk f-CNT batch. The analysis indeed demonstrates that all samples are functionalized but there are too many variables (amount of f-CNTs in sample under test, illumination, etc) to be able to draw any statistical analysis from it.

The transformation experienced by the CNTs during functionalization is schematized in Fig. 5.1. It consists of two subsequent chemical reactions where (1) is the initiator and (2) is the functionalizer. The procedure and chemical amounts are expressed per gram of CNTs but the CNTs are usually processed in batches of 1 to 10 g. The detailed chemical treatment is listed in Table 5.1.

Fig. 5.1: Chemical route followed by the CNTs using BuLi as initiator to graft epoxide branches on the sidewalls.

Table 5.1: The chemical reaction route.

Process Step	Process Condition	Remarks
Prepare a solution of 1000 mg CNTs and 200 ml toluene	This step is done in a glove box under Argon dry atmosphere. The solution is sealed in a bottle and bath sonicated during 4 hrs to split the vertically aligned CNT bundles.	Anhydrous toluene must be used to prevent exposing BuLi to water. Sonication separates the CNTs so that some sidewalls of CNTs are not masked inside bundles during the chemical attack.
Add 5 ml of 2 mol.L ⁻¹ BuLi	Stir during 1 hr.	The charged CNTs disperse naturally by electro-repulsion. The suspension is stable as long as the bottle remains sealed.

Add 0.80 ml of epichlorohydrin	Stir 1 hr at 20°C. After stirring the bottle can be unsealed and the f-CNTs exposed to ambient atmosphere.	Solution turns pale yellow due to the formation of LiCl. When stirring stops, the f-CNTs sediment slightly due to the absence of charge. The f-CNTs are stable to exposition to humidity.
Centrifuge the solution at 11000 G for 30 minutes	Gently pour out the liquid phase supernatant to leave the bulk precipitate at the bottom of the tube.	A small fraction of the f-CNTs are lost in the supernatant because solubility is drastically improved in toluene.
Add toluene to the paste, stir the solution for 30 min, centrifuge at 11000 G for 30 minutes and pour out the supernatant.	Lower grade toluene can be used during this step and it is done under ambient atmosphere under a fume hood similarly to the rest of the procedure.	Toluene is used once to remove most of the remaining LiCl ionic molecules.
Add acetone to the paste, stir the solution for 30 min, centrifuge at 11000 G for 30 minutes and pour out the supernatant.	Repeat this step twice.	Acetone is a good volatile solvent to remove toluene and other residual chemicals from the solution.
Evaporate solvent in a vacuum oven at 30°C during 1 hour	Keep the paste far from the heating elements of the oven. Cover the Petri dish with a funnel to avoid sputtering during evaporation.	Ensure a mild oven temperature to avoid spontaneous polymerization of the epoxide functional molecules.

A few direct observations are made during the chemical process. As soon as BuLi is added to the solution, a uniformly black mixture is observed (Fig. 3.13). This mixture remains uniformly black as long as the bottle is sealed. After 1 month no visible changes and no sedimentation could be observed from a sample bottle. The electro-repulsive forces disperse the CNTs uniformly forming a homogenous suspension. This is an indication that the CNTs are almost all chemically attacked. Using an optical microscope, a droplet of the solution is trapped between two glass blades (Fig. 5.2 (a)). Pieces of broken glass are inserted between the two blades to allow a thick sample of the solution to be analyzed. Comparatively, pure CNTs dispersed by sonication in an equal proportion of toluene are analyzed (Fig. 5.2 (b)). Even in very thin films, bundles can be observed when the CNTs are not treated.

Fig. 5.2: 500 X optical microscope view of CNTs in solution: (a) f-CNTs, (b) pure CNTs.

5.3 Composite fabrication

During the fabrication of the composite material, the f-CNT powder is mixed by overhead mechanical stirring in an epoxy resin. The mechanical stirrer used is a EUROSTAR Power Control Visc P4 from IKA[®] WERKE. The particularity of the stirrer model used is that it keeps a constant rotational speed independently of the change in viscosity that occurs in the composite material. Thus, it ensures that the same dispersion parameters are being used for the different samples made.

Table 5.2: Physical properties of the epoxy resins as reported in the technical data sheet and material safety data sheet available on demand from the manufacturers.

	EPON 828	EPICOTE 1006A Part A
Viscosity (P)	110 – 150	10 – 13
Specific Gravity	1.16	1.05
Epoxide Equivalent Weight (g/eq)	185-190	185-192
Number Average Molecular Weight (u)	≤ 700	≤ 300

The two different epoxy resins used during this study have their physical properties summarized in Table 5.2. The values indicated are measured at 25°C. As shown, the only difference between the two resins is in its number average molecular weight and this parameter has obvious repercussions on the viscosity. As a consequence of the functionalization, the CNTs disperse more easily in the epoxy resins because of the nanotube surface non-uniformities which prevent bundling and because of the oxirane content of the bonded molecules which favor chemical compatibility with the resin.

As the solubility of the f-CNTs is better than pristine CNTs, after a few minutes of stirring in 250 ml of resin, the mixture looks uniformly black. However, to ensure that the homogenization is of a good quality the composite mixture is stirred for 4 hours at a constant stirring rate of 70 rpm. Because of the relatively high viscosity of the EPON 828 resin, a higher stirring rate tends to introduce air bubbles in the mixture. Air inclusion results in small pores inside the solid samples after curing (Fig. 5.3). Porosity affects the uniformity and reproducibility of the mechanical properties of the composite material and should be avoided as far as possible. Thus, this stirring rate is kept constant and to remain consistent with the fabrication of different epoxy composite samples, the same stirring rate and stirring time is used for both resins. Slower stirring rates, on the other hand, do not induce any porosity but cause the homogenization time to be longer. Once stirred, the composite resin remains homogenous for months. No changes in properties are noted over 6 months.

Fig. 5.3: Samples of epoxy composite after curing presenting numerous pores. Sample (a) consists of EPON 828 stirred at 120 rpm and sample (b) is EPICOTE at 180 rpm.

The viscosity analysis of the epoxy resin is performed during the stirring process and for both resins similar trends are noted. Using a Brookfield viscometer,

measurements are made at 5 rpm at 0, 24 and 48 hrs. Fig. 5.4 shows the viscosity of the composite resin does not vary much with low wt % of f-CNT addition at time 0 hr (purple). However, if the samples are stirred for 24 hrs, the viscosity increases noticeably and the presence of f-CNTs makes the change even more drastic. Moreover, what is also particular to the samples containing f-CNTs is that the viscosity remains unchanged after 24 hrs of shelf, unlike the pure resin. This is due to homogeneous distribution of the f-CNTs in the resin which imposes permanent physical changes to the system.

Fig. 5.4: Viscosity measurements of the epoxy resin during stirring. The three samples are made up of EPICOTE 1006A. Sample (A) is the pure resin, sample (B) is the resin with 0.1 wt% f-CNTs and sample (C) is the resin with 0.2 wt % f-CNTs. The yellow bar represents the viscosity measurements made after 24 hrs of rest subsequent to the measurement in blue.

In order to fabricate the solid composite material, a curing agent must be added to the composite resin. Each epoxy resin is mixed with its associated hardener which is provided by the manufacturer. The properties of the two curing agents are listed in Table 5.3. They both consist of at least one diamine or triamine species and the

crosslinking chemistry that occurs between such amines and the epoxy resins is an addition polymerization. As there are no byproducts formed, there is no degassing if the blending ratio is applied with precision and if the two components are thoroughly mixed.

Table 5.3: Properties of the two curing agents as reported in the technical data sheet and material safety data sheet available on demand from the manufacturers. Unless specified, the values correspond to measurements made at 25°C.

	EPIKURE 3202	EPICOTE 1006A Part B
Crosslinking Molecules	N-aminoethyl piperazine 70% Triethylenetetramine 30%	Isophoronediamine
Viscosity (P)	0.2	0.3
Specific Gravity	0.98	1.03
Blending Ratio	100:20	100:60
Gel Time (min)	21	67 at 20°C

Inverting the curing agents or using the same curing agent for both resins result in composites having partially uncured areas. It can be seen on Fig. 5.5 (a) that during the grinding of the sample, there is a viscous flow which results in an uneven surface made up of nodules and voids. The surface of the samples also looks sweaty at the naked eye and a magnified view shows grooves which channel liquids at the surface (Fig. 5.5 (b)). It is also reported that when the curing agent is mixed to the composite resin, CNTs tend to bundle again [209]. This bundling is explained by the change in ionic strength induced by the hardener addition which disrupts the electrostatic repulsion stability. Moreover, since the diffusion coefficient is inversely proportional to viscosity, the agglomeration is also explained by the reduction in viscosity which

results from the initial stage of hardener addition, just before polymerization starts to take place. Thus, a strategy which consists of dribbling the hardener at a constant rate using a syringe is used to prevent such an occurring (Fig. 5.6). The method ensures that the hardener addition is systematically the same such that its impact on the change in viscosity and ionic strength of the composite is negligible due to progressive low volume addition. The time taken to dispense the hardener is 2 min and the total mixing time is 10 min.

Fig. 5.5: SEM pictures of epoxy composite samples which are not cured completely. Sample (a) is the trench view and sample (b) is the surface view of the composite.

Fig.5.6: Sketch of the experimental setup to introduce the hardener in the composite.

The technique that is employed to cure the composite material is compression molding. After mixing, the viscous composite solution is poured in an aluminum mold. The mold consists of two 1.5 cm thick slabs which compress a thin aluminum sheet of 3 mm containing the relevant sample patterns (Fig. 5.7). Four steel quick-release pins located at each corner of the slabs are used as aligners and compressors when tightened. The size and shape of the patterns depend on the sample geometry required by the equipments used for mechanical characterization. For example, for dynamical mechanical testing, rectangular samples of 60 mm $\times$ 12 mm $\times$ 3 mm are made while, for thermo-mechanical testing, cylindrical samples of 5 mm in diameter and 3 mm in thickness are prepared.

Fig. 5.7: Design of the aluminum mold to cure the epoxy composite.

The heating profile is shown in Fig. 5.8. During the first 60 minutes the temperature of the composite is raised while no compression is applied so that degassing of eventual residual chemicals and water desorption can occur concurrently with a total reticulation of the polymer. Then, after cooling the composite to 40°C, the pins are tightened so as to compress the thin aluminum sheet containing the composite

and the temperature is ramped up to 100°C and maintained for 120 minutes. Finally, the temperature of the sample is ramped down again to ambient temperature and the samples uncasted from the mold. The advantages of using this curing method is that, at the first stage, it allows a proper degassing of all the non-polymeric chemicals present in the mixture. Then, the samples are sealed and compressed so that they are not in contact with the ambient atmosphere during the curing phase. This prevents surface glossy effects which usually occur due to the oxidation of exposed surfaces and often initiate surface cracks [210]. Moreover, this strategy also prevents the samples from enduring unnecessary additional compressive and expansion cycles during curing. All these factors have an impact on the repeatability of the characterization results obtained for a specific mass ratio of CNTs added to the epoxy.

Fig. 5.8: Curing profile of the composite.

A series of samples containing different wt % of CNTs are prepared to compare the evolution in mechanical and thermal properties of the composite with respect to different amounts of fillers added. Composites containing between 0.1 to 7 wt % CNTs are made using almost the same protocol. For samples made up of pristine CNTs, the blending time is 24hrs. It should be pointed out that the saturation in

solubility of f-CNTs in epoxy resins occurs at a rather low weight percentage, and the addition of CNTs in an epoxy resin has an increasing impact on the viscosity of the resulting material. Consequently, the workability becomes difficult for weight percentages above 7 % for EPICOTE 1006 A and 5 % for EPON 828. As a result, this represents the upper limit of CNT addition.

5.4 Optical and microscopic characterization

Fig.5.9: Sample on the left contains 0.1 wt % of vertically aligned grown f-CNTs and on the right 0.1 wt % of randomly grown untreated CNTs

There are visible differences between composite samples made of randomly grown CNTs, vertically aligned grown CNTs and vertically aligned grown f-CNTs. As shown in Fig. 5.9, the sample on the right is pale brown and has numerous dark spots while the sample on the left is much darker without any spots. In terms of dispersion,

these two samples represent the two extremes that are realized in this study; that is, CNT bundles and f-CNTs. The cloudy regions which are seen on the left sample are surface irregularities due to the plastic pan in which these few epoxy composite demonstration sample are cured. However, these irregularities disappear when the sample surface is polished (Fig. 5.10a). Moreover, samples cured in the aluminum molds for thermo-mechanical characterization are regular in shape and have uniform surfaces (Fig 5.10b).

Fig. 5.10: Samples of epoxy composite containing f-CNTs. (a) Same sample as the one in Fig. 5.9 left, but after surface polishing. (b) Selection of samples used for thermo-mechanical characterization.

To analyze the dispersed CNTs in the epoxy matrix, several methods are employed:

- Fracture of the composite at room temperature
- Fracture or elongation of the composite at high temperature
- Chemical attack of the epoxy matrix at room temperature
- Chemical attack of the epoxy matrix at room temperature followed by elongation at high temperature

The chemical attack is based on the reaction of epoxies with hydrogen peroxide due to its fair resistance to this chemical. To do so, solid samples of the composite are placed

in a 33 % concentrated hydrogen peroxide solution on an IKA Vibrax® orbital shaker at slow speed for at least 6 hours. The epoxy matrix is attacked by hydrogen peroxide while leaving the CNTs unaffected. Progressively, when the epoxy residues get slowly washed away, the CNT network which is within the matrix stands out. The samples are then dried up in a vacuum oven at 80°C for two hours and analyzed using a SEM.

Fig. 5.11: Room temperature fracture of composite samples made up of randomly grown CNT bundles dispersed in EPON 828 epoxy resin. (a) Non-functionalized. (b) Functionalized. (c) Magnification of (b). (d) Magnification of (c).

The first characterization set concerning the dispersion of CNTs in epoxy matrices is related to the dispersion of randomly grown CNTs. As mentioned before, such CNTs

are entangled similarly to wool balls and it is not an obvious task to untangle them. Fig. 5.11 (a) shows the picture of a composite sample made up of as-grown CNT bundles dispersed in the epoxy by mechanical stirring. It can be observed that the bundles are still present but, more importantly, it can also be seen that the wettability of the bundle surface is relatively poor with respect to the epoxy as shown by the sharp boundary identified by the red arrows. The sample shown in Fig. 5.11 (b), however, consists of the same CNTs but treated following the chemical route described above. Even though, it is clear that bundles are still present in the sample, a change in wettability is visible. At higher magnifications (Fig. 5.11 (c) & (d)), a clear boundary between the CNT bundle and the epoxy matrix is still not apparent.

Fig. 5.12: Room temperature fracture of a composite sample made up of vertically aligned grown and functionalized CNTs dispersed in EPON 828 epoxy resin. (a) Surface of the fractured area. (b) Magnification of (a). (c) Magnification of (b). (d) Magnification of (c).

The same kind of characterization is also carried out on epoxy composite samples containing vertically aligned grown CNTs which are functionalized using the same above mentioned strategy. As shown in Fig. 5.12 (a) and (b), a rough fractured surface is indicative of a tough material. Moreover, no agglomerations of CNTs can be observed while scanning the fractured plane. Furthermore, long single CNTs sticking out of the surface cannot be seen either, indicative of a good CNT to matrix adhesion. The only visible traces of CNTs are the short tips (~ 100 nm) that protrude from the surface (Fig. 5.12 (d)). This kind of CNT pull out is conform to the description of the ineffective length [119] discussed in Chapter 2.

Fig. 5.13: Epoxy composite consisting of f-CNTs dispersed in EPICOTE 1006A epoxy resin. Sample elongated at 150°C. (a) Slit showing CNTs still linking the two sides of the matrix. (b) Single CNT under elongation having 4 different diameters. (c) and (d) Mode I fracturing at the failure zone showing the different deformation stages.

Another approach to analyze f-CNTs in the epoxy matrix is to heat a sample above T_g before fracturing it. In doing so, the matrix is softer and more malleable which favors more plastic deformation before failure. Fig. 5.13 shows examples of such samples which are analyzed along fractured zones. The first remark is about the CNTs that align and remain bonded to both sides of the slit even though the matrix failed (Fig. 5.13 (a)). More interestingly, Fig. 5.13 (b) shows the pulling of a single f-CNT and what can be noticed is a peeling of the nanotube bearing about 4 different diameters. The smallest one ($\phi 4$) can be explained by the inner tubes which are not functionalized on the side walls but may have been functionalized at the tip. Then, in ascending diameter order, the next one ($\phi 3$) may be the outermost functionalized wall to which some epoxy molecules have bonded explaining its relatively big size. However, there is no known mechanism explaining why these epoxy molecules are not interdependent of both the f-CNT and the bulk matrix. Finally, the two other diameters ($\phi 1$ and $\phi 2$) which can be observed are obviously epoxy shells due to their relatively big sizes of about 400nm and 300nm respectively. It appears that the epoxy which is located at the immediate vicinity of the f-CNTs behaves differently from the bulk epoxy.

This remark is more explicitly explained by Fig. 5.13 (d) where the delamination occurring is similar to a Mode I fracturing. Indicated by the red arrow, point (1) shows a CNT which is still inside the matrix at a delaminating interface. Then, in a region where delamination is more significant, point (2) indicates another CNT which is pulled out from both surfaces but still surrounded by the epoxy. Finally, when delamination is even more important, point (3) shows a bare CNT with no more epoxy wrapping it. Thus, point (3) in Fig. 5.13 (d) is similar to ($\phi 3$ and $\phi 4$) in Fig. 5.13 (c)

where the CNTs are almost bare. This situation is not peculiar because it is expected that the CNT delaminates at some point. However, point (2) in Fig. 5.13 (d) is similar to (ϕ 1 and ϕ 2) in Fig. 5.13 (c) where it appears that the surrounding epoxy matrix is more interdependent to the CNT than to the bulk epoxy. Discussions about this phenomenon follow in the next chapter on the mechanical characterization of the composite.

Fig. 5.14: Epoxy composite sample consisting of 5 wt % f-CNTs dispersed in EPON 828 epoxy resin after mild attack by hydrogen peroxide. (a) – (d) Analysis of different areas of the sample.

The rather big diameter pull outs visible during elongation could also be explained by CNT bundles present in the sample. Thus, to unveil this ambiguity, the method adopted is to chemically attack the matrix in order to visualize better the CNT

configuration inside. As shown in the four captions of Fig. 5.14, even in a very dense dispersion of 5 wt % of f-CNTs, the disposition only consists of individual nanotubes surrounded by epoxy. A similar observation is made for samples consisting of 7 wt % of f-CNTs in EPICOTE 1006A (Fig. 5.15 (a) & (b)). By treating the same kind of sample for a longer period in hydrogen peroxide, the f-CNTs can be visualized directly (Fig. 5.16 (a) & (b)). In this case, a very compact network of f-CNTs can be

Fig. 5.15: Epoxy composite sample consisting of 7 wt % f-CNTs dispersed in EPICOTE 1006A epoxy resin. After curing, the sample undergoes mild chemical attack by hydrogen peroxide.

seen with some remaining pieces of epoxy. Here again, it can be deduced that the wettability of the f-CNTs with epoxy is high due to a visible good contact angle between the two species. Moreover, it can also be observed that the CNT network is compact to such a level that there would hardly be free space for more CNTs. That is, this ratio of 7 wt % may not be far from a kind of saturation point beyond which the CNTs may probably bundle again due to a lack of interstitial epoxy resin.

Fig. 5.16: 7 wt % f-CNTs dispersed in EPICOTE 1006A epoxy resin and attacked by hydrogen peroxide after curing. (b) is the magnification of (a).

Fig. 5.17: Epoxy composite sample after prolonged chemical attacked by hydrogen peroxide

Under strong chemical attack by hydrogen peroxide, almost no epoxy matrix remains and the f-CNTs are revealed as a distribution of individual nanotubes (Fig. 5.17). An

interesting observation about this network is that almost no tips are visible. They almost all seem to be trapped in the remaining epoxy matrix. Said differently, the CNT tips tend to retain the epoxy matrix more than the sidewalls. This implies that either the tip has a better wettability than the sidewall or the functionalization of the CNTs is more important at the tips resulting in a good bonding with the matrix. Further SEM analysis indeed shows that the sidewall of straight CNTs have a lesser tendency to be surrounded by epoxy (Fig. 5.18). Greater amounts of residual epoxy are mostly found at the CNT tips (Fig. 5.18 (a) & (b)) and curved sidewalls (Fig. 5.18 (c) & (d)). Thus, this may be an indication that the functionalization method adopted in this thesis essentially attacks the defect sites present on the nanotube, with a lesser tendency to attack the good crystalline parts.

Fig. 5.18: f-CNTs tips (a) & (b) and bent sidewalls (c) & (d) adhering to the epoxy matrix.

Finally, the same method is applied to observe the dispersion of non-chemically treated vertically-aligned-grown CNTs which apart from being blended for a longer time (24 hrs) are processed in the same way as the other composites. The longer mixing time is because, after a few hours, black layers of composite and interlaced transparent epoxy resin are usually still visible. As the target of making pristine CNT / epoxy composite samples is for mechanical characterization comparison, the focus is to achieve a relatively good dispersion even if it is at the detriment of a good process technique. As shown in Fig 5.19, the CNTs seem to be unbundled even if a few bundles can be sparingly seen (Fig 5.19 (b)). Nevertheless, even if the CNTs are densely packed and exhibit some kind of alignment (Fig. 5.19 (a)), the dispersion does not seem to be bad. Thus, the samples are retained for mechanical testing.

Fig. 5.19: Pristine CNTs blended in EPON 828. (a) Dense pack of CNTs with some visible bundles. (b) Closer range showing a bundle on the bottom right.

5.5 Discussion

From the different SEM observations it can be deduced that the covalent functionalization method is able to improve the dispersion of CNTs in an epoxy resin thus resulting in a uniform distribution of fillers in the solid matrix. It can also be

observed that the functionalization seems to improve the surface energy with respect to epoxy. Moreover, the very particular observation made in Fig. 5.13 suggests that the epoxy found in the region surrounding the CNT behaves differently from the bulk epoxy. In a range of several 100 nm the epoxy seems to exhibit like a viscoelastic material which is not characteristic of epoxies. Very recently some research work have been initiated by a few groups to explore the eventuality that the material constituting the matrix indeed forms an interphase around CNT fillers. This possible occurrence is discussed further in Chapter 7 devoted to the mechanical characterization of the epoxy composite.

5.6 Conclusions

A composite material consisting of f-CNTs in an epoxy matrix is prepared by simple stirring of the fillers in the resin. Functionalization is shown to improve the fabrication process of the composite. The single step strategy consisting of mixing a pre-functionalized CNT powder in the epoxy resin can, in principle, be performed at any stage of the fabrication of an IC packaging composite. It does not raise any chemical incompatibility issue with other additives because the chemical property of the CNTs is that of the resin itself. In the next chapters, the mechanical and thermal properties of the composite are measured and analyzed. Moreover, they are compared to the properties of the pure epoxy resin and to the composites made up of pristine CNTs.

CHAPTER 6

MECHANICAL CHARACTERIZATION OF THE COMPOSITE MATERIAL

6.1 Introduction

As mentioned in Chapter 2 it is strongly believed in the scientific community that the two main challenges related to an efficient mechanical reinforcement of CNTs in polymers are first, a homogeneous dispersion of the nano-fillers in the matrices and second, a good interfacial load transfer between the two components. Windle reported though that a too strong interfacial transfer can be disastrous for the reinforcement fillers because, upon strong mechanical stress of the composite, the fillers would break [211]. Moreover, he demonstrates that for very strong interfacial stress transfers the aspect ratio of the fillers does not need to be as high as those of CNTs. Even if the statements are true, the point that should be mentioned is that the composite is not made up of a single nanotube but of a network of numerous nanotubes arranged arbitrarily such that, macroscopically, in any direction there is a huge amount of parallel CNTs which share the load. Moreover, the objective should not only be focused on preserving the fillers but also to conserve the bulk composite. The composite material should be analyzed as a whole, including the epoxy matrix and its mechanical limits. Thus, if in a specific direction the bulk material reaches a loading point where the internal stress distribution is quasi-uniformly equal to a few TPa per CNT without any failure of the matrix, then it can be considered as a good achievement.

SEM pictures show that the chemical treatment improves the dispersion of the CNTs. Moreover, based on the same pictures one can also notice some improvements in epoxy adhesion to the CNT sidewalls. The objective now is to evaluate whether this strategy indeed turns out to be advantageous in terms of bulk mechanical strengthening. A general observation made from the literature is that people very

seldom talk about the nano-scale properties of the composite matrix. In the case of epoxies, it should be pointed out that the pre-polymer molecules present in the resin are of about the same length order as the CNT fillers. This occurring is specific to nano-sized fillers incorporated in macromolecular materials and it is rational to matter about the potential impact that this size correspondence may have on the reinforcing ability of the dual material. Indeed, the interaction between the epoxy molecules and the CNT sidewalls cannot be assumed as being the same as for micro and milli-sized fillers such as carbon fibers. This is the reason why, besides comparing different CNT types (functionalized, pristine,...), two different epoxies are also used for this mechanical comparative analysis. As mentioned before, the only difference between the two epoxies is in the average molecular mass of the pre-polymer. In choosing two epoxies with a remarkable difference in molecular length, the aim is to investigate whether this physical property has an impact on the filler/matrix interface and thus on the mechanical properties of the composite. However, it should be noted that this parameter also has an impact on the viscosity of the resin and this usually results in slight differences in CNT dispersion.

6.2 Dynamic Mechanical Analysis

To evaluate the changes induced by the f-CNT fillers on the mechanical properties of the epoxies, a dynamic mechanical analysis (DMA) is carried out. The equipment used to do this characterization is a DMA Q800 from TA Instruments. DMA is a very useful method to investigate the elastic, elasto-plastic and viscoelastic dynamic characteristics of materials. It consists of evaluating the vibrational response of the material to a forced oscillating movement. More specifically, the configuration used to test the samples is the three points bending beam. This configuration is considered

to be the most accurate method to evaluate the glass transition temperature (T_g) and the storage and loss moduli of strong thermosets [212] at varying temperatures.

Fig. 6.1: Experimental disposition of the sample under test.

T_g is the temperature at which the molecules start having long-range segmental mobility in the amorphous phase of polymers. It is the boundary which demarcates the glass phase of polymers from its rubbery phase. In general, any factor that affects segmental mobility will affect T_g . This includes factors that influence the nature of the moving segment, chain stiffness or steric hindrance, and those that influence the free volume available for segmental motion. The storage and loss modulus represent respectively the portion of the energy stored and lost by the polymer under the application of an external force. The energy stored is related to the elastic behavior of the material and its ability to resist deformations whereas energy lost is associated with heat dissipation of the material and the onset of permanent changes in shape [213]. $\tan \delta$ is defined as the ratio between the storage and loss modulus of the material and thus determines the dynamic behavior of the material.

One important parameter related to the experimental setup used for the test is the geometry factor (GF). This parameter determines the optimal dimensions of the sample to be tested and the best experimental conditions under which the sample should be tested. It is defined by the equipment manufacturer by [214]:

$$GF = \left[\frac{L^3}{48I} + S(1 + \nu) \frac{L}{2A} \right] \quad (6.1)$$

where L is the sample length, I is the geometric moment ($= \frac{1}{12} T^3 W$ for rectangular samples), A is the cross sectional area, ν is the Poisson's ratio, S is the shearing factor (~ 1.5), T is the sample thickness and W is the sample width. Based on the sample dimensions, the GF is of 166. According to the specifications of the equipment, for such a GF, the 3 point bending configuration can measure the modulus in a range going from 10 MPa to 1000 GPa. Moreover, the parameter settings for the DMA are: static force, $F_0 = 1$ N, force track (autostrain) of 150 %, amplitude of 30 μ m, frequency of 1 Hz, temperature range of 25°C to 150°C and a temperature ramping, $K = 3^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. They correspond to the optimal set of parameters recommended by the equipment manufacturer to characterize a high modulus thermoset.

The sample is placed in the isolated DMA chamber (Fig. 6.1) where ambient air is purged and replaced by N_2 . The system is then heated to 25°C and maintained under isothermal conditions during 5 minutes to ensure that the sample is uniformly heated. Then, the oscillating force is applied to the sample and the temperature is ramped up. The oscillating axis which applies the force is also connected to a probe which records the deformations of the sample and the phase difference between applied force and deformation. A purely elastic material has a phase shift of 0° while a purely viscous

material has a phase shift of 90° (See Annex B) and viscoelastic materials have phase shifts in-between these two intervals. Consequently, DMA simultaneously measures the modulus of the material and its viscoelastic properties over a spectrum of temperature.

Fig. 6.2: Storage modulus of epoxy composite samples made up of vertically-aligned grown, untreated CNTs dispersed in EPON 828.

For each epoxy composition, about 10 samples are fabricated and, by visual inspection, the 5 best are used for DMA testing. Then, the mean value of the extracted data is calculated and plotted. Fig. 6.2 shows the storage modulus of epoxy composite samples which are made up of EPON 828 epoxy resin blended with chemically untreated CNTs that are grown by a vertical alignment method. The graph shows that the addition of pristine CNTs indeed raises the modulus of the composite but, by using the volume fraction rule (*described in Chapter 2*), the improvement is not representative of the amount of CNTs added. Moreover, the gradient of the curves for composite samples before T_g do not follow the same trend as the pure epoxy samples.

It appears that the moduli of the composite samples are more sensitive to temperature than the pure epoxy is.

By studying the storage modulus of composite samples made up of f-CNTs (Fig. 6.3), the first comparative observation is that the reinforcement of epoxy composite samples made up of high wt % f-CNT addition (5 wt %) is almost the same as that of pristine CNTs. That is, the relative improvement is not remarkable as compared to low wt % CNT addition.

Fig. 6.3: Storage modulus of epoxy composite samples made up of vertically-aligned grown f-CNTs dispersed in EPON 828.

The slope of the curve for samples constituted of 0.5 wt % f-CNTs is smoother than that of samples bearing 5.0 wt % f-CNTs. This implies that, at low wt % f-CNT addition, the composite is mechanically more resistant during temperature elevation. Moreover, the slope follows the same trend as that of pure epoxy samples, which

means that the limit of the composite material, in this case, is dictated by the limit of the matrix. By comparing these two graphs we thus observe that the chemical treatment applied to the CNTs does not have much impact on the mechanical properties of the composite material at high wt % but it does for lower wt % and more specifically at higher temperatures. Moreover, an additional set of samples made up of only 0.1 wt % of f-CNTs show that for even lower amounts of f-CNTs added, the relative reinforcement is even better in terms of volume fraction addition. The graph shows that at 25°C there is an increase of modulus of 40% which is maintained until 90°C. Using the volume fraction rule, this implies that the tensile strength of the CNT fillers is roughly 2 TPa.

To evaluate whether the trend is the same for an epoxy resin made up of shorter prepolymer strands, the same analysis is made with samples made up of EPICOTE 1006A and f-CNTs (Fig 6.4). As this epoxy resin is less viscous, samples made up of bigger amounts of f-CNTs have also been prepared for comparison. However, even in this case the observation is that big amounts of f-CNTs do not have a big relative reinforcement impact on the composite. For 7 wt % the results are even dramatic with a fall in modulus over the whole temperature spectrum below T_g . Moreover, the relative improvement at 0.5 wt % f-CNT addition is less than those obtained for samples shown in Fig. 6.2 and Fig. 6.3 meaning that, even at low wt % CNT addition, the reinforcement effect is not very good. Nevertheless, at 0.5 wt % the slope of the curve before T_g is flatter than that of the pure epoxy. This implies that, within this temperature interval, the composite is slightly more mechanically resistant during temperature rise. That is, the f-CNTs dictate the composite mechanical property below T_g .

Fig. 6.4: Storage modulus of epoxy composite samples made up of vertically-aligned grown f-CNTs dispersed in EPICOTE 1006A.

From the review paper of Coleman et al. [215] an interesting method is introduced to compare the relative improvement in modulus of composites fabricated using different techniques as it is the case in this thesis. It consists of calculating the increase in modulus with respect to the amount of CNTs added:

$$\eta_E = \frac{(E_c - E_m)}{V_f} \quad (6.2)$$

where η_E is the efficiency, E_c is the modulus of the composite, E_m the modulus of the pure material and V_f is the volume fraction of CNTs added.

Fig. 6.5: Comparative efficiency of the different composites.

When the calculations are made for the samples that are evaluated in this thesis, we observe that the efficiency is indeed better for low wt % of CNT addition (Fig. 6.5). Moreover, the graph also shows that the reinforcement is much better if the epoxy resin is made up of longer pre-polymer molecular strands. Finally, we notice that for 0.5 wt % a slight improvement is also noticed for f-CNTs as compared to pristine CNTs (red arrow). It should be mentioned that the efficiency calculations are based on the moduli at 25°C and that when the same calculations are performed with the moduli at higher temperatures, the relative improvement between 0.5 wt % f-CNTs and pristine CNTs is even more consequent.

As mentioned above, DMA also simultaneously measures the loss modulus of the composite samples. The analysis of the loss modulus leads to useful information about the phase transitions occurring inside the materials. Fig. 6.6 shows the loss modulus of EPON 828 epoxy composite samples containing untreated CNTs. The first

observation is that, at low wt % CNT addition, there is no change in T_g . However, at high wt %, there is a 10°C reduction in T_g . The same cannot be said for EPON 828 epoxy samples containing f-CNTs (Fig. 6.7). Whatever the amount of f-CNT added, between 8 to 10°C reduction in T_g is observed. Even more interestingly, for EPICOTE 1006A epoxy composites containing f-CNTs, there is a monotonous increase in T_g from 44°C for pure epoxy to 60°C for 7 wt % load composite.

Fig. 6.6: Los modulus of epoxy composite samples made up of pristine CNTs in EPON 828. The T_g is indicated by the red dotted line.

Fig. 6.7: Los modulus of epoxy composite samples made up of f-CNTs in EPON 828. The T_g is indicated by the red dotted line.

Fig. 6.8: Loss modulus of epoxy composite samples made up of pristine f-CNTs in EPICOTE 1006A. The T_g is indicated by the red dotted line.

The plateaus before T_g also reveal useful information about the epoxy composite energy loss in plastic deformation. For untreated CNTs in EPON 828 (Fig. 6.6), there is a gradual increase in energy loss while for f-CNTs in the same resin no noticeable energy loss is observed. Peculiarly, for EPICOTE 1006A, at low wt % there is a small raise in energy loss which becomes even more consequent when higher wt % of f-CNTs are added.

6.3 Discussion on experimental results

The experimental results obtained by DMA needs to be discussed further. More specifically, some reflections are needed to draw a physical interpretation from this set of data. Likewise, the conflicting results observed on the mechanical strength improvement of CNTs in polymers have recently started to trigger thoughts. The main discussions converge towards the dominating effects of the interphase present around the CNTs. Windle states that the enormous specific surface area of CNTs implies that the interphase polymer layers which are at the immediate vicinity of the sidewalls finally represent a dominant fraction of the polymer such that, finally most of the polymer matrix thus behaves like an interphase [211]. He also mentions that in the case of crystalline polymers, nanoparticle surfaces can act like nucleation seeds for crystal growth. This is a key point in understanding the mechanical effects induced by the addition of CNTs in polymers and that the nucleation effect may not only be limited to crystalline polymers. Indeed, it is reasonable to think that the relative similarity in dimensions of the pre-polymer molecules and the CNT fillers may finally not only lead to untangling the CNT fillers but also to the ordering of the pre-polymer molecules. That is, during CNT dispersion, the nanotubes that flow through the resin may “comb” the polymer molecules and improve their dispersion. During the

dispersion, the polymer molecules may also wrap the CNTs and the continuous viscous flow probably aligns the molecules around the nanotube. The polymer dispersion and wrapping are very dependent on of polymer properties and more specifically on the length of the polymer strands, their flexibility and adhesion to the surface of the CNTs. This would corroborate with the different trends of change in T_g observed for the various samples. Indeed, the conformation of a polymer has a direct impact on T_g [27]. Moreover, this could also explain why experimental results on modulus tend to vary so much in the literature.

For the composites that are presented in this thesis, even if no dispersion differences are visible by SEM there may be differences in molecular disposition and arrangement of the polymer around the CNTs. These differences should be variations in the way the molecules wrap the CNTs. Long molecules tend to be more flexible and adhere to curved surfaces, leading to helical structures around the fillers. Shorter molecules, on the other hand, tend to be stiffer and to stick to the fillers along the axis of symmetry [216]. Nevertheless, in both cases this polymer adhesion may give rise to an aligned stacking up of molecules around the CNT thus leading to a localized nematic phase in the immediate vicinity of the fillers [217] (Fig. 6.9).

Fig. 6.9: Possible organization of the epoxy pre-polymer molecules around the CNTs. (a) Long pre-polymer strands. (b) Short pre-polymer strands.

The consequence of this polymer arrangement around the molecules is that it may, in turn, lead to tightly packed polymer bundles that exhibit properties different from the bulk polymer. This corroborates with the findings of Brinson et al. about interphase effects between CNT fillers and a polymer matrices [218] who states that the interphase region may be made up of either polymer strands stuck on the surface of the nano-fillers [219, 220], the selective flow of long or short molecular weight molecules to the surface [221] or an altered crosslink density of the surface molecules [222]. Moreover, they also demonstrate that interphases effects are increased if the CNTs are functionalized [223, 224]. As stated by Brinson et al. [218], among the different side effects that may be induced by this eventuality, the most dominating should be:

- An alignment of the pre-polymer molecules around the CNTs,
- An alteration of the cross-linking of these layers during polymerization,
- Sliding of the layers during mechanical stress.

Therefore, in the case of epoxies, a reduction in cross linking combined with an alignment of the molecules may give rise to viscoelastic interphase properties different from the bulk thermoset. Back to the samples, the reason why CNT reinforcement is not efficient for high wt % addition is explained by the overlapping, interaction and destructive interference of the interphases. Indeed, when too much CNT fillers are added in a composite, the minimum amount of matrix material necessary to constitute the interphases is lacking. Thus, the entire matrix has the properties of an interphase, with major alterations in cross-linking. So, the binding role of the epoxy matrix is not properly accomplished.

The discussion that follows on T_g is based on the elements presented by Crowie and Arrighi [225]. T_g in polymers is the temperature above which the molecular chains start having free motion. Even though T_g is not fully understood at the present stage, a lot of information already exists to try to interpret the mechanisms which are responsible for and the factors which affect this transition. Below T_g , polymers are in a glassy state and the molecular chains are fixed so that only intra-molecular motion is allowed. However, as the temperature is raised, the energy absorbed results in a relaxation of the matrix due to an improved mobility of the molecules. As the temperature approaches T_g , the mobility of the chains increases until they are almost free to move under the action of an external force.

Various factors affect T_g in polymer composites. If the polymer matrix is totally amorphous with no degree of crystallization, the chains tend to occupy more space than they would in a semi-crystalline state. This open structure gives rise to free space which allows the molecules to move without restraint and thus favors a low T_g .

However, this same amorphous state is also responsible for a random disposition of the molecules which are thus meshed up and, as a result, lose some degree of liberty to motion thus leading to a high T_g . Therefore, polymer chain conformation results in two opposing phenomena. When CNTs are added to the polymer, the complexity of the system grows. Indeed, as mentioned before, the presence of interphase may reduce the cross-linking density around the fillers and thus lower the T_g . Moreover, as mentioned above, CNTs may also affect the degree of crystallinity of the polymer resulting in the two opposing effects.

If the CNTs are functionalized, the system becomes even more complex because the functional molecules can be responsible of three effects: affecting the cross-linking density, creating surface non-uniformities which result in an increase in matrix/filler frictional force (higher T_g) and allow voids at the interface which favor polymer chain motion (lower T_g). The only difference observed between pristine and f-CNTs in EPON 828 is that a disparity occurs just for low wt % addition, where T_g is lowered for f-CNTs. However, at high wt %, T_g is lowered in both cases. Factors which are responsible for a lower T_g in this case can be either a reduction in the cross-linking density of the polymer matrix or the creation of interfacial voids or both. As the lowering in T_g is also observed for high wt % addition of pristine CNTs bearing no functional molecules and thus no interfacial voids, this is a confirmation that functionalization reduces the cross linking density and thus increases the interphases effects in composites. Indeed, no changes in T_g are observed when 0.5 wt % pristine CNTs are added to the resin while changes are observed when as few as 0.1 wt % f-CNTs are added.

The fact that f-CNT addition increases T_g in EPICOTE 1006A but reduces T_g in EPON 828 can only be explained by a difference in interfacial polymer chain conformation of the two species. Here again, this is the manifestation of an interphase effect where, short chains may probably align along the f-CNTs and thus become nucleation points for crystal formation. The more f-CNTs are added, the bigger is the effect as shown by the monotonous increase in T_g . However, long pre-polymer chains, on the other side, may induce amorphosity in the composite but the effect is not proportional to the amount of f-CNTs added because the base epoxy is already an amorphous material.

Finally, the reason why EPON 828 gives better results than EPICOTE 1006A may be because, as shown in Fig. 6.9, long pre-polymer chains would rather tend to wrap the f-CNTs in a helical manner while short chains would adhere to the sidewalls along the tube. In principle, sidewall alignment should favor interphase sliding. However, helical structures, which have molecular chains almost perpendicular to the CNT axis, should act oppositely by creating resistance to deformation due to increased frictional forces (viscosity). Also, the difference in plateaus observed before T_g is probably because: the low adhesion between the EPON 828 matrix and pristine CNTs results in plastic deformation due to sliding of the fillers in the matrix. However, the good adhesion between the f-CNTs, the interphase and EPON 828 matrix maintain the composite constituents together, allowing only elastic deformation. However, for EPICOTE 1006A, even if there is a good adhesion between the f-CNTs and the interphase, the molecular alignment is prone to plastic deformations when high wt % of fillers are added.

6.4 Finite element model of composite debonding

There are a few models developed to simulate the various mechanical effects induced by the presence of an interphase around CNTs but to our knowledge there is only one which investigates the debonding effects of CNTs due to the difference in adhesion of the interphase. The adhesion between the matrix, interphase and CNT is crucial in determining the reinforcement effects caused by the CNT and the role of the interphase in the system. The model is developed by Needleman et al. [218] and consists of a 2D finite element model of a multi-layer system comprising a CNT and the bulk matrix sandwiching the interphase material. Needleman et al. characterize the CNT as a linear elastic solid while they model the matrix as a von-Mises solid with non-hardening plastic properties for strains of up to about 0.3. The interface, on the other hand, is defined by a varying elastic cohesion relation that depends on the tangential and normal displacement of the CNT. Even if their model gives interesting results about CNT to interphase delamination it does not take into account the possible delamination between the interphase and the matrix. Such an occurring is likely to happen in specific cases where the bulk matrix is made up of a material which does not allow polymer chain flow and the interphase does. Based on the SEM picture shown in Fig. 5.13 (b), it is speculated that this can be the case for the samples made up of f-CNTs in EPICOTE 1006A because the bulk matrix is a cross-linked thermoset and the interphase is probably constituted of aligned pre-polymer molecules with altered cross-linking.

Thus, using COMSOL Multiphysics, a simple model based on the method of Needleman et al. is developed with the following few differences that first, two interfaces are defined and second, the bulk matrix is configured as a thermoset while

the interphase is configured as a thermoplastic (Fig. 6.10). Based on the mean dimensions provided by the CNT manufacturer, the modeled CNT is of 50 nm in diameter and 16 μm long. The thickness of the interphase is quasi-arbitrarily chosen to be 25 nm based only on the observation of the SEM picture. The length of the bulk material is of 20 μm and, as shown in Fig. 6.10, the right side is fixed and a tension is applied to the left side.

Fig. 6.10: Model of a CNT inside an epoxy matrix with an interphase

The corresponding point to point contact surfaces between the layers are determined by creating identity pairs and imprints. However, with this procedure gaps can be formed between the contact surfaces due to the structure of the finite elements. Thus, a parameter called the repair tolerance must be chosen with care to inform the simulator about the maximum allowed gaps during mesh formation. A repair tolerance of $5 \times 10^{-10}\text{m}$ is chosen for this model because it is the best balance between computing time and model accuracy. Smaller values of the repair tolerance do not contribute in improving the accuracy of the model but affect the computing time. The correct determination of the repair tolerance is essential to prevent the different structures to interpenetrate each other during mismatched mechanical displacements. The identity pairs are then configured to become contact pairs by setting the CNT and

matrix surfaces to behave as the master boundaries and the interphase surfaces to behave as the slave boundaries. This choice is based upon the relative difference in mechanical strength of the two interfacial materials and to the most likely resulting deformation tendency when the two materials are sliding on each other.

The whole structure is meshed in triangular finite elements by putting particular emphasis on the interfaces. The contact surfaces of the interface defined as the slave boundaries are designed with a finer mesh size than that of the CNT and epoxy contact surfaces defined as master boundary because it is expected that the viscoelastic polymer will undergo more deformations than the CNT and matrix. The maximum element size of the matrix is 50 nanometers, its element size scaling factor is set to 1, the element growth rate is set to 1.5, the mesh curvature factor is set to 0.6, the mesh curvature cutoff is 0.03 and the resolution of narrow regions is 0.5. Further to that, a refinement of slave boundaries is performed. The maximum element size at the slave boundary is 10 nanometers and its element growth rate is 1.45. The mesh features are chosen such that the maximum element size is at most as big as the diameter of the CNTs, and the special resolution of the model is of the order of the CNT diameter. The system is then solved for static mechanical responses. The solver used is the linear system SPOOLES with a preset relative tolerance of 1×10^{-9} m. In the solver, the damped Newton and augmented Lagrangian solver parameters are also included with a tolerance of 5×10^{-10} m to improve the solving procedure of the software and ensure its convergences.

6.4.1 Modeling results and discussion

By varying the adhesion between the interfaces and the viscoelastic properties of the interphase, the model is solved several times. There is no reason why the cross-linking between the matrix and interphase should not occur. Thus, the matrix / interphase interface is set as good adhesion. Covalent bonding between the interphase and the CNT wall should in principle provide a good adhesion but the sample shown in Fig. 5.13 is prepared at high temperature. Thus, if the interphase is above T_g it is likely that the material has a reduced viscosity. Therefore, both the viscoelastic properties of the interphase and the CNT interface are set with reduced viscosity. In doing so, the simulation result obtained is shown in Fig. 6.11. The three constituting materials have indeed moved with an augmented dislocation of the CNT which pulls out from the interphase. The color code is a rainbow spectrum where blue and red represent a maximum and a minimum displacement respectively. Assuming that the bulk matrix fractures, the result may look quite similarly to the observed SEM.

Fig. 6.11: CNT pull out from the interphase.

Using the same model to simulate the composite made up of f-CNTs and EPON 828 where helical wrapping probably takes places around the CNT, the matrix interface is set with a lower adhesion but the CNT interface is set with a higher adhesion. The reason why the matrix adhesion is purposely set to a lower value than the CNT adhesion is that, due to the probable helical arrangement of the pre-polymer molecules, the cross-linking may be altered. The result is shown in Fig. 6.12 where the color code is a rainbow spectrum representing the stress with red and blue respectively maximum and minimum. The contour bars represent the displacement.

Fig. 6.12: Stress and displacement for an interphase having a good adhesion with the CNT.

If this result indeed represents the real situation, it implies that, even if the adhesion with the interphase is good and that the CNTs take a maximum of load, the matrix interface with the interphase may still be weak. Thus, it would mean that, by improving the CNT interface adhesion, the problem has been slightly displaced a few nanometers away with a weak matrix interface adhesion. Simulations only cannot predict whether this occurring is an advantage because it still provides a way to control interfacial parameters and provide reasonable reinforcement or a disadvantage because the reinforcing effects are too small. The inability of the model to give better predictions is due to the fact that there are too many physical variables that are unknown and given arbitrary values during the simulation.

6.5 Conclusions

In this chapter, epoxy composite materials prepared using various combinations of epoxy resins and CNTs are tested for their thermo-mechanical properties. CNTs improve the mechanical strength of the composite when these conditions are met:

- CNTs are properly chemically functionalized
- Small amounts of f-CNTs are used
- The epoxy resin pre-polymer molecules meet some specific geometrical specifications such as a minimum length

Using small quantities of f-CNT fillers is not only a potential advantage but it also seems to be a constraint due to the apparent inability to put more. The interphase between the f-CNTs and the bulk epoxy matrix has a dominating effect on the composite.

Finally, what can be drawn from this study is that the behavior of CNTs in epoxy matrices is more similar to that of a copolymer system than to fillers incorporated in a binding matrix. The epoxy resin pre-polymer and the CNTs are of about the same length and the chemistry to combine these two constituents is very complex and is yet to be polished up. Moreover, the ratio of the two parts plays a determining role in the outcome of the resulting composite. Thus, we are very far from the science of traditional glass fibers or carbon fibers incorporations in resins. There is still a lot of work to be done to determine whether CNTs can be substitutes for these traditional micro-sized fibers. The intrinsic properties of CNTs are very different from micro-fibers. At the present time, the weaving of CNTs to form micro-sized fibers still seems to be a non-financially feasible option. Moreover, the first attempts reported in the literature do not give very conclusive results.

CHAPTER 7

THERMAL AND ELECTRICAL CHARACTERIZATION OF THE COMPOSITE

7.1 Introduction

In this chapter, a thorough thermal and electrical characterization is performed on composite samples which are fabricated using the procedure described in Chapter 5. The objective is to analyze whether there are changes and improvements in thermal dissipation of the epoxy due to the presence of f-CNT fillers. Moreover, since the application of this research work is to fabricate a good thermally conductive but electrically insulating composite, the dielectric properties are also analyzed. As mentioned before the strategy is to covalently functionalize the CNT fillers so that the electrical conductivity is drastically reduced while still maintaining enough crystal integrity for the heat to be transported by lattice vibration. Thus, what is investigated in this chapter is whether molecular bridges must be set between the CNT fillers and the epoxy matrix in order to ensure a better phonon transport. Therefore, the target is to evaluate if the selective covalent functionalization of CNTs not only prevents electrical transport but also favors the phonon interfacial transport. Consequently, both the chemical attack of the CNT crystal structure and the molecules used to connect it to the matrix are factors which alter the free flow of charge carriers. The mechanical characterization of the composite materials described in the previous chapter shows that the optimal combination of CNT fillers is when less than 1 wt % of f-CNTs is added to EPON 828 (Fig. 6.5). Thus, the samples tested in this chapter respect these conditions.

7.2 Thermal Characterization

To characterize the composite for thermal dissipation enhancement a calorimetric analysis of the different samples using a modulated differential scanning calorimeter (m-DSC) TA 2920 from TA Instruments is performed based on the standardized

ASTM E1952–06 test method. Small shreds of the composites contained in aluminum pans are disposed in the m-DSC under nitrogen gas atmosphere with a gas flow of 50 mL/min. The chamber temperature is equilibrated at 20°C and maintained so during 10 minutes to ensure that the sample is at thermal equilibrium. The temperature is then ramped up at a rate of 3°C /min and sinusoidally varied at a rate of $\pm 3^\circ\text{C} / 100 \text{ sec}$ until the temperature of 120°C is reached. The interval between 20°C and 25°C is not taken into account in the data analysis because it is a period during which the modulation conditions of the equipment are allowed to stabilize.

Fig. 7.1: Specific heat capacity of the composite for different weight percentage of CNT addition.

Fig. 7.1 shows the specific heat capacity (c_p) of the composite containing different amounts of f-CNTs and measured at various temperatures. Even for low wt % of f-CNTs added, an increase in c_p is observed. Most of the curves (except 0.125 and 1 wt %) exhibit the same monotonous trend as the one consisting of pure epoxy. It is deduced that this uniform increase in c_p with respect to temperature is mainly related

to the linear temperature dependence in c_p of the amorphous matrix below T_g [225]. However, for the sample containing 1 wt% of f-CNTs, this different trend is attributed to the CNT-related temperature dependence in c_p which is quadratic until approximately 50°C as reported by [226] and is more visible in this sample due to the bigger amount of CNTs involved. Conversely, it is believed that the distorted curve of the sample containing 0.125 wt % of f-CNTs is related to the 55°C flash point of the epoxy which implies that the samples bearing 0.125 wt % of f-CNTs are not completely polymerized during the curing process.

Fig. 7.2: Isothermal change in specific heat capacity with respect to the f-CNT concentration. Measurements made at 100°C.

In Fig. 7.2 the c_p of the composite is plotted with respect to the percentage of f-CNTs added, measured at 100°C. The isothermal increase in c_p follows a smooth curve which can be split into two regions. A linear fit of each region is shown on Fig. 7.2. The first degree polynomial of each fit is used to identify the c_p of f-CNTs by applying a mass fraction rule. For low concentrations of f-CNTs the calculated c_p is

218.5 J/gK and for higher concentrations $c_p = 51.1$ J/gK, with a threshold of about 0.15 wt %. Thermal conductivity measurements are not possible yet because of a lack of equipment availability to measure the thermal diffusivity. However, the few models that are developed to investigate the effects of an interphase on the thermal transport of CNT composites use thermal conductivity as a comparative evaluation. Thus, it is not possible at the present time to do a convenient fitting of a theoretical model. Nevertheless, the trend of c_p in Fig. 7.2 is the same as the thermal conductivity trend in the model of Seidel and Lagoudas who evaluate the effects of the Kapitza resistance of the interphase on the global thermal conductivity of the bulk material [227]. If thermal diffusivity is assumed to be constant or vary only a little, we can assume that the model would fit the experimental results. However, Kapitza resistance is not enough to give a physical interpretation to this dual slope curve. It is then deduced that this result is most likely to be related to the f-CNT dispersion within the epoxy matrix. Indeed, above the 0.15 wt % threshold, the f-CNT concentration is too high to maintain the existence of a network of quasi-isolated rectilinear f-CNTs. Thus, at this concentration, the formation of dense networks of f-CNTs becomes unavoidable. Consequently, the interphase surrounding the f-CNTs start overlapping and this phenomenon seemingly has a destructive effect on the thermal transport. Therefore, the f-CNTs surrounded by a distorted interphase are less efficient in absorbing the surrounding thermal energy and this has a negative impact on the expected c_p enhancement with respect to the filler concentration. This negative effect on the enhancement in c_p may be due to the disruption in organization occurring on the interphase molecules when they overlap due to CNT proximity, thus leading to phonon scattering. Consequently, the optimal CNT concentration for c_p enhancement

is around 0.15 wt % even if mild improvements can still be obtained above this concentration.

A Raman spectroscopy analysis is also performed to study the vibrational modes of the composite material. The interest is more particularly oriented towards the compatibility in phonon modes between the epoxy matrix and the CNT fillers. Using a Renishaw InVia Reflex Raman Microscope, two different set of samples are characterized at room temperature using a laser of 488 nm wavelength and an objective of 50X. First, the pure epoxy is studied and then a composite sample made of 1 wt % of CNT fillers is analyzed. Fig. 7.3 shows the experimental results obtained for the two samples. The first striking information that can be extracted from the spectrum is that the epoxy matrix has a phonon mode similar in frequency to the G band of the CNTs. Thus, if the interfacial boundary resistance is low, the heat transport taking place along the CNTs via the tangential modes can be transferred to the epoxy matrix without any frequency shifts resulting from phonon-phonon couplings. Consequently, this effect may have a positive repercussion on the phonon mean free path in the composite. The D band of the CNTs in the composite spectrum can also be observed. The relatively large and shouldered D band may indicate that defect sites exist in various forms on the CNTs due probably to the functionalization at these defect sites.

Fig. 7.3: Raman spectroscopy of pure epoxy polymer and f-CNT / epoxy composite.

There is however an unexpected mode that appears in the spectrum of the composite at 1140cm^{-1} . The same peak is observed by Huang et al. [228] and is interpreted as being related to the electron delocalization associated with the presence of polyaniline. In another study performed by Hulman et al. [229], the resonant Raman analysis result in the same phenomenon but the reasons given to justify the band are either a major shift of the G band or a resonant peak unique to the (5,1) chirality of SWNTs. Surprisingly, the same band appears in the Raman spectroscopy of nano-sized diamond but much disagreement occurs in the interpretation of that band. Very diverse interpretations such as a tetrahedrally bonded carbon phase [230, 231], a transverse optical phonon band in amorphous diamond [232], the presence of trans-polyacetylene at the grain boundary of the nano-crystals [233-237], and hexagonal nano-structured diamonds [238] are attributed to that band. It is believed that the very dissimilar context in which the experiments take place may help to dissipate some controversy. Since there is evidently no trace of trans-polyacetylene in the composite,

that interpretation can be phased out, at least in our case. The only common cause that may give rise to such band is, in our opinion, related to the hybridization state of carbon. In this case, the sp^2 hybridization state of some carbon atoms present in the CNTs are altered to sp^3 hybridization due to the covalent bond formation of the grafted functional molecules. However, the shape of those sp^3 carbon atoms is expected to be deformed to a uniform tetrahedral due to the stress induced by the strong honeycomb structure of CNTs. Likewise, in diamond crystals, the sp^3 hybridization state is also expected to be deformed at the surface of the crystal due to a lack of bonding. However, that effect can only start to be detectable when the proportion of surface atoms is roughly the same as that of the core atoms. This very classical effect of nanostructures may bring forward the presence of an intermediate hybridization state between sp^2 and sp^3 as the one modeled by Titantah and Lamoen [239]. Thus, the non-tetrahedral sp^3 bonding states may be responsible for the atypical phonon mode present in both species.

7.3 Electrical characterization

As mentioned above, the objective is to make an epoxy composite with enhanced thermal dissipation properties without losing the dielectric nature of the pure epoxy. Thus, besides going through the thermal characterization of the composite material that is synthesized, some tests to explore any potential changes in electrical properties that may be incurred due to the addition of CNTs are also performed. Using a four point electrical probe, resistivity tests are carried out on the samples. However, all the samples with less than 1 wt % exhibit resistivities which are above $1\text{ G}\Omega\text{m}$ with no breakdown voltage until 80 V. This resistivity being the measuring limit of the

equipment, there is no way to determine the exact value of the resistivity for samples having less than 1 wt %. Thus, such values are not plotted in the I-V curve (Fig. 7.4).

Fig. 7.4: Electrical resistivity characterization of the epoxy composite samples

Moreover, higher potentials could not be tested due to the limit of the signal generator. Since there are no visible changes in surface resistivity as compared to the pure epoxy, A dielectric analysis of a few samples are also performed. Using a dielectric analyzer DEA 2970 from TA Instruments, four thin film squared samples using gold plated electrodes are tested and the change in real and imaginary permittivity over a temperature range of 30°C to 110°C are measured. The samples are tested at different temperatures because of the expected application of the composite. The experiment is performed at frequencies of 1, 10, 100 and 300 kHz with a temperature ramping of 5°C/min. The measured imaginary permittivities for 10, 100 and 300 kHz are all below 0.1 for the whole temperature range and the three curves were almost flat and overlap. However, a more noticeable permittivity variation can be observed for 1 kHz. Thus, the results displayed in Fig. 7.5 only concern measurements made at 1 kHz for

the four samples. The first sample is made up of pure epoxy and the second one consists principally of pristine CNTs which are held together in the form of a film by blending it with a few drops of epoxy. The two other samples consist of an epoxy composite with 0.25 wt % of CNT fillers, one with pristine nanotubes and the other one with f-CNTs. Over that temperature range, the samples are tested for changes in complex permittivity, ϵ^* defined as:

$$\epsilon^* = \epsilon' + \epsilon'' \quad (7.1)$$

where ϵ' is the real permittivity and ϵ'' is the imaginary permittivity [240-241]. The imaginary permittivity is also called the loss factor because it is an indication of a material's electromagnetic waves attenuation capability and is expressed as:

$$\epsilon'' = \frac{\sigma}{\omega \epsilon_0} \quad (7.2)$$

Thus, at constant frequency the electrical conductivity of the material is directly proportional to the imaginary permittivity. Therefore, by comparing the imaginary permittivity of the four samples one is able to evaluate variations in electrical conductivity with respect to temperature and CNT contents.

Fig. 7.5 shows both the real and imaginary permittivity of the samples. While the sample made up essentially of pristine CNTs (pure CNT sample) shows obvious signs of a metallic behavior because of the higher imaginary permittivity, the three other samples are dielectric. However, the addition of pristine CNTs affects the low permittivity of the original epoxy while the addition of f-CNTs does not. As it can be noted from the graph, the use of f-CNTs conversely has a slight beneficial effect on the permittivity of the composite by lowering it as compared to the pure epoxy within some temperature intervals. Thus, the functionalization method developed has a negative effect on the electrical conductivity of the nanotubes both in dc and ac

regimes. This implies that the chemical treatment that has been developed is well adapted to the use of CNT fillers in an epoxy matrix for the fabrication of a dielectric composite.

Fig. 7.5: Comparative permittivity of epoxy composites containing pristine and functionalized MWNTs. A) Real permittivity. B) Imaginary permittivity.

7.4 Conclusions

This chapter devoted to the transport in epoxy composite materials demonstrates that dielectric epoxy composites with improved thermal conductivity and high electrical resistivity can be made by focusing on phonons as a means of heat transport while cutting off electron mobility. To do so, CNT fillers bearing a high thermal conductivity are added to the epoxy matrix without affecting the conductivity of the epoxy matrix. Particular attention is paid to the thermal contact resistance between the epoxy matrix and CNT fillers. Indeed, it appears that the interphase present between the bulk matrix and fillers play a role in the thermal conductivity of the composite. Indeed, covalent molecular links between the matrix and fillers are not enough to enhance the phonon transport. The arrangement of the pre-polymer interphase molecules surrounding the CNTs also impacts on the ability of the nanotubes to diffuse heat. Thus low wt % must also be targeted so that interactions that would tend to disorganize the arrangement of the molecules can be avoided. For 0.15 wt % f-CNT addition, 22 % c_p enhancement is observed.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

A new method is proposed in this thesis to take advantage of the known exceptional mechanical and thermal properties of CNTs as fillers in dielectric epoxy composites for IC packaging applications. The proposed method consists of covalently bonding molecules having the same chemistry as the targeted epoxy matrix so that, during the fabrication of epoxy composite, the CNT interface is more compatible with the epoxy matrix and also takes part in the polymerization process. The precursor used for functionalization is the same as that used in fabricating epoxy pre-polymers. An extensive experimental characterization is also provided in the thesis to prove the occurrence of the functionalization. Moreover, the f-CNTs fabricated prove to be easier to disperse and thus facilitate the epoxy composite fabrication process. However, the observations made from the characterization of the composite material are that the bottlenecks are not only related to the integration process of the CNT but also the properties of the CNT fillers within the matrix. It appears that due to the apparent formation of an interphase during the composite fabrication, restrictions in CNT amount must be obeyed so that the full potential of fillers can be exploited both in mechanical reinforcement and thermal dissipation enhancement. Moreover, it has also been demonstrated that CNT fillers are not suitable for any kind of epoxy resins. Perhaps, this observation may be extrapolated to other polymers. This thesis contributes in giving a better understanding about the most likely constitution of the interphase and its properties.

8.2 Future work

Based on the work presented in this thesis and on literature publications, it appears that there is still a lot of research to be performed before developing a method that can truly exploit optimally the full potential of CNTs. Thorough experimental analysis must still be done to understand even better the mechanisms at the interface of CNTs. Moreover, narrowing down to processes that are industrializable render the development even more difficult. Future aspects of this research work include exploring other chemical routes and observe if these induce potential impacts on the interphase and thus on the bulk composite. Thus, based on the specifications of IC packaging materials, a study must be carried out to explore whether CNTs can indeed be integrated in such composites. Finally, an area which is really interesting and would deserve to be explored, is to consider the addition of small amounts of CNTs in epoxies as that of a copolymer instead of a filler and then to use this material as a base resin to develop new composites with the addition of traditional micro-fibers.

Publications and patent

International Journals & Conferences

- 1 "Nano-tailoring of carbon nanotube as nano-fillers for composite materials applications"
Charles Baudot, Cher Ming Tan, Charles Wang
Nanoelectronics Conference, INEC 2008. 2nd IEEE International, Pages: 570-572 (2008).
- 2 "Solubility, dispersion and bonding of functionalised carbon nanotubes in epoxy resins"
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- 3 "Application of FTIR for the study of functional molecules grafting on carbon nanotubes"
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Patents

- 1 "Epoxy functionalized carbon nanotubes and methods of forming the same"
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Annex A. Fundamentals of Thermodynamics

A.1 Thermodynamic properties of materials - Thermodynamic equilibrium

The equilibrium of a system is an important notion for the experimentalist because it is the only state during which any measurements can be made on the system. A system is said to be in thermodynamic equilibrium if the following three conditions are satisfied:

1. Mechanical equilibrium – All the mechanical forces acting on the system are in equilibrium with the forces exerted by the system.
2. Thermal equilibrium – The macroscopic temperature of the system is uniform so that there are no heat exchanges from one part of the system to another.
3. Chemical equilibrium – The number of particles in each phase is constant in the system.

Reversible changes: A reversible process is defined as one which may be exactly reversed to bring the system back to its initial state with no other changes in the surroundings. Imagine a change in the system which is made in such a way that the system remains in equilibrium at all times. Such a change is called quasistatic. A reversible process involving a large change proceeds through a series of quasistatic states; each change is made so that the system remains in equilibrium at all stages. Undoing the process step by step would return the system to the same original state.

Internal energy: The internal energy, U of an infinitesimal macroscopic system is its total energy measured in a reference space with respect to which the system is at rest. Hence, the internal energy of a system consists of the sum of kinetic energies due to

the motion, translation, rotation and vibration of its constituting particles and the interaction potential energy associated with the interaction of the particles with external or internal fields. The potential energy includes the energy of all the chemical bonds.

Entropy: In classical thermodynamics, entropy, when multiplied by a specific temperature, can be understood as a measure of the amount of energy in a physical system at a specified temperature that cannot be used to do thermodynamic work; *i.e.*, work mediated by thermal energy. More precisely, in any process where the system will give up an amount of energy, its entropy will fall by ΔS , and a quantity of at least $T_R \Delta S$ of that energy will be given up to the system's surroundings as unusable heat (T_R is the temperature of the system's external surroundings). Otherwise the process will not go forward.

In statistical thermodynamics, entropy is defined as a measure of the statistical disorder of the thermodynamic system, the amount of uncertainty that would remain about the exact microscopic state of the system, given a description of its macroscopic properties. It can be shown that this definition of entropy reproduces all of the properties of the entropy of classical thermodynamics.

A.2 Laws of thermodynamics

Zeroth law: If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.

First law: At macroscopic equilibrium the total internal energy of an isolated system is constant.

$$U = \text{constant} \quad (\text{A.1})$$

If the system is allowed to interact and thus goes from one macroscopic state to another, the resulting change in internal energy is written in the form:

$$\Delta U = -W + Q \quad (\text{A.2})$$

where W is the macroscopic work done by the system as a result of the system's change in external parameters and Q is the heat absorbed by the system.

Second law: In any process in which a thermally isolated system goes from one macrostate to another, the entropy tends to increase:

$$\Delta S \geq 0 \quad (\text{A.3})$$

If the system is not isolated and undergoes a quasi-static infinitesimal process in which it absorbs an infinitesimal amount of heat dQ , then

$$dS = \frac{dQ}{T} \quad (\text{A.4})$$

where T is a quantity characteristic of the macrostate of the system and is called the absolute temperature of the system.

Third law: The entropy of a system has the limiting property:

$$\lim_{T \rightarrow 0^+} S = S_0 \quad (\text{A.5})$$

where S_0 is a constant independent of all parameters of the particular system.

A.3 Extensive and Intensive parameters

If a system is doubled, all parameters that are also doubled are said to be extensive.

However, all those which remain the same are said to be intensive.

Fig. A.1: Extensive and intensive parameters of a thermodynamic system.

As shown in Fig. A.1, V and N are extensive parameters. V/N and T are intensive parameters.

A.4 Equations of state

A system in equilibrium can be fully described using the three variables S , V and N .

From those, we can write a function that will relate the state of the system. The partial derivative of the function of state of the internal energy $U(S, V, N)$ is expressed by:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,N} dS + \left(\frac{\partial U}{\partial V} \right)_{S,N} dV + \left(\frac{\partial U}{\partial N} \right)_{S,V} dN \quad (\text{A.6})$$

from which we can define three state variables using the equations of state:

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \quad \mu_e = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (\text{A.7})$$

Thus,

$$dU = TdS - pdV + \mu_e dN \quad (\text{A.8})$$

If two systems are in thermodynamic equilibrium, their three intensive parameters T , p and μ remain the same. Such a function contains all the information to describe the

state in which a system is. However, it is not always practical to work with such parameters. So, it is often useful to describe other functions of state.

By making a Legendre transformation between two conjugate variables in Eqn. A.8, other state functions can be derived. These state functions also contain all the information about the equilibrium state of a system but for different sets of parameters.

The free energy, F

$$F(T, V, N) = U(S, V, N) - TS \quad (\text{A.9})$$

Thus,
$$dF = -SdT - pdV + \mu_c dN \quad (\text{A.10})$$

Enthalpy, H

$$H(S, p, N) = U(S, V, N) + pV \quad (\text{A.11})$$

Thus,
$$dH = TdS + Vdp + \mu_c dN \quad (\text{A.12})$$

Free enthalpy, G (Gibbs enthalpy)

$$G(T, p, N) = F(T, V, N) + pV \quad (\text{A.13})$$

Thus,
$$dG = -SdT + Vdp + \mu_c dN \quad (\text{A.14})$$

Grand potential, J

$$J(T, V, \mu) = F(T, V, N) - N\mu_c \quad (\text{A.15})$$

Thus,
$$dJ = -SdT - pdV - Nd\mu_c \quad (\text{A.16})$$

A.5 Heat capacities

It is sometimes more convenient to express the internal energy, U in terms of the three independent variables T , V and N . However, as T is not a state variable of U , the function does not contain all the information about the equilibrium state of the system. Nevertheless, such a formulation makes experimental measurements more obvious.

$$dU(T, V, N) = \left(\frac{\partial U}{\partial T} \right)_{V, N} dT + \left(\frac{\partial U}{\partial V} \right)_{T, N} dV + \left(\frac{\partial U}{\partial N} \right)_{T, V} dN \quad (\text{A.17})$$

Three new partial derivatives are thus introduced in this expression, the first one being extensive and the two others intensive. The first one is called the specific heat at constant volume (also called the calorific capacity at constant volume):

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{V, N} \quad (\text{A.18})$$

It is a measure of the variation of the internal energy for a variation in temperature of a closed system. It is often expressed in a normalized way:

$$c_v = \frac{C_v}{N} = \frac{1}{N} \left(\frac{\partial U}{\partial T} \right)_{V, N} = \left(\frac{\partial u_N}{\partial T} \right)_{v_N} \quad (\text{A.19})$$

However, it is sometimes more convenient to measure the heat capacity at constant pressure. In liquids and solids for example, the change in pressure that is necessary to maintain the volume constant can be very high. Thus, instead of maintaining the volume constant, the pressure is kept constant. To obtain an expression of the heat capacity at constant pressure, enthalpy must be expressed as a function of T , p and N . Here again, that function does not contain all the information about the system because T is not a state variable of H .

$$dH(T, p, N) = \left(\frac{\partial H}{\partial T} \right)_{p, N} dT + \left(\frac{\partial H}{\partial p} \right)_{T, N} dp + \left(\frac{\partial H}{\partial N} \right)_{T, p} dN \quad (\text{A.20})$$

From that relation, we define the first partial derivative as the specific heat at constant pressure (also called the calorific capacity at constant pressure):

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{p, N} \quad (\text{A.21})$$

The connection between C_p and C_v can be made using the Clapeyron relation:

$$C_p - C_v = \frac{\alpha^2 TV}{\beta_T} \quad (\text{A.22})$$

where α is the coefficient of thermal expansion, and β_T is the isothermal compressibility of the material.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (\text{A.23})$$

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (\text{A.24})$$

It can be noted that for an ideal gas, the relation is simplified to:

$$c_p - c_v = k_B \quad (\text{Mayer relation})$$

where k_b is the Boltzmann constant.

Annex B. Mechanical properties of materials

B.1 Permanent deformation - The tension test

The objective of performing the mechanical analysis of a material is to determine the temporary or permanent structural changes that are incurred on it as a result of an external force. There is a series of different cases that should be considered in the course of such a study. Each case distinguishes itself by relating a unique structural evolution to specific external conditions. A material that restores to its original morphology after the action of a temporary force is said to undergo elastic deformation. In most cases, this material feature may imply that no alterations have occurred in the material and this aspect is of crucial importance under consideration during materials development.

Besides analyzing the extent under which a material behaves elastically, another important feature is to explore the response of the material when it goes beyond that point. Different materials behaviors can follow, ranging from complete rupture to permanent deformations. A material that undergoes permanent changes in shape is said to behave plastically. The characterization of such a property is generally performed by proceeding to a tensile test of a specimen of the material. It consists of applying a tensile stress, σ on a uniform sample and raising it gradually while measuring the resulting strain, ϵ . It is very difficult to pin point the exact moment at which a material shifts from an elastic behavior to a plastic behavior because this transition is very gradual. Thus, another strategy commonly used is to distinguish

between those two different materials properties and the localization of that specific in-between turning point as the yield strength (σ_y). It consists of drawing a line parallel to that of the linear elastic regime with an offset of typically 0.2% in the strain and determining the point at which this line cuts the stress-strain curve (Fig B.1).

Fig. B.1: Determination of the yield strength of a material.

Fig. B.2: Plastic flow of a material beyond the yield length.

Beyond the yield strength, any increase in tensile strain is associated with an increase in tensile stress. This phenomenon is a consequence of the material's resistance to plastic deformation and it is referred to as the work hardening of the material. The material will undergo such a plastic flow with an increase in tensile stress up to a limit

referred to as the tensile strength (Fig. B.2). Past this point the material experiences elongation more and more easily until the fracture point

B.2 Fluidic properties of materials

Some solids such as most metals do not undergo a lot of plastic deformation. The yield strength of these solids is very near to its tensile strength which in turn is also near to its fracture point. However, other solid such as polymers can experience a wide stage of plastic deformation. During this stage, the polymer molecules flow through the solid resulting in a permanent reorganization of its internal structure which accounts for the permanent deformation. This macro-molecular flow does not occur without any resistance though. Besides the fact that the polymer molecules are meshed up together, there are also dipole forces of attraction that oppose to molecular circulation. To describe this phenomenon, it is necessary understand first some aspects of fluidic flow.

B.2.1 Viscosity

In order to understand the viscosity of a flowing fluid, the simplest case is to consider a purely viscous laminar flow.

Fig. B.3: Definition of the viscous flow of a material.

To model the flow of such a fluid, we consider that it is made up of a series of layers, each flowing at a different rate following a velocity gradient oriented in the y -axis direction. As shown in Fig. B.3, at a point y , the velocity is $u = dx/dt$ and at $y + dy$, it is $u + du$. The displacement gradient of the fluid, also oriented in the y -axis direction is called the **shear strain** and is denoted by the annotation γ .

The rate at which the shear strain changes, denoted $\dot{\gamma}$, is in this case:

$$\dot{\gamma} = \frac{d}{dt}(\gamma) = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{d}{dy}\left(\frac{dx}{dt}\right) = \frac{du}{dy} \quad (\text{B.1})$$

Another important property to describe a viscous flow is the shear stress, denoted τ , which is defined as the force acting on the fluid divided by the cross-sectional area of a layer.

$$\tau = \frac{F}{A} \quad (\text{B.2})$$

finally, the last definition is the viscosity, denoted η , which is described as being the ratio of the shear stress to the shear rate:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (\text{B.3})$$

For Newtonian fluids, η is a constant of linear proportionality:

$$\tau(\dot{\gamma}) = \eta \dot{\gamma} \quad (\text{B.4})$$

Fluids which do not obey Newton's model are known to be either dilatant (shear-thickening) or pseudoplastic (shear-thinning) (Fig. B.4).

Fig. B.4. Graph showing the behavior of different viscous materials.

There is also another category of fluids the viscosity of which exhibits a reversible time dependant behavior. When a shear stress is applied on the fluid the viscosity will change until the force applied is stopped. The term used to denote a fluid whose viscosity rises is rheopectic and the term used to denote one that falls is thixotropic (Fig. B.5).

Fig. B.5: Graph showing behavior of time dependant viscous materials.

B.2.2 Viscoelasticity

Linear viscoelasticity is the simplest form of combined viscosity and elasticity. Because a wide range of materials exhibit both properties, it is essential to understand how to merge those behaviors in a single model. Many materials, however, can be accurately modeled only by using complex combinations. Nevertheless, in order to describe the basics of the interaction between viscosity and elasticity in a material, a simple model is enough.

It is often very convenient to describe a material in terms of basic mechanical objects. To describe an elastic and a viscous behavior, respectively, a spring and a dashpot can be used (Fig. B.6). The pure linear elastic deformation and linear viscous flow can be thus expressed as using those two objects.

Fig. B.6: Two simple mechanical objects used to describe the elastic and viscous behavior.

So, to describe the mechanical response of a material to a linear shear deformation, a combination of both models can be used by putting a number of each object in a network of series and parallel arrangements. A simple arrangement consists of putting two of them in series in the, so called, Maxwell element (Fig. B.7).

Fig B.7: Maxwell element showing a spring and a dashpot in series.

The shear strain of the element is:

$$\gamma = \gamma_{dashpot} + \gamma_{spring} \quad (B.5)$$

The shear rate is:

$$\dot{\gamma} = \dot{\gamma}_{dashpot} + \dot{\gamma}_{spring} \quad (B.6)$$

$$\Rightarrow \dot{\gamma}(\tau) = \frac{\tau}{\eta} + \frac{\dot{\tau}}{G} \quad (\text{B.7})$$

B.3 Deformation of materials

When a force is exerted on a material, there is a work done on it. Depending on the nature of the force, F the expression of the work done is as shown in Fig. B.8, B.9 & B.10.

B.3.1 Shear

Fig. B.8: Definition of the shear stress applied on a material.

B.3.2 Uniaxial tension

Fig. B.9. Definition of the tensile stress applied on a material.

B.3.3 Isotropic compression:

Fig.B.10: Definition of the isotropic compression applied on a material.

From the first law of thermodynamics, the differential form of the internal energy is:

$$dU = TdS - dW + \mu dN$$

If no matter is lost or gained, $dN = 0$. So, if we combine the different expressions of work done, we obtain:

$$dU = TdS - pdV + Fdl + V \tau d\gamma \quad (\text{B.8})$$

If we consider the case of pure isotropic compression, then it follows that $d\gamma = 0$. Because the change in length is already accounted in the change in volume, $dl = 0$. So, we end up with a simple expression from which two partial derivatives can be deduced:

$$dU = TdS - pdV \quad (\text{B.9})$$

$$\Rightarrow p = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T \quad (\text{B.10})$$

These equations indicate that there are two terms contributing to the isotropic pressure: the first one is related to the internal energy of the molecules of the material. This storage of energy is in the form of intermolecular elastic translations, vibrations and rotations. The second term is related to the change in entropy of the system. Under compression, the ability of the molecules of the material to move to different configurations will decrease. Thus, some of the entropy of the system will be lost. These microscopic concepts about energy storage and loss, introduce the notions of storage and loss modulus.

B.4 Dynamic properties of materials

An important aspect about materials is its response to a continuously varying external environment. This situation is often met in IC packaging due to the variations in stress and thermal situation resulting from the operation of the IC. Thus, it is necessary to understand how to characterize materials properly in dynamic environment.

B.4.1 Dynamic mechanical testing

By applying a variable strain to a material, the response of the latter can give very interesting information about its viscous and elastic properties. For example when a sinusoidal strain is applied to a purely linear elastic material:

$$\gamma = \gamma_o \sin \omega t \quad (\text{B.11})$$

where ω is the angular frequency and γ_o is the amplitude of the strain, the resulting stress will be:

$$\tau = G \gamma_o \sin \omega t \quad (\text{B.12})$$

in phase with the strain. However, if the same strain is applied to a purely linear viscous material, the stress will be:

$$\tau = \eta \omega \gamma_o \cos \omega t \quad (\text{B.13})$$

90° out of phase of the strain. For a material which exhibits both properties, the response will be in between these two limits. Thus, to express the full mechanical response of such a material, both components must be taken into account. A very suitable way to do so is to use the complex notation:

$$\tau^* = \tau' + i \tau'' \quad (\text{B.14})$$

where τ^* denotes the complex stress of the material, τ' is the in-phase stress and τ'' is the out of phase stress. Similarly, the complex modulus is defined as:

$$\begin{aligned} G^* &= G' + i G'' \\ &= \frac{\tau'}{\gamma_o} + i \frac{\tau''}{\gamma_o} \end{aligned} \quad (\text{B.15})$$

and the complex viscosity:

$$\begin{aligned}
 \eta^* &= \eta' - i\eta'' \\
 &= \frac{\tau^*}{\dot{\gamma}_0} \\
 &= \frac{\tau'}{\dot{\gamma}_0} - i \frac{\tau''}{\dot{\gamma}_0}
 \end{aligned}
 \tag{B.16}$$

where $\dot{\gamma}_0 = i\omega\gamma_0$. The term G' is referred to as the storage modulus and it represents the energy stored elastically in the material. The term G'' is referred to as the loss modulus and accounts for the energy lost in terms of heat dissipation by the material. Another quantity that can be defined from this study is the loss tangent (also called *tan delta*):

$$\tan \delta = \frac{\tau''}{\tau'} = \frac{G''}{G'} = \frac{\eta''}{\eta'}
 \tag{B.17}$$

which is the phase difference between the storage modulus and the loss modulus.