Universitatea *Transilvania* din Braşov

HABILITATION THESIS

Tailoring the effective properties of hybrid polymer based composite materials

Domain: Mechanical Engineering

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Abstract

The overall aim of the work is to provide comprehensive means of predicting and characterizing the properties of principal hybrid polymer based composite architectures that can simultaneously yield results of practical utility. This is accomplished by comparing, whenever possible, the theoretical predictions for the effective properties to available experimental data.

The present work is divided into two parts. Part I deals with the author's scientific achievements that enabled to characterize quantitatively the main effective properties of self-developed hybrid polymer based composite architectures and different theoretical and computer-simulation methods used for comparison. Part II describes the author's scientific backgrounds in connection with the approached subject and identifies future directions for professional and academic evolution and development.

The introductory chapter in Part I was reserved to the state-of-the-art in the subject intended to be covered with the main body of the habilitation thesis. This was done on purpose to illustrate the importance of developed subject that is under continuous evolution and that expanded after herein author's first contributions. It is noteworthy that significant advances have been made recently in the quantitative characterization of hybrid composite materials of any type both theoretically and experimentally.

The general objectives were underlined and concise delivered to give the reader a preview of the concepts that will be discussed specifically in the subsequent chapters. Indirectly, they point toward one of the main aims of this work, namely to provide a direction for systematically analysis of hybrid polymer based composite materials.

Chapter 2 was dedicated to the brief presentation of individual materials' selection, manufacturing issues, details on hybrid microstructures and finally, some practical information on experimental devices and settings considered. Practically, reproducibility issue of the experimental data processing can be potentially addressed through sharing these particular information results.

Chapter 3 provides a review of the theoretical models used deploying a multi-step homogenization scheme, particular developed by the herein author, to apply for individual combinations and effective property under consideration. These theoretical models were selected due to their ability to describe the 'details of the microstructures' (i.e. constitutive volume fractions, orientations, sizes, shapes, spatial distributions and surface areas of interfaces, etc.) and ability to encompass particular information that can be ascertained in practice.

In the light of above, particular concerns was given to those structure/property relations that can be easily understood by apprentices, unaccustomed researchers on engineering field and finally, to materials' designers bounded by cost and time to perform measures on their mechanical applications for all possible combinations, phase properties and microstructures aimed to be developed.

Chapter 4 extensively approaches the effective mechanical, dynamical, linear thermal expansion and thermo- and electrical conductivities of particular hybrid polymer based composites developed. These effective material properties were retrieved by subjecting the various hybrid composite specimens to extreme environmental temperature range to address the sustainability issue and some practical implementation considerations.

Over the entire sections of this chapter was followed the same formalism, including: section's objectives, applied standards used to run the exploratory tests, particular and representative experimental curves, details on the retrieved values, predicted over recovered data comparison relevant for the effective property vs. micro-structural dependence description and analysis.

Structural design and applications emerging from this cannot be sough strictly to comply or use solely the mechanical properties. In the mechanical engineering field, the applications are driven by a multitude of influencing factors whose cross-dependencies can be regarded to the seemingly different effective properties considered here.

Moreover, the experimental data can be effectively translated to practice and have important implications for the optimal design of composites. Space limitations and overcome the settled objectives do not enable us to treat, in any detail, the cost and error minimization topics identified as the major issues that benefit from the herein retrieved information.

General conclusions presented in Chapter 5 provide the merits of the theoretical predictions, the main reasons behind the effective property's behavior during the conditions imposed within the experimental runs and a unified framework to study a variety of different hybrid composite architectures with their tailored effective properties.

Additionally, these can be regarded as an ex-ante foundation and conditionality for further hybrid polymer based composited architectures tailored from natural reinforcements and matrices under the so called 'green' composites material category. In the light of previous mentioned and with respect to the effective properties of hybrid polymer based composites, further directions for scientific research were identified and briefly described at the beginning of Part II of the work.

Specific citation to the literature used, both own published contributions between 2006 to 2015 and other sources have been kindly provided at the end of Part II as references. These were used in correlation to the section's subject and can be easily identified and suitable checked. It is noteworthy that few sections contain unpublished work of undersigned used to clarify some aspects related to the effective property under discussion and provided to enable readers to comprehend the ongoing discussions and related conclusions.

Rezumat

Teza de abilitare a fost elaborată în vederea furnizării unei perspective de abordare sistemică a principiilor și metodelor de identificare și caracterizare a proprietăților de material pentru anumite clase de compozite polimere hibride cu potențial de utilizare într-o gamă largă de aplicații inginerești. Din considerente practice, selecția constituenților și a arhitecturilor claselor reprezentative de compozite hibride s-a efectuat ținând cont de experiența autoarei și a rezultatelor preliminare obținute din simulări numerice.

Lucrarea este structurată în două părți. Partea I prezintă rezultatele științifice ale autoarei ca urmare a derulării cercetărilor experimentale în vederea determinării proprietăților claselor de structuri compozite polimere hibride elaborate coroborat cu rezultatele simulărilor numerice utilizând modele teoretice multi-scalare. Partea II cuprinde o descriere succintă a realizărilor din perspectiva contribuțiilor științifice materializate în lucrări științifice, prezentări publice, cărți/capitole care au permis identificarea unor potențiale direcții de cercetare și evoluție profesională.

Capitolul 1 conține aspecte ce vizează dinamica principalelor problematici abordate în literatura de specialitate în strânsă corelație cu subiectul tezei. Scopul principal a vizat oferirea unui referențial pentru subiectul abordat dar și sublinierea importanței acestuia ce poate fi evidențiat prin lucrările de specialitate apărute în ultimii ani.

În cadrul aceluiași capitol au fost enunțate concis obiectivele generale ale tezei de abilitare pentru a permite o vedere de ansamblu asupra conceptelor care vor fi detaliate în cadrul lucrării și a scopului principal pentru care aceasta a fost elaborată, și anume analiza proprietăților de material a principalelor clase de compozite polimere hibride.

Capitolul 2 a fost rezervat prezentării succinte a principalelor aspecte cu privire la selecția constituenților, tehnologiilor de fabricare utilizate, particularităților micro-structurale și echipamentelor de testare experimentală suplimentate cu condițiile de utilizare prestabilite. Detaliile oferite sunt conforme cu deontologia cercetării științifice care presupune furnizarea de informații care să permită reproductibilitatea datelor furnizate.

Capitolul 3 a fost destinat principalelor modele teoretice utilizate în procedurile de omogenizare multi-fază elaborate de către autoare pentru analiza diverselor combinații de arhitecturi hibride și estimarea proprietăților acestora. Modele teoretice au fost riguros selectate datorită capacității acestora de a încorpora detalii cu privire la microstructura materialelor (ex. concentrația constituenților, dimensiune, formă, distribuție, etc.) dar și a unor informații suplimentare cu relevanță în utilizarea aplicativă a acestora.

Suplimentar, s-a acordat o atenție deosebită prezentării acelor relații de dependență structură/proprietate care pot asimilate și înțelese cu ușurință de către doctoranzi și tinerii cercetători, dar și de către inginerii proiectanți care nu au posibilitatea de a realiza și testa practic combinațiile de materiale ce se urmăresc a fi utilizate în structurile mecanice vizate.

Capitolul 4 abordează detaliat proprietățile mecanice, dinamice, termice și electrice ale materialelor compozite polimere hibride elaborate. Suplimentar, au fost evidențiate și modificările induse de condiționarea eșantioanelor față de anumiți factori de mediu în scopul clarificării anumitor aspecte de ordin practic și evidențierii sustenabilității acestora.

Structura capitolului a fost concepută astfel încât informațiile detaliate să fie prezentate conform următorului formalism: enunțarea obiectivelor pentru fiecare categorie de proprietate de material abordată → specificarea standardele utilizate în derularea testărilor experimentale → reprezentări grafice ale proprietăților și variații ale acestora în funcție de anumiți factori de influență → furnizarea de valori experimentale pentru justificarea afirmațiilor și observațiilor → comparații teoretico-experimentale relevante pentru proprietatea de material în funcție de anumiți descriptori micro-structurali.

În acest context, este imperativ să se țină cont de faptul că atât etapele de proiectare/modelare a structurilor mecanice și implementarea practică efectivă a acestora nu mai pot fi abordate strict dintr-o perspectivă restricționată la proprietăților mecanice ale acestora. Aplicațiile din domeniul ingineriei mecanice sunt condiționate de o multitudine de factori de influență care aparent nu au nimic în comun cu tipul de proprietăți de material prezentate în această lucrare dar cu care, în realitate, se află într-o strânsă dependență.

Suplimentar, datele experimentale prezentate în acest context pot fi efectiv transpuse în practică și prezintă implicații majore în proiectarea optimală a materialelor compozite. În acest context, se impune menționarea faptului că în cadrul lucrării nu au fost abordate aspecte cu privire la componenta financiară pentru dezvoltarea acestor tipuri de compozite hibride și nici cele cu privire la modul de minimizare a erorilor de proiectare, identificate ca cele mai stringente aspecte care se impun a fi tratate în conjuncție cu subiectul acesteia.

Concluziile generale prezentate în cadrul Capitolului 5 evidențiază caracterul unitar al lucrării prin reformularea succintă și particularizată a celor mai importante rezultate obținute în urma testărilor și comparațiilor teoretico-experimentale, rezultate care pot fi utilizate în studiul unei game diverse de compozite polimere hibride cu proprietăți de material impuse.

Complementar, acestea pot fi catalogate ca fiind fundamente și condiționalități pentru clasa de compozite hibride armate cu constituenți și rășini polimere naturale și care constituie una dintre tendințele din domeniu. În aceste circumstanțe, identificarea și prezentarea unor potențiale direcții de cercetare viitoare, așa cum au fost descrise succint în partea introductivă a celei de-a doua părți a lucrării, s-au dovedit a fi o consecință firească.

Referințele bibliografice utilizate, care includ atât publicațiile autoarei între anii 2006 și 2015 cât și a altor cercetători, au fost furnizate la finalul lucrării. Acestea sunt în strânsă conexiune cu subiectul abordat și pot fi identificate cu ușurință în fluxul publicațiilor din principalele baze de date. Anumite date nepublicate de autoare au fost incluse deliberat pentru a permite înțelegerea afirmațiilor și concluziilor prezentate la acea categorie de proprietăți.

Contents

Part I. Scientific and professional achievements

Scientific and professional achievements

The main research and scientific achievements of herein undersigned cannot be viewed without accounting the approaches within the PhD thesis delivered by the same author, entitled ‘*Contributions to the analyzing the correlations between the tension level and the physical properties characteristic of certain materials by using non-destructive testing methods (sound, visual)*’.

The overall systematic study and outcomes of above enabled development of research skills, interest for composite materials from both processing and testing perspectives, enabling thus all the scientific achievements that naturally followed. It was clear that performing measurements on materials for all possible constitutive properties and microstructure is prohibitive due to time and cost. Hence, theoretical methods and techniques were needed to be deployed to provide a systemic approach of the composite classes’ material properties.

In the light of the importance of determining the effective properties of polymer based composites, a vast body of literature has evolved based on direct measurements and theoretical techniques. Some of them will be referred in the subsequent chapter in relation to the subject of this habilitation thesis to give the reader a framework to acknowledge the importance and prevalence of the novelty of this particular work beyond the time scale of reporting.

The ability to tailor hybrid polymer composites with a unique spectrum of properties taking advantages of structure/property relations and wide deployed measuring techniques represents the chief aims of this habilitation thesis and has important implications for improved materials, their processing and engineering applications.

Many of the models, methods and results in this habilitation thesis were developed during the last decade and published as referred throughout the subsequent chapters of part I. Space limitation does not permit us to treat, in any details, cases in the elasticity and conduction issues in which the multiphase interfaces of the hybrid composites are characterized as imperfect or no ideal. These will remain to be developed somewhere into the future proven the maintained interest on the subject.

From the design and practical standpoints, it is desirable to understand the importance of effective material properties measured values and their dependence on structural levels, details on their microstructure and individual constitutive, environmental conditioning and other influencing factors. Indeed, the latest numerical predictions around the mechanical structures made of polymer composite materials emphasized the idea of achievable error minimization through using the measured effective material properties.

Finally, with respect to the academic and professional achievements, these will be detailed in part II of the work since these are closely to the mid and long term intentions for career development.

Chapter 1 – 'State-of-the-art' related to the approached subject

Research is to see what everybody else has seen, and to think what nobody else has thought.

Albert Szent - Gyorgyi

1.1 Designing hybrid polymer composite materials

Research conducted on hybrid composites, predominantly based on intermingled carbon and glass fibre fabrics, can be traced back to the early 1970s, from the work of Bunsell and Harris (1974) or Summerscales and Short (1978, 1980), that were among the first in the investigation of the mechanical properties of various material combinations in view of their prospective use as lightweight load bearing composite structures [1-3]. Since then, a variety of combinations emerged as viable architectures to produce fibre reinforced polymer (FRP) composites.

Literature is abundant in references on hybrid composite materials, generally, and polymer based, particularly. Ashby (2003, 2011) is one of the scholars who succeeded to define and formulate concisely the concept of hybrid materials – "combinations of two or more materials assembled in such a way as to have attributes not offered by either one alone" [4, 5]. In addition, he underlined the ingredients to be used in hybrid material design, including: the choice of materials to be combined, their configuration, their relative volume fraction and the scale length of the structural unit.

One may acknowledge the prevalence of three types of hybridization architectures regarded as *interlayer*, *intralayer* and *intrayarn*. The interlayer hybridization implies reinforcement mixing on the layer level while the intralayer configurations within each layer. The first architecture is the most common configuration as it handy to be manufactured. On the other hand, the latter is rather difficult to be produced but proved to yield improved mechanical properties as reported by Pegoretti et al. [6] and Fukunaga et al. [7].

In the light of above, numerous combinations emerged and studied by researchers from property prediction point of view, cost and performance, behavior under various loading conditions and application potential based on different scenarios. With respect to the latter, "the best of both", "the rule of mixtures", "the weaker link dominates" and "the least of both" were the main scenarios that emerged in the attempting of answering the questions arose: What is a hybrid material? When is hybrid a material? How does it behave while subjected to a certain loading condition?

One of the first review on hybrid composites was written by Kretsis in 1987 [8]. The author focused especially on hybrid composites based on epoxy resins reinforced with synthetic fibers, carbon and glass, especially continuous and unidirectional oriented, from effective mechanical properties of view.

Since then, a wide range of materials was found to challenge the benchmarks. Thus, natural constitutive were preferred and leading the last decades of research as direct consequence of focused concerns about environmental issues. In addition, they naturally followed the searching for an answer to the question: “Are natural fiber composites superior to glass fiber reinforced composites?” [9-11].

One of the fundamental parameters in the hybrid polymer based composites design is the *hybrid ratio* that is acknowledged to have a direct influence on the overall performance of structure. This is intimately connected to the *hybrid effect* that is generally assessed while approaching such materials’ architectures.

Noteworthy, the most comprehensive and employed definition of the hybrid effect was given by Marom et al. in 1978 [12]. According to their findings, deviation from linear rule of mixtures (RoM) can be modified to be used to predict a large spectrum of mechanical properties in addition to the failure strain. Consequently, positive and/or negative hybrid effects result from these predictions and used to quantify the examined property. The aforementioned rule is known in literature as the *linear rule of hybrid mixtures* (RoHM) and, unfortunately, has some major drawbacks as debated by Swolfs et al. (2014) [13].

There are many influencing factors that can be identified to influence the hybrid effect. High-performance composites require outstanding returns from their individual constituents, both reinforcement and matrix. Without limiting them, the nature, distribution, amount, layering pattern and individual features of the constitutive strongly influence the effective material properties. Subsequently, material selection must be tackled as sharing the same importance in the composite design. Other parameters, such as fiber-matrix interface, inter-laminar strength and fracture toughness, can be also considered to influence the hybrid effect.

Theoretical predictions developed to address microstructure-property connection have a long and venerable history, attracting the attention of some of the luminaries of science, including Maxwell, Rayleigh and Einstein. Since their early work on the properties of heterogeneous materials, there has been an explosion in the literature on this subject, one of the outstanding contributors being Torquato (2002) [14].

In the most general sense, the overall properties of heterogeneous materials can be predicted using expressions developed based upon the variational principles, local and homogenized solutions to the problems, phase-interchange relations, exact solutions, effective medium approximations, rigorous bounds, cross-property relations, etc.

It is noteworthy that these significant advances have enabled investigators to break through the limits of models and further, to compute property estimates that depend on other requirements imposed real materials. The ability to tailor composites with unique spectrum of properties rests fundamentally on the systematic approach to relate the effective properties to the microstructure by means of accurate expressions. One can then relate changes in the microstructure quantitatively to changes in the macroscopic property.

Nonetheless, the exponential upbringing that can be seen with respect to hybrid composite materials development is driven mostly by industry pressure. Material designers and manufacturers seem to be endlessly in the search of novel combinations bounded by requirements that allow fast architecture optimization in terms of cost minimization, high performance and lightweight condition.

Hybrid polymer composites were developed mostly using thermosetting resins, ranging from epoxy to polyester and poly vinyl ester, etc. Epoxy resins and derived blends were preferred due to their versatility in use with all manufacturing technologies, good compatibility with almost all types of fibers, both synthetic and natural.

The consumption of composites, either thermoplastics or thermosetting, is controlled by user market demand. The ability to adapt these materials to economic and technical market requirements relays on the innovation in terms of both materials and processes, supplemented by adaptability to the environmental constrains (i.e. circular 3R concept - recycling, reusing and remanufacturing) as outlined, for example, by Biron (2014) [15].

These composites found their niche in engineering applications were solely two-phase constitutive lead, viewing them, mostly like an alternative instead of replacements. Thus, civil and automotive engineering, marine and aerospace, biomedical and sensing devices were several application domains of these modern composite architectures [16-20]. A balance in cost and performance can be sized behind each material design while used in aforementioned structural applications.

Certainly, the study of hybrid composite materials is a multidisciplinary endeavor that overlaps with various branches of material science, engineering, applied mathematics, etc. The ability to tailor hybrid composites with a unique spectrum of properties relies on relating the effective properties to the microstructure and correlation of experimental retrieved data with theoretical predicted values, bounded by certain processing conditions.

1.2 Material properties of hybrid polymer composites

The effective material properties of a hybrid polymer based composite depend on the reinforcements' volume fraction, geometrical parameters (e.g. length, shape, etc.), orientation and layering type, supplemented by interface interactions with the matrix system. The overall behavior of resulted hybrid material is dictated by each of and every component. The synergetic effects based on contribution of all constitutive forming the composite was outlined by Wang and Pan (2008) [21].

In addition, constitutive individual properties and their compatibility were directing towards maximum hybrid results as reported by several research groups, both theoretically and experimentally through systematic studies, challenging thus the state-of-the-art results (Faruk et al., 2012; Ahmad et al., 2004; Jawaid et al., 2011; Ashori et al., 2010) [10, 16, 22, 23].

Next, both theoretical and experimental approaches, individually or intermingled, will be discussed in the view of highlighting the significant progresses. In addition, a connection with engineering applications is aimed further to strengthen the individual research results from subsequent chapters. To be able to foster the herein author's research contribution, paper collection and ex-ante development, it will be employed a back and forth approach with respect to the scientific literature referring.

Before commencing, it is desirable to recall the comprehensive collection of micro-mechanical based models, ranging from two to multiphase systems, accompanied by graphical representation of predicted values under each composite class that was co-authored by Motoc Luca (2009) [24]. A large number of theoretical models for prediction of effective properties for two and multiphase materials were covered. These include elastic modulus, thermal and electrical conductivities and coefficient of thermal expansion, respectively.

The advent on scale transition modeling methods relays on the outstanding work of Berryman (1996, 2001, 2014), individually or co-authored, who proposed several effective medium approximations for elastic constants of random composites to the alternative of the familiar rigorous bonds [25-27]. Furthermore, insight into the various methods enabled boosting a number of new effective medium approximations that can be viewed as natural variants and/or combinations of the existing ones.

Additionally, a comprehensive systemic approach on the overall response parameters of materials with micro-heterogeneities and defects (i.e. cracks, cavities, inclusions, etc.) was generously provided by Nemar-Nasser and Hori (1999) [28]. In summary, within the sixth chapters subdivided into sections, the basic idea of a heterogeneous *representative volume element* (RVE) and *repetitive unit cells* (RUCs) were extensively extrapolated; linearly elastic solids with micro-inclusions were tackled in such that their elastic response were captured, followed by fundamentals on elastic solids with distributed in-homogeneities, including cavities, inclusions and cracks. Furthermore, in most cases the models were accompanied by application examples.

In particular, focused approaches on *Mori-Tanaka* principles and results were tackled due to the formalism enabling interesting applications. This trend was followed by other researchers like Wu & Weng (2000), Thomsen & Pyrz (2001), Dong et al. (2005), Tan et al. (2005), Bohm & Nogales (2008), Mercier & Molinari (2009), Peng et al. (2009), Lu (2013) and recently by Liu & Huang (2014) [29-37].

Put in a nutshell, the above references fail to address directly the concept of hybrid composite materials and associated overall properties from *Mori-Tanaka* expression's point of view. On the other hand, the corresponding formalism can be extrapolated to encompass this class of hybrid composite materials as suggested by Berryman (see ref. above) or Kanaun & Jeulin (2001) [38]. Nonetheless, their findings can be ranked as fundamental in the continuously accelerating learning and developing process related to the issue.

Likewise, theories should be placed into the practical context by their theoretical underpinnings in a clear and concise manner, and illustrate their utility for the design and analysis of hybrid composite materials, generally, and polymer based particularly. An excellent reference with respect to above is the co-authored book of Aboudi (2012) [39].

They succeeded to address directly the issues of multi-scale modeling methods as developed under a micromechanical approach, based on hierarchical, synergistic or concurrent strategies used that systematically pass information on bottom-up or top-down manners.

In summary, the micromechanical based approaches deployed were sought as a range of methods from *fully analytical* (e.g. rule of mixture (ROM) and *Mori-Tanaka*) to *fully numerical* (e.g. finite-element analysis (FEA) and molecular dynamics (MD)), or from *semi-analytical* (e.g. Generalized Method of Cells (GMC)) to *fully numerical*. The key point behind the development of all the theories presented relayed on the balance between fidelity and efficiency that was met while applied to multi-scale modeling of composite materials. Therefore, these can assist in designing the hybrid composite materials themselves as well as the structures comprised of them.

Furthermore, noteworthy can be ranked the review of Gibson (2010) with respect to the research activity and publications in multifunctional materials and structures that succeeded to identify the most appealed topics on the aforementioned [40]. Besides of establishing a road map on the hot topics focusing on multifunctional materials, including hybrid composites driven by application oriented approaches, the author urged on the “need for development of more analytical models to compliment the experiments."

Likewise, recently Lee et al. (2012, 2015) approached and adapted log-normal and generalized extreme value (GEV) *statistical functions* to predict the effective elastic moduli for multiphase hybrid composites [41, 42]. The idea of employing statistical functions to predict the material properties in composites is not a new one. The highly potential of the statistical methods relay on their versatilities, easy to be understand but difficult to be implemented due to several key factors related to the structure that must be accounted. In particular, author’s theoretical and experimental platform enabled a more insightful understanding with respect to the class of hybrid composite materials, generally, and it is enough thoughtfully to allow expandability, particularly.

Mechanical properties of hybrid composites

The existing analytical models for the effective mechanical properties are based or derived from the well-known *Voigt* model that served as a benchmark for validation. As mentioned before, since it is providing the upper bound for many material properties, including elastic modulus, positive and negative effects can be outlined further. The effects are deemed positive when the mechanical properties relay above the predicted trend and vice versa when the opposite occurs.

The *linear rule of the hybrid mixture* (RoHM), as it is referred the basic model from above provide acceptable predictions of the effective elastic properties for simple or simplified combinations, but the accuracy and applicability are rather limited (Teodorescu et al., 2008; Fu et al., 2002) [43, 44]. It is extremely difficult to predict the hybrid effects and overall properties, especially flexural/tensile strength and derived elastic moduli, since they depend upon the several key factors and appreciably overestimate the property under the focus.

To overcome these limitations, different researchers were either introducing empirical parameters to account for certain structure characteristics, combined several theoretical models for complex composite architectures or running finite element based simulations (Dong et al., 2015; Mishnaevsky and Dai, 2014; Dong et al., 2013; Benveniste, 2008; Afonso and Ranalli, 2005; Mori and Tanaka, 1973; Christensen, 1990; Hashin and Shtrikman, 1962) [45-52].

Noteworthy within the above is the contribution of Mishnaevsky and Dai (2014) on computation modeling techniques of hybrid and hierarchical nano reinforced polymer based composites' structure-properties relationships. They argued in favor of glass/carbon-fiber hybrid composites that exhibit a higher stiffness and lower weight and/or strength with the increase in the carbon content as compared with their counterparts. Further, addition of nano reinforcement can drastically increase the fatigue lifetime of these composites.

The effects of the reinforcement clustering, individual material properties of constitutive on the overall composite behavior under mechanical loading were accounted by the above referred majority in terms of effect upon the elastic modulus and strength. Further, Chiang et al. (2005), Lua (2007), Teodorescu et al. (2009), Wu (2009) [53-56] proved that mechanical property improvement failed to hold in all polymer based composites. The latter can be regarded to few influencing factors that were individually identified, monitored and debated.

In materials testing, flexural strength is most commonly determined through 3-point bending test. It was reported that the flexural strength, and the inter-laminar shear strength (ILSS) are strongly influenced by the hybrid design and depend on the reinforcing fiber position (Yahaya et al., 2015; Ary Subbagia et al, 2014; Amico et al., 2010; Reiss et al., 2007) [57-60].

Carbon fiber (CF) based composites were one of the most tailored architectures due to some drawbacks of this reinforcement, including susceptibility to stress concentration due to it's to brittleness, recycling potential and associated manufacturing costs. To overcome these drawback researchers called on the hybridization procedure with direct benefits in cost and effective material properties.

Literature reports on several *synthetic/synthetic* hybrids that were developed among first to exploit the synergetic effects of the combinations. Thus, Manders and Bader (1981) reported on flexural properties of glass and carbon fibers hybrid composites [61]. According to their findings, the failure strain of carbon phase increased as the relative proportion of carbon fiber was decreased, and as the carbon fiber was more finely dispersed. They called this behavior as a hybrid effect and reported an enhancement in failure strain of up to 50%.

Further, Selmy et al. (2012) accounted 'hybridization' based on the same type of material used as reinforcement but a different shape/distribution/volume fraction such as unidirectional and random glass fibers [62]. Their findings indicated that the in-plane shear properties (i.e. shear strength and modulus) of unidirectional fiber composite can be considerably improved by incorporation of random glass fiber to proffer structural composite architectures.

Next, Ary Subagia et al. tailored different hybrid architectures out of carbon fiber (CF) and basalt fiber (BF) by various stacking the individual layers as the outer- or innermost layers using a vacuum-assisted technique [58]. They concluded that all stacking sequences exhibited a positive hybridization effect. In addition, higher flexural strength and modulus were obtained for hybrid architectures were the carbon fiber based plies were layered on the compressive side.

Hybrid polymer based composite architectures were tailored by Ahmad et al. (2004) out of glass, Kevlar and carbon woven fibers embedded within two different matrices: epoxy and polyester resins. Their results shown linear increase in tensile strength with an increase in volume fraction fabric for both polyester and epoxy based composites. In addition, the hybrid composites have shown up to more than 100% increase in modulus of polyester composites while glass fabric reinforced polyester composites showed high tensile properties [16].

Next, Valenca et al. (2015) reported on the mechanical behavior of hybrid epoxy based composites using Kevlar and glass fibers as constitutive [63]. The structural composites developed performed excellent in tensile, bending and impact tests comparatively with their counterparts. Earlier, Dutra et al. (2000) reported on impact performance of a mixture of polypropylene and carbon fibers as reinforcing elements into an epoxy matrix [64]. They argued on the improved properties of hybrids in comparison with CF based composites.

Hybrid composite architectures tailored out of basalt fibers (BF) with either glass or carbon fibers were reported previously by Czigany (2006), Che et al. (2009), Carmisciano et al. (2011) [65-67]. As forecasted, the experimentally retrieved mechanical properties are higher for hybrids out of carbon and basalt fibers comparatively with their counterparts. Fiber orientation and surface treatment were tackled and considered as influencing factors upon the mechanical properties, both stress and elastic modulus in tensile and flexures, respectively. In addition, the results point toward property improvement in case of increased fiber/matrix adhesion.

Another hybrid class further developed has been the *synthetic/natural* reinforcement type combination. These hybrids were developed to overcome the problems associated both with synthetic and natural reinforcements. The latter are known for their susceptibility to moisture, their incompatibility with the hydrophobic polymer matrix, lack of the established manufacturing process that limits their performance and use in structural applications (Priya et al., 2006; Reis et al., 2007; Almeida et al., 2012, 2013; Dhakal et al., 2013; Mansor et al., 2013; Romanzini et al., 2013) [59, 68-73].

Experimental tensile testing procedure is often considered in conjunction with unidirectional fibers. Zhang et al. (2013) investigated the tensile and interfacial properties of few hybrid architectures tailored by different stacking unidirectional flax and glass fibers. They concluded that tensile properties of the hybrid architectures were improved with the increase of glass content. The stacking sequence was shown to influence the tensile strength, but not the tensile modulus.

A recent paper on *natural/natural* reinforced hybrid polymer composites was co-authored by Alavuuden et al. (2015) on banana and kenaf reinforcements, differently weaved, namely, plain and twill, following the work of Boopalan et al. (2013) [74, 75]. Their findings revealed that plain type reinforcements shown improved tensile properties compared to the twill type in all the fabricated composites. Furthermore, the maximum increase in mechanical strength was observed in the plain woven hybrid composites rather than in randomly oriented composites.

Scale transition and temperature dependence of the mechanical property enabled hybrid particle-fiber polymer composite analysis and overall behavior enhancements. With regard to aforementioned, the work of Li et al. (2014) can be viewed as representative for the potential in improving mechanical and thermo-mechanical properties of the fiber-reinforced composite by using multi-scale carbon hybrids [76]. They argued on the multi-scale hybridization of carbon nanotubes (CNTs) with micro-particles and about the opportunities in fostering high-performance multifunctional polymer based composites.

Further on the previous issue, the work of Lin et al. (2012) on the mechanical and wear properties of hybrid carbon fibers (CF) and nano-ZrO_2 particles embedded within a polyetheretherketone (PEEK) polymer matrix can be regarded as a contribution on structural composites [77]. In addition, nano sized particles embedded into the polymer matrix enabled stress release at the fiber/matrix interface, and thus excellent effective properties.

Besides aforementioned, Rahmanian et al. (2014) or Qin et al. (2015) tackled the issue of mechanical properties of multiscale hybrid polymer composites out of carbon fibers (CF) while Gamze Karsli et al. (2014) employed short glass fibers [78-80]. Unsurprisingly, all works report on improvements on the monitored mechanical property along with arguments in favor of synergetic effects.

Researchers tackled the *environmental influences* (e.g. moisture absorption) and *atmospheric*, *accelerated* or *thermal aging effects* upon the mechanical properties of hybrid composites during their studies aiming a comprehensive perspective on tailored materials. Among these can be mentioned the contributions of Barjasteh et al. (2009, 2012), Boualem & Sereir (2011), Burks & Kumosa (2012), Tsai et al. (2009) [81-85]. The conclusion underpinning their research resides in the unchanging or small discrepancies in the monitored effective properties due to the above mentioned external influences.

Dynamic mechanical properties of hybrid composites

Dynamic mechanical analysis (DMA) proved to be a useful tool in the study of polymer based composite materials' behaviour under various temperatures, frequency or external loading conditions. Measurements can be conducted either by applying a periodic load to gather the resulting deformation or by applying a constant load (or a displacement) to obtain creep (or relation) data. Information on loading modes, calibration methods, sample conditioning and particular data acquisition can be found in the comprehensive and commonly referred work of Menard (2008) [86].

Temperature-dependent dynamic mechanical properties, such as storage modulus, loss modulus and mechanical damping (i.e. loss factor), allow a closer monitoring of the level of interactions (i.e. adhesion) between the polymer matrix and the reinforcements. In addition, *Cole-Cole* or *Cole-Davisson* plots proved to be the most expressive and useful data processing tools in sizing the constitutive influence.

Literature provides numerous references focusing on the fibre reinforced polymer composites and their dynamical material properties revealing their inherent structure related particularities and thermal history during their manufacturing (Idicula et al., 2005; Mohanty et al., 2007; Deng et al., 2007; Bai et al., 2008; Ornaghi et al, 2010; Almeida et al., 2012; Faguaga et al., 2012; Romanzini et al., 2012 and 2013) [70, 73, 87-93]. Both organic and inorganic fibres were considered as high-potential reinforcement candidates for the different polymer based composite architectures and dynamic mechanical analysis (DMA) as the most-used testing method in order to size the overall material behaviour under shock and vibrations.

Thermo-mechanical models using temperature-dependent mechanical properties of fibre reinforced polymer composites can be traced around ‘80s. A compressive review of these models was reported by Mahieux et al. (2001, 2002) [94, 95]. In addition, a Weibull-type function was developed to describe the elastic modulus change over the full range of transition temperatures. The model is consistent only with thermoplastic materials (e.g. PEEK, PMMA, PPS, etc.) and cover a wide range of temperatures. Other empirical models were developed by Springer (1984) or Gu and Asaro (2005) [96, 97].

Noteworthy, the majority of researchers report on both retrieved static and dynamic mechanical properties for their tailored composite samples. Surprisingly, none explicitly addressed the particular issue of similarities between experimentally retrieved values from above configurations, although, in principle, they should be the same (Lee-Sullivan et al., 2000; Shao et al., 2000) [98, 99].

Numerous research papers approaching the subject of dynamic properties of hybrid polymer based composite can be traced as experiencing an exponential increase in the last decade. Surprisingly, majorities focus upon the synthetic/natural reinforcement combinations as it was the subject preferred and developed by numerous researchers. Recently, scale transition enabled tunings with respect to the hybrid architectures as reported by Diez-Pascual et al. (2011) [100].

In addition, effectiveness of reinforcements and adhesion factor can be traced and further used to assess the effectiveness of stress/strain between the reinforcements and matrix and their interface bonding (Idicula et al., 2005; Romanzini et al., 2013) [73, 93]. The constant related to the effectiveness of reinforcements envisages that the higher its value the lower the effectiveness of the reinforcement combination. Next, it is acknowledged that composites with poor interface bonding tend to dissipate more energy than that with good interface bonding, as shown by Tan et al. (1990) [101].

Thermo-physical properties of hybrid composites

Uncontrolled thermal expansion in polymer based composites, especially those designed for structural applications, can be considered nuisances that preclude precision in these architectures. To mitigate the effects, the constitutive can be selected with matching *coefficients of thermal expansion* (CTE) at interfaces or tailored so that varies within a certain range (Kelly et al., 2005, 2006) [102, 103].

References that can be traced in literature generally approach the subject of *thermal expansion* in particle reinforced composites for energy harvesting applications, power electronic, electronic packaging, sensing devices, actuators, polymer based composite architectures tailored to attain negative coefficients or to withstand extreme environments, etc. (Hatta et al., 2000; Zhao et al., 2007; Bai, et al., 2008; Tsai et al., 2009; Jefferson et al., 2009; Boualem et al., 2011) [81, 83, 92, 104-106].

Further, rather contraction effects than expansion responses from constitutive were often considered in the composite design for those architectures intended to be developed to be used in harsh environments. Carbon fibers (CF) were again among the preferences, especially for applications dedicated to high temperatures. Noteworthy, studies are scarcely in literature about the thermo-physical changes occurring in these types of reinforcements, especially within extreme temperature range. Noticeable are those conducted by Sauder et al. (2002), Pradere and Sauder (2008), Gabr et al. (2015) [107-109]. The above covers solely the class of two-phase composites and can be used strictly to account the subject as uncovered and expandable.

Carbon fibres naturally exhibit different CTE responses along their longitudinal and transversal directions and are usually selected as reinforcements for multi-layered polymer composite structures to tailor their overall CTE. On the other hand, its counterpart, glass fibers exhibit positive CTE on both directions, longitudinal and transversal. Through ‘smart’ combination of reinforcements, it can be tailored an ‘ideal’ hybrid composite architecture exhibiting zero thermal expansion. Unfortunately, reality departs far beyond these ideal depicted scenarios.

In the herein context, Praveen et al. (2011) reported on CTE in case of a hybrid carbon-glass composite for applications at cryogenic temperatures [110]. Research conducted shown that a 80:20 relative hybrid ratio supplemented by a 30° and 0° orientation of carbon and glass constitutive, respectively, yield to a near zero overall CTE as the temperature was lowered from room temperature to 125 K.

In the light of the above, noticeable is the research of Esposito et al. (2013) with respect of polymers’ CTE measurements at cryogenic temperatures with the aid of optical sensors, namely fiber Bragg grating [111]. Fiber Bragg’s grating sensors were employed due to their capability to allow measurements in extreme environmental conditions as well as their high immunity toward external electromagnetic interference factors. The procedure can be accounted for hybrid polymer composites’ characterization as reliable.

Attempts for overall CTE dependence on fiber orientation was carried out by Tezvergil et al. (2003) on particle/fiber hybrid polymer composites [112]. The ANOVA analysis revealed strong dependences between the fiber orientation and temperature range particular to each hybrid specimen. In addition, their findings suggest that the anisotropic nature of fiber-reinforced composites exists also in connection to the CTE values.

Among earliest published contributions on the particle/fiber-reinforced hybrid composite architectures' CTE belong to Dzenis (1989) and Camacho et al. (1990) [113, 114]. Accompanying theoretical predictions covered the influences of fiber aspect ratio, isotropic and anisotropic fiber materials, planar, three-dimensional or arbitrary fiber orientation, solid spherical reinforcements. Agreement between predicted values and experimental values was argued. Their hybrid structures were designed for very high speed integrated circuit (VHSIC) board applications.

Further, scale transition enabled particle/particle hybrid composite development out of micron size silicon dioxide (SiO2) and graphitized carbon nano-fiber (CNF) particles, respectively, as reported by Jang et al. (2011) [115]. The effect of filler loading was investigated with respect to both mechanical and thermal stability of the hybrid composite materials. Their findings revealed that the addition of 3% weight fraction of SiO2 particles along with 3% weight fraction of CNF improved damping loss factors by 15.6% at room temperature and thermal stability with up to 15% from retrieved diminished CTE values.

Entirely nano-sized particles tailored as hybrid particle/particle polymer composite architectures were developed and investigated by Jin and Park (2012) [116]. They monitored the thermal stability in alumina (Al_2O_3) and silicon carbide (SiC) nano-particles embedded within a DGEBA resin, in addition to dynamic mechanical and curing behavior, followed by thermal mechanical properties as the filler content increased. Their findings revealed that the coefficient of thermal expansion of hybrid composite samples at the glassy and rubbery regions decreased with the increase of the filler content.

Modeling and numerical predictions of thermal expansion of entirely fibrous composites were tackled for various reinforcements' shape and orientation, different material combination, and accounting fiber/matrix interactions by Price et al. (2006); Papanicolaou et al. (2009); Nayak et al. (2009); Tsukamoto (2011), Dzenis (1989) [113, 117-120].

More recently, Lu (2013) approached the aforementioned subject in his attempt to clarify some confusing aspects concerning of the *Mori-Tanaka* model for CTEs [35]. Corrections were introduced by using derived expressions of the initial model followed by comparison with other models. Accompanying debate favors the *Mori-Tanaka* model, and a practical expression was proposed to the prospective users.

Another property accounted in composite material development and characterization is *thermal conductivity*, especially for applications aiming power electronics, microelectronics, energy harvesting and storage, sensors and transducers, etc. (Alsina et al., 2005; Han et al., 2011; Mallick et al., 2011; Otiaba et al., 2011) [121-124].

In the light of above, a comprehensive work was carried out by Lee et al. (2006) that investigated various inorganic fillers including aluminum nitride (AlN), wollastonite, silicon carbide whisker (SiC) and boron nitride (BN) with different shape and size, alone or in combination [125]. Their findings substantiate the effects of hybridization toward the increase of thermal conductivity due to the enhanced connectivity offered by structuring filler with a high aspect ratio. Next, for given filler loading, the use of larger particle and surface treated filler resulted in composite materials with enhanced thermal conductivity.

Out of aforementioned, several references tackled the modeling or numerical predictions' available methods to further aid thermal analysis of the polymer based composite architectures under the focus. Among them, micromechanics theoretical models are prevailing and considered among the best quantitative predictors of the overall composite material property considered.

Noteworthy, the contribution of Sevostianov (2012) can be ranked as comprehensive, proven the cross-property connection approach on thermal expansion and thermal conductivity [126]. Its mathematical development covered a wide range of reinforcements, proven different shape and orientation, enabling quantitatively characterization of microstructures involving mixtures of diverse inhomogeneities. In addition, he debated on the limitation induced by familiar models developed by Turner (1946), Kerner (1956), Thomas (1960), Schapery (1968), Fahmi and Ragai (1970), Van Fo Fay (1971), Tummala and Friedberg (1970), Sevastianov (2007), etc. [24], [127]. The results were consistent with experimental data available in literature and aforementioned approaches.

Thermal conductivity of particle reinforced polymer composites were extensively investigated by Hatta and Taya (1991) who’s theoretical models are among the best predictors for this material property [128, 129]. Further, more comprehensively can be ranked the paper of Bigg (1995) who extended the above concepts to spherical and irregular shape fillers [130]. In addition, experimental methods, including steady and unsteady state techniques were also reviewed in the light of thermal conductivity retrieval, especially for applications like heat exchangers where is of primary importance.

Thermal conductivities of hybrid epoxy composites reinforced with different particle fillers were investigated by various researchers, such as: Choi & Kim (2013) who used aluminum oxide and aluminum nitride fillers, Teng et al. (2012) that approached the issue by using functionalized multi-walled carbon nano-tubes and aluminum nitride or Zhou et al. (2010, 2013) that employed hybrid multi-walled carbon nano-tube and micro silicon carbide fillers or flake graphite and carbon nano-fillers. Kandare et al. (2015), on the other hand, reported on epoxy composites based on carbon fibers mixed with nano-inclusions (e.g. silver and graphene) by exploiting the synergy of latter [131-135].

In addition, in the work of Pak et al. (2012) was tackled the synergistic effect sizable in the thermal conductivity overall property of thermoplastic composites reinforced with boron nitride and multi-walled carbon nano-tube fillers, while Kumar Reddy et al. (2014) reported on cow dung powder filled glass-polyester composites [136, 137].

With respect of above, despite the attempts in upbringing effective thermal conductivity enhancement on investigated *particle-particle* or *particle-fiber* thermosetting composites, to exploit the synergetic effects due to particle reinforcement compatibilities and to argue against the effectiveness of proposed combination, one might observe that scale transitions do not necessarily represent a viable solution in terms of the application potential.

Further, remarkable can be raked the contribution of Chen and its co-authors (2015) on thermal conductivity enhancement as a result of hybridization in polymer based composites [138]. They developed a two-step analytical model for the effective thermal conductivity prediction of epoxy composites containing hybrid single-walled carbon nano-tubes (SWCNTs) and graphite nano-platelets (GNPs) fillers [138]. Their results proved to be high consistent with reported data, and synergetic effects were envisaged into debate around the hybrid ratio.

Previously, Goyal et al. (2012) were investigated the electrically conductive thermal interface materials reinforced with hybrid graphene-metal particle fillers [139]. The experimental retrieved values shown that nano-particle size graphene fillers were responsible for the highly enhancement of the effective thermal property and this particular finding is important for the thermal management of advanced electronics and optoelectronics devices.

Through-thickness and out-of-plane thermal conductivities of 3D woven carbon fiber reinforced polymer composites were investigated by Schuster and his co-workers (2008) [140]. Theoretical modeling by the finite-element method was also employed to enhance their predictive expressions and experimental results. Next, challenging can be sought the perspective of considering thermal conductivity as a design aspect to be varied by fiber architecture and equal to mechanical design criteria such as Young’s modulus or strength.

The above resulted from previous contributions of Krach and Advani (1996), Kulkarny and Brady (1997), Thomann et al. (2004), Turias et al. (2005), etc. [141-144]. These references fail to address directly the subject of effective thermal conductivity estimation or predictions, being of importance if further developments on the issue it will be tackled. Generally, they aimed thermal conductivity property recovery for two-phase polymer based composites, reinforced with unidirectional or commingled fibers, experimentally and theoretically.

Electrical properties of hybrid composites

Inasmuch as the property is sharing the same importance in hybrid composite design and applications and despite the scarcity of reports in literature, knowledge on it has important implications for the optimal design of composites. The latter are particularly important in developing functional composites that differ from structural ones in the sense that their properties are quite different from those of the matrix materials and reinforcements, and it is far from that based on the law-of-mixture type formula. Composite materials that are exhibiting a “coupling” behavior are often referred to as *smart composites* or *multi-functional materials* (Newnham et al., 1978) [145].

First of all, there is necessarily to clarify the meaning of the *electronic composite* as most comprehensively defined by Taya (2008) like a material: "whose function is primarily to exhibit electromagnetic, thermal, and/or mechanical behavior while maintaining structural integrity" [146]. Therefore, not only electronic behavior should be sought during investigations but its physical and coupling behavior must be included. In addition, referring to its co-authored papers, the theoretical models developed accounted for the percolation and microscopic conduction mechanism irrespective of the reinforcements type, shape, size and volume fraction [147].

The properties of electronic composites can be tailored to meet specific applications, like those in electronic packaging: printed circuit boards (PCBs), thermal interface materials (TIMs), or like micro-electromechanical systems (MEMS) and BioMEMS where their functions are multi-fold: active sensing and housing.

To the best of author's knowledge, tenuity on the relaxation processes *modeling* techniques applied to hybrid polymer based composites can be found. Beyond these shortcoming El Hasnaoui et al. (2014) reported on dielectric properties of an epoxy-resin matrix with randomly dispersed carbon black nano particles in various amounts [148]. The analysis of the temperature dependence of electric permittivity using the *Vogel-Tammam-Fulcher* and *Havriliak-Negami* formalisms revealed the existence of carbon black/matrix interaction.

Early stages on electronic composite development focused on using mainly carbon black (CB) as conductive filler embedded within a high-density polyethylene (HDPE) matrix (Novak et al., 2005) or the combined effect while mixing with carbon fiber in polyethylene or polyethylene/polypropylene blends or other polymer matrices (Shen et al., 2011; Jin et al., 2013; Othman et al., 2013; Puertolas & Kurtz, 2014) [149-153].

In addition, noteworthy are the *particle-fiber* hybrid architectures tailored out of synthetic fibers, including carbon and glass mixed with carbon black. Moreover, recent scientific contributions approached the synthetic/natural combinations under the *fiber-fiber* category (e.g. PP/jute yarn commingled fabric) (Wichmann et al., 2006; Lonjon et al., 2012; Yamamoto et al., 2012; Gejo et al., 2013) [154-157].

Furthermore, following the work of Yang et al. (2007) on electrical properties of different hybrid carbon fiber reinforced plastics (CFRP), Yao et al. (2008) reported on dielectric constants on epoxy based composites tailored out as a combination of basalt and Kevlar fibers [158, 159]. Their experimental data agreed with the predicted results, and a positive hybrid effect was reported in all composites. Once again, carbon and Kevlar fibers proved outstanding competitors both individually or in combination with other types of materials.

Noteworthy, Zhan et al. (2011) reported on an unusual combination among chicken feather and glass fibers and related electrical properties, identifying as having potential application in printed circuit boards (PCBs) [160]. In addition, they argued on the manufacturing costs and sustainability of the chicken feather fibers' presence within their tailored hybrid composite architectures.

A comprehensive review was carried out by Thomassin et al. (2013) on polymer/carbon based composites as electromagnetic interference (EMI) shielding materials [161]. The paper was divided into five sections focusing on: electromagnetic theory and the main parameters that influence the related property of the materials, description and classification of various materials envisioned for reaching high EM absorption performances with respect to the different carbon fillers, combination and/or comparison of the latter with other fillers, and finally description of few composite architectures.

Scale transition enabled dielectric relation processes monitoring in hybrid composites tailored from carbon nano-tubes (CNT), carbon black (CB) and carbon nano-fibers (CNF). For example, Al-Saleh and Saadeh (2013) reported on the electrical properties and electromagnetic interference shielding effectiveness in the X-band frequency range, underlining that no synergy outcome on their overall conductive properties was found, while Zheming et al. (2010) reported on reduction in electrical resistivity and percolation threshold along with increase on the graphite oxide content [162, 163]. Opposite, da Silva et al. (2013) succeeded to outline the synergetic effect with respect to the electrical conductivity of hybrid composites based multi-wall carbon nano-tube (MWCNT) reinforced blend of poly-vinylidene fluoride (PVDF) and poly-pyrrole (PPy) polymer matrix [164].

Additionally, Yang et al. (2011), Yu et al. (2011), Zhang et al. (2012), Salinier et al. (2013), Yan et al. (2014), Motaghi et al. (2014) and recently Yan et al. (2015) tackled and generously reported on synergetic effects in hybrid carbon fillers reinforced polymer composites [165-170]. In summary, they reported excellent electric performance in temperature response, energy efficiency and operation within temperature range at given applied voltage in addition to enhanced dielectric properties.

Changes in material use patterns and the corresponding opportunities along the value-chains, fostered green composites as the main issue of intensive research in the last decade. Essentially, as debated in the previous sections, an insight on the effective dielectric properties of green hybrid composites was tackled. Thus, Jayamani et al. (2014) reported on dielectric constant, dissipation factor and dielectric loss factor of jute/bamboo natural fibers reinforced with polypropylene and unsaturated polyester hybrid composites [171]. Moreover, they further argued against the influence in increased jute volume fractions on the monitored dielectric properties, on the irrelevance of the polymer matrix contribution and alkali treatment of the natural fibers.

1.3 Conclusions

The previous sections aimed to address the main challenges on the route of development high performance polymer composite materials out of various constitutive combinations and architectures, including issues on synthesis, characterization and property modeling or simulation. Reflections on their overall behavior, interferences and synergies with direct consequences on their balanced properties should carefully be considered further while tailoring their architectures.

As the industry demand is skyrocketing around synthetic materials that impair supremacy either with natural or 3^R materials (i.e. recycled, reused, recovered), scientists acknowledged the importance of hybridization for both research and industrial purposes.

In this regard, experts view on the challenges of existing and future trends on the approached herein subject may help to overcome the gaps along each road map set individually or within a mix of accustomed and innovative issues. Furthermore, smart specializations become not only desirable but compulsory and novel tools and research technologies emerged to reduce cost and spread information within participants.

The opportunities for these improvements can lie within: design, recycling, manufacturing processes, multi-scale approaches, availability, cost, substitution, etc. To promote understanding, inter- and intra- effective communication and interaction with outstanding worldwide research achievements and outcomes, focused actions should be employed to enable paradigm changes.

A sustainable development approach towards hybrid composite materials' deployment and 'smart' management tackles all underlined challenges in a comprehensive way by taking into account: a balance of economic, social and environmental aspects, a life cycle perspective and the direct implication of relevant actors (e.g. researchers, industry players, etc.).

1.4 Research general objectives

Motivated by aforementioned outlined contributions, trends and research concerns, supplemented by a wide variety of applications, the herein contribution complied with the general quest for high-performance materials tailored as hybrid composite architectures envisaged by the mainstream field of research.

Further, it is considered to comply with the prevailing paradigm underpinned by the research community and acknowledged and accepted by business leaders and entrepreneurs proven the generated data. However, translated into practice these might give rise to some lock-in situation due to dogmatic views of different interest groups. Consequently, a balanced disposal in approaching the herein scientific information is both encouraged and desirable.

Therefore, the present contribution *primary aims* to provide and foster a research framework on high-performance polymer based hybrid composite materials and their effective material properties by comprehensive characterization and computer aided numerical simulation to enable structural and/or other emerging engineering applications.

More specifically, the herein habilitation thesis strives to address:

Objective 1 – issues to tackle in relation to hybrid polymer based composite architecture design, e.g. identifying cut-offs with respect to the material selection and compatibility issues attainment, expanding and enlargement novel micromechanical based relationships to be used in conjunction with the effective material property addressed, underline of potential transition within the multi-scale transition through simulation and modeling, etc.

Objective 2 – facilitating understanding of employed material characterization method and/or set up in conjunction with particular hybrid polymer based composite architectures in order to ensure mutual awareness, knowledge transfer and fostering between scientific researchers, specifically, and industry players and other actors, generally.

Objective 3 - providing input to further debates on hybrid polymer based composite materials' synthesis and characterization, full implementation of the existing state-of-art in the particular field approached or related scientific domains through smart specialization of various stakeholders (e.g. young researchers, master and doctoral students, industry specialists, etc.).

In order to achieve these objectives, the herein scientific contribution will feature, inter alia:

1. An update on the scientific achievements and experts' views on the challenges of existing and future trends in hybrid polymer based composite materials, prior and post published references of the herein author.
2. Outlines of the inter-linkages between hybrid composite materials' design, manufacturing and characterization on future prospective applications, on the role of scientific data availability, understanding and use in the world-wide context of research and innovation.
3. Providing pointers to the systemic approach applied while tackled the herein subject, balanced views and expanded research description developed throughout the individual chapters into a fashionable and contemporary manner.

Chapter 2 – Design of experiments

Taking into account the general objectives stated in the previous chapter, the experimental research carried out was centered both on different hybrid polymer based composite architectures' manufacturing and testing with the aim of overall material properties' retrieval.

Due to the complexity and availability of the research equipments, the experimental research related to the individual material property under the focus was carried out in several locations:

- Mechanical analysis lab within Mechanical Engineering Department, Faculty of Mechanical Engineering, 'Transilvania' University of Brașov, Romania.
- Thermal analysis lab within Materials Science Department, Faculty of Materials Science and Engineering, 'Transilvania' University of Brașov, Romania.
- Dynamic mechanical analysis lab within Netzsch GmbH, Selb, Germany.
- Electromagnetic Compatibility and Electrical Systems lab within Electrical Engineering and Applied Physics Department, Faculty of Electrical Engineering and Computer Science, 'Transilvania' University of Brașov, Romania.

Hybrid polymer based composites - architectures and synthesis

The manufacturing aspects were tackled by tailoring few hybrid polymer based composites' architectures based on their constitutive features under the following categories:

- Hybrid particle-particle reinforced polymer based composite materials.
- Hybrid particle-fiber reinforced polymer based composite materials.
- Hybrid fiber-fiber reinforced polymer based composite materials.

The hybrid polymer composite architectures were developed using the following manufacturing technologies:

- Closed molding manufacturing process in case of particle-particle specimens.
- Open molding based on wet lay-up technology manufacturing process in case of both hybrid particle-fiber and fiber-fiber specimens.

Regarding hybrid composites' specimen synthesis, from the polymer matrix perspective, several courses of actions were taken during and after manufacturing procedures to be able to provide fully cured specimens under each category.

Thus, several temperature ranges were considered in each case under debate, depending especially on the polymer resin used. The temperature values and the extent in which these were influencing the retrieved property under discussion will be underlined next.

Reinforcements used to develop the hybrid polymer based composites can be assigned to the class of the most employed type of engineering materials: *glass* and *carbon*. Despite their shapes, geometries, distribution or combination within the entire hybrid composite structures, they were selected to balance the overall properties and indirectly address the cost-effectiveness issue.

The latter will be not developed or exploited explicitly, individually or related to one of the effective material properties, even it concerns the herein undersigned researcher's interest.

Types of constitutive

Within the context of the herein contribution, two different types of reinforcements was deployed, namely: *fibers* and *particles*. The previous was long, random or unidirectional disposed, different material types (e.g. glass and carbon), while the latter considered 'ideal' spherical shaped but different size particles (e.g. iron, graphite, alumina, carbon, etc.). The content (i.e. volume fraction) of each constitutive was determined accordingly to the previous versions of ASTM D3171: 2015 [172].

The matrices embedding the reinforcements were different thermosetting polymer resins, ranging from unsaturated polyester, epoxy, to polyvinyl acetate polymers enabling polymerization at room temperature in the presence of corresponding hardener. Since they are commercial resins, their behavior it's supposed to produce unsurprisingly effects.

Hybrid particle-particle composites

Specimens manufactured under this class represent a mixture of different particle sizes of iron and graphite powders embedded in a commercially available polyvinyl acetate polymer matrix up to a 70% total reinforcement content. The individual relative particle content varied from 30% up to 50% for the iron component and was selected as reference in the analysis.

In Fig. 1 it can be seen the internal distribution of phases from a cross-sectional area of a *particle-particle* hybrid specimen (i.e. 30% iron particles mixed along with 40% graphite particles within a PVAc polymer matrix) on the left side, whereas on the right an excerpt from a *particle-fiber* hybrid composite (i.e. 10% of iron particles embedded with random E-glass fibers into an unsaturated polyester resin).

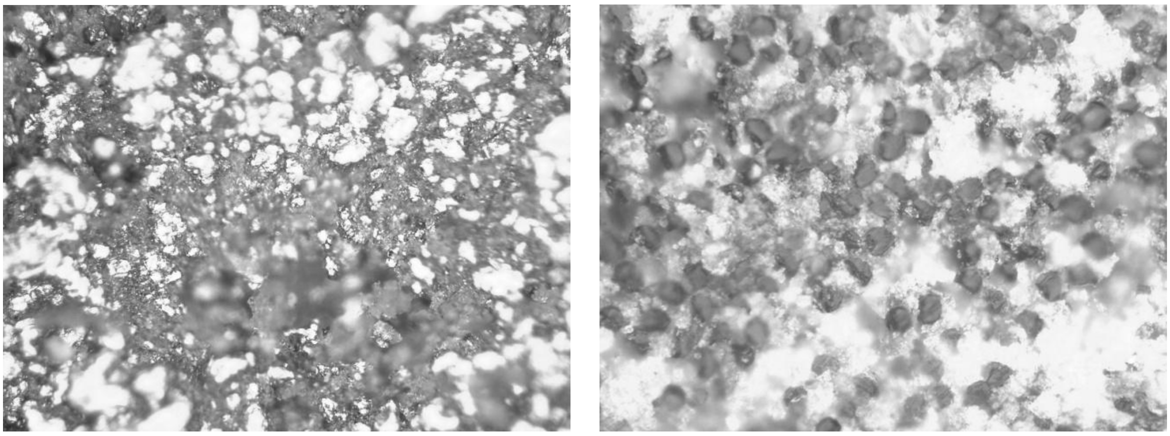

Fig. 1 *Micrographic views on particle-particle (left) and particle-fiber (right) hybrid composites developed*

Hybrid particle-fiber composites

Particle-fiber hybridization, generally, is due to overcome problems encountered during composites manufacturing while deploying polymer matrices that condensate (e.g. unsaturated polyester resins, etc.) such as little cavities or voids near the specimens' surface.

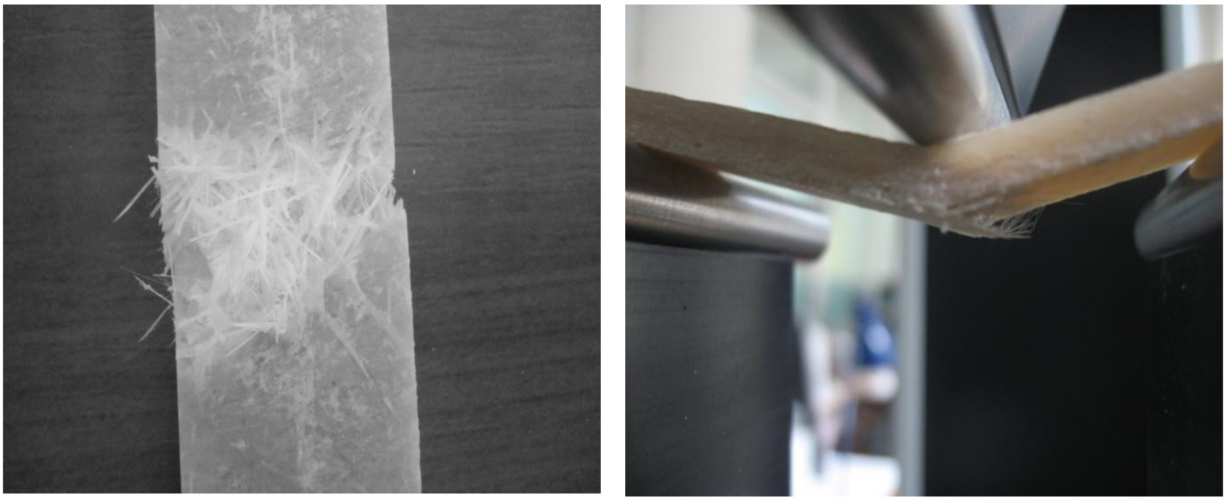

Fig. 2 *Composite breakage in tensile (excerpt, left) and flexure (right)*

Thus, in Fig. 2 (left and right) was provided some excerpts from the experimental side, namely a close view on the hybrid particle-fiber polymer composite specimen after a tensile test as well as specimen layering while subjecting to it to flexure testing.

Hence, by adding a stress release agent during the polymer composite manufacturing processes the above surface-related problems can be discarded. In the light of hybridization issue, by addition of a second phase, improvements on one or several effective properties might be attained.

With respect to both extensive and comprehensive research work carried out by the author on the particle-fiber polymer reinforced composite materials it can be stated that the experimental approaches were accomplished on two types of particle reinforcements, namely ceramic and metallic ones. On the other hand, relating the random E-glass fibers (i.e. under Multistrat^{TM} Mat ES 33-0-25 trade name, from Johns Manville, USA), consistency was kept both on their volume fraction (e.g. 45%) within the overall volume fraction of hybrid reinforcements and layer numbers (e.g. five layers).

Moreover, since details on the data retrieved by subjecting the hybrid composite specimens to a comprehensive characterization will be provided in the subsequent chapters, it should be emphasized that these were considered to apply to unconditioned or environmentally conditioned specimens depending on the particular engineering structural deployment to match with.

Hybrid fiber-fiber composites

Specimens manufactured under this class represent a mixture of different stacked sequences of unidirectional carbon fibers and random E-glass fibers embedded within an unsaturated polyester resin (n. SYNOLITE 8388 P2 from DSM Composite Resins, Switzerland). The sequence of the UD layering stacking sequence is provided in Table 1. The constitutive used as reinforcements were: chopped strand mat (n. GF; MultiStrat™ Mat ES 33-0-25 from Johns Manville, USA), and unidirectional (n. CF; Panex® 35 from Zoltek Co., USA) carbon fibers.

Table 1 - Hybrid composites samples' layer architecture

Samples	Layer sequence	No. of layers
Sample 1	1 GF/1GF/1GF/1GF/1GF	5
Sample 2	1 GF/1GF/1CF/1GF/1GF	5
Sample 3	1 GF /1CF/1 GF /1CF/1 GF	5

Types of research equipments involved

- *Mechanical properties*, including tensile and flexural properties, were retrieved in accordance with SR EN ISO 527-1:2000 and SR EN ISO 14125:1998 standards using LS100 and LR5K Plus devices from Lloyd Instruments (United Kingdom) – load cells used in tensile testing - 100 kN and in 3-point bending - 5 kN; different crosshead speeds – 1 mm/min or 5 mm/min, acquisition software Nexygen Plus™.
- *Dynamic mechanical properties* were retrieved in accordance with ASTM D5023-07 using a DMA 242 C analyzer from Netzsch GmbH (Germany) – 3-point bending mode, oscillating frequency of 1 Hz, various temperature range (e.g. - 40°C up to 150°C), scan rate of 3 K/min, controlled atmosphere, cooling agent - liquid nitrogen.
- *Thermo-physical properties* – Thermal expansion tests were performed on a differential dilatometer DIL 420 PC/1 from Netzsch GmbH (Germany), in accordance with ASTM E228-11 and DIN 53752-A standards - dynamic heating ramp was set out a temperature mode, temperature range – between 25°C and 250°C, heating rate of 1 K/min. The software includes semi-automatic routines for correction of the sample holder expansion, as well as, computation of the expansion coefficients, onset and peak temperatures, inflection points, rate of expansion etc.
- *Thermo-physical properties* – Thermal conductivity tests were performed using a C-THERM TCi from Mathis Instruments Ltd (United Kingdom) within the temperature range from 20 °C up to 150 °C.
- *Electrical properties* were retrieved by the aid of a self-developed experimental configuration centered on the 4-terminal method using a LCR meter (Hewlett-Packard Co., USA).
- *Morphology* was investigated by a digital microscope CCD video camera aided enabling image visualization on an LCD monitor and use of multiple functionalities (i.e. image acquisition, processing and characterization, etc.) and different settings, especially magnification regarded.

General considerations and specifications

Generally, the aforementioned mentioned values under each experimental device's setup considerations were preserved and used in case of hybrid *particle-fiber*, fiber-fiber and *particle-particle* polymer composites architectures.

Variations from previous were considered while monitoring and sizing the influence of the experimental environment and running conditions upon the effective properties and performances of hybrid polymer based samples under consideration.

Therefore, for comparison purposes other dynamic temperature programs were used in connection with the thermo-physical changes monitoring (i.e. linear coefficient of thermal expansion) to underline the retrieved values consistency irrespective to the environmental settings.

Variations in experimental set-ups and specimen geometry were individually addressed and considered for the hybrid composites under debate (e.g. tensile replaced by compression in particle-particle hybrid composites samples, etc.). In addition, information on constitutive shape, dimensions, orientation and distribution was accounted individually for each combination under debate to enable microstructure related effective property quantification.

Dynamic mechanical properties were considered only for a single frequency (i.e. 1 Hz) that was considered to be the most significant and relevant value. Researchers accustomed with the experimental device and runs can deploy a magnifying constant to get a picture at which extend can be used the tailored composite architecture in mechanical structures subjected to the dynamical loading conditions.

In temperature related overall properties, the reported data corresponds to the second or to the next thermal cycles, irrespective to the temperature programs selected to run the measurements. The reasons behind this should be related mainly to the manufacturing conditions, namely to the removal of the thermal-history and other volatiles from the specimens' surfaces.

With respect to the electrical properties, these were considered in the absence of environmental temperature variation and strongly limited by the experimental configuration used. Despite this, the experimental results are consistent with theoretical predictions and other values reported in literature. Noteworthy, is the scarcely use of experimental devices to retrieve this particular property and references in literature, especially on the hybrid polymer based composite materials.

Chapter 3 – Theoretical micromechanical based approaches

Theoretical predictions of hybrid composites' effective material properties are currently under extensive approaches due to the requirements involving expertise and subject understanding. Due to heterogeneous nature of these types of materials, scale transitions from macro to micro and reverse are employed by the instrumentality of mean-field homogenization methods.

Thus, micro to macro transition needs the presence of a *representative volume element* (RVE) containing all inclusions that better describe the hybrid composite structure, sufficiently large to represent the underlining heterogeneous microstructure and a homogenization method to find the macro constitutive response of the previous.

In Fig. 3 are plotted several of the RVEs used by the herein researcher in few of the authored or co-authored scientific papers referred [55, 173-181].

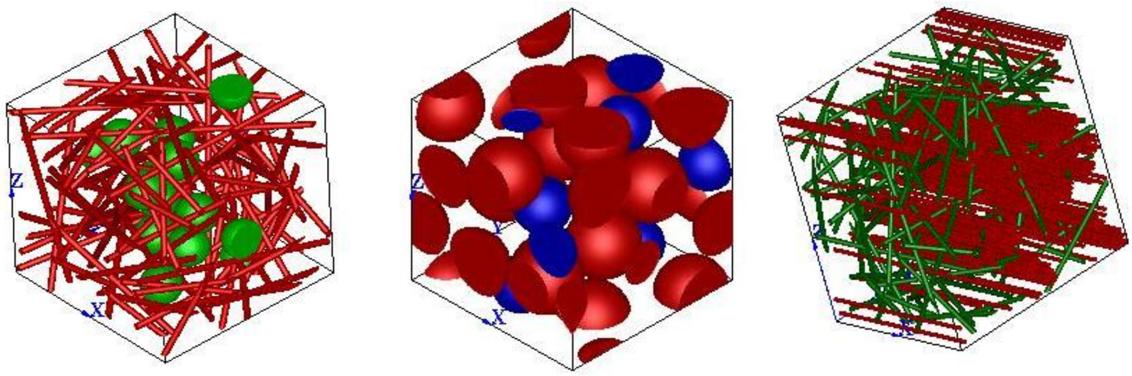

Fig. 3 *RVEs used in effective material properties predictions in case of hybrid particle-fiber (left), particle-particle (middle) and fiber-fiber (right) architectures*

Two distinct courses of actions were followed to predict the effective material properties of the hybrid polymer based composites under the focus:

- numerical predictions by the aid of a professional multi-scale modeling software platform from e-Xstream Engineering;
- numerical predictions based on theoretical models by the aid of commercially available software (e.g. Excel from Microsoft Office, PTC Mathcad, Matlab, Maple, Mathematica, etc.).

It is beyond the purpose of the herein thesis to debate on the advantages and disadvantages on using the aforementioned, even several mentions were made in the articles referred within this chapter.

A large collection of micromechanical models was extensively presented, augmented and debated by the herein contributor in one of her co-authored book [24]. Particular theoretical models were selected and presented next based on their frequency in use and not on their accuracy or accompanying mathematical formalism, while others only referred to as listed in Table 2.

Table 2 - Expressions of theoretical models used in hybrid composites properties predictions

Hybrid composite architectures	Property predicted	Theoretical model	References
Hybrid particle-particle polymer composites	Mechanical	Mechanics of Materials, Mori-Tanaka, RoHM	[24], [182], [183]
	Thermo-physical (thermal expansion)	Mori-Tanaka, Double inclusion	[24],[181],[184],[185], [186], [187], [188]
	Electrical	Maxwell, Clausius-Mossoti, Milton, Pal, Bruggeman, Hashin-Shtrikman	[24], [177], [180], [189], [190]
Hybrid particle-fiber polymer composites	Mechanical	Milton, Mechanics of Materials, Halpin-Tsai, RoHM	[24], [173], [183]
	Dynamic mechanical	Mori-Tanaka, Halpin-Tsai	[191], [192]
	Thermo-physical (thermal expansion and conductivity)	Mechanics of Materials, Maxwell, Levin-Hashin-Shtrikman, Hashin-Rosen, Christensen, Chamis, Ziebland	[179],[193],[194],[195]
Hybrid fiber-fiber polymer composites	Thermo-physical	Shapery, Hopkins-Chamis, Geier, Mori-Tanaka	[176], [178]

3.1 Effective elastic modulus

The micromechanical models were developed mainly in terms of reinforcement and matrix volume fractions even the weight fraction is more favorable to be applied in industry since the manufacturing equipments normally uses gravimetric feeding systems. Nonetheless, the simple relationship between the volume and weight fractions in single phase composite materials can be written as follows:

$$V_f = \frac{\frac{W_f}{\rho_f}}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}} \tag{3.1}$$

where V_f is the filler's (either fiber or particle) volume fraction, W_f is the filler's weight fraction whereas W_m is the matrix weight fraction, ρ_f and ρ_m representing the filler's and matrix materials density.

On the other hand, for a hybrid composite architecture, the individual filler contribution inside the overall reinforcement's volume fraction can be determined by using the following expressions:

$$V_{f1} = \frac{\dfrac{W_{f1}}{\rho_{f1}}}{\dfrac{W_{f1}}{\rho_{f1}} + \dfrac{W_{f2}}{\rho_{f2}} + \dfrac{W_m}{\rho_m}} \text{ and } V_{f2} = \frac{\dfrac{W_{f2}}{\rho_{f2}}}{\dfrac{W_{f1}}{\rho_{f1}} + \dfrac{W_{f2}}{\rho_{f2}} + \dfrac{W_m}{\rho_m}} \quad (3.2)$$

where V_{f1} and V_{f2} are the volume fraction of the individual fillers embedded with the polymer system.

Rule of the hybrid mixtures (RoHM) is one of the simplest predictors that can be used for preliminary design situations where precision and accuracy of the properties are not of primary importance. In order to predict the effective elastic modulus of the hybrid composites the individual elastic modulus of phases should be determined first and then incorporated into the RoHM equations. Thus, neglecting the interactions between the individual phases, the effective elastic modulus of the hybrid composite can be evaluated using the following expression:

$$E_c = E_{c1} \cdot V_{c1} + E_{c2} \cdot V_{c2} \quad (3.3)$$

where $V_t = V_{f1} + V_{f2}$ is the total reinforcement volume fraction, $V_{c1} = {}^{V_{f1}}\!/_{V_t}$ the volume fraction of the first phase and $V_{c2} = {}^{V_{f2}}\!/_{V_t}$ the volume fraction of the second phase.

Positive and negative hybrid effect can be further defined and used to quantify any positive or negative deviation of the retrieved elastic modulus of the hybrid composite from the predicted value using RoHM equation. With respect to the elastic strength of the hybrid composite architecture, it can be estimated in the same manner using the above concept.

As it can be seen, other parameters associated with the properties of the reinforcements such as dimension, shape and distribution are excluded from the above expressions, thus resulting in a decrease in the accuracy of predicted mechanical property.

Literature reports on prevalence of other micromechanical models used to predict the stiffness of single system composite materials. These models where approached extensively by the herein author in the co-authored book, for each type of reinforcement (e.g. long and random fibers, particles, voids, etc.) (Curtu & Motoc Luca, 2009) [24]. Among them, *Halpin-Tsai* and *Tsai-Pagano* are widely deployed for either random discontinuous or short fibers, as well as for particles reinforcements.

Furthermore, besides prediction within a single step (e.g. RoHM model) a combination of different micromechanical models can be considered to apply in order to predict the effective mechanical properties (i.e. elastic modulus, elastic strength, etc.). Thus, a multi-step homogenization scheme can be developed individually for hybrid polymer composite architectures under the focus. Next, is tackled the issue of multi-step homogenization principle followed by practical examples developed by the author.

3.2 Effective complex elastic modulus

Hybrid particle-fiber polymer composites

A *multi-step homogenization scheme* was developed to predict the effective dynamic-mechanical properties (i.e. E-modulus and viscosity) in case of herein particle-fiber polymer based composites, consisting of two homogenization steps after decomposition. The multi-step method is capable of delivering excellent predictions when the right choice of the homogenization schemes is made.

The general assumptions made with respect to the phases are referring to their isotropy accompanied by void content neglecting.

In the first step level, a *Mori-Tanaka* homogenization scheme was applied to the particles embedded in different volume fractions within the polymer matrix. This enabled a so-called *equivalent matrix* whose properties will be used to replace the matrix in the second step. The homogenization scheme was chosen due to its capability in predicting excellent results for small-volume factions of the fillers.

According to the model, the complex elastic modulus of the equivalent matrix is defined in terms of complex bulk and shear moduli as:

$$E_{em}^{*} = \frac{9 \cdot K_{em}^{*} \cdot G_{em}^{*}}{3 \cdot K_{em}^{*} + G_{em}^{*}} \tag{3.4}$$

where

$$K_{em}^{*} = K_{m}^{*} + \frac{V_p \cdot K_{m}^{*} \cdot \left(K_{p}^{*} - K_{m}^{*}\right)}{K_{m}^{*} + \zeta \cdot \left(1 - V_p\right) \cdot \left(K_{p}^{*} - K_{m}^{*}\right)} \tag{3.5}$$

is the complex bulk modulus, while

$$G_{em}^{*} = G_{m}^{*} + \frac{V_p \cdot G_{m}^{*} \cdot \left(G_{p}^{*} - G_{m}^{*}\right)}{G_{m}^{*} + \varsigma \cdot \left(1 - V_p\right) \cdot \left(G_{p}^{*} - G_{m}^{*}\right)}. \tag{3.6}$$

In the above expressions, ζ and ς parameters depend on the matrix's Poisson ratio:

$$\zeta = \frac{1 + \nu_m}{3 \cdot \left(1 - \nu_m\right)}, \varsigma = \frac{2 \cdot \left(4 - 5\nu_m\right)}{15 \cdot \left(1 - \nu_m\right)}. \tag{3.7}$$

Next, in the second step a homogenization scheme was chosen to account the fibers' orientation (i.e. randomly) and the mathematical formalism from general composite materials' theory was employed to provide an estimate on the complex modulus. Thus, the general expression can be written as:

$$E_c^* = \frac{3}{8}E_L^* + \frac{5}{8}E_T^*, \tag{3.8}$$

where the complex moduli in longitudinal and transversal directions, respectively, where replaced with the well known expressions from *Halpin-Tsai* model. The latter represents one of the best predictors in terms of mechanical/dynamic-mechanical properties and then often used in micromechanical based approaches and predictions. Accordingly, the above expression changes to:

$$E_c^* = \frac{3}{8}\frac{E_{em}^* \cdot \left(1 - 2\xi\eta_L^* V_f\right)}{1-\eta_L^* V_f} + \frac{5}{8}\frac{E_{em}^* \cdot \left(1 + 2\eta_T^* V_f\right)}{1-\eta_T^* V_f}. \tag{3.9}$$

The parameters η_L^* and η_T^* can be written in terms of individual constitutive mechanical properties and a shape factor (ξ) defined as a ratio of fibers' length (l) to their diameter (d), as following:

$$\eta_L^* = \frac{\dfrac{E_f^*}{E_{em}^*} - 1}{\dfrac{E_f^*}{E_{em}^*} + 2\xi},\ \eta_T^* = \frac{\dfrac{E_f^*}{E_{em}^*} - 1}{\dfrac{E_f^*}{E_{em}^*} + 2}. \tag{3.10}$$

where the storage and loss components can be expresses such as:

$$\eta_L' = \frac{\dfrac{E_f'}{E_{em}'} - 1}{\dfrac{E_f'}{E_{em}'} + 2\xi},\ \eta_L'' = \frac{\dfrac{E_f'}{E_{em}'} tg\delta_f - tg\delta_{em}}{\dfrac{E_f'}{E_{em}'} tg\delta_f + 2\xi tg\delta_{em}} \tag{3.11}$$

in the longitudinal direction, and

$$\eta_T' = \frac{\dfrac{E_f'}{E_{em}'} - 1}{\dfrac{E_f'}{E_{em}'} + 2},\ \eta_T'' = \frac{\dfrac{E_f'}{E_{em}'} tg\delta_f - tg\delta_{em}}{\dfrac{E_f'}{E_{em}'} tg\delta_f + 2tg\delta_{em}}. \tag{3.12}$$

in the transversal direction, respectively.

In the above expressions, the subscripts stand for: *c* – composite, *p* – particle, *f* – fiber, *m* – matrix, *em* – equivalent matrix, *L* – longitudinal direction, *T* – transversal direction, while the general form of the complex property (i.e. elastic modulus, model's parameters, etc.) - $P^* = P' + iP''$ was individually particularized in terms of their storage (*P'*) and loss (*P''*) components.

On the other hand, mathematical manipulation and factor collection related to damping factor provided a relatively complicated expression, as it can be seen next:

$$tg\,\delta_c = \frac{3\cdot tg\,\delta_{em}\cdot\left(1+2\xi\eta''_L V_f\right)\cdot\left(1-\eta''_T V_f\right)+5\cdot tg\,\delta_{em}\cdot\left(1+2\eta''_T V_f\right)\cdot\left(1-\eta''_L V_f\right)}{3\cdot\left(1+2\xi\eta''_L V_f\right)\cdot\left(1-\eta''_T V_f\right)+5\cdot\left(1+2\eta''_T V_f\right)\cdot\left(1-\eta''_L V_f\right)}\cdot\frac{\left(1-\eta'_L V_f\right)\cdot\left(1-\eta'_T V_f\right)}{\left(1-\eta''_L V_f\right)\cdot\left(1-\eta''_T V_f\right)} \tag{3.13}$$

The predicted effective elastic moduli are following the general increasing trend with the constitutive volume content. This reveals the consistency of the applied homogenization schemes, both combined and individually.

Other theoretical models that can be deployed to roughly estimate the dynamic mechanical properties are the *rule of mixtures (RoM)* and/or *inverse rule of mixtures (iRoM)*. Literature acknowledges them as the *Voigt* and *Reuss* models. These models provide the lower and the upper limits of the predicted elastic values that bound the other predicted and/or retrieved values.

Accordingly, the complex modulus and damping factor of a composite material out of two constitutive are expressed as following:

$$E_c^* = E_r^* V_r + E_m^* V_m \tag{3.14}$$

$$tan\,\delta_c = \frac{E'_r V_r \tan\delta_r + E'_m V_m \tan\delta_m}{E'_r V_r + E'_m V_m} \tag{3.15}$$

in case of the *Voigt* or *RoM* model, whereas

$$\frac{1}{E_c^*} = \frac{V_r}{E_r^*} + \frac{V_m}{E_m^*} \tag{3.16}$$

$$tan\,\delta_c = \frac{(\tan\delta_r + \tan\delta_m)(E'_m V_r + E'_r V_m) - (1-\tan\delta_r \tan\delta_m)(E'_r V_m \tan\delta_r + E'_m V_r \tan\delta_m)}{(1-\tan\delta_r \tan\delta_m)(E'_m V_r + E'_r V_m) + (\tan\delta_r + \tan\delta_m)(E'_r V_m \tan\delta_r + E'_m V_r \tan\delta_m)} \tag{3.17}$$

in case of the *Reuss* or *iRoM* model, whereas E^*, V and $tan\,\delta$ stand for the complex modulus, volume fraction of individual constitutive and mechanical loss factor, respectively. Next, for hybrid composite architectures, the above can be used as expressed in the previous section in case of the elastic modulus derived from *rule of hybrid mixtures* (RoHM).

Kinetic parameters estimation

Due to experimental related restrictions in DMA data available for hybrid polymer composite architectures investigated (i.e. one heating rate) a modified *Coats-Redfern* formalism can be deployed to estimate the kinetic parameters during the glass transition. Simple mathematical manipulation in the method's expression leads directly to the following:

$$ln\left(-ln\left(1-\alpha_g\right)/T^2\right)=ln\left(A_g R/\beta E_{A,g}\right)\cdot\left(1-2RT/E_{A,g}\right)-\left(E_{A,g}/RT\right) \quad (3.18)$$

where α_g is the conversion degree of the glass transition, T is the temperature, R is the universal gas constant (8.31J/mol K), A_g is the corresponding pre-exponential factor from Arrhenius law, β is the constant heating rate (set to 1 in this work) and $E_{A,g}$ is the activation energy.

Furthermore, the dynamic mechanical properties (e.g. complex modulus, either storage or loss modulus) can be expressed in function of the conversion degree such as:

$$E_{exp} = E_g\left(1-\alpha_g\right)+E_r\alpha_g\left(1-\alpha_d\right) \quad (3.19)$$

where E_{exp} is the experimentally retrieved dynamic property and α_d is the conversion degree during decomposition. Since decomposition was not recorded for the hybrid polymer based composite materials, the parameter will be neglected. Thus, the above expression allows the conversion degree at glass transition estimation proven the E_g and E_r will be taken from the glassy and rubbery plateau in storage/complex modulus variation with temperature.

3.3 Effective thermal expansion and thermal conductivity

Hybrid particle-particle polymer composites

This section briefly describes the concepts behind the theoretical models that were deployed to predict the thermal expansion coefficients of multi-phase particle reinforced composites. Thus, among all available theoretical predictions, partially debated in the co-authored book (Curtu and Motoc Luca, 2009) were selected the most expressive and extensively used models referred as *Mori-Tanaka* and *double inclusion* prediction schemes [24]. Since it's beyond the purpose of this habilitation thesis to expand the tensor formalism behind both theoretical approaches, reader is kindly redirected to works of Mori-Tanaka (1973) and Nemat-Nasser and Hori (1999) [28], [52].

Double inclusion method was proposed for better account for interaction between the inclusion and the matrix and between the inclusion and inclusion. The inclusions have an ellipsoidal form and can be aligned or randomly oriented in pane or in space. For the herein purpose, spherical shape inclusions were selected in the software simulation environment. On the other hand, the *Mori-Tanaka* scheme does not account a particular microstructure. For the case of randomly oriented ellipsoidal inclusions, it is still not known to have associated any microstructure even its predicted values of thermal properties can be shown to remain inside the *Hashin-Shtrikman* bounds.

In addition, when the double cells have the same shape and orientation of the enclosed inclusion, the results provided are similar to those predicted by *Mori-Tanaka* homogenization scheme.

A computer software program (see details provided in Chapter 2) was used to predict the effective thermal expansion coefficients of various particle-particle polymer composites accounting for different particle concentrations and distribution.

Hybrid particle-fiber polymer composites

Effective thermal expansion

The same concept of *multi-step homogenization* scheme is applied in order to retrieve the effective CTE of the hybrid polymer based composite samples. Within the first step, the *equivalent matrix* was derived through homogenization of random E-glass fibers and unsaturated polyester matrix followed by embedding the second phase (e.g. ceramic particles) into the previously homogenized matrix.

Mechanics of materials scheme was used to predict the CTE values of random, long E-glass fibers embedded with the polymer matrix, using the following expression:

$$\alpha_{em} = \frac{\alpha_L + \alpha_T}{2} + \frac{\alpha_L - \alpha_T}{2} \frac{E_L - E_T}{E_L + (1+2\nu)E_T} \tag{3.20}$$

where α_L, α_T, E_L, E_T and ν represents the equivalent thermal and mechanical properties of a fictive layer of a unidirectional fibers reinforced composite having the same volume fraction and material composition as the composite structure under analysis. In the previous expression, the longitudinal and transversal coefficients of thermal expansion can be predicted using the same assumptions as above. Thus, the CTE in the longitudinal direction of fibers can be predicted using:

$$\alpha_L = \frac{1}{E_L}\left(\alpha_f^L E_f V_f + \alpha_m E_m V_m\right) \tag{3.21}$$

whereas, the in the transversal direction to the fibers using:

$$\alpha_T = \left(1+\nu_f\right)\alpha_f^T V_f + \left(1+\nu_m\right)\alpha_m V_m - \alpha_L \nu \tag{3.22}$$

respectively.

In the second step, two theoretical models, developed in the literature and most used in predictions, for a particle reinforced composite material combination will be employed to predict the overall coefficient of thermal expansion. Firstly, were used the expression of the *Levin-Hashin-Shtrikman* theoretical model:

$$\alpha_c = \left(1-V_p\right)\alpha_{em} + V_p \alpha_p + \frac{\alpha_p - \alpha_{em}}{\frac{1}{K_p} - \frac{1}{K_{em}}}\left[\frac{1}{K_c} - \left(\frac{1-V_p}{K_{em}} + \frac{V_p}{K_p}\right)\right] \tag{3.23}$$

and next, the one developed by *Hashin-Rosen*:

$$\alpha_c = \alpha_p + \left(\alpha_{em} - \alpha_p\right)\frac{K_p - K_c}{K_p - K_{em}} \tag{3.24}$$

Both theoretical models were developed using the assumption of a perfect bonding between the phases and in case of particle reinforced composites yield an exact solution for the CTE. In reality however, perfect bonding does not exist.

In previous expression, the subscripts stand for: *c*- hybrid composite, *em* – equivalent matrix, *p* – particle constitutive whereas K is the bulk modulus and *α* individual thermal expansion coefficient, etc.

Effective thermal conductivity

The concept of *multi-step homogenization scheme* was deployed on *thermal conductivity* property predictions for the particle-fiber reinforced polymer composites under the study. Studies were conducted on the variation with the volume fraction of the filler, ceramic or metallic, using, firstly, the *Maxwell* type approximation. Accordingly, the thermal conductivity of the *equivalent matrix* having as phases the dilute distribution of the particles embedded within the polymeric matrix was predicted first since the model yield useful estimates of the effective property considered. The particles were assumed as having an ideal shape and uniformly distributed within the matrix.

The *Maxwell* approximation is an explicit scheme that yields the effective properties by direct substitution [14]. Hence, the effective thermal conductivity of the particle-matrix combination can be predicted using:

$$k_{em} = k_m + 3k_m V_p \frac{k_p - k_m}{k_p + 2k_m} \tag{3.25}$$

Next, for the fiber-equivalent matrix homogenization step exact predictors were used to evaluate the effective thermal conductivities of the hybrid combinations. The models used enable predictions on longitudinal and transversal directions of the fibers embedded within the matrix. All the models provide the same expression for the thermal conductivity on longitudinal directions, as follows:

$$k_c^L = k_f V_f + k_{em}\left(1 - V_f\right) \tag{3.26}$$

and different formula on the transversal direction. Hence, according to the model developed by *Christensen*, the thermal conductivity on longitudinal direction can be predicted using:

$$k_c^T = k_{em} + \frac{k_{em} V_f}{\frac{1 - V_f}{2} + \frac{k_{em}}{k_f - k_{em}}} \tag{3.27}$$

whereas, according to *Chamis* and *Ziebland* via:

$$k_c^T = \left(1-\sqrt{V_f}\right)k_{em} + \frac{k_f k_{em}\sqrt{V_f}}{k_f - \left(k_f - k_{em}\right)\sqrt{V_f}} \tag{3.28}$$

$$k_c^T = \frac{k_{em}k_f}{k_{em}V_f + k_f\left(1-V_f\right)} \tag{3.29}$$

Since it is generally impossible to determine exactly the effective properties of hybrid composite architectures, irrespective of the reinforcement geometry and distribution, any rigorous statements about these properties must take the form of bounds.

For the thermal conductivity, two classes of improved bounds can be used, *Wiener* and the well-known *Hashin-Shtrikman* bounds. As it can be seen, the *Wiener* bounds are simple the *rule of mixtures* (RoM) and *inverse rule of mixtures* (iRoM) gathered together:

$$k_c^{low} = \frac{1}{\sum_{i=1}^{n}\frac{V_i}{k_i}} \tag{3.30}$$

$$k_c^{upper} = \sum_{i=1}^{n} V_i k_i \tag{3.31}$$

Thus, the effective thermal conductivity is bounded by the arithmetic mean of the phase thermal conductivities and from below by the harmonic mean of the phase thermal conductivities. References acknowledge these results as *one-point bounds* since they involve information of up to the level of the volume fraction [14].

On the other hand, the well-known *Hashin-Shtrikman* bounds are known as *two-point bounds*, actually the best possible bounds on the effective thermal conductivity of two-phase isotropic three-dimensional composites given just volume fraction information.

$$k_c^{low} = k_m + \frac{3k_m\left(\dfrac{V_p}{1+\dfrac{3k_m}{k_p-k_m}} + \dfrac{V_f}{1+\dfrac{3k_m}{k_f-k_m}}\right)}{V_m + \dfrac{V_p}{1+\dfrac{3k_m}{k_p-k_m}}\dfrac{3k_m}{k_p-k_m} + \dfrac{V_f}{1+\dfrac{3k_m}{k_f-k_m}}\dfrac{3k_m}{k_f-k_m}} \tag{3.32}$$

$$k_c^{upper} = k_p + \frac{3k_p\left(\dfrac{V_m}{1+\dfrac{3k_p}{k_m-k_p}} + \dfrac{V_f}{1+\dfrac{3k_p}{k_f-k_p}}\right)}{V_p + \dfrac{V_m}{1+\dfrac{3k_p}{k_m-k_p}}\dfrac{3k_p}{k_m-k_p} + \dfrac{V_f}{1+\dfrac{3k_p}{k_f-k_p}}\dfrac{3k_p}{k_f-k_p}} \tag{3.33}$$

In the above expressions, the subscripts stand for: *c* – composite, *p* – particle, *f* – fiber, *m* – matrix, etc.

Inter alia, the bounds are particular useful because they are usually exact under certain conditions, can be used for comparison purposes against the experimental data and provide a unified framework to study other types of effective properties.

Hybrid fiber-fiber polymer composites

The micromechanical models deployed for the expansion coefficients of fiber-reinforced composites were selected to address the problem of transverse isotropy particular to UD carbon fibers. Hence, the following models were employed to predict the thermal expansion coefficients along both longitudinal and transversal in-plane directions, as was proven to minimize relative errors [24], [178].

The micromechanical models below uses the same expression for the linear thermal expansion coefficients along the longitudinal directions of the fibers, as following:

$$\alpha_c^L = \frac{\alpha_f^L E_m V_f + \alpha_m E_m (1-V_f)}{E_f V_f + E_m (1-V_f)} \tag{3.34}$$

whilst by the differences arise along the transversal direction. Thus, Poisson’s ratio of the reinforcements was accounted by *Schapery* while deriving the model for thermal expansion coefficients on transversal directions:

$$\alpha_c^T = (1+\nu_f)\alpha_f^L V_f + (1+\nu_m)\alpha_m (1-V_f) - \alpha_c^L \nu_c \tag{3.35}$$

On the other hand, the *Hopkins-Chamis* model accounts for a broad range of fiber distribution and orientations. The model was derived around the elastic and thermal properties of constitutive, matrix and fibers, as well as their concentrations. The expressions is:

$$\alpha_c^T = \frac{E_m}{E_c^T}\left[(1-V_f)\alpha_m + \frac{\alpha_m\sqrt{V_f} - V_f\left(\alpha_m - \alpha_f^T\right)}{1-\sqrt{V_f}\left(1-\dfrac{E_m}{E_f}\right)}\right] \tag{3.36}$$

where

$$E_c^T = (1 - V_f) + \frac{\sqrt{V_f}}{1 - \sqrt{V_f}\left(1 - \frac{E_m}{E_f}\right)} \tag{3.37}$$

Another micromechanical based predictor for thermal expansion coefficient along transversal direction is the one developed by *Geier*. Like above, the model accounts for the elastic and thermal expansion coefficient individual properties of the reinforcements:

$$\alpha_c^T = \alpha_f^T V_f + (1 - V_f)\left[\alpha_m + (\alpha_m - \alpha_f^L)\frac{\nu_m + \nu_f \frac{E_m}{E_f^T}}{V_f + (1 - V_f)\frac{E_m}{E_f^L}} V_f\right] \tag{3.38}$$

3.4 Effective electrical conductivity

The same *multi-step homogenization scheme* was deployed to predict the effective electrical conductivities of hybrid particle-particle composites. Consequently, in the dilute limit all effective media theories in electro-composite materials are reduced to *Maxwell*'s expression:

$$\sigma_c = \sigma_m + \sigma_m \cdot \frac{3 \cdot (\sigma_p - \sigma_m)}{\sigma_p + 2 \cdot \sigma_m} \cdot V_p \tag{3.39}$$

where σ_c is the electrical conductivity of the composite material, σ_m is the conductivity of the matrix phase, σ_p represent the particles conductivity and V_p is the particle concentration.

Remark: All above notations are preserved and used in the next derived relationships. Supplementary, ideal spherical shape, isotropic media and perfect matrix/filler interface were assumed.

The other theoretical models extend calculations beyond the dilute range. Among the best predictors is the *Maxwell-Wagner* expression, known also as the *Maxwell-Garnett* equation or *Wiener*'s derived rule:

$$\sigma_c = \frac{2 \cdot (\sigma_p - \sigma_m) \cdot V_p + (\sigma_p + 2\sigma_m)}{(\sigma_p + 2\sigma_m) - (\sigma_p - \sigma_m) \cdot V_p} \tag{3.40}$$

Another theoretical model was developed by *Meredith* and *Tobias* that extended Fricke's treatment on ellipsoidal particles by using half of the total particle content to predict an equivalent electrical conductivity of the resulted composite and next by using as the matrix constitutive while mixing with the other half of particle content. The expressions are as following:

$$\sigma_c = \sigma_m \cdot \frac{(1+V_p)\cdot(2+V_p)}{(1-V_p)\cdot(2-V_p)} \tag{3.41}$$

that is valid for conductive particles phase, and

$$\sigma_c = \sigma_m \cdot \frac{8\cdot(2-V_p)\cdot(1-V_p)}{(4+V_p)\cdot(4-V_p)} \tag{3.42}$$

for insulating particles, respectively.

All electrical conductivities can be regarded to lie between some lower and upper two-point bounds. Among all expressions reported in literature, the more rigorous bounds are those proposed by *Hashin* and *Shtrikman*:

$$\sigma_c^{low} = \sigma_m \cdot (1-V_p) + \sigma_p \cdot V_p - \frac{V_p \cdot (1-V_p)\cdot(\sigma_p - \sigma_m)^2}{\sigma_m \cdot V_p + \sigma_p \cdot (1-V_p) + \sigma_m} \tag{3.43}$$

$$\sigma_c^{upper} = \sigma_m \cdot (1-V_p) + \sigma_p \cdot V_p + \frac{V_p \cdot (1-V_p)\cdot(\sigma_p - \sigma_m)^2}{\sigma_m \cdot V_p + \sigma_p \cdot (1-V_p) + \sigma_m} \tag{3.44}$$

When $\sigma_p \geq \sigma_m$ is satisfied, $\sigma_c^{low} \leq \sigma_c \leq \sigma_c^{upper}$ and, as expected, these are exact through second order in the difference in the phase conductivities [14, 24]. On the other hand, *Milton*'s expressions belong to the three-point bounds for two-phase isotropic media. He derived a lower bound that applies when the aforementioned inequalities hold and was written in the form:

$$\sigma_c^{low} = \sigma_m \cdot \frac{1+(1+2V_p)\cdot\left(\dfrac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right) - 2\cdot\left((1-V_p)\cdot\xi - V_p\right)\cdot\left(\dfrac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right)^2}{1+(1-V_p)\cdot\left(\dfrac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right) - \left(2\cdot(1-V_p)\cdot\xi + V_p\right)\cdot\left(\dfrac{\sigma_p-\sigma_m}{\sigma_p+2\sigma_m}\right)^2} \tag{3.45}$$

In previous expression the bound depends not only on V_p but also on the three-point micro-structural parameter ξ that lies in the closed interval [0, 1]. The latter always improve upon the two-point *Hashin-Shtrikman* bounds.

Next, a notorious approximation scheme used to predict the overall conductivity is the differential effective-medium estimate introduced by *Bruggeman*. The approximation relays on the incremental homogenization principle, used for spherical conductive inclusions and expressed as follows:

$$\sigma_c = \sigma_m \cdot (1-V_p)^{-3} \tag{3.46}$$

Another theoretical model used to predict the effective electrical conductivities of particle-particle polymer based composites was that developed by *Pal*. It uses the same differential effective-medium scheme as above but on high volume content of fillers. One of the expressions developed can be used in the following form:

$$\left(\frac{\sigma_c}{\sigma_m}\right)^{1/3} \cdot \left(\frac{\sigma_p - \sigma_m}{\sigma_p - \sigma_c}\right) = exp\left(\alpha \cdot V_p\right) \tag{3.47}$$

whereas the modified form account a maximum concentration of particle constitutive that can be embedded within the matrix, like below:

$$\left(\frac{\sigma_c}{\sigma_m}\right)^{1/3} \cdot \left(\frac{\sigma_p - \sigma_m}{\sigma_p - \sigma_c}\right) = \left(1 - \frac{V_p}{V_p^{max}}\right)^{-\alpha V_p^{max}} \tag{3.48}$$

Remark: Debates on the above expression can be carried by further considering the conductive or insulating nature due to fillers' and matrix materials type. This debate enables a customization and comparison with other appropriate theoretical schemes (i.e. Maxwell or *Maxwell-Wagnar*, etc.).

Chapter 4 – Effective measured properties. Results and discussion

4.1 Mechanical properties

Specific objectives:

- To deploy acquired proficiency through debating on mechanical properties of hybrid composites manufactured.
- To track structural performance of hybrid polymer composite specimens.
- To debate on the effective mechanical properties as result of hybridization and environmental conditioning.

In composite materials' testing, especially concerning the hybrid architectures, flexural properties (i.e. E-modulus, strength and strain to failure) are widely retrieved through 3-point bending experimental configurations as specified by ASTM D7264/D7264 M:2015 while tensile properties in accordance with ASTM D3039:2014 [182, 183]. The subsequent data were retrieved by approaching the above investigation setup but not limited to these.

In addition, since the specimens are being subjected to various environmental conditions (e.g. moisture, low temperature environments, etc.) a recent version of ASTM D5229/D5229 M:2014 was considered to apply [184].

The subsequent reported data and discussion relay on information provided in the authored and co-authored scientific papers or invited presentations [173, 185-190]. Readers are kindly advised for further readings on other referred co-authored papers [43, 55, 174, 191-194]. Some of the graphs were plotted differently than those presented in the cited articles and included into the subsequent discussion to provide a comprehensive view on the approached issue.

4.1.1 Hybrid particle-fiber polymer composites

Hybrid composites properties from tensile tests

This particular type of experimental testing in order to retrieve the mechanical properties of herein hybrid polymer based composite was carried out to prove a comprehensive insight on the issue. Additionally, engineering applications and other practical related issues seldom imply or refer to it.

In Fig. 4 is being plotted the Young modulus retrieved experimentally from tensile tests for all particle-fiber polymer based composites herein, whereas in Fig. 5 the stress-strain dependence on ceramic fillers embedded in different volume fraction.

As it can be seen, the nature and volume fraction of fillers used influence the magnitude of the retrieved mechanical property. In addition, the linear increase of stress-strain dependencies enables facile Young modulus retrieval.

Furthermore, if the *hybrid rule of mixtures* (RoHM) is being accounted for the effective elastic modulus particular about the particle-fiber combinations herein, a positive hybrid effect is encountered. This hybrid effect highlights the synergistic based changes in the mechanical properties due to the various combinations of particle and random glass fibers. For example, for the hybrid specimens tailored out of iron fillers the following corresponding values to the % error were obtained: 0% - 71.68%; 5% - 68.10% and 10% - 74.86%.

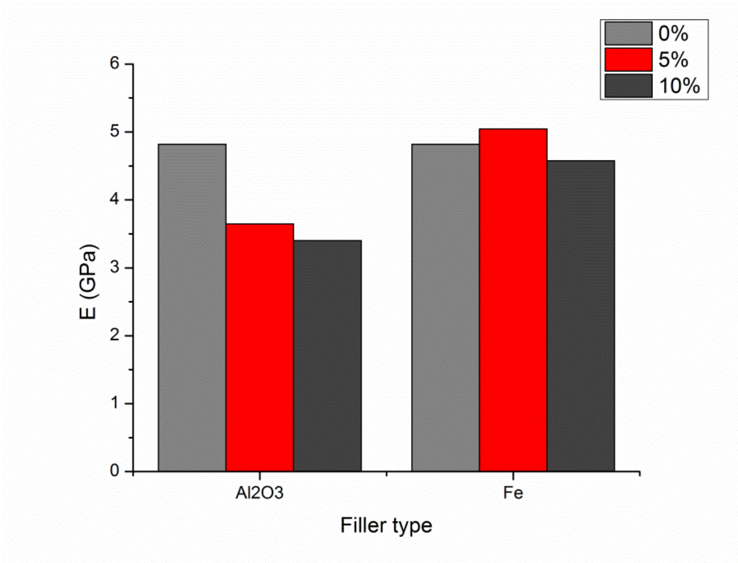

Fig. 4 *Particle-fiber hybrid composites' Young modulus from tensile tests*

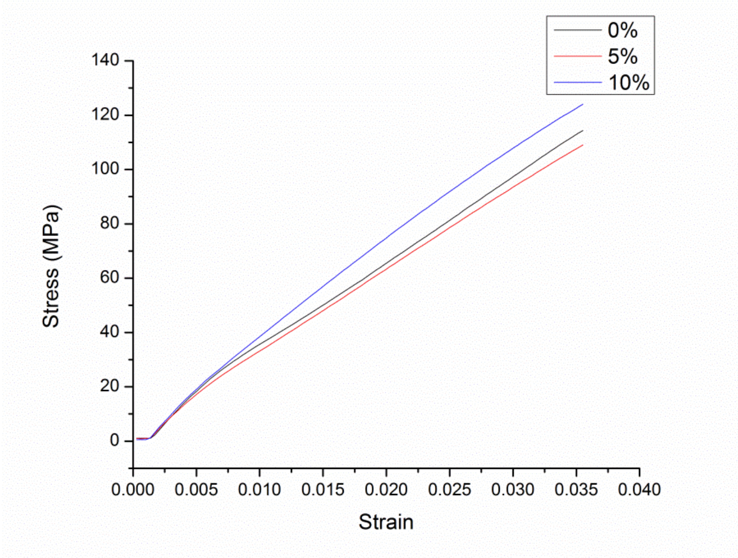

Fig. 5 *Stress-strain curves from tensile tests on ceramic fillers hybrid composites*

Hybrid composites properties from 3-point bending tests

In Fig. 6 is being plotted the Young modulus retrieved experimentally from tensile tests for all particle-fiber polymer based composites herein, whereas in Fig. 7 the maximum stress-strain dependencies on ceramic fillers embedded in different volume fraction.

As it can be seen, like previously, the nature and volume fraction of fillers used influence the magnitude of the retrieved mechanical property. Moreover, particles' volume fraction increases diminish stress development within the hybrid polymer composite specimen and thus relation in the stress-strain dependencies and abrupt breakage during further loadings.

It should be underlined that strength of hybrid particle-fiber polymer composites relies on fillers' parameters (e.g. shape, size) and loading (e.g. volume fraction) as well as interface adhesion. The primary role of reinforcements is to enable a larger filler/matrix interface that further contributes to its crystallization process and structure modification in the neighborhood of reinforcements' surface.

Furthermore, without debating on the issue, there are differences on the Young modulus from tensile and flexure testing. These differences can be sized in values plotted in the Fig. 8 and can be regarded mainly to the applied loading type since the experiments used the same precision while recording data.

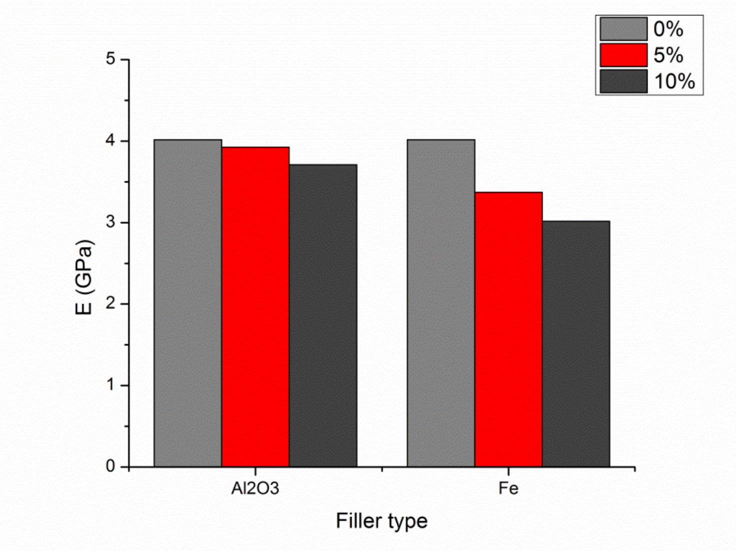

Fig. 6 *Particle-fiber hybrid composites' Young modulus in flexure*

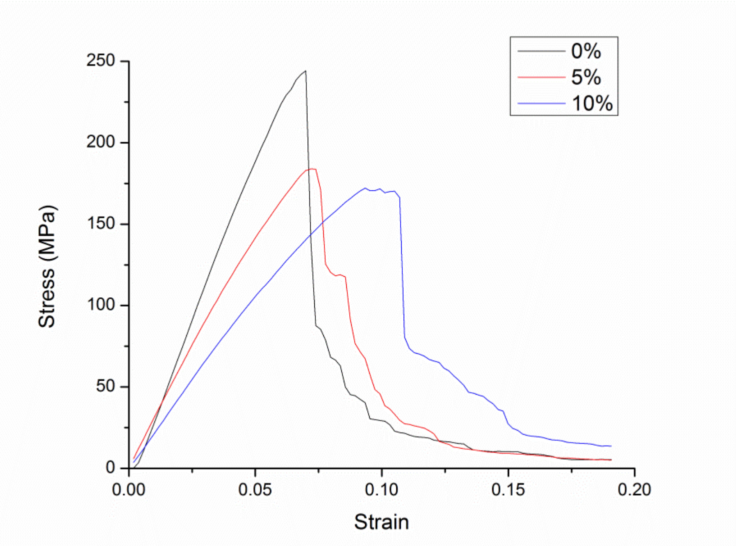

Fig. 7 *Stress-strain curves from flexure tests on ceramic fillers hybrid composites*

In Fig. 8 is being plotted the percent difference (% difference) between the experimental retrieved values, the Young modulus in tensile and flexure corresponding to individual polymer composite specimen class. These differences between the experimental values reveal the effectiveness of the particle filler type as reinforcement, and can be used as an indicator to the faction volume in which should be embedded. The latter, particular applies to the ceramic fillers.

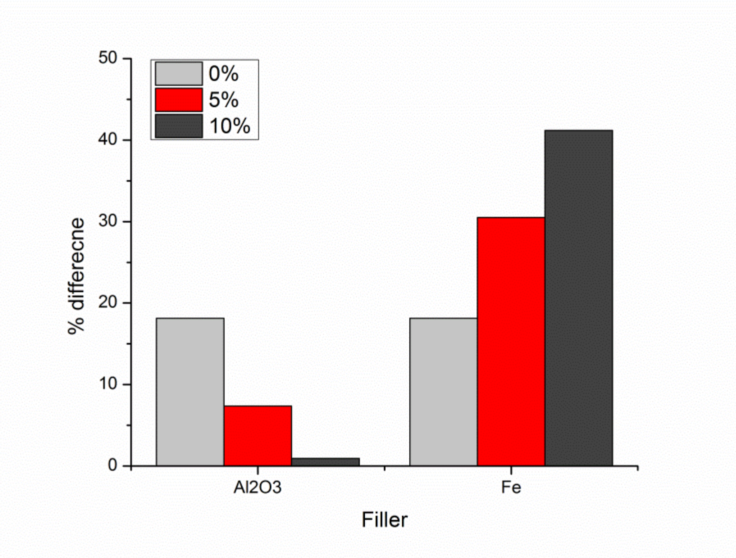

Fig. 8 *Percent difference between the experimental retrieved Young modulus from tensile and flexure testing*

In Fig. 9 was plotted the theoretical predicted values for metallic and ceramic particles reinforced along with E-glass fibers to hold a total volume fraction of 45% in the unsaturated polyester resin used as matrix material (see materials in previous chapter). The data were plotted out of records and referred in the co-authored paper [195].

With respect on the above, supplementary information on provided values should be compulsory to enable understanding. Thus, the theoretical values correspond to the values computed using a homogenization scheme developed to be applied within successive steps by deployment of *Mori-Tanaka* (particle – matrix) and *Halpin-Tsai* (equivalent matrix – random fibers) micromechanical models.

Noteworthy, the synergetic effects due to the particle-fiber combination on the mechanical property under debate can be sized whilst comparing with the theoretical predicted values from the *rule of the mixtures* (RoM) and the *rule of the hybrid mixtures* (RoHM).

Consequently, in Fig. 10 is being plotted the percent relative error between the theoretical values from the above models and the experimentally retrieved ones from tensile and 3-point bending tests corresponding solely to the metallic inclusions. As it can be seen, there is a slight difference between the experimental values from both mechanical runs.

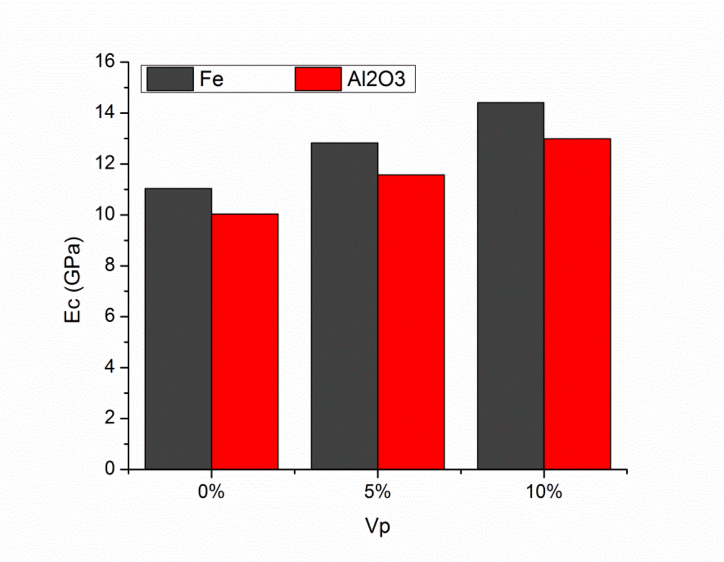

Fig. 9 *Theoretical predicted values based on the multi-step homogenization scheme used for particle-fiber reinforced polymer composites*

Thus, in all cases, irrespective of the filler's volume fraction, a positive hybrid outcome is encountered revealing the effectiveness of this phase within the reinforcement combination. The magnitude of the relative error highly depends on the predicted values. The latter is related to the highest value of elastic modulus from all theoretical predictions that can be carried out as shown and extensively debated by the herein author in reference [24].

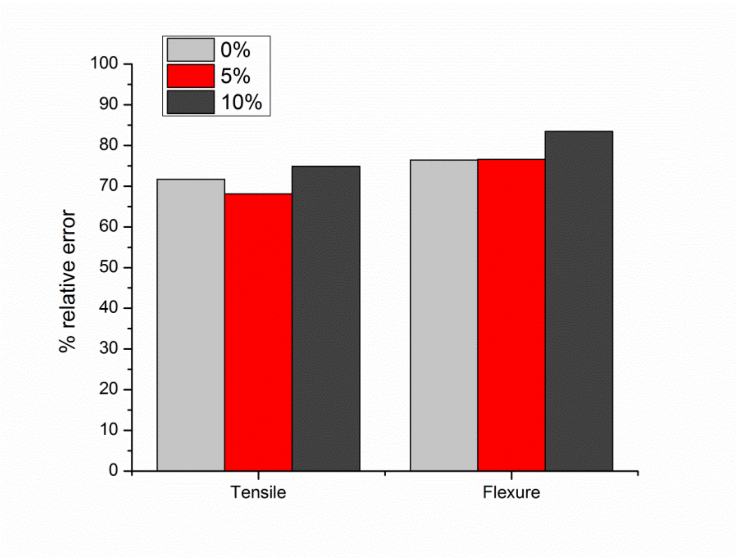

Fig. 10 *Percent relative error between theoretical and experimental Young modulus*

Put into a nutshell, the aforementioned approach can be carried out on all predictable values using models of mechanics at various scale levels (e.g. macro, micro, etc.). It is beyond the purpose of herein contribution for further development of the aforementioned issue since all the results will be of some magnitude less than the above represented ones. Furthermore, reader is kindly advised to conduct the simulation by deploying individual properties of constitutive from reliable and trustful sources.

Environmental effects on flexural properties

Application areas of hybrid polymer based composites imply exposure to various environments from extreme temperature to moisture, atmospheric aging to hygrothermal, etc. Within the herein context, environmental effect upon expansion behavior of hybrid composite specimens was extensively approached by exposing:

a) the specimens to temperature variation ranging from -10 °C to +40 °C within a controlled temperature enclosed structure, under a desert condition simulated thermal cycle, 7 days long, 24 hours/day (see Table 3);
b) the specimens to a constant low temperature of -35 °C, 7 days long, 24 hours/day, relative humidity 45%.

Table 3 – Extreme environment temperature program

Temperature [^{0}C]	Relative humidity level [%]	Time [h]
-10	45	8
0	50	1
10	50	1
20	55	1
30	60	1
40	65	8

In Fig. 11 is being plotted the elastic modulus in flexure for hybrid Al_2O_3 particle-fiber specimens under consideration, previously conditioned under extreme temperature environments as depicted above. Plotted data correspond to the computed mean value out of measures carried on 5 representative specimens.

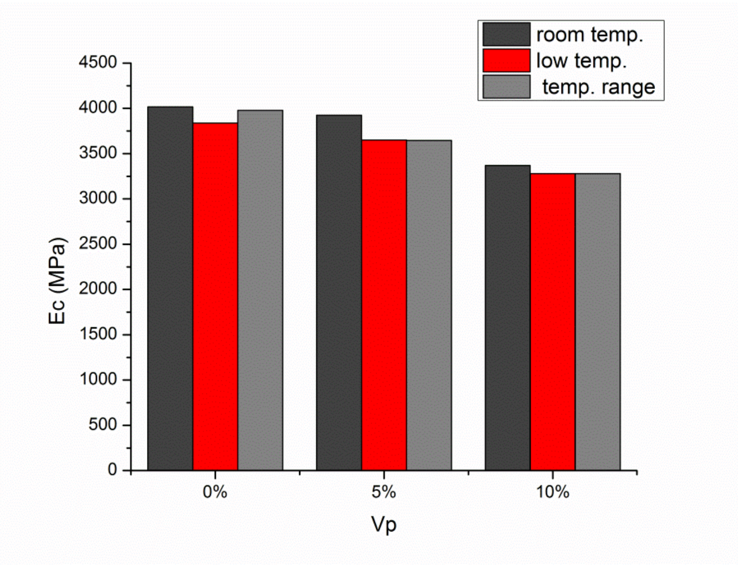

Fig. 11 *Mean elastic modulus in flexure for Al_2O_3 fillers hybrid composites*

As it can be seen from above, the overall elastic modulus in flexure is experiencing a decrease if the hybrid polymer based composite specimens are being prior conditioned to extreme various environmental regimes. This behavior should be assigned to the polymer matrix degradation that slightly influences the effective values retrieved. In case of metallic inclusions embedded along with E-glass random fibers all from above apply.

In addition, irrespective of the extreme environmental conditions considered, there are little discrepancies between the experimental values within individual categories. Strictly referring to the available experimental data and accounting the time scale monitoring of the hybrid specimens under debate, one may conclude that these withstand various environmental conditions.

Furthermore, decrease in the retrieved experimental values accounted the presence of the particle fillers in different volume fractions. The general rule asserting the following: ‘any increase in the filler’s volume fraction ascertains an increase in the corresponding property’ is ensued straightforward.

Additionally, irrespective of the constitutive particle filler nature and environmental conditioning, the load vs. extension or load vs. time curves retrieved experimentally resembles on their tendency. The aforementioned can be sized from the corresponding graphical representation in Fig. 12 retrieved for low temperature preconditioned iron particle-fiber hybrid composite specimens on their different volume fraction of fillers.

Moreover, as it can be seen, all specimens experience a linear variation with applied load over a long time until delamination occurs on the opposite side, followed by a relative abrupt failure. The latter can be regarded both to the samples’ morphology and previous environmental conditioning, as well as to the experimental settings (e.g. load and velocity).

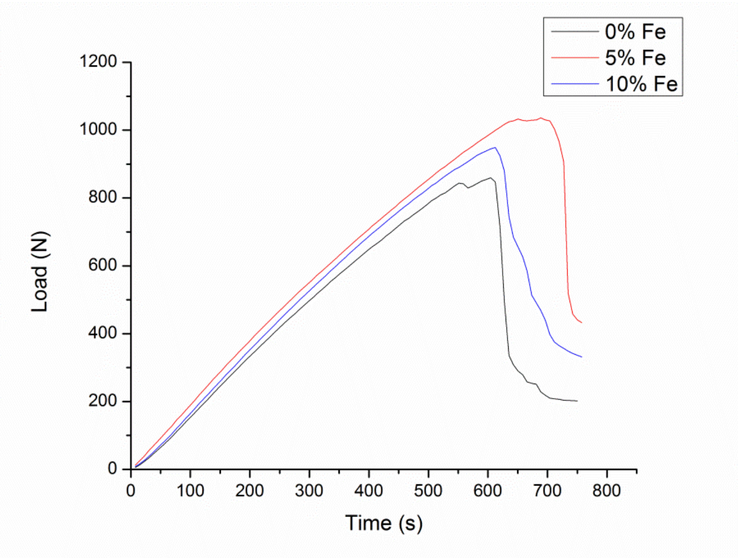

Fig. 12 *Load vs. time evolution curves on low temperature preconditioned iron particles reinforced hybrid polymer specimens in flexure*

Furthermore, to emphasis the effectiveness of the particle fillers as reinforcement within the hybrid polymer composite architectures, a percent difference (% difference) among the Young modulus in flexure retrieved for each environmentally conditioned (i.e. low and range temperatures) against to the unconditioned specimens are being plotted in Fig. 14.

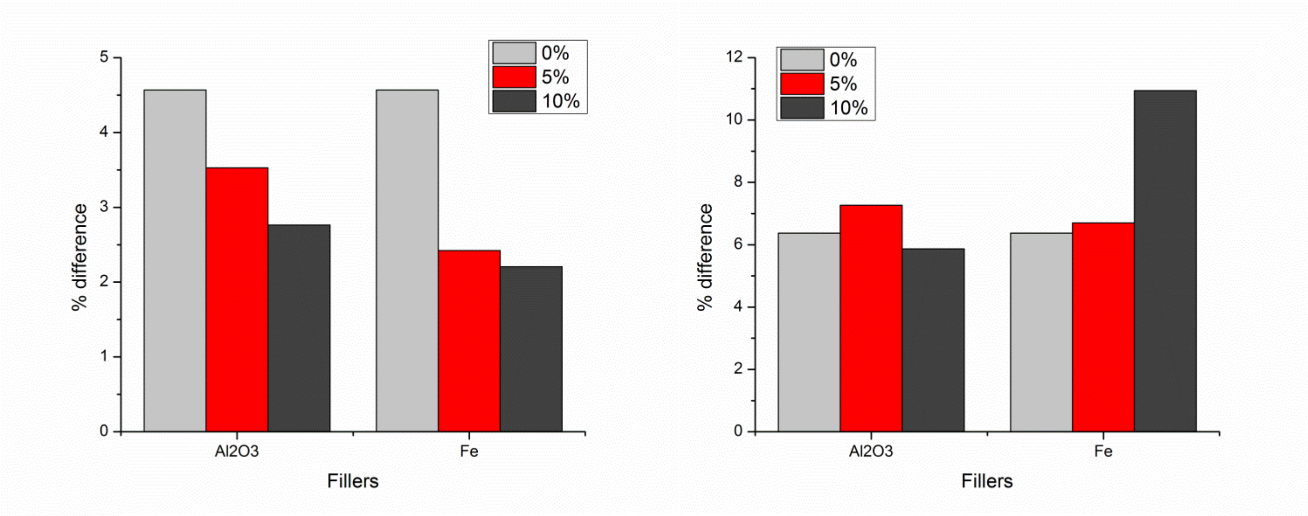

Fig. 13 *Percent difference between Young modulus in flexure: room and low temperature conditioned (left); room and temperature range (right)*

As it can be seen, in all cases, the tendency seems to be kept from one particle reinforcement type to the other. Relatively large differences are encountered for low temperature conditioned polymer composite specimens as the particle volume fraction increases.

4.1.2 Hybrid fiber-fiber polymer composites

Load-deflection curves recorded for the hybrid unsymmetrical and reference composite specimens, as plotted in Fig. 14, are subjected to changes with a positive shift while partially substitution the glass fibers with carbon fibers.

All specimens exhibited a linear relationship up to a certain load level followed by a small undeviating trend close to their ultimate stress before experiencing an abrupt, almost constantly, load drop at increasing extension.

The effective composite's elastic modulus is another dependent material property on the fibre volume fraction. Thus, the experimental flexural modulus was found to be lower than the tensile modulus as the content of UD carbon fibres' increases. This it can be sized by looking at the values provided in Table 4.

The decrease in the flexural modulus can be regarded both as compressive and shear failure types that are the predominant failure mechanisms governing these hybrid composite architectures. Tensile failure is uncommon in flexural tests, so it is unlikely to occur. The majority of specimens failed by matrix cracking combined with glass fiber breakage at their tensile face.

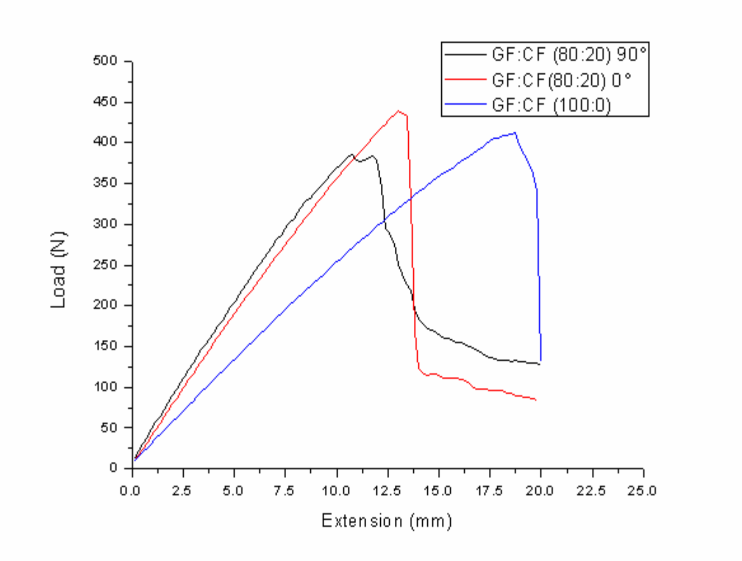

Fig. 14 *Load vs. extension curves for unsymmetrical hybrid and reference composites in flexure*

Despite all differences that can be regarded to the UD carbon fiber' content, orientation and stacking sequences, it can be seen that positive hybrid effects exist for all polymer based composite architectures.

Table 4 - Effect of UD carbon fibers' orientation and content on tensile and flexural properties of composite specimens

Sample architecture	UD CF orientation	Tensile		Flexural	
		Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
GF:CF(100:0)		116.17 ± 0.04*	4.81 ± 0.03	38.10 ± 0.04	4.68 ± 0.03
GF:CF(80/20)	0°	295.6 ± 0.03	14.64 ± 0.09	25.15 ± 0.05	4.74 ± 0.07
	90°	95.8 ± 0.02	7.60 ± 0.05	32.40 ± 0.04	4.23 ± 0.07
GF:CF(60/40)	0°	331.37 ± 0.01	16.21 ± 0.07	108.12 ± 0.05	4.48 ± 0.05
	90°	93.15 ± 0.04	7.22 ± 0.05	118.14 ± 0.04	4.21 ± 0.04

* Standard error

Inconsistencies between the experimental values, proven various UD carbon fibres orientation and content, can be ranked as being relatively low for data retrieved based on the flexure tests in comparison with the tensile tests where a severe drop of approximately 50% in the elastic modulus was found to occur for the same composite architecture but different UD carbon fibre orientation.

Moreover, the discrepancies between the hybrid composites' overall strength are evenly more accentuated, especially in the composite architectures with longitudinal (0°) oriented UD carbon fibres.

Thus, the flexural properties of hybrid composites under the focus can be regarded to depend mainly on the stacking sequence, individual reinforcement material and orientation with respect to the mechanical applied load.

Furthermore, as expected, the higher the CF contents the best mechanical performance over the other hybrid or reference architectures, irrespective of the orientation with external applied load. In addition, these increase values can be regarded to the fibre-matrix adhesion and interfacial strength.

The effective mechanical properties of these hybrid composites are being also influenced by the capacity of stress transferring between the fibre-matrix interfaces and fibres' different breakage mechanisms.

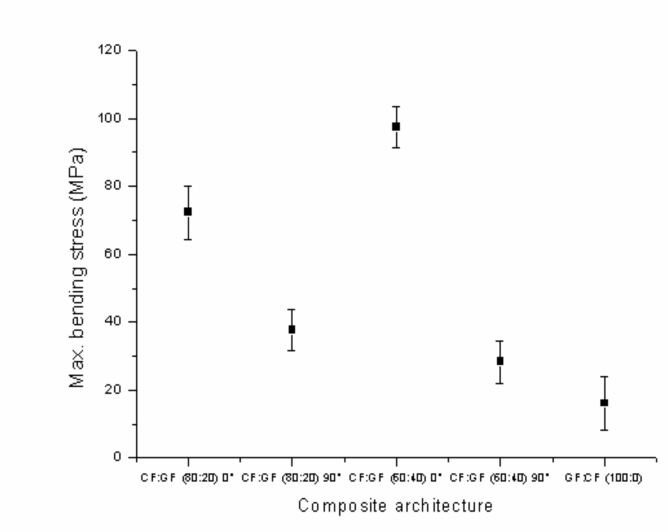

Fig. 15 *Mean maximum bending stress values retrieved for the hybrid fiber-fiber polymer composite specimens*

Fig. 15 refers to the maximum bending stresses at maximum extension for all hybrid polymer composites plus reference specimen. Data scattering can be regarded to the increase of the UD carbon fibre's content as well as to their orientation with the external load.

These are provided to give reader a perspective on the experimental values retrieved and are particular useful in structural applications of these type of composite materials. Furthermore, it should be desired to have supplementary information on the breakage mechanisms and the initiation of failure on all hybrid composite architectures.

Furthermore, it was beyond of the purpose of this topic to retrieve the mechanical parameters for different setup values that can be imposed even it is supposed to be highly influenced. Further studies tackling the issues can be carried out in order to contribute to both database and knowledge enhancement on these composite architectures since they can be deployed effectively in a wide range of engineering applications.

4.2 Dynamic mechanical properties

Specific objectives:

- To deploy acquired proficiency through debating on dynamic mechanical properties of hybrid composites manufactured.
- To track temperature dependencies of effective dynamic mechanical properties in hybrid polymer composite specimens.
- To debate on the dynamic mechanical properties due to hybridization.

As it was previously stated in Chapter 1, the main *influencing factors* upon the effective material properties of polymer based composites, generally, and hybrid ones, particularly, have to be identified by looking to the composites: architecture, constitutive (e.g. volume fraction, orientation, materials, etc.), manufacturing technology, prior and post-processing of individual or overall structure and last to the experimental conditions selected.

The latter out of aforementioned influential factors and consequently, sources of errors associated with experiments envisages: type of load, frequency, clamp, specimen geometry, temperature program, etc.

The dynamic mechanical properties of polymer based composite materials are temperature-dependent properties. At each temperature, the polymer composite structures can be considered as a mixture of materials in various states, with different overall properties.

According to ISO 6721-1:2011, the *storage modulus* E΄represents the stiffness of a visco-elastic material and is proportional to the energy stored during a loading cycle while the *loss modulus* E" is defined as being proportional to the energy dissipated during one loading cycle. The *loss factor* tan δ is the ratio of loss modulus to storage modulus. It is a measure of the energy lost, expressed in terms of the recoverable energy, and represents mechanical damping or internal friction in a viscoelastic system. The loss factor tan δ is expressed as a dimensionless number. A high tan δ value is indicative of a material that has a high, non-elastic strain component, while a low value indicates one that is more elastic [196].

The subsequent reported data and discussion relay on information provided in the authored and co-authored scientific papers or invited presentations [195, 197-200]. All specimens were subjected to applied mechanical load by layering in three-point bending mode and using temperature ranges as described in chapter 2. Some of the graphs were plotted differently than those presented in the cited articles and included into the subsequent discussion to provide a comprehensive view on the approached issue.

4.2.1. Hybrid particle-fiber polymer composites

Storage modulus (E')

As shown in Fig. 16, the storage modulus of the hybrid particle-fiber polymer based composites under the focus varies significantly when subjected to high temperatures. As it can be seen, two transitions (i.e. glass and leathery to rubbery) and three different states (i.e.

glassy, leathery ad rubbery) can be identified for the herein unsaturated polyester thermosetting resin used as matrix material. Since the experiment was stopped at 180°C a second decrease associated to the rubbery to decomposed state could not be recorded.

In the temperature range between -25° up to 25°C, the unsaturated resin can be characterized as preserving intact its primary and secondary polymer bonds. The associated variation is almost constant its values are the highest among all the recorded ones. This polymer state is referred to as the glassy state.

Furthermore, from ceramic particles influences point of view an increase in the relative volume fraction towards to an increase in the corresponding storage modulus. These tendencies are being kept over the entire temperature range, for all recorded polymer states as well as for dynamic mechanical components (see Fig. 16).

Next, when the temperature increases the *leathery* polymer state, is being reached. This is compromising intact primary bonds and broken secondary polymer bonds that are causing both a drop in the dynamic mechanical modulus and an increase in the viscosity.

As the temperature is raised further, between 150° up to 180°C, the primary and secondary bonds remains unchanged as previously, but the molecular structure get entangled. In this case, the *rubbery* state is not so well captured in the experimental data. The small segment associated to this temperature range can be assigned better to the transitions form the leathery to the rubbery state and to what is following naturally due to the temperature increase.

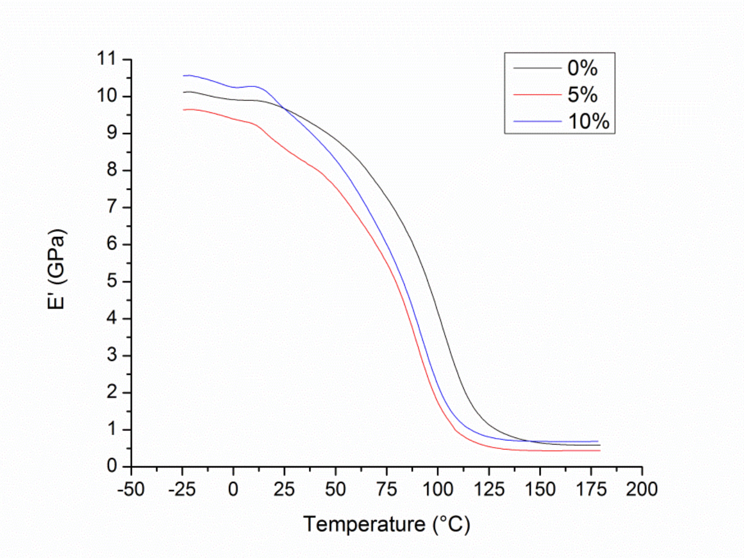

Fig. 16 *Particle content effects on the storage modulus at different temperatures*

Loss modulus (E”)

In Fig. 17 was represented the variation of the loss modulus with temperature for both polymer based hybrid composites and reference architecture.

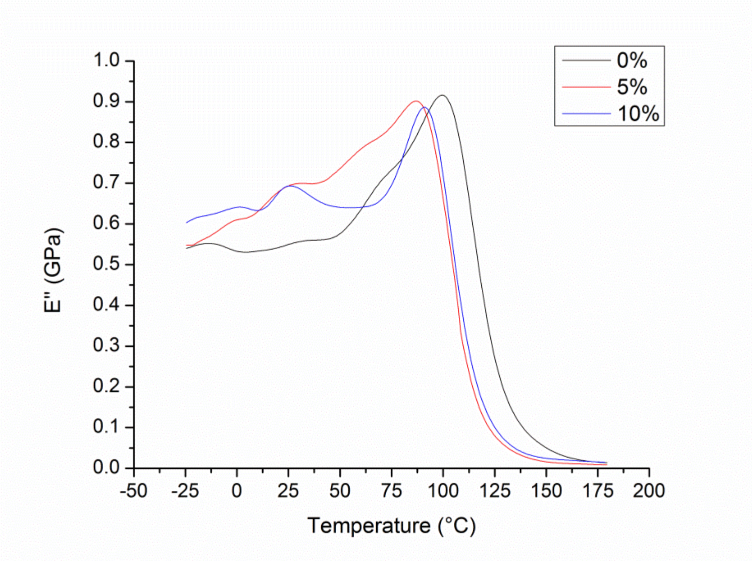

Fig. 17 *Particle content effects on the loss modulus at different temperatures*

As it can be seen, the incorporation of the particle phase causes a broadening of the loss modulus peak that can be attributed both to the inhibition of the relation process and different arrangements of the cross-linking segments of the unsaturated polymer matrix.

Furthermore, all randomly variations until the peaks are being reached can be assigned to the polymer network that breaks its secondary bonds while preserving unchained the primary ones. The glassy to leathery transition reveals better this increase of viscosity.

Damping factor/loss tangent (tan δ)

As one of the important parameters that provide a balance between the elastic and viscous phase of polymer based composite materials, this material property reveals the influence of the constitutive, in terms of type, distribution and compatibilities upon the damping behavior of the structures.

In Fig. 18 is being represented the variation of loss tangent with temperature for particle-fiber reinforced polymer composites. As it can be seen, the Tg (i.e. glass transition temperature) is around 125 °C for the solely random E-glass reinforced system, whereas for the other hybrid structures encounters a negative shift towards 100 °C. This negative shift in Tg values reveals the fact that the ceramic particles phase are effective as a reinforcing material and stress relaxing agent. Furthermore, this shift it can be associated with the increased mobility of the polymer chains at the constitutive interfaces.

From manufacturing point of view this is a positive measure that can be taken to release the internal stress during the polymerization step, proven the highly condensation nature of the unsaturated polyester resin.

Next, the addition of second phase (i.e. particles) lowers the Tg of the overall hybrid composite structure. Lower Tg values represent a less reticulated system, which yields smaller network degree density.

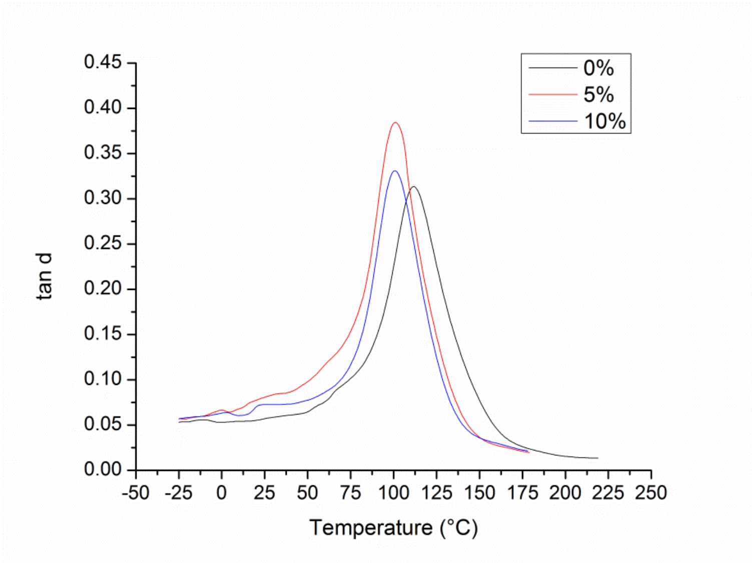

Fig. 18 *Damping factor variation with temperature in particle-fiber hybrid architectures*

In Table 5 was listed the Tg values retrieved from the damping factor and loss modulus curves. These values are usefully in assessing the hybrid composite's behavior in shock and vibrations as recommended by ASTM D 4065:2001 [201]. Furthermore, the importance of Tg relays on its practical significance since provides information regarding the thermal limits in use of structures or components, their frequency and temperature-dependent damping, influence of the constitutive on the mechanical properties, degree of curing or post-curing, etc.

Table 5 - Peak height and Tg temperatures (from tan δ and E" curves)

Sample architecture	Peak height of tan δ curve	Temperature [° C]	
		Tg from tan δ	Tg from E"
GF: CP 0%	0.3762	91.2	89.0
GF: CP 5%	0.3030	87.4	85.0
GF: CP 10%	0.5182	86.2	81.3

Cole-Cole plots

The *Cole-Cole* diagram of the hybrid composite structures for different particle volume fraction is presented in Fig. 19. As it can be seen, for the 0% particle reinforced architecture, the spherical ideal shape was retrieved whereas an increase in the particle content reveals departures from this shape. The latter is indicating the heterogeneity of the hybrid structure while the shapes of the curves' points towards to a relatively good reinforcement/matrix interface.

In Fig. 20 and Fig. 21 are being represented the predicted data vs. experimental retrieved values and the relative error between these types, respectively.

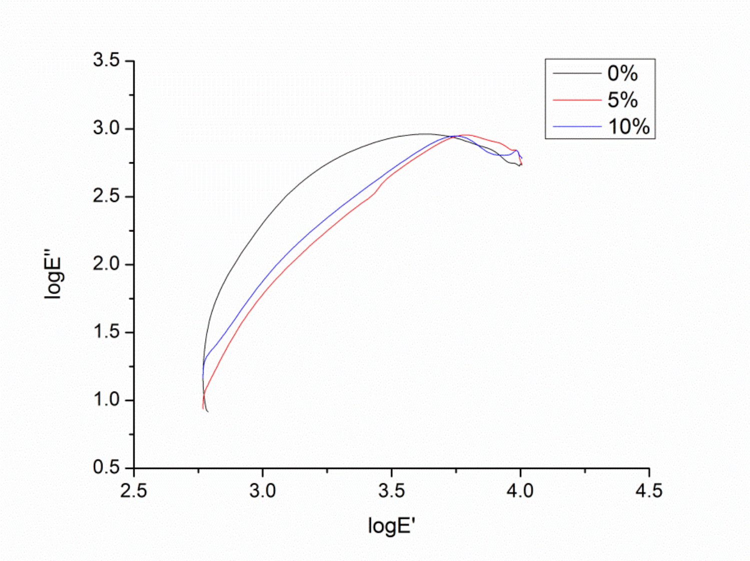

Fig. 19 *Cole-Cole diagrams for the particle-fiber polymer composites*

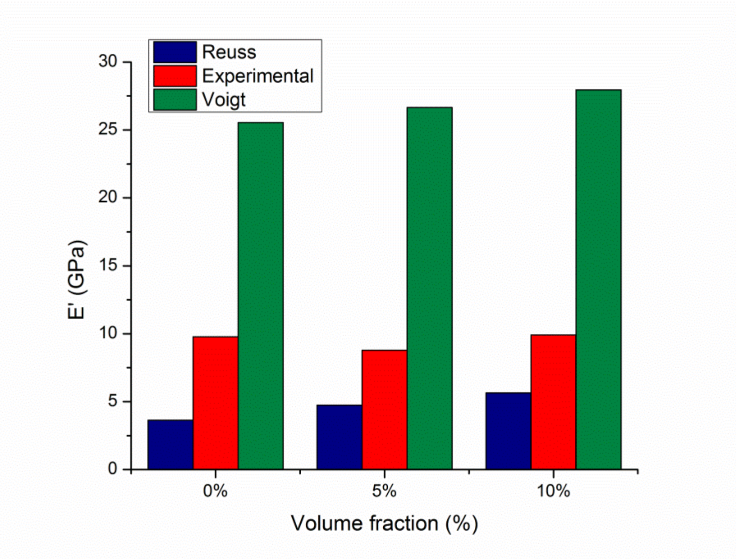

Fig. 20 *Theoretical vs. experimental data values accounting for different particle fractions*

As it can be seen from Fig. 20, the experimental values retrieved from the storage modulus curves as values recorded at room temperature (i.e. 23 °C) are bounded by the theoretical predicted values based on micromechanical models developed by *Reuss* (iRoM and iRoHM) and *Voigt* (RoM and RoHM). These bounds correspond to the extreme values that can be retrieved for the Young modulus of the composites proven the ideal case considered while the assumptions were made.

With respect to the data plotted in Fig. 21, these correspond to the relative error between each theoretical micromechanical model considered and the experimental retrieved data. As it can be seen from the figure, the experimental values are relatively closer to the *Voigt* model meaning that, in this case, a simple addition of individual dynamic mechanical properties of constitutive can provide a quick assessment of the overall dynamic mechanical properties of the hybrid composite architecture.

Further, since all deviations between the elastic modulus of the hybrid composites from the RoHM equation and the actual modulus values are positive, a positive hybrid effect results.

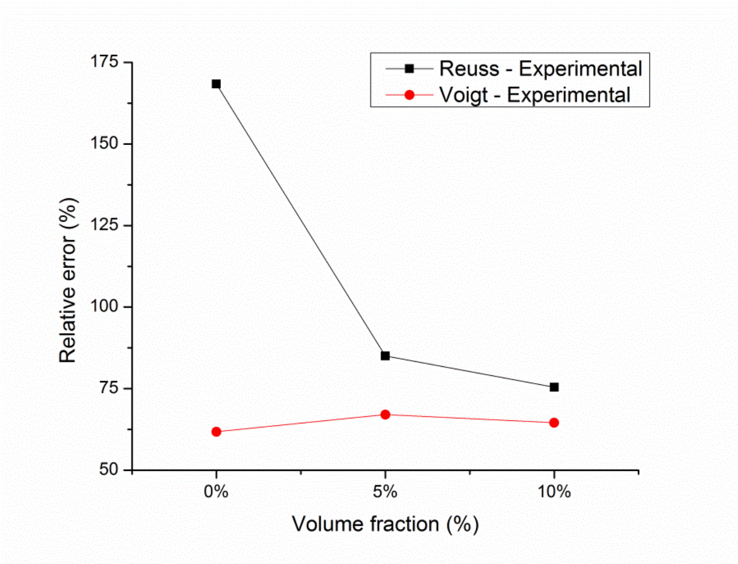

Fig. 21 *Relative errors accounting for different particle volume fractions*

Kinetic parameters identification

Based on related expression in chapter 1, a plot of $ln\left(-ln\left(1-\alpha_g\right)/T^2\right)$ against $1/T$ was provided in Fig. 22. Simple linear regression applied to the selected data (n. correlation factor 0.97) followed by parameter identification from slope value provided enables glass transition associated energy of activation retrieval. The activation energy, $E_{A,g}$ was calculated to be 2.04 kJ/mol as provided in Table 6. Next, this value was substituted to enable retrieval of pre-exponential factor A_g (see provided values).

With respect to the value predicted for energy of activation, one might debate on the relatively small value retrieved compared with other polymer materials. The latter can be assigned to the polymer used as matrix in this hybrid composite architecture that is an unsaturated polyester resin. Apart for being one of the less costly material often employed by manufacturers it's polymerization process strongly depend on several factors such as: storage environment, manufacturing conditions, content of relaxing agents, etc. The activation energy strongly depends upon the constitutive content within the composite and reveals the effectiveness in stress transfer between the particles, fibers and matrix. Further insights into the issue should be closely approached.

Furthermore, one may further use the kinetic parameters to predict the temperature-dependent complex/storage or loss modulus and deploy an error minimization scheme between theoretical predicted and experimentally retrieved values. Consequently, the above formalism can be applied to the loss modulus experimental values and may be used to model the temperature-dependent viscosity. Since the viscosity in the leathery and rubbery states appears to be different, the analysis should be individually carried out. It is beyond the purpose of this work to further debate on the issue.

Table 6 - Kinetic parameters associated to glass transition in hybrid particle-fiber composites

T (°C)	α_g (%)	A_g ($x10^{-7}$ min^{-1})	$E_{A,g}$ (kJ/mol)
75	40	37.07	2.04
80	50	40.57	
90	65	43.30	
95	75	48.21	
100	85	57.50	
110	95	68.12	

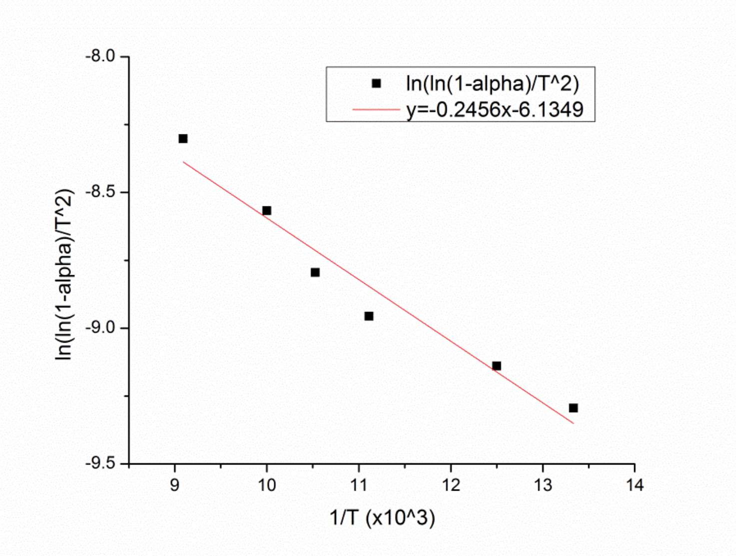

Fig. 22 *Linear regression plots for activation energy identification*

4.2.2. Hybrid fiber-fiber polymer composites

Further research development in the chapter's issue aimed to size the influence of the constitutive material type, content and different orientation upon the overall dynamic mechanical properties of fiber-fiber type hybrid polymer based composite structures.

Thus, long fibers with different distributions (i.e. random and unidirectional) and materials' type (i.e. glass and carbon) were differently stacked, symmetrical and non-symmetrical, to provide the hybrid composite architecture.

Storage modulus (E')

In Fig. 23 were plotted the storage modulus variation with temperature for the reference (i.e. GF:CF(100:0) architecture) and both longitudinally and transversal oriented UD carbon fibers' reinforced hybrid composites under discussion.

Accordingly, one might observe that E' values decrease as the number of the UD carbon fiber ply-ups increases and changes their orientation with respect to the general reference system. The latter can be regarded to the fact that the modulus of elasticity of the UD carbon fiber is much lower in the transversal direction than in the longitudinal direction.

Addition of carbon fiber ply-ups was expected to lead to an increase of the E' modulus of these architectures of polymer based composites.

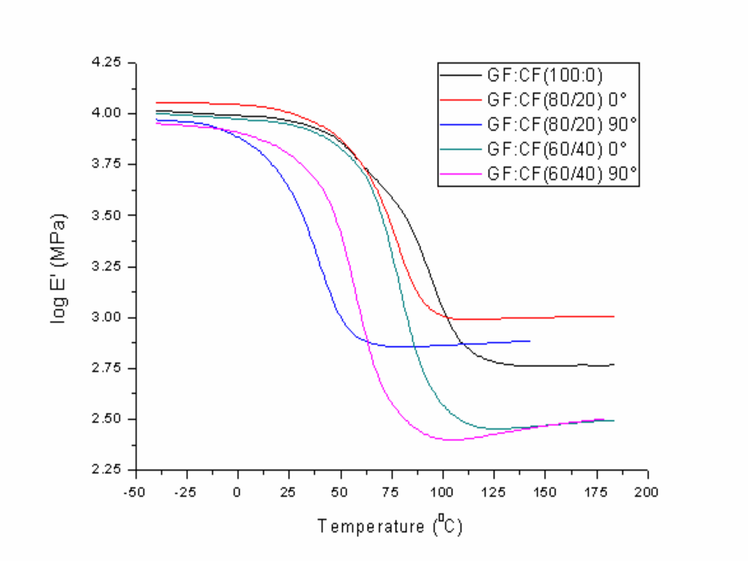

Fig. 23 *Reinforcements' volume fraction and UD fiber orientation effects on the storage modulus at different temperatures*

As temperature increases, close to glass transition temperature (Tg), the E' of the reference and hybrid fiber-fiber composites experience a sharp decrease indicating that the structures are passing through the glass/rubbery transition stage.

Further, above Tg, the storage modulus of the reference is lower than that of GF:CF(80:20), having UD carbon fibers both 0° and 90° oriented but higher than that of GF:CF(60:40), of same type. The latter can be regarded to the increases in molecular mobility of the polymer chains above Tg temperature, as well as to the UD carbon fiber content and temperature dependence.

Loss modulus (E'')

Like above, the loss modulus preserves the same tendency of high values over the temperature range for reduced numbers of carbon fiber ply-ups embedded within the hybrid composite architectures (see Fig. 24).

The E" values recorded from the glassy plateau reveal the influence of the UD carbon fibers content on the overall dynamic property. Thus, an increase in the UD fiber volume fraction is leading to a decrease of the E" values that can be regarded to the carbon fibers' behavior with the increase of temperature.

A discrepancy can be observed throughout the transition region, especially for the maximum E" in case of GF:CF (60:40) and reference specimens. This can be attributed to the inhibition of the relaxation process within the composite structures with the addition of the UD carbon fibers as a supplementary phase. However, GF:CF (80:20) hybrid composite architecture has resulted in higher E" values within temperature range above its Tg.

Below the Tg values of each specimen, the E'' curve for reference is closer to the curve retrieved for the GF:CF(80:20) architecture, whereas after these values, is getting nearer to the curve retrieved for the GF:CF (60:40) combination, proven the longitudinal orientation of the UD carbon fibers.

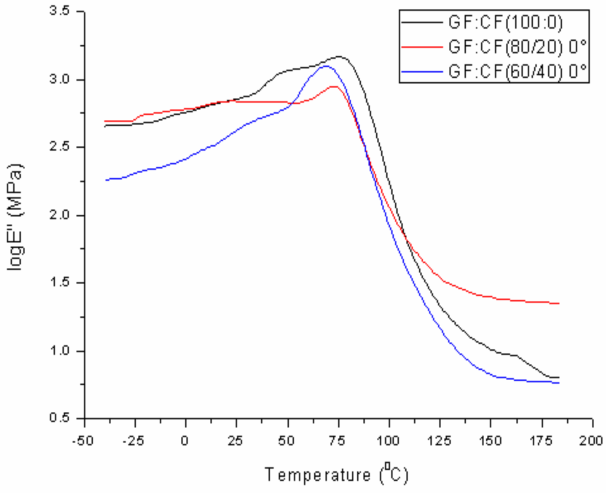

Fig. 24 *Reinforcements' volume fraction and UD fiber orientation effects on the loss modulus at different temperatures*

Damping factor/loss tangent (tan δ)

In Fig. 25 was plotted the tan δ curves function of temperature, accounting for different UD carbon fiber content and orientation, whereas in Table 7 were provided the Tg values retrieved from the tan δ and the E" curves. The latter are the most relevant performance indicators of hybrid composites' behavior in shock and vibrations.

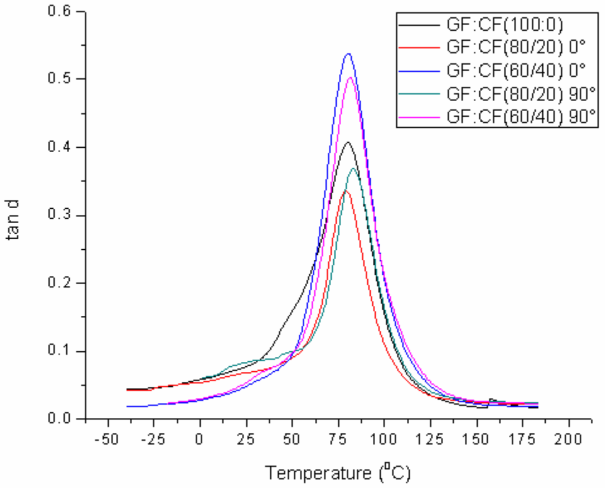

Fig. 25 *Damping factor variation with temperature and UD fiber orientation in fiber-fiber hybrid composite architectures*

Table 7 - Peak height and Tg temperatures (from tan δ and E” curves)

Sample architecture	UD CF orientation	Peak height of tan δ curve	Temperature [° C]	
			Tg from tan δ	Tg from E”
GF:CF(100:0)	-	0.3762	91.2	89.0
GF:CF(80:20)	0°	0.3030	87.4	85.0
	90°	0.3241	88.4	83.6
GF:CF(60:40)	0°	0.5182	86.2	81.3
	90°	0.4782	88.0	83.4

Noteworthy can be considered the small shift experienced by the loss factor while UD carbon-fiber content and orientation change. The shifts in Tg values are positive and thus can be viewed to reveal the effectiveness of the GF and CF fibers as reinforcing agents and have not to be linked to any post-curing effects.

Concerning the reference comparison issue, it can be observed that the tan δ peak of symmetrically stacked UD carbon fibers are lower than of non-symmetrical architectures, either 0° or 90° oriented. This envisages that an increase in the carbon fibers’ content will carry into a greater extent of applied stress allowing a small part of it to strain the fiber/matrix interfaces.

Cole-Cole plots

In Fig. 26 (a) and (b), were provided the *Cole-Cole* plots of the dynamic moduli for the reference and hybrid polymer composite structures accounting for different UD carbon fiber content and orientation. The *Cole-Cole* graphs consists in plotting the loss modulus data as a function of the storage modulus.

As it can be seen, both content and orientation of the UD carbon fiber contribute to the *Cole-Cole* plot shape changes. While in case of the 0° disposed UD carbon fibers, the changes give rise to imperfect semicircular shapes to the *Cole-Cole* plots, for their reverse configuration (i.e. 90°), the form of plots changes to an irregular shape.

These imperfections indicate that there is heterogeneity among the glass and carbon fibers along the specified direction and the transversal isotropy of the CF reinforcement. Further insights in the adhesion between fibers and polymer matrix should be considered. Since the polymer matrix deployed is an unsaturated resin matrix, it is expected to have voids near the fiber/matrix interface that can be accounted to provide this departure from the ideal spherical shape.

In addition, because the unsaturated polyester resin is a condensation resin, it is expected to react with the volatiles, and other impurities form the reinforcement surface. This is unlikely to occur in that extend to exert a severe impact on the formation of perfect bonding at interfaces.

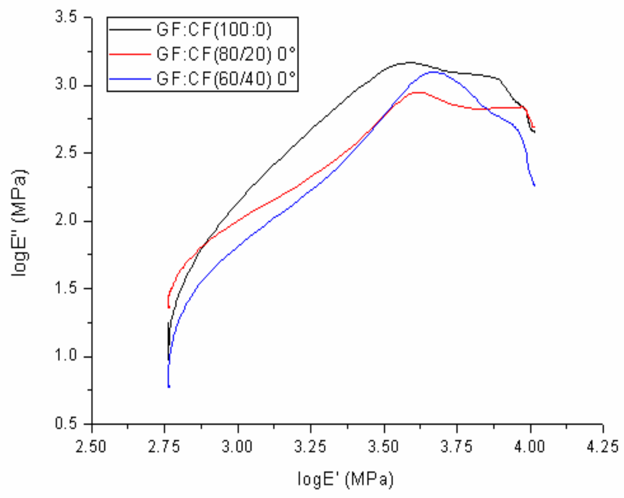

Fig. 26 *(a) Cole-Cole diagrams in 0° oriented UD carbon fibers of hybrid fiber-fiber polymer composites*

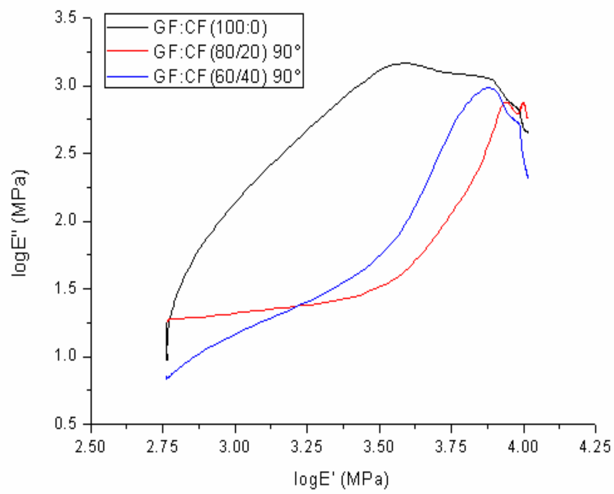

Fig. 26 *(b) Cole-Cole diagrams in 90° oriented UD carbon fibers of hybrid fiber-fiber polymer composites*

Finally, the reader should recall the importance of the DMA experiments for practical applications, including: influence of the fiber reinforcement on mechanical parameters, use of the dynamic elastic moduli to compute the temperature dependence of composite mechanical strength, identification of ageing state, polymer's matrix degree of curing and post curing, polymer composite's thermal degradation, etc.

In the light of above, the extent to which similar correlations can be drawn and exploited for other polymer matrices, stacking sequence layer of synthetic reinforcements and various orientations remains to be tackled in further studies once they have been identified and ranked as potential interesting.

4.3 Thermo-physical properties

Specific objectives:

- To deploy acquired proficiency through debating on thermo-physical changes in hybrid composite architectures.
- To track thermo-physical changes in hybrid polymer composite specimens function of structural parameters and/or external loading conditions.
- To debate on the hybrid effects on the overall thermo-physical property, both expansion and conductivity, from the contribution of individual reinforcements.

The influencing factors as acknowledged from previous chapters will be closely monitored and referred herein. These include information on laminates: architecture, constitutive (e.g. volume fraction, orientation, materials, etc.), manufacturing technology, prior and post-processing of individual specimens and last to the experimental conditions selected.

The latter out of aforementioned influential factors and consequently, sources of errors associated with experiments envisages: temperature program, specimen geometry, thermocouple position with respect to the specimen, specimen layering, etc.

The experimental measurements are being considered to comply with the general principles stated with the last amendments on ASMT E 473:2014 [202] and principles stated with ASTM E831:2014, ASTM D696:2008 or ISO 11403-2:2012 on thermal measurements, generally and linear expansion, particularly [203-205]. In addition, since the specimens are being subjected to various environmental conditions (e.g. water immersion, moisture, low temperature environments, etc.) some other standards are being accounted to apply, namely ASTM D570:98 (2010) E1 and ASTM D5229/D5229 M:2014 [184, 206].

The subsequent reported data and discussion relay on information provided in the authored and co-authored scientific papers or invited presentations, partially or entirely referred [176, 178, 179, 181, 207-212].

4.3.1 Hybrid particle-fiber polymer composites

Thermal expansion

The dilatometer used for this work was equipped with a fused silica sample holder and pushrod. The contact force of the pushrod was 2.5 N. The temperature measurement at the sample was done using a type E thermocouple. The system's influence was diminished using the calibration correction. The calibration run was carried out under the same conditions as used for the specimens.

The samples' length was about 25 mm. Each individual sample was tested in a controlled air atmosphere between 25 °C and 250 °C at a heating rate of 1 K/min following two successive runs. The first one removes thermal history particular about specimens' manufacturing while the second run enabled to retrieve the thermal property foreseen.

In Fig. 27 is being plotted the instantaneous experimentally retrieved CTE values of particle-fiber reinforced polymer composites subjected individually to successive thermal runs. The composites where labeled differently in this particular plot, with the following significance on the particle volume fraction (n. the fiber reinforcement retained the same volume fraction): sample 1 – 0%, sample 2 and 3 – 5% and 10% Al_2O_3 fillers, sample 4 and sample 5 – 5% and 10% Fe fillers, respectively.

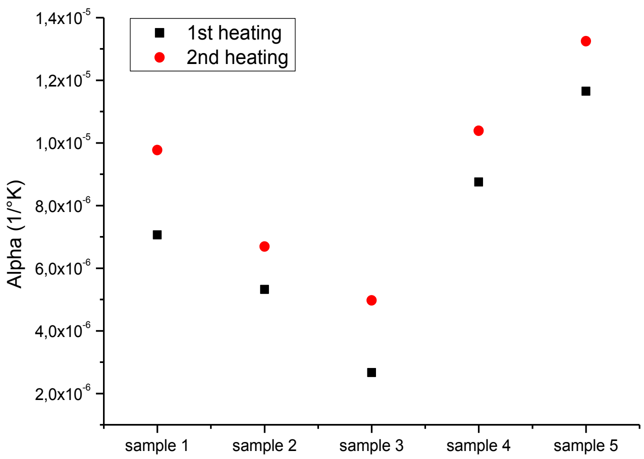

Fig. 27 *Instantaneous CTE values (at 25 °C) for samples undergoing two successive scans*

Differences on the CTE values retrieved at room temperature are relatively small and can be regarded to thermal stress induced during the manufacturing, residue removal from the specimens' surface (e.g. wax, surface conditioners, etc.) and air trapped at the surface as the result of the polymerization process.

The values of instantaneous coefficients of thermal expansion of particle-fiber reinforced polymer based composites under the focus are summarized in Table 8. These were retrieved from the instantaneous CTE variation with temperature for different instances of the latter.

Table 8 – Instantaneous CTE values of particle-fiber polymer composites

Temperature [^{0}C]	Reference sample [x10^{-6}/^{0}C]	5% particles [x10^{-6}/^{0}C]		10% particles [x10^{-6}/^{0}C]	
		Al_2O_3	Fe	Al_2O_3	Fe
25	31.434	36.789	31.903	41.237	29.624
50	21.809	13.326	25.045	12.579	24.826
100	1.2586	2.8613	4.4431	3.8404	4.6403
150	5.2118	3.4754	4.8478	4.4835	4.7307
200	4.2617	2.1328	4.9412	1.3774	4.6980
250	2.6055	1.5667	2.4167	3.4394	2.5823

In Fig. 28 was plotted the predicted theoretical values using the *Mori-Tanaka* scheme vs. experimentally retrieved ones for all polymer hybrid composite specimens. As it can be seen, all CTE values are experiencing a decrease with the particle concentration increase, irrespective of the filler material type used. Moreover, the differences on the predicted values and those retrieved from test runs can be regarded to the limitation of the scheme deployed that can provide relatively accurate values only for small particle concentrations.

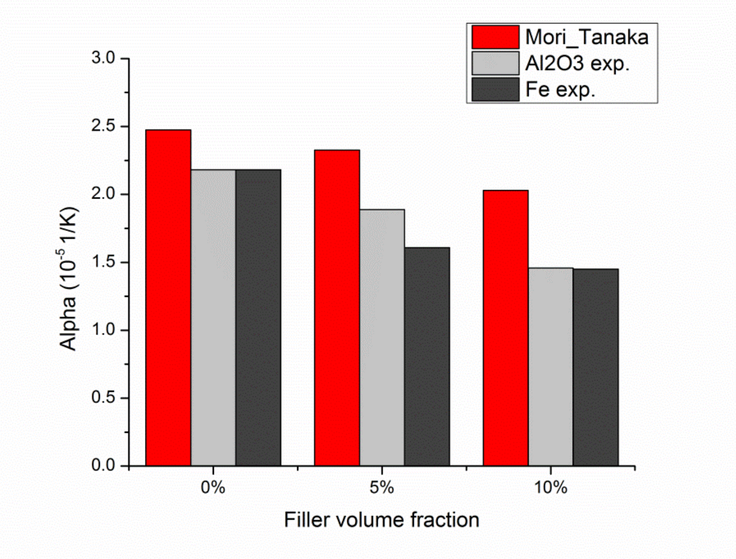

Fig. 28 *Comparison on theoretical predicted vs. experimental retrieved CTE values*

Environmental effects on thermal expansion

Application areas of hybrid polymer based composites imply exposure to various environments from extreme temperature to moisture, atmospheric aging to hygrothermal, etc. Within the herein context, environmental effect upon expansion behavior of hybrid composite specimens was extensively approached by exposing:

c) the specimens to hygroscopic environment followed by monitoring the water intake along 1 week, 1 month and 3 months, respectively, at room temperature, unchanged atmospheric conditions;
d) the specimens to temperature variation ranging from -10 °C to +40 °C within a controlled temperature enclosed structure, under a desert condition simulated thermal cycle, 7 days long, 24 hours/day (see Table 3);
e) the specimens to constant low temperature of -35 °C, 7 days long, 24 hours/day, relative humidity 45%.

Water intake in hybrid particle-fiber reinforced polymer composites exhibited a Fickian behavior, namely a increasing uptake with the first days followed by a constant variation for the remaining time interval. Since the issue was not of primary interest in terms of diffusion coefficients or maximum water intake retrieval, these can be made available at the request. Consequently, regarding the water intake influence upon the hybrid composites' expansion behavior and related properties, next figures captured the effects.

A. Specimen conditioning under hygroscopic environments

This type of experimental runs is far the most time consuming among all the works considered for particle-fiber hybrid polymer based composites' comprehensive characterization. The main objective of this work was to underline that irrespective of the environmental conditioning such is this case of long time exposure to water the hybrid composite specimens fails to undergone dramatic changes in their expansion coefficients, thus revealing structural stability.

In Fig. 29 is being plotted the instantaneous CTE variation with temperature for all representative hybrid particle-fiber composite specimens having ceramic fillers in various volume fraction by prior subjecting 1 week long to water environment. As it can be seen and in accordance with above, there are no large discrepancies between the values apart from the one revealed during the recordings for the 10% filler hybrid specimen. Thus, within 50 °C – 75 °C range, these deviations can be regarded both to the water evaporation and phase transitions particular to the unsaturated polymer resin.

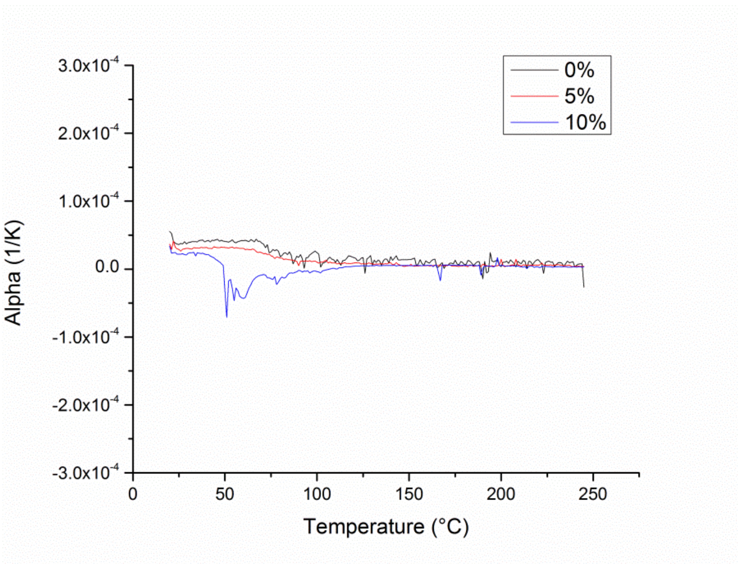

Fig. 29 *Overall CTE temperature variations after water exposure along 1 week*

Furthermore, long exposure time intervals - 1 week, 4 weeks and 12 weeks, respectively, reveals the same tendency as mentioned above, as it can be sized by scrutinize the plots in Fig. 30. The spikes need to be regarded to the temperature step used to retrieve the experimental values set to 1 K/min that is of high precision and proved unpractical from several reasons.

On the other hand, the thermal strain developed within hybrid particle-fibre composites prior subjected to water environments seems to reveal the same tendencies irrespective of the time length for immersion as it can be seen in Fig. 31. Thus, the higher the volume fraction of the ceramic filler embedded within the composite architecture the more relaxed get the thermal strains developed within as temperature rises.

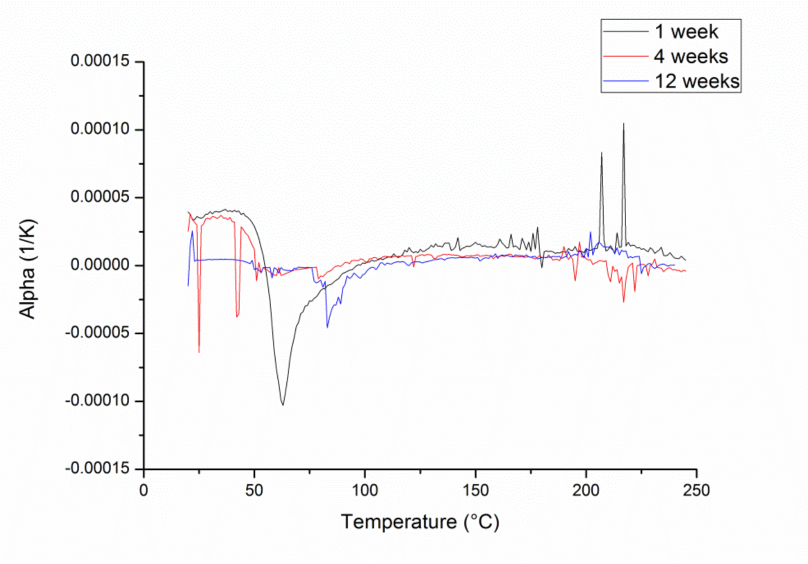

Fig. 30 *CTE temperature variations in reference specimens subjected to water exposure*

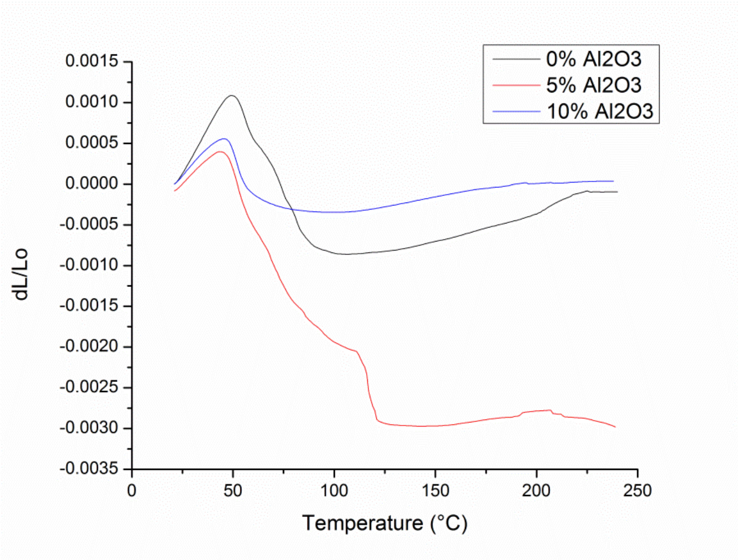

Fig. 31 *Thermal strain fields' evolution within composites after 12 week of water exposure*

For example, within the temperature range 125 °C to 250 °C, thermal strain relaxing occurs precipitously within the 10% ceramic fillers hybrid composite specimens. This can be better sized by taking a closer look to the Fig. 32 added as supplement. As it can be seen, irrespective of the time length under water exposure, the thermal strain fields' evolution maintains the same tendencies until the water evaporates from the hybrid specimens' surface and then goes to phase transitions particular about the polymer systems under temperature variations. Moreover, in all cases, the polymer matrix reaches its Tg value around 65 °C that is particular to the system deployed.

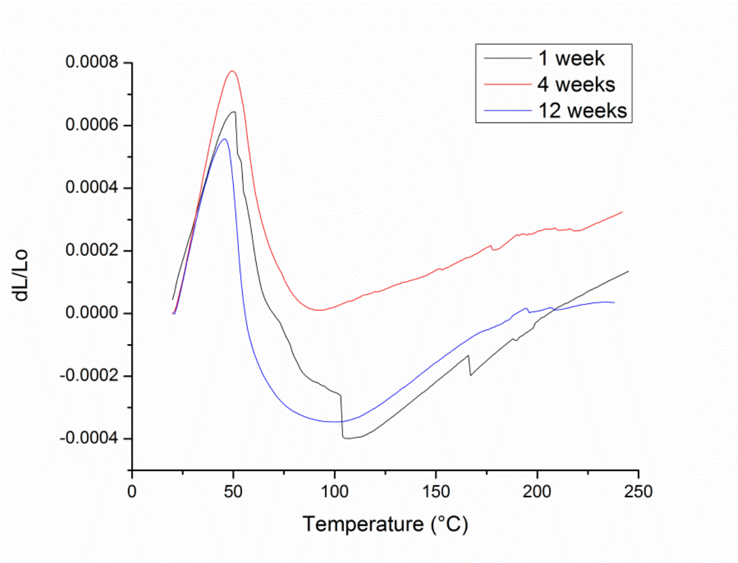

Fig. 32 *Thermal strain fields' evolution within 10% Al_2O_3 specimens under water exposure*

B. Specimen conditioning under temperature variation

In Table 9 and Table 10 are provided the instantaneous CTE values of ceramic fillers hybrid polymer based composite specimens prior undergoing temperature variation conditioning, as reported by the herein author [211].

Table 9 - Instantaneous CTE vales of conditioned and unconditioned hybrid composites

Temperature [^{0}C]	Reference sample [x10^{-6} /^{0}C]		5% Al_2O_3 particles [x10^{-6} /^{0}C]		10% Al_2O_3 particles [x10^{-6} /^{0}C]	
	no cond.	cond.	no cond.	cond.	no cond.	cond.
25	31.434	30.099	36.789	35.132	41.237	17.542
50	21.809	20.097	13.326	7.4007	12.579	12.809
100	1.2586	2.5620	2.8613	3.2002	3.8404	3.6432
150	5.2118	4.9643	3.4754	9.6350	4.4835	4.3506
200	4.2617	4.1582	2.1328	1.4232	1.3774	1.5914
250	2.6055	1.0194	1.5667	2.6413	3.4394	1.0726

Table 10 - Peak values with the instantaneous CTE temperature variations

	Reference sample		5% Al_2O_3 particles		10% Al_2O_3 particles	
	no cond.	cond.	no cond.	cond.	no cond.	cond.
Temperature [^{0}C]	22.1	57.4	124.4	56.7	79.9	89.4
CTE max [x10^{-3} /^{0}C]	0.0026	0.9095	0.04053	0.8150	0.0679	0.0215

Moreover, in Fig. 33 is being plotted the thermal strain fields recorded with temperature range for the reference, as well as the hybrid polymer composites prior experiencing a temperature range environmental conditioning. This particular environmental conditioning has a practical importance and resembles identically the atmosphere of the Sahara's 24-hour temperature interval.

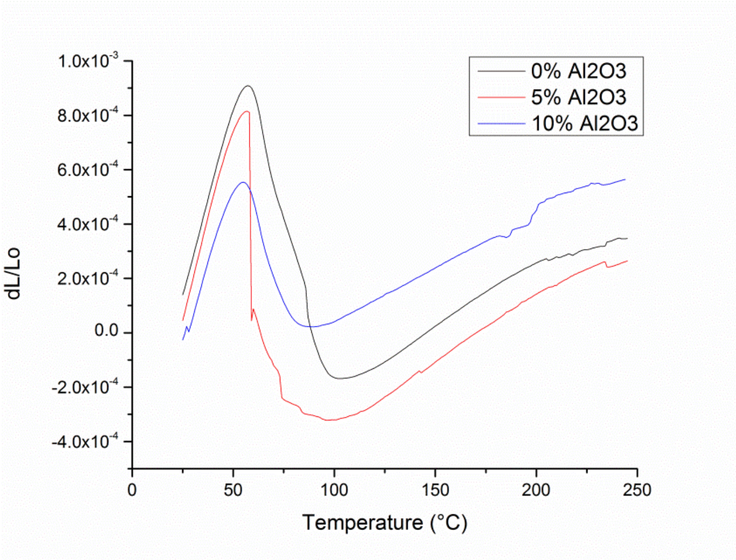

Fig. 33 *Thermal strain fields' evolution within samples prior undergoing temperature range*

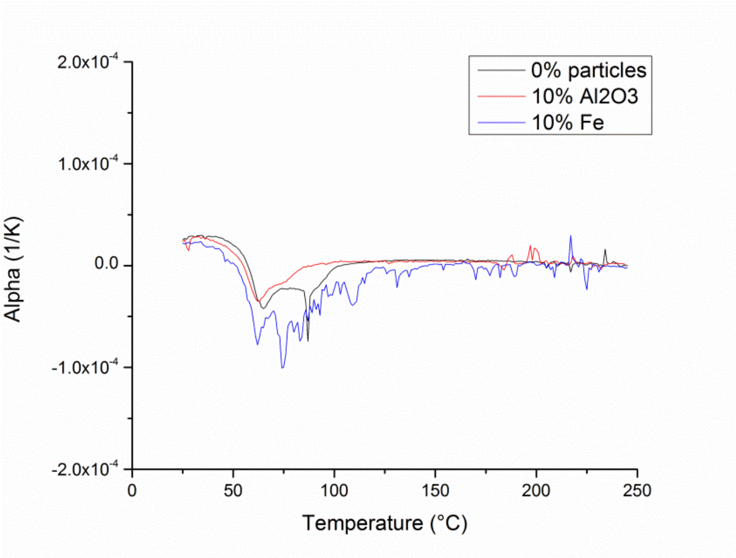

Fig. 34 *CTE temperature variations in samples prior subjected to temperature range*

On the other hand, Fig. 34 plots the instantaneous linear CTE retrieved for reference specimens and the 10% fillers (i.e. ceramic and metallic) prior subjected to temperature range environmental conditioning.

As it can be seen there are small differences between the values irrespective of the fillers' material type, even the metallic ones are showing more abrupt variations.

In addition, the same variation reveals more spikes comparative with the other ones. This can be regarded to the higher susceptibility of this hybrid composite specimen to the environmental conditioning regime considered prior to thermal runs.

On the other hand, theoretical predictions considered for these particular cases deployed the *multi-scheme homogenization* technique developed around *mechanics of materials'* combination with either *Levin-Hashin-Shtrikman* or *Hashin-Rosen* micromechanical models (see corresponding section with Chapter 3). In Fig. 35 were plotted these predicted values against those from experimental runs for reference and different concentrations of Al_2O_3 particle reinforcements.

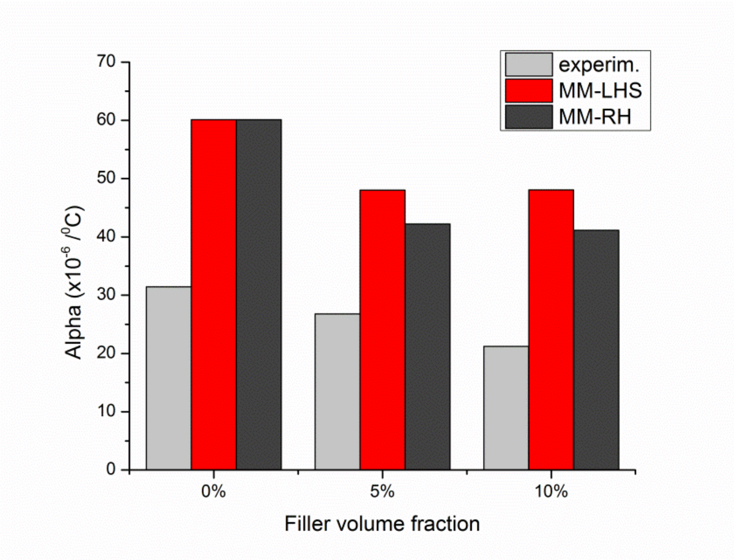

Fig. 35 *Theoretical predicted vs. experimental retrieved CTE values for Al_2O_3 fillers*

Paying attention to the plotted values, both predicted and experimentally retrieved, it might be identified the identical trends followed by these. Thus, the experimental recorded values are undergoing a decrease trend with the increase in the concentration of the particle phase as those from predictions. Furthermore, the differences should be accounted to the schemes deployed that belong to improved bounds that provide useful estimates of the thermal property for a range of volume fractions.

C. Specimen conditioning under constant low temperature

Concerns about materials' properties environmentally conditioned to low and cryogenic temperature range, prior or during test runs, captured attention due to several practical reasons, including their application potential, sustainability and their behavior.

Experimental runs considered therein aimed approximately the same issues as above. Consequently, the reference and particle-fibre hybrid polymer based structures prior undergoing low temperature range as described (see Chapter 2) are found to experience different behaviour during their thermal-physical change monitoring.

In Fig. 36 was plotted the thermal strain fields recorded for different concentration of Al_2O_3 particle reinforcements prior subjected to low temperature conditinings.

There is no reasonable explanation on the 5% Al_2O_3 hybrid polymer based specimen, and the general trends are the get relaxation behavior within the hybrid structures as the particles' concentration increase.

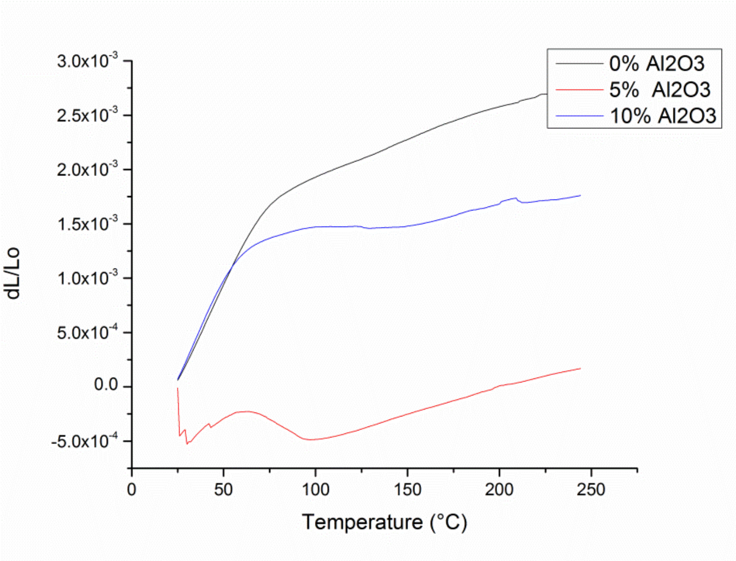

Fig. 36 *Thermal strain fields' evolution within composites prior undergoing low temperature*

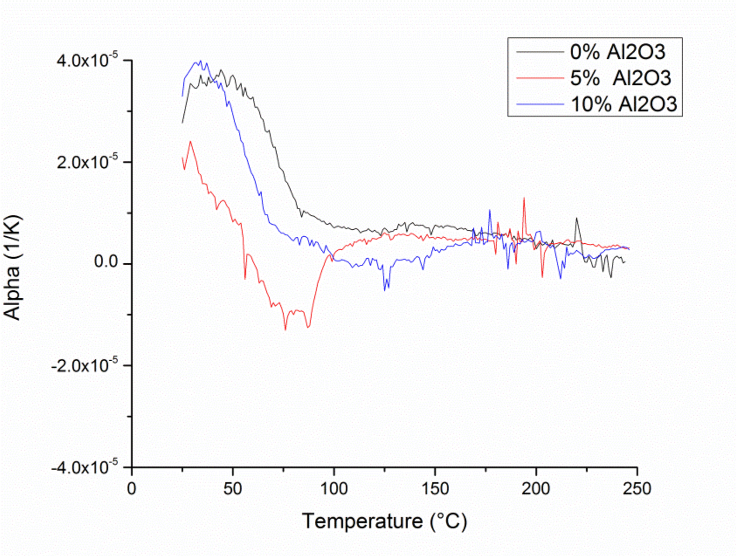

Fig. 37 *Overall CTE temperature variations after low temperature exposure*

The same as above holds with respect to the instantaneous CTE variation with temperature, as it can be sized from the Fig. 37. Similarly to the temperature range environmental conditioning plots, the spikes from the recorded values can be regarded to the induced micro-cracks from the samples' surface as well as to the moisture removal.

Thermal conductivity

This material property is particular important while designing composite panels or structures acting as thermal insulators (e.g. civil engineering, transport, aerospace, encapsulated electronic devices, etc.).

The measuring principle is rather simple but effective and provides a quick retrieval of the property. In addition, since *thermal effusivity* represents another important parameter to be accounted in thermal related design processes, proven the practical significance (i.e. measure of the material's ability to exchange thermal energy with its surroundings) it was accounted as well herein.

In Fig. 38 was plotted the experimental values and the predicted effective thermal conductivities based on lower bounds of the multi-level theoretical models from expressions in Chapter 3. As it can be seen, the experimental values fall between the lower *Hashin-Shtrikman* limit and lower Wiener bound, encountering higher values for the Al_2O_3 reinforced hybrid composite structures.

Supplementary, the increase of the particle content within the composite structure results to an increase of the effective measured material property as is well acknowledged within the literature. The above can be better sized in terms of the computed relative error between the predicted values and experimentally retrieved ones, as plotted in Fig. 39.

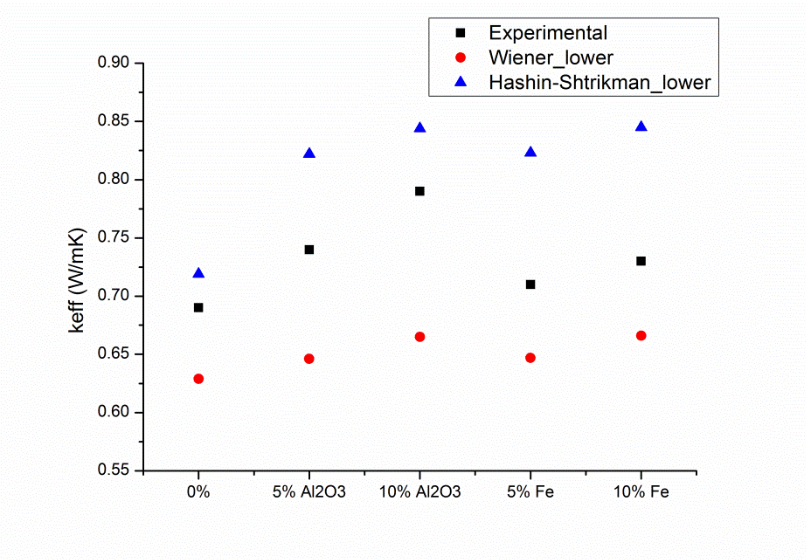

Fig. 38 *Effective thermal conductivities – experimental vs. theoretical predicted*

In Fig. 40 was plotted the effusivity experimental retrieved values for the hybrid composite samples under the study for different particle volume fractions. As it can be seen, the same remarks as in case of effective thermal conductivity holds, namely an increase of the overall material property with the increase of the particle content. Due to the dilute content of the particle inclusions, their contributions to the effective thermal conductivity and effusivity of the hybrid configurations approached is scarcely, the random E-glass fibers are remaining as a leading constitutive influencing the overall behavior.

Furthermore, the higher the volume fraction of the particle type constitutive, the approximately the same turn to be the polymer composites' abilities to exchange thermal energy with their surroundings. This finding is particular important for electronics industry applications including printed circuit boards.

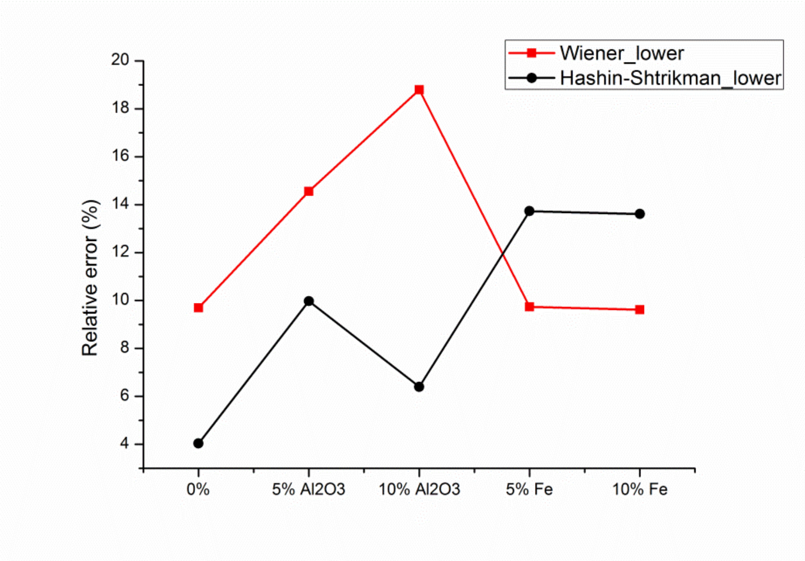

Fig. 39 *Relative errors between the experimental and predicted thermal conductivities*

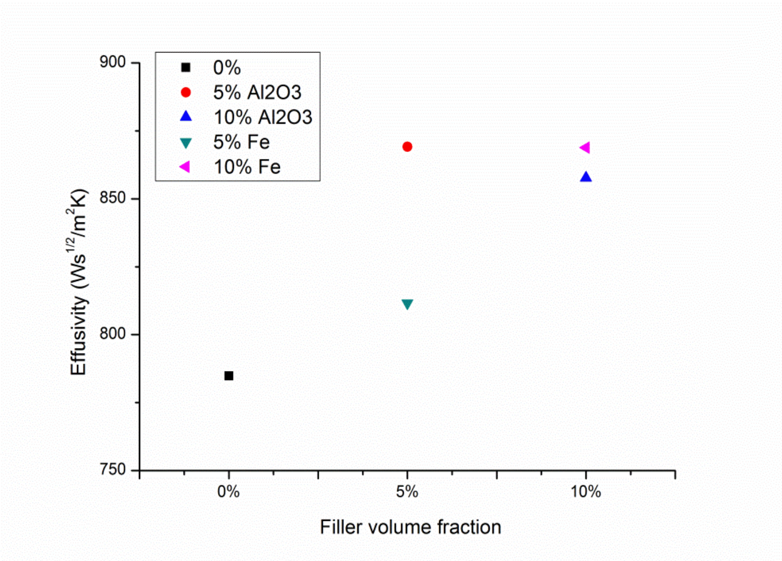

Fig. 40 *Thermal effusivity experimental values of the hybrid composite structures*

The micromechanical models used for comparison purposes within the process of effective thermal conductivities tailoring process were selected due to values predicted, as it can be seen from Fig. 38 and Fig. 39 (n. see Chapter 3 for related expressions). Thus, the lower and upper bounds trends can be sized from Fig. 41.

It should be emphasized the fact that all the values predicted based upon the micromechanical bounds, irrespective of the approximations used to develop them, lies between the values derived for the *Hashin-Shtrikman* bonds. This is the beauty of the latter bonds since they apply for a wide range of constitutive shapes and orientations and do not imply a certain type of microstructure to be used with.

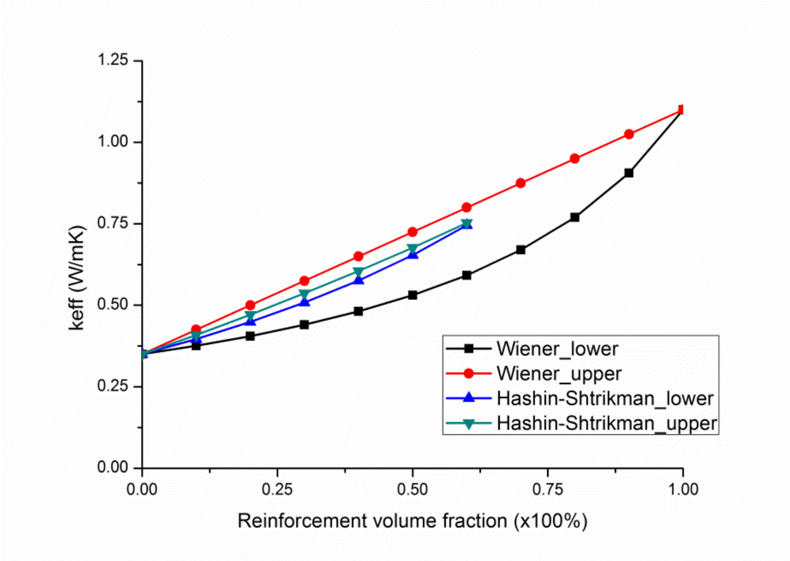

Fig. 41 *Lower and upper thermal conductivity bounds for E-glass fiber reinforced sample*

4.3.2. Hybrid fiber-fiber polymer composites

The influence of individual material type and fiber orientation within a composite structure was highlighted in case of hybrid structures made from different UD carbon fiber and random E-glass plies using various stacking sequences. Accordingly, in Fig. 42 and Fig. 43 were plotted the thermal strain fields recorded over the imposed temperature range and instantaneous effective linear coefficient of thermal dilatation.

As it can be seen from Fig. 42, specimen's thermal strain field highly depends on the number of UD carbon fiber based plies as well as their orientation with respect to the principal direction. Carbon fibers are generally known for their negative expansion behavior not to mention their different behavior on longitudinal and transversal directions, respectively.

This it can be seen on the thermal strain recorded for UD carbon fibers embedded as 20% and 40% relative content into the hybrid polymer composite structure. Furthermore, 20% carbon fiber longitudinally disposed hybrid composite specimen exhibited approximately same thermal strain field as 40% carbon fibers transversely disposed sample. Within reference composite sample, thermal expansion occur unrestricted and due to simple contribution of constitutive – random E-glass fibers and unsaturated polyester resin.

In addition to above, instantaneous coefficient of thermal expansion reveals the same behavior. As it can be seen from Fig. 43, hybrid composite specimens reveal a linear behavior within temperature range exceeding Tg irrespective of UD carbon fiber's orientation with the thermocouple head's position. In addition, CTE curve's peaks indicate the Tg values associated with the polymer resin while their magnitude the influence of the constitutive content. Comparatively with the Tg values retrieved from DMA measurements discrepancies can be easily identified and regarded to the equipments used and measuring principles. The latter are to be considered an additional source of errors.

On the other hand, particular to these composite architectures and their constitutive, higher peak values are revealing the hybrid architectures whose UD carbon fibers are transversally oriented with the thermocouple head irrespective of their content.

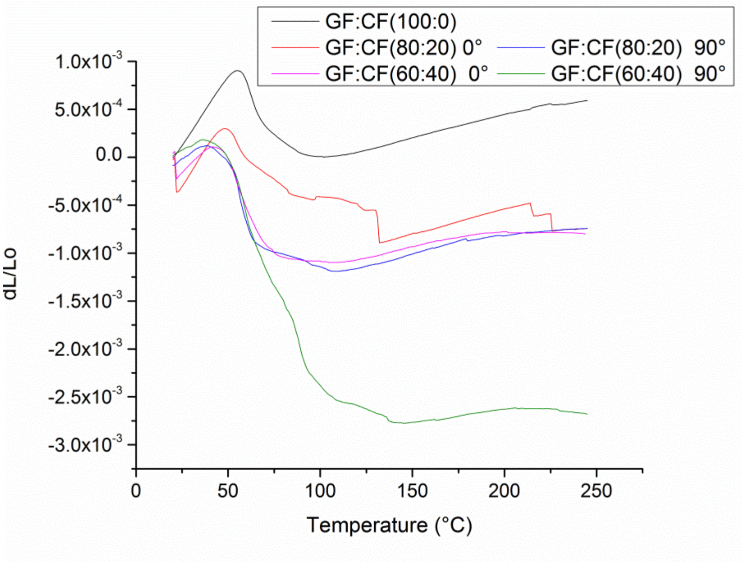

Fig. 42 *Thermal strain fields' evolution within the composite specimens*

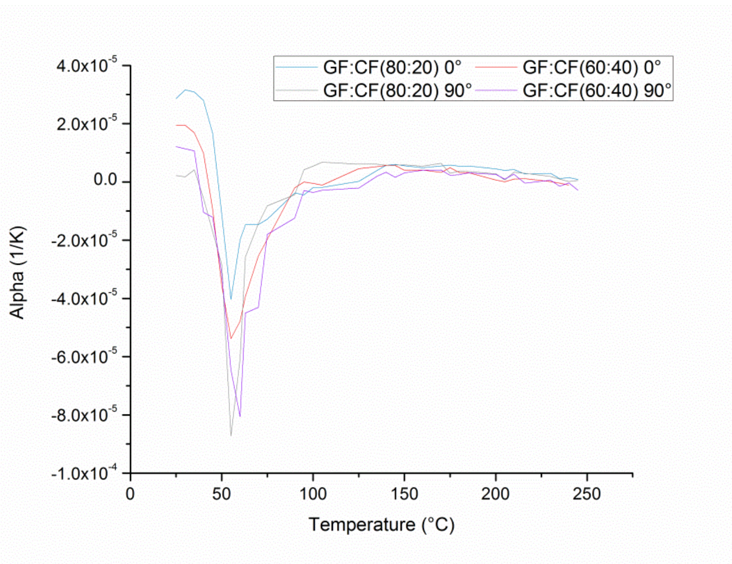

Fig. 43 *Instantaneous effective CTE temperature variations accounting different content and orientations of UD carbon fibres within the composite architectures*

A. Specimen conditioning under temperature variation

Further, the hybrid composite specimens were being subjected to temperature variation ranging from -10 °C to +40 °C within a controlled temperature enclosed structure, under a desert condition simulated thermal cycle, 7 days long, 24 hours/day, like previously.

Particular to this case are the thermo-physical effects that were captured along the longitudinal direction along the UD carbon fiber, known for its transversal isotropy.

Moreover, graphical representations were adapted to apply to the style used to report with this contribution. For further comparison with other hybrid fiber-fiber polymer based architectures please refer to the co-authored paper [178].

Differences can be accounted if the hybrid fibre-fibre polymer composite specimens are being subjected to environmental conditioning such is the low-temperature exposure used. These can be easily observed by looking to Fig. 42 and Fig. 44 representing the thermal strain fields developed within the specimens with temperature increase up to 250 °C. Thus, an increase of UD carbon fibre layer numbers impacts the thermal strain instantaneous values recorded for a particular temperature by lowering them.

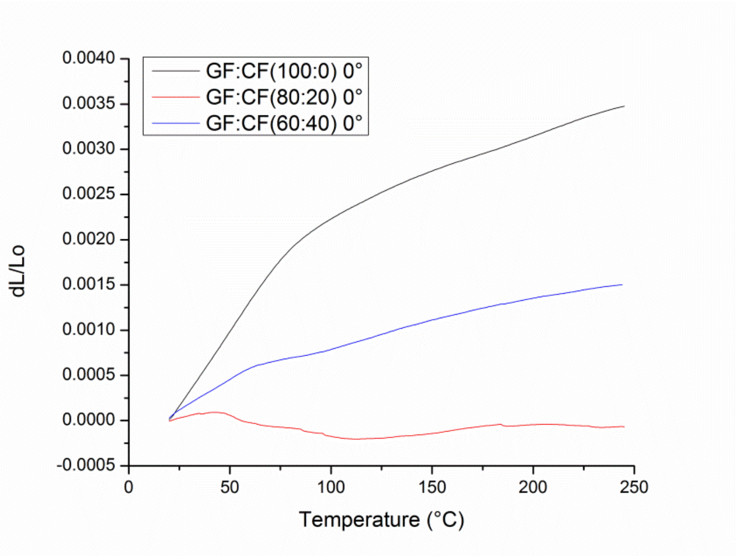

Fig. 44 *Thermal strain fields' evolution within the composite specimens*

In addition, as it can be seen from Fig. 45, the low temperature preconditioning regime induces the occurrence of more peaks in the instantaneous overall CTE field over the temperature range, having a highly departure from the linear variation up to temperatures corresponding to the glass transition temperature of the polymer matrix (around 70 °C). These can be associated to the micro cracks induced during the low temperature environmental conditioning and polymer thermal conditioning during the temperature rise. Matrix degradation proceeds gradually in the first thermal cycling and then more rapidly in the second thermal cycle.

In Fig. 46 was plotted the mean values of the effective CTE based on statistical manipulation of the experimental recorded data for all the thermal cycles applied upon the hybrid composites analyzed, with or without preconditioning to a low temperature environment. As it can be seen, the previous remarks hold and are more clearly seen in the plotting, the lower effective mean CTE being retrieved for the GF:CF (60:40) specimen whose CF has the highest number of layers.

In Fig. 47 was represented the relative error compute accounting the effective CTE values predicted based on the *Mori-Tanaka* homogenization scheme and experimental mean values retrieved from the second thermal runs.

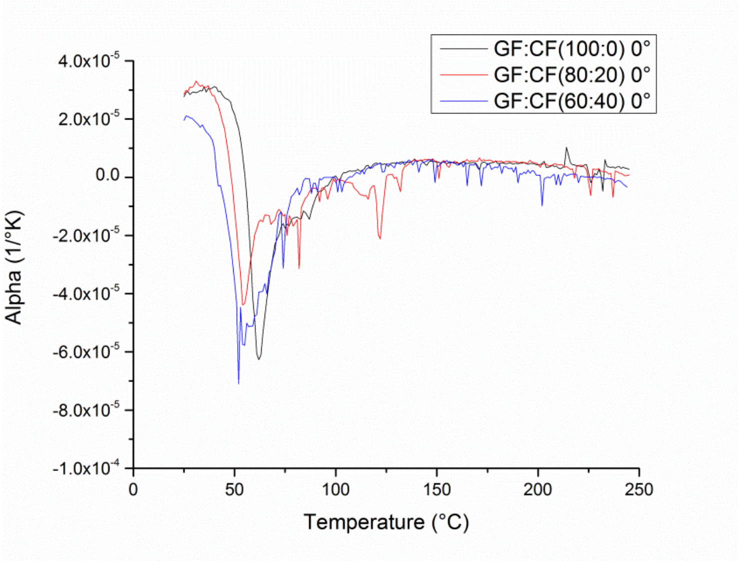

Fig. 45 *Instantaneous effective CTE variations with temperature*

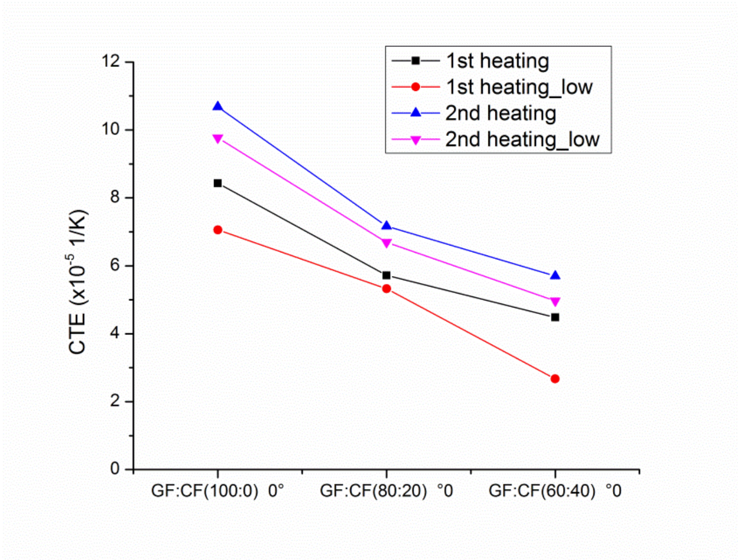

Fig. 46 *Effective CTE mean values from successive thermal cycles*

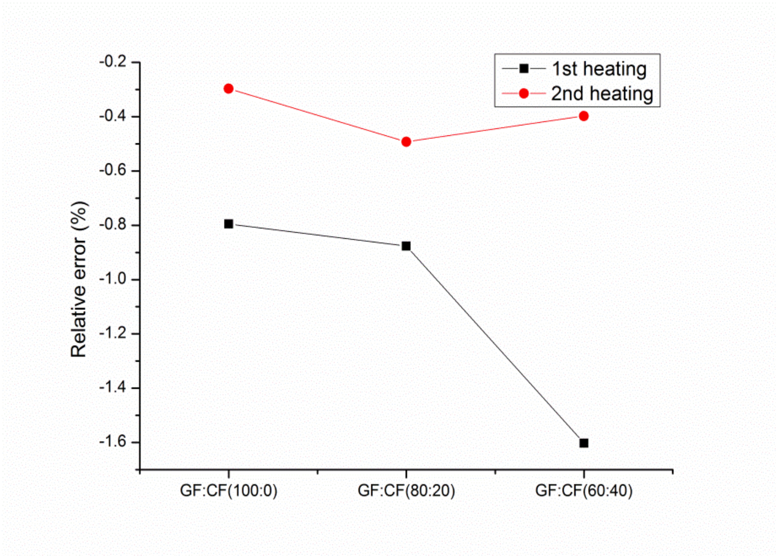

Fig. 47 *Relative error from experimental and micromechanical predictions*

4.3.3. Hybrid particle-particle polymer composites

Thermal expansion in particle-particle hybrid polymer based composite was retrieved by subjecting the specimens to temperature variations. Thermal loading is experiencing a dynamic ramp by heating and cooling up/down to/from 150 ^{0}C with a heating step of 1 K/min under the static air atmosphere.

In Fig. 48 and Fig. 49 is being plotted the thermal strain fields' variation with temperature as developed within the hybrid particle – particle composites during the dynamic heating ramp, as well as the related instantaneous CTE data.

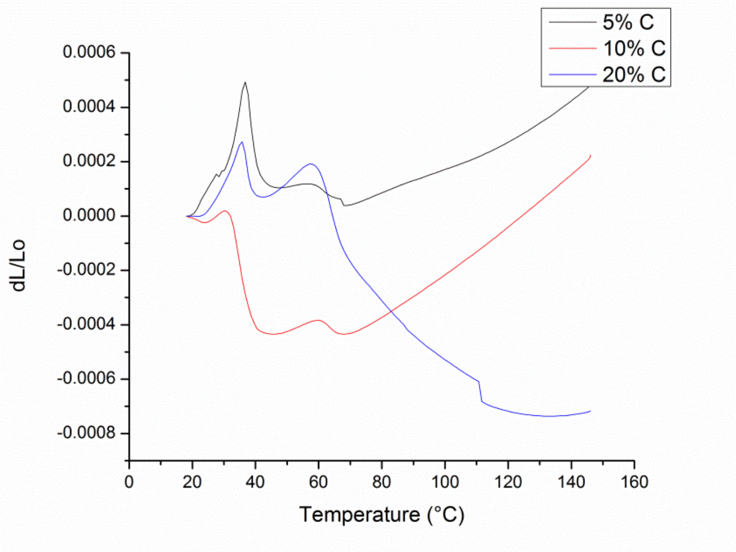

Fig. 48 *Thermal strain fields developed within hybrid composites during heating*

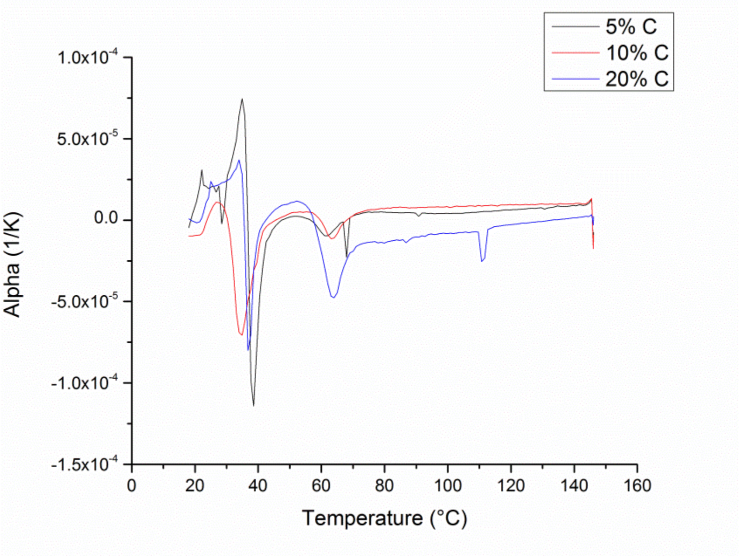

Fig. 49 *Instantaneous CTE variations with temperature during the heating step*

With respect to the CTE plot, the peaks around 40 °C should be associated to the polymer glass transition and residual thermal strains from manufacturing phase. In addition, the spikes from the plot should be neglected since they represent the consequence of the temperature step imposed within the temperature program.

In Table 11 and Table 12 are provided the instantaneous and peak CTE values retrieved during the thermal loading while subjecting the specimens to two successive heating cycles. In the light of aforementioned, the peak values and temperature values were occurring are important only from the polymer matrix behavior monitoring while temperature increases.

Table 11 - Instantaneous CTE values in particle-particle hybrid polymeric composite

Temperature [^{0}C]	Reference sample [x10^{-6}/^{0}C]		5% C particles multiphase composite [x10^{-6}/^{0}C]		10% C particles multiphase composite [x10^{-6}/^{0}C]	
	1st cycle	2nd cycle	1st cycle	2nd cycle	1st cycle	2nd cycle
20 (heating)	14.087	12.899	11.742	13.459	10.996	15.548
50 (heating)	4.7076	14.637	2.0925	10.834	4.2966	2.4086
100 (heating)	8 .2254	12.088	4.1026	10.928	8.3001	9.6639
150 (max.)	9.5383	10.833	4.7260	10.902	4.7654	10.915
100 (cooling)	13.091	12.962	13.236	14.269	12.359	12.465
50 (cooling)	17.538	17.946	23.458	23.759	24.122	24.859
20 (cooling)	15.880	16.010	20.810	20.946	20.097	20.479

In addition, as it can be seen, there are small differences between the linear CTE values recorded from the heating and cooling steps, respectively for the same temperature.

Table 12 – Peak values retrieved from instantaneous thermal expansion variation recorded

Composite samples	Heating		Cooling	
	T [^{0}C]	CTE max [x10^{-3}/^{0}C]	T [^{0}C]	CTE max [x10^{-3}/^{0}C]
Reference composite 70% Fe	32.6 145.5	0.2695 0.7860	42.7 -	-0.3942 -
Multiphase composite 5% C, 65% Fe	36.7 145.8	0.4935 0.4919	42.3 -	-1.1101 -
Multiphase composite 10% C, 60% Fe	146	0.2271	46.2	-1.3163

Negative CTE values were obtained in the cooling step for all polymer based composites, both reference and particle-particle hybrid combinations, as can be sized in Table 12, revealing a contraction rather than expansion within the specimens.

Moreover, the experimental values are not revealing high differences as the carbon particle concentration increase. The latter can be sized from the data plotted in Fig. 50 that corresponds to the predicted and experimental retrieved ones. This can be regarded to the relatively small dimension size of the carbon particles with respect to the second metallic phase.

Hence, predictions made using the well-known *Mori-Tanaka* approximations highly departure from the experimental retrieved values in comparison with the double inclusion results. These can be regarded to the fillers' dispersion and agglomeration within the polymer matrix and to reinforcements/matrix interfaces.

In addition, it should be accounted the issue with respect to the limitations imposed by the *Mori-Tanaka* scheme that provided good results only for reinforcement concentrations less than 50%.

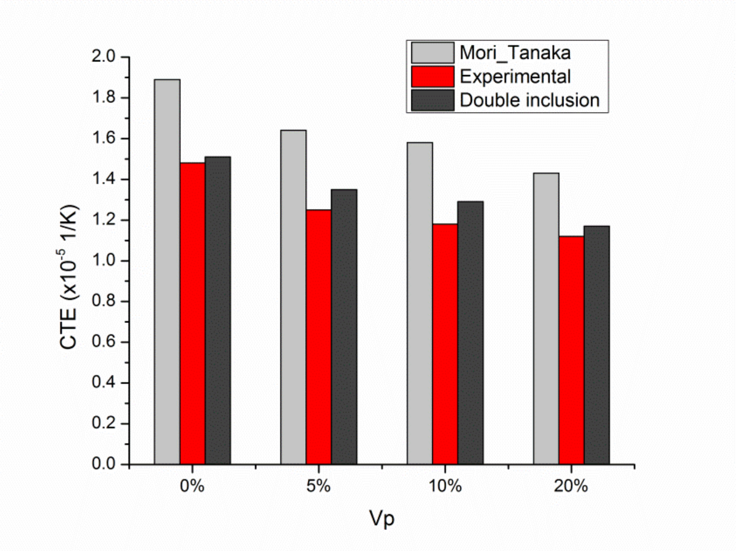

Fig. 50 *CTE mean experimental values vs. micromechanical predicted*

In the light of above, it should be mentioned the fact that the *Mori-Tanaka* homogenization scheme do not account any microstructure. More specifically, the model does not used as inputs information on the reinforcement distribution, shape and orientation and only for the particular case of aligned and small shape dimensions provide effective property values that are closer to those predicted by the *double inclusion* model proposed by Hori and Nemat-Nasser (see ref. [28]).

Furthermore, the homogenization scheme deployed within this sections were selected for their wide use in literature and numerous references approaching either differences or drawbacks of both and other related models. The interested reader is directed to the work of Willis, Ponte Castaneda, Torquato, et. al (see ref. [14]).

The results provided in this section are specific important since aided the understanding of a particular hybrid particle-particle combination selected due to is outstanding characteristics of the individual constituents. This combination enabled further to develop a hybrid composite architecture suited to be used as material for a sensor device despite the uncontrolled distribution of the distinctive reinforcements that can be sought to highly impeding the overall performance of the latter.

In addition, these can be used to supplement the author's available database and enable further research directions for studies for other particular hybrid combinations that be tailored.

4.4. Electrical properties

Specific objectives:

- To deploy acquired proficiency by tracking and debating on dielectric properties of particle-particle hybrid composite architectures.
- To track dependencies of hybrid composite's effective dielectric property upon various influencing factors.
- To debate on influence of constitutive individual material properties on overall dielectric property.

The subsequent reported data and discussion relay on information provided in the authored and co-authored scientific papers or invited presentations, partially or entirely referred [180, 213-217]. Supplementary, some particular issues were included from the co-authored patents no. 123411/2012 and no. 126789 A0/2011.

Remark: In the herein chapter will be tackled only the dielectric values retrieved on the particle-particle hybrid polymer specimens due to the limitations imposed by the experimental devices that enabled runs on highly conductive phases, at room temperature and absence of an experimental device enabling temperature dependent runs.

4.4.1. Hybrid particle-particle polymer composites

Electrical conduction in composite materials, according to the percolation theory, characterizes the connectivity properties in random geometries and practical applications. A focused analysis reveals the fact that a system containing fillers of different conductivities undergoes phase transition of metal-dielectric type. Estimation of charge carrier concentration of an extrinsic semiconductor has to consider both electrons and holes concentrations determined by the intrinsic ionization processes.

The electrical resistance of hybrid particle-particle composite samples was being retrieved by applying a constant current from a current generator through two external contacts followed by the measurement of the voltage between other two different contacts, as depicted by the herein author [218].

In Fig. 51 was shown the variation of electrical resistance function of applied current intensity for identical hybrid polyvinyl acetate resin (PVAc) based specimens reinforced with conductive particles, iron and graphite, embedded as 40% and 30% individual volume fractions, respectively.

As it can be seen, the retrieved values experience an exponential decrease with the increase in applied intensity that can be regarded as the *Joule-Lenz* effect that is particular about the extrinsic semi-conductive material type like those herein. As temperature rises, the ionization processes within the structure intensify to extend where all the donor impurities will be ionized.

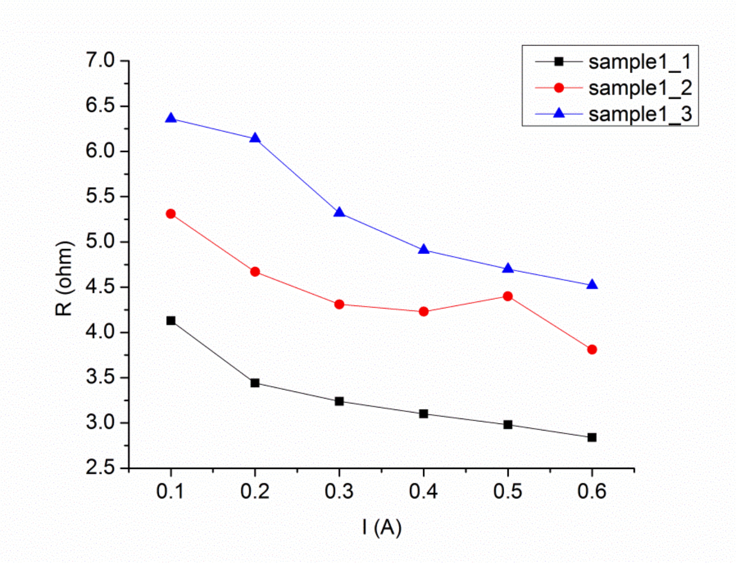

Fig. 51 *R(I) variation with applied current intensity for multi-phase composite specimens*

Differences between the recorded values can be viewed from individual particles' contact point of view, being widely acknowledged that the electrical conductivity in particle reinforced polymer composites is primarily resulted from above.

Furthermore, electrical conductivity further depends upon the constitutive shapes, individual material properties of theirs and applied voltage. Next, as stated in Chapter 1, electrical conduction in composite systems comprising an intricate network of conducting and insulating phases are determined by two mechanisms, *percolation* in a continuous conductive network and/or *tunneling* between insolated conducting particles. Both phenomena are present and responsible for electrical conduction in herein hybrid particle-particle composites.

The clustering effect and dispersion of conductive phases within the hybrid structure cannot be accounted directly from the measured data. These can be regarded to influence the effective conductive property and should be tackled as further issues.

In Fig. 52 is shown the effective resistance dependence on applied external current intensity for different hybrid particle-particle composites that corresponds to 30%, 40% and 50%, respectively individual volume fraction of conductive iron particles.

As it can be seen from figure, retrieved experimental data follow the same exponential decrease with applied current intensity for different relative iron particle content. Supplementary, effective resistivity reveals higher values with the increase of single conductive phase relative volume fraction while keeping unchanged the total particle loading. With respect to the retrieved trend, it follows the theoretical behavior of composite materials where the electrical conductivity increases as the constitutive volume increases.

A closer look to the experimental data reveals that the electrical resistivity decreases strongly with the increase of the conductive fillers’ volume fractions and increase of the current density.

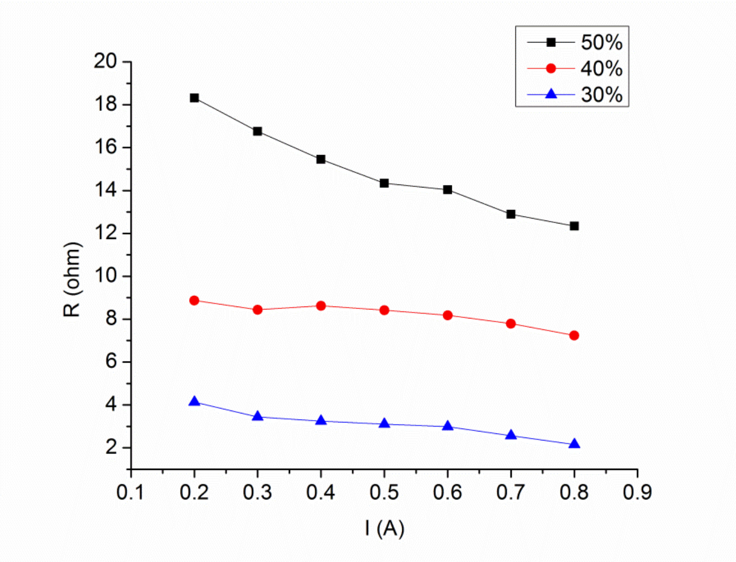

Fig. 52 *R(I) variation for different volume fraction of iron particles*

Noteworthy is the influence of polymer resin upon the effective electrical conductivity as shown in several co-authored papers [180, 213, 214, 217]. The above issue has not been approached since the hybrid particle reinforced specimens were manufactured based only on PVAc polymer resin. The latter is known for its insulating character and low conductivity exhibited that recommend for wide applications in electronic industry.

Departure of prediction from actual values allowed assessments of either a positive or negative hybrid effect for this material property. Thus, estimates provided using composite micromechanical models as written and debated in Chapter 3 were used along with the computed mean values of conductivity values (i.e. $\sigma = \frac{h}{R \cdot A} = \frac{4 \cdot h}{R \cdot \pi \cdot d^2}$, where h is specimen height, R is specimen's resistance and d is the sample's diameter, etc.).

Noticeable are the predicted mean values based on the recorded data on electrical resistivity that are particular about semiconductor materials. Thus, as it can be seen from Fig. 53 the experimentally retrieved values are lower compared with predictions based on combined *Pal* and *Hashin-Shtrikman*. On the other hand, the 3-point approximation model of *Milton* seems to provide approximately similar results. Consequently, low percentage error values were found as it can be seen from data in Fig. 53.

A closer look on percent error of predicted and absolute effective conductivities provided function of the relative volume fraction of iron particles reveal the hybrid effects encountered. Thus, deviation from theoretical predictions shows a positive hybrid effect for all values of relative iron content, 30% to 50%. These values reveal also departure from the other data set of prediction made using 3-point approximation formula developed by *Milton*. On contrary, the latter revealed negative hybrid results with the addition of iron particles. Thus, if the relative content is being kept at 30% only a -6.5% difference is encountered whereas with the increase of phase content the departures rise up to approximately -55% and -70%, respectively.

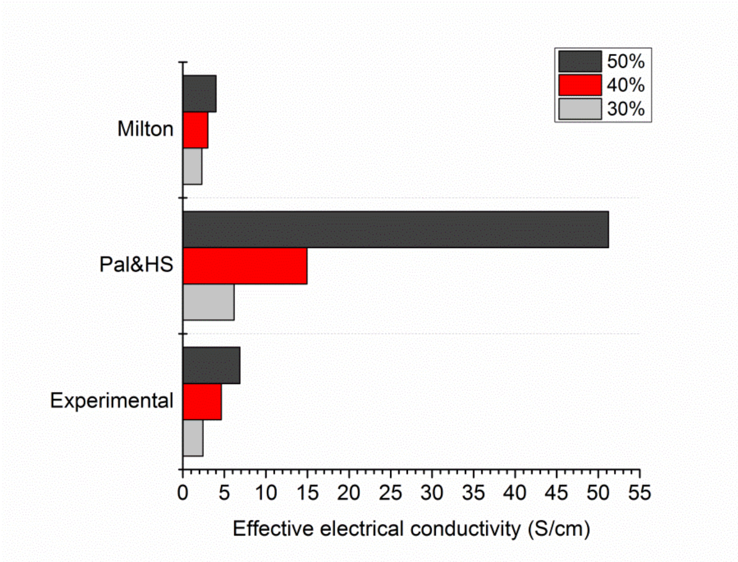

Fig. 53 *Comparative theoretical-experimental data on effective electrical conductivity for different relative content of iron particles*

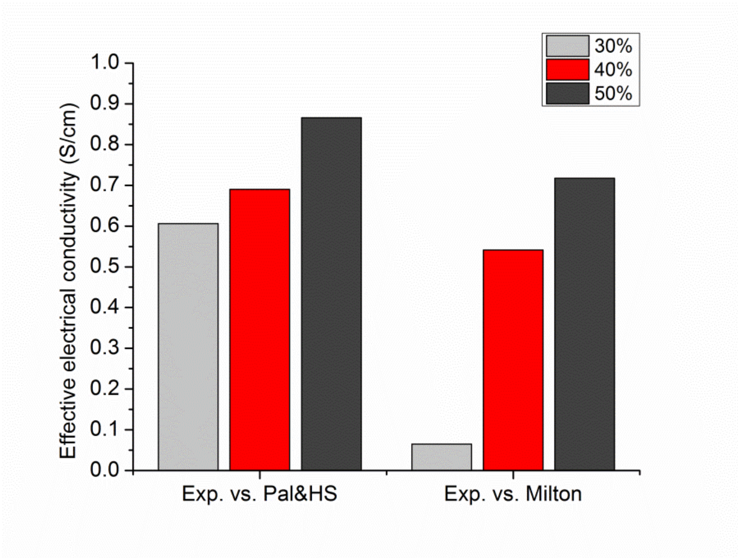

Fig. 54 *Absolute values of relative percent error from experimental and predicted values on effective electrical conductivities of hybrid composites*

Data plotted in Fig. 54 were unpublished and used herein to highlights the positive or negative effects of the effective electrical conductivity with modification of the fillers' content. It is widely acknowledged in literature that hybrid ratio is among the fundamental parameter for polymer based composites that directly affect the performance of structure (Short & Summerscales, 1980) [3]. From this perspective, the above underline the synergetic effects due to hybridization of different types of conductive phases on this particular material property.

Furthermore, the values plotted in Fig. 55 correspond to different relative iron particle contents embedded within PVAc polymer matrix as predicted using the aforementioned micromechanical models on electrical conductivity.

The 3-point approximation formula captures the sensitivity of electrical conduction to microstructure in contrast to the *Hashin-Shtrikman* bound. Moreover, it proves to yield good approximations of the effective electrical conductivity of the hybrid composite structures. However, its utility has yet to be fully explored.

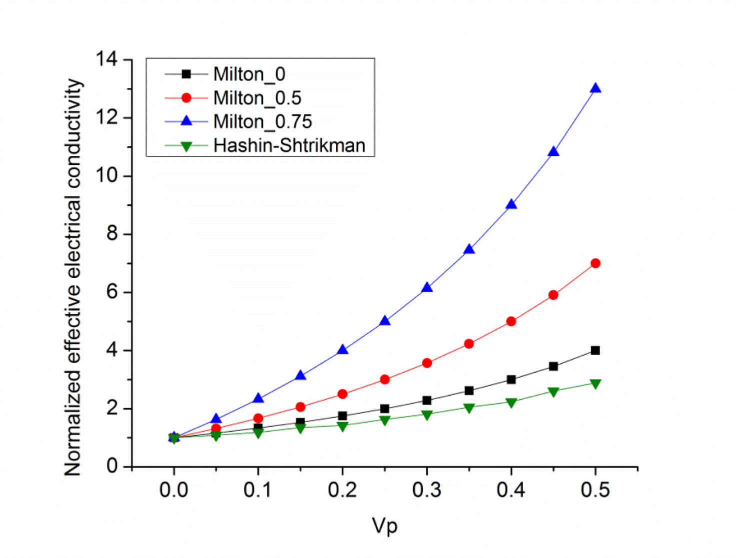

Fig. 55 *Effective electrical conductivity function of relative iron particle content in hybrid iron-graphite reinforced PVAc based composites*

The above predictions cannot be sought to yield basic results since an important aspect was omitted from the approximations, namely the percolation threshold issue. A variety of techniques exist to estimate the percolation thresholds of continuum models or to account these in the numerical simulations. It is beyond the purpose of herein work to debate on the issue. Thus, the section cannot be closed without accounting the percolation threshold within few predictions carried out by the author but unpublished yet and further considered under development.

Double inclusion model was considered to apply for prediction of electrical properties (i.e. conductivity and resistivity) of few particle-particle hybrid architectures embedded within the same PVAc polymer matrix: 65% Fe and 5% C, 60% Fe and 10% C, 55% Fe and 15% C and a 70% Fe set as a reference sample. The percolation threshold was set to 0.2 whereas the percolation exponent to 2, and a multi-level homogenization scheme was applied. The aforementioned values were set out after several trials for the numerical predictions and can be assigned to more practical issues and account the previous findings.

Thus, in Fig. 56 was plotted the electrical conductivity values predicted accounting the previous restrictions set out prior initiating the numerical simulations, whereas in Fig. 57 the same property accounting a 0.3 percolation threshold and different percolation exponential values (i.e. 2, 2.5 and 3, respectively).

As it can be sized in the above graphical representations, the higher the carbon filler's content, an increase in the effective conductivity of the hybrid composite is obtained. The latter signify the effectiveness of the carbon particle phase as reinforcement.

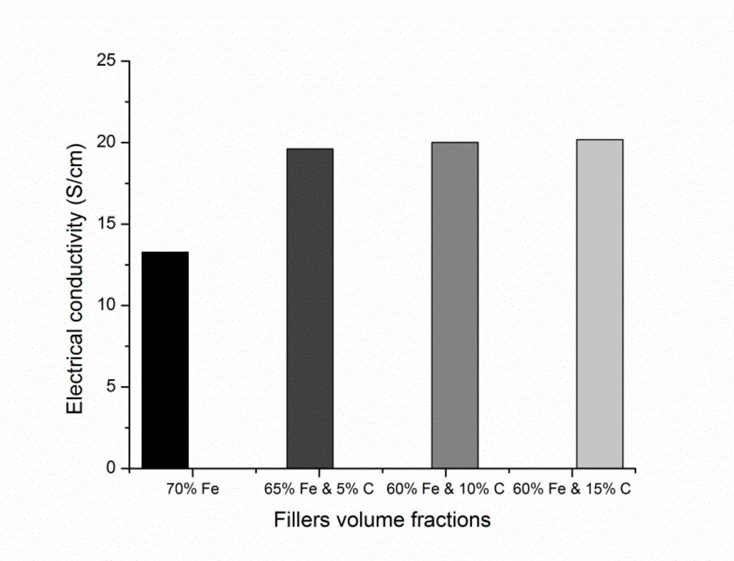

Fig. 56 *Effective predicted electrical conductivity values for a 0.2 percolation threshold*

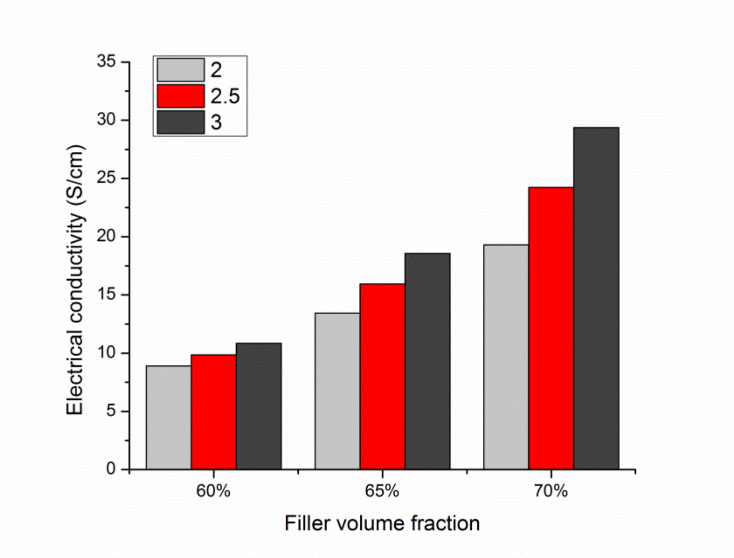

Fig. 57 *Effective predicted electrical conductivity values for different exponential values*

No attempt was made to cover the extensive literature concerning the direct calculation of effective electrical properties of these random media via computer simulations. However, it is useful to point out that there is a variety of simulation methods that can be used and will be deployed in future studies.

Consequently, contrast bounds or cluster bounds can be considered next in order to predict the effective electrical properties of conductive inclusions embedded within a conductive/nonconductive polymer matrix material.

As a final remark, we note that, estimates of the percolation properties and critical exponents identified as susceptible for variations underlined within the present section it will be closely approached and debated.

Chapter 5 – Conclusions on the original work

Tailoring hybrid polymer composite materials process is a multidisciplinary endeavor that overlaps with various branches of engineering, material science, applied mathematics and chemical physics. In some cases, the boundaries set with these disciplines are due to particular methods, models and results that can be applied to study hybrid composite materials and vice versa.

The ability to tailor hybrid polymer composites with a unique spectrum of properties rests fundamentally on the ability to relate the effective properties to the microstructure, one of the essential aims of this habilitation thesis. Furthermore, the availability of predictable material properties shortens the manufacturing cost associated with structural components in *mechanical engineering applications* (e.g. aircraft, space vehicles, automobiles, insulation, heat exchangers, recreational products, micro electromechanical systems, etc.) as primary aimed by developers.

The reader has to account that the content of herein work was already published and indexed in worldwide data bases (i.e. Web of Knowledge, Google Scholar, Scopus, etc.). Similar research activities were carried in relation to above, and those stated in the following section of the next chapter. The results should be sought as part of an ongoing publishing activity in co-authored peer-review journals.

Mechanical properties of hybrid polymer composites

- Elastic properties of *particle-fiber* hybrid polymer combinations are highly influenced both by the volume fraction of particle reinforcements and material type (i.e. ceramic, metallic) in addition to their geometry, shape and distribution. Viewed from a material type perspective, some might behave as manufacturing induced stress relaxing agent whereas some as inhibitors.
- Positive hybrid effects were obtained in all cases against the predicted values using *rules of the hybrid mixtures* (RoHM) model irrespective of the reinforcement type.
- Discrepancies between effective elastic moduli retrieved from tensile and flexure testing were found that relay on the experimental principle deployed, test parameters set and different reinforcement material type.
- The higher the particle volume fraction of the filler the smaller the differences between the retrieved elastic moduli in case of ceramic fillers, while using metallic reinforcements this reverses. In addition, differences between the elastic moduli from tensile and flexure tests account approximately for 35% and 45% while embedding the metallic constitutive in 5% and 10% volume fractions, respectively.
- Environmentally hybrid polymer composite conditioning (e.g. low temperatures, temperature range, water immersion, etc.) further impacts the experimentally retrieved elastic property in some extends, thus revealing information on materials' sustainability and hints on the drawbacks resulted from the manufacturing technology deployed.

- Differences between the effective elastic properties of environmentally conditioned and unconditioned hybrid particle-fiber polymer composites are higher if specimens were prior subjected to range temperature in comparison with those undergoing low temperatures (i.e. approximately 6 to 8% versus values < 4%).
- In the light of above, these differences should not be sought negatively or highly impacting the hybrid composite behavior while used as material in structural components. Moreover, prior environmentally conditioned hybrid composite specimens are experiencing longer stress-strain dependence until the first signs of delamination appear opposite to the applied load, irrespective of the reinforcement type.
- On the other hand, the elastic properties in *fiber-fiber* hybrid polymer composites have to account supplementary fiber parameters (e.g. orientation) and stacking sequence. For particular architectures herein, the experimental flexural modulus was found to be lower than the tensile modulus as the content of carbon fibre increases.
- A severe drop of approximately 50% in the elastic modulus was found to occur for hybrid polymer composite architecture accounting the same carbon fibre orientation and stacking sequence while performing bending test versus tensile runs.
- Carbon fiber reveals its effectiveness while embedded as reinforcement irrespective of the stacking layer sequences. This can be sized on the elastic properties that improve while the reinforcement content increases.
- The effective mechanical properties of these hybrid composites are being also influenced by the capacity of stress transferring between the fibre-matrix interfaces and fibres' different breakage mechanisms.
- It was shown that hybrid composites' strength is strongly influenced by reinforcements/matrix interface because depend on effective stress between constitutive and matrix.
- Conversely, the effective stiffness of hybrid composite architectures depends significantly on constitutive loading and not on reinforcements/matrix adhesion, since these have higher individual elastic properties comparatively with polymer matrix.
- A critical evaluation of experimentally retrieved data and available predicted values was provided in order to enable information gathering on strengthening and stiffening mechanisms in these tailored hybrid particle-fibre and fibre-fibre polymer composites.

Dynamic mechanical properties of hybrid polymer composites

- The effect of hybridization on the dynamic mechanical properties was approached for both *particle-fiber* and *fiber-fiber* polymer composites. The *particle-particle* hybrid specimens failed to be tested for their dynamic properties due to their geometry.
- Generally, in all cases the storage and loss modulus revealed the same tendencies, namely a decrease as the temperature increases, which is associated with the softening of the unsaturated polyester or epoxy matrices at higher temperatures.
- A single frequency value (i.e. 1 Hz) was used for the dynamically applied load upon all hybrid composite specimens while preserving the same temperature range, from 25 °C to 250 °C.

- The resin systems (i.e. unsaturated polyester and epoxy resins) match well with the reinforcements revealing the absence of additional relaxation peaks in the experimentally retrieved curves.
- The storage moduli of *particle-fiber* hybrid polymer composites are experiencing an increase with increasing of the particle content that can be regarded as the reinforcement effect imparted by the constitutive that are more rigid than the polymer matrix.
- On the other hand, the loss modulus curves are being distributed over a wider range. Since these are indicative of the dissipated energy, the negative shift as the ceramic filler content increases and broadening of the loss modulus peak can be attributed to the relaxation processes within the hybrid composite.
- Damping factors used further to characterize the hybrid composite specimens, reveal the same negative shift recorded around glass transition temperature value as the particle content phase increases revealing thus an increase in the mobility of polymer molecules on the particle/fiber/matrix interfaces.
- Cole-Cole diagrams plotted to indicate the extent of departure from the ideal shape with the content increase reveal the heterogeneity of the hybrid polymer composites as well as the relatively good reinforcements/matrix interface.
- Micromechanical predictions made using *linear rules of hybrid mixture* (RoHM) and *inverse rules of hybrid mixture* (iRoHM) reveal differences while comparing with the experimental retrieved values.
- In addition, positive hybrid effects were revealed by all composite specimens, irrespective of the particle filler content.
- Likewise, the dynamic mechanical characteristics of *fiber-fiber hybrid* polymer composites experience the same tendencies on their storage and loss moduli variation as the temperature increase.
- In relation to above, the transversal isotropy number and number of stacking layers particular about the carbon-fiber reinforcement phase are strongly influencing both effective storage and loss moduli.
- The storage modulus of the hybrid composite specimens experiences a strong decrease as the number of the UD carbon-fiber ply-ups increases and transversally disposed with respect to the general reference system.
- On the other hand, the loss modulus reveals small differences and the same wide-range distribution over the temperature range as the number of carbon-fiber layer increases and longitudinally disposed with respect to the general reference system.
- Furthermore, the positive shifts on the damping factor recorded for all hybrid composite specimens reveal the effectiveness of both fibers (i.e. GF and CF) as reinforcements irrespective of their stacking sequence, layer number and orientation
- Individually tackled Cole-Cole plots, for both longitudinal and transversal disposed carbon-fibers, reveal the heterogeneity of the hybrid fiber-fiber composite specimens and suitable indicators on the relatively good fibers/matrix interfaces.

- All the experimental findings reveal the effectiveness of the carbon-fiber as reinforcement in various polymer composites architectures as well as its behavior while disposed differently with respect to the loading direction.

Thermo-physical changes of hybrid polymer composites

- Generally, thermal stress and instantaneous linear coefficient of thermal expansion of herein tailored polymer composites are strongly affected by the same identified influencing factors as above, namely constitutive individual properties and reinforcement parameters (i.e. shape, orientation, concentration, etc.).
- In addition, both thermal properties experience an increase as temperature increases up to glass transition temperature, and successive runs have to be applied to remove thermal history from the manufacturing steps.
- In tailored *particle-fiber* hybrid polymer composites both thermal strain fields developed within specimens and instantaneous CTE variation with temperature reveal a decrease if particle filler concentration's increases irrespective of their material type.
- Theoretical predictions on effective CTE reveal the same decreasing tendency as the particle content increases and relatively large differences when compared with the experimentally retrieved values.
- The environmental conditioning steps considered prior property estimation reveal discrepancies on recorded thermal strain fields and instantaneous CTE variation with temperature for hybrid architectures while particle content increases. These differences can be seen in all records irrespective of the environmental conditioning regime applied.
- In addition, these should be regarded to the polymer matrix degradation nearby the composite's surface due to environmental conditioning induced micro-cracks, water removal and not to structural changes within the hybrid architecture.
- Moreover, these differences are less significant if hybrid composite specimens undergo a low-temperature program comparatively with temperature range or hygroscopic environmental conditioning.
- In tailored *fiber-fiber* hybrid polymer composites a supplementary influencing factor has to be accounted, namely fibers' orientation along to the measuring head direction.
- Like above, both thermal strain fields and instantaneous CTE are experiencing differences as temperature increases due to both constitutive concentration and orientation.
- The increase of UD carbon-fiber layers number and accounting their transversal isotropy as orientation with the measuring head changes, a lowering in both thermal strain and instantaneous CTE values can be easily highlighting.
- The findings are consistent with the other references with literature that classified this type of material as 'negatively' behaving. The later signify that this type of material highly contributes to the lowering of the property under consideration.
- Instantaneous CTE curves enable supplementary property retrieval, namely polymer's matrix glass transition temperature from the corresponding value at the curve peak.

This parameter is particular important while testing a novel polymer matrix and a tailored hybrid composite architecture. Unfortunately, huge discrepancies were found to apply for this temperature value (e.g. 30 °C) comparatively with DMA or DSC measurements. Consequently, the later measurement test runs are favored.

- The *particle-particle* tailored hybrid polymer composites accounted the same influencing factors as previously, namely constitutive shape, distribution and concentration.
- The thermal properties were highly influenced by aforementioned, and the same overall thermal property lowering effect was gathered as the concentration of the carbon particle reinforcement increased.
- The numerous spikes in the CTE curve, irrespective of the carbon particles' concentration, can be regarded both to the temperature step set to record the experimental values as well as to the reinforcement/matrix interfaces that undergo changes as temperature increases.
- Furthermore, the instantaneous CTE variation with temperature range enables to retrieve supplementary information on the polymer matrix, namely those on glass temperature.
- In addition, the positive shift encountered with the carbon particle concentration increases reveals the prevalence of relaxation phenomenon at the reinforcements/matrix interface.
- As previously underlined, glass temperature transition value differs from that foreseen through DSC measurements (see polymer’s technical sheet from the company's supplier). The latter measurement type is favored in literature.
- Theoretical predicted vs. experimentally retrieved CTE values shown small discrepancies if the double inclusion method was accounted comparatively with the well-known *Mori-Tanaka* model.
- In relation to above, these differences should be sought from the necessity to account other influencing factors, including their distribution and agglomeration within the polymer matrix.

Electrical properties of hybrid polymer composites

- These types of measurements were carried out solely on *particle-particle* polymer composites and envisaged the influences particular about the constitutive combination, individual geometry and distribution-related specificities.
- From experimental retrieved values, one should acknowledge that electrical conductivity of herein tailored hybrid polymer combinations’ ranks within semiconductor range (i.e. 10^{-2} to 10^{2} $\Omega \cdot m$) and increases with the increase of current density. The latter can be regarded to electro-thermal effects within the composite structure.
- In addition, effective electrical resistivity of herein hybrid polymer specimens experiences an abrupt decrease with the increase on the metallic particle volume fraction and increase of the current density applied upon these.

- Differences between the experimentally retrieved and predicted values of effective electrical conductivities (e.g. *Milton* and *Hashin-Shtrikman* bounds) should be sought to relay on the reinforcements' distribution and agglomeration within the hybrid composite structure that highly contributed to particle-particle interfaces enabling the conductive paths.

In summary, the previous experimental research on tailored hybrid polymer based composites of a different reinforcement kind (i.e. particle-fiber, fiber-fiber or particle-particle) must not be considered as 'science for the sake of science'.

Herein tailored hybrid polymer based combinations emerged to address some practical applications requested by several industry players during the long-term partnership or momentary solicitation or to enable research project outcomes as part of the undersigned contract with the *Romanian Executive Unit for Financing Research, Innovation and Development in Higher Education* (http://uefiscdi.gov.ro/).

The micromechanical models deployed were selected on purpose by accounting the wide experience on macro- and micro-scale theoretical approaches prior their use in scientific articles (n. peer-review journals or conference proceedings) or books (n. including book chapters). References provided at the end of this work contain supplementary information on the aforementioned and in few particular cases detailed discussions were presented to highlight both differences and similitude.

In the light of above, noteworthy is the multi-scale transition interest due to widely use of nano-particle reinforcements with various polymer matrices in order to enhance one of the chief aimed properties. The beauty of numerical simulations carried out at this scale level consists in the deployment of micromechanical models to predict the effective property under consideration. It is the opinion of this author that a cross-fertilization of ideas between all the approaches with respect to the effective properties under debate, at a different scale, will be mutually beneficial.

Space limitations and departure from the main objectives of this habilitation thesis will not permit us to treat, in any detail the natural-synthetic reinforcements' combination embedded in polymer matrices tailored with natural derivatives. Readers are informed on the availability of such experimental data covering all the herein material properties approached (see ref. [219] on partial delivered results). These findings are under the ongoing process of being published in the peer-review journals, and were intentionally omitted from the body of this work.

All the related achievements should be sought to comply with the main trends of other research groups from national and European institutes and universities. Furthermore, the experimental results were gathered from devices complying with the highest quality standards in the domain that compete with similar.

Part II. The evolution and development plans of scientific and academic career

Directions of scientific research

Beyond the 'state-of-the-art' of physical and mechanical properties of hybrid composites

In light of the above review, the major contribution that is foreseen by author concerns with the fostering of novel hybrid woven out of solely synthetic/natural fibres or combinations of their (e.g. inter, intra- or comingled) followed by emerging tailored architectures to address the performance criteria and optimization designs settings.

More specifically, further emerging deployment mutually agree on:

- Avoidance of the variability in natural fibre properties related to the location and time of harvest, processing conditions as well as their sensitivity to temperature, moisture and UV radiation.
- Avoidance of the problems caused by the hydrophilic nature in case of cellulose/lignocelluloses fibres that greatly influence their mechanical properties.
- Necessity of additional modifications like in case of cellulose/lignocelluloses fibres whose surface properties need supplementary improvements (e.g. physical or chemical methods) to guarantee the compatibility between fibres and matrix material.
- Problems caused by the physical properties regarding to the fibre dimensions, defects, strength and structure encountered in case of natural fibres.

The 'state-of-the-art' with hybrid polymer based composites mechanical properties, gathered findings generated and related shortcomings on the: fibre/matrix materials' compatibility, reinforcement structure and chemical composition or manufacturing techniques are foreseen to allow a smooth transition to other types of hybrids. In this regard, innovation and creativity are desirable to surmount shortages of skills and fill-in gap with missing information.

Beyond the 'state-of-the-art' of dynamical mechanical properties of hybrid composites

With regard to related contributions depicted within habilitation thesis and other surveys on deployment of DMA technique will foreseen:

- Attempts for experimental research and data processing with aim of further comparison between the retrieved data from various DMA configurations (e.g. 3-point bending, penetration, double cantilever method, and single cantilever method) and hybrid polymer based composite architectures.
- Retrieved data processing (e.g. Cole-Cole plots, energy of activation, estimation of kinetic parameters, etc.) to size the contribution of the main influencing factors upon the dynamical behaviour and impact resistance of the constitutive over the temperature range settings.
- Drafting novel micromechanical based theoretical models to encompass the hybrid effect within the composite combinations to predict the temperature-dependent related properties.

- Mutually reinforcing theoretical predictions and experimentally retrieved values systemic approach to further assess the overall performance of the hybrid composite architecture under the focus.

Beyond the 'state-of-the-art' of thermal properties of hybrid composites

At a glance, Chapter 1 can be summarized as underpinning the recent contributions on thermal properties and temperature-related behaviour in hybrid polymer based composites, irrespective of reinforcement specificities. Consequently, these can be regarded to the natural trend in the materials' design and performance assignments by improving their structural functionality. Furthermore, from manufacturing processing point of view, knowledge on issue enables great thermal formability of these types of materials.

In the light of above, following the acknowledgement on 'state-of the-art' around the issue can be targeted new challenges, including:

- Monitoring and quantifying the thermal properties' changes of hybrid polymer based composites while subjected to thermal aging, thermal cycling or extreme thermal cycling conditions, both on in-situ or real manufacturing/working conditions.
- Evaluation of kinetic parameters and degradation mechanism of hybrid polymer based composites under various temperature ranges using different thermal analysis methods (e.g. DSC, DMA, TGA) followed by further correlation with predicted data from several theoretical predictions developed and reported in literature.
- Assessment of thermal properties in hybrid polymer based composites subjected to extreme environmental loading conditions (e.g. cryogenic, elevated and high temperatures).
- Development of newly theory models related to dynamic properties to enable a better approach on distribution functions, both temperature and frequency related, toward a more realistic characterization of hybrid composites.

Beyond the 'state-of-the-art' of electrical properties of hybrid composites

Since dielectric spectroscopy of polymer based composite materials fail to capture researchers' interest due to several reasons, including the testing equipments acquisition high rate, a strong industrial interest on dielectric and electric properties of these materials can be identified. The latter can be regarded to the growing use of these materials in electronic devices, optoelectronic switches, printed board circuitry and microwave subassemblies for radar, fuel cell, etc.

Following this industry interest and acknowledging the information gaps within the scientific literature with respect to the issue, concerns should be addressed with respect to the:

- Dielectric behaviour of polymer matrices, including in-situ real time monitoring of kinetics and rheology of cure within a wide range of frequencies (i.e. 10^{-5} to 10^{11} Hz), temperature range (i.e. extreme low to very high) and correlation with other types of measurements.

- Dielectric properties' changes encountered for different hybrid polymer based composites architectures function of reinforcements' concentration, geometry, distribution, other prior specimen's conditioning, etc.
- Monitoring of relaxation phenomena and related parameters over the time and function of applied frequency, to enable information and knowledge gathering on the issue.

Beyond the 'state-of-the-art' of all effective material properties of hybrid composites

In addition, underpinning the advancements both in hybrid composites and related effective material properties, combinations of various efficient, cost-effective and environmentally friendly reinforcement materials that can be tailored in place of/along with fewer environmentally-friendly materials can be tackled. The hybridization process needs further attention both in terms of experimental research and theoretical approaches. Inter alia, multi-scale theoretical models are required to be developed to tackle the contributions of the constitutive. Nevertheless, particular concerns are given to:

- Setting a multi-scale modelling framework for prediction of the effective material properties (e.g. mechanical, thermal, dynamical, electrical, etc.) in case of the hybrid polymer based composite structures.
- Encompassing in the multi-scale models the non-linear behaviour due to the matrix material and sizing the influence of the fillers' length (e.g. short, continuous) on the effective properties of the hybrid polymer based composites developed.
- Development of theoretical models for temperature-dependent effective material properties' prediction at different states encountered during thermal conditioning (e.g. glassy, leathery, rubbery and decomposed).
- Considering coupled-analysis issues and dependencies for time shortening from the process and next, material design steps to be ready for manufacturing structure design levels.

Multi-scale engineering or *continuum modelling* of materials can be considered as further research directions proven the missing information available and weak understanding about the issue. In addition, semi-empirical models can be further developed to encompass the already identified influencing factors upon the effective retrieved material properties.

Evolution and development plans of professional career

Evolution of professional and academic career

European high-educational entities are facing a fierce pressure from political side as ‘knowledge economy’ concept is being widely embraced. In addition, smart specializations become not only desirable but compulsory with industry players and thus contribute to necessity of paradigm changes. Novel tools and teaching technologies emerged to reduce cost and spread information within participants. Some of them failed to produce their foreseen effects.

Consequently, in the absence of a clear measure of the educational output, competitions between universities to be top-ranked are fierce and unfortunately, still dependent on the different types of funding and managerial skills on how to attract.

The success of above higher educational models depend on their capability to integrate people, processes and mechanisms, apply related feedback loops to minimize drawbacks, develop expertise and understand needs. It is beyond the purpose of herein section to further debate on the issue. It should be referred only to understand the paradigm changes nowadays in the European higher educational systems and further the pressure upon small universities from emerging countries.

In the light of above, dynamic completion and adaption to the European and national requirements and needs that has to meet the agreed quality standards for education, particular higher education, is being foreseen and followed by the herein author and PhD supervisor candidate.

There are two pillars on which the academic career of the herein author was ongoing developed and characterized as relatively partially interconnected:

- Teaching activities – that can be viewed as addressing in present and covering less than 25% of the main interest field, namely composite materials, but enabling connection and knowledge transferred to other disciplines.
- Research activities – strongly focused on themes/subjects from the main research stream, both European and national, developed as project manager and team member; running under constant ant continuous development and information exchange with collaborators from specialities in strong connection with the author’s working field.

Nonetheless, both directions are considered to be developed in accordance with the Department of Material Science vision where the author is working within in the present, to the Mechanical Engineering field as the graduating domain and continuously enriched by added-value perspective embraced by the herein PhD supervisor candidate. Keeping the trend line imposed by European high-ranked universities is considered as an unceasing endeavor that cannot be sought to be hampered by language differences or distances, and it will be boosted by joint research programs or projects aimed to be submitted.

Teaching activity

The teaching career with 'Transilvania' University of Brasov was commencing with former Precision Mechanics Department, Faculty of Mechanical Engineering in 1992, after passing the entrance exams as junior assistant.

Since then, timely deployed professional evolution included new academic grades and roles (from laboratory and seminars supervision to lecture delivery):

- 1995 – 1999 – Assistant professor with *academic activities* covering course works and laboratories on high level language computer programming, geometrical and physical optics, optoelectronics; *research activities* covering optical systems for mechanical devices.
- 1999 – 2003 – Lecturer with *academic activities* covering course lectures on high level language computer programming, geometrical and physical optics, equipments for optical processing information, optoelectronics, computerized optical systems and clinical diagnosis; *research activities* covering optical systems for engineering materials testing; *management activities* involving students tutoring, undergraduate diploma/master dissertation papers advising.
- 2003 – 2012 – Associate professor with Department of Precision Mechanics and Mechatronics running *academic activities* tackling course lectures on high level language computer programming, virtual instrumentation, technical optics, optoelectronics, geometrical optics, computerized optical systems, and computational mechanics; *research activities* covering composite materials manufacturing, testing and characterizing; *management activities* tackling students tutoring, undergraduate diploma/master dissertation papers advising, monitoring and coordinating.
- 2012 – present - Associate professor with Department of Material Science running *academic activities* covering composite materials, materials selection, operational research, robotics; *research activities* relating composite materials manufacturing, testing and characterizing; *management activities* covering students tutoring, research projects proposal, Erasmus Plus coordination nominee as faculty responsible, etc.

Thus, day-to-day teaching activity is accomplished through routine activities within seminars and laboratory works accompanying delivered lectures, generally, and systemic and focused revision following the major trends worldwide, particularly. Further, practical implementation in relation to above it can be sized by looking to the delivered teaching supplements (e.g. academic lectures, seminar notes, laboratory description, etc.). Next, it should be emphases that the teaching process is running into a feed-back type loop, meaning that the evaluation and self-assessment of the current activities are continuously monitored, both externally and internally, by expert bodies and academia beneficiaries.

In addition, since the teaching methods are subjected to changes, it is acknowledged the necessity for continuous learning in order to adapt and update the curricula and teaching resources to the nowadays information technology oriented course.

Noteworthy, is the involvement in the Erasmus Plus program as faculty coordinator (since 2013) enabling thus bilateral agreement and students' exchanges from/to highly-ranked universities in Europe (e.g. Spain, Italy, Portugal, England, Belgium, etc.).

Furthermore, during these teaching experiences exchange and acknowledges of various institutional habits and internal/external procedures in transferring credits, a co-authored article tackling the above issue was published and indexed with ISI Web of Knowledge [220]:

- Ferrandiz Bou, S., Pop, A. P., Lopez Martinez, J., Motoc Luca, D.- *Adapting to the new ECTS programme. Comparison of the evolution of the materials course in Romania and Spain.* INTEND 2011: 5th International Technology, Education and Development Conference, 2011: p. 4027-4033.

Moreover, it should be mentioned the position of visiting professor with University of Valencia held from 17 to 25 April, 2012 to deliver lectures with M.Sc. specialization in Computer-Aided Design and Manufacturing.

- Title of lecture delivered: *Challenging the classical path: new approaches in polymer based composites modeling and simulation*.

Concerning the publishing activity, the herein contributor co-authored up to present 12 books (5 – unique author, 4 – first author) and several chapters included in international published books, approaching various subjects particular about the lectures delivered or to the research activity. Selected writings (related to the herein subject and particular to Mechanical Engineering field) include:

- Szava I., Ciofoaia V., Motoc Luca D., Curtu I. - *Metode experimentale în dinamica structurilor mecanice* (en. *Experimental methods in mechanical structures dynamics*), Ed. Universităţii "Transilvania" din Braşov,2001, ISBN 973-9474-40-3 (262 pag)
- Motoc Luca D. – *Materiale compozite cu pulberi: analiză, modelare, fabricare şi testare ultrasonică* nedistructivă (en. *Particle reinforced composite materials: analysis, modelling, manufacturing and non-destructive ultrasonic testing*), Ed. Universităţii „Transilvania” din Braşov, 2005, ISBN 973-635-527-6 (250 pag)
- Curtu I., Motoc Luca D. – *Micromecanica materialelor compozite. Modele teoretice* (en. *Composite materials micromechanics. Theoretical models*), Ed. Universităţii „Transilvania” din Braşov, 2009, ISBN 978-973-598-469-4 9 (206 pag)

Research activities

The research activity on composite materials, generally, can be regarded to the studies initiated and developed while delivering the PhD thesis entitled “*Contributions to analyzing the correlations between the tension level and the physical properties particular about certain materials by using non-destructive testing methods (sound, visual)”* in 2002, in the field of Mechanical Engineering, specialization Strength of Materials, Elasticity and Plasticity.

The main objective of the thesis was to analyze, predict and model the mechanical properties of several self-manufactured particles reinforced polymer based composite materials and retrieve their elastic properties using nondestructive testing methods.

The most outstanding contributions in relation to above targets the different experimental nondestructive testing methods used, classical and laser-ultrasonic, that enabled elastic properties' retrieval at values closer to the predicted ones. The latter were being approached by deployment of various micromechanical models, and finite element based simulations.

During this period (from 1996 to 2002), all the skills particular about a research activity have been acquired, including selection, synthesis, optimization and testing of composite materials irrespective of the filler type, number of phases, dimension, orientation and distribution.

Furthermore, confidence and thorough experience were gained while tackling various testing facilities enabling material characterization, generally, and hybrid polymer composites, particularly. These include materials' properties such as: mechanical (tensile, compression, bending), dynamical (DMA), thermal (DIL), electrical, etc. with or without subjecting the environmental conditioning resembling their practical use.

Translated into practice, the aforementioned materialized in the research project granted and run as project manager, entitled "*Advanced research aiming the development of multiphase polymeric composite materials with improved mechanical and physical properties*" during 2007-2010 under PNII-CNCSIS, IDEI Program.

In relation to above, more than 15 published articles (ISI proceedings, Scopus) and papers in the main stream journals, worldwide conferences' attendance, 5 published chapters in international books and one patent proposal (title - *Pressure-force transducer embedded in concrete pillars)* can be mentioned to be the main outcomes from the project.

To sum up, the publishing activity related to the research work can be summarized as: 40 articles (ISI Web of Knowledge, Scopus or Google Scholar indexed), 2 patents (one awarded in 2012, no. RO 123411 - *Adjusting resistor made of a piezo-resistive based effect composite material*), 5 chapters in books, 2 projects run as project manager, team member in 3 projects (after 2000), etc.

Nonetheless, these further contribute to the enhancement of international visibility, quantified in terms of Hirsch index type: ISI Web of Knowledge – 4, Scopus – 1, Google Scholar – 5 and citation in indexed published articles (journals like: Fibers and Polymers, Industrial and Engineering Chemistry Research, Journal of Thermal Analysis and Calorimetry, Composites B, Journal of Optoelectronics and Advanced Materials, etc.). Next, is should be mentioned the position held as reviewer for the following ISI journals: Journal of Thermal Analysis and Calorimetry, Textile Research, Journal of Applied Polymer Science.

Other responsibilities related to the scientific activity include the nomination as member of Scientific Committee of CEEC TAC 3 – 3rd International Conference on Thermal Analysis and Calorimetry, Ljubljana, Slovenia (2015, http://www.ceec-tac.org/conf3), member of

Organizing Committees of COMAT 2014 – The 5th International Conference on Advanced Composite Materials Engineering (https://sites.google.com/site/comat2014); BRAMAT 2015 – 9th International Conference on Material Science and Engineering, Brasov, Romania (http://www.bramat.ro) or chairman of section assigned to International Conferences:

- 2011 – 4th International Conference on Computational Mechanics and Virtual Engineering COMEC 2011, Brasov, Romania;
- 2010 – Production management section within the 7th International DAAAM Baltic, Tallinn, Estonia
- 2010 – 3rd International Conference Advanced Composite Materials Engineering, Brasov, Romania
- 2010 – New materials and Traffic Pollution and Noise sections within the 11th International Congress on Automotive and Transport Engineering, Brasov, Romania.

Internationalization within 'Transilvania' University of Brașov can be viewed as an ongoing and up-down and conversely running process, and consequently, profoundly influencing not only the structures but mentalities. In these circumstances, preservation of present international/European relationships is not only desirable but indispensable.

In the light of above, can be viewed the nomination of herein author as PhD external evaluator for 2 thesis delivered in:

- March 2011, Polytechnic University of Valencia, Thesis title – *Using natural based plasticizers to obtain flexible PVC low environmental impact*, Author: Octavio Angel Fenollar Gimeno, PhD supervisors: Juan Lopez Martin, Rafael Antonio Balart Gimeno.
- March 2012, Polytechnic University of Valencia, Thesis title – *Structural optimization of topological defined morphological structures using genetic algorithms*, Author: Samuel Sánchez Caballero, PhD supervisors: Vicente Jesus Seguí Llinares, Jose Enrique Crespo Amorós y Miguel Ángel Sellés Cantó.

A great honour was the invitations from the Romanian Academy, on behalf of Thermal Analysis and Calorimetry commision, to deliver the following presentatios:

- *Dynamic mechanical properties of basalt/flax and carbon/flax hybrid polymer composites* (2015)
- *Towards "all green" hybrid polymer composites tailored by the aid of DMA investigations* (2014).

Development plans for professional and academic career

The professional and academic career development plans are complying with the present ongoing path but are foreseen to rise exponentially once awarded the PhD supervision title. This relay on the professional and academic experience acquired so far, on the leadership attainments from research projects' management and on identified need concerning the openness toward international joint research and exchange programs acknowledged more profoundly since appointed as Erasmus coordinator at faculty level.

Expected outcomes and future dimensions

Teaching related:

- Continuously improvements of the existing curricula and lecture content in accordance with the quality in the higher education regulations and European trends.
- Deployment of modern teaching techniques, methods and instruments to enable flexibility and enhanced interactivity with attendee and further raise their implication and interest in the learning process, individually and in working groups.
- Identification, selection and close monitoring of potential students to be involved into research type activities, joint groups of discussions and academia-industry partnerships to stimulate entrepreneurship thinking and behaving.
- Development of strategies for mitigating skill shortages by proposal of new syllabi and training courses to bridge existing knowledge gap and already identified skill shortages, either in compressed schedule (i.e. courses of single or multiple days) or several modules.
- Proposal and implementation plans for transformational courses by fast-track curricula for mixed-background engineering B.Sc. graduates to quickly gain knowledge and experience comparable with that of a M.Sc. from related engineering fields they are working within.
- To apply for the position of full professor acknowledging the importance of the position and liabilities emerging from this, as well as the role and implications.

Scientific research related:

- To foster and continue the herein described research activities' spirit of an interconnected and multidisciplinary approach while aiming to tailor, develop and subject to comprehensive testing the future materials designated for structural engineering applications.
- To further promote the ongoing research activities by transferring the results into journal articles from the main stream of indexed journals (desirable to be ranked as having an IF>2), deliver presentations with international conferences and publish chapters/books accepted by prestigious publishing houses, apply for national/international patents on novel or adapted products/processes from the identified engineering applications.
- To strategically attract potential candidates owing unboosted skills for research activities, passion and creativity unleashed and let to flourish during the team/working groups' consolidation while running experiments under the research programs or projects by further directing toward doctoral studies.
- To propose research topics in accordance with the current scientific trends within the field of mechanical engineering and to coordinate doctoral thesis, both individually or under joint supervision, by close collaboration with colleagues from Romanian universities/research institutes or abroad.

- To further identify and attract public and/or private financing sources to enable research activities development, equipment acquisition or access to other research facilities.
- To consolidate the present collaboration and further develop other working relationships for joint research and publishing activities, to foster applications for research funds by gathering experts under a multidisciplinary partnership.
- To promote the scientific research outcomes of the group, department and/or faculty to belong with, by any legal means, resources and professional position and further contribute to their augmentation on the overall ranking with 'Transilvania' University.

Conclusions

Nonetheless, the entire experience and knowledge acquired over more than 20 years of presence in teaching and research activities with 'Transilvania' University, through dynamical and consistent involvement, essentially contribute to the position, vision and present attitude of the undersigned.

Put in a nutshell, several things should be tackled differently in the light of the present experience. Since implication and venture are the main words used to define my personality, future can be unpredictable and provocative. In addition, creativity and inventiveness will naturally follow 'what do you think about this?'

In summary, the past and present approaches as well as the future intentions on research topics in connection with polymer based composite materials can be viewed to comply with the main research themes and Horizon 2020 priorities in all pillars: pillar I – Excellent Science, pillar II – Industrial Leadership and pillar III – Societal Challenges. Consequently, concerns and actions it will be taken to get involved in research groups pursuing to apply for grants from the ongoing programs under aforementioned.

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