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MSc. Thesis

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Development of Nanohybrid Polyurethane Coatings with Self-Healing Properties

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Abstract

In recent years, self-healing materials have been a subject of increased research interest due to their ability to self-repair damages either autonomically or by external stimuli, extending their lifetime or therefore assisting in the reduction of waste. Polyurethanes represent one of the most promising materials to use towards this direction. In particular, waterborne polyurethane dispersions (WPUDs) are widely used in coatings giving the additional advantage of the reduction of volatile organic compounds (VOCs) in the environment in comparison with the traditional coatings which are solvent-based. At the same time, inorganic and / or graphitic nano-additives are widely used to improve the mechanical, thermal, optical and electronic properties of a polymeric matrix resulting in polymer nanocomposites with an overall optimized behavior.

In this work, nanohybrid polyurethane coatings were developed and their self-healing properties were evaluated. 2D materials like graphitic carbon nitride, g-C₃N₄, graphene oxide, GO, and $Ti_3C_2T_x$ which belongs to the newly emerged class of Mxenes were dispersed in the polymeric matrix. The intrinsic self-healing mechanism of the WPUD can be improved by the presence of the inorganic compounds as they are anticipated to provide more hydrogen bonds due to the nitrogen and/or oxygen functional groups that exist on their surface or due to their ability to dissipate heat faster and thus increase the mobility of the polymer chains. Following the nanoadditives synthesis, the materials were thoroughly characterized via X-ray Diffraction, XRD, Differential Scanning Calorimetry, DSC, as well as Raman and Infrared Spectroscopy, ATR-FTIR, measurements. WPUD nanocomposites were fabricated in different concentrations ranging between 0.05 - 1% wt. to investigate the effect of the additive content on the final properties. The PU/g-C₃N₄ nanocomposites were prepared via solid-liquid mixing while the PU/GO and $PU/Ti_3C_2T_x$ via liquid-liquid mixing to avoid sedimentation problems. All nanocomposites were structurally and thermally characterized and no difference was observed in comparison to the properties of the pure PU due to the small amount of the nano-additives. Finally, coatings of all nanocomposites were fabricated by drop casting on silicon wafers. The coated surfaces were scratched creating deep and shallow cracks, using a razor blade and their self-healing efficiency was evaluated in two different temperatures (i.e., 75oC and 90oC). The healing procedure was monitored utilizing a Polarized Optical Microscope equipped with a Linkam heating stage. A quantification of the healing results was attempted by using mean grey value analysis. Similarities and differences were observed depending on the additive used; in certain cases, the self-healing ability of the pure polyurethane was found enhanced in the nanocomposites and the healing rate was found much higher, due to either better heat dissipation and / or the enhanced ability for hydrogen bond formation.

Development of the polymer nanocomposite coatings with enhanced self-healing efficiency is anticipated to enhance their usage as varnishes in wooden floors as well as paints in the car industry.

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"In the midst of winter, I found that there was within me an invincible summer. And that makes me happy. For it says that no matter how hard the world pushes against me, within me there is something stronger, something better pushing right back. Where there is no hope, we must invent it."

Albert Camus

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1.Introduction

1.1 Polymers

Polymers are macromolecules that consist of repetitive units, which are called monomers, covalently bonded between them.¹ The two large polymer categories, are based on their origin, i.e., the one consists of the synthetic polymers (e.g. poly (styrene), poly (propylene), poly (amides)) and the other of natural ones (e.g. DNA, RNA, proteins, cellulose). These materials are being used for their fascinating properties which arise from their large degree of polymerization, referred as N, which is defined as the number of the repetitive units of the polymer chain, and their molecular weight, which is the weight of the repetitive units multiplied by the polymerization degree.² Polymers are being used in a wide variety of applications due to a plethora of properties such as adhesive, insulating, environmental, biodegradable etc.;³ one of the most promising and fascinating properties is their self-healing ability.⁴

1.2 Classification of polymers

1.2.1 Topology

Polymers can be categorized based on their architecture (topology) which describes the shape of the polymer chain. Whatever the origin of the polymer is, natural or synthetic, the polymer chain can have linear, branched, cross-linked, star shaped and dendrimer architecture.⁵

Linear polymers are flexible chains where the monomers are connected end to end in a single chain (Fig.1). The chains interact all together with physical attractions, usually Van der Waals forces.⁶ Linear polymers can be crystalline or semi-crystalline as the single chains can be packed resulting in high density. Some examples of linear polymers are poly (isoprene), poly (propylene), poly (styrene), poly (methyl methacrylate), poly (amides) and poly (vinyl chloride).⁶



Figure 1. Linear polymer configurations⁷

Branched polymers are linear polymers that have side chains (i.e. branches) of the same composition growing out from the main polymer chain (Fig. 2).⁶ These branches appear due to side reactions during the polymerization process affecting the polymer properties, e.g. the density of these polymers is reduced due to the loose packing of the polymer chains. The most common branched polymer is Low Density Polyethylene (LDPE).⁶



Figure 2. Branched polymer configuration⁸

Star shaped polymers are molecules consisting of three or more polymeric chains which emanate from a central point referred as core (Fig. 3).⁹ Their main advantage, compared to linear polymers, is that they consist of smaller molecular weights resulting in more compact structures and thus can be used a variety of applications (commercial thermoplastic elastomers, drug release in target cells, etc.).¹⁰ Finally, cross linked polymers consist of linear polymers, where their chains are covalently bonded forming a network. The vulcanization of rubber is considered to have resulted in the first cross linked polymer.¹¹ Polymer networks, instead of dissolving in good solvents, as conventional polymers do, they swell (Fig. 4).¹²



Figure 3. Star shaped polymer configuration⁹



Figure 4. Cross linked polymer configuration¹³

1.2.2 Chemical composition

Polymers can also be classified based on their chemical composition. The two most common categories are homopolymers and copolymers. Homopolymers consist of one type of monomers where in copolymers two or more monomers constitute the polymeric chain.^{12, 2} Depending on the sequence of monomers, different categories of copolymers can be distinguished (Fig.5).

- i) Block copolymers; Blocks of different monomers compose the polymeric chain
- ii) Graft copolymers; Blocks of different monomers are grafted as branches onto the polymeric chain
- iii) Statistical copolymer; No periodicity among different monomers can be observed
- iv) Alternating copolymer; Different monomers are alternating along the polymeric chain
- v) Periodic copolymer; A standard periodicity along the chain can be observed ¹²



Figure 5. Classification of copolymers based on their chemical composition¹⁴

1.2.3 Morphology

Polymers can be also classified based on their morphology, meaning the arrangement of the polymeric chains on a large scale. Three categories can be distinguished; crystalline, amorphous, semi-crystalline.

- Crystalline polymers: A periodicity is apparent in the arrangement of the polymeric chains (e.g., parallel arranged chains), and by decreasing the temperature an ordered structure, on a large scale, can be appeared by a process called crystallization (Fig. 6). ¹²
- Amorphous polymers: Polymeric chains are randomly arranged in space presenting no periodicity and by decreasing the temperature the chains do not orientate but retain their random arrangement (Fig. 6). ¹²
- Semi-crystalline polymers: Polymers that consist of both crystalline and amorphous regions. Most polymers are not completely crystalline and thus belong in this category (Fig. 6).¹²



Figure 6. Morphology of polymers¹⁵

1.3 Self-healing ability of polymers

Self-healing is the ability of a material to repair since it has suffered some damage. By imitating biological systems, which process their own self-healing mechanisms, it is possible for polymers to reshape through physical or chemical approaches at a molecular level.⁴ The physical self-healing mechanisms include interchain diffusion, phase separated morphologies and shape memory effects while the chemical approach is based on the introduction of covalent, free radical or supramolecular dynamic bonds in the polymeric matrix.⁴ However, there are some self-healing approaches that combine both physical and chemical mechanisms such as the enhancement of Van der Waals forces, the incorporation of microcapsules or the cardiovascular network filled with reactive fluids.⁴

1.3.1 Physical approaches

A common self-healing mechanism is the interchain diffusion which can be expressed in five different steps; segmental surface rearrangements, surface approach, wetting, diffusion and randomization. After the physical damage on the material, the segmental surface rearrangements begin (above the glass transition temperature of the polymer) and the process is highly affected by the topology of the polymer, the roughness of the damaged surfaces and the molecular weight.⁴ Then, in the second step, the two separated surfaces are getting close and a physical and/or chemical self-healing process initiates at a molecular level. When the two surfaces reach each other, a wetting process occurs, as an interface is being formed, and finally the diffusion and randomization of the polymeric chains takes place, as the material returns to its initial shape (Fig. 7).⁴



Figure 7. Interchain diffusion self-healing approach of polymers⁴

Another physical approach to self-healing is by inducing two different separated morphologies in a copolymer.⁴ This usually occurs in copolymers where the chain consists of soft and hard segments and this enhances the ability of storing and losing mechanical modulus which is pivotal when it comes to self-healing.⁴ According to the literature, polymers with phase separated morphologies, e.g. a material with rubber elasticity and thermoplastic stiffness or tough copolymers combined with flexible polymeric segments, tend to respond to external stimuli (heat, light, electrical or magnetic fields) resulting in enhanced self-healing abilities (Fig. 8).⁴ Similar to the interchain diffusion healing mechanism, some polymers consist of two different interdigitated phases which tend to flow back to their initial shape upon physical damage.⁴



Figure 8. Phase separated morphology self-healing mechanism⁴

Finally, shape memory effect is the ability of a material to "remember" its initial shape, and return to it after an external or internal stimulus.⁴ It is reported that the effect is a result of hydraulic shrinking and swelling, triggering the movement of the polymeric chains and finally returning to its initial structure (Fig. 9).⁴ The ability of a polymer to memorize its shape is closely dependent to its synthetic route and more precisely to its topology.⁴ Under certain stimuli such as heat, light or mechanical deformation, a polymer can reform back to its memorized shape through entropy driven chain or mass flow movements.⁴



Figure 9. Shape memory effect self-healing mechanism⁴

1.3.2 Chemical approaches

Dynamic covalent bonds

One of the most known chemical approaches is the Diels-Alder (DA) reaction which occurs between dienes and olefins, called dienophiles forming cyclohexenes.¹⁶ The dienes are conjugated and include furan products e.g. furan, furfuryl alcohol, furfuryl amine etc. and the olefins include maleimide compounds such as maleic hydride, maleimide and bismaleimide. The DA is a reversible reaction and upon heating the configured cyclohexenes are destroyed and by lowering the temperature the reforming of cyclohexenes can be observed proving the reversibility of the reaction (Fig. 10).¹⁶ This reversible process allows the change in the shape of the material and enhances its self-healing ability.¹⁶



Figure 10. Reversible Diels-Alder reaction, enhancing the self-healing ability of a polymer¹⁷

Another common chemical approach are the disulfide bonds which are abundant in nature as their main purpose is to maintain the tertiary structure of proteins.¹⁶ Disulfide bonds can be easily destroyed by heat, light or mechanical stimulus but they can also be reshaped when exposed to suitable temperature or pH environment.¹⁶ By exploiting the weak dynamic covalent network provided by the disulfide bonds, these reversible bonds reinforce the polymeric material with improved self-healing properties at lower temperatures. In order to take advantage of the reversibility of disulfide bonds, small molecules (e.g. Hydroxyethyl disulfide (HEDS)) containing disulfide bonds are introduced in the polymeric matrix.¹⁶

Similar to disulfide bonds, imine bonds are weak and unstable creating a network of reversible bonds.¹⁶ The imine bond, which is a double bond between carbon and nitrogen, is the product of the condensation of a carbonyl containing compound (e.g. aldehyde, ketone) and an amine containing compound (e.g. primary amines, hydrazine, hydroxylamine). Under acidic conditions the imine bond, as it is pH responsive, intensifies the self-healing ability of a polymer (Fig. 11).¹⁶



Figure 11. Imine exchange reaction example; Formation and decomposition of carbinolamine¹⁸

Dynamic non-covalent interactions

A non-covalent interaction which affects the self-healing efficiency of polymers is their crystallinity. Crystalline or semi-crystalline polymers by definition, consist of crystalline areas where "crystals" are formed due to the well-ordered structure of the polymer chains.¹⁶ When the polymer is heated above its melting temperature (T_m) its fluidity increases and thus its shape can be easily reformed. On the contrary, when the polymer is below its T_m the agility of the polymer is decreased and so the chains cannot move or change their orientation.¹⁶ Crystalline polymers such as polycaprolactone (PCL), poly(lactic acid) (PLA) and polyethylene, possess the ability of shape memory and as a result, when a crack appears on their polymeric matrix, by increasing the temperature, the crystals 'flow' on the cracked area reforming their initial shape.¹⁶ After that, by lowering the temperature and ''freezing'' the chains, the polymer can be fully reformed returning to its initial shape resulting in a successful self-healing procedure.¹⁶

Another common approach is the hydrogen bonding which is a supramolecular interaction where a hydrogen atom is bonded with a more electronegative atom, usually Fluorine, Nitrogen or Oxygen.¹⁶ The pairing of these atoms can occur due to the fact that the hydrogen atom is positively charged and acts as an electron donor where the F, O, N atom has a negative charge and acts as an electron acceptor. When the atoms of the polymeric chains are hydrogen bonded, a non-covalent dynamic network is created and by the increase of temperature the bonds are disconnected.¹⁶ In the same manner, by lowering the temperature the electrostatic interactions take place where the hydrogen bonds are reconnected forming the physically cross-linked network. It is evident that

hydrogen bonds act as molecular switches in the non-covalent dynamic network of the polymeric chains equipping the material with great self-healing properties (Fig.12).¹⁶ The self-healing ability of hydrogen bonding can be enhanced by exploiting the shape memory effect of polymers.¹⁶ This usually happens when hydrogen bonds create a permanent network, and the self-healing ability mostly depends on the shape memory effect. Polyurethanes are the most common such example as the hydrogen bonds do not create a dynamic cross-linked network but a permanent one where due to the shape memory effect the material maintains its initial shape. This happens due to the structure of the polymeric chain which consists of hydrogen bonded soft and hard segments.¹⁶



Figure 12. Hydrogen bonding self-healing mechanism¹⁹

Similar to hydrogen bonding, ionic interactions can act as molecular switches in a dynamic crosslinked network.¹⁶ These networks contain ionic bonds where under humidity conditions the ions are positively and negatively charged resulting in a disconnection and finally the destruction of the cross-linked network.¹⁶ When heated and dried, the charged ions are reconnected through ionic interactions and as a result the network is reformed, providing the material with excellent selfhealing properties. The respective materials contain ionic structures such as thiobetaine, carboxypyridyl zwtitterion and imidazolium ions which are highly sensitive to water molecules. Alike to hydrogen bonding self-healing mechanism, shape memory effect can greatly enhance the self-healing properties of the material.¹⁶

1.3.3 Physico-chemical approaches

A recent approach to self-healing materials is the exploitation of the effect of Van der Waals forces among the chains of a polymer.⁴ When the attractive interactions are disturbed due to physical damage, the entangled chains will flow to reach a more favorable energy state, filling the wound and as a result, enhancing the self-healing ability of the material (Fig. 13).⁴ This process is more common in alternating or random copolymers where their interdigitated chains behave like "keys-and locks". Fundamentally, Van der Waals forces enhance the cohesive energy between the copolymer chains and force them to reach the most beneficial energy state while at the same time the material is being reshaped.⁴



Figure 13. Van der Waals assisted self-healing mechanism⁴

One category of the first heterogeneous self-healing systems was based on the so called extrinsic self-healing mechanisms, and that is in the encapsulation of reactive liquids that crack and release the self-healing agent upon physical damage.⁴ The main idea is that the reactive fluid upon its release will be polymerized and fill the opened wound (Fig. 14).⁴ This approach imitates the blood clotting wound but the main disadvantage of the artificial self-healing is its one time self-repair as micro- or nano- capsules can be used once.



Figure 14. Encapsulation of spherical microcapsules in polymer matrix enhancing the self-healing ability⁴

In the same manner, the polymer can be reinforced with two kind of void fibers that are arranged in a way to create a network. The fibers are filled with two different reactive agents, one being the resin and one being the cross linker.⁴ Upon cracking, the fibers release the fluids resulting in the cross linking and polymerization of the resin and can therefore heal the crack (Fig. 15).⁴



Figure 15. Cardiovascular network of fibers filled with reactive fluids⁴

1.4 Polyurethanes: Structure, Properties and Applications

Polyurethanes are polymeric materials used in a wide variety of applications exploiting their fascinating properties, i.e. mechanical, physical, biological etc.²⁰As far as their chemical structure is concerned, polyurethanes mainly consist of an O-R and an NH-R group, bonded on the same carbonyl carbon (Fig. 16).²¹ The main reagents for the polyurethane synthesis are a reacting polyol and the appropriate isocyanate (e.g. di-isocyanate, polymeric isocyanate etc.) along with a proper catalyst and a variety of additives. The resulted polymeric chain consists of soft and hard segments and many different types of polyurethanes can be produced depending on the synthetic route; rigid polyurethane foams, flexible polyurethane foams, thermoplastic polyurethanes etc.²⁰

1.4.1 Structures of Polyurethanes

The most commercially used member of the polyurethane family are the rigid foams which are being used as insulators for energy saving applications.²² For their synthesis, usually, bio-based or plant-based polyols like castor or vegetable oil are being used, reacting with the appropriate isocyanate forming the rigid foam. The mechanical and physical properties of the foams depend on the type of the used polyol as mentioned above. The properties are also affected by the category of the hydroxyl group which is present in the polyols, i.e., whether it is a secondary or a primary hydroxyl group. According to the literature, the reaction between a primary hydroxyl group and the isocyanate is faster than using a secondary one.²²

In contrary to the rigid foams, flexible polyurethane foams consist of block copolymers and the degree of their flexibility depends on the phase separation between the soft and hard segments of the polymeric chain.²³ The ratio of the segments, and thus the flexibility, along with certain properties of the resulted foams (e.g. density, durability, tearing resistivity, surface elasticity etc.) can be modified by polymer's synthetic route.²⁰ Due to their special properties as mentioned above, flexible foams are commercially extensively used in household products, such as cushions, carpets, furniture, and in the heavy industry (e.g. biomedicine, automotive and packaging).²⁰



Figure 16. Synthesis reaction of polyurethanes²¹

Thermoplastic polyurethanes (TPUs) is one of the most common structures which exploit the properties of a thermoset polymer along with the physical properties of a polyurethane as already mentioned.²⁰ TPUs are flexible, elastic and non-fragile materials while being resistant to stretching, friction and heat. There are many synthetic routes to produce TPUs using extrusion, compression, injection molding etc. TPUs present great thermal stability, as no weight loss can be observed for temperatures up to 235 °C. Moreover, the glass transition temperature (T_g) is evaluated at 85 °C indicating that these materials are suitable for automotive, footwear and constructive applications.^{24,25}

Polyurethane ionomers contain ionic groups along the polymeric chain. This structure offers additional properties to the polyurethane such as improved dispersibility in polar solvents and enhanced thermal and mechanical properties.²⁶ A crucial ability of an ionomer polyurethane is its shape memory effect which is a thermo-responsive property due to which the material can remember its initial shape and return to it if any change occurs. The shape memory effect results from the presence of soft and hard segments of the polyurethane with the hard segments being responsible for the frozen phase and thus the memory of the permanent shape, and the soft segments being responsible for the reversible phase. The material is able to return to its initial shape above a characteristic switch temperature.²⁶ The T_g and the soft segments are closely related to the switch temperature whereas the ratio of soft and hard segments affects the shape memory effect procedure.²⁰

Finally, waterborne polyurethane dispersions are simply fabricated in water via a two-step emulsification process.²⁷ These dispersions are mainly used as coatings and adhesives taking advantage of the solvent and can be applied in a plethora of commercial products as they are eco-friendly and non-toxic. Furthermore, WPUDs have the particular advantage that the viscosity of the dispersion is not related to the polymer molecular weight.²⁰

1.4.2 Properties of Polyurethanes

The great advantage of WPUDs is their adjustable viscosity. In contrast with the conventional PUs, as mentioned above, WPUDs present low viscosity which is independent of the molecular weight or the content of solid compounds in the dispersion.²⁸ The viscosity can be adjusted by the addition or decrease of thickening agents or water. Moreover, the ratio of isocyanates and hydroxyls (NCO/OH) of the PU can affect the increase or decrease of viscosity.²⁹ By increasing the molar ratio, the content of polar bonds increases and thus the polymeric chains agglomerate resulting in an increased viscosity. In the same manner, by decreasing the NCO/OH ratio, the viscosity of the dispersion is greatly reduced.²⁹

As far as their thermal properties, polyurethanes are thermoplastic materials, the morphology of which varies from amorphous to semi-crystalline polymers.³⁰ The polymeric chain of a polyurethane consists of hard and soft segments as already mentioned. The soft segments are composed of polyols, with a T_g lower than room temperature and the hard segments consist of isocyanates with a T_g higher than room temperature. The hard segments due to the polar bonds are highly attracted resulting in an orientation and finally in a phase separation of soft segments.²⁸ Depending on the synthetic route, the ratio of the segments can define the crystallinity of the polymer.³⁰ It is reported that when the content of hard segments in the polymeric chain is over

35% a regular arrangement of these segments can be achieved and as a result a semi crystalline polymer is formed.³⁰

Polyurethanes exhibit excellent self-healing properties due to their chemical and rheological properties as mentioned above. It is considered to be one of the most promising polymeric materials used in self-healing applications as there is abundance of investigations according to the literature.³¹ Almost all of the above-discussed self-healing mechanisms can be achieved using PUs as the polymeric matrices with emphasis on those involving supramolecular approaches and more precisely hydrogen bonding self-healing mechanisms.^{31,32} PUs consist of dynamic bonds on their polymeric chain due to the presence of ureas which provide the self-healing abilities of the material. Although, in linear PUs, these bonds can enhance the self-healing up to a certain point beyond which no effect can be exhibited. On the other hand, cross-linked PUs exhibited far better self-healing results, indicating that modifications concerning their dynamic bonds are crucial. This can be achieved by incorporating inorganic materials in the polymeric matrices, modifying the polymer's structure or enhancing the mobility of the chains by heat and / or presence of hydrogen bonds.³¹ Xiao et al. proved that PUs are sufficient self-healing materials as they tested two different self-healing approaches.³³ First, a scratch was made on a waterborne PU film and was tested on a hot plate at 100°C. The PU exhibited great results as in ten minutes the crack was no longer visible and the film was completely healed. The second approach was studied by creating a PU strip and stretching it until its fatigue. After that, a treatment at 100°C was made for 36 hours until the material achieved a self-healing efficiency up to 92.29%.³³ Similarly, Jian et al. created PU strips which were cut in half and were heated at 60°C for 12 hours. The crack could almost be distinguished after 12 hours.³⁴ Hu et al. proposed PUs that consist of many hydroxyl groups in their polymeric matrix. These PUs exhibited healing efficiency up to 90% when exposed to heat due to the formation of hydrogen bonding between the polymeric chains.³⁵ WPUDs contain Diels-Alder moieties have been developed and apart from their great mechanical properties, they exhibited a healing efficiency up to 80-95% in room temperature.³⁵ Finally, WPUDs consisting diselenide groups, presented a healing efficiency more than 90% when exposed to visible light for 48 hours. Moreover, they presented great healing repeatability.³⁵

1.4.3 Applications of Polyurethanes

Polyurethanes are among the most industrially utilized polymeric materials due to the variety of their physical and chemical properties which can be modified to reach the needs of an application or a product.³⁶ PUs are dominating the industry when it comes to coatings, adhesives, sealants and elastomers (CASE) due to their excellent adhesion, chemical stability, low temperature flexibility and abrasion resistance.³⁶ It is also reported that PUs have been extensively used for the fabrication of paints and other surface coating materials.³⁶ Apart from their surface applications, PUs are used in the automotive industry, as many parts such as seats, windows, ceiling, bumpers etc., are PU based. In general PUs are mainly preferred for the fabrication of these parts over a metal because it can drastically reduce the weight of a car and hence make it more efficient in its performance.³⁶ Moreover, PU foams are widely used in the manufacturing industry due to their low density, and thus stiff and light components can be fabricated that can be used in aircrafts, automotive and marine boats.³⁷

PUs are also widely used in medical applications as general purpose tubing, surgical drapes, catheters, hospital bedding and other injection-molded equipment owing to their availability and great mechanical and physicochemical properties.³⁷ One of the most significant applications, due to the biocompatibility of the PUs, is their use in short-period implants. It is reported that the embodiment of PUs in medical-related applications offer the fabrication of cost effective, high toughness and resilient materials in order to replace the conventional and widely used ceramics and metal alloys.³⁷ Moreover, the biodegradability of the PUs enhance the performance and usage of the implants and medical-related materials.

Finally, many investigations have been made for the fabrication of antibacterial coatings by incorporating the PUs in the antibacterial coating materials as it is reported that PUs are capable of enhancing the antibacterial and anti-fouling properties.³⁷

Finally, PUs are used in specific applications such as top coatings or carpet underlay foams.³⁷ They are utilized to offer floors durability, ease of maintenance and aesthetic pleasure. By incorporating PU foams in household carpets or floors their lifespan rises while they offer frictional resistance and self-cleaning abilities when coated on floors, as well.³⁷ For packaging applications, PUs can be used as printing ink or as packaging foams. It is reported that plasticizers for packaging applications were fabricated using PU and palm olein or castor oil. The produced resin presented high flexibility and great mechanical and freezing resistivity. Also, PU foams offer versatility and cost effectiveness when are incorporated into packaging materials.³⁷

1.5 2D Nanoadditives

1.5.1 Graphitic-Carbon Nitride (g-C₃N₄): Structure, Synthesis, Properties and Applications

Structure of g-C₃N₄

Graphitic carbon nitride has attracted a lot of attention due to its unique optoelectronic properties and its high applicability in various fields (photovoltaics, biosensing, photocatalysis etc.).³⁸ It is a two-dimensional material beyond graphene (Fig. 17 (a)) that consists of a regular arrangement of triazine units.³⁹ In 1996 it was predicted that carbon nitride has five different structures including α -C₃N₄, β -C₃N₄, c-C₃N₄, p-C₃N₄ and g-C₃N₄. Apart from g-C₃N₄, the other four structures belong to super hard materials which is the reason why graphitic carbon nitride is customized.³⁸ Two condensation states can be distinguished as the major structural units of a single sheet of the g-C₃N₄; the first one consists of s triazine units with a regular position of the single carbon vacancies while the second one is formed by tri s triazine/heptazine compounds. In the literature it is mentioned that the tri-s-triazine-based g-C₃N₄ is more stable than the s-triazine-based one (Figure 17 (b)).⁴⁰



Figure 17. a) Bulk structure of g-C₃N₄; grey color represents Carbon atoms and blue color Nitrogen atoms, respectively⁴¹ and b) Triazine (left) and Tri-s-triazine (right) based connection patterns³⁸

Synthesis of $g-C_3N_4$

The most common and efficient methods for the preparation of $g-C_3N_4$ are both top-down and bottom-up methods. The bottom-up approach refers to the creation of nanoparticles through chemical reactions between atoms, ions and molecules. On the contrary, methods for crushing or breaking the bulk material into many components to create nanoparticles are used in the top-down approach.⁴²

Top-down methods

A common top-down method is calcination where the main idea is to weaken the Van der Waals forces between the layers of bulk $g-C_3N_4$.³⁸ Calcination occurs upon the heating of solids, towards the removal of volatile compounds, like the oxidation of mass, etc.⁴³ Studies by Niu et al. and Li et al. proposed an optimum calcination temperature for $g-C_3N_4$ nanosheets up to 500 °C.^{44,45} By heating the bulk material under Ar₂ or ammonia gas, nanosheets with improved catalytic properties can be produced (Fig 18).³⁸



Figure 18. The calcination process followed for g-C₃N₄ nanosheets synthesis³⁸

Liquid phase exfoliation (LPE) is another popular top down method which is a simple approach assisted by the application of an external force (ultrasonic wave, pressure or thermal energy) and is considered as suitable for the preparation of low dimensional materials.³⁸ To evaluate the degree of exfoliation, two critical factors should be taken into account; a) the solvent and b) the energy input. Due to the presence of Van der Waals interactions between the layers of the bulk material, an energy barrier should be overcome in order the exfoliation to take place. Therefore, it is obvious that the exfoliation degree may vary, depending on the solvent medium characteristics (surface tension, boiling point, polarity etc.).⁴⁶ Except from the selected solvent's characteristics, the applied energy input on the bulk material, using bath or probe assisted sonication, may also affect the degree of exfoliation. This is due to the shear forces and cavitation bubbles, originated by the ultrasounds, which can completely or partially exfoliate the multi-layered bulk materials to few or single layered ones.^{38, 44}

Bottom-up methods

g-C₃N₄ can be produced by simple condensation methods as well. Wang et al. proposed a threestep condensation reaction of dicyandiamide (DCDA) which includes the removal of ammonia upon thermal treatment, thus promoting the formation of g-C₃N₄ network. Throughout the condensation, the rejection of ammonia forces nitrogen compounds to self-assemble into melamine at 240°C and consequently into melem at 390°C, which respectively may result in the formation of g-C₃N₄ network at 520°C (Fig 19).⁴⁷



Figure 19. Condensation reaction from DCDA to g-C₃N₄⁴⁷

A solid-state reaction is a widely used bottom-up method and can be carried out through contact, nucleation, reaction and crystal growth between solid materials at high temperatures.³⁸ Kouvetakis et al. successfully used a solid-state reaction to produce C_3N_4 thin films using 2,4-difluoro-6-bis(trimethylsilyl)imido-1,3,5-triazine and 2,4-dichloro-6-bis(trimethylsilyl)imido-1,3,5-triazine as precursors.³⁸ Morphology, crystallinity, dimensionality and properties of g-C₃N₄ may differ due to variations in the synthetic parameters such as the temperature and pressure.³⁸ According to the literature, in many reactions the change of one parameter may alter the material's properties as stated by Zhang et al and Gu et al.^{48,49}

Solvothermal is a method in which a reaction between the original mixture and an organic or nonaqueous solvent takes place into a sealed system at certain pressure and temperature conditions. As a result, the products of the reaction exhibit high crystallinity, uniform morphology and good dispersibility.³⁸ The first synthesis of g-C₃N₄ according to this procedure was made by Montigaud et al. who used melamine and cyanuric chloride in triethylamine under 130 MPa and 250 °C. Any differentiation in the solvent and the reaction conditions may yield g-C₃N₄ with different crystallinity, morphology and dispersibility.³⁸

And finally, thermal decomposition of cyanuric triazide (2,4,6-triazido-1,3,5-triazine) is an endothermic reaction which can be used to produce bulk g-C₃N₄ in which chemical decomposition occurs by heating in high temperature and pressure.⁵⁰ It is the most common method used to

produce large quantities of $g-C_3N_4$ due to its ease of processing, the abundance of resources and its low cost. Liu et al. proposed that $g-C_3N_4$ can be produced by the thermal decomposition of melamine.⁵¹ Similar to cyanuric trizide, upon heating melamine, an endothermic reaction occurs forming melam, melem and melon. By further heating the melem and melon products, $g-C_3N_4$ is synthesized (Fig. 20).⁵¹



Figure 20. Synthesis of g-C₃N₄ by the thermal decomposition of melamine⁵¹

Properties of g-C₃N₄

Graphitic carbon nitride has attracted a lot of attention among the 2D nanomaterials due to its unique physicochemical properties.⁵² Mortazavi et al. experimentally determined its band gap at 2.7 eV, indicating its highly promising applicability in optoelectronic devices.⁵² In a related context, Konofaos et al. and Derradji et al. explored that carbon nitride thin films with higher nitrogen content exhibited lower resistivity and higher dielectric constant respectively compared to the ones with lower nitrogen content.^{53,54} Derradji et al. also demonstrated a proportional relationship between conductivity and the content of the nitrogen atoms existed in a g-C₃N₄ film, since higher percentage of nitrogen atoms implies higher conductivity. However, it should be noted that this relationship exists only in the case that the nitrogen concentration (nitrogen atoms) is up to 18%.⁵⁴

As for the optical properties, Giusto et al. observed that carbon nitride films exhibited the highest intrinsic refractive index (n_D =2.43) for polymers to date.⁵⁵ g-C₃N₄ films highly emit blue fluorescence under UV irradiation. The photoluminensce (PL) spectra of films differ from that in powder form due to the manifold transitions between different energy levels under light stimulation. However, similarities in the spectra of the two forms can be observed when the film thickness is larger than 1 µm due to the increased condensation of the forerunner.⁵⁵

g-C₃N₄ has been widely also used in photocatalytic applications due to its ability to harvest solar energy.⁵⁶ Thanks to its "green" properties like non-toxicity and high recyclability, g-C₃N₄ could ideally replace the conventional TiO₂ based photocatalysts, which are harmful to humans and animals when being inhaled. However, low absorption in visible light, fast recombination of the excited electrons and low surface area remain a bottleneck towards its extended use.⁵⁶ In the field of electrocatalysis, carbon nitride can be applied in Hydrogen Evolution Reaction (HER) due to its superior electrochemical properties. HER technology is based on water splitting via electrolysis producing molecular hydrogen; therefore, electrocatalyst materials are required.⁵⁷ Due to restricted resources and the high cost of Pt-based catalysts, the most widely used in electrocatalytic reactions metal free catalysts have attracted a lot of interest thanks to their high reactivity and their great availability. In this context, g-C₃N₄ can be considered as an excellent stable and efficient

electrocatalyst mainly thanks to its electronic structure, its high nitrogen content and its unique thermal and chemical properties.⁵⁸

Finally, concerning its mechanical properties, in terms of flexibility, Cai et al. used a strip consisted of a $g-C_3N_4$ based coating (10 µm thickness, 3 cm width, 1.5 cm length) in test conditions of clamping and stretching at a certain speed. The film strip exhibited a tensile strength up to 0.1 GPa and could elevate a 25,000 times heavier object.⁵⁹ Arazoe et al. reported, following nanoindentation analysis, that the reduced Young modulus and the hardness of the strip are 12GPa and 1GPa, respectively.⁶⁰ Carbon nitride strips were also pliable and could remain intact after continuous bending and unbending distortions.⁵⁹

Applications of g-C₃N₄

The photocatalysts based on $g-C_3N_4$ are mainly used a) for pollutants' degradation and for water splitting applications.³⁸ According to Qiang et al., $g-C_3N_4$ nanosheets present a higher surface area and better optical properties compared to the bulk material, exhibiting a band gap of 2.7 eV.³⁸ In another study by Niu et al., $g-C_3N_4$ nanosheets were used as the catalyst material to split water and generate hydrogen.⁶¹

Moreover, the photocatalytic reduction of nanosheets can promote the conversion of CO_2 to chemicals and fuels (e.g. methanol fuel, methane, acetic acid).⁶² As shown, the adsorption energy of CO_2 molecules was reduced from -0.99 to -1.37 eV upon the use of g-C₃N₄ nanosheets instead of the bulk form. Moreover, since g-C₃N₄ nanosheets tend to exhibit larger specific area than the bulk material, more active sites and thus enhanced photocatalytic activity exist.³⁸

 $g-C_3N_4$ nanosheets have been extensively incorporated in various environmental applications due to their superior capability to photodegrade many organic pollutants such as phenol, rhodamine B (RhB), tetracycline or 2,4-dichlorophenol.³⁸ The photocatalytic oxidation of the nanosheets can be also used for sterilization and self-cleaning applications.³⁸

The nanosheets also display high fluorescence quantum yield and high specific surface area and therefore, they can be incorporated in sensing applications.⁶³ In this framework, Zhang et al. designed and developed a g-C₃N₄ nanosheet–MnO₂ composite based sensor. The developed sensor was very fast and accurate for the detection of glutathione in aqueous solutions, as displayed in Fig. 21.⁶³



Figure 21. g-C₃N₄ nanosheet–MnO₂ composite for sensing glutathione⁶³

 $g-C_3N_4$ can be used in energy storage applications too, as Wu et al. proposed.⁶³ High density lithium can be interposed into the triangular space between the triazine units of $g-C_3N_4$. In this context, it was reported that interconnection between Li atoms and nitrogen spaces is very strong

and thus it could be ideal for energy storage.⁶³ In addition, lithium-carbon nitride composites can be used either as the anode or the cathode material in lithium-based batteries providing great potential for hydrogen storage, since the hydrogen adsorption energy of lithium is ideal for hydrogen sorption (Fig. 22).⁶³



Figure 22. Lithium- g-C₃N₄ monolayer. Black, orange, and red balls represent C, N, and Li atoms, respectively⁶⁴

1.5.2 Graphene Oxide (GO): Structure, Synthesis, Properties and Applications

Structure of graphene oxide (GO)

Graphene is a one atom thick sp² hybridized planar sheet in a hexagonal honeycomb lattice with exceptional properties such as high specific surface area, high intrinsic mobility, high Young's modulus, etc.⁶⁵ It has been extensively studied for applications in nanoelectronics, Li-ion batteries, supercapacitors etc. and many different synthetic routes have been reported for its synthesis; the top-down approaches include mechanical and chemical exfoliation and chemical synthesis while the bottom-up approaches include pyrolysis, epitaxial growth, and chemical vapor deposition.⁶⁵ Alongside with graphene, graphene oxide (GO) has been considerably studied as a graphene derivative with unique properties and applications.⁶⁶

Many different models, experimentally and theoretically, have been reported by Hoffman and Holst⁶⁷, Reuss⁶⁸, Scholz and Boehm⁶⁹ and many more⁶⁶ in the effort of understanding the GO structure.⁶⁶ GO consists of a hexagonal carbon network and in contrary to graphene, it consists of both sp² and sp³ hybridized carbon atoms (Fig. 23). The sp³ hybridized carbons exist due to the presence of the oxygen functional groups in the GO lattice.⁶⁶ The oxygen functional groups are hydroxyls, epoxies and carboxylic acids which are covalently bonded to the carbons so the lattice is separated in oxidized and unoxidized regions. The oxygen functional groups can protrude over, under or from the side of the lattice.⁶⁶



Figure 23. 2D (left) and 3D (right) representation of GO structure⁷⁰

Synthesis of GO

GO can be produced by chemical synthesis via three available routes; Brodie method, Staudenmaier method and Hummers method (Fig. 24).⁶⁵ The main idea of all three routes is the oxidation of graphite using strong acids and oxidants such as concentrated sulfuric acid (H_2SO_4), nitric acid and potassium permanganate.⁶⁵ It should be noted that the oxidation degree of the synthesized GO varies depending on the stoichiometry, reaction conditions, etc.⁶⁵

The first attempt for GO synthesis was made in 1856 by B. C. Brodie who investigated the reactivity of graphite.⁷¹ The oxidizing agent that he used was potassium chlorate (KClO₃). By oxidizing graphite with many oxidizing agents, Brodie achieved to unravel the GO structure for the first time. In this route, graphite was mixed with a solution of potassium chlorate and nitric fuming acid (HNO₃) and was heated at 60°C for four consecutive days.⁷¹ The resulted carbon, hydrogen and oxygen composition was evaluated as $C_{11}H_4O_5$ with a C/O ratio of 2.2; this result was confirmed by multiple oxidative treatments.⁷¹ The developed GO presented sufficient dispersibility in water but it agglomerated in a slightly more acidic environment. The main disadvantages of Brodie's method are the time required for the synthesis and the hazardous reagents that are used.⁶⁵

L. Staudenmaier modified Brodie's method by altering the addition of the potassium chlorate and alongside adding sulfuric acid (H_2SO_4) in the solution.⁷¹ Staudenmaier proposed that the potassium chlorate should be added in small portions in order to gradually decrease the danger of the explosive byproducts and heat evolution. Moreover, the acidic environment caused by the sulfuric acid dramatically decreased the reaction time.⁷¹ The main advantage of Staudenmaier's method is that it constitutes a one step process.⁶⁵ In 1937, Hoffman elevated Staudenmaier's method by using potassium chlorate and nonfuming nitric acid and thus the resulted GO presented lower oxygen content than the previous methods (C/O ratio 2.5).⁷¹ It is reported that the concentration of the nitric acid greatly affects the oxidation level of GO. The lower the concentration of the acid, the higher the oxidation of GO.⁷¹

Hummers' method is the one that is being extensively used as it is the most conventional and fast method.⁷¹ In this method, graphite is mixed with a solution of an excess of potassium permanganate (KMnO₄), sulfuric acid and sodium nitrate (NaNO₃) and the reaction lasts from 8 to 12 hours. After the reaction, the excess potassium permanganate is neutralized with a solution of H_2O_2 .⁷¹ The resulted GO presented a C/O of 2.2, similar to that of Brodie's method. The advantage of this method is that is constitutes the faster and safest route to GO synthesis but it is not an environmentally friendly method as NO_x bi-products are produced.⁷¹



Figure 24. All chemical synthetic routes of GO⁷²

Properties of GO

Graphene and its derivatives have been widely investigated for their excellent sensing properties.⁷³ Flexible and wearable sensors, biosensors, photodetectors and many more devices have been fabricated exploiting the abilities of the mono- and few- layer GO. Singh et al. proposed that graphene sheets and especially GO sheets are ideal for sensing applications as different types of molecules can be detected on their surface.⁷³ A change of the resistivity of the GO sheet is observed when a molecule is detected by an electron exchange between the molecule (whether is a donor or acceptor) and the GO sheet.⁷³ Some et al. studied the GO sensors in high acidic (PH=1) and basic (PH=11) environments for the detection of Volatile Organic Compounds (VOCs) such as methanol, ethanol, Tetrahydrofurane (THF), acetone, diethylamine, hydrazine and nitromethane.⁷⁴ In the acidic environment the sensor presented great results as all of the compounds were detected at a concentration of 500 parts per billion (ppb). Methanol, ethanol and THF were detected at 90% relative humidity RH, acetone at 80% RH, diethylamine and hydrazine at 60% RH and nitromethane at 50% RH.⁷⁴ It is reported that the high sensitivity of GO depends on the abundant oxygen groups on its surface which enhance the electron exchange with the gas molecules.⁷⁴ GO consists also of great electronic properties and the key factor of these properties is the understanding of its band structure. Huang et al. suggested that the GO energy gap varies depending on its oxidation degree, chemical composition and atomic structure.⁷⁵ Many studies have been accomplished on a theoretical level as far as GO's band gap analysis is concerned. Ito et al. studied GO models where only epoxy groups exist on its surface and calculated through DFT calculations different bandgaps for different O/C ratios.⁷⁶ These O/C ratios were 0.125, 0.167, 0.25, and 0.5 with the corresponding bandgaps being 0.02, 0.22, 1.44, and 3.39 eV, respectively (Fig 25).⁷⁶ Yan et al. studied ordered structures of high and partially oxidized GO.⁷⁷ The fully oxidized structures presented bandgaps between 2 and 4 eV where the bandgap of the partially oxidized GO depends on the ratio of epoxy and hydroxyl groups. It is also reported that besides the ratio of the oxygen functional groups, GO's bandgap can be tuned by alternating the distribution of the functional groups on the sheet (Fig 26).⁷⁶



Figure 25. Bandgap values of GO containing different ratios of epoxy groups⁷⁶



Figure 26. Bandgap values of GO with different distribution of oxygen functional groups⁷⁶

Alike to graphene, GO exhibits excellent mechanical properties as Liu et al. suggested.⁷⁸ Similar to the electronic properties, the mechanical properties of GO depend on the ratio and distribution of the oxygen functional groups. The Young's modulus (E) and the intrinsic energy τ_c of the multilayer GO vary from 6-42 GPa and 76-293 GPa respectively, depending on its chemical structure. Moreover, Liu et al. proposed that the Young's modulus of few-layer GO can be greatly increased up to 200 GPa and for monolayer GO Gomez-Navvaro et al. evaluated its Young's modulus via Atomic Force Microscopy (AFM) to 250 GPa.⁷⁹

Graphene is known to be the best heat conductive material with its thermal conductivity varying between 2000 and 5000 W·m⁻¹·K⁻¹ (Fig. 27).⁸⁰ Compared to graphene, GO presents two to three orders of magnitude lower thermal conductivity. As Yang et al. investigated, the decrease in graphene oxide's thermal conductivity depends on the oxidation degree and its lattice defects.⁸⁰ Two main categories of structural defects can be distinguished in GO; the first one is the projection of the oxygen functional groups of the sheet and the second one is the absence of an atom of the lattice that disturbs the ideal structure.⁸¹



Figure 27. GO's protrusion and vacancy defects⁸⁰

It is reported that the number of the defects on the GO sheets can affect the thermal conductivity more significantly than its oxidation degree.⁸⁰ Yang et al. studied the thermal conductivity of GO with different ratios of oxidation degrees and various distributions of the oxygen functional groups and came up to the conclusion that these factors can slightly affect its thermal conductivity. On the other hand, with the increase of the vacancy defects, the thermal conductivity was dramatically reduced. Although, when the vacancy defect ratio was over 2% no decrease of the thermal conductivity was observed.⁸⁰

GO can be used in a broad range of environmental applications due to its excellent electron mobility, high surface area and its tunable electronic band structure.⁸² Ye et al. investigated its Hydrogen Evolution Reaction (HER) efficiency using different GOs with bandgaps ranging from 2.4-4.3 eV under mercury light irradiation.⁸³ GOs with higher oxidation degree presented higher bandgaps and insufficient light absorption and thus they were modified by reducing a number of oxygen functional groups.⁸³ Jian et al. studied the correlation between the OH/H ratio on a GO sheet and its environmental properties.⁸⁴ He reported that GO with a 40-50% coverage of hydroxyls and a 2:1 ratio of OH: H are suitable for oxidation and reduction reactions but especially for water splitting applications and a ratio of 1:1 of OH: H with a 50% coverage is ideal for photo catalysis in visible-light.⁸⁴

GO is considered to possess great optical properties in comparison to graphene.⁸⁵ The oxygen functional groups can turn the zero-bandgap graphene into a semiconductor or even an insulator. The most studied optical property of GO is its absorbance where Dimiev et al. suggested that the electron transitions can be observed mainly in the ultraviolet with a little extension of the phenomenon on the visible spectrum.⁸⁵ The main electron transition is the $\pi \rightarrow \pi^*$ which occurs due to the C=C bonds of GO where this transition can produce in-phase or out of phase π and π^* orbitals (Fig. 28 (A) and (B)).⁸⁵ The π to π^* transition is induced due to the lower energy of the π orbital compared to π^* allowing the orbital change of the photon and thus a broad peak at 230 nm can be observed.⁸⁵ Although, this is not the only electron transition that takes place in the GO molecular orbitals. A shoulder at 300 nm appears due to the n $\rightarrow \pi^*$ transitions caused by the C=O bonds from the oxygen functional groups where an electron from a lone pair non-bonding n orbital

jumps to the antibonding π^* orbital via photon absorption (Fig. 28 (C)).⁸⁵ The non-bonding n orbital is in-between the π and π^* and thus the $n \rightarrow \pi^*$ transition is energetically lower than the $\pi \rightarrow \pi^*$. As a result, the transition is red-shifted on the absorption spectrum (Fig. 29).⁸⁵



Figure 28. (A) The π orbitals of C=C bonds. (B) The π^* orbitals of C=C bonds. (C) The π , π^* and n energy states and the transitions between them⁸⁵



Figure 29. Absorbance spectrum of GO⁸⁵

Applications of GO

One of them most common potential applications of GO are the electronics and especially the fabrication of novel electrodes. The conventional electrodes used for electronic devices are usually made of silver tin (Sn)-doped indium dioxide (In₂O₃) which are transparent and present great conductivity but lack mechanical resilience and their high brittleness leads to fatigue when they are mechanically strained.⁷³ The solution to this problem was proposed by Liang et al. as they constructed silver nanowires (AgNW) doped with GO to create conductive, transparent and flexible electrodes for electronic devices.⁸⁶ A composite material of GO-AgNW and poly (ethylene terephthalate) was synthesized for the fabrication of the electrodes. The GO-AgNW/PET electrodes presented great flexibility in both large sheets and thin films (Fig. 30 (a), (b)), a sheet resistance of 14 Ohm/sq.⁸⁶ and 88% transparency at 550 nm. Furthermore, the sheets resistance was increased by 2-3% after repeating 12,000 bending cycles at a bending radius of 4mm evaluating its great flexibility (Fig. 30 (c)).⁸⁶



Figure 30. a) Flexible sheet of GO-AgNW/PET composite. b) GO-AgNW/PET composite bent to 4mm radius. c) Change of relative resistance GO-AgNW/PET electrode during repeated bending cycles⁸⁶

The energy storage and more precisely the hydrogen storage has been extensively studied in order to solve today's energy problem. Hydrogen storage by graphene nanosheets has been investigated without encouraging results since graphene's weak hydrogen adsorption energy (1.2 kJ mol⁻¹) results in low storage capacity which is less than 2 wt%.⁸² Kim et al. studied the hydrogen adsorption capacity of GO, by modifying the interlayer distance and the pore size, resulting in an increase of 4.8 wt% and reported that the optimum interlayer distance is 6.5 Å.⁸⁷ Moreover, the oxygen functional groups of GO make conjugates with metals which enhance its adsorption capacity.⁸² Wang et al. calculated that titanium (Ti) atoms can be coupled with the hydroxyl groups on the GO sheet (Fig. 31); each Ti atom is capable of binding more than one hydrogen molecule and thus higher adsorption capacity can be achieved.⁸⁸



Figure 31. Ti doped GO with multiple hydrogen adsorption sites⁸⁸

One of the most promising environmental applications of GO, and graphene derivatives in general, is their ability to capture harmful and toxic gases for both humans and the environment.⁸² The oxygen functional groups of the GO sheets are excellent spots for the covalent or non-covalent bonding of these gases (CO₂, CO, NO₂ and NH₃).⁸² In addition, GO sheets have exhibited notable catalytic performance in the conversion of these gases to useful energy resources. Fet al. reported that the few-layer GO is capable of binding harmful CO₂ molecules produced by the greenhouses especially under humidity conditions.⁸² Water molecules can assist the incorporation and retention of CO₂ on the GO sheet through repulsive forces between the CO₂ atoms and the oxygen functional groups. It has been also reported that GO can be effectively used for the removal of other hazardous gases such as NO_x, formaldehyde, H₂S and others, as the oxygen functional groups enhance the chemisorption of the molecules of these chemical vapors.⁸²

Since GO consists of excellent sensing properties too, biological sensors have been fabricated for the detection of biomolecules or biomarkers.⁸⁵ The most well-known technique for the construction of the biosensors depends on the fluorescence resonance energy transfer phenomena (FRET) which is the photoexcitation transfer from a donor fluorophore to an acceptor molecule.⁸⁵ GO depending on its oxidation degree can have fluorescence ranging from the infrared to the ultraviolet part of the spectrum. It is ideal for the fabrication of biosensors since it can both act as a donor, due to its photoluminescence properties, or as an acceptor when it behaves as a semimetal.⁸⁵ The sensing ability of GO depends on the interaction of the oxygen functional groups and the biomolecules of interest. Furthermore, the performance of a GO based biosensor can be enhanced due to the hydrophilicity of the GO sheets which enables secondary interactions with diols, amines and phenyls.⁸⁵

1.5.3 Mxene (Ti₃C₂T_x): Structure, Synthesis, Properties and Applications

Structure of Mxenes

Since the isolation of graphene, a broad investigation on the synthesis and characterization of different 2D materials has been portrayed.⁸⁹ As a result, innovative 2D materials are emerging such as transition metal dichalcogenides, boron nitride etc. A new intriguing category of 2D materials are Mxenes which are considered to be very promising due to their excellent properties and appealing applications.⁸⁹ Mxenes are layered materials with the general formula of $M_{n+1}X_nT_x$, where M are elements from third to sixth group of the periodic table, X is carbon or nitrogen and T are surface terminations such as O, OH, F and/or Cl (Fig. 32) which are bonded on the surface of the M layers.⁸⁹ In a single Mxene sheet, the n+1 layers of the early transition metals (where n=1-3) are interdigitated with n layers of the X elements in a honeycomb lattice which occupy the neighboring octahedral sites resulting in different HCP structures (Fig. 33).⁸⁹



Figure 32. Composition elements of Mxenes⁸⁹



- M (one or more different transition metals)
- X (C, N or CN)
- T_x (surface functional groups: =O, –OH, –F, or –Cl)

Figure 33. Main structure of the basal plane of Mxenes⁹⁰

Vahid Mohammadi et al. reported that the Mxene sheets can consist of more than one transition metals resulting in two main categories; solid solutions and ordered structures.⁹¹ In solid solutions, transition metals are randomly arranged between the different atomic layers where in the ordered structures, a periodicity in the arrangement of the elements can be observed. In plane (i-Mxenes) and out of plane (o-Mxenes) Mxenes can be distinguished depending on the atomic layers of transition metals, whether they exist on the same or in separate planes (Fig 34).⁹¹ It is exhibited that the ideal composition of the i-Mxenes, refereeing to the transition metals, has a ratio of 2:1 and the difference between the atoms sizes should be at least 0.2 Å and in the case of o-Mxenes the ideal composition could have a ratio of 2:1 or 2:2.⁹¹



Figure 34. Structures of Mxenes with different transition metal compositions⁹¹

3.3.2 Synthesis of Mxenes

Mxenes can be prepared by the etching of the metallic bonds of their bulk precursor MAX.⁹² The latter has the general formula $M_{n+1}AX_n$ where M and X are the transition metals and surface terminations respectively as mentioned above. A is an element from group IIIA or IVA of the periodic table.⁹² MAX can be synthesized via physical vapor deposition, chemical vapor deposition (CVD), combustion synthesis etc. and after appropriate treatment, Mxenes can be produced.⁹² In the MAX phase the M-A bond is metallic and the M-X can be either ionic or covalent so the main idea for the Mxene synthesis is the breakage of the metallic bonds through selective etching agents. It is reported that different etching agents produce Mxenes with different surface terminations and therefore the properties of the produced Mxenes may vary.⁹² Many synthetic routes of Mxenes have been reported such as etching using aqueous acids or molten salts, electrochemical etching, hydrothermal etching etc.⁹³ The main factors for the synthetic route and conditions are the A element and the transition metal. The acid etching method is used when the A element is Aluminum (Al) or Silicon (Si) while the molten salt method is used when the A element is Al, Si, Zinc (Zn) or Gallium (Ga).⁹² As for the transition metal, metals with high degree

of reactivity decreases the requisite energy to break the M-A bond and thus exfoliate the MAX to Mxene. The reaction conditions are milder when the reactivity decreases from left to right across the periodic table and thus harsher conditions are required for Chromium (Cr), Molybdenum (Mo) and Tungsten (W) than Titanium (Ti), Zirconium (Zr) and Hafnium (Hf).⁹²

The first attempt of the Mxene synthesis through aqueous acids etching was made by Naguib et al. where a 50% mixture of Ti₃AlC₂ and Hydrofluoric acid (HF) was made and stirred at room temperature for 2 hours.⁹³ HF was selected as a strong corrosive acid and for its ability to react with the A element of the Mxene and break the covalent bonds with the transition metals. HF can selectively etch the aluminum layer of the bulk MAX phase as it can only react with the A element (Fig. 35) and it is reported that the etching process occurs from the edges of the layers to the inside.⁹³ Through the whole etching reaction, AlF₃ and H₂ are produced as bi-products, and thus Mxenes etched in HF are always terminated by -OH and -F groups or atoms respectively (Fig. 36). After the etching reaction the AlF₃ groups are intercalated in the MAX layers. The presence of the H₂ can expel the AlF₃ groups and as a result the layers of the Ti₃C₂T_x are opened ending up in an accordion like structure (Fig. 37). According to the literature, HF etching procedure can be used for most Al containing MAX phases such as Ti₂AlC, Nb₂AlC and V₂AlC.⁹³



Figure 35. Selective Al etching using HF as etching agent⁹²

$$Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2$$
 1

$$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2$$
 2

$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$$
 3

Figure 36. Chemical reactions through the HF etching process resulting in -OH and -F terminations⁹²


Figure 37. Accordion like structure of Ti₃C₂ Mxene after HF etching⁹²

Due to the strong corrosivity and hazardness of HCl, Ghidiu et al. proposed a solution etching agent consisting of LiF and HCl as a safer and easier approach towards Mxene synthesis.⁹⁴ The composition of the Mxene and the etching time are strongly correlated to the MAX phase. It is reported that Ti_3AlC_2 can be successfully etched by LiF/HCl to form Ti_3C_2 and furthermore the Mxene can be easily delaminated to a few-layer material after the etching process due to the intercalation of the cations produced by the fluoride salt.⁹³ As a result, in comparison with the HF etching process, using LiF/HCl is not only a safer approach to prepare Mxenes but also the product is of higher purity with enhanced properties due to the presence of cations.⁹³ Liu et al. investigated the preparation of $Ti_3C_2T_x$ using different salts such as NaF, KF, NH₄F and concluded that the positive ions of Na⁺, K⁺, NH₄⁺ can successfully etch the Al layer affecting the surface structure and thus the surface properties of the prepared Mxene.⁹⁵

The preparation approaches of Mxenes can be affected by high temperatures.⁹³ The conventional methods, as described above, occur in an open environment and the synthesis temperature cannot exceed 100 °C due to the risk of boiling and thus the evaporation of the etchant.⁹³ It is possible for a reaction to take place in a closed environment, such as an autoclave, and temperatures higher than 100 °C can be achieved. This method is called hydrothermal etching, and in comparison, with the reactions in an open environment, tends to be safer and faster as it takes place in sealed reactors. Wang et al. proposed the hydrothermal etching of Ti₃AlC₂ to Ti₃C₂ using NH₄F as etchant in a sealed Teflon-lined autoclave at 150 °C for 24 hours resulting in a product of high purity.⁹³ During the process, the NH₄F was hydrolyzed producing HF which reacted with the Al layers of the MAX phase. The main limitation of the hydrothermal etching is the sensitivity of Mxenes to oxidization, especially in high temperatures, so this method is not applicable to all MAX phases.⁹³

Another approach towards Mxene synthesis is the electrochemical etching where the presence of an electric field can selectively etch the layer of the A element between the two M layers.⁹³ The MAX phase is mixed with the etching solution, which consists of an electrolyte, and two electrodes are placed inside the mixture. By applying a voltage difference on the electrodes two anodic and two cathodic reactions take place on the interface of the electrodes.⁹³ The voltage difference can be controlled within the range of the reaction potential between the A and M layers of the MAX phase and the selective removal of the A element occurs.⁹³ Sun et al. introduced the electrochemical etching by removing the Al layer from porous Ti₂AlC electrodes to form Ti₂CT_x Mxene sheets on the electrolyte, and the etching time estimated to 120 hours. Finally, Ti₂C Mxene was synthesized on the interface of the electrodes via electrochemical etching.⁹⁶ The main limitation of this approach is the formation of carbide-derived carbon (CDC) layers which

cover the unreacted MAX phases during the electrochemical process, and this is the main reason that electrochemical etching cannot be used for mass production.⁹³ To avoid this phenomenon, an intercalator is being used (e.g. tetramethylammonium ion) which dissociates the layers of the MAX phase and allows the etching ions to react with the deeper A layers of the MAX phase.⁹³ Jin et al. suggested that Ti_3C_2 Mxene could also be prepared via electrochemical etching by using Ti_3AlC_2 electrodes in an aqueous electrolyte solution of tetramethylammonium hydroxide and ammonium chloride.⁹³ The corrosion of the electrodes allow the formation of the Mxene sheets on their interface. The chloride ions are used to break the Ti-Al bonds and the presence of ammonium hydroxide (NH₄OH) serves as an intercalator as discussed above (Fig. 38)⁹³.



Figure 38. a) Electrochemical etching of Ti₃AlC₂ b) electrochemical cell structure⁹³

Molten salt etching

Molten salt etching technique is widely used for the production of non-Al containing, and in particular nitride based, Mxenes.⁹³ The etching of nitride based Mxenes has been unsuccessful in aqueous etchants due to the high energy barrier transition from the MAX phase to Mxene structure $(T_{n+1}AlN_n \text{ to } T_{n+1}N_n)$ and thus the selective etching of Al could not occur.⁹³ Urbankowski et al. suggested the molten salt etching approach of Ti₄AlN₃ MAX phase using a molten salt such as KF, NaF and LiF under Argon atmosphere at 550 °C for 0.5 hour to produce Ti₄N₃T_x Mxene. The limitation of this approach using fluoride salts is that the termination groups on the surface of the Mxenes are always fluorine groups.⁹³ Li et al. suggested an etching procedure using Lewis acid molten salts (ZnCl₂, NaCl, KCl) to successfully etch Zinc-based MAX phases (Ti₃ZnC₂, Ti₂ZnC, V₂ZnC) at 550 °C by the replacement reaction of molten zinc chloride (ZnCl₂).⁹³ Li et al. also proposed the etching of Silicon, Zinc and Germanium based MAX phases by mixing them with Lewis acidic molten salts and heating upon 750 °C. For the etching of Ti₃SiC₂ MAX phase, cooper (II) chloride (CuCl₂) was used and as a product, a mixture of Ti_3SiT_x/Cu mixed powder, after the selective etching, was obtained. For the removal of the Cu particles, ammonium persulfate solution (APS $(NH_4)_2S_2O_8$) was used where finally the pure $Ti_3C_2T_x$ Mxene was produced with O and Cl terminations on its surface (Fig. 39).⁹³



Figure 39. Schematic diagram of molten salt etched Ti_3SiC_2 a) MAX phases submerged in CuCl₂ molten salt at 750 °C. b),c) $Ti_3SiC_2/CuCl_2$ reaction for $Ti_3C_2T_x$ formation d) Removal of Cu particles using APS.⁹³

Mxenes properties

The physicochemical properties of Mxenes are strongly correlated with their structure and surface functionalization.⁹¹ Mxenes behave as metals when it comes to their electrons transport, meaning that their resistivity is linearly decreased with the temperature. However, by changing the transition metal and the structure of the M layer, whether it is a solid solution or ordered structure, Mxenes can behave like semiconductors with a negative temperature dependence resistivity (e.g. Mo₂CT_x, Nb₂CT_x, V₂CT_x).⁹¹ The surface groups are crucial for the electronic properties of Mxenes as without surface termination they tend to behave as metals where the free electrons of the M layers act as carriers. By modifying the surface, the density of states (DOS) changes and a shift in the Fermi level is observed, making Mxenes electronically tunable (Fig. 40).⁹¹ Vahid Mohammandi et al. showed that Ti₃C₂T_x has a metallic conductivity, but when its surface is modified with Mo atoms, which replace the outer Ti layer, and its structure converts to *o*-Mxene, a semiconducting behavior is observed.⁹¹ Finally, the electronic properties of Mxenes depend on the flake size, stoichiometry and the defects of the M and X sub lattices (mostly vacancies) as larger flakes with fewer defects present higher interflake electron transport and their conductivity can reach up to 20,000 S cm^{-1.91}



Figure 40. Density of states of Ti₃C₂O₂, Ti₃C₂(OH)₂, Ti₃C₂F₂ exhibiting the dependence of surface chemistry to the electronic properties⁹¹

Similar to electronic properties, optical properties of Mxenes depend on the type and structure of the M and X layers along with the surface termination.⁹¹ In general, Mxenes present strong absorption in the ultra-violet (UV) range and consist of transversal plasmon resonances in the visible and near infrared (vis-NIR) spectrum.⁹¹ However different Mxenes absorb and reflect in different regions of the vis-NIR spectrum emitting different plasmonic colors (Fig. 41). For example, $Ti_3C_2T_x$ has a green color in transmission and a purple one in reflection exhibiting a characteristic absorbance peak at 770 nm where V_2CT_x has a greenish blue color in transmission and a brownish gold in reflection without an absorbance peak in the vis-NIR spectrum.⁹¹ In solid solution Mxenes, the ratio of the two different transition metals is of high importance as different ratios result in different plasmonic colors. It is reported that by decreasing the n value of Mxenes (M_{n+1}X_nT_x) a blue shifting on the excitation peaks of their optical phenomena can be observed.⁹¹



Figure 41. Colloidal solutions of different Mxenes emitting different colors depending on their structure⁹¹

Computational studies predicted the high elastic modulus of Mxenes since the investigation of their mechanical properties is at a very early stage.⁹¹ Until now, only $Ti_3C_2T_x$ and $Nb_4C_3T_x$ thin films and single flakes have been tested concerning their mechanical properties.⁹¹ Films of Ti_3 - C_2T_x , with a thickness of 940 nm, showed a tensile strength of 560 MPa where the monolayer exhibited a Young's modulus of 330 GPa.⁹¹ The Nb₄C₃T_x single layer Young's modulus was measured to be 390 GPa which is lower than the predicted value due to the presence of point defects and surface terminations. Moreover, its tensile strength was found to be 26 ± 1.6 MPa. According to the literature, nitride based Mxenes are considered to have higher in plane Young's modulus than the carbide-based ones.⁹¹

Since Mxenes have recently been developed, only a few reports have been published so far referring to their thermal properties.⁹⁷ Their thermal conductivity has been obtained both theoretically and experimentally using the equation $\kappa = \alpha \cdot C_p \cdot \rho$ where κ is the thermal conductivity, α is the thermal diffusivity, C_p the specific heat capacity and ρ is the density of the Mxene.⁹⁷ It is reported that the theoretically calculated values of the thermal conductivity tend to be higher than

those experimentally defined due to multiple defects, mainly vacancies, which cannot be predicted and included in the theoretical calculations.⁹⁷ Thermal diffusivity is the main factor for the calculation of thermal conductivity and there is only one reference for its calculation in pure Mxene thin films.⁹⁷ Wu et al. calculated the thermal diffusivity of a $Ti_3C_2T_x$ thin film using a transient electrothermal technique (TET) based on Joule heating mechanism and resulted in a temperature dependent thermal diffusivity ranging from 2.68 $\cdot 10^{-6}$ m² s⁻¹ at 307 K to 3.06 $\cdot 10^{-6}$ m² s⁻¹ at 352 K.⁹⁸

Finally, an exceptional property of Mxenes is their ability to convert light to heat.⁹⁷ This phenomenon is attributed to their localized surface plasmon resonance (LSPR) which is mainly observed in materials with broadband light absorption. When the incident light and Mxenes conduction electrons have similar frequencies, then the photon energy can be effectively absorbed in the NIR region and afterwards be converted into heat.⁹⁷ The photothermal conversion can be quantified by estimating the light absorption and conversion efficiency for different structures of Mxenes. Yu et al. reported that for most Mxenes the extinction coefficient ranges from 35.4 L g⁻¹ cm⁻¹ to 52.8 L g¹ cm⁻¹ at 808 nm and 1064 nm respectively which is much higher than ordinary highly absorptive 2D materials, such as reduced graphene oxide, which presents an extinction coefficient at 24.6 L g⁻¹ cm⁻¹ measured at 808 nm.⁹⁷ Moreover, the photothermal conversion efficiencies of Mxenes are far better compared to the extensively used 2D materials such as black phosphorus. Black phosphorus has an efficiency of approximately 30% at 908 nm where Mxenes, up to now, show an efficiency higher than 35%. Apart from the heat conversion, Mxenes with double transition metal carbides are expected to have promising heat-induced antibacterial effect under irradiation but further investigation is crucial to extract adjective results as only few reports have been published.⁹⁷

Mxenes applications

As mentioned earlier, there is the urgent need for hydrogen production as a promising alternative of clean energy.⁹⁹ Mxenes have been studied experimentally and theoretically for their efficiency as electro- and photo- catalysts for the production of hydrogen via hydrogen evolution reaction (HER). Ti_2CT_x , $Ti_3C_2T_x$, $Mo_2C_2T_x$, with –O and –OH groups as terminations, were experimentally tested and considered to be the most promising catalysts due to their conductance under standard conditions.⁹⁹ As a result, they possess the ability to transfer charge during catalytic reactions and taking into account Gibbs free energy, they have the ideal value of 0 eV. That articulates that Mxenes with -O and -OH termination groups are considered to be ideal 2D catalysts.⁹⁹ It is reported that $Mo_2C_2T_x$ present higher HER activity from Ti_2CT_x for hydrogen production using water but Ti₃C₂T_x present the higher values of hydrogen production via HER when ammonia borane (BH₆N) is used.⁹⁹ Another emerging energy application is the fabrication of energy storage devices. 2D materials have been extensively studied as appropriate materials for hydrogen storage due their high specific surface area.⁹⁹ From all the investigated Mxenes as hydrogen storage materials, Sc₂C stands out as it owns the largest surface area and a storage capacity of 9.0 wt% which is relatively high compared to conventional 2D materials.⁹⁹ Furthermore, there is a challenge of fabricating alkali-based batteries with high gravimetric energy voltage and density. Khazei et al. reported that when ions, such as Li⁺, Na⁺, K⁺, Mg²⁺, NH₄⁺ and Al³⁺, intercalated between the layers of $Ti_3C_2T_x$ a high capacitance up to 350 F cm⁻³ can be achieved.⁹⁹

Like most 2D materials, Mxenes have been tested for the fabrication of sensing devices.¹⁰⁰ A wide variety of chemical compounds can be detected such as relative humidity, enzymes, gases (NH₂, NH₃, NH₄, H₂O₂), macromolecules, cancer biomarkers and many more. The constructed sensing devices exploit the metallic conductivity, biocompatibility, the adsorption sites and their high dispersibility in aqueous media.¹⁰⁰ The above benefits result in devices with low signal to noise ratio, low detection limit and high sensing sensitivity.¹⁰⁰ Computational calculations exhibited that Mo₂CO₂ and V₂CO₂ can detect very low concentrations of NO and Nb₂CO₂ and Ti₂CO₂ are considered to be ideal for the detection of NH₃. Further investigations presented that Mxenes can sufficiently detect hydrogen, methane and CO₂ at ambient conditions.¹⁰⁰ Mxene based sensors present far better results than conventional sensors such as hydrogels or MoS₂ ones as they present great stability, high sensitivity, and fast response and are fully compatible and applicable through wearable devices in human skin for the detection of humidity or other compounds during subtle human activities (blinking, handwriting etc.).¹⁰⁰

Wearable and portable electronic devices are fabricated to be lightweight and flexible with great mechanical properties.¹⁰¹ Thus, these devices demand materials with similar properties. The current devices are widely using tin-doped indium oxide (ITO) due to its excellent optoelectronic properties such as low sheet resistance, 10-100 Ω sg⁻¹ and high transmittance, i.e., 85%.¹⁰¹ Still, its brittleness and high-temperature processing for its thin film fabrication, limits its implementation in these devices. To avoid these limitations, electrodes based on nanomaterials such as graphene and carbon nanotubes have been fabricated but still their low electrical conductivity is a huge limitation for their usage.¹⁰¹ Therefore, Mxenes are considered to be ideal materials for the fabrication of transparent flexible electrode materials. As Shahzad et al. reported, Mxenes are capable of being used at optoelectronic devices and applications such as liquid crystal displays (LCDs), touch panels, solar cells and high performance transparent and conductive electrodes due to their high conductivity and high optical transparency.¹⁰¹ Halim et al. fabricated transparent films by sputtering depositing the Ti₃AlC₂ MAX phase films, followed by the removal of the Al layers, and synthesized $Ti_3C_2T_x$ transparent films with 19 nm thickness and a transmittance of 90% in the visible (Vis)-to-infrared (IR) range.¹⁰¹ Zhang et al., reported that $Ti_3C_2T_x$ is ideal for the fabrication of electrodes used in field effect transistors (FETs), correlating the thickness of the films with their electronic properties. They noted that thin films of $Ti_3C_2T_x$ are preferred for optoelectronic applications as their properties are enhanced by decreasing the thickness of the film.¹⁰¹

1.6 Nanocomposites

An efficient way to improve the properties, and therefore to increase the applications, of polymeric materials is the addition of inorganic compounds which have at least one dimension in the nanometer scale in the polymeric matrices.^{102,103,104,105} The resulted materials are called nanocomposites and they consist of many interfacial regions between the polymer and the inorganic compound which exhibit fascinating properties compared with the pure polymer, such as increased modulus, strength, heat resistance etc.^{106,107} The key factor considering the properties of the fabricated nanocomposites is the ratio between the volume and the surface of the inorganic filler.¹⁰⁸ One interesting category of polymer nanocomposites is the one that consists of two-dimensional layered materials. In this case, three types of nanocomposite structures can be obtained, according to the interactions between the polymer matrix and the inorganic filler; conventional composites (micro composites), intercalated nanocomposites and exfoliated nanocomposites (Fig. 42).^{108, 109, 110, 111, 112, 113, 114, 115}



Figure 42. Nanocomposite structures using inorganic layered fillers a) microcomposite, b) intercalated nanocomposite, c) exfoliated nanocomposite¹⁰⁸

In the first case, the polymer is unable to mix with the inorganic filler and thus the microcomposite is fabricated where two separate phases can be distinguished (Fig. 42 (a)). Not many differences between the properties of the microcomposite and the polymer can be observed.¹⁰⁸ In the case where a polymer can be interacted favorably with the inorganic filler, two different morphologies

can be distinguished; intercalated nanocomposites (Fig. 42 (b)) and exfoliated nanocomposites (Fig. 42 (c)). In the first case, the polymer chains are intercalated between the inorganic layers, but the layers remain well ordered and uniformly structured while in the case of the exfoliated nanocomposite the layers are dispersed in the polymer matrix losing their initial orientation.¹⁰⁸ There are many differences in the resulting properties and applications as in the case of the exfoliated nanocomposites, a larger surface area between the polymer and the filler can be achieved.¹⁰⁸

According to the literature, the most common nanoadditive in polyurethane matrices are colloidal silica which are incorporated to improve the physical properties of the polymer.¹¹⁶ The PU/silica nanocomposites can be easily prepared with an in-situ hydrolysis and condensation of silane-terminated oligomers. This has as a result the increase of the storage moduli of the nanocomposites; both their tensile strength and elongation at break increased proportionally with the addition of silica nanoparticles presenting a strong dependence on concentration. As for the thermal properties, the glass transition temperature, T_g of the composites constantly increases as the size of the silica particles increases and reaches its maximum value when particles with diameter that ranges between 28-66 nm are used.¹¹⁷

Many reports in the literature investigate the effect of the 2D nanoadditives in polymers and in particular in PU matrices. A widely used nanoadditive in PU matrices is organoclays. It is reported such nanocomposites even at a concentration of 4.2% wt., present a tensile modulus which is double than that of the pure PU while their tensile strength was increased more than 50%. Moreover, the nanocomposites presented higher temperature resistance than the pure polymer.

Madhab et al. suggested that the addition of very low concentrations of GO in thermoplastic PU has a remarkable effect concerning the PU's mechanical properties.¹¹⁸ By the addition of 0.1% wt. GO, the nanocomposite presented 280% increase in tensile strength and 410% increase in toughness while the elongation at break increased from 588% to 1066%.¹¹⁸ Wong et al. developed an rGO polyurethane composite based on Diels-Alder reaction with enhanced self-healing abilities using microwaves.¹¹⁹

The properties of the PU can be also improved by incorporating $Ti_3C_2T_x$. Gao et al. presented the improvement of the mechanical and rheological properties of the nanocomposites compared with the pure PU by incorporating low concentrations of the nanoadditive.¹²⁰ A nanocomposite with 0.5% wt. additive exhibited increased tensile strength and elongation at break by 41.2% and 15.4% respectively.¹²⁰ It is reported that the enhancement of the above properties is due to the formation of hydrogen bonds between the PU and the $Ti_3C_2T_x$.¹²⁰ However, for concentrations higher than 0.5% wt., the mechanical properties deteriorate due to the aggregation of the inorganic nanoadditive. As for the rheological properties, the viscosity of the nanocomposites is greatly increased compared with the pure PU which indicates that the presence of $Ti_3C_2T_x$ restricts the movement of the polymeric chains due to the strong interactions between them.¹²⁰ Many other reports have investigated the thermal diffusivity and conductivity using Mxene based polymer composites or hybrid nanostructures resulting in high values of thermal conductivity proving that Mxenes can be considered as appropriate thermal conductors for various applications (thermal energy storage, thermoelectric devices, sensors etc.).⁹⁷

Finally, the addition of $g-C_3N_4$ in the PU matrices had an effect in their mechanical and thermal properties as Liao et al. suggested.¹²¹ Again, the nanoadditive increased the tensile strength of the

pure PU as it restricts chains mobility and thus a less flexible material was produced. However, this effect occurred up to the concentration of 1% wt. For nanocomposites with higher concentration, the g-C₃N₄ flakes agglomerated and lower density cross linked composites were fabricated resulting in decreased mechanical properties.¹²¹ Furthermore, it is reported that g-C₃N₄ alters the thermal stability of pure PU due to the formed cross-linked network as, the nanocomposite decomposed in higher temperatures.¹²²

Whereas there are certain works that investigate the effect of layered additives in the mechanical and thermal properties of polyurethanes, there are not many reports investigating their effect on the PU self-healing ability.

1.7 Current Work

In this work, the enhancement of the self-healing ability of waterborne polyurethanes was investigated via the development of nanocomposites which consist of 2-dimensional graphitic and inorganic additives like $g-C_3N_4$, GO and $Ti_3C_2T_x$. The nano-additives were selected based on their ability to form multiple hydrogen bonds assuming that this would drastically improve the self-healing process and / or their efficiency in heat conduction that is anticipated to increase chain mobility. $g-C_3N_4$ behaves as physical and chemical cross-linker which is expected to improve the self-healing properties of a polymeric matrix.¹²³

GO is assumed to assist the healing efficiency of PU by improving the intrinsic healing mechanism of hydrogen bonding due to its high heat capacity and the oxygen functional groups that exist on its surface.

Finally, $Ti_3C_2T_x$ was selected as it is assumed that the dynamic hydrogen network of the PU will be improved by two main factors; heat conductance and T_x terminations. Due to Mxenes high thermal conductance, it is presumed that sufficient heat will be dissipated in the polymer matrix and thus the mobility of the polymeric chains will be improved. The second factor that is expected to assist the self- healing mechanism are the T_x terminations of $Ti_3C_2T_x$ (-O, -OH) which will affect the healing process similar to g-C₃N₄ as mentioned above. In all cases, nanocomposites with concentration between 0.05 - 1% wt. were prepared to avoid aggregation of the nano-additives.¹²³ Subsequently, all initial materials as well as their nanocomposites were thoroughly characterized via X-ray Diffraction, XRD, Differential Scanning Calorimetry, DSC, as well as Raman and Infrared Spectroscopy, ATR-FTIR, measurements to evaluate their structure, thermal and spectroscopic behavior. The coated surfaces were scratched creating deep and shallow cracks, using a razor blade and their self-healing efficiency was evaluated in two different temperatures (i.e., 75°C and 90°C). The healing procedure was monitored utilizing a Polarized Optical Microscope.

2. Experimental

2.1 Materials

The materials used for the present thesis were; a waterborne polyurethane dispersion (WPUD), graphitic-carbon nitride nanosheets (g-C₃N₄ NSs), graphene oxide (GO) and exfoliated Mxene $Ti_3C_2T_x$. WPUD was provided by Megara Resins, S.A. under the product name of SNP-P-47 (P47), g-C₃N₄ NSs were synthesized in collaboration with members of the Transparent and Conductive Materials group (TCM) at IESL-FORTH, GO and $Ti_3C_2T_x$ were prepared at the Hybrid Nanostructures group at IESL-FORTH.

2.2 Materials synthesis

2.2.1 Synthesis of WPUD

The pure P47 WPUD was provided by Megara Resins S.A. It was prepared via a prepolymerization method by adding negatively charged building blocks. A polyurethane prepolymer was prepared through the reaction of the polycarbonate polyol, with the molecular weight of M_w =1000 g/mol and an OH value ~110mg(KOH)/g, and isophorone diisocyanate (IPDI).



Fig 43. Synthetic procedure of P47 WPUD via the pre-polymerization method

Following the formation of the urethane blocks, a different building block was added, i.e. 2,2-Bis(hydroxymethyl)propionic acid (BisMPA), which assisted the urethane blocks to be stably dispersed in water. Alongside with BisMPA, 8% of proglyde solvent was added in order to control the viscosity of the PU. In the next step, the prepolymer was neutralized by the addition of trimethylamine and the product of the reaction was dispersed in water. Finally, the bipartite of the polymeric chains took place by the addition of the ethyl diazoacetate reagent (EDA) to increase

the molecular weight (Fig. 43). As a result, a WPUD was obtained with a ratio hard to soft segments, NCO/OH=1.4, pH=7.2, percentage of solid parts in the dispersion, 37.31% and minimum film forming temperature, MFFT=- 3.6° C.

The full characterization of the WPU is provided in chapter 3.

2.2.2 Synthesis of g-C₃N₄

For the preparation of polymer nanocomposites, g-C₃N₄ nanosheets (NSs) were utilized. g-C₃N₄ was obtained by thermal exfoliation of bulk g-C₃N₄ (Fig. 44),¹²⁴ which was prepared by the thermal polycondensation of melamine. In particular, melamine (50 g) was placed into an alumina crucible with a cover in a muffle furnace and heated at 510 °C for 2 h and 530 °C for 2 h under air flow (heating rate 2 °C min⁻¹). For the synthesis of the NSs, the bulk powder was thermally exfoliated by placing 5 g of the bulk powder in an open ceramic container and by heating it at 580°C for 2h with a ramp rate of 2 °C/min.¹²⁴



Fig 44. Synthetic procedure of bulk g-C₃N₄ and g-C₃N₄ NSs¹²⁴

2.2.3 Synthesis of GO

Graphene oxide was chemically prepared from bulk graphite using a modified Hummer's method.¹²⁵ In particular, 1g of graphite powder was placed in a 600ml beaker with a large stirring magnet. Afterwards, 46ml of sulfuric acid (H_2SO_4) were added using a 50 ml siphon and the mixture was left stirring for 20 min. Then, 1g of sodium nitrate (NaNO₃) was added slowly as the reaction is exothermic (Eq. 1); the container of the reaction was placed in an ice-bath. The mixture was left stirring for 1h. The reaction that takes place is:

 $2 \text{ NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{ HNO}_3 + \text{Na}_2\text{SO}_4 (1)$

 $NaNO_3$ is being used as an oxidizing agent as the intercalation of H_2SO_4 cannot take place without the agent. When one hour had passed, 6g of potassium permanganate (KMnO₄) was added very slowly and in small amounts due to the violently exothermic reaction which produce dimanganese

heptoxide (Mn_2O_7) (Eq. 4). When KMnO₄ is added to the solution a thick green color is observed and the following reactions take place:

 $KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3 HSO_4^- (2)$ $KMnO_4 \rightarrow K^+ + MnO_4^- (3)$ $MnO_3^+ + MnO_4^- \rightarrow Mn_2O_7 (4)$ $GIC + Mn_2O_7 \rightarrow Graphene Oxide + by-products (5)$

At this stage, the bulk graphite is in the form of the intercalated graphite compound (GIC) in which the layers are intercalated with the molecules of H₂SO₄. Following the addition of KMnO₄ the mixture was left stirring for 24h. After the 24h, the solution was stirred at 35°C for an additional 1h and 40 min. Afterwards, the temperature was raised at 90°C for 40 min and then the beaker containing the dispersion was removed from the hot plate. 200 ml of di-ionized (DI) water were added followed by 20 ml of hydrogen peroxide solution (H₂O₂, 30%). The additional water exfoliated further the graphite flake while H₂O₂ is added to stop the oxidation and remove any traces of excess KMnO₄. Finally, the entire dispersion was centrifuged at 4200 rpm for 20 min for the separation of the solid GO from the supernatant. The sediment was washed with 200 ml of warm DI-water at 65°C. The final step was to wash the GO with DI-water at room temperature, to neutralize the oxidizing agents until the mixture's pH reached 6-7. At the end, the pure sediment was left to dry overnight at 60°C and once water was fully evaporated it was pulverized using a pestle and mortar until it was in the form of fine powder.

2.2.4 Synthesis of Ti₃C₂T_x

Ti₃C₂T_x was prepared by its precursor MAX phase, Ti₃AlC₂, via etching using HCl 6M as etchant as suggested by the literature.¹²⁶ Initially, the highly concentrated 10M HCl was diluted to 6M by mixing 14ml of DI-H₂O with 26ml HCl 10M in a 100ml beaker and thus 40ml of HCl 6M was obtained. In a plastic round bottom flask, HCl is added along with 1.2g NaF which is in excess. NaF is slowly added to the flask due to its exothermic dissolution and to avoid sedimentation that is observed when the addition is rapid. When NaF is completely dissolved, the flask is placed on a hotplate at 65°C and then 1g of Ti₃AlC₂ is added. Immediately, the flask is connected to a reflux, to control the evaporation of the solvent, and remains under constant stirring at 500 rpm for 72h. After three days the dispersion is collected from the flask and is centrifuged for 10min at 4500 rpm for the removal of the byproducts of the reaction and also for the increase of the pH by dissolving the remained HCl, mixing the solution with water. The process ends after 20 centrifugations when the measured pH had reached the value of 6. In the final step, the diluted dispersion is placed in a filter paper for one day to separate the solvents from the solids and after filtration the filter paper is placed in a hood for one day for the complete evaporation of the volatile moieties. Finally, the powder is placed in an oven at 100°C under dynamic vacuum conditions for its complete drying.

2.3 Preparation of polymer nanocomposites

Polymer nanocomposites of all three 2D nanofillers were fabricated using as polymer matrix WPUD P47. g-C₃N₄, GO and Ti₃C₂T_x were dispersed in P47 dispersion in suitable concentrations so that the final compositions of the nanocomposites were 0.05% wt., 0.1% wt., 0.2% wt. and 1% inorganic part. As mentioned above, the WPUD consists of 37% solid components and 63% water. Therefore, by calculating the appropriate quantities, for the fabrication of 2ml of each nanocomposite, 5,34g of the WPUD and 0.001g, 0.002g and 0.004g and 0.02g of the nanoadditive were used.

2.3.1 Preparation of P47/g-C₃N₄ nanocomposites

For the fabrication of the P47/g-C₃N₄ nanocomposites 5.34g of P47 polyurethane dispersion were placed in four different 22ml vials as mentioned above. Then 0.001g, 0.002g, 0.004g and 0.02g of g-C₃N₄ NSs in thin powder form were weighed in a 5-digit analytical balance and were placed in the corresponding vial for the fabrication of the four different concentrations of 0.05% wt., 0.1% wt., 0.2% wt. and 1%. Each PU/g-C₃N₄ dispersion was left for 24h stirring at 350 rpm using a magnetic stirrer. After 24h the 0.05% wt., 0.1% wt. and 0.2% wt. dispersions were homogeneous as no sedimentation or agglomeration of the g-C₃N₄ NSs could be seen. The 1% wt. dispersion was inhomogeneous and exhibited high degree of agglomeration and thus no further investigation was occurred (Fig 45).



Fig 45. P47/g-C $_3N_4$ nanocomposite dispersions with 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. composition from left to right

2.3.2 Preparation of P47/GO nanocomposites

Similar to P47/g-C₃N₄ nanocomposites, for the fabrication of 2 ml of P47/GO nanocomposites 5.34g of the PU were initially placed in four different 22ml vials for the synthesis of the four different concentrations. Same as before, 0.001g, 0.002g, 0.004g and 0.02g of GO were weighed in powder form and placed in the corresponding vial. Initially, GO was dispersed in the polymer matrix in powder form but the dispersions were inhomogeneous even after constant stirring at 350 rpm for 24h as high sedimentation was observed. Therefore, for the successful fabrication of the nanocomposites, before placing GO in the polymer matrix it was dispersed in water as GO is highly hydrophilic. 0.001g, 0.002g and 0.004g and 0.02g of GO were weighed in powder form and placed in four different vials of 22ml and with a Gilson pipette, 5ml of DI-water were placed in the vials containing GO. Then, all four different concentrations were ultra-sonicated using an ultrasonic probe for 5 min and after this, homogenous dispersions of GO in water could be seen. Finally, for the synthesis of the P47/GO composites a solution blending method was used. The GO/water dispersions were placed in four different 22ml vials containing 5.34g of WPUD P47. After the mixing, where no sedimentation was observed, the vials were placed on a magnetic stirring hot plate at 60 °C for 72h for the complete evaporation of the solvent (Fig 46).



Fig 46. P47/GO nanocomposites at 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. composition from left to right

2.3.3 Preparation of P47/Ti₃C₂T_x nanocomposites

A similar synthetic procedure was followed for the synthesis of P47/Ti₃C₂T_x nanocomposites. $Ti_3C_2T_x$ was dispersed in the polymer matrix in powder form. 0.001g, 0.002g, 0.004g and 0.02g of $Ti_3C_2T_x$ were weighed in a 5-digit analytical balance and placed in four different 22ml vials. Then in each vial, 5.34g of P47 polyurethane dispersion were placed and nanocomposites of 2ml final volume were made at 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. compositions. All four vials were placed on a stirring hot plate at 350 rpm for 24h. After 24h inhomogeneous dispersions were observed and high sedimentation was presented which implies that $Ti_3C_2T_x$ is unable to be dispersed in the PU in powder form. After that, in order to achieve homogenous nanocomposites dispersions, a liquid-liquid mixing method was implemented using a stable dispersion of the $Ti_3C_2T_x$ and the PU dispersion. 0.1g of $Ti_3C_2T_x$ were weighed and placed in a weighed 22ml vial along with 15ml of DI-H₂O and were left under constant stirring for 24h to exfoliate the material. After stirring, the dispersion was sonicated for 1h at 60% amplitude in an ice bath to avoid overheating. Then, in order to obtain the stable dispersion, the vial was centrifuged at 3000 rpm for 30 minutes. With a Pasteur pipette all of the supernatant was carefully collected, weighed and placed in a different 22ml vial. The remaining sedimentation was left in a hood for 7 days and then in a vacuum oven for 5 days at 100°C for the complete evaporation of the solvent. The dried sediment was weighed again and by subtracting the mass of the sediment from the initial mass of $Ti_3C_2T_x$ (i.e. 0.1g), the concentration of the stable dispersion was evaluated to be 2 mg/ml. Finally, 0.5ml, 1ml, 2ml and 10 ml were placed in four different vials with a Gilson pipette for the fabrication of 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. concertation nanocomposites respectively. Then 5.34g of pure PU were placed in each vial and were left on a stirring hot plate at 60°C at 350 rpm for the evaporation of the solvent. The prepared nanocomposites are presented in Fig. 47. Again, the 1% wt. concentration nanocomposite presented high sedimentation and thus it could not be further investigated.



Fig 47. P47/Ti₃C₂T_x nanocomposites at 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. composition from left to right

2.4 Procedure for the self-healing investigation of polymeric coatings

To investigate the self-healing ability of the nanocomposites, 0.3g of each sample were drop casted on a ~4 cm² silicon wafer creating a thin film. The samples were left in a hood for 7 days for the evaporation of the solvent (i.e., water) and after the one week they were placed in a vacuum oven at 90°C and were constantly weighed until the mass remained the same confirming that the solvent was completely evaporated. After that, a crack was made manually on the surface of each sample using a sharp blade for the evaluation of the coatings self-healing ability. The sample was placed in a sealed heating stage under constant flow of N₂ gas to prevent the decomposition of the coatings and the crack was monitored through a polarized optical microscope (POM) by taking pictures at different time points (Fig. 48). The self-healing ability of shallow and deep cracks was investigated at two different temperatures (i.e. 75°C, 90°C) and three measurements were occurred for each nanocomposite in order to evaluate the result (Appendix 1)



Fig 48. Self-healing process of polymeric coatings; a) unscratched polymeric film b) razor blade used for scratches c) scratching procedure d) POM used for monitoring the healing ability of the coatings

2.5 Experimental techniques

All synthesized materials and nanocomposites were characterized with various techniques for the evaluation of their structural and thermal properties. The experimental instruments and the measurements conditions are described below.

X-Ray Diffraction (XRD)

X ray diffraction is a powerful, non-invasive analytical technique used to investigate the crystal structure of materials. In this technique, the sample is bombarded with X-rays which pass through the material and are diffracted in the crystal lattice producing a characteristic diffraction pattern. This pattern contains valuable information about the structure of the material such as unit cell dimensions, presence of defects, size of crystallites etc.¹²⁷

The pattern is formed when the interaction of the incident X-rays with the sample satisfy the Bragg's law, $n \cdot \lambda = 2 \cdot d \cdot \sin \theta$ where n is the order of diffraction (i.e. an integer representing the number of wavelengths), λ is the wavelength of the incident radiation, d is the distance between the neighboring planes of atoms in the crystal lattice and 2 θ is the angle of diffraction.¹²⁷

The characteristic patterns of materials are collected using an X-ray diffractometer. Diffractometers consist mainly of three elements; an X-ray tube, a sample holder, and an X-Ray detector. The X-Rays are produced in a ray tube by a heating filament in order to produce electrons. When the electrons have sufficient energy to displace the inner shell electrons of the material, characteristic X-Ray beams are produced and are accelerated towards the targeted material which finally are detected and produce the final XRD pattern (Fig. 49).¹²⁸



Figure 49. Instrumentation of an X-Ray diffractometer¹²⁹

In this work, the XRD characterization technique was implemented for the structural evaluation of both PU and 2D nanomaterials but also for the investigation of the structural properties of the fabricated nanocomposites. All measurements were carried out using a Bruker D8 Advance diffractometer using a CuK α radiation at a wavelength of λ =1.5406 Å. All data were collected over a 2 θ range of 5°- 60° with a step of 0.01°.

Differential Scanning Calorimetry (DSC)

Calorimetry is widely used as a characterization technique to investigate the thermal properties of a material and in particular to establish a correlation between the temperature and the physical properties of substances. The most popular calorimetry is the differential scanning calorimetry (DSC) which measures the change of material's thermal properties with temperature or time (at a specific temperature). DSC measures the amount of heat that is emitted or absorbed by the sample as temperature changes in comparison with a reference material (Fig. 50).¹³⁰ This characterization technique is mainly used for the determination of critical transition temperatures of materials such as; glass transition, melting and crystallization temperatures. Moreover, a variety of other measurements are available using DSC such as thermal curing, heat history, specific heat capacity etc.¹³¹



Figure 50. Instrumentation of DSC¹³¹

In this work, DSC was used for the investigation of the thermal properties of pure materials and their nanocomposites using a DSC250 by TA Instruments under constant flow of N₂ gas. All data were collected over a temperature range of -100 °C to 100 °C with a step of 0.1°C/min. Two thermal cycles were carried out in order to erase the thermal history and humidity of the materials.

ATR-IR Spectroscopy

Infrared spectroscopy is a non-destructive spectroscopic technique that provides information related to the presence or absence of specific functional groups, as well as the chemical structure of polymeric materials.¹³² In this spectroscopic technique the molecules absorb energy in the infrared range of the spectrum, which causes them to rotate and vibrate.¹³³ Molecular vibrations can be distinguished in two main categories; stretching and bending. Stretching is the continuous change of a bond between two atoms while bending is the change of the angle between two bonds. The resulted IR spectrum captures these vibrational modes of molecules that absorb different frequencies of the incident light within the infrared region. The only bonds that are visible in an infrared spectrum are those that undergo a change to their electronegativity.¹³³



Figure 51. Instrumentation of an IR Spectrometer¹³⁴

Conventional IR instruments include a radiating source, a wavelength selector, a sample container, a transducer (detector) and a signal processor (Fig. 51). The type of sources, transducers and beam splitters vary whether the measurements are performed in near-, mid- and far- IR region. Most organic compounds are identified in the mid-IR region.¹³³

In this work, Attenuated Total Reflectance (ATR)-IR spectroscopy was used for the structural evaluation of materials in order to recognize their characteristic absorbance peaks. All attenuated total reflectance (ATR) absorbance spectra were carried out using an ATR/FT-IR spectrometer (Vertex 70v; Bruker Optik GmbH, Rosenheim, Germany) coupled with a Bruker A225/Q Platinum ATR unit (Bruker Optik GmbH, Rosenheim, Germany) with single reflection diamond crystal.

Raman Spectroscopy

Raman spectroscopy is a powerful, non-invasive tool that offers information on disorder, edge and texture boundaries, thickness, doping etc. of both solid and liquid compounds.¹³⁵ It is a light scattering technique where the valuable information of molecules is obtained based on the interactions between a monochromatic laser beam, which is used as a light source, and matter.¹³⁶ The scattered light is mainly at the same wavelength with that of the incident light which provides no information about the material. Nevertheless, a small amount of this light is scattered at different wavelengths which is called Raman or inelastic scattering and contains the information about the chemical structure of the substance.¹³⁶ Similar to infrared spectroscopy, Raman spectra contain a number of peaks presenting the intensity and the wavelength of the inelastic scattered light. Each peak reveals a significant vibration of the molecular bonds of the substance providing both quantitative and qualitative information. The main difference compared with the infrared spectroscopy is that Raman scattered light is emitted only by molecular bonds that undergo a change in their dipole moment.¹³⁶

Raman spectrophotometers contain a monochromatic laser beam as light source, usually in 532 or 1064 nm, a beam splitter, focusing lenses, filters and a CCD camera as a detector (Fig. 52).¹³⁶ In this work Raman spectroscopy was implemented for the determination of the structure of the materials and the success of their synthesis which can be defined by the qualitative analysis of their D and G Raman bands of their spectrum. All Raman spectra were collected using a LabRAM HR; HORIBA FRANCE SAS with Modified Raman microscope.



Figure 52. Raman spectrophotometer instrumentation¹³⁷

Polarized Optical Microscopy (POM)

Optical microscopy, which is often referred as light microscopy, is a widely used, non-invasive technique in many fields of science such as biology, materials science etc.¹³⁸ The fundamental principles of optical microscopy are based on the interaction of the incident light with the sample and the optical elements used in an optical microscope (objective lens, condenser lens etc.). Finally, the micro structure of a sample can be magnified and become visible by the human eye.¹³⁸ There are many types of optical microscopies such as confocal, bright field, fluorescence etc. and in our case the polarized optical microscopy was used. Polarized optical microscopy is an expertized microscopy technique that provides information on the structure of materials taking advantage of the anisotropy in their optical properties and more precisely the anisotropy of their refractive index which is called birefringence.¹³⁸



Figure 53. Polarized Optical Microscope instrumentation¹³⁸

As all microscopes, a polarized microscope consists of an unpolarized light source, usually a halogen lamp or an LED and its beam passes through a polarizer which is placed beneath the specimen stage (Fig. 53). The polarizer is a filter which has the ability to selectively transmit the light waves that oscillate in a specific plane and at the same time block the light waves that are perpendicular to that plane. As a result, all light waves vibrate in the same plane of polarization and polarized light is produced.¹³⁸

Similar to all microscopes, POM consist of an objective lens which enhances the light after interacting with the sample. Above the objective lens, there is a second polarizing filter called analyzer which is placed perpendicular to the polarizer and is directed at the same angle to that of

the polarizer.¹³⁸ This filter is used to analyze the polarized state of the light and more precisely it adjusts the retardation and interference of the light waves. It can be rotated in order to control its angle with the polarizer and thus the amount of the light that passes through. This offers the ability to visualize different interference colors in several levels of retardation in the sample and thus these color differentiations provide information about sample's thickness and birefringence.¹³⁸ Finally, compensators are placed into the optical path and they are used to enhance the visibility of birefringent colors as they adjust the relative phase of the polarized light waves causing interference patterns which generate colorful images.¹³⁸

In this work, the self-healing ability of the coatings was monitored utilizing a polarized optical microscope AX10 provided by Nanolane and images of the samples, at selected temperatures, were taken using a ProgRes CT5 camera provided by Jenoptik.

3. Results and discussion

Following the materials and nanocomposites preparation, they were all thermally, structurally and spectroscopically characterized for the evaluation of their successful synthesis. The abovementioned characterization techniques were implemented in order to confirm their structure and to investigate if the addition of the nanoadditives alters the structure and properties of the P47 PU.

3.1 Characterization of the P47 polyurethane

Initially, the properties of P47 polyurethane were investigated. Its thermal properties were evaluated using differential scanning calorimetry (Fig. 54). The DSC measurement confirmed the amorphous structure of the polyurethane, as the hard segments of its structure, which are the ones that define the crystalline areas of the material, are a very small part in comparison to the soft ones.³⁰ The only thermal transition that is exhibited is a broad T_g step at -12°C.



Figure 54. Differential Scanning Calorimetry, DSC measurement of P47 polyurethane

Moving on to the structural characterization, the XRD measurement of P47 is depicted in Fig. 55. The measurement presents a broad peak at 19.8° without any detectable sharp peaks which indicates again the amorphous structure of the material. Moreover, the angle of the peak is close to the observation in other polyurethane materials.¹³⁹ A small step appears at approximately 7.5° and an extremely low intensity broad peak at 42° which may both attributed to the crystal orientation of hard segments but since the PU does not contain high number of hard segments, no crystallinity is exhibited.¹⁴⁰ As a result, the amorphous structure of P47 is evaluated from both the DSC and XRD measurements as no crystallization or melting peaks are observed.



Figure 55. X-Ray diffraction, XRD measurement of P47 polyurethane

Finally, the rheological properties, in terms of viscosity, of P47 were investigated. Viscosity is defined as the resistance to flow and it is closely related to polymer's properties (shape memory effect, chain mobility etc.).^{12, 14} The viscosity of P47 was measured every seven days for approximately two months between 0.5 - 250 rpm at 25°C. In Fig. 56 all viscosity measurements are presented. The values are relatively low and high fluidity of the polymer is observed in accordance to its low molecular weight. Within approximately two months, the viscosity values are increased about half an order of magnitude. This could be attributed to the presence of the proglyde solvent as similar WPUDs which contain solvents such as proglyde or NMP have presented the same behavior and an overall increase in their viscosity is observed. Nevertheless, this solvent has been selected for a greener approach compared with similar WPUDs.



Figure 56. Viscosity measurements of P47 polyurethane

3.2 Characterization of bulk g-C₃N₄ and g-C₃N₄ NSs

The first nanoadditive that was characterized was g-C₃N₄. As mentioned earlier, the bulk structure was exfoliated and, in this work, the obtained nanosheets (NSs) were utilized for the preparation of nanocomposite coatings. Both bulk and NSs structures have been characterized for the evaluation of their synthesis. To begin with, in Fig. 57 the XRD characterization of both bulk g-C₃N₄ and NSs is presented. The pattern of bulk g-C₃N₄ presents a characteristic strong peak at $2\theta = 27.5^{\circ}$ and a small one at $2\theta = 13.0^{\circ}$. The main peak at 27.5 ° is attributed to the (002) plane corresponding to a d-spacing of 0.336 nm. This often refers to the interlayer distance of bulk g-C₃N₄. Lower angles indicate a larger d-spacing between the layers. Moreover, the peak at $2\theta = 13.0^{\circ}$ corresponds to the (100) plane with a d-spacing of 0.680 nm and represents the flat structural motif of the repeating tri-s-triazine units (intra-layer d-spacing).⁵⁰ When the bulk material is exfoliated the intensity of these peaks is decreased due to the smaller number of layers present in the periodic structure and due to the disappearance of the coherence of the structure and of the periodicity.¹²⁴



Figure 57. XRD measurement of bulk g-C₃N₄ and g-C₃N₄ NSs

Following the structural characterization, ATR-IR spectroscopy was utilized. In Fig. 58 the ATR-IR absorption spectra of the bulk g-C₃N₄ and the NSs are presented. Both spectra present similar peaks and by comparing their intensity, the successful exfoliation of the NSs can be observed.¹²⁴ More precisely, in the spectrum of bulk g-C₃N₄, the sharp peaks at 804 cm⁻¹ appears due to the breathing mode of the triazine units. In the region 3500-3000 cm⁻¹ the N-H stretching mode and the vibrations of the absorbed water are observed. The region from 1132 to 1627 cm⁻¹ is related to the C=N and C-N stretching mode of the aromatic CN heterocycles.¹²⁴ Furthermore, the region from 1132 to 970 cm⁻¹ is also associated to the oxygen-containing groups. When the exfoliation of the bulk g-C₃N₄ to NSs is successful, an increase in the intensities of the peaks at 1132, 1081 and 1011 cm⁻¹ is observed due to the oxidation of the layers during the oxidation process of the thermal exfoliation. In our case, the intensity of these peaks sharply rises which implies the successful fabrication of g-C₃N₄ NSs.¹²⁴



Figure 58. ATR-IR spectra of bulk g-C₃N₄ and g-C₃N₄ NSs

Finally, to complete the spectroscopic characterization of bulk $g-C_3N_4$ and define its defects, Raman spectroscopy was used. The Raman spectrum of the NSs could not be measured due to high fluorescence. Most of the 2D materials in Raman spectra present two discrete peaks, the socalled D and G bands.¹⁴¹ In Fig. 59 the Raman spectrum of bulk $g-C_3N_4$ is presented. As excitation source, a 1064 nm light was used. The peak at 706 cm⁻¹ corresponds to the breathing mode of sp² atoms in heptazine rings known as D peak, disorder band or defect band. The peak around 1238 cm⁻¹ is attributed to the stretching vibration mode of C-N heterocycles known as G band. When the ratio of the D band intensity to the G band intensity is close to one, then the material consists of a small number of defects. In our case this equals to 1.001 which exhibits low number of defects. Furthermore, a band near 1560 cm⁻¹ appears in the case where the g-C₃N₄ powder consists of many impurities. In our measurement, this band is not visible which proves the high purity of the synthesized material.¹⁴²



3.3 Characterization of Graphene Oxide, GO

GO was structurally characterized utilizing XRD measurements as presented in Fig. 60. The characteristic peak (002) is observed at 10.8° which represents the interlayer distance of the GO flakes and according to the literature that indicates that the synthesized GO is fully oxidized.¹⁴³ The d-spacing is 0.819 nm as calculated through Bragg's equation and the increase in the spacing is attributed to the presence of the oxygen functional groups (e.g. epoxy, hydroxyl, carboxyl and carbonyl groups) on the surface of the flakes.¹⁴³ Moreover, the characteristic peak of graphite at 26.5° has been vanished which proves again that the graphite flakes are successfully oxidized.¹⁴³



Figure 60. XRD measurement of GO

After that, in order to confirm and identify the presence of the oxygen functional groups on the surface of GO, ATR-IR spectroscopy was implemented and its absorption spectrum is shown in Fig. 61. The main absorption peak at 1618 cm⁻¹, which is also observed in graphite, is attributed to the double bonds of carbon atoms of the basal plane.¹⁴⁴ After the oxidation of graphene via Hummer's method, the peaks at 1049 and 1726 cm⁻¹ are emerging.¹⁴⁴ The peak at 1726 cm⁻¹ is ascribed to the presence of the double bonds of carbon and oxygen atoms while the peak at 1049 cm⁻¹ is attributed to their single bonds. Finally, a stronger intensity absorbance peak is exhibited at 3425 cm⁻¹ which implies the existence of both hydroxyl groups and water molecules.¹⁴⁴ All of the above peaks indicate the presence of the oxygen functional groups on the surface of the GO sheets and confirm its successful synthesis from pure graphite via a modified Hummer's method.¹⁴⁴



Figure 61. ATR-IR spectrum of GO

Finally, to determine the degree of the impurities of GO, Raman spectroscopy was used and its spectrum is depicted in Fig. 62. In general, the conventional Raman spectrum of GO presents the G band which corresponds to the E_{2g} phonon of the sp^2 carbon atoms and the D band, often referred as disorder band, which corresponds to the breathing mode of k-point phonons of A_{1g} symmetry.^{141Error! Bookmark not defined.} The Raman spectrum of the GO that was used in the present work has its D band at 1348 cm⁻¹ while the G band appears at 1588 cm⁻¹. Both of the bands appeared slightly shifted compared to the literature due to the presence of certain defects such as vacancies, grain boundaries etc.^{141Error! Bookmark not defined.} The ratio of the intensity of the two bands, i.e., I_D/I_G , indicates the quality of the product.¹⁴¹ The I_D/I_G is calculated to be 1.05 which proves the good quality of the material. Moreover, two lower intensity bands appear at 2700 and 2900 cm⁻¹ known as 2D and D + G band, respectively, which is an index of material's defects. Here, the bands are broadened which implies that the prepared GO contains some defects.^{141Error! Bookmark not} defined.



3.3 Characterization of Ti₃C₂T_x Mxene

The last inorganic nanoadditive that was characterized was $Ti_3C_2T_x$ which results from Ti_3AlC_2 MAX phase. The XRD measurements of both materials are shown in order to confirm the successful synthesis of $Ti_3C_2T_x$. MAX phase exhibits a plethora of crystalline peaks most of which vanish when the material is etched to its Mxene $Ti_3C_2T_x$ phase due to the elimination of the Al layer. More specifically, the peak from 23° to 34° is either decreased or disappeared from MAX to Mxene phase, due to the breakage of the covalent bonds between the Al and Ti atoms during the etching process.¹⁴⁵ The main peak that implies the formation of the Mxene phase is the (002) at 9.49° which corresponds to the interplanar spacing of Ti_3C_2 motifs.¹⁴⁵ In the etched Mxene the peak shifts to 6.3° , indicating the increase of the interlayer distance between the $Ti_3C_2T_x$ planes after etching and according to the literature verifies the successful synthesis of $Ti_3C_2T_x$ from MAX phase.¹⁴⁵



Figure 63. XRD pattern of MAX phase Ti₃AlC₂ and etched Mxene Ti₃C₂T_x

For the evaluation of the oxygen, chloride and titanium functional groups, ATIR-IR spectroscopy was used but due to high fluorescence none of the corresponding peaks were visible. However, the Raman spectrum of $Ti_3C_2T_x$ presented valuable information and is depicted in Fig.64. Various peaks are presented, exhibiting different vibrational modes.¹⁴⁶ The peaks that appear at 139, 261, 397 and 597 cm⁻¹ can be attributed to the nonstoichiometric titanium carbide compounds formed by the synthesis of $Ti_3C_2T_x$ from its precursor Ti_3AlC_2 MAX phase. Usually, two additional peaks should appear around 1300-1500 cm⁻¹, the D and G bands of carbon layers, which intensities ratio describe the defects of the prepared material. In our case, these peaks are not visible as there is low content of defects confirming that the $Ti_3C_2T_x$ has been successfully synthesized and that the obtained material is of high purity.¹⁴⁷



Figure 64. Raman spectrum of $Ti_3C_2T_x$

3.4 Structural and thermal characterization of polymer nanocomposites

Initially, all P47/g-C₃N₄ nanocomposites were characterized using XRD to identify their structure, and their measurements are presented in Fig. 65 (a). It is obvious that the amorphous structure of the polymer is still valid since the low concentrations of the additive are not enough to change the morphology of the polymeric matrix. The broad amorphous peak at 19.8° seems to remain the same as the concentration of g-C₃N₄ increases. At the same time, the low amount of the additive is the reason that its characteristic diffraction peaks could not be observed. Subsequently, their thermal properties were estimated via DSC measurements. In Fig. 65 (b) the Tg of P47 and nanocomposites is presented. The only thermal transition that can be observed in all nanocomposites is the glass transition as the amorphous structure remains regardless of the concentration of the additive. The T_g of the nanocomposite with 0.05% wt. concentration appears at -11°C which is almost the same as that of pure PU. By increasing the concentration of the additive by a factor of 2, i.e., the nanocomposite with 0.1% wt. concentration exhibits a Tg at -8°C while the 0.2% wt. concentration presents a Tg at -7°C. As a result, and taking into account the fact that the glass transition is a very weak and very broad transition, no dependence can be observed correlating the Tg and the concentration of g-C₃N₄ as it remains very similar in all nanocomposites. As a result, in any case the low concentrations of g-C₃N₄ do not alter either the structure or the thermal properties of P47.



Figure 65. a) XRD measurements of P47 and P47/g-C $_3N_4$ nanocomposites and b) DSC measurements of P47 and P47/g-C $_3N_4$ nanocomposites

The structural properties of P47/GO nanocomposites were evaluated via XRD measurements as well. In Fig. 66 (a) all measurements are presented and the amorphous structure of P47 does not change upon the addition of GO flakes in any concentration. However, the broad peak of the nanocomposites, presents a shift to lower angles compared with that of P47 which is observed at 19.8°. For the 0.05% wt. concentration nanocomposite, the peak shifts to 16.1° while for 0.1% wt. and 0.2% wt. concentration nanocomposite the peak shifts to 16.8° and returns 16.1° respectively. Finally for the 1% wt. concentration nanocomposite the peak shifts to 16.3°. The lower intensity peak at 42° of the pure PU presents a slight shift in all nanocomposites as well, but in this case the

shifting remains the same as all peaks appear at 39.5° . The diffraction peaks of the GO cannot be observed in this case as well due to its very low amount. Overall, the presence of the GO flakes is not capable of changing the amorphous structure of the polymer matrix and all nanocomposites present the same structure. Afterwards, the thermal properties of P47/GO nanocomposites were evaluated through DSC measurements (Fig. 66 (b)). The T_g, compared to that of the pure PU, appears to be unchanged as a very similar transition step is observed. The 0.05% wt. nanocomposite presents a T_g at -15°C where the ones with 0.1% wt., 0.2% wt. and 1% wt. exhibited the same T_g at -9°C. The addition of GO does not affect the thermal properties of pure PU as no differences in their glass transition temperatures are observed. The amorphous structure of pure PU does not change upon the addition of GO and no crystallinity is observed despite the presence of the flakes which was also confirmed by the XRD measurements.



Figure 66. a) XRD measurements of P47 and P47/GO nanocomposites and DSC patterns of P47 and P47/GO nanocomposites

Similar to g-C₃N₄ and GO nanocomposites, all Ti₃C₂T_x nanocomposites were structurally characterized via XRD measurements (Fig. 67 (a)). The concentration of Ti₃C₂T_x in the polymer matrix is relatively low and cannot change its amorphous structure. The broad amorphous peak at 19.8° is still visible in all nanocomposites, however it is shifted at 16.2°. The shifting can be attributed to the presence of Ti₃C₂T_x that may influence the characteristics of the amorphous structure since all nanocomposites exhibit the same behavior. In this case as well, no peak due to the inorganic additive can be observed. Following Ti₃C₂T_x nanocomposites structural characterization, their thermal properties were evaluated through DSC measurements (Fig.67 (b)). Their amorphous structure, which was confirmed through the XRD measurements, remained intact as no other thermal transitions, besides glass transition, were observed. All nanocomposites exhibit almost the same glass transition temperature, T_g. More precisely, the 0.05% wt. nanocomposite presented a T_g at -9°C which is close to that of pure PU. Similarly, both 0.1% wt. and 0.2% wt. concentrations nanocomposites exhibited the same T_g at -11°C. The T_g of pure PU and the T_g of the nanocomposites are considered to be the same since their deviation is of no importance. As a result, the incorporation of Ti₃C₂T_x does not affect the thermal properties of the polymeric matrix.



Figure 67. a) XRD measurements of P47 and P47/ $Ti_3C_2T_x$ nanocomposites and b) DSC patterns of P47 and P47/ $Ti_3C_2T_x$ nanocomposites

3.5 Investigation of P47 and P47/nanocomposites self-healing efficiency

Initially, the self-healing properties of the pure polyurethane were evaluated. The self-healing abilities of the coatings were studied on deep and shallow cracks where the healing procedure was monitored via POM. In Fig. 68 images of shallow and deep cracks are presented. Shallow cracks are approximately 5µm and deep cracks approximately 20µm



Figure 68. Example of images depicting a) shallow and b) deep cracks as monitored initially through the optical microscope

The investigation of the self-healing properties of both pure PU and nanocomposites was made within an hour since no effect is observed after. In Fig. 69 the healing procedure within 24 hours of pure PU and all nanocomposites of 0.2% wt. concentration are presented exhibiting that after one hour the healing results remain the same.



Figure 69. Self-healing process of deep cracks of pure P47 (first row) and P47/g-C₃N₄, GO, Ti₃C₂T_x nanocomposites at the concentration of 0.2% wt. (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30, 60 min and 24 hours from left to right
3.5.1 Self-healing investigation of P47

Initially the self-healing efficiency of P47 polyurethane was investigated for shallow cracks at 75°C (Fig. 70). In all cases, a triplet of coated surfaces was tested to verify the results. By comparing the images of the cracks within one hour, a slight healing is observed as a gradual fading of the crack occurs. This implies that at this temperature there is some healing efficiency of the cracks but it is not enough to completely heal them and this result is observed and confirmed for all three measurements.

The healing of the crack can be attributed to the molecular mobility of the chains under high temperatures and thus the plentiful dynamic hydrogen bonds of the isocyanates and polyols that separated by the crack are re-formed, upon heating, resulting in the partial self-healing ability of the polyurethane.¹⁴⁸ It is reported that the hard segments of the polyurethane are mainly responsible for the self-healing process while the increase in soft segments has a negative effect as they reduce the density of the possible hydrogen bonds and the flexibility of the polymer chain which are crucial factors for the self-healing process.¹⁴⁹ P47 has a ratio of hard to soft segments, i.e. isocyanates to polyols, equal to 1.4 (NCO/OH=1.4), i.e., the hard segments prevail numerically to the soft ones and as a result they participate in the self-healing process. Moreover, the shape memory effect of the polyurethanes could drastically enhance its self-healing ability as the material remembers its initial shape and returns to it when it undergoes the thermodynamic process of heating. The heat dissipation in the polymeric matrix triggers the abundant hydrogen bonds of the polyurethane resulting in an efficient self-healing procedure.¹⁵⁰



Figure 70. Self-healing process of three different measurements of shallow cracks of P47 at 75°C at 0,1,5, 30 and 60 min from left to right

After testing the healing efficiency of the shallow cracks at 75°C, deep cracks were studied in the same temperature to investigate the correlation of P47's healing efficiency with the crack's dimensions. It is assumed that in the same temperature, deep cracks will heal slower as the reconnection of the polymeric chains is more difficult, due to the wider gap, and thus worse healing results will be observed. This seems to apply in our case as all cracks appear to be slightly healed, but after one hour the cracks are still visible, and compared with the images at 0 min not much

difference can be observed (Fig. 71). As a result, the temperature has an effect concerning the healing efficiency and it is clear that in the same conditions shallow cracks can be healed faster confirming that there is a correlation of cracks dimensions and their healing efficiency.



Figure 71. Self-healing process of three different measurements of deep cracks of P47 at 75°C at 0, 1, 5, 30 and 60 min from left to right

After the healing efficiency investigation of P47 at 75°C, a similar work was performed at 90°C to study if the hydrogen bonding network is temperature dependent and thus, higher temperatures will lead to better healing results. Initially the shallow cracks were tested, as presented in Fig. 72. It is obvious that all cracks have completely disappeared within an hour which could possibly be attributed to the higher temperature as chains tend to have higher mobility.¹⁴⁸ The results are impressive since the cracks at 90°C show a significant degree of healing even after 5 minutes. These results lead to the conclusion that the healing behavior of P47 is indeed correlated with the temperature and it is clear that shallow cracks are fully healed at 90°C compared with the corresponding cracks at 75°C.

Moving on, the healing of deep cracks was investigated at 90°C, as well, to determine if the trend that was observed for the smaller cracks remains. In Fig.73 the results on the healing of deep cracks are presented. The crack in all three measurements has been slightly healed although its wide gap is still visible. The temperature in this case has affected the healing efficiency but it is insufficient to fully heal the cracks. Compared with the deep cracks at 75°C, the results are not far better and thus there is no correlation between the temperature and the cracks healing, as proposed for the shallow ones. For deeper cracks, the effect of temperature is not that evident.

To sum up, the healing results of P47 were excellent in shallow cracks at 90°C while the deep cracks in the same temperature exhibited poor healing efficiency. However, at 75°C both shallow and deep cracks present the same healing efficiency as the cracks appear to be healed to some degree within an hour but the cracks are not much different than those at 0 min. In both cases the temperature enhanced cracks healing ability although deep cracks healing efficiency remained unaffected by the increase of the temperature.



Figure 72. Self-healing process of three different measurements of shallow cracks of P47 at 90°C at 0, 1, 5, 30 and 60 min from left to right



Figure 73. Self-healing process of three different measurements of deep cracks of P47 at 90°C at 0, 1, 5, 30 and 60 min from left to right

3.5.2 Self-healing investigation of polymer nanocomposites

Taking into account the healing results of P47 that were described above, the investigation of how the presence or the amount of the different nano-additives affect its healing was performed. Both shallow and deep cracks were evaluated at 75°C whereas studies only for deep cracks were performed at 90°C since the neat PU had a good performance at the specific temperature and cracks sizes.

Initially, the P47/g-C₃N₄ nanocomposites were evaluated and their self-healing process for shallow cracks at 75° C are presented. The corresponding images for the neat P47 are shown as well for comparison.

It is obvious that the composites seem to heal faster than the pure PU as the crack has almost vanished within an hour. In all three concentrations the nanocomposites are healed faster than the P47. As a first estimation, $g-C_3N_4$ seems to enhance the self-healing ability of P47 and it is presumed that the hydrogen bonds of the $g-C_3N_4$ NSs have effectively improved the intrinsic self-healing mechanism of the polyurethane.



Figure 74. Self-healing process of shallow cracks of pure P47 (first row) and P47/g-C₃N₄ nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

After studying the shallow cracks, deep cracks were tested in all samples in order to draw conclusions referring to the self-healing ability of $P47/g-C_3N_4$ nanocomposites. In Fig. 75 the healing results are presented. In this case, the results exhibit that $g-C_3N_4$ does not contribute on the intrinsic self-healing mechanism of P47 as all cracks seem almost intact in all three nanocomposites of different concentration. Compared with the healing results of P47, all three nanocomposites seem to not only have no effect in P47's healing efficiency but maybe slow down

the healing process. The initial cracks at 0 min are almost the same with the ones observed after 1 hour confirming that the presence of the nanoadditive had a negative effect on the self-healing abilities of P47. This could be attributed to the constraints that the surfaces impose to the motion of the chains lowering their mobility at the specific temperature, making it difficult for the hydrogen bonding network to be reformed. As a result, the presence of the g-C₃N₄ in deeper cracks cannot assist the healing process by providing more hydrogen bonds.¹⁵¹



Figure 75. Self-healing process of deep cracks of pure P47 (first row) and P47/g-C₃N₄ nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

Finally, the healing efficiency of the nanocomposites for deep cracks at 90°C was evaluated as presented in Fig. 76. It is clear that the healing efficiency of P47 has been enhanced in this case as in all concentrations, within an hour, the crack has disappeared leaving only a trace. The trace at 1 hr of the P47 is still clear while in the case of the nanocomposites it can hardly be seen proving that $g-C_3N_4$ can assist the healing mechanism of P47. Therefore, the combination of the high temperature with the presence of $g-C_3N_4$ has led to the significant enhancement of the P47's healing abilities. The healing result is independent of the nanoadditives concentration as in all three concentrations a similar result is observed.



Figure 76. Self-healing process of deep cracks of pure P47 (first row) and P47/g-C₃N₄ nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

To sum up, g-C₃N₄ NSs seem to improve the healing-ability of pure PU at certain temperatures. For shallow cracks at 75°C, an enhancement can be observed for all three nanocomposites. For deep cracks at 75°C a decrease in the healing efficiency of the nanocomposites is observed, compared with P47, and thus the healing-process is slowed down by the presence of g-C₃N₄. Nevertheless, the same result is observed for all three concentrations. Finally, for deep cracks at 90°C the best healing results are observed in the nanocomposites as the healed cracks present significant differences in comparison with the corresponding cracks of neat P47 under the same conditions proving that high temperature and the presence of g-C₃N₄ in the polymeric matrix can lead to great healing efficiency.

Following the study of the nanocomposites that comprise of $g-C_3N_4$, the P47/GO nanocomposites self-healing efficiency was investigated. Initially, shallow cracks at 75°C were tested and the healing results for all nanocomposites are presented in Fig. 77. As a first estimation, the results are not so encouraging since the presence of GO may only slightly assist the healing process. More precisely, a slight improvement of the cracks depth within an hour can be observed in all concentrations, except the 0.1% wt. concentration nanocomposite. The healed cracks, compared with the P47, seem to be hardly better but no great differences are observed. At this temperature, the presence of GO might enhance the healing ability of the polymer but not to a great degree. The traces of the cracks are still visible within an hour but appear more healed than that of P47. The results are independent of the concentration as all healed cracks exhibit the same healing efficiency. In the case of 0.1% wt. concentration nanocomposite, the crack seems to remain

completely unchanged and the presence of GO appear to decrease the healing efficiency of P47. Since higher and lower concentrations presented better healing results, this behavior cannot be attributed to the presence of GO in the polymeric matrix. However, this result has been confirmed from all three repeatable measurements for this concentration (Appendix 1).



Figure 77. Self-healing process of shallow cracks of pure P47 (first row) and P47/GO nanocomposites at concentrations of 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. (second, third, fourth and fifth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

Subsequently, deep cracks were tested in the same temperature and the healing results are presented in Fig. 78. The healing efficiency of the nanocomposites does not seem to differ from that of P47 in this case as well and a similar behavior with the one described for the shallow cracks is observed. The deep cracks are slightly healed within one hour but their healing efficiency appears to be in the same degree with that of P47 and as a result the presence of the GO flakes does not enhance the healing efficiency regardless of the concentration as all nanocomposites exhibit the same behavior. On the other hand, the healing efficiency does not seem to be slowed down and is completely independent by the GO's presence.



Figure 78. Self-healing process of deep cracks of pure P47 (first row) and P47/GO nanocomposites at concentrations of 0.05% wt., 0.1% wt., 0.2% wt. and 1% wt. (second, third, fourth and fifth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

Finally, deep cracks were tested in 90°C and their results are presented in Fig. 79. A similar behavior as the previous self-healing measurements is presented. To begin with, all nanocomposites, exhibit the same behavior regardless of the GO concentration and their healing efficiency does not seem to differ than that of P47. In the case of 0.05% wt. and 0.2% wt. concentrations the nanocomposites behavior might be interpreted as an improved healing ability but their initial cracks compared with that of P47 might be slightly shallower and thus better healing results may be observed. However, considering the shape and the size of their initial cracks, the nanocomposites healing degree seems to be the same as that of P47. Again, the presence of GO neither improves nor slows down the healing process. The behavior of P47 is completely unaffected by the presence of GO.



Figure 79. Self-healing process of deep cracks of pure P47 (first row) and P47/GO nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third, fourth and fifth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

To sum up, the presence of GO in the polymeric matrix did not exhibit encouraging results as almost all cracks remained visible within one hour. More specifically, shallow cracks at 75°C seem to be slightly more healed than P47 and in this specific case the presence of GO might enhance to a small degree the healing procedure. However, this result may not be fully attributed to the GO flakes as the initial cracks in the nanocomposites may be shallower than that of P47 and thus better healing results are expected. The deep cracks at both 75 and 90°C retained the same healing degree with P47 in all cases, and thus the presence of the GO flakes does not offer any assistance in the nanocomposite healing efficiency. Moreover, the results are independent of the GO's concentration as the same behavior is observed in all nanocomposites. However, the healing process is not slowed down by the agglomeration of the flakes as proposed by the literature.¹⁵²

Finally, the self-healing properties of P47/Ti₃C₂T_x nanocomposites were estimated. At first, the shallow cracks at 75°C were investigated and all results are presented in Fig. 80. By comparing the healing results of the nanocomposites with these of P47, it is clear that the presence of $Ti_3C_2T_x$ does not improve the healing efficiency. Within an hour, the nanocomposite cracks do not differ from that of P47 and this behavior is observed regardless of the nanoadditive's concentration. The

nanocomposites and the P47 healing degree appears to be almost the same and thus no assistance is provided in the polymeric matrix by $Ti_3C_2T_x$. However, the presence of the inorganic nanoadditive does not decrease the healing efficiency, which is completely independent by it. Again, the initial cracks at 0 min may be slightly different but the healing degree appears to be the same in all nanocomposites and P47.



Figure 80. Self-healing process of shallow cracks of pure P47 (first row) and P47/Ti₃C₂T_x nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

Moving on to the deep cracks at 75°C, some differences between the nanocomposites and P47 can be observed (Fig. 81). The nanocomposite with 0.05% wt. concentration seems to be slightly better healed than the P47 when comparing their images at 0 and 60 min. The cracks at 0 min look almost identical and even within a minute, the nanocomposite's crack appears to be more healed. Within an hour better self-healing results are observed than P47. However, for the 0.1% wt. and 0.2% wt. concentration nanocomposite, the results seem to differ and no improvement in the healing efficiency can be observed. This may be attributed to the formation of agglomerates which hinder the motion of the polymer chains.



Figure 81. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x nanocomposites at concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right

Finally, the healing ability was investigated for deep cracks at 90°C (Fig. 82). A similar behavior to the one of deep cracks at 75°C is observed. Compared with the P47 results, the nanocomposite with 0.05% wt. concentration appears to be more healed, however, to a small degree, indicating that the presence of $Ti_3C_2T_x$ might have an effect in this very low concentration. By increasing the nanoadditive's concentration, the healing results are getting worse and a delay in the healing process is observed. All traces of the cracks are still visible within an hour however one should take into account differences in the initial size of the crack as well. Nevertheless, the healing degree of the nanocomposites appears lower than that of P47. Again, the same conclusion as before can be extracted, that the higher concentrations of $Ti_3C_2T_x$ may lead to the delay of the healing process due to the formation of aggregates and not even the higher temperature is capable of overcoming this problem.



Figure 82. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x nanocomposites at the concentrations of 0.05% wt., 0.1% wt. and 0.2% wt. (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

Summarizing, the healing results of the P47/Ti₃C₂T_x nanocomposites were not so encouraging but some conclusions can be extracted based on their behavior. At first, at low temperatures the presence of $Ti_3C_2T_x$ seems to have no effect referring to the healing abilities of P47. Nor improvement or decrease in the healing efficiency is observed and this behavior remains the same for all nanocomposites. Moving on to the deep cracks, almost the same behavior in all nanocomposites is exhibited. In both temperatures (i.e., 75 and 90°C) the 0.05% wt. concentration nanocomposite seem to have slightly better healing results than P47 while the two higher concentrations (i.e., 0.1% wt. and 0.2% wt. concentrations) appear to slow down the healing process. This result could be attributed to the formation of agglomerates at higher concentrations which cause a decrease in the mobility of the chains.

3.5.3 Grey value analysis

Following the qualitative interpretation of the results, an attempt was made for their quantitative analysis. This was attempted by calculating the mean grey values of each crack. The grey value of a crack is defined as the contrast difference between the crack and its background. Through appropriate software, a bar capable of measuring the grey level of crack's color and the grey level of its background was used. As a result, a plot was extracted that correlates the grey values of a crack with the corresponding pixels, and a wide peak can be observed which represents crack's depth. For the quantification of the results, the grey values of each crack at 0 min were compared with those at 1 hr and a healing efficiency was calculated by comparing their areas. Finally, these healing efficiencies for the nanocomposites were compared to those of P47 to confirm the effect of the nano-additive on the process. Since the way that this analysis is performed is not optimized yet we chose to show certain examples only. More specifically, the grey values of P47 and P47/g-C₃N₄ nanocomposites for shallow cracks a 75°C (Fig. 83) and of P47 and P47/Ti₃C₂T_x nanocomposites for deep cracks at 90°C (Fig. 84) are presented. In the first case, the healing percentages prove that $g-C_3N_4$ has an effect in the P47's matrix as by increasing its concentration better healing results are observed as the volume of the crack seems to decrease. The healing efficiency increases systematically with nanoadditive concentration from 21% for the neat P47 to 36% for the nanocomposite with 0.05% wt. concentration and to 59% and 64% for concentrations of 0.1 and 0.2% in g-C₃N₄, respectively. This result is in agreement with the optical evaluation of the cracks where similar trends were observed. In the case of the $P47/Ti_3C_2T_x$ nanocomposites the healing efficiency is almost the same for the nanocomposite with 0.05% wt. as it increases from 66% to 69%. However, for higher concentrations the healing efficiency dramatically decreases, as 0.1% and 0.2% wt. concentrations exhibit 49% and 51% respectively. This result is in accordance with the optical interpretation as the same behavior is observed in the corresponding images. However, it should be noted that the grey values analysis is a time-consuming and difficult process which can be affected by many factors. The results may vary depending on the length of the measuring bar, the measured area (as different grey levels may exist along the crack), crack's shape and size or crack's contrast. For this, the analysis has to be very precisely done in order to produce representative results and further investigation is necessary in order to constitute a conventional tool.



Figure 83. Mean grey values of a) P47 and P47/g- C_3N_4 nanocomposites at the concentrations of b) 0.05% wt., c) 0.1% wt. and d) 0.2% wt. for shallow cracks at 75°C



Figure 84. Mean grey values of a) P47 and P47/Ti₃C₂T_x nanocomposites at the concentrations of b) 0.05% wt., c) 0.1% wt. and d) 0.2% wt. for deep cracks at 90°C

4.Conclusions

In the present thesis the self-healing ability of polyurethane nanocomposites was evaluated. Motivated by the interesting properties of nanocomposites comprising of 2D nanomaterials, 2D inorganic and graphitic additives are utilized as ideal candidates for the enhancement of the intrinsic self-healing mechanism of pure PU. This choice is based on two reasons, the first being that the functional groups that are present on the surface of the nanoadditives may enhance the hydrogen bonding between them and the polymeric chains whereas the second one is that their heat conducting properties can enhance the mobility of the chains and thus the hydrogen bonding via heat dissipation.

In this work, three different 2D materials, graphitic carbon nitride nanosheets, $g-C_3N_4$ NSs, graphene oxide, GO and $Ti_3C_2T_x$ Mxene, were incorporated in a waterborne polyurethane dispersion, WPUD, which was based on a polycarbonate polyol. Initially, the 2D inorganic nanoaddititives were isolated from their bulk structure. In the case of $g-C_3N_4$ the bulk form was synthesized by thermal polycondensation of melamine and the NSs were isolated by thermal oxidation of the bulk $g-C_3N_4$. Graphene Oxide, GO was synthesized via a modified Hummer's method and $Ti_3C_2T_x$ was prepared by etching the MAX phase Ti_3AlC_2 using HCl. After their synthesis, the materials were characterized using XRD, DSC, Raman and IR spectroscopy for the evaluation of their structure, functional groups and thermal properties.

For the preparation of the nanocomposites, $g-C_3N_4NSs$ were dispersed in powder form in the PU matrix via solid-liquid mixing by weighing the appropriate mass while GO and $Ti_3C_2T_x$ were dispersed via liquid-liquid mixing to avoid sedimentation problems. For GO nanocomposites, hybrids with concentrations of 0.5-1% wt. were prepared whereas the concentrations that were investigated for $g-C_3N_4$ and $Ti_3C_2T_x$ were 0.05% wt., 0.1% wt., and 0.2% wt. since for the 1% wt. sedimentation was observed.

At first, the nanocomposites were thermally and structurally characterized via DSC and XRD measurements to investigate the effect of the presence and / or the concentration of the additive on the structure and thermal properties of the pure PU. Little to no differences were observed and the amorphous structure of the polymer remained intact in all cases. All DSC measurements exhibited a similar T_g step with slight deviations. The XRD measurements for g-C₃N₄ nanocomposites presented no difference compared to the one of the neat P47 as the amorphous peak of the polymer can be observed at the same angle for the nanocomposites. For GO and Ti₃C₂T_x nanocomposites the XRD measurements show a shift of the diffraction peak to lower angles ~4°, but the amorphous structure is still observed for all measurements.

Finally, the healing procedure of all nanocomposites in the different concentrations was monitored through polarized optical microscopy in two different temperatures (i.e., 75° C, 90° C) for cracks of two different sizes (shallow and deep) on the surface of each sample made manually using a razor blade. The procedure was monitored within one hour since no effect was observed after this time interval. Eventually, the evaluation of the results was made by comparing the width of the cracks at t=0 min with that of t=1 hr by optical observation.

For the pure PU at 75°C a partial healing of the crack can be observed for both shallow and deep cracks, since its trace is still visible even after one hour. A similar behavior is observed for the deep cracks at 90°C, however at this temperature shallow cracks are completely healed within an hour indicating that the temperature has an effect in shallow cracks and higher temperatures can enhance the intrinsic healing mechanism of PU.

P47/g-C₃N₄ nanocomposites seem to have a better healing efficiency especially than pure PU for shallow cracks and higher temperatures. More specifically, shallow cracks heal faster compared with the pure PU while for deeper ones, higher temperatures are required as at 75°C they exhibit poor healing results whereas at 90°C they show great healing efficiency confirming that higher temperatures can enhance PU's healing mechanism.

Our results are not so encouraging in the case of the P47/GO nanocomposites. Overall, the presence of GO does not improve significantly the healing efficiency of the PU since the healing degree of the nanocomposites remains almost the same.

Finally, for the P47/Ti₃C₂T_x nanocomposites no healing efficiency is observed for shallow cracks as the same traces are observed after one hour with that of pure PU. For deep cracks, a different behavior is observed. The nanocomposites with low $Ti_3C_2T_x$ concentration, might slightly enhance the healing process but for higher concentrations a decrease in their healing efficiency is observed. This behavior is exhibited for both temperatures and this might be attributed to the formation of agglomerates which prevent the chain motion and therefore decrease the healing efficiency.

Although the investigation of the healing efficiency of the nanocomposites was performed in the best possible way, it should be noted that its determination in a nanocomposite coating, consists of many limitations. To begin with, since the crack is done manually using a razor blade, it is almost impossible to repeatedly scratch cracks with the exact same width and depth. As a result, differences in crack's dimensions may lead to different results referring to their healing efficiency as shallower and thinner cracks seem to heal faster than the deeper and wider ones. For this, an automated system that creates identical cracks is necessary and is proposed as a future work; this would allow the investigation of effect of the crack size on self-healing. Furthermore, an additional difficulty observed is that different nanoadditives lead to different nanocomposites mechanical properties and different force is required to produce cracks with standard dimensions. Finally, the grey value investigation of the healing process of a crack is empirical and constitutes an approach in measuring the contrast between two spots. As in all microscopic techniques, it is very difficult to define the exact same position that one can place the scale bar to evaluate the color difference. This is something that should be done more automatically in the future. In general, more investigation upon the grey value analysis is required for the objective quantification of the results.

As far as the scientific part is concerned, in the future, a more detailed investigation of the temperature and the concentration effect on the self-healing ability of nanocomposites need to be performed. Moreover, different nanoadditives can be utilized, along the directions indicated by the current work on the self-healing mechanisms that would enhance the final healing efficiency. Examples of such nanomaterials can be reduced graphene oxide, r-GO and / or r-GOs with varying degree of reduction. Such an approach could enhance the healing efficiency both by dissipating

heat and providing more hydrogen bonds in the polymeric matrix in order to finally be possible to be produced large scale products with excellent self-healing properties.

The present investigation was made for the improvement of the intrinsic healing ability of the WPUD in order to provide valuable information for the fabrication of polymer coatings that could be potentially utilized as varnishes for wooden flooring surfaces as well as paints in the car industry.

Appendix 1

All repeatable measurements for P47/g-C_3N_4 nanocomposites for shallow and deep cracks at $75^{\rm o}C$ and $90^{\rm o}$



Figure 85. Self-healing process of shallow cracks of pure P47 (first row) and P47/g- $C_3N_40.05\%$ wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 86. Self-healing process of shallow cracks of pure P47 (first row) and P47/g-C₃N₄ 0.1% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 87. Self-healing process of shallow cracks of pure P47 (first row) and P47/g-C₃N₄0.2% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 88. Self-healing process of deep cracks of pure P47 (first row) and P47/g-C₃N₄0.05% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 89. Self-healing process of deep cracks of pure P47 (first row) and P47/g- $C_3N_40.1\%$ wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 90. Self-healing process of deep cracks of pure P47 (first row) and P47/g-C₃N₄0.2% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 91. Self-healing process of deep cracks of pure P47 (first row) and P47/g- $C_3N_40.05\%$ wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Figure 92. Self-healing process of deep cracks of pure P47 (first row) and P47/g- $C_3N_40.1\%$ wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Figure 93. Self-healing process of deep cracks of pure P47 (first row) and P47/g- $C_3N_40.2\%$ wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

All repeatable measurements for P47/GO nanocomposites for shallow and deep cracks at 75 $^{\rm o}{\rm C}$ and 90 $^{\rm o}$



Figure 94. Self-healing process of shallow cracks of pure P47 (first row) and P47/GO 0.05% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 95. Self-healing process of shallow cracks of pure P47 (first row) and P47/GO 0.1% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 96. Self-healing process of shallow cracks of pure P47 (first row) and P47/GO 0.2% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 97. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.05% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 98. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.1% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 99. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.2% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 100. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.05% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Figure 101. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.1% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Figure 102. Self-healing process of deep cracks of pure P47 (first row) and P47/GO 0.2% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

All repeatable measurements for P47/Ti_3C_2T_x nanocomposites for shallow and deep cracks at 75 and 90°C



Fig 103. Self-healing process of shallow cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.05% nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Fig 104. Self-healing process of shallow cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.1% nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Fig 105. Self-healing process of shallow cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.2% nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Fig 106. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.05% nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Figure 107. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.1% wt. nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Fig 108. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.2% nanocomposite in three different measurements (second, third and fourth row respectively) at 75°C at 0, 1, 5, 30 and 60 min from left to right



Fig 109. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.05% nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Fig 110. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.1% nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right



Fig 111. Self-healing process of deep cracks of pure P47 (first row) and P47/Ti₃C₂T_x 0.2% nanocomposite in three different measurements (second, third and fourth row respectively) at 90°C at 0, 1, 5, 30 and 60 min from left to right

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