NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY "POLITEHNICA" BUCHAREST

DOCTORAL SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

SUMMARY DOCTORAL THESIS

STUDIES AND RESEARCH ON NEW PA6/HGB/MWCNT HYBRID MATERIALS FOR THE TRANSPORTATION INDUSTRY

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TABLE OF CONTENTS

Keywords used in the doctoral thesis: Acrylonitrile Butadiene Styrene, Artificial Intelligence, 3-aminopropyltriethoxysilane or Silane Coupling Agent, American Society for Testing and Materials, Body in White, Computer-Aided Design, Corporate Average Fuel Economy, Dynamic Mechanical Analysis, Differential Scanning Calorimetry, Energy Dispersive X-Ray Analysis, Fourier-Transform Infrared Spectroscopy, Hollow Glass Bubbles, High- Resolution Scanning Electron Microscopy, 3-Aminopropyl-triethoxysilane, 98% (APTES, Silane Coupling Agent), Multi-Walled Carbon Nanotubes, Sodium Hydroxide, Nitrile Butadiene Rubber, Polydimethylsiloxane, Scanning Electron Microscope Analysis, Selective Laser Sintering, Twin Screw Extruder

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INTRODUCTION

Nowadays the acceleration of new technology and AI set us on a continuous journey which is sometimes more on the fast forward gear; all the trends and latest gadgets made us forget the real source of our culture, of our past, or even our initial target. In today's world, there is a need for new materials and technology more than ever; these accelerations in upgrades bring a considerable challenge from the tiniest manufacturer to the substantial one. The trend started to switch from competition to collaboration; there is a visual turn in the world when it comes to manufacturing and processing. Today the need is yet again about numbers but on top of that sits the quality and perfection when it comes to products and services. All of the greatest producers have started to focus their attention on quality and perfection rather than volume and quantity.

The focus is more on customer needs and the voice of the public started to be more and more heard. Being in a crisis where recycling started to be more than a challenge when it comes to scraping a product than it was 10 years ago. The era of technology brings at the same time the biggest challenge we have ever had; eventually, that challenge is the recyclability of parts and how these composites will end. This unprecedented stage forced regulations to be more severe when it comes to pollution; hence all these ambitious targets set by the government were prioritised and carefully monitored. More industries started to feel this "pain" and the new set of rules started to challenge the way they behave in the world; most importantly started to challenge the way they handle a process from the early stages to developing, testing, producing and disposing them securely. In some cases, most of the challenges are pointing more toward getting more funds out of these companies' budgets.

The incentives and taxes changed our perception of living, thinking and working in society and forced us to adapt more and fast to the new era. For example. there are several challenges facing the transportation sector, especially the automobile industry, including meeting the requirements imposed by the European Union and global legislation considering the CO_2 outputs for every kilometre travelled. Starting with the year 2021 a new fleet average limit has been applied in the European Union (EU) which impacted all the manufacturers that exceed the limit of 95g CO_2/Km, with an incentive tax of €95 for every exceeded gram of carbon dioxide per kilometer [1]. On top of that, in June 2022 the European Union (EU) went further and adopted a new set of rules to reduce CO_2 pollution to 0 by 2050. To reach climate neutrality by 2050, all car manufacturers from the EU will produce cars, trucks and vans with 0 CO_2 tailpipe pollution starting in 2035 [2]. Electric powertrain development and lightweight materials are two key strategies for this challenge. Lightweighting effectively reduces fuel use in internal combustion engines and improves the range of electric vehicles. Composite polymers [3, 4] can be key in reducing vehicle weight due to their excellent specific properties, eventually, this will bring an increased cost for the new materials that are less explored for now. In some cases, the costs for composite polymers can exceed the cost [5] of the usual material by 20 times over the standard materials [6]. However, lower cost options exist for RP utilization, including injection moulding [7, 8], of short fibre reinforced polymers such as polypropylene (PP) and polyamide (PA). Short fibres can be in the form of glass fibre (GF) [9] or carbon fibre (CF) depending on the performance and cost targets. This doctoral thesis aims to investigate a potential state-of-the-art composite material that incorporates polymer composite material containing fillers of carbon nanotubes with multi-walls (NC7000 grade) and glass spheres (iM16K grade).

Previous studies [10, 11] revealed that notable improvements in mechanical performance can be achieved when polymers composited are used with hollow glass bubbles [12]. This project will specifically target opportunities for lightweighting using HGB and MWCNT as a filler for automotive polymer systems. PA will be investigated as this is the most common structural thermoplastic matrix material. Following a detailed state-of-the-art review, a sinterization of hollow glass spheres will explore the way the treatment with APTES can bring the adhesion morphology to another level; eventually, the obtained granules from the extrusion process will allow the test specimens to be fabricated by injection moulding of flat plaques. It is hoped that light-weighting potential will arise by two routes; firstly, the use of HGB should lead to a reduction in the density of the composites. Secondly, improvements in water absorption and high performance may lead to dielectric properties. HGBs and MWCNTs are used as lightweight fillers in composite polymers such as syntactic foam; the syntactic foam from these microbubbles gives its lightweight, low density, low thermal conductivity, and good dielectric properties, which other foams do not offer in the end.

This Doctoral thesis brings the potential of a new material which aims to open new limits and horizons in polymer composite materials; this explores how both the development and manufacturing of new composite materials can touch better ways when it comes to polymer materials and processing. All tests and developments are expected to fill the existing gap in the literature; eventually, this will bring unimaginable value to the market.

PART I

CHAPTER 1

LITERATURE REVIEW, THESIS OBJECTIVES STATE-OF-THE-ART

Literature Review and General Considerations

Chapter 1 presents the current state of literature and where the general considerations are situated at the moment. It enhances the state of the materials and the overall information about how the obtaining process for composite polymers with dielectric properties has been studied so far. Furthermore, this chapter presented the usage of hybrid materials in the automotive industry and how these composite materials have been used until now in the past 2 decades; eventually, this will open a new era of smart materials and their usage. Chapter 1 is a good reference, considering the work done by other researchers and this helped to understand better where the literature review is situated in connection with the current state. In this chapter the start of the discussion is about previous studies made on PA6, MWCNT HGB; eventually, this will explore more of the targeted properties for hybrid materials and what other research colleagues have done so far. Literature review and previous investigations for density determination, mechanical properties, measurement of the contact angle, water absorption and determination of dielectric/ electric properties are being exposed. This chapter explored the need for smart materials in the current market and what are the current opportunities which can evolve in-depth study considering the current doctoral research

Materials science or materials science and engineering is an interdisciplinary field, which aims to discover and describe new materials, especially solid materials. The origin of this science dates back to the enlightenment period when scientists used knowledge in the fields of chemistry, physics, and engineering to scientifically explain ancient observations related to metallurgy and mineralogy according to *M.D. Eddy et.al* [13]. Materials science and engineering is a field of technology that is in constant progress and to appreciate its importance it is sufficient to specify that the current technological changes in any productive activity are determined by a common criterion – materials.

Through impressive efforts, the specialists in the engineering of materials manage to create new materials or transform the existing ones to satisfy complex requirements in a highly evolved field of use. If some materials are fully known, others are in the design testing phase when they have an essential role in the calculation programs and the capacity of computer tools that are in turn dependent on the development materials. A unitary technical education in the field of materials in which the study of materials is an essential formative component is indispensable more so because today empiricism is strongly affected by donate mics of scientific innovation. To increase the efficiency of the scientific paper, it was decided to strike a balance between the fundamental theoretical aspects addressed and the practical applications in many fields of engineering. New materials are created every year, with the aim to be used in industries such as transportation, aviation, medicine, science, and many others; having a specific scope of solving problems or filling the gap using their unique properties. So far there were discovered around 100,000 types of materials and polymer composites and every year this number is increasing.

This research paper focuses on detail in the preparation of the materials for the extrusion process and obtaining the granules for the injection moulding which will take place in the production of tensile/bending specimens, but also in the interpretation of the final mechanical results obtained at the end of this study. This project aims to research a novel composite material for use in automotive structures that has isotropy properties, thermal properties (to resist in a range of temperatures between -50°C: 60°C), improved dielectric properties, to offer light-weighting potential, cost-effective and environment-friendly. The characterization of physical properties for composites will likely include the determination of composite apparent density, volume fraction, adhesion of HGB to the matrix and preliminary treatment with NaOH and APTES; dispersion of HGB and other fibres, mechanical performance (tensile, fatigue, crush), thermal characteristics, water absorption, the measurement of the contact angle and the determination of dielectric/ electric properties.

Other Hybrid Applications for Similar Composite Materials

The demand in the automotive sector for higher comfort is represented by vehicles that have low emissions of CO_2 pollution. Regarding the high comfort for the reduction of interior noises, it is more associated with weight. This is why applications of so-called hybrid materials or intelligent materials are suitable for use in the overall realization of adaptive systems. Materials that have piezometric films or fibres are easy to place in both the thin ceiling and the dashboard. Investigations [14 , 15] have shown that dynamic structure behaviour is important in adaptive system design. Many of these investigations can demonstrate that the use of sophisticated models represents a high computational time effort. The results of this model from these studies were presented for a straight steel plate with piezometric sheet inserts.

Polymers Overview (PA)

Nylons or polymers as they are often called, represent one of the most used plastic materials nowadays, due to their excellent properties such as resistance to electrical stress, resistance to high temperatures, good performance in injection applications and many others. As already known polymers are considered to bring high-performance properties with their performance to have a good resistance to increased temperatures, mechanical force, electrical stress and many others. Polymers are known to be in various types, but the most used in the market are polyamide 66 and polyamide 6. There are of course some significant characteristics and properties between these two and some of them are making a difference in sample production when some properties are expected to be brought to light more.

Hollow Glass Bubbles (HGB)

Hollow glass bubbles, known also as hollow glass microspheres or microbubbles are ultra-lightweight inorganic composite material which has been used in the past decade. This material contains tiny glass bubbles or glass spheres, filled with air; thanks to their low dimension (approximately: 18–65 µm/ micrometre) have a very high resistance to high loading such as crush strength (approximately 27 00 PSI) [16]. There are recommendations for the usage of hollow glass bubbles in other applications such as polymer composite applications and those recommendations are specifically for the preparation of the material in the first instance. Because these glass spheres have low dimensions is very easy to damage them before material mixing, also worth mentioning that if are used as bulk there are chances of miss mixing homogeniously. For that is worth applying a pre-treatment before mixing the material with other composites. Treatment with APTES or known silane coupling agent, has become very popular in application with hollow glass bubbles; this agent not only helps in creating good coating adhesion on glass spheres but ensures the connection between hollow glass bubbles and other materials is bonding correctly and efficiently at the same time. However, at the same time, the number of studies made so far is limited as well, and there is not so much information in the literature about this. There is of course some data available, but the reduction in investigations and studies around this subject created a gap in the market. Because of that one of the reasons for using hollow glass bubbles in our research study is also to identify the right procedure and the correct mixture for the materials that will be used further down. For this research, the selection was made between iM30K and iM16K due to their great properties at high pressure, resistance at strength and durability. These two grades [17] can withstand 27 00 PSI deformation resistance (for iM30K), respectively 16 000 PSI (for iM16K).

Multi-Walled Carbon Nanotubes (MWCNTs)

Multi-walled carbon nanotubes, also known as carbon nanotubes, are one of the best options used in composite materials selection when it comes to weight reduction, strength and good dielectric/ electric properties. This material has been widely used in the past decade but there is still a gap in the market when it comes to research information. The selection for NC7000 in this matter for the research was mainly to fulfil the initial scope in plastic applications, having the opportunity to use this material later on high-quality products. One of the main benefits of NC7000 is the common usage in injection moulding, and extrusion processes and not only, with great records in such an environment, having a low grade of failure in applications that follow these steps. It is expected to explore a state-of-the-art within this doctoral research, where multi-walled carbon nanotubes are expected to target both, density reduction and good dielectric properties alongside other opportunities that overcome the needed information in the current market.

Targeted Properties for Hybrid Materials

Hybrid materials also known as composite materials are those types of composites with unique properties, which can change their colour, shape, structure or even some of the characteristics under a certain force, degree or external environment. These materials can rapidly change their state such as their form; from solid to liquid and vice versa by just being exposed to a warm/ cold environment; these can be included in a wide range of alloys with memory or piezoelectric materials.

Determination of Material Density

Density determination in plastic polymers plays a vital role in material selection because allows us to identify where these materials can be used in the industry and what their best applicability is for them [18, 19]. In this research, the density of each polymer composite sample has been calculated using the Buoyancy Method, known as Archimedes' Principle [20, 21]. There are studies [22] that investigated how density can be determined better and of course methods, as well as the well-known Archimedes Principle can be used to estimate, and some cases have the right density for the object/ material other parameters are well known. In this research, it is expected that a reduction in density will be visible as soon as the composite material uses the addition of materials mentioned above (HGB and MWCNT). Nowadays, there is a need for lightweight products where the cost per part and delivery has increased due to the thought sanctions imposed by various governments. As specified above, mainly in the transportation industry and not only, weight reduction is an important factor when the usage of materials is considered before designing a new material/ product.

In the current state, it is expected that this doctoral research will create new opportunities in density determination, considering the polymer composite will contain hollow glass bubbles and MWCNTs. Both, HGB and multi-walled carbon nanotubes are lightweight and have a low density, such as 1.14 g/cc for PA6, 0.075 g/cc for MWCNT, respectively 0.46 /cc for HGB. Determination of properties before the usage of material in applications is important to determine whether or not the material created, fulfils the expected properties. In the current case, the right process and procedure have been followed and used, to ensure good practice and usage of the materials will be done based on test results and investigations which are used as both references from previous research studies and experience/ expertise in the field.

Determination of Mechanical Properties

Determination of mechanical properties is known for the physical properties a material withstands when a force is applied on its own. The importance of mechanical properties determination for a material or sample is primordial, because this will dictate the limits of this, such as the elongation, tensile strengths, fatigue limit, hardness or elasticity. There are many ways [23, 24] that can determine the tests presented above, and in this case, the usage of material can be done within safe limits when such determinations are known. In this case for the current study, the determination of mechanical properties such as flexural modulus or elongation at strength/ tensile strength are wanted to be determined, even if the usage of the material is not intentionally supposed to have high mechanical loads.

Determination of mechanical properties has become more and more accessible, due to various options in prediction for this matter. Studies [25] revealed how this can be possible, even if used in unprecedented situations. Mechanical properties of polymer composite are not impossible to predict when are know all the parameters; eventually, this can give important information about the material which can help more in the studies, even if the actual sample, the material was not physically tested just yet.

Determination of the Contact Angle

The determination of the contact angle is the drop of a liquid on a solid object or sample. Using this measurement will immediately give an indication of how the material behaves in a wet environment, such as if loves water this will be hydrophilic, whereas if it has a resistivity to the water this will be hydrophobic.

Studies [26, 27] have shown how the influence of a liquid can impact the properties of a material or an object; therefore, the determination of contact angle and ensuring where the balance sits for a composite material when used in the market is even significant. Literature [28] investigated the measurement of contact angle and carefully observed what is the direct relation between the liquid and the tested object. Even if the simplicity of this test, as is sounded to be easy, sometimes can be very challenging. It has been confirmed that behind all these experiments, there needs to be an equilibrium in the modern literature. There are circumstances when this test went beyond its limits, and the measurements of the contact angle were done in-depth, such as it has been confirmed that in the modern laboratory, even the water/ liquid droplet on the surface can be measured, such as speed, weight, angle and the distance between droplets or even the shapes of them.

Determination of the Water Absorption

Previous studies [29, 30] have shown how other parts have been investigated and how their usage is linked to performance and applicability. There are cases [31, 32] where the materials need to withstand challenging conditions and have to meet certain properties such as good mechanical performance, good resistance in wet environments or present good corrosion resistance. In general, the main challenge is when a material is continuously exposed to a wet environment because as already known water accelerates the material aging in any circumstances. The best example of a material that resists in a wet environment is represented by the water absorption test [33]. A material water intake always brings disadvantages such as reducing the strength properties or even the impact of the glass transition temperature, eventually, this is directly linked to the amount of absorbed liquid [34, 35]. There are cases when water uptake on multilayer films [36] can cause water intake to increase due to the plasticization and swelling of the polymer composite structure due to the attraction of the hydrophilic areas. Water molecules' presence [37] in polymer composites sometimes can create difficulties, eventually, this is down to the creation of a bond cluster or in some cases [38] is due to their increased mobility [39]. Water uptake can affect the properties of composites, such as the mechanical properties [40]; for example, on the injected moulded samples from a polyamide-based with 30 wt% bamboo-based biochar filler, the increased strengths on the final component reached a lower water absorption [41, 42].

Literature [43] has shown the side effect of water absorption on composite materials, such as polymer-based and how the numerical solution of the water can be precisely calculated with various equations [44, 45] such as Fick's equation diffusion model [46, 47] Therefore, using this diffusion model confirmed in further studies [48, 49] how the water intake measurements for several polymer composites were predicted by only using as an indicator their hydrophobic characteristics or Tg. One important indicator when using composite polymers in liquids is being triggered by the amount of mass that is added compared to the initial mass of the material before being immersed in water.

Eventually, water uptake can lead sometimes to a decrease in mechanical properties and a decrease in polymer composite usage [50]. Additionally, the automotive industry's demand for materials that have reduced both water absorption and weight is particularly on a scale that continuously rising every year. Because of that the majority of industries, especially the automotive industry is continuously looking for better options when it comes to materials usage, such as materials which can help in fuel consumption; eventually, these materials can bring other benefits as well as efficiency and increased in vehicle speed [51, 52].

Determination of Dielectric Properties

Considering current literature [53, 54] it has been proved once again that the usage of composite materials with specific properties that are being used in certain applications was always a challenge. To have a well-balanced material with certain properties, the experience of multidisciplinary teams sometimes needs to compromise other aspects of the final product. The progress of the development of electronic systems in the previous years, brought improvements in results such as in the electronic systems, considering the multitude of fields of activities, as well as automotive, space, medicine, railway, and many other industries. By doing that, researchers opened a new era for smart applications [55, 56] and the usage of materials, eventually, this challenged the creation of composite materials which can be tailored based on the desired application that followed to be used. Team collaboration across various domains, having the same scope made this journey achievable and created great success in creating materials to resolve certain issues in the field [57, 58].

The Need for Studying Hybrid Materials

Nowadays, lightweight materials in the automotive industry are also known as materials with a weight reduction of the vehicle mass. Body-in-White (BIW) is a traditional name for the body of the vehicle but is also recognized as a stage in automobile manufacturing where the body frames are joined together. This process takes place before paint, chassis assemblies or finishing components (seats, electronics, glass, locks/handles) are integrated into the common structure. We can admit that each material was important at one time and was considered a material of the future based on the actual performance it offered and how it was used in engineering to add to the process [59]. In 1913 steel was introduced into the mass production of automotive structures by Henry Ford. In the 1950s, more than 75% of car components contained steel. Since then, the vehicle construction process has evolved every decade [60].

The big differences between the past and present are the specifications: performance, safety, exterior features, interior features, technical features, efficiency, compliance, handling, etc. All of these specifications are possible thanks to the new hybrid materials that are on the market today. Using aluminium chassis can reduce the weight by 30% less than using steel. Making a car with an aluminium chassis will have better energy absorption and the vehicle will be much safer. In addition, 95% of the interior and exterior body components have also been improved over the past 60 years in the carmaker's portfolio.

CHAPTER 2

OBJECTIVES, RESEARCH METHODS, AND EQUIPMENT USED

Purpose and Objectives

Chapter 2 describes the purpose and objectives of the doctoral thesis, what methods were used to assess those objectives and eventually, in the end, what equipment was used during the investigation process to obtain the wanted results for this study. The conceptual model from this research well embedded with the synthesis of the investigated materials has made it possible to analyse better in this chapter all the methods, working steps, and laboratory instruments. General objectives and the elaboration of the conceptual model are being explored in more detail such as all the working preliminary steps that were taken from the initial phase to the development of the material the analysis methods and all the laboratory equipment used for creating this investigation.

The doctoral thesis entitled "Studies and Research on PA6/ HGB/ MWCNT Hybrid Materials for the Transportation Industry" has the main purpose of designing, obtaining, characterizing and optimizing three-dimensional nanomaterials based on HGB and MWCNT, with the potential for obtaining reliable material with dielectric properties, low water absorption and reduced density. These materials intend to fill the gap in the current literature and additionally to fill the purpose within the transportation industry and not only. It is expected that in the upcoming chapters, a state-of-the-art will explore in depth one of the greatest opportunities that has been investigated so far. The correlation between the 3 types of composite materials such as PA6, HGBs and MWCNTs will open new limits in the manufacturing process; eventually, this will explain the current need in the market.

Elaboration of the Conceptual Model of the Research

The conceptual model for this doctoral research was elaborated and represents a stepping stone because opens new opportunities to the market. This study investigates not only the originality of a new composite material, but it demonstrates how the composition of a new material can be done differently. To obtain certain results it was designed a set of steps that were carefully monitored to ensure the development of the study was done by the book. In other words, all phases of the development of this material needed to be respected are presented below by categories. Each category represents a milestone which the composite material went through. Considering the timeline and the laboratory apparatus available at that time, these points were created in such a way that each phase followed a logical order.

I. Material Simulation and CAE Analysis.

This initial stage represents the identification of the optimal condition for the synthesis of the 3D CAD model, such as developing the initial simulation using tools that CATIA V5 offers, such as the Measure Inertia Tool or Density Automation Determination.

II. HGB Surface Treatment.

This secondary stage represents the identification of the ideal structure for the pre-treatment of hollow glass spheres (HGBs) with sodium hydroxide (NaOH) such as for enhancing a better surface preparation for the coupling agent. As soon as this phase was completed, the follow-up treatment of the same bubbles with a silane coupling agent such as APTES was used immediately to create an improved surface adhesion in the mixture composition.

III. Material Processing and Sample Production.

This represents one of the most important stages from this investigation such as the development of the composite sample and the required samples that were needed for this study to take place. As well as both the extrusion process and granulation highlighted how the preparation and mixture of the filler variation took place in the development. Is worth mentioning that after all the completion within this stage from the injection moulding process and producing the sample eprouvettes was a conformation the mixture and moulding process had closed nicely.

IV. Morpho Structural Characterization.

This last stage enhanced both the characterization of the obtained samples through the determination of serial ways, such as density, contact angle measurement, water absorption, dielectric properties and mechanical performance; as well as identification of each material and how this homogeneous commerce, eventually being confirmed with scanning electron microscopy (SEM) and fourier transform infrared spectroscopy analysis (FTIR).

PART II

CHAPTER 3

RESEARCH AND EXPERIMENTAL STUDIES, ORIGINAL CONTRIBUTIONS

Simulation And Design Of Hybrid Materials

Chapter 3 focuses on the simulation and design of the hybrid material. In this chapter is worth mentioning that all the element selection and meshing were done thanks to the current CATIA V5 software, using the tools from Computer Aided Engineering (CAE) for the mesh simulation. Eventually, these tools helped to create a design of experiments for the wanted parts. From the element selection, and meshing to the optimization concept, this chapter revealed the advantages of using these tools.

Optimisation Concept

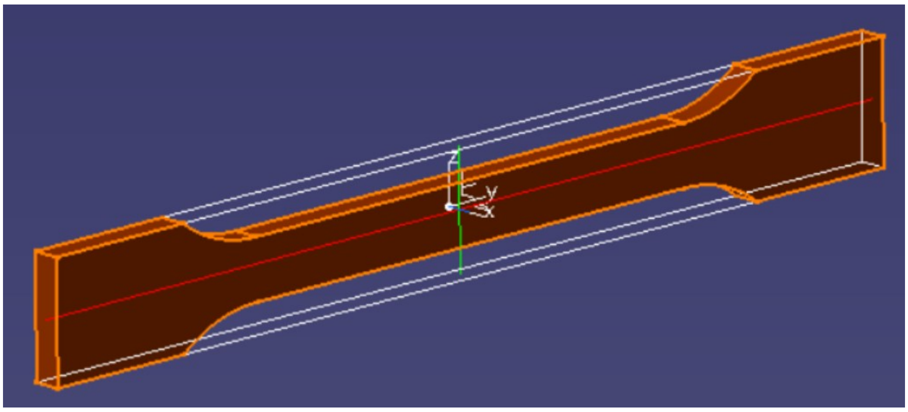


Figure 3.1: 3D Model Resurfacing of the ISO 527/2 Tensile Sample [168]

The optimization concept in a simulation environment is a good opportunity to improve the model to ensure the research will deliver the results wanted. There are of course several advantages that are not easily forgotten when optimizing a model concept **Figure 3.1** from the initial phase.

The first advantage is cost efficiency: in a 3D environment in general there are no cost implications or if they are, will be very low compared to a physical model optimization. It reduces the risk of the additional funds required for manufacturing processes, tooling modification, labour implication, raw material, and time frame; whereas in a 3D model, the design can be virtually optimized and can be created as much literation as needed by saving the resources and time.

Computer-Aided Engineering (CAE) Simulation Program

As mentioned in Chapter 3, the optimization concept or the simulation stage has been an important phase in the initial study [61] because helped to understand better which type of polymer (PA6 or PA66) should be more explored for this research and revealed what the differences between these 2 polymers [62]. The performance of the tensile simulation was done by using Catia-V5, function Simulation Analysis.

Table 3.1: Short Comparison of the Test Samples after the Simulation when using PA66 [168]


Reference

PA66

PA66-10MWCNT

PA66-20MWCNT

PA66-30MWCNT

PA66-10CF

PA66-20CF

PA66-30CF

CHAPTER 4

MATERIALS AND METHODS USED FOR OBTAINING AND CHARACTERIZATION OF HYBRID PA6/ HGB/ MWCNT MATERIALS

Materials Used and Specimen Preparation

Chapter 4 explores the materials methods used for the characterization of hybrid PA6/ HGB/ MWCNT composite materials and the overall original contributions. This chapter presented all the used materials during the investigation together with the preparation stages for all the specimens. Eventually, these were carried out using methods for obtaining and characterization, such as extrusion process and granulation and even injection moulding and sample production. Is worth mentioning, that this chapter presents in-depth morpho structural characterization methods such as FTIR- Fourier Transform Infrared Analysis, and HR-SEM – High-Resolution Scanning Electron Microscopy Analysis. Still, this phase discussed the physical and surface characterization, such as density determination, contact angle measurement, water absorption and determination of dielectric properties.

Specimen formulation represents a combination of two, such as literature [63] reference and personal contribution within this investigation. There are other studies [64] where separate polymers with either HGBs or MWCNTs were done following various applications. Having that said, this initial point was used as a reference for the current study, which combined with personal contribution, explored a new technique to develop and study new mixture variation types, that other colleagues did not try before. The preparation of all 12 variations was done under certain criteria divided into multiple trial days and sequences until the optimal composition had been reached. Is worth mentioning before doing the mixture variation for this study, a set of tests and investigations were done to identify the optimal condition for both hollow glass bubbles and surface treatment with APTES. Literature [65] played an important role in this investigation as well as personal contribution such as developing a new method of sinterization of glass bubble surface with sodium hydroxide, which eventually allowed us to prepare the glass sphere surface for the final treatment with 3-aminopropyltriethoxysilane.

This allowed for the enhancement of new material compositions such as described in **Table 4.1.**

Specimen Formulation

Table 4.1: Illustration of each Variation Type of PA6/HGB/MWCNT Formulations

No.	Variation Type	PA6 (wt.%)	HGB (wt.%)	MWCNT (wt.%)
1	PA6	100	0	0
2	PA6-30HGB	70	30	0
3	PA6-40HGB	60	40	0
4	PA6-15MWCNT	85	0	15
5	PA6-20MWCNT	80	0	20
6	PA6-10HGB-S-2MWCNT	88	10	2
7	PA6-10HGB-S-4MWCNT	86	10	4
8	PA6-10HGB-S-6MWCNT	84	10	6
9	PA6-20HGB-S-2MWCNT	88	20	2
10	PA6-20HGB-S-4MWCNT	86	20	4
11	PA6-20HGB-S-6MWCNT	84	20	6
12	PA6-30HGB-S-2MWCNT	88	30	2
13	PA6-30HGB-S-4MWCNT	86	30	4
14	PA6-30HGB-S-6MWCNT	84	30	6

The sequence of each sample variation took place following some important steps; initially, as described above were tree trials which defined the amount of filler and dosage that needed to be used in the mixture. Therefore, the exact quantities could be measured and predicted before the physical work begins. After the preparation of each material sample, the mixture begins by weighing carefully the necessary amount needed for each variation type.

Hollow Glass Bubbles Surface Treatment

Functionalization of HGBs with Sodium Hydroxide and APTES

A series of treatment and pre-treatment sequences were done in accordance to identify the optimal condition for both hollow glass bubbles and the right mixture composition for polyamide 6 and multi-walled carbon nanotubes. Initially, this started with 3 main trials, to determine which recipe should be used for the bulk material. This trial not only saved and preserved time and material amount, but helped to identify optimal conditions such as the amount of the filler, temperatures, time and laboratory mechanisms needed for the study to be conducted as per book.

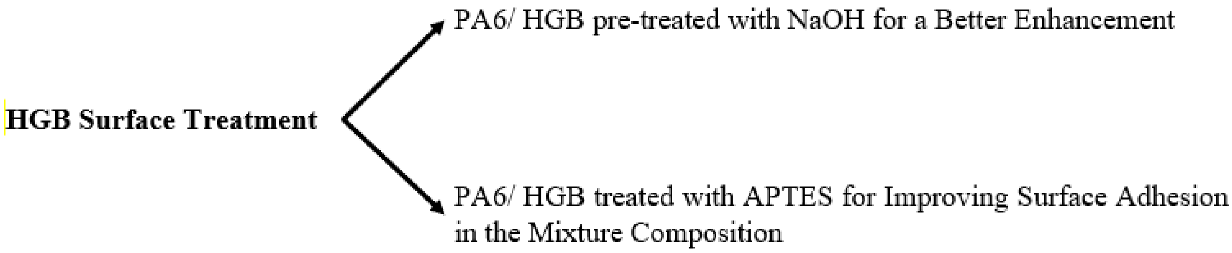


Figure 4.2: Schematic Illustration of Functionalization for HGBs with Sodium Hydroxide and APTES

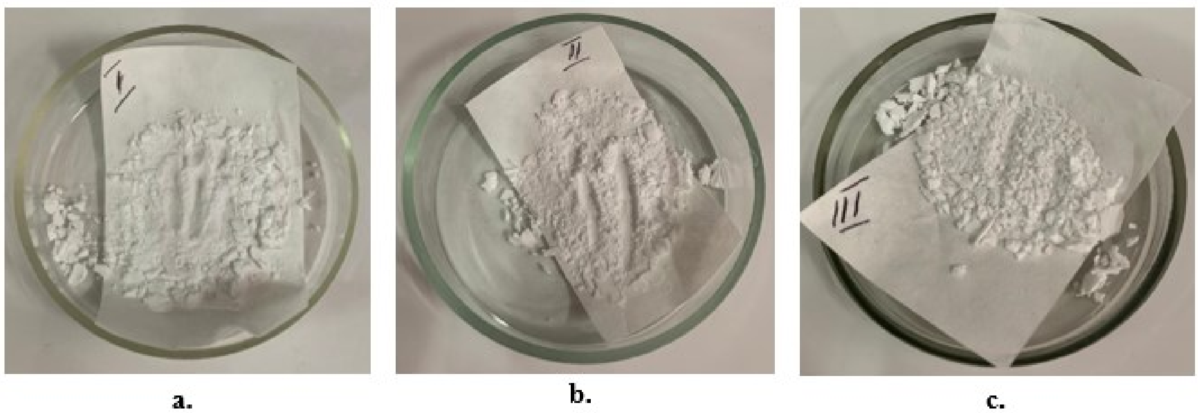


Figure 4.3: Illustration of all 3 stages in the Treatment Preparation of HGB

Method for Obtaining and Characterization

Extrusion Process and Granulation

Previous studies and current literature [66, 67] proved once again that the extrusion process is often used in various production processes, eventually, this created a wide cross-sectional profile for the plastic parts. The material preparation [68, 69] stage is primordial in the initial phase as this will define the robustness of the final part. Mixing the materials [70, 71] with an extruder is a key stage regarding the material development, because all these stages from the material amount, material preparation, and extrusion times, but also the stationary times in the extruder, must be well-defined. For this study, 14 types of variations (**Table 4.2**) for the extrusion process were used.

The type of extruder used for this study was a conventional twin-screw extruder with 4 different zones of temperatures with the mixture process for the materials in the loading bay, which was called initially zone 0 or feeding zone. Each variation had the composition carefully selected based on initial preparations and quantity volume measurements. The extrusion process identified as one of the most important stages of the entire preparation process; eventually, this was needed to be prepared in advance and various scrap samples were done to ensure the laboratory extruder was calibrated accordingly.

Table 4.2: Materials variation type for the extrusion process

Number	Variation Type
1	PA6
2	PA6-30HGB
3	PA6-40HGB
4	PA6-15MWCNT
5	PA6-20MWCNT
6	PA6-10HGB-S-2MWCNT
7	PA6-10HGB-S-4MWCNT
8	PA6-10HGB-S-6MWCNT
9	PA6-20HGB-S-2MWCNT
10	PA6-20HGB-S-4MWCNT
11	PA6-20HGB-S-6MWCNT
12	PA6-30HGB-S-2MWCNT
13	PA6-30HGB-S-4MWCNT
14	PA6-30HGB-S-6MWCNT

The creation of the 14 types of variations was conceived on the basis of the studied literature and on the basis of the exploration of new variations, which have been less studied until now.

The calculation of the amount of material of the variations in each composition was carried out volumetrically.

The problem in this case started to rise when the treated materials passed through zone 1 of the extruder, which had a temperature above 150 ˚C. As already known APTES or silane coupling agents are over 90% material based on alcohol or made from materials with similar properties which are inflammable and easy to burn when exposed to high temperatures. Because of that the trial phase challenged the zones in the extruder such as were needed to set up and prepare for the study to begin. In the end, the optimal condition was stabilised at a constant screw speed (rpm) for each variation and all 4 temperature zone were better controlled during the entire study.

Injection Moulding and Sample Production

PA6 polymer composite which was prepared with both fillers HGB and MWCNT was mixed accordingly as a first stage, then was extruded and eventually injected moulded based on each variation type. The different composites [72, 73] were prepared with an extruded equipped with a corotating twin-screw extruder which has the performance of a speed per screw at 40 rpm, and at a zone temperature for the profile between 220–240 ˚C. All the composites were stirred and premixed by being fed simultaneously and tumbling into the extruder. The injection moulding process is a process that usually produces parts from plastic, but also from heat-resistant material or other materials such as metals. The device available at the time of the research was a Minijet Pro type device, from the manufacturer Thermo Fisher Scientific, which used a Haake piston injection moulding system.

Test samples were produced from both grades such as *ISO 527* usually used for Tensile and Elongation at Break as well and *ASTM D790* mainly used for Flexural Strength and Modulus using injection moulding, eventually, samples were produced with a moulding apparatus Haake Minijet Pro [74] from Thermo Fisher Scientific, which operates at a zone temperature of 250˚C each and a pressure force of 650 bar holding in the piston for 15 seconds; eventually, the parts resulted from this process were used eventually used for the water absorption test as well. The obtained samples after the injection process were of 2 types, namely:

-*ISO 527/2* [75] the standard itself specifies the test normal conditions for the determination of the right elongation properties of extrusion and moulding plastics, considering the general principles given by the specification.

-*ASTM D790* [76]; the standard itself specifies the test normal conditions for the determination of the right flexural properties, which represents the type of specimens generally used when performing flexion/ bend.

CHAPTER 5

EXPERIMENTAL RESULTS CONCERNING HYBRID MATERIALS AND OBTAINING PA6/ HGB/ MWCNT; ORIGINAL CONTRIBUTION

Chapter 5 presents all the experimental results concerning hybrid materials PA6/ HGB/ MWCNT and all the original contributions. This chapter reveals all the initial phases, from

HGB pre-treatment to achieving good adhesion with PA6 matrix to HGB treatment with APTES, H_2O and Ethanol. Thanks to SEM-Scanning Electron Microscopy Analysis and FTIR-Fourier Transform Infrared Analysis the adhesion of NaOH onto the hollow glass bubble surface was confirmed. Eventually, this was taken further to the extrusion process and granulation which embedded the preparation of the hybrid material by the extrusion process. Furthermore, FTIR and SEM confirmed that a homogeneous mixture successfully enhanced the polymer composition. In the end, experimental specimens were carefully prepared and presented for the injection mould process.

SEM Analysis of HGB surfaces before APTES treatment

Scanning electron microscopy can provide pictures of a test sample/ sample in general by examining the surface using a beam that is focused based on the electrons; these electrons are generated by the electron source, and these are emitted when their thermal energy applies to the work function of the material source.

Figure 5.l: Neat Hollow Glass Bubbles

Preliminary HGB Surface Treatment with APTES

The first trial contained 5 grams of hollow glass bubbles (HGBs), stirred in an aqueous solution in which the solvent was based on both 66ml of distilled water (H_2O_d) and 10ml of silane coupling agent (KH550/ APTES).

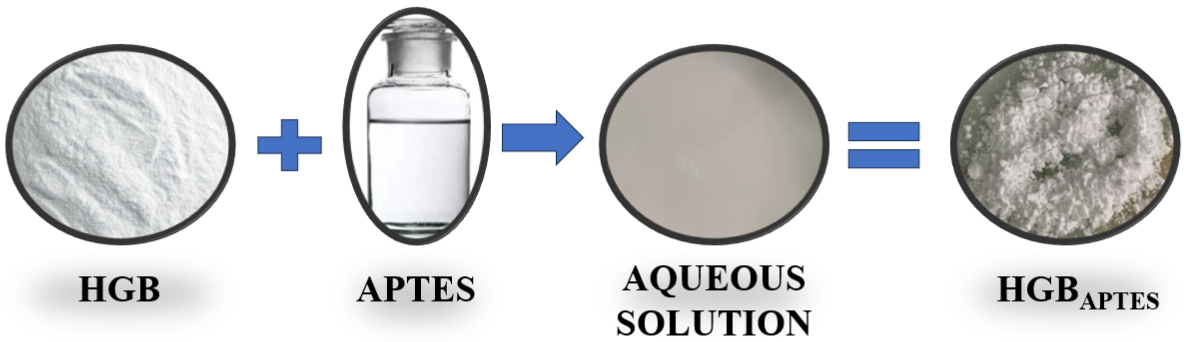


Figure 5.3: Illustration of HGB Treated with Silane Coupling Agent

SEM for the Preliminary Research on HGB_{NaOH} treatment with APTES

The morpho-structural characterization of the obtained composite materials was highlighted by a wide range of measurements according to the main factors that influence their structure and texture. Characterizations were performed using high-resolution SEM and FTIR spectra analysis. Techniques that allowed investigations regarding the synthesized composite materials' size, shape, and density. Subsequently, the scanning performance of the composite based on HGB and MWCNT was evaluated on multiple samples. The study of characterizations and evaluations of the properties of the synthesized materials took into account the methods of obtaining used that led to complex structures in terms of purity, composition, size and distribution for each material. A wide range of analyses was chosen to provide a complex characterization of materials, the use of a single characterization technique being relevant to us in terms of their characteristics.

FTIR for the Preliminary Research on HGB_{NaOH} treatment with APTES

The molecular structure of HGB_{NaOH} and APTES was confirmed using an FTIR system from Thermo Scientific Nicolet iS10. **Figure 5.13** shows FTIR spectrums of HGB_{NaOH} modified using the last three mixture techniques (8, 9 and 10 from **Table 5.1-***see above*). The FTIR curve of HGB_{NaOH} from all three mixtures does show a significant characteristic peak between 2500 - 3500 cm^{-1}, which corresponds to the primary amine in HGB_{NaOH} -APTES.

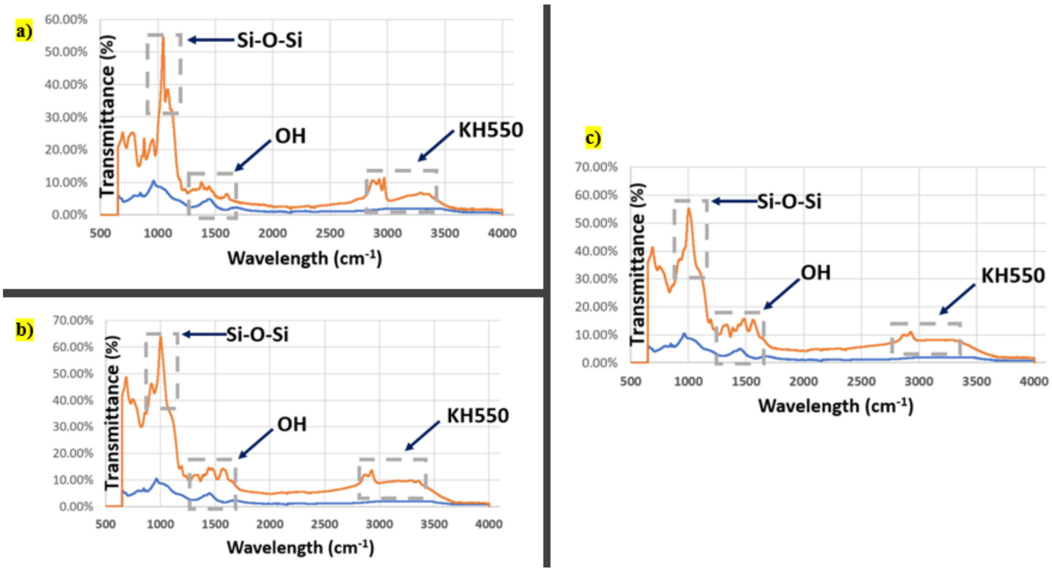


Figure 5.13: FTIR Spectrum images of HGB_{OH} modified with:

(a): APTES, **(b):** APTES-Ethanol, **(c):** APTES-H_2O_d

FTIR wavelength of HGB_{NaOH} revealed the characteristic stretching peak between 1000 - 1100 cm^{-1} and that is the correlation of the Si-O-Si bond. The spectral region presents a peak between 2000 - 2300 cm^{-1} corresponding usually to the CO_2. For a better surface adhesion of APTES, NaOH was used to attach hydroxyl groups on the surface of HGB for the subsequent reaction with a coupling agent in the fabrication of amino-terminated HGB_s. It is worth mentioning despite the treatment of HGBs with APTES, it was an agglomeration on the bubble surface which can be correlated between SEM (Figure 5.12b and Figure 5.12c) with the corresponding FTIR (Figure 5.13b and Figure 5.13c). It is assumed that the higher the number of APTES in the composition, the stronger the mixture structure of HGB_{NaOH} becomes, eventually this composition can create a strong crust which eventually will break and impact the hollow glass spheres; this assumption will affect the mixture overall and the benefits of using HGB in the composition will not bring the same values as expected.

Hybrid Materials Preparation by Extrusion Process

The extrusion process and granulation have been by far one of the most important stages of this development process. Having that said, preliminary preparation for the polymer composite material and the other fillers used in this research investigation need to be with careful attention all parameters used for preparation have to have clear indications; eventually following with careful attention to both references and personal decisions which will contribute in the end at personal contribution and originality of the thesis. The extrusion process consists of several preparatory stages, each with particular importance, such as:

The below table (**Table 5.2**) describes all 14 variations, with all the parameters recorded during the processing process, such as extrusion. During all individual mixtures, it was observed an interesting behaviour such as when using a material with hollow glass bubbles treated with silane coupling agent aqueous solution, the extrusion process was challenged due to the inflammable composition from the APTES itself.

Table 5.2: Extrusion conditions used for each type of variation.

No.	Variation Type	Temperature (˚C)/ screw				Screw Speed (rpm)	Extrusion Time Mixture
		Zone 1	Zone 2	Zone 3	Zone 4		
1	PA6	220	230	240	240	40	7 min 30 sec
2	PA6-30HGB	220	230	240	240	40	12 min
3	PA6-40HGB	220	230	240	240	40	9 min 40 sec
4	PA6-15MWCNT	220	230	240	240	40	24 min
5	PA6-20MWCNT	220	230	240	240	40	36 min 30 sec
6	PA6-10HGB-S-2MWCNT	220	230	240	240	40	11 min
7	PA6-10HGB-S-4MWCNT	220	230	240	240	40	10 min 40 sec
8	PA6-10HGB-S-6MWCNT	220	230	240	240	40	10 min 37 sec
9	PA6-20HGB-S-2MWCNT	220	230	240	240	40	10 min
10	PA6-20HGB-S-4MWCNT	220	230	240	240	40	23 min 55 sec
11	PA6-20HGB-S-6MWCNT	220	230	240	240	40	32 min 10 sec
12	PA6-30HGB-S-2MWCNT	220	230	240	240	40	30 min
13	PA6-30HGB-S-4MWCNT	220	230	240	240	40	19 min
14	PA6-30HGB-S-6MWCNT	220	230	240	240	40	20 min

Hybrid Materials Preparation by Granulation Process

Once the samples were obtained from the extrusion process, they were left for a few hours to set (approximately 6 hours), and for the samples to dry and cool down. The granulation itself was mainly represented by the breaking down of the composite polymer obtained from the injection moulding such as plastic wire, in other cases where the extrusion nozzle was removed, the obtaining of the samples was based on lumpy big parts of plastic composition with other fillers (**Figure 5.16**).

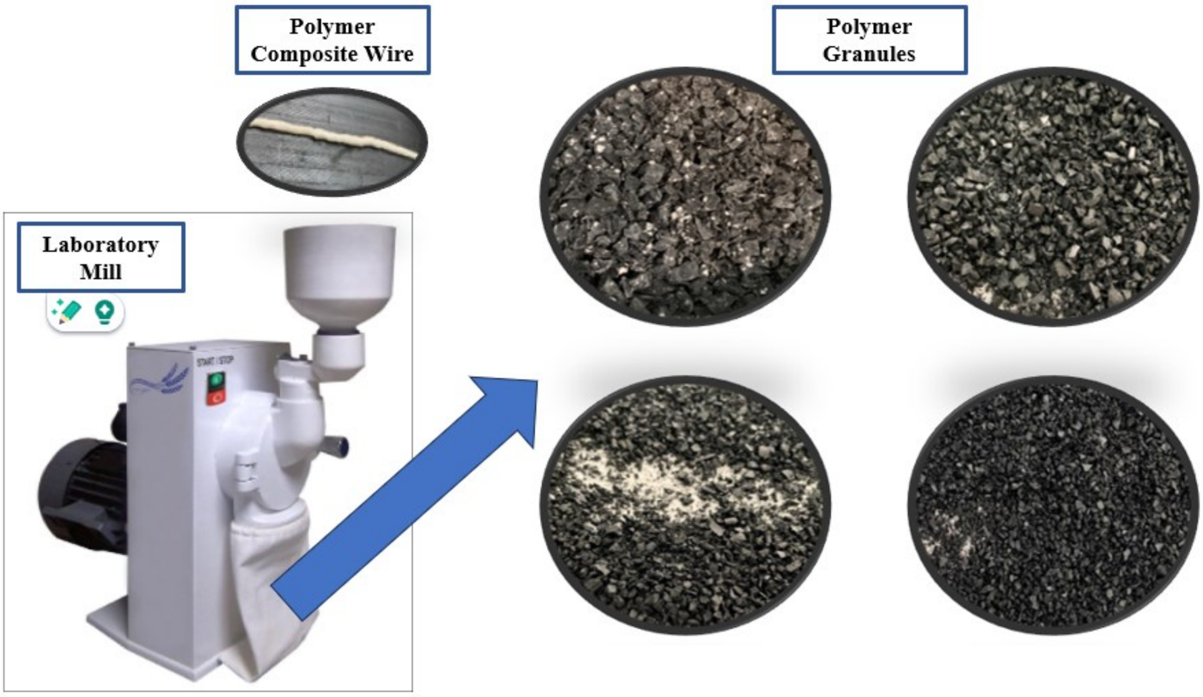


Figure 5.16: Illustration of Granulation Process from Wire to Pellets

Experimental Specimen Preparation for the Injection Moulding Process

The experimental preparation of the specimens concerning the injection moulding process is a stage where the confirmation of the entire work will be evident in the final samples. Further, these samples are due to be tested and validate the initial presumptions, such as the wanted properties from the new material such as performance and weight reduction.

During this process, challenges did not hesitate to appear, such as some variations (number 2, 3 and 13) could not be performed due to the high aqueous solution of coupling agent from the glass spheres composition. There were cases where for some parts, due to the high gases formed inside the cylinder (samples 2 and 3); eventually, such high pressures from the piston system, were pushed out along with the material, hence the injection process could not be completed *(***Figure 5.22***)*.

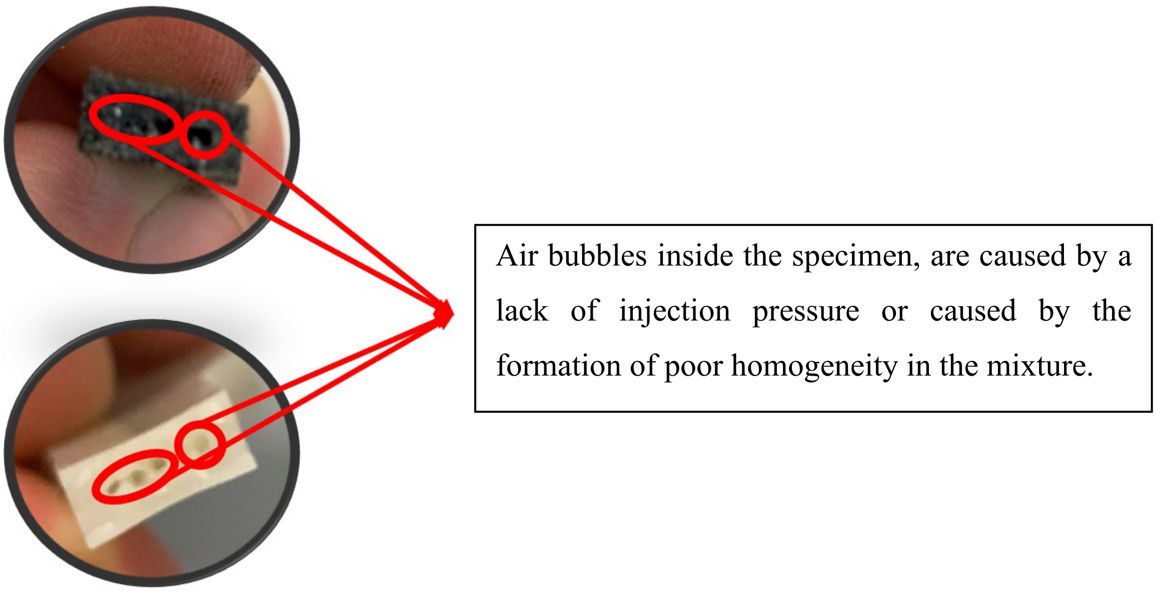


Figure 5.22: Example of Samples formed with Air Bubbles/ Holes inside due to Low Injection Pressure.

CHAPTER 6

PHYSIC-MECHANICAL CHARACTERIZATION OF PREPARED SPECIMENS; EXPERIMENTAL RESULTS

Chapter 6 represents the milestone where the physic-mechanical characteristics of prepared specimens are presented carefully based on the experimental results. In this chapter, density determination test results confirmed once again the usage of new composite material on the market. Is worth mentioning that mechanical properties were confirmed by both routes, such as the tensile and elongation at break and the flexural strength and modulus.

Mechanical Properties Determination

Mechanical properties determination in plastic materials represents an important factor from a sample characteristic. Having a material with good mechanical properties such as tensile or flexural strength is a bonus, depending on the applications. Of course, not all applications require good mechanical properties, some of the applications do not even require having this property at all. Even if the material was not designed to withstand any mechanical force, it intended to be a support and have other applications in use, the determination of mechanical properties was performed anyway. The determination of these properties helped to understand what the limits and characteristics of this composite material are.

Tensile and Elongation at Break

The performance of this test made it possible to understand if both the characteristics and the stretching forces before breaking are within the limits. Using the reference from the simulation, made it possible to understand better if the CAE was matched on match to the real-life tests.

The simulation test could not be performed due to various reasons but one of the principles applied in the test was all down to the preparation stages and the way the samples must behave during the simulation. As presented in **Figure 6.2** the eprouvettes must be fixed at one point to have stability when the tensile starts to occur. The idea of the simulation is down to the force that takes for the sample to break and also defines the peak where the material starts to change in phase from solid form to an elastic state; eventually, this is when the deformation takes place. The apparatus used to perform the tests to determine the tensile properties of plastic materials was an Instron 3382 type. Tested samples were checked under the same conditions, such as a tensile speed of 10 mm/min, at a room temperature of 23 ˚C and a humidity of 50%.

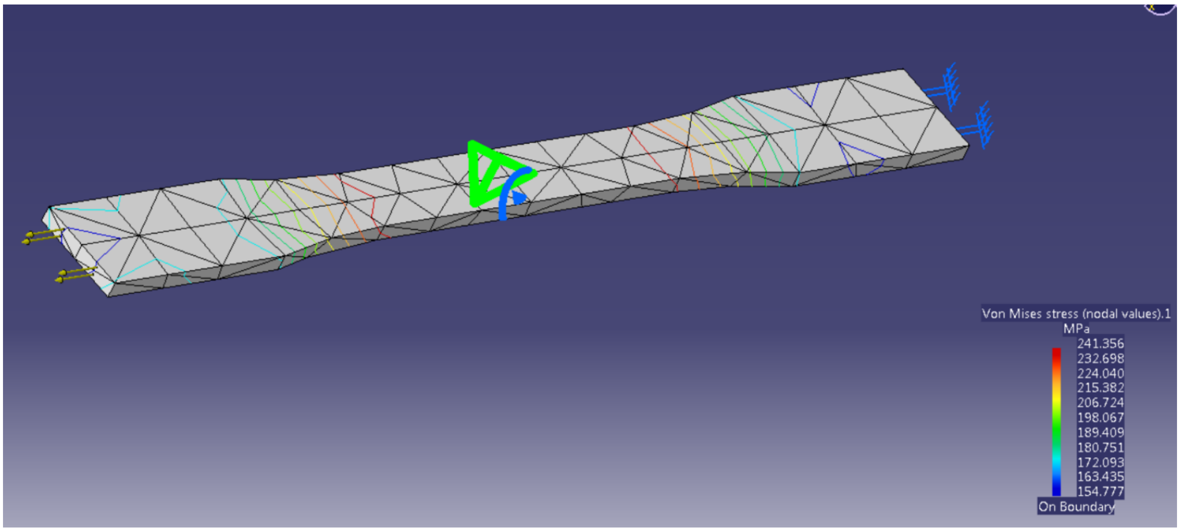


Figure 6.2: Tensile Sample Illustration in Catia V5

One of the advantages, in this case, was that samples from the previously prepared variations for this study were tested, one by one. For conducting the tests, the steps specified in the standards were followed after which the test samples were prepared with great care.

CHAPTER 7

CONTACT ANGLE AND WATER ABSORPTION OF PA6/ HGB/ MWCNT OBTAINED HYBRID MATERIALS

Chapter 7 presents the results of the measurement for the contact angle, as well as the determination of the water absorption on PA 6 using HGB and MWCNT. In this chapter the results are discussed and concluded based on the current need, referencing the current literature.

Contact Angle Determination

For this study were made multiple measurements, such as for both the glossy and the matte side. Of course, a single plate on one side could also be used and can make as many measurements as wanted on a surface and then the contact angle results can be averaged. The tested plates in this study were washed in advance, rinsed with a lot of distilled liquid, and let for a day to dry naturally; eventually, were measured 2 plates per sample on both sides, glossy and matte - the data results are entered in **Table 7.1**.

Table 7.1: Contact Angle for each Sample Type

No.	Sample Type	Average Angle [Θm]
1	PA6	73.4 ± 3.26
2	PA6-30HGB	74.5 ± 1.17
3	PA6-15MWCNT	115 ± 1.44
4	PA6-10HGB-2MWCNT	85.0 ± 1.84
5	PA6-10HGB-4MWCNT	90.2 ± 1.54
6	PA6-10HGB-6MWCNT	95.1 ± 4.22
7	PA6-20HGB-2MWCNT	90.3 ± 3.77
8	PA6-20HGB-4MWCNT	95.4 ± 3.97
9	PA6-20HGB-6MWCNT	100.9 ± 3.21
10	PA6-30HGB-2MWCNT	95.9 ± 1.72
11	PA6-30HGB-4MWCNT	100.5 ± 3.75
12	PA6-30HGB-6MWCNT	106.5 ± 2.25

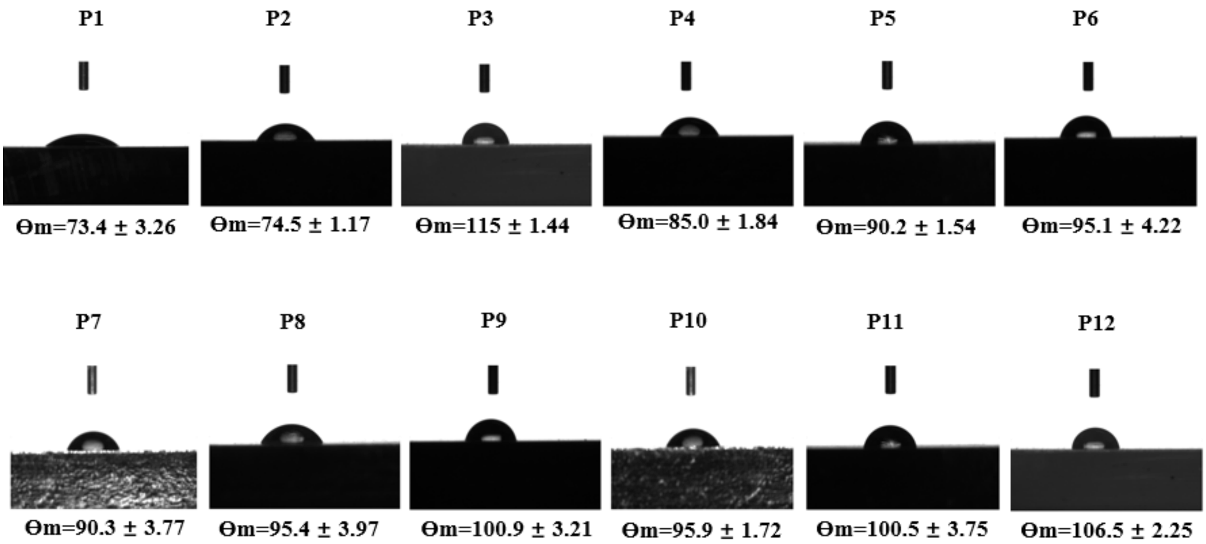
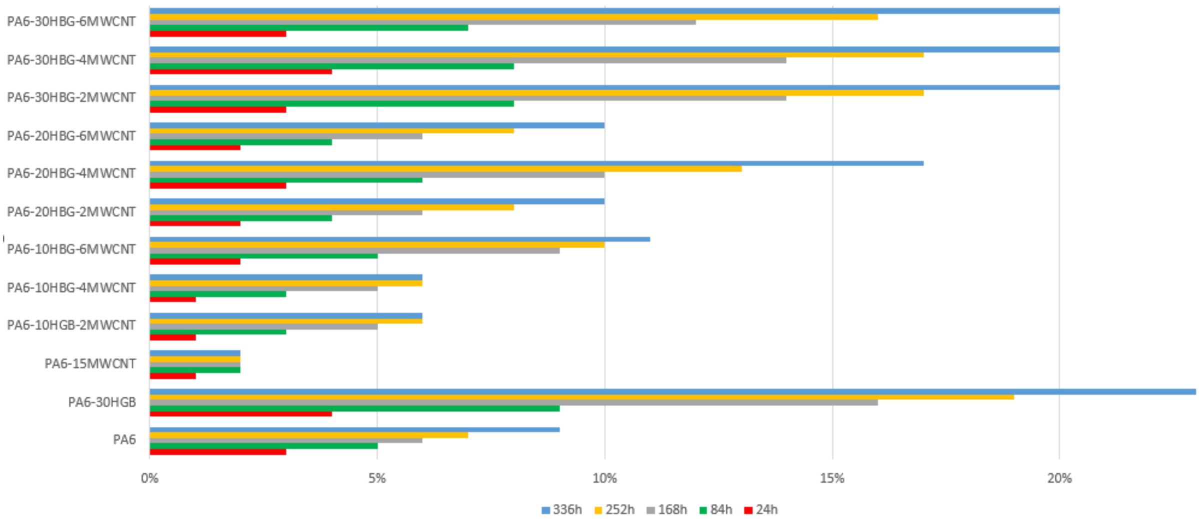


Figure 7.1: Contact Angles of the Water Drop for all Composite Samples

Figure 7.1 shows the correlation between the contact angle test results from the test and the picture of all composite samples. The smaller the contact angle, the more hydrophilic the surface. Hydrophilicity decreases as the contact angle increases, and when it reaches 90 degrees, the surface is considered hydrophobic. Depending on what has been added to the composite samples, the angle decreases or increases, increasing or decreasing the hydrophilicity of the surface.

The Water Absorption on Polyamide 6 (PA6) using MWCNT and HGB

The water absorption test on polymer composite materials or plastic materials is a good indication of discovering the material resistance in a wet environment. On top of that, this will



identify if any of the properties the material has will be affected. The tested specimens were placed in a recipient full of distilled liquid for the next 24 hours, at a constant room temperature of 23°C entirely immersed. The specimens were removed from the water after 24 hours (±1h), cleaned with a material cloth and then using a laboratory scale, each sample was weighted to identify the impact of water uptake during the conducted test (**Table 7.2**). The assumption has been made for the samples with high loading of HGB to have a higher amount of water uptake, as those samples, in particular, were treated before with APTES to ensure the connection between material in the mixture. It is to be noted that the samples with APTES were still wet in the composition when were used for the injection moulding process.

Figure 7.2: Water Uptake Percentage at Different Hours

Figure 7.2 which displays the water uptake for different loading of HGBs and MWCNTs, enhances how the tested epruvets have a connection between them. Not to be forgotten that for the first 14 days during the water uptake test, the intake for the samples was significantly more considering the other end of 21 days from the entire cycle; eventually, this is because the samples hit the well-known saturation liquid limit. The equation created by Fick [77] is often used to identify the moisture diffusion curves for the studied materials [78]. This equation can be used equally for both hot and humid water uptake input, which enhances the possibility of directly linking any changes in T_g with the moisture content.

Still, **Figure 7.2** shows the correlation between the increase in the water intake and immersion treatment time for the tested samples, which gradually increased. Eventually, this may have a bigger impact for samples that contain loading of HGB filler, where the loading filler is linked to the immersion time under the water; eventually, the % of the water that was stored during the test will have a better impact on those samples. This study further indicates the usage of fillers such as MWCNT loads can lead to improved water resistance for the polymer composite (samples 3). The addition of such fillers can significantly impact the reduction of water uptake on the component and present desirable applicability when samples with the above filler are being used in an environment that has a decreased wet percentage compared with the polymer reference. As presented above samples that hit the saturation limit are known as the normalized water intake samples, furthermore, the reference polymer states a lower % such as 9% compared with the neat granules which stated the highest water intake amount; eventually, this can increase up to 11% in a shorter period.

CHAPTER 8

DETERMINATION OF DIELECTRIC PROPERTIES

Chapter 8 presents the determination of the dielectric properties and the determination of the composite material. This chapter is presented in more detail with facts and results, such as graphs and tables which are the right composite polymer material mixture types that exceeded in this field. Is worth mentioning that the test results obtained from this investigation are as well as part of a state-of-the-art, which once again did not disappoint. Still in this chapter, further discussion related to the need to composite material and the linkage between dielectric properties take place.

Identification And Characterization of Dielectric Properties

As described above at 4.3 dielectric properties were checked for the obtained hybrid composite test coupons. The injected moulding test samples were tested for dielectric properties, which are shown in **Figure 8.1**; eventually, the test results are described as the variations of tan δ and ε_r' with frequency for both PA6-HGB-MWCNT and neat PA6 composites at 30 °C. ε_r' for both composites PA6-30HGB-4MWCNT and PA6-10HGB-4MWCNT are significantly higher compared to the reference (PA6) for the entire frequency range; this sign can indicate that new dipoles were introduced in the polyamide 6 during the initial preparation of the polymer composites. Considering this, a remarkable increase in ε_r' values at low frequencies when presented with all composite materials as well; but in this case, their variation is significantly slower on the way to a higher frequency.

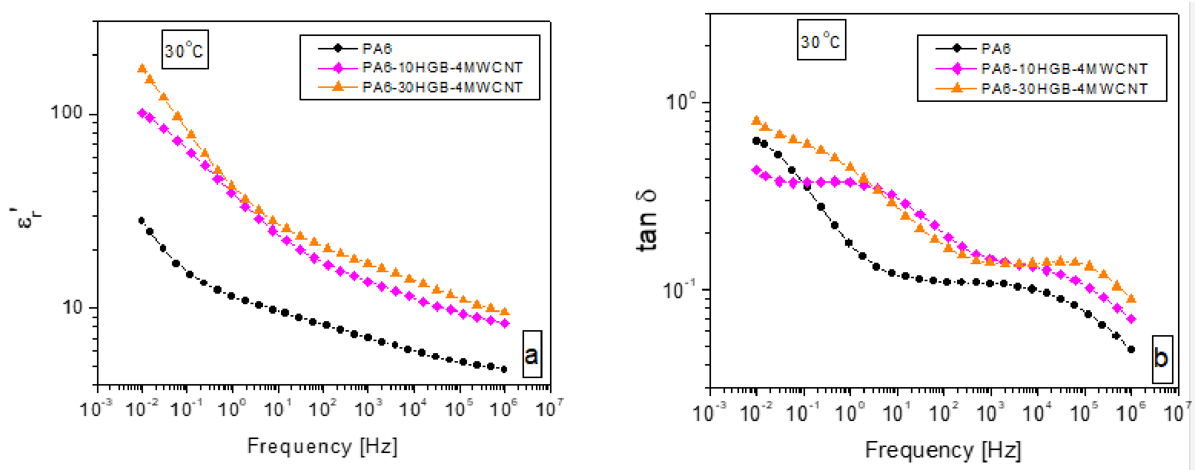


Figure 8.1: Frequency alteration of ε_r' (a) & tan δ (b) for the Polyamide

On top of that, this can only indicate that the accumulation of the space charge in the electrodes resulted in being described as electrode polarization, this is directly related to the increased tan δ and ε_r' values at low frequencies [79]. **Figure 8.1b** describes the loss of tangent values which seems to be higher considering the PA6 reference across the entire frequency range. As described by Joncher's Universal Law the complex conductivity σ' which is discovered in most of the materials that have dielectric properties is frequency-dependent based on the behaviour of the real part.

(**Equation 8.1**)

$a\sigma'(\omega) = \sigma_{DC} + \sigma_{AC} = \sigma_{DC} + a\omega^{n}$, values between 0 and 1 are taken by the exponent n, whereas a is the real coefficient.

Figure 8.1 presents for both PA6-HGB-MWCNT and PA6 composites at a temperature of 30°C, the dielectric spectrum of σ' is presented as a graduate growth of σ' in the numerical plot; eventually, this can only indicate that for the PA6 the capability law variation of σ_{AC} is the dominant. Additionally, 10^{-2} Hz represents the power of values between 10^{-12} to 10^{-11} S/m; eventually, this only results in the material having insulating properties in all cases for all tested samples. In general, this effect triggers a decrease in DC for the material. Usually, this happens because of the ion signals rather than the effect of the creation of conductive leads often being influenced by the addition of MWCNT.

CHAPTER 9

PERSONAL CONTRIBUTION AND FINAL RESULTS

Chapter 9 represents the last chapter of this doctoral thesis, eventually at this stage, all the conclusions from the entire study. In this chapter are presented all the personal contributions and the final results, such as conclusions, together with thesis originality and all personal contributions. Is worth mentioning this chapter presents the future research direction as well as how this composite polymer material can open new limits in the market when it comes to smart polymer composites.

Final Conclusions

The present doctoral thesis entitled "Studies and Research on PA6/ HGB/ MWCNT Hybrid Materials for the Transportation Industry", shows what are the great opportunities in using materials in composite applications. Moreover, these types of materials will be more often used in the industry, and eventually, this will bring polymer composite production to another level.

Thesis Originality and Personal Contributions

This research brought several continuous contributions to the current literature state. Personal findings and original contributions enhanced the unicity of all presented studies from this paper. All the important test results presented above created a well-rounded state-of-the-art. This scientific study led to a multitude of new answers which were carefully presented while the presentation of each test has been commerce in the current state. To highlight better the original contributions, several research activities were considered that helped in the organization, presentation and testing of composite materials obtained. Among them, the following are presented:

- The design and treatment of HGB with APTES of hybrid materials, in which the active sodium hydroxide (NaOH) played a vital role in linking on top of the HGB surface the hydroxyl groups for the subsequent reaction with a coupling adhesion agent concerning the fabrication of HGBs.
- Development of a conceptual research model that materialized in synthesis methods for each component of the hybrid structures as well as morphological and electrochemical characterizations: morpho-structural characterization by scanning electron microscopy (SEM), determination of materials, structure and purity by Fourier transform infrared (FTIR) and establishing the elemental composition by volumetric measurement of each sample.
- The creation of a new polymer composite material, such as PA6-10HGB-4MWCNT, which represents in the end a state-of-the-art in the current phase of literature. This new material aims to explore new limitations withing the polymer composite on the open market. Is worth mentioning this material has explored a better density, very good water absorption properties, acceptable mechanical properties and comparable contact angle measurements when was comparing to the polymer 6 reference.

Future Research Direction

This doctoral thesis has proved to be a successful state-of-the-art and has clear prospects for further development in several directions, such as:

- Continuation of tests to establish the optimal composition for introducing even more properties for this smart composite material.
- Is worth mentioning as future research direction, there is a need in improving the mechanical performance of the current discovered material. Having this property improved due to the reduction in fillers such as hollow glass microspheres and multi-walled carbon nanotubes will potentially increase the material elasticity, eventually, improved properties in mechanical loading will arise.
- Determination and characterization of other filler composite mixtures that can improve the properties of this obtained hybrid composite material.
- Application where weight reduction is a must, such as lightweight plastic components, such as plastic covers based on the cabin side.

- Dashboard components, such as under-bonnet components where the reduction in weight is required, or components that are reduced in density
- Other interior applications that need to be low in density or weight.

- Plastic components which are not exposed to mechanical force or any other exterior loading.
- Components which are free of breakage or do not present any risk of being exposed to exterior damage or breakage.
- Applications such as the low risk of being broken or hit such as interior components used more for protection or isolation, mainly in the interior which does not interact with the exterior hits.
- Plastic wiper protection, air intake or any other plastic component assembly,
- Exterior parts, such as front shield protection,
- Any other applications such which require water resistance, such surfaces need to be hydrophobic or reject water.
- Front bumper plastic protection, headlight plastic protection, undercover shield or plastic shield.
- Exterior applications, that are intended to protect or withstand harsh conditions, such as temperature variability.
- Any other applications such which require high resistance in wet environments or are at risk for liquid split.
- battery cable isolators, or this investigation have the possibility to expand studies on serial production for electric car batteries.
- Any other applications such as LCDs or monitors can have a great potential for the usage of composite polymer material, such as applications where dielectric properties are a must.

APPENDIX A

Published Scientific Articles in the Field

ISI Articles

1. ***Andrei-Ionut PERDUM*** *and Alexandra BANU*, The Influence of Water Absorption on Reinforced Polymers (FRP) using MWCNT and HGB, Revue Roumaine de Chimie, 2023, 68(1/2), 101-107.
   doi: 10.33224/rrch.2023.68.12.10

2. ***Andrei-Ionut PERDUM****, Alexandra BANU, Roxana TRUSCA, Cornelia MARINESCU*, Hollow Glass Microspheres Treated with Silane Coupling Agent, U.P.B. Sci. Bull., Series B, Vol. 84, Iss. 4, 2022, ISSN 1454-2331.

ISI Conference Volumes

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2. ***Andrei-Ionut PERDUM*** "Cost Impact on Changing the Aluminium with Fibre Reinforced Polymers (FRP) in the Automotive Industry" Proceedings of the 37th International Business Information Management Association (IBIMA), 30-31 May 2021, Cordoba, Spain, ISBN: 978-0-9998551-6-4, ISSN: 2767-9640

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